Hierarchy equations of motion

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What is HEOM?

- Hierarchy equation of motion
- Numerically exact solution to non-relativistic time dependent Schrodinger equation for a specific Hamiltonian

$$H_T = H_s + H_b + V(s,b)$$

Density matrix

- Let $|\psi\rangle$ be the wavefunction of any system
- Density matrix is an operator: $\hat{\rho} = |\psi\rangle\langle\psi|$
- It is an equally complete description of the state as $|\psi\rangle$

Density matrix

- For example, expectation value of any operator is:

$$\langle\psi|\hat{A}|\psi\rangle = Tr[\hat{A}\hat{\rho}]$$

Proof: Let $A|i\rangle = a_i|i\rangle$,

$$\langle\psi|\hat{A}|\psi\rangle = \sum_i \sum_j \langle\psi|i\rangle\langle i|\hat{A}|j\rangle\langle j|\psi\rangle$$

$$= \sum_i a_i \langle i|\psi\rangle\langle\psi|i\rangle$$

$$= \sum_i \langle i|\hat{A}\hat{\rho}|i\rangle$$

$$= Tr[\hat{A}\hat{\rho}]$$

Density matrix properties

1. $Tr[\hat{\rho}] = 1$
2. $\hat{\rho}^2 = \hat{\rho}$ (for a pure system, i.e. system has a wavefunction)
3. $\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right]$

Reduced density matrix

- Consider the Hamiltonian: $H_T = H_s + H_b + V(s,b)$
- If $|\psi\rangle$ of total system is known, how do we describe state of the system?

- Does the system have a wavefunction?
  - Not necessarily!

- In this case state of the system is described by a density matrix

Reduced density matrix

- Consider the Hamiltonian: $H = H_s + H_b + V(s,b)$
- Density matrix of the system is called reduced density matrix: $\hat{\rho}_s$
- We want $\hat{\rho}_s$ to satisfy the relation: $\langle \hat{A}_s \rangle = Tr_s\left[\hat{A}_s \hat{\rho}_s\right]$
- This implies $\hat{\rho}_s = Tr_B[\rho]$ (trace over bath space)

- What is the equation of motion of $\hat{\rho}_s$?

Hierarchy Equation Of Motion

$$H_S = \sum_{i=1}^{N} \epsilon_i |i\rangle\langle i| + \sum_{ij}^{N} V_{ij} |i\rangle\langle j|$$

$$H_B = \sum_i \left(\frac{p_i^2}{2m} + \frac{1}{2} m\omega_i^2 x_i^2 \right)$$

$$V_{sb} = \sum_j |j\rangle\langle j| \sum_i c_{ji} x_i$$

Spectral density: $J_j(\omega) = \frac{1}{\hbar} \sum_i \frac{c_{ji}^2}{2m\omega_i} \delta(\omega - \omega_i)$

Tanimura and Kubo, JPSJ **58**, 1199 (1989)

Bath correlation function

- $C_j(t) = \langle u_j(t) u_j(0) \rangle$ $\quad u_j(t) = \sum_i c_{ji} x_i\,(t)$

$$= \frac{1}{\pi} \int_0^\infty d\omega \, \frac{J_j(\omega) e^{i\omega t}}{1 - e^{-\beta\hbar\omega}}$$

- If $J_j(\omega) = \frac{2\lambda_j \gamma_j}{\hbar} \frac{\omega}{\omega^2 + \gamma_j^2}$, then $C_j(t) = \sum_{m=0}^{\infty} c_{jm} \exp(-\nu_{jm} t)$

$$\nu_{j0} = \gamma_j, \; \nu_{jm>0} = \frac{2\pi m}{\beta\hbar},$$

$$c_{j0} = \frac{\gamma_j \lambda_j}{\hbar} \left(\cot\left(\frac{\beta\hbar\gamma_j}{2} \right) - i \right), \; c_{jm>0} = \frac{4\lambda_j \gamma_j}{\beta\hbar^2} \frac{\nu_{jm}}{\nu_{jm}^2 - \gamma_j^2}$$

Yan and Xu, ARPC **56**, 187 (2005)

Hierarchy Equation Of Motion

$$\dot{\hat{\rho}}_{\boldsymbol{n}} = -\frac{i}{\hbar}[H_s, \rho_{\boldsymbol{n}}] - \sum_{j=1}^{N}\sum_{m=0}^{M} n_j \nu_{jm} \rho_{\boldsymbol{n}} - i \sum_{j=1}^{N}\sum_{m=0}^{M} \left[|j\rangle\langle j|, \rho_{\boldsymbol{n}_{jm}^{+}}\right]$$

$$-i \sum_{j=1}^{N}\sum_{m=0}^{M} n_{jm} \left(c_{jk} |j\rangle\langle j| \rho_{\boldsymbol{n}_{jm}^{-}} + c_{jm}^{*} \rho_{\boldsymbol{n}_{jm}^{-}} |j\rangle\langle j| \right)$$

- Proof: Strumpfer and Schulten, JCP **131** 225101 (2009) (proof in SI) https://aip.scitation.org/doi/full/10.1063/1.3271348

Tanimura and Kubo, JPSJ **58**, 1199 (1989)

Hierarchy

$$\boldsymbol{n} = (n_{10}, n_{11}, \ldots, n_{1M}, n_{20}, \ldots, n_{2M}, \ldots, n_{N0}, \ldots n_{NM})$$
$$\rho_{\boldsymbol{n}=\boldsymbol{0}} = \rho_S$$

N =total number of system levels

M= number of terms in the expansion of bath correlation function

$$C_j(t) = \sum_{m=0}^{M} c_{jm} \exp(-\nu_{jm} t)$$

L = depth of hierarchy = $\sum_i \sum_j n_{ij}$

Initial Condition

- $\rho(t = 0) = \rho_s(0) \; \frac{e^{-\beta H_B}}{Tr\left[e^{-\beta H_B}\right]}$
- $\rho_{\boldsymbol{n}\neq 0}(0) = 0$

Faster converging HEOM!

$$\tilde{\rho}_{\boldsymbol{n}} = \left(\prod_k n_k!\ |c_k|^{n_k}\right)^{-\frac{1}{2}} \rho_{\boldsymbol{n}}(t)$$

$$\tilde{\rho}_{\boldsymbol{n}=0} = \rho_{\boldsymbol{n}=0}$$

$$\dot{\tilde{\rho}}_{\boldsymbol{n}} = -\frac{i}{\hbar}[H_s, \tilde{\rho}_{\boldsymbol{n}}] - \sum_{j=1}^{N}\sum_{m=0}^{M} n_{jm}\nu_{jm}\tilde{\rho}_{\boldsymbol{n}} - i\sum_{j=1}^{N}\sum_{m=0}^{M}\sqrt{(n_{jm}+1)c_{jm}}\left[|j\rangle\langle j|, \tilde{\rho}_{\boldsymbol{n}_{jm}^{+}}\right]$$

$$-i\sum_{j=1}^{N}\sum_{m=0}^{M}\sqrt{\frac{n_{jm}}{c_{jm}}}\left(c_{jk}|j\rangle\langle j|\tilde{\rho}_{\boldsymbol{n}_{jm}^{-}} + c_{jm}^{*}\tilde{\rho}_{\boldsymbol{n}_{jm}^{-}}|j\rangle\langle j|\right)$$

Shi, Chen, Nan, Xu, and Yan, JCP **130,** 084105 (2009)