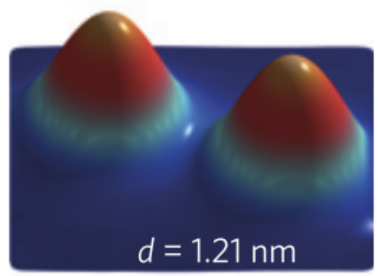
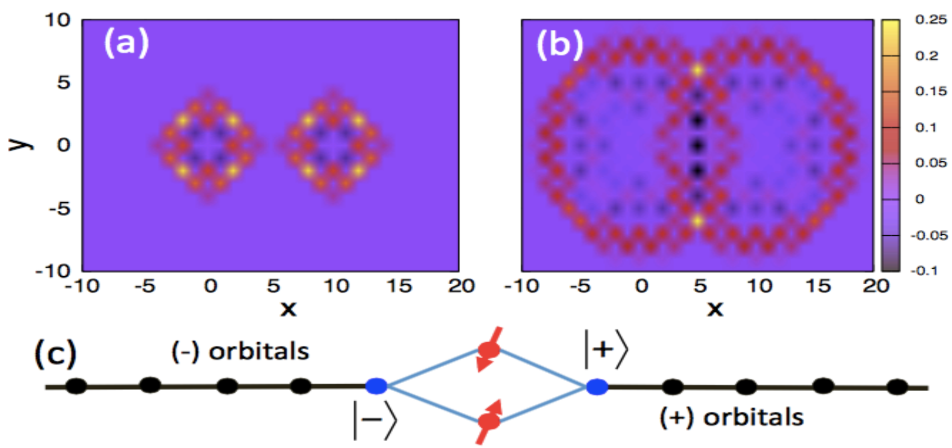
Iron chef: Recipes for building magnetic structures atom by atom

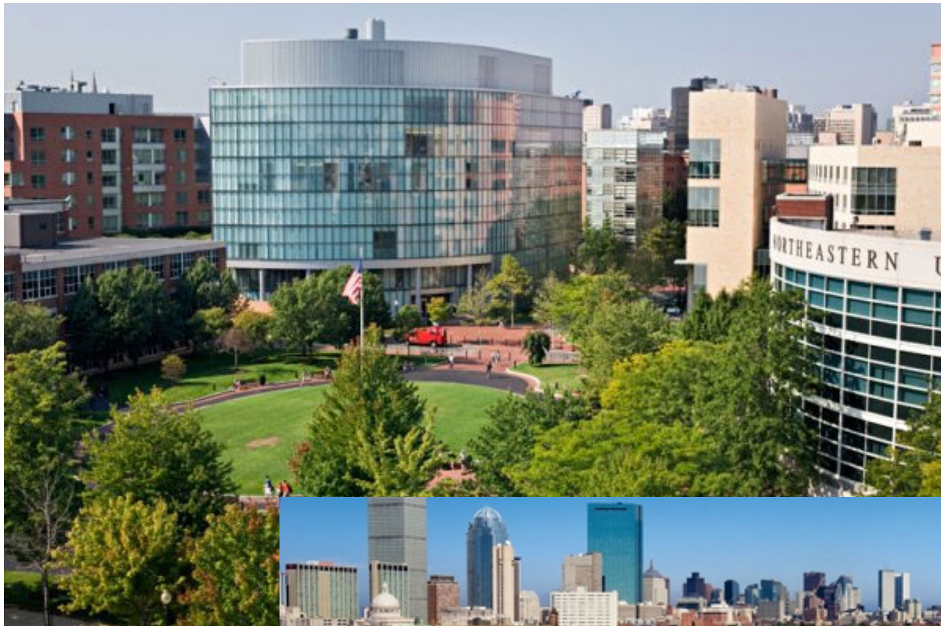
Adrian Feiguin

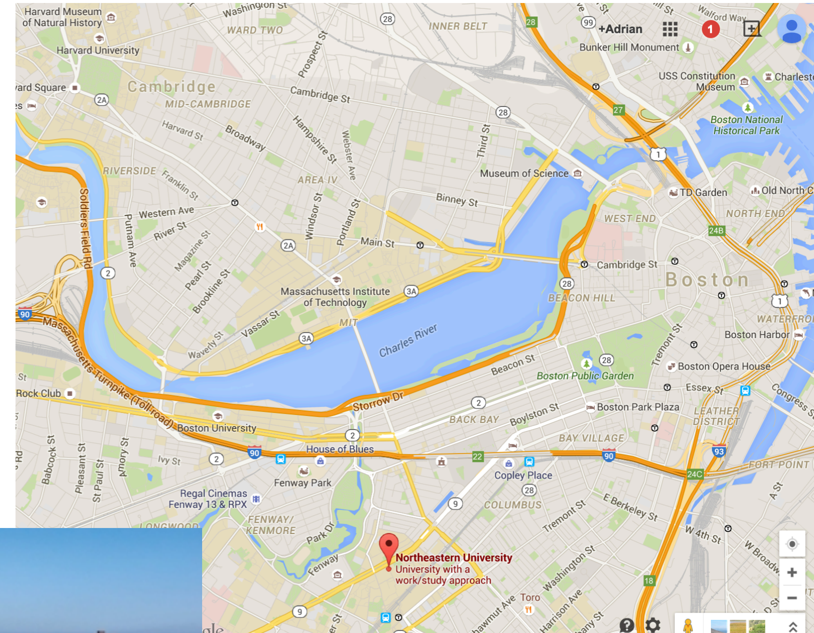
Northeastern University (Boston)





Northeastern University





Boston

Assistant chefs

Carlos Busser

Andrew Allerdt

References:

A.Allerdt, C. A. Büsser, S. Das Sarma, A. E. Feiguin (in preparation).

A. Allerdt, C. A. Büsser, G. B. Martins, and A. E. Feiguin, Phys. Rev. B 91, 085101 (2015).

C. A. Büsser, G. B. Martins, and A. E. Feiguin, Phys. Rev. B 88, 245113 (2013).

Motivation I: Permanent magnets are of strategic importance for modern technology

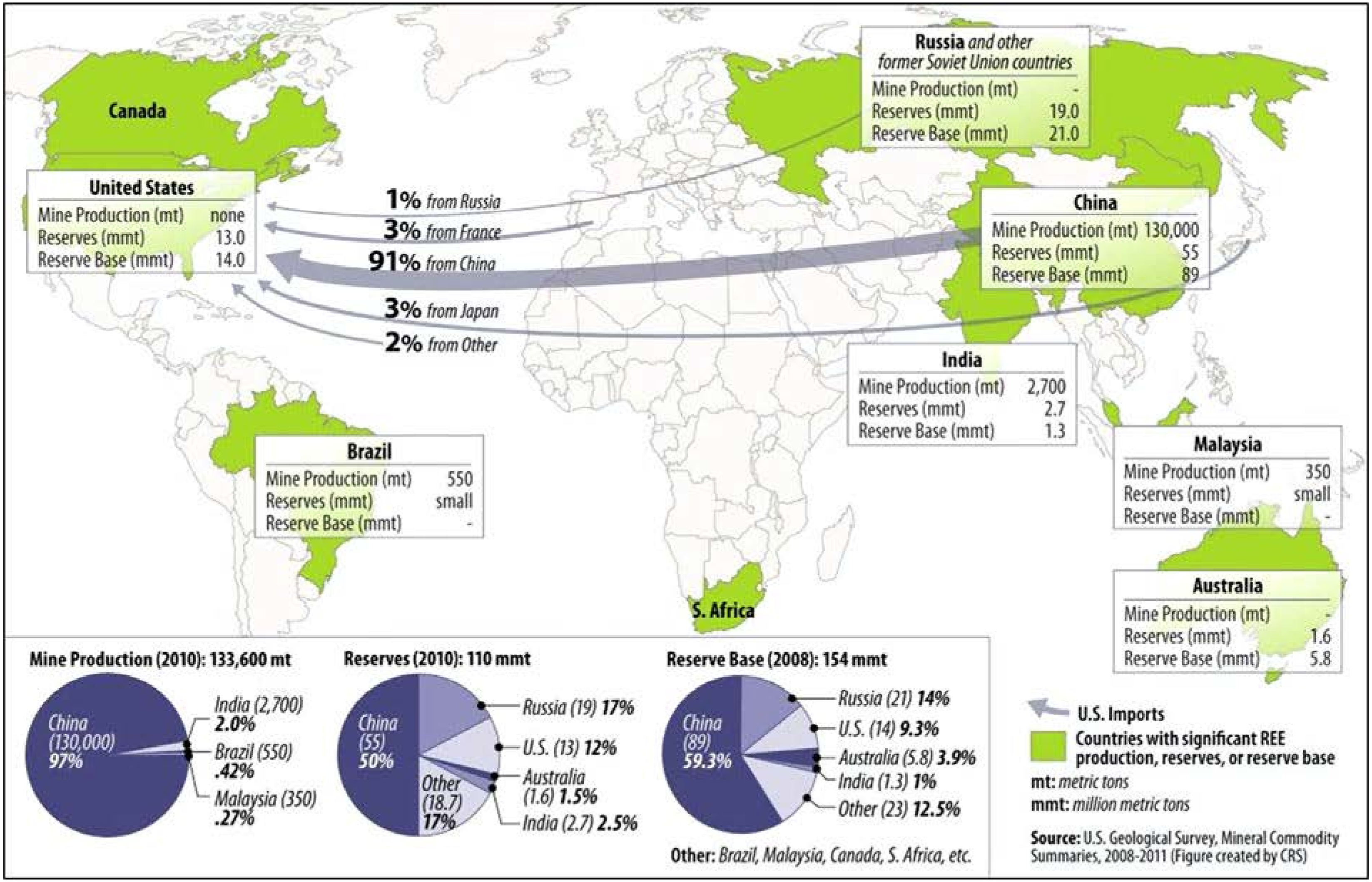
Data & Electronics

Energy Conversion

Computer and office automation	• Computer hard drives • CD-ROM spindle motors and pick-up motors	**Consumer electronics**	• cameras • speakers • cell phones
Automotive & transportation	• starter motors • electric steering • sensors • instrumentation gauges	**Medical industry**	• magnetic resonance imaging equipment • surgical tools • medical implants
Factory automation	• magnetic couplings • servo motors • generators • magnetic bearings	**Alternative energy**	• hybrid/electric vehicles • wind power systems • power generation systems • energy storage systems
Appliances & systems	• portable power tools • household appliance motors • scales • air conditioners	**Military**	• weapons systems • vehicles, watercraft, avionics • communications systems, radar satellites

Courtesy of Luke G. Marshall: Table adapted from: Lewis, L. H. & Jiménez-Villacorta, F. “Perspectives on Permanent Magnetic Materials for Energy Conversion and Power Generation.” Metall. Mater. Trans. A 44, 2–20 (2012).
Systems information from USMMA RE-Weapons Systems DoD Supply Chain Assessment, 10/07/2010: http://bit.ly/1THp1uM

RE-elements supply chain



M. Humphries. “Rare Earth Elements: The Global Supply Chain.” Congressional Research Service 7-5700, R41347, 2011.

RE-elements supply chain
An strategic priority area

Figure 1. Short-Term (0–5 years) Criticality Matrix

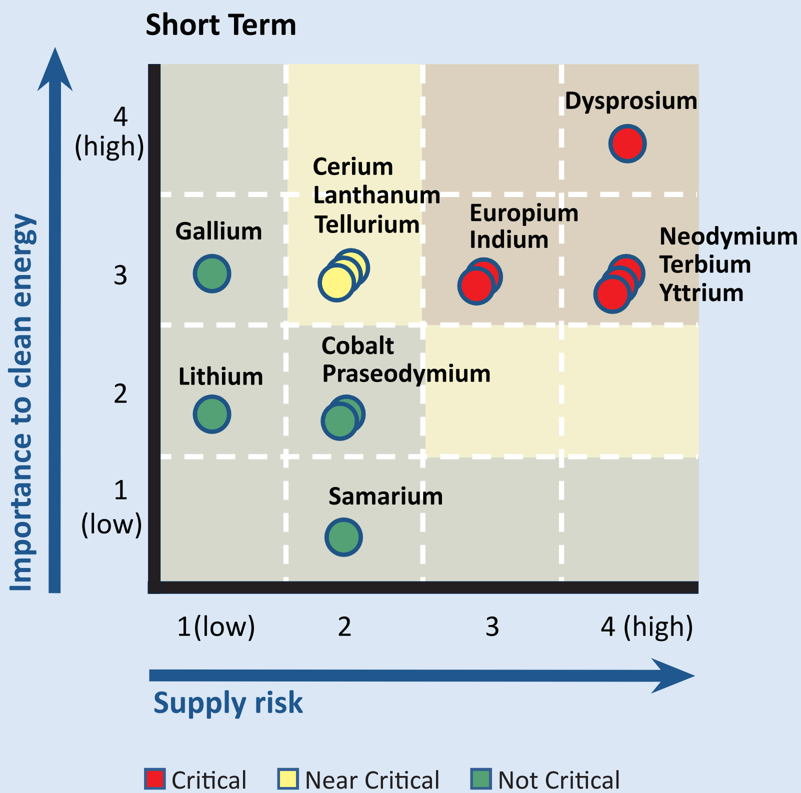
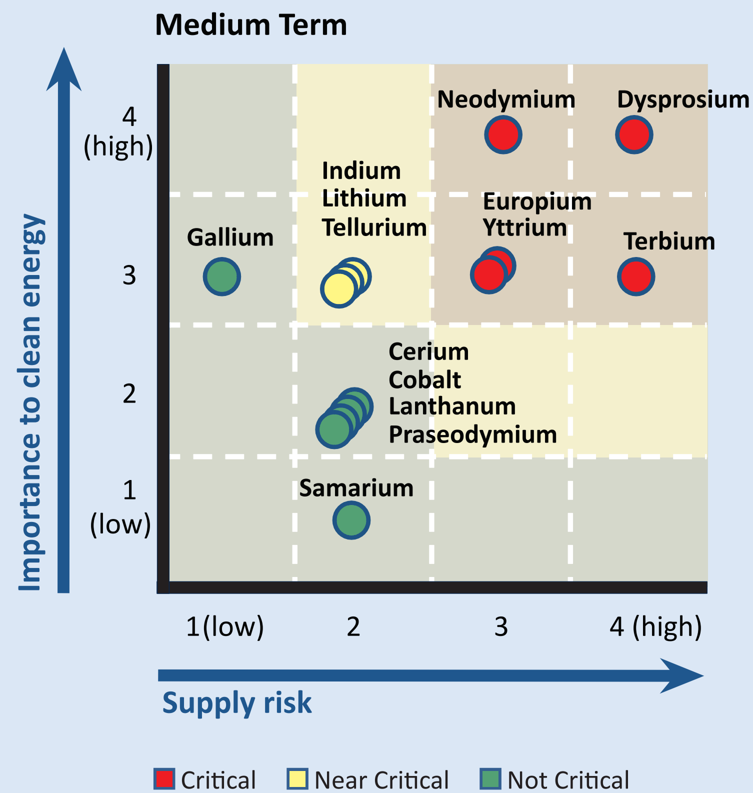
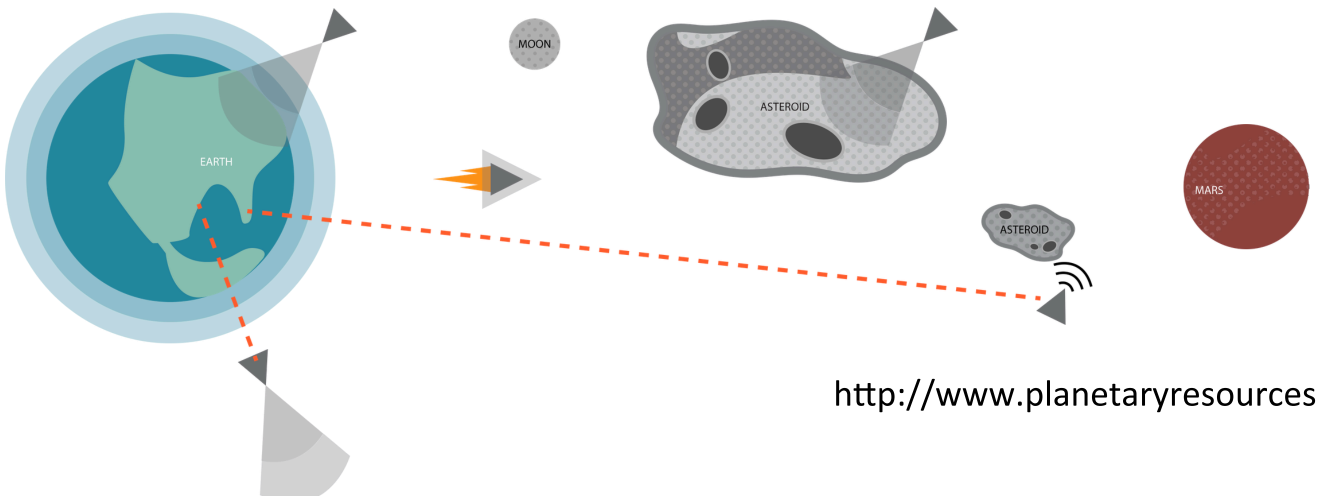


