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Libra *Summer School and Workshop 2024*
HEOM

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Fundamentals of HEOM with Libra

See here

https://compchem-cybertraining.github.io/Cyber_Training_Workshop_2021/files/Jain-HEOM.pdf

System-bath Hamiltonian for HEOM

Temen, S.; Jain, A.; Akimov, A. V. *IJQC* **2020**, *120*, e26373.

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$$H = H_s + H_b + H_{sb,1}$$

$$H = \sum_{n,m=0}^{N-1} |n\rangle H_{nm} \langle m| + \sum_{n=0}^{N-1} |n\rangle \sum_{b=0}^{N_n-1} \left(\frac{p_{b,n}^2}{2} + \frac{1}{2}\omega_{b,n}^2 x_{b,n}^2 \right) \langle n| + \sum_{n=0}^{N-1} |n\rangle F_n \langle n|.$$

$$H_s = \begin{pmatrix} E_0 & V_{01} & \cdots \\ V_{10} & E_1 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

$$F_n = \sum_{b=0}^{N_b-1} f_{b,n} x_{b,n}.$$

$$H_b = \sum_{n=0}^{N-1} \sum_{f=0}^{F-1} \{ |n > \frac{p_f^2}{2m_f} + \frac{1}{2} m_f \omega_{n,f}^2 q_f^2) < n| \}$$

$$J_n(\omega) = \frac{\pi}{2} \sum_{b=0}^{N_n-1} \frac{f_{b,n}^2}{\omega_{b,n}} \delta(\omega - \omega_{b,n}).$$

$$H_{sb,1} = \sum_{n=0}^{N-1} s_n \sum_{f=0}^{F-1} \{ |n > c_{n,f} q_f < n| \}$$

$$J_n(\omega) = \frac{\eta\gamma\omega^2}{\omega^2 + \gamma^2}.$$

Debye spectral density

$$J(\omega) = \frac{\lambda}{2} \frac{\omega\omega_c}{\omega^2 + \Omega^2}$$

$$J(\omega) = \frac{\pi}{2} \sum_{j=1}^{N} \frac{c_j^2}{\omega_j} \delta(\omega - \omega_j).$$

η – bath reorganization energy

$\gamma = \frac{\Gamma}{\hbar}$; Γ – system-bath interaction energy

λ – bath reorganization energy

$$\omega_f = \Omega \tan\left(\frac{\pi}{2}(1 - \frac{f+1}{F+1}) \right) \forall f = 0, \ldots, F-1$$

$$\frac{\lambda}{2} = \eta \qquad \gamma = \Omega \qquad \omega_c = \Omega\omega$$

$$f_{b,n} = s_n c_{n,f}$$

$$c_f = -\omega_f \sqrt{\frac{2\lambda}{F+1}} \forall f = 0, \ldots, F-1$$

Wu, D.; Hu, Z.; Li, J.; Sun, X. JCP 2021, 155, 224104

The Hierarchy of Equations

Temen, S.; Jain, A.; Akimov, A. V. *IJQC* **2020**, *120*, e26373.

J. Strümpfer, K. Schulten, J. Chem. Theory Comput. 2012, 8, 2808;
Q. Shi, L. Chen, G. Nan, R.-X. Xu, Y. Yan, J. Chem. Phys. 2009, 130, 084105;
L. Chen, R. Zheng, Q. Shi, Y. Yan, J. Chem. Phys. 2009, 131, 094502.

$$\dot{\rho}_{\mathbf{n}} = -i[H,\rho_{\mathbf{n}}] - \sum_{m=0}^{M-1}\left(\sum_{k=0}^{K} n_{mk}\gamma_{mk}\right)\rho_{\mathbf{n}} + \rho_{\mathbf{n}}^{(+)} + \rho_{\mathbf{n}}^{(-)} + T_{\mathbf{n}}.$$

$$\rho_{\mathbf{n}}^{(+)} = -i\sum_{m=0}^{M-1}\left[Q_m, \sum_{k=0}^{K}\rho_{\mathbf{n}_{mk}^{+}}\right].$$

