Breaking symmetry in time-dependent electronic structure theory to describe spectroscopic properties of non-collinear and chiral molecules.

Joshua Goings
Thursday, May 25, 12:30 pm
Advisor: Xiaosong Li

Thank you to the Li research group,

My committee,

Xiaosong Li
Stefan Stoll
David Masiello
Matt Bush
Jim Pfaendtner

My family and friends

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My family and friends

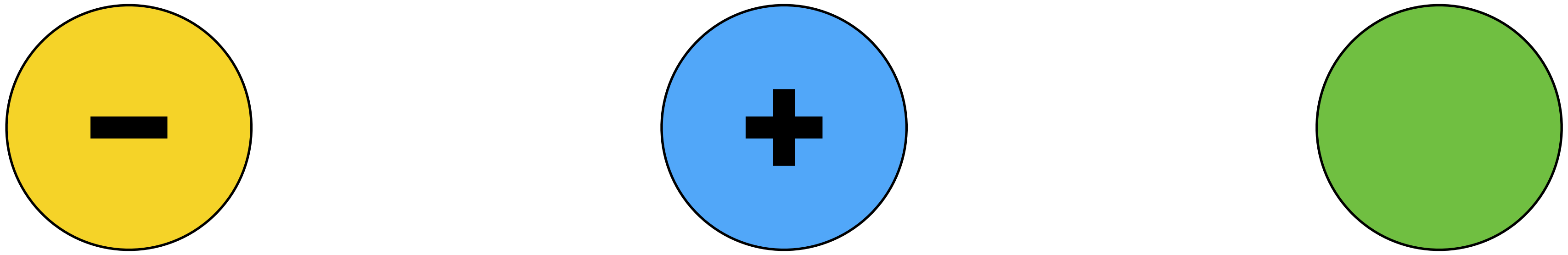
…speaking of…

I know many of my family and friends aren’t chemists.

What the *heck* did I spend the past 5 years doing?

Chemistry is the study of matter.

All matter consists of three things.

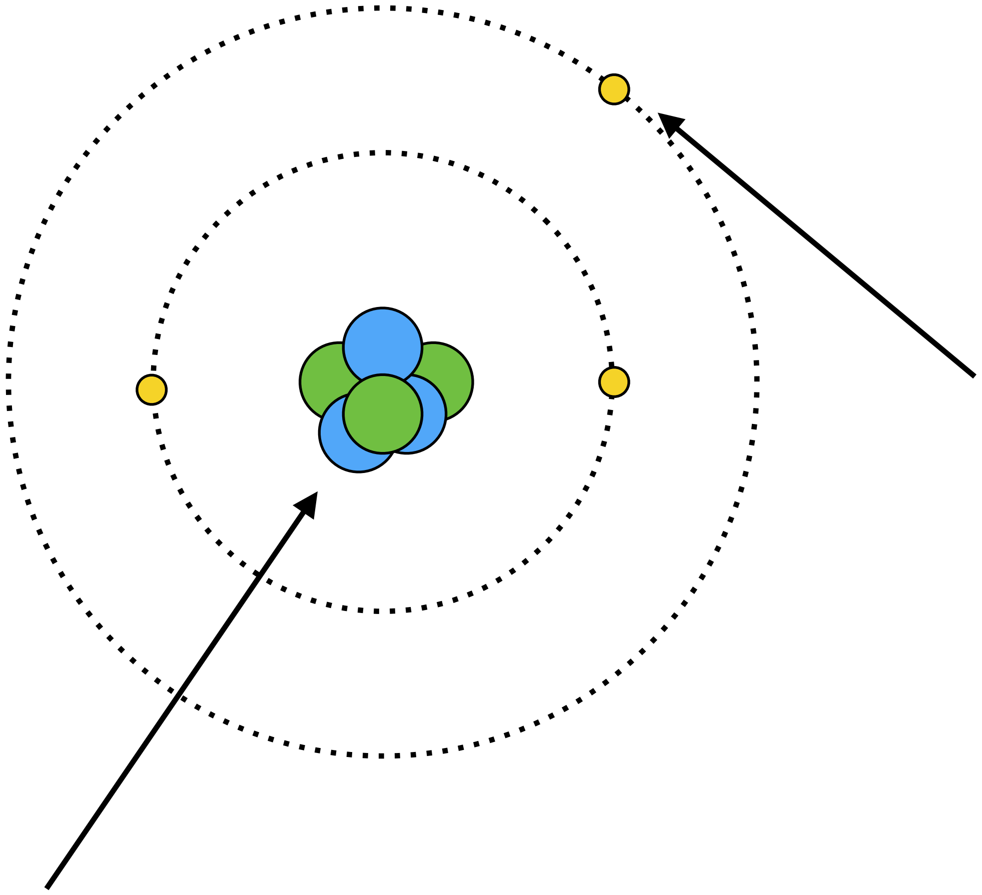


electrons

protons

neutrons

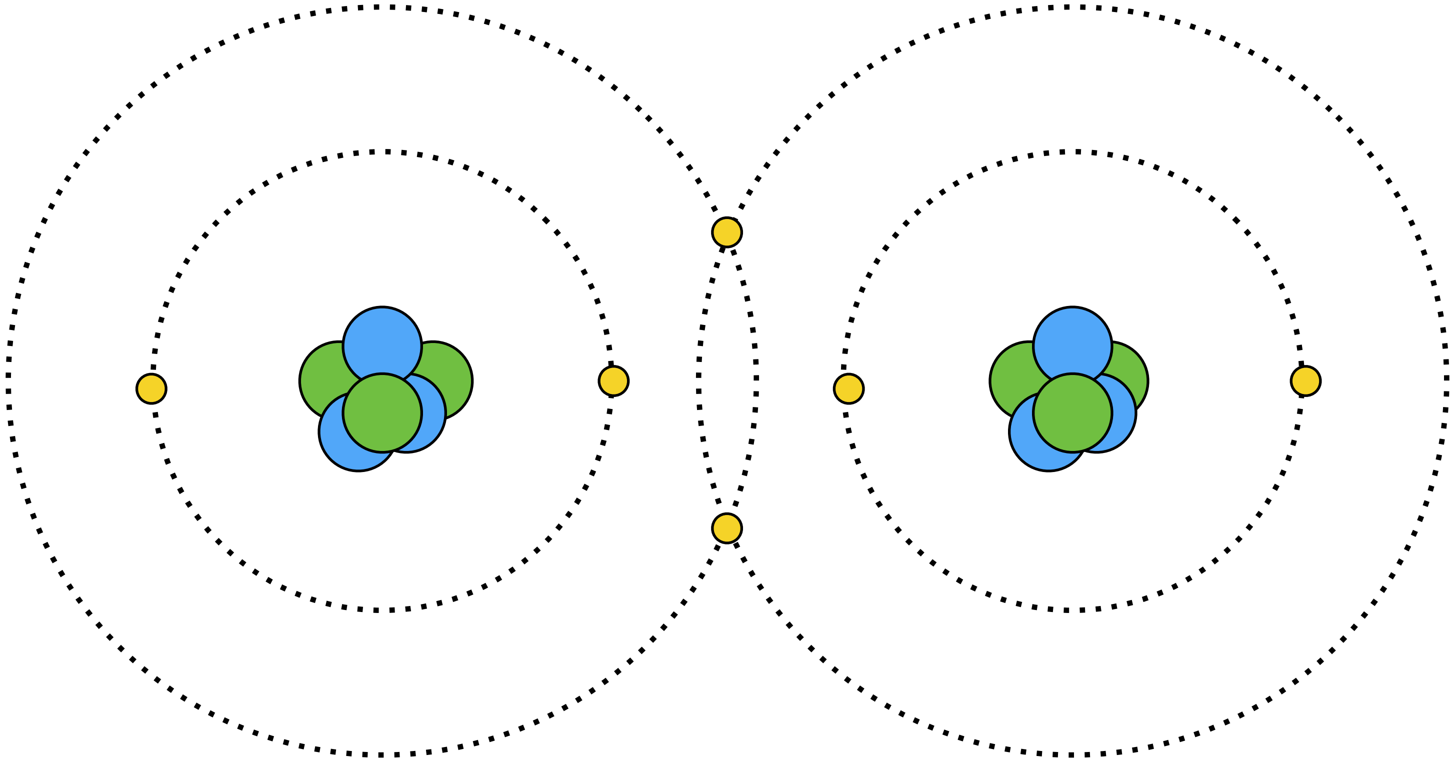
These three types of particles combine to make atoms.



electrons

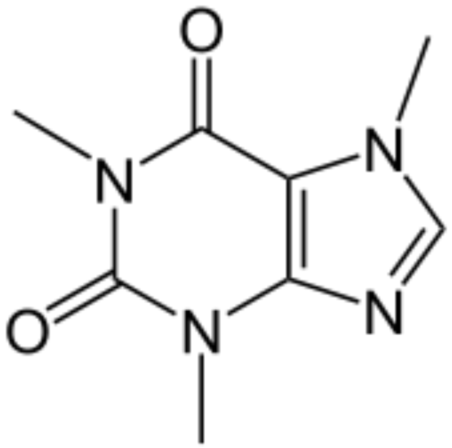
nucleus

Atoms can combine to form molecules.



They do this by sharing electrons.

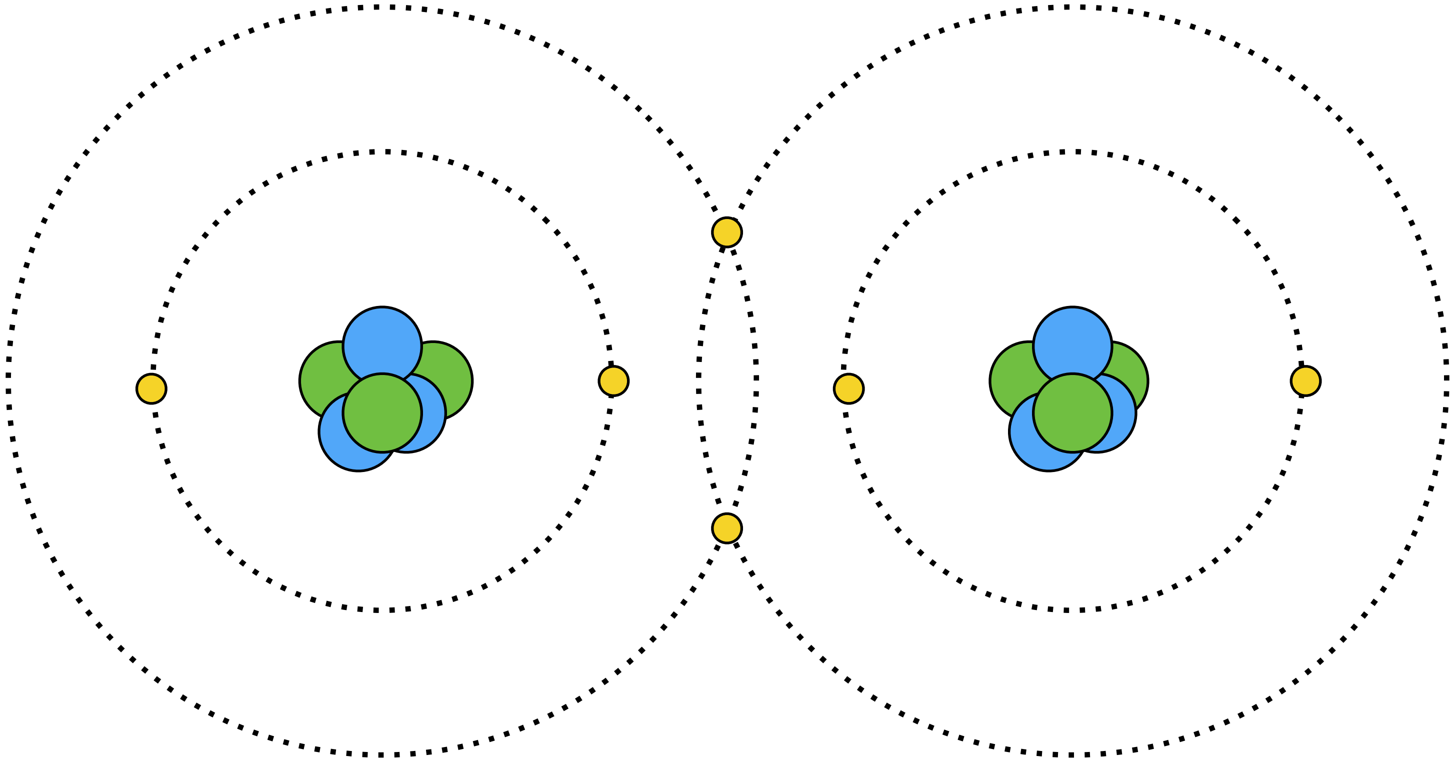
Atoms can combine in many ways to create an incredible diversity of molecules and compounds

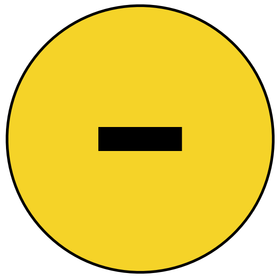


caffeine

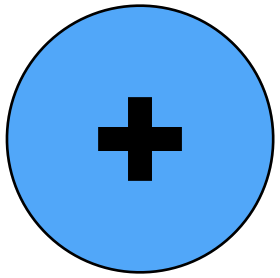
Anything you can touch, taste, smell, see…
…all come from combining these three particles, ⊖ ⊕ ●,
in different ways.

How is it that these three particles can lead to the world we experience?

