Single Magnetic Atom on a Surface: Anisotropy Energy and Spin Density

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The desire of higher-density magnetic data storage is becoming more emergent to conform to the explosive growth of today’s information industry. The continued downscaling of storage bits will require significant enhancement of magnetic anisotropy energy (MAE) per atom to overcome the fundamental, superparamagnetic limit. Single-atom magnetic anisotropy on surfaces serves as an important bottom-up approach of such enhancements. A surface magnetic adatom no longer has the isotropic orbital electronic structures of its free atom, and consequently its spin-orbit couplings (SOC) vary in different spin orientations. Such an anisotropy is not only technologically relevant to the smallest magnetic storage bit that can be built, but also of great scientific interest for its fascinating quantum effects. Pioneering experiments have been able to measure the MAE of single transition-metal atoms and dimers on surfaces, followed by computational studies that are consistent with the measurements. Among those experiments, scanning tunneling microscopes (STM) can even reach atomic sites of a CuN surface. There is even a very recent STM study that can fabricate a bistable atomic-scale antiferromagnet, which enables a low-temperature demonstration of dense nonvolatile storage of information. However, the magnetic properties of such adatoms, e.g. spin density, have not yet been understood in simple, atomic-scale microscopic pictures. Also, MAE of non-transition-metal atoms, the rare earth for example, have not been explored, and are potential candidates with even higher single-atom MAE so that one may build atomic-scale storage bits in the future.

We start this study from first-principles calculations of a single rare-earth atom Dysprosium (Dy) on a CuN surface. Analysis of subshell quantum numbers, orbital shapes, and occupations of the $4f$ orbitals leads to simple explanation of the calculated spin-density distribution of the Dy atom. The success of such orbital analysis is then duplicated to the previously studied single Fe atom on the same surface, showing that this simple picture works independently for both the transition-metal $d$ and rare-earth $f$ orbitals. This work of Dy on a CuN surface is also the first study of the MAE of a single rare-earth atom on a surface, which is calculated by first principles to be a factor of five larger than the previously largest single-atom MAE, Co on the Pt surface.

II. COMPUTATIONAL APPROACHES

We construct a supercell of 5-layer Cu(100) slabs, place N and Dy atoms on the surface in the same way as the density-functional-theory (DFT) studies of single Fe and Mn adatoms, and then perform DFT calculations using the basis set of all-electron full-potential linearized augmented plane wave (FP-LAPW) or generalized-gradient approximation makes the $4f$ orbitals be pinned at the fermi level and causes a fractional $4f$ occupation, inconsistent with the photoemission measurements of rare-earth nitride bulks, and this problem was shown to be resolved by performing a DFT+U calculations instead. To find the correct $U$ and $J$ values for DFT+U, we perform PBE+U calculations and inspect the $4f$ occupation number $n_{4f}$ of Dy on the CuN surface with a series of $U$ and $J$. When $J = 0$, and $U$ ranges from 0 to 9 eV (noting that $U = 0$ denotes PBE itself), the occupation number stays at $n_{4f} = 9.6$ regardless of the $U$ value used. This means that with solely $U$ turned on, the unphysical fermi-level pinning of one of the $f$ states remains the same as the naive PBE. If $J$ is turned on to be a positive value 1.2 eV at $U = 9$ eV, the $f$ state originally pinned at fermi-level lowers in energy, and becomes fully occupied. However, the occupation number then becomes $n_{4f} ≈ 10$, inconsistent with the typical $n_{4f} ≈ 9$ in either a DFT+U calcula-
have determined that $U = 6 \text{ eV}$ and $J = -0.8 \text{ eV}$ yields a $4f^9$ configuration that agrees with both the DFT+U calculation of a DyN bulk\textsuperscript{13} and the CASSCF calculation of a DyCl\textsubscript{3} molecule\textsuperscript{18}. Atomic charges and spins are calculated by Bader analysis\textsuperscript{20}.

