ESI for: Valence electrons in lanthanide-based single-atom magnets: paradigm shift in 4f-magnetism modeling and design.

Vasilii Dubrovin,[a] Alexey A. Popov [*a] and Stanislav M. Avdoshenko [*a]

[a)]*Leibniz Institute for Solid State and Materials Research Dresden, Helmholtzstraße 20, 01069 Dresden, Germany.*

Abstract The detailed electronic structure of single atomic magnets is a crucial bit in the further understanding and design of a new generation of monoatomic magnetic elements on surfaces and in molecules. Control and manipulation of the single atomic state, as well as long relaxation of magnetization, have been demonstrated for lanthanide atoms on carefully chosen supporting substrates. However, these convincing experiments are puzzling by insufficient theoretical description, usually omitting the valence electrons of lanthanide atoms. In this work, starting with an idea of the inevitable need of local d- and p-shell electrons for a proper description of the magnetic states of lanthanide atoms, we rationalized the electronic structure and magnetic properties of Ho atom on the MgO substrate using ab initio multiconfigurational approaches. By doing so, we obtained the solution which complements experimental observations and has been able to pin-point the atomic state which most likely to be responsible for the exceptional magnetic properties of Ho on MgO. This study demonstrates that new paradigms are needed for understanding and interpretation of the lanthanide single-atomic magnets.

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1. An example of the ASE-based python script for structure generation:

```python

import numpy as np
from ase.io import write
from ase import Atoms, Atom
from ase.lattice.compounds import Rocksalt

ho = Atoms('Ho', positions=[[0, 0, 0]])

ii=3
lat=4.212

bulk = Rocksalt(size=(ii, ii, 2), symbol=("Mg", "O"), latticecon=lat, pbc=True)
bulk.set_pbc = [ii*lat, ii*lat, 30]

print bulk.get_cell()
pos = bulk.get_positions()
pos += np.array([-10./2., -10./2., -12.5])
bulk.set_positions(pos)

bulk = ho + bulk

bulk.set_cell(np.array([[ii*lat, 0., 0.],[0., ii*lat, 0.], [0., 0., 50.]]))
bulk.pbc=[True,True,True]
bulk.center()


write('mol_mgo.pdb', bulk)
write('mol_mgo.cif', bulk)
write('mol_mgo.xyz', bulk)

from ase.visualize import view
view(bulk)

```

2. Computational details for VASP DFT:

Table SI1: Example of VASP optimization file
INCAR
PREC = Normal
ENMAX = 400
ISMEAR = 0 ; SIGMA = 0.1
IBRION = 1
IVDW=11
LREAL=Auto
NSW = 400
EDIFFG = -0.005
ALGO = F
NCORE= 24
LORBIT=11
ISPIN = 2

3. Basic DFT results for Ho|MgO system:

Table SI2:Charges and relative energies						
System	O-site			B-site		
	PP, Ho3+	PP,Er3+	PP,Er2+	PP, Ho3+	PP,Er3+	PP,Er2+
ΔE(eV)	0.00	0.00	0.00	0.52	0.49	0.39
Δq(e)	0.10	0.10	0.28	0.71	0.76	0.35
Ho-O(Å)	2.07	2.06	2.19	1.63	1.62	2.00

145 atoms, Lattice="12.636 0.0 0.0 0.0 12.636 0.0 0.0 0.0 30.0"