Figure 2. Medium-Term (5–15 years) Criticality Matrix



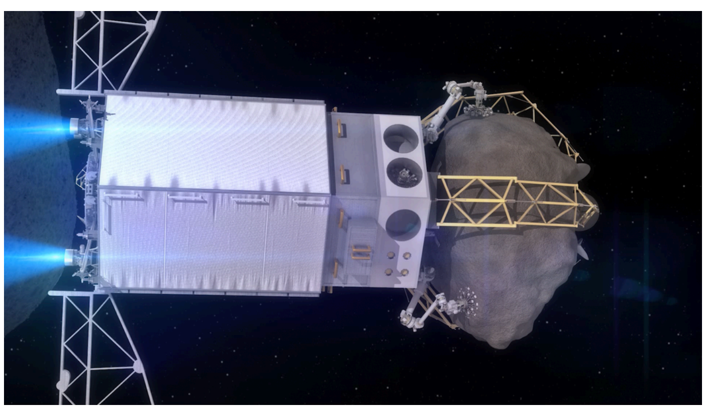
DOE Report, 2010 (see also DOD reports)

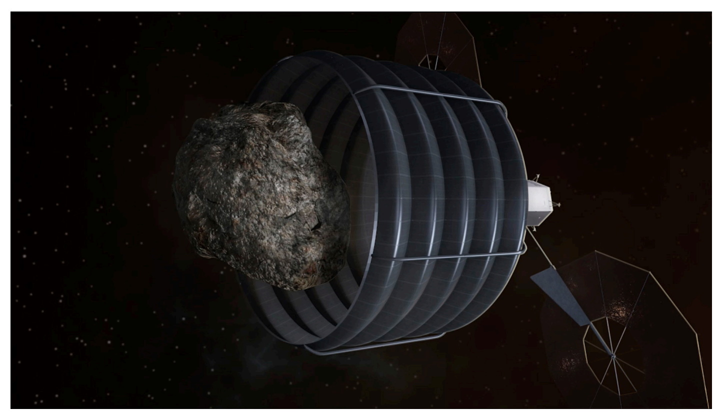
(Possible and likely) Solution: Asteroid Mining



http://www.planetaryresources.com

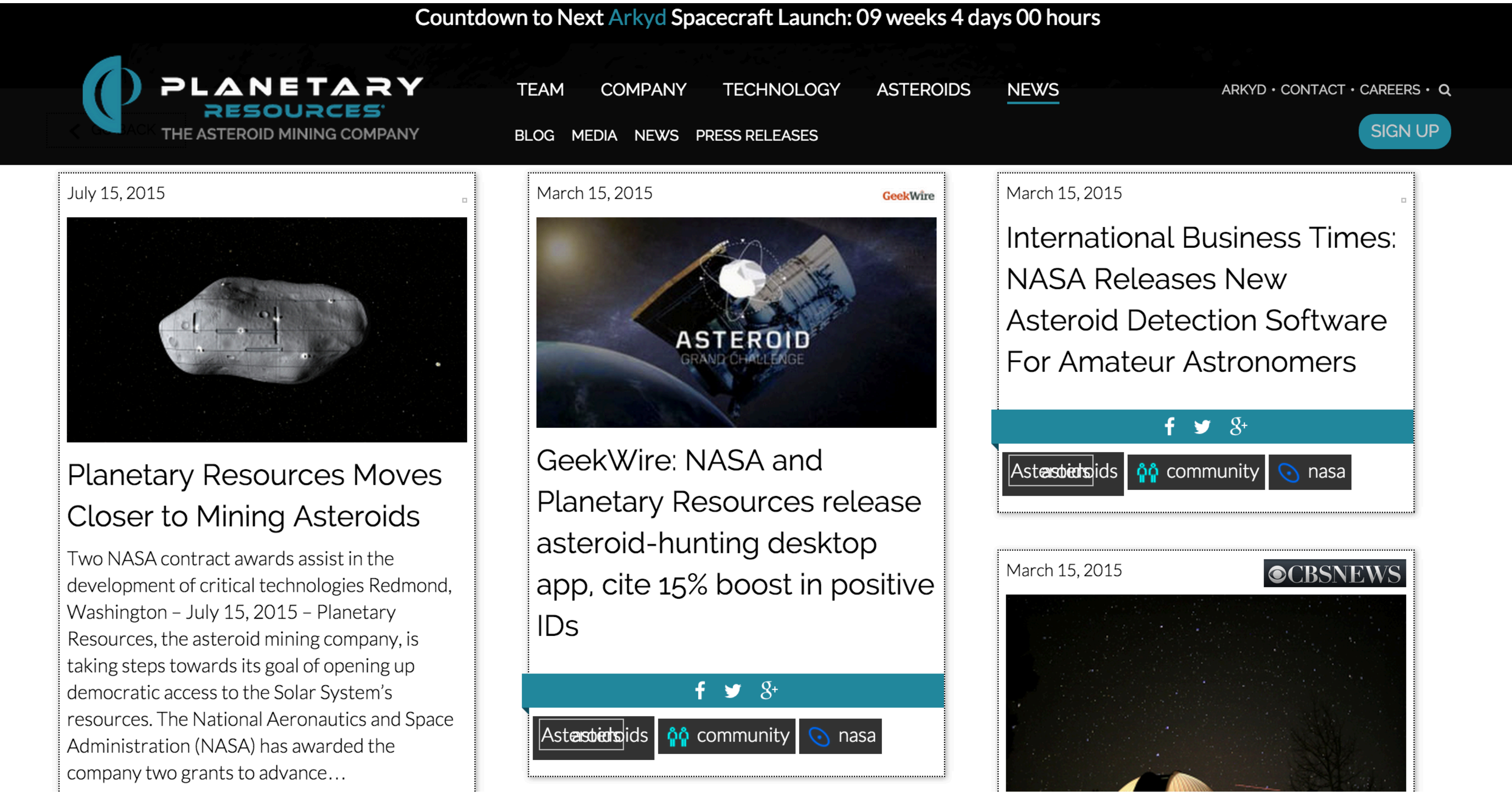
Asteroid Redirect Mission (NASA and Planetary Resources)





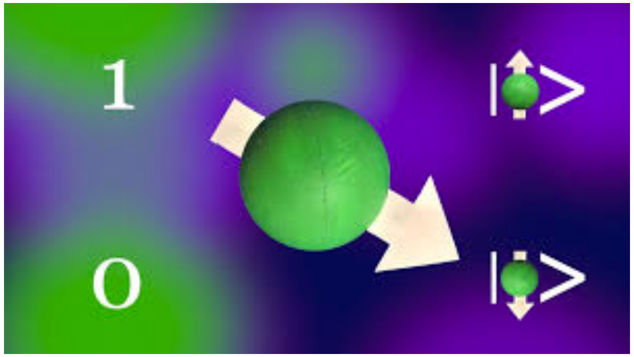
Asteroid mining

http://www.planetaryresources.com



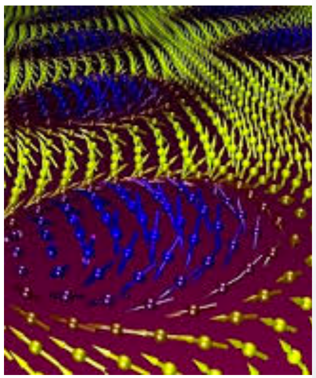
Motivation II: "Spintronics"

- Information is stored into spin as one of two possible orientations
- Spin lifetime is relatively long, on the order of nanoseconds
- Spin currents can be manipulated
- Spin devices may combine logic and storage functionality eliminating the need for separate components
- Magnetic storage is nonvolatile
- Binary spin polarization offers the possibility of applications as qubits (quantum "spins transistors") in quantum computers
- High speed, low power consumption
- Atomic scale devices

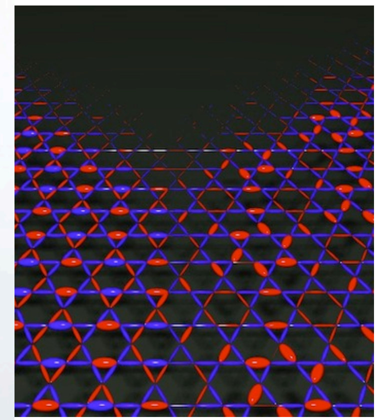


Motivation III: fundamental physics and exotic states of matter

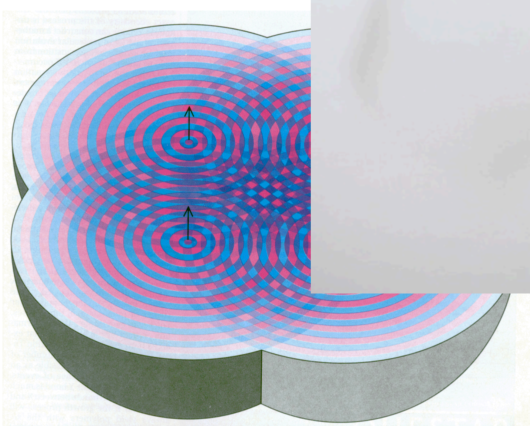
Topological s



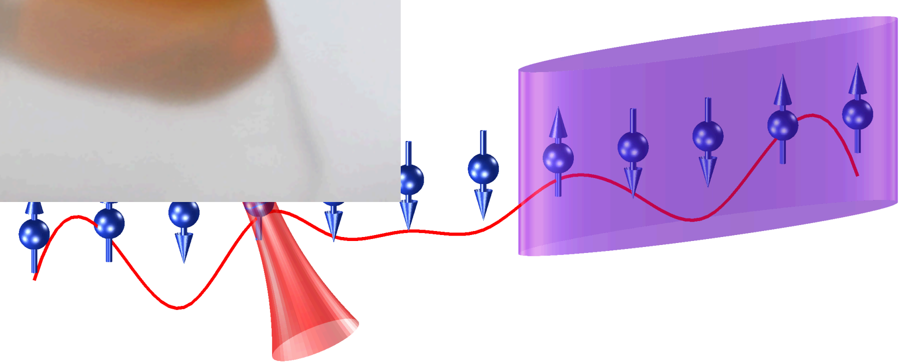
Spin liquids



Spin gla



-body localization



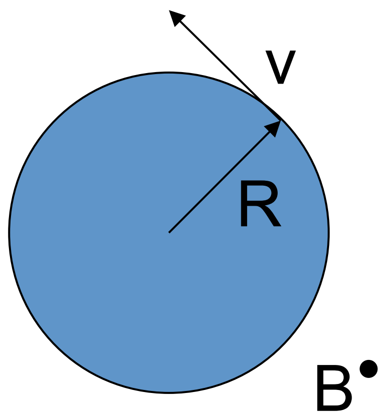
Classical magnetism (or lack thereof)

The *Bohr-van Leeuwen* theorem

Simple proof:

$$\mathbf{F} = q\mathbf{v} \times \mathbf{B}$$ Perpendicular to velocity

$$\int \mathbf{F} \cdot dl = \int \mathbf{F} \cdot \mathbf{v} dt = q \int (\mathbf{v} \times \mathbf{B}) \cdot \mathbf{v} dt = 0$$ No work



No work = no change in energy = no magnetization!!!

Actual proof:

$$Z = \int \prod_i d\mathbf{r}_i d\mathbf{p}_i \exp[-\beta H(\{\mathbf{r}_i, \mathbf{p}_i\})] \qquad H = \sum_i \frac{[\mathbf{p}_i + e\mathbf{A}(r_i)]^2}{2m} + other\ terms$$

The vector potentials can be "gauged out", the integral is independent of B

$$\mathbf{M} = -\left(\frac{\partial F}{\partial \mathbf{B}}\right)_{T,V} = -\frac{1}{\beta}\left(\frac{\partial \log Z}{\partial \mathbf{B}}\right)_{T,V} = 0 \quad !!!$$

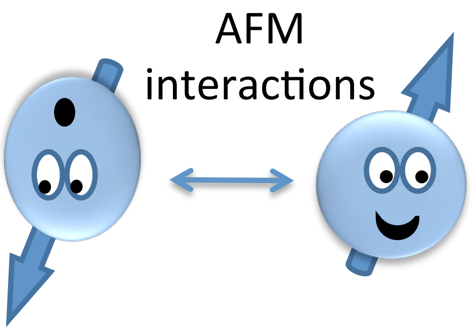
The Bohr-van Leeuwen theorem shows that magnetism cannot be accounted for ***classically***. In particular, it also rules out classical ferromagnetism, paramagnetism, and diamagnetism ***(In equilibrium!)***.

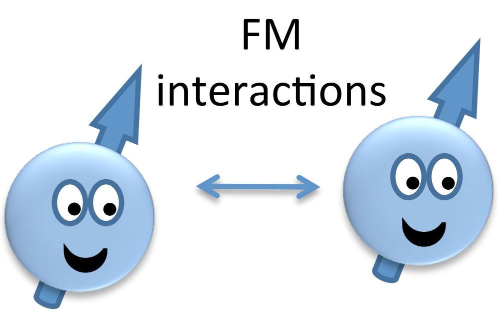
Magnetism is a quantum phenomenon!

