Cost-efficient normal-order and Wick's theorem based many body approach for thermal properties and quantum dynamics for both electronic and vibronic problems

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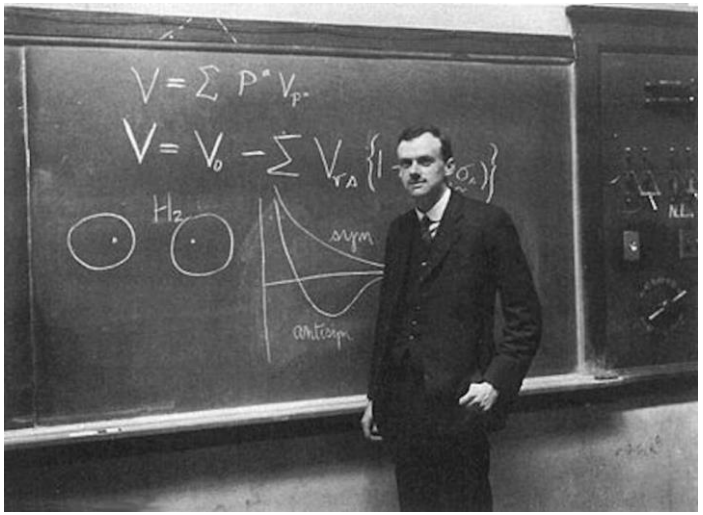
Mini Symposium

Wednesday, November 6th, 2019

Outline

- Formal theory
- Basics: normal order and Wick's theorem
- Imaginary time propagation: temperature dependencies and thermal effects
- Real time propagation: time dependency and quantum dynamics
- Current and future project
- Incorporate temperature effect for strong correlated electronic structure
- Develop efficient computational approach to simulate quantum dynamics for non-adiabatic vibronic model.
- Modeling molecular magnetism

Formal theory



Genralized Wick's theorem

- Normal order and contraction

$$a_i^\dagger a_j = \{a_i^\dagger a_j\} + \overline{a_i^\dagger a_j} = \{a_i^\dagger a_j\} + \mathrm{f_i}\delta_{ij}$$

- Commutation for bosons

$$\left[a_i^\dagger, a_j\right] = a_i^\dagger a_j - a_i a_j^\dagger = \delta_{ij}$$

- Anti-commutation for fermions

$$\left[a_i^\dagger, a_j\right]_+ = a_i^\dagger a_j + a_i a_j^\dagger = \delta_{ij}$$

Kutzelnigg, W., & Mukherjee, D. (1997). Normal order and extended Wick theorem for a multiconfiguration reference wave function. *The Journal of chemical physics*, *107*(2), 432-449.
Kong, L., Nooijen, M., & Mukherjee, D. (2010). An algebraic proof of generalized Wick theorem. *The Journal of chemical physics*, *132*(23), 234107.

Real / Imaginary time propagation

- Thermal density matrix: imaginary time propagation

$$\hat{D} = e^{-\beta \hat{H}}$$

$$\frac{d\hat{D}}{d\beta} = -\hat{H}\,\hat{D}$$

- Schrödinger equation : real time propagation

$$|\Psi\rangle = e^{-i \hat{H} t}|\Psi_0\rangle$$

$$i\frac{d|\Psi\rangle}{dt} = \hat{H}|\Psi\rangle$$

Coupled cluster reformulation

- Thermal density matrix: imaginary time propagation

$$\widehat{D} = \{e^{\hat{S}}\}\,\widehat{D}_0$$

many body operator equation

$$\frac{d\,\hat{S}}{d\beta} = \left(\{e^{\hat{S}}\}\widehat{H}\right)_{connected}$$

CC amplitude equation

$$\left\langle \{\Omega_\nu^{\mathrm{I}}\}\left\{\frac{d\,\hat{S}}{d\beta}\right\}\right\rangle = \langle\,\{\Omega_\nu^{\mathrm{I}}\}\left(\{e^{\hat{S}}\}\widehat{H}\right)_{connected}\rangle$$