Table SI3: Optimized O-site structure							
Ho	6.318000	6.318000	8.741266				
Mg	0.000000	0.000000	29.997986	O	0.000000	0.000000	2.096616
Mg	0.000000	2.106059	2.090909	O	0.000000	2.106707	29.949516
Mg	2.106059	0.000000	2.090909	O	2.106707	0.000000	29.949516
Mg	2.106312	2.106312	29.999743	O	2.106763	2.106763	2.099111
Mg	4.212536	0.000000	30.001322	O	4.213612	0.000000	2.099290
Mg	4.210928	2.106755	2.095642	O	4.214085	2.107899	29.954492
Mg	6.318000	0.000000	2.093215	O	6.318000	0.000000	29.954310
Mg	6.318000	2.106778	30.001946	O	6.318000	2.112359	2.106445
Mg	8.423464	0.000000	30.001322	O	8.422388	0.000000	2.099290
Mg	8.425072	2.106755	2.095642	O	8.421915	2.107899	29.954492
Mg	10.529941	0.000000	2.090909	O	10.529293	0.000000	29.949516
Mg	10.529688	2.106312	29.999743	O	10.529237	2.106763	2.099111
Mg	0.000000	4.212536	30.001322	O	0.000000	4.213612	2.099290
Mg	0.000000	6.318000	2.093215	O	0.000000	6.318000	29.954310
Mg	2.106755	4.210928	2.095642	O	2.107899	4.214085	29.954492
Mg	2.106778	6.318000	30.001946	O	2.112359	6.318000	2.106445
Mg	4.213033	4.213033	30.003563	O	4.217562	4.217562	2.111148
Mg	4.209115	6.318000	2.095941	O	4.214490	6.318000	29.956844
Mg	6.318000	4.209115	2.095941	O	6.318000	4.214490	29.956844
Mg	6.318000	6.318000	30.000678	O	6.318000	6.318000	2.105825
Mg	8.422967	4.213033	30.003563	O	8.418438	4.217562	2.111148
Mg	8.426885	6.318000	2.095941	O	8.421510	6.318000	29.956844
Mg	10.529245	4.210928	2.095642	O	10.528101	4.214085	29.954492
Mg	10.529222	6.318000	30.001946	O	10.523641	6.318000	2.106445
Mg	0.000000	8.423464	30.001322	O	0.000000	8.422388	2.099290
Mg	0.000000	10.529941	2.090909	O	0.000000	10.529293	29.949516
Mg	2.106755	8.425072	2.095642	O	2.107899	8.421915	29.954492
Mg	2.106312	10.529688	29.999743	O	2.106763	10.529237	2.099111
Mg	4.213033	8.422967	30.003563	O	4.217562	8.418438	2.111148
Mg	4.210928	10.529245	2.095642	O	4.214085	10.528101	29.954492

