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Very weak bonds to artificial atoms formed by quantum corrals

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We explored the bonding properties of the quantum corral (a circle of 48 iron atoms placed on a copper surface) reported by Crommie, Lutz and Eigler in 1993, along with variants, as an artificial atom using an atomic force microscope (AFM). The original corral geometry confines 102 electrons to 28 discrete energy states, and we find that these states can form a bond to the front atom of the AFM with an energy of about 5 millielectron volts. The measured forces are about 1/1000 of typical forces in atomically resolved AFM. The confined electrons showed covalent attraction to metal tips and Pauli repulsion to CO-terminated tips. The repulsion at close distance was evident from the response of corral states created by deliberately placing single iron atoms inside the corral. The forces scaled appropriately with a 24-atom corral.

Artificial atoms are structures that confine a fixed number of electrons in a small space such that these electrons show discrete energy levels (1). The original quantum corral, a circular arrangement of 48 Fe atoms with a radius of $r_c = 7.13$ nm (2) on a Cu (111) surface, was created by atomic manipulation (3) with a scanning tunneling microscope (STM). We studied the chemical bonding of this artificial atom (and structures with extra Fe atoms and a smaller 24-atom corral) with single atom metal tips and CO-terminated tips of an atomic force microscope (AFM) (4). We observed an attractive interaction between the corral states and the front atom of the metal tip for core-core distances of the front atom of the tip and the plane of the surface Cu atoms from 620 to 440 p.m. (6.2 to 4.4 Å). The measured bonding energy between the single atom metal tip and the artificial atom of 5 meV is only a fraction of the van der Waals (vdW) bonding energy between two xenon atoms that amounts to 35 meV (5). The CO terminated tip can approach the surface down to a distance of 410 p.m., it interacts repulsively with the corral states. Because of the weak interaction, a reasonable signal-to-noise ratio is only obtainable up to a distance of about 490 p.m.

The artificial atom manifested by the corral states does not contain a fixed number of electrons as it is connected to an electron reservoir from the Cu substrate. We show below that the corral should contain ≈ 102 electrons. The $\psi_{n=5,l=0}$ state, where n denotes the radial zeroes of the wavefunction and l is the angular momentum, has a calculated energy that is exactly at the Fermi level E_F and as the levels are broadened, this state is expected to be half-filled. Thus, the expected electron occupation is 101 electrons if the energy of the $\psi_{5,0}$ state exactly matches E_F , but the ± 10 meV uncertainty in that energy can lead to variations. In addition, attractive

interaction with the AFM tip will shift the energy of this state to lower values, causing increased filling, and repulsive interaction will cause the opposite effect. Experimentally, the attractive interaction with a metal tip led to an occupation of up to 0.95 electrons for each of the two spin states in the $\psi_{5,0}$ state, whereas repulsive interaction with a CO terminated tip reduced it to 0.65, leading to a total occupation between 101.9 and 101.3 electrons.

A scanning tunneling microscopy (STM) image of the 48-atom quantum corral (2) was recorded with a CO-terminated metal tip [Fig. 1A; see section 1 in (6) for experimental details] resolved both the Cu surface atoms as well as the confined-electron eigenstates [see section 2 in (6) for a comparison to the data obtained with a metal tip]. The two-dimensional (2D) nature of the quantum corral originated from the surface states that exist on closely packed noble metal surfaces such as Cu(111) (7). Figure 1B shows the overall energy scale, where E_0 is below the vacuum level by the work function = 4.94 eV (8) plus the occupied range of the surface band given by 440 ± 10 meV (9). The unperturbed surface state on Cu(111) can be described by a 2D quasi-free electron gas with a quadratic energy dispersion of $E^*(k) = \hbar^2 k^2 / (2m^*)$, where $\hbar$ is Planck's constant divided by 2π and the effective mass m^* is 0.38 ± 0.02 times the electron mass (9) (Fig. 1C); the wave vector $\mathbf{k}$ is parallel to the surface, with a Fermi wave vector of $k_F = 2\pi/\lambda_F \approx 2.1$ nm⁻¹ and $\lambda_F \approx 3$ nm (10).

The Fe adatoms repulsively scatter the surface state, and the iron ring forces the modified surface states into a potential energy landscape that can be reasonably modeled by a disc of radius r_c with hard-wall confinement (2, 11–13). The solutions of the Schrödinger equation for the hard-wall model are

$$\psi_{n,l}(r, \phi, z) = C_{n,l} \cdot J_l(\rho_{0n,l} \cdot r / r_c) \cdot e^{il\phi} \cdot e^{-z/(2\lambda_B)} \quad (1)$$

in the following referred to as Bessel-type eigenstates. Each state with angular momentum $l \cdot \hbar$ in z direction, where l can be negative and positive, can be occupied by two electrons

(spin up/down). The constant $C_{n,l}$ is a normalization constant, $J_l(\rho)$ is the Bessel function of the first kind of order l with n th zero $\rho_{0,n,l}$ [figs. S3 to S5 and table S1 in section 3 in (6)], r is the radial distance from the center of the corral, ϕ is the azimuthal angle and $\lambda_B = 42.1$ pm is the decay length of the electron density described by the Bessel-type eigenstates into the vacuum for all n, l .

