Supplemental Material for
Magnetic character of holmium atom adsorbed on platinum surface

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SUPERCELL MODEL

FIG. S1: (Color online) Schematic supercell model for Ho adatom on Pt(111).

BATH STATE PARAMETERS USED IN DFT+ED

TABLE S1: 4f-states occupations $n_{5/2}^f$ and $n_{7/2}^f$, and bath state parameters $\epsilon_{5/2,7/2}^l$ (eV), $V_{5/2,7/2}^l$ (eV) for bulk Ho, and Ho adatom on Pt(111) surface in the hcp and fcc positions from LDA calculations.

| Material      | $n_{5/2}^f$ | $n_{7/2}^f$ | $\epsilon_{5/2}^l$ | $V_{5/2}^l$ | $\epsilon_{7/2}^l$ | $V_{7/2}^l$ |
|---------------|-------------|-------------|---------------------|-------------|---------------------|-------------|
| hcp-Ho-bulk   | 5.99        | 4.56        | -0.09               | 0.15        | 0.105               | 0.11        |
| hcp-Ho@Pt     | 5.93        | 4.62        | 0.20                | 0.095       | -0.06               | 0.087       |
| fcc-Ho@Pt     | 5.93        | 4.73        | 0.25                | 0.097       | -0.065              | 0.087       |

CHOICE OF THE DOUBLE-COUNTING

No unique choice of the double counting exists in DFT+U and DFT+ED calculations, and “physical” arguments prevail in the choice of $W_{dc}$. In previously reported LDA+Hubbard I calculations (HIA) for the bulk Ho [1], the $W_{dc}$ was fixed to adjust the position of the first multiplet peak below $E_F$, which was measured by experimental valence-band photoelectron spectroscopy (PES) [2].
Since no PES results exist for Ho@Pt, we assumed the transferability of $W_{dc}$, and performed the DFT+ED calculations for the bulk Ho in the paramagnetic state ($\Delta_{ex}=0$ in Eq. (1) of the main text) making use of the experimental lattice parameter value $a$ and the $c/a$ ratio. The resulting densities of state (DOS) obtained in DFT+ED with “fully localized” limit (FLL) [3] and “around-mean-field” (AMF) [4] flavours for $W_{dc}$ are shown in Fig. S2. The FLL results are in striking disagreement with the experimental data [2]. DFT+ED-AMF gives the positions and the spectral shape of the occupied 4$f$-states in a reasonable agreement with the experiment (first multiplet peak at 3.3 eV below $E_F$), and a bit worse for the empty 4$f$-states (first multiplet peak at 3.8 eV above $E_F$). Comparison with experimental valence-band photoelectron spectroscopy (PES) is often taken as important criterion of truthfulness of electronic structure calculations. Thus, we conclude that AMF flavour is a better approximation, and places the 4$f$-level $\epsilon_f$ in Eq. (1) correctly. Therefore, this form of $W_{dc}$ is used in the further calculations.

In Fig. S2C we show the total DOS per Ho atom for comparison with the results of [5]. There is a good agreement between these two calculations. The difference in the energy positions of the $f$-peaks is caused by a different choice of $W_{dc}$. In [5], it was adjusted so that the position of the first multiplet peak below $E_F$ matched the experimental PES.
RESULTS OF DFT+HIA CALCULATIONS.

We performed the DFT+HIA calculations without hybridization term in Eq. (1) of the main text. For the \textit{fcc-Ho@Pt}, the ground state of the Ho adatom, the solution of Eq. (3) of the main text, has $\langle n_f \rangle = 10.18$ \textit{f}-electrons. The out-of-plane directed spin $M_S$, and the orbital $M_L$ magnetic moments for the \textit{f}-shell calculated using the
local Green function Eq. (2) are shown in Table S2, in comparison with previously reported DFT+U results of [6, 7]. Note that DFT+U results were obtained with the same Korringa-Kohn-Rostoker (KKR) method [8] and differ for a reason which is not completely clear. It is seen that the DFT+U results exceed substantially the experimental values for both $M_S$ and $M_L$ obtained in the XMCD experiments [9] shown in Table I of the main text. The use of DFT+HIA brings the results closer to the XMCD [9] data for both the spin $M_S$ and the orbital $M_L$ components of the total moment $M_T$. No noticeable differences are found for Ho@Pt in fcc and hcp positions.