### III. RESULTS

As already pointed out in the previous Fe study\textsuperscript{16}, when an adatom is deposited onto the Cu site of the surface, it establishes polar covalent bonds with the nearest-neighbor N atoms that replaces the original CuN binding network. The calculated electron density of a Dy atom in the CuN surface is shown in Fig. 1a, together with the previously calculated Fe re-presented. As one can see, the Dy atom, sitting even higher on top of the surface, attracts its neighboring N atoms further out of the surface than the Fe case. We have also calculated that Dy and its neighboring N are +1.3 and −1.2 charged respectively. Compared with the +0.9 and −1.4 charged Fe and its neighboring N respectively, the Dy-N bond of the Dy system has a polarity approximately the same as the Fe-N.

By pointing the Dy spin in the hollow, N-row, and out-of-plane three symmetry directions (to be called $x$, $y$, and $z$ respectively) in our PBE+U total-energy calculations with SOC included, we obtain the Dy MAE $E(\hat{n})$ of $\hat{n} = \hat{e}_x$, $\hat{e}_y$, and $\hat{e}_z$, and compare it with the Fe case, as shown in the level diagram in Fig. 1b. One notices that in contrast to the Fe case, the most-preferred magnetization axis of Dy is oriented in the out-of-plane direction, while both atoms have their least-preferred axis pointing in the hollow direction. The MAE of Dy is basically one order of magnitude larger than that of Fe, and is five times larger than the 6meV MAE of Co on the Pt surface\textsuperscript{17}, the largest single-atom MAE reported previously.

The previously studied Fe on the surface has 13.5% of spin density extends into the surrounding atoms with the spreading primarily along the N-row direction\textsuperscript{16}. In contrast to Fe, when calculating Dy on the same surface, we find that a net spin of $S = 2.9$ is localized at the Dy atom, and $S = 2.9$ by including the spin of all atoms, indicating that there is no spin spreading. The $S = 2.9$ of Dy includes two parts of contribution from our analysis, $S = 2.5$ from the localized electronic configuration (4$f^9$)\textsuperscript{5} (within the Dy muffin-tin sphere), and $S = 0.4$ from the delocalized (6$s5d$)\textsuperscript{10} (out of the muffin-tin sphere but within the Bader basin), where 6$s5d$ denotes a hybridized molecular orbital\textsuperscript{21}. The significant reduction of spin spreading when replacing Fe by Dy is obviously because the Dy 4$f$ orbitals are more localized than the Fe 3$d$. Another interesting feature is the shape of the spin density. When looking closely at the spin isosurfaces of the Dy and Fe atoms along all three crystal-symmetry directions in Fig. 1h, the shapes of Dy and Fe are found to be approximately a hexagon and a square, respectively, along either the N-row or out-of-plane direction, while

![Figure 1: (a) Electron density contour of a single Dy on the CuN surface along the N-Dy-N raw and the out-of-plane direction, in comparison with the Fe case. The numbers inside the circles indicate the net charge on selected atoms. (b) Level diagrams in scale showing the calculated MAE of Dy and Fe on the CuN surface, respectively. The Fe case is done by Shick et al. (c) Calculated spin-density isosurfaces (second row, blue) of Dy on CuN at the magnitude of 0.05e/\text{a}_0^3 within a 3×3×3\text{Å}^3 cube centered at the Dy nucleus, by looking (left to right) along $x$, $y$, and $z$ directions. Each stick-ball structure corresponds to one of the three directions. The purple surfaces are the corresponding Fe spin density for comparison.](image-url)
suggests that the hexagonal spin density is related to the
and are different from the rest three. The six-petal shape
of subshell symmetries, the cubic and the general sets
rarely shown in literatures, have two commonly used sets
As an example, we plot the 4f orbitals, from left to right: (upper)
following well-known subshell symmetries, \( n = 3 \) and \( n = 4 \),
where blue (red) zones denote positive (negative) values. (a)
The general set, from left to right: (upper) \( yz^2 \), \( z(z^2 - 3x^2) \),
\( x(x^2 - 3y^2) \), (lower) \( z^3 \), \( z(x^2 - y^2) \), \( y(3x^2 - y^2) \). The \( xyz \) orbital
is plotted in the inset at the right-lower corner. (b) The \( \{ L_z \} \)
fully-polarized set, from left to right: (upper) \( yz^2 \), \( z(z^2 - 3x^2) \),
\( x(x^2 - 3y^2) \), (lower) \( yz^2 \), \( x^2 \), \( y(3x^2 - y^2) \). All six orbitals have
a unique six-petal shape. The only exceptional shape of the \( xyz \) orbital is plotted in the inset at the right-lower corner.

