
# The MP/SOFT methodology for simulations of multidimensional quantum dynamics

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$$i\hbar \frac{\partial |\Psi_t\rangle}{\partial t} = \hat{H}|\Psi_t\rangle \longrightarrow |\Psi_t\rangle = e^{-i\hat{H}t/\hbar}|\Psi_0\rangle$$

*where* $$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$$

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + V_1(\hat{x}_1) + \sum_{j=2}^{N}\left(\frac{\hat{p}_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2\hat{x}_j^2 + \frac{1}{2}c_j\hat{x}_1\hat{x}_j^2\right),$$

where $m_j = 1.0$ a.u., $\omega_j = 1.0$ a.u. and $c_j = 0.1$ a.u. for $j = 1$—N with N = 1—20.

## Numerically Exact Methods for Multidimensional Wave-Packet Propagation Based on Expansions of Coherent-States/Configurations

- Multiconfigurational time dependent Hartree (MCTDH) method
  Meyer, Burghardt, Cederbaum, Worth, Raab, Manthe, Makri, Miller, Thoss, Wang

- Time dependent Gauss-Hermit (TDGH) method
  Billing

- Multiple Spawning (MS) method
  Ben-Nun and Martinez

- Coupled Coherent States (CCS) technique
  Shalashilin and Child

- Matching-Pursuit Split-Operator Fourier Transform (MP/SOFT) method
  Wu, Chen, Batista

## Time-Sliced Simulations of Quantum Processes

$$\langle \mathbf{x}|\Psi_t\rangle = \int d\mathbf{x}_0 \langle \mathbf{x}|e^{-i\hat{H}(t_n-t_0)/\hbar}|\mathbf{x}_0\rangle\langle \mathbf{x}_0|\Psi_0\rangle,$$

The essence of the approach is to time-slice matrix elements of the quantum mechanical propagator by repeatedly inserting the resolution of identity

$$\hat{1} = \int \mathbf{dx}|\mathbf{x}\rangle\langle\mathbf{x}|,$$

yielding

$$\langle \mathbf{x}_n|e^{-i\hat{H}(t_n-t_0)/\hbar}|\mathbf{x}_0\rangle = \int \mathbf{dx}_{n-1}\ldots\int \mathbf{dx}_1\langle \mathbf{x}_n|e^{-(i/\hbar)\hat{H}(t_n-t_{n-1})}|\mathbf{x}_{n-1}\rangle \ldots\langle \mathbf{x}_1|e^{-(i/\hbar)\hat{H}(t_1-t_0)}|\mathbf{x}_0\rangle,$$

where $t_0 < t_1 < \ldots < t_{n-1} < t_n$. For sufficiently thin time slices (i.e., when $\tau = t_k - t_{k-1}$ is sufficiently small) each finite-time propagator can be approximated by a semiclassical (*e.g.*, HK SC-IVR) or a quantum-mechanical expansion (*e.g.*, Trotter expansion).

Trotter Expansion (Strang Splitting)

$$\left|\Psi_t\right\rangle = e^{-i\hat{H}t/\hbar}\left|\Psi_0\right\rangle$$

$$e^{-(i/\hbar)\hat{H}\tau} \approx e^{-(i/\hbar)\hat{V}\tau/2}\mathrm{FT}^{-1}\, e^{-(i/\hbar)\frac{\mathbf{p}^2}{2m}\tau}\mathrm{FT}\, e^{-(i/\hbar)\hat{V}\tau/2}.$$

Here, $\hat{H} = \frac{\mathbf{p}^2}{2m} + \hat{V}(\mathbf{x})$, and FT indicates the action of the multidimensional Fourier transform.

# MP/SOFT Method


Wu,Y.; Batista, V.S. *J. Chem. Phys.* (2003) **118**, 6720

Wu,Y.; Batista, V.S. *J. Chem. Phys.* (2003) **119**, 7606

Wu,Y.; Batista, V.S. *J. Chem. Phys.* (2004) **121**, 1676

Chen, X., Wu,Y.; Batista, V.S. *J. Chem. Phys.* (2005) **122**, 64102

Wu,Y.; Herman, M.F.; Batista, V.S. *J. Chem. Phys.* (2005) **122**, 114114

Wu,Y.; Batista, V.S. *J. Chem. Phys.* (2006) **124**, 224305

Chen, X.; Batista, V.S. *J. Chem. Phys.* (2006) **125**, 124313

Chen, X.; Batista, V.S. *J. Photochem. Photobiol.* (2007) **190**, 274

Kim, J.; Wu, Y.; Batista, V.S. *Israel J. Chem.* (2009) **49**, 187

Chen, X.; Batista, V.S. *J. Chem. Phys.* (2010) **in prep.**

Wu,Y.; Batista, V.S. *J. Chem. Phys.* **121**, 1676 (2004)