The discrete energy spectrum of the Bessel-type eigenstates (Fig. 1D) showed energy level broadening caused by scattering and coupling to the bulk substrate (2, 11). Five of these states were visible by STM at low bias as their energy eigenvalues were near E_F ; $\psi_{5,0}$ was exactly at the Fermi energy E_F and $\psi_{4,\pm 2}$, $\psi_{2,\pm 7}$ were 8 and 7 meV below E_F , respectively. Because of the ± 10 meV uncertainty in the occupied range of the surface band and the uncertainty of the effective mass, the occupation of each spin state in $\psi_{5,0}$ could be anywhere between 0 and 1. Because of the finite energy width of the $\psi_{5,0}$ state, its occupation would be 0.5 if the occupied range of the surface band was exactly 440 meV and $m^* = 0.38 m_e$. The occupation of the $\psi_{5,0}$ state was modified by the tip-sample interaction.

Figure 1E shows the surface charge density σ_{Fermi} of these five states when fully occupied by a total of ten electrons, the dashed line is σ_{Fermi} with empty $\psi_{5,0}$ states. The experimental STM data of Fig. 1A, fig. S1A in (6), and fig. 2B in (2) resemble σ_{Fermi} . The remaining 92 electrons have an energy far below E_F . Thus, a total of 102 electrons occupy the corral if the $\psi_{5,0}$ states are filled, yielding an average surface charge density of $\sigma_{\text{av}} = 102 e/(\pi r_c^2) = 0.639$ e/nm². In the profile of the calculated total surface charge density σ_{total} (Fig. 1F), the dashed line is σ_{total} without the contribution of $\psi_{5,0}$ states. The surface charge density of the radially rippled disc-shaped cloud of electrons in the corral was very dilute compared to natural atoms. For example, Cu has an atomic radius of 127.5 pm and an average surface charge density for its 11 valence electrons of ~ 215 e/nm² when projected on a plane (14), or ~ 340 times the surface charge density of the corral.

To investigate the bonding properties of the quantum corral, we used frequency-modulation AFM (15), which can achieve atomic resolution and deliver low-noise force spectroscopy (16, 17). We use two types of AFM tips, single-atom metal tips that often form strong bonds with conventional atoms (18), and CO-terminated metal tips (19) that are usually chemically inert (20) and interact mainly through Pauli repulsion (21, 22). Electrostatic interactions of the corrugated electron states caused only negligible interaction forces [see section 4 in (6)].

The interaction of the surface and corral states with a single-atom metal AFM tip is shown in Fig. 2, A to E, and a CO-terminated AFM tip in Fig. 2, F to J. The scan size was confined to the central area of the ring to prevent the tip from colliding with the Fe corral atoms. A constant height mode at

close distance was required because the vdW force between tip and sample was $\sim 10\,000$ times larger than the bonding force between quantum corral and tip, and a very small change in height would induce a large change in vdW forces. Careful checks ruled out cross talk between current and force [see section 5 in (6)].

The raw data of the frequency shift recorded with a single-atom metal tip (Fig. 2A) was low-pass filtered to produce Fig. 2B. Both attractive and repulsive interactions apparently scaled well with the total charge density [see section 6 in (6)], so in Fig. 2C, we compared a frequency shift profile (left vertical axis) taken at constant height to the reverse total charge density of the corral states (right vertical axis, reversed) from Fig. 1F. The comparison of frequency shifts to surface charge densities is motivated by prior experiments on the interaction of metal tips with adatoms (18) and CO tips with organic molecules (20) as well as calculations on Pauli repulsion of CO tips (21, 22) where the force and thus the frequency shift was approximately proportional to the charge density. The decrease of the ripples' contrast with distance on an (x, z) plane can be seen in Fig. 2D, and Fig. 2E displays the exponential fading with distance of frequency shift and force (fit line in Fig. 2E). The experimental decay length of $\lambda_{\text{met}} = 55.7$ pm is near the calculated decay length of the charge density of the Bessel-type eigenstates $\lambda_B = 42.1$ pm of Eq. 1. The acquisition of this low-noise data requires an averaging technique that is explained in section 7 in (6).

The data for a CO terminated tip (Fig. 2, F to J) had two marked differences compared to the metal tip data. First, as expected from previous studies (23, 24), we observed an attractive (dark) image of the Cu(111) surface atoms spaced by 255 pm in Fig. 2F. Second, the faint contrast of the ripples caused by the Bessel-type eigenstates was repulsive and only $\sim 10\%$ of the magnitude for the metal tip of Fig. 2A at the same height z . The low-pass filtered version (Fig. 2G) of Fig. 2F showed the ripples more clearly but suppressed the atomic surface lattice.

