Nonadiabatic Charge and Energy Transfer







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Motivation









Challenge:
$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H},\hat{\rho}(t)]$$

- High-dimensional (open) systems (nuclei, electrons, photons)
- Compatible with both model Hamiltonians and *ab initio* methods.
- "Accuracy" in different physical and chemical settings.
- Computational cost less than or equal to ...



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- High-dimensional systems (nuclei, electrons, photons)
- Compatible with both model Hamiltonians and *ab initio* methods.
- "Accuracy" in different physical and chemical settings.
- Computational cost less than or equal to ... MEAN FIELD THEORY.
- Systematic improvability would also be nice....





- Quantum classical dynamics and Ehrenfest mean-field theory
- The Nakajima-Zwanzig generalized quantum master equation
- Trajectory-based dynamics methods via wavefunction ansatze



$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H},\hat{\rho}(t)]$$



 $\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H},\hat{\rho}(t)]$

 $\hat{\rho}_W(R,P) = (2\pi\hbar)^{-3N} \int dZ \, e^{iP \cdot Z/\hbar} \langle R - \frac{Z}{2} | \hat{\rho} | R + \frac{Z}{2} \rangle$



 $\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H},\hat{\rho}(t)]$

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$$(\hat{A}\hat{B})_W(R,P) = \hat{A}_W(R,P)e^{\hbar\Lambda/2i}\hat{B}_W(R,P)$$



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 $\left(\hat{A}\hat{B}\right)_{W}(R,P) = \hat{A}_{W}(R,P)e^{\hbar\Lambda/2i}\hat{B}_{W}(R,P)$

$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -\frac{i}{\hbar} \left(\hat{H}_W(R,P) e^{\hbar \Lambda/2i} \hat{\rho}_W(R,P,t) - \hat{\rho}_W(R,P,t) e^{\hbar \Lambda/2i} \hat{H}_W(R,P) \right)$$



$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -\frac{i}{\hbar} \left(\hat{H}_W(R,P) e^{\hbar \Lambda/2i} \hat{\rho}_W(R,P,t) - \hat{\rho}_W(R,P,t) e^{\hbar \Lambda/2i} \hat{H}_W(R,P) \right)$$

$$\mu = (m/M)^{1/2}$$



$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -\frac{i}{\hbar} \left(\hat{H}_W(R,P) e^{\hbar \Lambda/2i} \hat{\rho}_W(R,P,t) - \hat{\rho}_W(R,P,t) e^{\hbar \Lambda/2i} \hat{H}_W(R,P) \right)$$

$$\mu = (m/M)^{1/2}$$

$$\frac{\partial \hat{\rho}'_{W}(R',P',t')}{\partial t'} = -i(\hat{H}'_{W}(R',P')e^{\mu\Lambda'/2i}\hat{\rho}'_{W}(R',P',t') - \hat{\rho}'_{W}(R',P',t')e^{\mu\Lambda'/2i}\hat{H}'_{W}(R',P'))$$



Quantum-Classical Dynamics

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} &= -\frac{i}{\hbar} \left[\hat{H}_W(R,P), \hat{\rho}_W(R,P,t) \right] \\ &+ \frac{1}{2} \left(\left\{ \hat{H}_W(R,P), \hat{\rho}_W(R,P,t) \right\} - \left\{ \hat{\rho}_W(R,P,t), \hat{H}_W(R,P) \right\} \right) \end{aligned}$$

$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -i\hat{\mathscr{L}}\hat{\rho}_W(R,P,t)$$



Kapral and Ciccotti, JCP, 1999.

