A variational surface hopping algorithm for the sub-Ohmic spin-boson model

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September 1, 2014 - Brasov, Romania
Simulating Physics with Computers

Richard P. Feynman
Quantum Mechanics at Work in Photosynthesis: Algae Familiar With These Processes for Nearly Two Billion Years

ScienceDaily (Feb. 4, 2010) — A team of University of Toronto chemists have made a major contribution to the emerging field of quantum biology, observing quantum mechanics at work in photosynthesis in marine algae.

See Also:

Plants & Animals
- Biology
- Botany
- Cell Biology

Matter & Energy
- Physics
- Quantum Physics
- Quantum Computing

Reference
- Mechanics
- Quantum number
- Biophysics
- Quantum tunnelling

"There's been a lot of excitement and speculation that nature may be using quantum mechanical practices," says chemistry professor Greg Scholes, lead author of a new study published in Nature. "Our latest experiments show that normally functioning biological systems have the capacity to use quantum mechanics in order to optimize a process as essential to their survival as photosynthesis."

Special proteins called light-harvesting complexes are used in photosynthesis to capture sunlight and funnel its energy to nature's solar cells -- other proteins known as reaction centres. Scholes and his colleagues isolated light-harvesting complexes from two different species of marine algae and studied their function under natural temperature conditions using a sophisticated laser experiment known as two-dimensional electronic...
FMO trimers in green sulfur bacteria

Figure 1

(a) Top-view of the Fenna-Matthews-Olson (FMO) protein trimer from green sulfur bacterium *Prosthecocobloris aestuarii*. The protein is depicted in yellow, and the bacteriochlorophyll (BChl) molecules are in green. (b) The FMO protein is located between the light-harvesting antenna (chlorosome) and the reaction center, with the C3 symmetry axis of the trimer perpendicular to the membrane plane of the baseplate. (c) Side view of the BChl arrangement in the FMO trimer. Seven BChl a molecules belonging to one of the monomeric subunits are highlighted in black. The BChl numbers correspond to the original labeling used in Reference 14.
Light-Harvesting System in Purple Bacteria
A. The electron-hole distance: Frenkel or Wannier exciton?
   Models based on Frenkel exciton (e.g. Meir, Zhao, Chernyak & Mukamel JCP 1997; Zhao, Meier et al., J. Phys. Chem. B 1999).

B. Energy transfer mechanisms (the size of exciton):
1. Förster Incoherent hopping (Markovian) process (small polaron).
2. Coherent exciton migration. (large polaron).
How does a superradiant patch move?

Proposed: “Super-transfer” of a superradiant patch?

Greg Scholes, *Chem Phys* 2002; Lloyd & Mohseni, *New J Phys* 2010.

→ *motion of a large polaron*?!
Dirac-Frenkel time-dependent variation

1. Description of the relaxation process of the photo-excited state:

Initial state:

\[ |D(t = 0)\rangle = \sum_n \alpha_n \hat{a}_n^+ |0\rangle_{\text{ex}} |0\rangle_{\text{ph}}, \quad \sum_n |\alpha_n|^2 = 1 \]

I.e., at \( t = 0 \), there are no phonon displacements on the molecular ring, and the exciton number on the entire ring is 1.

Since \( \left[ \sum_n \hat{a}_n^+ \hat{a}_n, \hat{H} \right] = 0 \), the exciton number on the ring is conserved.

In the process of the relaxation, the quantum state of the system can be approximated, for example, by the Davydov \( D_1 \) Ansatz:

\[
|D_1(t)\rangle = \sum_n \psi_n(t) \hat{a}_n^+ |0\rangle_{\text{ex}} \otimes \exp \left( \sum_m \left[ \lambda_{n,m}(t) \hat{b}_m^+ - \lambda_{n,m}^{*}(t) \hat{b}_m \right] \right) |0\rangle_{\text{ph}}
\]

where \( \sum_n |\psi_n(t)|^2 = 1 \), \( \lambda_{n,m}(t = 0) = 0 \)

Variational parameters
2. Two simplified forms of the $D_1$ Ansatz

**$D_2$ Ansatz:**

\[|D_2(t)\rangle = \sum_n \psi_n(t) \hat{a}_n^+ |0\rangle_{ex} \otimes \exp\left(\sum_m \left[ \lambda_m(t) \hat{b}_m^+ - \lambda_m^*(t) \hat{b}_m \right]\right)|0\rangle_{ph}\]

