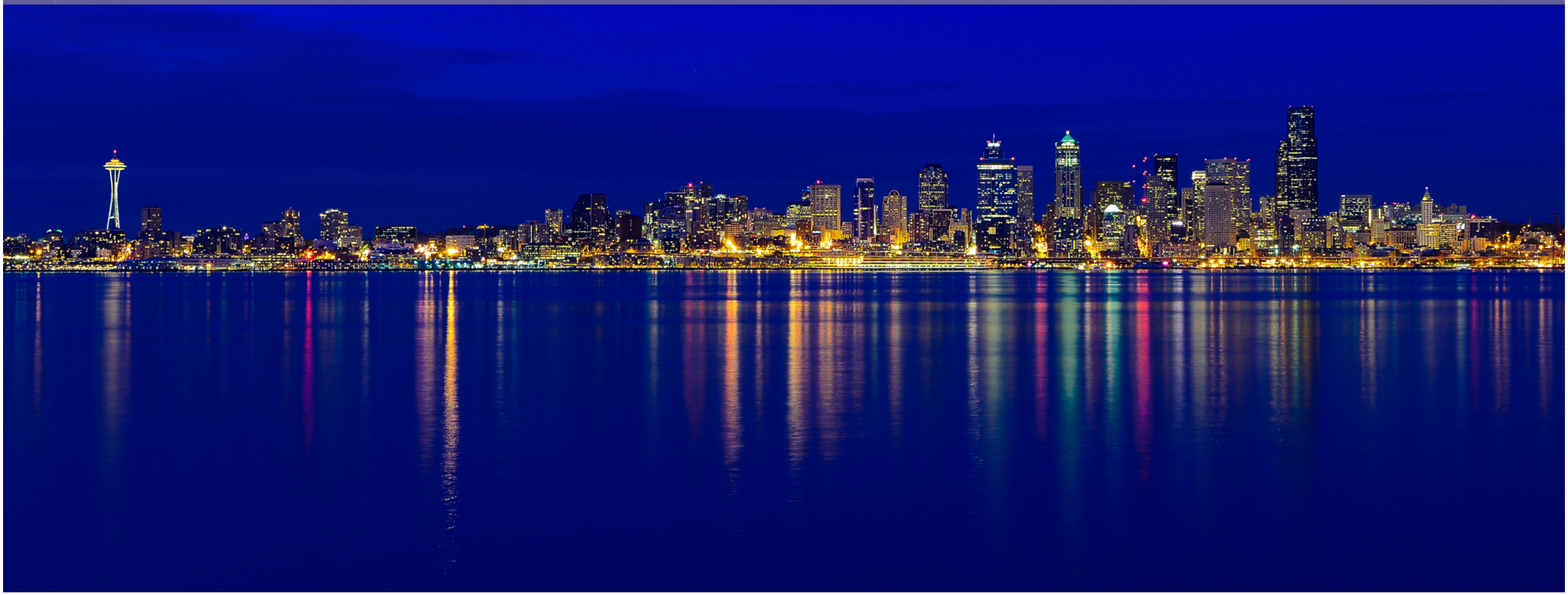
Two-Component Ehrenfest Dynamics

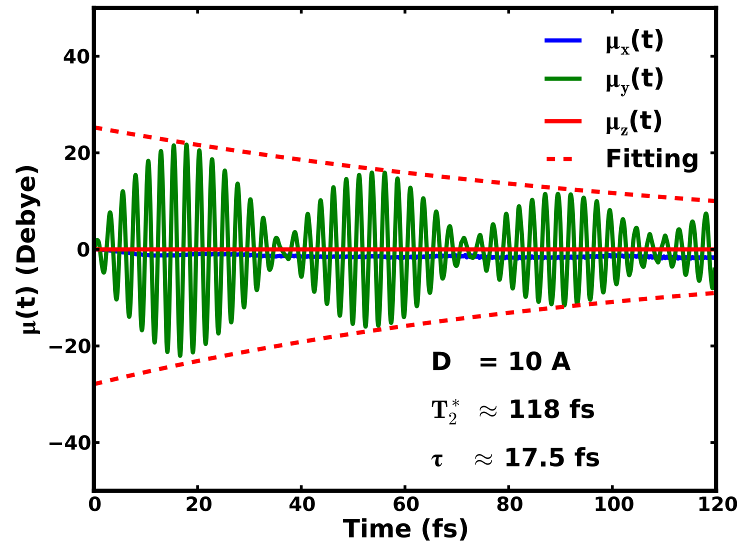


Li Research Group

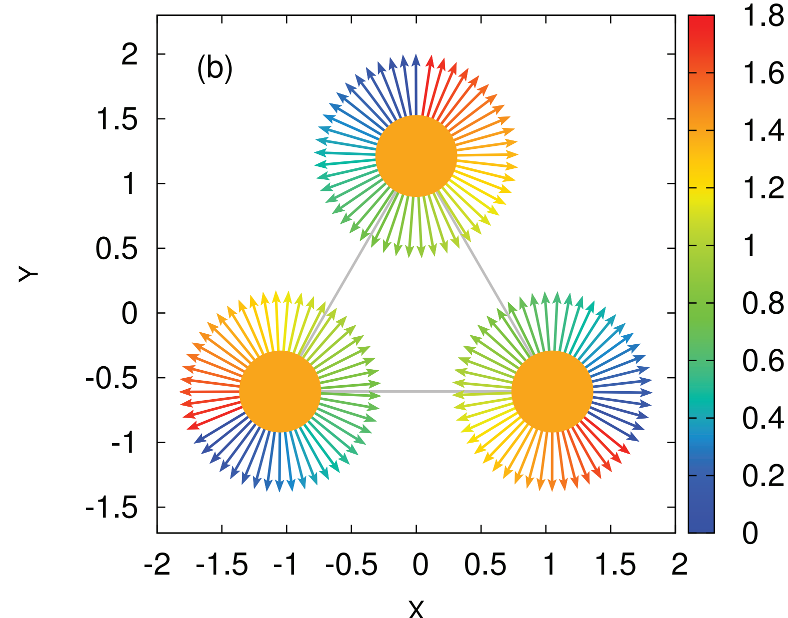
University of Washington, Seattle

Outline

- Quantum Electronic Dynamics Background
  - Decay of Coherent-Exciton



- Time-Dependent Two-Component HF/DFT Theory
  - Spin-Frustration Dynamics
  - Spin-Wave
  - Two-Component Ehrenfest

