Universität Rostock
Traditio et Innovatio

INSTITUT FÜR PHYSIK

VIBRONIC SPECTROSCOPY WITH CLASSICAL TRAJECTORIES

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الصندوق القطري لرعاية البحث العلمي
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FERMI'S GOLDEN RULE

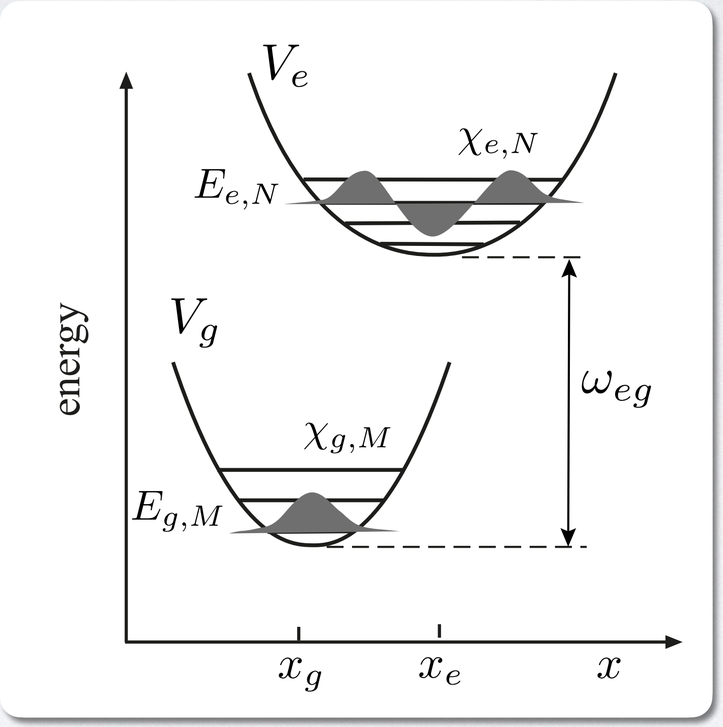
- vibronic absorption spectrum

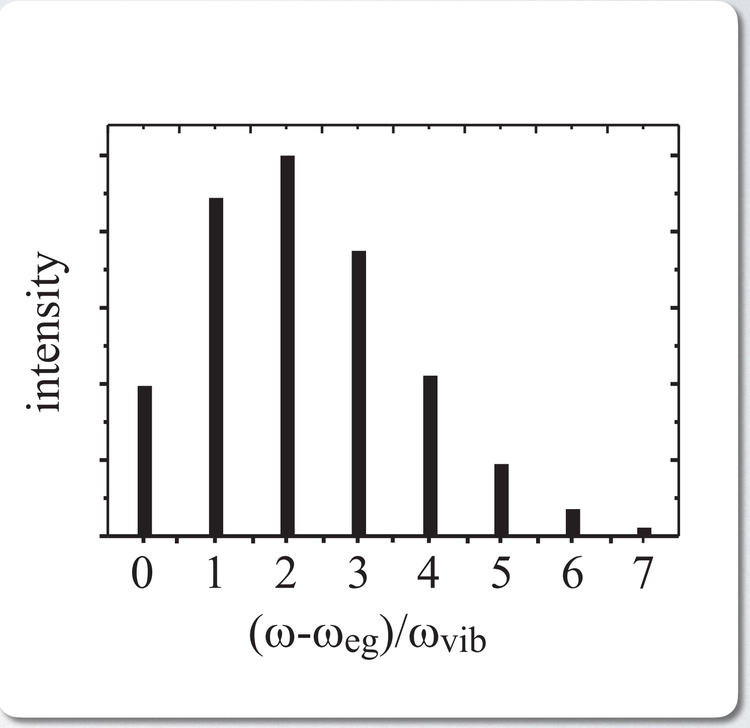
$$\alpha(\omega) = \frac{1}{Z_{\text{vib}}} \sum_{MN} e^{-\beta E_{g,M}} |\langle \chi_{e,N} | \hat{d}_{eg} | \chi_{g,M} \rangle|^2 \delta(\hbar\omega - \hbar\omega_{eg} - (E_{e,N} - E_{g,M})) \qquad (\beta = 1/k_{\text{B}}T)$$

- dipole moment operator

$$\hat{d} = \hat{d}_{eg}(\mathbf{x}) |e\rangle\langle g| + \text{h.c.}$$

- shifted oscillator model

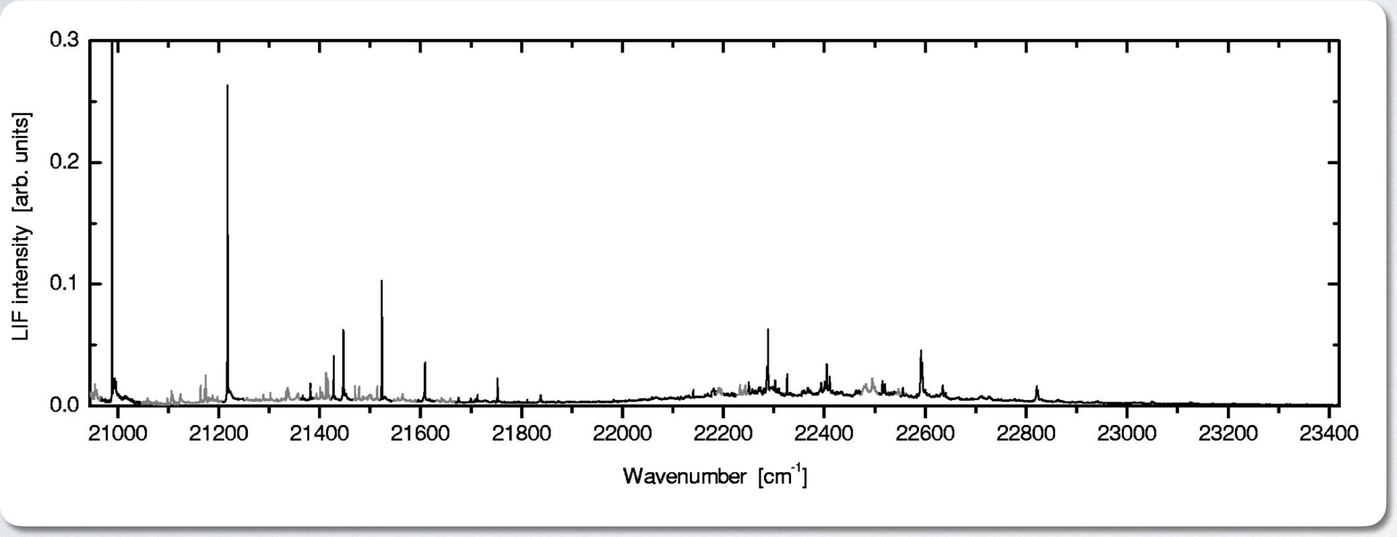




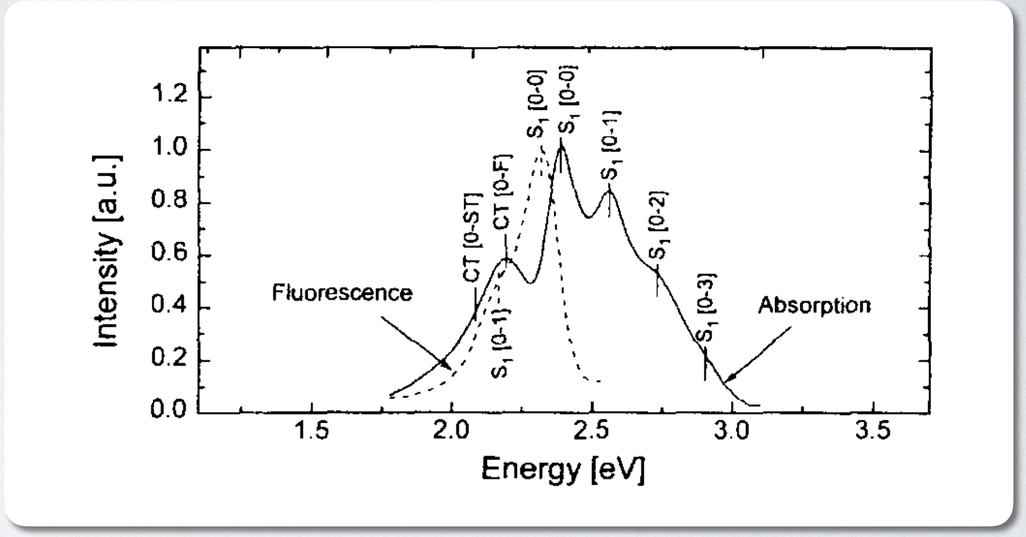
$$\alpha(\omega)|_{T=0} = \frac{|d_{eg}|^2}{\hbar} e^{-\Delta g^2} \sum_{M=0}^{\infty} \frac{\Delta g^{2M}}{M!} \delta(\omega - M\omega_{\text{vib}})$$

VIBRONIC ABSORPTION SPECTRA

PTCDA in He



PTCDA in DMSO



- multi-mode & anharmonic case
- condensed phase: system-environment coupling

Wewer et al. JCP 120, 1239 (2004); Bulovic et al. Chem. Phys. 210, 1 (1996)

AGENDA

Goal: nuclear quantum dynamics effects in vibronic spectroscopy with classical trajectories

This talk:

- time-dependent formulation of vibronic absorption spectra
- classical trajectories in common approaches
- generalized time-correlation functions
- Matsubara dynamics

THE HELLER FORMULA

$$\alpha(\omega) = \frac{1}{Z_{\text{vib}}} \sum_{MN} e^{-\beta E_{g,M}} |\langle \chi_{e,N} | \hat{d}_{eg} | \chi_{g,M} \rangle|^2 \delta(\hbar\omega - \hbar\omega_{eg} - (E_{e,N} - E_{g,M}))$$

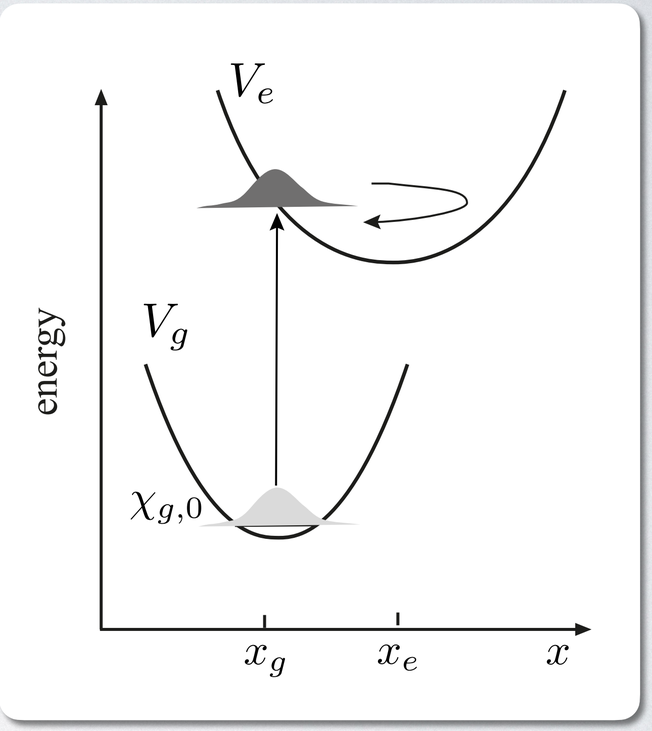
- using Fourier-integral representation of delta function

