Ehrenfest Dynamics with Decoherence and Detailed Balance



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Nijjar, Jankowska, Prezhdo J. Chem. Phys. 150, 204124 (2019)



Ehrenfest Quantum-Classical Dynamics

$$rac{d}{dt}\langle A
angle = rac{1}{i\hbar}\langle [A,H]
angle + \left\langle rac{\partial A}{\partial t}
ight
angle$$
 quantum expectation values follow classical-like equations of motion $mrac{d}{dt}\langle x
angle = \langle p
angle, \ rac{d}{dt}\langle p
angle = - \langle V'(x)
angle$

Couple quantum expectation values (electrons) to classical variables (nuclei)

Gives mean-field (average) trajectory



Ehrenfest theorem



Problems with Ehrenfest



- 1. Branching average surface is not physical
- 2. Equilibrium Ehrenfest cannot properly transfer energy from quantum to classical
- Decoherence phonons should induce electronic decoherence, e.g. quantum Zeno effect



Ehrenfest vs. Surface Hopping



- 1. Can be derived
- 2. Requires fewer trajectories, no need to sample stochastic hops

How to introduce decoherence and detailed balance into Ehrenfest?



Coherence Penalty Functional

Akimov, Long, Prezhdo, J. Chem. Phys. 140, 194107 (2014)

Penalize development of coherence

Step 1: Meyer/Miller/Stock/Thoss classical mapping

$$i\hbar \frac{\partial c_i(t)}{\partial t} = \sum_i \left[E_i(R(t)) \delta_{i,j} - i\hbar \frac{P}{M} d_{ij} \right] c_j(t) \qquad \begin{aligned} q_i &= \operatorname{Re}(c_i) \\ p_i &= \operatorname{Im}(c_i) \end{aligned}$$
$$H = \sum_i \frac{E_i}{2\hbar} \left(q_i^2 + p_i^2 \right) - \frac{P}{M} \sum_{i,j} d_{ij} p_i q_j \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \dot{q}_i = \frac{\partial H}{\partial p_i} \end{aligned}$$

- Mapping of quantum dynamics into classical dynamics allows more intuitive picture
- No approximations are made, though no computational gain either



Coherence Penalty Functional

Akimov, Long, Prezhdo, J. Chem. Phys. 140, 194107 (2014)

Penalize development of coherence

Step 2: analyze coherence in Meyer/Miller/Stock/Thoss mapping

$$i\hbar \frac{\partial c_i(t)}{\partial t} = \sum_i \left[E_i(R(t))\delta_{i,j} - i\hbar \frac{P}{M}d_{ij} \right] c_j(t) \qquad \begin{array}{l} q_i = \operatorname{Re}(c_i)\\ p_i = \operatorname{Im}(c_i) \end{array}$$
$$H = \sum_i \frac{E_i}{2\hbar} \left(q_i^2 + p_i^2 \right) - \frac{P}{M} \sum_{i,j} d_{ij} p_i q_j \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \dot{q}_i = \frac{\partial H}{\partial p_i} \end{aligned}$$
$$\left[(q_i^2 + p_i^2)(q_j^2 + p_j^2) = |c_i^* c_j|^2 \right]$$

- Coherence between a pair of states is quantified by square of corresponding off-diagonal element of density matrix
- Maps onto quartic term in classical Hamiltonian



Coherence Penalty Functional

Akimov, Long, Prezhdo, J. Chem. Phys. 140, 194107 (2014)

Penalize development of coherence

Step 3: add decoherence into mapped Schrodinger equation

$$i\hbar \frac{\partial c_i(t)}{\partial t} = \sum_i \left[E_i(R(t)) \delta_{i,j} - i\hbar \frac{P}{M} d_{ij} \right] c_j(t) \qquad \begin{array}{l} q_i = \operatorname{Re}(c_i) \\ p_i = \operatorname{Im}(c_i) \end{array}$$
$$H = \sum_i \frac{E_i}{2\hbar} \left(q_i^2 + p_i^2 \right) - \frac{P}{M} \sum_{i,i} d_{ij} p_i q_j \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \dot{q}_i = \frac{\partial H}{\partial p_i}$$
$$\tilde{H} = H + \sum_{\substack{i,j \\ i \neq j}} \lambda_{ij} \left(q_i^2 + p_i^2 \right) \left(q_j^2 + p_j^2 \right) \qquad \begin{array}{l} \text{large coherence = large energy} \\ \lambda_{ij} - \text{decoherence rate} \end{array}$$