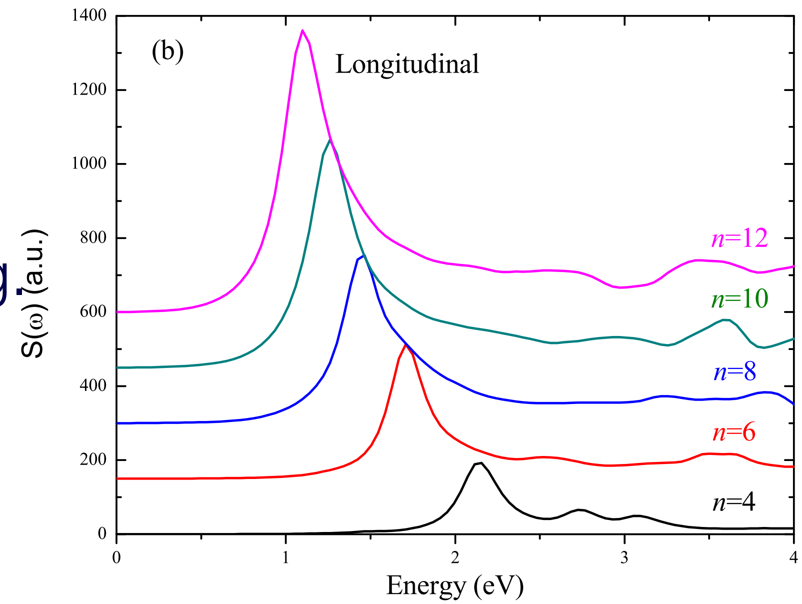


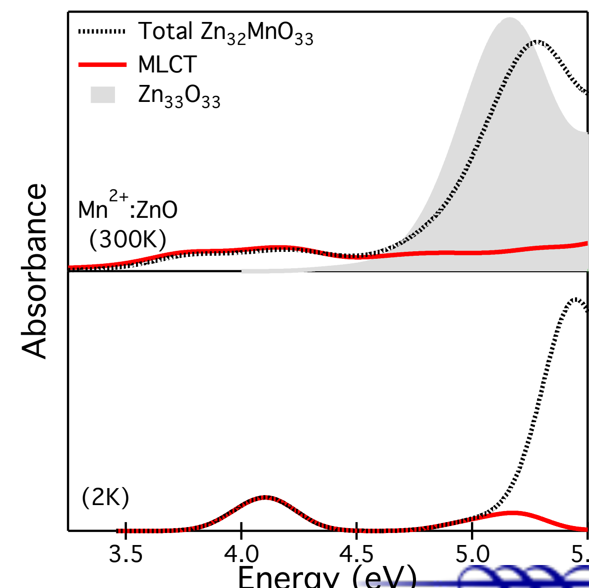
TD Electronic Structure Theory

$$i\frac{d}{dt}\Psi(t) = \hat{H}(t)\Psi(t)$$

$$\Psi(t) = \Phi(r)\cdot\Phi(R)$$

- Expansion in terms of perturbations (e.g. electric field)
  - First order approximation: RPA, linear response TDDFT
  - Second order approximation: quadratic response, two-particle propagator
- Real-Time Integration
  - Non-equilibrium quantum dynamics
  - Linear and non-linear optical properties





X. Li, *et. al.* "*An Efficient Method for Calculating Dynamical Hyperpolarizabilities using Real-time Time-dependent Density Functional Theory*," JCP, 2013, 138, 064104.

N. Govind, *et al.* "*Near and Above Ionization Electronic Excitations with Non-Hermitian Real-Time Time-Dependent Density Functional Theory*", JCTC, 2013, 9, 4939

TDDFT Electronic Dynamics

$$i\frac{d}{dt}\Psi(t) = \hat{H}(t)\Psi(t)$$

$$\Psi(t) = \Phi(r)\cdot\Phi(R)$$

- Unitary Transformation TDDFT

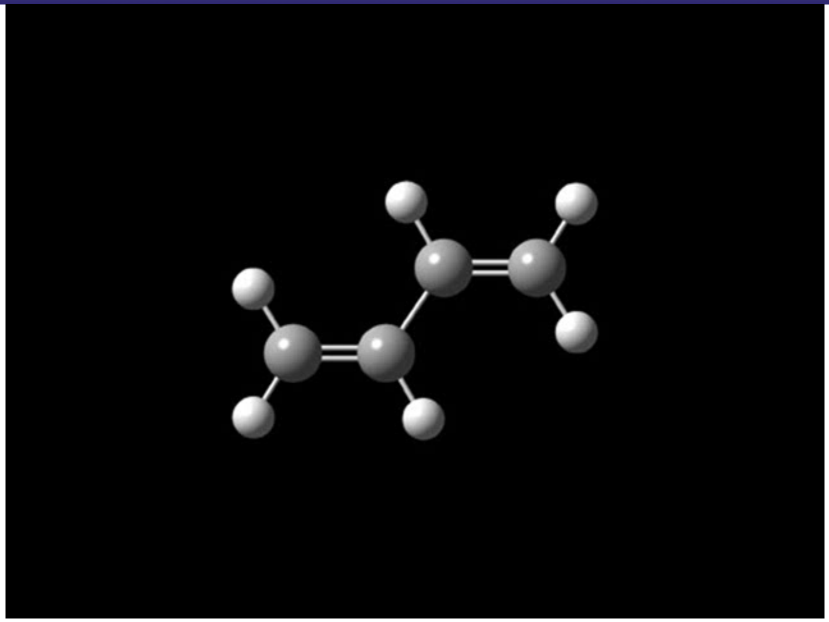
$$i\frac{d\mathbf{P}(t_k)}{dt} = [\mathbf{K}(t_k),\mathbf{P}(t_k)]$$

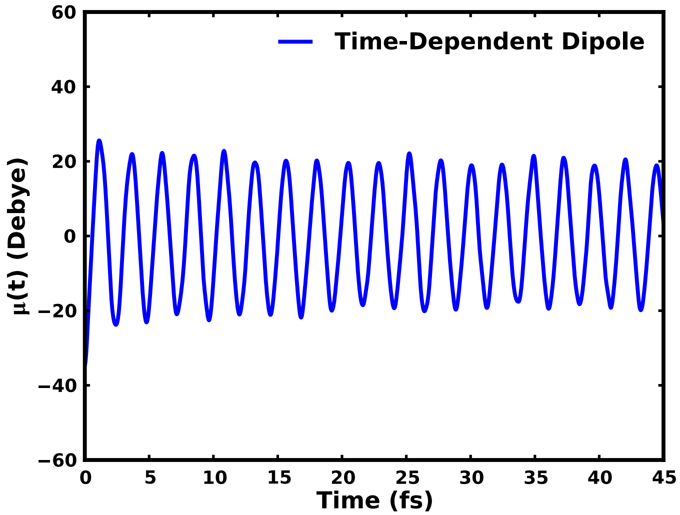
$$\mathbf{P}_{k+1} = \mathbf{U}(t_k)\cdot\mathbf{P}(t_{k-1})\cdot\mathbf{U}^{\dagger}(t_k)$$

$$\mathbf{U}(t_k) = \exp[i\cdot 2\Delta t_e\cdot\mathbf{K}(t_k)]$$

$$\mathbf{C}^{\dagger}(t_k)\cdot\mathbf{K}(t_k)\cdot\mathbf{C}(t_k) = \varepsilon(t_k)$$

$$\mathbf{U}(t_k) = \mathbf{C}(t_k)\cdot\exp[i\cdot 2\Delta t_e\cdot\varepsilon(t_k)]\cdot\mathbf{C}^{\dagger}(t_k)$$