- Schrödinger equation : real time propagation

$$|\Psi\rangle = \{e^{\hat{S}}\}|\Psi_0\rangle$$

many body operator equation

$$i\frac{d\,\hat{S}}{d\tau} = \left(\{e^{\hat{S}}\}\widehat{H}\right)_{connected}$$

CC amplitude equation

$$i\left\langle \{\Omega_\nu^{\mathrm{I}}\}\left\{\frac{d\,\hat{S}}{d\tau}\right\}\right\rangle = \langle\,\{\Omega_\nu^{\mathrm{I}}\}\left(\{e^{\hat{S}}\}\widehat{H}\right)_{connected}\rangle$$

Current & future projects

- Incorporate temperature effect in electronic structure
- Compute auto corr
  photo-electronic sp
  model
- Modeling molecul

Compute thermal effects

- Algorithm: compute Reduced Density Matrix (RDM) through imaginary time integration

Amplitude equation

$$-\frac{ds_0}{d\beta} = R_0(\boldsymbol{H}) - \mu R_0(\boldsymbol{\delta})$$

$$-f\bar{f}\frac{ds_i^a}{d\beta} = R_i^a(\boldsymbol{H}) - \mu R_i^a(\boldsymbol{\delta})$$

$$-f^2\bar{f}^2\frac{ds_{ij}^{ab}}{d\beta} = R_{ij}^{ab}(\boldsymbol{H}) - \mu R_{ij}^{ab}(\boldsymbol{\delta})$$

Grand canonical constraints

$$\mu = \frac{\sum_p R_p(\boldsymbol{h},\boldsymbol{s})}{\sum_p R_p(\boldsymbol{\delta},\boldsymbol{s})}$$

1-RDM:

$$d_p^q = \langle \hat{p}^\dagger \hat{q}\{e^{\hat{S}}\}\rangle = \\ = f\delta_{pq} + f\bar{f}s_p^q$$

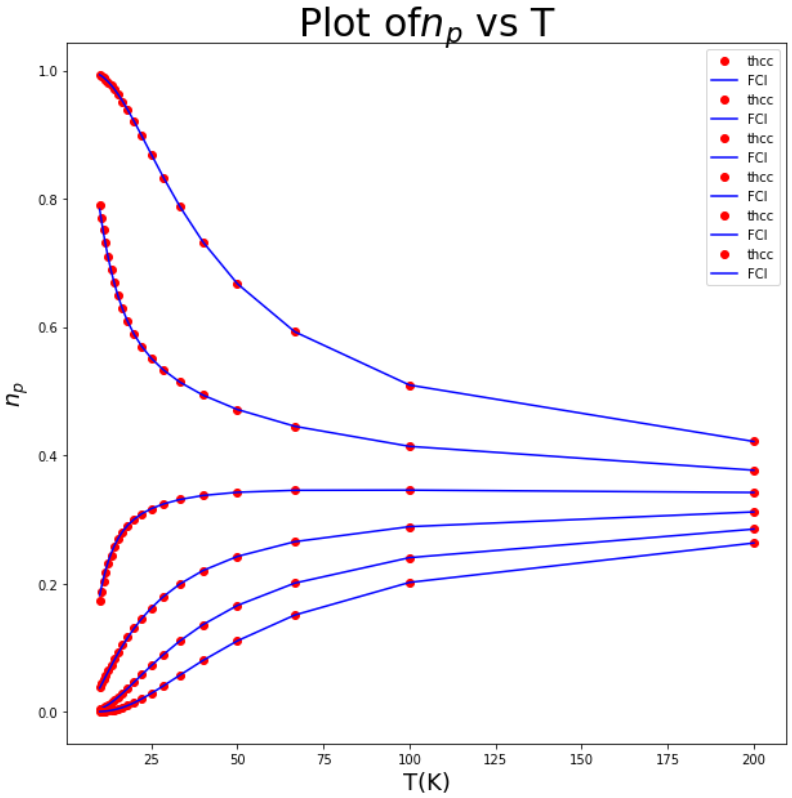
2-RDM:

