The mechanisms underlying the enhanced resolution of atomic force microscopy with functionalized tips

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Abstract. By functionalizing the tip of an atomic force microscope (AFM) with a molecule or an atom that significantly contributes to the tip–sample interaction, the resolution can be dramatically enhanced. The interaction and therefore the resolution crucially depend on the chemical nature of the tip termination. Employing a tip functionalized with a CO molecule, atomic resolution of a pentacene molecule was recently demonstrated. In this work, the interaction between the CO tip and the pentacene imaged are studied with first principles calculations. The calculated frequency shifts compare very well with the experiment. The different energy contributions are analyzed and the Pauli energy is computed. We demonstrate that the source of the high resolution is Pauli repulsion, whereas van der Waals and electrostatic interactions only add a diffuse attractive background.

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1. Introduction

With the invention of scanning tunneling microscopy (STM) [1], resolving individual surface atoms became possible. However, as the tunneling current is primarily sensitive to the local electron density of states close to the Fermi level, resolving single atoms within a molecule remains a great challenge. In recent years, non-contact atomic force microscopy has become a competitive tool in the characterization of nanostructures on the atomic scale [2], and impressive progress has been made. Atoms were resolved with chemical identification [3]; the magnetic exchange force was measured with atomic resolution [4]; individual atoms were manipulated [5, 6], and the forces during atomic manipulation were determined [7]. In investigations of single molecules, atomic resolution was achieved on single-walled carbon nanotubes [8, 9], and the force needed to switch a molecular conformation was measured [10]. Even higher resolution with a non-contact atomic force microscope (AFM) was achieved by functionalizing the tip with a CO molecule [11]. The atomically well-defined tip terminations, which allow the short-range chemical forces to be probed, are the key to achieving this goal. In this paper, we present a detailed analysis of density functional theory (DFT) calculations that were carried out to understand the imaging mechanism and origin of the high lateral resolution. This paper is organized as follows. We begin by describing, in section 2, the high-resolution imaging of a pentacene molecule using non-contact AFM, and the separation of the force contributions of the metal tip and the CO molecule. In section 3, we present a computation of the interaction between the tip and the pentacene molecule. The computational details are given, the frequency shifts are computed, the different energy contributions are analyzed and the Pauli energy is computed. Finally, in section 4, a short summary and conclusion are given.

2. Non-contact atomic force microscope (AFM) measurements of a pentacene molecule

2.1. High-resolution image of a pentacene molecule

Atomically resolved AFM measurements of pentacene on both a Cu(111) substrate and an NaCl insulating film are presented. In the short-range regime of forces, it is desirable to work with...
Figure 1. (a) Ball-and-stick model of the pentacene molecule. The carbon atoms are numbered from 1 to 22. (b) The frequency shift $\Delta f$ at constant height AFM of pentacene on Cu(111) using a CO-functionalized tip. Imaging parameters: STM set point parameters $I = 110$ pA, $V = 170$ mV, tip height $z = -0.1$ Å (with respect to the STM set point above Cu(111)) and oscillation amplitude $A = 0.2$ Å.

A pentacene molecule as shown in figure 1(a) was imaged using non-contact AFM on Cu(111) with a CO-functionalized tip. The image is shown in figure 1(b). For this image, a CO molecule was deliberately picked up with the tip, leading to significantly increased resolution. From previous investigations it is known that the CO molecule is adsorbed with the carbon atom...
towards the metal tip [14, 15]. The AFM image in figure 1(b) was recorded in constant-height mode, i.e. the tip was scanned without z-feedback parallel to the surface while the frequency shift $\Delta f$ was being recorded. The frequency shift is the detuning of the resonance frequency $f_0$ of the tuning fork due to the tip–sample interactions. In this and all following measurements, the tip height $z$ is given with respect to the STM set point $z_{sp}$ over the substrate. When we acquire an AFM image, we first position the tip above the bare substrate near the molecule using constant-current feedback. We then open the feedback circuit and apply an additional offset $z$ to the tip height, i.e. $z = 0$ Å corresponds to the tip height when using the STM feedback with the set point parameters above the bare substrate. In constant-height mode, the tip is then scanned on a plane that is defined by the STM set point parameters, the offset $z$ and the global tilt of the sample surface which is compensated. Constant-height operation is critical as it allows stable imaging in the region where the frequency shift is a non-monotonic function of the tip height.