Quantum-Classical Dynamics

$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -\frac{i}{\hbar} \left[\hat{H}_W(R,P), \hat{\rho}_W(R,P,t) \right] + \frac{1}{2} \left\{ \left\{ \hat{H}_W(R,P), \hat{\rho}_W(R,P,t) \right\} - \left\{ \hat{\rho}_W(R,P,t), \hat{H}_W(R,P) \right\} \right\}$$

$$\hat{H}_W = H_e(X) + \hat{H}_s(\hat{q}) + \hat{V}_c(\hat{q}, R)$$





Surface Hopping

- A natural choice for trajectory-based simulations is to work in the adiabatic basis, which often leads to surface-hopping type algorithms.
 - e.g. Fewest Switches Surface Hopping (FSSH)
- However, other (more rigorous) surface-hopping schemes are also available
 - e.g. Momentum-jump approximation to the QCLE





QCLE - Surface Hopping





Hierarchy of Trajectory Based Approaches





$$\hat{\rho}_s(t) = \int dX \; \hat{\rho}_W(X,t)$$

 $\rho_e(X,t) = \mathrm{Tr}'\hat{\rho}_W(X,t)$



Mean Field Theory is "Uncorrelated" Quantum-Classical Dynamics

$$\hat{\rho}_s(t) = \int dX \, \hat{\rho}_W(X,t) \qquad \qquad \rho_e(X,t) = \mathrm{Tr}' \hat{\rho}_W(X,t)$$

$$\hat{\rho}_W(X,t) \equiv \hat{\rho}_s(t)\rho_e(X,t) + \hat{\rho}_{cor}(X,t)$$



Mean Field Theory is "Uncorrelated" Quantum-Classical Dynamics

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$$\frac{\partial \rho_e(X,t)}{\partial t} = \left\{ H_e + \mathrm{Tr}' \hat{V}_c \hat{\rho}_s(t), \rho_e(X,t) \right\}$$



$$\frac{\partial \rho_e(X,t)}{\partial t} = \left\{ H_e + \mathrm{Tr}' \hat{V}_c \hat{\rho}_s(t), \rho_e(X,t) \right\}$$

$$\dot{R}(t) = rac{P(t)}{M}, \quad \dot{P}(t) = -rac{\partial V_{\mathrm{eff}}(R(t))}{\partial R(t)}.$$



$$\frac{\partial \rho_e(X,t)}{\partial t} = \left\{ H_e + \mathrm{Tr}' \hat{V}_c \hat{\rho}_s(t), \rho_e(X,t) \right\}$$

$$\dot{R}(t) = rac{P(t)}{M}, \quad \dot{P}(t) = -rac{\partial V_{\mathrm{eff}}(R(t))}{\partial R(t)}.$$

$$\frac{\partial \hat{\rho}_s(t)}{\partial t} = -\frac{i}{\hbar} \Big[\hat{H}_s + \int dX \, \hat{V}_c \rho_e(X,t), \hat{\rho}_s(t) \Big]$$



Heat Transport through a Molecular Junction



$$g_{\lambda}(\omega) = \frac{\pi}{2} \xi_{\lambda} \omega \exp(-\omega/\omega_{c,\lambda})$$



Heat Transport through a Molecular Junction





AK, JCP 2019

Heat Transport through a Molecular Junction



AK, JCP 2019

Spontaneous Emission of Radiation (in a Cavity)





Spontaneous Emission of Radiation (in a Cavity)







Norah Hoffmann et al., PRA 2019

Spontaneous Emission of Radiation (in a Cavity)