TABLE S2: Spin ($M_S$), and orbital ($M_L$) magnetic moments (in $\mu_B$) and 4$f$ occupation $n_f$ of the Ho adatom on Pt(111) from DFT+HIA calculations with $\Delta_{ex} = 10$ meV.

| Site        | $n_f$ | $M_S$ | $M_L$ | $n_f$ | $M_S$ | $M_L$ |
|-------------|-------|-------|-------|-------|-------|-------|
| DFT+U [6]   | N/A   | 4.1   | 5.6   | N/A   | 3.9   | 5.45  |
| DFT+U [7]   | 10.14 | 3.91  | 5.88  | 10.14 | 3.91  | 5.88  |
| DFT+HIA     | 10.18 | 3.28  | 5.16  | 10.17 | 3.25  | 5.17  |

DETAILS OF THE DFT+ED CALCULATIONS.

| Energy (meV) | $\langle L_z \rangle$ | $\langle S_z \rangle$ | $\langle J_z \rangle$ |
|-------------|----------------------|----------------------|----------------------|
| 0.0         | 5.32                 | 1.67                 | 7.00                 |
| 9.8         | 4.59                 | 1.39                 | 5.98                 |
| 15.8        | -0.01                | 0.02                 | 0.02                 |
| 17.6        | 0.72                 | 0.28                 | 1.00                 |
| 22.8        | -0.74                | -0.24                | -0.98                |
| 26.5        | 1.47                 | 0.52                 | 2.00                 |
| 29.0        | 3.83                 | 1.14                 | 4.97                 |
| 33.4        | -5.33                | -1.66                | -6.99                |
| 36.4        | 2.25                 | 0.74                 | 2.99                 |
| 36.5        | -1.38                | -0.44                | -1.82                |
| 37.6        | -4.62                | -1.38                | -6.00                |
| 39.2        | 2.92                 | 0.89                 | 3.82                 |
| 45.8        | 6.13                 | 1.86                 | 8.00                 |
| 50.9        | -2.29                | -0.70                | -2.99                |
| 51.7        | -3.88                | -1.12                | -5.00                |
| 57.6        | -3.09                | -0.90                | -4.00                |
| 83.1        | -6.15                | -1.86                | -8.00                |

| Energy (meV) | $\langle L_z \rangle$ | $\langle S_z \rangle$ | $\langle J_z \rangle$ |
|-------------|----------------------|----------------------|----------------------|
| 0.0         | -6.08                | -1.87                | -7.95                |
| 0.0         | 6.08                 | 1.87                 | 7.95                 |
| 6.5         | -4.10                | -1.26                | -5.37                |
| 6.5         | 4.10                 | 1.26                 | 5.37                 |
| 7.9         | 0.00                 | 0.00                 | 0.00                 |
| 11.7        | -1.34                | -0.41                | -1.75                |
| 13.2        | -0.51                | -0.17                | -0.68                |
| 13.2        | 0.51                 | 0.17                 | 0.68                 |
| 14.8        | 0.00                 | 0.00                 | 0.00                 |
| 17.1        | -0.01                | 0.00                 | -0.01                |
| 20.2        | 0.01                 | 0.00                 | 0.01                 |
| 24.8        | -3.16                | -0.95                | -4.11                |
| 24.8        | 3.16                 | 0.95                 | 4.11                 |
| 26.6        | 0.00                 | 0.00                 | 0.00                 |
| 26.6        | -2.02                | -0.61                | -2.63                |
| 26.6        | 2.02                 | 0.61                 | 2.63                 |

TABLE S3: (Color online) The magnetic moments and energies from Eq. (1) of the main text for spin-polarized case (left panel, also shown in Fig. 2(A) of the main text); for paramagnetic case (right panel, also shown in Fig. 2(B) of the main text).

$$\begin{bmatrix} 0.035 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.012 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.014 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & -0.059 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.000 & 0.014 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.012 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.001 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.035 & 0.000 & 0.000 & 0.000 \\ \end{bmatrix} \begin{bmatrix} -0.001 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & -0.012 \\ 0.000 & -0.013 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.037 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & -0.049 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.037 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & -0.013 & 0.000 \\ -0.012 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & -0.001 \\ \end{bmatrix}$$

TABLE S4: (Color online) fcc-Ho@Pt(111): Self-consistent $\Delta_{C_{5v}}$ (eV) determined from the local hamiltonian Eq. (4) of the main text from the spin-polarized calculations with $\Delta_{ex} = 10$ meV (left panel); from the paramagnetic calculations (right panel).
INELASTIC SCANNING TUNNELING SPECTRA

The IETS is described with the total hamiltonian of the form [10]

\[ H = H_{\text{tip}} + H_{\text{sur}} + H_{\text{imp}}, \]

(S1)

where \( H_{\text{tip}} = \sum_{k,\sigma} \epsilon_{k,\sigma}^{(\text{tip})} a_k^{\dagger} a_k \) corresponds to the electrons in the tip with energies \( \epsilon_{k,\sigma}^{(\text{tip})} \) and \( H_{\text{sur}} = \sum_{k,\sigma} \epsilon_{k,\sigma}^{(\text{sur})} b_k^{\dagger} b_k \) describes the electrons in the surface with energies \( \epsilon_{k,\sigma}^{(\text{sur})} \). The adatom hamiltonian \( H_{\text{imp}} \) is given by Eq. (1) of the main text with eigenvalues \( \epsilon_M \) and eigenvectors \( |M\rangle \).