- Classical dynamics avoids high energy, i.e. high coherence regions
- Original Schrodinger equation becomes nonlinear



Estimating Decoherence Rates for Condensed Phase Applications Akimov, Prezhdo, J. Phys. Chem. Lett. 4, 3857 (2013)

- System-bath thinking allows simple, 1-parameter model. (Decoherence is more complex in small systems.)
- Applications allow classical path approximation, since fluctuations are larger than geometry differences.
- Decoherence = pure-dephasing of optical response theory. Nuclei fluctuate in equilibrium, while electrons evolve in a highly non-equilibrium manner.





Estimating Decoherence Rates for Condensed Phase Applications Akimov, Prezhdo, J. Phys. Chem. Lett. 4, 3857 (2013)

2nd order cumulant approximation to the pure-dephasing function $D_{ij}(t) = \exp\left[-\frac{1}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' C_{ij}(t'')\right]$ $C_{ij}(t) = \langle \delta E_{ij}(t) \delta E_{ij}(0) \rangle$ $\delta E_{ij}(t) = E_{ij}(t) - \langle E_{ij} \rangle$



Energy gap autocorrelation function Gaussian fit of decay of D(t) gives decoherence rate



Estimating Decoherence Rates for Condensed Phase Applications Akimov, Prezhdo, J. Phys. Chem. Lett. 4, 3857 (2013)



- 1) Gap fluctuation is large (usually if gap itself is large)
- 2) Autocorrelation function of gap fluctuation decays fast



Ehrenfest with Detailed Balance

Bastida, Cruz, Zuniga, Requena, Miguel Chem. Phys. Lett. 417, 53 (2006)

- 1) Fermi's golden rule: transition rate proportional to coupling squared
- 2) Rates can be obtained from correlation functions
- 3) Quantum correction to classical correlation functions give more accurate rates
- 4) Quantum correlation functions satisfy detailed balance, while classical correlation functions do not

|NAC|² ~ Rate ~ Correlation Function ~ Quantum Correction

=> Scale NAC by Square Root of Quantum Correction



Quantum Corrections to Classical Correlation Functions

Egorov, Skinner Chem. Phys. Lett. 293, 469 (1998)

$$G(t) = \langle A(t) A(0) \rangle$$

= Tr[e^{-\beta H}A(t) A(0)]/Tr[e^{-\beta H}]

$$A(t) = e^{iHt/\hbar}A e^{-iHt/\hbar}$$

$$\hat{G}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t \, \mathrm{e}^{i\,\omega t} G(t)$$

$$\hat{G}(-\omega) = e^{-\beta \hbar \omega} \hat{G}(\omega)$$

$$\hat{G}_{cl}(-\omega) = \hat{G}_{cl}(\omega)$$

Classical limit, h=0, detailed balance is lost Scale classical by $exp [-\beta h\omega]$ (Classical ACF has no imaginary part)



Quantum Corrections to Classical Correlation Functions

Egorov, Skinner Chem. Phys. Lett. 293, 469 (1998)

$$Q(\omega) = \frac{2}{1 + e^{-\beta \hbar \omega}}$$

Simplest, used by Bastida et al. real part of quantum ACF = classical $RE G(t) = G_{cl}(t)$

$$Q(\omega) = \frac{\beta \hbar \omega}{1 - e^{-\beta \hbar \omega}}$$

 $Q(\omega) = \mathrm{e}^{\beta \hbar \omega/2}$

Harmonic approximation

Schofield $G(t) = G_{cl}(t + i\beta\hbar/2)$

|NAC|² ~ Rate ~ Correlation Function ~ Quantum Correction
=> Scale NAC by Square Root of Quantum Correction