Norah Hoffmann et al., PRA 2019

The Generalized Quantum Master Equation: Reduced Dynamics

Liouville – von Neumann Equation

 $\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H},\hat{\rho}(t)]$



 $\hat{\mathcal{P}}_{\mathcal{A}}^{eq}$ is the dense $\hat{\mathcal{S}}_{\mathcal{A}}$ is a pure bath $\hat{\mathcal{O}}_{\mathcal{A}}$ is a pure bath $\hat{\mathcal{O}_{\mathcal{A}}$ is a pure bath $\hat{\mathcal{O}}_{\mathcal{A}}$ is a pure ropalso assume that the initial state the marster care be factorized in the following mann $\hat{H}_b)$ $\frac{1}{\partial t}\hat{\rho}(t) = -\frac{1}{\hat{\rho}} \begin{bmatrix} \hat{H} \\ \hat{\rho}(t) \end{bmatrix}_{eq} \hat{\rho}(t) = \hat{\rho} \begin{bmatrix} \hat{H} \\ \hat{\rho}(t) \end{bmatrix}_{eq} \hat{\rho}_{b} \hat{\rho}_{$ (24) $\frac{\partial \hat{H}_{i}}{\partial \hat{H}_{i}}$ where $\langle \cdots \rangle_{eq} = Tr_b(\underbrace{\cdots \hat{\rho}_b^{eq}})$ denotes the equilibrium bath av $e s_{i-1}$ rs/2f. the correction Projection Appte _____Operators rally sa $\frac{\exp(\overline{Sec.}^{BH})}{\operatorname{Sec.}^{H}}$ such a condition neral cases it can be simply Algebra Aphte density en in rative 40 its thermal average.²² operneorborated nal assumption is that the ther luced dynamics of the subsystem are as enotime coolution of the subsystem RDM is given by the formally rexact ANakajima-Zwanzig mensitions assumptions fond may $\overline{proceed}^{solv}$ describe the K-(Tukes (dynamics of the super GQME, t^0 Nakajima-Zwar GQME, t^0 Nakajima. Zwanzie. Mori Nakajima, Zwanzig, Mori $d\tau \mathcal{K}(\tau) \hat{o}(t - \tau)$ (25)

Monte is naturally satisfied nowever in general cases it can be simply ventile $G_{\text{eneralized Quantum Master Equation}}^{\text{incorporated by redefining } \hat{\Lambda}}$ relative to its thermal average.²² Under these conditions, the time evolution of the subsystem RDM is given by the formally exact Nakajima-Zwanzig omen-nsition $\frac{d}{dt}\hat{\rho}_{s}(t) = -i\mathcal{L}_{s}\hat{\rho}_{s}(t) - \int_{0}^{t} d\tau \mathcal{K}(\tau)\hat{\rho}_{s}(t-\tau),$ $\frac{d}{dt}\hat{\rho}_{s}(t) = -i\mathcal{L}_{s}\hat{\rho}_{s}(t) - \int_{0}^{t} d\tau \mathcal{K}(\tau)\hat{\rho}_{s}(t-\tau),$ Not so simple: $\mathcal{K}(\tau)$ nsition (25)l, such ven by



method to phopolipe hated by the family of the first of t the wirdes General the chieves and it of the subsysweights that the state superior is given by the formally exact Nakajwhrae-Zwanzig stem many eases. In this, section, we show how the formally exact Nakajwhrae-Zwanzig $d\tau \mathcal{K}(\tau) \hat{\rho}_{s} (\tau) = d\tau'_{s} \tau'_{s} \tau$ this as ben Grand Menority the EQME for mal (m) to Shapproach the allows for the generation of long $\mathcal{L}_{sb}e^{i\mathcal{L}_{sb}}$ and $\mathcal{L}_{sb}e^{i\mathcal{L}_{sb}}$ at the evolution in the adjustion of the second se hadradatised thamics d Estimates of longer. I, induction of the reduced $\mathcal{L}_{sb}\mathcal{P}$ Another insertion of the reduced $\mathcal{L}_{sb}\mathcal{P}$ Another insertion of the reduced $\mathcal{L}_{sb}\mathcal{P}$ and the the reduced $\mathcal{L}_{sb}\mathcal{P}$ are the reduced $\mathcal{L}_{sb}\mathcal{P}$ and $\begin{array}{l} \underset{t \neq k}{\overset{\text{gr}}{\underset{\text{into (30)}}{\overset{\text{gr}}{\underset{\text{above yield}(\tau)}{\overset{\text{gr}}{\underset{\text{st}}}}}} = \underbrace{(28)}_{i} \hat{H}_{s} \text{followFhe} \\ \underset{t \neq k}{\overset{\text{gr}}{\underset{\text{st}}}} \underbrace{(\tau_{\tau}) + i}_{k} \underbrace{(\tau_{\sigma}) \neq k}_{s} \underbrace{(\tau_{\tau}) + \tau'_{i}}_{k} \underbrace{(\tau_{\tau}) + \tau'_{i}}_{2} \underbrace{(\tau_{\tau}) + \tau'_{i}}_{k} \underbrace{(\tau_{\tau}) + \tau'_{i}}_{k}$ **brome**reduced 14104-5 Α. $d\tau' \mathcal{K}_3(\tau_w + e\tau') \mathcal{K}_2(\tau), J_0$ (3) Here d by ${}^{b}\text{ext}_{\mathcal{K}_{1}(\tau)} = Tr_{b} \int_{\mathcal{K}_{2}} \mathcal{L}_{2} e^{-i\mathcal{K}_{3}^{\tau}} \mathcal{L}_{2} + \hat{\ell}_{2} e^{-i\mathcal{K}_{3}^{\tau}} \mathcal{L}_{2} + \hat{\ell}_{$ vhere $\{e^{-i\mathcal{L}}\mathcal{K}\mathcal{L}(f)\}$ $Tr_b\{e^{i\mathcal{L}}\mathcal{K}\mathcal{L}(f)\}$ $Tr_b\{e^{i\mathcal{L}}\mathcal{K}\mathcal{L}(f)\}$ $Tr_b\{e^{i\mathcal{L}}\mathcal{K}\mathcal{L}(f)\}$ ly on nemory Kertesimoratien de treu sipoutautosistem de treu ngth Qiang Shi and Eitan Geva, J. Chem. Phys., 2003 SCIID Dopayate the Selest creat RDWervars in program States Real Andrew Monthly

