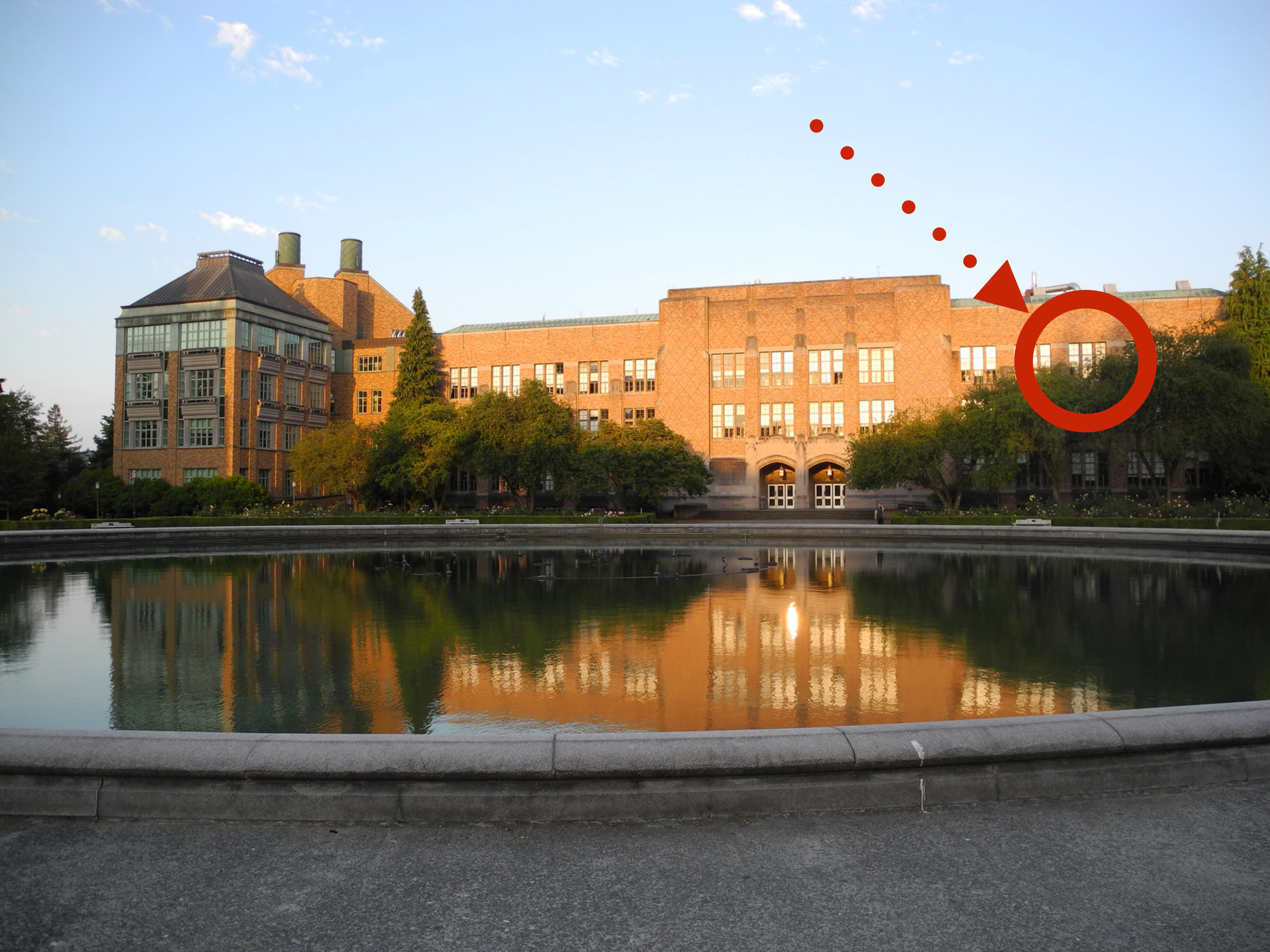
Explorations into Molecular Magnetism

Joshua Goings
University of Washington, Seattle, WA

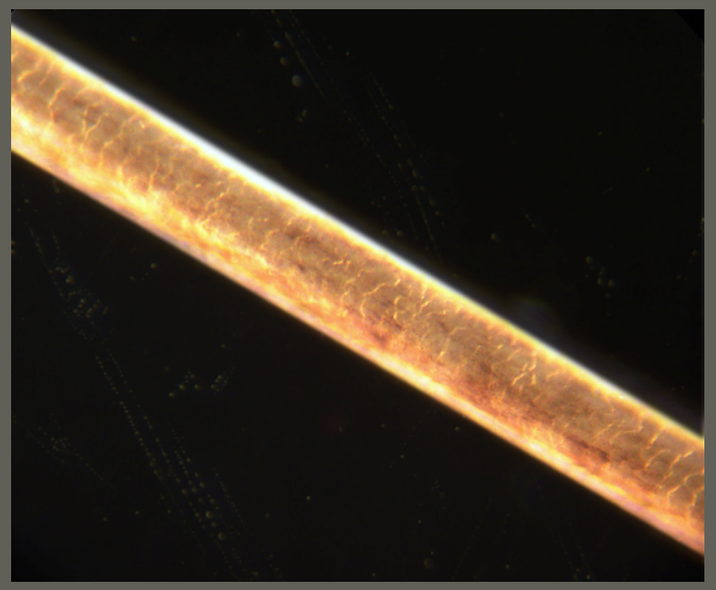
UNIVERSITY of WASHINGTON

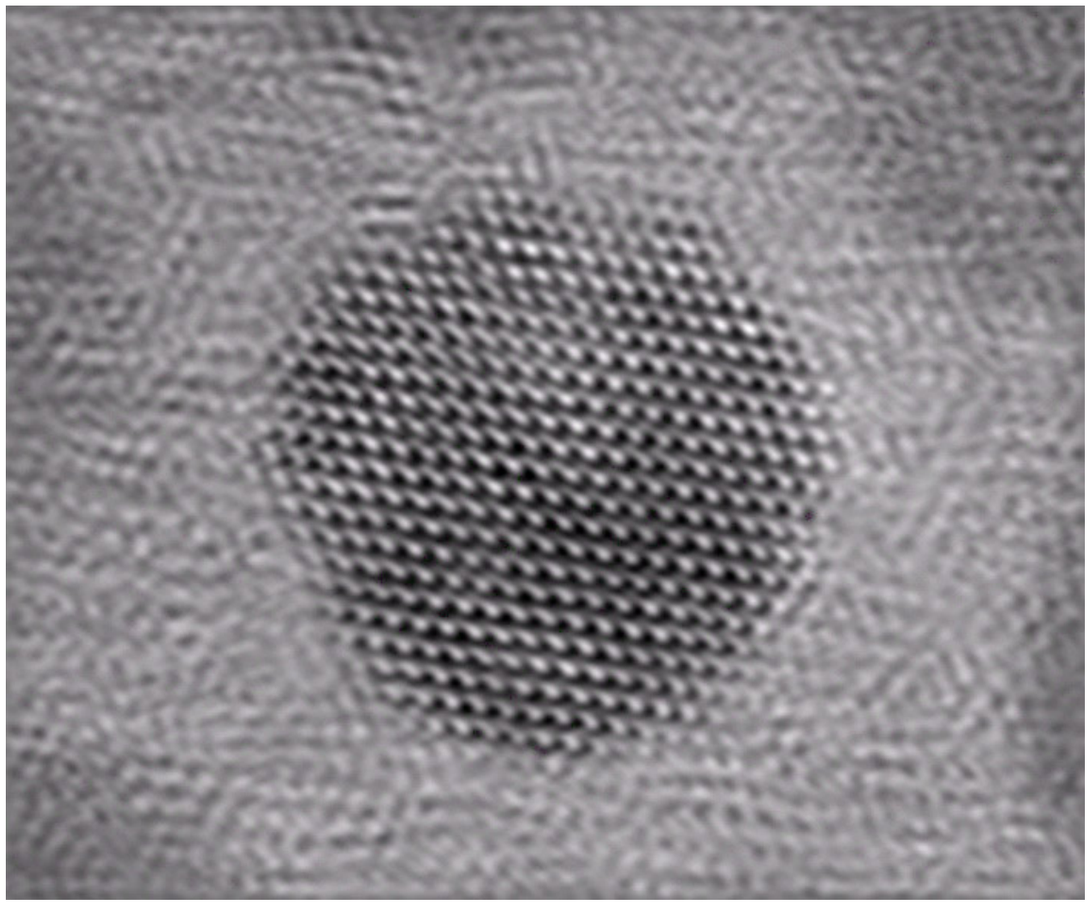



uw
Li Research Group
LABMEN

Our big focus is using computers to predict properties of nanomaterials, e.g. quantum dots

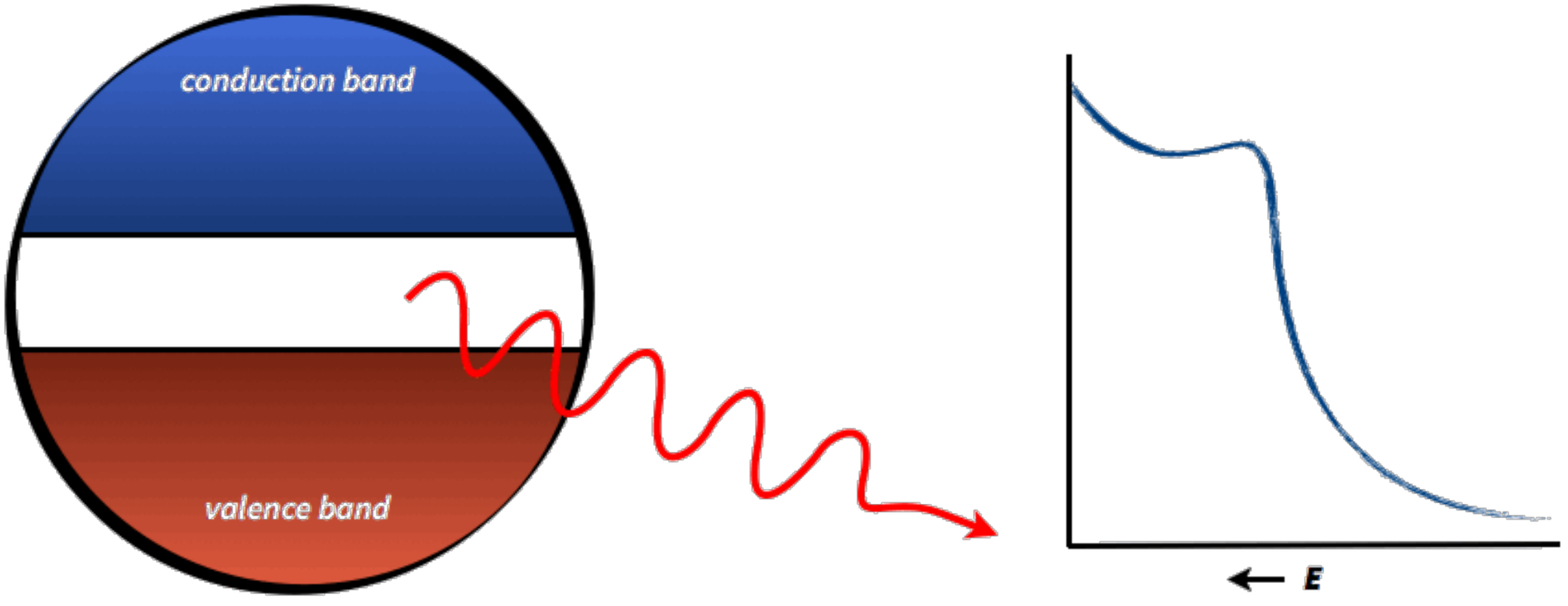
10,000 times
smaller than
diameter of
a human hair





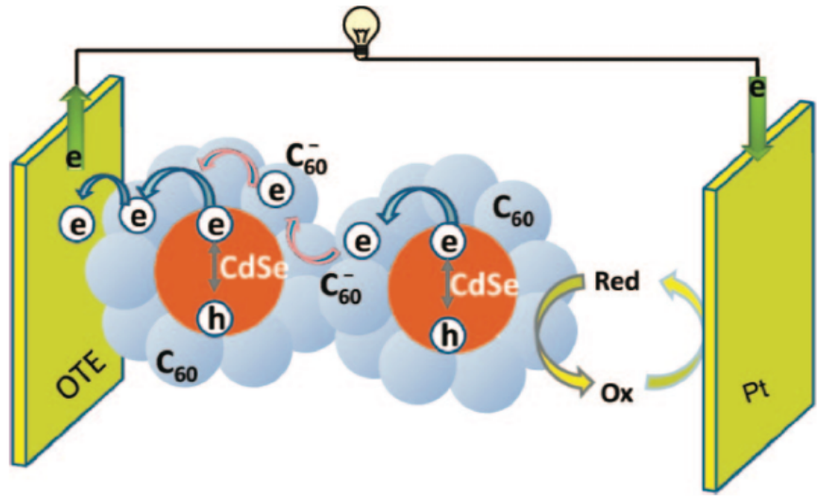
You could fit
3,000,000
end-to-end across
the width of
your thumb