The red trace in Fig. 2H shows an experimental frequency shift profile at constant height, again compared to a profile of the total charge density of the electrons in the corral. The fit between the experimental data and the total charge density was reasonable, except for the central peak that was much higher in the total charge density compared to the experimental data. A nearly perfect fit was obtained by setting the occupancy of each of the two spin states in $\psi_{5,0}$ that was closest to E_F to 0.7 [section 8 in (6); the reasoning for that occupancy discussed below]. Figure 2I showed the contrast evolution as a function of distance z , where the fit line in Fig. 2J resulted in a decay length of $\lambda_{\text{CO}} = 50.4$ p.m., again near the calculated vertical decay length of the charge density from Eq. 1 of $\lambda_B = 42.1$ pm and slightly less than for the metal tip with $\lambda_{\text{metal}} = 55.7$ p.m.

We conclude for the analysis of the data in Fig. 2 that the corral artificial atom interacted with the AFM probe tips in a similar way as natural atoms or molecules. For the metal tip, we observed covalent bonding, that is, an attractive interaction with the 2D corral atom. For a CO terminated tip, we observed Pauli repulsion between tip and the 2D corral atom (20).

Back-action in the measurement of a quantum state is a basic principle of quantum mechanics, and the proximity of the AFM tip will alter the corral quantum mechanical states, just as surface atoms interact via surface states (25–27). One effect of observation is the alteration of energy eigenvalues $E_{n,l}$ under the influence of an external potential V_{ts} where the shifted energy $E_{n,l}^*$ is approximated by perturbation theory:

$$E_{n,l}^* = E_{n,l} + \langle \psi_{n,l} | V_{ts} | \psi_{n,l} \rangle \quad (2)$$

Of all the occupied states in the quantum corral, the $\psi_{5,0}$ state was most sensitive to occupation changes induced by the tip-sample interaction as its energy eigenvalue is directly at E_F [see table S2 in (6) and Fig. 1D], and the finite width of the eigenstate energies must be considered. The quantum corral was coupled strongly to the Cu(111) substrate (11–13), which broadens the energy levels, as found experimentally in (2). According to the hard wall model, the energy of the $\psi_{5,0}$ state is exactly 440 meV [table S2 in (6)]. Given that the occupied range of the surface state band has some uncertainty [440 ± 10 meV (9)], the $\psi_{5,0}$ state should be about half-filled if the AFM tip is far away.

A repulsive interaction with the tip, where $\langle \psi_{5,0} | V_{ts} | \psi_{5,0} \rangle > 0$, reduces the filling of the $\psi_{5,0}$ state, and an attractive interaction with its negative matrix element increases its filling [see fig. S11 in (6)]. AFM can measure V_{ts} by integrating the force from a large distance to a close distance. All occupied states contribute to the force, but only the five occupied states with $l = 0$ are present in the center of the corral, and the weight of the five occupied states $\psi_{n,0}$ is proportional to the square of their respective amplitudes at $r = 0$. Thus, we can estimate the energy shift for one electron in a $\psi_{5,0}$ state to be -0.8 meV for the metal tip and $+130$ μ eV for the CO-terminated tip for the closest distance z that was probed in the center of the corral. When adding up the contribution of all occupied states in the center of the corral $\psi_{n,0}$ from $n = 1$ to 5 as explained in section 9 in (6), we obtained a bond energy for the metal tip of -5 meV and an (anti-) bond energy of about $+1$ meV for the CO-terminated tip. The repulsive interaction of the CO terminated tip led to a lower occupation of the $\psi_{5,0}$ state than what was observed for the attractive metal tip [section 8 in (6)]. Furthermore, close inspection of Fig. 2D shows that the height ratio (HR) between the central negative peak and the peaks left and right to it decreased when increasing the distance z from the minimum of 490 pm to 570 p.m., whereas the data for the CO tip in Fig. 2I

indicated that the HR rose slightly for increasing distances. The data showed that the attractive interaction of the metal tip led to a substantial increase of the population of the $\psi_{5,0}$ state but the weak repulsive interaction of the CO terminated tip only slightly depopulated it (6).

The perturbation caused by the tip on the corral states, based on the traces that make up Fig. 2D, is shown in Fig. 3A. The HR between the central peak and its two peaks next to it (Fig. 3B) decreased from ~ 2.2 at 440 pm away to ~ 1.2 for 540 pm away for the metal tip, but for the CO tip, it increased from ~ 0.6 to ~ 0.9 over the same distance range. The HR is related to the occupation of the $\psi_{5,0}$ state (Fig. 3B), and the reduction with the CO tip fits to a repulsive interaction that partially depopulated this state.