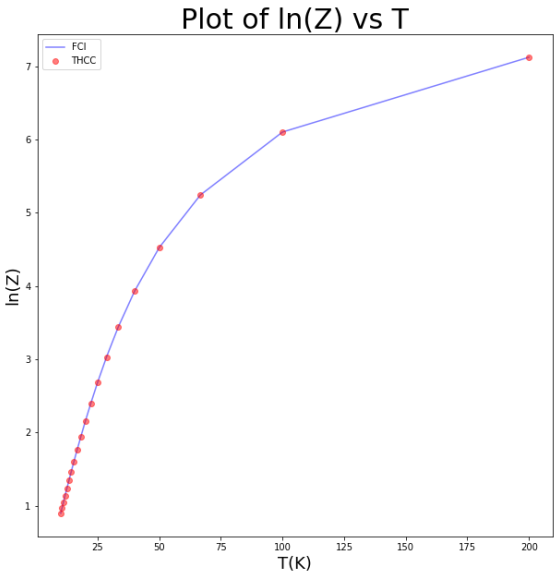
$$d_{pq}^{rs} = \langle \hat{p}^\dagger \hat{q}^\dagger \hat{r}\,\hat{s}\{e^{\hat{S}}\}\rangle \\ = g(\boldsymbol{\delta},\boldsymbol{S})$$

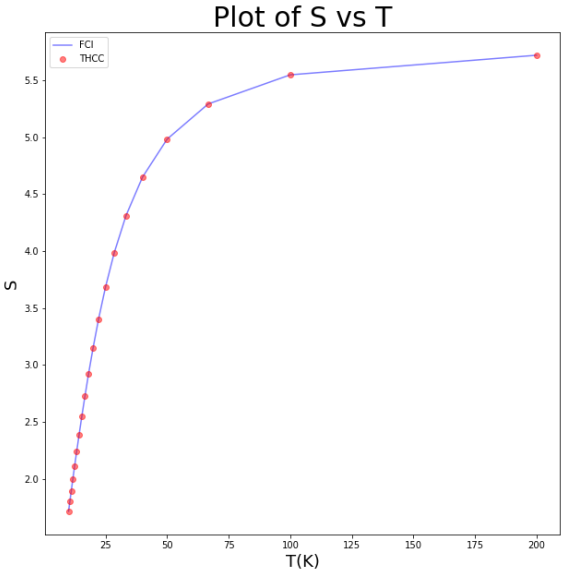
Compute thermal effects

- Tests on model systems

$$\hat{H} = \sum_{p} h_p^p \{\hat{p^\dagger}\hat{p}\} + \sum_{p,q} v_{pq}^{pq} \{\hat{p^\dagger}\hat{q^\dagger}\hat{q}\hat{p}\}$$







Compute thermal effects

Issues

- We have verified that this coupled cluster formalism under no constraints is equivalent to the Contracted Schrödinger Equation (CSE) developed by Mukherjee et al

- As in CSE, we get into to trouble on finding the general N-representability constraints for 2-RDMs

Mazziotti, D. A. (2012). Significant conditions for the two-electron reduced density matrix from the constructive solution of N representability. *Physical Review A*, *85*(6), 062507.

Mukherjee, D. (1995). A coupled cluster approach to the electron correlation problem using a correlated reference state. In *Recent progress in many-body theories* (pp. 127-133). Springer, Boston, MA.

