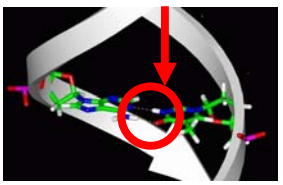
Methodenentwicklung:
Lichtinduzierte Dynamik großer molekularer Systeme

Kooperation: TP C2

Quanten-klassische Dynamik

Klassische Dyn. / Quanten-Dyn.

Massen: M / Massen: m



Gemischt quanten-klassische Dynamik: Konsistente Kopplung ?!?

Liouville-von Neumann Gleichung

$$\partial_t \hat{\rho}(t) = -\frac{i}{\varepsilon}\left[\hat{H}(t), \hat{\rho}(t)\right]_-$$

Hamilton-Operator

$$\hat{H}(t) = -\frac{1}{2}\left(\frac{\varepsilon}{i}\nabla_R\right)^2 - \frac{1}{2}\left(\frac{1}{i}\nabla_r\right)^2 + U(r,R) - F_0\left(\frac{\gamma\omega}{\varepsilon}t\right)\cos\left(\frac{\omega t}{\varepsilon}\right)\mu(r,R)$$

Massenverhältnis: $\varepsilon = \sqrt{\frac{m}{M}}$

Zeitskalen: $\gamma = \frac{T}{\tau}$ mit $T = \frac{2\pi}{\omega}$

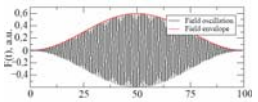
Adiabatische Floquet-Zustände

$$\hat{\mathbf{H}}(R,F_0) = \mathbf{E}(R,F_0) + \frac{1}{2}\left(\left(\frac{\varepsilon}{i}\nabla_R\right)^2\mathbf{1} + 2\frac{\varepsilon}{i}\mathbf{C}(R,F_0)\cdot\left(\frac{\varepsilon}{i}\nabla_R\right)\right) - i\gamma\omega\,\mathbf{G}(R,F_0)\hat{F}_0 + O(\gamma,\varepsilon^2)$$

Nichtadiabatische Kopplungen

$$C_{ij}(R,F_0) = \langle\varphi_i(R,F_0)|\nabla_R|\varphi_j(R,F_0)\rangle$$

$$G_{ij}(R,F_0) = \langle\varphi_i(R,F_0)|\nabla_{F_0}|\varphi_j(R,F_0)\rangle$$



Quanten-klass. Liouville-Gleichung

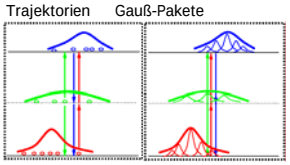
$$\partial_t \boldsymbol{\rho}_W = -\frac{i}{\varepsilon}[\mathbf{E},\boldsymbol{\rho}]_- - i\gamma\omega\hat{F}_0[\mathbf{G},\boldsymbol{\rho}]_- - [\mathbf{C}\cdot P,\boldsymbol{\rho}]_- + \frac{1}{2}[\mathbf{E},[\mathbf{C},\nabla_P\boldsymbol{\rho}]_-]_- - P\cdot\nabla_R\boldsymbol{\rho} + \frac{1}{2}[\nabla_R\mathbf{E},\nabla_P\boldsymbol{\rho}]_+ + O(\varepsilon)$$

- Partielle Wigner-Transformation
- Nur führende Terme in $\boldsymbol{\varepsilon}, \boldsymbol{\gamma}$

Numerische Lösungsverfahren

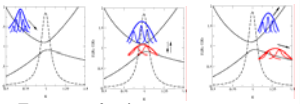
Partikel-Verfahren

Trajektorien / Gauß-Pakete



- Monte-Carlo basierte Darstellung
- Bessere Abtastung durch GP'e

Explizite Integration (Linien-Meth.)