Main contribution for free atoms:

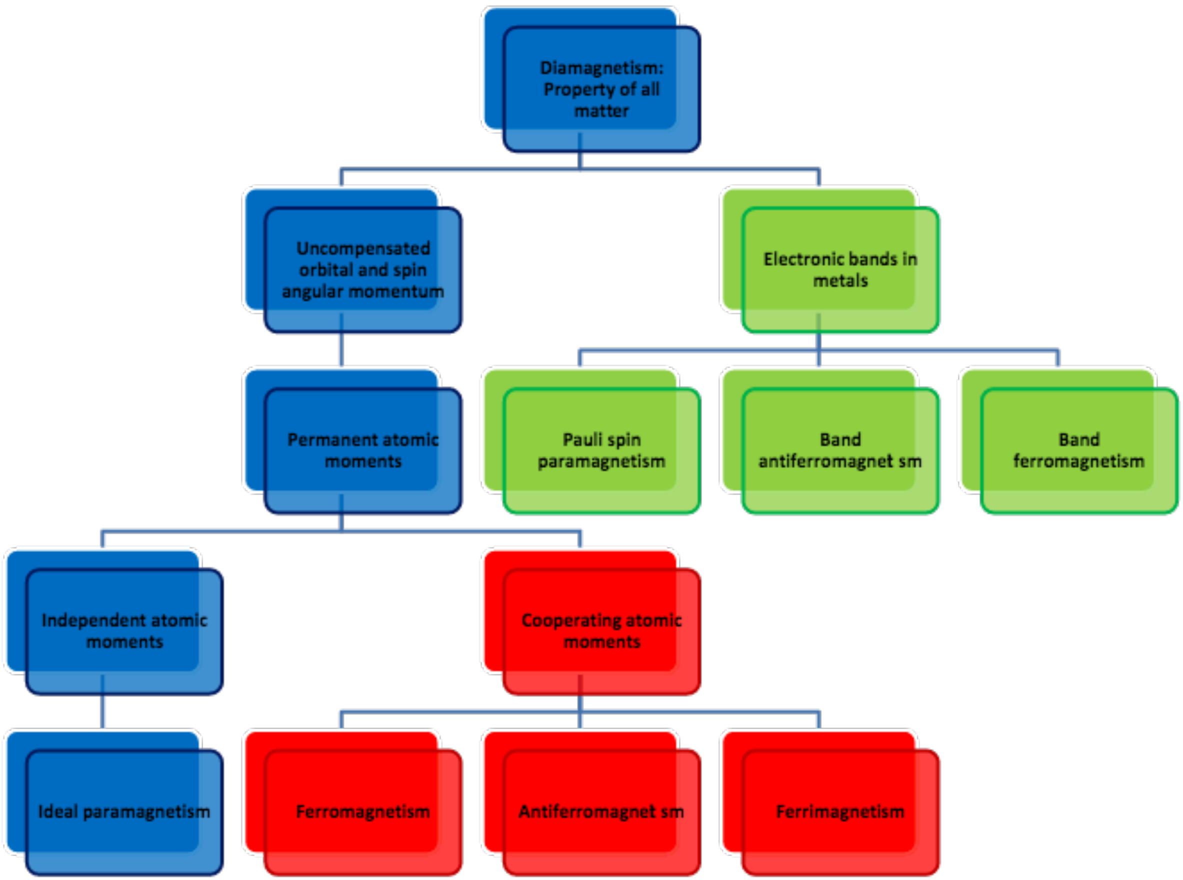
- spins of electrons
- orbital angular momenta of electrons
- Induced orbital moments

Electronic structure	Moment
H: 1s	**M** ~ **S**
He: $1s^2$	**M** = **0**
unfilled shell	**M** ≠ **0**
All filled shells	**M** = **0**





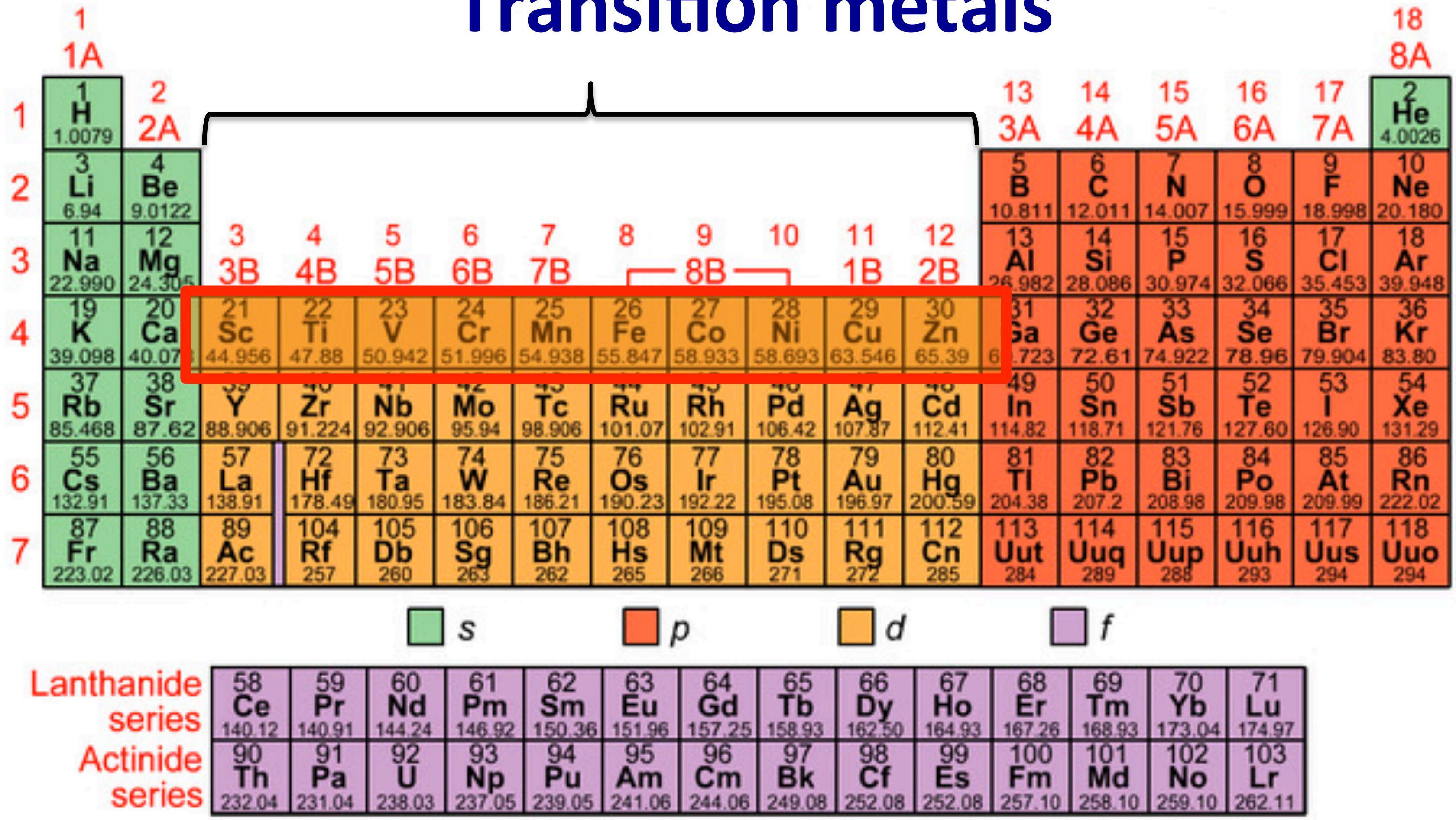
Various types of magnetism



Magnetism in the solid state is much rarer than in gases, since in gases atoms preserve their partially filled shells

Source: www.boundless.com

Solution: dope with Rare Earths and Transition metals



Colors represent *s*, *i*, *d*, and *f* blocks

Source: www.boundless.com

Hund's Rules

For filled shells, spin orbit couplings do not change order of levels.

Hund's rule (L-S coupling scheme):
Outer shell electrons of an atom in its ground state should assume
1.Maximum value of S allowed by exclusion principle.
2.Maximum value of L compatible with (1).
3.J = | L−S | for less than half-filled shells.
J = L + S for more than half-filled shells.

Causes:
1. Parallel spins have lower Coulomb energy.
2. e's meet less frequently if orbiting in same direction (parallel Ls).
3. Spin orbit coupling lowers energy for $L \cdot S < 0$.

Mn^{2+}: $3d^5$ (1) $\rightarrow S = 5/2$ exclusion principle $\rightarrow L = 2+1+0-1-2 = 0$

Ce^{3+}: $4f^1$ $L = 3, \ S = ½$ (3) $\rightarrow J = | 3 - ½ | = 5/2$ ${}^2F_{5/2}$

Pr^{3+}: $4f^2$ (1) $\rightarrow S = 1$ (2) $\rightarrow L = 3+2 = 5$ (3) $\rightarrow J = | 5 - 1 | = 4$ ${}^3H_4$

Iron Group Ions

Table 2 Effective magneton numbers for iron group ions

Ion	Configuration	Basic level	$p(\text{calc}) = g[J(J+1)]^{1/2}$	$p(\text{calc}) = 2[S(S+1)]^{1/2}$	$p(\text{exp})^a$
Ti^{3+}, V^{4+}	$3d^1$	$^2D_{3/2}$	1.55	1.73	1.8
V^{3+}	$3d^2$	$^3F_2$	1.63	2.83	2.8
Cr^{3+}, V^{2+}	$3d^3$	$^4F_{3/2}$	0.77	3.87	3.8
Mn^{3+}, Cr^{2+}	$3d^4$	$^5D_0$	0	4.90	4.9
Fe^{3+}, Mn^{2+}	$3d^5$	$^6S_{5/2}$	5.92	5.92	5.9
Fe^{2+}	$3d^6$	$^5D_4$	6.70	4.90	5.4
Co^{2+}	$3d^7$	$^4F_{9/2}$	6.63	3.87	4.8
Ni^{2+}	$3d^8$	$^3F_4$	5.59	2.83	3.2
Cu^{2+}	$3d^9$	$^2D_{5/2}$	3.55	1.73	1.9

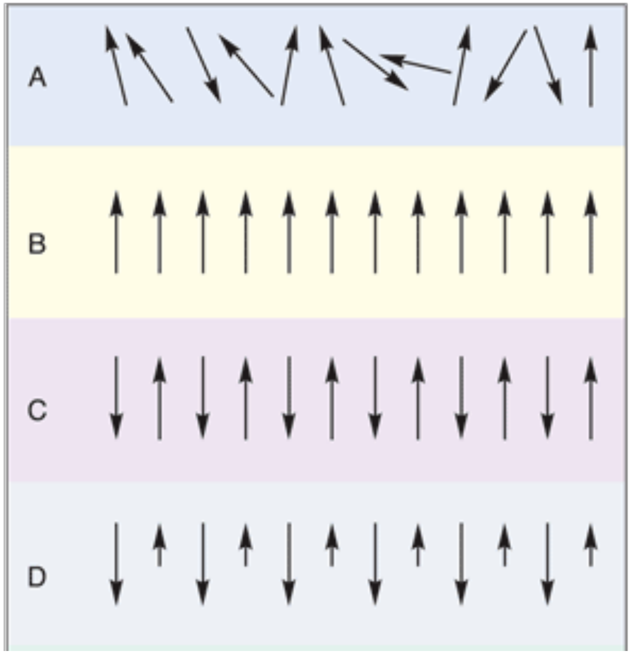
[a] Representative values.

$L = 0$

In these ions, the magneton numbers agree well with the spin prediction, as though the orbital moment were not present (it's said to be "quenched")

From Kittel's "Solid State Physics"

(Some) Types of magnetism

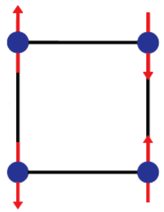


Paramagnetism

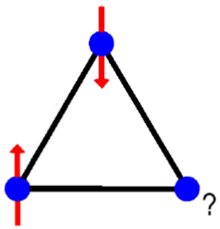
Ferromagnetism

Anti-Ferromagnetism

Ferrimagnetism



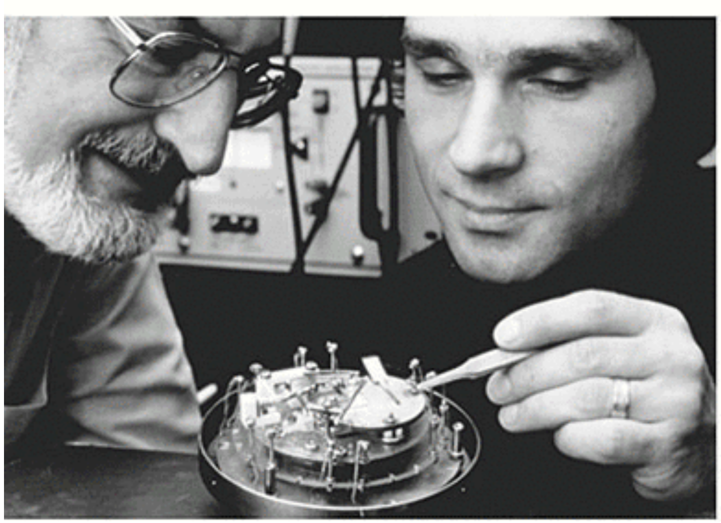
Square Lattice
Unfrustrated



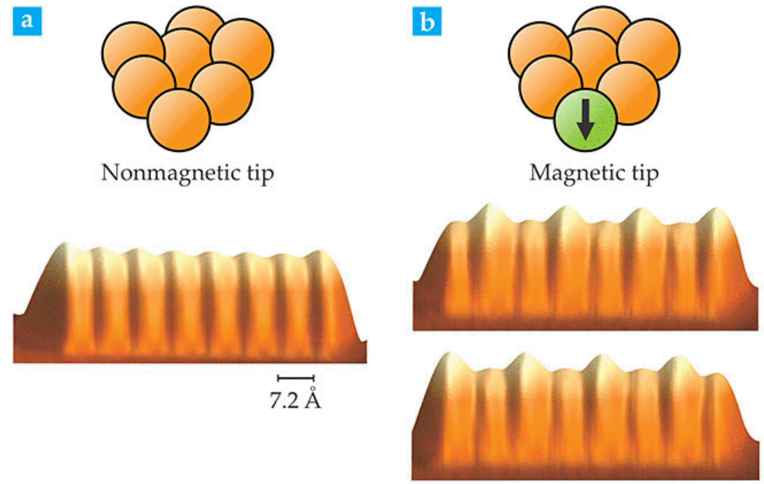
Triangular Lattice
Frustrated

Anti-Ferromagnetic interactions can yield counter-intuitive states of purely quantum origin, such as "spin-liquids"

The power of STM



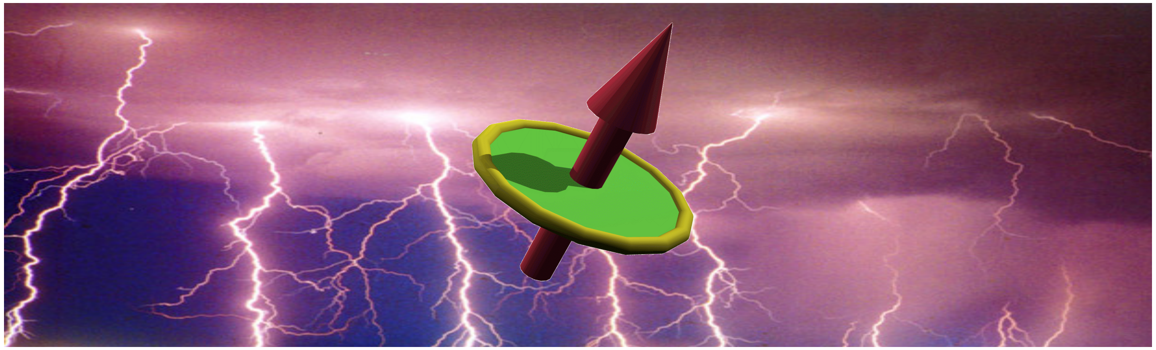
Gerd Binnig and Heinrich Rohrer
1986 Nobel Price



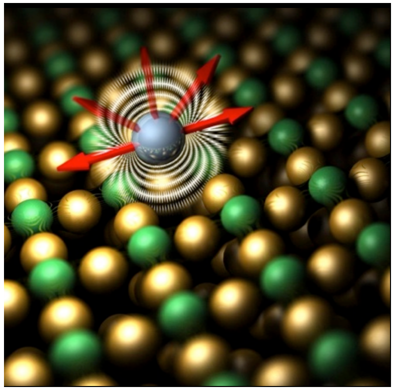
- STM provides a tool for constructing magnetic structures atom by atom
- STM-based spectroscopies can probe magnetic interactions with atomic resolution, such as:
  - Interplay between a local spin and its local environment
  - accessing multi-spin systems and probing for many-body effects

Andreas Heinrich, Physics Today (March 2015)

Coupling between spins and their environment



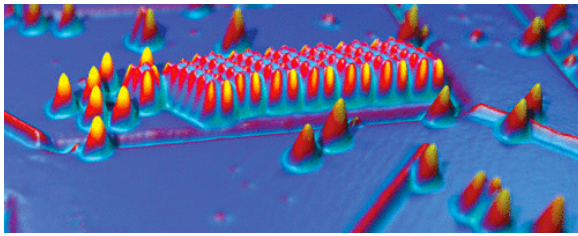
In some cases, such as in quantum information processing, spins are extremely sensitive to decoherence, a randomization of the spin state caused by entanglement with the environment



In other circumstances, this coupling is crucial, and can be used to engineer magnetic structures with arbitrary interactions

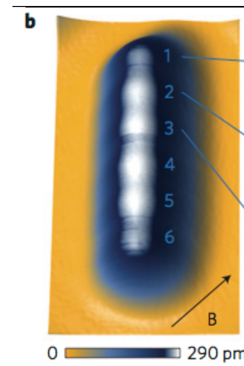
Atomic scale magnetic structures

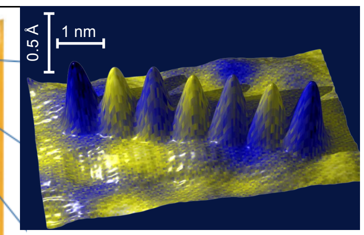
Ladders and magnetic clusters



S. Loth et al
Science (2013)

Spin chains

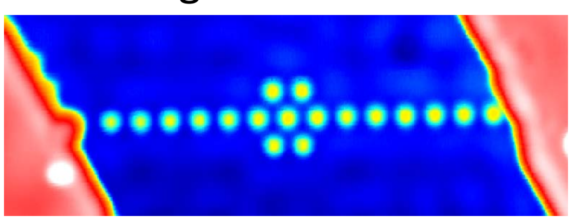




Khajetoorians et al
Nat. Phys. (2012)