Vibronic model

- Non-adiabatic vibronic model Hamiltonian:

$$\hat{H} = \sum_{a,b} \hat{h}_b^a |a\rangle\langle b|$$

$$\hat{h}_b^a = h_b^a + h_b^{ai} a_i + h_{bi}^a a^i + h_{bj}^{ai} a_i a^j + h_{bij}^a a^i a^j + h_b^{aij} a_i a_j$$

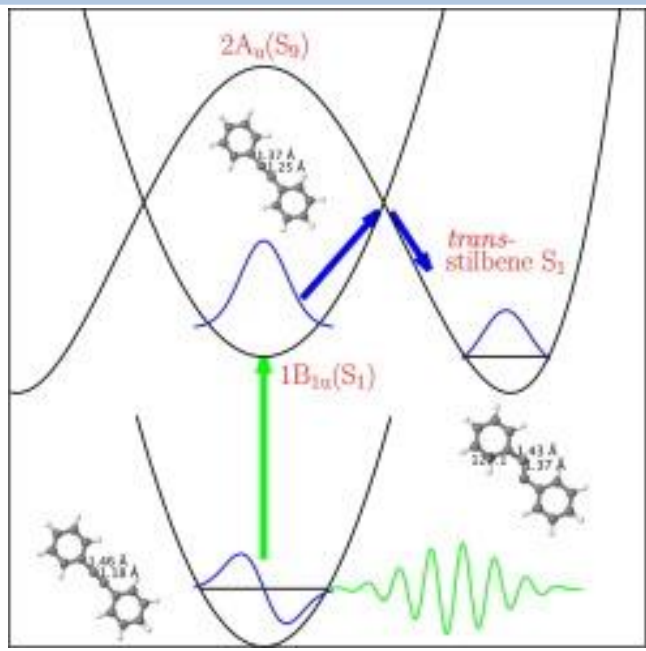
- Quantum dynamics though real time integration

$$i\left\langle \{\hat{\Omega}_v^{\dagger}\}\left\{\frac{d\hat{S}}{d\tau}\right\}\right\rangle = \langle \{\hat{\Omega}_v^{\dagger}\}\left(\hat{H}\,\{e^S\}\right)_{connected}\rangle$$

$$i\frac{d\hat{g}_b^a}{d\tau} = \left\langle \left(\hat{H}\{e^S\}\right)_{connected}\right\rangle_b^a$$

- Compute auto correlation function and power spectrum

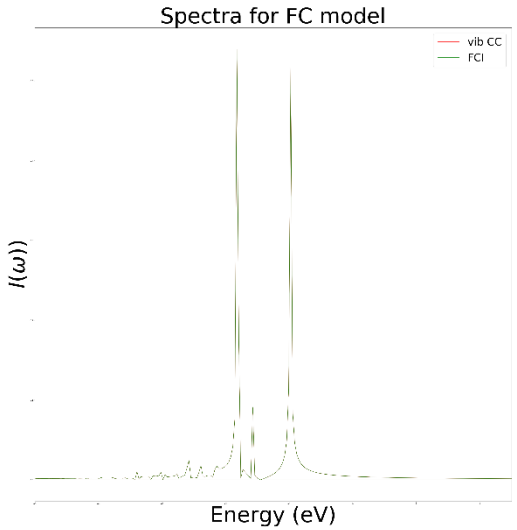
$$C(\tau) = \sum_{a,b} X_a \left(e^{\hat{g}(\tau)}\right)_b^a X^b \xrightarrow{\text{Fourier Trans}} I(\omega)$$