equation: 

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\begin{align*}
\vec{L} \cdot \hat{e}_i &= |L_z|, \quad \text{with eigenvalues } |m| = 3 = l. \\
\text{Due to the reflection symmetry of these orbitals in the }
\hat{e}_i \text{ directions, their angular-momentum polarization has an}
\text{sign ambiguity. The full polarization of } |L_z| \text{ of these}
\text{six } 4f \text{ orbitals can be further visualized clearly by looking}
\text{at their orbital shapes. As one can see in Fig. 2b, the}
\text{above mentioned six fully-polarized } 4f \text{ orbitals have an}
\text{unique six-petal shape, and can be grouped into three}
\text{pairs. Each pair of orbitals have the same coordinate axis as}
\text{their central symmetry axis, and are related to each}
\text{other by exchanging their in-plane axes. The most obvious}
\text{full polarization can be realized for the } y(3x^2 - y^2) \text{ and}
\text{ } x(x^2 - 3y^2) \text{ orbitals, which are eigenstates of } |L_z|
\text{ with eigenvalues } |m| = 3, \text{ and have } z \text{ as their central}
\text{axis. Similarly, each of the rest four fully-polarized}
\text{orbitals have their central axes as their polarization}
\text{directions. The only exception, the } xyz \text{ orbital, has eight}
\text{lobes pointing to the corners of a cube.}
\text{Our calculations show that the Dy } 4f \text{ majority-spin}
\text{states are all fully occupied and are very low-lying,}
\text{extremely atomic-like levels. The orbital analysis of this}
\text{work does not depend on the details of the Dy } 4f
\text{majority-spin states as long as all of them are fully}
\text{occupied, and their details are not presented here. For}
\text{minority-spin states, we plot their PDOS in Fig. 3b, and}
\text{find that } xz^2 \text{ and } y(3x^2 - y^2) \text{ are mainly occupied, and}
\text{ } yz^2 \text{ and } x(x^2 - 3y^2) \text{ slightly occupied. The occupation}
\text{numbers of the rest of the } 4f \text{ minority-spin states are}
\text{negligible. The } 5d\text{fs electron mentioned in a previous}
\text{paragraph is mostly delocalized out of the Gd muffin-tin}
sphere, and has a negligible PDOS within that sphere.}
show that all the majority-spin states are fully occupied or almost empty. The PDOS of three of the subshells are plotted separately in each inset solely for the purpose that all PDOS are better visualized.

The Dy 4f orbitals are rather localized as indicated from a previous paragraph that they have an approximate 0.4 Å radius. It is a good approximation to think of these orbitals in the way of electronic configurations of an atom, and therefore the nontrivial occupation (neither fully occupied nor completely empty) is determined for each orbital from the area under the curve below the Fermi level. The PDOS thus implies an approximately 4f⁹ configuration for the Dy atom itself.

The conventional quantization axes of the Fe 3d PDOS are oriented in the way that the x axis points along the hollow direction, y along the N row, and z out of plane. Such PDOS have been presented in Ref. 9,11, and show that all the majority-spin states are fully occupied. We re-calculate the PDOS and plot the minority spins in Fig. 3b. The minority-spin PDOS show that x² − y² is fully occupied, z² partially occupied, and the rest three minority-spin states basically empty. The partially occupied spin-minority z² prohibits us from establishing a simple picture of either the spin-density shape or the SOC. However, one may notice that the z² and x² − y² PDOS profiles depend nontrivially on the choice (or interchange) of the coordinate axes, while the xy, yz and zx (see the insets of Fig. 3b) have trivially the same set of PDOS profiles with interchange of PDOS labels corresponding to the interchange of the coordinate axes. Therefore we search for z² and x² − y² minority-spin PDOS of all three possible assignments of coordinate axes, i.e., the hollow, N-row, and out-of-plane directions are x, y, and z axes, respectively, and the cyclic permutations. In all three axis assignments, all the majority-spin states are always fully occupied, and the xy, yz and zx minority-spin always empty, while the z² and x² − y² minority-spin states have specially simple occupations as shown in Fig. 3b, under a particular assignment of new axes: the hollow, N-row, and out-of-plane directions are z₁, x₁, and y₁ axes, respectively. In this new coordinate system, only the z² (or equivalently x² in the old coordinates) orbital has paired spins, while the rest four all unpaired.