In the AFM image, the five phenyl rings with hexagonal shape are clearly resolved. We observe local maxima of the frequency shift above the edges of the hexagons, near the carbon atom positions, and minima above the centers of the carbon rings (hollow sites). This agrees with the measurements on single-walled carbon nanotubes [8] and graphite [16]. Even the positions of the hydrogen atoms within the pentacene molecule can be resolved. Finally, the pentacene molecule is surrounded by an attractive region.

The measured frequency shift surfaces for five tip heights $z$ are shown in figure 2. By capturing a 3D field [17] of the frequency shift with $80 \times 40 \times 3100$ data points in a box of $25$ Å $\times 12.5$ Å $\times 13$ Å above a pentacene molecule the measured frequency shifts were determined as a function of the height. For values of tip heights $z$ larger than 4.2 Å, we recorded only frequency shifts $\Delta f$ smaller than 0.5 Hz. The molecule was imaged as a featureless depression with an attractive interaction for tip heights larger than 2 Å. With decreasing tip height, the frequency shift decreased before reaching a minimum of about $-4$ Hz above the molecular center for a tip height $z$ of 1.8 Å. From this tip height onwards, we began to observe corrugation on the atomic scale. When we decreased the tip height further, the frequency shift increased above the pentacene again. Finally, for a tip height of 1.2 Å, the frequency shift becomes even positive over some parts of the molecule. For this tip height, which is the regime of maximal attractive forces, we achieved the highest contrast and lateral resolution. Generally, the lateral contrast of the frequency shift increased with decreasing tip height. Decreasing the tip height further would result in instabilities and, finally, in lateral or vertical manipulation of the molecule. For the smallest accessible tip height of 1.2 Å, we measured an attractive force of 110 pN above the central phenyl ring. Above the positions of the carbon atoms, the forces were significantly smaller and ranged between 60 and 90 pN.

We summarize that for large tip heights the molecule is imaged as a featureless depression indicating attractive interaction. Only for smaller tip heights does a positive contribution to the frequency shift with atomic contrast appear. This suggests that the region of atomic contrast stems from repulsive interactions, which will be discussed later in detail.

2.2. Separation of the contributions of the Au tip and the CO molecule

In the following, we concentrate on the investigation of pentacene on an NaCl (2 ML)/Cu(111) substrate. We estimate the contribution from the metallic tip behind the CO molecule, which later helps for a quantitative comparison between theory and experiment. From the measurements, we separate the force contributions of the Au tip and the CO molecule. The
Figure 2. 3D contours of the measured frequency shift $\Delta f$ for five different tip heights $z$. The contour area is 23.6 Å × 10.6 Å. The heights $z$ are given with respect to the STM set point of $I = 2$ pA, $V = 200$ mV above the NaCl (2 ML)/Cu(111) substrate.

Vertical forces $F_z$ were extracted using the method of Sader and Jarvis [18]. We first measured the forces using an Au tip without a CO molecule at the apex, as shown in figure 3(a). After measuring the forces with the Au tip, we picked up a CO molecule and under otherwise identical experimental conditions measured the forces again, which are shown in figure 3(b). The fact that the set point $z_{sp}$ has changed when picking up the CO molecule has been taken into account. Typically, the set point $z_{sp}$ was reduced by 0.5–1.5 Å when picking up a CO molecule, i.e. the tip was driven towards the sample by the constant-current feedback after picking up the CO molecule. The rather large range of this decrease of the set point $z_{sp}$ is probably due to different tip geometries and adsorption of the CO molecule on different tip atoms. Note that the CO molecule might not always adsorb at the foremost tip atom. The heights $z$ in figure 3 are all given with respect to the set point of the CO tip. The force acting between the CO tip and the pentacene contains contributions due to interactions of the CO molecule with the pentacene and contributions of the comparably large Au terminated tip behind the CO molecule. Figure 3(c) shows the difference between the force acting on the entire CO tip from figure 3(b) and the force acting on the metal tip without CO molecule from figure 3(a). This yields a good estimate of the force contribution of the CO molecule only, without the metal part of the tip. As can be seen clearly in figure 3(a), there is no atomic corrugation when scanning with the bare Au tip. Only
Figure 3. The forces above the long axis of a pentacene molecule using an Au and a CO tip as a function of the lateral position $x$. Lines with the same color correspond to the same absolute tip height. (a) The force $F_z$ between an Au tip and the pentacene molecule on an NaCl (2 ML)/Cu(111) substrate. (b) The force $F_z$ of the same Au tip functionalized with a CO molecule and the same pentacene molecule. (c) The force between the CO molecule and the pentacene, i.e. the difference between the force of the Au tip (a) and the Au tip with a CO molecule (b). The height $z$ is given with respect to the STM set point ($I = 2$ pA, $V = 200$ mV) for the CO tip above the NaCl (2 ML)/Cu(111) substrate.