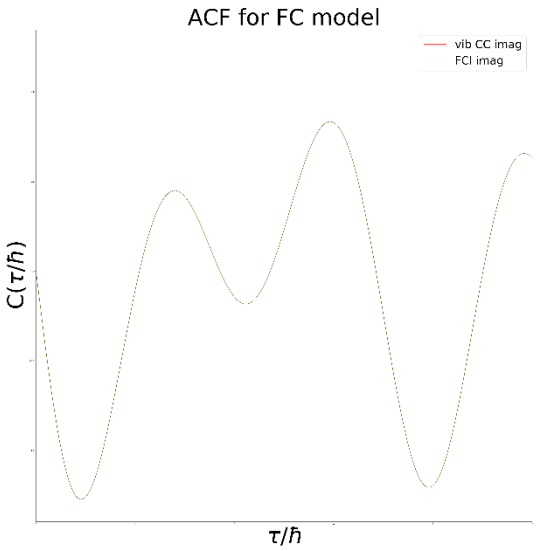


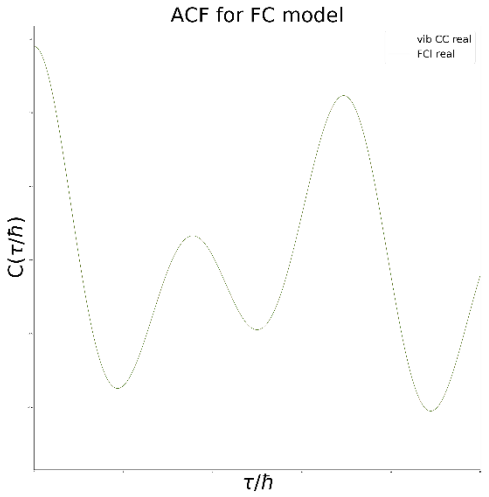
Vibronic model

- Numerical results

Pure FC model: The electronic states are decoupled from vibrational states: $\hat{H}_b^a = \hat{0}\ if\ a \neq b$





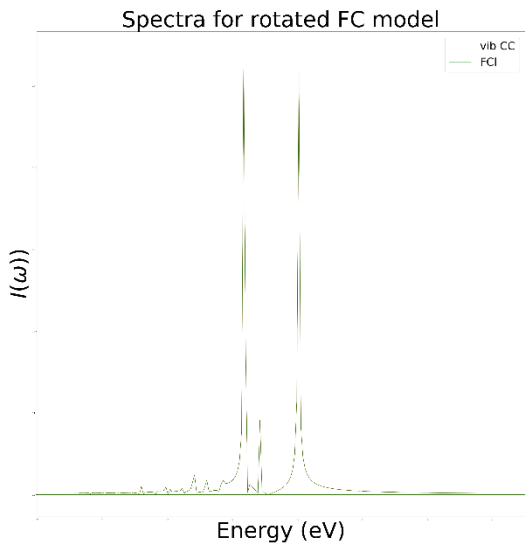


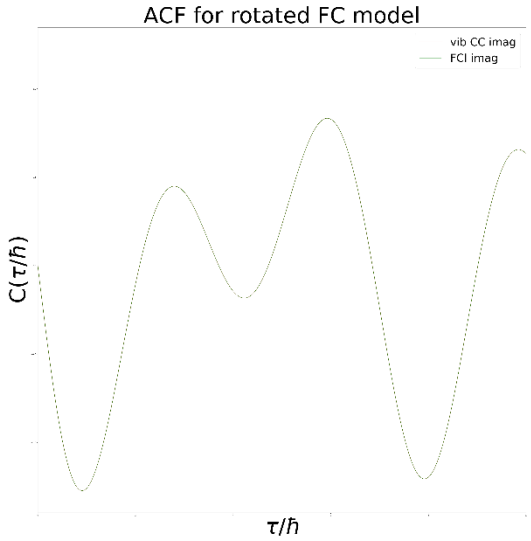
Vibronic model

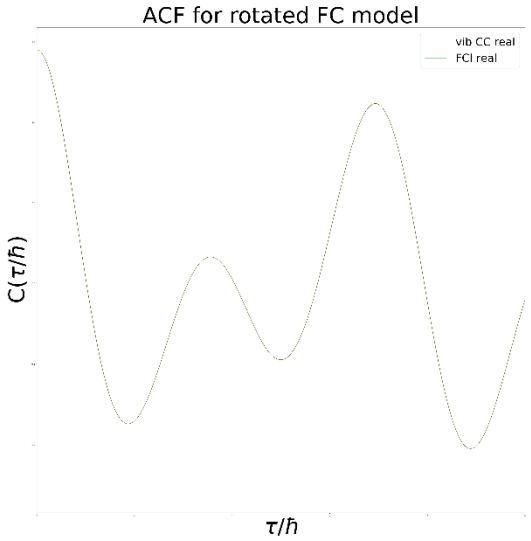
- Numerical results

The rotated FC model: Pure FC vibronic model is transformed through a rotation operator for electronic states