$$\delta(\omega) = \frac{1}{2\pi} \int dt e^{i\omega t}$$

- time correlation function (TCF) expression

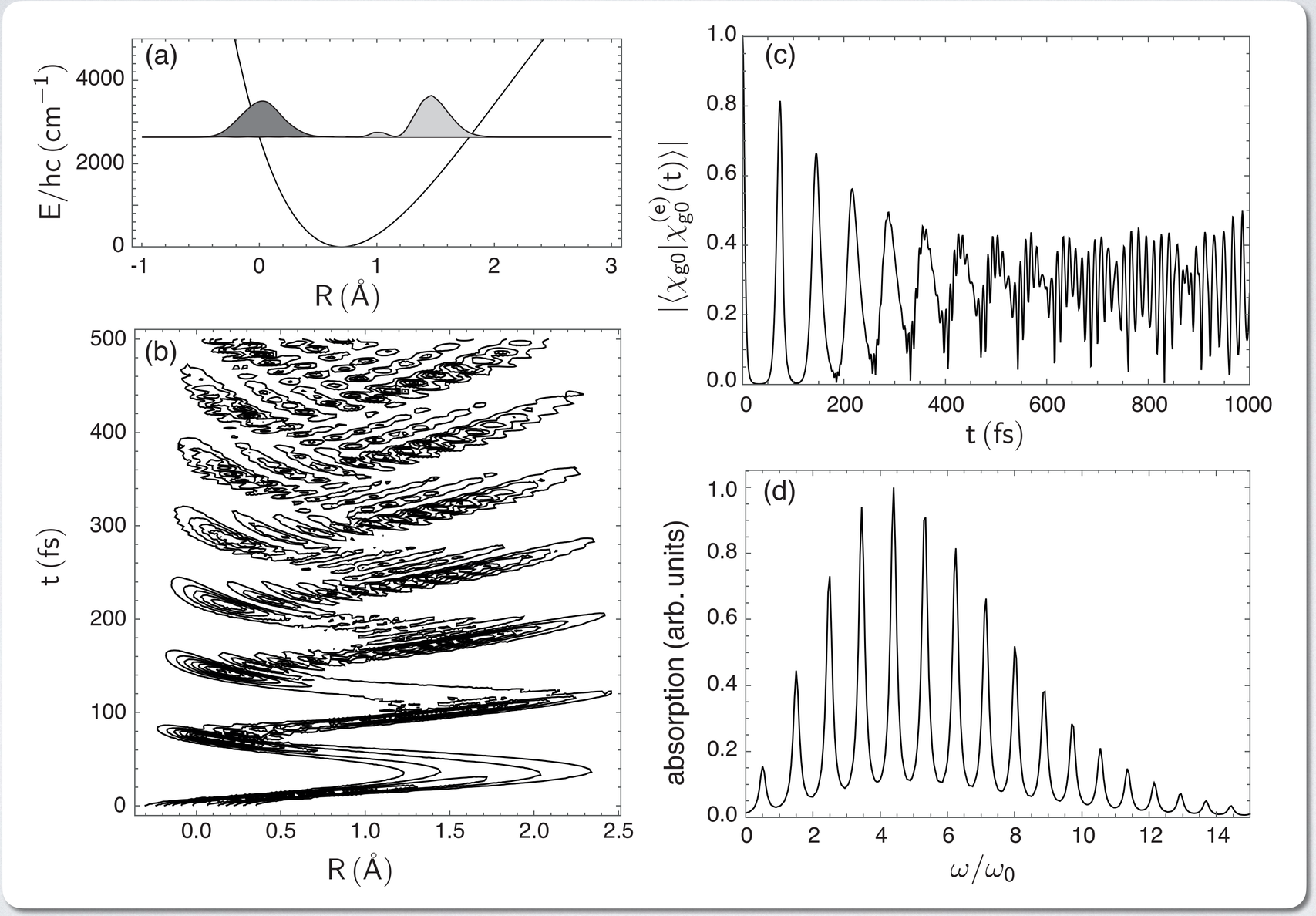
$$\alpha(\omega)|_{T=0} = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle \chi_{g,0} | e^{i\hat{H}_g t/\hbar} \hat{d}_{ge} e^{-i\hat{H}_e t/\hbar} \hat{d}_{eg} | \chi_{g,0} \rangle$$

- same information, but obtained using time-domain techniques



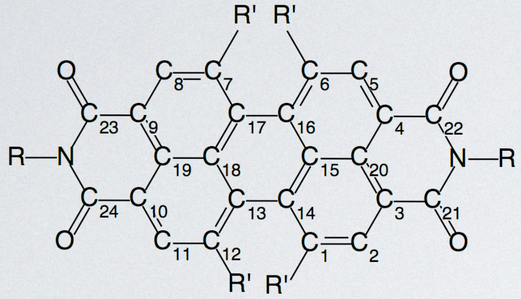
E. J. Heller, JCP 68, 3891 (1978)