Ehrenfest with Detailed Balance

Bastida, Cruz, Zuniga, Requena, Miguel Chem. Phys. Lett. 417, 53 (2006)

$$V_{jk}^{\mathrm{qc}} = \left(\frac{2}{1 + \mathrm{e}^{-\hbar\omega_{kj/KT}}}\right)^{1/2} V_{jk}$$

scale off-diagonal matrix elements of Hamiltonian

symmetrize to ensure dynamics keeps probabilities positive

$$V_{jj}^{\text{sqc}} = V_{jj} \qquad c_k = \rho_k e^{i\theta_k}$$

 $= V_{kj}^{\text{sqc}} = \rho_k V_{jk}^{\text{qc}} - \rho_j V_{kj}^{\text{qc}}$

Schrodinger equation becomes nonlinear, because modified coupling depends on wavefunction



Ehrenfest with Decoherence and Detailed Balance

Nijjar, Jankowska, Prezhdo, J. Chem. Phys. 150, 204124 (2019)

- Decoherence: Coherence Penalty Functional J. Chem. Phys. 140, 194107 (2014)
- Detailed balance: Chem. Phys. Lett. 417, 53 (2006)

$$\operatorname{Im}\left[\tilde{H}_{ij}\right] = \operatorname{Im}\left[H_{ij}\right] \cdot \rho_{j} \sqrt{\frac{2}{1 + \exp\left(\frac{\Delta E}{k_{B}T}\right)}} - \rho_{i} \sqrt{\frac{2}{1 + \exp\left(\frac{-\Delta E}{k_{B}T}\right)}}$$

$$\operatorname{Re}\left[\tilde{H}_{ij}\right] = \operatorname{Re}\left[H_{ij}\right] + \sum_{\substack{i,j \\ i\neq j}} \lambda_{ij} \left(q_i^2 + p_i^2\right) \left(q_j^2 + p_j^2\right).$$



Time-Domain DFT for Nonadiabatic Molecular Dynamics

Craig, Duncan, Prezhdo Phys. Rev. Lett. 95, 163001 (2005)

Electron density derives from Kohn-Sham orbitals $\rho(x) = \sum_{p} |\varphi_{p}(x)|^{2} \qquad |\Psi\rangle = |\varphi_{p}(x_{1},t)\varphi_{q}(x_{2},t)\dots\varphi_{v}(x_{N},t)\rangle_{SD}$ DFT functional H depends on nuclear evolution R(t)Variational principle gives $i\hbar \frac{\partial \varphi_p(x,t)}{\partial t} = H\varphi_p(x,t) \quad p = 1,2...$ Orbitals are expanded in adiabatic KS basis $\varphi_p(x,t) = \sum c_p^{\alpha}(t)\chi^{\alpha}(x)$ $H(x;R(t))\chi^{\alpha}(x;R(t)) = \varepsilon^{\alpha}(R(t))\chi^{\alpha}(x;R(t))$ $i\hbar c^{\alpha} = \sum_{\beta} c^{\beta} \left(\varepsilon^{\beta} \delta_{\alpha\beta} - i\hbar \left\langle \chi^{\alpha} \left| \vec{\nabla}_{R} \right| \chi^{\beta} \right\rangle \cdot \vec{R} \right)$



Time-Domain Kohn-Sham Equations: Ehrenfest vs. Surface Hopping

<u>Ehrenfest</u>: adiabatic KS basis can be viewed as *numerical representation* Stier, Prezhdo JPC-B 106 8047 (2002)
 main challenge – evaluation of NA coupling



 Decoherence/Detailed Balance: require definition of "states"
 KS basis gives 0th order adiabatic states

Craig, Duncan, Prezhdo PRL 95, 163001 (2005)





Many-Body Kohn-Sham Basis

Craig, Duncan, Prezhdo *Phys. Rev. Lett.* **95,** 163001 (2005) Akimov, Prezhdo, *J. Theor. Comp. Chem.* **9**, 4959 (2013)