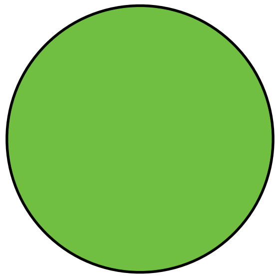




electrons



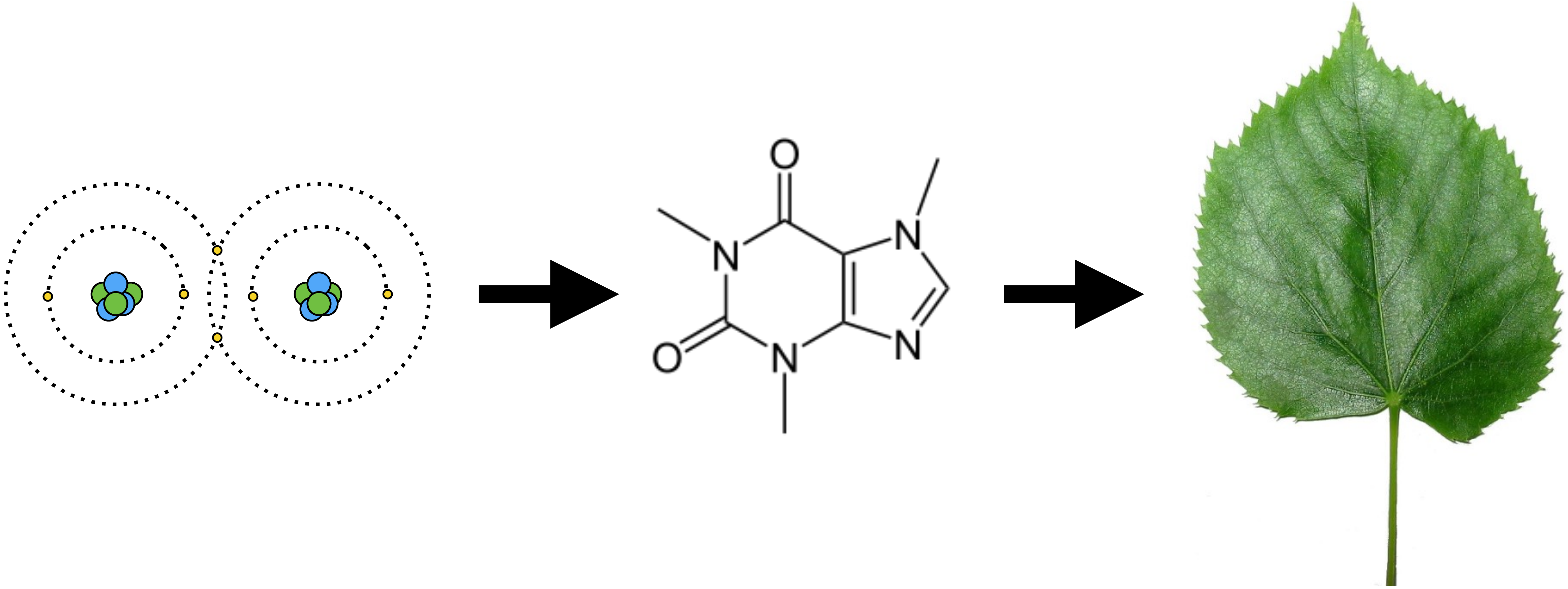
protons



neutrons

Most of it comes from how the electrons organize themselves!

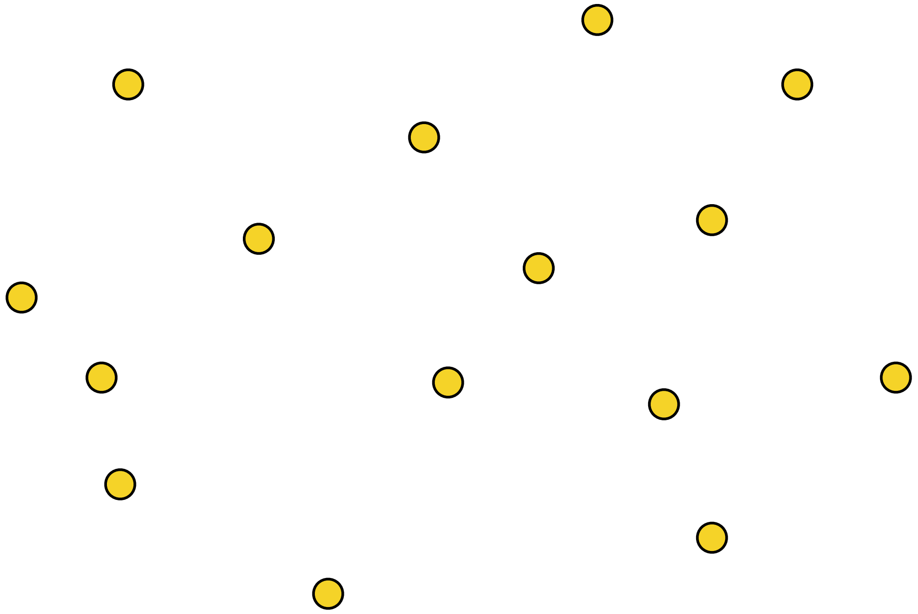
My area of chemistry focuses on
electronic structure theory



basically, I study how electrons organize themselves in molecules, and how this leads to the stuff we experience

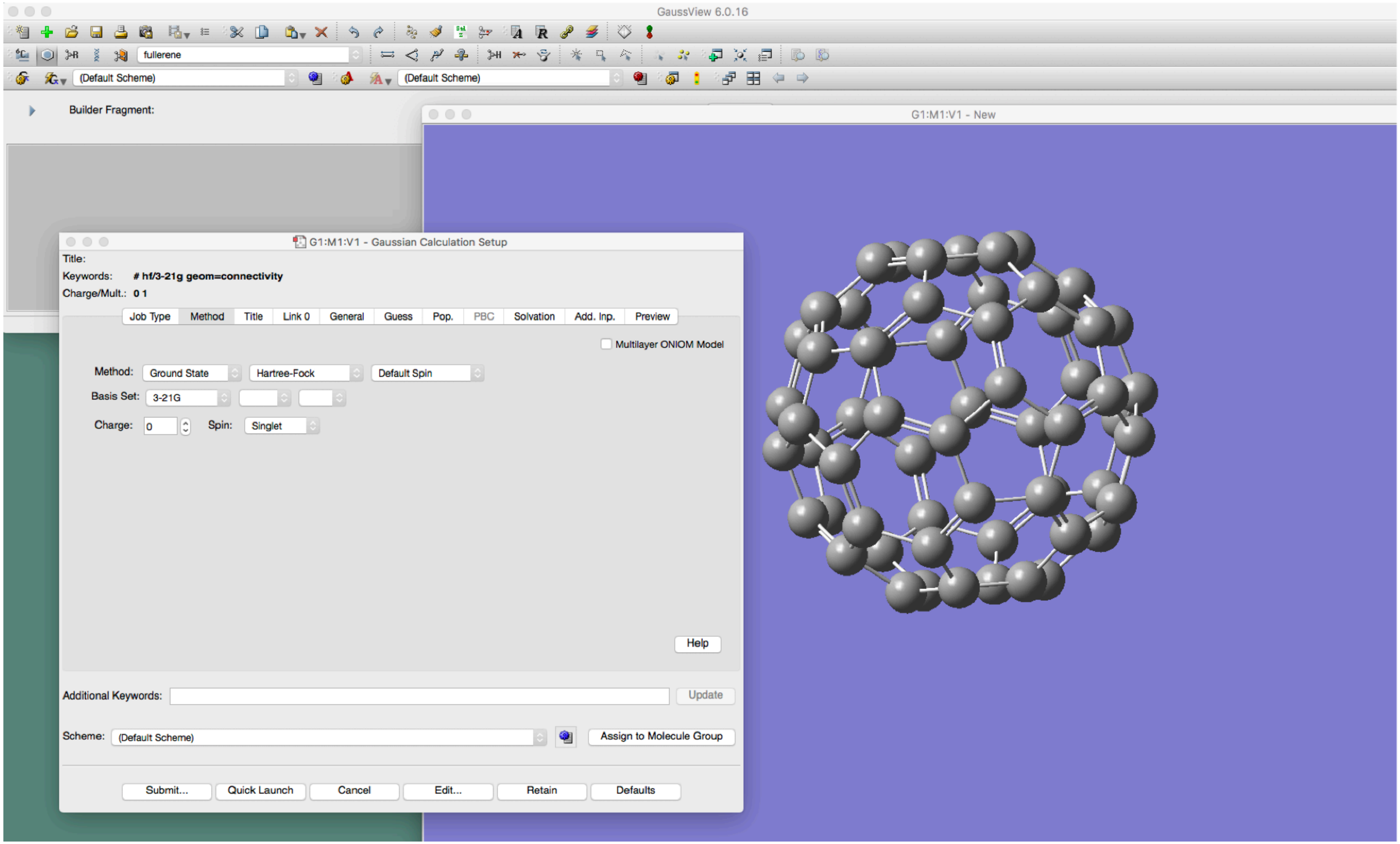
I do this by **describing the electrons mathematically**.

Predicting the behavior of electrons is **extremely difficult**



molecules may have hundreds or thousands of electrons, and if one moves, they all respond (correlation).

My work developed both **mathematical models** to describe molecules, as well as **programming** the math so a computer could solve the equations



Title:
Keywords: **# hf/3-21g geom=connectivity**
Charge/Mult.: **0 1**

Method: Ground State, Hartree-Fock, Default Spin
Basis Set: 3-21G
Charge: 0
Spin: Singlet

Additional Keywords:
Scheme: (Default Scheme)

In particular, I study and apply computational methods to **spectroscopy**, which is the **interaction of light and matter.**

Every molecule interacts with light differently,
and has a **unique spectrum** — like a fingerprint.

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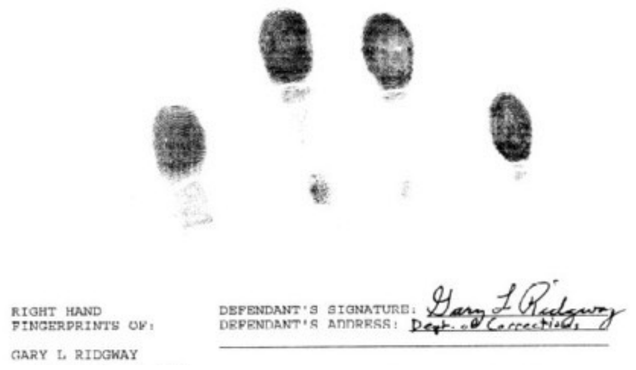

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GARY L RIDGWAY

DEFENDANT'S SIGNATURE: Gary L Ridgway
DEFENDANT'S ADDRESS: Dept. of Corrections

Green River killer

In particular, I study and apply computational methods to **spectroscopy**, which is the **interaction of light and matter.**

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Green River killer

tomato soup

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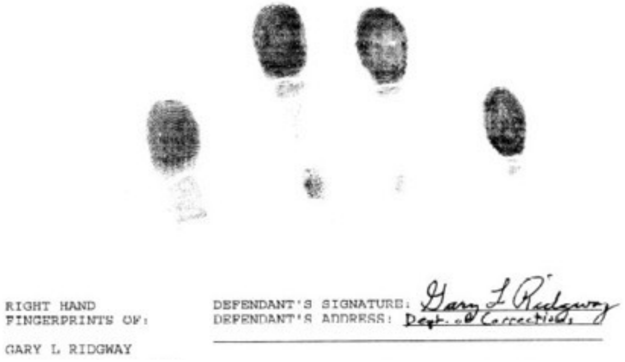

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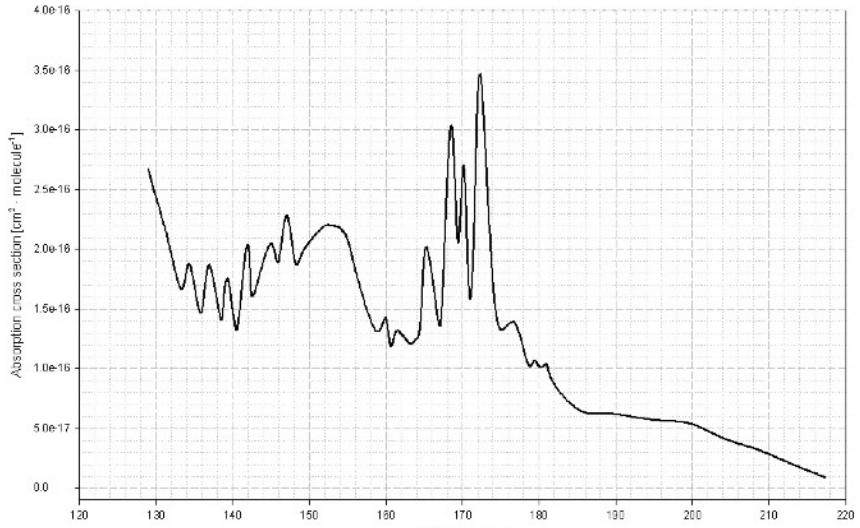

VUV absorption cross sections of cyclopropene c-C_3H_4 at 298 K,
Robin et al., J. Chem. Phys. 51 (1969) 45

cyclopropene

It's kind of like a barcode in that way, and most of my work goes into **predicting what the spectrum** will look like.

So in sum, I study:

how electrons organize in molecules (**electronic structure theory**)
how this affects the way they interact with light (**spectroscopy**)

So in addition to predicting how molecules interact with light, which gives us a way of identifying molecules…

…We can also hope to use these results to help develop **better medicines, better chemicals, and better devices**.

Breaking symmetry in time-dependent electronic structure theory to describe spectroscopic properties of non-collinear and chiral molecules.

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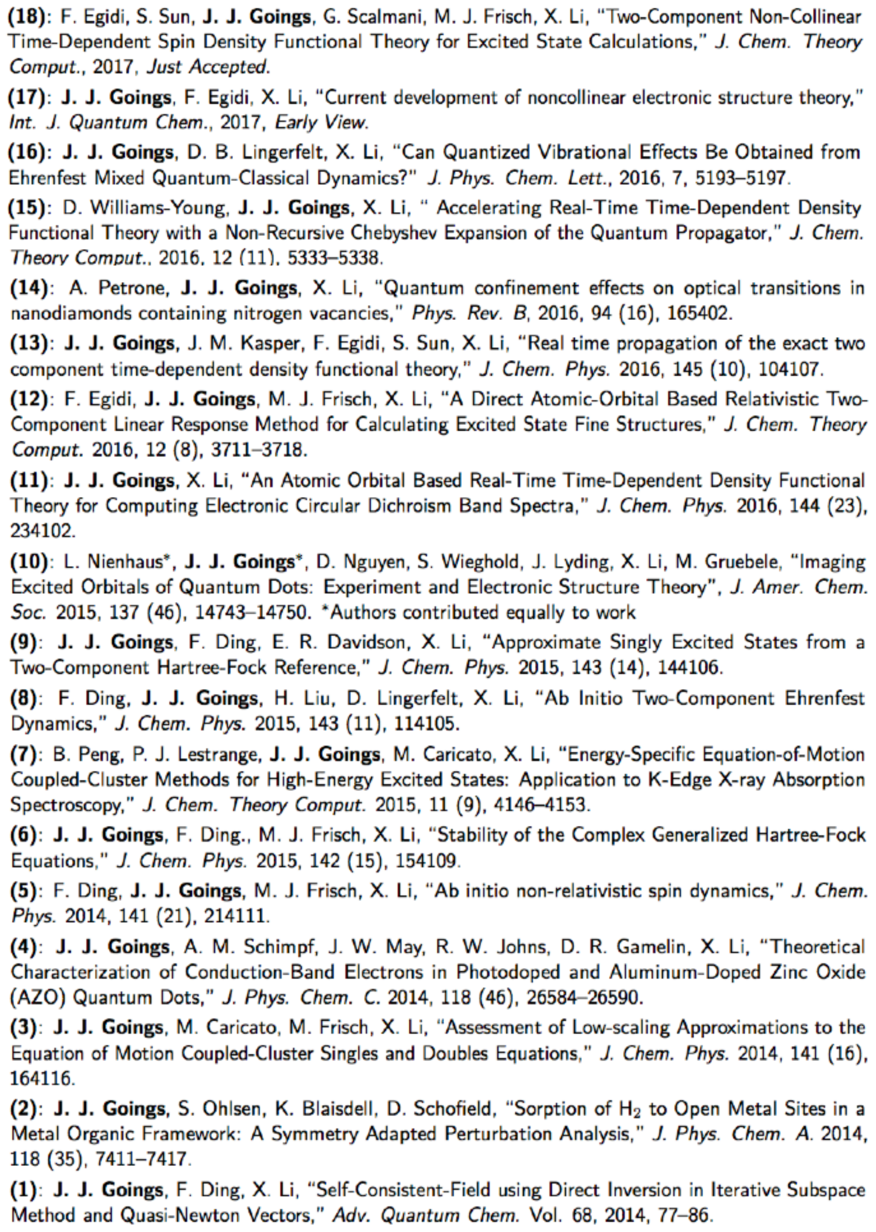
Over the past 5 years…

I've written 18 peer-reviewed papers



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(6): **J. J. Goings**, F. Ding., M. J. Frisch, X. Li, "Stability of the Complex Generalized Hartree-Fock Equations," *J. Chem. Phys.* 2015, 142 (15), 154109.