IV. DISCUSSION

With the orbital quantum numbers and occupation numbers determined, we now try to explain the spin-density shape of a Dy atom on the CuN surface. By starting with the top view, one notices that the x(x² − 3y²) and y(3x² − y²) orbitals both have the six-petal shapes centered about the z-axis. As we have identified from the PDOS analysis that y(3x² − y²) has roughly paired spins, while x(x² − 3y²) has roughly an unpaired spin. The spin density shape along the xy plane are therefore dominated by the x(x² − 3y²) majority spin alone. Observing the shape of the x(x² − 3y²) orbital, one then realizes that the hexagonal shape of the Dy spin density from a top view in Fig. 1 is essentially the consequence of the unpaired x(x² − 3y²) orbital (see Fig. 4a). Similarly, the z(z² − 3x²) and xz² orbitals, both with a six-petal shape centered about the y-axis, contribute to the hexagonal spin density by looking along the y direction. However, the yz² and zy² orbitals, centered about the x-axis, both have unpaired spins. Their two six-petal shapes with 30° relative to each other result in a slightly-round-shape spin-density by looking along the x direction. We can even further understand the unique dent at the y ends of the spin isosurface by the following analysis. The only unpaired orbital that carries a lobe in the y direction is yz², as can be seen in Fig. 4a, and all the rest have nodes along y. On the other hand, both the other two axes receive lobe contribution from two unpaired-orbitals, e.g., x(x² − 3y²) and zy² both contribute lobes along x. Con-
sequences of the spin-unpaired $z_1 x_1$ and $y_1 z_1$ orbitals, respectively, while the round shape from the hollow-site side view is the combination of the spin-unpaired $x_1^2 - y_1^2$ and $z_1 x_1$ orbitals. One also notice that the spin isosurface has a dent only at the $z_1$ ends. Similar to the way of explaining the Dy spin-isosurface dent, such a dent is the consequence that both the $x_1$ and $y_1$ ends have lobe contributions from the $x_1^2 - y_1^2$ orbital, while $z_1$ has no lobe contribution mainly due to the fact that the $z_1^2$ orbital is spin-paired.

V. CONCLUSION

The STM moving-atom technique has demonstrated its capability of building, manipulating, and measuring a single atomic spin in a well-characterized environment. First-principles calculations conclude that such an atomic spin forms a surface-embedded molecular magnetic structure, as well as, reproduce the measured magnetic anisotropy axes. As an ongoing study of the STM-engineered adatoms, this work is the first attempt to understand the spin density of a surface magnetic atom in a simple, atomic-scale microscopic picture. This is achieved by analyzing the occupations, shapes, and angular moments of its individual localized orbitals. These localized orbitals include both the well-known $d$ orbitals of the transition-metal atoms and the nontrivial $f$ of the rare-earth. We determine an unconventional set of $4f$ subshell quantum numbers and an unconventional set of $3d$ quantization axes that can be used to analyze the shape of the spin density. The spin-density shape of a magnetic adatom is explained by simply counting the occupation of each individual subshell and spin state of the atom’s localized orbital. These studies provide an important microscopic picture of the atomic-scale origins of magnetization distribution. We have also done the first computational study of a single rare-earth atom on a surface. The calculation predicts a record-high MAE of 31 meV. All these theoretical and computational realizations, combined with continuing experimental innovations, may lead to further engineering of the single-atom magnetic anisotropy, further exploration of the smallest magnetic storage bit, and new fascinating applications of atomic-scale magnetism.

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21 The Dy 4f, 5d, and 6s have radii of 0.4, 1.4, and 2.0 Å, respectively. As a result, the 4f contributes a much larger radial part \(dV(r)/dr\) to the SOC than 6s5d. In fact, the 6s5d orbital is mainly distributed out of the Dy muffin-tin sphere, and its SOC is not included in this calculation.
22 See, for example, [http://winter.group.shef.ac.uk/orbitron](http://winter.group.shef.ac.uk/orbitron)