

Putting a spin on time dependent electronic structure theory

**Joshua Goings
General Exam**

Thursday, May 14, 10:00am CHB 339

Thank you to General Exam Committee

Xiaosong Li (chair)

Jim Pfaendtner (GSR)

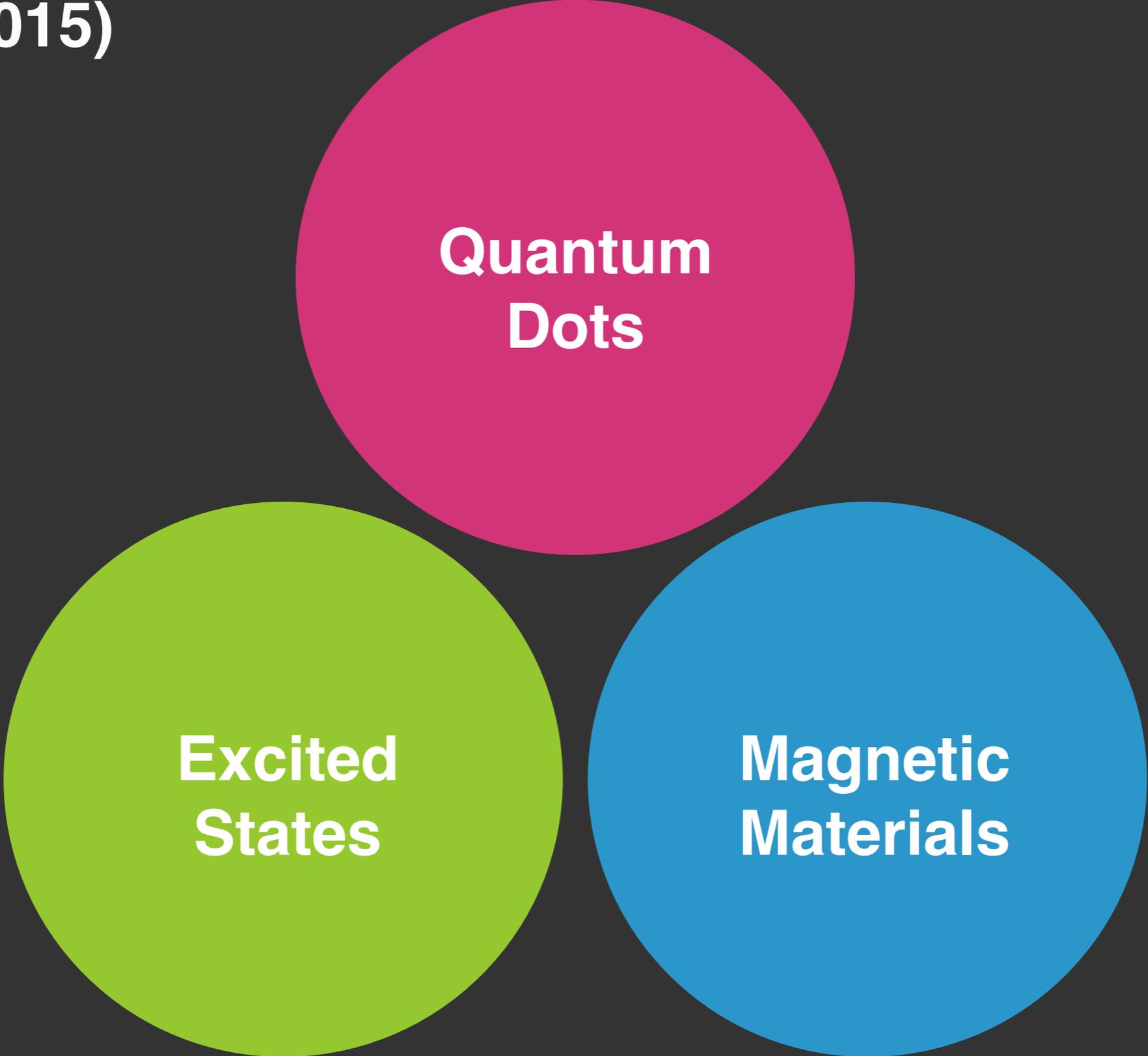
Matthew Bush

David Masiello

Stefan Stoll

How can we **predict** and **understand**
the **electronic** and **magnetic responses**
of **molecules** and **nano-materials**?

Research Directions (2014—2015)



**Quantum
Dots**

**Excited
States**

**Magnetic
Materials**

Research Directions (2014–2015)

Excited States

1. Goings, J. J., Caricato, M., Frisch, M. J., & Li, X. (2014). JCP, 141(16), 164116.

Quantum Dots

2. Goings, J. J., Schimpf, A. M., May, J. W., Johns, R. W., Gamelin, D. R., & Li, X. (2014). JPC C, 118(46), 26584.

Magnetic Materials

3. Ding, F., Goings, J. J., Frisch, M. J., & Li, X. (2014). JCP, 141(21), 214111.

4. Goings, J. J., Ding, F., Frisch, M. J., & Li, X. (2015). JCP, 142(15), 154109.

Other

5. Goings, J. J., Ohlsen, S. M., Blaisdell, K. M., & Schofield, D. P. (2014). JPC A, 118(35), 7411.

6. Goings, J. J., Ding, F., & Li, X. (2014). Proceedings of MEST 2012: Electronic Structure Methods with Applications to Experimental Chemistry, 68, 77.

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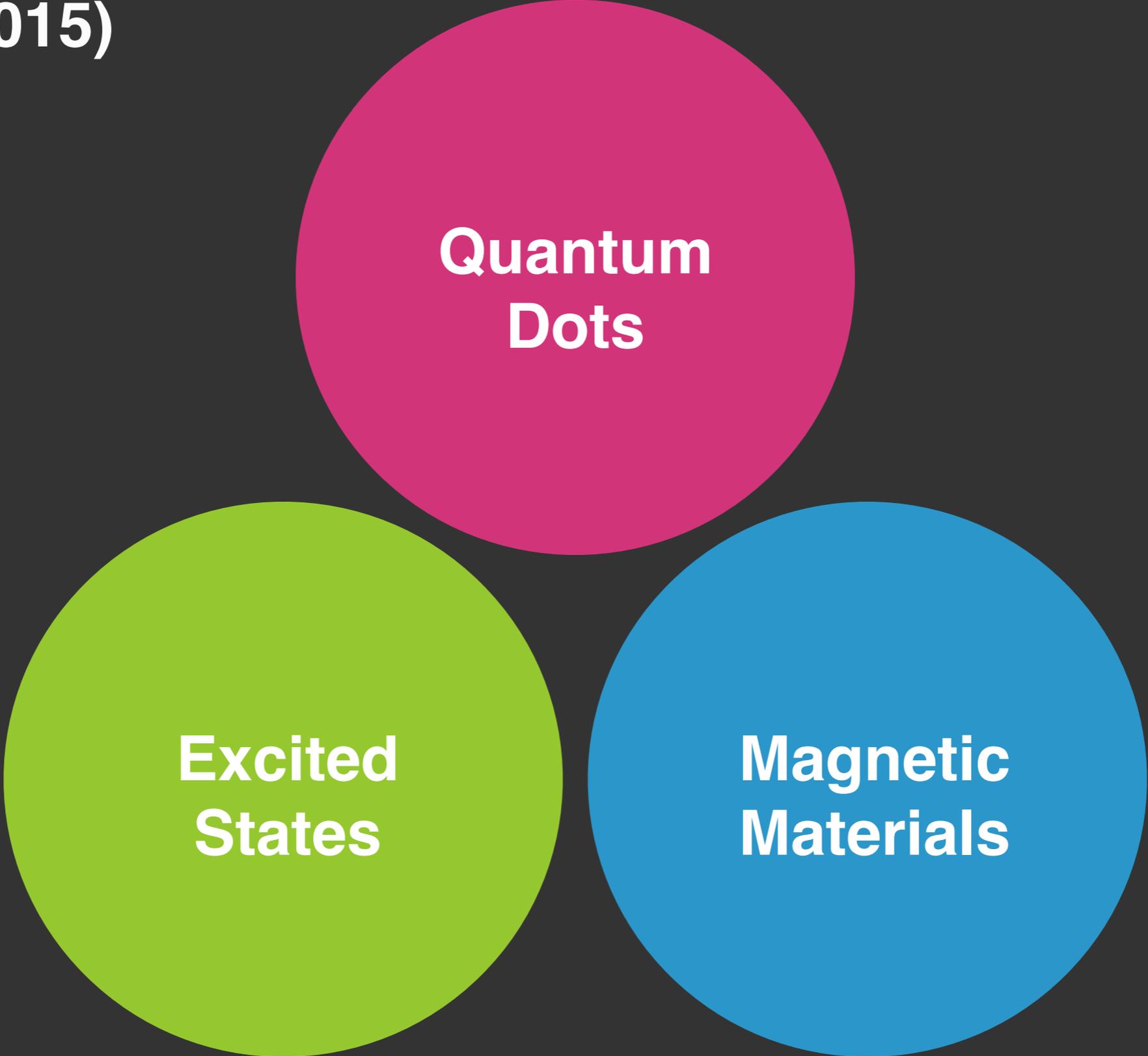
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Research Directions (2014—2015)