Spinelli et al
Nat. Mat. (2014)

Magnetic devices

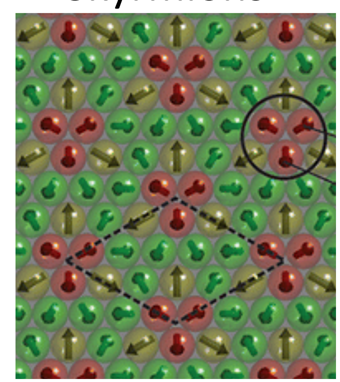


Khajetoorians et al
Science (2011)

Frustration

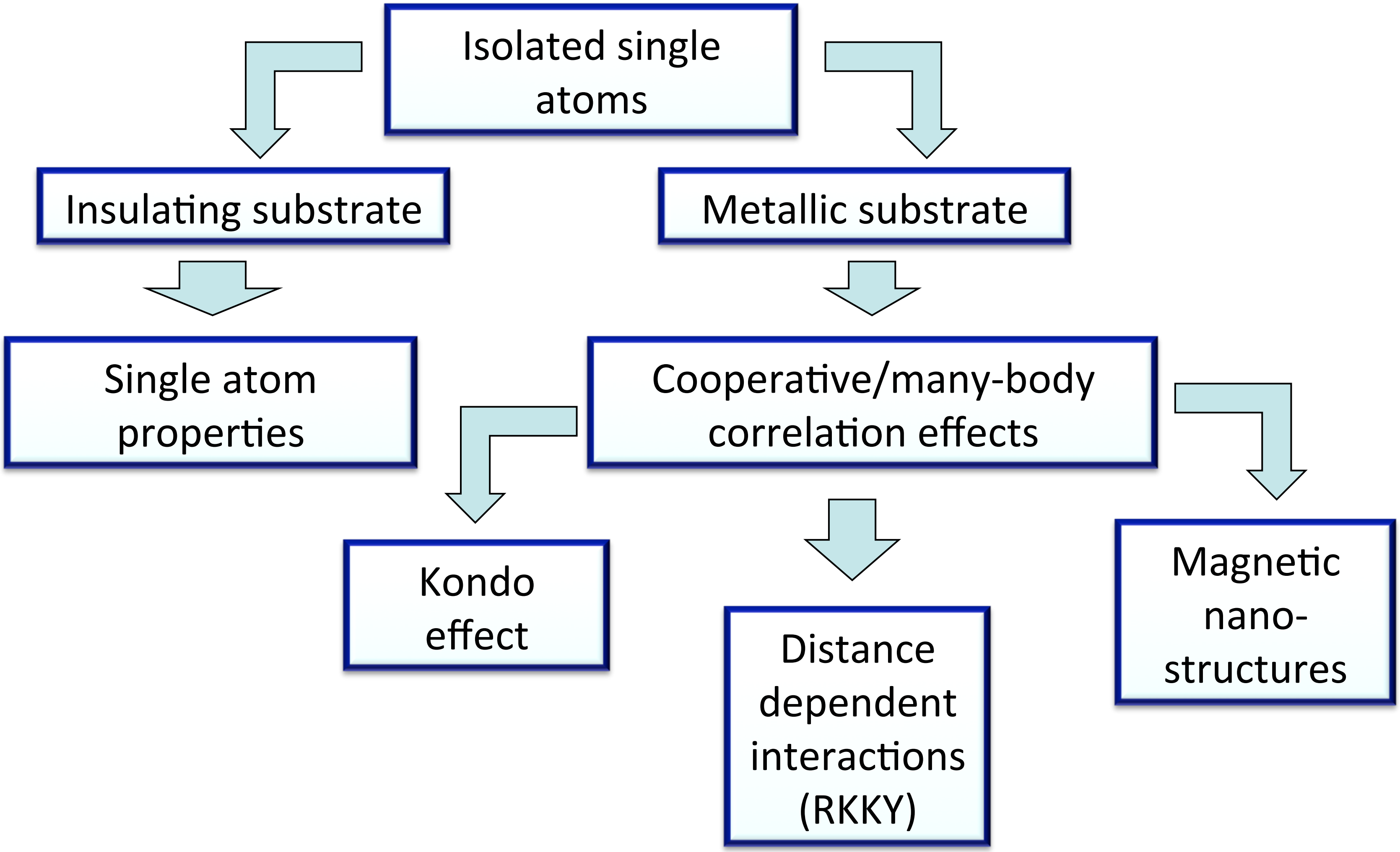
Khajetoorians et al
Science (2011)

Skyrmions

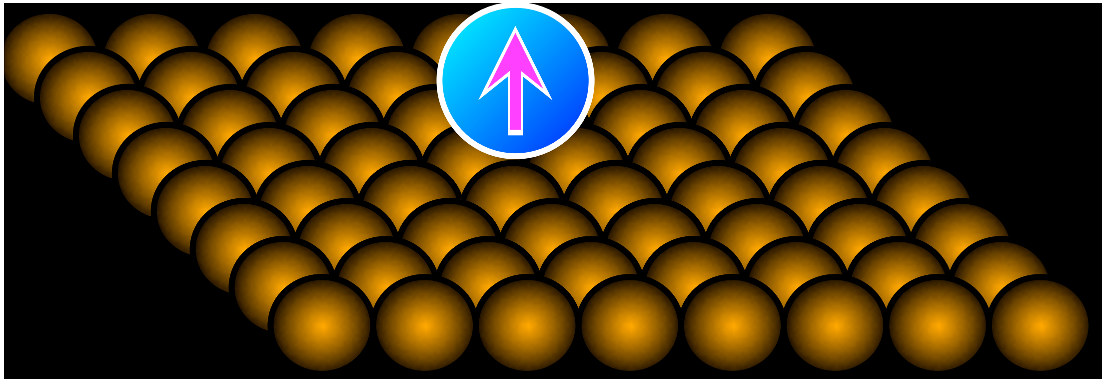


Von Bergmann
Nano. Lett. (2015)

From single atoms to magnetic structures



The single-impurity (Kondo) problem

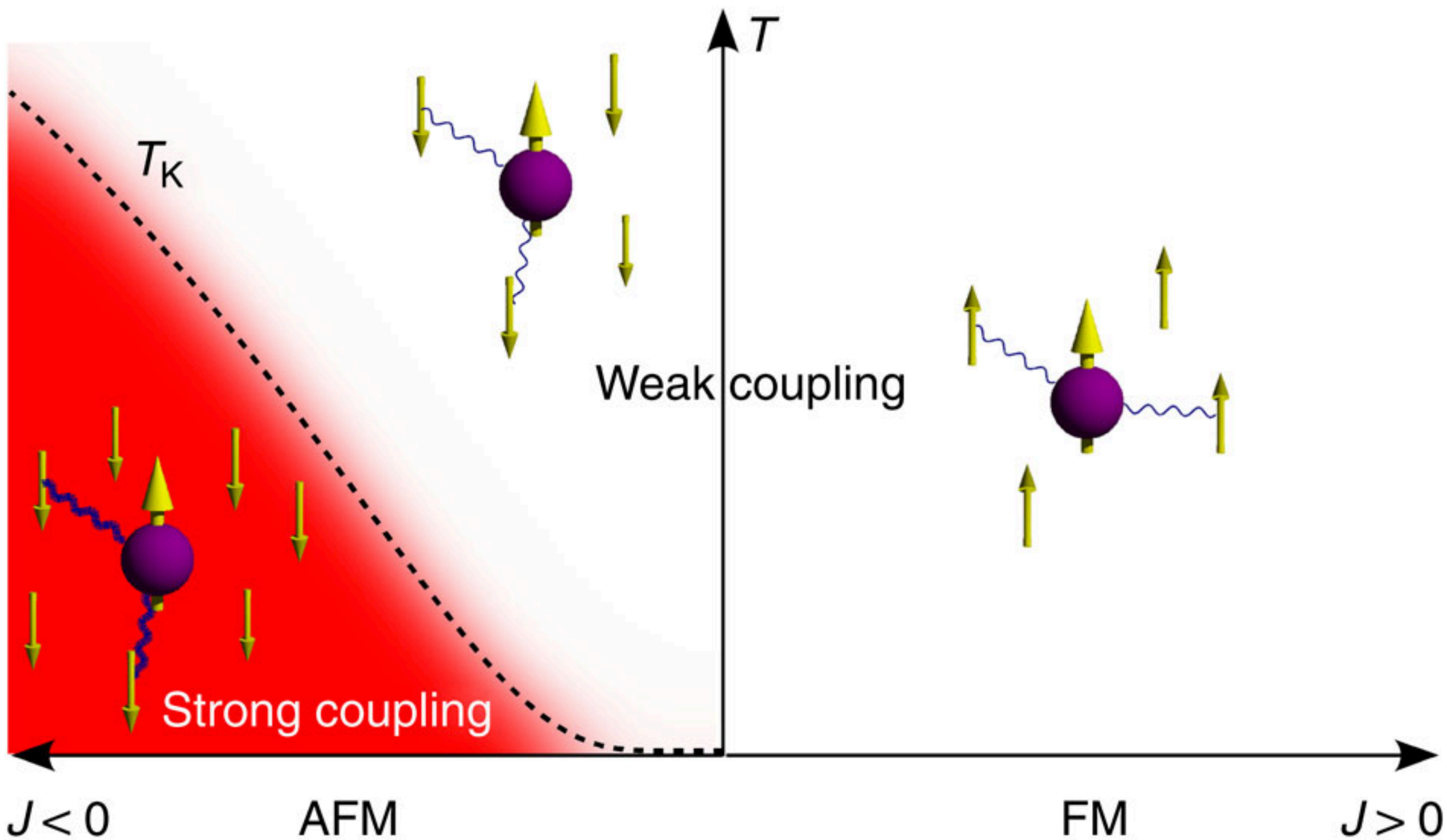


Lattice details and dimensionality do not play a relevant role in the **universal** physics of the single impurity, unless:

- There is a gap (band insulators)
- a pseudogap (graphene)
- a “patological” DOS (van Hove singularity)
- Small system (Kondo box)

Wilson: Regardless of the dimensionality, the Kondo problem is essentially one-dimensional .
It can be solved with Numerical Renormalization Group (Wilson, Krishnamurthy, Wilkins), or Bethe Ansatz (Tsvelik, Andrei).

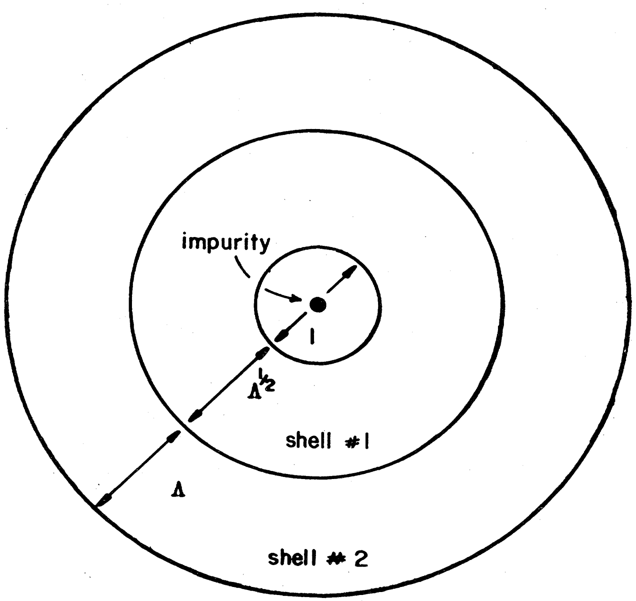
A single magnetic impurity: The Kondo problem

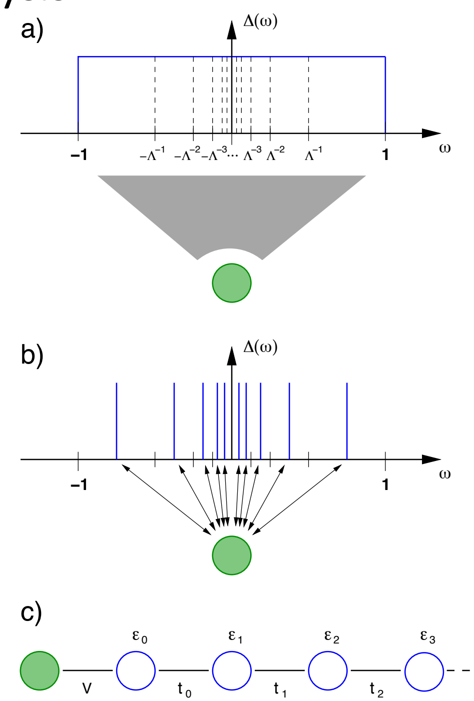


Yong-Hui Zhang, Nature Comm. (2013)

Wilson's NRG approach

- Change of basis: Pick orthogonal discretized shells around the impurity with spherical (s-wave symmetry --All other symmetry channels are ignored, it can be shown that they don't play a role)
- The farther the state, the closer it is to the Fermi energy
- A "lambda" or logarithmic discretization of the spectrum increases resolution around the Fermi energy and enables an RG analysis

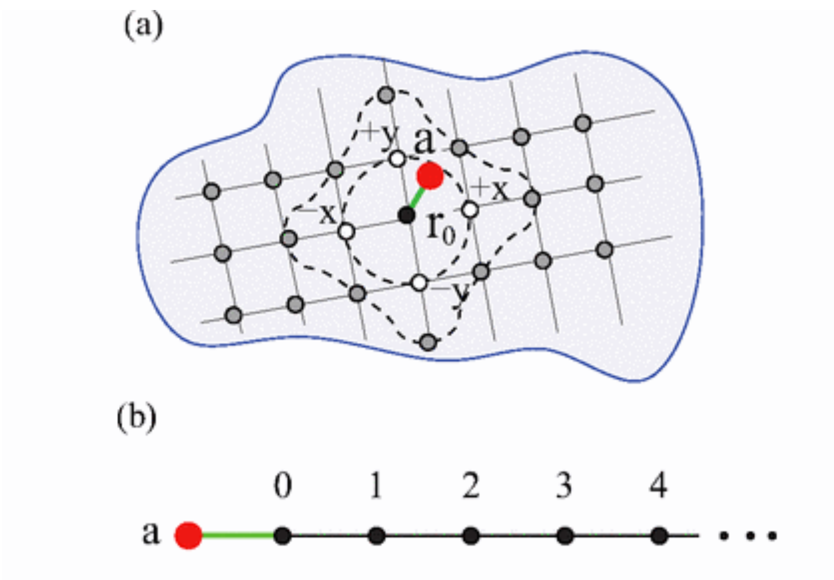




Wilson's RMP(75), Bulla, Costi, Pruschke, RMP(08).

Introducing the lattice

We choose a basis of concentric orbitals that expand radially from the impurity a la Wilson. The are generated by the action of the non-interacting hopping terms.