Note that the blue trace in Fig. 3B rose to larger HRs for distances decreasing to 440 p.m., indicating increasing attraction that led to the loss of the front atom of the tip when approaching closer [see section 10 of (6)]. However, the transition from attraction to repulsion between the metal atom and the corral states for very close distances could be inferred from the response of the corral states when placing an Fe adatom at the center of the corral. Placing the adatom as a substitute for the tip directly on the Cu substrate at a core distance of ≈ 200 pm to the surface plane should reduce the occupation of the $\psi_{5,0}$ state if it interacts repulsively, as shown as an STM topograph in Fig. 3C. In a constant-height AFM image of a frame with size 4.7 nm (Fig. 3D; see the green square in Fig. 3C), a trace through that image did not allow a clear assessment that the occupation of the $\psi_{5,0}$ state has changed as expected. However, scanning along a trace with a length of 12 nm (red line in Fig. 3C) covered a sufficiently large width of the corral states. In the experimental frequency shift (Fig. 3E), the green dashed line (total charge density for empty $\psi_{5,0}$ states) is lower than the black dashed curve (total charge density for a fully occupied $\psi_{5,0}$ state—note reversed scales). The match of the green dashed line to the experimental data in red suggests that the $\psi_{5,0}$ state is indeed empty [see fig. S22 in (6)].

We used STM to confirm the depletion of the $\psi_{5,0}$ state. If the two electrons that occupy the state were forced into the Cu substrate, the effect is larger in STM, which probes 10 versus 102. In Fig. 3C, the similar height of second and third rings of the corral states was confirmed by analyzing the traces in Fig. 3F. The red line is the experimental topographic trace, and the dashed blue and green lines show the surface charge densities at the Fermi level with a fully occupied and an empty $\psi_{5,0}$ state, respectively. The dashed green line with the empty $\psi_{5,0}$ state again showed better agreement to the experimental data in red outside the locations where the Fe adatoms (center and corral) contributed strongly to the current, as the tunneling channel into those states were not contained in the simulations.

Moving the additional adatom outside of the center lifts the degeneracy of $l \neq 0$ states with $\cos(l\phi)$ and $\sin(l\phi)$ azimuthal functions. The perturbative energy shift described in Eq. 2 is only valid for non-degenerate states, so we needed to compose new linear combinations of the degenerate $\pm l$ solutions expressed in Eq. 1 that diagonalize the perturbation operator. For the $\psi_{2,\pm 7}$ states, we created two linear combinations of the angular functions $\exp(\pm il\phi)$. The even solution $\cos(l\phi) = (\exp(il\phi) + \exp(-il\phi))/2$ has a maximal interaction with the extra atom at $\phi = 0$ and the odd solution $\sin(l\phi) = (\exp(il\phi) - \exp(-il\phi))/2i$ has a minimal interaction at this angle. If the atom interacts repulsively, the energy eigenvalue of the $\cos(l\phi)$ -solution will be higher than the one of the $\sin(l\phi)$ -solution such that the population of the $\cos(l\phi)$ -solution decreases.

Figure 3G shows the adatom at $x \approx 4$ nm where the $\psi_{2,\pm 7}$ states have a local maximum. The perturbation imposed by the adatom leads to the emergence of angular ripples with a $\sin^2(7\phi)$ dependence and 14 azimuthal local minima for angles $\phi_m = 2\pi m/14$ where m is an integer that runs from 0 to 13. Figure 3H shows the more precise numerical calculation with the tight-binding based code KWANT (28), explained in detail in section 11 in (6). The tight binding simulation of Fig. 3H revealed subtle details not observed in modelling by Bessel type eigenstates of Eq. 1. For example, the potential energy imposed by the 48 Fe atoms is not exactly invariant with the azimuthal angle ϕ , but invariant with respect to rotations of multiples of 60° . This shows up both in experiment and calculations, as the central rings in Fig. 3, G and H, are clearly hexagonal.

We repeated these measurements for a smaller corral with a radius of $r_c' = 3.565$ nm and 24 atoms and obtained similar bonding properties, where Fig. 4A shows an STM topograph. A constant height AFM scan indicated by the frame in Fig. 4A is shown in Fig. 4B. The energy spectrum of the 24 atom corral has only 10 states with 6 different eigenvalues ($\pm l$ states are degenerate) below E_F (Fig. 4C). The average surface charge density of the 24 atom corral is similar to the 48 atom corral, but its magnitude σ_{total} varies about three times as much, displayed in Fig. 4D. Correspondingly, the force contrast is about three times as high as for the 48 atom corral (Fig. 2E). To study the bonding properties of the small corral, we performed constant height AFM line scans over a height range from 450 to 1100 pm as shown in Fig. 4E, and the contrast is plotted as a function of distance over a height range from 450 to 550 pm in Fig. 4F. The decay rate of the contrast with distance is at $l_{\text{met}}' = 50.5$ pm again near the calculated value of $l_B = 42.1$ p.m. [see section 12 in (6) for more details].

STM has proven to be very useful for the study of quantized surface states (29–34), but it relies on tunneling electrons from the tip to the surface quantum state and to the bulk (or reverse), i.e., on transport. AFM not only allows to

study the chemical bonding properties of these states, but also images stationary states that do not contribute to conduction [see section 13 in (6)].

