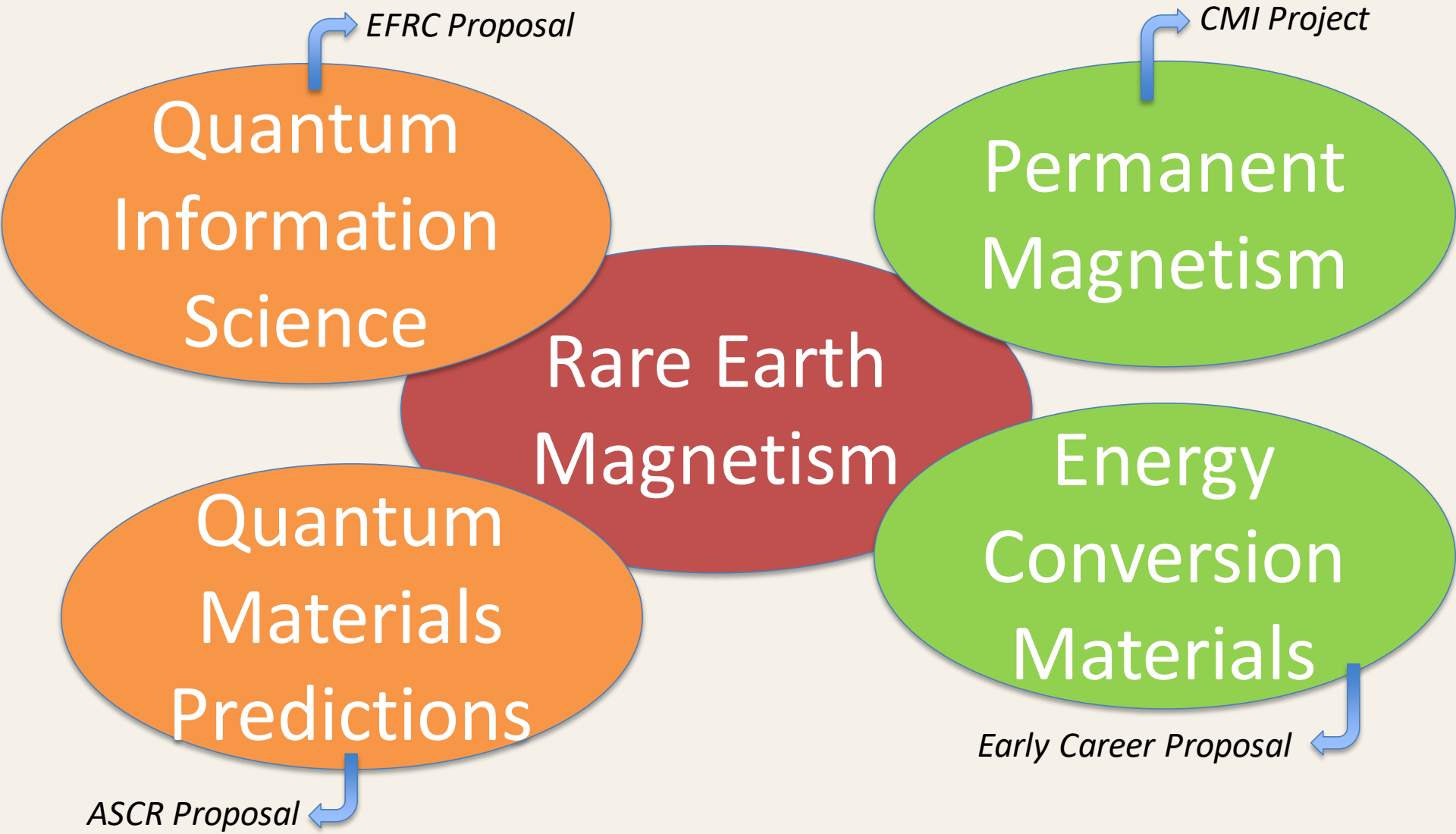
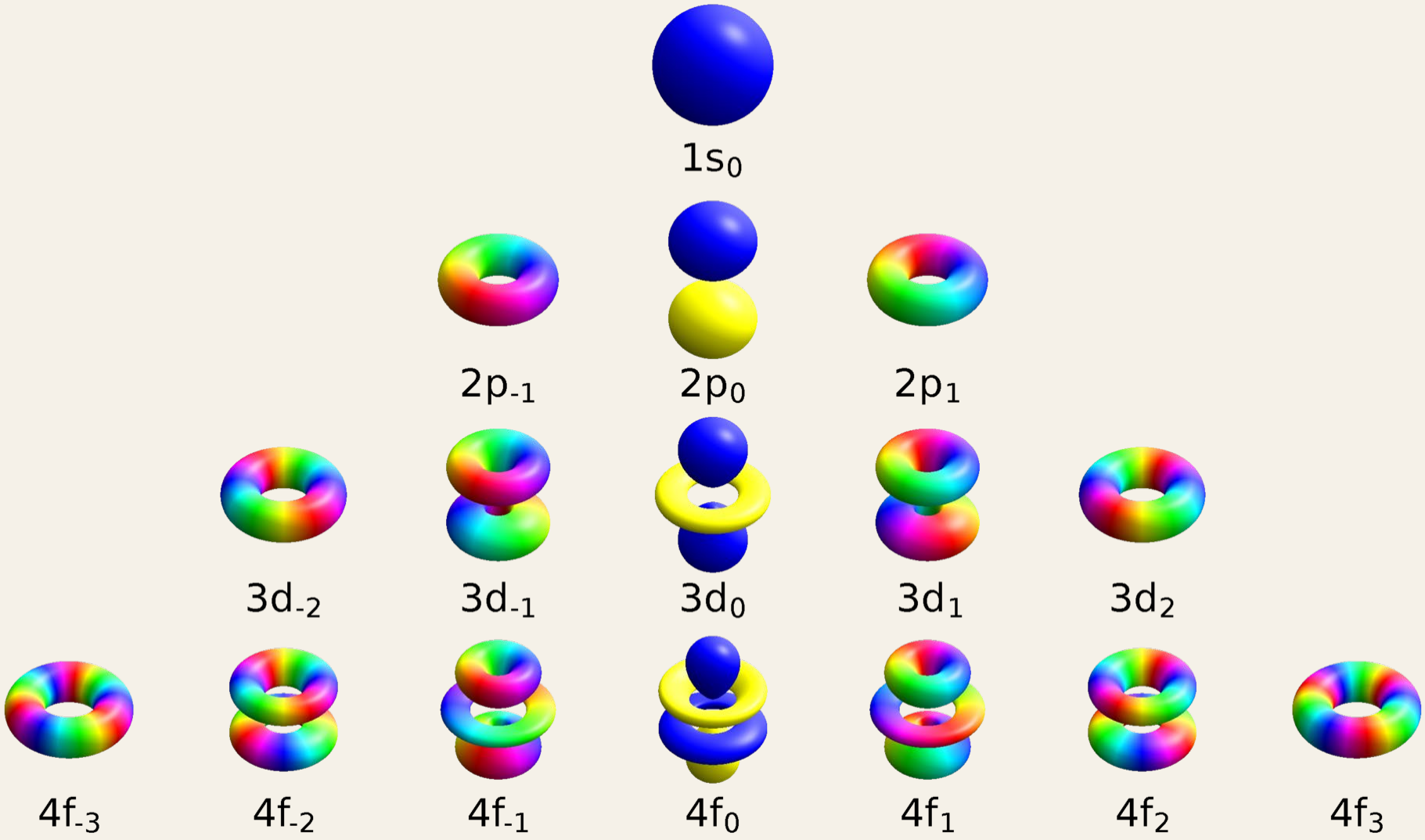
# Symmetry and topology of rare-earth magnetic materials