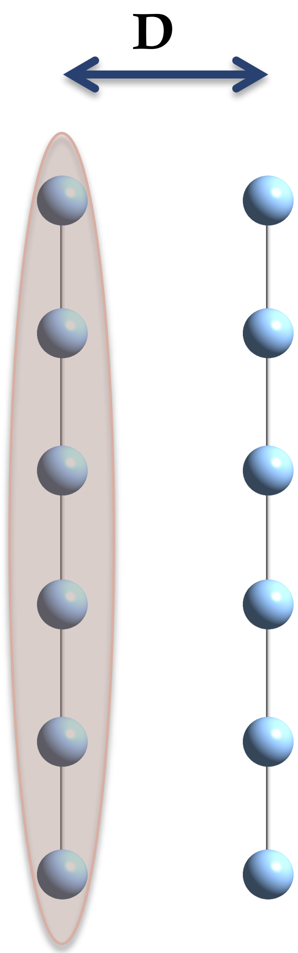


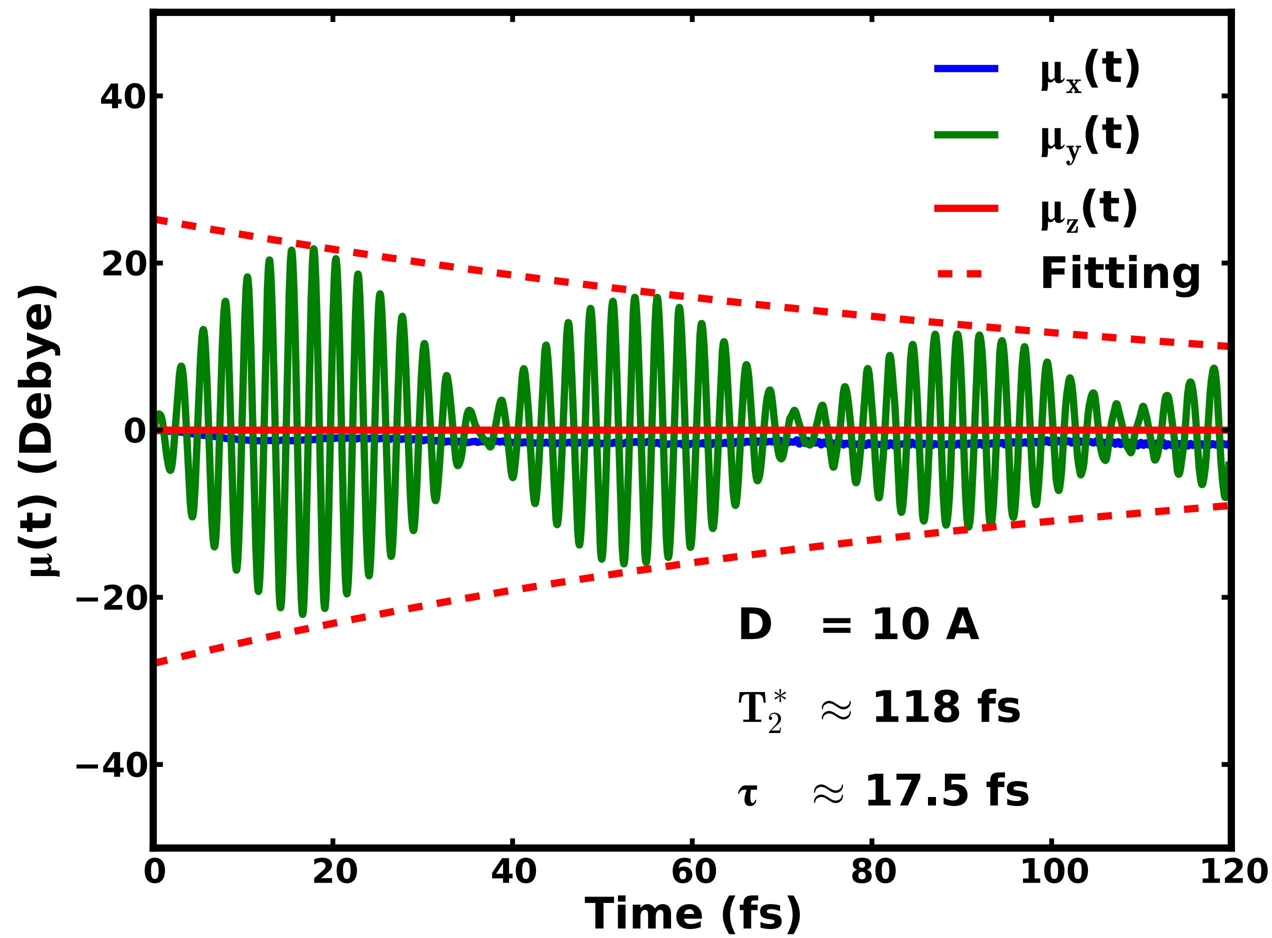
See references from Li group from the past 10 years

Exciton Decoherence

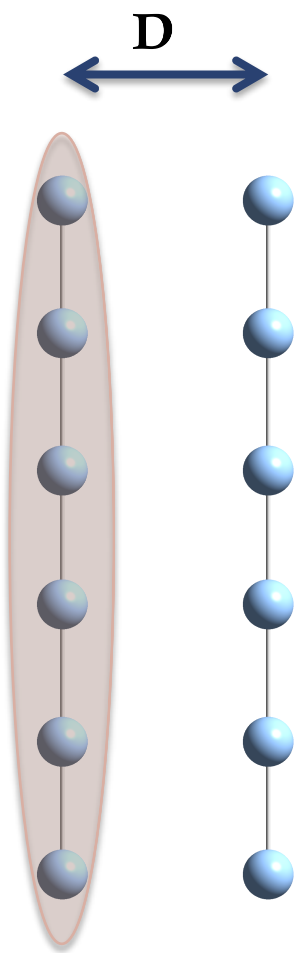
$$\mu_1(t) = \mathbf{Tr}[\mathbf{P}'_{11}(t)\cdot\mathbf{d}'_{11}] + \frac{1}{2}\mathbf{Tr}[\mathbf{P}'_{12}(t)\cdot\mathbf{d}'_{12}] + + \frac{1}{2}\mathbf{Tr}[\mathbf{P}'_{21}(t)\cdot\mathbf{d}'_{21}]$$

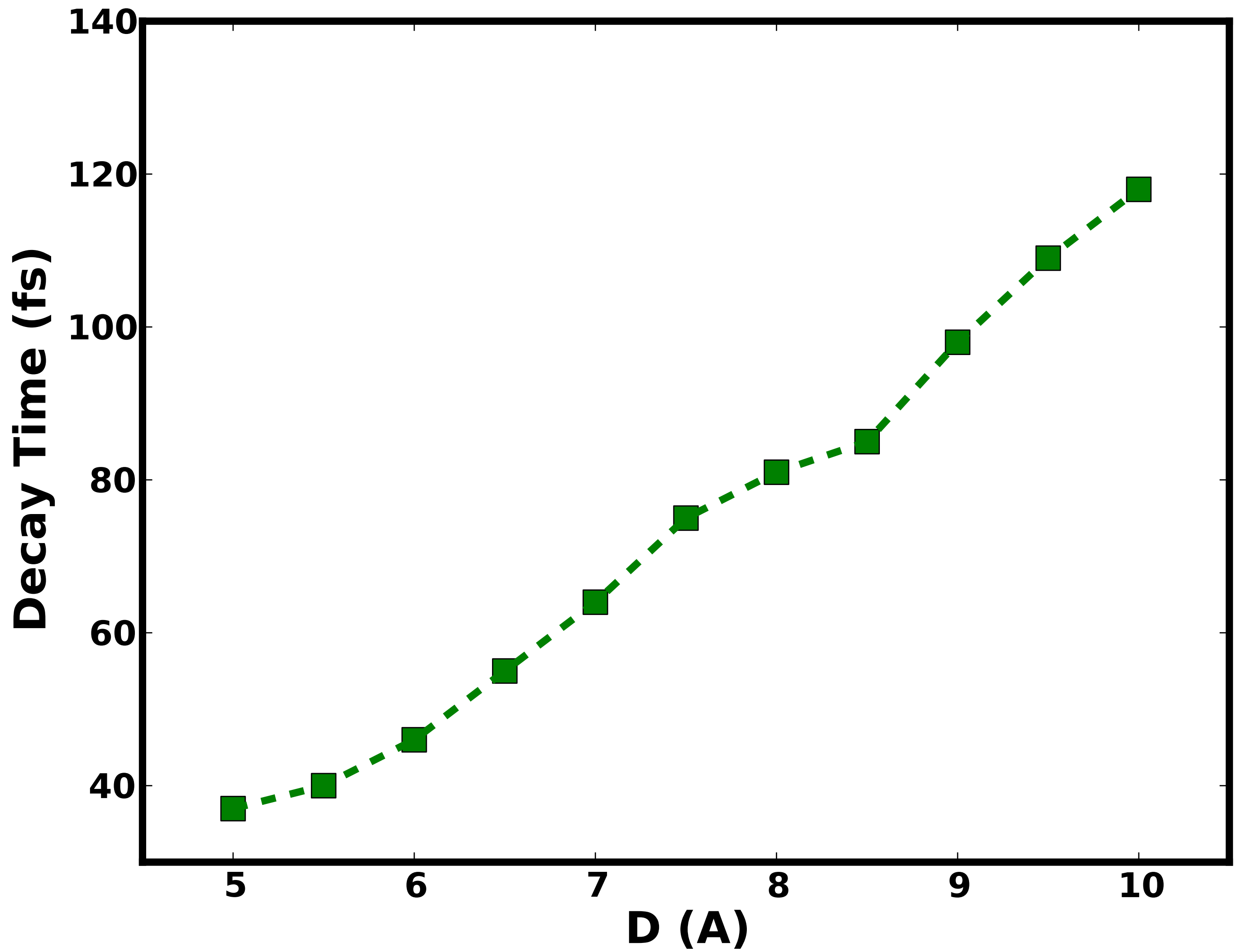
$$\rho_{12}(t) = \rho_{12}(0)e^{-i\omega t}e^{-i\Delta\omega t}e^{-t/T_2^*}$$