1. Choose the seed:

$$\left|\Psi_0\right\rangle = c^\dagger_{r_0}\left|0\right\rangle$$

2. Lanczos Iteration:

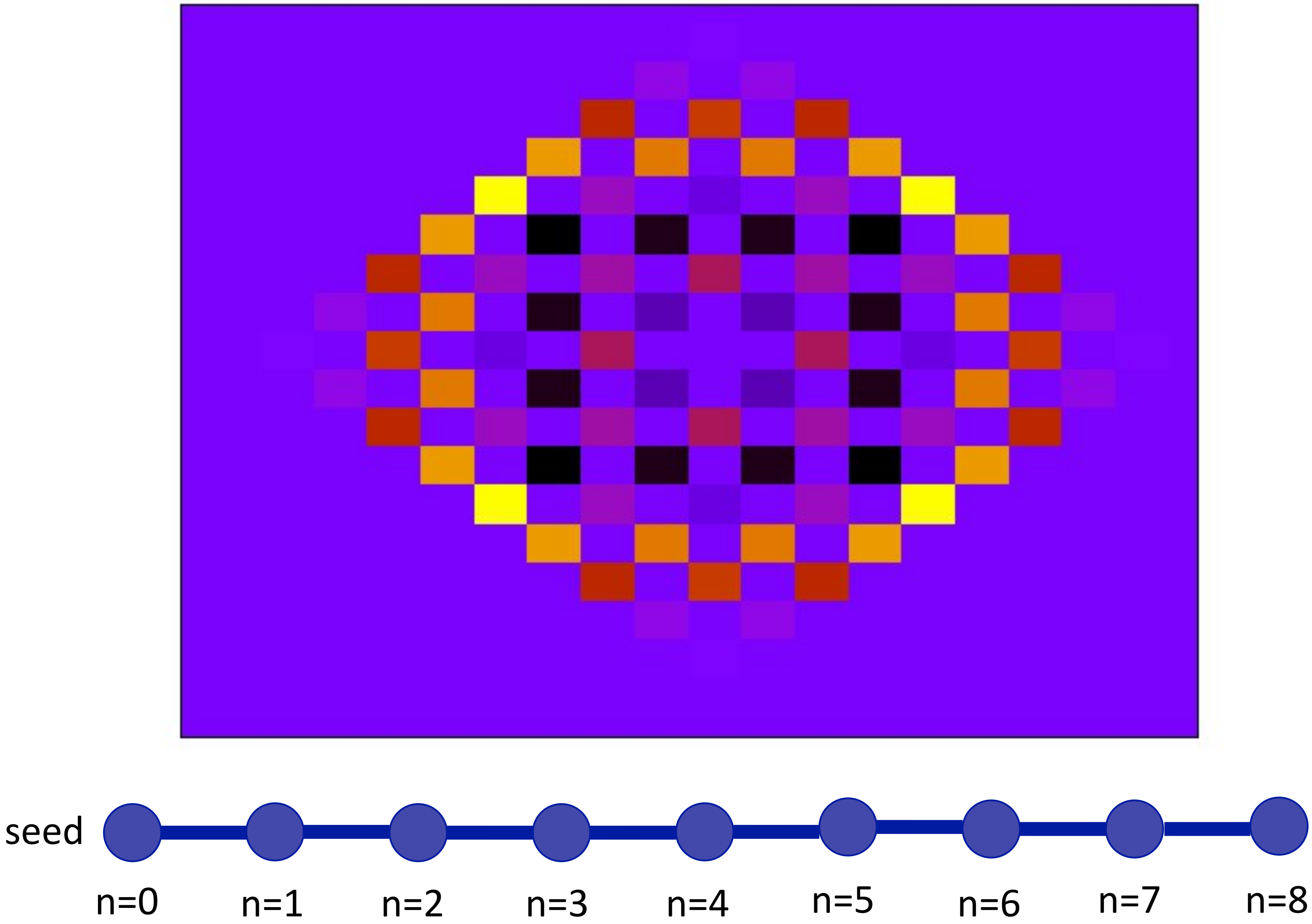
$$\left|\Psi_1\right\rangle = H\left|\Psi_0\right\rangle - a_0\left|\Psi_0\right\rangle$$

$$\left|\Psi_{i+1}\right\rangle = H\left|\Psi_i\right\rangle - a_i\left|\Psi_i\right\rangle - b_i^2\left|\Psi_{i-1}\right\rangle$$

$$a_i = \frac{\left\langle\Psi_i\middle|H\middle|\Psi_{\mathrm{i}}\right\rangle}{\left\langle\Psi_i\middle|\Psi_i\right\rangle} \quad b_i = \frac{\left\langle\Psi_i\middle|\Psi_{\mathrm{i}}\right\rangle}{\left\langle\Psi_{i-1}\middle|\Psi_{i-1}\right\rangle}$$

C. A. Busser, G. B. Martins, and A. E. Feiguin, Phys. Rev. B **88**, 245113 (2013).
R. Haydock, V. Heine, and M. Kelly, Journal of Physics C: Solid State Physics **5**, 2845 (1972).

Lanczos Orbitals



The equivalent chain

Same as Wilson's approach, the Hamiltonian now is in Tri-Diagonal Form:

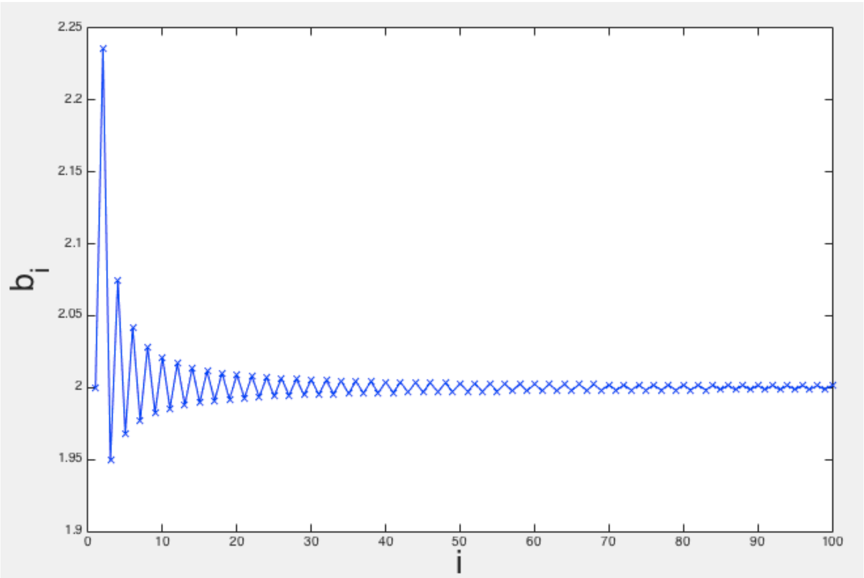
$$H_{band=}\begin{pmatrix} a_0 & b_1 & 0 & 0 & 0 \\ b_1 & a_1 & b_2 & 0 & 0 \\ 0 & b_2 & a_2 & b_3 & 0 \\ 0 & 0 & b_3 & a_3 & \ddots \\ 0 & 0 & 0 & \ddots & \ddots \end{pmatrix}$$

Can study systems with L^d sites, keeping only ~O(L) orbitals!

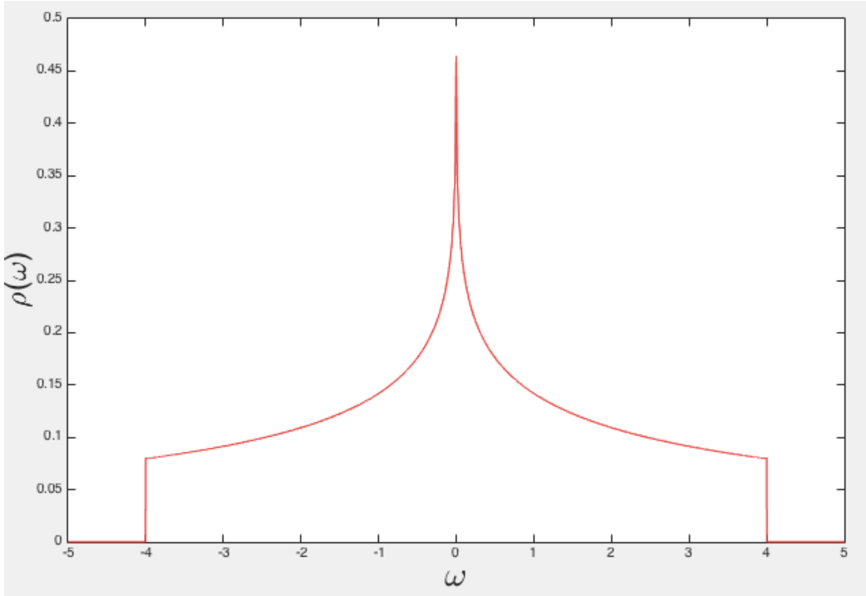
$$H_{band} = \sum_{i=1}^{N}(b_i c_i^{\dagger} c_{i-1} + h.c.) + \sum_{i=0}^{N} a_i n_i$$

Example: Square Lattice

New "Hopping"

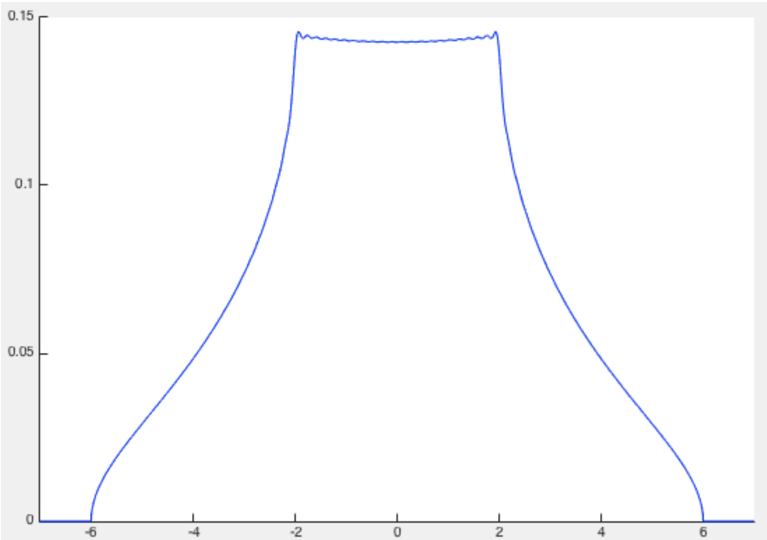


LDOS

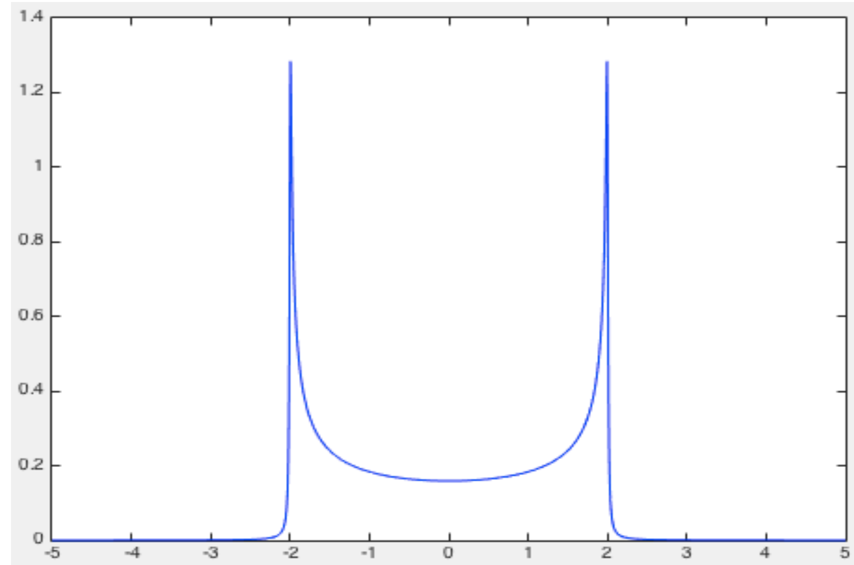


$$\rho_0(\omega) = -\frac{1}{\pi}\lim_{\eta\to 0}\operatorname{Im} G_0(\omega + i\eta)$$

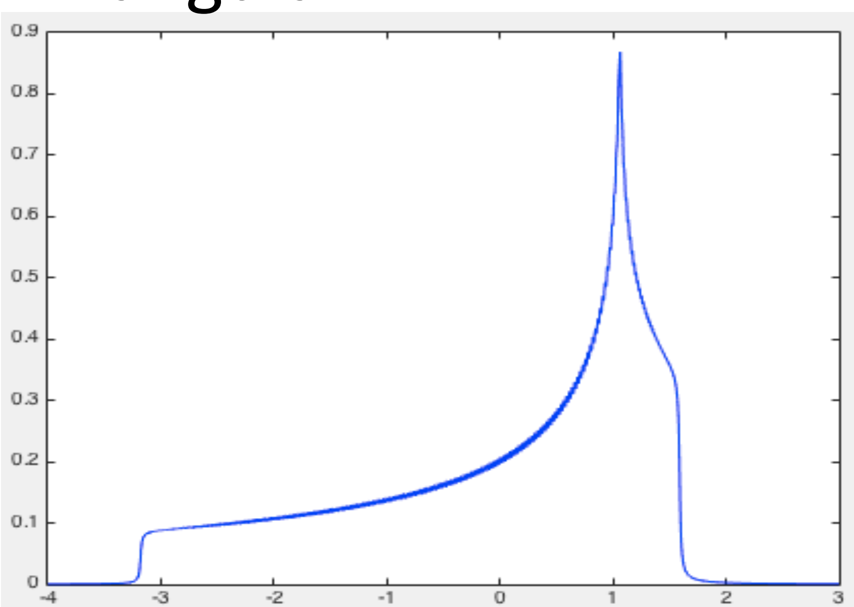
Cubic



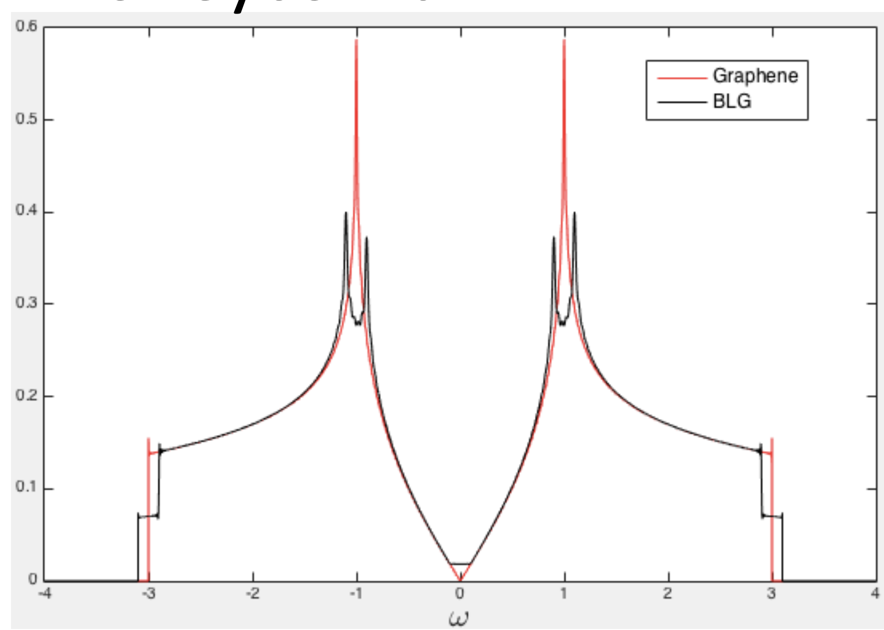
1D chain



Triangular



Honeycomb

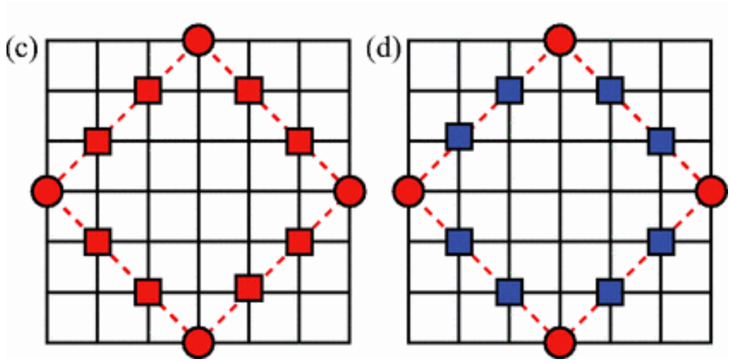


The effective Hamiltonian

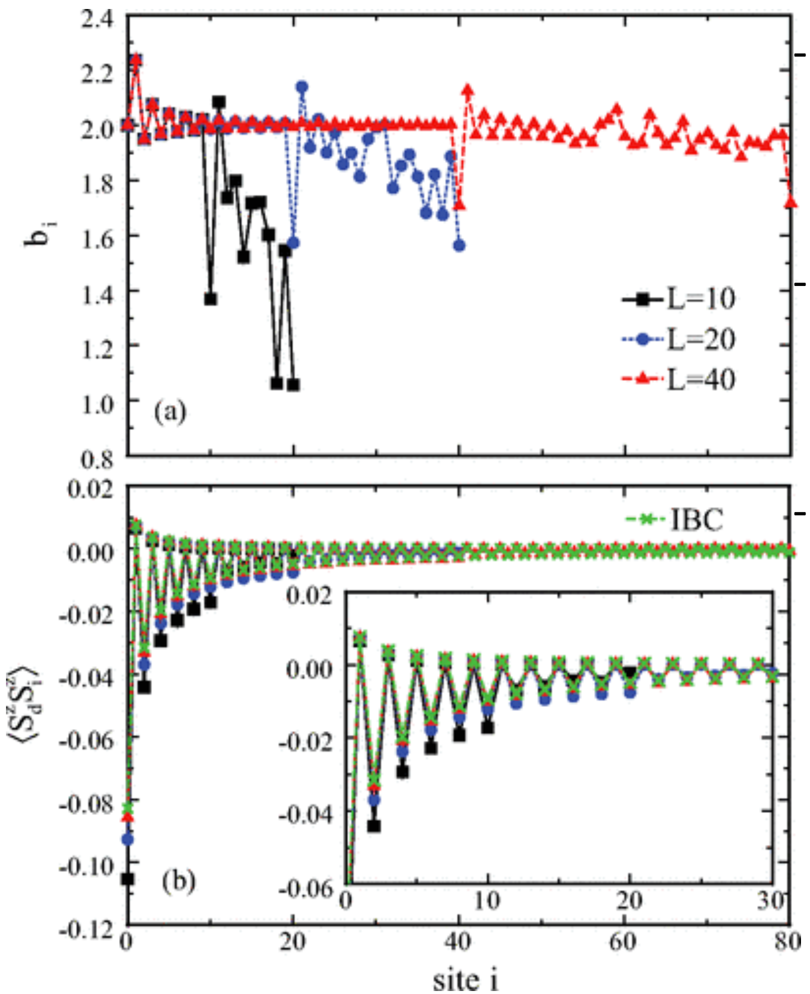
- The impurity is connected to the first site of the chain (which remains in a real space representation), and the many-body terms only act on that link.
- The impurity (rigorously) only couples to the "s-wave" channel.
- The effective one-dimensional system can be effectively solved with DMRG.