Durga Paudyal

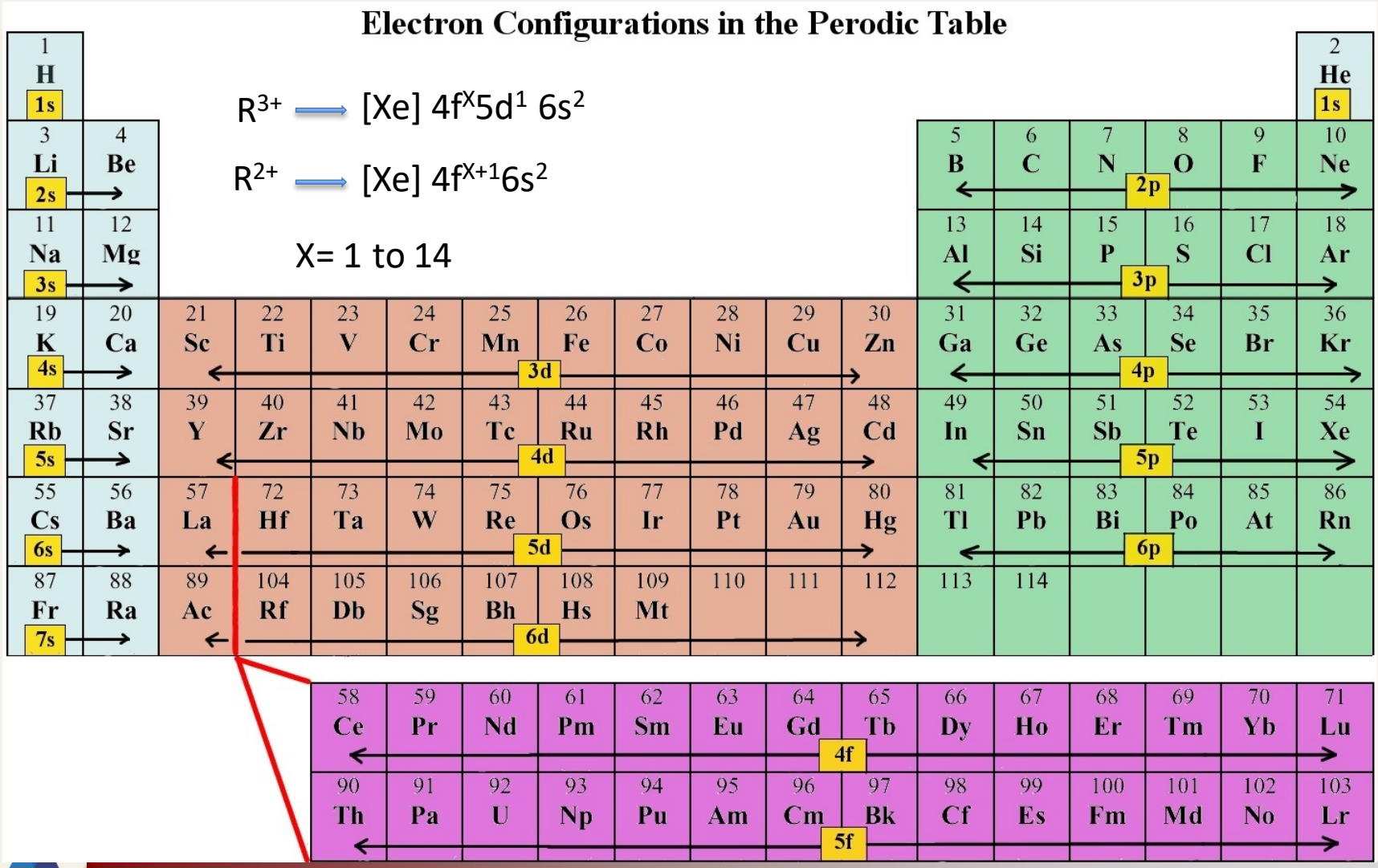
# Research Focus



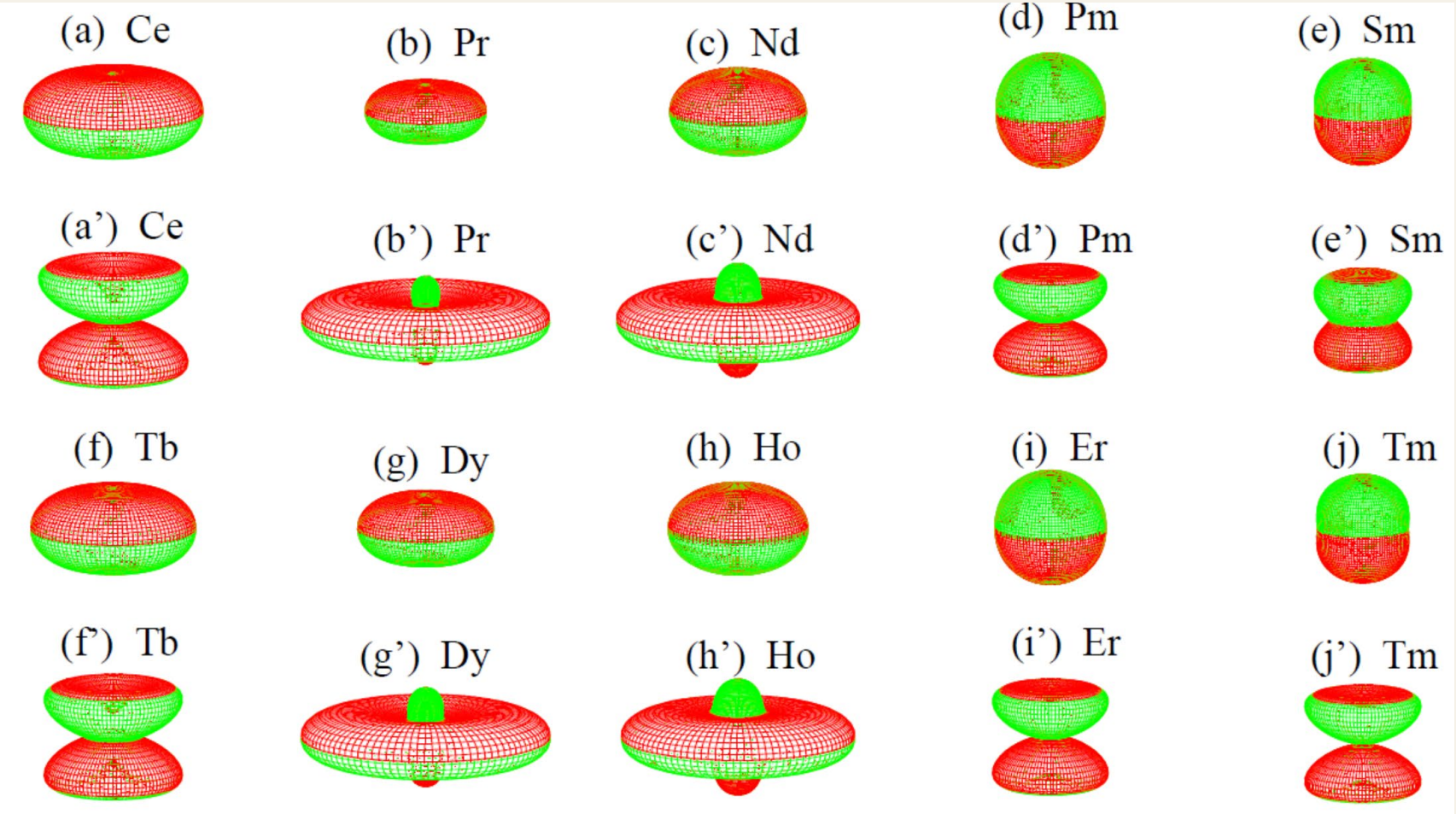
# Topology of Atomic Orbitals



# Rare Earths

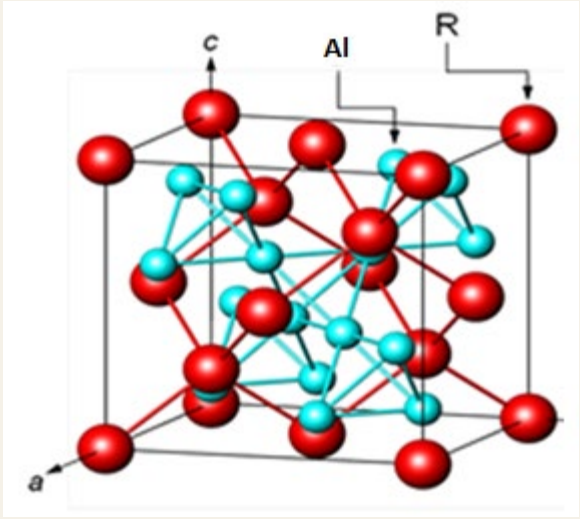

Electron Configurations in the Perodic Table
$R^{3+}$ ⟶ [Xe] $4f^X5d^1\ 6s^2$
$R^{2+}$ ⟶ [Xe] $4f^{X+1}6s^2$
X= 1 to 14
1 H 1s
2 He 1s
3 Li 2s
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
2p
11 Na 3s
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
3p
19 K 4s
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
3d
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
4p
37 Rb 5s
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
4d