when the tip is functionalized with a CO molecule can the atomic corrugations be observed as shown in figure 3(b). Furthermore, the comparison of the measurements with and without CO molecule shows that 65% of the force stems from the CO molecule and not from the large metal tip behind the molecule. This is rather surprising because the metal tip is large when compared with the CO molecule. However, the CO molecule keeps the Au tip far enough away from the pentacene so that the short-range interaction primarily results from the CO molecule and not from the Au tip. This fact justifies omitting the Au tip in the following when calculating the tip–sample interaction. Furthermore, separating the forces makes it possible to quantitatively compare experiment with theory.

3. Computation of the interaction between the tip and the pentacene molecule

3.1. Computational details

To elucidate the origin of the observed atomic contrast, we computed the energies, forces and frequency shifts. We carried out DFT calculations [19, 20] employing the highly optimized code
We applied the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [21] and employed \textit{ab initio} norm-conserving pseudopotentials [22]. van der Waals (vdW) forces are non-local correlations that are beyond the scope of local density approximation (LDA) and generalized gradient approximation (GGA). This limitation was overcome by adding a dispersion energy contribution in the form of $C_6/R^6$ to the DFT energy, which has been proved to be an appropriate approach in earlier works [23]. The pseudopotentials were created with the scheme of Troullier and Martins [24]. The pseudopotentials were further transformed into fully separable Kleinman–Bylander pseudopotentials [25], with the $p$-potential chosen as the local potential, except in the case of the hydrogen atoms, for which the $s$-potential was chosen as the local potential. The electron density was calculated from one $k$-point, the $\Gamma$-point. The wave functions were expanded into plane waves [26] with a kinetic energy of up to 200 Ryd. Such a large kinetic energy cut-off is necessary, because the interaction energies are in the range of tens of meV, and they have to be converged so that their error is smaller than 0.1 meV. The equilibrium lattice parameters of the molecules were found by minimizing the total energy and relaxing the ions until the forces were smaller than 1 pN. We only included the pentacene molecule and the CO molecule in our calculations and neglected both the substrate and the metallic part of the tip. We assumed that the CO molecule is oriented perpendicularly to the plane of the pentacene molecule, with the oxygen atom pointing towards the pentacene. To check this, we performed calculations in which we allowed the atoms of both molecules to relax and permitted a tilt of the molecular axis of the CO. We found that for the experimental tip heights, relaxing the atoms did not change the results. Therefore, to reduce computational time, the atomic positions were not relaxed in the following calculations. Furthermore, the calculations indicated that the CO molecule holds a small dipole moment oriented towards the pentacene, i.e. the oxygen atom carries a small positive partial charge. However, for the experimental tip heights, the main contribution to the attractive interaction is given by the vdW interaction and only a small contribution can be attributed to electrostatic interaction.