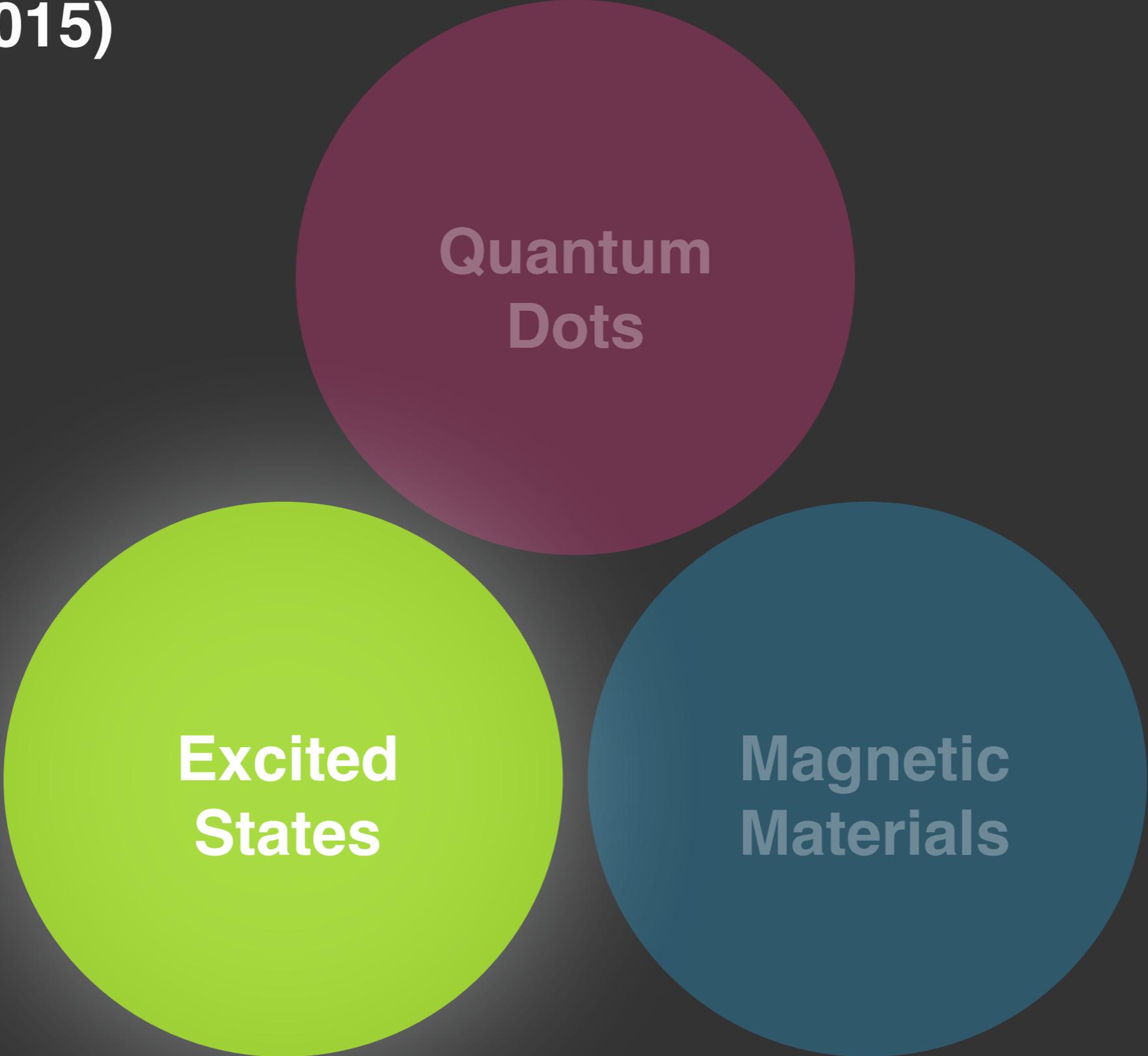


**Quantum
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Research Directions (2014—2015)



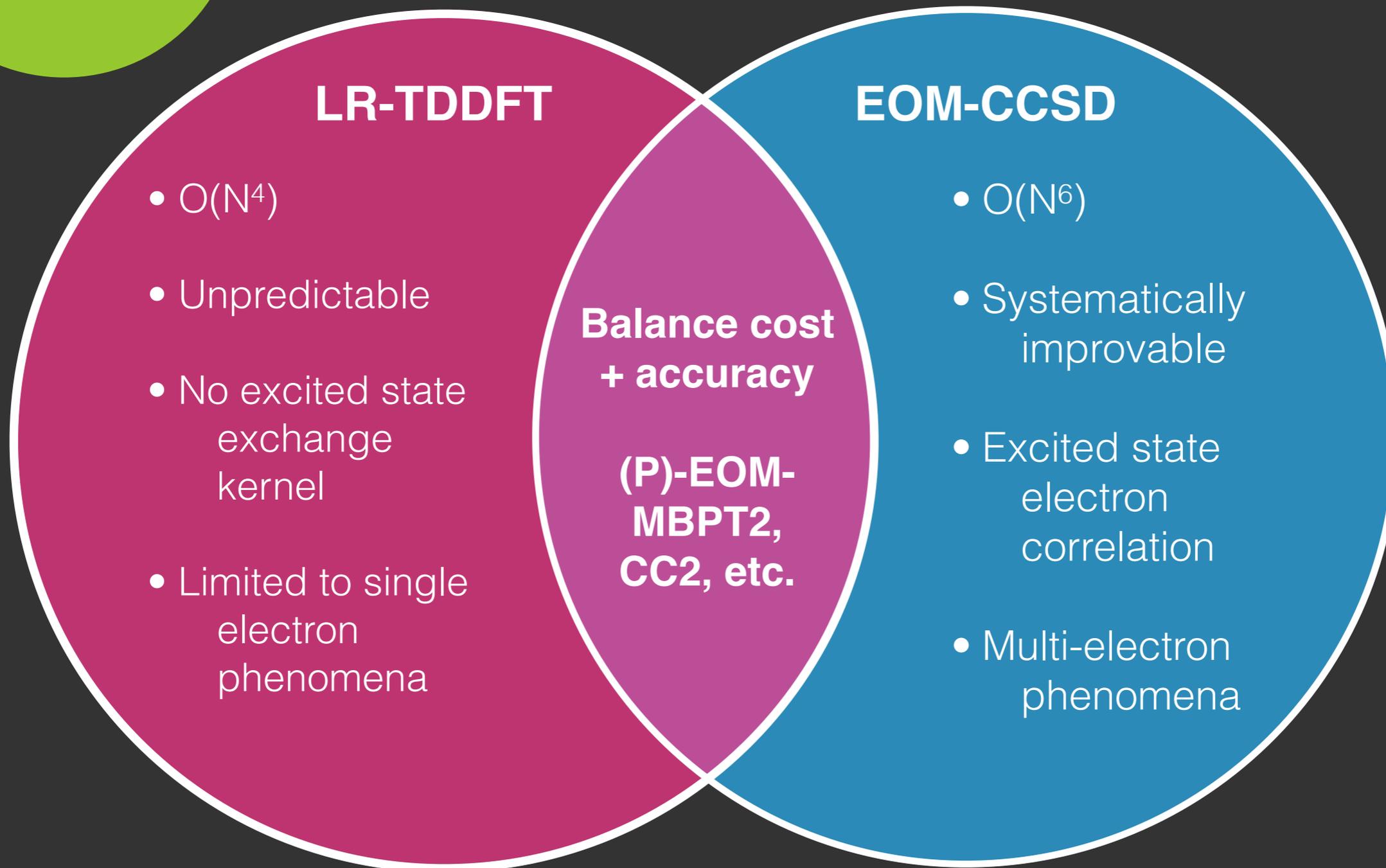
Quantum
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Excited States

Balancing Cost + Accuracy of Electronic Excited State Methods

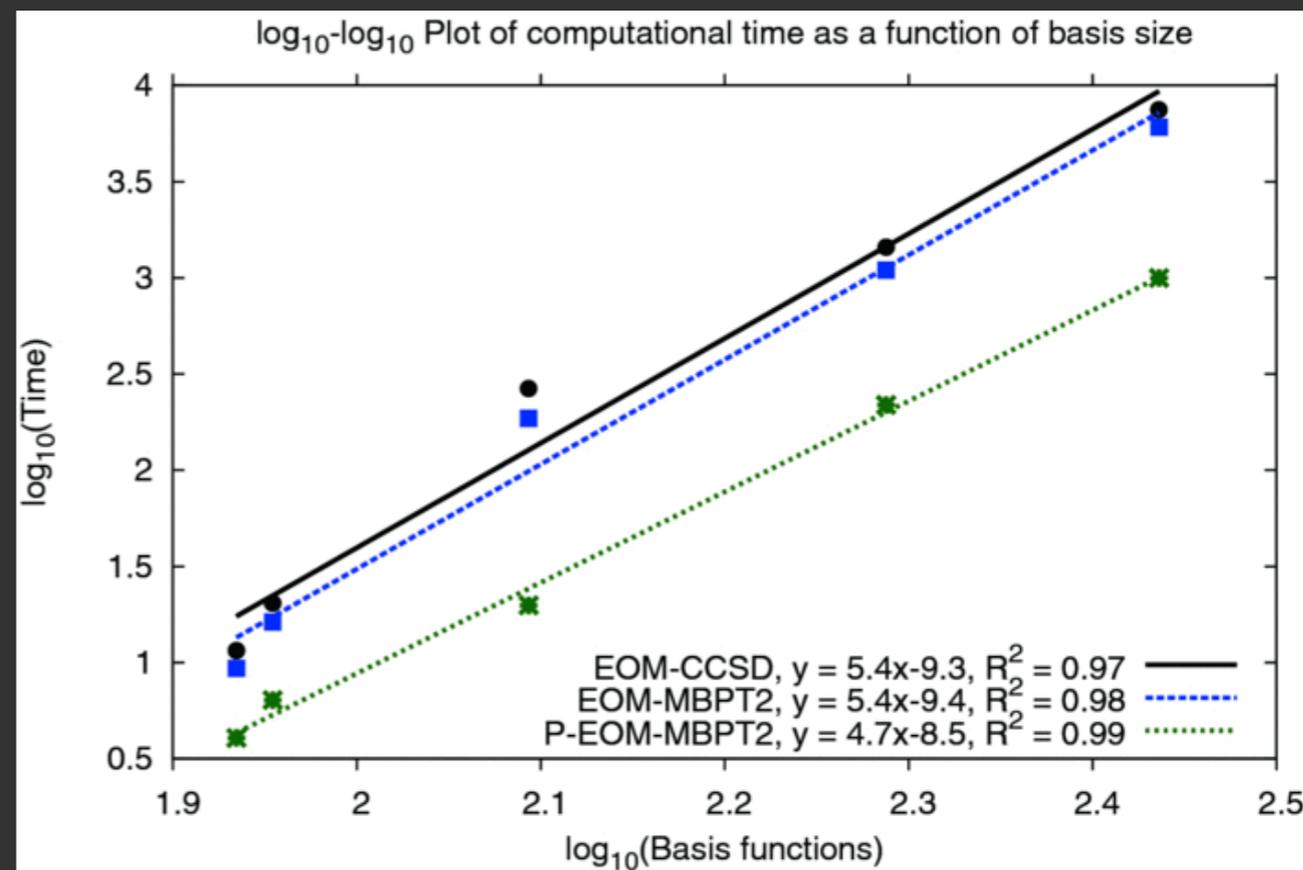


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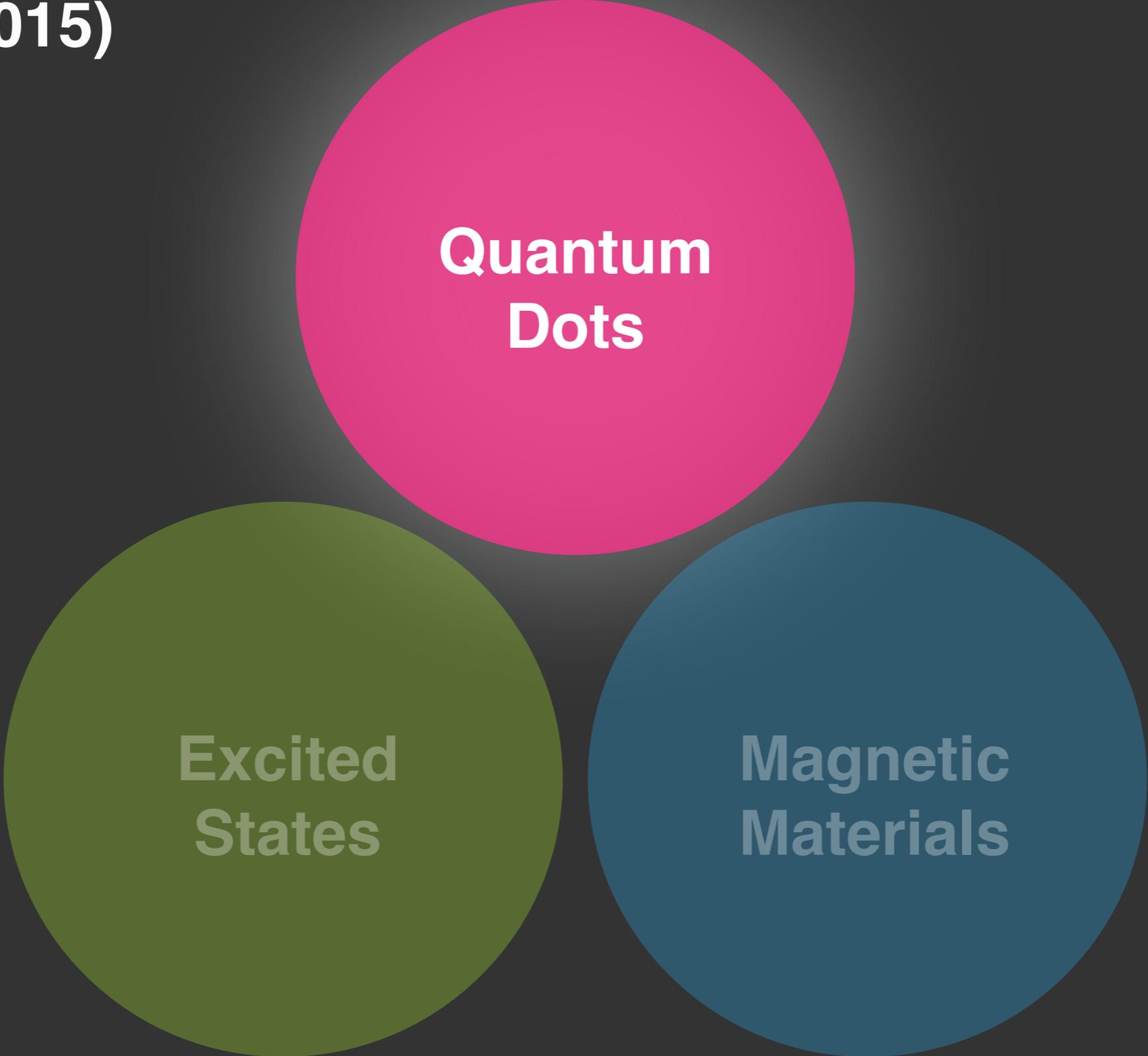
Excited States

Balancing Cost + Accuracy of Electronic Excited State Methods

- Applied perturbation theory to coupled cluster (CC) equations
- Reduced computational time of CC equations by an order of magnitude
- Accuracy generally outperforms density functional theory



Research Directions (2014—2015)