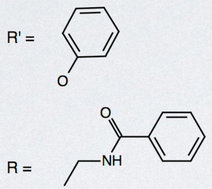
SIMPLE EXAMPLE: MORSE OSCILLATOR

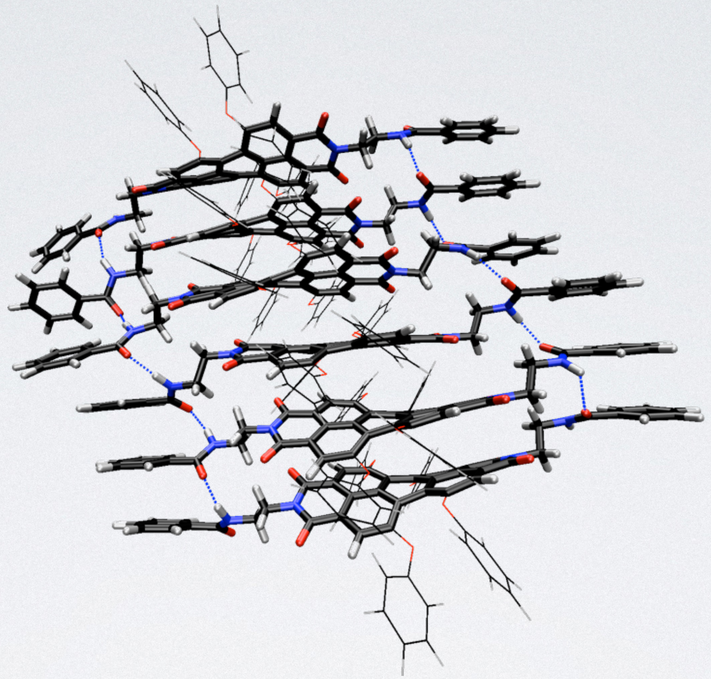


A LESS SIMPLE EXAMPLE

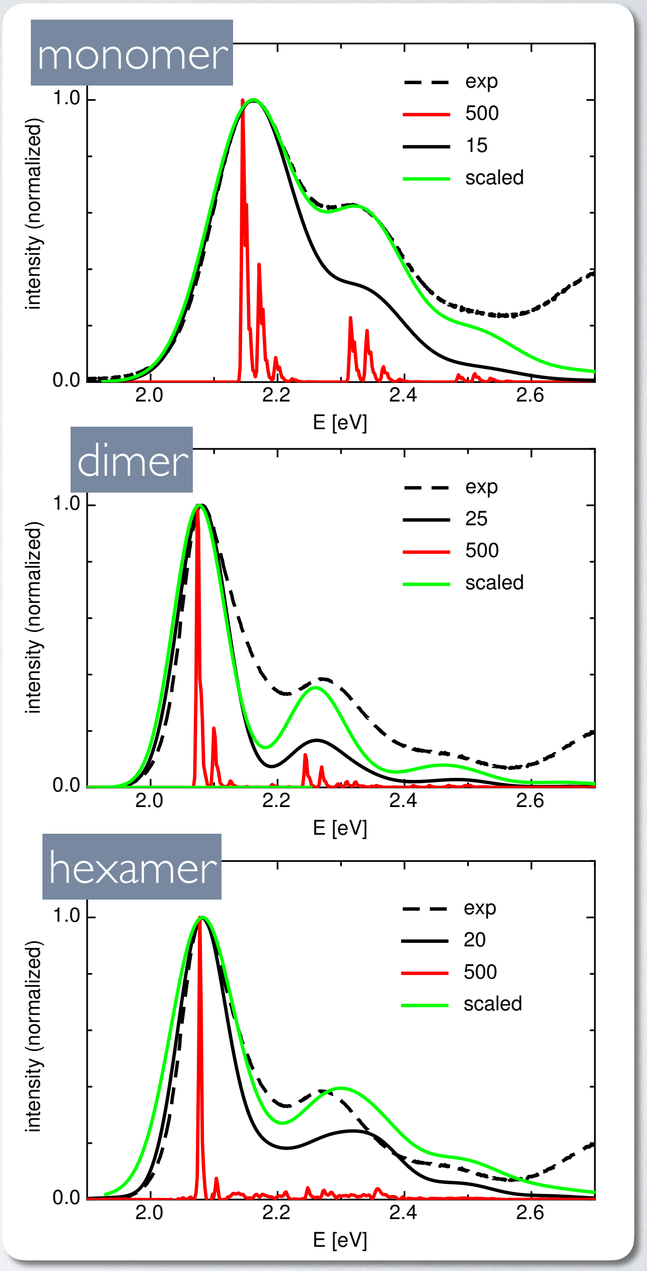
- PBI aggregate





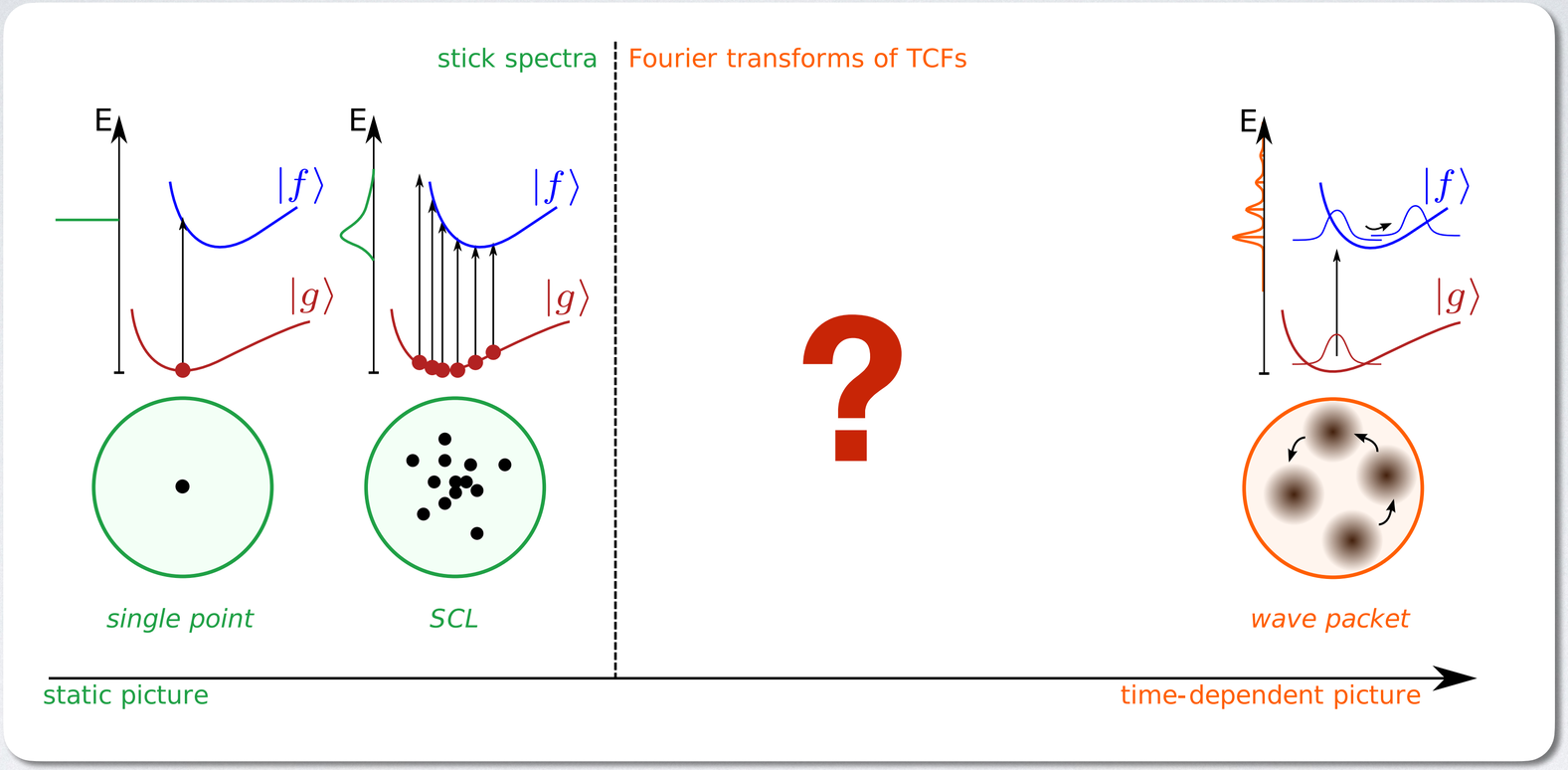


- MCTDH model of n-mer with n x 5 modes
- but…. curse of dimensionality



D. Ambrosek et al., JPCA 116, 11451 (2012)

COMMON TRAJECTORY APPROACHES



- Heller's wave packet formulation (time-dependent)
- single point + empirical broadening (static)
- sampling of configurations (static)

DYNAMICAL CLASSICAL LIMIT (DCL)

$$\alpha(\omega) = \frac{1}{2\pi\hbar Z_{\text{vib}}} \sum_M \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle \chi_{g,M} | e^{-\beta E_{g,M}} e^{i\hat{H}_g t/\hbar} \hat{d}_{ge} e^{-i\hat{H}_e t/\hbar} \hat{d}_{eg} | \chi_{g,M} \rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt e^{i\omega t} C(t)$$

$$C(t) = \frac{1}{Z_{\text{vib}}} \text{tr}_{\text{vib}} [e^{-\beta \hat{H}_g} e^{i\hat{H}_g t/\hbar} \hat{d}_{ge} e^{-i\hat{H}_e t/\hbar} \hat{d}_{eg}] = \langle e^{i\hat{H}_g t/\hbar} \hat{d}_{ge} e^{-i\hat{H}_e t/\hbar} \hat{d}_{eg} \rangle_{\text{vib}}$$

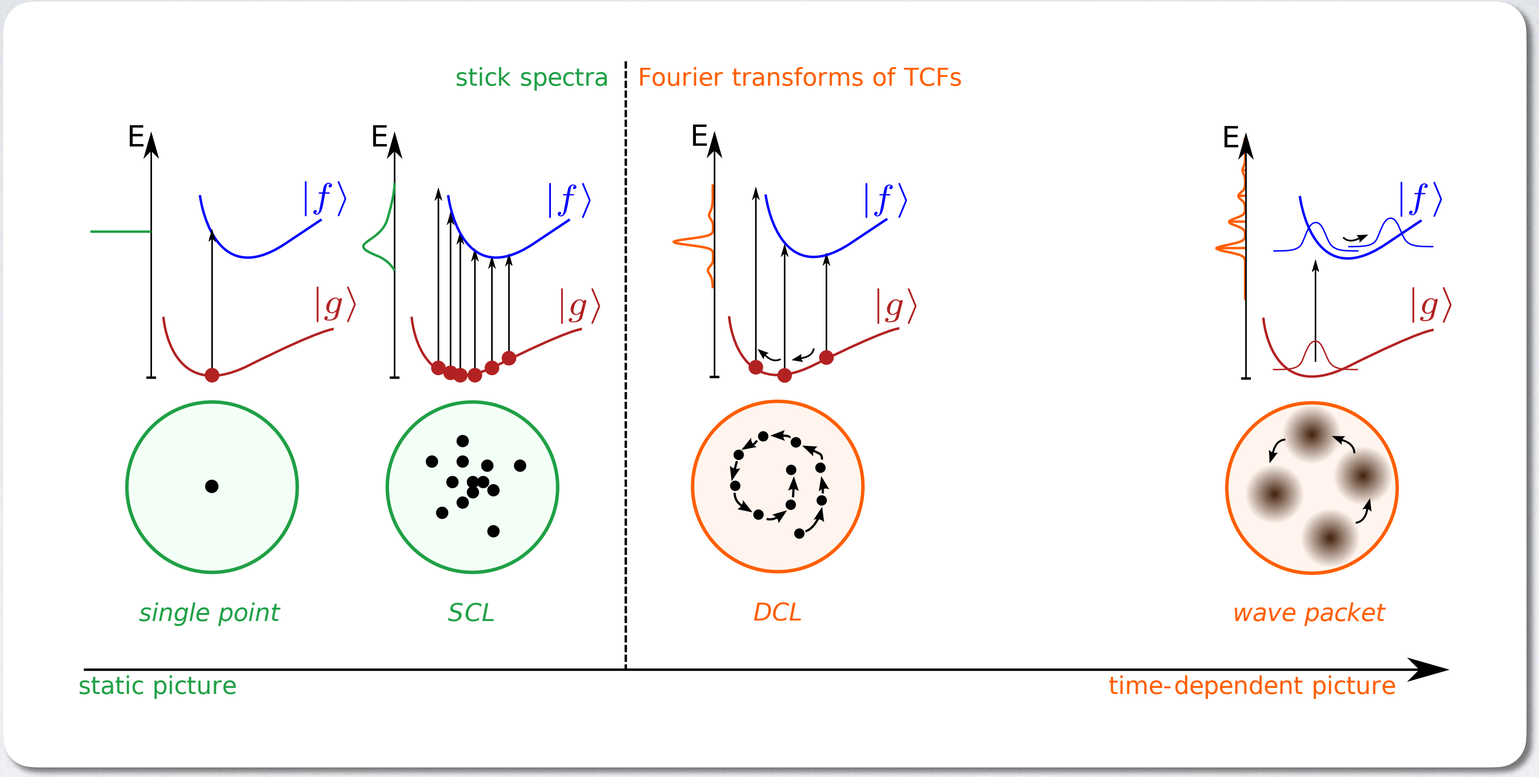
- use interaction representation to introduce energy gap fluctuations

$$e^{-i\hat{H}_e t/\hbar} = e^{-i\hat{H}_g t/\hbar} \exp_+ \Big[-i \int_0^t d\tau \hat{\Delta}_{eg}(\tau) \Big]$$

$$\hbar \hat{\Delta}_{eg}(t) = e^{i\hat{H}_g t/\hbar} (\hat{V}_e - \hat{V}_g) e^{-i\hat{H}_g t/\hbar}$$

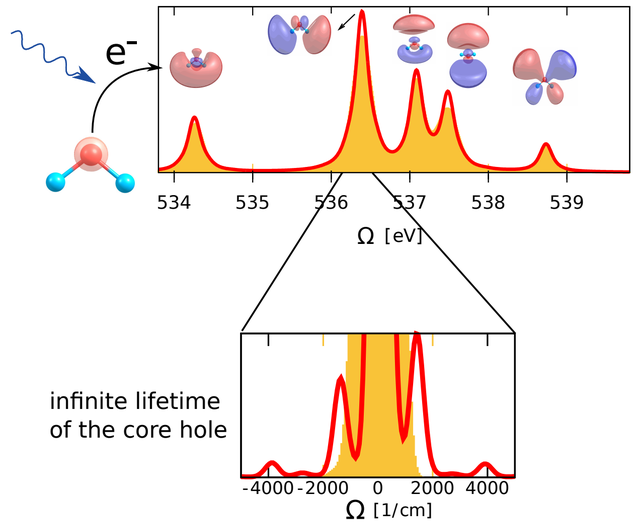
$$C(t) = \langle \hat{d}_{ge}(t) \exp_+ \Big[-i \int_0^t d\tau \hat{\Delta}_{eg}(\tau) \Big] \hat{d}_{eg}(0) \rangle_{\text{vib}}$$

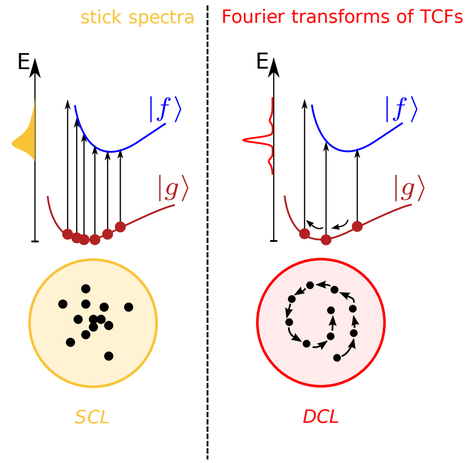
$$C_{\mathrm{DCL}}(t) = \frac{1}{Z_{\mathrm{cl}}} \int \mathrm{d}\mathbf{x}_0 \mathrm{d}\mathbf{p}_0 e^{-\beta H_g(0)} d_{ge}(\mathbf{x}_t) d_{eg}(\mathbf{x}_0) \exp\Big[-i \int_0^t d\tau \Delta_{eg}(\mathbf{x}_\tau) \Big]$$



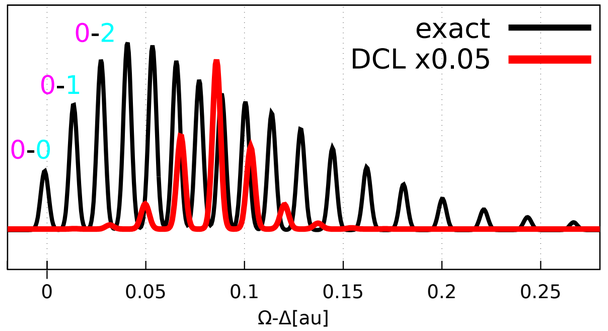
- only ground state trajectories are required
- readily interface with standard classical molecular dynamics codes
- extension to nonlinear spectroscopy straightforward

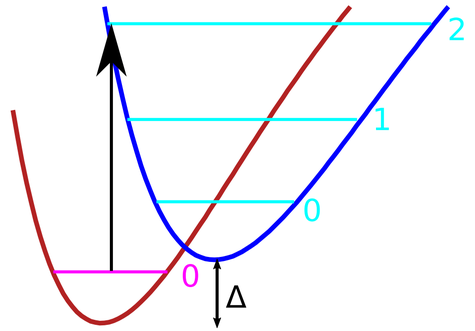
- XAS of gas phase water





- OH stretch of H_2O (1D)