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
5p
55 Cs 6s
56 Ba
57 La
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
5d
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
6p
87 Fr 7s
88 Ra
89 Ac
104 Rf
105 Db
106 Sg
107 Bh
108 Hs
109 Mt
110
111
112
113
114
6d
58 Ce
59 Pr
60 Nd
61 Pm
62 Sm
63 Eu
64 Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
70 Yb
71 Lu
4f
90 Th
91 Pa
92 U
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cf
99 Es
100 Fm
101 Md
102 No
103 Lr
5f

# Anisotropic Rare Earth Ions

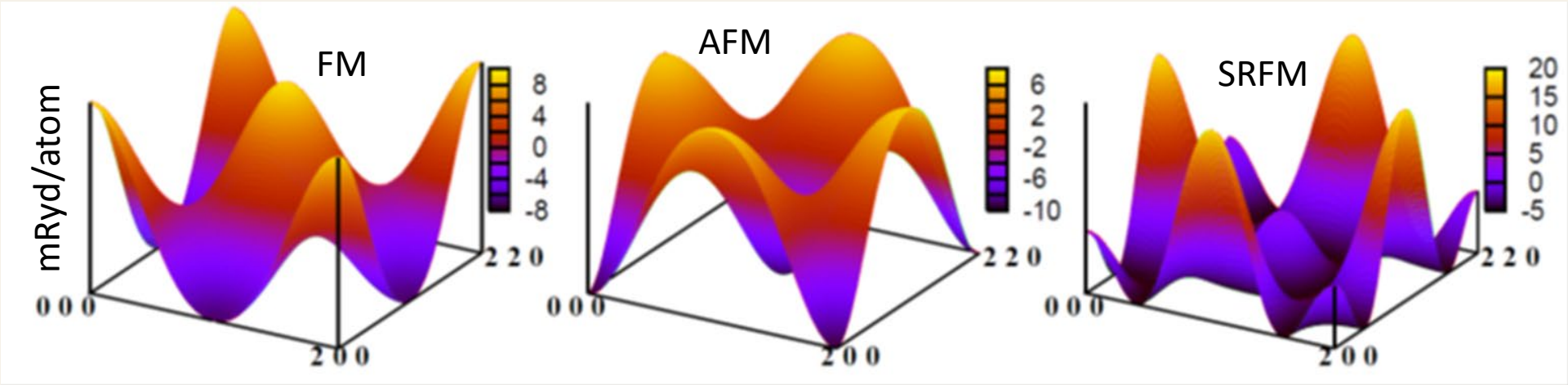


# Short Range Ferromagnetism

Effective magnetic surface potentials calculated from density functional theory (DFT)