Quantum Confinement

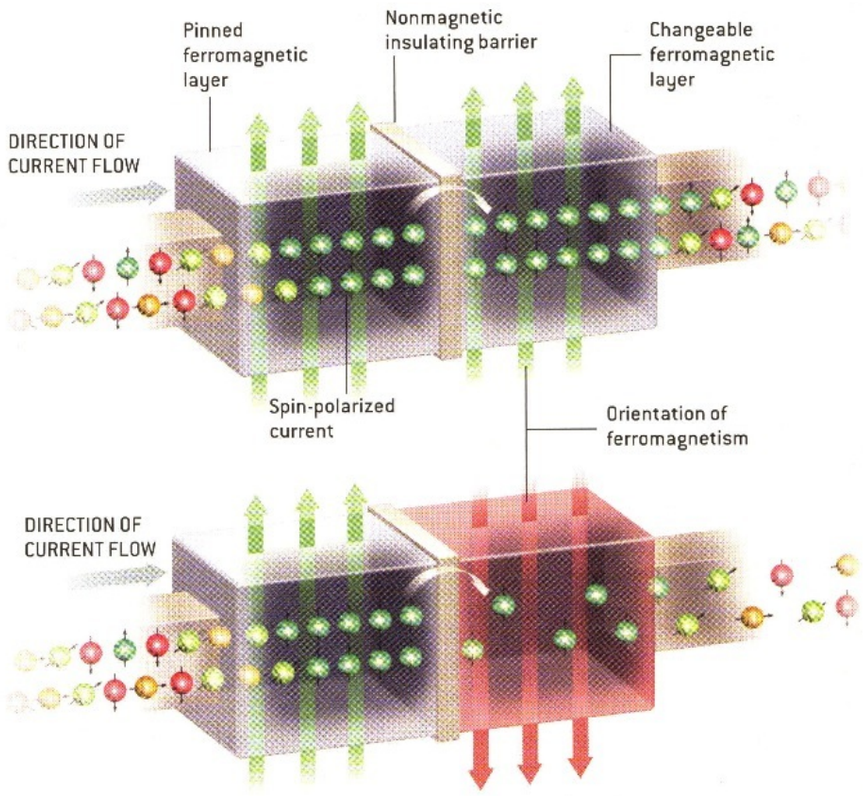


Photovoltaics and Spintronics

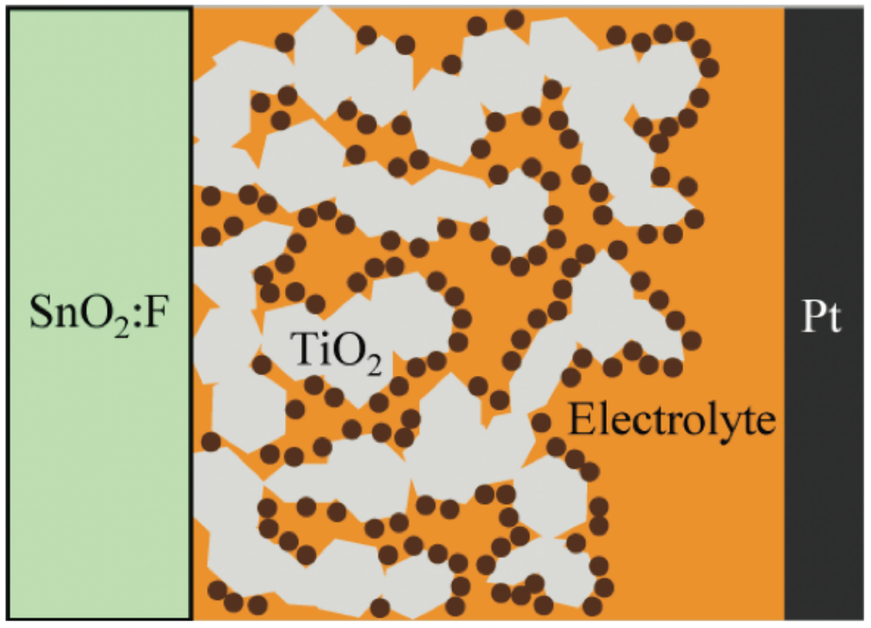
Ginger Research Lab, UW Chemistry



Kamat, et al. JACS, 2008

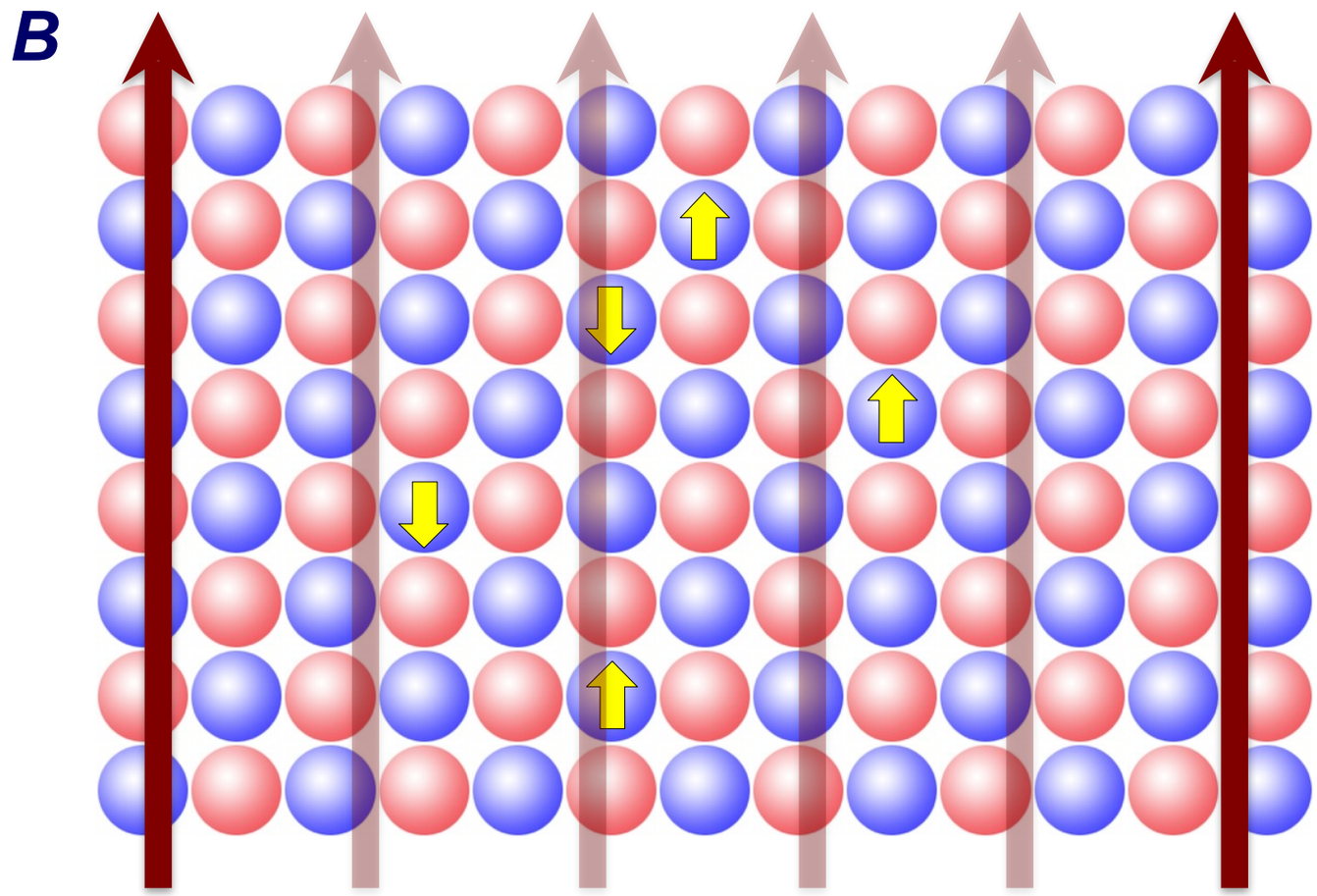


Scientific American, June 2002



Sargent, et al. ACS Nano, 2010

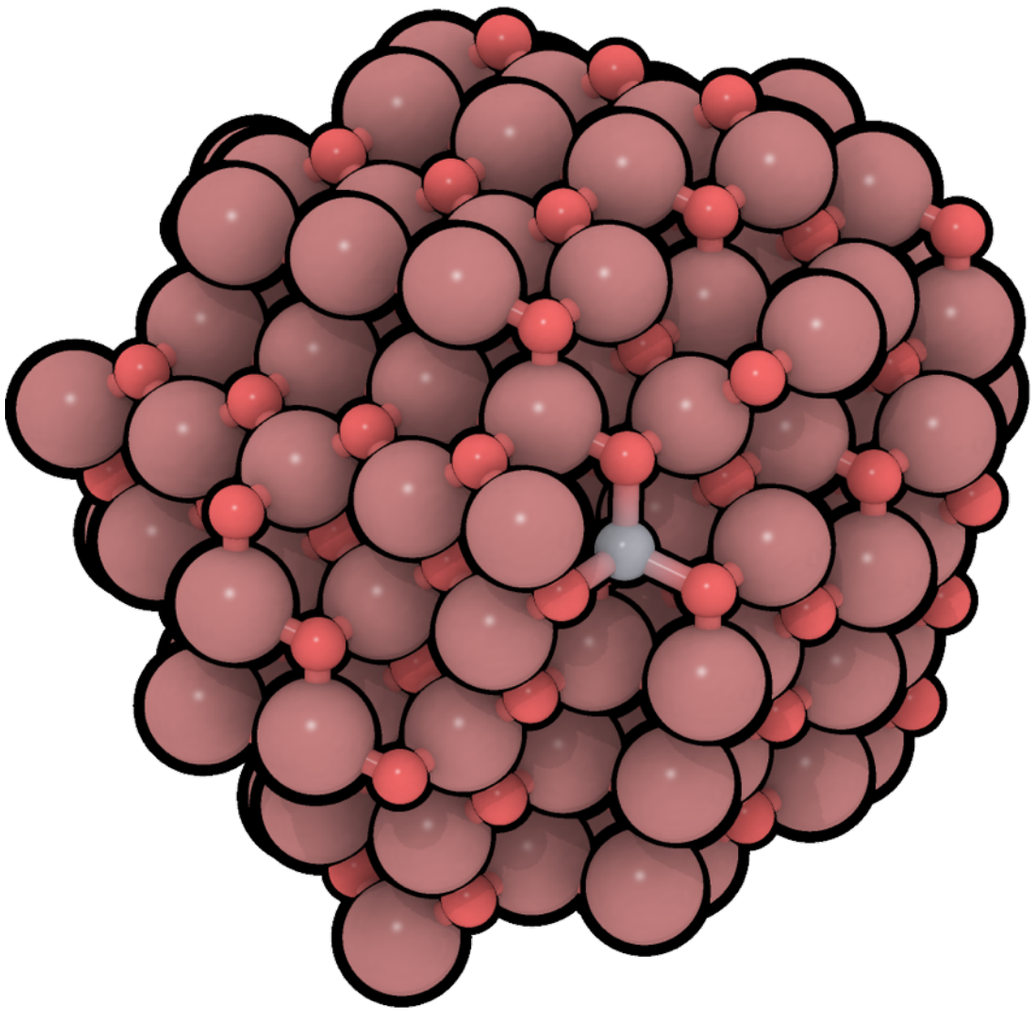
Diluted Magnetic Semiconductors (DMS)



$T < T_C$

✓ magnetization
✓ additional absorption features

These magnetic dopants interact strongly with certain other dopants that may lead to



New superconductors

High-temp ferromagnets

Incredibly small hard drives

Super-fast processors

The problem is no one really knows how this works.

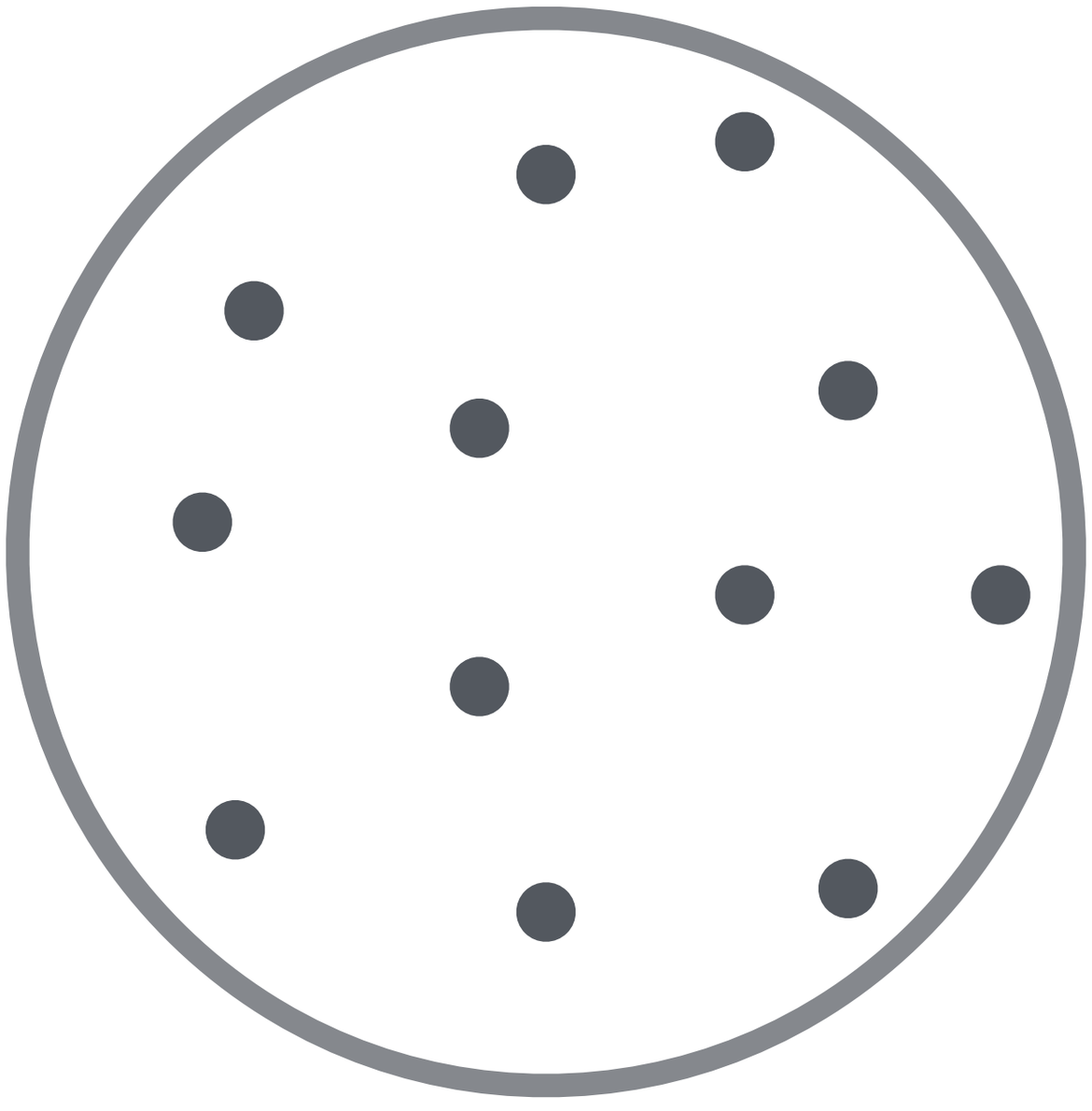
I use **quantum chemistry** to simulate these materials on supercomputing clusters

Hartree-Fock is a computational method for studying electrons in molecules

Instead of studying many electrons at once, we look at each electron individually moving in the field of the other electrons.

“Molecule”

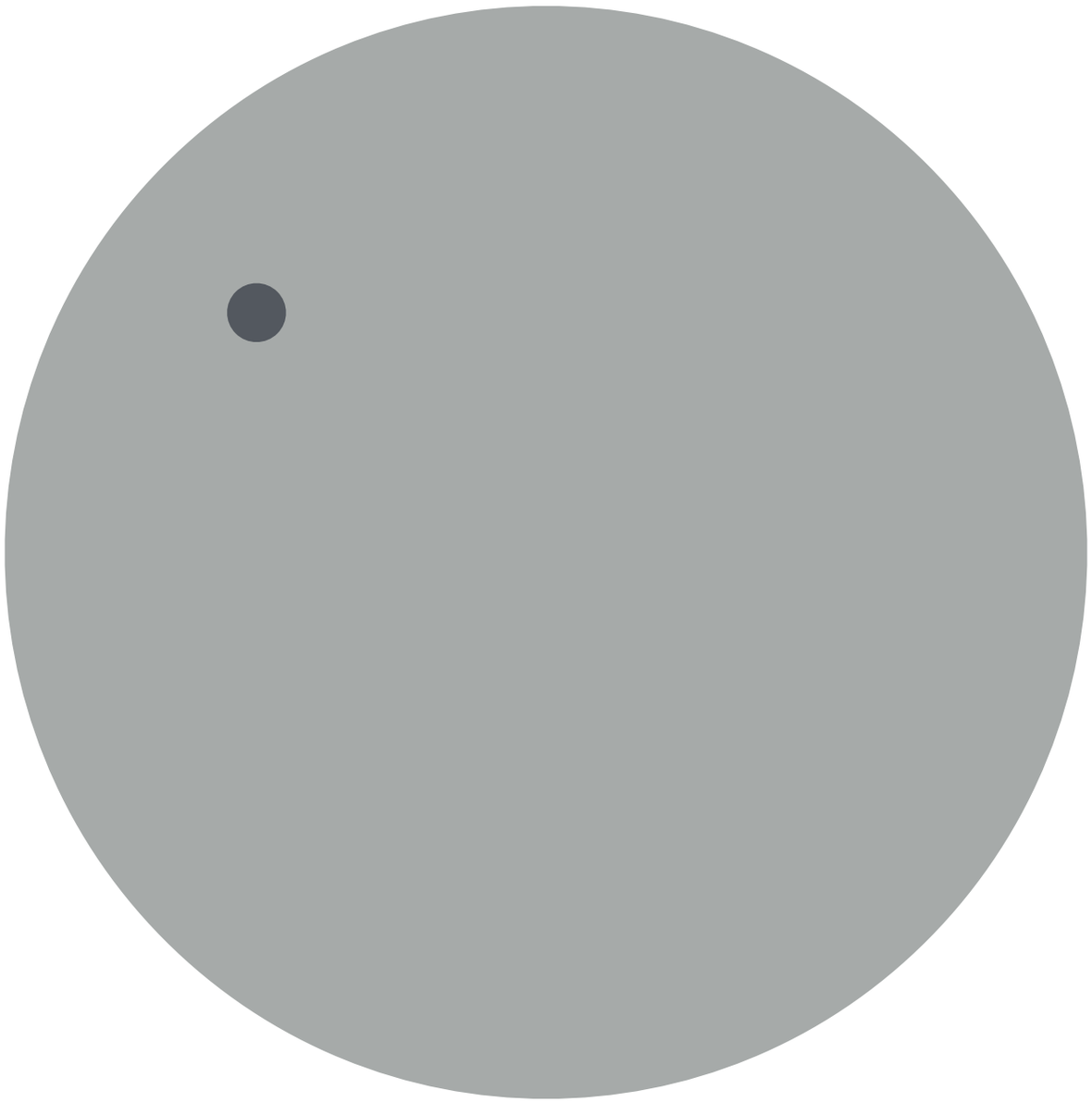
- electron



“Molecule”