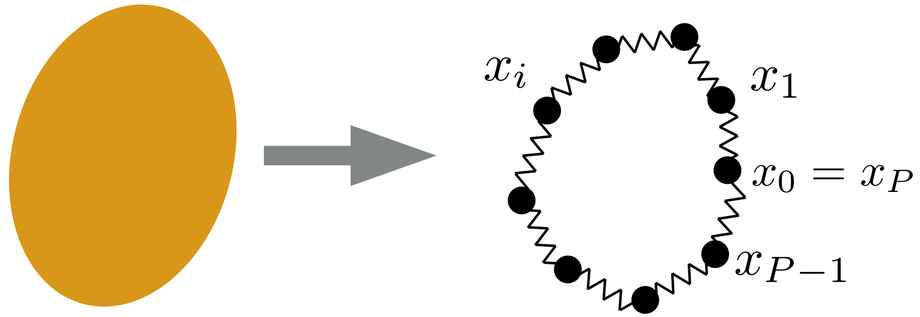
- what's missing?
  - on the ground state: nuclear quantum effects (ZPE, tunneling)
  - on the excited state: info about accessible potential, nonadiabatic effects

S. Karsten et al., JPCL 8, 992 (2017), & JCP 146, 224203 (2017)

IMAGINARY-TIME PATH INTEGRALS

- method to capture quantum effects on statistical distribution
- mapping onto dynamics of classical ring polymer in configuration space

$$\langle \hat{A}\hat{B} \rangle = \frac{1}{Z}\mathrm{tr}[e^{-\beta\hat{H}}\hat{A}\hat{B}] = \lim_{P\to\infty}\frac{1}{Z_P}\int d\mathbf{x}e^{-\beta U(\mathbf{x})}A(\mathbf{x})B(\mathbf{x})$$



quantum distribution ring polymer

$U(\mathbf{x})$: harmonic springs + physical potential

- formally exact expression, allows to describe quantum effects on equilibrium properties using classical trajectories

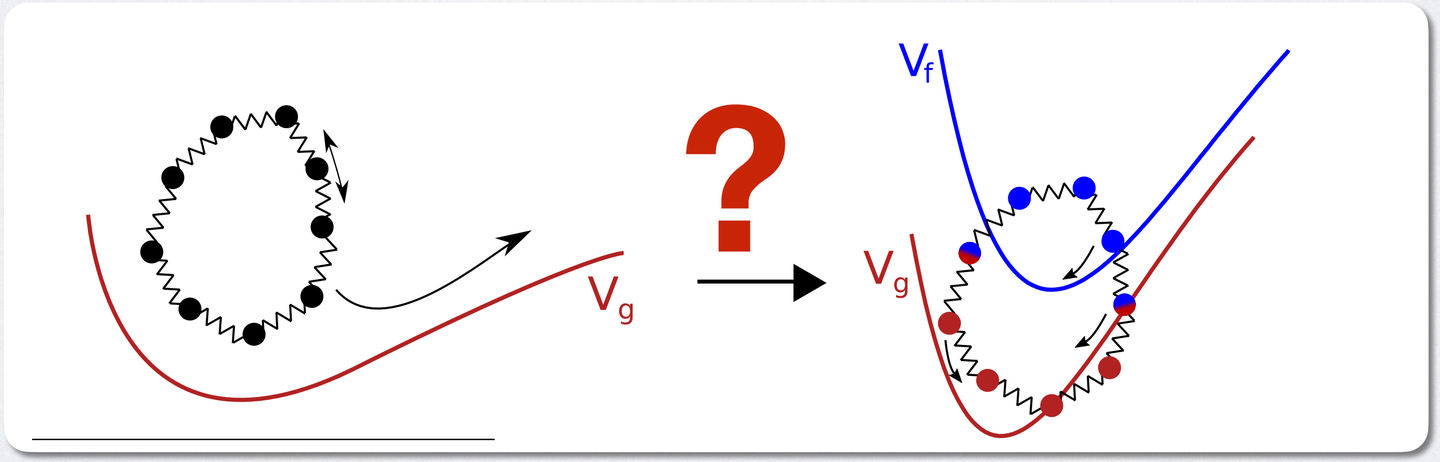
R.P. Feynman & A.R. Hibbs, Quantum Mechanics and Path Integrals, McGraw Hill, 1965

RING-POLYMER MOLECULAR DYNAMICS (RPMD)

- original path-integral formulation for static case only
- for spectroscopy TCFs are needed

$$C_{AB}(t) = \langle \hat{A}(0)\hat{B}(t)\rangle = \frac{1}{Z}\mathrm{tr}[e^{-\beta\hat{H}}\hat{A}(0)\hat{B}(t)] \qquad \hat{B}(t) = e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}$$

- RPMD makes use of ring polymer expression and takes trajectories that were intended for sampling only (not rigorous except, e.g., harmonic oscillators)
- vibrational dynamics via dynamics of ring polymer



I. R. Craig, D. E. Manolopoulos, JCP 121, 3368 (2004); S. Habershon et al. Annu. Rev. Phys. Chem. 64, 387 (2013)

TCF: CLASSICAL LIMIT

- absorption spectrum

$$\alpha(\omega) \propto \int \mathrm{d}t e^{-i\omega t} C_{AB}(t) = C_{AB}(\omega) \qquad (\hat{A} = \hat{B} = \hat{d})$$

- properties of quantum TCF

$$C_{AB}(t) = \langle \hat{A}(0)\hat{B}(t) \rangle = \frac{1}{Z}\mathrm{tr}[e^{-\beta \hat{H}} \hat{A}(0)\hat{B}(t)]$$

$$C_{AB}(t) = C^{*}_{BA}(-t) \quad \leftrightarrow \quad C_{AB}(\omega)/C_{BA}(-\omega) = \exp(\beta\hbar\omega)$$

- simple classical approximation does not fulfill detailed balance

$$C_{AB,\mathrm{class}}(t) = C_{BA,\mathrm{class}}(-t) \qquad \leftrightarrow \qquad C_{AB,\mathrm{class}}(\omega)/C_{BA,\mathrm{class}}(-\omega) = 1$$

- large number of classical correction schemes derived from equivalent quantum formulations

R. Ramírez et al., JCP 121, 3973 (2004)

KUBO-TRANSFORMED TCF

- introduce imaginary-time shifted TCF

$$C_\lambda(t) = C_{AB}(t + i\lambda\hbar) = \frac{1}{Z}\mathrm{tr}[e^{-(\beta-\lambda)\hat{H}}\hat{A}(0)e^{-\lambda\hat{H}}\hat{B}(t)]$$

- Kubo-transformed TCF

$$C_{\mathrm{Kubo}}(t) = \frac{1}{\beta}\int_0^\beta d\lambda C_\lambda(t) = C_{\mathrm{Kubo}}(-t)$$

- most classical-like TCF

- de facto best method for vibrational (IR) spectroscopy

$$\alpha(\omega) \propto \int dt e^{-i\omega t} C_{\mathrm{Kubo}}(t) = \frac{1}{\beta}\int_0^\beta d\lambda C_\lambda(\omega)$$

R. Ramírez et al., JCP 121, 3973 (2004)

GENERALIZED TCF

- relation between Fourier-transforms of original and imaginary-time shifted TCF

$$C_{AB}(\omega) = \int dt e^{-i\omega t} C_{AB}(t) = C_\lambda(\omega) e^{\lambda\hbar\omega}$$

- ad-hoc generalization suggested by identity

$$\frac{1}{\beta}\int_0^\beta d\lambda W(\lambda) C_\lambda(\omega) = \frac{1}{\beta}\int_0^\beta d\lambda W(\lambda) e^{-\lambda\hbar\omega} C_{AB}(\omega) = p(\omega) C_{AB}(\omega)$$

- given a weight-function W the spectrum of the original TCF can be recovered

$$C_{AB}(\omega) = p^{-1}(\omega) \int dt e^{-i\omega t} \frac{1}{\beta}\int_0^\beta d\lambda W(\lambda) C_\lambda(t)$$

- in practice one is searching for approximations to the generalized TCF

$$C_W(t) = \frac{1}{\beta}\int_0^\beta d\lambda W(\lambda) C_\lambda(t)$$

S. Karsten et al., JCP 148, 102337 (2018)

RPMD & GENERALIZED TCF

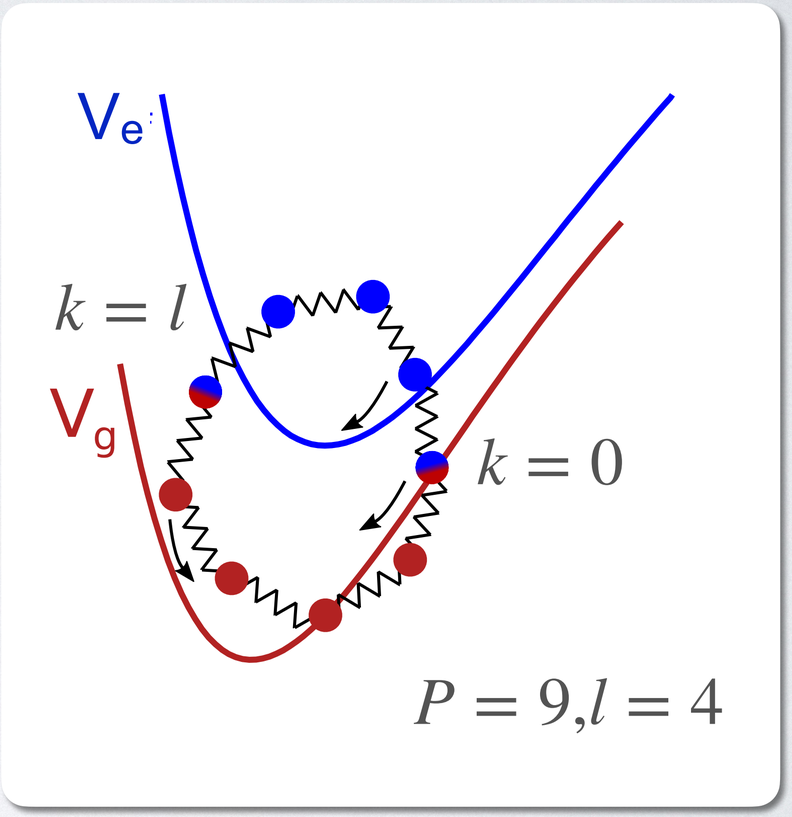
- generalized TCF can be combined with RPMD idea to include nuclear quantum effects

- leads to dynamics on ‚both potentials'

$$U_l(\mathbf{x}) = K_{\mathrm{poly}}(\mathbf{x}) + \frac{1}{P}\Big[\sum_{k=0}^{l} \eta_k V_e(\mathbf{x}_k) + \sum_{k=l}^{P} \eta_k V_g(\mathbf{x}_k)\Big]$$

$$K_{\mathrm{poly}}(\mathbf{x}) = \sum_{k=0}^{P-1} \frac{P}{2\beta^2\hbar^2}(\mathbf{x}_k - \mathbf{x}_{k+1})^{\mathrm{T}}\mathbf{M}(\mathbf{x}_k - \mathbf{x}_{k+1})$$