$$\begin{split} |\varphi_{a}\varphi_{b}\cdots\varphi_{p}\rangle &= \sum_{\substack{j\neq k\neq\cdots\neq l\\N_{e}}}^{N_{e}} C_{j\cdots l}(t) |\tilde{\varphi}_{j}\tilde{\varphi}_{k}\cdots\tilde{\varphi}_{l}\rangle \\ i\hbar\frac{\partial}{\partial t}C_{q\cdots v}(t) &= \sum_{a\cdots p}^{N_{e}} C_{a\cdots p}(t) [E_{q\cdots v}\delta_{aq}\cdots\delta_{pv} \\ &+ \mathbf{D}_{a\cdots p;q\cdots r}\cdot\dot{\mathbf{R}}]. \end{split}$$
$$\mathbf{D}_{a\cdots p;q\cdots r}\cdot\dot{\mathbf{R}} = -i\hbar\langle\tilde{\varphi}_{a}\tilde{\varphi}_{b}\cdots\tilde{\varphi}_{p}|\frac{\partial}{\partial t}|\tilde{\varphi}_{q}\tilde{\varphi}_{r}\cdots\tilde{\varphi}_{v}\rangle$$

D is non-zero only if different in one orbital, very sparse Multiple excitons in $Si_{29}H_{24}$: 25 VB and 24 CB orbitals **98,101 states** = ground+600SE+97,500DE



Hyeon-Deuk, Prezhdo Nano Lett. 11, 1845 (2011); ACS Nano 6, 1239 (2012)

Why Kohn-Sham Representation Works?

S. Fischer, B. Habenicht, A. Madrid, W. Duncan, O. V. Prezhdo, *J. Chem. Phys.* **134**, 024102 (2011)

- KS close to LR/TDDFT (in contrast to HF and CIS)
- No bond-breaking, conformational changes.
- Many-electrons, single excitation small perturbation
- Averaging over many initial conditions and pathways



1600



Classical Path Approximation to "Surface Hopping"

Prezhdo, Duncan, *Prog. Surf. Sci.* **84**, 30 (2009) Akimov, Prezhdo, *J. Theor. Comp. Chem.* **9**, 4959 (2013)

- 1. **Precompute trajectory** to drive electron dynamics
- 2. DFT functional depends on ground state density, even though the true density does evolve

Justification:

- 1. Thermal fluctuations are larger than differences in equilibrium geometries of ground and excited electronic states
- 2. Excitation of 1 or 2 electrons out of hundreds does not change density and forces much

Key Advantages:

- One ground state trajectory, instead of 1000 excited; still quantum dynamics for electronic state populations
- 2. Update DFT functional every femtosecond not attosecond; electronic and nuclear timestep separation (1as & 1fs)



PYXAID: PYthon eXtension for Ab Initio Dynamics

Akimov, Prezhdo, J. Theor. Comp. Chem. 9, 4959 (2013) *ibid.* 10, 789 (2014)

Python interfaced with Quantum Espresso, VASP

In DFTB+: Pal, Trivedi, Akimov, Aradi, Frauenheim, Prezhdo *JCTC* 12 1436 (2016) Fragment approach in Gamess: Negben, Prezhdo

JPC A **120** 7205 (2016)



Overview of NAMD methods Perspective Article in JPC Lett. 7 2100 (2016)



Ehrenfest with Decoherence and Detailed Balance

Nijjar, Jankowska, Prezhdo, J. Chem. Phys. 150, 204124 (2019)

Detailed balance

$$\operatorname{Im}\left[\tilde{H}_{ij}\right] = \operatorname{Im}\left[H_{ij}\right] \cdot \left|\rho_{j}\sqrt{\frac{2}{1 + \exp\left(\frac{\Delta E}{k_{B}T}\right)}} - \rho_{i}\sqrt{\frac{2}{1 + \exp\left(\frac{-\Delta E}{k_{B}T}\right)}}\right|$$

<u>Decoherence</u>

$$\operatorname{Re}\left[\tilde{H}_{ij}\right] = \operatorname{Re}\left[H_{ij}\right] + \sum_{\substack{i,j \ i \neq j}} \lambda_{ij} \left(q_i^2 + p_i^2\right) \left(q_j^2 + p_j^2\right).$$



Ehrenfest-DBB reproduces initial rates, but dynamics slows down as system approaches equilibrium

Qiu, Nazin, Ho Science 299, 542 (2003); Jankowska, Prezhdo, JPCLett. 9, 3591 (2018)



Other Modifications of Ehrenfest

Stochastic Mean-Field (SMF) – decoherence gives branching Prezhdo J. Chem. Phys. **111** 8366 (1999)