Photo-induced Electron Transfer







Disparate Time Scales in the Electron – Transfer Regime Lead to Massive Computational Speed-ups



Donor State Population Evolution







Pfalzgraff, Kelly, and Markland, JPCL, 2015.

Electron Transfer Rates



Exciton Transport in LHC-II





Exciton Transport in LHC-II



W. Pfalzgraff, A. Montoya-Castillo, A. Kelly, and T.E. Markland, JCP, 2019.





Exciton Transport in LHC-II









Going Beyond Mean Field Theory: Mapping - QCLE

$$H_m(\mathcal{X}) = \frac{P^2}{2M} + V_0(R) + \frac{1}{2\hbar} \overline{h}^{\lambda\lambda'}(R)(r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'})$$



Going Beyond Mean Field Theory: Mapping - QCLE

$$H_m(\mathcal{X}) = \frac{P^2}{2M} + V_0(R) + \frac{1}{2\hbar} \overline{h}^{\lambda\lambda'}(R)(r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'})$$

$$\dot{r}_{\lambda} = \frac{\partial H_m}{\partial p_{\lambda}}, \quad \dot{p}_{\lambda} = -\frac{\partial H_m}{\partial r_{\lambda}}, \quad \dot{R} = \frac{\partial H_m}{\partial P},$$
$$\dot{P} = -\frac{\partial H_m}{\partial R} + \frac{\hbar}{8\rho_m^{\mathcal{P}}} \frac{\partial \overline{h}^{\lambda\lambda'}}{\partial R} \left(\frac{\partial^2}{\partial r_{\lambda'}\partial r_{\lambda}} + \frac{\partial^2}{\partial p_{\lambda'}\partial p_{\lambda}}\right) \rho_m^{\mathcal{P}}$$



Going Beyond Mean Field Theory: Mapping - QCLE

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Going Beyond Mean Field Theory

$$H_m(\mathcal{X}) = \frac{P^2}{2M} + V_0(R) + \frac{1}{2\hbar} \overline{h}^{\lambda\lambda'}(R)(r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'})$$

Poisson Bracket Mapping Equation

$$\frac{\partial}{\partial t}\rho_m^{\mathcal{P}}(\mathcal{X},t) = \left\{H_m, \rho_m^{\mathcal{P}}\right\}_{\mathcal{X}} \equiv -i\mathcal{L}_m^{PB}\rho_m^{\mathcal{P}}(\mathcal{X},t)$$