- details of partitioning depend on intrinsic and external weights



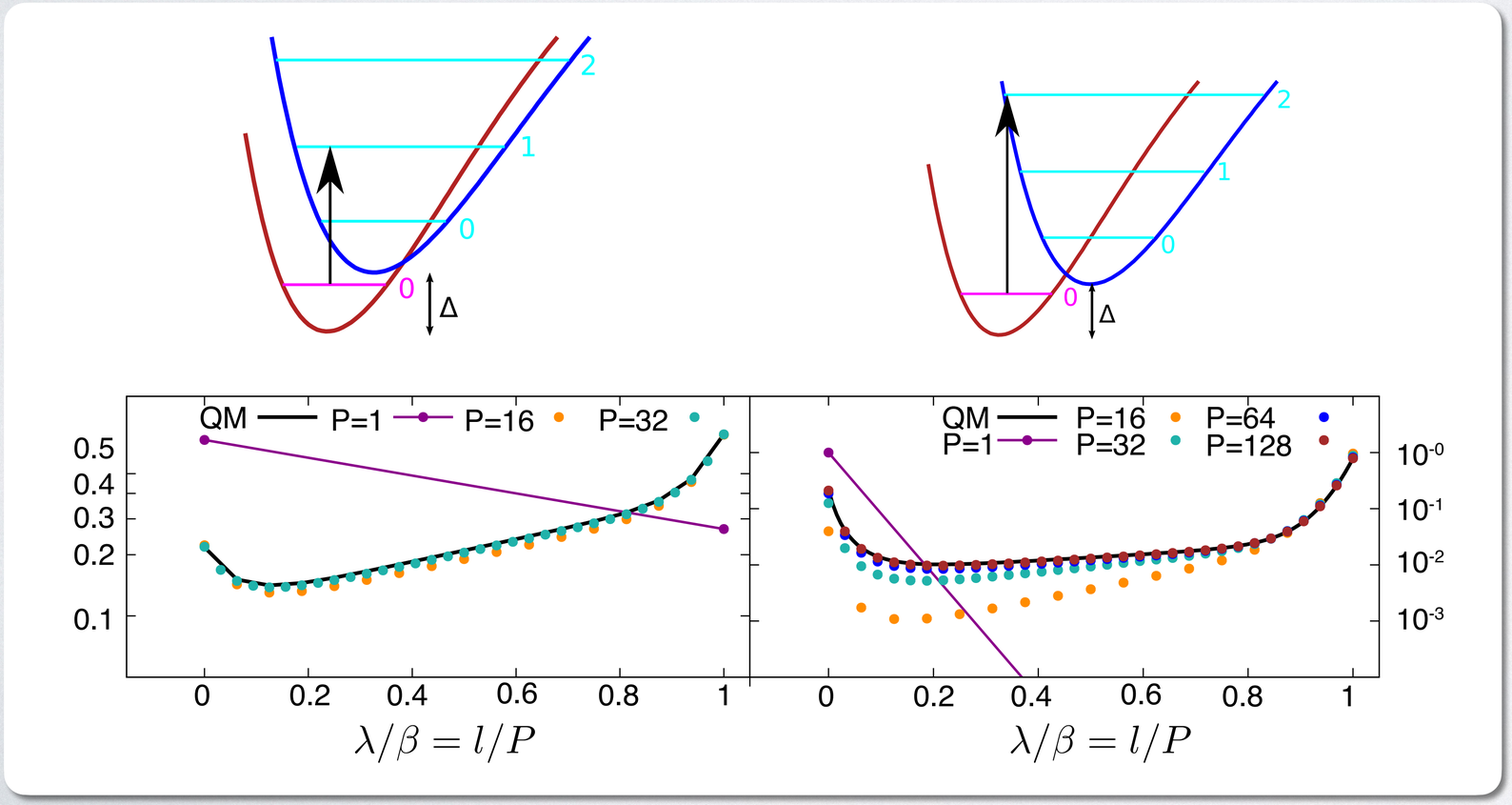
$\eta_k = 0\,(l = 0, P)$

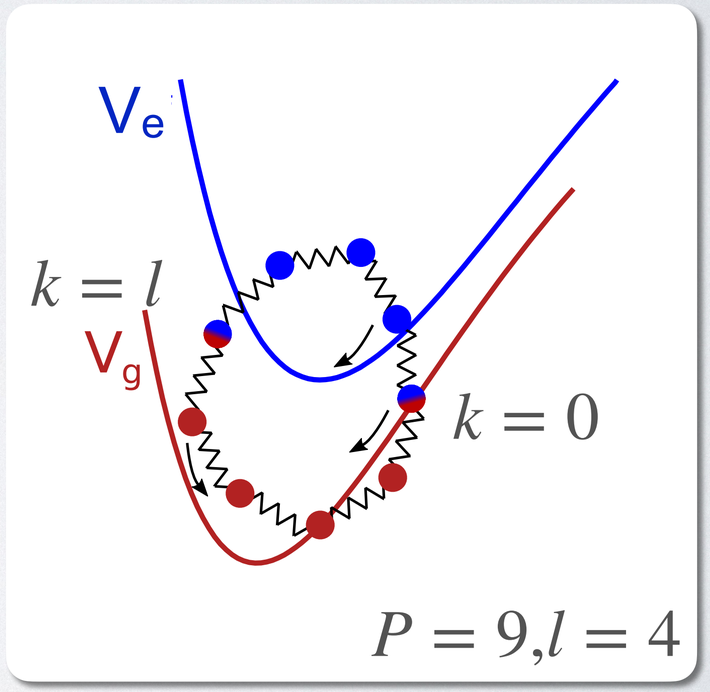
$\eta_k = 1/2\,(k = 0, l, P)$

- generalized TCF expression applied to vibronic transition

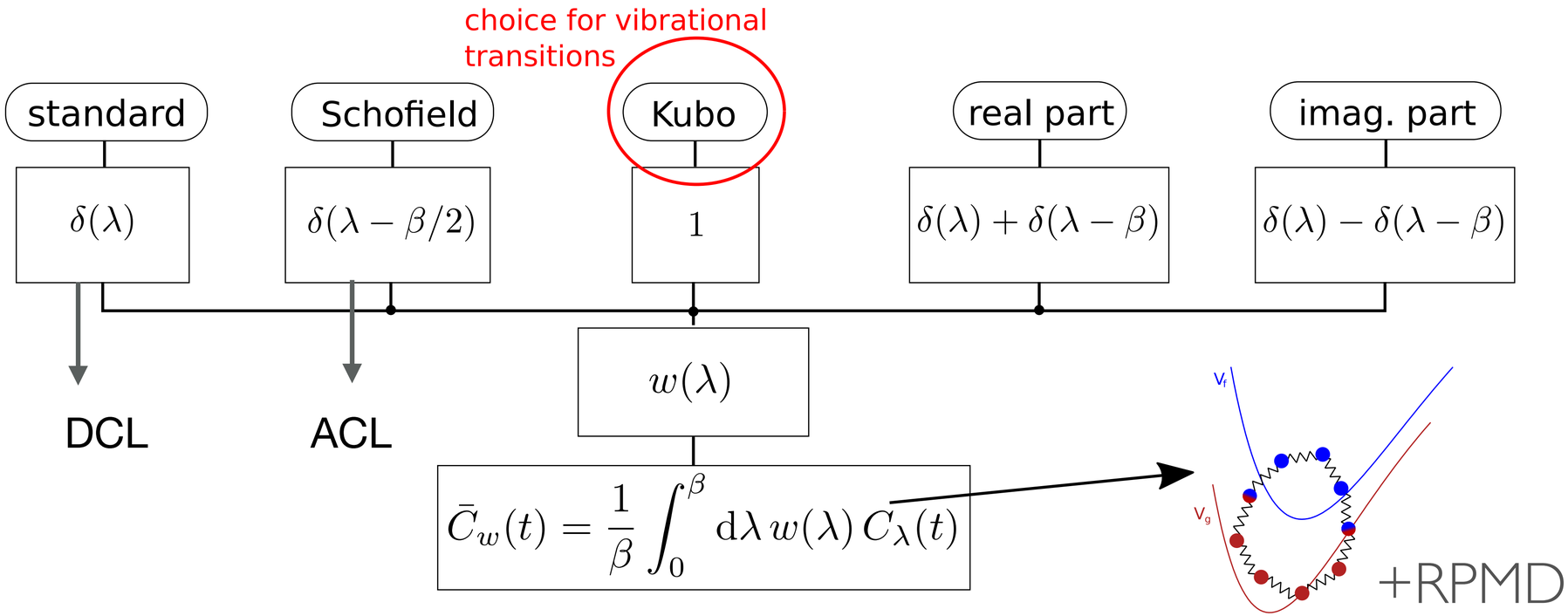
$$C_W(t) = \frac{1}{P}\sum_{l=0}^{P} \eta_l \, W(\lambda_l) \, \xi_{\lambda_l} \langle d_{ge}(\mathbf{x}_l) d_{eg}(\mathbf{x}_0(t)) e^{i/\hbar \int_0^t d\tau [V_e(\mathbf{x}_0(\tau) - V_g(\mathbf{x}_0(\tau)]} \rangle_{\lambda_l} \qquad \lambda_l = l\beta/P$$

external & intrinsic weights $\xi_{\lambda_l} = Z_{\lambda_l}/Z$





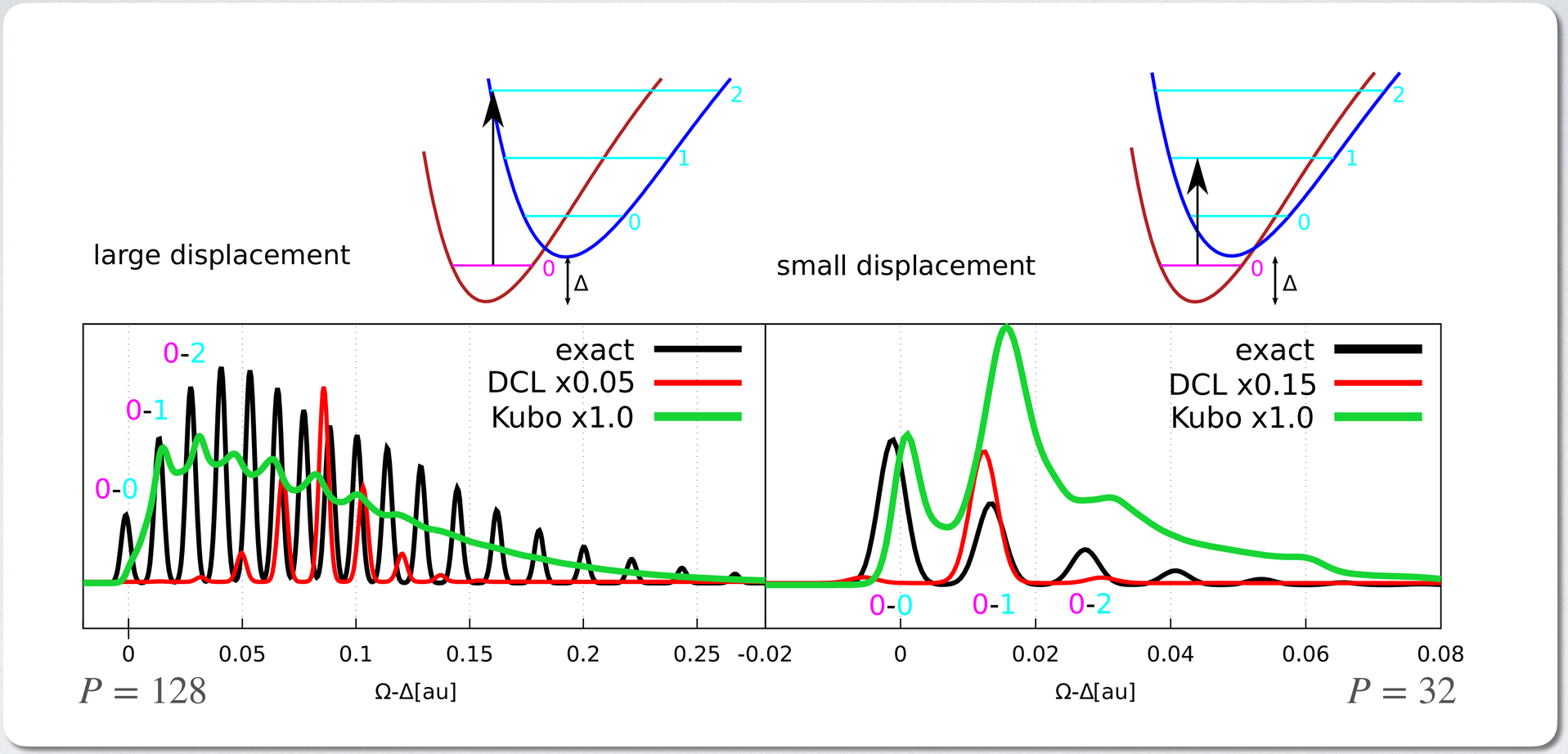
RELATION TO OTHER SCHEMES



- common quantum correction schemes are recovered by special choice of $\mathbf{W}$
- but - new scheme opens way to infinitely many new TCFs