**$\tilde{D}$ Ansatz:**

\[|\tilde{D}(t)\rangle = \sum_n \psi_n(t) \hat{a}_n^+ |0\rangle_{ex} \otimes \exp\left(\sum_m \left[ \left( \beta_{m-n}(t) - \lambda_m(t) \right) \hat{b}_m^+ - \left( \beta_{m-n}^*(t) + \lambda_m^*(t) \right) \hat{b}_m \right]\right)|0\rangle_{ph}\]
3. Time evolution equations of the Davydov Ansätze

Schrödinger Equation

Dirac-Frenkel time-dependent variational method

Equations of the motion of the variational parameters

\[ L = \langle \Phi(t) | \frac{i\hbar}{2} \frac{\partial}{\partial t} - \hat{H} | \Phi(t) \rangle \]

\[ \frac{d}{dt}(\frac{\partial L}{\partial \alpha^*_m}) - \frac{\partial L}{\partial \alpha^*_m} = 0 \]

For $D_2$ Ansatz, for example, EOMs are derived for a diagonally-coupled system:

\[ \dot{\lambda}_q(t) = -i \omega_q \left[ g_q \sum_n |\psi_n(t)|^2 e^{-inq} + \lambda_q(t) \right] \]

\[ -i \dot{\psi}_n(t) = J [\psi_{n+1}(t) + \psi_{n-1}(t)] \]

\[ -\psi_n(t) \left\{ \sum_q \omega_q |\lambda_q(t)|^2 + \sum_q \omega_q g_q \left[ \lambda_q(t)e^{i\phi_n} + c.c. \right] - \frac{1}{2}i \sum_q \left[ \dot{\lambda}_q(t)\dot{\lambda}_q^*(t) - c.c. \right] \right\} \]
Equations of the motion of the $D_2$ variational parameters for an off-diagonally coupled system

$$-i \dot{\lambda}_q(t) = \frac{1}{2} \omega_q \phi (1 - e^{-iq}) \sum_n \left[ \psi^*_n(t) \psi_{n+1}(t) + c.c. \right] e^{-in\phi}$$

$$-\omega_q \left[ g_q \sum_n |\psi_n(t)|^2 e^{-in\phi} + \lambda_q(t) \right]$$

$$-i \dot{\psi}_n(t) = \psi_{n+1}(t) \left\{ J - \frac{1}{2} \phi \sum_q \omega_q (1 - e^{-iq}) \left[ \lambda_q(t)e^{i(n+1)} - \lambda^*_q(t)e^{-in\phi} \right] \right\}$$

$$+ \psi_{n-1}(t) \left\{ J - \frac{1}{2} \phi \sum_q \omega_q (1 - e^{iq}) \left[ \lambda^*_q(t)e^{-in\phi} - \lambda_q(t)e^{i(n-1)} \right] \right\}$$

$$- \psi_n(t) \left\{ \sum_q \omega_q |\lambda_q(t)|^2 + \sum_q \omega_q g_q \left[ \lambda_q(t)e^{in\phi} + c.c. \right] - \frac{1}{2} i \sum_q \left[ \dot{\lambda}_q(t) \lambda^*_q(t) - c.c. \right] \right\}$$
Initial state: at $t = 0$, exciton amplitude is localized at site $n = 0$ and $n = 1$. 

$|\psi_n(t)|^2$

$|\lambda_n(t)|$

$J = 0.1$, $W = 0$, $S = 0$, $\phi = 1$

$J = -0.1$, $W = 0$, $S = 0$, $\phi = 1$
Polaron Dynamics of D1 Ansatz with realistic LH2 Frenkel exciton Hamiltonian; Initial State: Singly excited at site 0, $\xi_n(0)=0$.
S. Ganapathy et al, *PNAS*. 2009, 106, 8525
Calculated spectra: linear absorption

\[ \tilde{F}(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty F(t) e^{i\omega t} dt \]

For \( D_2 \) Ansatz:

\[
\begin{align*}
 F(t) &= \mu^2 N \sum_n \psi_n(t) \exp \left( -\frac{1}{2} \sum_q |\lambda_q(t)|^2 \right), \\
 \psi_n(0) &= \delta_{n,1}, \quad (n = 1, 2, ..., N) \\
 \lambda_q(0) &= 0, \quad (q = -\frac{N}{2} + 1, -1, 0, 1, ..., \frac{N}{2})
\end{align*}
\]