$\hat{H}_b^{a(rot)} = U_c^a \, \hat{H}_d^{c(FC)} U_b^{\dagger d}$ and the rotation matrix $U \equiv \begin{bmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{bmatrix}$



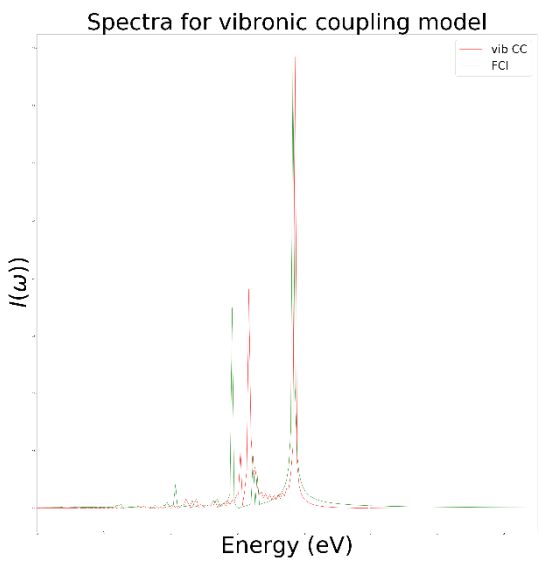


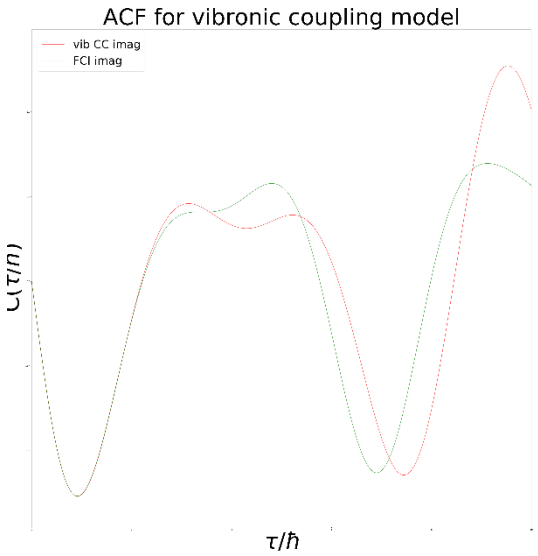


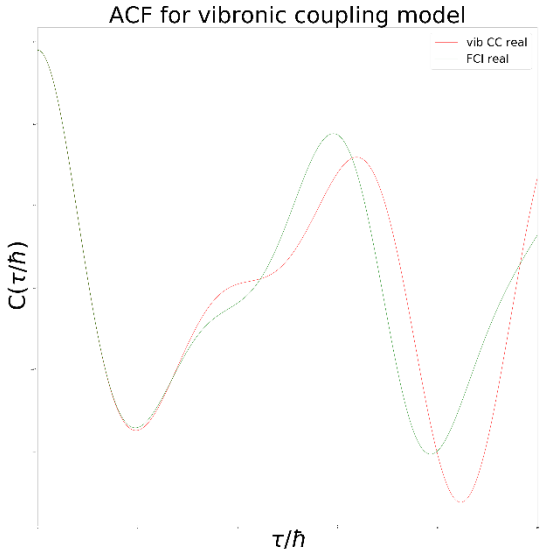
Vibronic model

- Numerical results

General vibronic model







Vibronic model

Discussion

- Based on the numerical simulation of model system, the approach is exact for diagonal FC model.
- The approach is invariant under global unitary transformation of electronic states as well
- We think/hope this approach is exact for up to quadratic vibronic models.