(5): F. Ding, **J. J. Goings**, M. J. Frisch, X. Li, "Ab initio non-relativistic spin dynamics," *J. Chem. Phys.* 2014, 141 (21), 214111.

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(1): **J. J. Goings**, F. Ding, X. Li, "Self-Consistent-Field using Direct Inversion in Iterative Subspace Method and Quasi-Newton Vectors," *Adv. Quantum Chem.* Vol. 68, 2014, 77–86.

But I am only going to discuss a couple.

My research addressed:

1) What are two-component electronic structure methods, and how do we ensure that the solutions are stable?

2) How can we extend two-component methods to include relativistic effects, as well as how we can compute absorption spectra *via* an explicitly time-dependent (real-time) approach?

3) How we can modify the real-time methods to obtain circular-dichroism spectra, which relies on a magnetic response an electric field

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Most electronic structure methods retain
some sort of spin symmetry.

We don’t always want this.

This symmetry might break due to…

…**geometry** of the system,
…external **magnetic** fields,
…or **internal** symmetry breaking terms
in the Hamiltonian

Hartree-Fock seeks to minimize the energy of a single Slater Determinant (independent particle model, IPM)

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

This leads to an eigenvalue equation with Fock operator **F**

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}$$

Very generally, **F** is written as

$$\left(\begin{array}{cc} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{array} \right) \qquad \mathbf{F}^{\sigma\tau} = \mathbf{h}^{\sigma\tau} + \delta_{\sigma\tau} \left[\mathbf{J}^{\alpha\alpha} + \mathbf{J}^{\beta\beta} \right] - \mathbf{K}^{\sigma\tau}$$

In general, we expect the Fock operator (and its solutions) to have the same symmetries as the electronic Hamiltonian

All symmetry operations can be represented by similarity transformations.

$$\hat{g}\hat{H}\hat{g}^{-1} = \hat{H}, \qquad (\forall \hat{g} \in \mathcal{G}).$$

It's usually the case that the similarity transformations are also (anti-)unitary.

We seek transformations such that

$$\hat{U}\begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix}\hat{U}^{-1} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix}$$

This has the effect of adding constraints to the wave function, which simplifies the equations we must solve

Depending on the symmetry we want to enforce, we can simplify the structure of the Hartree-Fock equations

$$\hat{U}\begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix}\hat{U}^{-1} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix}$$

Unrestricted Hartree Fock (UHF):

$$\mathbf{F} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{F}_{\beta\beta} \end{pmatrix}$$

*symmetric to one spin rotation axis

Restricted Hartree Fock (RHF):

$$\mathbf{F} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{F}_{\alpha\alpha} \end{pmatrix}$$

*symmetric to all spin rotations

Any time we make the Fock operator invariant
to some symmetry, we add a constraint.

More constraints can only raise the energy
of a variationally optimized solution.

Eliminating all symmetry constraints related to spin and time reversal, we get the complex generalized Hartree-Fock equations (GHF).

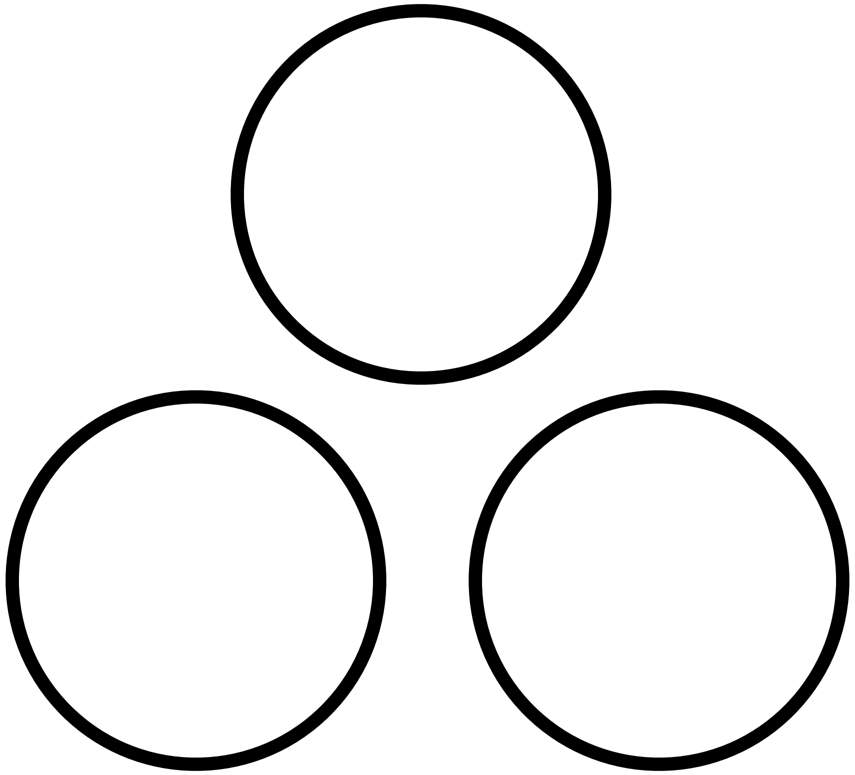
Solutions may be complex-valued and mixed spin,
and historically is an uncommon method.

One of the first problems I ran into was that simply “doing” GHF didn’t always give us the lower energy solution.

More degrees of freedom = greater chance you land at energetic saddle point

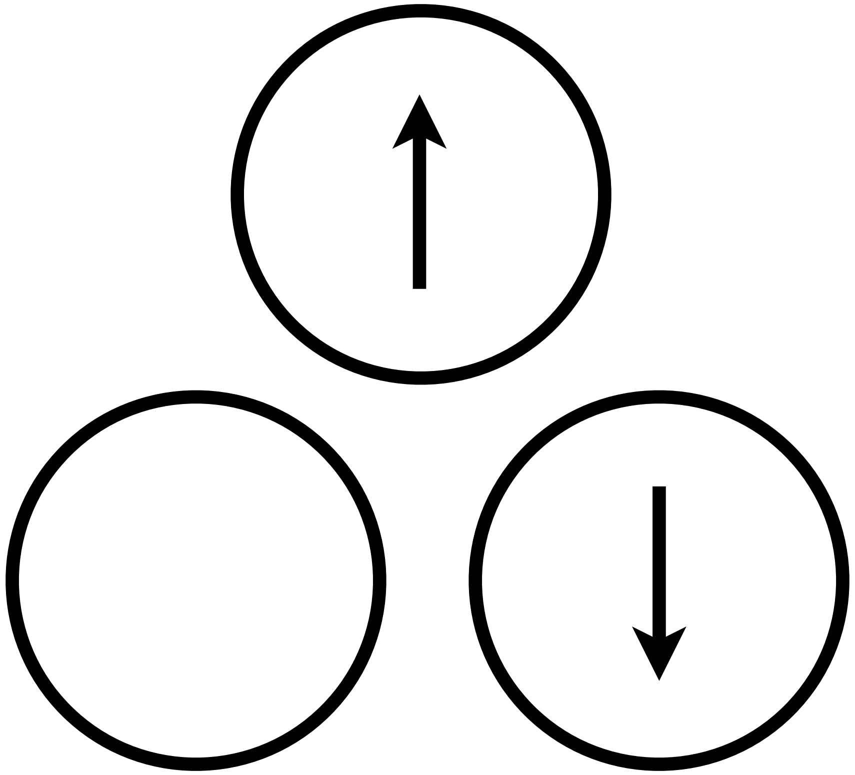
A great example comes from spin-frustrated systems.

What are spin-frustrated systems?



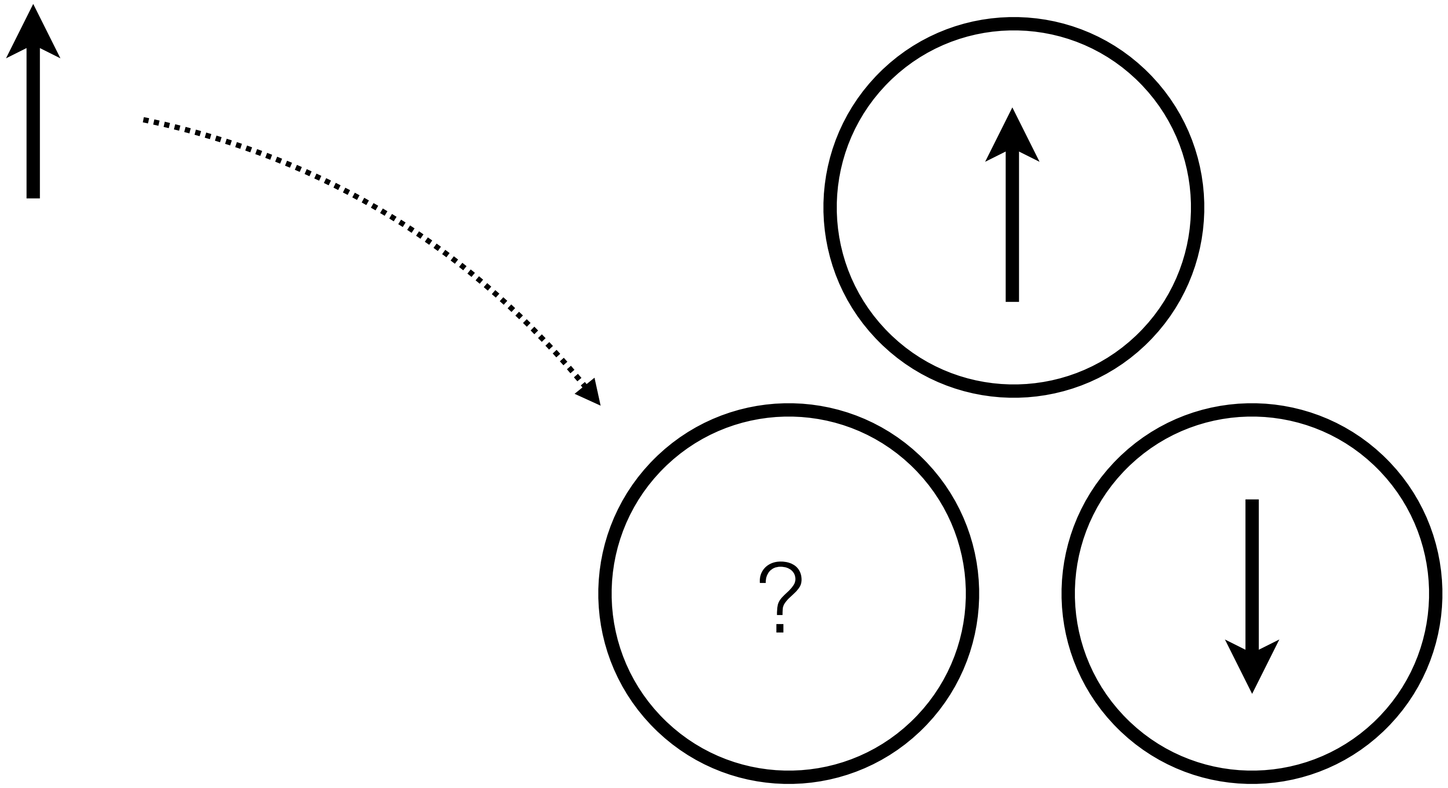
Take a three site lattice

What are spin-frustrated systems?



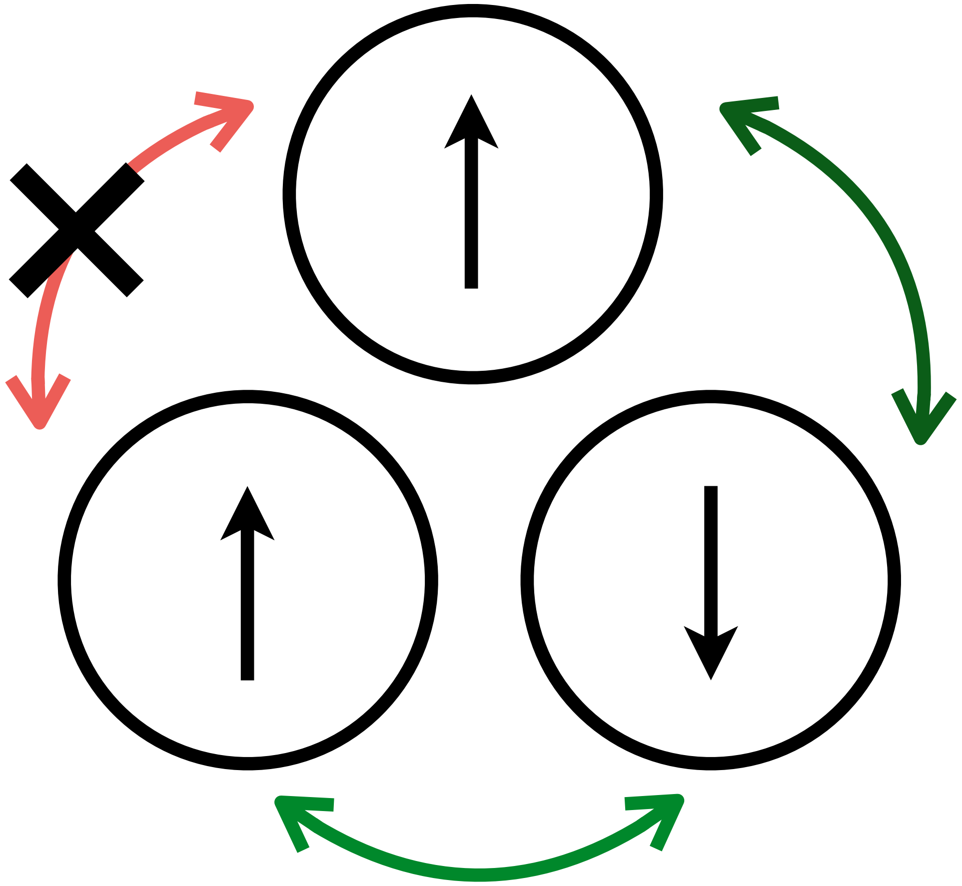
Add two electrons.
(Assume anti-ferromagnetism favored).

