Ehrenfest and Car-Parrinello Molecular Dynamics with Adaptive Mass

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Schrödinger equation & Born-Oppenheimer MD

- Schrödinger eigenvalue problem

$$\hat{H}(X)\Phi(X) = E\Phi(X)\,,$$

with the Hamiltonian operator, $\hat{H}(X) = -\frac{1}{2}M^{-1}\Delta_X + V(X)$.

- The BOMD fixes an electronic eigenstate

$$V(X)\Psi_0(X) = \lambda_0(X)\Psi_0(X)\,,$$

which leads to the dynamical system

$$\ddot{X}_t = -\lambda_0'(X_t).$$

Ehrenfest MD

- The Ehrenfest molecular dynamics

$$\ddot{X}_t = -\frac{\langle \psi_t, \nabla V(X_t)\psi_t \rangle}{\langle \psi_t, \psi_t \rangle}$$

$$\dot{\psi}_t = -i\hat{M}^{1/2}\left(V(X_t) - \frac{\langle \psi_t, V(X_t)\psi_t \rangle}{\langle \psi_t, \psi_t \rangle} \right) \psi_t.$$

- $\hat{M}$ is an artificial mass parameters.
- The Car-Parrinello molecular dynamics, $\ddot{\psi}_t = \cdots$.

Motivation

- Large $\hat{M}$ required when λ_0 is close to λ_1.
- #time-steps, $N = \mathcal{O}(\sqrt{\hat{M}})$.

- How to choose $\hat{M}$?

Using adaptive mass in molecular dynamics

- Adaptive algorithm:

$$\hat{M}(t) := \frac{1}{\epsilon^2} \cdot \max\left(1, \frac{1}{|\bar{\lambda}_1(X_t) - \bar{\lambda}_0(X_t)|^4}\right),$$

- Electron eigenvalues are approximated by Rayleigh quotient

$$\bar{\lambda}_0(X_t) := \frac{\langle \psi_t, V(X_t)\psi_t \rangle}{\langle \psi_t, \psi_t \rangle}, \qquad \bar{\lambda}_1(X_t) := \frac{\langle \dot{\psi}_t, V(X_t)\dot{\psi}_t \rangle}{\langle \dot{\psi}_t, \dot{\psi}_t \rangle}.$$

A two dimensional problem

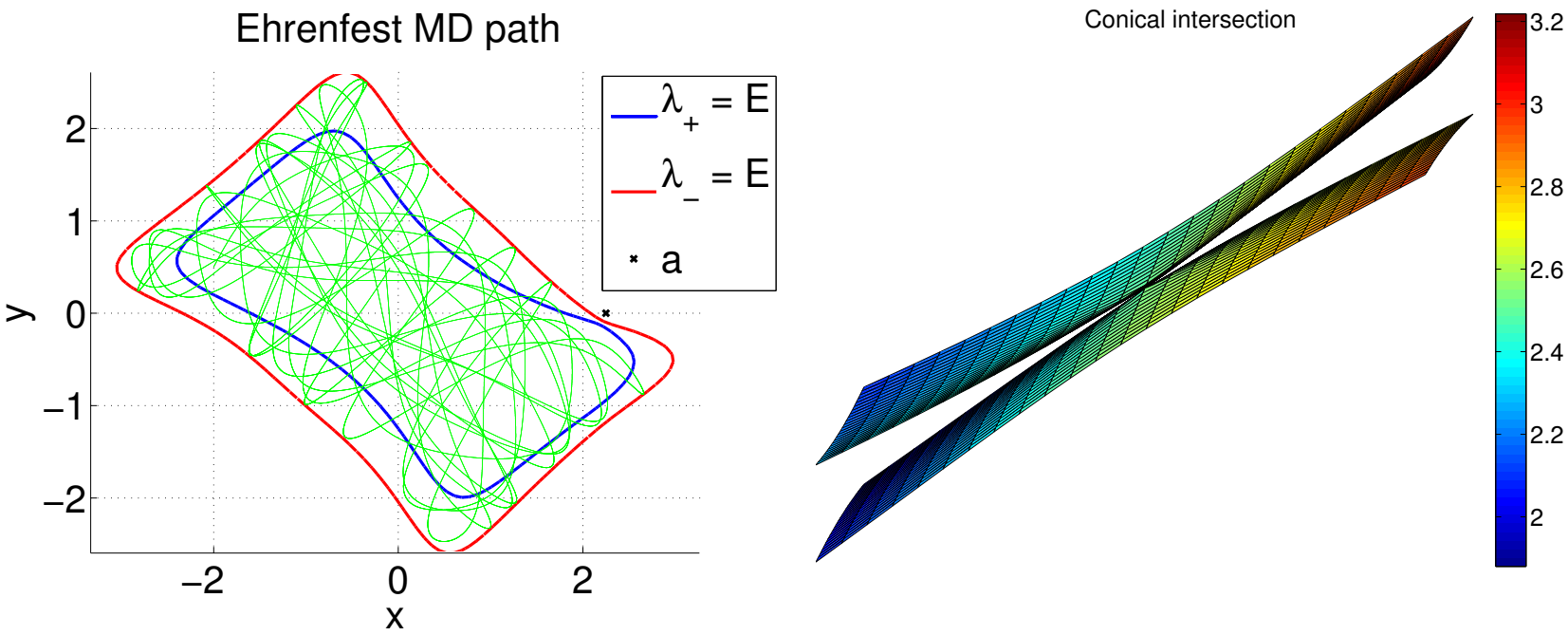

Figure: (Left) MD path, (Right) Conical intersection.

A two dimensional problem

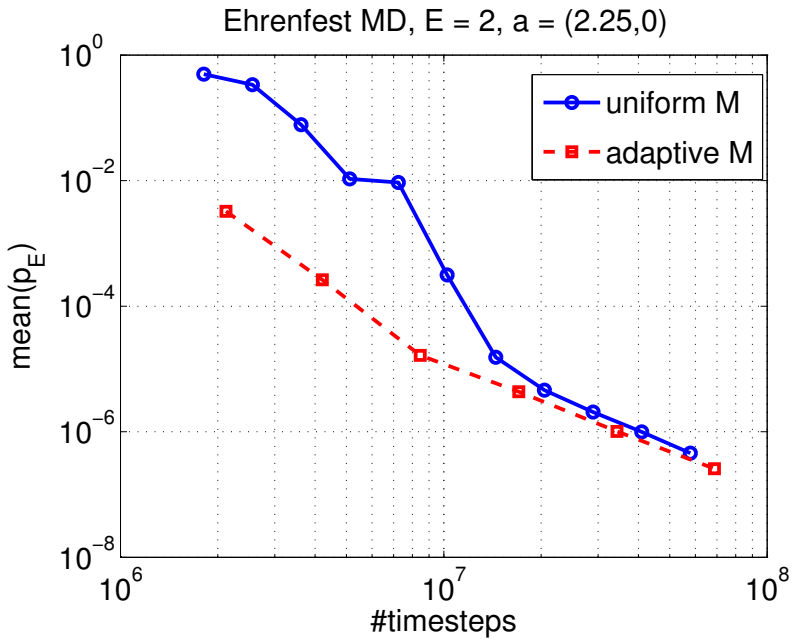

Figure: The simulation is computed for time $t = [0, 2000]$.

Questions?

Thank you!