**Quantum
Dots**

**Excited
States**

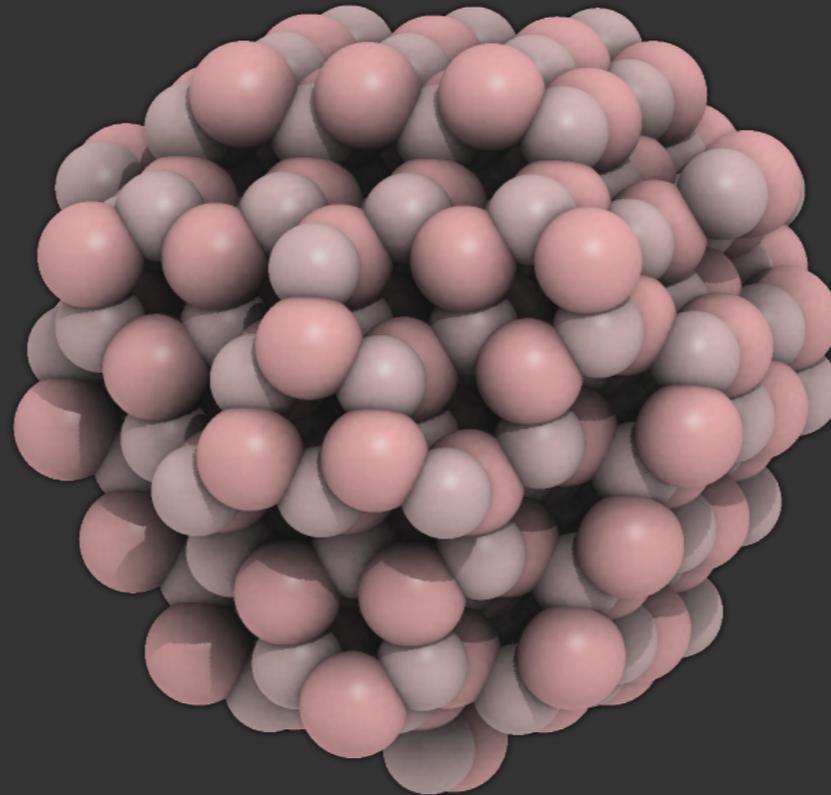
**Magnetic
Materials**

**Quantum
Dots**

**Understanding Dopant Influence
on Excitations in n-type Quantum Dots**

$\text{Al}^{3+}:\text{ZnO}$

**extra conduction
band electron
tough to oxidize**



$e^{-}:\text{ZnO}$

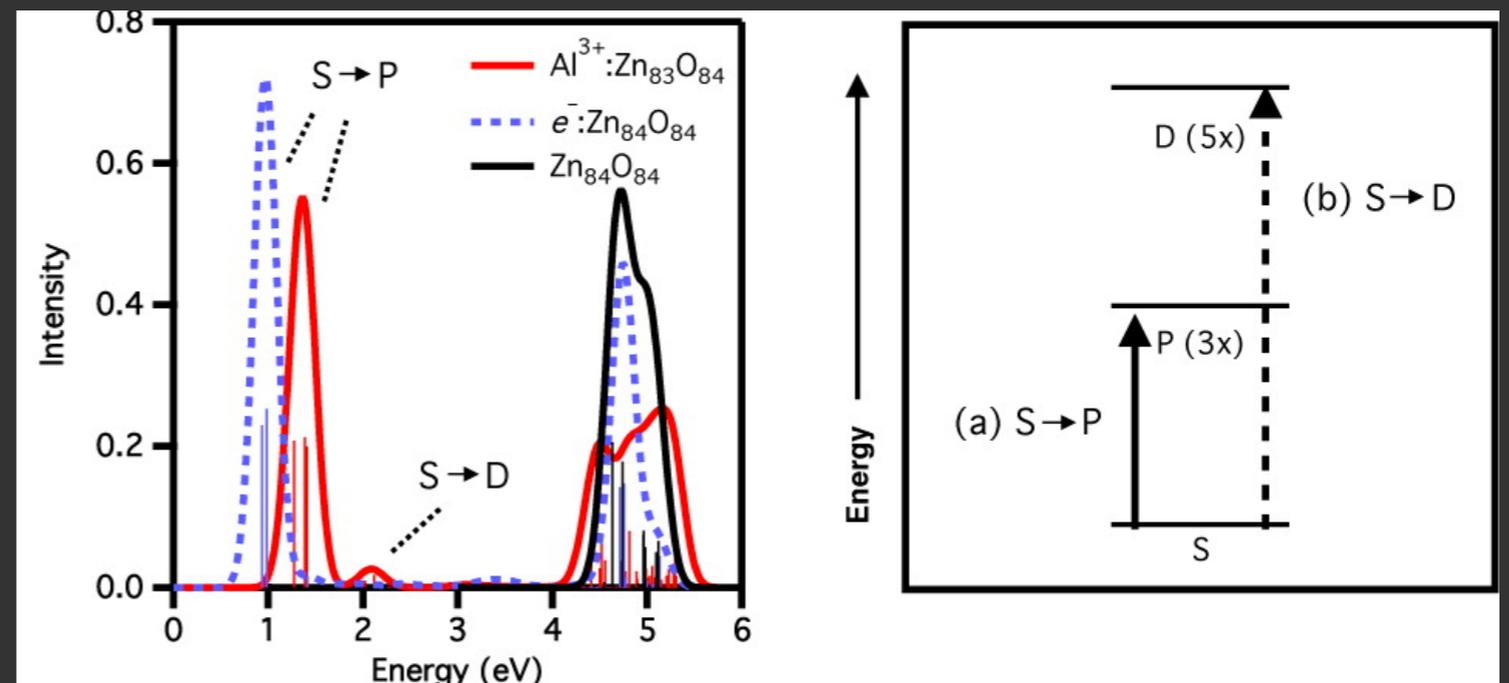
**extra conduction
band electron
easy to oxidize**

Goings, J. J., Schimpf, A. M., May, J. W., Johns, R. W., Gamelin, D. R., & Li, X. (2014). Theoretical Characterization of Conduction-Band Electrons in Photodoped and Aluminum-Doped Zinc Oxide (AZO) Quantum Dots. JPC C, 118(46), 26584-26590.

Quantum Dots

Understanding Dopant Influence on Excitations in n-type Quantum Dots

- n-type ZnO QDs
- UV-Vis spectra from aluminum doped and photodoped QDs
- Rationalized theoretical/experimental results in terms of particle-in-a-sphere

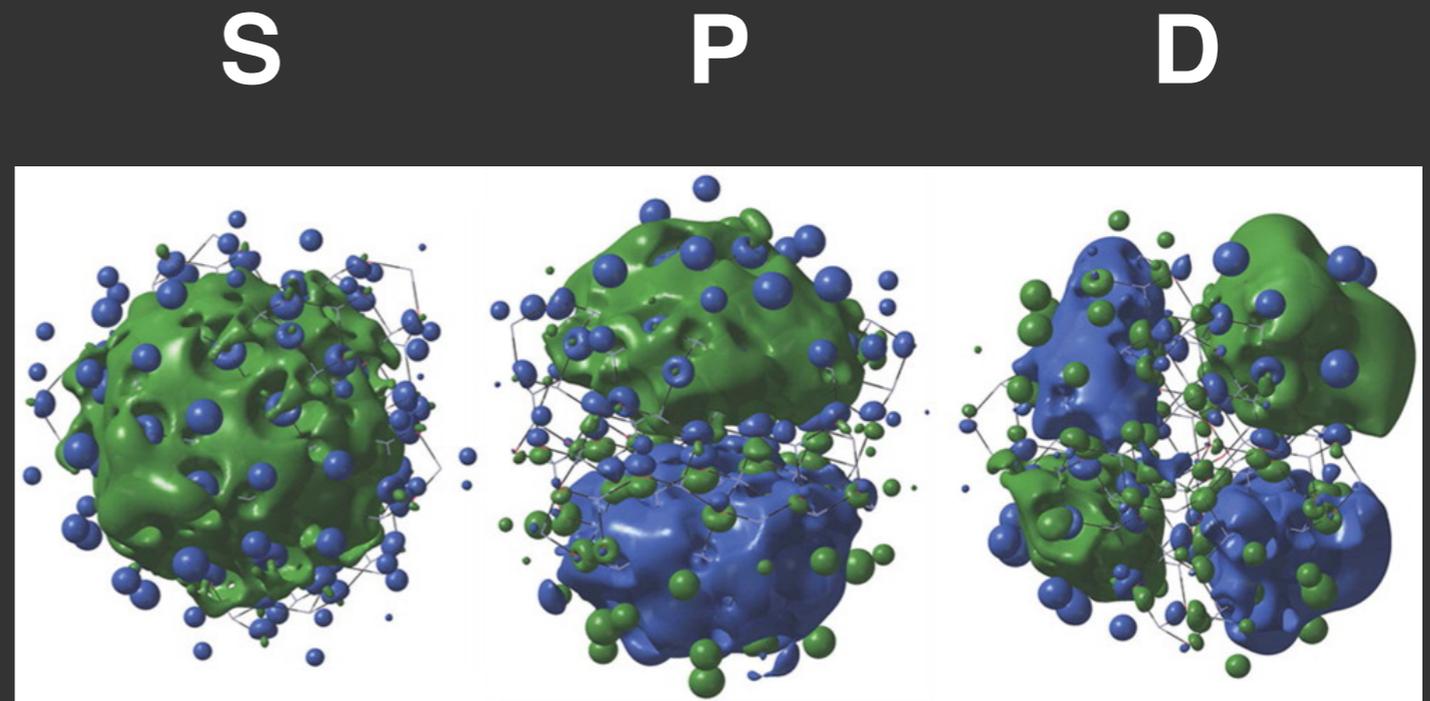


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Quantum Dots

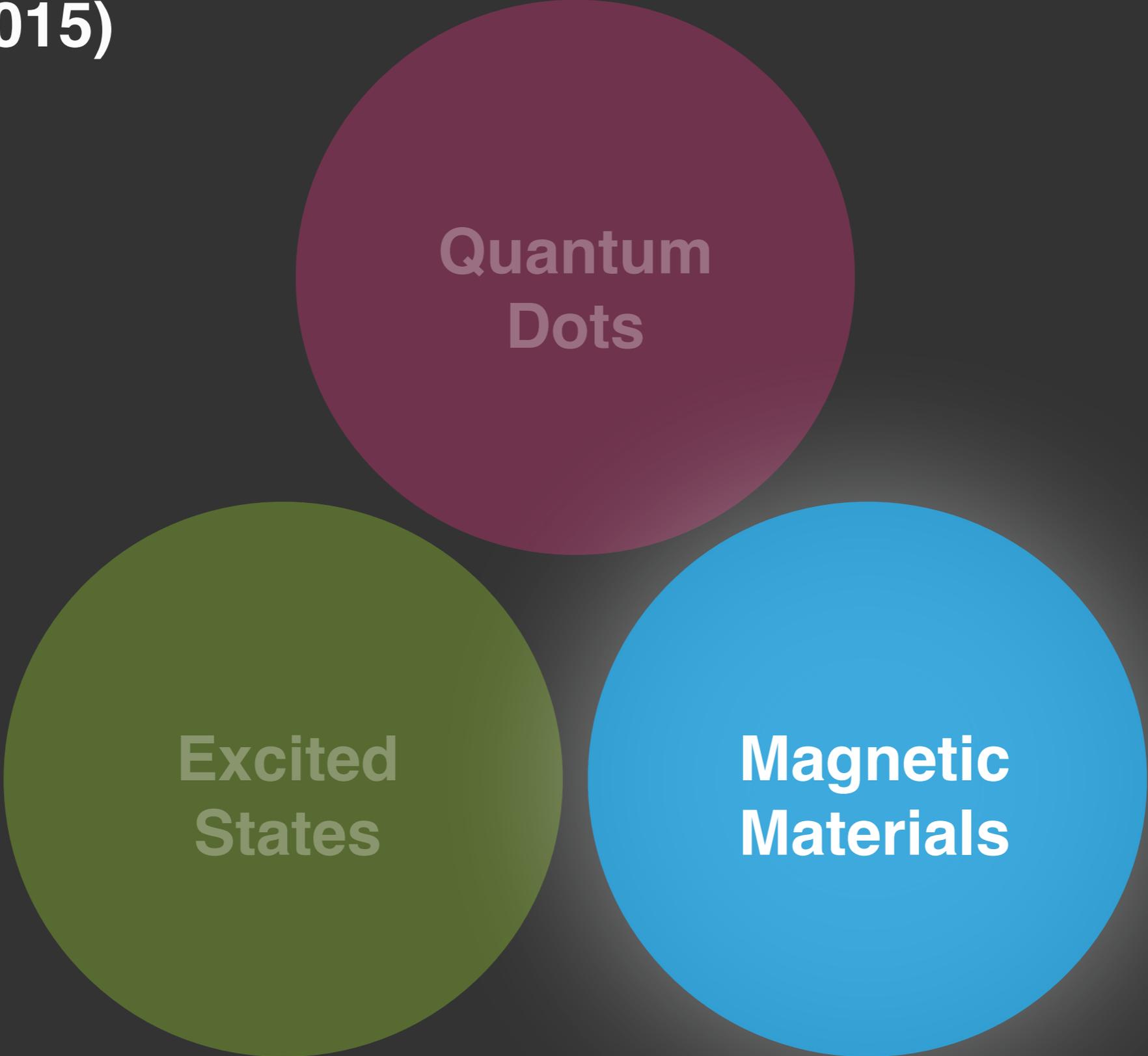
Understanding Dopant Influence on Excitations in n-type Quantum Dots

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Research Directions (2014—2015)



Quantum
Dots

Excited
States

Magnetic
Materials

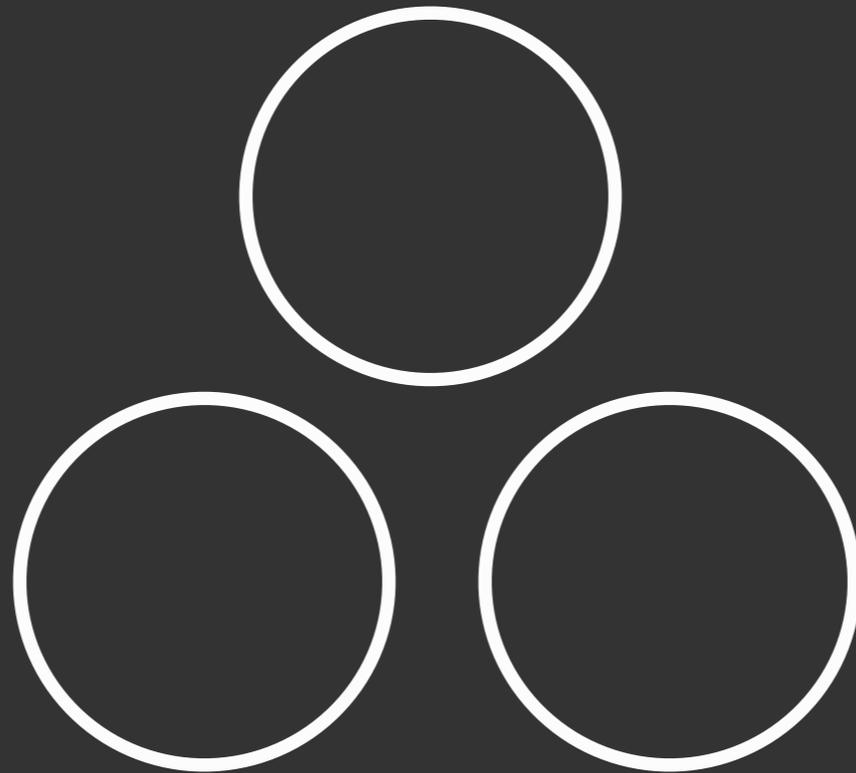


Magnetic Materials

Exploring spin-frustrated molecules with the generalized Hartree Fock (GHF) method

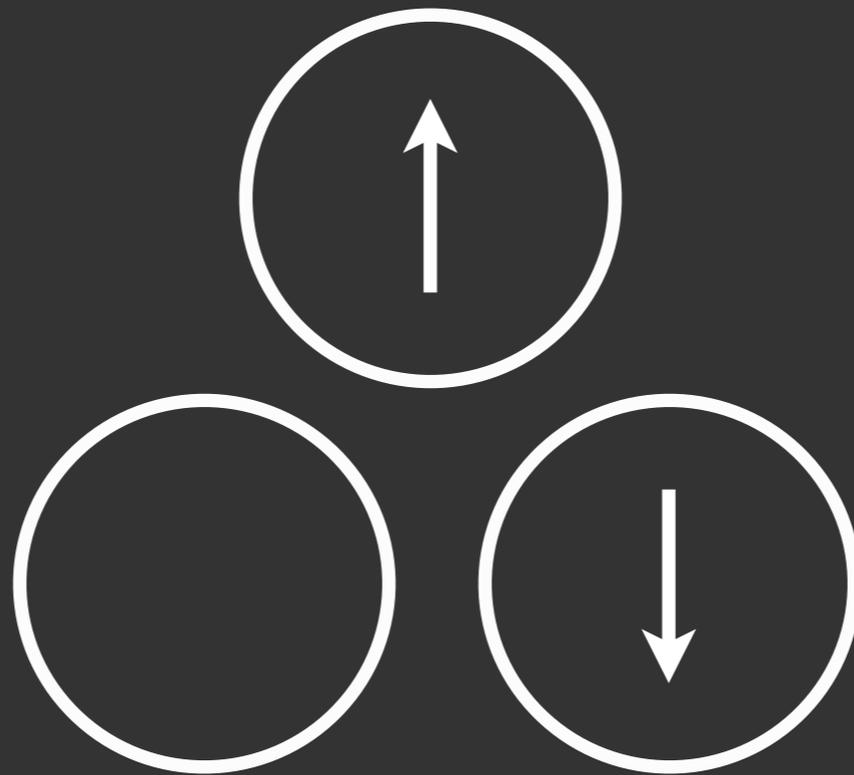
Goings, J. J., Ding, F., Frisch, M. J., & Li, X. (2015). Stability of the complex generalized Hartree-Fock equations. The Journal of chemical physics, 142(15), 154109.