Observations:

- The entanglement in free fermionic systems can be understood in terms of the number of channels times the entanglement of a 1d chain.
- All the terms in the "s-wave" Hamiltonian have the same sign.
- The other channels with different symmetry will form their own chains and will not couple to the impurity.
- **Many states in the density of states (an exponential number) **do not** contribute to the physics!!!**



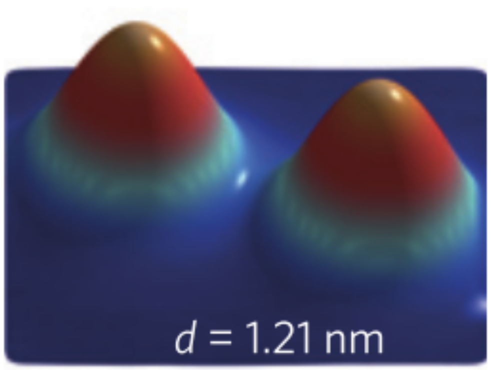
Finite size effects



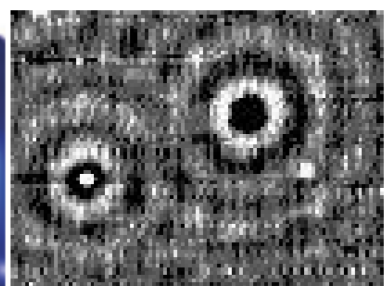
- In finite systems, when orbitals reach the boundary, they "bounce back" and retrace their path.
- Unless the lattice has the same symmetry of the orbitals, the channels will couple at the boundary.
- Typically, one considers "infinite system/ thermodynamic boundary conditions", where the orbitals expand indefinitely (same as Wilson's RG)

(Some) Outstanding issues in multi-impurity problems

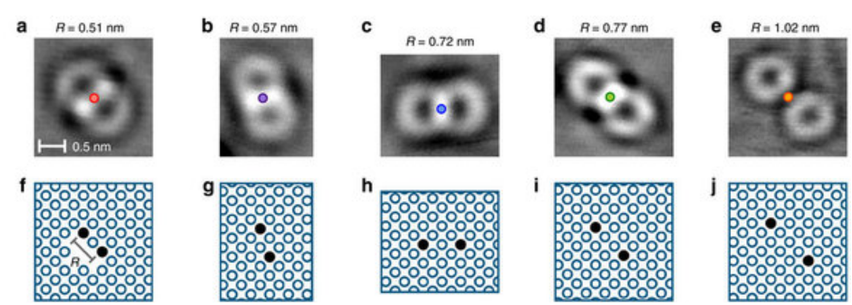
- Non-perturbative effects and competition between Kondo and RKKY interactions.
- Directionality of the RKKY interaction.
- Ferromagnetism.
- Underscreening effects.
- Surface and (chiral) edge states.
- Nozieres's exhaustion problem and fate of the Kondo cloud.
- Superconductivity and Shiba states.



Khajetoorians, A. A., Wiebe, J., Chilian, B., Lounis, S., Blügel, S., Wiesendanger, R.,*Nature.* 8, 497-503. (2012)

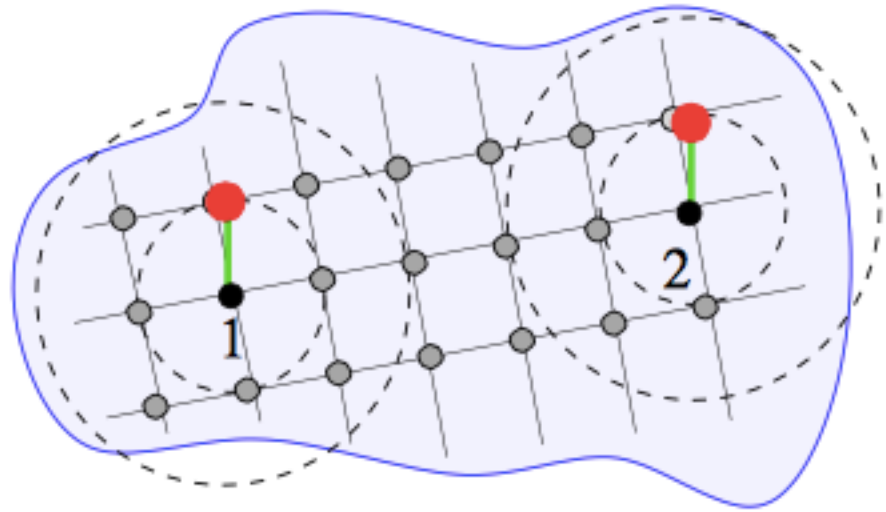


Wahlström, E.,Ekvall, I Olin, H., Walld, L. Appl. Phys. A 66, S1107-S1110 (1998)



Prusser et al, Nature Communications 5, 5417 (2014)

Two-impurity problem



1. Choose Seeds:

$$|\alpha_0\rangle = c^{\dagger}_{r_1}|0\rangle$$

$$|\beta_0\rangle = c^{\dagger}_{r2}|0\rangle$$

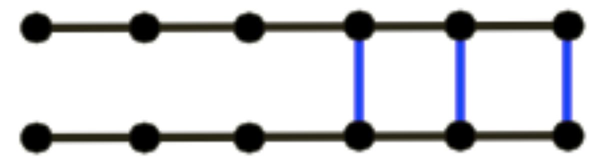
2. Block Lanzcos[1] Iteration:

$$|\alpha_1\rangle = H|\alpha_0\rangle - a_0^{\alpha\alpha}|\alpha_0\rangle - a_0^{\alpha\beta}|\beta_0\rangle$$

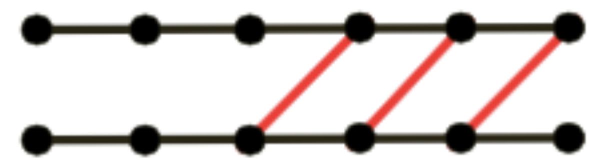
$$|\beta_1\rangle = H|\beta_0\rangle - a_0^{\beta\beta}|\alpha_0\rangle - a_0^{\beta\alpha}|\beta_0\rangle$$

$$|\lambda_{i+1}\rangle = H|\lambda_i\rangle - \sum_{\gamma} a_i^{\lambda\gamma}|\gamma_i\rangle - \sum_{\gamma} b_i^{\lambda\gamma}|\gamma_{i-1}\rangle$$

R=7



R=6



J. K. Cullum and R. A. Willoughby, *Lanczos Algorithms for Large Symmetric Eigenvalue Computations: Vol. 1: Theory* (SIAM, Philadelphia, 2002), Vol. 41.
See also T. Shirakawa, S. Yunoki, PRB (14)

Block Tri-Diagonal Form:

$$H_{band=}\begin{pmatrix} A_0 & B_1 & 0 & 0 & 0 \\ B_1 & A_1 & B_2 & 0 & 0 \\ 0 & B_2 & A_2 & B_3 & 0 \\ 0 & 0 & B_3 & A_3 & \ddots \\ 0 & 0 & 0 & \ddots & \ddots \end{pmatrix}$$

$A_m, B_m = n \times n$ Matrices.

n = # of ‘seeds’ or impurities.

See also: Phys. Rev. B 90, 195109 (14). Tomonori Shirakawa and Seiji Yunoki

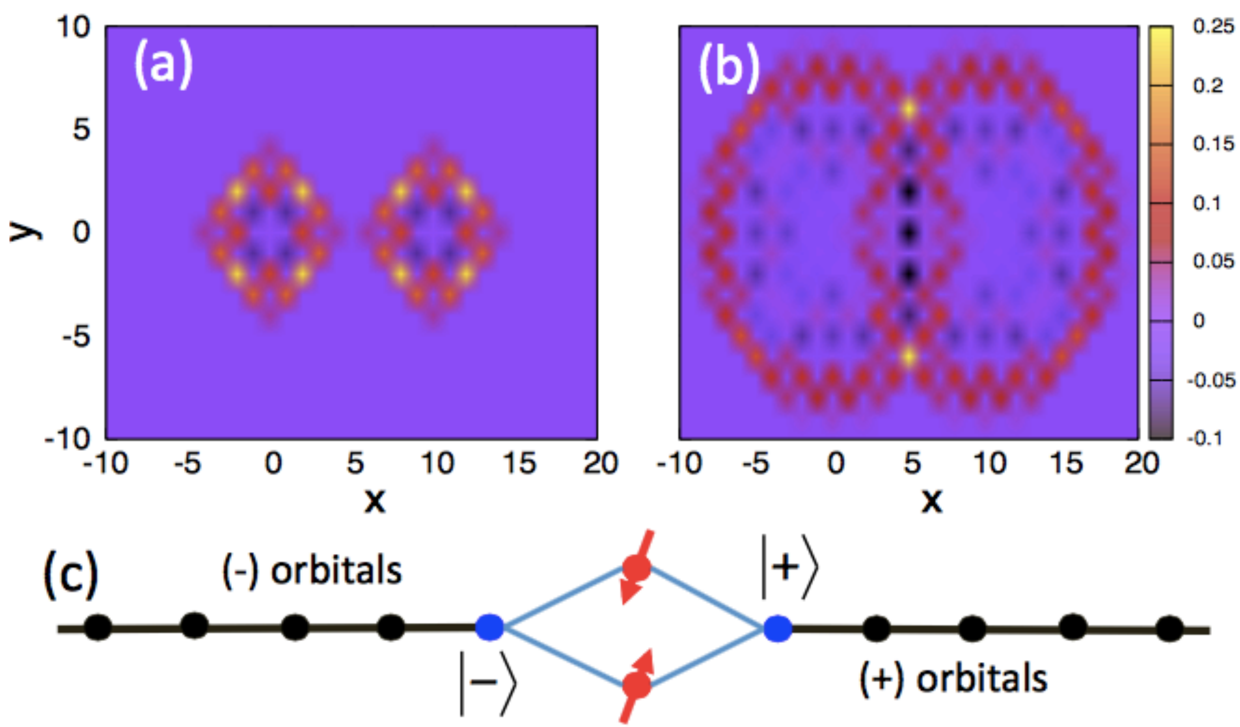
Mapping to Chains (Two impurities)

1. Choose symmetric and anti-symmetric seeds:

$$\left|+\right\rangle = \tfrac{1}{\sqrt{2}}\left(c_1^\dagger + c_2^\dagger\right)\left|0\right\rangle = \tfrac{1}{\sqrt{2}}\left(\left|1\right\rangle + \left|2\right\rangle\right)$$

$$\left|-\right\rangle = \tfrac{1}{\sqrt{2}}\left(c_1^\dagger - c_2^\dagger\right)\left|0\right\rangle = \tfrac{1}{\sqrt{2}}\left(\left|1\right\rangle - \left|2\right\rangle\right)$$

2. Iterate the same as the single impurity case for each seed.



Two-impurity Kondo problem

$$H = H_{band} + J_K\left(\vec{S}_1 \cdot \vec{s}_{r_1} + \vec{S}_2 \cdot \vec{s}_{r_2}\right)$$

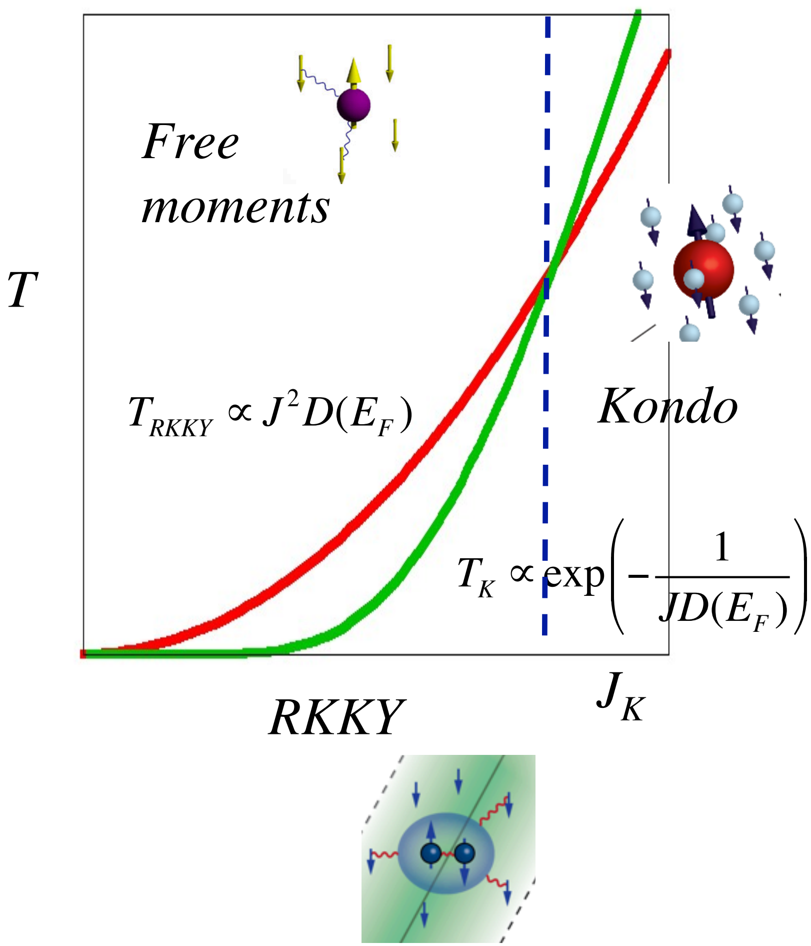
After rotating to the new basis :

$$V = \frac{J_K}{2}(\mathbf{S}_1 + \mathbf{S}_2) \cdot \sum_{\mu,\eta,\gamma=\pm} c^{\dagger}_{\gamma\mu}\vec{\sigma}_{\mu\eta}c_{\gamma\eta}$$
$$+ \frac{J_K}{2}(\mathbf{S}_1 - \mathbf{S}_2) \cdot \sum_{\mu,\eta,\gamma=\pm} c^{\dagger}_{\gamma\mu}\vec{\sigma}_{\mu\eta}c_{-\gamma\eta}$$