P. Schofield, PRL 4, 239 (1960)

PERFORMANCE OF STANDARD METHODS



- DCL fails (see above)
- Kubo performance depends on systems parameters

TOWARDS NEW TCFS

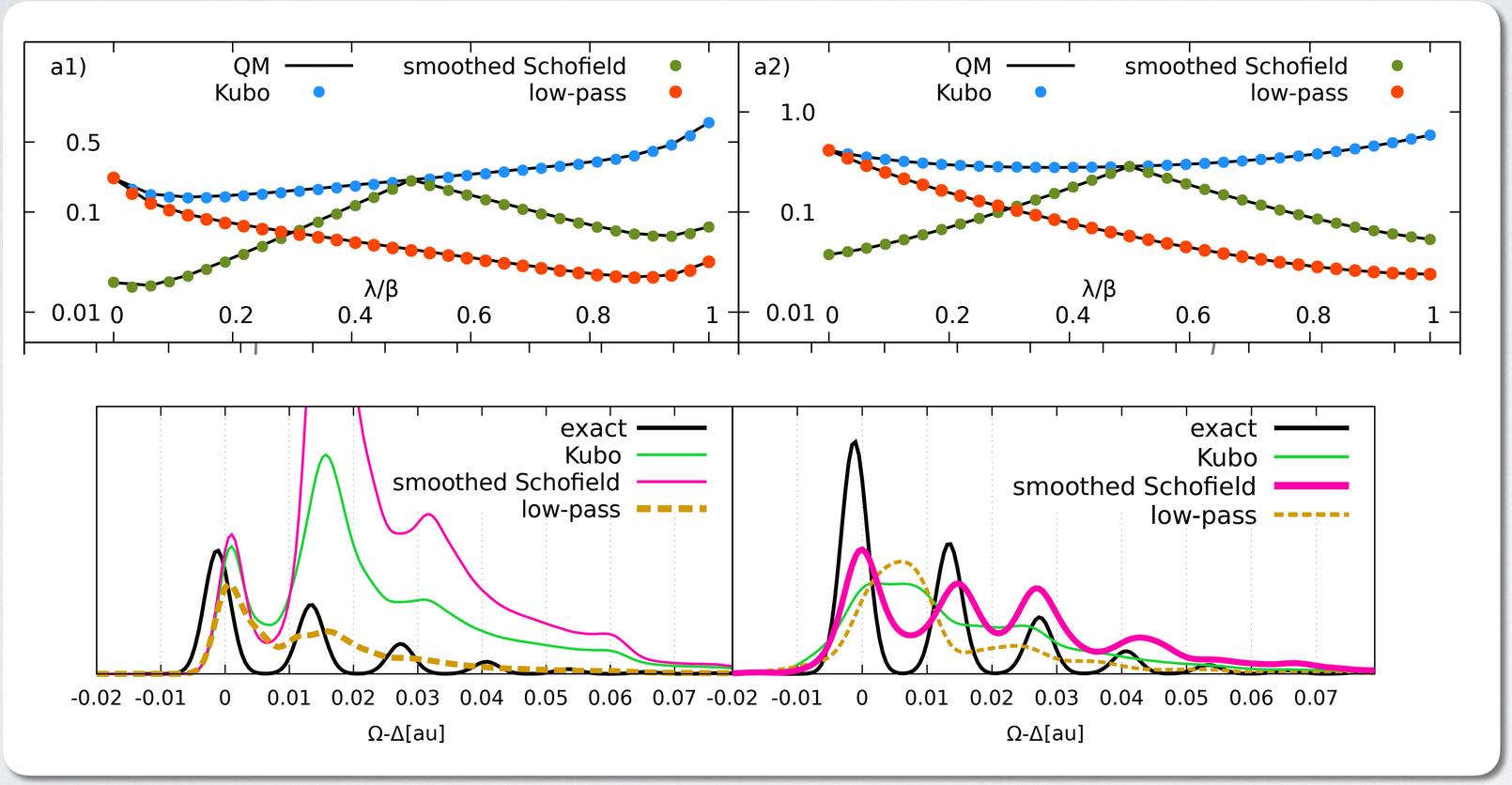
smoothed Schofield

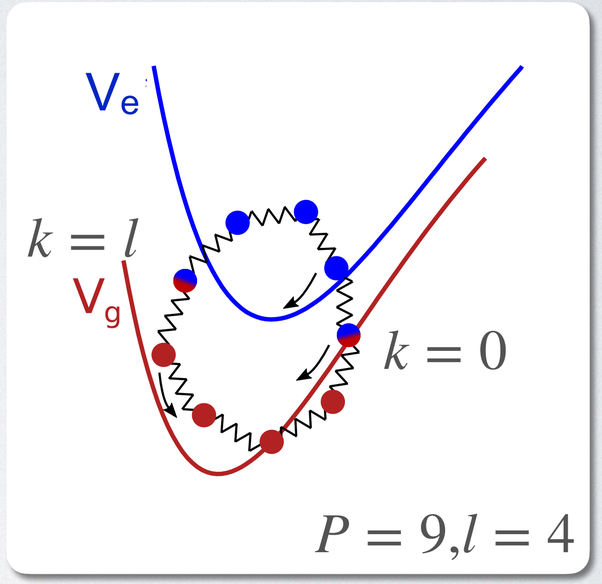
$$W_{\text{Schofield}}(\lambda) = \delta(\lambda - \beta/2) \rightarrow e^{-|\lambda-\beta/2|\epsilon}$$

Kubo with low-pass filter

$$W_{\text{Kubo}}(\lambda) = 1 \rightarrow e^{-\lambda\epsilon}$$

$W(\lambda_l)\,\xi_{\lambda_l}$

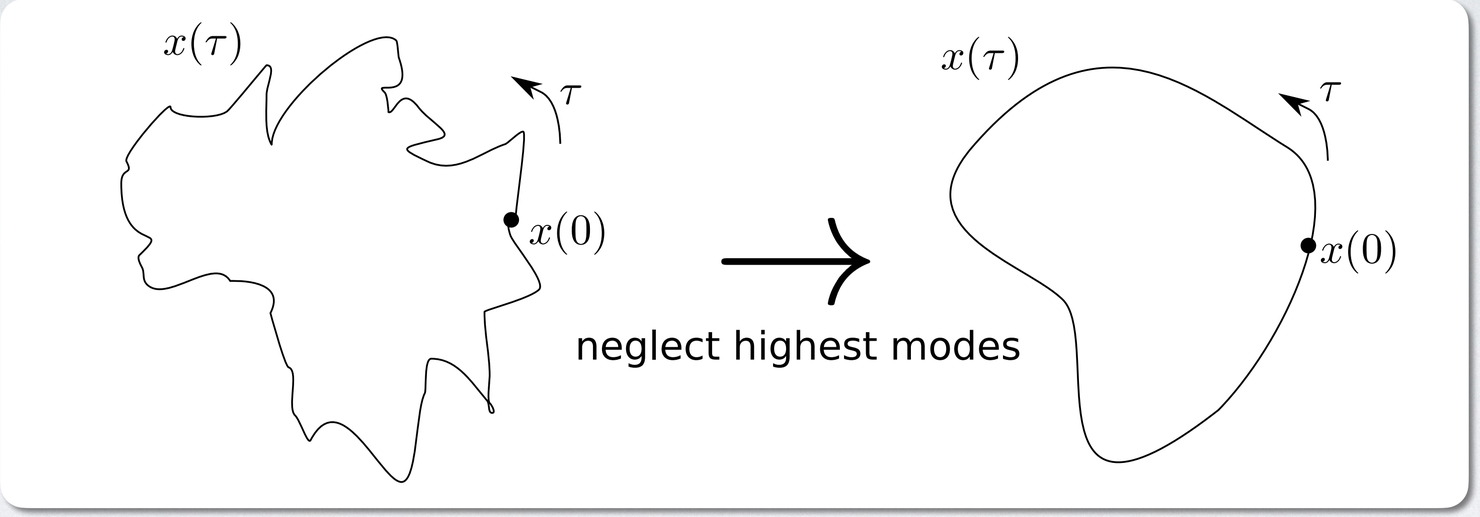




- low-pass Kubo works for $\beta\hbar\omega_g = 18.6$
- smoothed Schofield works for $\beta\hbar\omega_g = 5$

MATSUBARA DYNAMICS

- dynamic PI-based approach to TCFs developed for vibrationally spectroscopy
- in that case rigorous up to the Matsubara approximation



- only <u>smooth</u> imaginary-time paths contribute to TCF
- dynamics of smooth paths classical, but gives correct quantum statistics
- RPMD & centroid MD are limiting cases of Matsubara dynamics

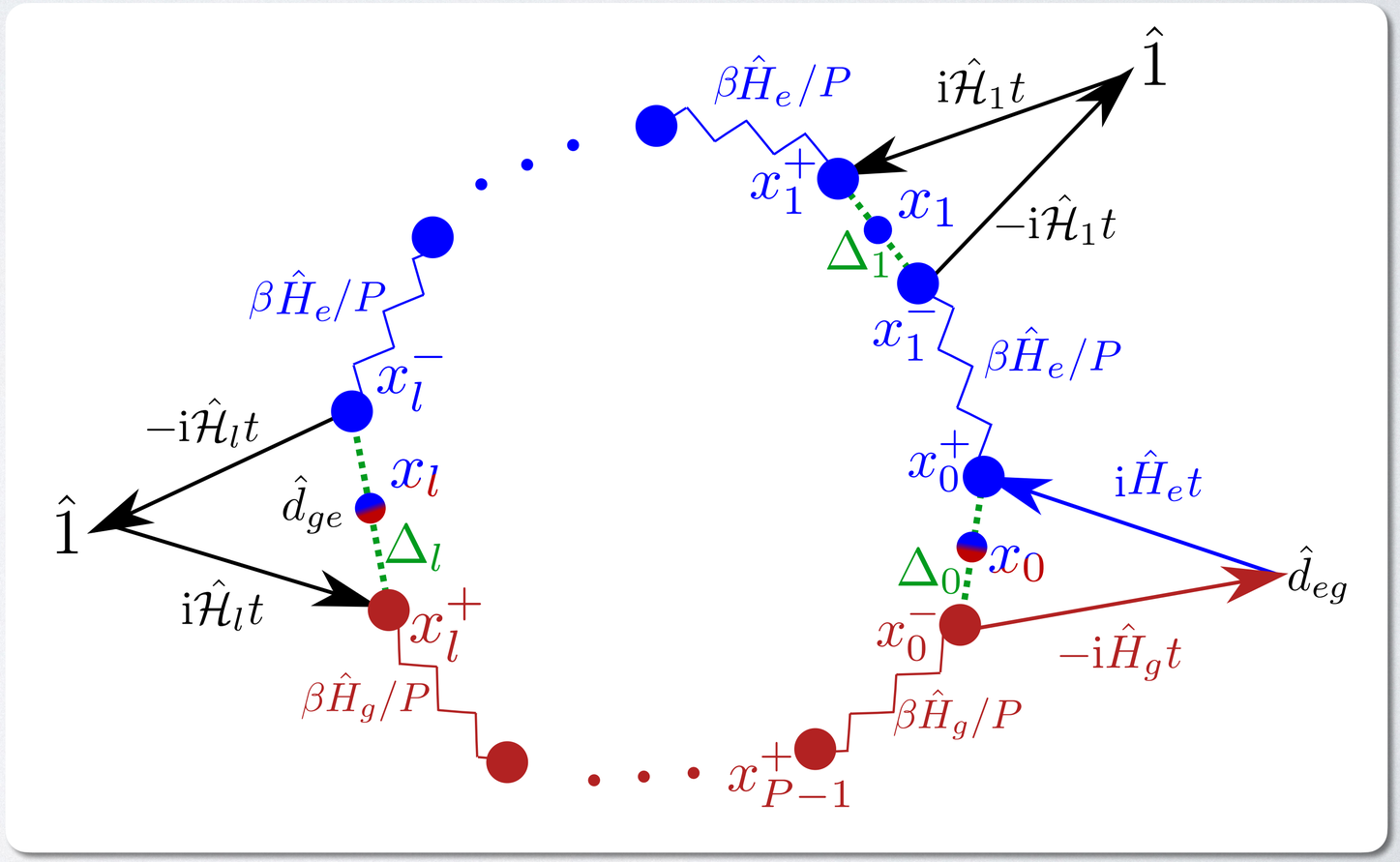
T. Hele et al., JCP <u>142</u>, 134103 (2015); S. C. Althorpe, Eur. J. Phys. B <u>94</u>, 155 (2021)