### 3.2. Computation of the frequency shift

To obtain the vertical force acting on the CO molecule and the corresponding frequency shift, we calculated the total energies of the CO molecule and the pentacene for five different intermolecular distances $d$. The distance $d$ denotes the distance of the CO carbon atom to the plane of the pentacene atoms. The relation of the distance $d$ to the experimental tip height $z$ will be given later. The interaction energies $E_{\text{int}}$ are then obtained by subtracting the total energies of the CO molecule and pentacene from the total energy of the combined system. These interaction energies were fitted by a Lennard-Jones-type potential of the form

$$E_{\text{int}}(d) = \left( \frac{a}{d} \right)^b - \left( \frac{u}{d} \right)^v \text{[meV]}. \quad (1)$$

The first term describes the repulsive interaction and the second the attractive interaction. Not only the parameters $a$ and $u$ but also the exponents $b$ and $v$ were extracted by fitting. The DFT energies and the corresponding Lennard-Jones fit for the CO molecule located above the center of the pentacene molecule are shown as a function of the distance $d$ in figure 4(a). The resulting fit parameters are $a = 6.01 \ \text{Å}$, $b = 12.63$, $u = 9.47 \ \text{Å}$ and $v = 6.08$. For each lateral
Figure 4. (a) The computed interaction energies and the corresponding Lennard-Jones fit for the CO molecule above the center of the pentacene molecule, as a function of the intermolecular distance $d$. The force $F_z$ (b) and frequency shift $\Delta f$ (c) computed from the Lennard-Jones fit, as a function of the intermolecular distance $d$.

position, these parameters are determined separately. Moving laterally away from the pentacene molecule, all four parameters gradually decrease and approach zero, as both repulsive and attractive forces decrease.

In figure 4(b), the vertical force $F_z$ is shown, which was extracted by differentiating the Lennard-Jones fit function with respect to $d$:

$$F_z(d) = -\frac{\partial E_{\text{int}}(d)}{\partial d}.$$ 

(2)

The frequency shift $\Delta f$ shown in figure 4(c) is extracted by differentiating the force $F_z$:

$$\Delta f = -\frac{f_0}{2k_0} \frac{\partial F_z(d)}{\partial d}.$$ 

(3)

In principle, one has to take into account the tip amplitude when calculating the frequency shift. However, for amplitudes of 0.2 Å the corrections are minimal and can be omitted. When obtaining the curves in figures 4(b) and (c) by differentiating, the curve shapes remain similar. However, the minima are shifted to larger distances with each derivative. Whereas the interaction energy has its minimum at 4.09 Å, the force has its minimum at 4.53 Å and the frequency shift has its minimum at 4.96 Å. We exploit this characteristic later to understand the cause of the atomic contrast. The frequency shift was calculated for a lateral grid of $x$ and $y$ positions with a spacing of 0.2 Å and for five distances $d$ using the above-described method. The computed frequency shifts are shown in figure 5. The atomic distance of the CO molecule to the pentacene could not be determined in the experiment exactly, and therefore the experimental tip heights $z$ are given with respect to the STM set point. To determine the relationship between the tip height $z$ and the distance $d$, we compare the experimental and calculated frequency shifts. Applying the relationship $z \approx d - 3.55$ Å, the two frequency shifts exhibit very similar behavior. For distances $d$ larger than 7.75 Å, the calculated frequency shift

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is rather small and appears as a featureless attractive depression. With decreasing distance, the frequency shift increases. It starts to exhibit atomic corrugations for a distance of approximately 5.35 Å. The minimum of the frequency shift is reached at a distance of approximately 4.95 Å. The atomic contrast increases further for smaller distances. Experiment and theory agree well and show maximal negative frequency shifts of the order of $-2.5$ Hz above the hollow sites of the pentacene molecule. In contrast, the frequency shifts above the C–C bonds are less negative and can even become positive for small heights and distances. For a distance $d$ of 4.75 Å, the attractive force above the central phenyl ring reaches a value of 90 pN, which is in good agreement with the experimental value of 110 pN. However, the computed atomic corrugations, i.e. the differences in the frequency shift above the C–C bond and the hollow site, are always overestimated in theory compared with experiment. This becomes even more pronounced in the short-range regime for distances smaller than 4.95 Å. Furthermore, in the computations, the C(1)–C(2), C(10)–C(11), C(12)–C(13) and C(21)–C(22) bonds at the end of the pentacene show a large repulsive contribution for distances smaller than 5.35 Å.