REFERENCES AND NOTES

1. M. A. Kastner, Artificial atoms. *Phys. Today* **46**, 24–31 (1993). [doi:10.1063/1.881393](https://doi.org/10.1063/1.881393)
2. M. F. Crommie, C. P. Lutz, D. M. Eigler, Confinement of electrons to quantum corrals on a metal surface. *Science* **262**, 218–220 (1993). [doi:10.1126/science.262.5131.218](https://doi.org/10.1126/science.262.5131.218) [Medline](#)
3. D. M. Eigler, E. K. Schweizer, Positioning single atoms with a scanning tunnelling microscope. *Nature* **344**, 524–526 (1990). [doi:10.1038/344524a0](https://doi.org/10.1038/344524a0)
4. G. Binnig, C. F. Quate, C. Gerber, Atomic force microscope. *Phys. Rev. Lett.* **56**, 930–933 (1986). [doi:10.1103/PhysRevLett.56.930](https://doi.org/10.1103/PhysRevLett.56.930) [Medline](#)
5. S. Kawai, A. S. Foster, T. Björkman, S. Nowakowska, J. Björk, F. F. Canova, L. H. Gade, T. A. Jung, E. Meyer, Van der Waals interactions and the limits of isolated atom models at interfaces. *Nat. Commun.* **7**, 11559 (2016). [doi:10.1038/ncomms11559](https://doi.org/10.1038/ncomms11559) [Medline](#)
6. See the supplementary materials.
7. A. Zangwill, *Physics at Surfaces* (Cambridge Univ. Press, 1988).
8. P. O. Gartland, S. Berge, B. J. Slagsvold, Photoelectric work function of a copper single crystal for the (100), (110), (111), and (112) faces. *Phys. Rev. Lett.* **28**, 738–739 (1972). [doi:10.1103/PhysRevLett.28.738](https://doi.org/10.1103/PhysRevLett.28.738)
9. S. D. Kevan, Effective-mass theory of simple surface states. *Phys. Rev. B Condens. Matter* **34**, 6713–6718 (1986). [doi:10.1103/PhysRevB.34.6713](https://doi.org/10.1103/PhysRevB.34.6713) [Medline](#)
10. M. F. Crommie, C. P. Lutz, D. M. Eigler, Imaging standing waves in a two-dimensional electron gas. *Nature* **363**, 524–527 (1993). [doi:10.1038/363524a0](https://doi.org/10.1038/363524a0)
11. E. J. Heller, M. F. Crommie, C. P. Lutz, D. M. Eigler, Scattering and absorption of surface electron waves in quantum corrals. *Nature* **369**, 464–466 (1994). [doi:10.1038/369464a0](https://doi.org/10.1038/369464a0)
12. M. F. Crommie, C. P. Lutz, D. M. Eigler, E. J. Heller, Quantum corrals. *Physica D* **83**, 98–108 (1995). [doi:10.1016/0167-2789\(94\)00254-N](https://doi.org/10.1016/0167-2789(94)00254-N)
13. G. A. Fiete, E. J. Heller, Colloquium: Theory of quantum corrals and quantum mirages. *Rev. Mod. Phys.* **75**, 933–948 (2003). [doi:10.1103/RevModPhys.75.933](https://doi.org/10.1103/RevModPhys.75.933)
14. Here, we only count the 11 valence electrons of Cu as its core electrons have much more negative bonding energies, while the 102 corral electrons are all in a very narrow energy range from -5.38 eV to -4.94 eV. We project the valence electrons onto the surface area of the atom to obtain a surface charge density rather than calculating a volume charge density. The reason is that the experimental situation of a 2D surface imposes a strong asymmetry between the in-plane coordinates x , y or r , and z , the coordinate normal to the surface.
15. T. R. Albrecht, P. Grütter, D. Horne, D. Rugar, Frequency modulation detection using high-Q cantilevers for enhanced force microscope sensitivity. *J. Appl. Phys.* **69**, 668–673 (1991). [doi:10.1063/1.347347](https://doi.org/10.1063/1.347347)
16. R. García, R. Perez, Dynamic atomic force microscopy methods. *Surf. Sci. Rep.* **47**, 197–301 (2002). [doi:10.1016/S0167-5729\(02\)00077-8](https://doi.org/10.1016/S0167-5729(02)00077-8)
17. S. Morita, F. J. Giessibl, E. Meyer, R. Wiesendanger, *Noncontact Atomic Force Microscopy* (Springer, 2015), vol. 3.
18. M. Ternes, C. González, C. P. Lutz, P. Hapala, F. J. Giessibl, P. Jelínek, A. J. Heinrich, Interplay of conductance, force, and structural change in metallic point contacts. *Phys. Rev. Lett.* **106**, 016802 (2011). [doi:10.1103/PhysRevLett.106.016802](https://doi.org/10.1103/PhysRevLett.106.016802) [Medline](#)
19. L. Bartels, G. Meyer, K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, G. Ertl, Dynamics of electron-induced manipulation of individual CO molecules on Cu(111). *Phys. Rev. Lett.* **80**, 2004–2007 (1998). [doi:10.1103/PhysRevLett.80.2004](https://doi.org/10.1103/PhysRevLett.80.2004)
20. L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, The chemical structure of a molecule resolved by atomic force microscopy. *Science* **325**, 1110–1114 (2009). [doi:10.1126/science.1176210](https://doi.org/10.1126/science.1176210) [Medline](#)
21. N. Moll, L. Gross, F. Mohn, A. Curioni, G. Meyer, The mechanisms underlying the enhanced resolution of atomic force microscopy with functionalized tips. *New J. Phys.* **12**, 125020 (2010). [doi:10.1088/1367-2630/12/12/125020](https://doi.org/10.1088/1367-2630/12/12/125020)
22. N. Moll, L. Gross, F. Mohn, A. Curioni, G. Meyer, A simple model of molecular imaging with noncontact atomic force microscopy. *New J. Phys.* **14**, 083023 (2012). [doi:10.1088/1367-2630/14/8/083023](https://doi.org/10.1088/1367-2630/14/8/083023)
23. B. Schuler, W. Liu, A. Tkatchenko, N. Moll, G. Meyer, A. Mistry, D. Fox, L. Gross,