Mg	6.318000	8.426885	2.095941	O	6.318000	8.421510	29.956844
Mg	6.318000	10.529222	30.001946	O	6.318000	10.523641	2.106445
Mg	8.422967	8.422967	30.003563	O	8.418438	8.418438	2.111148
Mg	8.425072	10.529245	2.095642	O	8.421915	10.528101	29.954492
Mg	10.529245	8.425072	2.095642	O	10.528101	8.421915	29.954492
Mg	10.529688	10.529688	29.999743	O	10.529237	10.529237	2.099111
Mg	0.000000	0.000000	4.207293	O	0.000000	0.000000	6.349656
Mg	0.000000	2.099898	6.302523	O	0.000000	2.104675	4.200330
Mg	2.099898	0.000000	6.302523	O	2.104675	0.000000	4.200330
Mg	2.104835	2.104835	4.209318	O	2.100367	2.100367	6.350844
Mg	4.210876	0.000000	4.210258	O	4.203615	0.000000	6.350402
Mg	4.197407	2.091491	6.309551	O	4.213570	2.105212	4.204366
Mg	6.318000	0.000000	6.303501	O	6.318000	0.000000	4.197187
Mg	6.318000	2.096376	4.210279	O	6.318000	2.070342	6.339797
Mg	8.425124	0.000000	4.210258	O	8.432385	0.000000	6.350402
Mg	8.438593	2.091491	6.309551	O	8.422430	2.105212	4.204366
Mg	10.536102	0.000000	6.302523	O	10.531325	0.000000	4.200330
Mg	10.531165	2.104835	4.209318	O	10.535633	2.100367	6.350844
Mg	0.000000	4.210876	4.210258	O	0.000000	4.203615	6.350402
Mg	0.000000	6.318000	6.303501	O	0.000000	6.318000	4.197187
Mg	2.091491	4.197407	6.309551	O	2.105212	4.213570	4.204366
Mg	2.096376	6.318000	4.210279	O	2.070342	6.318000	6.339797
Mg	4.211533	4.211533	4.228113	O	4.204398	4.204398	6.342846
Mg	4.098708	6.318000	6.351775	O	4.235539	6.318000	4.247107
Mg	6.318000	4.098708	6.351775	O	6.318000	4.235539	4.247107
Mg	6.318000	6.318000	4.169284	O	6.318000	6.318000	6.681078
Mg	8.424467	4.211533	4.228113	O	8.431602	4.204398	6.342846
Mg	8.537292	6.318000	6.351775	O	8.400461	6.318000	4.247107
Mg	10.544509	4.197407	6.309551	O	10.530788	4.213570	4.204366
Mg	10.539624	6.318000	4.210279	O	10.565658	6.318000	6.339797
Mg	0.000000	8.425124	4.210258	O	0.000000	8.432385	6.350402
Mg	0.000000	10.536102	6.302523	O	0.000000	10.531325	4.200330
Mg	2.091491	8.438593	6.309551	O	2.105212	8.422430	4.204366
Mg	2.104835	10.531165	4.209318	O	2.100367	10.535633	6.350844
Mg	4.211533	8.424467	4.228113	O	4.204398	8.431602	6.342846
Mg	4.197407	10.544509	6.309551	O	4.213570	10.530788	4.204366
Mg	6.318000	8.537292	6.351775	O	6.318000	8.400461	4.247107
Mg	6.318000	10.539624	4.210279	O	6.318000	10.565658	6.339797
Mg	8.424467	8.424467	4.228113	O	8.431602	8.431602	6.342846
Mg	8.438593	10.544509	6.309551	O	8.422430	10.530788	4.204366
Mg	10.544509	8.438593	6.309551	O	10.530788	8.422430	4.204366

Mg	10.531165	10.531165	4.209318	O	10.535633	10.535633	6.350844

Table SI4: Optimized B-site structure							
Ho	5.246813	7.388927	8.512234				
Mg	0.000367	-0.000762	29.987520	O	0.003656	-0.004130	2.104713
Mg	-0.002307	2.103582	2.085206	O	-0.000538	2.104843	29.957737
Mg	2.105998	-0.005973	2.088401	O	2.107589	-0.004068	29.959617
Mg	2.103164	2.102312	29.988749	O	2.107738	2.102339	2.104598
Mg	4.211182	-0.000833	29.983745	O	4.214799	-0.012479	2.110468
Mg	4.210295	2.098560	2.083886	O	4.212860	2.104275	29.960686
Mg	6.319351	0.006294	2.084343	O	6.317498	0.000758	29.959668
Mg	6.319031	2.105647	29.983910	O	6.315570	2.117645	2.110712
Mg	8.426058	0.003240	29.988636	O	8.420890	0.003215	2.104670
Mg	8.423274	2.111423	2.088858	O	8.421254	2.109069	29.960130
Mg	10.532007	0.001928	2.085180	O	10.530714	0.000105	29.957705
Mg	10.529642	2.105954	29.988556	O	10.525994	2.109565	2.105292
Mg	-0.003679	4.209472	29.988690	O	-0.003653	4.214650	2.104735
Mg	-0.006714	6.316175	2.084377	O	-0.001273	6.317999	29.959686
Mg	2.100516	4.206825	2.084105	O	2.105902	4.212547	29.960563
Mg	2.100161	6.315062	29.976683	O	2.113962	6.322491	2.111201
Mg	4.209467	4.206485	29.977571	O	4.217369	4.220772	2.111732
Mg	4.203530	6.309737	2.051307	O	4.211024	6.316191	29.944816
Mg	6.318094	4.207951	2.071106	O	6.315872	4.214195	29.953265
Mg	6.318908	6.316700	29.962272	O	6.310819	6.324756	2.089488
Mg	8.424330	4.211241	29.983065	O	8.411172	4.224411	2.115123
Mg	8.427644	6.317514	2.071126	O	8.421370	6.319686	29.953297
Mg	10.524171	4.212304	2.088890	O	10.526495	4.214284	29.960143
Mg	10.529869	6.316410	29.983955	O	10.517896	6.319970	2.110732
Mg	0.000001	8.424263	29.983649	O	0.011893	8.420675	2.110459
Mg	0.005400	10.529435	2.088384	O	0.003551	10.527926	29.959590
Mg	2.101436	8.424001	2.071744	O	2.107199	8.421283	29.953306
Mg	2.104823	10.530566	29.982990	O	2.117378	10.518042	2.114609
Mg	4.210377	8.424950	29.963658	O	4.219172	8.416269	2.089468
Mg	4.211462	10.533911	2.071760	O	4.214172	10.528259	29.953296
Mg	6.325813	8.432061	2.051314	O	6.319315	8.424494	29.945032
Mg	6.320447	10.535349	29.976768	O	6.312988	10.521560	2.111160
Mg	8.429103	8.426143	29.977578	O	8.414798	8.418215	2.111711
Mg	8.428720	10.535114	2.084075	O	8.423007	10.529651	29.960517
Mg	10.536965	8.425282	2.083893	O	10.531243	8.422726	29.960645
Mg	10.533257	10.532502	29.988705	O	10.533203	10.527848	2.104582