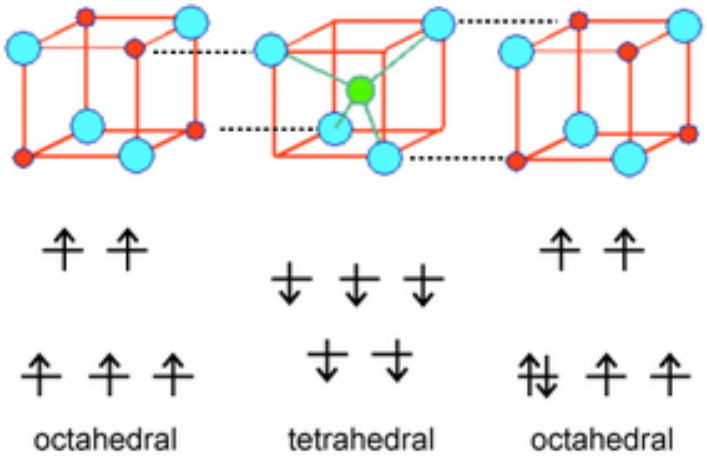
a) The theory can not be improved by adding higher order $\hat{S}$ amplitudes

b) Numerical issues with time integrations need resolution (debug the current code as well)

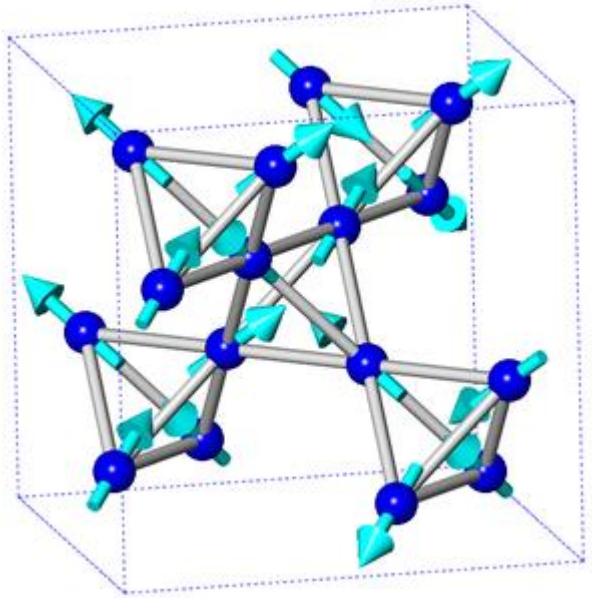
c) Further rigorous prove needed to verify the claim that this approach is exact.

- Real molecular system could be tested and compared with experimental data and potentially substitute current MCTDH method.

Modeling magnetism



Ferromagnetic order



Frustrated magnetism

- Adapt Heisenberg effective model Hamiltonian with second quantization

$$\widehat{H}_{eff} = -2J \sum_{p=1}^{N} \boldsymbol{S_p} * \boldsymbol{S_{p+1}}$$

- Apply thermal CC approach to compute partition function and thermal properties

Summary

- We develop a class of normal order and Wick's theorem based quantum many body theory

Thermal CC equation:

$$\frac{d\,\hat{S}}{d\beta} = \left(\{e^{\hat{S}}\}\hat{H}\right)_{connected}$$

Time dependent CC equation:

$$i\frac{d\,\hat{S}}{d\tau} = \left(\{e^{\hat{S}}\}\hat{H}\right)_{connected}$$

- Based upon this theory, we devise cost-efficient computational approaches to simulation thermal effect of electronic structure and dynamics of vibronic model

- We expect to apply this novel approach to investigate some interesting phenomenon for molecular systems

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+more

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Questions