3.3. Analysis of the energy contributions and computation of the Pauli energy

The computed frequency shift for the distance $d = 4.75$ Å is shown as a 2D contour in figure 6(a). Instead of studying the frequency shifts, we concentrate in the following on
Figure 6. 2D contour plots of the frequency shift and several energies of the CO molecule above the pentacene molecule. (a) The computed frequency shift $\Delta f$ for an intermolecular distance of $d = 4.75 \text{ Å}$. (b) The interaction energy $E_{\text{int}}$ for a distance of $d = 3.86 \text{ Å}$. (c) The contribution of the kinetic energy $E_{\text{kin}}$ to the interaction energy. (d) The contribution of the vDW energy $E_{\text{vdW}}$ to the interaction energy. (e) The contribution of the sum of the electrostatic and exchange correlation energies $E_{\text{el}} + E_{\text{xc}}$ to the interaction energy. (f) The interaction energies $E_{\text{int}}(\uparrow\uparrow)$ calculated using the wavefunctions of the isolated CO and pentacene molecules without orthogonalizing them. (g) The Pauli energy $E_{\text{Pauli}} = E_{\text{int}} - E_{\text{int}}(\uparrow\uparrow)$. (h) The interaction energy $E_{\text{int}}^{nsc}(\uparrow\downarrow)$ using the wavefunctions of the isolated CO and pentacene molecules and orthogonalizing them.

interaction energies, which are more easily accessible. The calculated interaction energy for a distance of $d = 3.86 \text{ Å}$ is shown in figure 6(b). When using a 0.89 Å shorter distance, the energy surface exhibits a similar contour as the frequency shift in figure 6(a). The excellent agreement
Figure 7. The frequency shift and several energies of the CO molecule above the long axis of the pentacene molecule. (a) The computed frequency shift $\Delta f$ for an intermolecular distance of $d = 4.75 \text{ Å}$. For a distance of $d = 3.86 \text{ Å}$, the interaction energy $E_{\text{int}}$ and the interaction energy $E_{\text{int}}^{\text{nsc}}(\uparrow \downarrow)$ were computed using the wavefunctions of the isolated CO and pentacene molecules and orthogonalizing them. (b) The interaction energy $E_{\text{int}}$, the contribution of the kinetic energy $E_{\text{kin}}$ to the interaction energy, the contribution of the vdW energy $E_{\text{vdW}}$ to the interaction energy, the contribution of the sum of the electrostatic and exchange correlation energies $E_{\text{el}} + E_{\text{xc}}$ to the interaction energy, the interaction energy $E_{\text{int}}(\uparrow \uparrow)$ computed using the wavefunctions of the isolated CO and pentacene molecules without orthogonalizing them, and the Pauli energy $E_{\text{Pauli}} = E_{\text{int}} - E_{\text{int}}(\uparrow \uparrow)$.

between the interaction energy and frequency shift is shown in figure 7(a). Their curve shapes as a function of distance agree very well, as has been shown in the previous section.

We examined the individual contributions of the interaction energies to gain deeper physical insight. The total energy in DFT is the sum of energies of four different physical origins: kinetic, vdW, electrostatic and exchange correlation energies. The kinetic and exchange correlation energies are not proper observables in DFT, and therefore caution has to be used when interpreting these contributions. The contribution of the kinetic energy $E_{\text{kin}}$ to the interaction energy is shown in figure 6(c), that of the vdW energy $E_{\text{vdW}}$ in figure 6(d) and the sum of the contributions of the electrostatic energy and the exchange correlation energy $E_{\text{el}} + E_{\text{xc}}$ in figure 6(e). The different contributions are also shown above the long axis of the pentacene in figure 7(b). The only repulsive interaction arises from the kinetic energy. Both the
vdW energy and the sum of the electrostatic and exchange correlation energies exhibit attractive interactions. In contrast to the vdW energy contribution, both the kinetic energy contribution and the electrostatic and exchange correlation energy contributions exhibit atomic corrugations and are much larger than the interaction energy. However, the two contributions are not observables and mostly compensate for each other so that the resulting corrugations in the interaction energy are much smaller, which can be clearly seen in figure 7(b). Furthermore, caution has to be exercised when interpreting the energies in figures 6 and 7 quantitatively. The proportions of the different contributions of the interaction energy are different for different distances $d$, and to obtain the same image, we chose a smaller distance for the energy image than for the frequency shift image. For example, for larger distances, the long-range vdW interactions might contribute more than the electrostatic interactions when calculating the frequency shift image.