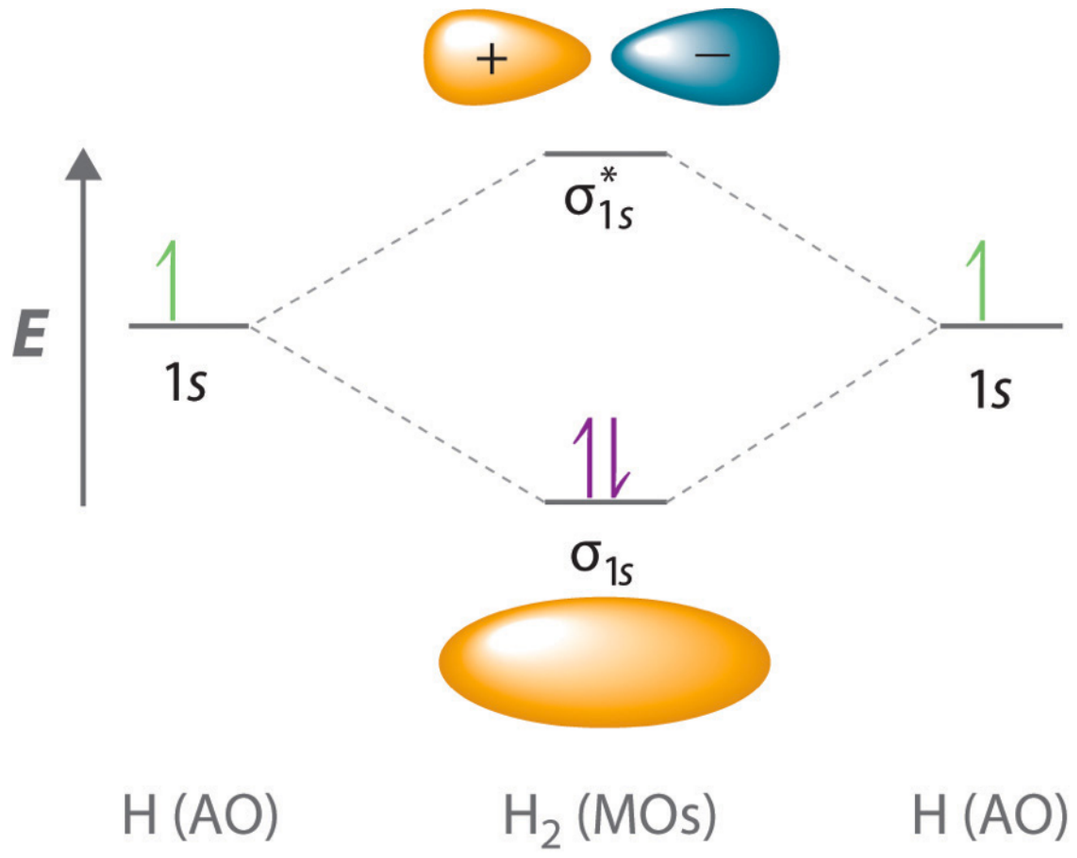
electron

“smeared” electron cloud

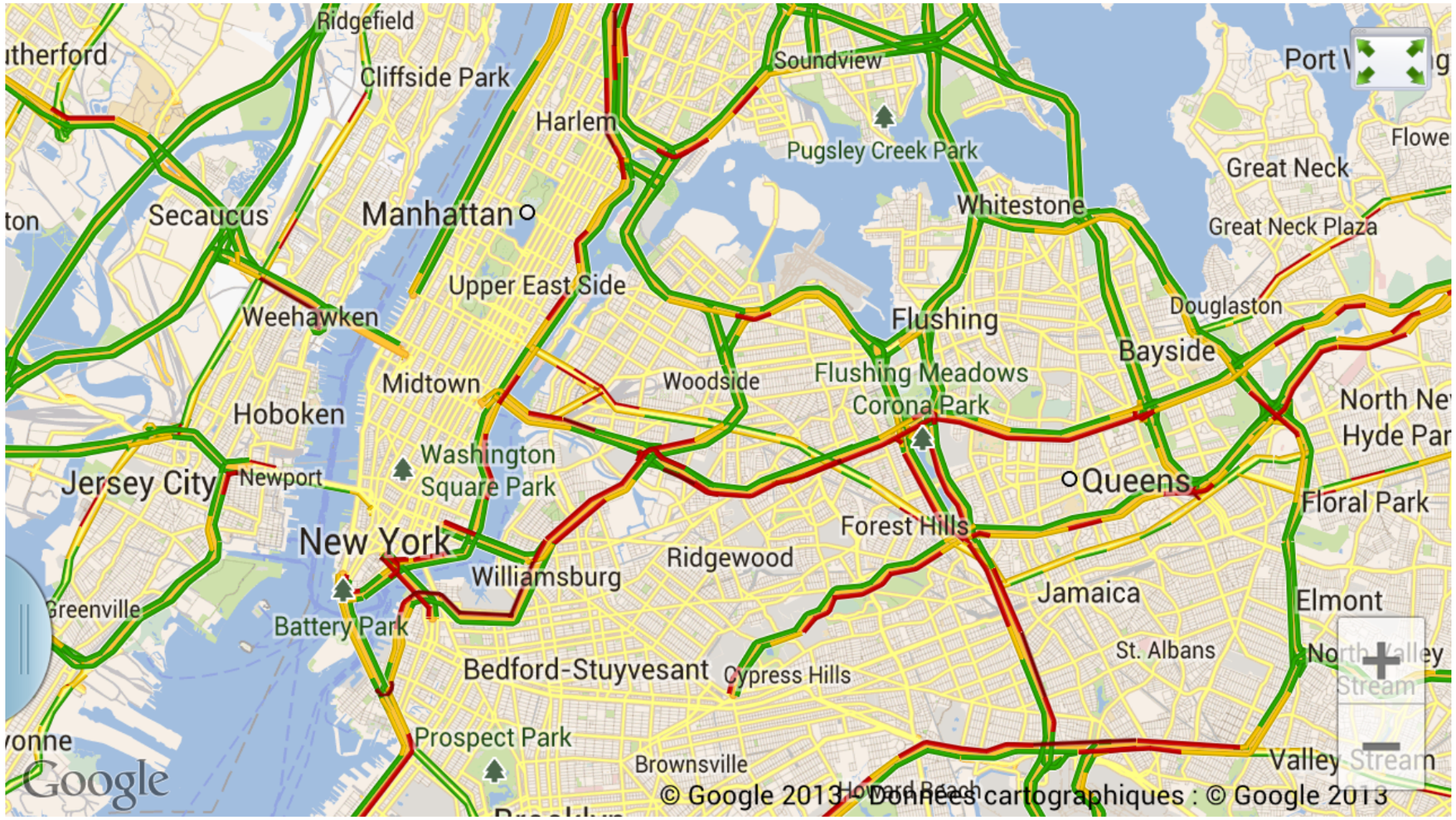


The function that describes how the electron moves in the "mean field" of the other electrons is its orbital.

Hartree Fock theory is the basis of Molecular Orbital theory!



Less formally, Hartree Fock is the Google Maps of chemistry



All the cars are smeared out into “traffic density”

All the electrons are smeared out into “electron density”

But what sort of interactions should we consider?

Quantum chemists try to solve

$$\hat{H}\Psi = E\Psi$$

$\hat{H}$ the Hamiltonian describes interactions between electrons

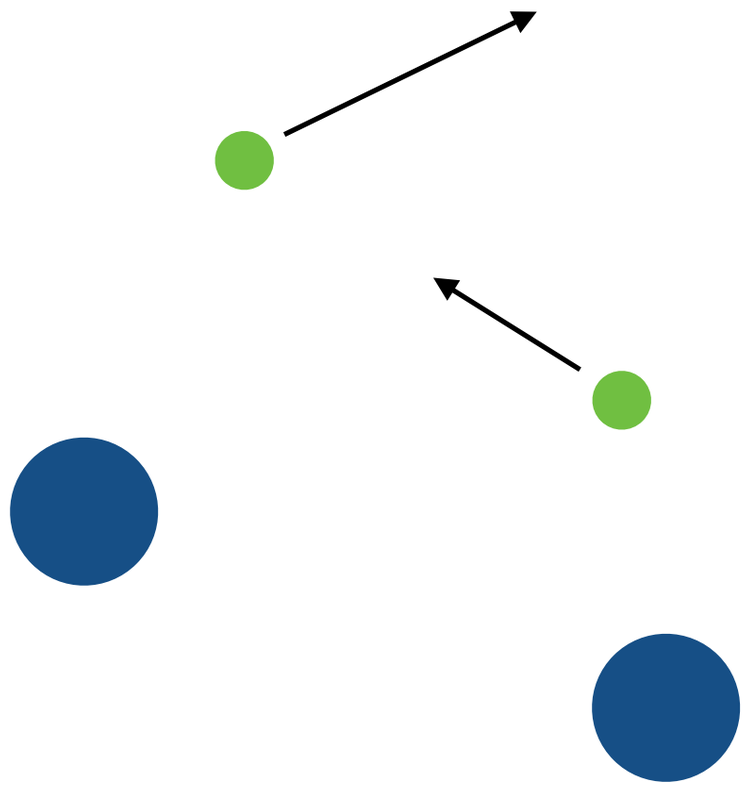
Ψ the wavefunction describes the molecule

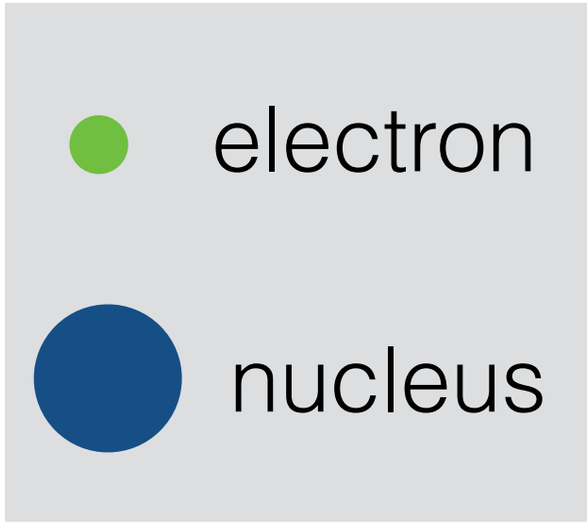
E is the energy of the system

This is the **Schrodinger Equation**
(and is in general impossible to solve)

For molecules, the Hamiltonian describes five interactions

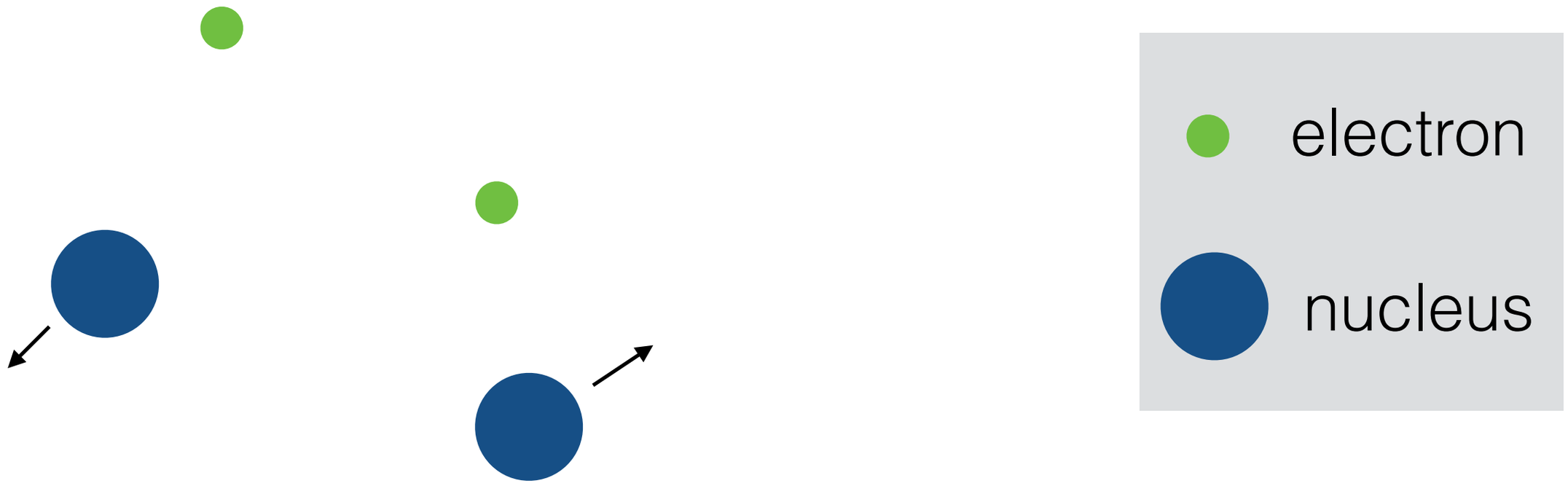
$\hat{H}$ = electron kinetic energy





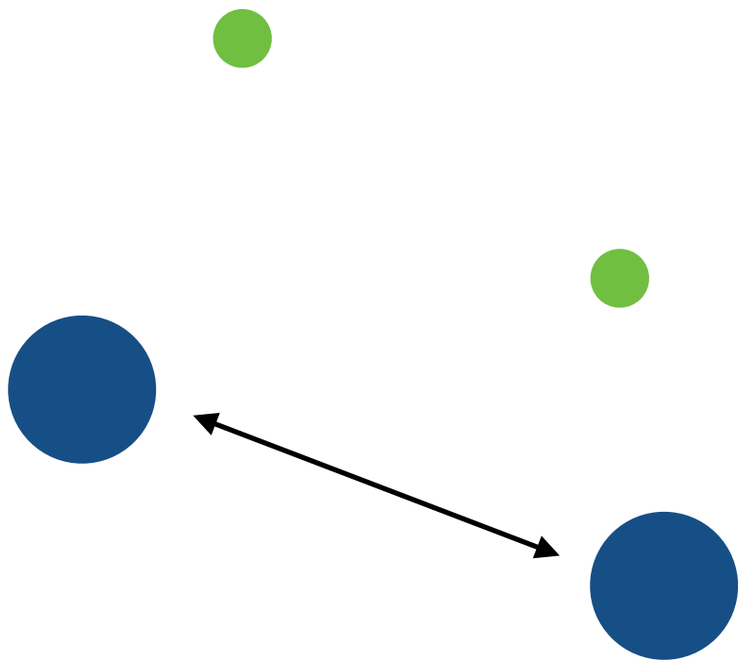
For molecules, the Hamiltonian describes five interactions

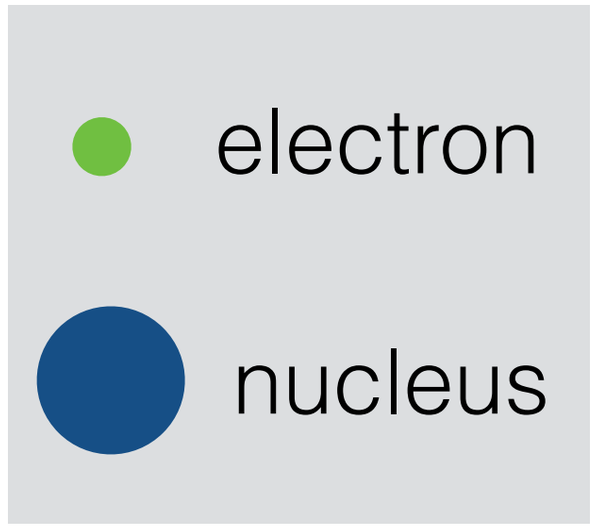
$\hat{H}$ = electron kinetic energy + nuclei kinetic energy



For molecules, the Hamiltonian describes five interactions

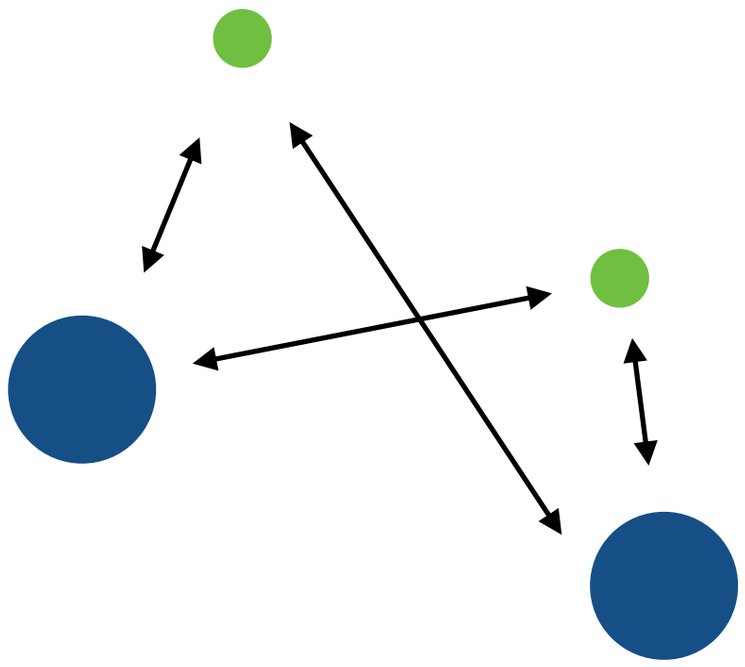
$$\hat{H}$$ = electron kinetic energy + nuclei kinetic energy + nuclear-repulsion

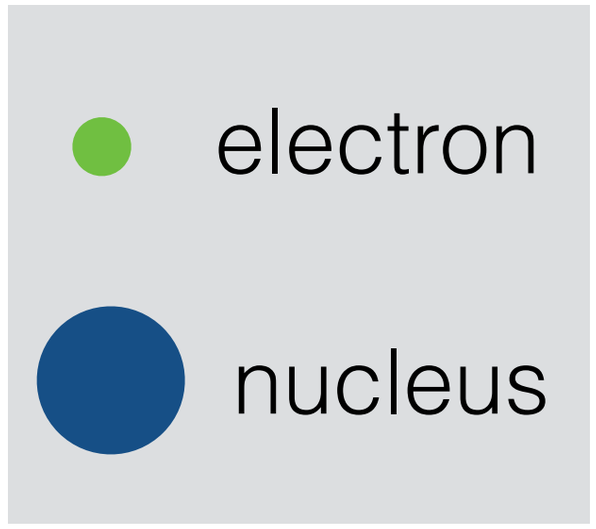




For molecules, the Hamiltonian describes five interactions

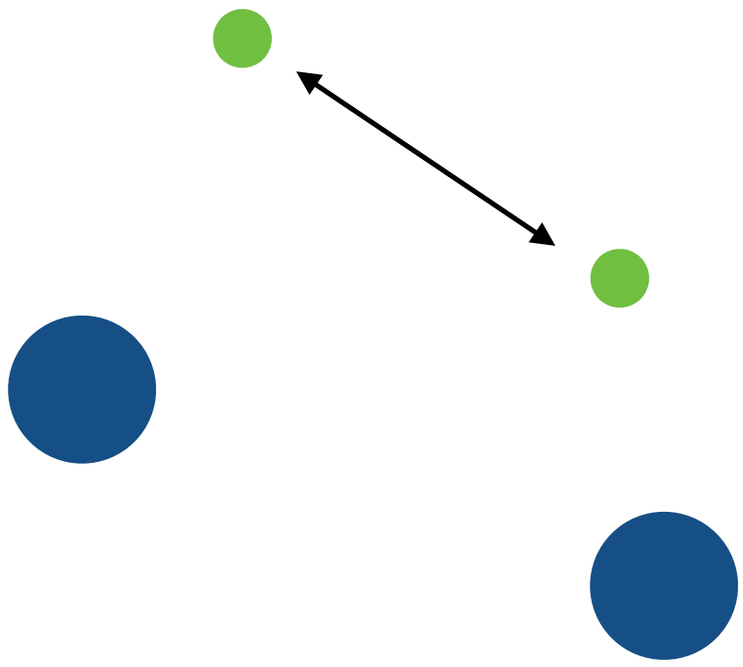
$$\hat{H}$$ = electron kinetic energy + nuclei kinetic energy
+ nuclear-repulsion + electron-nuclear attraction





For molecules, the Hamiltonian describes five interactions

$$\hat{H}$$ = electron kinetic energy + nuclei kinetic energy
+ nuclear-repulsion + electron-nuclear attraction
+ electron-electron repulsion



electron

nucleus

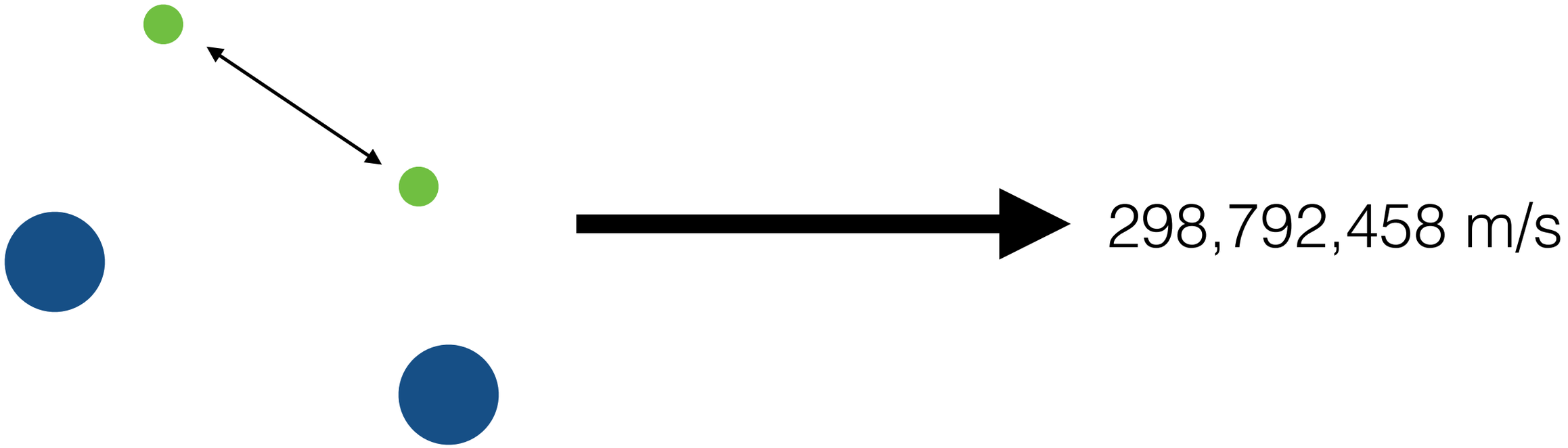
What's missing?