$(Pr,Er)Al_2$




*PRB 2014, 2016*

# Density Functional Theory & Beyond

- The external potential (and hence the total energy), is a unique functional of the electron density
- The functional that delivers the ground state energy of the system gives the lowest energy if and only if the input density is the true ground state density
- Full potential to go beyond atomic sphere approximation
- Onsite electron correlation, excited state, and dynamical mean field models for more accurate description of occupied and unoccupied 4f states
- Spin orbit coupling to calculate direction dependent magnetic moments and magneto-crystalline anisotropy energy

# Density Functional Theory & Beyond

Spin orbit coupling

$$\frac{1}{2m^2c^2r}\frac{dv}{dr}\,\mathbf{s}\cdot\mathbf{l}.$$

Crystal Field

$$v_{\mathrm{cf}}(\mathbf{r}) = -\int \frac{e\rho(\mathbf{R})}{|\mathbf{r}-\mathbf{R}|}\,d\mathbf{R}$$

$$v_{\mathrm{cf}}(\mathbf{r}) = \sum_{lm} A_l^m r^l Y_{lm}(\hat{\mathbf{r}})$$

Crystal field makes a contribution to the potential energy of a 4*f* electron

# Density Functional Theory & Beyond

## Magneto-crystalline anisotropy energy

Magnetocrystalline anisotropy energy (MAE) as the total energy difference with magnetic moment aligned along the planar and c-axis directions [$E_{hkl} - E_{001}$]

Anisotropic energy density relation

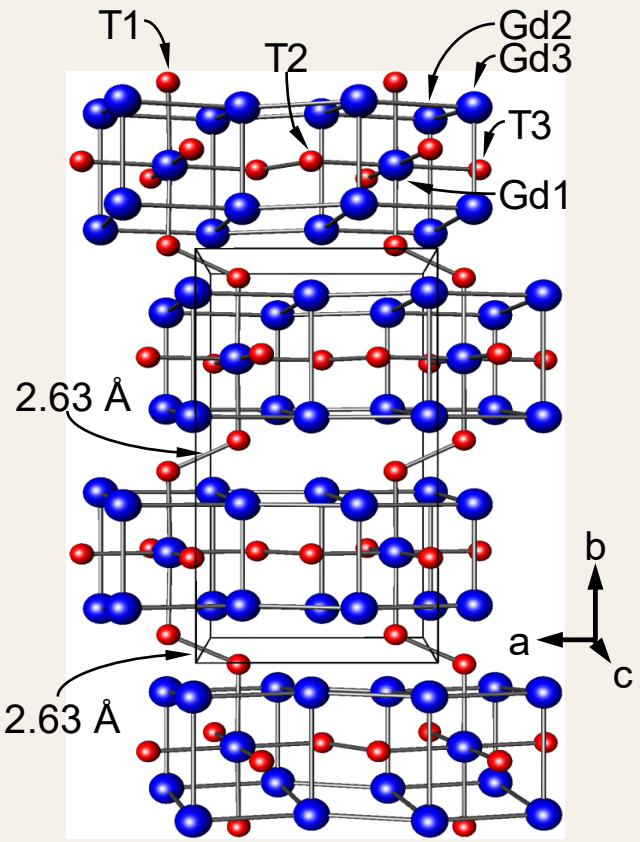
*PRB 2017*

$$\frac{E_a}{V} \approx \frac{\kappa_2}{2}(3\cos^2\theta - 1) + \frac{\kappa_4}{8}(35\cos^4\theta - 30\cos^2\theta + 3)$$

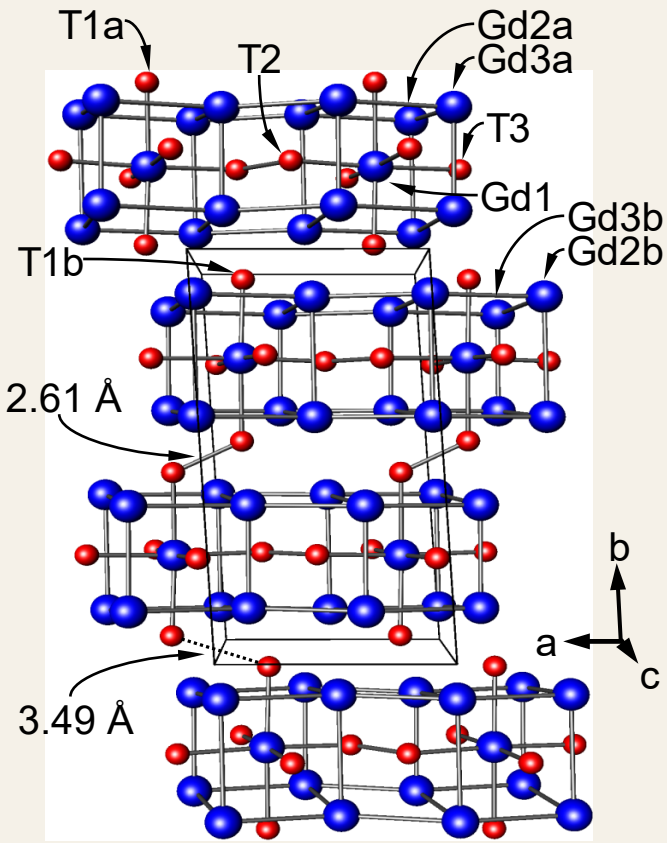
$\kappa_2$ (second-order) and $\kappa_4$ (fourth-order) coefficients are products of the corresponding quadrupolar/octupolar moments and crystal-field parameters