## Analytically Continued MP/SOFT Method

- **Step [1]**: Decompose $\langle \mathbf{x}|\widetilde{\Psi}_t\rangle \equiv \langle \mathbf{x}|e^{-\frac{i}{\hbar}\hat{V}(\mathbf{x})\frac{dt}{2}}|\Psi_t\rangle$ in a matching-pursuit coherent-state expansion:

$$\langle \mathbf{x}|\widetilde{\Psi}_t\rangle \approx \sum_{j=1}^{n} c_j \langle \mathbf{x}|j\rangle,$$

where

$$c_j \equiv \begin{cases} \langle 1|\widetilde{\Psi}_t\rangle, & \text{when } j=1, \\ \langle j|\widetilde{\Psi}_t\rangle - \sum_{k=1}^{j-1} c_k \langle j|k\rangle, & \text{otherwise.} \end{cases}$$

Here, $\langle \mathbf{x}|j\rangle$ are N-dimensional coherent-states,

$$\langle \mathbf{x}|j\rangle \equiv \prod_{k=1}^{N} A_j(k) e^{-\gamma_j(k)(x(k)-x_j(k))^2/2}\, e^{i\, p_j(k)(x(k)-x_j(k))}$$

with complex-valued coordinates $x_j(k) \equiv c_j(k) + i d_j(k)$, momenta $p_j(k) \equiv g_j(k) + i f_j(k)$, and scaling parameters $\gamma_j(k) \equiv a_j(k) + i b_j(k)$. The normalization constants are $A_j(k) \equiv (a_j(k)/\pi)^{1/4} \exp[-\frac{1}{2}a_j(k)d_j(k)^2 - d_j(k)g_j(k) - (b_j(k)d_j(k) + f_j(k))^2/(2a_j(k))]$.

- **Step [2]**: Analytically Fourier transform the coherent-state expansion to the momentum representation, apply the kinetic energy part of the Trotter expansion $e^{-\frac{i}{\hbar}\frac{\mathbf{p}^2}{2m}\tau}$, and analytically inverse Fourier transform the resulting expression back to the coordinate representation to obtain the time evolved wavefunction:

$$\langle \mathbf{x}|\Psi_{t+\tau}\rangle = \sum_{j=1}^{n} c_j e^{-\frac{i}{\hbar}V(\mathbf{x})\frac{dt}{2}}\langle \mathbf{x}|\widetilde{j}\rangle,$$

where

$$\langle \mathbf{x}|\widetilde{j}\rangle \equiv \prod_{k=1}^{N} A_j(k) \sqrt{\frac{m}{m+i\tau\hbar\gamma(k)}}$$
$$\times \exp\left(\frac{\left(\frac{p_j(k)}{\hbar\gamma(k)} - i(x_j(k)-x(k))\right)^2}{\left(\frac{2}{\gamma(k)}+\frac{i2\tau\hbar}{m}\right)} - \frac{p_j(k)^2}{2\gamma(k)\hbar^2}\right).$$

## Matching-Pursuit Coherent-State Expansion

- **Step [1.1]**: Maximize the norm of the overlap of a trial coherent-state with the target state $|\langle j|\widetilde{\Psi}_t\rangle|$. Define $|1\rangle$ according to the optimum parameters and the expansion coefficient $c_1$ as the overlap. Therefore,

$$|\widetilde{\Psi}_t\rangle = c_1|1\rangle + |\varepsilon_1\rangle, \tag{-5}$$

- **Step [1.2]**: Goto [1.1], replacing $|\widetilde{\Psi}_t\rangle$ by $|\varepsilon_1\rangle$. Therefore,