From the experiment, we concluded that the atomic contrast probably stems from a repulsive interaction and as only the kinetic energy in figure 6(c) leads to a repulsive contribution, we suggest that it is the cause of the atomic corrugations. The kinetic energy is closely linked to the Pauli repulsion or Pauli exclusion principle. The Pauli exclusion principle states that no two electrons may occupy the same quantum state simultaneously [27], which implies that the total wavefunction is antisymmetric. When two electrons of the same spin state intersect in space, their orthogonalized wavefunctions take on larger slopes to keep their overlap zero. The increase in slope causes an increase in kinetic energy, which is a large portion of the Pauli repulsion. The Pauli energy can be defined as the energy difference between orthogonalized and non-orthogonalized wavefunctions:

$$E_{\text{Pauli}} = E_{\text{int}}(\uparrow\downarrow) - E_{\text{int}}(\uparrow\uparrow). \quad (4)$$

In our case, when the CO molecule approaches the pentacene, the CO wavefunctions start to overlap with the pentacene wavefunctions. As the wavefunctions inherently are not orthogonalized, they start to minimize their overlap by increasing their slopes and therefore the interaction energy. To calculate the Pauli energy in equation (4), we employ the already computed total interaction energy $E_{\text{int}}$ for the first term $E_{\text{int}}(\uparrow\downarrow)$. The second term $E_{\text{int}}(\uparrow\uparrow)$ is calculated by first determining the wavefunctions of the isolated CO molecule and isolated pentacene. Using these wavefunctions, the interaction energy is calculated in the standard DFT way, but without orthogonalizing them. As the Pauli energy is a difference of two total energies, it is, in contrast to kinetic energy, a proper observable.

The interaction energy $E_{\text{int}}(\uparrow\uparrow)$ without orthogonalizing the wavefunctions of the two molecules is shown in figures 6(f) and 7(b). It is only attractive over the pentacene and exhibits no atomic corrugations. As the wavefunctions are not orthogonalized, they remain unaltered. Therefore, the kinetic energy of the interacting system is equal to the sum of the kinetic energies of the two isolated molecules for all lateral positions and distance, and the contribution of the kinetic energy to the interaction energy $E_{\text{int}}(\uparrow\uparrow)$ is always zero. As the contribution of the vdW energy is added semiempirically and depends only on the atomic positions, it is exactly the same as that for the self-consistent calculations shown in figures 6(d) and 7(b). The sum of the contributions of the electrostatic and exchange correlation energies is again attractive. However, it is smaller in magnitude and exhibits no atomic corrugations. This results in an interaction energy $E_{\text{int}}(\uparrow\uparrow)$ without orthogonalizing the wavefunctions, which is attractive but has no atomic corrugations.

As a next step, we calculated the Pauli energy, which is shown in figures 6(g) and 7(b). It is completely repulsive and exhibits the atomic corrugations observed in the interaction energy.
The fact that the Pauli repulsion stems from the overlap of the wavefunctions is the reason for the observed high resolution and strong enhancement of the atomic-scale contrast. The wavefunctions of the CO molecule are strongly localized and exhibit small lateral dimensions, which leads to the high resolution. Because molecular wavefunctions increase exponentially towards the molecule, the Pauli repulsion increases exponentially when the CO molecule approaches the pentacene, which causes the strong atomic contrast. Now, we compare the Pauli and the kinetic energy in figures 6 and 7(b). As expected, they show very similar behavior. The kinetic energy is proportional to the Pauli energy and is larger by a factor of approximately 1.9.