# Energy Conversion Materials: Magnetocaloric Effect in $Gd_5Si_2Ge_2$

**Orthorhombic below ~270 K**




**Monoclinic above ~270 K**




*PRB 2006*

# Magnetic exchange interactions and Curie temperature

- **Heisenberg Hamiltonian with zero magnetic field**

$$H = \sum_{i} \sum_{\delta} J_{i,i+\delta} \vec{S}_i \vec{S}_{i+\delta}$$

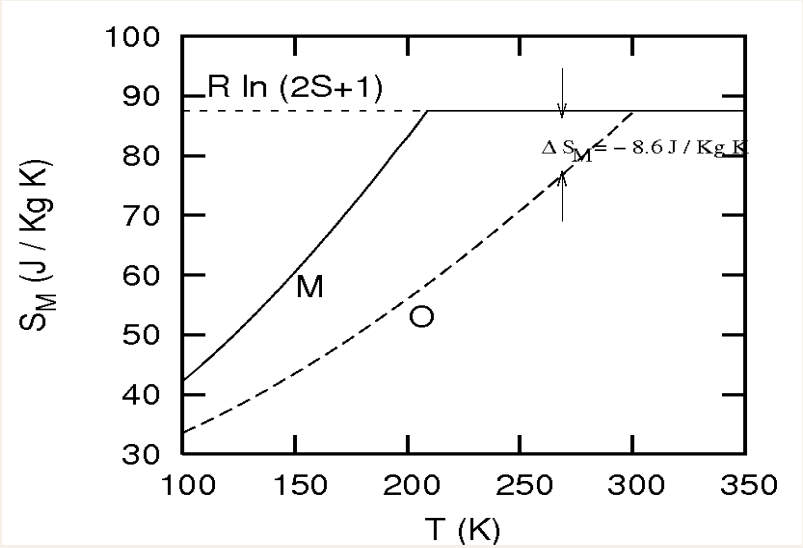
- **Curie temperature in the mean field approximation**

$$T_C = ZJ \frac{S(S+1)}{3k_B} = \frac{2}{3} \frac{E_{AFM} - E_{FM}}{k_B} = \frac{2}{3} \frac{J_O}{K_B}$$

# Magnetic entropy change, magnetic free energy and magnetostructural transition in $Gd_5Si_2Ge_2$

**Magnetic entropy**

$$S_M \approx R\left[\ln(2J+1) - \frac{3}{2}\left(\frac{J}{J+1}\right)\sigma^2 - \frac{9}{20}\frac{(2J+1)^4-1}{[2(J+1)]^4}\sigma^4\right]$$

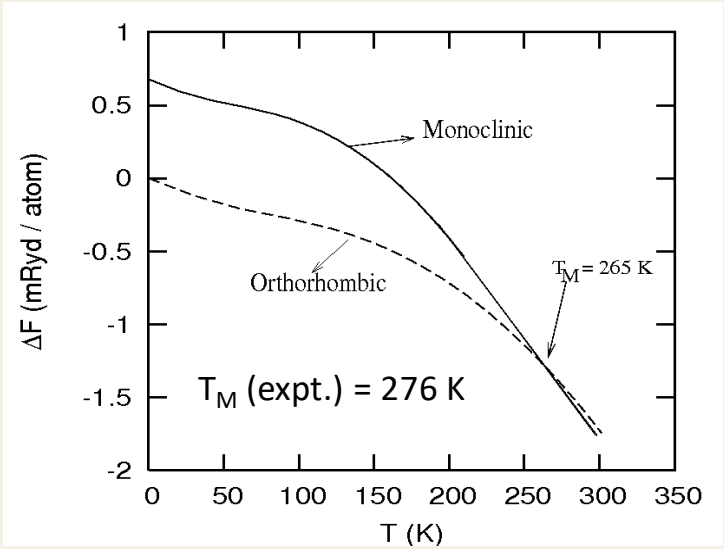



**Magnetization**

$$\sigma = \frac{M}{M_S} = \tanh\left[\frac{3J}{J+1}\frac{M}{M_S}\frac{T_C}{T}\right]$$

**Magnetic free energy**

$$F = -\frac{3}{2}\frac{J}{J+1}RT_C\sigma^2 - TS_M$$




At $T_M$, $U_1 - T_M S_1 = U_2 - T_M S_2$

**Magnetic entropy change** $\Delta S_M = \frac{U_1 - U_2}{T_M}$

*PRB 2006*

# Permanent Magnetism

With Post-Doc Renu Choudhary

## Motivation

Prediction of new disruptive permanent magnetic materials that have high uniaxial magneto-crystalline anisotropy and magnetic moment with reduced critical elements

## Goals and Objectives

Identify and employ novel methods to exploit 4f-elements for use in various novel rare earth element (REE) magnets

Theoretical assessment of optimal structural geometries to help accelerate the development of new materials with large magnetic anisotropies, moments, and magnetic transition temperatures

# Anisotropy and quenched orbital moment in Sm-Co magnets

## Achievement

Using electronic structure modeling, strong quenching of orbital magnetic moment was identified as the prime cause of unusually high magnetic anisotropy in $SmCo_5$

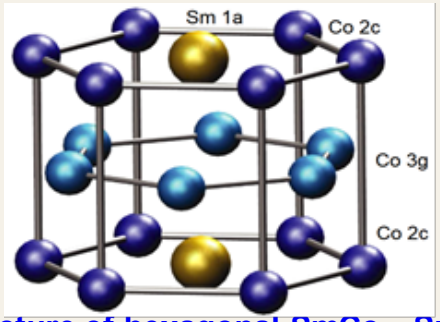
## Significance and impact

- Demonstration of validated theory and modeling techniques to resolve unsolved key permanent magnet parameters such as magnetic anisotropy and orbital moment emerging from rare-earths
- Sm-Co magnets offer relatively high energy-product at high-temperature suitable for technological applications from electric vehicles to wind turbines

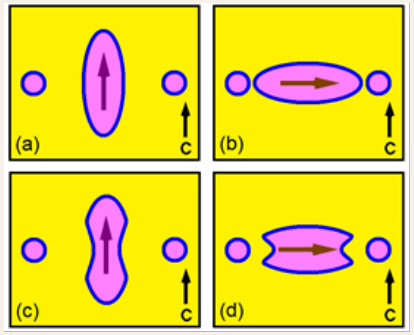
## Details and next steps

- Electronic structure of the Sm atoms violates Hund's rules and the orbital moment is strongly quenched providing strong anisotropy and net 4f moment
- Rationalizing the orbital-moment quenching in terms of the dependence of the 4f charge distribution, a long-run future research will be necessary to reconcile experiment, sub-lattice model, and ab-initio theory

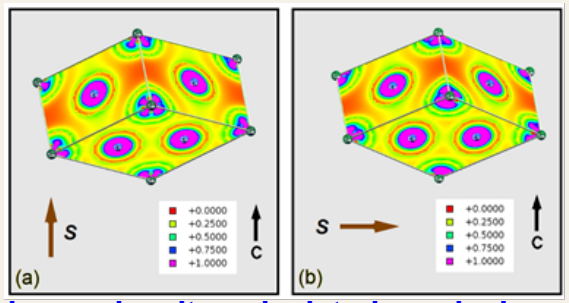
B. Das, R. Choudhary, R. Skomski, B. Balasubramanian, A. K. Pathak, D. Paudyal, and D. J. Sellmyer, Anisotropy and Orbital Moment in Sm-Co Permanent Magnets, Phys. Rev. B **100**, 024419 (2019).