Magnetic Materials



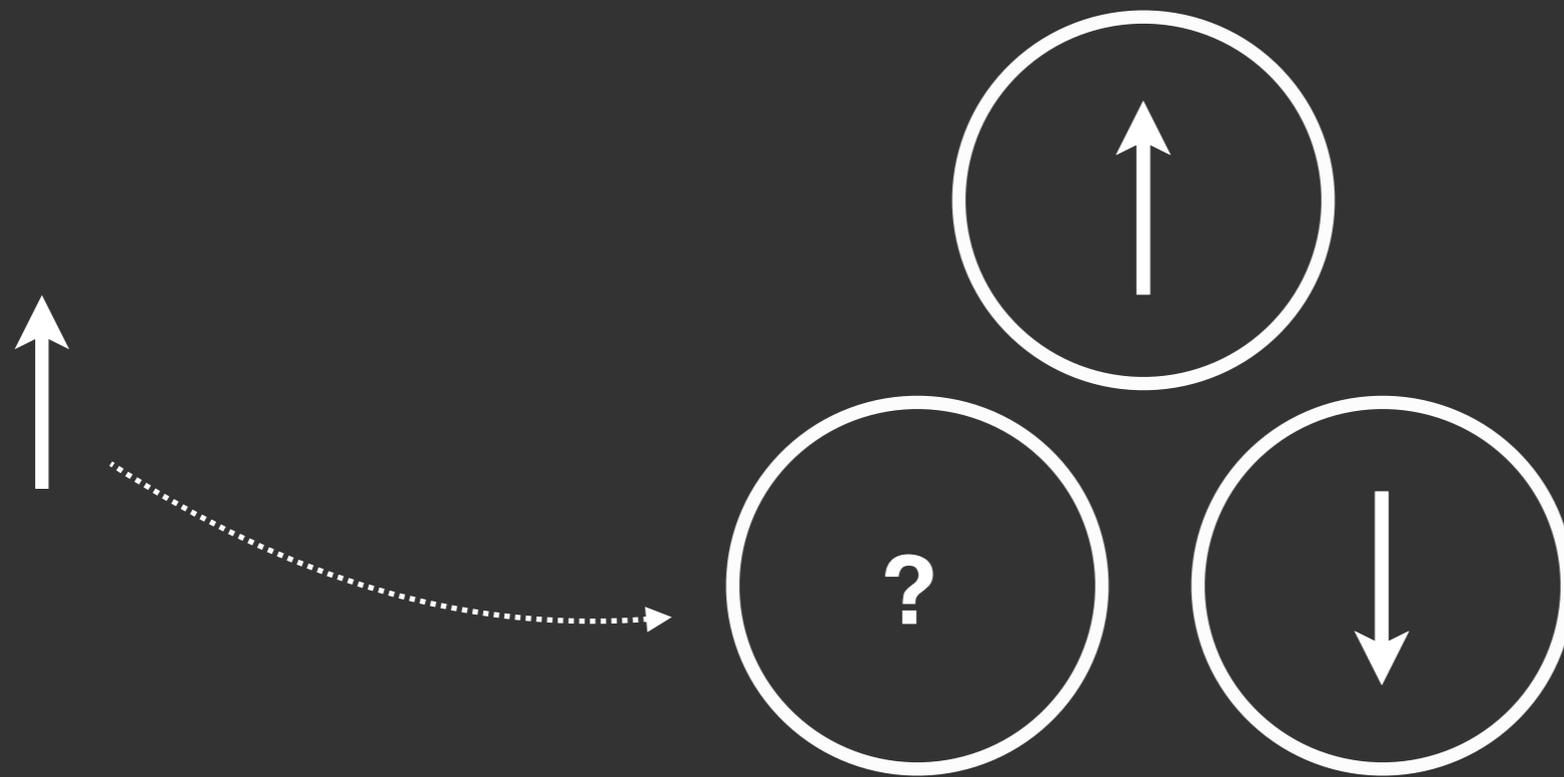
Take a three site lattice

Magnetic Materials



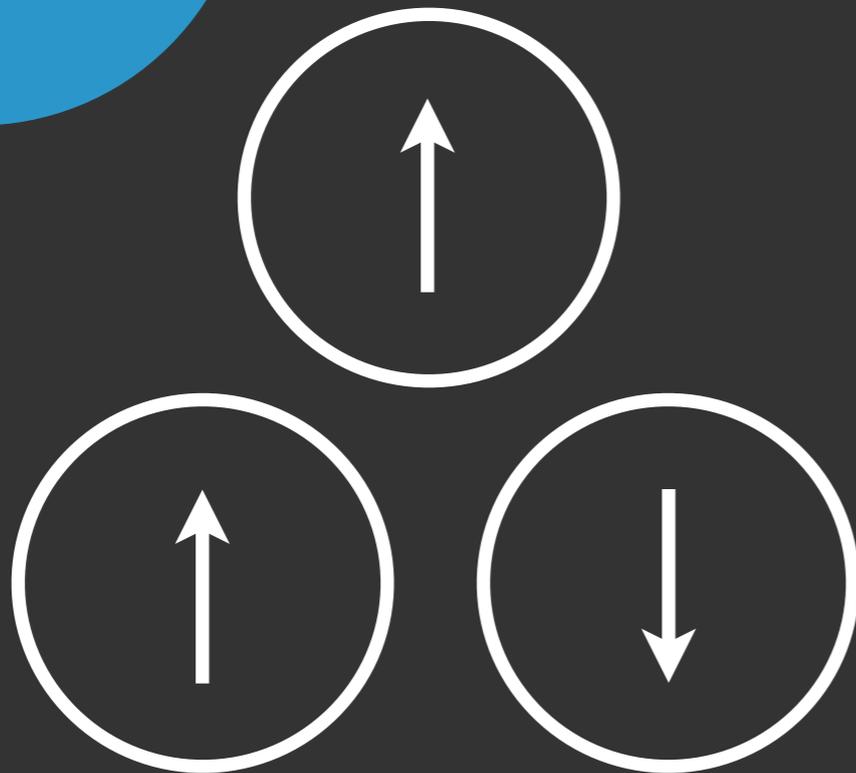
**Now add two electrons
(assume antiferromagnetism is favored)**

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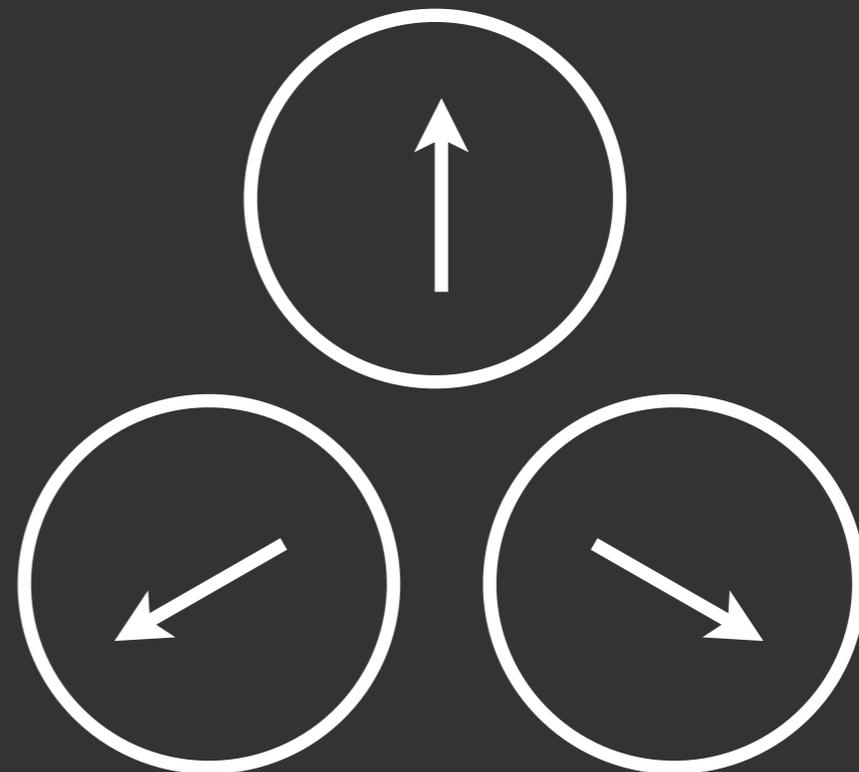


**Now add the third electron.
No orientation simultaneously favors
all anti-ferromagnetic interactions.**

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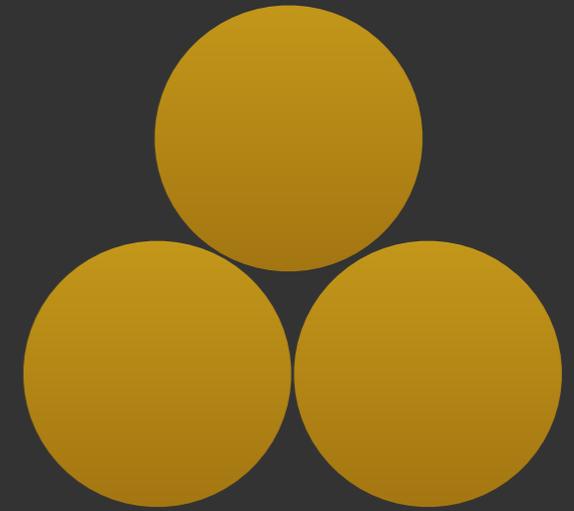
Collinear



Non-collinear

**Conventional methods force you to pick a collinear configuration.
Few methods can give you non-collinear state.**

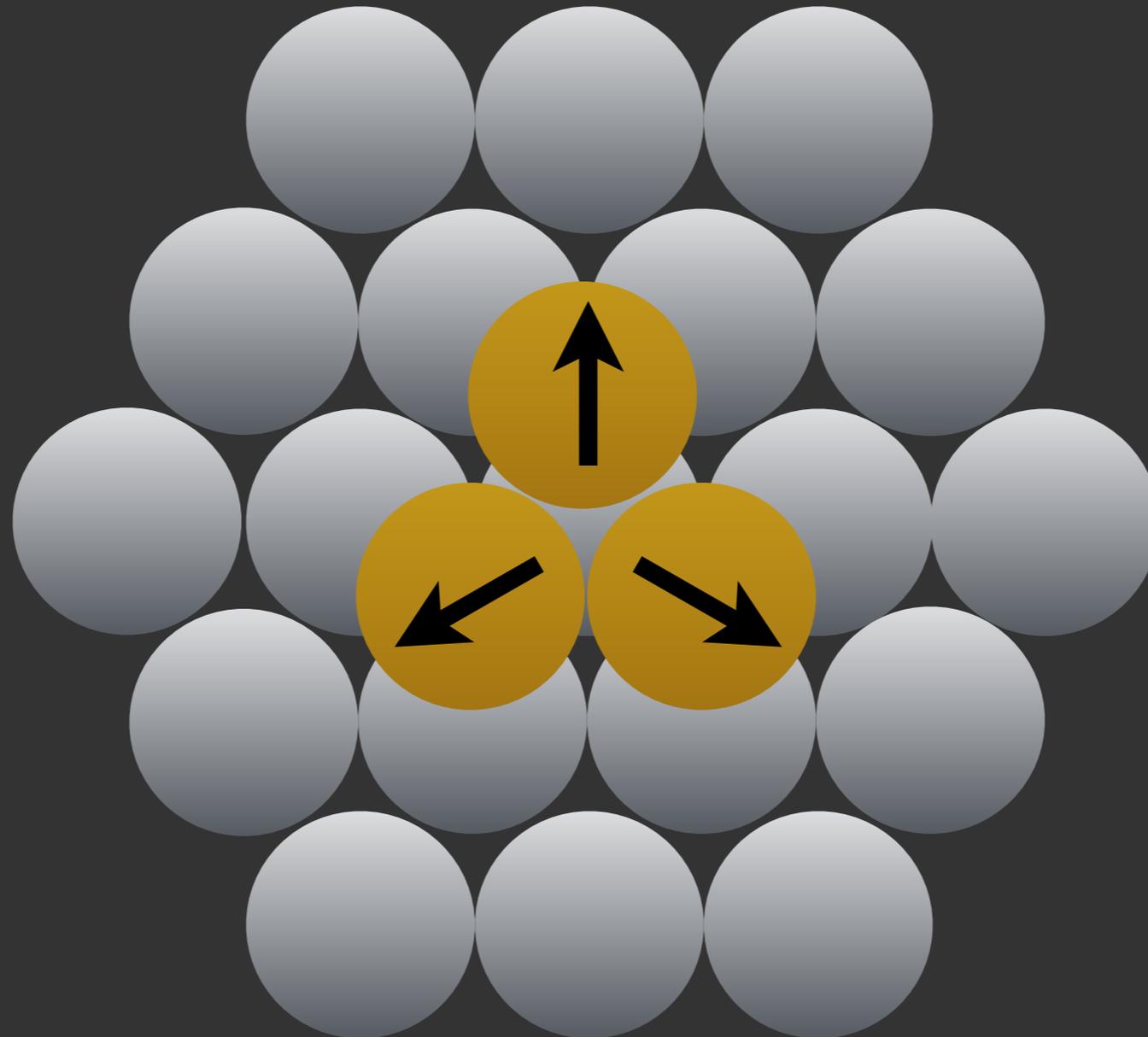
Magnetic Materials



via STM

Ag fcc(111) surface

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Can we describe this with Hartree Fock (HF)?