Exciton Decoherence

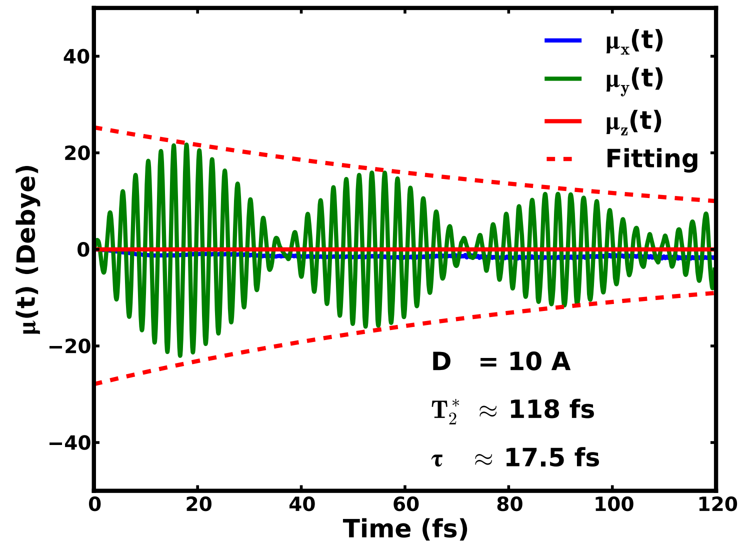


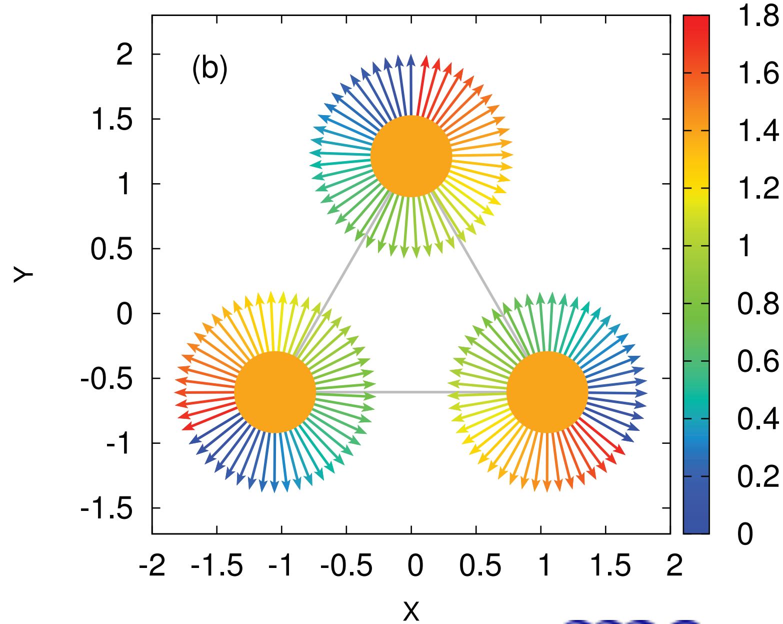


B. Peng, D. B. Lingerfelt, C. M. Aikens, X. LI, J. Phys. Chem. C, 2015, 119, 6421

Outline

- Quantum Electronic Dynamics Background
  - Decay of Coherent-Exciton
- Time-Dependent Two-Component HF/DFT Theory
  - Spin-Frustration Dynamics
  - Spin-Wave
  - Two-Component Ehrenfest

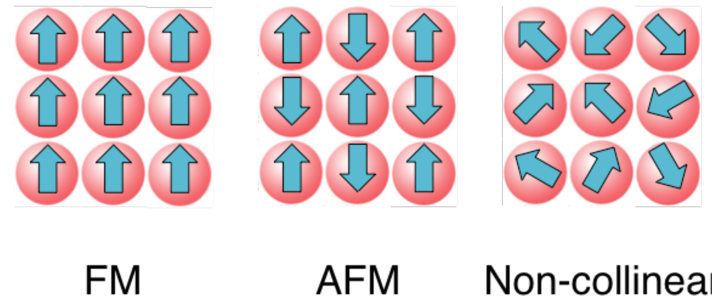


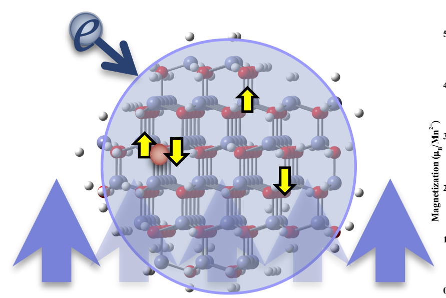


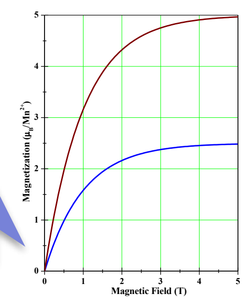
Spin…

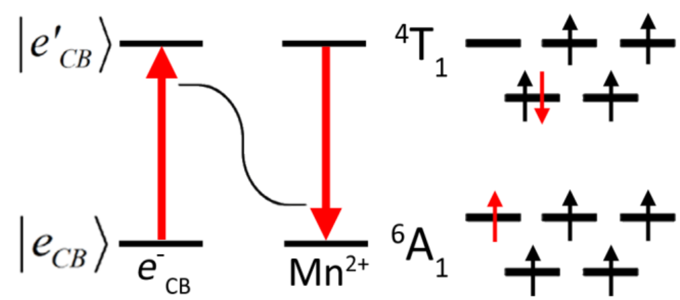
- Spin-driven Chemical Processes
  - NMR, EPR…
  - Intersystem crossing
  - Zero-field splitting and non-collinear spin system
  - Magnetization
  - Spin-crossover
  - Spin-flip Auger
  - Spin-echo
  - …

- TD-Dirac Equation
  - Full relativistic treatment of four-component spinor
    - Certain approximations are sufficient for chemistry





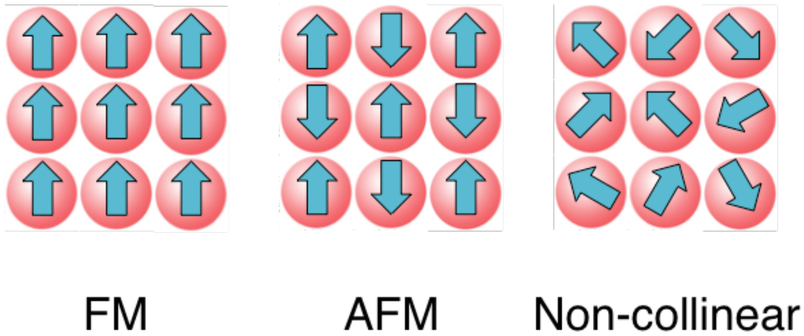




TD-2C-Spinor (TDHF$_{2c}$)