For the spin-flip tunneling,

\[ H_{\text{tun}} = \sum_{\sigma \neq \sigma'} \tau_{\sigma\sigma'} \tilde{J}_{\sigma\sigma'} \left( a_k^{\dagger} b_{k'}^{\dagger} + b_k^{\dagger} a_{k'} \right). \]

(S2)

In the above equation \( \tau_{\sigma} \) are the Pauli matrices, \( J_{\alpha} \) are the total moment operators (\( \alpha = x, y, z \)), and \( g \) is the Lande factor. The \( t_1 \) tunnelling matrix element is proportional to the square of hybridization parameters \( V_k \) shown in Table S1.

The differential conductance \( G = \frac{\partial I}{\partial V} \) is, [10]

\[ G = G_S \sum_{MM'} \sum_{s=\pm 1} P_M |\langle M | \tilde{J} | M' \rangle|^2 \left( \frac{1}{1 - e^{\beta(\Delta_{M'\text{'},M}-sV)}} + \frac{\beta(\Delta_{M'\text{'},M}-sV)}{4 \sinh^2 \left( \frac{\beta(\Delta_{M'\text{'},M}-sV)}{2} \right)} \right), \]

(S3)

where, \( \Delta_{M'\text{'},M} = \epsilon_{M'} - \epsilon_M \), \( P_M \) is the statistical weight of the eigenstate \( |M\rangle \), and \( G_S = (g-1)^2 t_1^2 \rho_{\text{sur}}(\epsilon_F) \rho_{\text{tip}}(\epsilon_F) \) proportional to the hybridization, and to the surface/tip DOS at the Fermi edge. \( V \) is an external voltage.

![FIG. S3: (Color online) Spin excitation spectrum of Ho adatom on Pt(111).](image-url)

The IETS spectrum for Ho adatom on Pt(111) in spin-polarized state (see Table S3) calculated using the model Eq. (S3) is shown in Fig. S3. It is seen that the calculation gives a shallow step at the voltage \( \pm 10 \text{ meV} \). Other step(s) occur at the higher energy range (over 40 meV).

The \( G_S \) in Eq. (S3) is proportional to the square of hybridization strength \( t_1 \) multiplied by a prefactor \( (g-1)^2 \) where \( g \) is the Lande factor. Assuming that the most important contribution to the tunnelling comes from the hybridization occurring in the vicinity of \( E_F \), and taking into account that the \( t_1 \sim |V_k|^2 \) shown in Table S1, we obtain the hybridization strength in the range of 12-23 meV. The prefactor \( G_S \) is reduced further by \( (g-1)^2 = 0.05 \) where the Lande factor \( g=1.23 \) for \( J = 8 \) many body state.
SCENARIO FOR MAGNETIC INSTABILITY OF Ho@Pt(111)

After the magnetic field is removed, the magnetization starts to evolve. We keep in mind that the 4f shell and 5d states can react differently, and that the latter is demagnetized faster than the former. This assumption is qualitatively consistent with recent experimental observation of a difference, by one order of magnitude, in the ultrafast magnetic moment dynamics of the localized 4f and itinerant 5d states in the RE metals [11].

We model this magnetic moment evolution in a simplified picture: we assume $\Delta_{ex} = 0$ while keeping all other parameters in Eq. (1) of the main text the same as in the spin-polarized case. The energy splitting of the seventeen lowest many-body eigenvalues of Eq. (1) for this intermediate state are shown in Fig. S4. Importantly, the lowest eigenstate, $|J = 8, J_z = 0\rangle$, has zero moment and is almost degenerate (within 1 meV energy difference) with a doublet $|J = 8, J_z = \pm 6.98\rangle$. The zero-field splitting becomes negligibly small, meaning that the system can go in and out of the magnetic state at no energy cost, thus it becomes magnetically unstable. Since the transition to this intermediate state is connected with the “fast” demagnetization of the 5d shell, the Ho adatom becomes magnetically unstable before the f-shell “slowly” transforms to the final fully relaxed paramagnetic state.

![Graph showing energy levels](image-url)

FIG. S4: (Color online) Scheme of quantum many-body levels of the lowest $J_f = 8.00$ multiplet obtained in Eq. (1) of the main text with the $\Delta_{CF}$ parameters for spin-polarized calculations and $\Delta_{ex} = 0$.

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