For \( \tilde{D} \) Ansatz:

\[
\begin{align*}
 F(t) &= \mu^2 N \sum_n \psi_n(t) \exp \left( -\frac{1}{2} \sum_q |\beta_q(t)e^{-i\phi} + \lambda_q(t)|^2 \right), \\
 \psi_n(0) &= \delta_{n,1}, \quad (n = 1, 2, ..., N) \\
 \beta_q(0) &= 0, \\
 \lambda_q(0) &= 0 \quad (q = -\frac{N}{2} + 1, -1, 0, 1, ..., \frac{N}{2})
\end{align*}
\]
**3rd order nonlinear two-dimensional spectra**

\[
\sigma^{(3)}(\omega_3, \tau_2, \omega_1) = \int_0^\infty \int_0^\infty R^{(3)}(\tau_3, \tau_2, \tau_1)e^{i(\omega_3\tau_3 + \omega_1\tau_1)}d\tau_3d\tau_1
\]

where \(R^{(3)}(\tau_3, \tau_2, \tau_1)\) is the 3rd order nonlinear response function which is a linear composition of \(R_1, R_2, R_3\) and \(R_4\):

\[
R_1(\tau_3, \tau_2, \tau_1) = \text{tr}\left[\hat{\mu}(\tau_1)\hat{\mu}(\tau_2 + \tau_1)\hat{\mu}(\tau_3 + \tau_2 + \tau_1)\hat{\mu}(0)\rho_0\right]
\]

\[
R_2(\tau_3, \tau_2, \tau_1) = \text{tr}\left[\hat{\mu}(0)\hat{\mu}(\tau_2 + \tau_1)\hat{\mu}(\tau_3 + \tau_2 + \tau_1)\hat{\mu}(\tau_1)\rho_0\right]
\]

\[
R_3(\tau_3, \tau_2, \tau_1) = \text{tr}\left[\hat{\mu}(0)\hat{\mu}(\tau_1)\hat{\mu}(\tau_3 + \tau_2 + \tau_1)\hat{\mu}(\tau_2 + \tau_1)\rho_0\right]
\]

\[
R_4(\tau_3, \tau_2, \tau_1) = \text{tr}\left[\hat{\mu}(\tau_3 + \tau_2 + \tau_1)\hat{\mu}(\tau_2 + \tau_1)\hat{\mu}(\tau_1)\hat{\mu}(0)\rho_0\right]
\]

where \(\hat{\mu} = \mu \sum_n \left[\hat{a}_n^+ |0\rangle_{\text{ex}} \langle 0| + |0\rangle_{\text{ex}} \langle 0| \hat{a}_n\right]\) is the transition dipole operator.

All the \(R_1, R_2, R_3\) and \(R_4\) are the 4-wave mixing correlation function:

\[
C_{4W}(t_4, t_3, t_2, t_1) = \text{tr}\left[\hat{\mu}(t_4)\hat{\mu}(t_3)\hat{\mu}(t_2)\hat{\mu}(t_1)\rho_0\right]
\]

\[
= \text{tr}\left[\hat{\mu}e^{i\hat{H}(t_3-t_4)} \hat{\mu}e^{i\hat{H}(t_2-t_3)} \hat{\mu}e^{-i\hat{H}(t_2-t_1)} \hat{\mu}\rho_0\right]
\]

\[
= \mu^2 \sum_n \sum_m \langle 0,0 | \hat{a}_m e^{i\hat{H}(t_3-t_4)} \hat{\mu}e^{i\hat{H}(t_2-t_3)} \hat{\mu}e^{-i\hat{H}(t_2-t_1)} \hat{a}_n^+ |0,0\rangle
\]

And this 4-wave mixing correlation function can be calculated numerically with a Davydov Ansatz.
$S = 2.0, \ J = 0.5, \ W = 0.1, \ \phi = 0$

**k$_I$ Signal**

(a) $t_2 = 0$

(b) Linear Absorption

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**k$_II$ Signal**

(a) $t_2 = 0$

(b) 2D ($\omega_1 = \omega_3$) Diag
Validity study: deviation vector of a trial state

\[ |\delta(t)\rangle \equiv \left( i\hbar \frac{\partial}{\partial t} - \hat{H} \right) |\Psi_D(t)\rangle \]

Amplitude of \( |\delta(t)\rangle \):

\[ \Delta(t) \equiv \sqrt{\langle \delta(t) | \delta(t) \rangle} \quad \leftarrow \text{Minimization leads to EOM !!} \]