$$\rho_{\mathbf{n}}^{(-)} = -i\sum_{m=0}^{M-1}\sum_{k=0}^{K} n_{mk}\left(F_{mk}c_{mk}\rho_{\mathbf{n}_{mk}^{-}} - c_{mk}^{*}\rho_{\mathbf{n}_{mk}^{-}}F_{mk}\right).$$

$$T_{\mathbf{n}} = \sum_{m=0}^{M-1}\Delta_K[Q_m,[Q_m,\rho_{\mathbf{n}}]].$$

$$\Delta_K = \sum_{n=0}^{\infty}\frac{c_{K+n}}{\gamma_{K+n}}.$$

$$C(t>0) = \sum_{k=0}^{K} c_k \exp(-\gamma_k t).$$

Quantum correlation function;

Matsubara expansion coefficients

$$c_0 = \frac{1}{2}\gamma\eta\left(\left[\tan\left(\frac{\gamma}{2k_B T}\right)\right]^{-1} - i\right),$$

$$c_k = \frac{4n\pi\eta\gamma}{(2k\pi)^2 - (\beta\gamma)^2} = \frac{4n\pi\eta\gamma}{\beta^2\left[\left(\frac{2n\pi}{\beta}\right)^2 - (\gamma)^2\right]} = 2\eta k_B T\frac{\gamma_0\gamma_n}{\gamma_n^2 - \gamma_0^2}, k \geq 1.$$

Matsubara frequencies

$$\gamma_0 = \gamma.$$

$$\gamma_n = \frac{2\pi n}{\beta} = 2\pi n k_B T, n \geq 1,$$

The indexing system

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M – the number of system levels;

K – the number of Matsubara frequencies

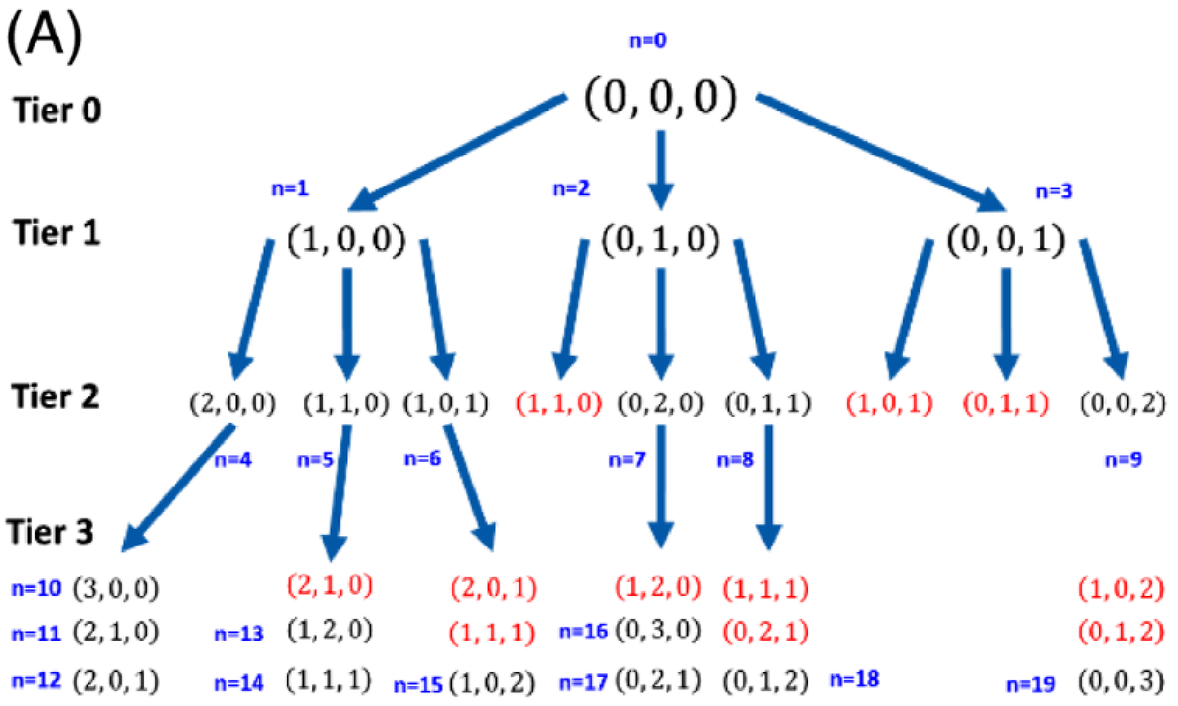
$$\mathbf{n} = (n_{00}, n_{01}, \ldots, n_{0K}, n_{10}, n_{11}, \ldots, n_{1K}, \ldots, n_{M-1,0}, n_{M-1,1}, \ldots, n_{M-1,K}).$$