What are spin-frustrated systems?

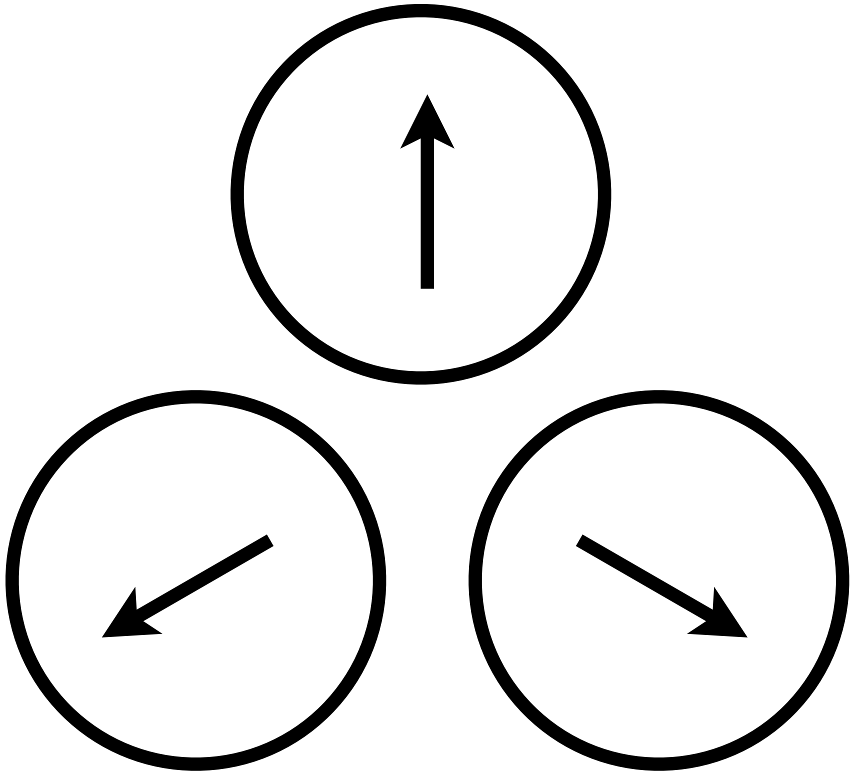


Now, add the third electron.
No spin orientation simultaneously favors
all anti-ferromagnetic exchange interactions

What are spin-frustrated systems?

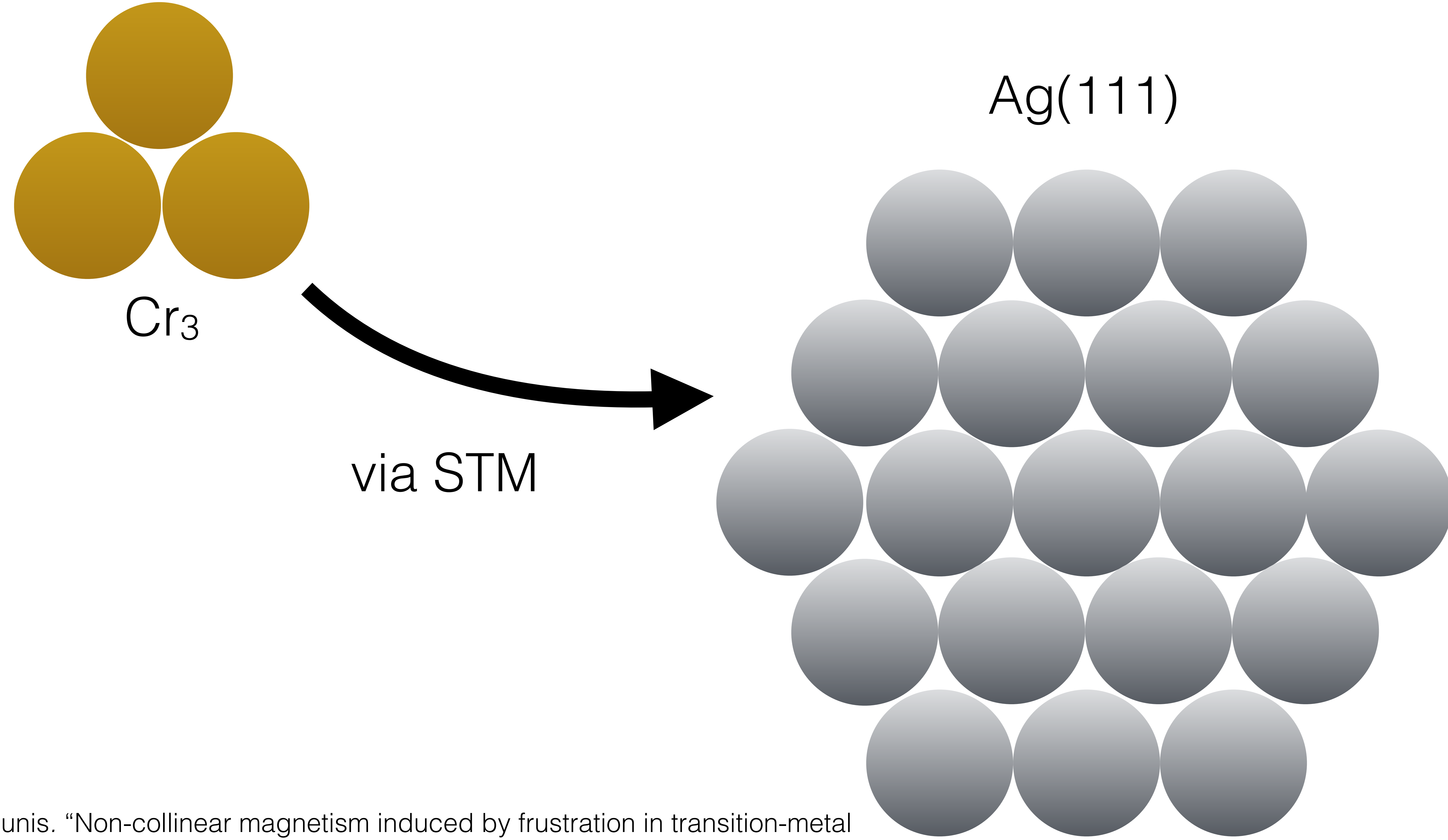


Collinear



Non-collinear

Generating non-collinear magnetism by spin frustration with transition metals



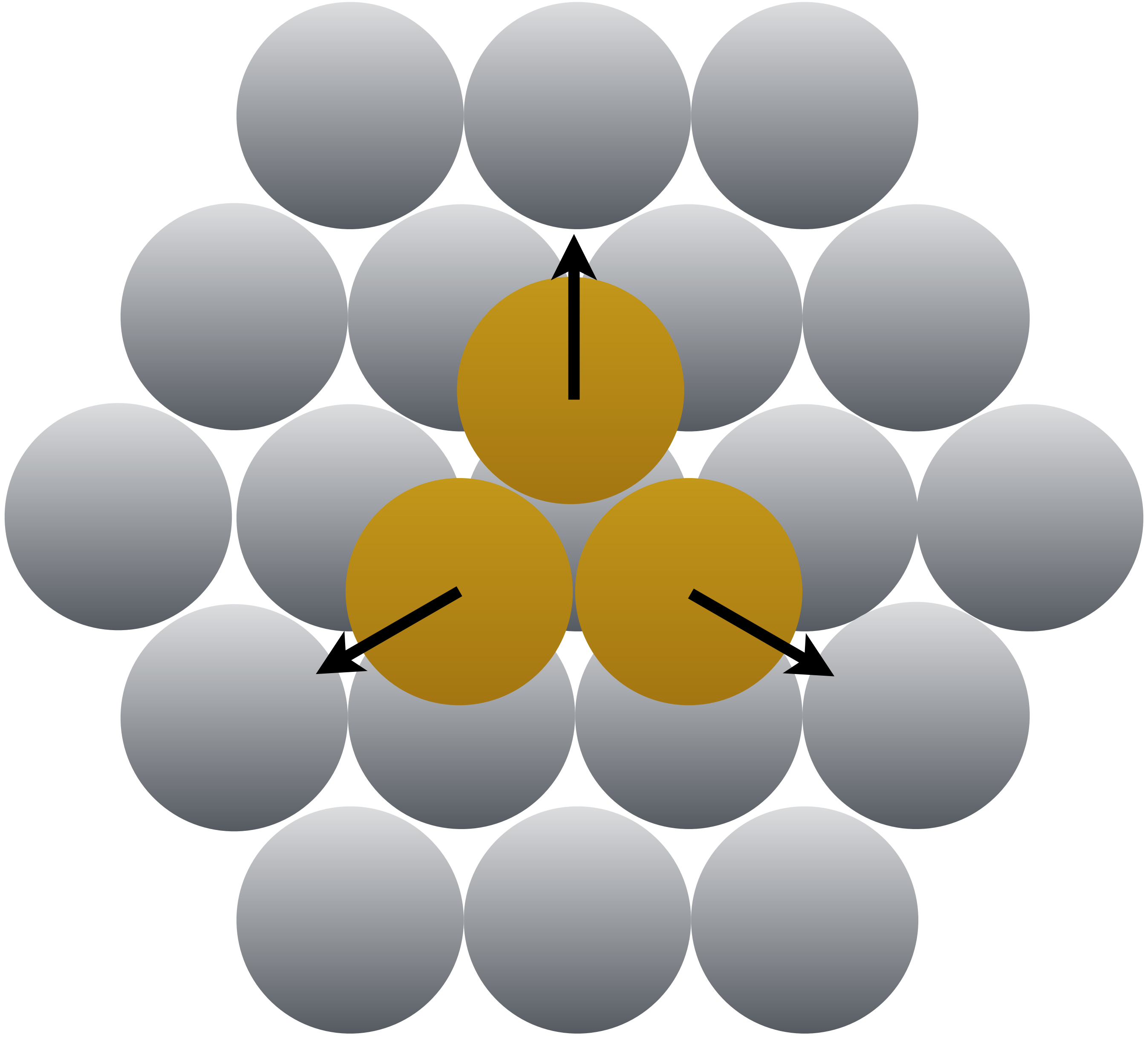
Cr_3

via STM

Ag(111)

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

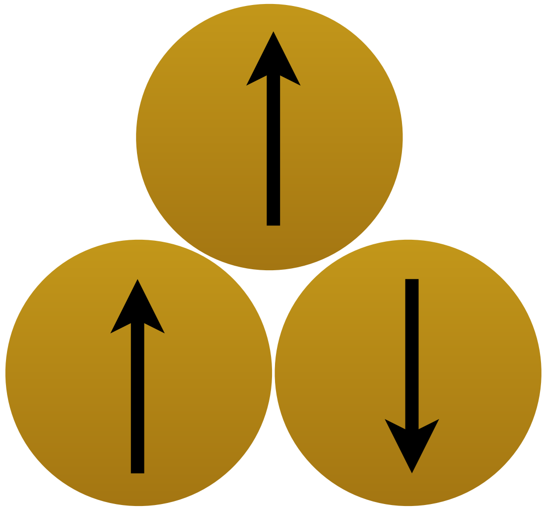
Generating non-collinear magnetism by spin frustration with transition metals



Lock metal trimer into D_{3h}

Problem: Just because you use GHF doesn't mean you converge to this lower energy solution!

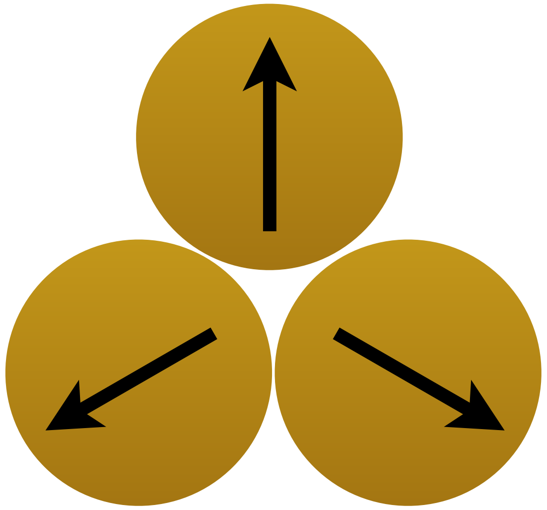
After many attempts with GHF…



Cr_3 / UHF / LANL2DZ

GHF lower in energy by 7.5 kcal mol^{-1}

D_{3h} / 2.89A



Cr_3 / GHF / LANL2DZ

Usually we landed on UHF solution(s).

Try changing initial guess, swapping orbitals, etc.

Is there a more robust way to get to GHF solution?

How do we get there?

Looking at how we change in energy
as we change orbital coefficients:

We wanted to find solutions that satisfied two conditions

(1) First variation equal to zero.
(2) Second variation greater than or equal to zero.

(1) is equivalent to Brillouin's theorem.
e.g. Fock matrix elements between occupied and virtual orbitals are zero. Satisfied if HF equations converged.

How do we get there?

(2) requires that the electronic Hessian is positive (semi) definite

In matrix form, this means

eigenvalues of $\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}$ need to be ≥ 0

$$A_{ia,jb} = \underbrace{(\epsilon_a - \epsilon_i)\delta_{ia,jb}}_{\text{orbital energy difference}} + \underbrace{\langle aj||ib\rangle}_{\text{orbital repulsion}} \qquad B_{ia,jb} = \underbrace{\langle ab||ij\rangle}_{\text{orbital repulsion}}$$

How do we get there?

Since all positive semi-definite matrices have positive (or zero) eigenvalues, we can determine if our solution is locally stable by diagonalizing the Hessian

If we run into negative eigenvalues, we pick the lowest one and its associated eigenvector (J).