- Adsorption geometry determination of single molecules by atomic force microscopy. *Phys. Rev. Lett.* **111**, 106103 (2013). [doi:10.1103/PhysRevLett.111.106103](https://doi.org/10.1103/PhysRevLett.111.106103) [Medline](#)
24. M. Emmrich, F. Huber, F. Pielmeier, J. Welker, T. Hofmann, M. Schneiderbauer, D. Meuer, S. Polesya, S. Mankovsky, D. Ködderitzsch, H. Ebert, F. J. Giessibl, Surface structure. Subatomic resolution force microscopy reveals internal structure and adsorption sites of small iron clusters. *Science* **348**, 308–311 (2015). [doi:10.1126/science.1219850](https://doi.org/10.1126/science.1219850) [Medline](#)
 25. J. Repp, F. Moresco, G. Meyer, K.-H. Rieder, P. Hyldgaard, M. Persson, Substrate mediated long-range oscillatory interaction between adatoms: Cu/Cu(111). *Phys. Rev. Lett.* **85**, 2981–2984 (2000). [doi:10.1103/PhysRevLett.85.2981](https://doi.org/10.1103/PhysRevLett.85.2981) [Medline](#)
 26. N. Knorr, H. Brune, A. Epplé, A. Hirstein, M. A. Schneider, K. Kern, Long-range adsorbate interactions mediated by a two-dimensional electron gas. *Phys. Rev. B Condens. Matter Mater. Phys.* **65**, 115420 (2002). [doi:10.1103/PhysRevB.65.115420](https://doi.org/10.1103/PhysRevB.65.115420)
 27. K. Morgenstern, K.-F. Braun, K.-H. Rieder, Direct imaging of Cu dimer formation, motion, and interaction with Cu atoms on Ag(111). *Phys. Rev. Lett.* **93**, 056102 (2004). [doi:10.1103/PhysRevLett.93.056102](https://doi.org/10.1103/PhysRevLett.93.056102) [Medline](#)
 28. C. W. Groth, M. Wimmer, A. R. Akhmerov, X. Waintal, Kwant: A software package for quantum transport. *New J. Phys.* **16**, 063065 (2014). [doi:10.1088/1367-2630/16/6/063065](https://doi.org/10.1088/1367-2630/16/6/063065)
 29. H. C. Manoharan, C. P. Lutz, D. M. Eigler, Quantum mirages formed by coherent projection of electronic structure. *Nature* **403**, 512–515 (2000). [doi:10.1038/35000508](https://doi.org/10.1038/35000508) [Medline](#)
 30. K. K. Gomes, W. Mar, W. Ko, F. Guinea, H. C. Manoharan, Designer Dirac fermions and topological phases in molecular graphene. *Nature* **483**, 306–310 (2012). [doi:10.1038/nature10941](https://doi.org/10.1038/nature10941) [Medline](#)
 31. K. Seufert, W. Auwärter, F. J. García de Abajo, D. Eciija, S. Vijayaraghavan, S. Joshi, J. V. Barth, Controlled interaction of surface quantum-well electronic states. *Nano Lett.* **13**, 6130–6135 (2013). [doi:10.1021/nl403459m](https://doi.org/10.1021/nl403459m) [Medline](#)
 32. A. A. Khajetoorians, D. Wegner, A. F. Otte, I. Swart, Creating designer quantum states of matter atom-by-atom. *Nat. Rev. Phys.* **1**, 703–715 (2019). [doi:10.1038/s42254-019-0108-5](https://doi.org/10.1038/s42254-019-0108-5)
 33. L. Yan, P. Liljeroth, Engineered electronic states in atomically precise artificial lattices and graphene nanoribbons. *Adv. Phys.* **X4**, 1651672 (2019). [doi:10.1080/23746149.2019.1651672](https://doi.org/10.1080/23746149.2019.1651672)
 34. S. E. Freney, S. T. P. Borman, J. W. Harteveld, I. Swart, Coupling quantum corrals to form artificial molecules. *SciPost Phys.* **9**, 085 (2020). [doi:10.21468/SciPostPhys.9.6.085](https://doi.org/10.21468/SciPostPhys.9.6.085)
 35. F. Queck-Scharrer, "Implementierung der Rastertunnelmikroskopie auf Isolatoren," PhD thesis, Physics Department, University of Regensburg, Regensburg, Germany (2019); <https://epub.uni-regensburg.de/38271/>
 36. Numerical data for: F. Stilp, A. Bereczuk, J. Berwanger, N. Mundigl, K. Richter, F. J. Giessibl, Very weak bonds to artificial atoms formed by quantum corrals, University of Regensburg (2021); <https://doi.org/10.5283/epub.45631>