$$\mathbf{n}^{+}_{mk} = (n_{00}, \ldots, n_{0K}, \ldots, n_{m0}, \ldots, n_{mk} + 1, \ldots, n_{mK}, \ldots, n_{M-1,0}, n_{M-1,1}, \ldots, n_{M-1,K}).$$

$$\mathbf{n}^{-}_{mk} = (n_{00}, \ldots, n_{0K}, \ldots, n_{m0}, \ldots, n_{mk} - 1, \ldots, n_{mK}, \ldots, n_{M-1,0}, n_{N-1,1}, \ldots, n_{M-1,K}).$$

Depth of hierarchy

$$n = tier(\mathbf{n}) = \sum_{m=0}^{M-1} \sum_{k=0}^{K} n_{mk}.$$



(B)

	index	$\mathbf{n}$	indices of $\mathbf{n}^{+}$	indices of $\mathbf{n}^{-}$
Tier 0	0	(0, 0, 0)	(1, 2, 3)	(−1, −1, −1)
	1	(1, 0, 0)	(4, 5, 6)	(0, −1, −1)
Tier 1	2	(0, 1, 0)	(5, 7, 8)	(−1, 0, −1)
	3	(0, 0, 1)	(6, 8, 9)	(−1, −1, 0)
	4	(2, 0, 0)	(−1, −1, −1)	(1, −1, −1)
	5	(1, 1, 0)	(−1, −1, −1)	(2 , 1, −1)
Tier 2	6	(1, 0, 1)	(−1, −1, −1)	(3, −1, 1)
	7	(0, 2, 0)	(−1, −1, −1)	(−1, 2, −1)
	8	(0 1, 1)	(−1, −1, −1)	(−1, 3, 2)
	9	(0 0, 2)	(−1, −1, −1)	(−1, −1, 3)

Scaled HEOM

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Q. Shi, L. Chen, G. Nan, R.-X. Xu, Y. Yan, J. Chem. Phys. 2009, 130, 084105;

$$\tilde{\rho}_{\mathbf{n}} = \left(\prod_{m=0}^{M-1} \prod_{k=0}^{K} n_{mk}! |c_{mk}|^{n_{mk}} \right)^{-1/2} \rho_{\mathbf{n}}. \qquad \tilde{\rho}_{\mathbf{0}} = \rho_{\mathbf{0}},$$

$$\frac{d\tilde{\rho}_{\mathbf{n}}}{dt} = -i[H,\tilde{\rho}_{\mathbf{n}}] - \sum_{m=0}^{M-1} \left(\sum_{k=0}^{K} n_{mk}\gamma_{mk} \right) \tilde{\rho}_{\mathbf{n}} + \tilde{\rho}_{\mathbf{n}}^{(+)} + \tilde{\rho}_{\mathbf{n}}^{(-)} + \tilde{T}_{\mathbf{n}}.$$

$$\tilde{\rho}_{\mathbf{n}}^{(+)} = -i \sum_{m=0}^{M-1} \left[Q_m, \sum_{k=0}^{K} \sqrt{(n_{mk}+1)|c_{mk}|}\, \tilde{\rho}_{\mathbf{n}_{mk}^{+}} \right]. \qquad \sqrt{(n_{mk}+1)|c_{mk}|} \rightarrow 1$$

$$\tilde{\rho}_{\mathbf{n}}^{(-)} = -i \sum_{m=0}^{M-1} \sum_{k=0}^{K} \sqrt{n_{mk}/|c_{mk}|} \left(F_{mk} c_{mk} \tilde{\rho}_{\mathbf{n}_{mk}^{-}} - c_{mk}^{*} \tilde{\rho}_{\mathbf{n}_{mk}^{-}} F_{mk} \right). \qquad \sqrt{n_{mk}/|c_{mk}|} \rightarrow n_{mk}$$