Spin doesn't show up in our Hamiltonian.

However, we need spin to describe magnetism.

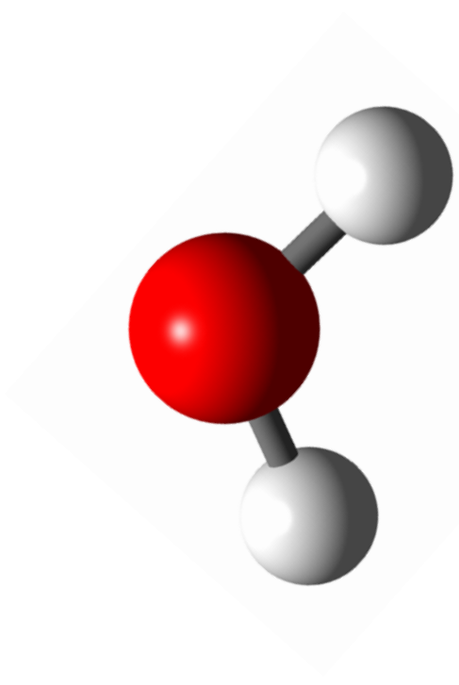
The origin of spin is actually really weird.

If we want to include spin, we actually have to think about how our equations change as we approach the **speed of light**.

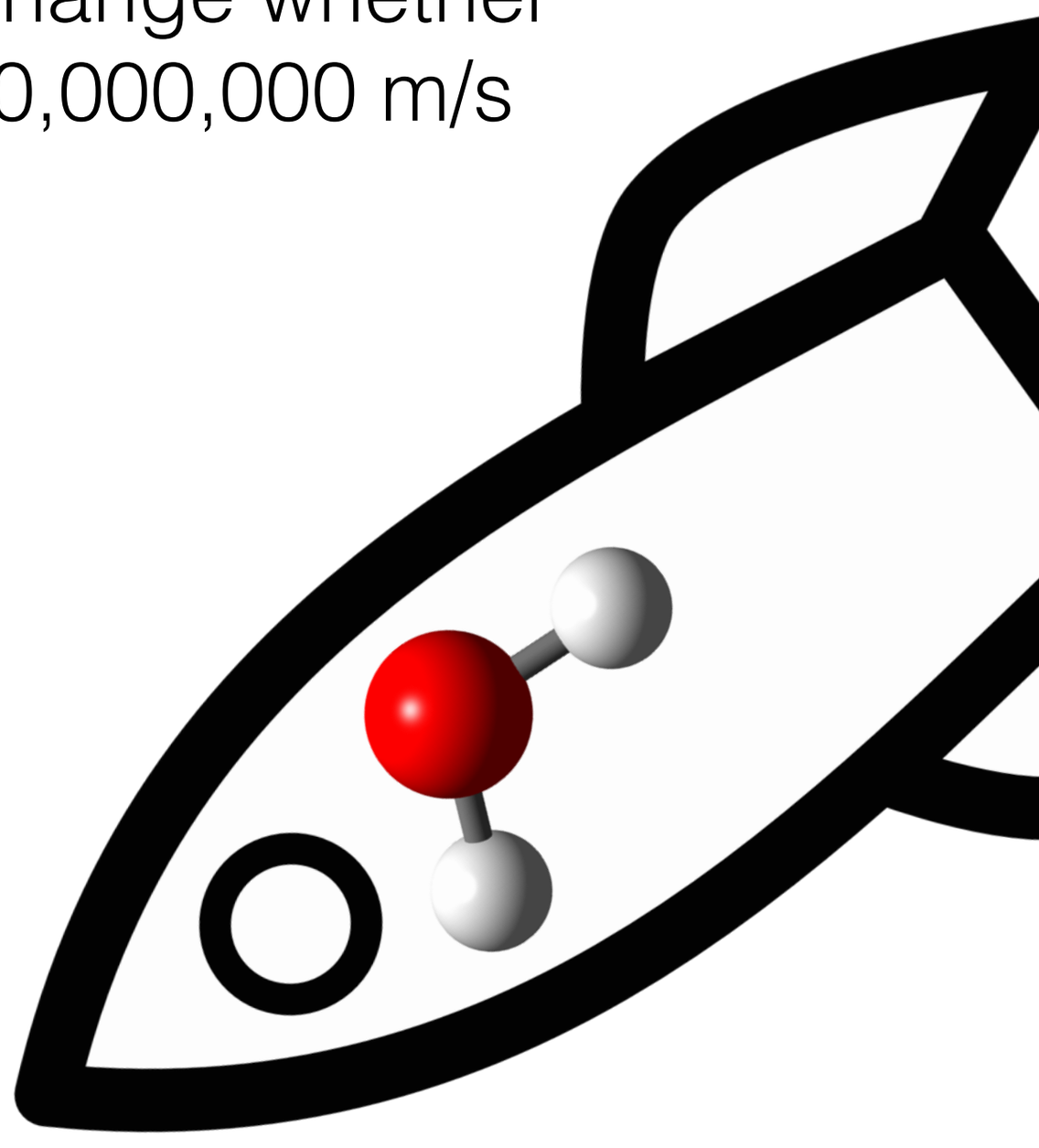


Einstein says our equations shouldn't change when we approach the speed of light

Chemistry shouldn't change whether we do it here or at 290,000,000 m/s



=



Mathematically, if require chemistry to be the same regardless of how fast we are moving…

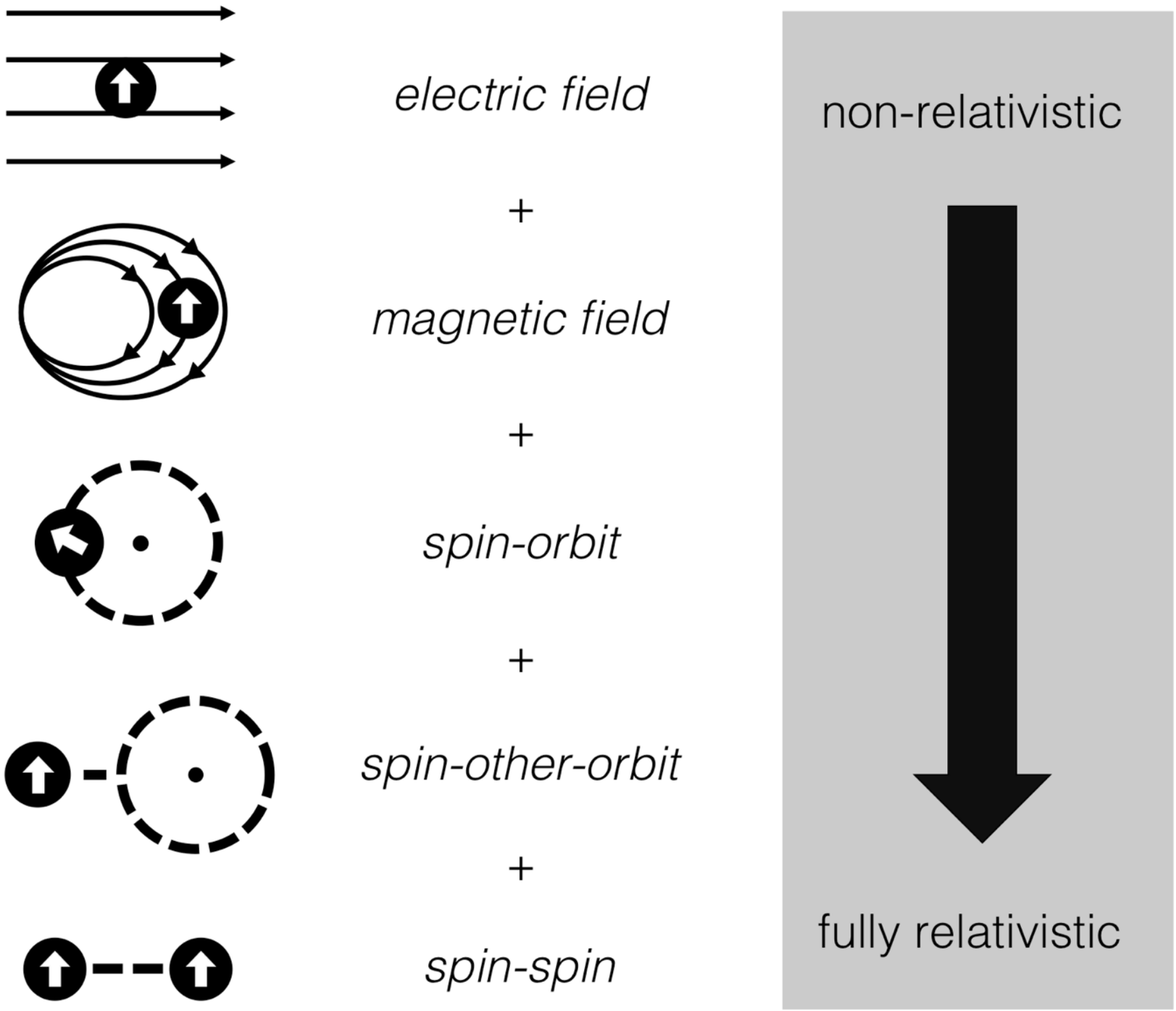
Spin shows up in our Hamiltonian

Interactions between spins show up

We get the proper description for
magnetism in molecules.

Actually doing this, however, is a very hard problem.

There are many types of spin interactions



A table from the back of “Theoretical Foundations of Electron Spin Resonance” (John Harriman)

These are just some of the spin interactions we might consider

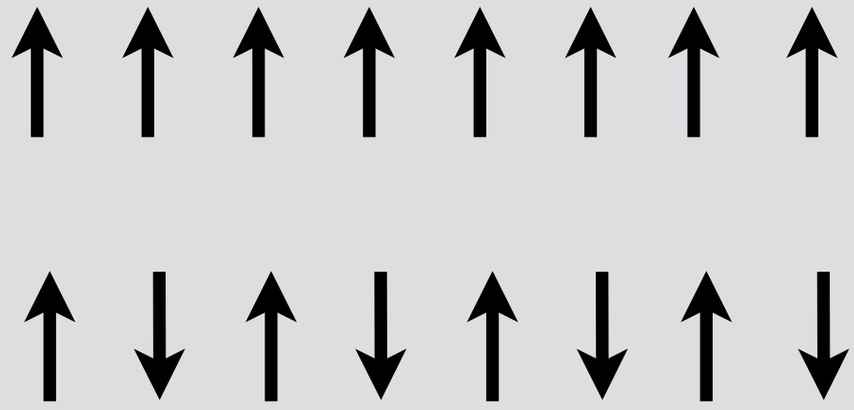
TABLE F-1 (*continued*)

Term	Description	Operator	Coeff. Atomic units
1.3	Electron–electron Darwin term	$\sum_{j<k}(-\pi\delta(\mathbf{r}_{jk}))$	$\alpha^2\mathscr{E}_0 a_0^3$
1.4	Electron–electron orbital interaction	$\sum_{j<k}\left[+\frac{1}{2}\left(\frac{\nabla_j\cdot\nabla_k}{r_{jk}}-\frac{(\mathbf{r}_{jk}\cdot\nabla_j)(\mathbf{r}_{jk}\cdot\nabla_k)}{r_{jk}^3}\right)\right]$	$\alpha^2\mathscr{E}_0 a_0^3$
1.5	Electron–electron orbital interaction	$\sum_{j<k}\left[+\frac{1}{4}\frac{1}{r_{jk}^3}(\mathbf{r}_{jk}\cdot\nabla_k-\mathbf{r}_{jk}\cdot\nabla_j)\right]$	$\alpha^2\mathscr{E}_0 a_0^3$
1.6	Electron–electron orbital interaction	$\sum_{j<k}[\pi\delta(\mathbf{r}_{jk})(\mathbf{r}_{jk}\cdot\nabla_j-\mathbf{r}_{jk}\cdot\nabla_k)]$	$\alpha^2\mathscr{E}_0 a_0^3$
Terms depending on spin but not field			
(Electron spin)			
2.1	Spin–orbit interaction	$\sum_{j,\nu}\left(-\frac{g'}{4}Z_\nu i\frac{k_0^2(\mathbf{r}_{j\nu})}{r_{j\nu}^3}\mathbf{S}_j\cdot(\mathbf{r}_{j\nu}\times\nabla_j)\right)$	$\alpha^2\mathscr{E}_0 a_0^3$
2.2	Spin–other-orbit interaction	$\sum_{j,k}'\frac{i}{r_{jk}^3}\mathbf{S}_j\cdot[(\mathbf{r}_{kj})\times\nabla_k]$	$\alpha^2\mathscr{E} a_0^3$
2.3	Electron–electron spin–orbit interaction	$\sum_{j,k}'\left(\frac{g'}{4}\frac{i}{r_{jk}^3}\mathbf{S}_j\cdot\mathbf{r}_{jk}\times\nabla_j\right)$	$\alpha^2\mathscr{E}_0 a_0^3$
2.4	Spin–spin dipolar interaction	$\sum_{j<k}\left(\frac{\mathbf{S}_j\cdot\mathbf{S}_k}{r_{jk}^3}-\frac{(\mathbf{S}_j\cdot\mathbf{r}_{jk})(\mathbf{S}_k\cdot\mathbf{r}_{jk})}{r_{jk}^5}\right)$	$\alpha^2\mathscr{E}_0 a_0^3$
2.5	*Spin–spin contact interaction*	$\sum_{j<k}\left(-\frac{8\pi}{3}\mathbf{S}_j\cdot\mathbf{S}_k\delta(\mathbf{r}_{jk})\right)$	$\alpha^2\mathscr{E}_0 a_0^3$
(Nuclear spin)			
2.6	*Nuclear dipole–dipole interaction*	$\sum_{\nu<\nu'}\frac{g_\nu g_{\nu'}}{4}\left[\frac{\mathbf{I}_\nu\cdot\mathbf{I}_{\nu'}}{R_{\nu\nu'}^3}-3\frac{(\mathbf{I}_\nu\cdot\mathbf{R}_{\nu\nu'})(\mathbf{I}_{\nu'}\cdot\mathbf{R}_{\nu\nu'})}{R_{\nu\nu'}^5}\right]$	$\left(\frac{m}{M_P}\right)^2\alpha^2\mathscr{E}_0 a_0^3$
7	*Nuclear quadrupole interaction*	$\sum_{j,\nu}\left[\frac{Q_\nu}{2I_\nu(2I_\nu-1)}\right]\left[\frac{I_\nu^2}{r_{j\nu}^3}-3\frac{(\mathbf{r}_{j\nu}\cdot\mathbf{I}_\nu)^2}{r_{j\nu}^5}\right]$	$\mathscr{E} a_0$
	Orbital hyperfine interaction	$\sum_{j,\nu}\frac{-g_\nu}{2}k_0(r_{j\nu})\frac{i}{r_{j\nu}^3}(\mathbf{r}_{j\nu}\times\nabla_j)\cdot\mathbf{I}_\nu$	$\left(\frac{m}{M_P}\right)\alpha^2\mathscr{E}_0 a_0^3$
	Orbital hyperfine correction	$\sum_{j,\nu}\frac{g_\nu}{4}k_0^3(r_{j\nu})\nabla_j^2\frac{i}{r_{j\nu}^3}(\mathbf{r}_{j\nu}\times\nabla_j)\cdot\mathbf{I}_\nu$	$\left(\frac{m}{M_P}\right)\alpha^2\mathscr{E}_0 a_0^5$
	Electron coupled nuclear spin–spin interaction	$\sum_j\sum_{\nu,\nu'}\frac{g_\nu g_{\nu'}}{8}\frac{k_0(r_{\nu j})}{r_{j\nu}^3 r_{j\nu'}^3}\times[(\mathbf{I}_\nu\cdot\mathbf{I}_{\nu'})(\mathbf{r}_{j\nu}\cdot\mathbf{r}_{j\nu'})-(\mathbf{I}_\nu\cdot\mathbf{r}_{j\nu})(\mathbf{I}_{\nu'}\cdot\mathbf{r}_{j\nu})]$	$\left(\frac{m}{M_P}\right)^2\alpha^4\mathscr{E} a_0^4$
	and nuclear spins)		
	Dipolar hyperfine interaction	$\sum_{j,\nu}\left(-\frac{gg_\nu}{4}k_0(r_{j\nu})\left[\frac{\mathbf{S}_{j\nu}\cdot\mathbf{I}_\nu}{r_{j\nu}^3}-3\frac{(\mathbf{S}_j\cdot\mathbf{r}_{j\nu})(\mathbf{I}_\nu\cdot\mathbf{r}_{j\nu})}{r_{j\nu}^5}\right]\right)$	$\left(\frac{m}{M_P}\right)\alpha^2\mathscr{E}$
	Fermi) contact hyperfine interaction	$\sum_{j,\nu}\frac{2\pi}{3}g'g_\nu\mathbf{S}_j\cdot\mathbf{I}_\nu\delta(\mathbf{r}_{j\nu})$	$\left(\frac{m}{M_P}\right)\alpha^2$

All magnetic materials have unpaired electrons.