**Crystal structure of hexagonal $SmCo_5$. Sm-1a, Co-2c, and Co-3g are three non-equivalent sites.**

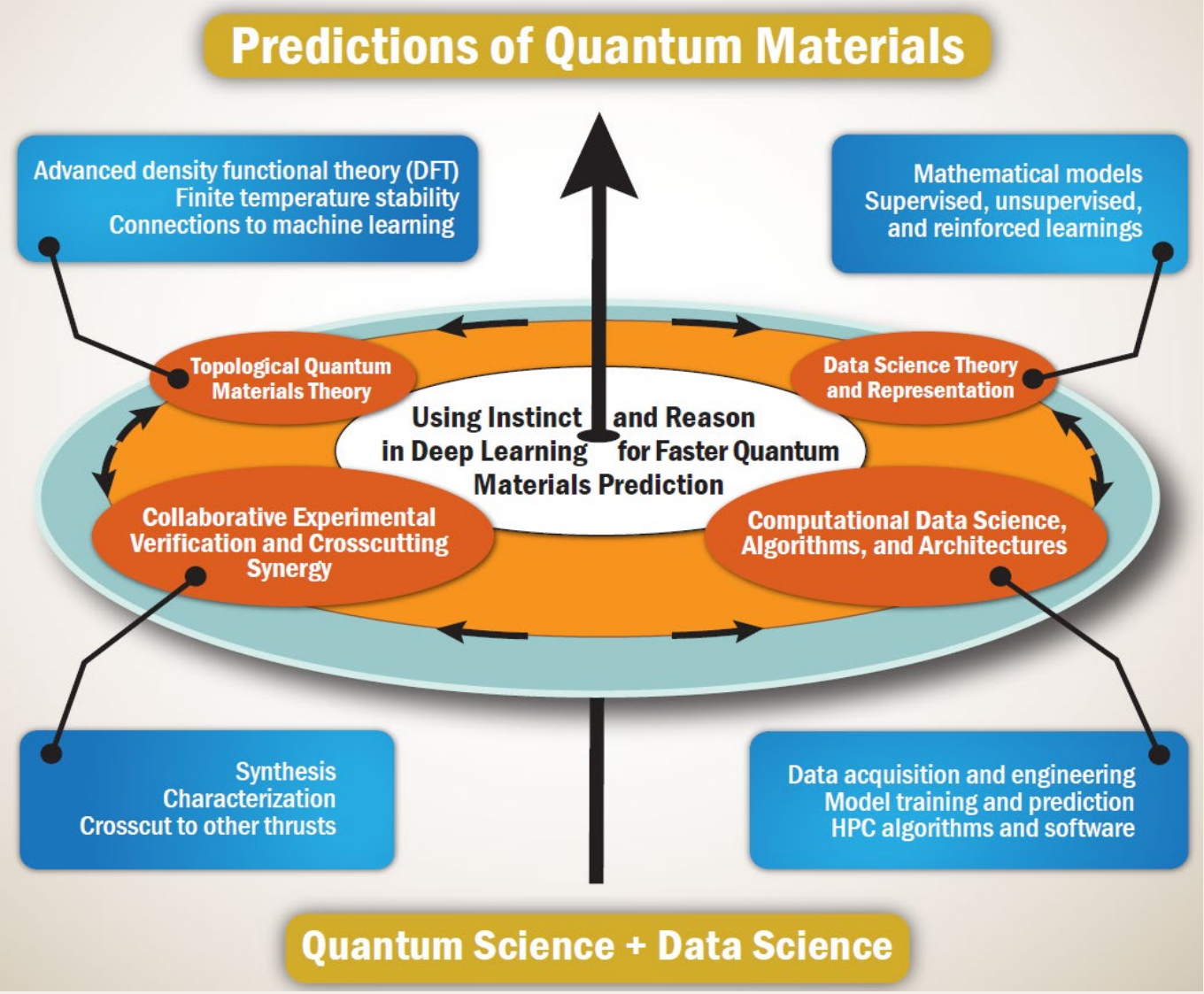



**(a) and (b) charge distribution and rare-earth moment in the easy and hard directions, (c) and (d) effect of crystal field on the charge distribution for the easy and hard directions**