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Hartree-Fock (HF): minimize the energy of a single Slater Determinant

$$E \leq \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

The solution is **variational**;
an upper bound to the exact energy.

This is an independent particle model (IPM).
It is the quantitative basis of molecular orbital theory.

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Types of Hartree-Fock

	Restricted (RHF)	Unrestricted (UHF)	General (GHF)
orbital	spatial	$\phi(\mathbf{r})\alpha(\omega); \phi(\mathbf{r})\beta(\omega)$	$\phi(\mathbf{r})\alpha(\omega) + \phi(\mathbf{r})\beta(\omega)$
\hat{S}^2	yes	no	no
\hat{S}_z	yes	yes	no
system	closed shell	open shell	spin frustrated



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Generalized Hartree Fock (GHF)

- GHF allows you to change spin smoothly



Magnetic Materials

Generalized Hartree Fock (GHF)

- GHF allows you to change spin smoothly
- Lowest energy HF solution possible



Magnetic Materials

Generalized Hartree Fock (GHF)

- GHF allows you to change spin smoothly
- Lowest energy HF solution possible
- Largely insensitive to guess multiplicity



Magnetic Materials

Generalized Hartree Fock (GHF)

- GHF allows you to change spin smoothly
- Lowest energy HF solution possible
- Largely insensitive to guess multiplicity
- Only HF method to treat spin frustration



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Problem:

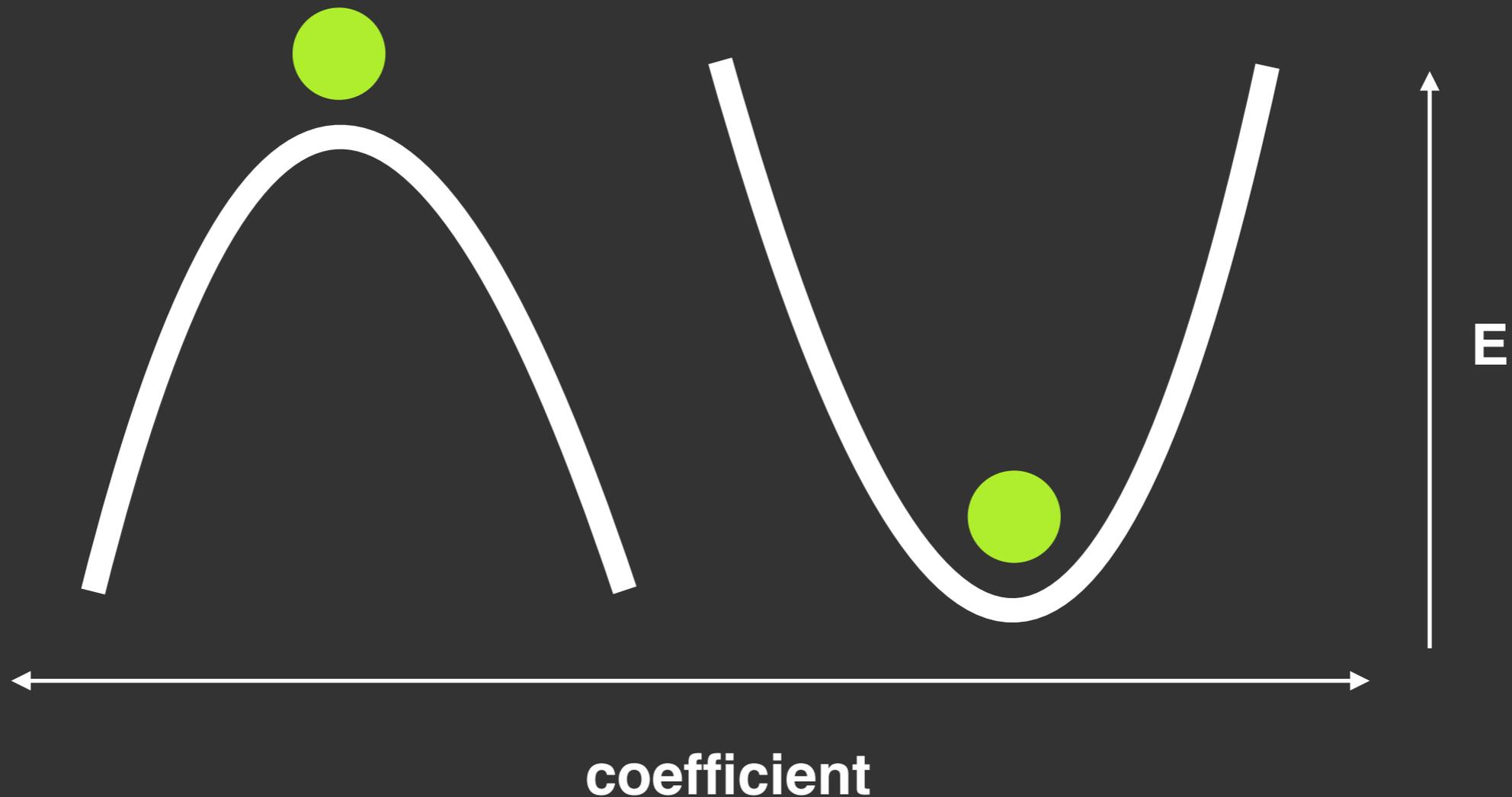
Just because you *can* get the lowest energy solution, doesn't mean you will.

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How to obtain GHF local minima?

unstable

stable



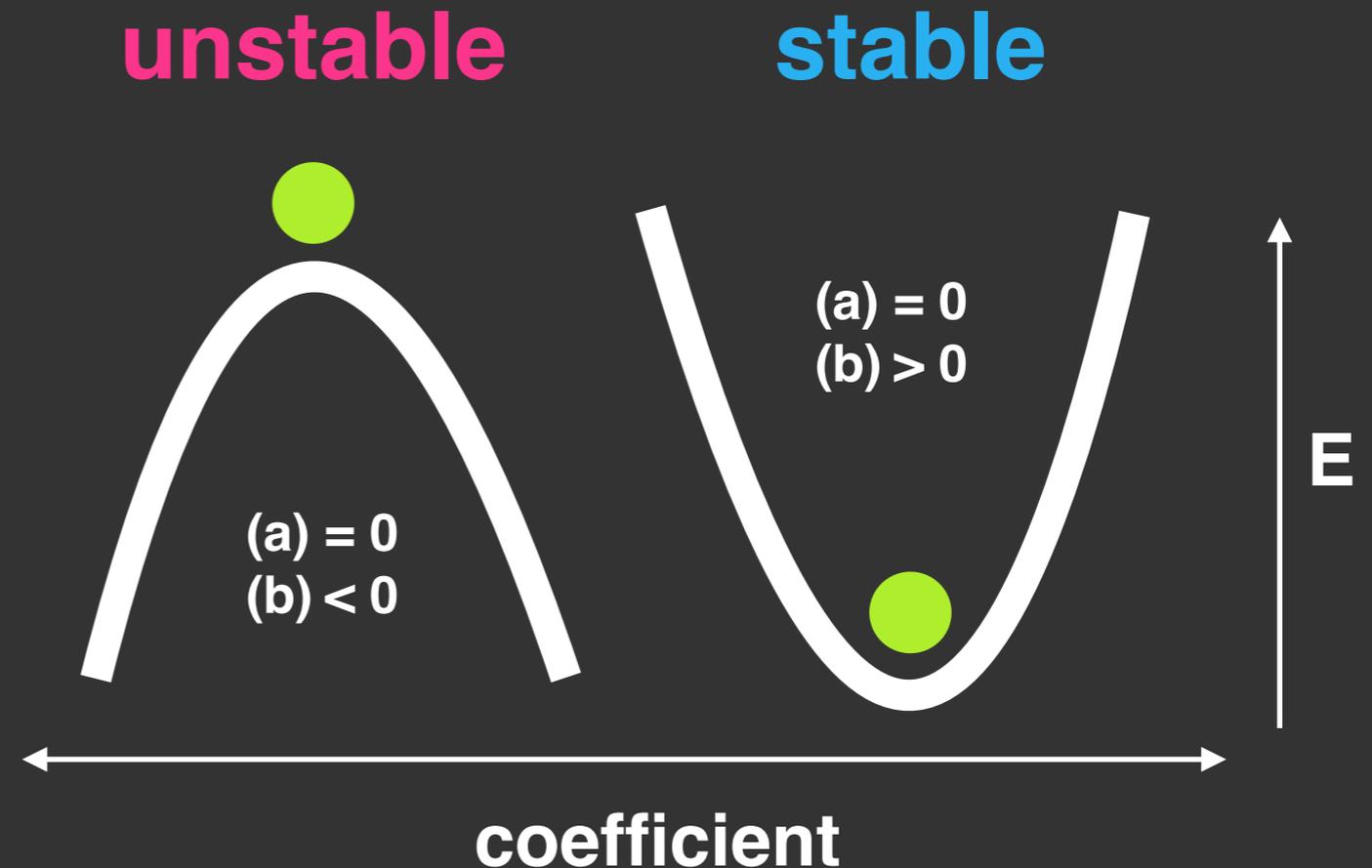
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How to obtain GHF local minima?

We want stable electronic solutions to the GHF model.

Local minima:

- (a) First variation equal to zero
- (b) Second variation greater than zero



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Differentiate E with respect to wave function coefficients

$$\frac{\partial E}{\partial q_i^a} = \begin{pmatrix} \langle \phi_i^a | \hat{H} | 0 \rangle \\ \langle 0 | \hat{H} | \phi_i^a \rangle \end{pmatrix} = \begin{pmatrix} f_{ai} \\ f_{ia} \end{pmatrix}$$

This must **equal zero**, known as **Brillouin's theorem**.

(Trivially satisfied as long as HF converges to *something*)

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Second derivative of energy with respect to wave function coefficients

$$\frac{\partial^2 E}{\partial q_i^a \partial q_j^b} = \begin{pmatrix} \langle \phi_i^a | \hat{H} | \phi_j^b \rangle & \langle \phi_{ij}^{ab} | \hat{H} | 0 \rangle \\ \langle 0 | \hat{H} | \phi_{ij}^{ab} \rangle & \langle \phi_j^b | \hat{H} | \phi_i^a \rangle \end{pmatrix}$$

The Hessian, which must be **positive definite** if our solution is to be a minimum.

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$$\text{Hessian} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}$$

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ia,jb} + \langle aj || ib \rangle, \quad B_{ia,jb} = \langle ab || ij \rangle$$

Compute eigenpairs of Hessian matrix.

If all eigenvalues are **positive**, we are at minima

If any eigenvalues are **negative**,
lower energy solution exists.

What if we run into instability?