Going Beyond Mean Field Theory: PBME

$$\overline{B(t)} = \int d\mathcal{X} \ B_m(\mathcal{X})\rho_m^{\mathcal{P}}(\mathcal{X},t)$$

$$\hat{\rho}_{m}^{\mathcal{P}}(X) = |m_{\lambda}\rangle \langle m_{\lambda} | \hat{\rho}_{m}(X) | m_{\lambda'} \rangle \langle m_{\lambda'} \rangle$$
$$\overline{B(t)} = \int d\mathcal{X} \ B_{m}^{\mathcal{P}}(\mathcal{X}) \rho_{m}^{\mathcal{P}}(\mathcal{X}, t)$$



$$P_{n \leftarrow m}(t) = \operatorname{Tr}\left[\hat{\rho}_{\mathrm{b}} |m\rangle \langle m| \,\mathrm{e}^{\mathrm{i}\hat{H}t} |n\rangle \langle n| \,\mathrm{e}^{-\mathrm{i}\hat{H}t}\right]$$

$$|n\rangle\langle n| = \frac{1}{S}\left(\hat{\mathbb{I}} + \hat{Q}_n\right)$$

$$\hat{Q}_n = (S-1) |n\rangle \langle n| - \sum_{m \neq n}^{S} |m\rangle \langle m|$$



$$P_{n \leftarrow m}(t) = \operatorname{Tr}\left[\hat{\rho}_{\mathrm{b}} |m\rangle \langle m| \,\mathrm{e}^{\mathrm{i}\hat{H}t} |n\rangle \langle n| \,\mathrm{e}^{-\mathrm{i}\hat{H}t}\right]$$

$$|n\rangle\langle n| = \frac{1}{S}\left(\hat{\mathbb{I}} + \hat{Q}_n\right) \qquad \qquad \hat{Q}_n = (S-1)|n\rangle\langle n| - \sum_{m \neq n}^{S} |m\rangle\langle m|$$

$$P_{n \leftarrow m}(t) = \frac{1}{S^2} \left(S + \operatorname{Tr} \left[\hat{\rho}_{\mathrm{b}} \hat{\mathbb{I}} \, \mathrm{e}^{\mathrm{i}\hat{H}t} \hat{Q}_n \mathrm{e}^{-\mathrm{i}\hat{H}t} \right] + \operatorname{Tr} \left[\hat{\rho}_{\mathrm{b}} \hat{Q}_m \mathrm{e}^{\mathrm{i}\hat{H}t} \hat{Q}_n \mathrm{e}^{-\mathrm{i}\hat{H}t} \right] \right)$$



$$\hat{Q}_n = (S-1) |n\rangle \langle n| - \sum_{m \neq n}^{S} |m\rangle \langle m|$$

$$P_{n \leftarrow m}(t) = \frac{1}{S^2} \left(S + \operatorname{Tr}\left[\hat{\rho}_{\mathrm{b}} \hat{\mathbb{I}} \, \mathrm{e}^{\mathrm{i}\hat{H}t} \hat{Q}_n \mathrm{e}^{-\mathrm{i}\hat{H}t} \right] + \operatorname{Tr}\left[\hat{\rho}_{\mathrm{b}} \hat{Q}_m \mathrm{e}^{\mathrm{i}\hat{H}t} \hat{Q}_n \mathrm{e}^{-\mathrm{i}\hat{H}t} \right] \right)$$

$$C_{\mathbb{I}Q_n}(t) = \left\langle \phi^a(\mathsf{X},\mathsf{P}) Q_n(\mathsf{X}(t),\mathsf{P}(t)) \right\rangle$$

 $C_{Q_mQ_n}(t) = \langle \phi^a(\mathsf{X},\mathsf{P}) Q_m(\mathsf{X},\mathsf{P}) Q_n(\mathsf{X}(t),\mathsf{P}(t)) \rangle$









 $\Psi(I,IL,L) = \psi(I,L)\chi(IL,L)$

Going Beyond Mean Field Theory (FIL $C_j(t)\phi_j(r)$ $\psi(r,t) = \sum_{j} \sum_{j} C_j(t)\phi_j(r)$ Recall: Mean Field Theory $\psi(r,t) = \sum_{j} \sum_{j} C_j(t)\phi_j(r)$, $\psi(r,t) = \psi(r,t)\chi(R,t)$