Phonon Energy of the System:

\[ E_{\text{ph}}(t) = \langle \Psi_D(t) | \hat{H}_{\text{ph}} | \Psi_D(t) \rangle \]

Relative Deviation of the Ansatz:

\[ \sigma \equiv \frac{\max\{\Delta(t)\}}{\text{avg}\{E_{\text{ph}}(t)\}}, \quad t \in [0, t_{\text{max}}] \]
Relative Deviation $\sigma$
Zero-K sub-Ohmic spin-boson dynamics

Results from (a) J. Chem. Phys. 138, 084111(2013); (b) Phys. Rev. Lett. 110, 010402(2013).
Surface hopping based on the Davydov Ansätze

(1) Initially, the spin is in the up state and the bosonic displacement follows the thermal distribution.

(2) The dynamics of both the spin and the bosons follows the Davydov Ansatz.

(3) The hopping criterion is:

$$\xi < \begin{cases} \rho_-(t) \exp[-(\epsilon_- - \epsilon_+)/k_B T], & \epsilon_- > \epsilon_+ \\ \rho_-(t), & \epsilon_- \leq \epsilon_+ \end{cases}$$

with a random number $\xi$ uniformly distributed in $[0,1)$. 
Comparison between our algorithm and QUAPI

(1) Our algorithm produces reliable results compared with that from QUAPI.

(2) The phase is conserved during the surface hopping.

(3) The detailed balance is fulfilled due to the hopping criterion we employ.
Time evolution of spin population

Strong coupling

(a) $\Delta=0.02$, $\alpha=0.05$

(b) $\Delta=0.06$, $\alpha=0.05$

(c) $\Delta=0.1$, $\alpha=0.05$

Weak coupling

(a) $\Delta=0.02$, $\alpha=0.01$

(b) $\Delta=0.06$, $\alpha=0.01$

(c) $\Delta=0.1$, $\alpha=0.01$
Comparison with the Marcus theory

Our results are in good agreement with that from the Marcus theory in the weak tunneling regime.
A variational approach to the ground state of the spin-boson model

1. A sophisticated multi-D, ansatz is introduced as the trial wave function.

\[ |\Psi\rangle = |+\rangle \sum_{n=1}^{N} A_n \exp \left[ \sum_{l} f_{n,l} \left( b^\dagger_l - b_l \right) \right] |0\rangle_{ph} \]

\[ + |-\rangle \sum_{n=1}^{N} B_n \exp \left[ \sum_{l} g_{n,l} \left( b^\dagger_l - b_l \right) \right] |0\rangle_{ph} \]

2. More than 100 random initial states are used in iteration procedure, and the target precision $10^{-14}$ is set.

\[ \frac{\partial H}{\partial x_i} - E \frac{\partial D}{\partial x_i} = 0 \]

where $E$ is the system energy, $H$ is the Hamiltonian expectation and $D$ is the normal of the wave function. $X_i$ denotes any variational parameter.

3. The extended simulated annealing algorithmic is adopted with the relaxation factor gradually decreasing from 0.1 to 0.001 to prevent from the trapping in metastable states.
Two-bath SBM with diagonal and off-diagonal coupling

\[ \hat{H} = \frac{\varepsilon}{2}\sigma_z - \frac{\Delta}{2}\sigma_x + \sum_{l,i} \omega_l b_{l,i}^\dagger b_{l,i} + \frac{\sigma_z}{2} \sum_l \lambda_l (b_{l,1}^\dagger + b_{l,1}) \]

\[ + \frac{\sigma_x}{2} \sum_l \phi_l (b_{l,2}^\dagger + b_{l,2}) , \]

where coupling strengths \( \lambda_l \) and \( \phi_l \) are determined by the spectral densities

\[
J_z(\omega) = 2\alpha \omega_c^{1-s} \omega^s, \quad J_x(\omega) = 2\beta \omega_c^{1-\bar{s}} \omega^\bar{s}.
\]

\( s(\bar{s}) \) is the spectral exponent and \( \alpha(\beta) \) is the coupling constant, corresponding to the diagonal (off-diagonal) coupling bath.

For simplicity, we focus on the case with the bias \( \varepsilon=0 \) and tunneling \( \Delta=0 \).
Acknowledgments

Yao Yao (surface hopping)

Nengji Zhou, Yao Yao, Ning Wu, Liwei Duan (spin-boson model)

Chen Lipeng, Jun Ye, Bin Luo, Jin Sun (polaron dynamics)

National Research Foundation, Singapore
(Project # NRF-CRP5-2009-04)
Our NTU research group