- **Trotter**-Aufspaltung: quant./klass./quant.-klass.
- **SHT**: surface hopping trajectories
- **SHG**: surface hopping Gaussians (auch nicht-lokale Operatoren)

Implizite Integration (Rothe-Methode)

TRAIL = **T**rapez **R**egel für **A**daptive **I**ntegration der **L**iouville Dynamik

(1) Zeitdiskretisierung:

Implizite Trapez-Regel

$$\left(\mathbf{I} - \frac{\tau}{2}\mathbf{L}\right)\boldsymbol{\rho}(t+\tau) = \left(\mathbf{I} + \frac{\tau}{2}\mathbf{L}\right)\boldsymbol{\rho}(t)$$

- symplektisch
- symmetrisch
- ⇒stationäre PDE im Phasenraum

(2) Ortsdiskretisierung (mit Gaußpaketen):

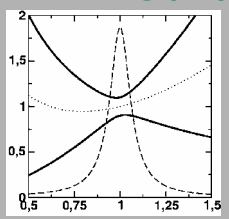
Globaler Fehlerschätzer

$$\varepsilon_\Gamma \approx \left\|\left(\mathbf{I} - \frac{\tau}{2}\mathbf{L}\right)\tilde{\boldsymbol{\rho}}(t+\tau) - \left(\mathbf{I} + \frac{\tau}{2}\mathbf{L}\right)\boldsymbol{\rho}(t)\right\|_{\{\mathbf{R},\mathbf{R}\}}$$

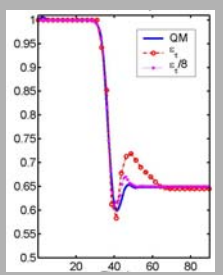
- Bewegliche Monte Carlo Punkte {Ri,Pi}
- Minimierung des Fehlers ⇒ Lineares Gl.-System
- Dynamische Erzeugung/Vernichtung von Gaußpaketen (nach lokalem Fehler)

Single crossing (1D)

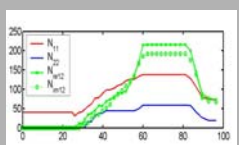
Potentiale /Kopplung



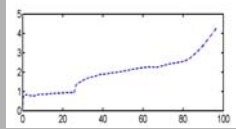
Populationsdynamik (TRAIL)



Partikelzahl

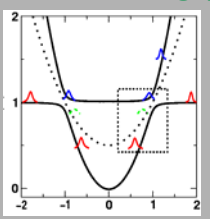


Zeitschritt

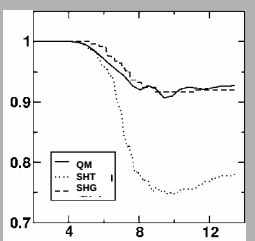


Double crossing (1D)

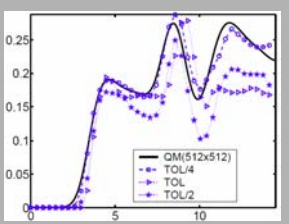
Potentiale /Kopplung



Population (surface hopping)

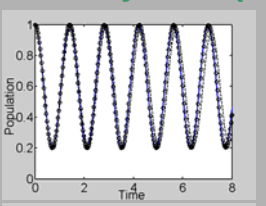


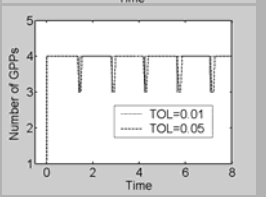
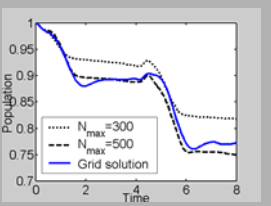
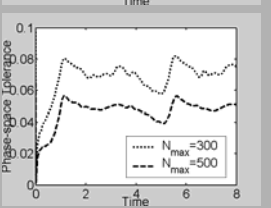
Population (TRAIL)



Spin boson systems (3D)

Rabi – Oszillationen (vertikal verschobene Oszillatoren)





Konische Durchschneidung (horizontal verschobene Oszillatoren)