Decoherence Induced Surface Hopping (DISH) – similar to SMF, but piece-wise continuous as regular SH Jaeger, Fisher, Prezhdo J. Chem. Phys. **137** 22A545 (2012)

Quantized Mean-Field – include zero-point motion Brooksby, Prezhdo, Chem. Phys. Lett. **346** 463 (2001)

Unravel Ehrenfest into Bohmian Ensemble – branching Prezhdo, Brooksby, *Phys. Rev. Lett.* **86** 3215 (2001)



$$\frac{|d\Psi\rangle}{=-iH|\Psi\rangle}dt - \frac{\gamma}{2} L^{+}L|\Psi\rangle dt + \sqrt{\gamma}L|\Psi\rangle dW$$

friction noise



Decoherence Induced Surface Hopping (DISH)

Jaeger, Fisher, Prezhdo J. Chem. Phys. 137, 22A545 (2012)

Evolve in an adiabatic state. Hop when a decoherence event occurs. Use normal quantum probabilities. Rescale velocity as before in SH.

Advantages

- 1. Includes decoherence
- 2. Gives branching
- 3. Nuclear evolution in pure states

Corresponds to a piece-wise continuous stochastic Schrodinger equation







Quantized Ehrenfest

C. Brooksby and O. V. Prezhdo, *Chem. Phys. Lett.*, **346** 463 (2001)



C. Brooksby and O. V. Prezhdo, *Chem. Phys. Lett.*, **346** 463 (2001) $d\langle Q \rangle = \langle P \rangle$ Ordinary dt Μ $\frac{d \langle P \rangle}{d = -M\Omega^2 \langle Q \rangle - \langle \Psi (q) | \nabla_q V (q, \langle Q \rangle) | \Psi (q) \rangle$ Mean-Field dt $\frac{d\langle Q^2\rangle}{dt} = \frac{2\langle PQ\rangle_s}{M}$ $\frac{d \langle P^2 \rangle}{d = -M\Omega^2 \langle PQ \rangle_s - 2 \langle P \rangle \langle \Psi (q) | \nabla_Q V (q, \langle Q \rangle) | \Psi (q) \rangle$ $\frac{d \langle PQ \rangle_{s}}{d Q} = \frac{\langle P^{2} \rangle}{d Q} - M\Omega^{2} \langle Q^{2} \rangle - \langle Q \rangle \langle \Psi (q) | \nabla_{Q} V (q, \langle Q \rangle) | \Psi (q) \rangle$ dt

QMF-2 equations require no new quantum calculation !



Ehrenfest to Bohmian Ensemble

O. V. Prezhdo, C. Brooksby *Phys. Rev. Lett.* 86 3215 (2001)

Ehrenfest: ions coupled to electronic average, one ion trajectory

$$M\ddot{X} = \left\langle \psi(x,t) \middle| - \nabla_X (V_X + V_{xX}) \middle| \psi(x,t) \right\rangle$$

x-electron; *X*-ion

<u>Bohmian</u>: ions coupled to one member of Bohmian ensemble of electrons => ensemble of ion trajectories

$$M\ddot{X}(x) = -\nabla_X (V_X(X) + V_{xX}(x,X))$$



Derivation: drop the quantum potential $Q(X) = -\frac{\hbar^2}{2m} \frac{\nabla_x^2 R}{R}$ for ions



Conclusions



- Ehrenfest requires fewer trajectories than surface hopping
- Decoherence needed to get correct rates
- Detailed balance needed to achieve equilibrium and study relaxation which competes with everything else
- Ehrenfest with decoherence and detailed balance captures essential physics
- Implemented with real-time TDDFT, can be applied to large systems





C Decoherence & Quantum Zeno Effect

O. V. Prezhdo, P. J. Rossky, *Phys. Rev. Lett.* 81, 5294 (1998)
O. V. Prezhdo, *Phys. Rev. Lett.* 85, 4413 (2000)

With decoherence: $P_{12} = |T_{12}|^2 + |T_{12}|^2 + ... |^2 T_{12}$ Without decoherence $P_{12} = |T_{12} + T_{12} + ... |^2$

Decoherence makes transitions less likely $|0.1|^2 + |0.1|^2 < |0.1 + 0.1|^2$

• atom

alive

dead

cat