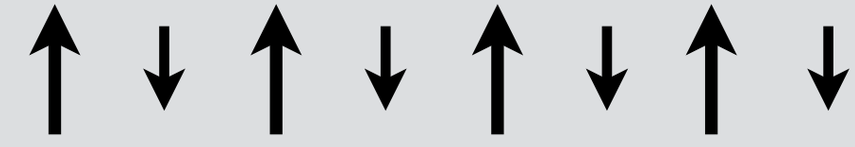
How the spins order determines the type of magnet (at 0K).

Ferromagnetic



Antiferromagnetic

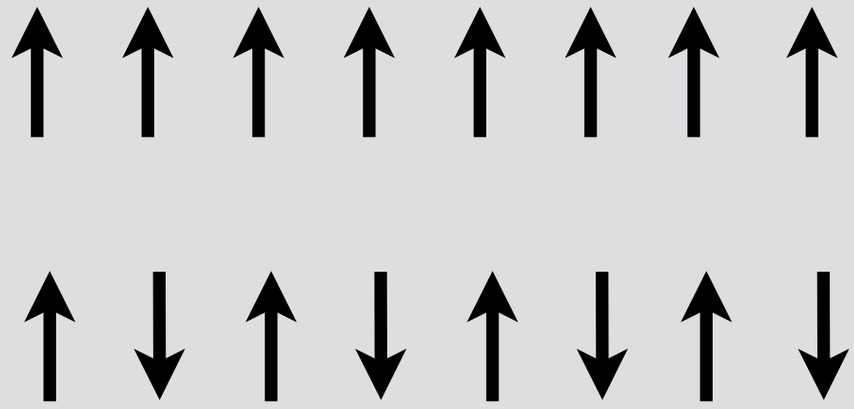
Ferrimagnetic



All these states are collinear.

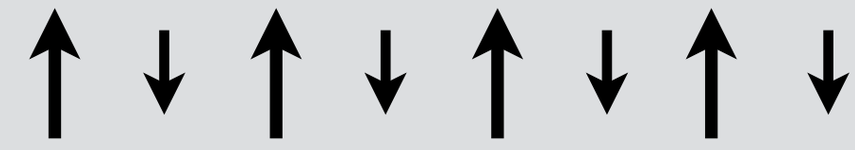
Spins point either up or down.

Ferromagnetic



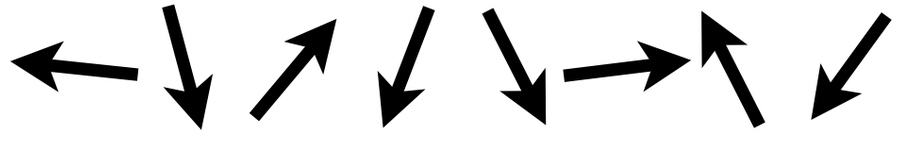
Antiferromagnetic

Ferrimagnetic



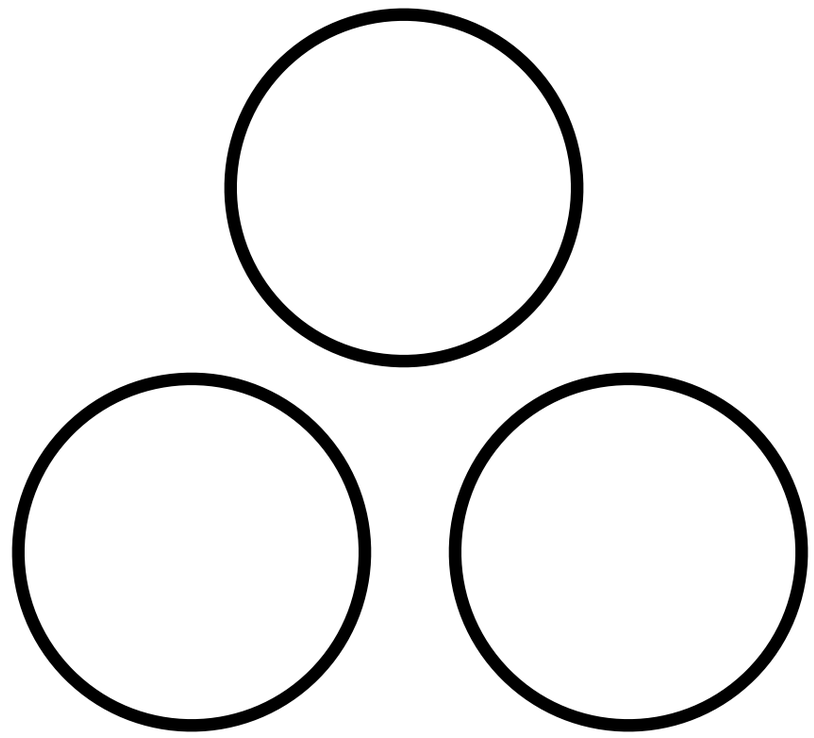
Heating up a magnet past its critical temperature gives us a disordered state

Paramagnetic



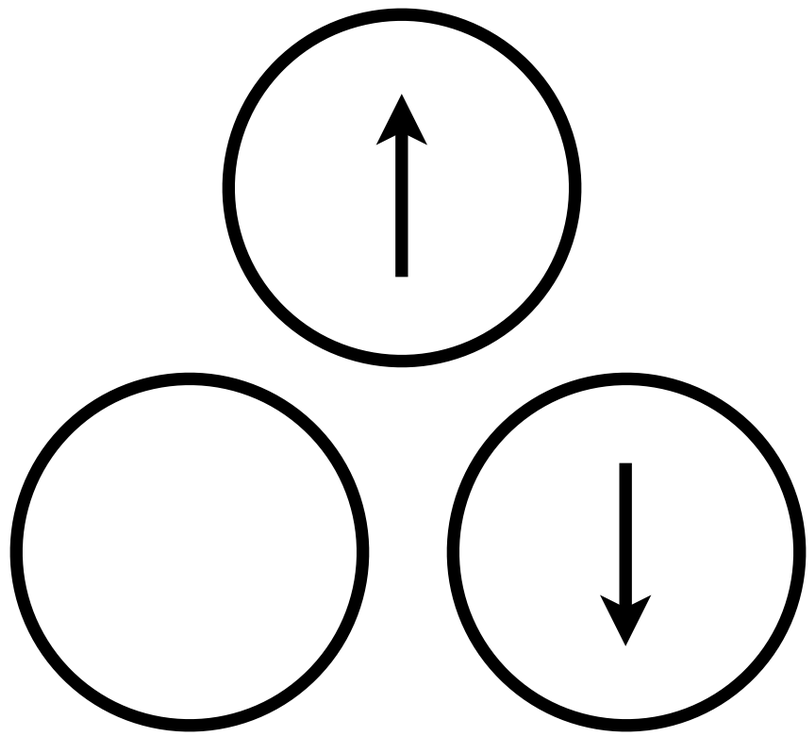
Is it possible to obtain a disordered state at absolute zero?

Spin frustration leads to non-collinear magnetism



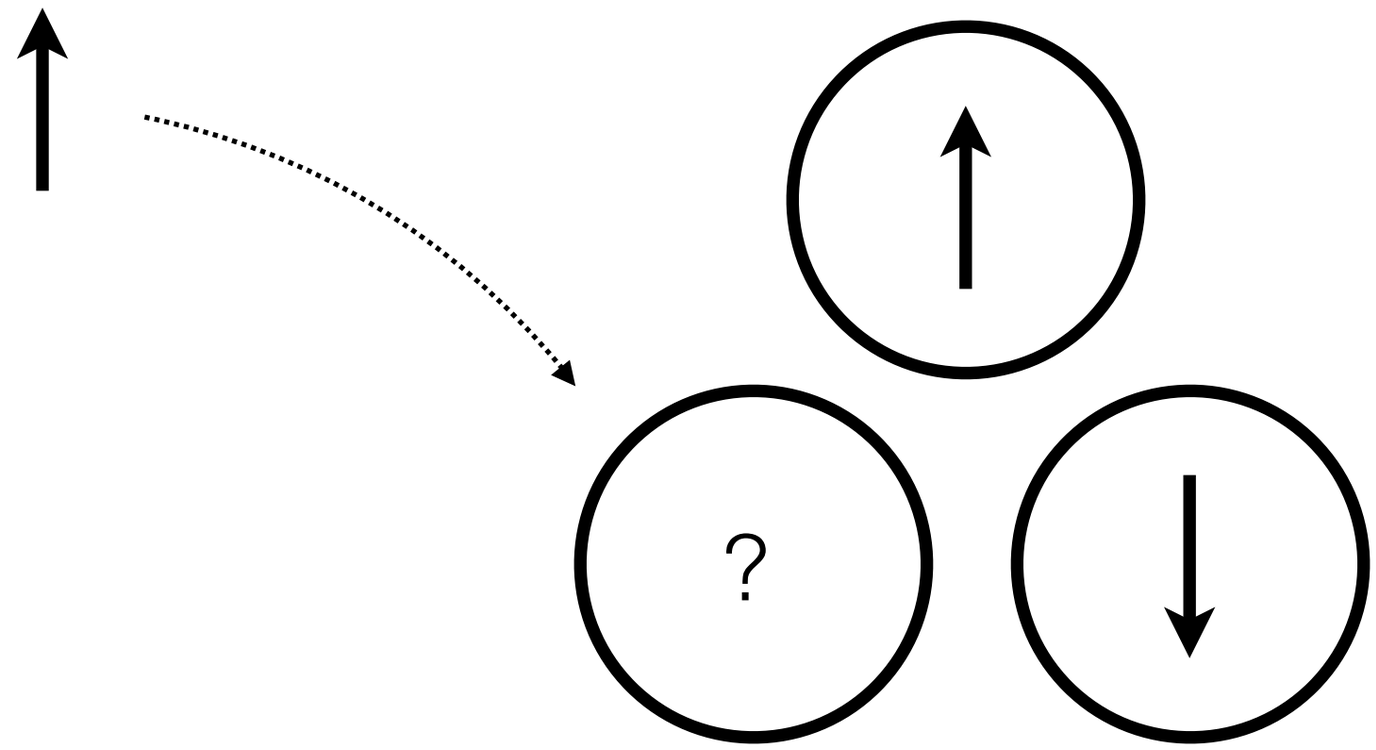
Take a three site lattice

Spin frustration leads to non-collinear magnetism



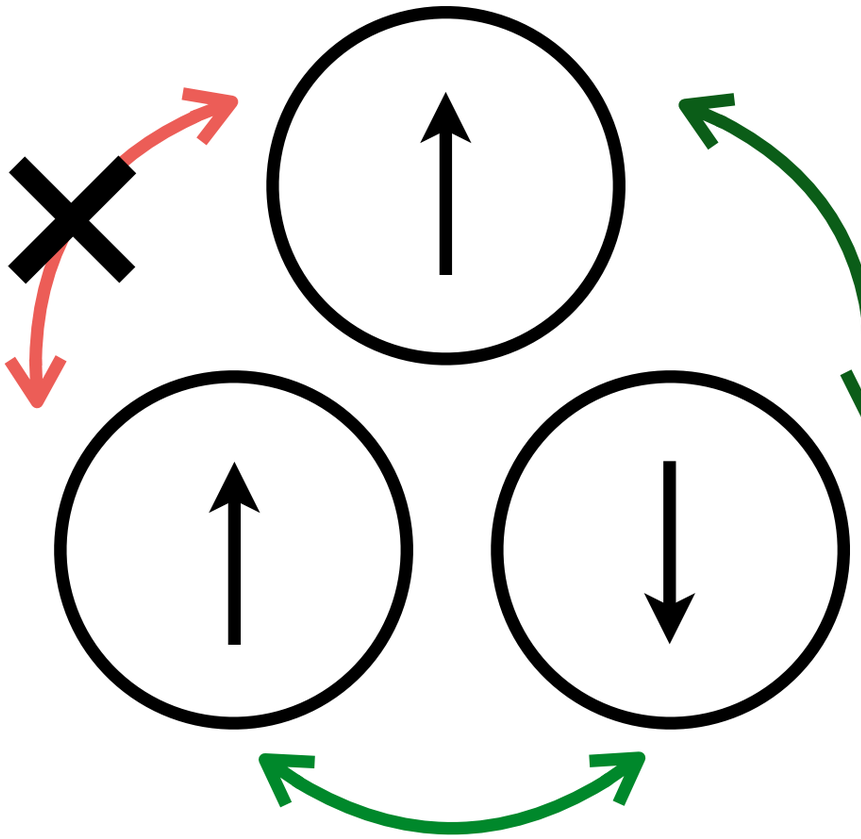
Add two electrons.
(Assume anti-ferromagnetism favored).

Spin frustration leads to non-collinear magnetism

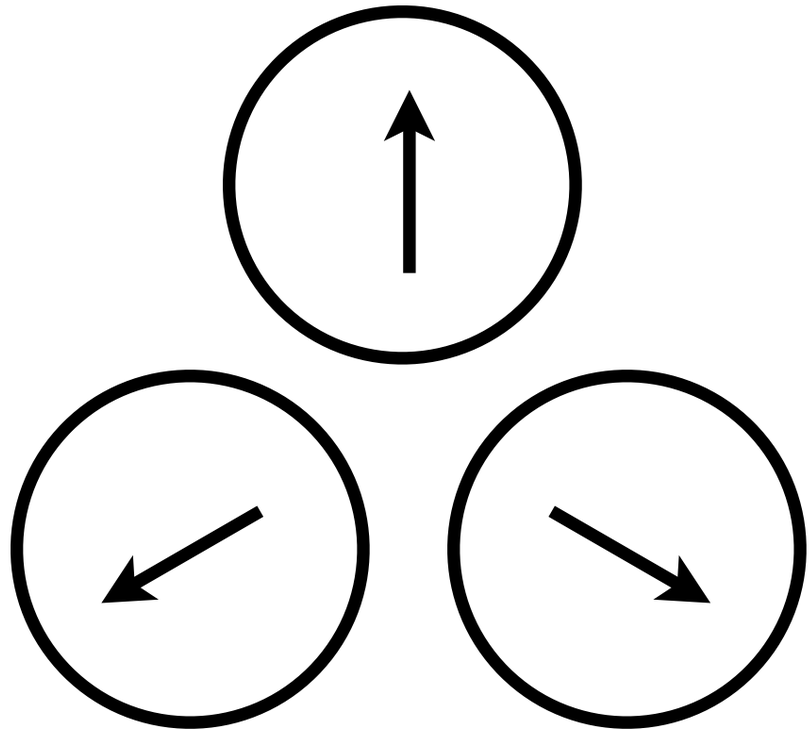


Now, add the third electron.
No spin orientation simultaneously favors
all anti-ferromagnetic exchange interactions