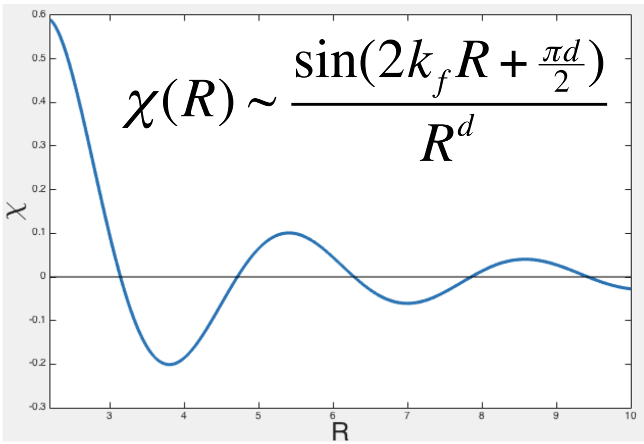
Identical to the Hamiltonian considered in NRG and theoretical calculations, but in "real space" (See work by Wilkins, Jones, Varma, Affleck, Ludwig, etc)

Our conventional understanding of the RKKY interaction

Doniach (1977)



$$J_{RKKY} = J^2 \chi(R)$$



- Continuum Model
- Uniform Electron Gas
- Quadratic Dispersion

Lindhard function on the lattice

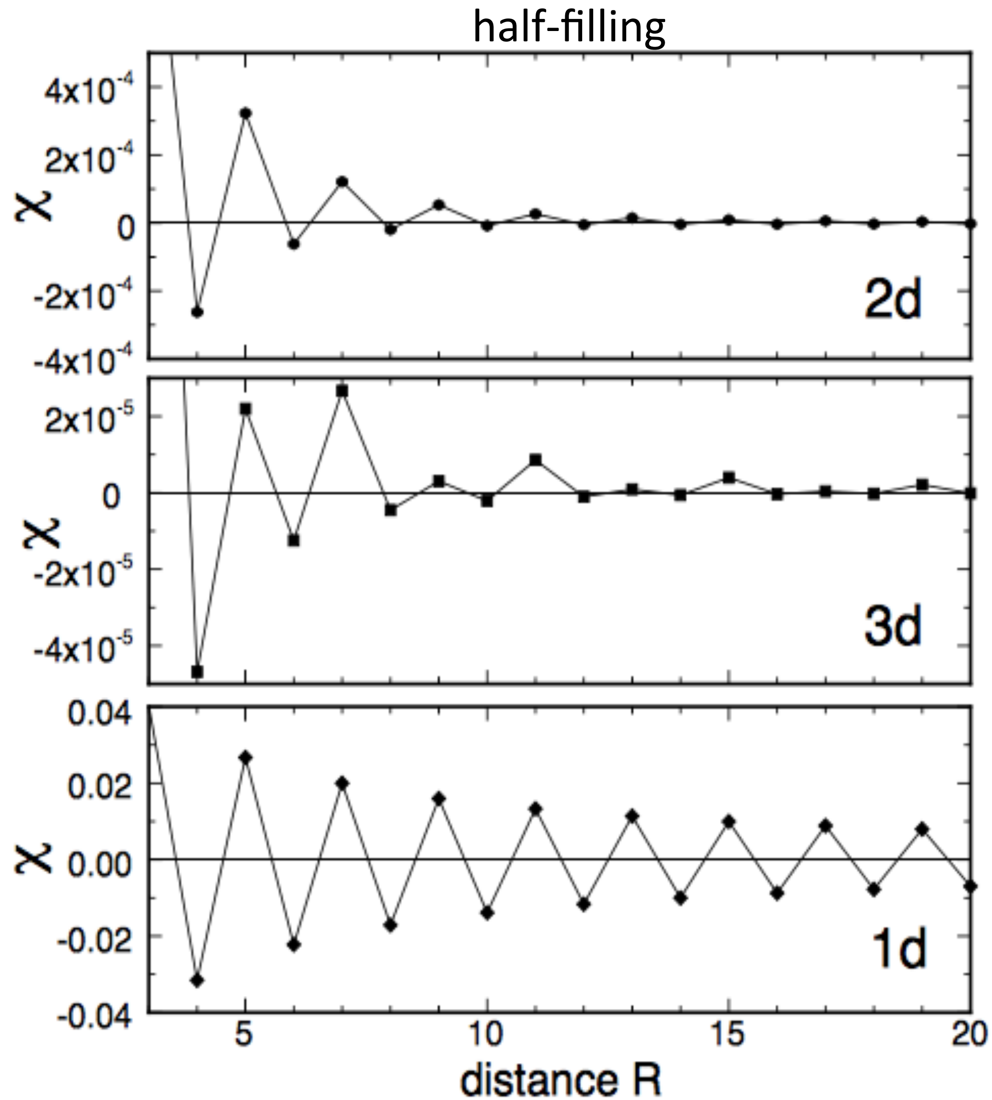
Lindhard function:

(Free electron susceptibility)

$$\chi(r_i,r_j) = -\frac{1}{2\pi}\mathrm{Im}\int_{-\infty}^{\infty} dE\, G_+\left(r_i,r_j,E\right)G_-\left(r_i,r_j,E\right)$$

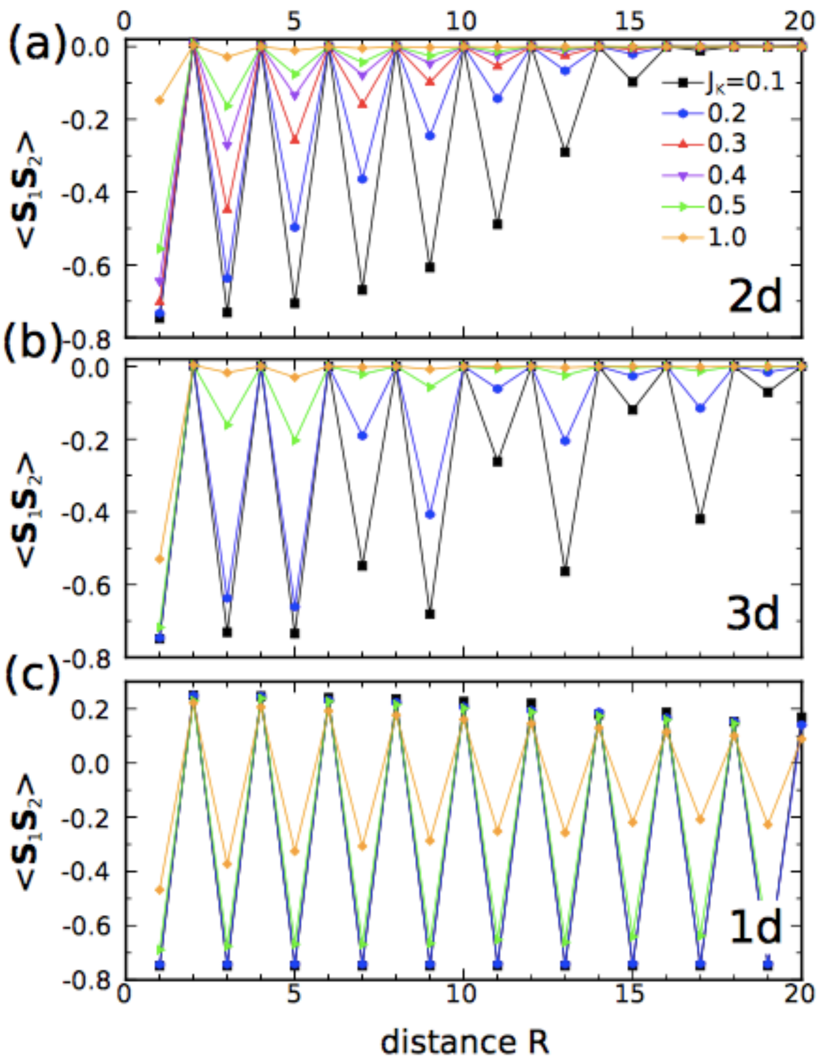
$$\chi(r_1,r_2) = 2\,\mathrm{Re}\sum_{E_n>E_f>E_m}\frac{\langle r_1|n\rangle\langle n|r_2\rangle\langle r_2|m\rangle\langle m|r_1\rangle}{E_n-E_m}$$

We expect the interactions to alternate between FM and AFM



Spin-Spin Correlations (half-filling)

DMRG, L=204, M~3000



In agreement with old QMC results on small lattices: Fye, Hirsch, Scalapino, PRB (87); Fye Hirsch, PRB (89); Fye, PRL (94).

QMC does not resolve Kondo physics due to finite temperatures.

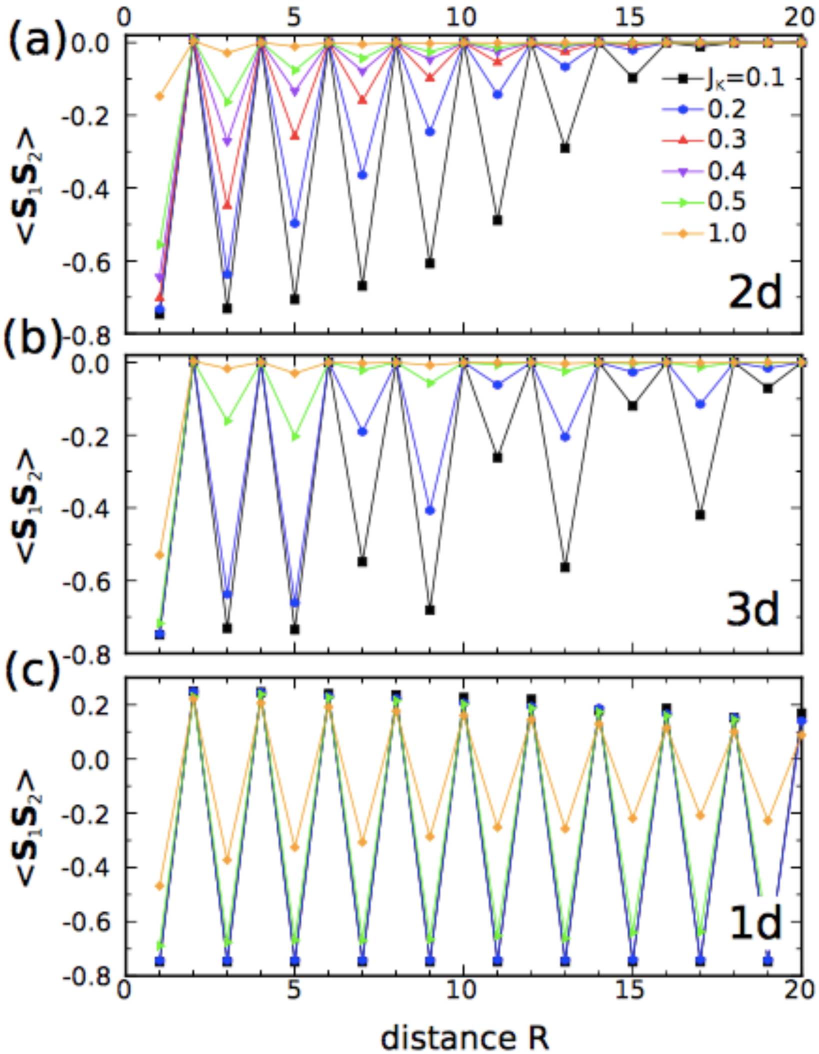
In 2D and 3D Kondo dominates when impurities are on same sublattice. FM only survives at very short distances! (Independent confirmation by A. Mitchell, Derry and Logan, PRB (2015)).

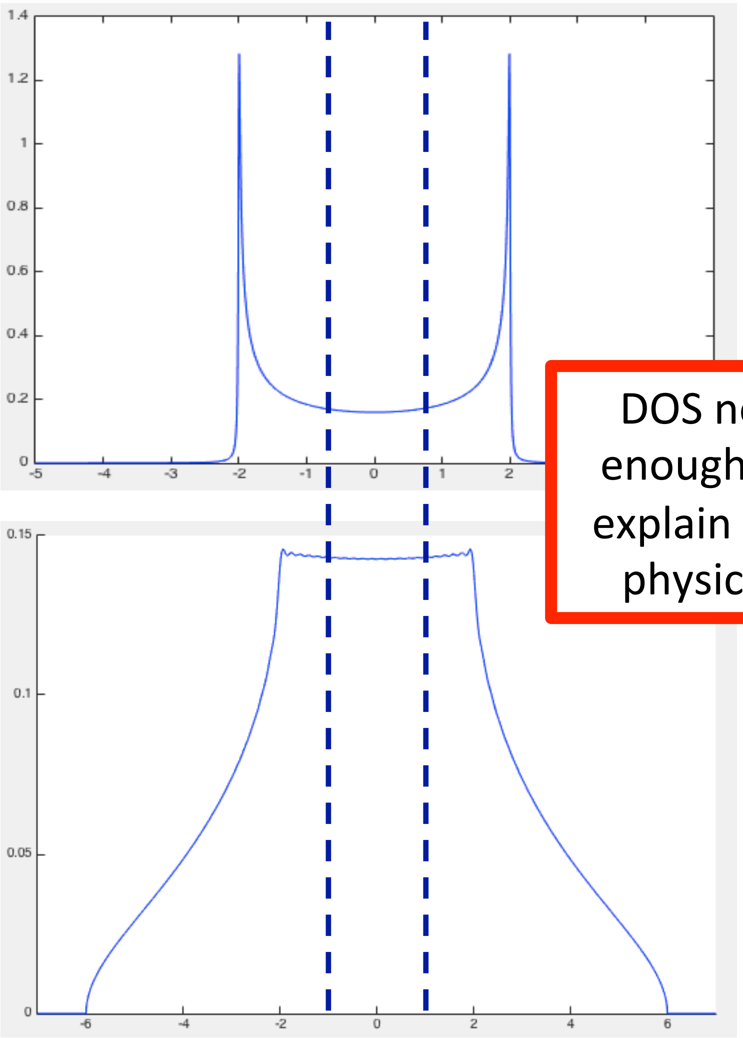
In agreement with Affleck and Ludwig, and Potthoff and Schwabe (See Schwabe's PhD Thesis, and references therein)

Andrew Allerdt, C. A. Büsser, G. B. Martins, and A. E. Feiguin PRB 91, 085101 (2015)

Spin-Spin Correlations (half-filling)

DMRG, L=204, M~3000





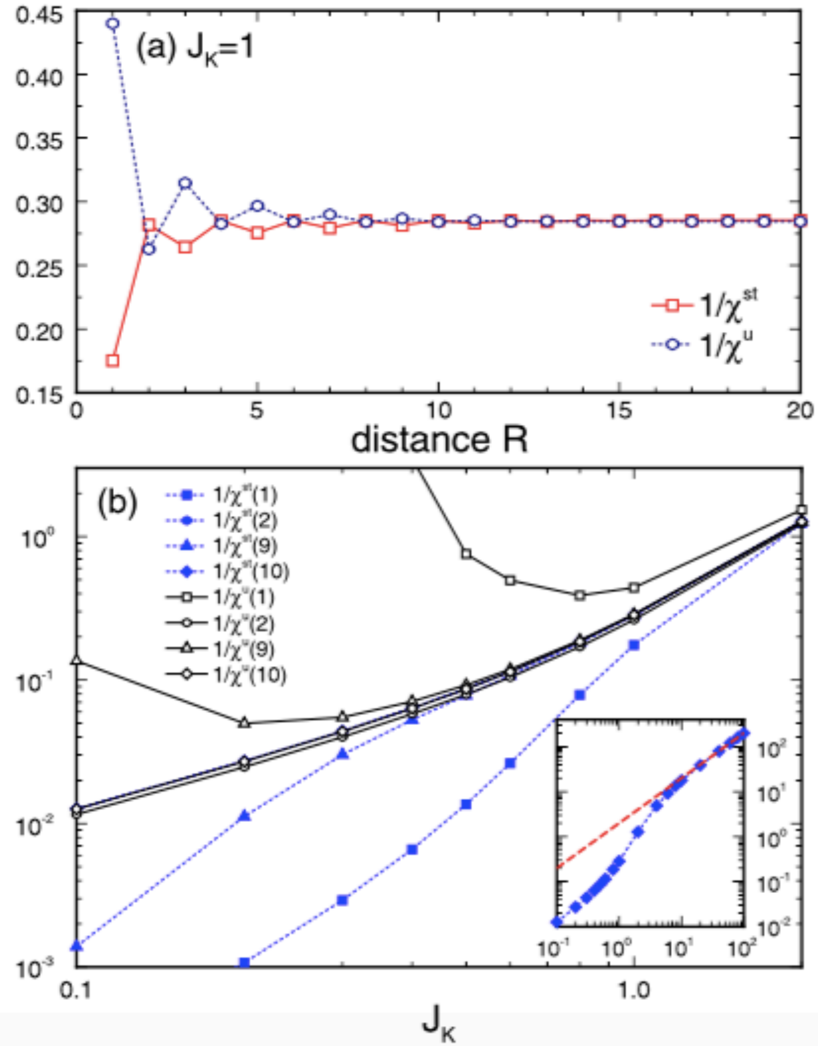
DOS not enough to explain the physics!