$$i\hbar \frac{\partial \Psi(r, R, t)}{\partial \Psi(r, R, t)} \stackrel{\hat{H}\Psi(r, R, t)}{= H\Psi(r, R, t)} = \hat{H}\Psi(r, R, t)$$
$$i\hbar \frac{\partial \Psi(r, R, t)}{\partial \Psi(r, R, t)} = \hat{H}\Psi(r, R, t)$$

ral form for the memory kernel, given above, is not straightforward to evaluate ection operator, \mathcal{P} . An elegant solution to this problem was presented by Sharmon presented by $\hat{\mathcal{P}}_{\mathcal{X}}(\hat{R},t)$ in $\hat{\mathcal{P}}_{\mathcal{X}}(\hat{R},t)$ following relation $\hat{\mathcal{P}}_{\mathcal{X}}(r,t)\hat{H}_{elec-nuc}(r,R)\psi(r,t)$ $\chi(R,t)$ is $\hat{\mathcal{P}}_{\mathcal{X}}(\hat{R},t)$ if $\hat{\mathcal{P}}_{\mathcal{X}}(\hat{R},t)$ is $\hat{\mathcal{P}}_{\mathcal{X}}(\hat{R},t)$ is $\hat{\mathcal{P}}_{\mathcal{X}}(r,t)\hat{H}_{elec-nuc}(r,R)\psi(r,t)$ is $\chi(R,t)$ $\hat{\mathcal{P}}_{\mathcal{X}}(\hat{R},t)$ $\hat{\mathcal{P}}_{\mathcal{X}}(r,t)\hat{\mathcal{P}}_{elec-nuc}(r,R)\psi(r,t)$ is $\chi(R,t)$ is $\hat{\mathcal{P}}_{\mathcal{X}}(r,t)\hat{\mathcal{P}}_{elec-nuc}(r,R)\psi(r,t)$ is $\chi(R,t)$ is $\hat{\mathcal{P}}_{\mathcal{X}}(r,t)\hat{\mathcal{P}}_{elec-nuc}(r,R)\psi(r,t)$ is $\hat{\mathcal{P}}_{\mathcal{X}}(r,t)\hat{\mathcal{P}}_{elec-nuc}(r,R)\psi(r,t)$ is $\hat{\mathcal{P}}_{\mathcal{X}}(r,t)\hat{\mathcal{P}}_{elec-nuc}(r,R)\psi(r,t)$ is $\hat{\mathcal{P}}_{\mathcal{X}}(r,t)$ is $\hat{\mathcal{P}}_{elec-nuc}(r,R)\psi(r,t)$ is $\hat{\mathcal{P}}_{elec-nuc}(r$

$$i\hbar \frac{\partial \psi(r,t)}{\partial t} \stackrel{=}{=} \left(\begin{array}{c} \hat{H}_{elec} - \hat{f}_{elec} (\chi(R,t)) \hat{H}_{elec-nuc}(R,t) \hat{f}_{elec-nuc}(r,R) \chi(R,t) \\ \hat{H}_{elec-nuc}(r,R) \chi(R,t) \end{array} \right) \stackrel{=}{\to} \left(\begin{array}{c} \hat{H}_{elec} - \hat{f}_{elec} (\chi(R,t)) \hat{f}_{elec-nuc}(r,R) \chi(R,t) \\ \hat{H}_{elec-nuc}(r,R) \chi(R,t) \end{array} \right) \stackrel{=}{\to} \left(\begin{array}{c} \hat{H}_{elec-nuc}(r,R) \chi(R,t) \\ \hat{H}_{elec-nuc}(r,R) \chi(R,t) \end{array} \right) \stackrel{=}{\to} \left(\begin{array}{c} \hat{H}_{elec-nuc}(r,R) \chi(R,t) \\ \hat{H}_{elec-nuc}(r,R) \chi(R,t) \end{array} \right) \stackrel{=}{\to} \left(\begin{array}{c} \hat{H}_{elec-nuc}(r,R) \chi(R,t) \\ \hat{H}_{elec-nuc}(r,R) \chi(R,t) \end{array} \right) \stackrel{=}{\to} \left(\begin{array}{c} \hat{H}_{elec-nuc}(r,R) \chi(R,t) \\ \hat{H}_{elec-nuc}(r,R) \\$$