We take a step (s) in the direction of the eigenvector and re-optimize.

$$\mathbf{C}' = e^{-s\mathbf{K}}\mathbf{C}$$

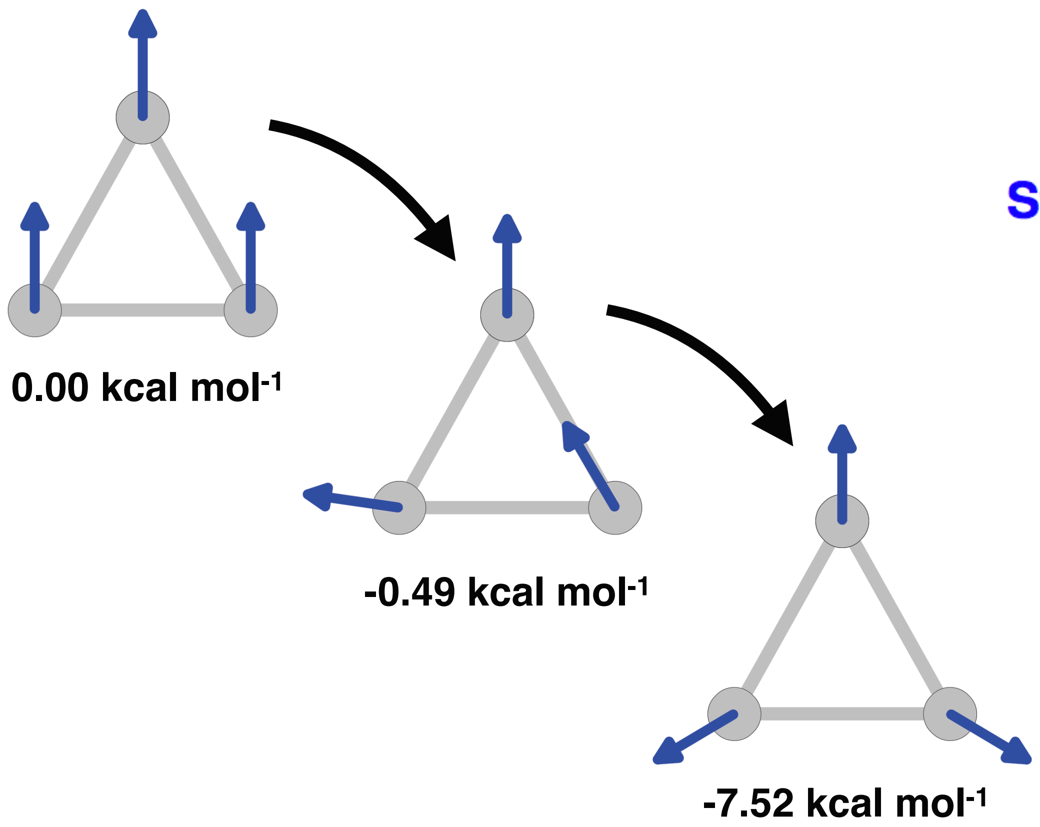
$$\mathbf{K} = \begin{pmatrix} \mathbf{0} & -\mathbf{J}^\dagger \\ \mathbf{J} & \mathbf{0} \end{pmatrix}$$

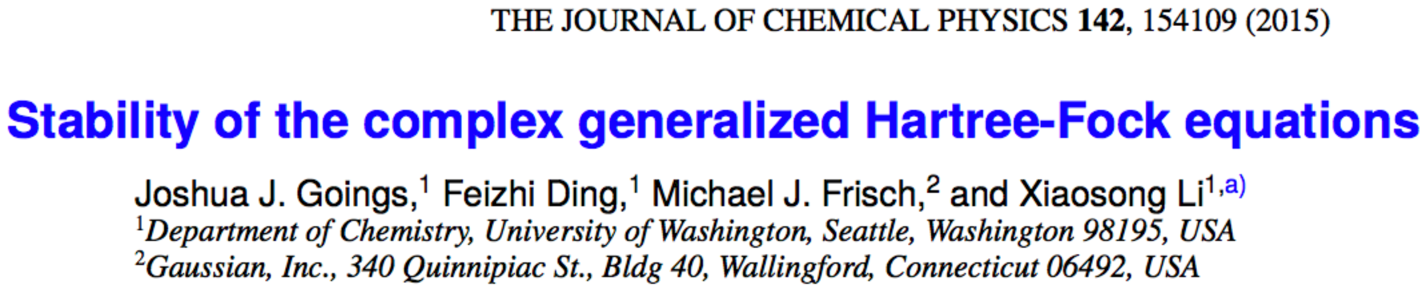
J is steepest-descent eigenvector, C and C’ are old and new orbitals

Conclusions:

If a lower-energy, lower-symmetry solution to the IPM exists, GHF can (in theory) find it.

We guarantee we are at a local minima by examining the eigenvalues of our Hessian. If we aren't, we have a defined method to move towards a local minima.

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Stability of the complex generalized Hartree-Fock equations

Joshua J. Goings,[1] Feizhi Ding,[1] Michael J. Frisch,[2] and Xiaosong Li[1,a)]

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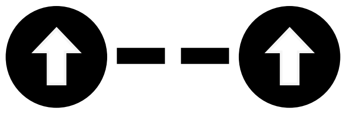
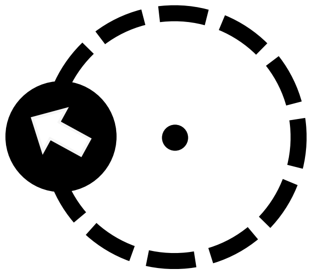
Cr_3 / GHF / LANL2DZ

D_{3h} / 2.89A

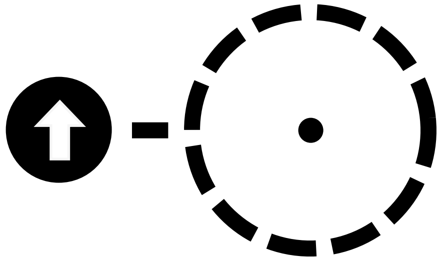
Two component GHF isn't just useful for spin frustrated systems. It is also a useful framework for including relativistic effects in your calculations.



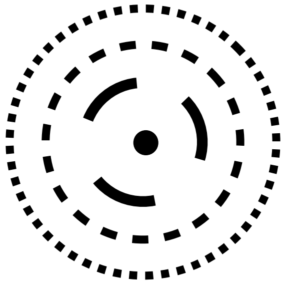
spin-spin interaction



spin-own-orbit interaction



spin-other-orbit interaction



orbital contraction

Not observable in themselves, but necessary to include for accurate descriptions of certain phenomena
(e.g. electronic excitations between spin states)

A relativistic theory of the electron is given by the Dirac equation

$$i\hbar\frac{\partial}{\partial t}\psi = c\alpha\cdot\left(-i\hbar\nabla\right)\psi + \beta mc^2\psi$$

Where

$$\alpha_k = \begin{bmatrix}\mathbf{0}_2 & \sigma_k \\ \sigma_k & \mathbf{0}_2\end{bmatrix}, k = x, y, z \qquad \beta = \begin{bmatrix}\mathbf{I}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & \mathbf{I}_2\end{bmatrix}$$

The equation is four-component, and in principle describes any spin-1/2 particle.

Because of the symmetry of the equation, it describes electrons as well as positrons

We care about electrons, and all two-component methods seek to decouple the positron and electronic solutions

e.g. from four-component Dirac-Fock

$$\mathbf{U}^{\dagger}\begin{pmatrix}\mathbf{H}^{LL} & \mathbf{H}^{LS} \\ \mathbf{H}^{SL} & \mathbf{H}^{SS}\end{pmatrix}\mathbf{U} = \begin{pmatrix}\mathbf{H}^{+} & 0 \\ 0 & \mathbf{H}^{-}\end{pmatrix}$$

Where each block is spin-blocked two-component, e.g.

$$\mathbf{H} = \begin{pmatrix}\mathbf{H}^{\alpha\alpha} & \mathbf{H}^{\alpha\beta} \\ \mathbf{H}^{\beta\alpha} & \mathbf{H}^{\beta\beta}\end{pmatrix}$$

No analytic expression for the decoupling operator!

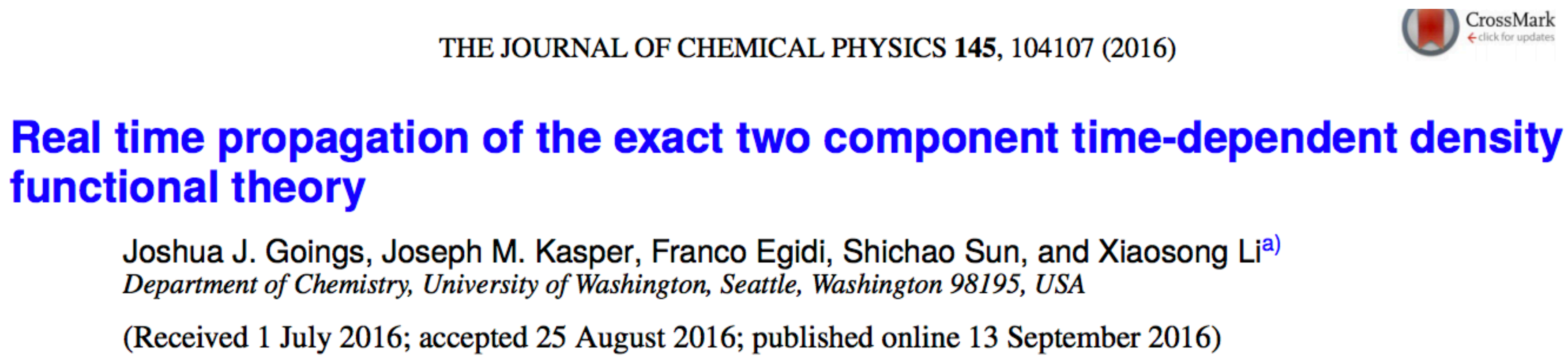
There are many ways we can accomplish the decoupling, most well-detailed in the literature.

$$\mathbf{U}^{\dagger}\begin{pmatrix}\mathbf{H}^{LL} & \mathbf{H}^{LS}\\ \mathbf{H}^{SL} & \mathbf{H}^{SS}\end{pmatrix}\mathbf{U}=\begin{pmatrix}\mathbf{H}^{+} & 0\\ 0 & \mathbf{H}^{-}\end{pmatrix}$$

DKH: Decoupling by nesting a series of unitary transformations

X2C: Decouple full equations through exact decoupling of one-electron parts

More important to our purposes is **utilizing their solutions in order to access spectroscopic observables**



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Real time propagation of the exact two component time-dependent density functional theory

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We want to use **explicitly time-dependent theory** to extract **absorption spectra** of atoms and molecules

This is a computationally efficient way of computing a full band spectrum

Furthermore, we want to allow for relativistic effects e.g. spin-forbidden transitions

Necessary for even qualitatively correct spectra.

The target quantity of interest is the frequency-dependent dipole-dipole polarizability

$$\boldsymbol{\alpha}(\omega) = \begin{pmatrix} \alpha_{xx}(\omega) & \alpha_{xy}(\omega) & \alpha_{xz}(\omega) \\ \alpha_{yx}(\omega) & \alpha_{yy}(\omega) & \alpha_{yz}(\omega) \\ \alpha_{zx}(\omega) & \alpha_{zy}(\omega) & \alpha_{zz}(\omega) \end{pmatrix}$$

The trace is proportional to the measured absorption spectra

Strategy:

Perturb the relativistic two-component solutions with an electric field, then correlate perturbation with time-dependent dipole moment

$$\mu_i(t) = \mu_i(0) + \int_{-\infty}^{t} \alpha_{ij}(t-\tau)E_i(\tau)d\tau + \cdots$$

time-dependent
electric dipole

dynamic
polarizability

applied
electric field

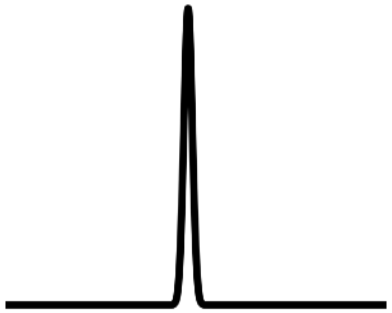
Carefully choosing our electric field, we can access $\alpha_{ij}(t)$

The electric field enters our 2c Hamiltonian as

$$\mathbf{F}_{\mathrm{E}}(t) = \mathbf{F}(t) - \sum_{q=x,y,z} E_i(t)\mathbf{d}_i \xleftarrow{} \text{dipole integrals}$$

Choosing electric field such that

$$E(t) = \begin{cases} E_{\max}, & 0 < t < \Delta t, \\ 0, & else \end{cases}$$



Our applied field is an effective delta pulse

This means the Fourier transform of

$$\mu_i(t) = \mu_i(0) + \int_{-\infty}^{t} \alpha_{ij}(t-\tau)E_i(\tau)d\tau$$

Is written simply as (convolution of Dirac delta)

$$\Delta\mu_i(\omega) = \alpha_{ij}(\omega)E_{\max} \quad \text{or,} \quad \alpha_{ij}(\omega) = \frac{\Delta\mu_i(\omega)}{E_{\max}} \propto S(\omega)$$

This governs the intensity of an absorption spectrum

We have a way of perturbing our system, now to solve in time

$$\frac{\partial}{\partial t}\begin{pmatrix} \mathbf{C}^{\alpha\alpha}(t) & \mathbf{C}^{\alpha\beta}(t) \\ \mathbf{C}^{\beta\alpha}(t) & \mathbf{C}^{\beta\beta}(t) \end{pmatrix} = -i\begin{pmatrix} \mathbf{F}^{\alpha\alpha}(t) & \mathbf{F}^{\alpha\beta}(t) \\ \mathbf{F}^{\beta\alpha}(t) & \mathbf{F}^{\beta\beta}(t) \end{pmatrix}\cdot\begin{pmatrix} \mathbf{C}^{\alpha\alpha}(t) & \mathbf{C}^{\alpha\beta}(t) \\ \mathbf{C}^{\beta\alpha}(t) & \mathbf{C}^{\beta\beta}(t) \end{pmatrix}$$

It can be shown that

$$\begin{aligned} \mathbf{C}(t) &\approx \exp\left(-it\mathbf{F}(t)\right)\ \mathbf{C}(0) \\ \mathbf{P}(t) &\approx \exp\left(-it\mathbf{F}(t)\right)\ \mathbf{P}(0)\,\exp\left(it\mathbf{F}(t)\right) \end{aligned}$$

We use the modified-midpoint unitary transformation (MMUT)

Modified Midpoint Unitary Transformation (MMUT)

$$\mathbf{C}^{\dagger}(t_n) \cdot \mathbf{F}(t_n) \cdot \mathbf{C}(t_n) = \boldsymbol{\epsilon}(t_n)$$

$$\begin{aligned}\mathbf{U}(t_n) &= \exp\big[-i \cdot 2\Delta t \cdot \mathbf{F}(t_n)\big] \\ &= \mathbf{C}(t_n) \cdot \exp\big[-i \cdot 2\Delta t \cdot \boldsymbol{\epsilon}(t_n)\big] \cdot \mathbf{C}^{\dagger}(t_n)\end{aligned}$$