- imaginary-time shifted TCF for electronic two-state problem (no weight function used!)

$$C_\lambda(t) = \frac{1}{Z}\mathrm{tr}_{\mathrm{vib}}[e^{-(\beta-\lambda)\hat{H}_g}\hat{d}_{ge}e^{-\lambda\hat{H}_e}e^{i\hat{H}_e t/\hbar}\hat{d}_{eg}e^{-i\hat{H}_g t/\hbar}]$$

- transformation to phase-space integral in spirit of path integrals

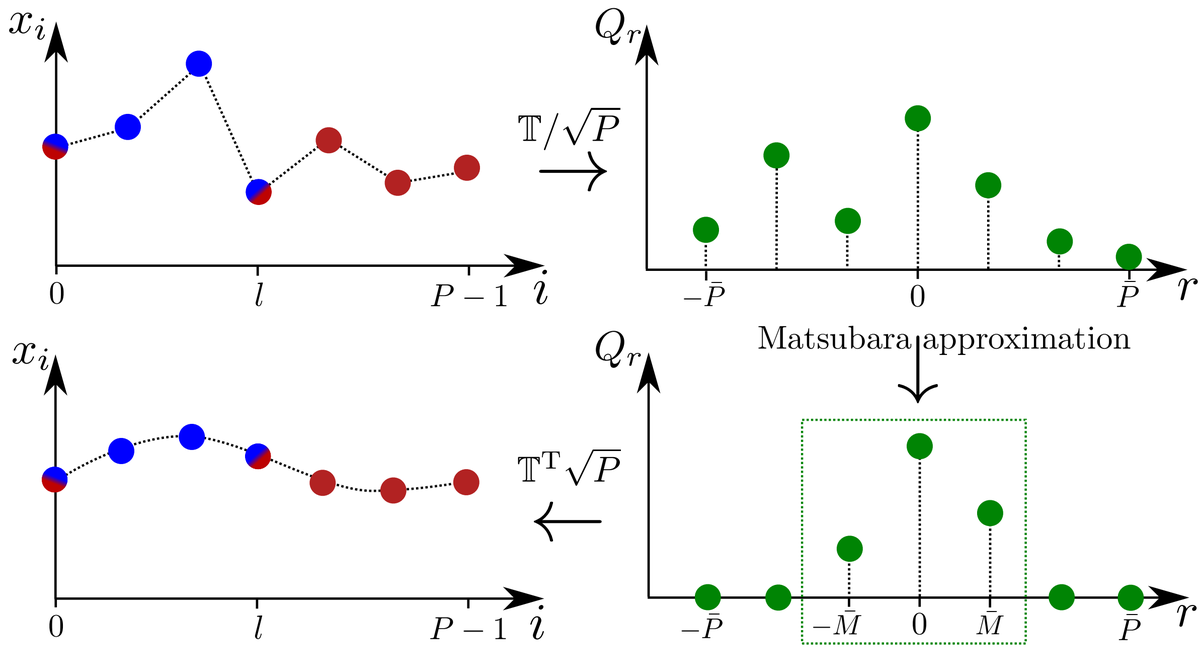
$$C_{\lambda_l}(t) = \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{p}\, A_l(\mathbf{x},\mathbf{p})B_l(\mathbf{x},\mathbf{p},t)$$



- time-independent part

$$A_l(\mathbf{x},\mathbf{p}) = \frac{1}{Z(2\pi\hbar)^P}\int d\mathbf{\Delta} e^{i\mathbf{p}\Delta/\hbar}\frac{1}{2}[\hat{d}_{ge}(x_l^+) + \hat{d}_{ge}(x_l^-)]\prod_{i=l}^{P-1}\langle x_{i+1}^- | e^{-\beta\hat{H}_g/P} | x_i^+\rangle \prod_{i=0}^{l-1}\langle x_{i+1}^- | e^{-\beta\hat{H}_e/P} | x_i^+\rangle$$

  - locally harmonic potentials w.r.t. distance between beads facilitates integration
  - Matsubara approximation $M \ll P$ $(\bar{M} = (M-1)/2)$



$\mathbf{Q}, \mathbf{\Pi}$: normal modes of free-particle ring polymer

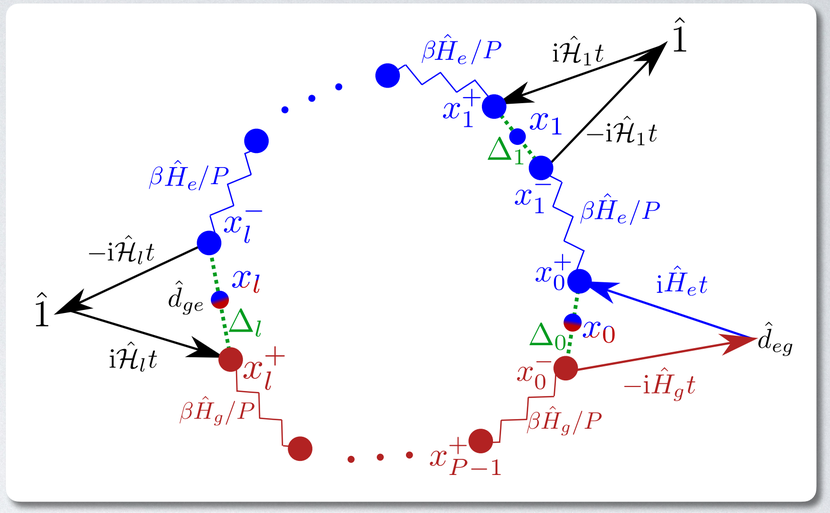
$$K_{\mathrm{poly}}(\mathbf{x}) = \sum_{k=0}^{P-1}\frac{P}{2\beta^2\hbar^2}(\mathbf{x}_k - \mathbf{x}_{k+1})^{\mathrm{T}}\mathbf{M}(\mathbf{x}_k - \mathbf{x}_{k+1})$$

- time-dependent part

$$B_l(\mathbf{x},\mathbf{p}) = \int d\mathbf{\Delta} e^{-i\mathbf{p}\mathbf{\Delta}/\hbar} \prod_{i=0}^{P-1} \langle x_i^+ | e^{i\hat{\mathscr{H}}_i t/\hbar} \hat{\mathscr{O}}_i e^{-i\hat{\mathscr{H}}'_i t/\hbar} | x_i^- \rangle$$

- time evolution w.r.t. full quantum Liouvillian
- trafo to Matsubara modes (plus sin/cos expansion) yields classical-like time evolution with phase factor

$$B_l(\mathbf{Q},\mathbf{\Pi},t) = d_{eg}(x_0(t)) \exp\Big\{\frac{i}{\hbar}\int_0^t d\tau [V_e(x_0(\tau) - V_g(x_0(\tau))]\Big\}$$



$$\hat{\mathscr{O}}_i = \hat{1},\ \forall i > 0 \quad \hat{\mathscr{O}}_0 = \hat{d}_{eg}$$

$$\hat{\mathscr{H}}'_i = \hat{\mathscr{H}}_i,\ \forall i > 0 \quad \hat{\mathscr{H}}'_0 = \hat{H}_g,\ \hat{\mathscr{H}}_0 = \hat{H}_e$$

- Hamilton EOM to obtain $x_0(t) = x_0[\mathbf{Q}(t)]$

$$\dot{\mathbf{Q}} = \frac{1}{m}\mathbf{\Pi} \qquad \dot{\mathbf{\Pi}} = -\nabla \mathscr{U}_l(\mathbf{Q})$$

- dynamics depends on choice of (arbitrary) Hamiltonians, here $\hat{\mathscr{H}}_i = (\hat{H}_g + \hat{H}_e)/2$

- TCF in Matsubara approximation

$$C_{\lambda_l}(t) \propto \int \mathrm{d}\mathbf{Q}\mathrm{d}\mathbf{\Pi}\, e^{-\beta[H_l(\mathbf{\Pi},\mathbf{Q})+i\mathbf{\Pi}^{\mathrm{T}}\mathbf{\Omega}\mathbf{Q}]}\, d_{ge}(x_l(\mathbf{Q}))\, B_l(\mathbf{\Pi},\mathbf{Q},t) \qquad [\mathbf{\Omega}]_{rs} = \frac{2\pi r}{\beta\hbar}\delta_{r,-s}$$

- difficult to converge due to ‚sign problem'
- <u>modified</u> Matsubara method
  - ad hoc modification of Matsubara density
  - exact for harmonic case and $\lambda = 0$ ($\mathbf{K}(\mathbf{Q})$: ground state Hessian)

$$i\mathbf{\Pi}^{\mathrm{T}}\mathbf{\Omega}\mathbf{Q} \rightarrow \frac{1}{2m}\mathbf{\Pi}^{\mathrm{T}}\mathbf{\Omega}^{\mathrm{T}}\mathbf{K}^{-1}\mathbf{\Omega}\mathbf{\Pi} + \frac{m}{2}\mathbf{Q}^{\mathrm{T}}\mathbf{\Omega}^{\mathrm{T}}\mathbf{\Omega}\mathbf{Q}$$

  - can be extended to anharmonic systems using (kind of) local harmonic approximation along imaginary time path