Steepest Descent Method

- 1. Take the most **negative eigenvalue** and eigenvector**
- 2. **Step wave function** in direction of eigenvector**
- 3. **Re-optimize** GHF solution.**

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Full details and working equations in the paper!



i, j, k, l refer to occupied orbitals, a, b, c, d refer to virtual orbitals, and p, q, r, s refer to any orbital. We also adopt Einstein summation, where the summation over common indices is implied. We begin with the Thouless representation of a single determinant. Thouless showed that any single Slater determinant can be transformed into another non-orthogonal single determinant via the transformation²¹

$$|\tilde{\phi}\rangle = e^{\hat{T}_1}|0\rangle, \quad (1)$$

where \hat{T}_1 is a single particle excitation operator

$$\hat{T}_1 = \sum_{ia} t_i^a \{a_i^\dagger a_i\}. \quad (2)$$

In order to ensure that the Thouless transformation is enacted by a unitary transformation, we insist on the condition that \hat{T}_1 is skew-Hermitian, i.e.,

$$\hat{T}_1 = -\hat{T}_1^\dagger \quad (3)$$

which implies that

$$t_i^a = -t_a^{i*}. \quad (4)$$

Consider the connected energy functional

$$E = \langle \tilde{\phi} | \hat{H}_N | \tilde{\phi} \rangle_c = \langle 0 | e^{\hat{T}_1} \hat{H}_N e^{\hat{T}_1} | 0 \rangle_c, \quad (5)$$

where

$$\begin{aligned} \hat{H}_N &= \hat{H} - \langle 0 | \hat{H} | 0 \rangle = \hat{F}_N + \hat{V}_N = f_{pq} \{a_p^\dagger a_q\} \\ &+ \frac{1}{4} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\} \end{aligned} \quad (6)$$

and \hat{H} is our Hamiltonian. \hat{F}_N and \hat{V}_N are the one- and two-body operators; the elements f_{pq} are the elements of the Fock matrix and $\langle pq || rs \rangle$ are the antisymmetrized two electron integrals. For this parameterized functional, expanding through second order in \hat{T}_1 gives

$$\begin{aligned} E &= \langle 0 | \hat{H}_N + \hat{T}_1^\dagger \hat{H}_N + \hat{H}_N \hat{T}_1 + \hat{T}_1^\dagger \hat{H}_N \hat{T}_1 + \frac{1}{2} \hat{T}_1^\dagger \hat{T}_1^\dagger \hat{H}_N \\ &+ \frac{1}{2} \hat{H}_N \hat{T}_1 \hat{T}_1 | 0 \rangle_c. \end{aligned} \quad (7)$$

Taking the first variation of E with respect to the Thouless parameters $q_i^a = (t_i^a, t_i^{a*})$ about $\hat{T}_1 = \hat{T}_1^\dagger = 0$, gives

$$\frac{\partial E}{\partial q_i^a} = \left(\begin{array}{c} \langle \phi_i^a | \hat{H}_N | 0 \rangle_c \\ \langle 0 | \hat{H}_N | \phi_i^a \rangle_c \end{array} \right) = \left(\begin{array}{c} f_{ai} \\ f_{ia} \end{array} \right) \quad (8)$$

which must equal zero if the energy functional is minimized. Thus, $f_{ia} = 0$ which are the off-diagonal elements of the Fock matrix, which is Brillouin's theorem. Taking the second variation of E with respect to the Thouless parameters yields

$$\frac{\partial^2 E}{\partial q_i^a \partial q_j^b} = \left(\begin{array}{cc} \langle \phi_i^a | \hat{H}_N | \phi_j^b \rangle_c & \langle \phi_{ij}^{ab} | \hat{H}_N | 0 \rangle_c \\ \langle 0 | \hat{H}_N | \phi_{ij}^{ab} \rangle_c & \langle \phi_j^b | \hat{H}_N | \phi_i^a \rangle_c \end{array} \right). \quad (9)$$

For the Hartree-Fock equations to be stable, the second variation must be positive semidefinite, i.e., $\delta^{(2)}E \geq 0$. Putting the second variation in matrix form, we obtain the Hessian

$$\left(\begin{array}{cc} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{array} \right), \quad (10)$$

where

$$A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ia,jb} + \langle aj || ib \rangle, \quad B_{ia,jb} = \langle ab || ij \rangle. \quad (11)$$

For the complex GHF equations, the orbital energies will be real as they are the eigenvalues of a Hermitian matrix. The antisymmetrized two-electron integrals, however, will be complex. Thus, in the complex GHF case, $\mathbf{A} \neq \mathbf{A}^*$ and $\mathbf{B} \neq \mathbf{B}^*$. At any stationary solution to the Hartree-Fock equations, the above Hessian may be constructed and diagonalized. Strictly negative eigenvalues indicate an instability, and the corresponding eigenvector indicates the direction in which the Hartree-Fock energy will decrease. This can be accomplished by taking the eigenvector corresponding to the lowest eigenvalue (steepest descent) and constructing a complex-valued $(2N \times 2N)$ mixing matrix \mathbf{K} , where N is the number of basis functions,¹

$$\mathbf{K} = \left(\begin{array}{cc} \mathbf{0} & -\mathbf{J}^\dagger \\ \mathbf{J} & \mathbf{0} \end{array} \right), \quad (12)$$

where \mathbf{J} is the $(O \times V)$ eigenvector corresponding to the lowest eigenvalue. This mixing matrix is exponentiated to give the unitary rotation matrix that transforms the old set of MO coefficients \mathbf{C} to a new set of rotated MO coefficients \mathbf{C}' ,

$$\mathbf{C}' = \mathbf{C} e^{-s\mathbf{K}}, \quad (13)$$

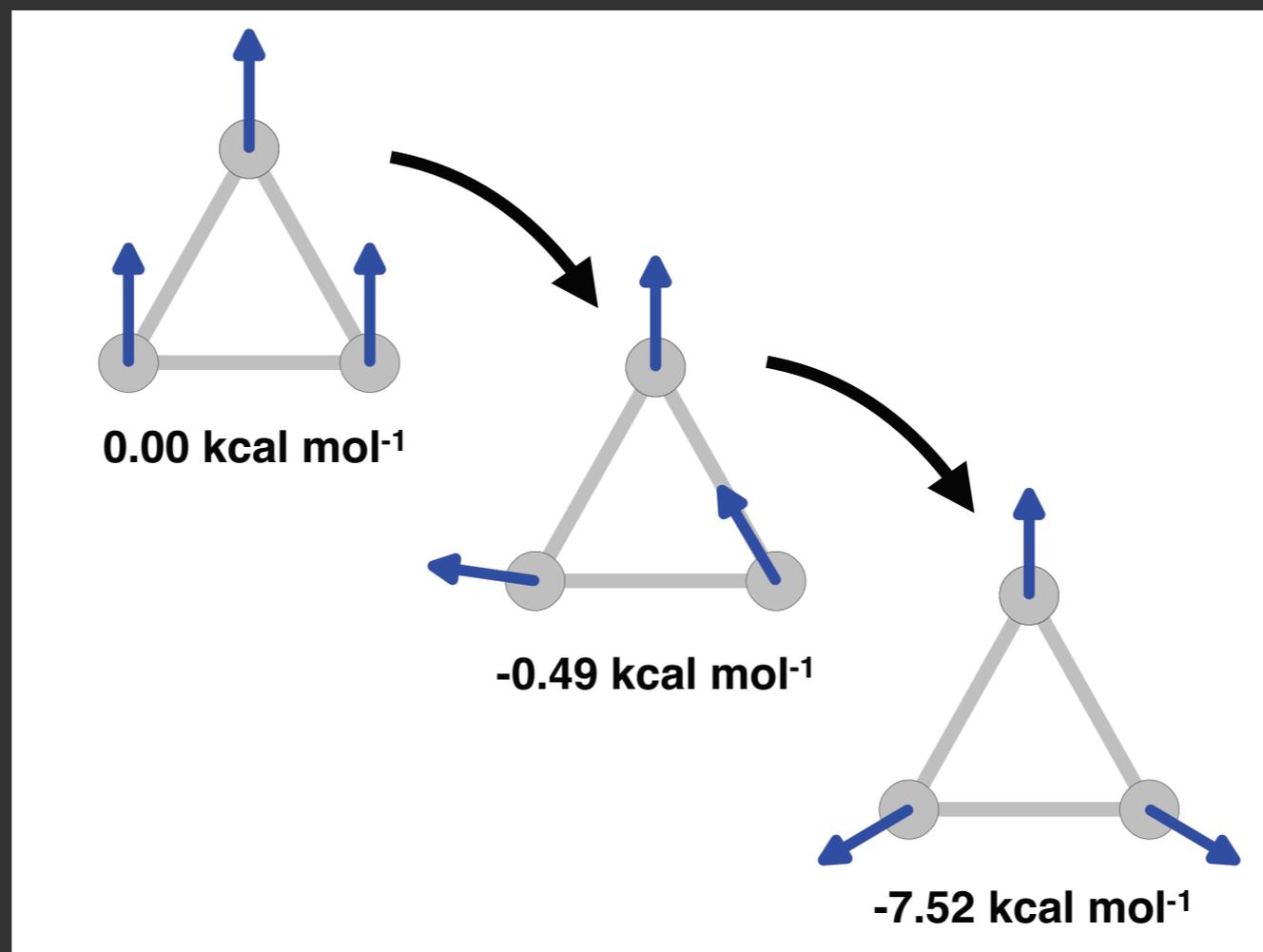
where s is some small step in the direction \mathbf{K} . The new rotated MO coefficients may be fed back into the SCF procedure and the Hartree-Fock solutions re-optimized. With a suitable step-size, the Hartree-Fock equations will converge to a lower energy solution, and the stability test may be performed again.

III. DISCUSSION

Among the first row elements, GHF solutions are rare. However, molecular systems involving geometric frustration are prime targets for a GHF analysis because their frustrated spins must break \hat{S}_z symmetry in order to minimize Pauli repulsion. Geometrically frustrated systems have long been a target for GHF and noncollinear DFT methods.⁷⁻¹⁴ Thus, to explore the applicability of our GHF stability tests, we examined a series of neutral hydrogen rings, ranging from 3 to 15 hydrogens. Each hydrogen was spaced 1 Å around a circle. The advantage of studying such a system is threefold: first, the system is simple enough that we can be guided by chemical intuition, second, at such a spacing, the hydrogen rings act similar to 1D hydrogen chains that prefer an antiferromagnetic alignment, and third, each odd-membered ring will be geometrically frustrated. There are few studies of hydrogen rings,^{22,23} but this appears to be the first to study the geometrically frustrated neutral, odd-numbered hydrogen rings. This geometric frustration means that a GHF solution must exist which minimizes the repulsion from the frustrated spin alignment. It bears mentioning that although the system appears to be artificial, equilateral H_3^+ is among one of the most common ions in interstellar gases,^{24,25} and H_3 has been observed experimentally.²⁶ Furthermore, recent combined theoretical/experimental reports have demonstrated the evidence of sigma-aromatic H_5^- when

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Looking for lowest energy solutions in spin frustrated rings



**Cr₃ : high-spin solutions unstable.
Lower energy non-collinear solution exists.**

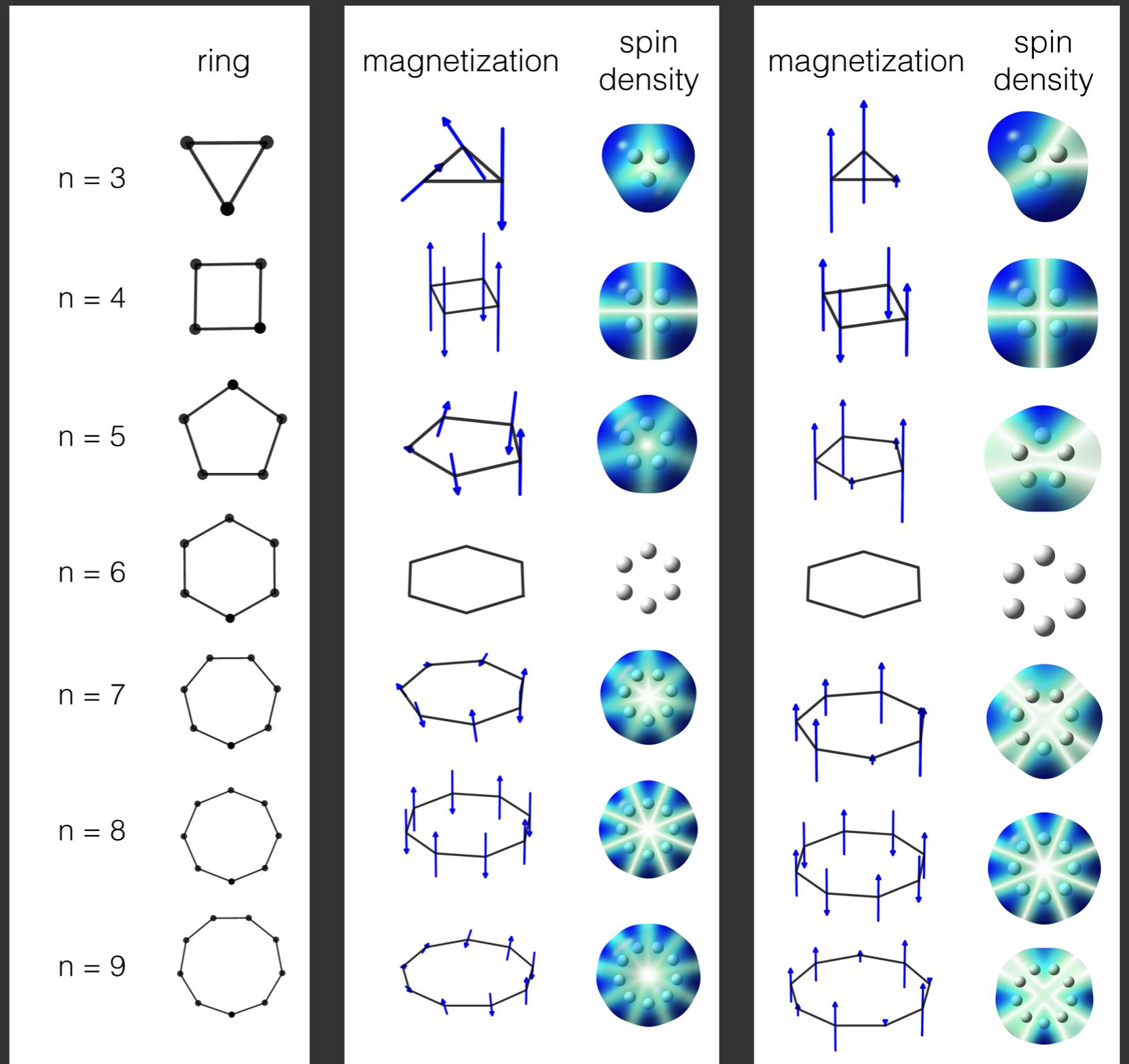
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Hydrogen rings

for odd-member rings, GHF lowest energy solution

GHF

UHF





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In summary:

GHF allows for the **lowest-energy HF solution**

Can **determine multiplicity** without user input

Can **handle spin frustrated** systems

Loses all good **spin quantum numbers**

Future outlook

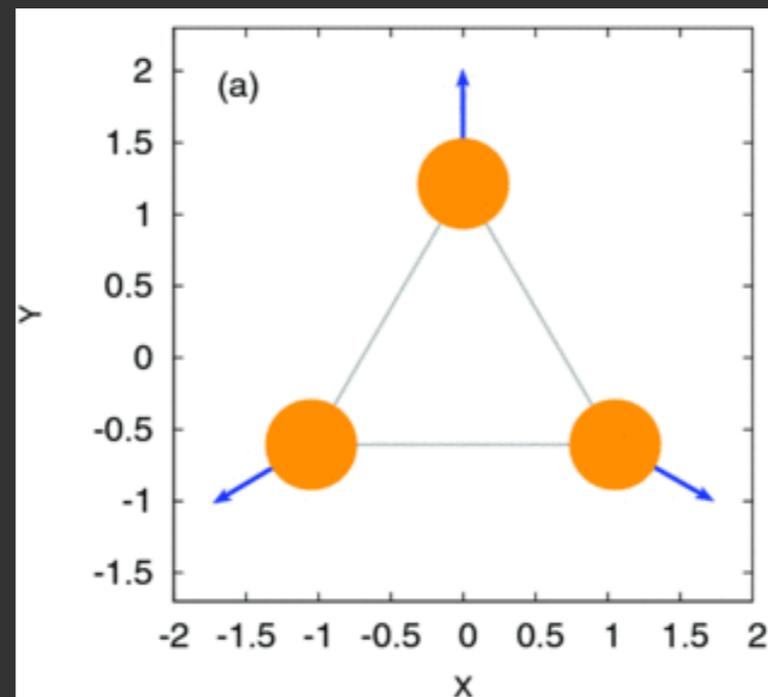
**GHF can handle spin transitions,
but lacks any spin operators
(only Coulomb exchange interaction)**

Including Arbitrary Magnetic Fields into *Ab Initio* Electron Dynamics

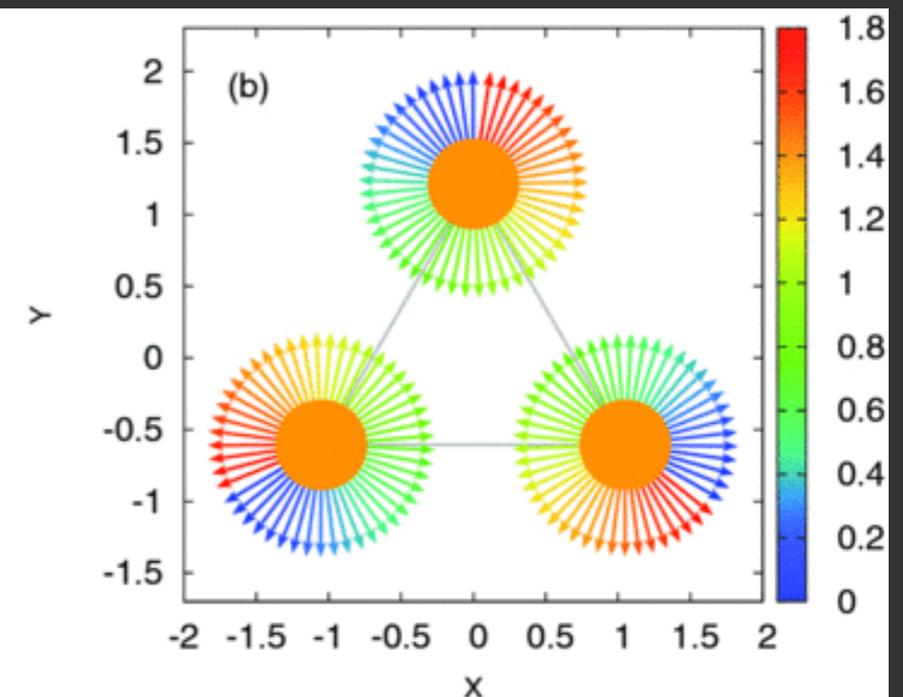
RT-TD-GHF

- Arbitrary magnetic field
- Magnetic moments precess with field
- No spin coupling!

Initial Magnetization



Time Evolution (ps)



Neutral Li_3 trimer, 20T field perpendicular to plane

Observation: TD-GHF allows smooth evolution of spin states, but **lacks spin coupling operators**

Can we extend this description by **adding explicit spin operators to the TD-GHF description?**

**Spin is a non-classical effect.
It arises from relativistic quantum mechanics.**

One electron, Dirac equation:

$$\begin{bmatrix} V & c\boldsymbol{\sigma} \cdot \boldsymbol{\Pi} \\ c\boldsymbol{\sigma} \cdot \boldsymbol{\Pi} & V - 2c^2 \end{bmatrix} \begin{bmatrix} \Psi^L \\ \Psi^S \end{bmatrix} = E \begin{bmatrix} \Psi^L \\ \Psi^S \end{bmatrix}$$

This replaces the one electron operators in GHF

Note four component:

$$\Psi^L = \begin{bmatrix} \Psi^{L\alpha} \\ \Psi^{L\beta} \end{bmatrix} \quad \Psi^S = \begin{bmatrix} \Psi^{S\alpha} \\ \Psi^{S\beta} \end{bmatrix}$$

For multiple electrons, we have the approximate interaction operator—the **Breit operator**

$$\hat{V}_{12} = \frac{q_1 q_2}{r_{12}} - \frac{q_1 q_2}{2} \left[\frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2}{r_{12}} + \frac{(r_{12} \cdot \boldsymbol{\alpha}_1)(r_{12} \cdot \boldsymbol{\alpha}_2)}{r_{12}^3} \right]$$

This replaces the two electron Coulomb operator

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0}_2 \end{pmatrix}$$

For multiple electrons, we have the approximate interaction operator—the **Breit operator**

$$\hat{V}_{12} = \frac{q_1 q_2}{r_{12}} - \frac{q_1 q_2}{2} \left[\frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2}{r_{12}} + \frac{(r_{12} \cdot \boldsymbol{\alpha}_1)(r_{12} \cdot \boldsymbol{\alpha}_2)}{r_{12}^3} \right]$$

(Coulomb) (Breit correction, note spin-dependence)

This replaces the two electron Coulomb operator

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0}_2 \end{pmatrix}$$

We can reduce to two component form

$$\begin{bmatrix} H_{LL} & H_{LS} \\ H_{SL} & H_{SS} \end{bmatrix} \begin{bmatrix} \Psi^L \\ \Psi^S \end{bmatrix}$$

$$U \begin{bmatrix} H_{LL} & H_{LS} \\ H_{SL} & H_{SS} \end{bmatrix} U^{-1} \rightarrow \begin{bmatrix} \tilde{H}_{LL} & 0 \\ 0 & \tilde{H}_{SS} \end{bmatrix}$$

Usually approximate

Off diagonal terms zero to some order

Order $1/c$ gives Breit-Pauli

Order V gives Douglas-Kroll-Hess

$$\Psi^L = \begin{bmatrix} \Psi^{L\alpha} \\ \Psi^{L\beta} \end{bmatrix}$$

$$\Psi^S = \begin{bmatrix} \Psi^{S\alpha} \\ \Psi^{S\beta} \end{bmatrix}$$

Uncertain best way to include these operators into the TDSE

	Four Component	Breit-Pauli (two component, $1/c$)	Douglas-Kroll-Hess (two component, V)
Naive cost?	$2(4N)^4$	$2(2N)^4$	$2(2N)^4$
Variational?	No (yes, in practice)	No	Yes
Interpretation?	Must account for positron-like component	Clear relation to spin-Hamiltonian	Spin-terms mixed

Future Roadmap

cheaper,
harder to code

response properties,
physical observables

DKH



picture-
change

**Property
Transf.**

spin-spin

Breit

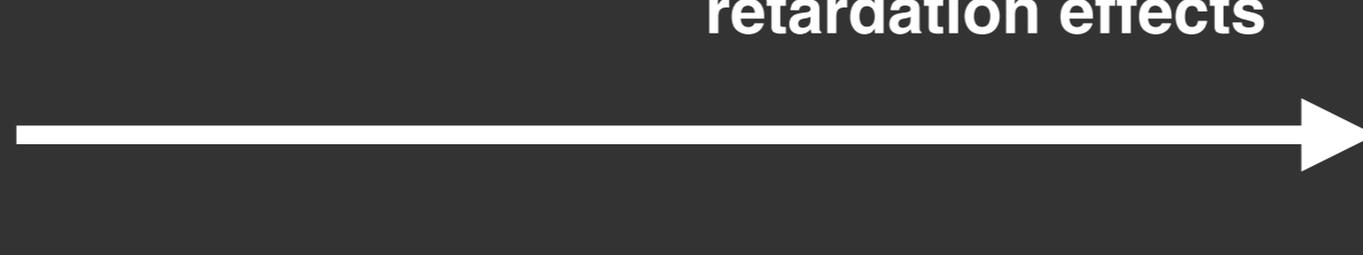


**Time
Domain**



retardation effects

4c



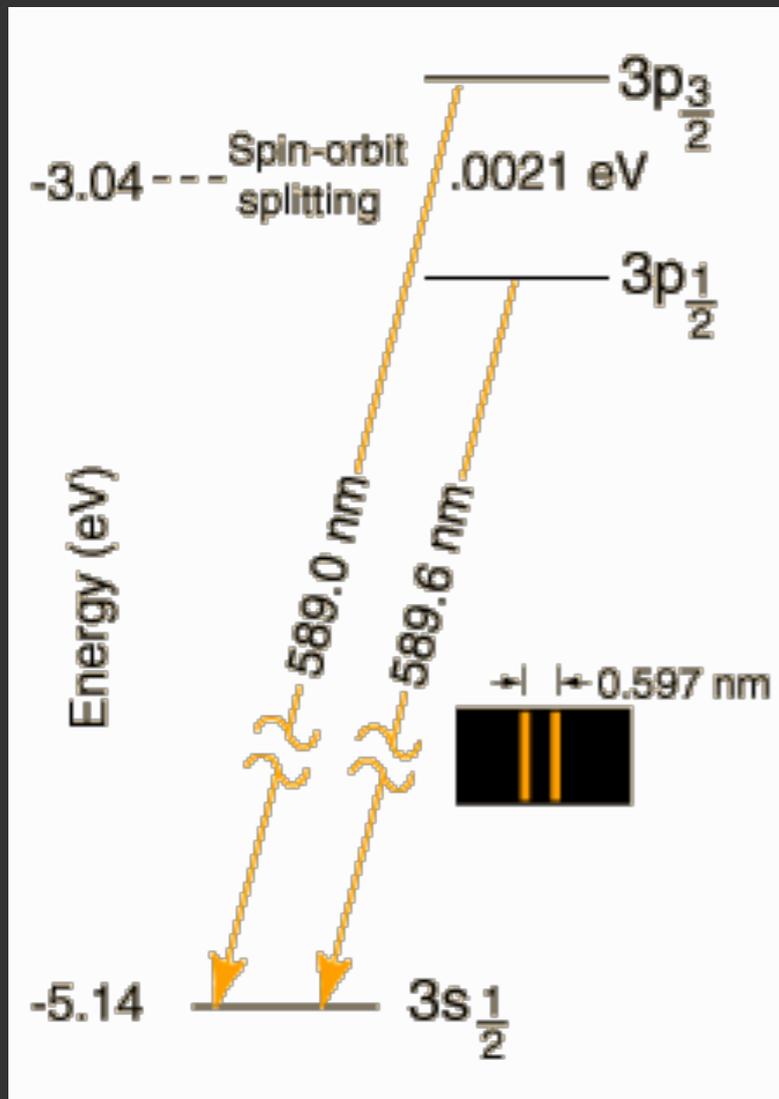
expensive,
simpler



**Spin-dependent electronic dynamics
Heavy-element response properties**

How can we **predict** and **understand**
the **electronic** and **magnetic responses**
of **molecules** and **nano-materials**?

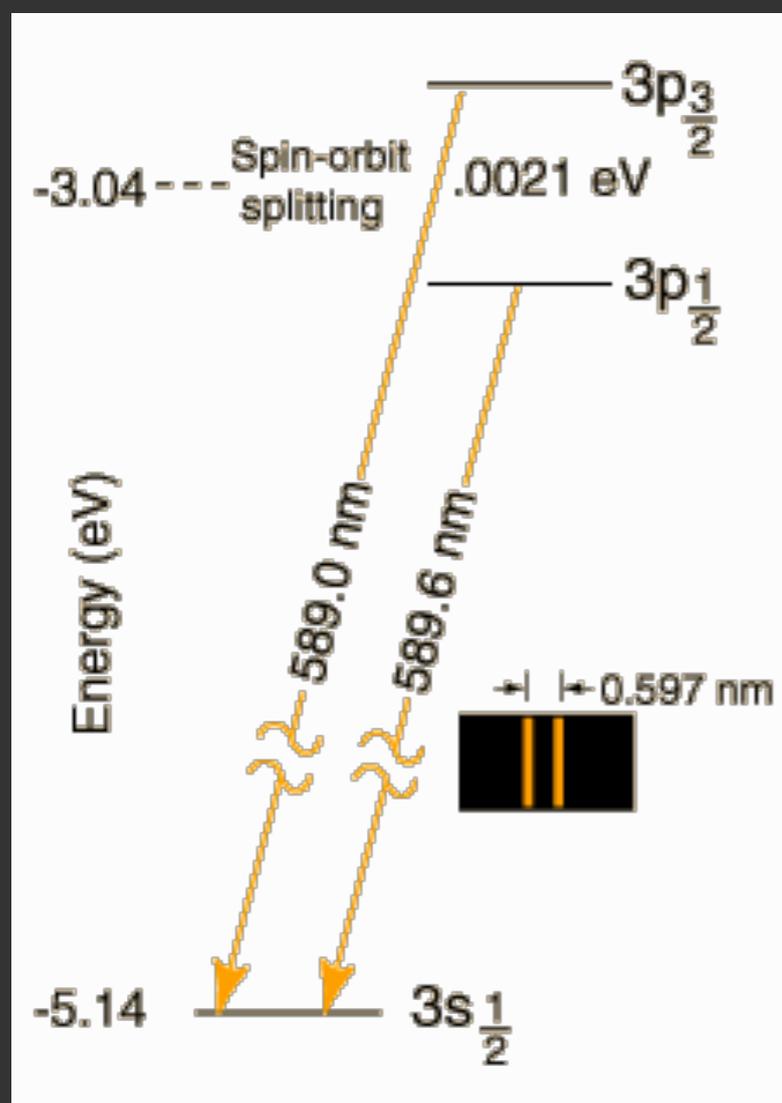
Maybe settle for atoms at the moment?