Propagate density **P** forward in time

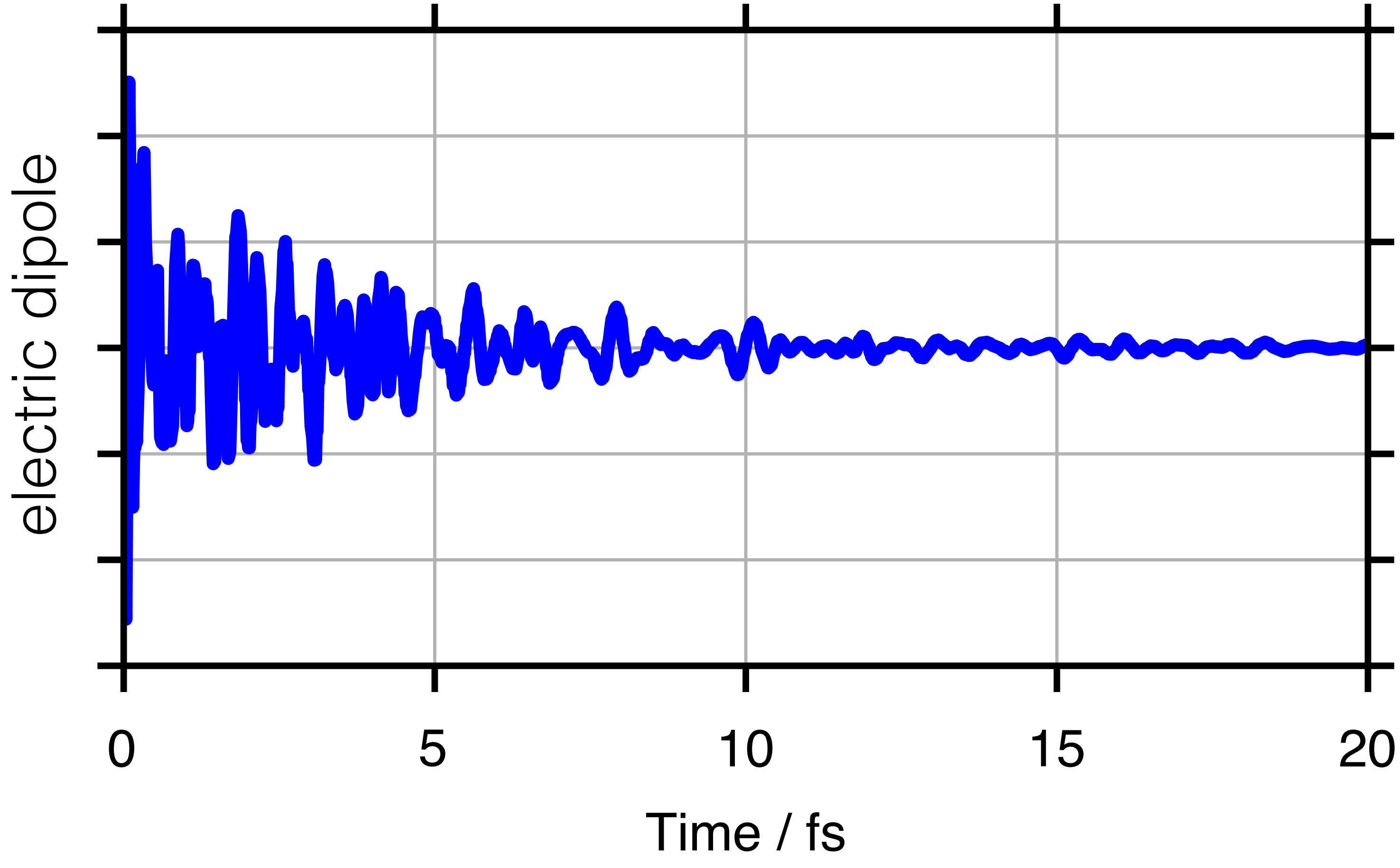
$$\mathbf{P}(t_{n+1}) = \mathbf{U}(t_n) \cdot \mathbf{P}(t_{n-1}) \cdot \mathbf{U}^{\dagger}(t_n)$$

At each time *t* we can compute the time-evolving dipole moment from a trace over the time-dependent density

“Perturbing-then-propagating” gives a time-dependent dipole

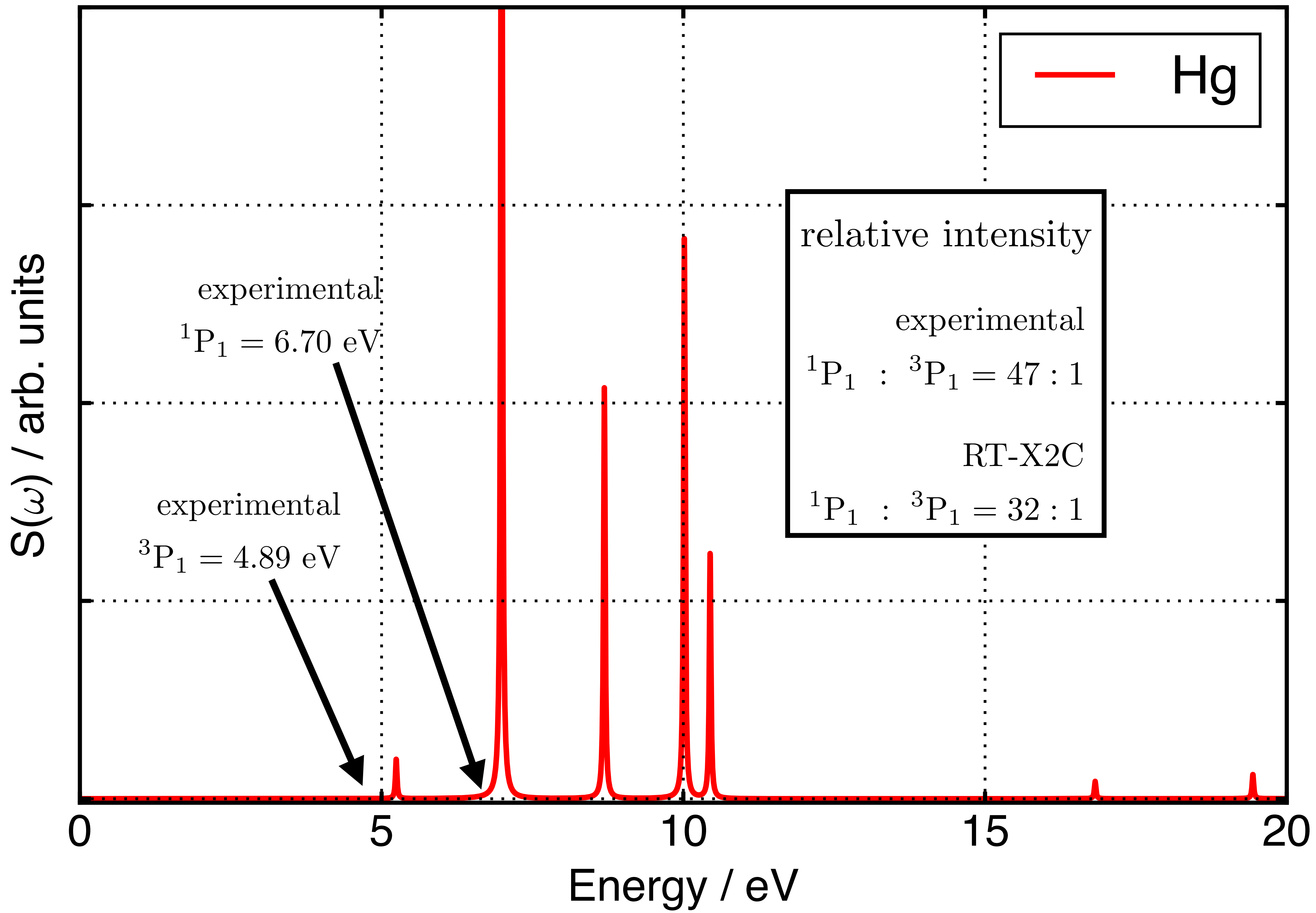
To give each peak a finite width,
we artificially damp by an exponential

$$\boldsymbol{m}'(t) = \boldsymbol{m}(t)e^{-t/a}$$



This effectively “dresses” each peak as a Lorentzian

Testing on atomic mercury, we get "spin-forbidden" transitions



experimental
$^1P_1 = 6.70$ eV

experimental
$^3P_1 = 4.89$ eV

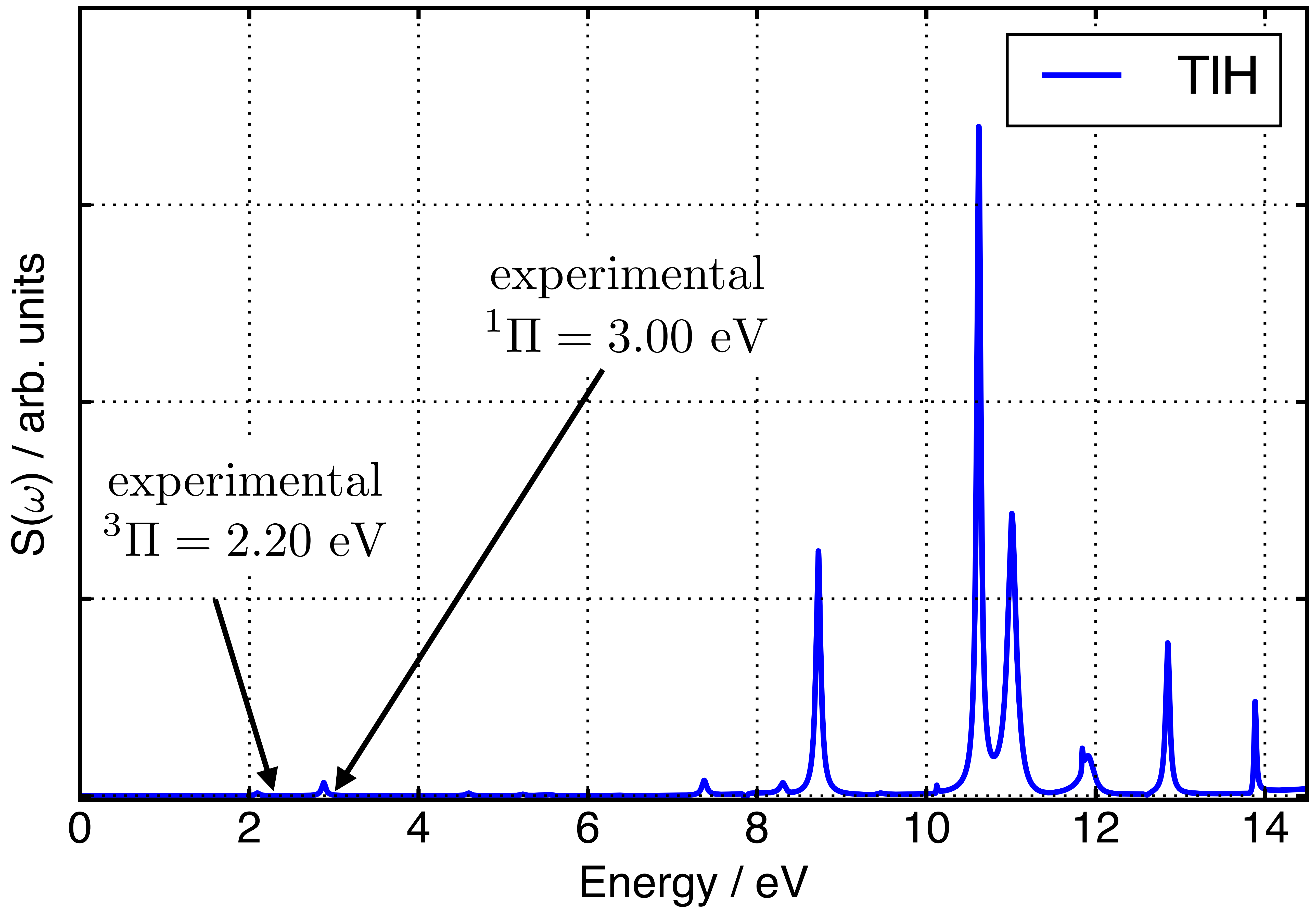
relative intensity

experimental
$^1P_1 : {}^3P_1 = 47 : 1$

RT-X2C
$^1P_1 : {}^3P_1 = 32 : 1$

Morton, Donald C. "Atomic data for resonance absorption lines. II. Wavelengths longward of the Lyman limit for heavy elements." *AJS* 130.2 (2000): 403.

Similar story for diatomic TlH



experimental
$^1\Pi = 3.00$ eV

experimental
$^3\Pi = 2.20$ eV

Movie time!

Conclusions:

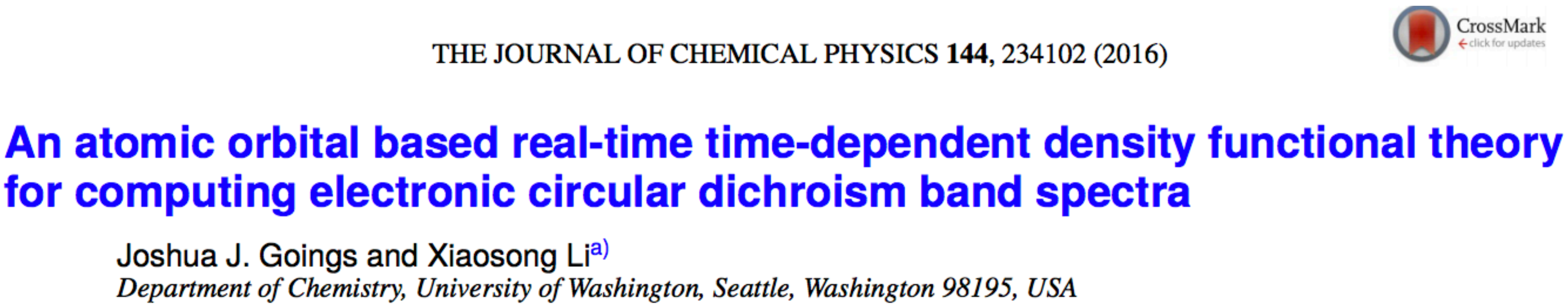
Relativistic effects can (variationally) be incorporated into two-component methods

By choosing a suitable perturbation, we can extract spectroscopic properties (e.g. absorption spectrum)

This gives an alternate (and, in some cases, more efficient) route to including relativistic effects in predicted spectra

We can do non-perturbative fields as well!