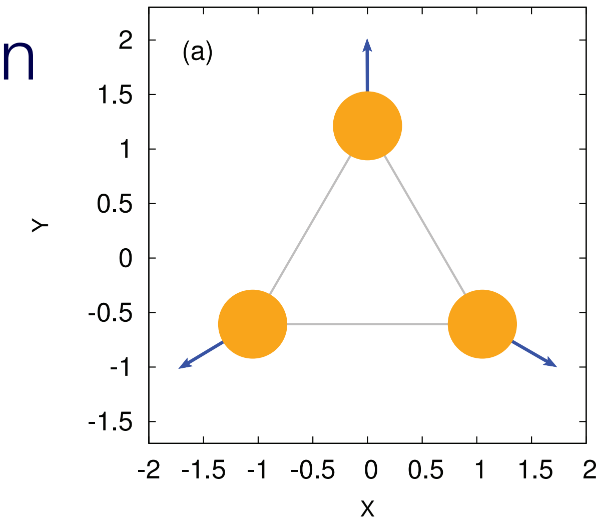
- Time-Dependent Two-component Spinor

$$\psi_k(\mathbf{x}) = \begin{pmatrix} \phi_k^{\alpha}(\mathbf{r},t) \\ \phi_k^{\beta}(\mathbf{r},t) \end{pmatrix}$$



- Dirac-Frenkel Time-Dependent Equation

$$i\frac{\partial}{\partial t}\left|\psi_k(\mathbf{x},t)\right\rangle = \hat{f}(t)\left|\psi_k(\mathbf{x},t)\right\rangle$$



2C-Spinor in a Static Magnetic Field

- Time-dependent von Neumann equation for non-relativistic two-component spinor in a static magnetic field

$$i\frac{\partial}{\partial t}\begin{pmatrix} \mathbf{P}^{\alpha\alpha}(t) & \mathbf{P}^{\alpha\beta}(t) \\ \mathbf{P}^{\beta\alpha}(t) & \mathbf{P}^{\beta\beta}(t) \end{pmatrix} = \left[\begin{pmatrix} \mathbf{F}^{\alpha\alpha}(t)+\mu_B B_z & \mathbf{F}^{\alpha\beta}(t)+\mu_B(B_x - iB_y) \\ \mathbf{F}^{\beta\alpha}(t)+\mu_B(B_x + iB_y) & \mathbf{F}^{\beta\beta}(t)-\mu_B B_z \end{pmatrix}, \begin{pmatrix} \mathbf{P}^{\alpha\alpha}(t) & \mathbf{P}^{\alpha\beta}(t) \\ \mathbf{P}^{\beta\alpha}(t) & \mathbf{P}^{\beta\beta}(t) \end{pmatrix}\right]$$

$$n(\mathbf{r},t) = \sum_{\mu\nu}\left[P_{\mu\nu}^{\alpha\alpha}(t) + P_{\mu\nu}^{\beta\beta}(t)\right]\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})$$

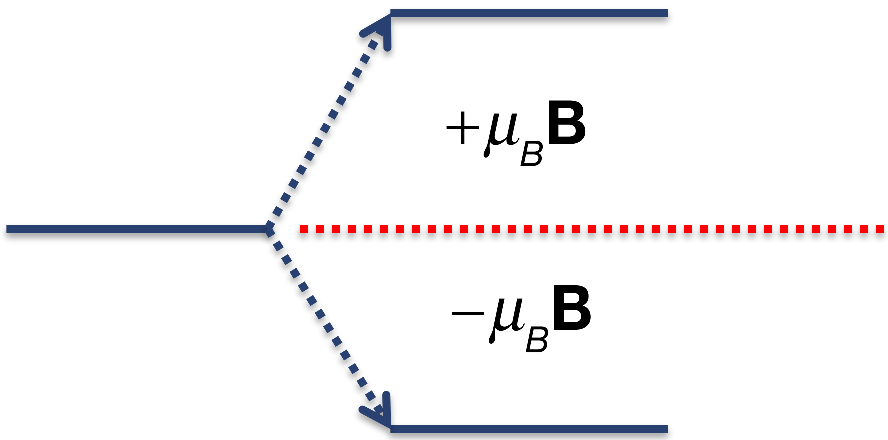
$$m_x(\mathbf{r},t) = \sum_{\mu\nu}\left[P_{\mu\nu}^{\alpha\beta}(t) + P_{\mu\nu}^{\beta\alpha}(t)\right]\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})$$

$$m_y(\mathbf{r},t) = i\sum_{\mu\nu}\left[P_{\mu\nu}^{\alpha\beta}(t) - P_{\mu\nu}^{\beta\alpha}(t)\right]\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})$$

$$m_z(\mathbf{r},t) = \sum_{\mu\nu}\left[P_{\mu\nu}^{\alpha\alpha}(t) - P_{\mu\nu}^{\beta\beta}(t)\right]\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})$$

X. Li, *et. al.* J. Chem. Phys., 2014, 141, 214111

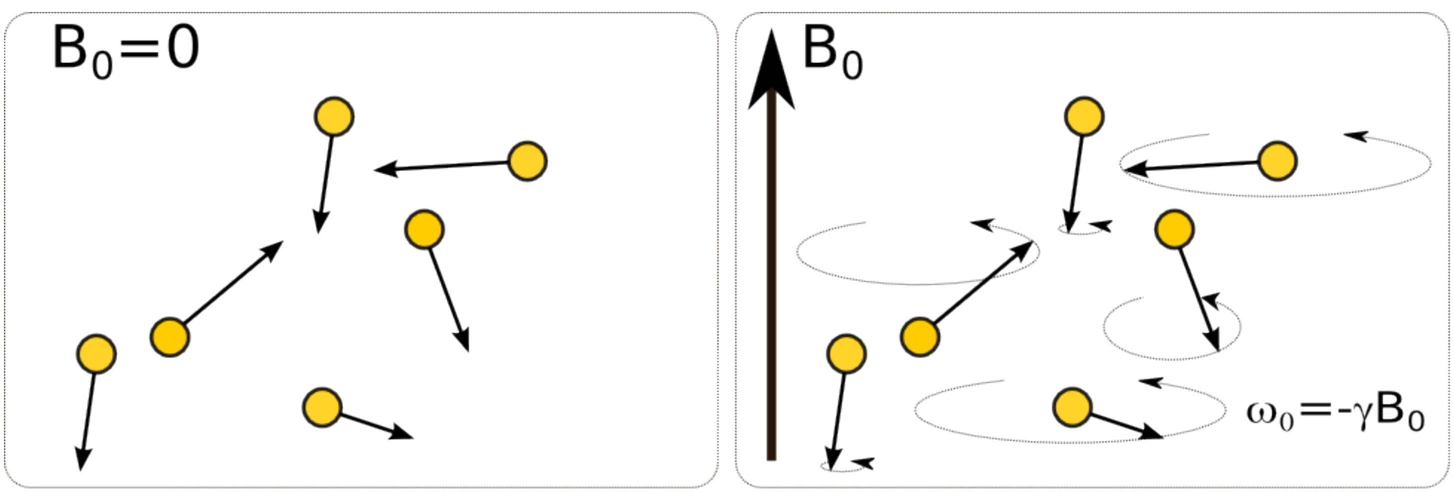
Larmor Precession



$$\Gamma = \mathbf{m} \times \mathbf{B} \rightarrow \omega_0 = 2\mu_B\mathbf{B}$$