Spin frustration leads to non-collinear magnetism



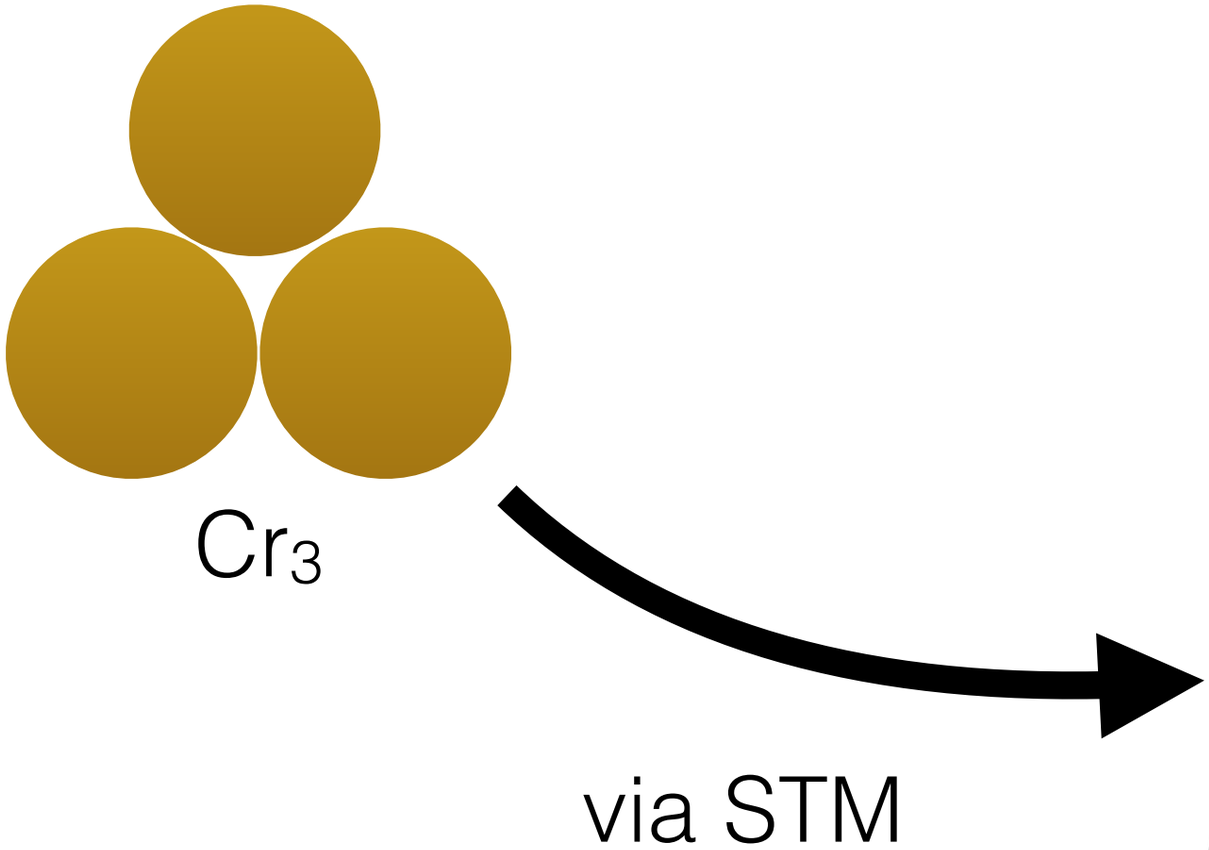
Collinear

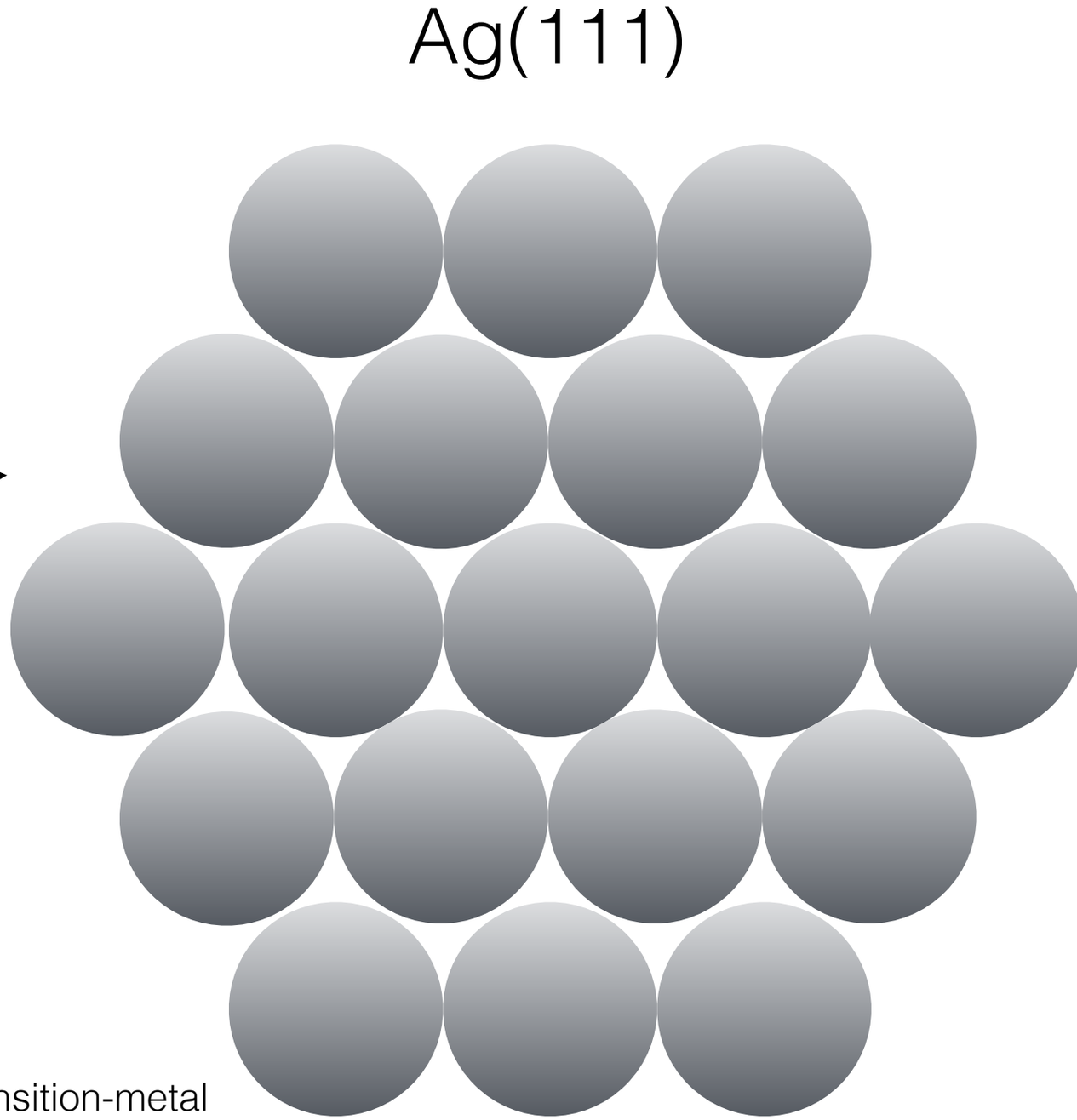


Non-collinear

Most electronic structure methods
cannot capture non-collinearity!

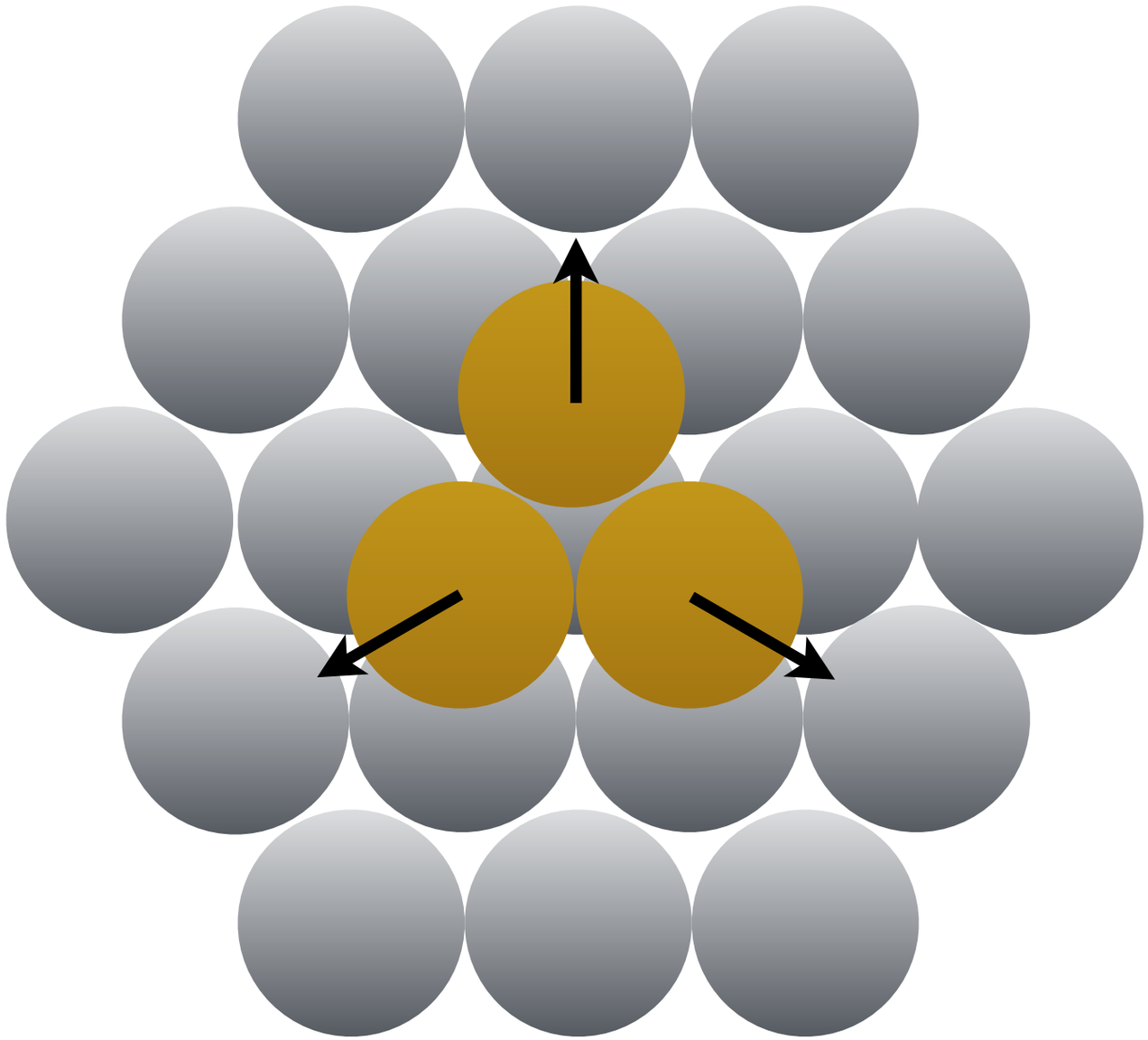
Generating non-collinear magnetism by spin frustration with transition metals





S Lounis. “Non-collinear magnetism induced by frustration in transition-metal nanostructures deposited on surfaces”. JPCM 26 (2014) 273201.

Generating non-collinear magnetism by spin frustration with transition metals



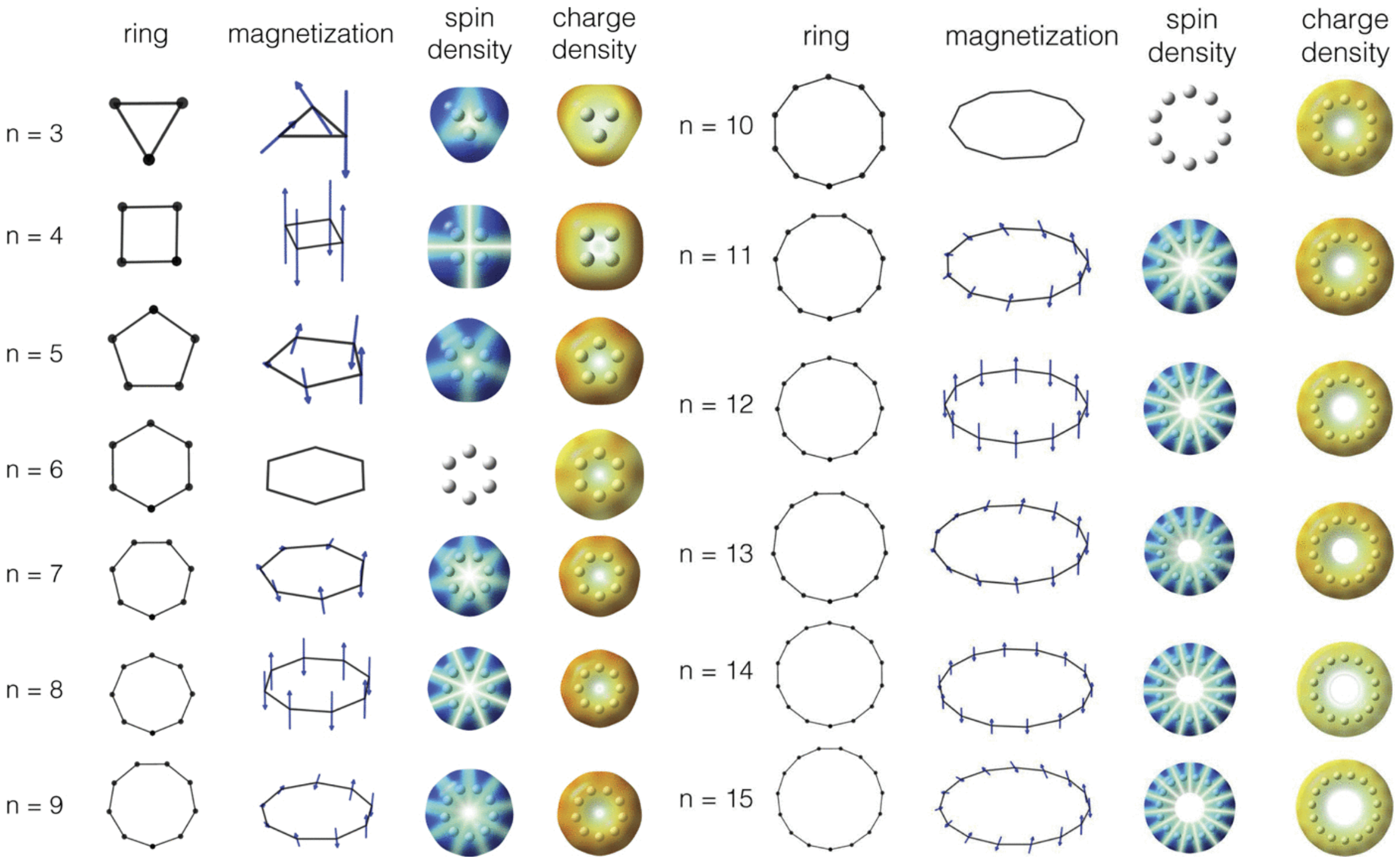
Lock metal trimer into triangle

THE JOURNAL OF CHEMICAL PHYSICS **142**, 154109 (2015)

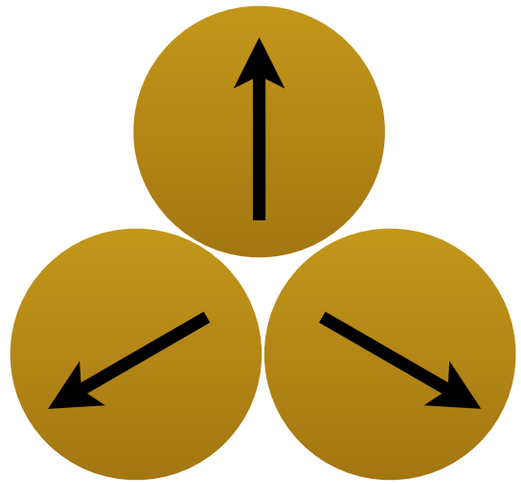
Stability of the complex generalized Hartree-Fock equations

Joshua J. Goings,[1] Feizhi Ding,[1] Michael J. Frisch,[2] and Xiaosong Li[1,a)]
[1]*Department of Chemistry, University of Washington, Seattle, Washington 98195, USA*
[2]*Gaussian, Inc., 340 Quinnipiac St., Bldg 40, Wallingford, Connecticut 06492, USA*

(Received 19 December 2014; accepted 2 April 2015; published online 16 April 2015)



These molecules are great for testing out ideas about magnetism because they have many competing magnetic interactions



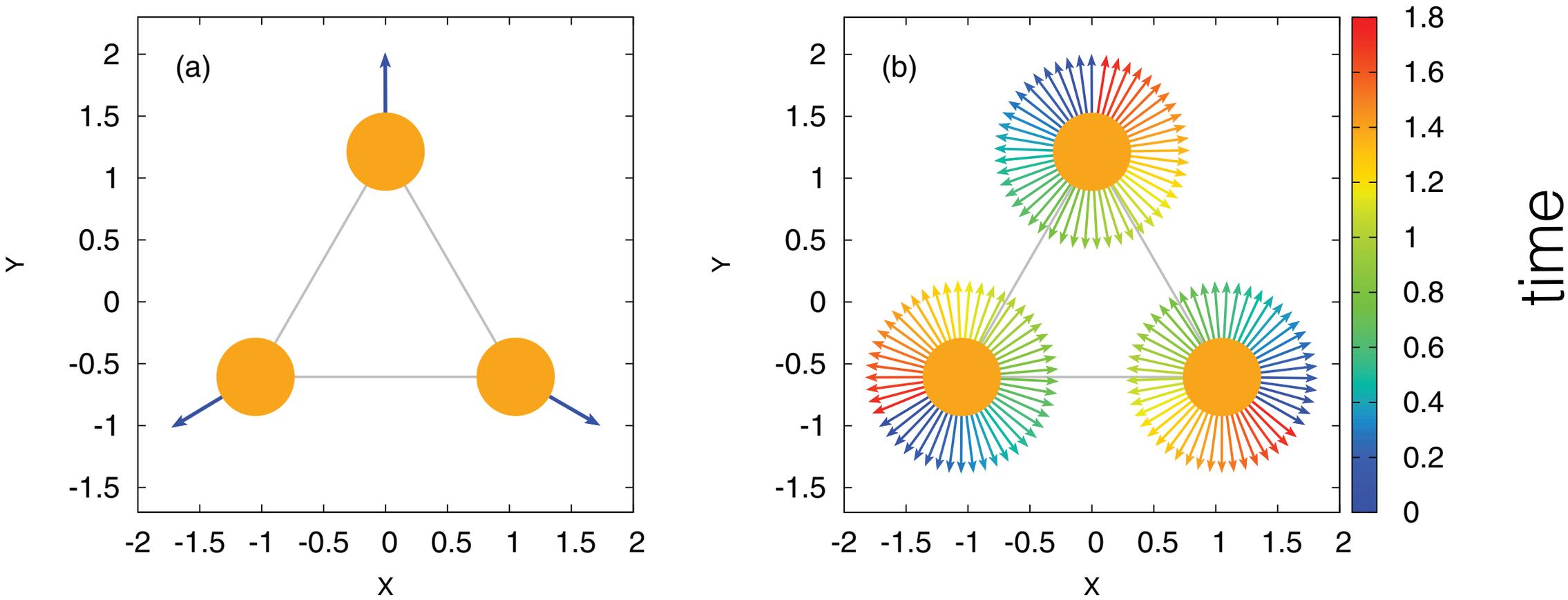
This understanding helps us understand more complicated interactions in quantum dots.