**The charge density calculated employing density functional theory calculations**

# Quantum Materials Predictions



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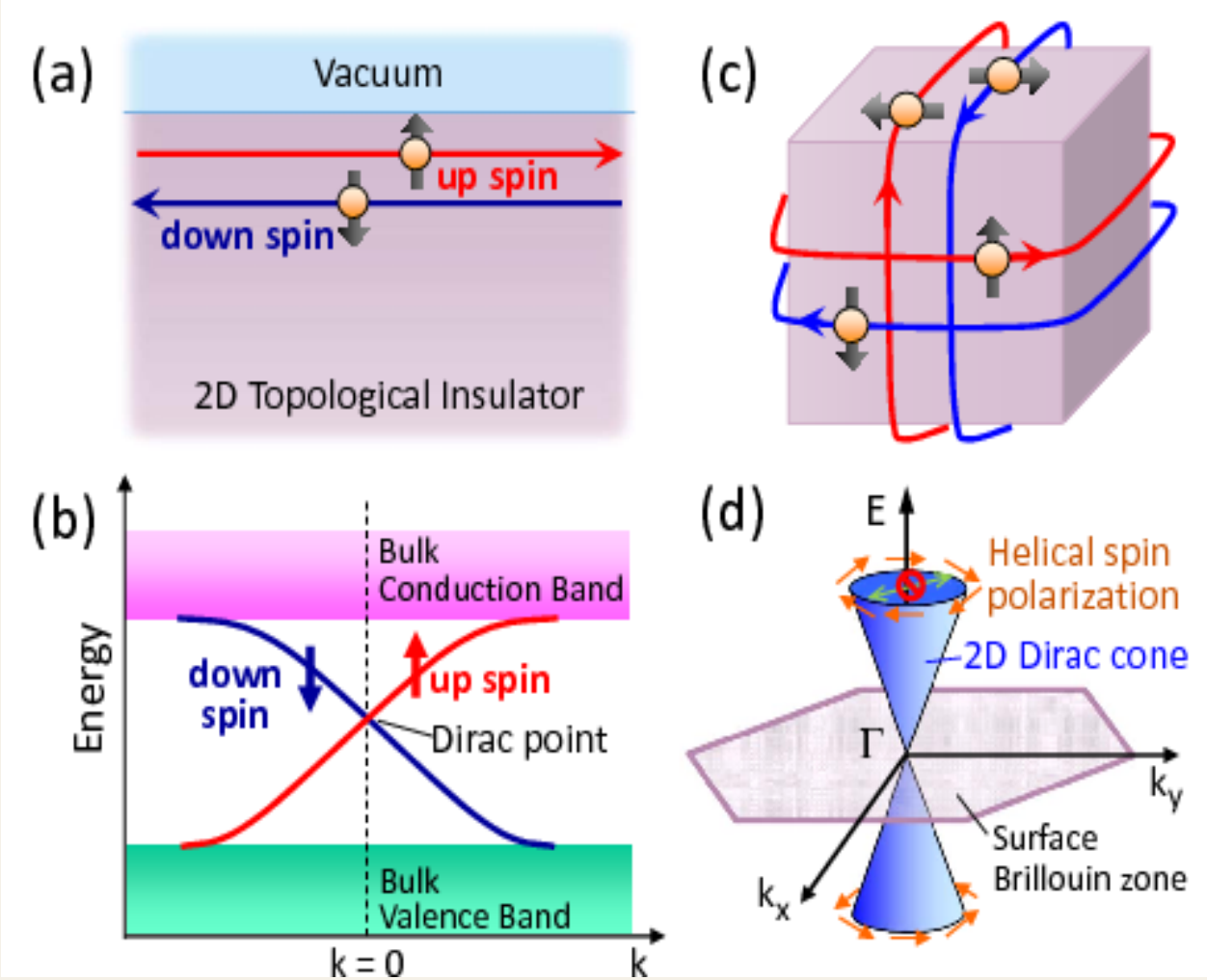
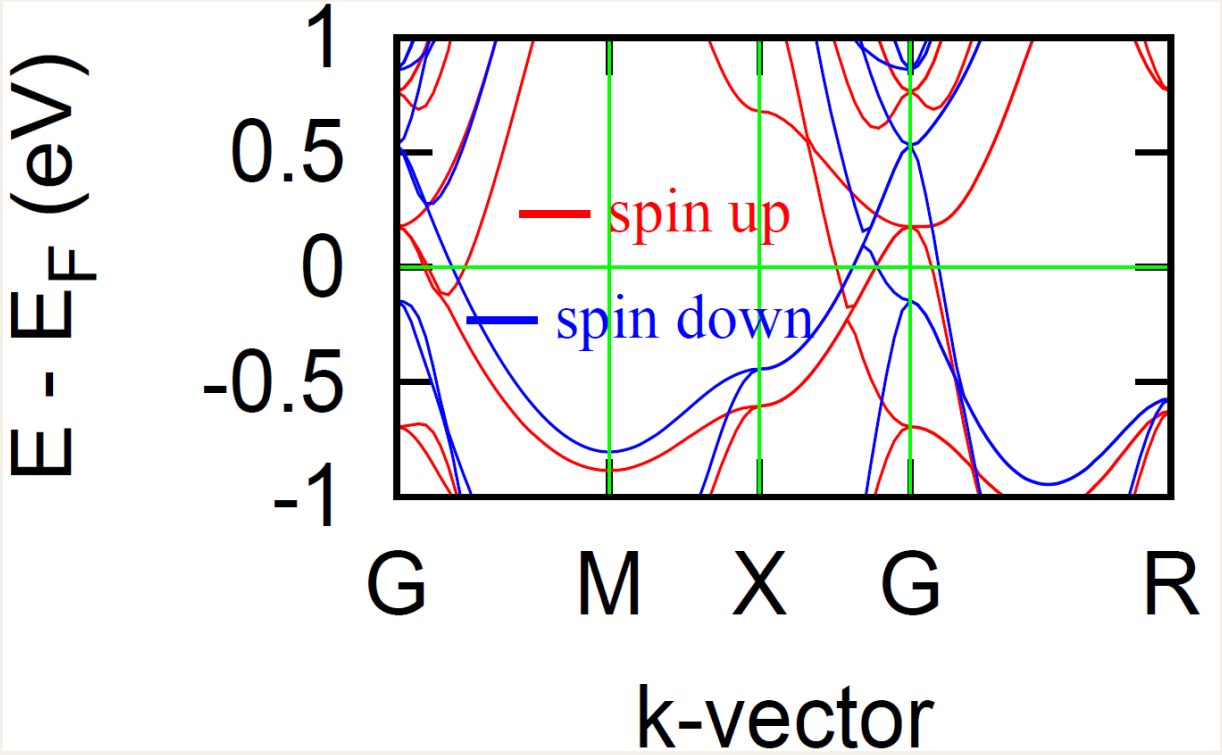
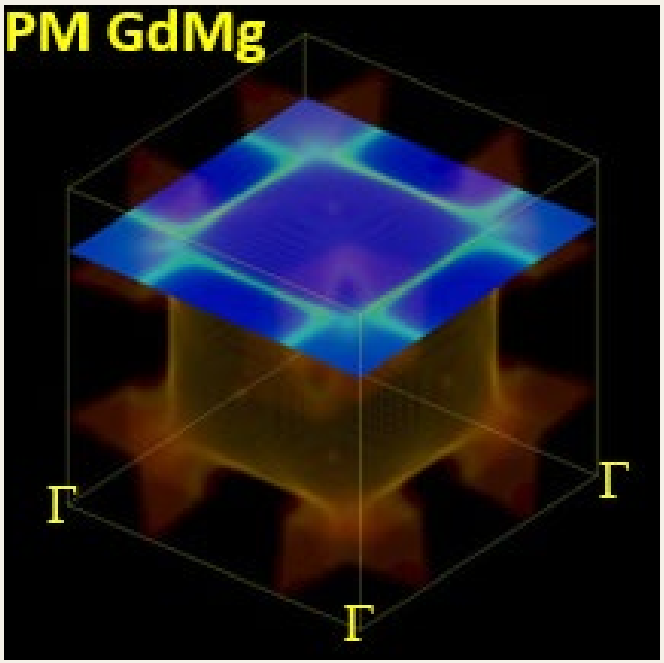