 37. F. J. Giessibl, The qPlus sensor, a powerful core for the atomic force microscope. *Rev. Sci. Instrum.* **90**, 011101 (2019). [doi:10.1063/1.5052264](https://doi.org/10.1063/1.5052264) [Medline](#)
 38. J. Welker, F. J. Giessibl, Revealing the angular symmetry of chemical bonds by atomic force microscopy. *Science* **336**, 444–449 (2012). [doi:10.1126/science.1219850](https://doi.org/10.1126/science.1219850) [Medline](#)
 39. F. Huber, F. J. Giessibl, Low noise current preamplifier for qPlus sensor deflection signal detection in atomic force microscopy at room and low temperatures. *Rev. Sci. Instrum.* **88**, 073702 (2017). [doi:10.1063/1.4993737](https://doi.org/10.1063/1.4993737) [Medline](#)
 40. C. J. Chen, *Introduction to Scanning Tunneling Microscopy* (Oxford Univ. Press, 1993).
 41. F. Huber, J. Berwanger, S. Polesya, S. Mankovsky, H. Ebert, F. J. Giessibl, Chemical bond formation showing a transition from physisorption to chemisorption. *Science* **366**, 235–238 (2019). [doi:10.1126/science.aay3444](https://doi.org/10.1126/science.aay3444) [Medline](#)
 42. J. A. Stroscio, D. M. Eigler, Atomic and molecular manipulation with the scanning tunneling microscope. *Science* **254**, 1319–1326 (1991). [doi:10.1126/science.254.5036.1319](https://doi.org/10.1126/science.254.5036.1319) [Medline](#)
 43. M. Schneiderbauer, M. Emmrich, A. J. Weymouth, F. J. Giessibl, CO tip functionalization inverts atomic force microscopy contrast via short-range electrostatic forces. *Phys. Rev. Lett.* **112**, 166102 (2014). [doi:10.1103/PhysRevLett.112.166102](https://doi.org/10.1103/PhysRevLett.112.166102) [Medline](#)
 44. O. Gretz, A. J. Weymouth, F. J. Giessibl, Identifying the atomic configuration of the tip apex using STM and frequency-modulation AFM with CO on Pt(111). *Phys. Rev. Res.* **2**, 033094 (2020). [doi:10.1103/PhysRevResearch.2.033094](https://doi.org/10.1103/PhysRevResearch.2.033094)
 45. I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, A. M. Baro, WSXM: A software for scanning probe microscopy and a tool for nanotechnology. *Rev. Sci. Instrum.* **78**, 013705 (2007). [doi:10.1063/1.2432410](https://doi.org/10.1063/1.2432410) [Medline](#)
 46. L. Gross, N. Moll, F. Mohn, A. Curioni, G. Meyer, F. Hanke, M. Persson, High-resolution molecular orbital imaging using a p-wave STM tip. *Phys. Rev. Lett.* **107**, 086101 (2011). [doi:10.1103/PhysRevLett.107.086101](https://doi.org/10.1103/PhysRevLett.107.086101) [Medline](#)
 47. R. P. Feynman, R. B. Leighton, M. Sands, *The Feynman Lectures on Physics II*. (Addison-Wesley, 1963).
 48. A. Liebig, A. Peronio, D. Meuer, A. J. Weymouth, F. J. Giessibl, High-precision atomic force microscopy with atomically-characterized tips. *New J. Phys.* **22**, 063040 (2020). [doi:10.1088/1367-2630/ab8ef4](https://doi.org/10.1088/1367-2630/ab8ef4)
 49. N. D. Lang, W. Kohn, Theory of metal surfaces: Charge density and surface energy. *Phys. Rev. B* **1**, 4555–4568 (1970). [doi:10.1103/PhysRevB.1.4555](https://doi.org/10.1103/PhysRevB.1.4555)
 50. F. J. Giessibl, A direct method to calculate tip-sample forces from frequency shifts in frequency-modulation atomic force microscopy. *Appl. Phys. Lett.* **78**, 123–125 (2001). [doi:10.1063/1.1335546](https://doi.org/10.1063/1.1335546)
 51. A. J. Weymouth, T. Wutscher, J. Welker, T. Hofmann, F. J. Giessibl, Phantom force induced by tunneling current: A characterization on Si(111). *Phys. Rev. Lett.* **106**, 226801 (2011). [doi:10.1103/PhysRevLett.106.226801](https://doi.org/10.1103/PhysRevLett.106.226801) [Medline](#)

