

# Coupling quantum corrals to form artificial molecules

Response to referee report 1: Robert Droste

We are grateful for the positive review that Robert Droste has submitted in response to our manuscript. We would like to thank him in particular for the time and effort he gave for his very thorough and insightful evaluation. This helps us to give clearer explanations and a fuller picture of our work. Below, we reply in detail to all comments.

## 1. Comment about the overlap integral:

“Concerning Fig. 2, the centre corral of the trimer has a slightly different area and confinement potential from those at the ends and therefore does not share the same wave function with the end sites. The overlap integrals in Eqs. (1) and (2) and that in Eqs. (3) through (5) are not identical. While I think that the approximation to treat them as such is justified, it would be good to briefly acknowledge this in the text.”

**Response:** It is certainly true that these overlaps are different. To approximate them as equal to each other allows us to find a solution using the five equations given in the text. This would otherwise not be possible because we would then have 6 unknowns but 5 equations.

**Action:** On page 5, we added the following sentence: "We make the assumption that the overlap integral is the same for the dimer and trimer."

## 2. Question about consistency of y-axes on differential conductance spectra

“Fig. 3 uses the label 'Corrected  $dI/dV$ ' while all other figures with conductance spectra read 'background corrected  $dI/dV$ '. Are both referring to the same procedure described in section 2 of the manuscript?”

**Response:** Indeed, all processing has been carried out in the same way.

**Action:** In the revised version, all labels have been made consistent.

## 3. Question about the formatting/representation of differential conductance spectra

“What are the faded dots that appear in the plots of conductance spectra? I assume that the lines represent the averages mentioned in section 2. Are the dots raw data? It would be good to have a brief explanation if both are to be shown.”

**Response:** Thank you for pointing this out. The dots represent the average of spectra taken at the same (or equivalent) sites and then divided by the average Cu(111) spectrum acquired with the same tip state. The smooth line above represents the moving average of this data.

**Action:** We've added the following sentence to the methods section: “In each spectrum shown, the faded points represent the data after the aforementioned procedure, while the solid line represents the moving average of the same data.”

#### 4. Indication of erroneously swapped marker colours

“Concerning Fig.3, I believe that there must have been a mix-up with the marker and curve colours. The red and green curves are nearly identical, even though they are seemingly measured at different locations. The red and blue curve are qualitatively different even though they have been acquired at symmetrically (nearly) identical points of the corral. The blue curve is the only data set showing a signature of the (2, 2)-state even though it has a nodal plane at the indicated location. Please double-check the assignments.”

**Answer:** The comment is totally correct, the positions of blue and green markers were swapped in the image. Thank you for noticing this.

**Action:** We have corrected this.

#### 5. Questions about the gradients of the plots in Figure 4 of the main text and the effective mass.

“Concerning the relationship between the corral size and on-site energy discussed in Fig. 4, I estimate the slope of the graph in Fig. 4c to be ca.  $-0.33 \text{ eVnm}^{-2}$  and that in Fig. 4f ca.  $0.66 \text{ eVnm}^{-2}$ . There are two issues here: First, why is the slope in Fig. 4c negative? I get  $m^* \approx -0.46m_e$  from my estimate. The value is the same as that reported in the paper, but what of the sign?”

**Response:** The slope should indeed be negative. In the original version, a constant term  $V_0$  was accidentally omitted from equation 6. As described in ref 36, the energies of a particle in a 2D box with finite barriers are given by

$$E = V_0 - \frac{2\hbar^2}{m^*} \left( \frac{u_{n_x}^2}{L_x^2} + \frac{u_{n_y}^2}{L_y^2} \right)$$

This equation naturally gives rise to a negative slope. We attach a document to clarify the origin of this equation further, also see reference 36 of the article.

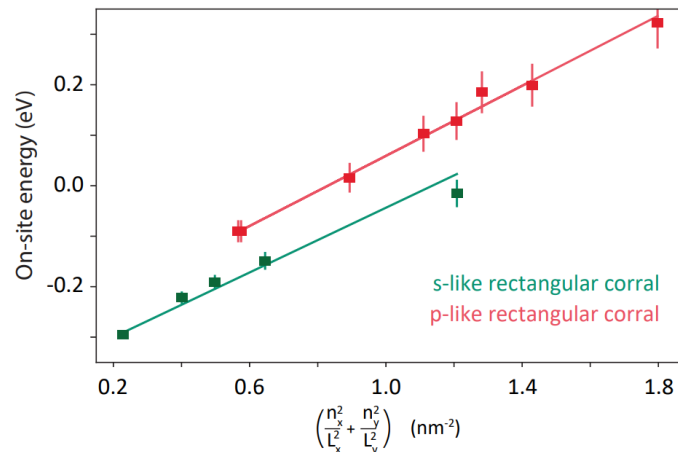
**Action:** We corrected equation 6 and added a more explicit reference to a textbook describing the particle in a 2D box with finite barriers.

c) “Second, the effective mass extracted from Fig. 4f comes to ca.  $1.3m_e$  for me. This is somewhat surprising. Why should  $m^*$  depend on the shape of the confining potential? A brief discussion would be good.”