$$|\varepsilon_1\rangle = c_2|2\rangle + |\varepsilon_2\rangle, \tag{-5}$$

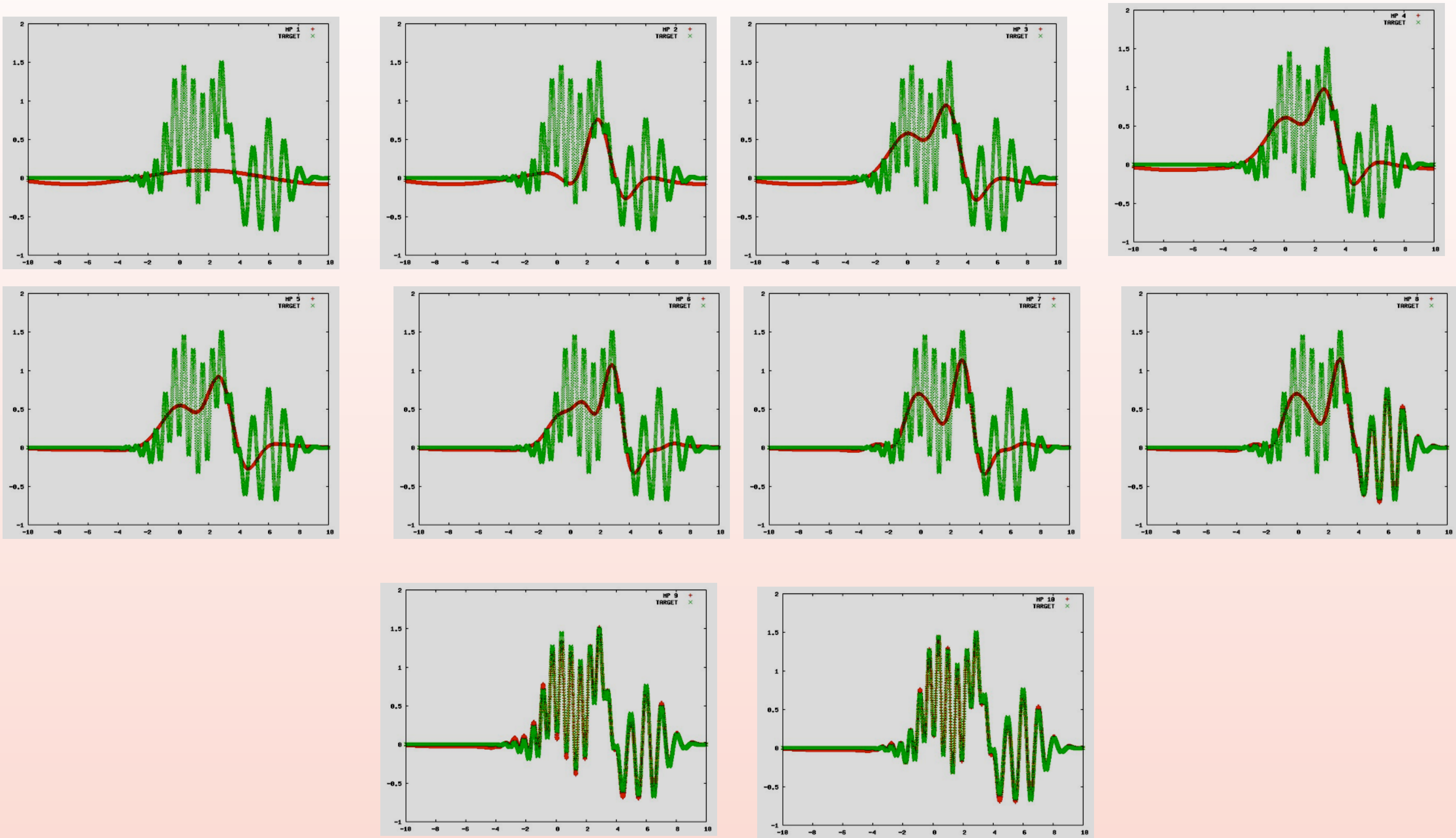
  where $c_2 \equiv \langle 2|\varepsilon_1\rangle$.

After $n$ successive orthogonal projections, the norm of the residual vector $|\varepsilon_n\rangle$ is smaller than a desired precision $\epsilon$,

$$|\varepsilon_n| = \sqrt{1 - \sum_{j=1}^{n} |c_j|^2} < \epsilon. \tag{-5}$$

Norm conservation is maintained within a desired precision.

# MP/SOFT Decomposition



Dr. Rajdeep Saha

# Contraction Mapping

$$Min\left[\left\|\varepsilon_1\right\|\right] \Leftrightarrow \partial\left\|\varepsilon_1\right\| / \partial\xi_j = 0, \xi_j = \left\{x_j, p_j, \gamma_j\right\}$$

$$x_j = \mathrm{Re}\left[\frac{\left\langle g_j\middle|\hat{x}\middle|\psi\right\rangle}{\left\langle g_j\middle|\psi\right\rangle}\right]$$

$$p_j = \mathrm{Re}\left[\frac{\left\langle g_j\middle|\hat{p}\middle|\psi\right\rangle}{\left\langle g_j\middle|\psi\right\rangle}\right]$$

$$\frac{1}{2\gamma_j} = \mathrm{Re}\left[\frac{\left\langle g_j\middle|\left(\hat{x}-x_j\right)^2\middle|\psi\right\rangle}{\left\langle g_j\middle|\psi\right\rangle}\right]$$

# Computation of Observables

**Absorption Spectrum:**

$$\sigma(\lambda) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, \xi(t)\, e^{i\omega t},$$

with $\omega = 2\pi c/\lambda$, and

$$\xi(t) \equiv \langle \Psi_0 \mid e^{-i\hat{H}t/\hbar} \mid \Psi_0 \rangle = \langle \Psi_0 \mid \Psi_t \rangle.$$