Same as the original equations

$$\tilde{T}_{\mathbf{n}} = \sum_{m=0}^{M-1} \Delta_K [Q_m, [Q_m, \tilde{\rho}_{\mathbf{n}}]].$$

But converges faster than the original equations

Convergence and complexity of the HEOM calculations

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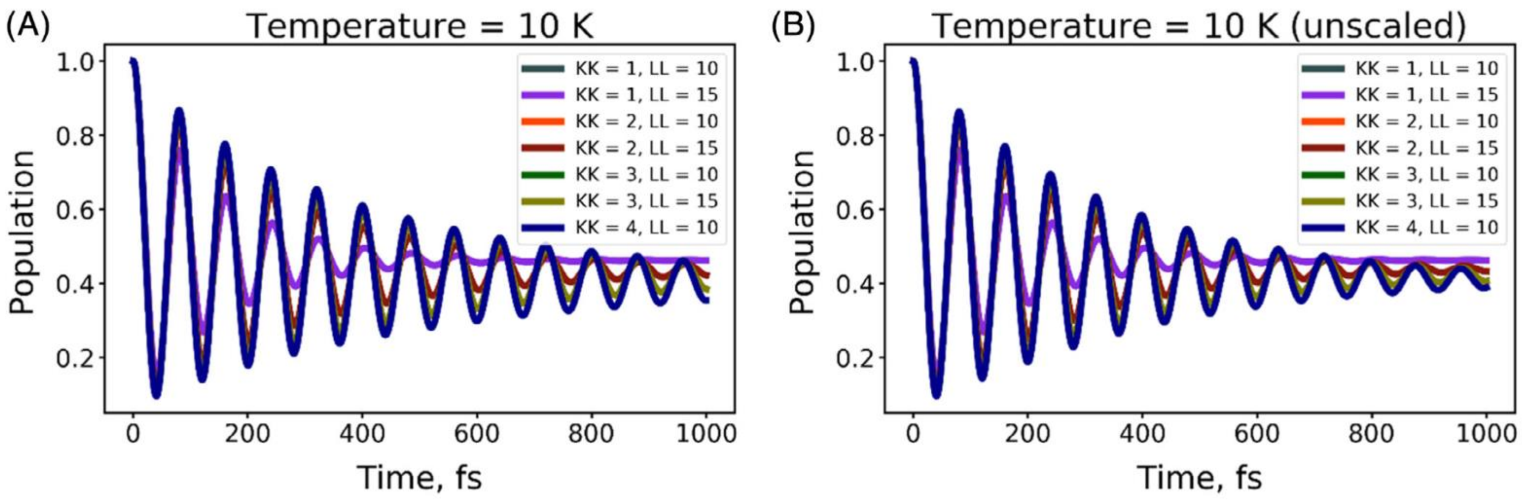

TABLE 1 The calculation timings are compared for different low temperatures at various hierarchy complexities

Hierarchy Parameters	Time per step (ms)					Number of auxiliary density matrices
	100 K	50 K	25 K	10 K	10 K (unscaled)	
KK = 1, LL = 10	16	17	18	18	5	1001
KK = 1, LL = 15	40	18	60	70	19	3876
KK = 2, LL = 10	94	119	143	153	38	8008
KK = 3, LL = 10	441	581	772	929	282	43 758
KK = 2, LL = 15	346	439	630	1007	287	54 264
KK = 4, LL = 10	1211	1399	1693	2060	1171	184 756
KK = 3, LL = 15	2664	2917	3344	4657	3261	490 314

Note: Lower temperatures have longer runtimes.

Spectra calculations

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Initial condition: $\rho_0(0) = |g\rangle\langle g|$

$$\langle \mu(t)\mu(0)\rangle_g = Tr[\rho_0(t)\mu].$$

$$I(\omega) = \frac{1}{\pi} \mathrm{Re}\left[\int_0^\infty dt e^{i\omega t} \langle \mu(t)\mu(0)\rangle_g\right],$$