**Response:** To derive a correct value of the effective mass, the finite barrier height should be taken into account. The energy equation provided for the triangular corrals is for systems with infinitely high potential barriers. This equation establishes the inverse relationship between area and energy. Indeed, using this equation and the gradient of the plot of the s-like state in figure 4.f will result in an effective mass of  $1.27m_e$ . However, the barriers in the experimental system are finite, so the effective mass calculated from the infinite barrier equation is not accurate. To see that this is the case, consider a rectangular corral with infinite barriers. The allowed energies for a particle in a 2D well with infinite barriers are given by

$$E = \frac{\hbar^2 \pi^2}{2m^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

Below, we show a plot of experimental on-site energy vs  $n_x^2/L_x^2 + n_y^2/L_y^2$ , where  $n_x$  and  $n_y$  are quantum numbers.



If we determine the effective mass from these plots using the equation given above, we find  $m^* = 1.17 \pm 0.01m_e$  and  $m^* = 1.08 \pm 0.01m_e$  for the s-like ( $n_x = 1, n_y = 1$ ) and p-like ( $n_x = 2, n_y = 1$ ) states, respectively.

Since the concept of the effective mass was defined to describe an electron in a (periodic) lattice, one would expect the effective mass for electrons in a quantum corral on Cu(111) to be close to that of the surface state electrons ( $\sim 0.42m_e$ ).

We have been unable to find an analytical solution of the Schrödinger equation for a particle in a 2D triangular box with finite barriers. Hence, we refrain from extracting a value of the effective mass.

## 6. Question about equation 7 and definition of terms

a) "Eq. (7) is a little difficult to follow. Under what conditions of the upper and lower expression after the curly braces in the equation hold?"

**Response:** We agree that the discussion related to eq. 7 was difficult to follow.

**Action:** We have modified the discussion about the 2D particle in a box with finite potential walls.

b) "What is  $V_0$  used in the definitions of  $u_0$  and  $v_i$ ? It seems that this is the height of the scattering potential discussed earlier, but there is no explicit assignment."

**Response:**  $V_0$  is indeed the potential barrier height.

**Action:** On page 7, we modified a sentence to make the meaning of  $V_0$  explicit: "To rationalize the experimental observations, we model our system using a particle-in-a-box model with finite potential barriers of height  $V_0 = 0.9 \text{ eV}$ "

c) "The quantity  $u_i$  is defined following Eq. (7), but does not seem to appear in it, nor in  $u_0$  or  $v_i$  defined before."

**Response:** Indeed, the definition is not clear. We have modified the text.

**Action:** We have modified the text, which now reads “The variables  $u_{nx}$  and  $u_{ny}$  take the role of quantum numbers. Their values are the solutions to the following set of three equations (where  $i$  denotes the x or y direction of the rectangular box)

$$u_i = \sqrt{u_{0i}^2 - v_i^2} \quad (7)$$

$$u_i = v_i \tan(v_i) \quad (8)$$

$$u_i = v_i \cot(v_i) \quad (9)$$

with  $u_i = \sqrt{2m^*(V_0 - E)}L_i / 2\hbar$ ,  $u_{0i} = \sqrt{2m^*V_0}L_i / 2\hbar$  and  $v_i = \sqrt{2m^*E}L_i / 2\hbar$ . No analytical solutions exist for these equations and one has to rely on graphical or numerical methods [36]. The solutions are given by the values of  $u_i$  where function (7) intersects function (8) or (9), and are denoted  $u_{ni}$ . For a given  $V_0$ ,  $L_i$  and effective mass, the values of  $u_{ni}$  are fixed, and can be thought of as analogous to the quantum number in the energy equation that describes a particle in a 2D rectangular box with infinite barriers.”

## 7. Question about coupling states

a) “On page 11, end of the first paragraph, the authors write: ‘The results reported here suggest that a full barrier would result in negligible coupling between states in a lattice and the surrounding 2DEG.’ I do not believe that the data presented support the claim with this level of generality.”

**Response:** We agree that this statement can be more precise. Our experiments provide an upper-limit to the coupling strength across a ‘full barrier’: any potential splitting of the bonding and antibonding states is smaller than the energy resolution of our experiments.

To further estimate the coupling in case of a full-barrier, we performed a muffin-tin calculation on a dimer using the largest square corral with a “full” barrier between corrals. In muffin tin, one adds broadening artificially, thus we can set it to a very low value to reveal the energy difference between bonding and antibonding states. This calculation reveals a splitting of only 11mV. For comparison, the dimer with the smallest gap width that we reported (calculated with muffin tin as well) had a 12mV difference in energy, which gave the parameters:  $\epsilon = -0.313$ ,  $s = 0.124$ ,  $t = -0.044$ .

**Action:** We have modified the sentence referred to by the referee to: “Our experiments provide an upper-limit to the coupling strength across a ‘full barrier’: any potential splitting of the bonding and antibonding states is smaller than the energy resolution of our experiments. A muffin-tin calculation using small broadening finds a peak splitting of 11 meV (suggesting an upper limit of the coupling strength of 5.5 meV).”

b) “It is clear from Fig. 4 that the broadening of the corral states is a function of the on-site energy and/or the corral area. It is difficult to imagine another mechanism than lifetime broadening from particle loss to the 2DEG and bulk states.”

**Response:** We agree with the referee.

## 8. Suggestion for changing the x-coordinate of figure 7

“Concerning Fig. 7, I would consider using the number of missing CO molecules as the x-coordinate of the plots in panels b and c. It seems a much more intuitive length scale given to me.”

**Response:** We feel that giving the gap size in nm is more general, and therefore more useful for future readers. Also note that the actual gap size that appears for a given CO depends on the direction along which the barrier is constructed on the surface, e.g. the size of the gap will be different for the close-packed direction  $[(1\bar{1}0)]$ , than for the  $(\bar{2}\bar{2}1)$  direction. We therefore prefer to keep the present x-coordinate.