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SUPPLEMENTARY MATERIALS

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Materials and Methods

Figs. S1 to S22

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References (37–51)

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Fig. 1. Quantum corral consisting of 48 Fe atoms on Cu (111). (A) Topographic STM image at a tip bias of -1 mV and a tunneling current of 20 pA using a CO terminated tip. The ring has a radius of 7.13 nm, the Cu atoms of the Cu(111) substrate appear as peaks with a height of ≈ 500 fm and a distance of 255 p.m. (B) Energy diagram of the electrons on the Cu(111) surface with vacuum level at 0 , the Fermi energy E_F at -4.94 eV, and the lowest energy of the surface state E_0 another -0.44 eV lower. (C) Energy spectrum of the occupied surface states on the Cu(111) surface with a shifted energy scale $E' = E - E_0$ and dispersion relation $E' = \hbar^2 k^2 / (2m^*)$. (D) Energy spectrum of the occupied corral states, characterized by the number of zeroes n and the angular momentum l . The states at the Fermi level (blue) are imaged by STM at low bias (2). (E) Calculated surface charge density σ_{Fermi} of the states at the Fermi level, dashed line without contribution of $\psi_{5,0}$. (F) Calculated surface charge density of all occupied states σ_{total} , dashed line without contribution of $\psi_{5,0}$. Surface charge densities are calculated using the Bessel-type eigenstates defined in (6).

Fig. 2. AFM data inside the quantum corral for a single atom metal tip (left column) and a CO terminated tip (right column). (A) Frequency shift data $\Delta f(x, y, z = \text{const.})$ with an attractive interaction between the probe tip and the Bessel-type eigenstates. (B) Low-pass filtered version of (A). (C) Profile line through the center of B and reversed total surface charge density of the corral. (D) Gray-scale representation of offset and slope corrected frequency shift $\Delta f_{\text{rel}}(x, 0, z)$. (E) Distance dependence of the contrast, defined as the difference between the average of the first and second maxima and the minimum in between. (F) Frequency shift data $\Delta f(x, y, z = \text{const.})$, showing attraction to the Cu surface atoms and repulsion to the Bessel-type eigenstates. (G) Low-pass filtered version of F, showing only the repulsion to the Bessel-type eigenstates. (H) Profile line through center of G compared to total charge density. (I) Gray scale presentation of offset and slope corrected frequency shift $\Delta f_{\text{rel}}(x, 0, z)$. (J) Contrast, defined by the difference between the first maximum at $x \approx \pm 1.3$ nm and the average between the first and second minimum, evolution as a function of vertical distance z . See section 7 in (6) for details of data extraction.

Fig. 3. Impact of the perturbation inflicted by the AFM tip [(A) and (B)] and a deliberately placed metal adatom inside [(C) to (H)]. (A) AFM traces (single atom metal tip) through the center of the corral for five different heights. (B) Relative depth of the central dip in traces from A as a function of distance z and corresponding occupation of $\psi_{5,0}$ with a metal tip (blue) and a CO terminated tip (yellow). (C) Topographic STM image of the corral with an extra Fe adatom located at the center of the corral. Tip bias -10 mV, current 10 pA (D) Constant height AFM data within green square in (C). (E) Off-center line trace of $\Delta f(x, y = 830 \text{ p.m.}, z = \text{const.})$, shown as red trace in (C) and comparison to total charge density σ_{total} (black) and σ_{total} minus the contribution of $\psi_{5,0}$ (green). (F) Central STM topography trace (red) through the corral with an additional adatom in its center and comparison to full contribution of $\psi_{5,0}$, $\psi_{4,\pm 2}$, and $\psi_{2,\pm 7}$ (blue) states and without the $\psi_{5,0}$ state (green). (G) Experimental topographic STM image of the corral with an extra Fe adatom located at $r = 4.048 \text{ nm}$ and $\phi = 0$. The states $\psi_{2,\pm 7}$ have a local maximum close to $r = 4 \text{ nm}$, therefore the $\cos^2(7\phi)$ component is lifted in energy and its occupation is reduced, while its $\sin^2(7\phi)$ component is affected less. Tip bias -10 mV, current 10 pA. (H) Calculated topographic STM image of G using the tight binding simulations (6). Note that the direct current channel into the corral atoms and extra Fe atom is not considered in the calculation, similar as in Fig. 3 of (11).

Fig. 4. Quantum corral with 24 Fe adatoms and a radius of $r_c' = 3.565$ nm. (A) STM topograph at tip bias -10 mV. (B) Constant height AFM data inside the corral. (C) Energy spectrum, states near E_F in blue. (D) Total charge density σ_{total}' (black) modeled by using a weight of 1 for all occupied states and charge density at the Fermi level σ_{Fermi}' (blue) modeled by a weight of 1 for the $y_{1,\pm 4}$ states and a weight of 0.4438 for the $y_{2,\pm 1}$ states [see section 12 of (6) for details]. (E) Frequency shift as a function of lateral and vertical coordinates y and z . (F) Plot of contrast in frequency shift as a function of vertical coordinate z showing an exponential decay with a decay length $l_{\text{met}}' = 50.5$ p.m.