Andrew Allerdt, C. A. Büsser, G. B. Martins, and A. E. Feiguin PRB 91, 085101 (2015)

Impurity Susceptibility

Staggered and uniform Susceptibility as a function of distance and J_K (coupling).

Linear contribution to T_K coming from "Kondo box"(*) physics (A. Schwabe, D. Gütersloh, and M. Potthoff, PRL. 109, 257202 (2012)).



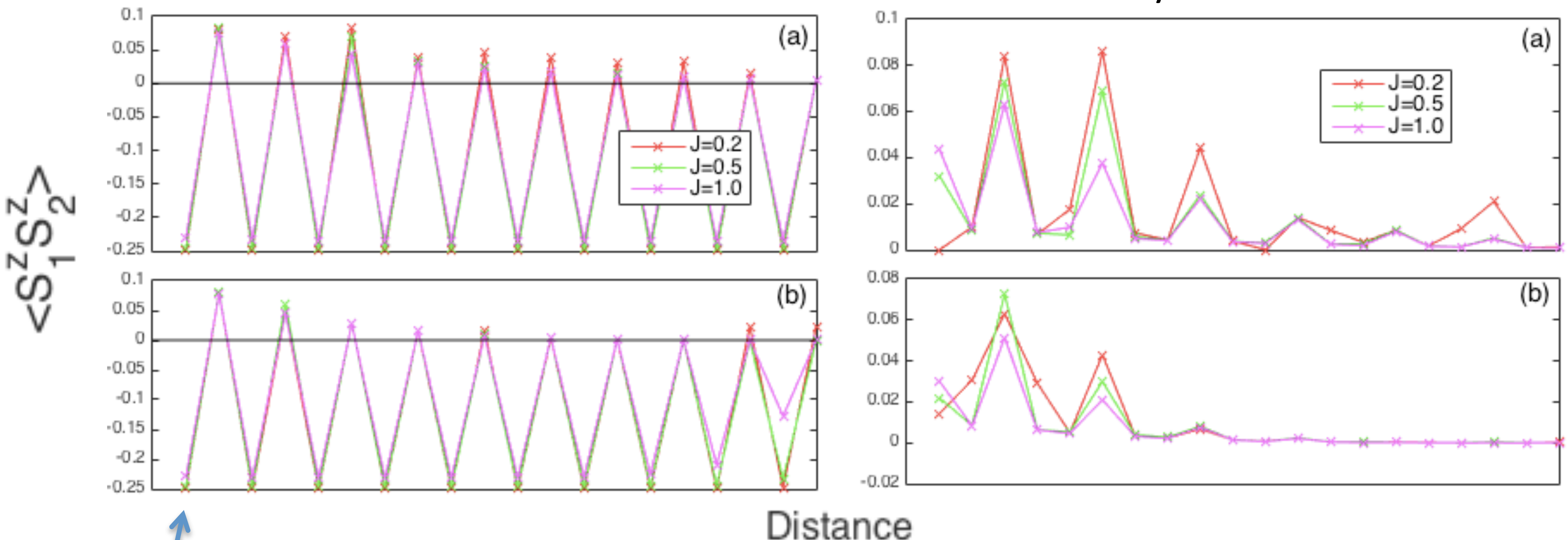
(*) W. B. Thimm, J. Kroha, and J. von Delft, Phys. Rev. Lett. 82, 2143 (1999); P. Schlottmann, Phys. Rev. B 65, 024420 (2001).
P. Simon and I. Affleck, Phys. Rev. Lett. 89, 206602 (2002).; P. Simon and I. Affleck, Phys. Rev. B 68, 115304 (2003).
T. Hand, J. Kroha, and H. Monien, Phys. Rev. Lett. 97, 136604 (2006); M. Hanl and A. Weichselbaum, Phys. Rev. B 89, 075130 (2014).

Graphene and bi-layer graphene

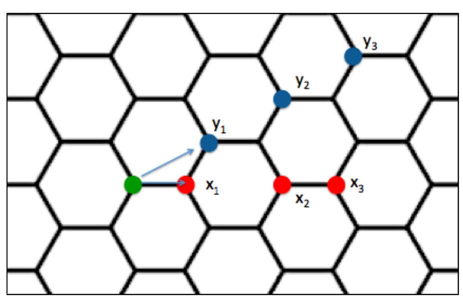
Half-filling

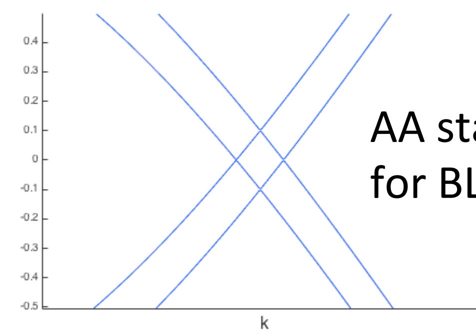
x-direction

y-direction



Free moment regime



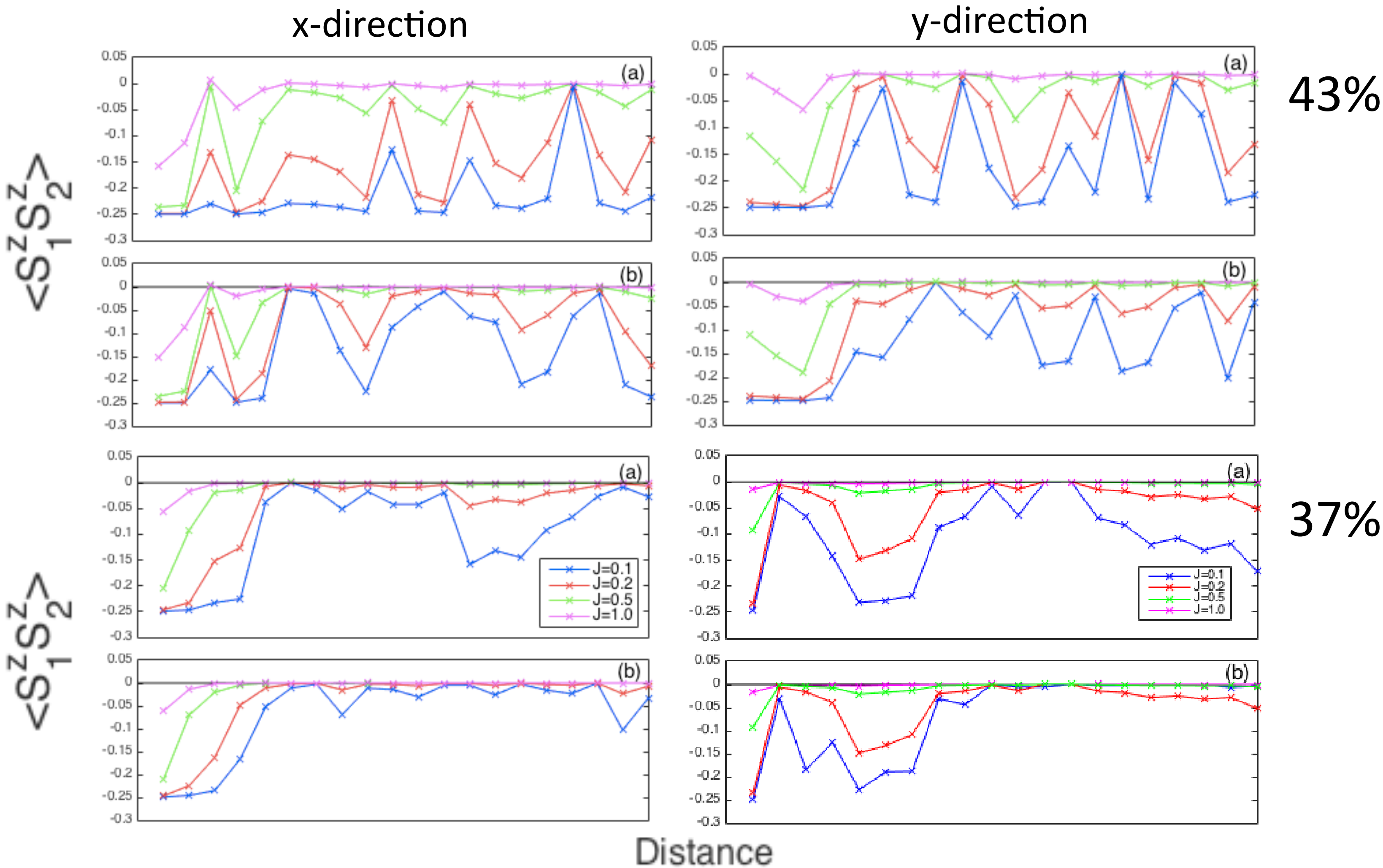


AA stacking for BLG

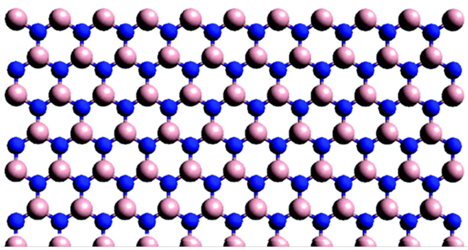
A. Allerdt, AEF (In preparation).

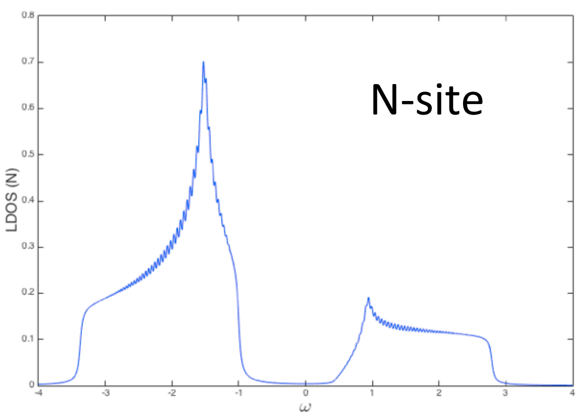
Graphene and bi-layer graphene

away from half-filling

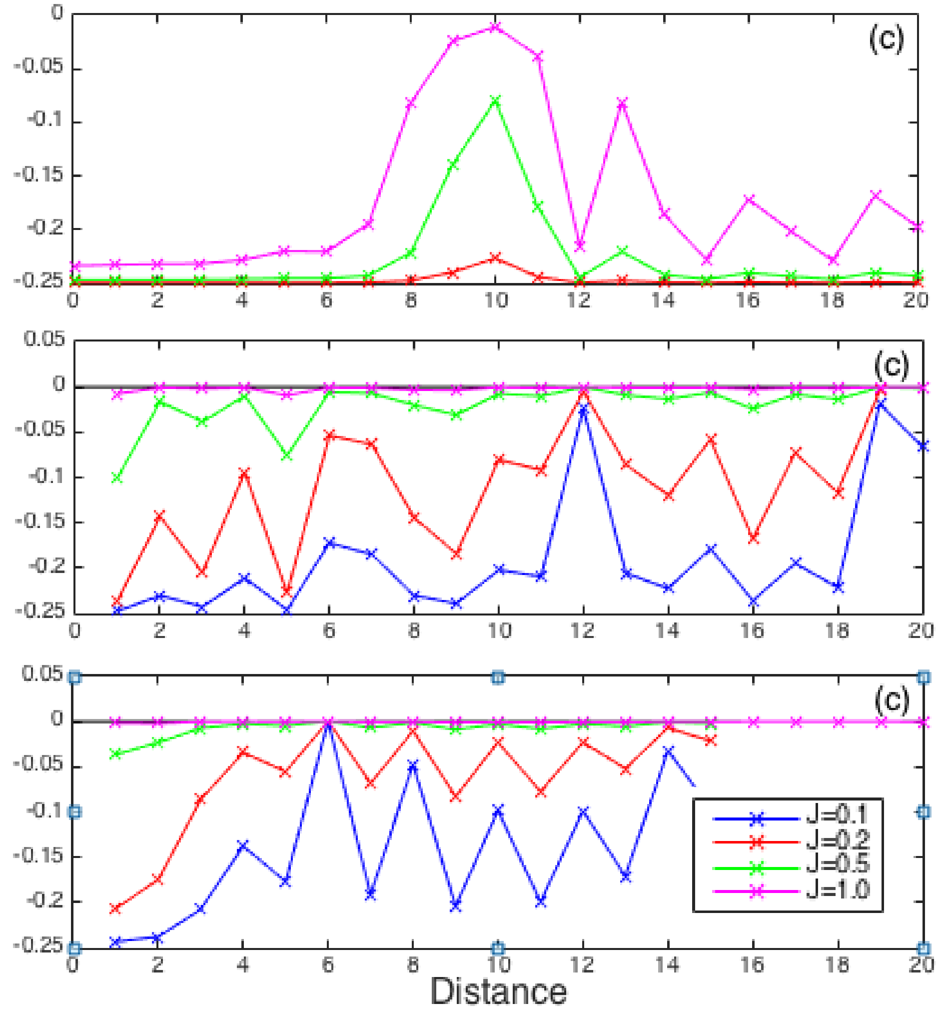


Boron Nitride





y-direction

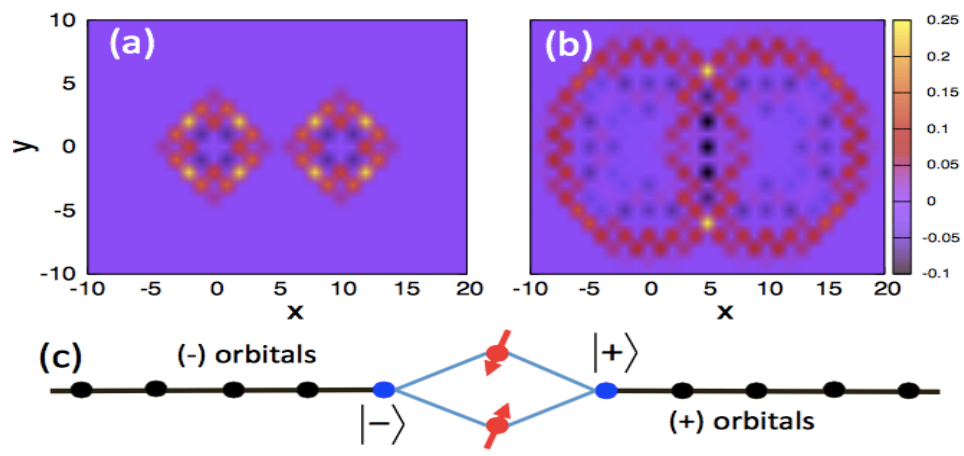


43%

37%

Conclusions (method)

- The mapping can be generalized to multi-impurity problems, with a number of chains equal to the number of impurities.
- Our method can be applied to more generic band structures, multi-orbital problems, disorder, and quantum chemistry.
- It can be applied to more complex problems with superconductivity and/or spin-orbit coupling.
- The equivalent Hamiltonian can be solved with other numerical methods besides DMRG.
- We can resolve arbitrary geometries/edges/surfaces. For instance, we can look at one impurity at an edge/surface, and another in the bulk (topological insulators, Shockley surfaces)



Conclusions (RKKY vs. Kondo)

- Lattice structure and dimensionality plays an important role in correlations and lead to non-universal behavior.
- Spin Correlations follow a non-perturbative behavior, departing from Lindhard function. - RKKY problem is non-trivial.
- The DOS is not enough to explain the physics on the lattice: wave functions are important!
- Ferromagnetism is not “stable” on the square and cubic lattices at half-filling. Kondo “wins”, consistent with Schwabe/Potthoff and Affleck/Ludwig arguments (Energetics + symmetry of the wave functions). (This is a zero-T result!)
- Many results in literature are misguided and assume a perturbative behavior - Experimentalists need new intuition based on new numerical methods.
- Graphene displays more robust ferromagnetism.

<u>Open issues:</u>

- Kondo box physics…
- Finite temperatures? Two-stage Kondo…
- Multi-impurity problem/exhaustion.
- Large spin: multi-orbital problem/more channels and Hund physics.
- More realistic models/more materials.
- Frustration