$$\mu_B = \frac{1}{2} \text{ (a.u.)}$$

$$1 \text{ a.u. } \mathbf{B} = 2.35 \times 10^5 \text{ T}$$



2cTDHF – Li atom

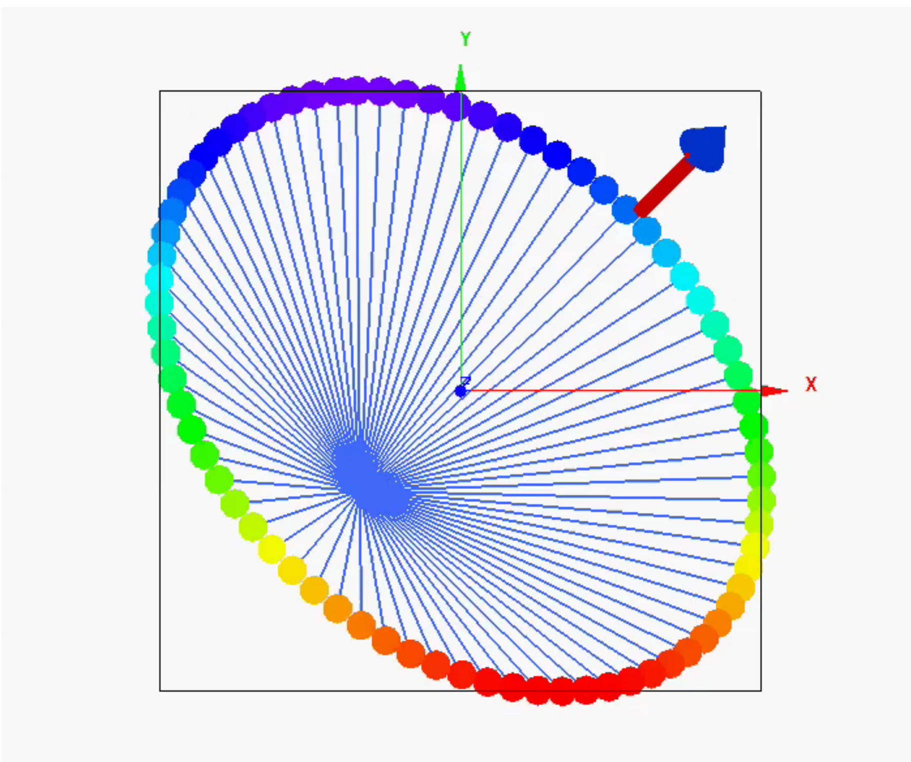
RT-TDGHF/STO-3G

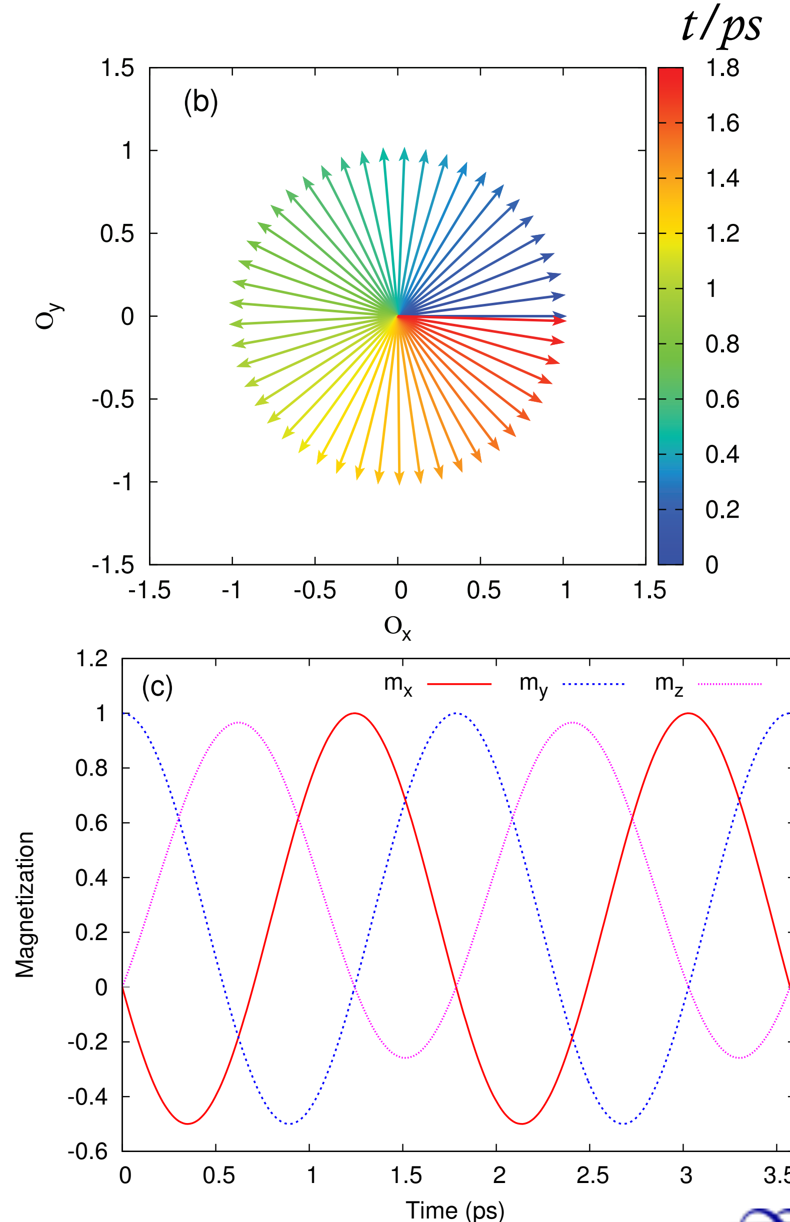
B=0.0000851 a.u. (20 T)

numerical :