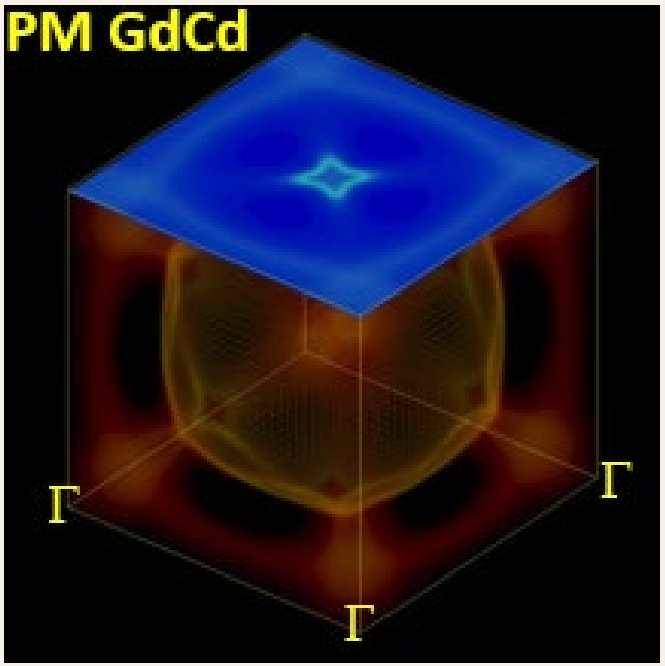
# Quantum Materials Predictions




Complex band at the G (Γ) point and in the GX (ΓX) high-symmetry direction

# Quantum Materials Predictions



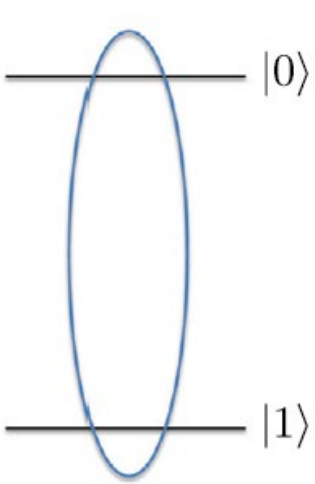



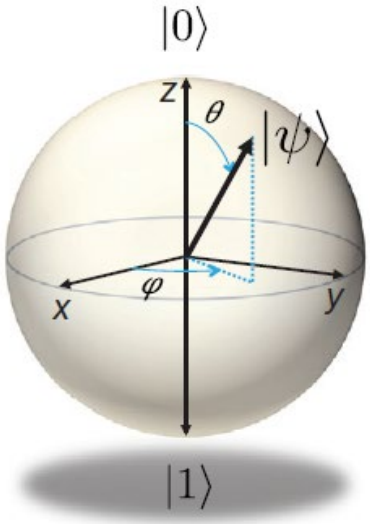

Wave vector (0 0 ½) nests large portions of parallel FS sheets, driving AFM correlations

A distinct topological transition – a hot spot formed around wave vector (½ ½ 0) when Mg is replaced by Cd, thereby suppressing the AFM and developing FM correlations

# Quantum Information Science

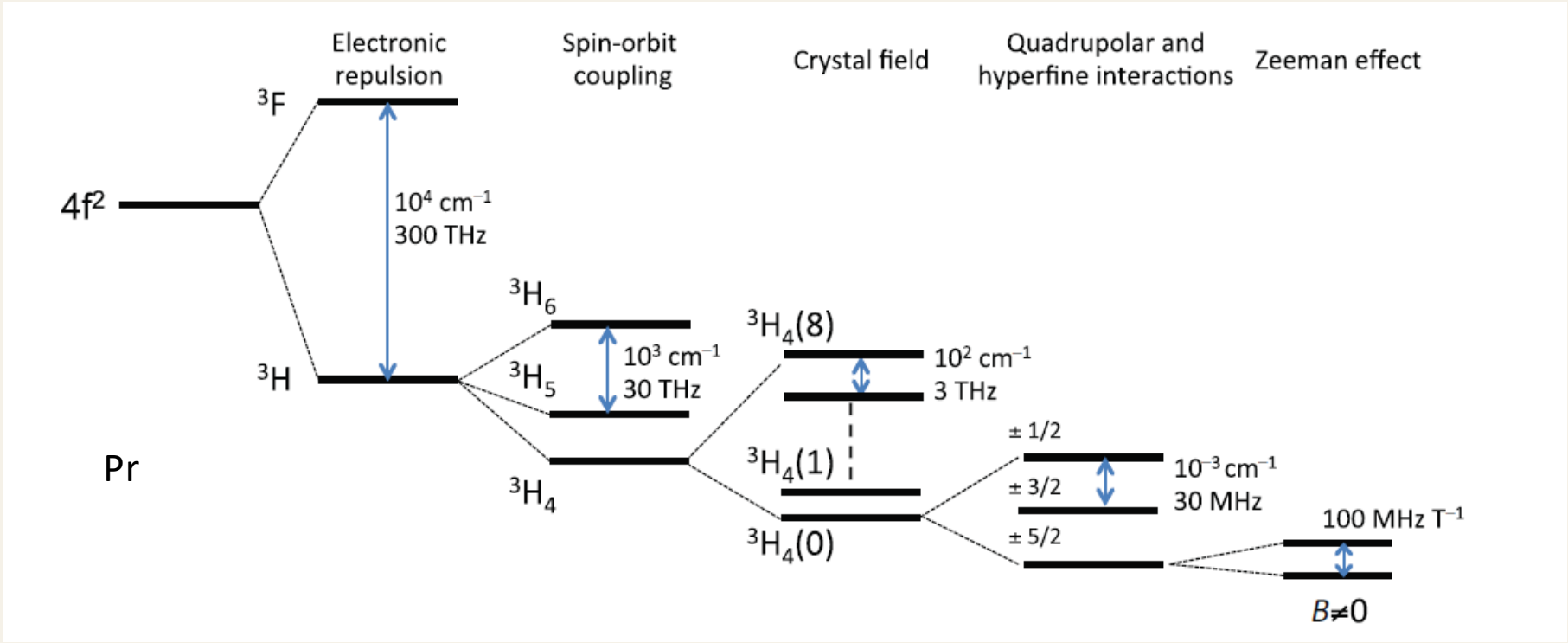
$$|\psi\rangle = \cos(\theta/2)|0\rangle + e^{i\phi}\sin(\theta/2)|1\rangle$$




$$|\psi\rangle = \cos(\theta/2)\,|0\rangle + e^{i\,\phi}\sin(\theta/2)\,|1\rangle$$

# Quantum Information Science




Interactions and partial energy-level scheme for $Pr^{3+}$ (I = 5/2). The degeneracy of the hyperfine levels is lifted by an external magnetic field

# Conclusion

Understanding of symmetry and topology will help build a foundation to discover quantum materials for current and future energy applications such as energy conversion, permanent magnet, and quantum information