Explicit time-dependent techniques are also useful for looking at other types of spectroscopy, regardless of components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An atomic orbital based real-time time-dependent density functional theory for computing electronic circular dichroism band spectra

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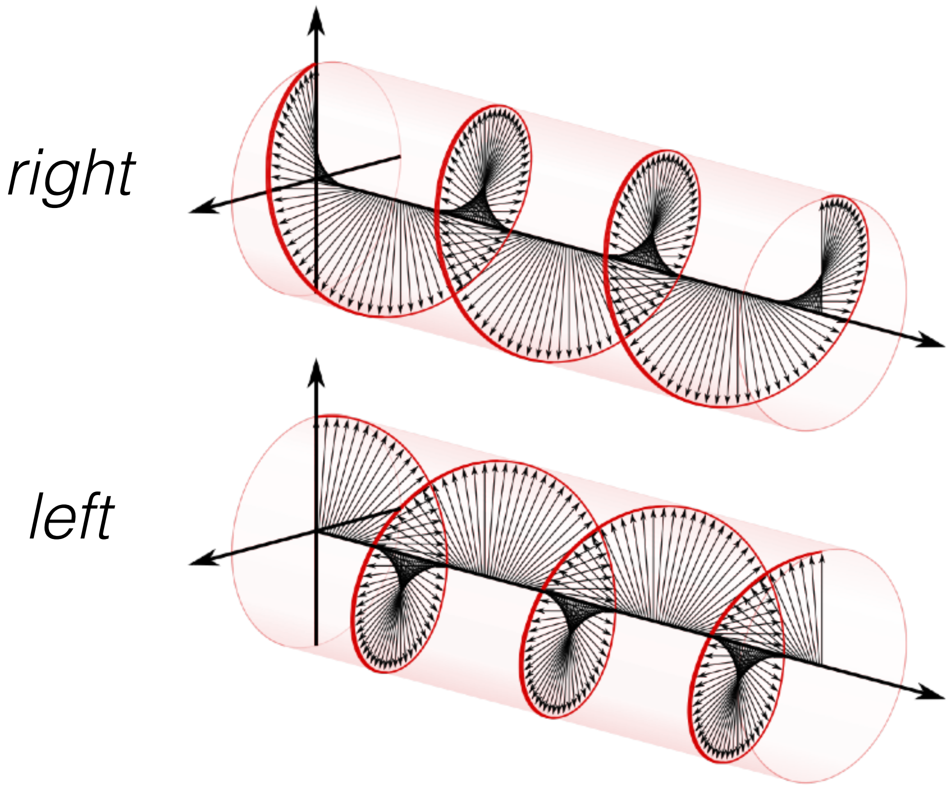
Circular dichroism, which is based on a magnetic response to an electric perturbation, is one such example.

Natural circular dichroism:

Differential absorption of circularly polarized light by chiral molecules

Gives a method of distinguishing enantiomers



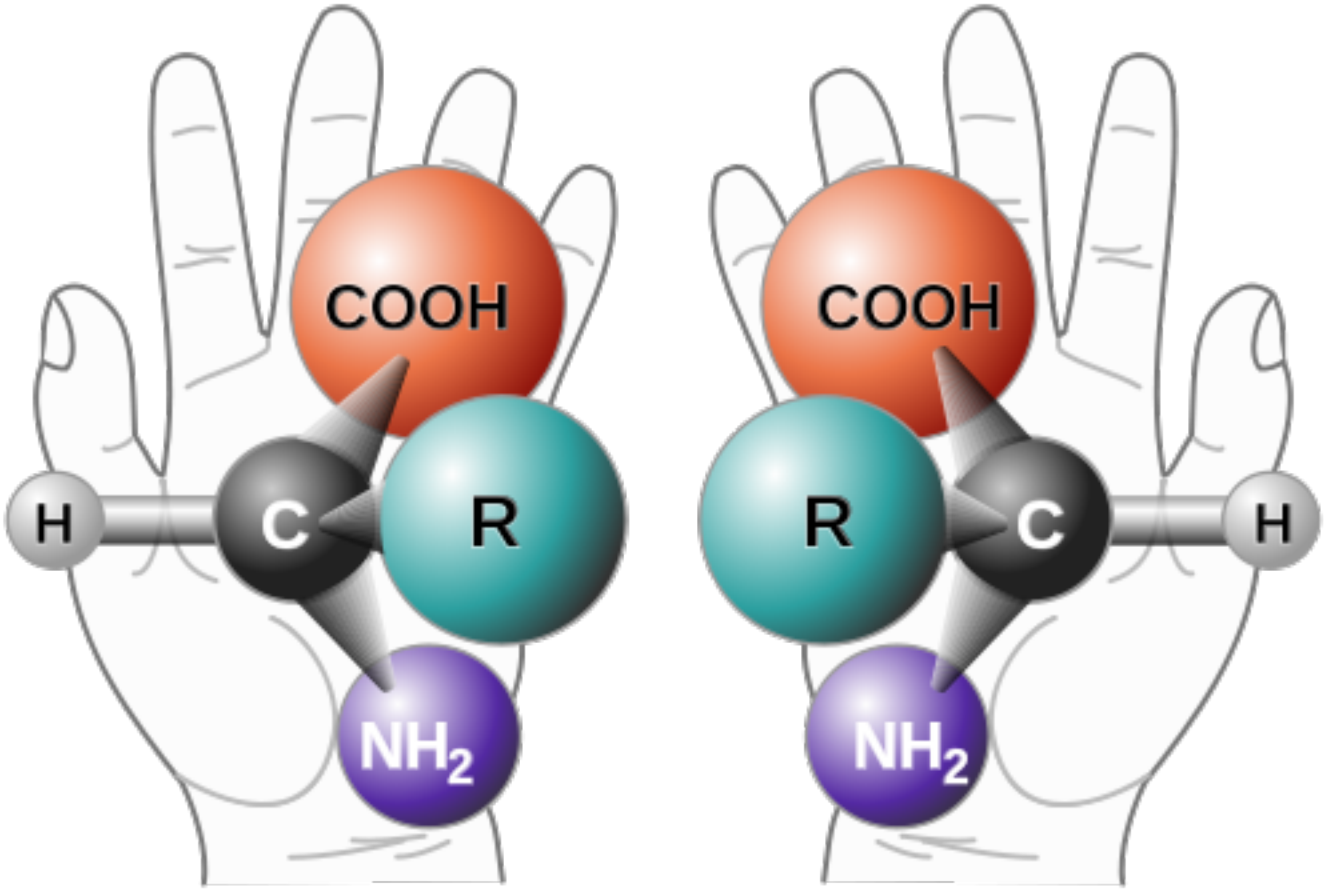


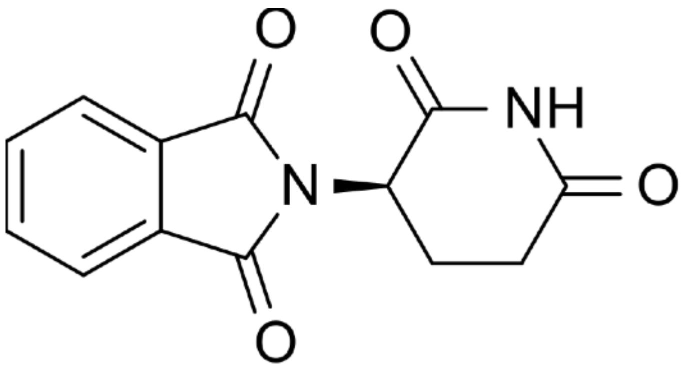
Image source: NASA (http://www.nai.arc.nasa.gov/)

By Dave3457 - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=9861553

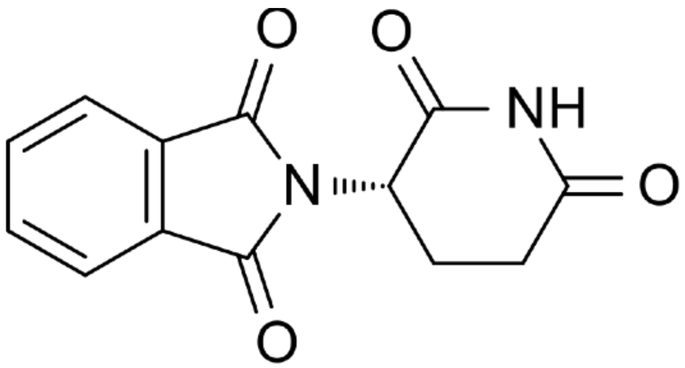
Why is this important?

Thalidomide tragedy

effective



(R)-thalidomide



(S)-thalidomide

tetragenic

Image source: Otis Historical Archives National Museum of Health and Medicine

In CD spectroscopy,
we usually care about rotatory strength

$$R(n \leftarrow 0) = \mathrm{Im}\langle 0|\boldsymbol{\mu}|n\rangle\langle n|\boldsymbol{m}|0\rangle$$

Which characterizes the intensity of an isotropic CD transition

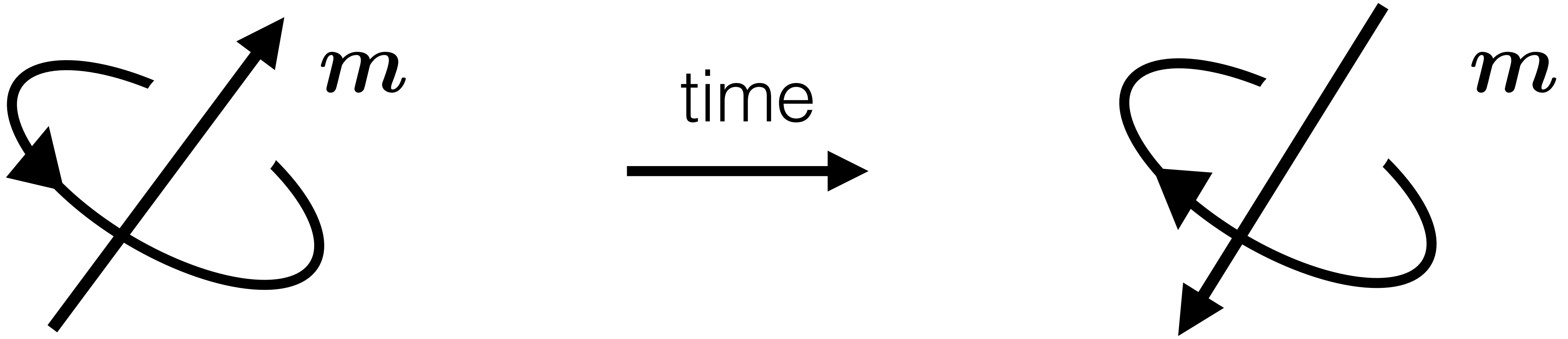
$\boldsymbol{\mu}$	electric dipole
$\boldsymbol{m}$	magnetic dipole

$$R(n \leftarrow 0) = \mathrm{Im}\langle 0|\boldsymbol{\mu}|n\rangle\langle n|\boldsymbol{m}|0\rangle$$

$\boldsymbol{\mu}$ electric dipole

$\boldsymbol{m}$ magnetic dipole

Chiral molecules can support an oscillating current density, which arises as a result of a perturbing electric field



It’s important to note that

$$R(n \leftarrow 0) = \mathrm{Im}\langle 0|\boldsymbol{\mu}|n\rangle\langle n|\boldsymbol{m}|0\rangle$$

Only holds for isotropic (non-oriented) systems

For oriented systems,
(especially in X-ray CD spectroscopy)
we must also include the induced
electric dipole — electric quadrupole

Getting good (experimentally meaningful) CD spectra
is not a trivial task

CD spectra can take positive and negative values

CD very sensitive to geometry,
functional / wave function, and basis

Vibronic effects (and VCD) further
complicate interpretation of spectra

Linear response:

TDDFT: Furche, 2001;
Autschbach, *et al.* 2002;
Stephens, *et al.* 2002;
Diedrich and Grimme 2003;
Caricato, 2014, 2015;
many more!

CC: Crawford, 2006;

Great if you want to study a specific transition,
gets expensive if you want the full band spectrum

Rotatory strength is given as

$$R(\omega) = \frac{\omega}{\pi c} \mathrm{Im}\left[\mathrm{Tr}\left(\boldsymbol{\beta}(\omega)\right)\right]$$

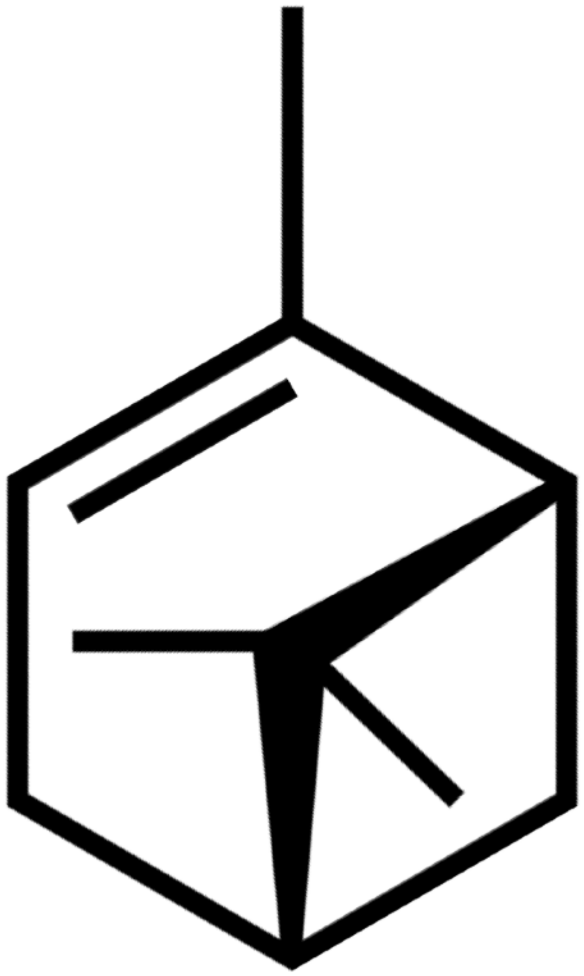
We can access magnetic-dipole—electric dipole polarizability from an explicit time-dependent approach

With a delta field, e.g. $E(t) = E\delta(t)$

$$\beta_{jk}(\omega) = \frac{ic}{\omega E_k} m_j(\omega)$$

Measure how much the magnetic dipole changes as a function of perturbing electric dipole