TD-DKH Sodium D-lines (daug-cc-pVTZ)

[eV]	1c-TD-DKH	2c-TD-DKH	Exp
${}^2S_{1/2} \rightarrow {}^2P_{1/2}$	1.9733	1.9730	2.1023
${}^2S_{1/2} \rightarrow {}^2P_{3/2}$	1.9733	1.9736	2.1044
Splitting	0.0000	0.0006	0.0021

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Splitting	0.0000	0.0006	0.0021

A lot more more needs to be done!

Future work



**Spin-dependent dynamics
and response theory**

Future work



**Spin in Time-
Dependent
Theory**

**Spin-dependent dynamics
and response theory**

Thank you!

**Li Group
Exam Committee
Ernest Davidson**



**Excited
States**

**Quantum
Dots**

**Magnetic
Materials**

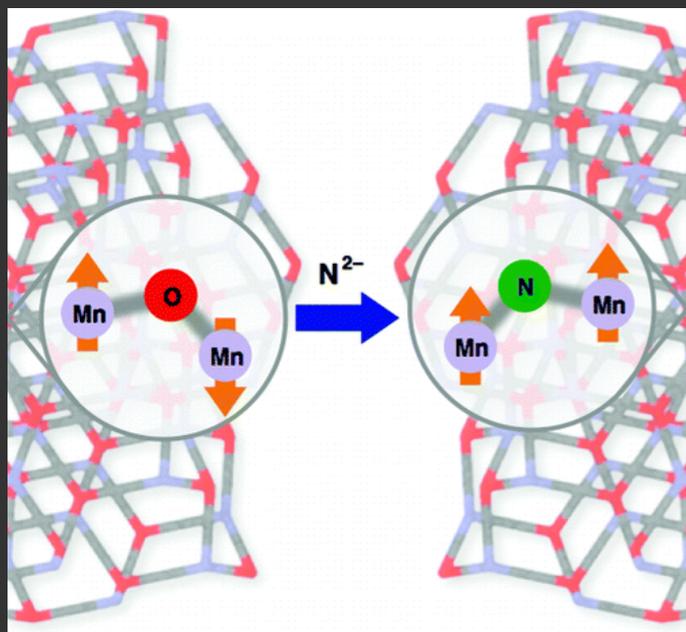


**Spin in Time-
Dependent
Theory**

Coupling between charge carriers and Mn^{2+} in ZnO QDs

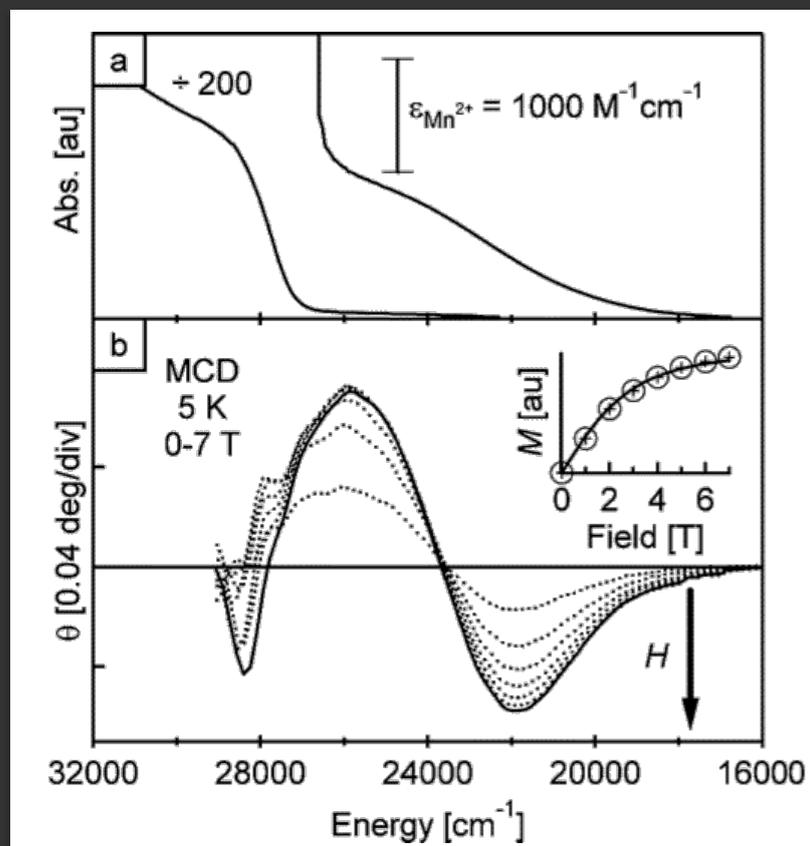
holes in p-type dopants couple with Mn^{2+} dimer

May, Joseph W., Ryan J. McMorris, and Xiaosong Li. JPCL 3.10 (2012): 1374-1380.

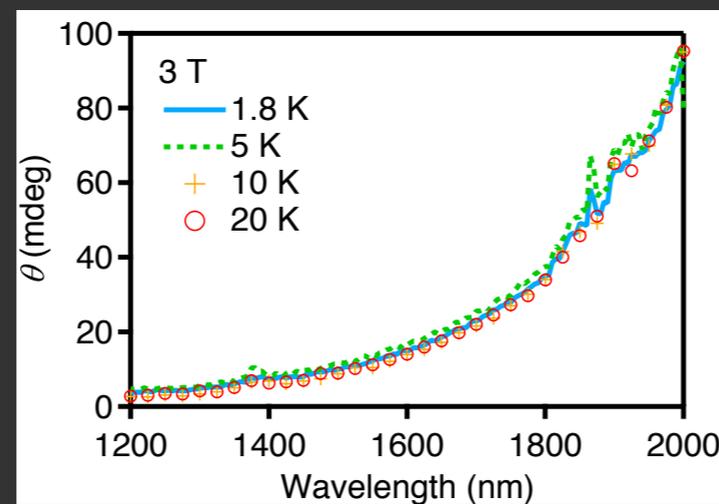
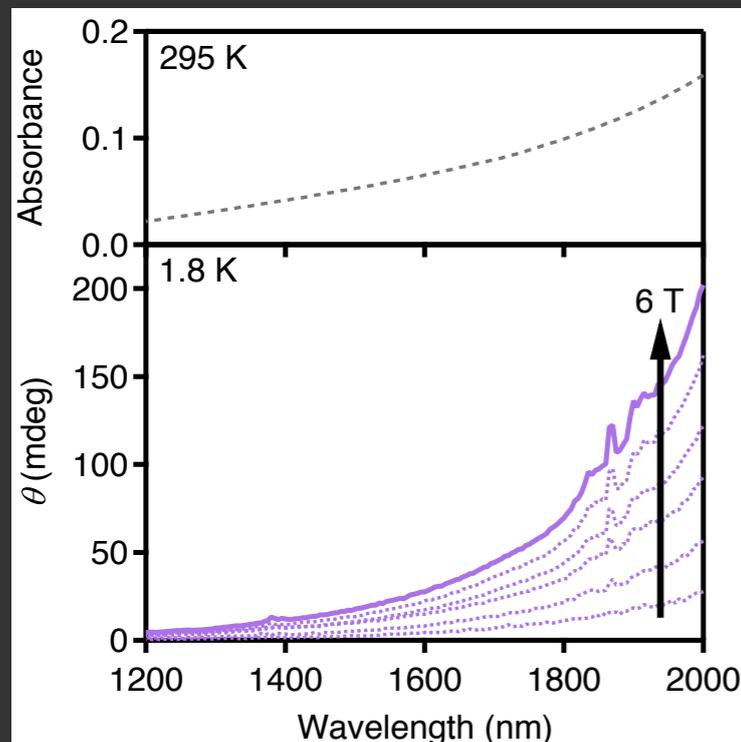


exciton couples to Mn^{2+} in ZnO QDs

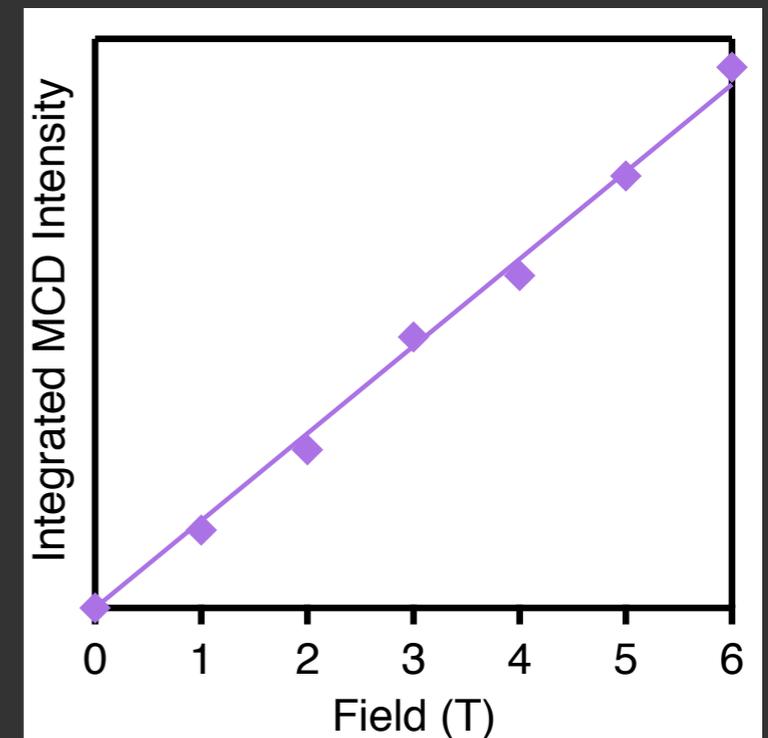
Norberg, Nick S., et al. JACS 126.30 (2004): 9387-9398.



It seems reasonable that excess CB electrons would couple to Mn



**Data courtesy
Dr. Alina Schimpf**

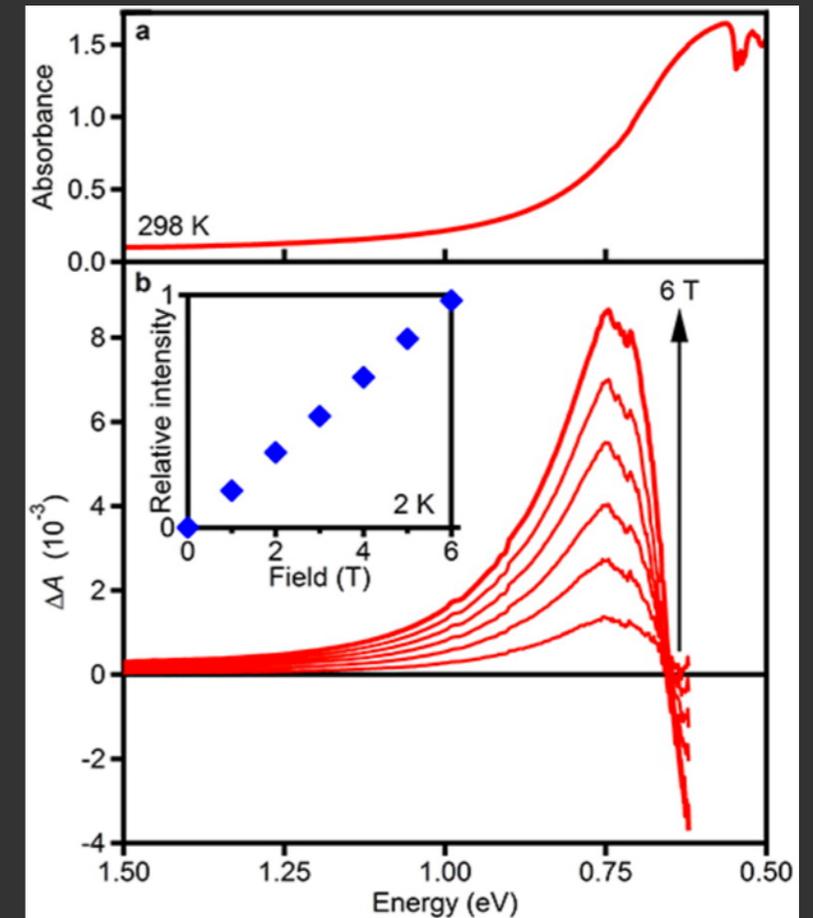


**$\text{Al}^{3+}:\text{ZnO}$ QDs; no evidence excess
electrons couple with Mn**

**Of course, similar story with
photodoped e⁻:ZnO**

**All systems studied so far are
heavily doped**

**Currently, Gamelin group
looking at low-carrier
concentrations**



Schimpf, A. M., Thakkar, N., Gunthardt, C. E., Masiello, D. J., & Gamelin, D. R. (2013). ACS Nano, 8(1), 1065-1072.

**Can we help explain this with spin dependent electronic
structure theory?**