ing this relation into (??) one finda

$$\begin{split} \psi(r,t) &= \sum_{j} C_{j}(t)\phi_{j}(r) \\ \textbf{Coupled Mean-Field Trajectories}(r,t) = \sum_{j} C_{j}(t)\phi_{j}(r) \\ \mathcal{C}_{j}(t)\phi_{j}(r) \\ \mathcal{C}_{j}(t)\phi_{j}(t)\phi_{j}(r) \\ \mathcal{C}_{j}(t)\phi_{j}(t)\phi_{j}(r) \\ \mathcal{C}_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(r) \\ \mathcal{C}_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t) \\ \mathcal{C}_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t) \\ \mathcal{C}_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t)\phi_{j}(t) \\ \mathcal{C}_{$$

Going Beyond Mean Field Theory

$$\langle \hat{B}(t) \rangle = \text{Tr}[\hat{B}(t)\hat{\rho}]$$

$$\begin{split} \langle \hat{B}(t) \rangle &= \sum_{\alpha\beta} \int \frac{d^2 z}{\pi^{N_b}} \int \frac{d^2 z'}{\pi^{N_b}} \{ \langle \alpha | \otimes \langle z | \} \hat{\rho} \{ |\beta\rangle \otimes |z'\rangle \} \\ &\times \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{-i\theta} \langle \psi(t,\theta) | \hat{B} | \psi(t,\theta) \rangle \end{split}$$



Going Beyond Mean Field Theory

$$\langle \hat{B}(t) \rangle = \text{Tr}[\hat{B}(t)\hat{\rho}]$$

$$\begin{split} \langle \hat{B}(t) \rangle &= \sum_{\alpha\beta} \int \frac{d^2 z}{\pi^{N_b}} \int \frac{d^2 z'}{\pi^{N_b}} \{ \langle \alpha | \otimes \langle z | \} \hat{\rho} \{ |\beta\rangle \otimes |z'\rangle \} \\ & \times \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{-i\theta} \langle \psi(t,\theta) | \hat{B} | \psi(t,\theta) \end{split}$$

$$|\psi(t,\theta)\rangle = \hat{U}(0,t)|\alpha\rangle \otimes |z\rangle + e^{i\theta}\hat{U}(0,t)|\beta\rangle \otimes |z'\rangle$$



Dynamics Algorithm from the Time-Dependent Variational Principle

$$|\tilde{\psi}(t)\rangle = |\alpha(t)\rangle \otimes |z(t)\rangle + |\beta(t)\rangle \otimes |z'(t)\rangle$$

$$L = i\hbar \frac{\langle \tilde{\psi}(t) | \dot{\tilde{\psi}}(t) \rangle - \langle \dot{\tilde{\psi}}(t) | \tilde{\psi}(t) \rangle}{2} - \langle \tilde{\psi}(t) | \hat{H} | \tilde{\psi}(t) \rangle$$



S. A. Sato, A. Kelly, and A. Rubio, Phys. Rev. B, 2018.

"Molecular Wires": Charge Transport and Polaron Formation







Holstein Polaron Model

$$\hat{H} = \hat{H}_{kin} + \hat{H}_{ph} + \hat{H}_{coup}$$

$$\hat{H}_{kin} = -t_0 \sum_{j} \left(c_j^{\dagger} c_{j+1} + c_{j+1}^{\dagger} c_j \right)$$

$$\hat{H}_{ph} = \omega_0 \sum_j a_j^{\dagger} a_j$$
$$\hat{H}_{coup} = -\gamma \sum_j \left(a_j + a^{\dagger} \right) \hat{n}_j$$

$$\lambda = \frac{\gamma^2}{2t_0\omega_0}$$

....



+ Periodic Boundary Conditions



Real-time Dynamics of Polaron Formation (at zero Kelvin)



S.A. Sato, A. Rubio, and A. Kelly, (In Progress)

Summary

- Trajectory-based quantum-classical approaches to quantum dynamics can accurately capture the physics of a wide range of energy and charge transfer problems.
- Applications to spectroscopy and transport properties are ongoing.