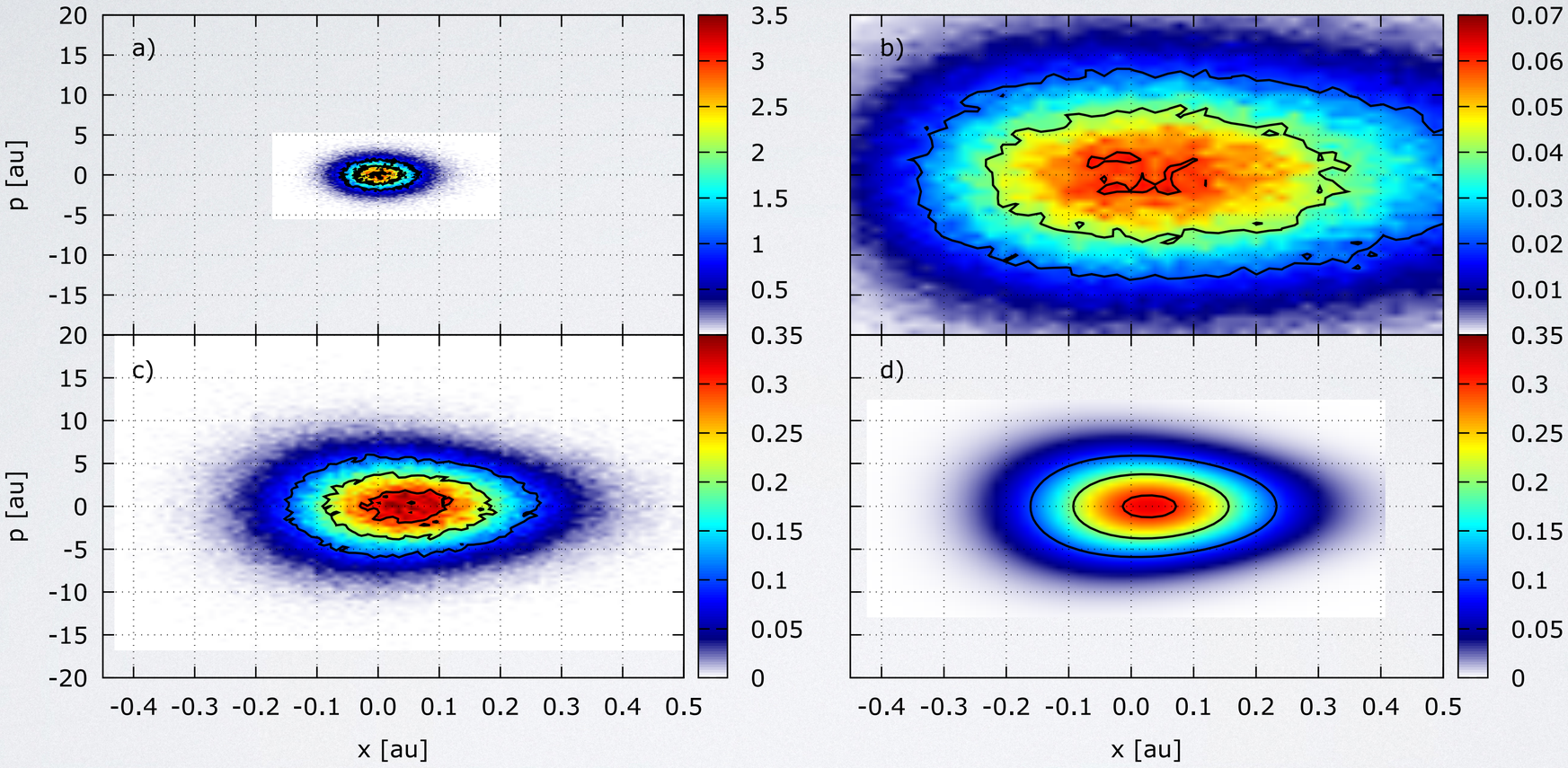
    ➡ problems expected for vanishing or negative curvature

S. Karsten et al., JCP <u>149</u>, 194103 (2018)

- anharmonic phase space probability densities (quartic potential)

classical Boltzmann

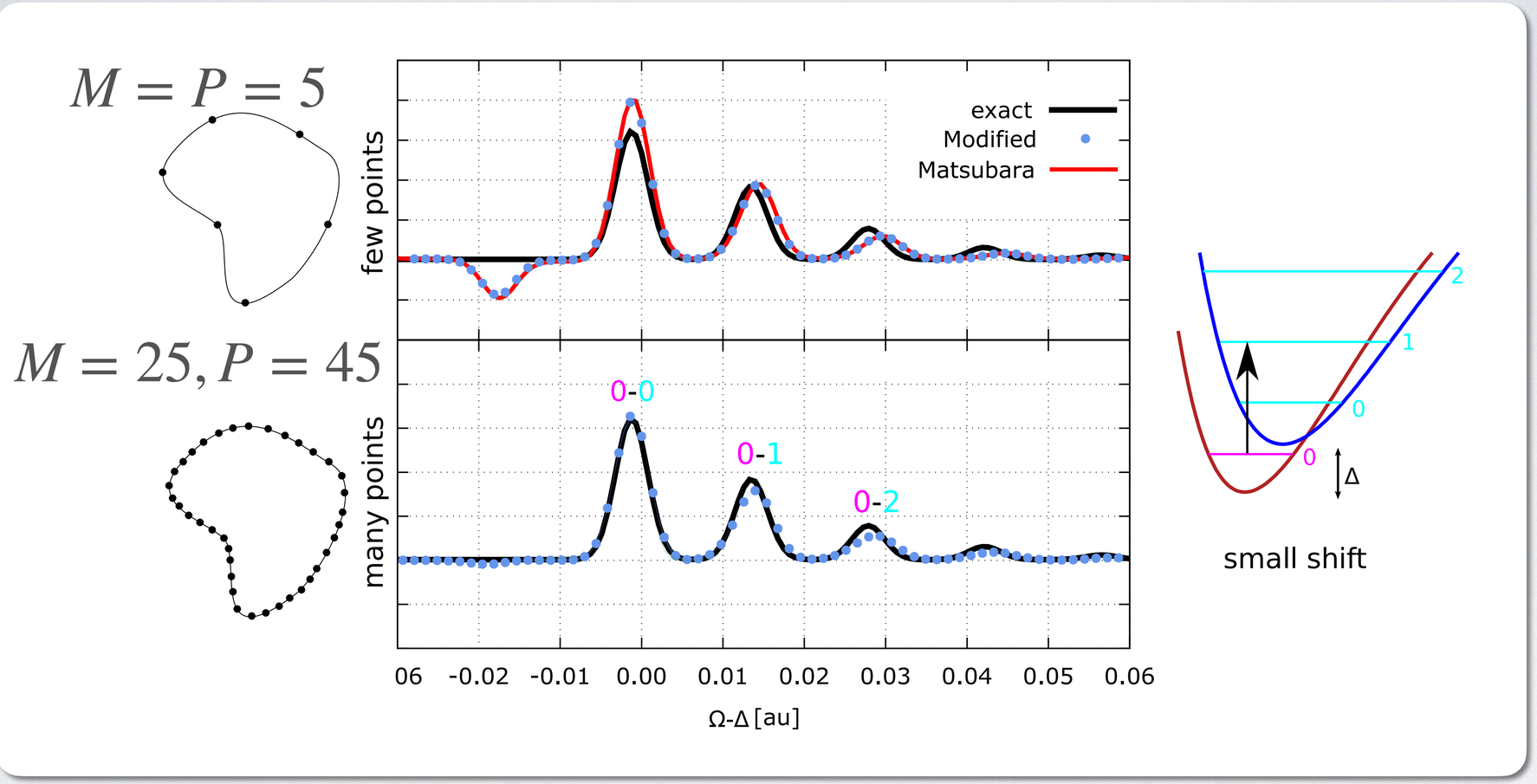
Matsubara („indirect sampling“)



modified Matsubara

exact

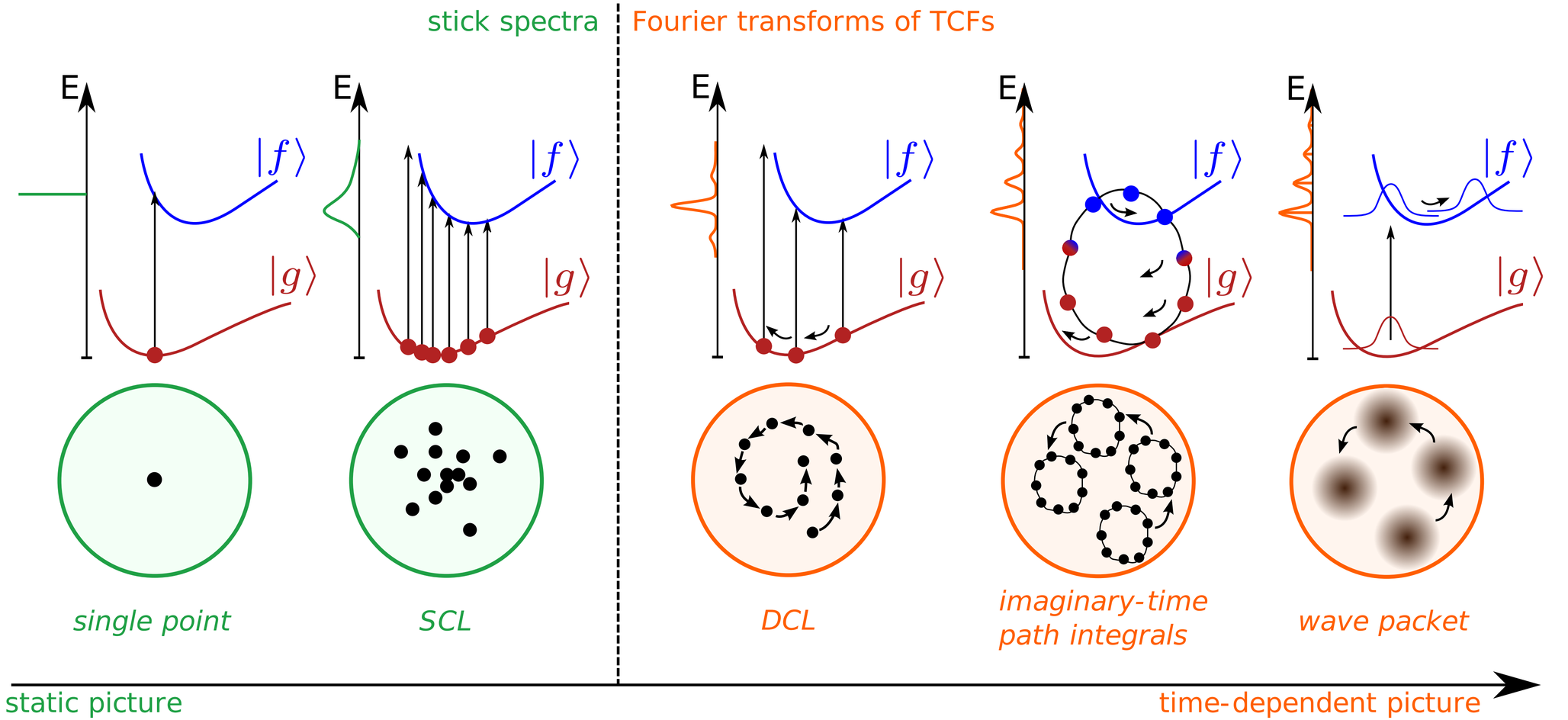
- performance of modified Matsubara method



10000 trajectories

- few points: Matsubara and its modification coincide (10 x more trajectories in former case)
- many points: Matsubara doesn't converge, modified remarkable accurate

SUMMARY


stick spectra
Fourier transforms of TCFs
E
$|f\rangle$
$|g\rangle$
single point
SCL
DCL
imaginary-time
path integrals
wave packet
static picture
time-dependent picture

OPEN QUESTIONS

- generalized TCF gives possibility to generate an infinite number of new TCFs
  - What's the best strategy for optimal choice of weight function?
- modified Matsubara method showed remarkable accuracy even for anharmonic systems
  - Why it works at all and what are the conditions under which it will fail?
- How to marry generalized TCFs and modified Matsubara?
- extension to nonlinear spectroscopy
- .....

Thanks for your attention!