Furthermore, we calculated the interaction energy $E_{\text{int}}^{\text{unc}}(\uparrow \downarrow)$ using the wavefunctions of the isolated CO and isolated pentacene molecules and orthogonalizing them, but not optimizing them any further. This interaction energy, shown in figures 6(h) and 7(a), compares very well with the fully self-consistent interaction energy $E_{\text{int}}$ in figure 6(b). This indicates that the molecules are inert and exhibit no binding interaction. The fact that the CO molecule is chemically inert facilitates the observed high atomic resolution, as the molecule can approach closer than the distance of maximum attraction without a bond forming.

3.4. Comparing the experiment with the computations

The experimental frequency shifts in figure 1(b) compare very well with the computed frequency shifts in figure 6(a). Most of the features are well reproduced and even the absolute values agree very well. With the above-described theoretical analysis, figure 1(b) can be much better understood. The vdW interaction and the electrostatic interaction show little lateral corrugation on the atomic scale and yield a diffuse attractive potential above the entire molecule, giving rise to the observed attractive region surrounding the molecules. The origin of the atomic contrast is the Pauli repulsion, which becomes significant when regions of high electron density overlap. These regions are concentrated on the atomic positions. Because the pi-orbitals are further extended and therefore heavily contribute to the Pauli repulsion, the C–C bonds are more pronounced than the C–H bonds of the pentacene molecule.

However, there are discrepancies between the experiment and the computations. In the experiment, the pentacene appears larger and distorted. The origin of this is not clear. It might be due to the fact that the substrate, the tip behind the CO or any relaxations of the CO molecule are not taken into account. The semiempirical treatment of vdW forces could also lead to errors. Another origin of the discrepancies could be the increasing influence of noise in the experimental data for small tip heights.

A further discrepancy arises at the end of the pentacene, where there is a positive frequency shift, i.e. comparably large repulsive contributions are observed for small distances. In the experiment, positive frequency shifts at the end were only observed when imaging the pentacene on a Cu(111) surface as shown in figure 1(b), where smaller tip heights can be achieved because of the stronger bonding of the pentacene to the substrate. There could be three reasons for this positive frequency shift. The first reason is that the C(1)–C(2), C(10)–C(11), C(12)–C(13) and C(21)–C(22) bonds have a higher bond order of 1.6 compared to the bond orders of the other C–C bonds, which range between 1.1 and 1.4. It is well known that organic molecules accumulate electrons at their ends where they, in principle, are truncated. This slightly larger electron density leads to stronger Pauli repulsion. This can be seen very well in the calculated frequency shifts, where the positive regions are only localized over these bonds. However, in the experiment, the regions above the C(1)–C(22) and C(11)–C(12) bonds also exhibit positive
frequency shifts. Therefore, two additional explanations come into consideration. One reason could be that in the experiment the pentacene is absorbed slightly bent such that the carbon atoms at the ends of the pentacene relax away from the substrate. When pentacene absorbs on a Cu(110) substrate, molecules are bent out of the surface plane by 0.4 Å from the center of the molecule that is closest to the Cu substrate [28]. Another reason could be that in the experiment the vdW interaction is decreasing faster towards the end of the molecule than in the computations. The smaller vdW interaction would then counter less of the Pauli repulsion. These two explanations would lead to positive frequency shifts over all bonds at the end of the pentacene.

4. Summary and conclusion

In this work, atomically resolved images of pentacene were presented that were obtained with non-contact AFM using a CO-functionalized tip. These images could be reproduced, and the underlying interactions were studied using first principles calculations. The different energy contributions of the CO tip and the pentacene were analyzed, and the Pauli energy was computed. We were able to conclude that Pauli repulsion is the source of the high resolution, whereas vdW and electrostatic interactions only add a diffuse attractive background with no atomic contrast. The Pauli repulsion exponentially increases with the overlap of the molecular wavefunctions. This explains the observed enhancement of the atomic scale contrast so that the atomic positions and bonds inside pentacene molecules can be resolved, revealing precisely the atomic molecular structure. We foresee that in the future, details of intermolecular bonds, such as the bond order and length, might be extracted even for molecules for which the precise structure is not known a priori. Probing the reactivity of different molecular sites with respect to a specific tip molecule or atom could yield detailed insights into chemical reactions and catalysis.

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