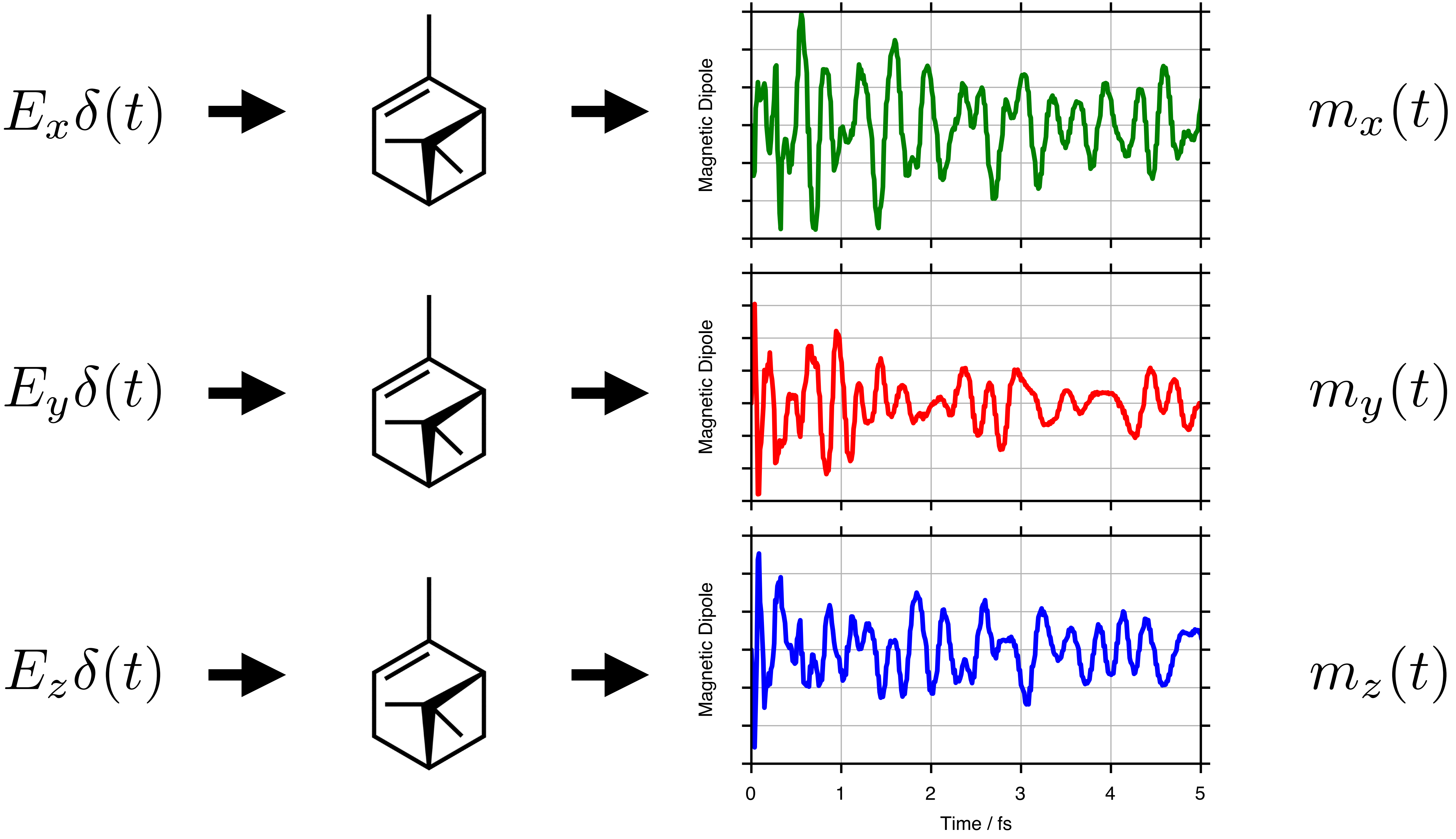
Example: RT-ECD with alpha-1,3-(R,R)-pinene



(R,R): North American

(S,S): European

Perturb with delta $E(t)$



$E_x\delta(t) \rightarrow \rightarrow m_x(t)$

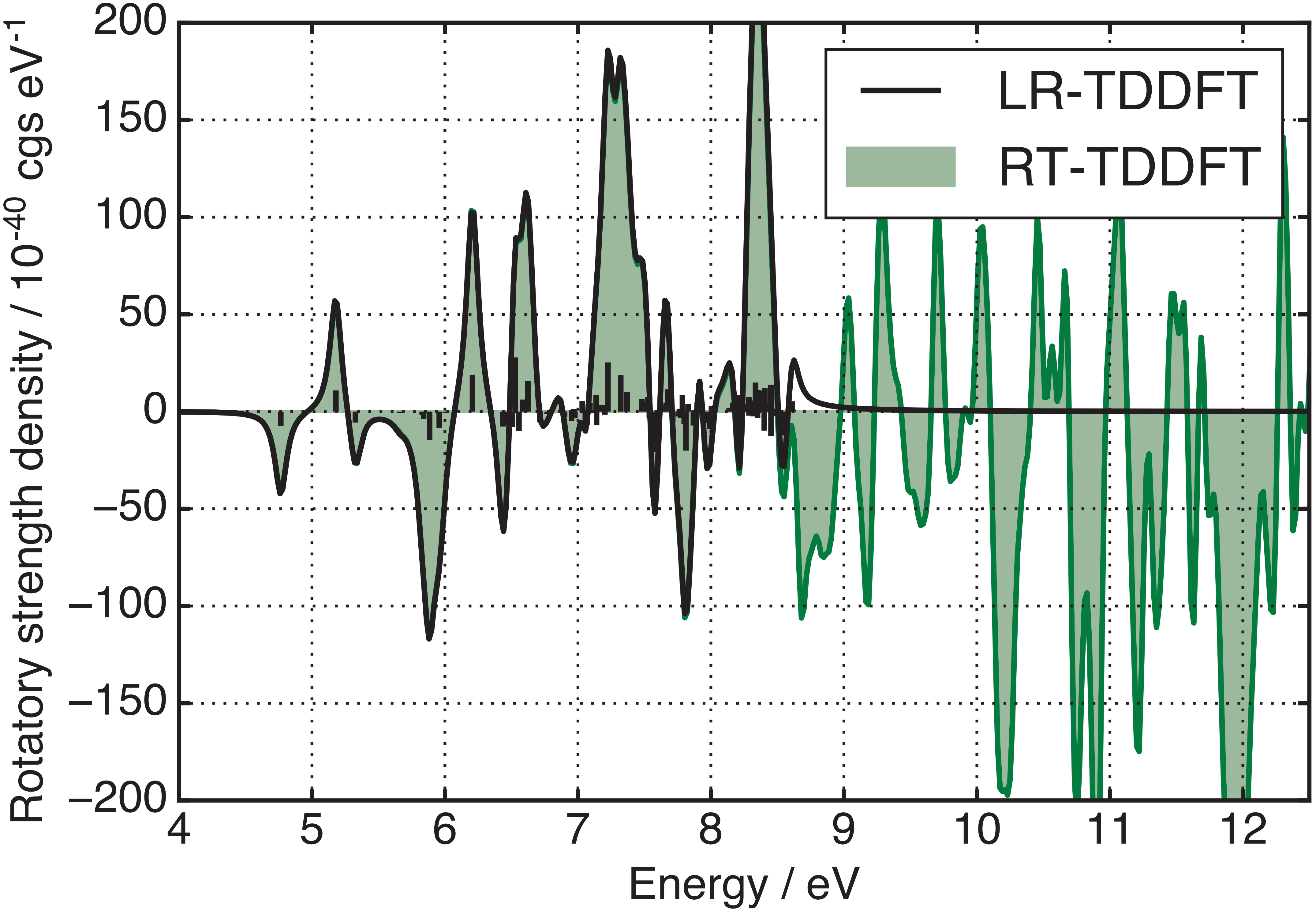
$E_y\delta(t) \rightarrow \rightarrow m_y(t)$

$E_z\delta(t) \rightarrow \rightarrow m_z(t)$

Fourier transforming TD magnetic dipole, substitute components

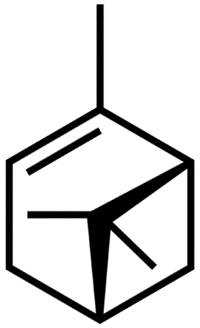
$$R(\omega) = \frac{i}{\pi}\mathrm{Im}\left[\mathrm{Tr}\left(\frac{m_j\left(\omega\right)}{E_j}\right)\right]$$

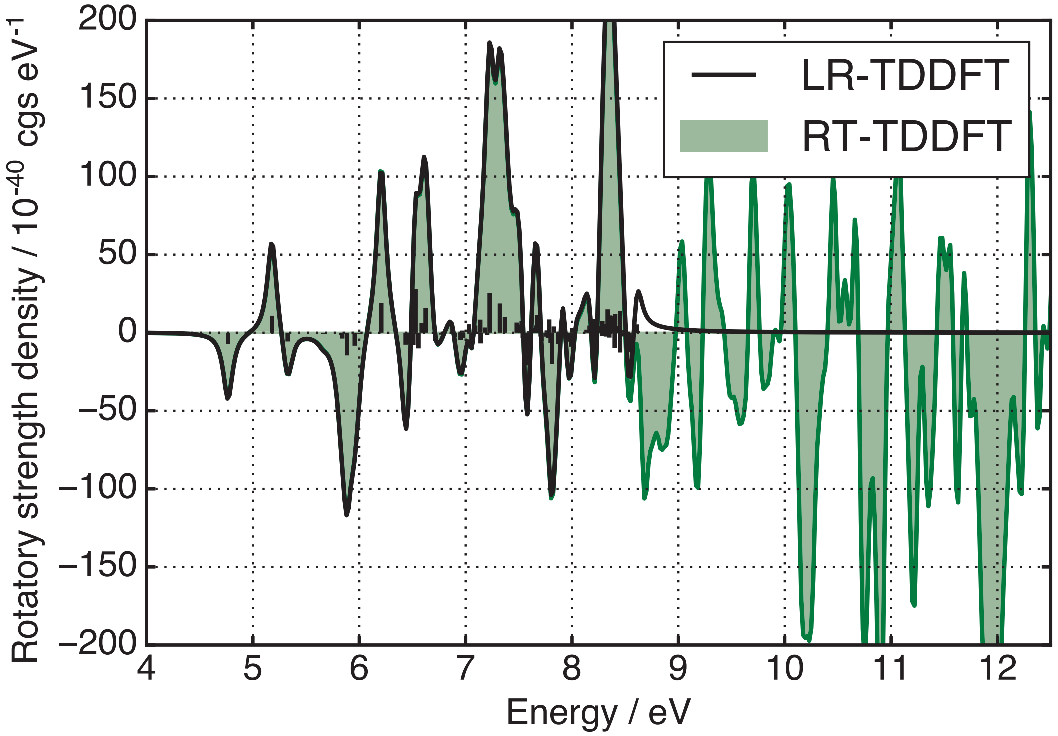
$$= \frac{1}{\pi}\mathrm{Re}\left[\mathrm{Tr}\left(\frac{m_j\left(\omega\right)}{E_j}\right)\right]$$



With a weak delta field, we can recover LR-TDDFT

B3LYP/6-31+G*



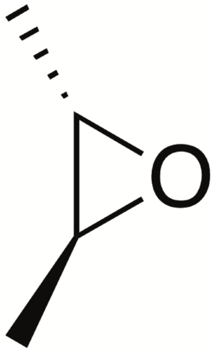


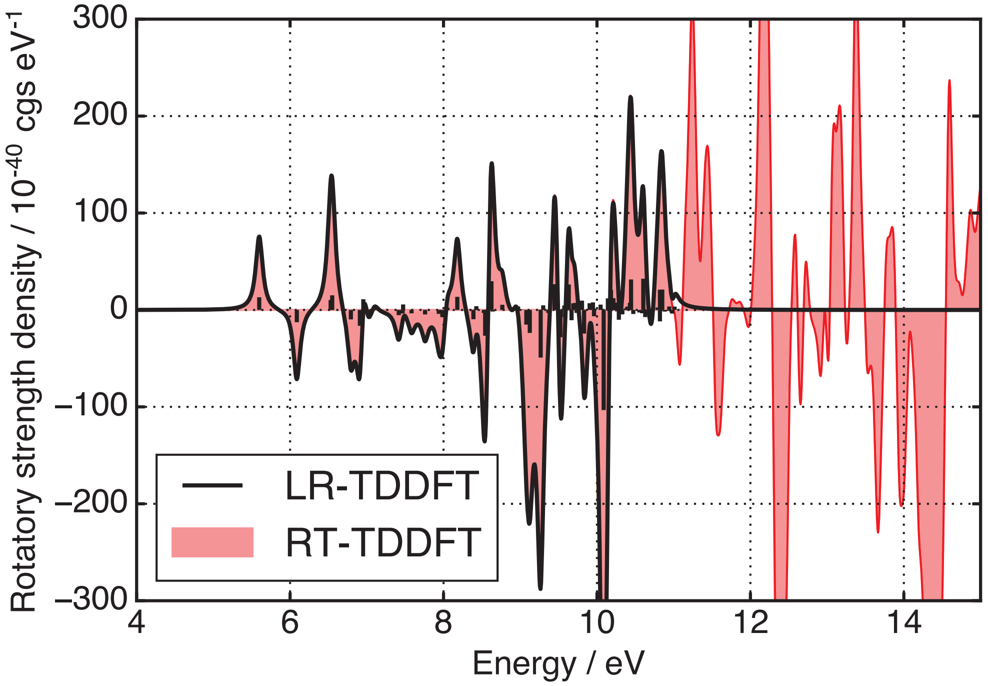
Compare to first 100 LR-TDDFT states

Resolution limited by propagation time

Here, at least 100 fs, 0.012 fs time step

2,3-(S,S)-dimethyloxirane





Conclusions:

Explicit time-dependent techniques can be extended to multiple types of spectroscopy

We showed this by deriving expressions for, and computing, circular dichroism

These techniques will be most efficient for large systems with a high density of states where many bands are of interest

Wrapping up…

We’ve showed how to get and check stability of two-component electronic structure methods

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How to use two-component methods to include relativistic effects for absorption spectra (real-time methods)

Wrapping up…

We've showed how to get and check stability of two-component electronic structure methods

How to use two-component methods to include relativistic effects for absorption spectra (real-time methods)

How to use the real-time techniques to other types of spectra, such as circular dichroism

Thank you

As an example…

The electronic Hamiltonian is invariant to unitary spin transformations about the z-axis.

$$\hat{U}(\theta, \mathbf{n}_z) = e^{i\theta \hat{S}_z}$$

So that: $e^{i\theta \hat{S}_z} \hat{H} e^{-i\theta \hat{S}_z} = \hat{H}$

For any real angle theta about the z-axis

We often claim UHF is invariant to $\hat{S}_z$

$$\hat{S}_z \propto \sigma_z = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}$$

Let’s show this (overlooking a few details).

$$\hat{U} \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix} \hat{U}^{-1} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix}$$

$$\begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & -\mathbf{F}_{\alpha\beta} \\ -\mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix}$$

Which is true if and only if $\mathbf{F} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{F}_{\beta\beta} \end{pmatrix}$