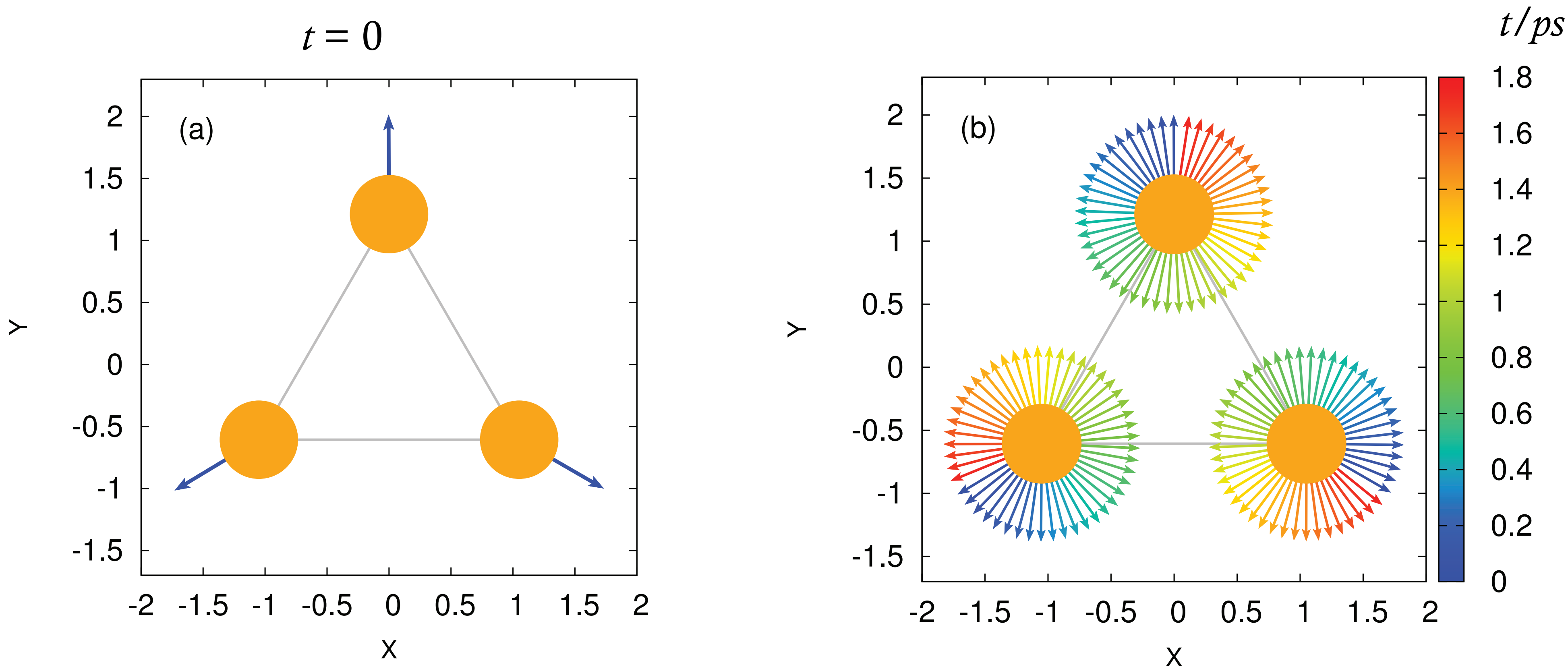
$T = \sim 17.9$ ps

ω_0=0.0000851 a.u. (18.7 cm^{-1})





2cTDHF – Li_3



RT-TDGHF/3-21G
B = 20 T

$T = \sim 17.9$ ps

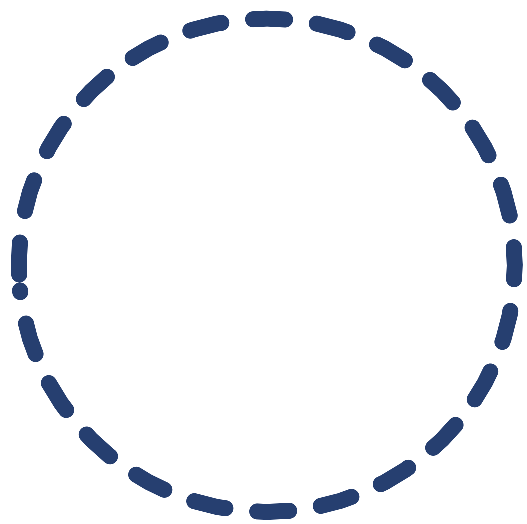
ω_0=0.0000851 a.u. (18.7 cm^{-1})

UNIVERSITY OF WASHINGTON

2cTDHF Spin-Wave H_{60}

At $t = 0$, S^2=2

2cTDHF/cc-PVDZ



2cTDHF/2cTDDFT Ehrenfest Dynamics

- Analytical force expression
  - Similar to X. Li et. al. "Ab Initio Ehrenfest Dynamics", J. Chem. Phys, 2015, 123, 084106

$$\mathbf{f}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = -\nabla_I \langle \Phi | H_{\text{el}} | \Phi \rangle$$

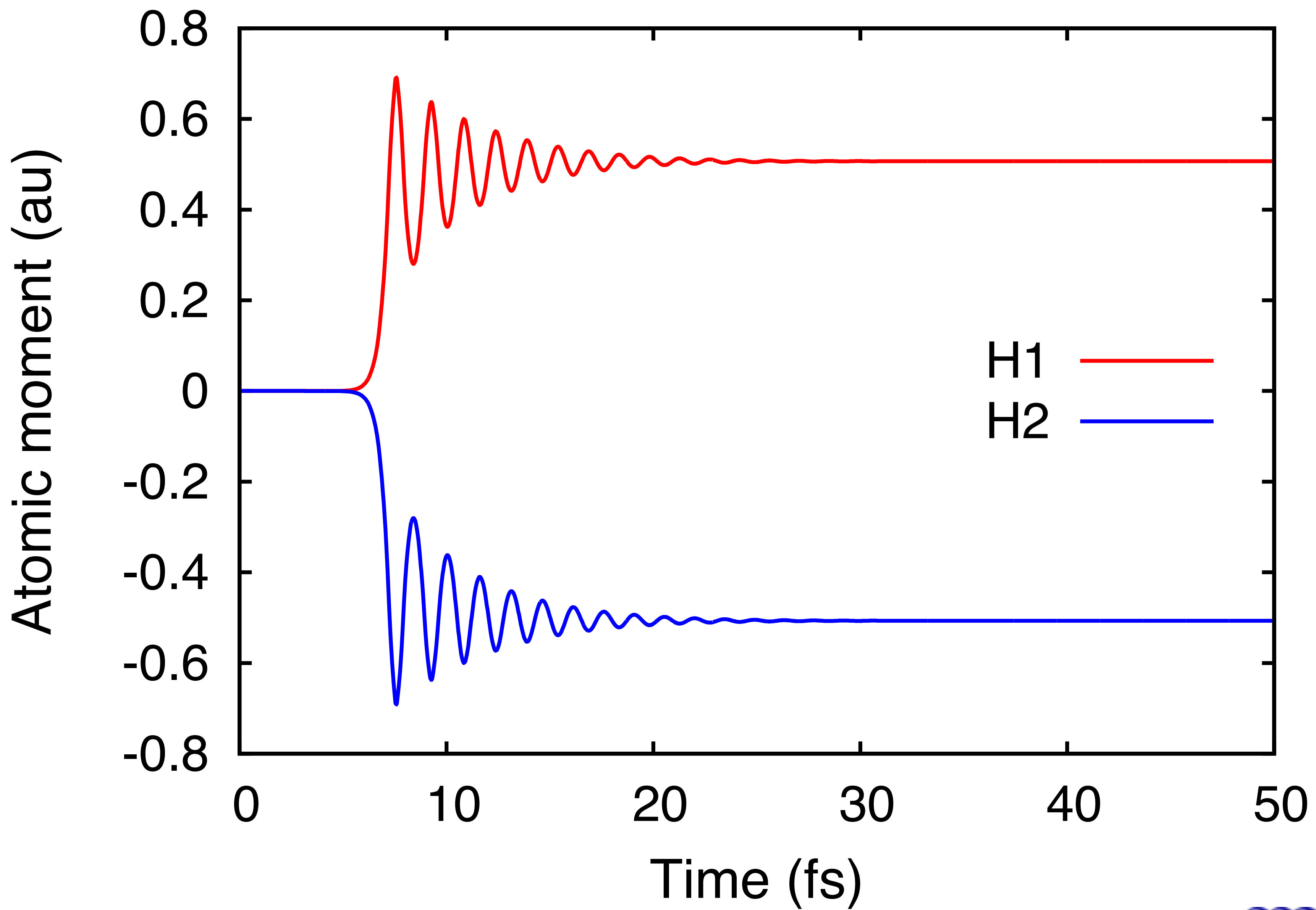
$$\mathbf{f}_I = \mathbf{f}_I^{\text{c}} + \mathbf{f}_I^{\text{nc}}$$

$$\mathbf{f}_I^{\text{c}} = -\text{Tr}\left\{ \sum_{\sigma} \left[\frac{d\mathbf{h}'^{\sigma\sigma}}{d\mathbf{R}_I}\mathbf{P}'^{\sigma\sigma} + \frac{1}{2}\frac{\partial \mathbf{G}'^{\sigma\sigma}}{\partial \mathbf{R}_I}\mathbf{P}'^{\sigma\sigma} \right] \right\}$$
$$+ \text{Tr}\left\{ \sum_{\sigma} \left[\mathbf{F}'^{\sigma\sigma}\mathbf{V}^{-1}\frac{d\mathbf{V}}{d\mathbf{R}_I}\mathbf{P}'^{\sigma\sigma} + \mathbf{P}'^{\sigma\sigma}\frac{d\mathbf{V}^T}{d\mathbf{R}_I}\mathbf{V}^{-T}\mathbf{F}'^{\sigma\sigma} \right] \right\} - \frac{\partial V_{nn}}{\partial \mathbf{R}_I}$$