THE JOURNAL OF CHEMICAL PHYSICS **141**, 214111 (2014)

Ab initio non-relativistic spin dynamics

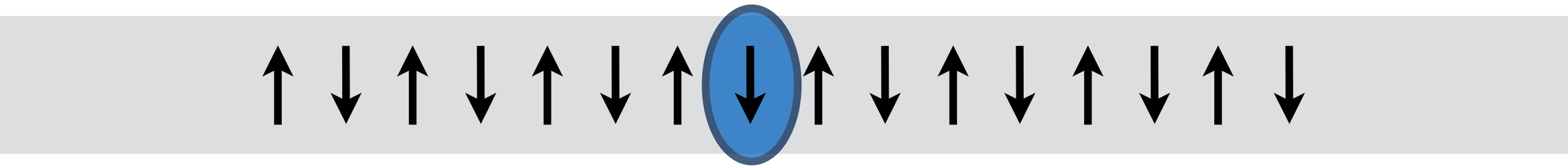
Feizhi Ding,[1] Joshua J. Goings,[1] Michael J. Frisch,[2] and Xiaosong Li[1,a)]
[1]*Department of Chemistry, University of Washington, Seattle, Washington 98195, USA*
[2]*Gaussian, Inc., 340 Quinnipiac St, Bldg 40, Wallingford, Connecticut 06492, USA*

(Received 29 August 2014; accepted 17 November 2014; published online 4 December 2014)

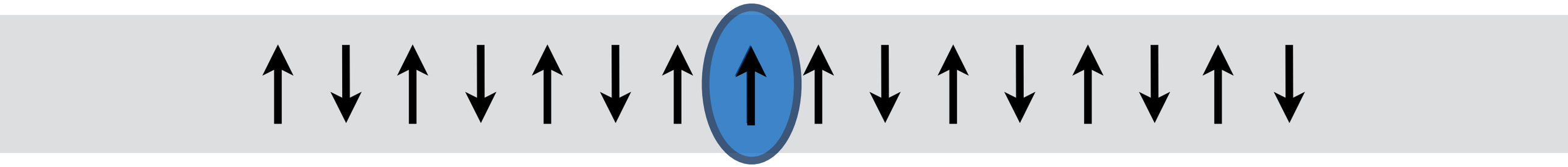


Applying a magnetic field (into page) causes spins to precess

Here we tried to model spin waves.



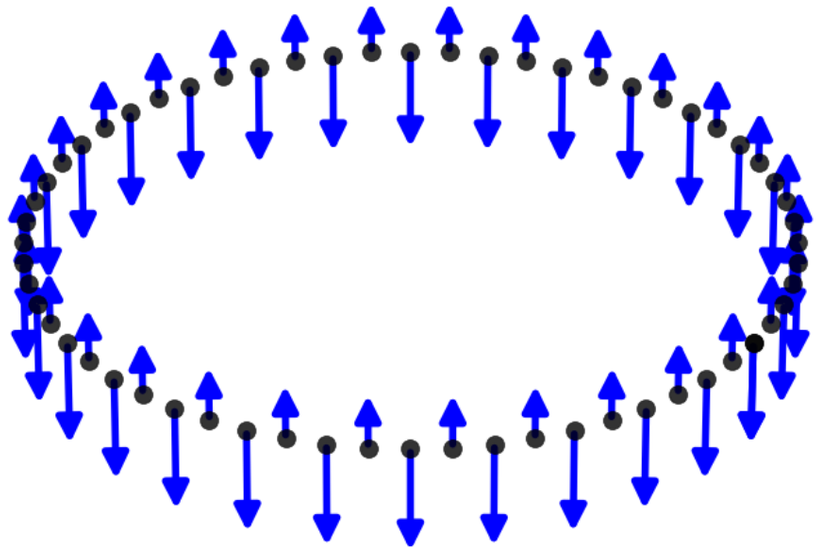
flip magnetic moment



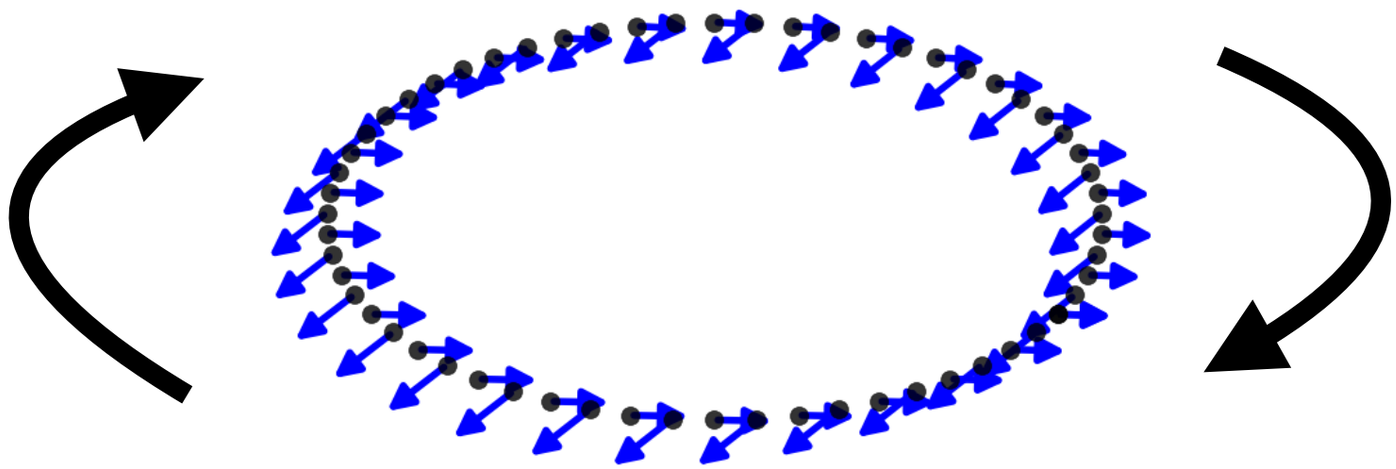
…and watch it go!

(movie)

Initial Spin-Flipped State



t ~ 20 fs

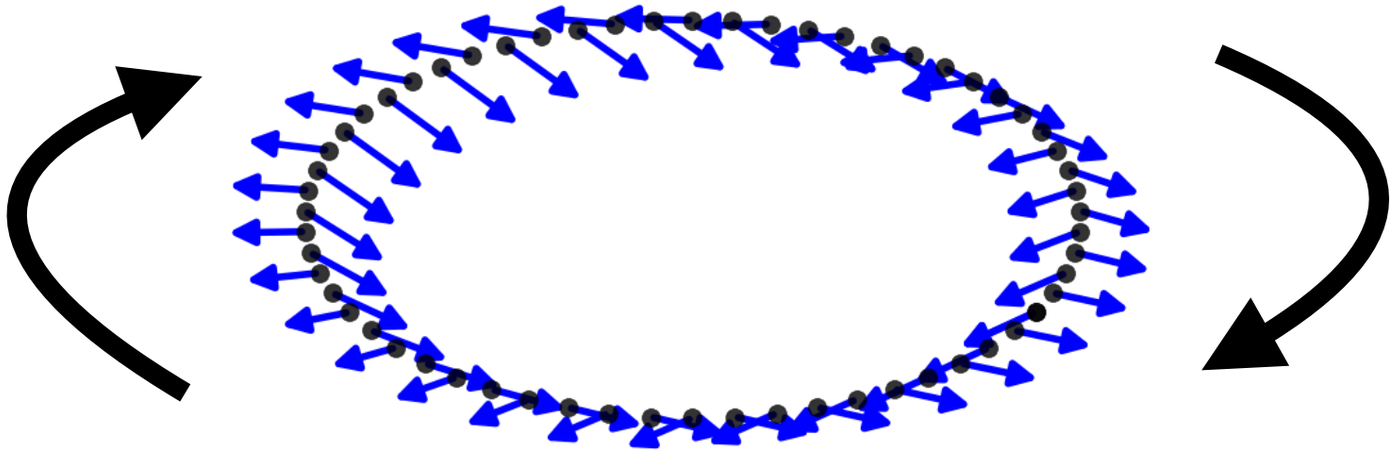


20 fs is to **1 s**

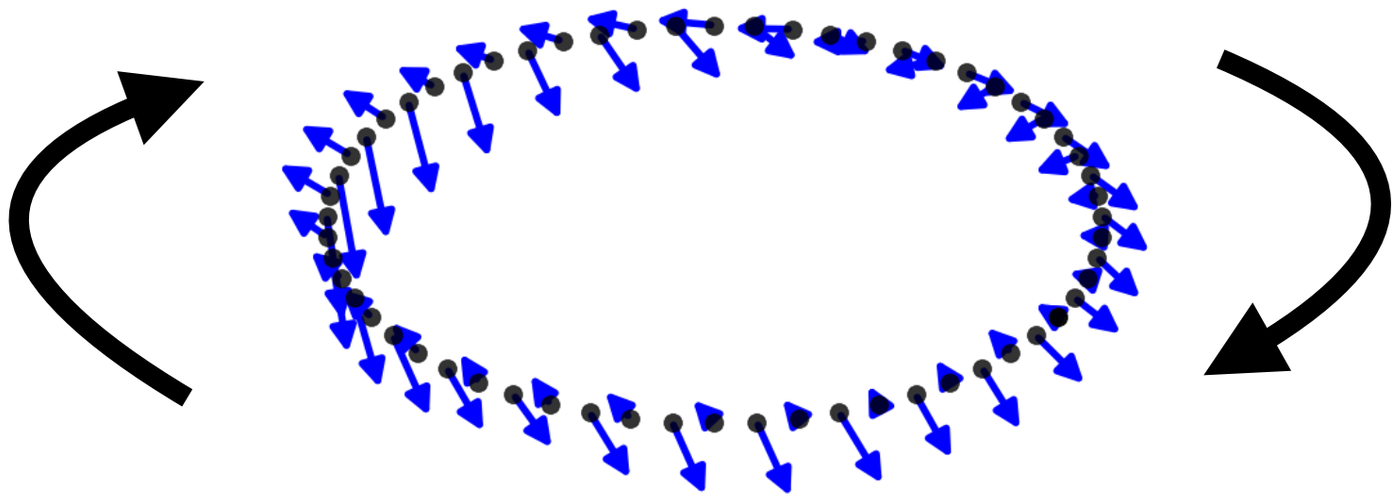
as

1 s is to **one million years**

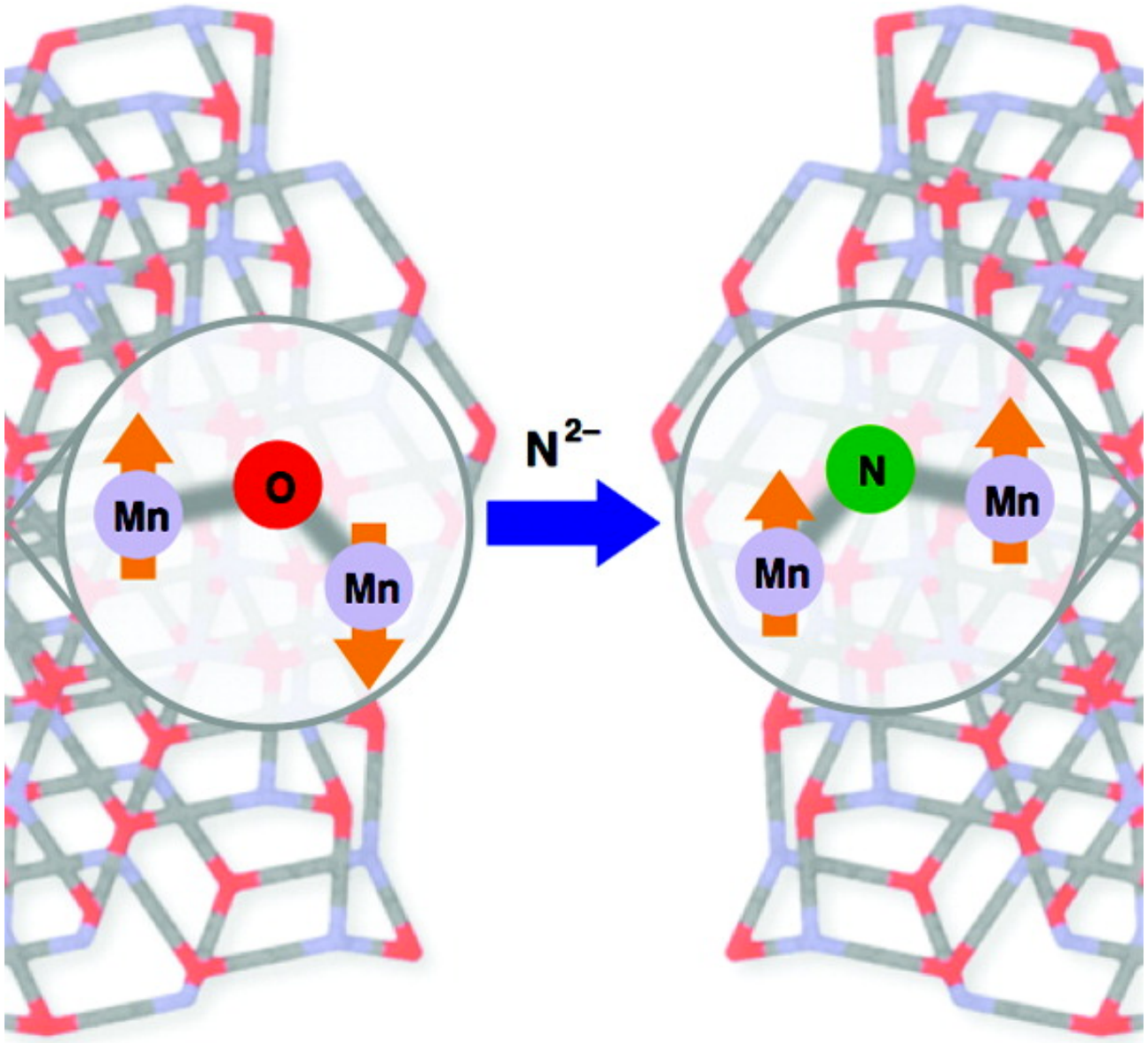
t ~ 40 fs



t ~ 60 fs



All these tools give us complementary information to interpret and explain what we see in the chemistry lab.



May, Joseph W., Ryan J. McMorris, and Xiaosong Li. "Ferromagnetism in p-Type Manganese-Doped Zinc Oxide Quantum Dots." The Journal of Physical Chemistry Letters 3.10 (2012): 1374-1380.

THE JOURNAL OF PHYSICAL CHEMISTRY C

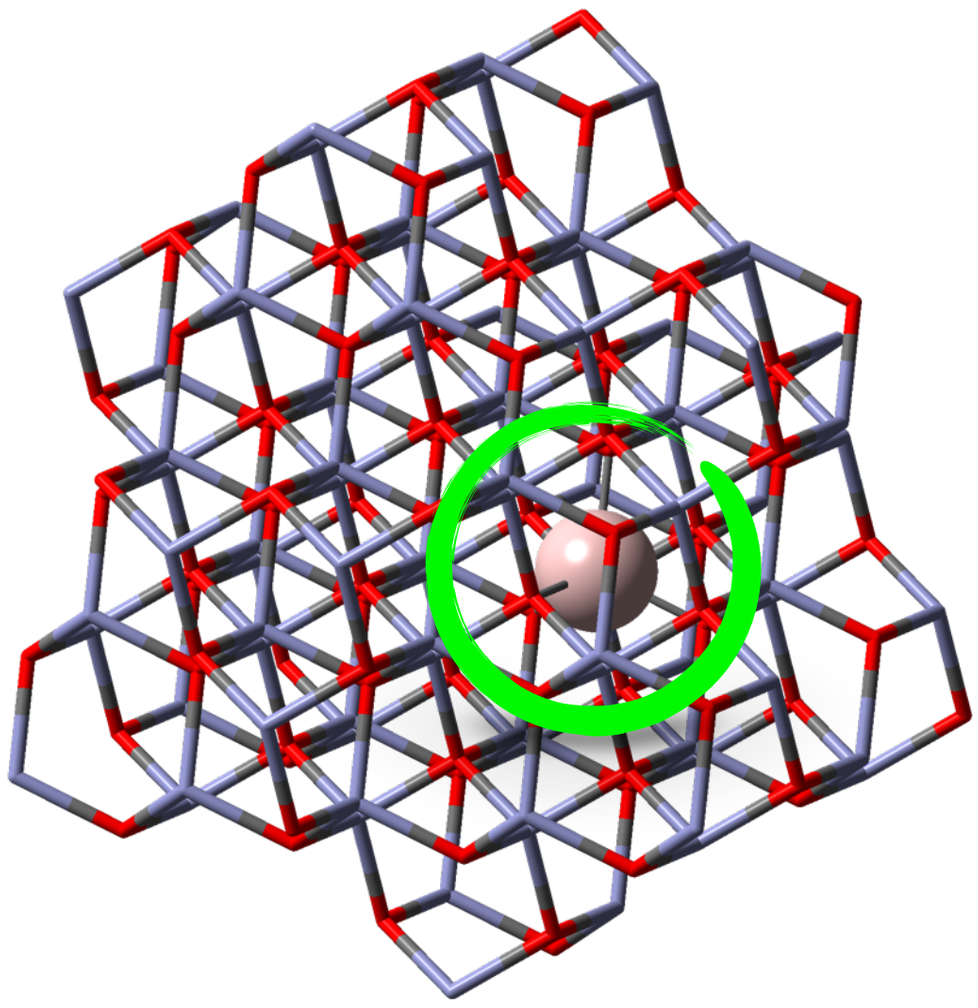
Article

pubs.acs.org/JPCC

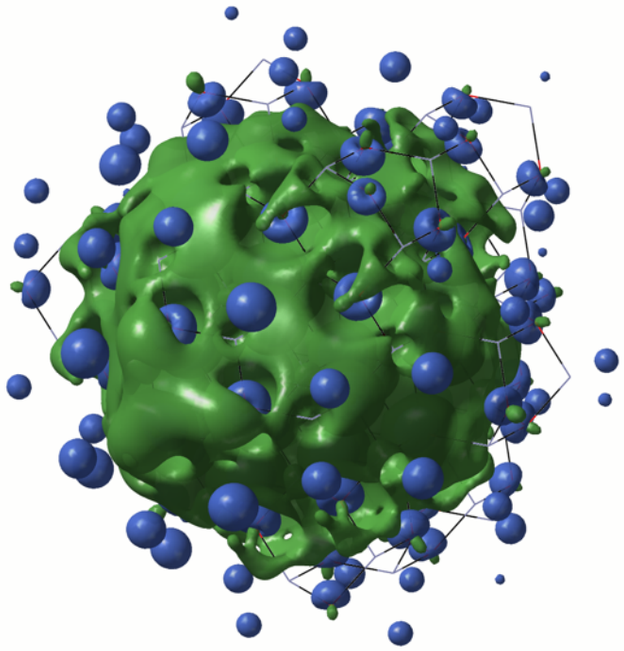
Theoretical Characterization of Conduction-Band Electrons in Photodoped and Aluminum-Doped Zinc Oxide (AZO) Quantum Dots