Mg	0.002147	-0.002615	4.206672	O	0.003772	-0.004306	6.353104
Mg	-0.011297	2.095650	6.308388	O	-0.002618	2.103542	4.205294
Mg	2.096001	0.001937	6.316553	O	2.113467	-0.013063	4.214448
Mg	2.100179	2.096055	4.204036	O	2.094768	2.093653	6.350382
Mg	4.211936	-0.002145	4.212734	O	4.212486	0.006363	6.364681
Mg	4.196410	2.084225	6.307437	O	4.214770	2.096475	4.203684
Mg	6.333239	0.019702	6.307303	O	6.315644	0.008208	4.203661
Mg	6.317524	2.106461	4.212663	O	6.317966	2.097327	6.365249
Mg	8.428805	0.009579	4.203931	O	8.433944	0.012073	6.350054
Mg	8.432231	2.103370	6.317214	O	8.414622	2.119349	4.215670
Mg	10.539788	0.010725	6.308329	O	10.531953	0.002122	4.205279
Mg	10.527231	2.108329	4.206907	O	10.524120	2.111377	6.353899
Mg	-0.009969	4.206712	4.203974	O	-0.012574	4.201586	6.350088
Mg	-0.020248	6.302336	6.307296	O	-0.008678	6.319853	4.203696
Mg	2.057896	4.164387	6.306832	O	2.105913	4.212385	4.204466
Mg	2.074309	6.312856	4.197447	O	2.059808	6.303121	6.321442
Mg	4.207284	4.180049	4.197045	O	4.199992	4.163731	6.322405
Mg	4.052211	6.155016	6.261185	O	4.238147	6.344172	4.258937
Mg	6.308232	4.146326	6.373767	O	6.307029	4.257514	4.262236
Mg	6.315491	6.320092	4.115238	O	6.228462	6.407067	6.885978
Mg	8.414822	4.220755	4.229094	O	8.394817	4.240754	6.381284
Mg	8.489253	6.327351	6.373747	O	8.378052	6.328539	4.262269
Mg	10.532195	4.203195	6.317197	O	10.516196	4.220918	4.215688
Mg	10.529138	6.317964	4.212700	O	10.538210	6.317575	6.365246
Mg	0.001616	8.423587	4.212732	O	-0.006919	8.423002	6.364711
Mg	-0.002414	10.539548	6.316571	O	0.012588	10.522020	4.214452
Mg	2.042881	8.416642	6.373601	O	2.150505	8.413161	4.260385
Mg	2.113266	10.522116	4.228426	O	2.128760	10.506693	6.377623
Mg	4.212679	8.422712	4.117899	O	4.276002	8.359692	6.875814
Mg	4.218833	10.592545	6.373587	O	4.222299	10.484943	4.260366
Mg	6.480422	8.583409	6.261020	O	6.291308	8.397414	4.258871
Mg	6.322467	10.561302	4.197354	O	6.332371	10.575754	6.321371
Mg	8.455475	8.428321	4.197012	O	8.471720	8.435574	6.322374
Mg	8.471076	10.577585	6.306698	O	8.423073	10.529649	4.204426
Mg	10.551236	8.439156	6.307481	O	10.539002	8.420803	4.203699
Mg	10.539340	10.535360	4.203983	O	10.541826	10.540743	6.350341