$$\mathbf{f}_I^{\text{nc}} = -\text{Tr}\left\{ \sum_{\sigma \neq \tau} \left[\frac{d\mathbf{h}'^{\sigma\tau}}{d\mathbf{R}_I}\mathbf{P}'^{\tau\sigma} + \frac{1}{2}\frac{\partial \mathbf{G}'^{\sigma\tau}}{\partial \mathbf{R}_I}\mathbf{P}'^{\tau\sigma} \right] \right\}$$
$$+ \text{Tr}\left\{ \sum_{\sigma \neq \tau} \left[\mathbf{F}'^{\sigma\tau}\mathbf{V}^{-1}\frac{d\mathbf{V}}{d\mathbf{R}_I}\mathbf{P}'^{\tau\sigma} + \mathbf{P}'^{\sigma\tau}\frac{d\mathbf{V}^T}{d\mathbf{R}_I}\mathbf{V}^{-T}\mathbf{F}'^{\tau\sigma} \right] \right\}$$

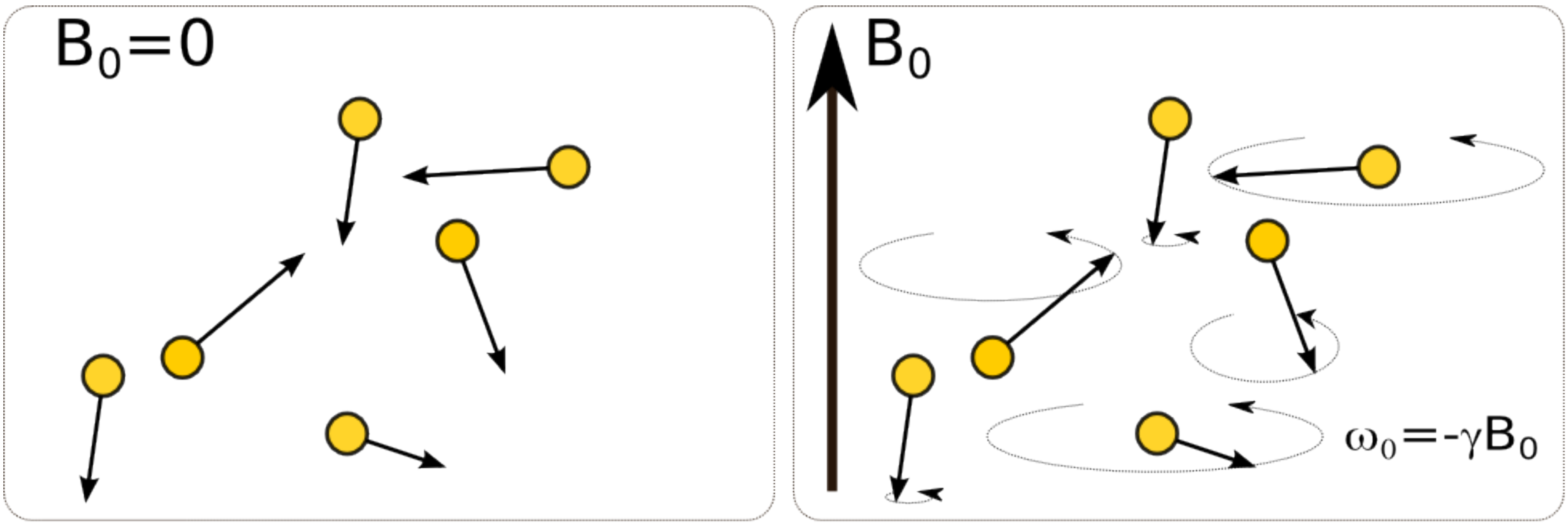
F. Ding, J. J. Goings, X. LI, to be submitted next week

H_2 Dissociation



F. Ding, J. J. Goings, X. LI, to be submitted next week

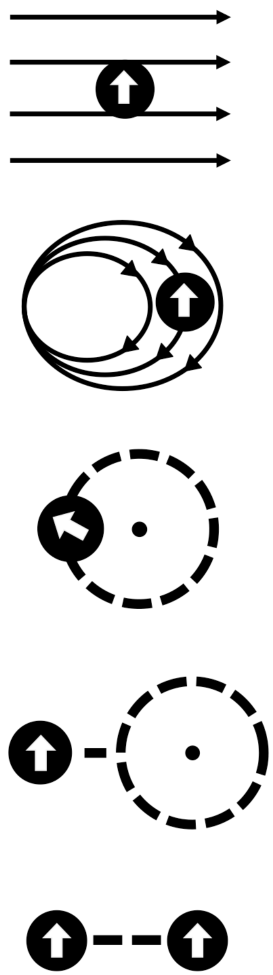
Spin…



$$\hat{H}_{SH} = \hat{H}_{LB} + \hat{H}_{BB} + \hat{H}_{SB} + \hat{H}_{SB}^{RMC} + \hat{H}_{SO}^{(1)} + \hat{H}_{SO}^{(2)} + \hat{H}_{SS} + \hat{H}_{MV} + \hat{H}_{Darwin} + \hat{H}_{SI} + \hat{H}_{LI}$$

TD-Schrödinger/Dirac Equation

UNIVERSITY OF WASHINGTON

Method		new physics	limit
TDHF		*electric field*	non-relativistic
		+	
TDGHF		*magnetic field*	
		+	
TDDCHF		*spin-orbit*	
		+	
TDDCBHF		*spin-other-orbit*	
		+	
		spin-spin	fully relativistic

UNIVERSITY OF WASHINGTON

Chronus Quantum Project

- Time-dependent theory – in both time- and frequency-domain; optical properties centric
  - High-order optical properties
  - Multi-dimensional spectroscopy
  - Transient absorption spectroscopy
  - Relativistic electronic structure theory
- Open-source, HGP+OS integral engine, LibInt (Valeev), TiledArray
- Beta testers can sign up at www.chronusquantum.org by the end of June

UNIVERSITY OF WASHINGTON

Acknowledgement

Group Members

- Dr. Alessio Petrone
- Dr. Franco Egidi
- Feizhi Ding
- Erica Chong
- Bo Peng
- David Lingerfelt
- Joshua Goings
- Patrick Lestrange
- David Williams-Young
- Hongbin Liu
- Sanjan Silwal

Former:

- Dr. Christine Isborn (Assistant Prof, UC Merced)
- Dr. Ekaterina Badaeva (Materials and Processes Engineer, Boeing)
- Dr. Yong Feng (Software Engineer, Yahoo)
- Dr. Wenkel Liang (Senior Associate, KPMG Data Analysis)
- Dr. Craig Chapman (Post-Doc, Northwestern U)
- Dr. Sean Fisher (Post-Doc, PNNL)
- Dr. Joseph May (High School Teacher, Las Vegas)
- Mr. Phu Nyugen (Amazon)

Collaborators

- Prof. Ernie Davidson (UW)
- Prof. Daniel Gamelin (UW)
- Prof. David Ginger (UW)
- Prof. Lin X Chen (Northwestern)
- Prof. Benedetta Mennucci (U of Pisa)
- Prof. Nadia Rega (U of Naples)
- Prof. Marco Caricato (U of Kansas)
- Prof. Christine Aikens (Kansas State U)