Joshua J. Goings, Alina M. Schimpf, Joseph W. May, Robert W. Johns, Daniel R. Gamelin,* and Xiaosong Li*

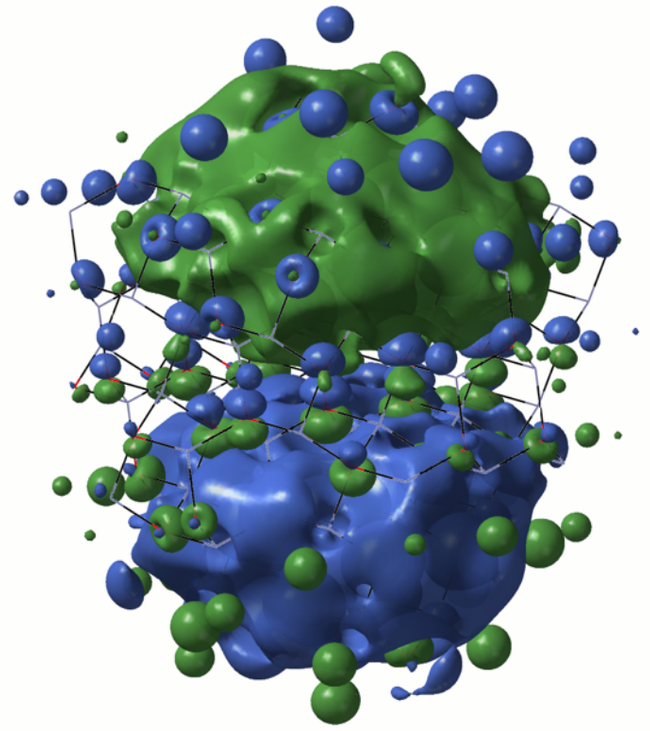
Department of Chemistry, University of Washington, Seattle, Washington 98195, United States



Give the quantum dots an extra electron by doping with aluminum…

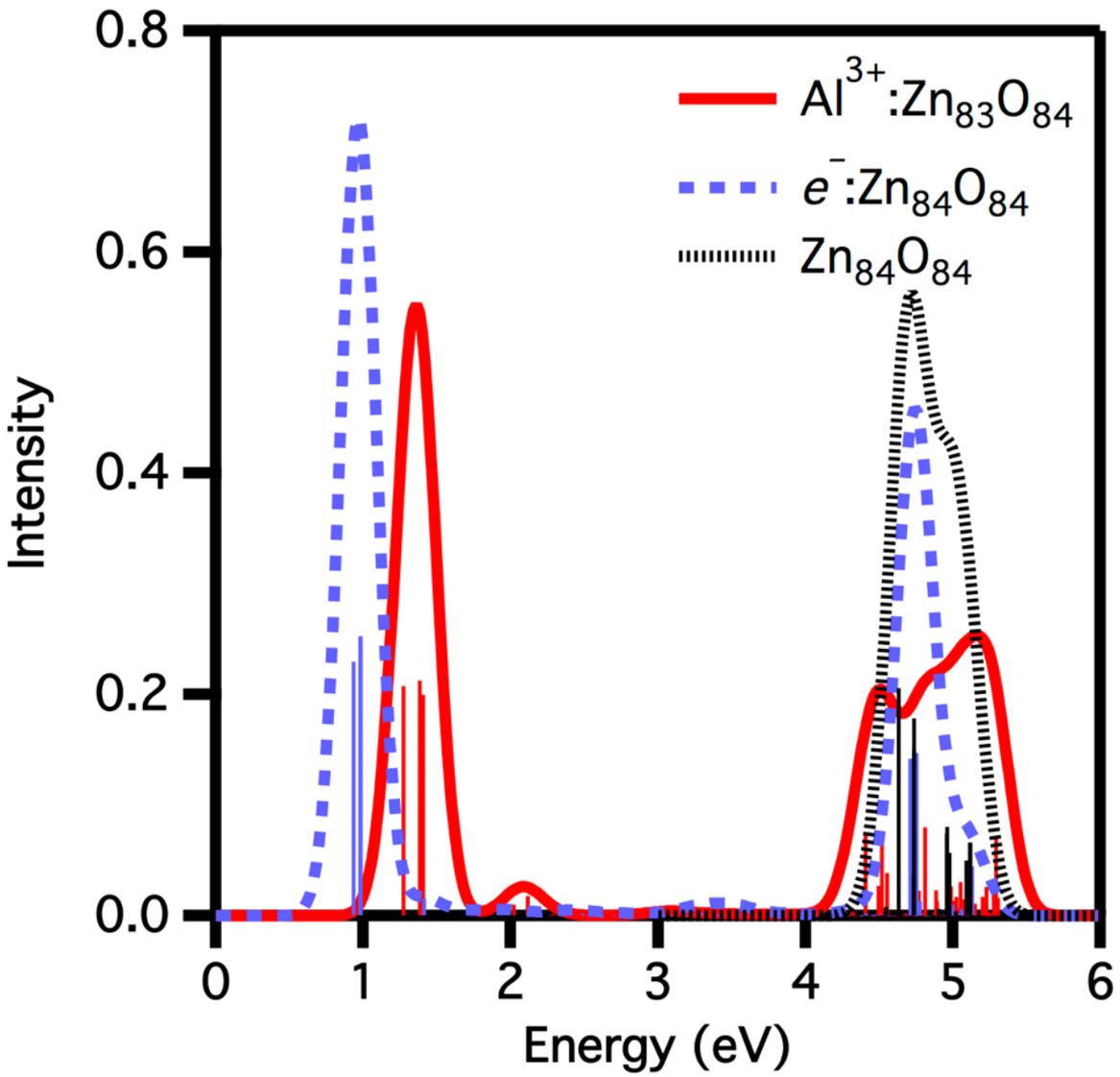


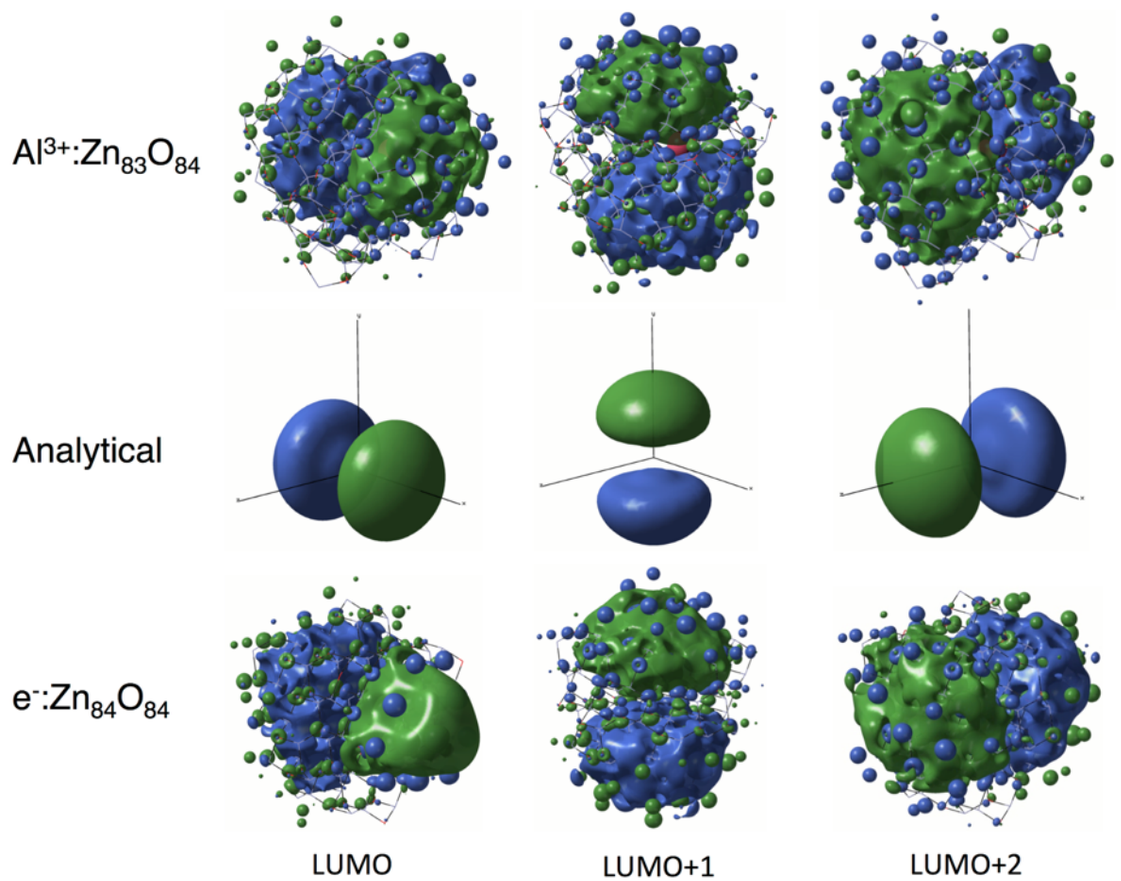
HOMO (s)



LUMO (p)

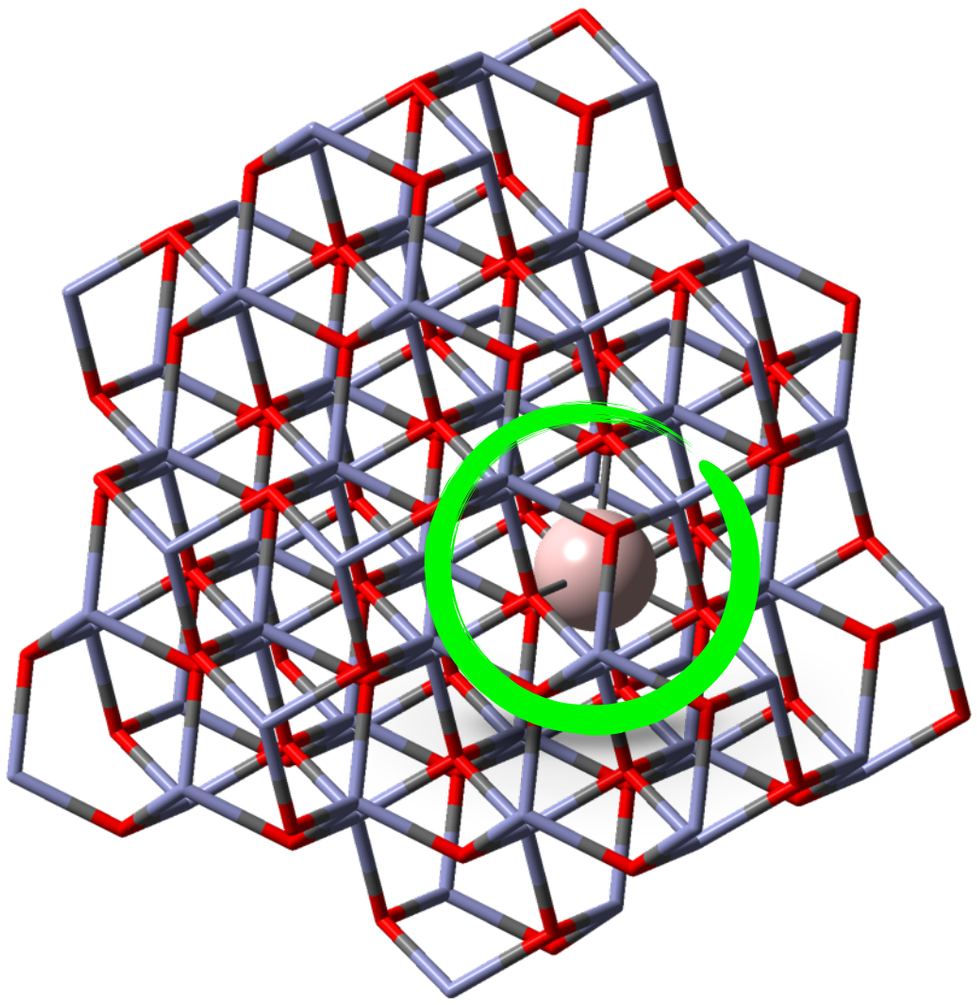
Quantum dot gets ‘atomic’ orbitals (“Super-orbitals”)


0.8
0.6
0.4
0.2
0.0
Intensity
0
1
2
3
4
5
6
Energy (eV)
$Al^{3+}:Zn_{83}O_{84}$
$e^-:Zn_{84}O_{84}$
$Zn_{84}O_{84}$


$Al^{3+}:Zn_{83}O_{84}$
Analytical
$e^-:Zn_{84}O_{84}$
LUMO
LUMO+1
LUMO+2

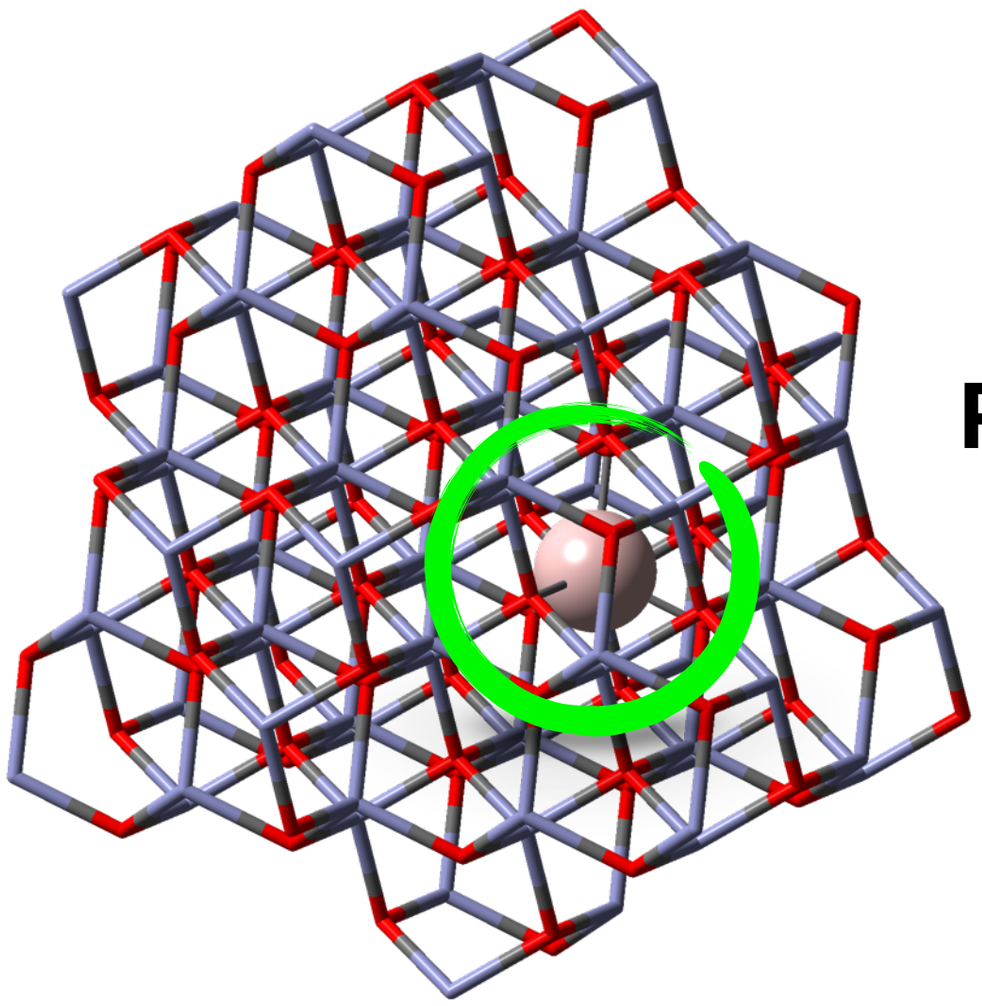
The “extra” electron carries a spin.
It *should* interact with magnetic centers.

We think it may make a good room-temperature magnet



The “extra” electron carries a spin.
It *should* interact with magnetic centers.

We think it may make a good room-temperature magnet



Part of the fun is seeing if it will!