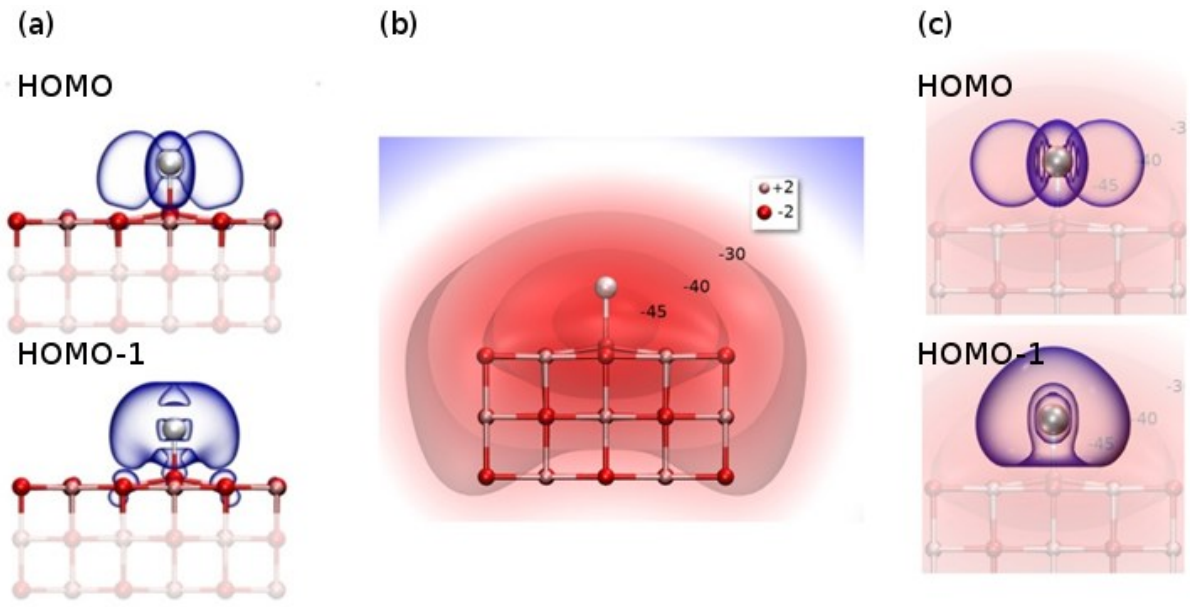

Figure S1 Molecular orbital densities of HOMO and HOMO-1 MOs obtained in full VASP/DFT/PBE consideration of the Ho|MgO system (a) and for single atom(Lu) modeling Lu|MgO at ORCA/DFT/PBE/SARC-DKH-TZVP (c), where MgO surfaces substituted by point charges with electrostatic potential (units k(T=300K)/e or 25 mV) (b).

Animation SI1

Evolution of natural spin densities for 149 SOC-states in modeling at RASSCF([$4f^{10}$, ($5d$ + $6p$)^1])/RASSI-SO/QZVP-RCC level.

Animation SI2

Evolution of natural spin densities for 120 SOC-states in modeling at RASSCF([$4f^{10}$, ($6p$)^1])/RASSI-SO/QZVP-RCC level.