**Time dependent reactant population:**

$$P(t) \equiv \langle \Psi_0 \mid e^{i\hat{H}t/\hbar} h(\mathbf{q}) e^{-i\hat{H}t/\hbar} \mid \Psi_0 \rangle,$$

Wu,Y.; Batista, V.S. *J. Chem. Phys.* **121**, 1676 (2004)

# Electron Tunneling in Multidimensional Systems

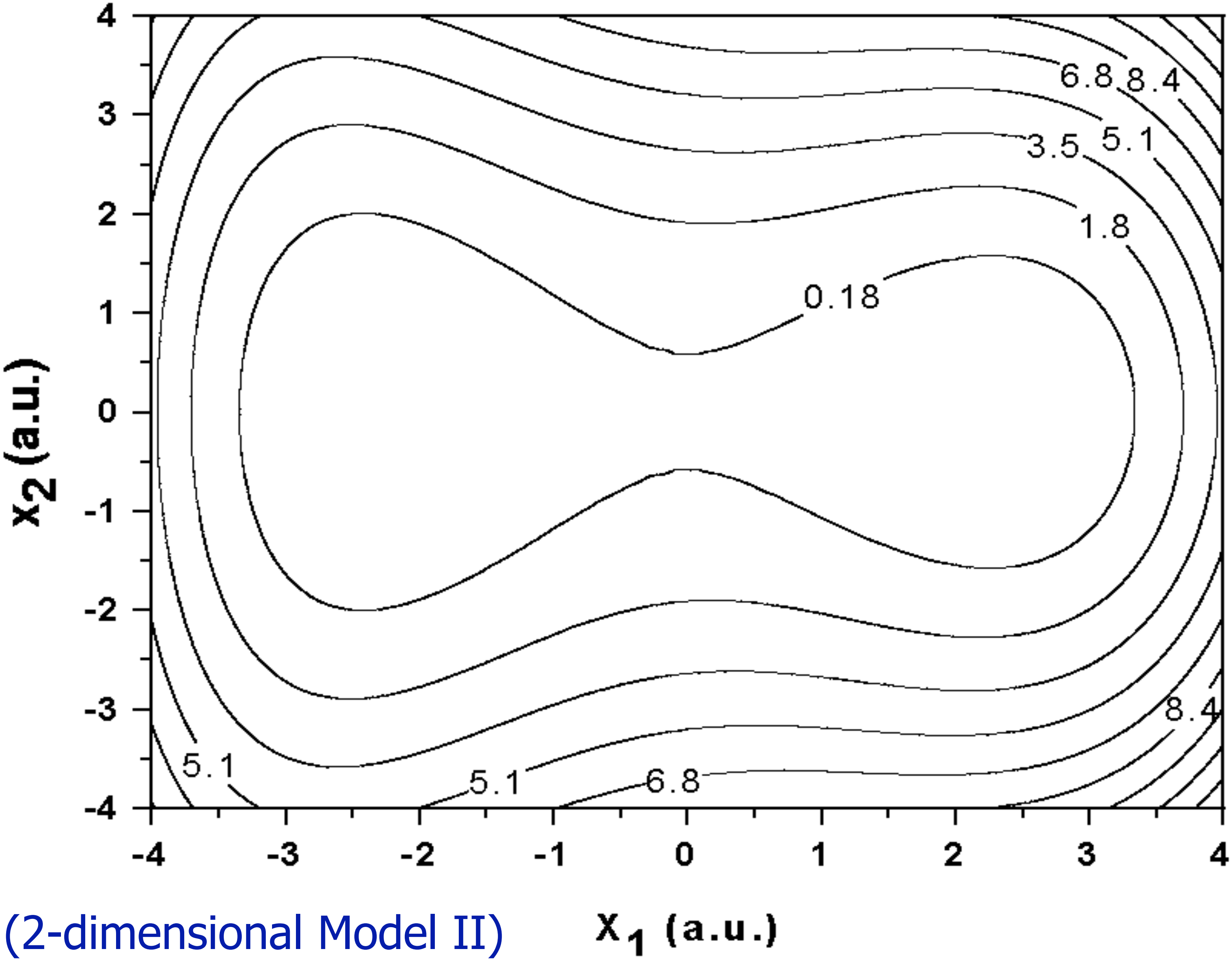
Model II

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + V_1(\hat{x}_1) + \sum_{j=2}^{N} \left( \frac{\hat{p}_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \hat{x}_j^2 + \frac{1}{2} c_j \hat{x}_1 \hat{x}_j^2 \right),$$

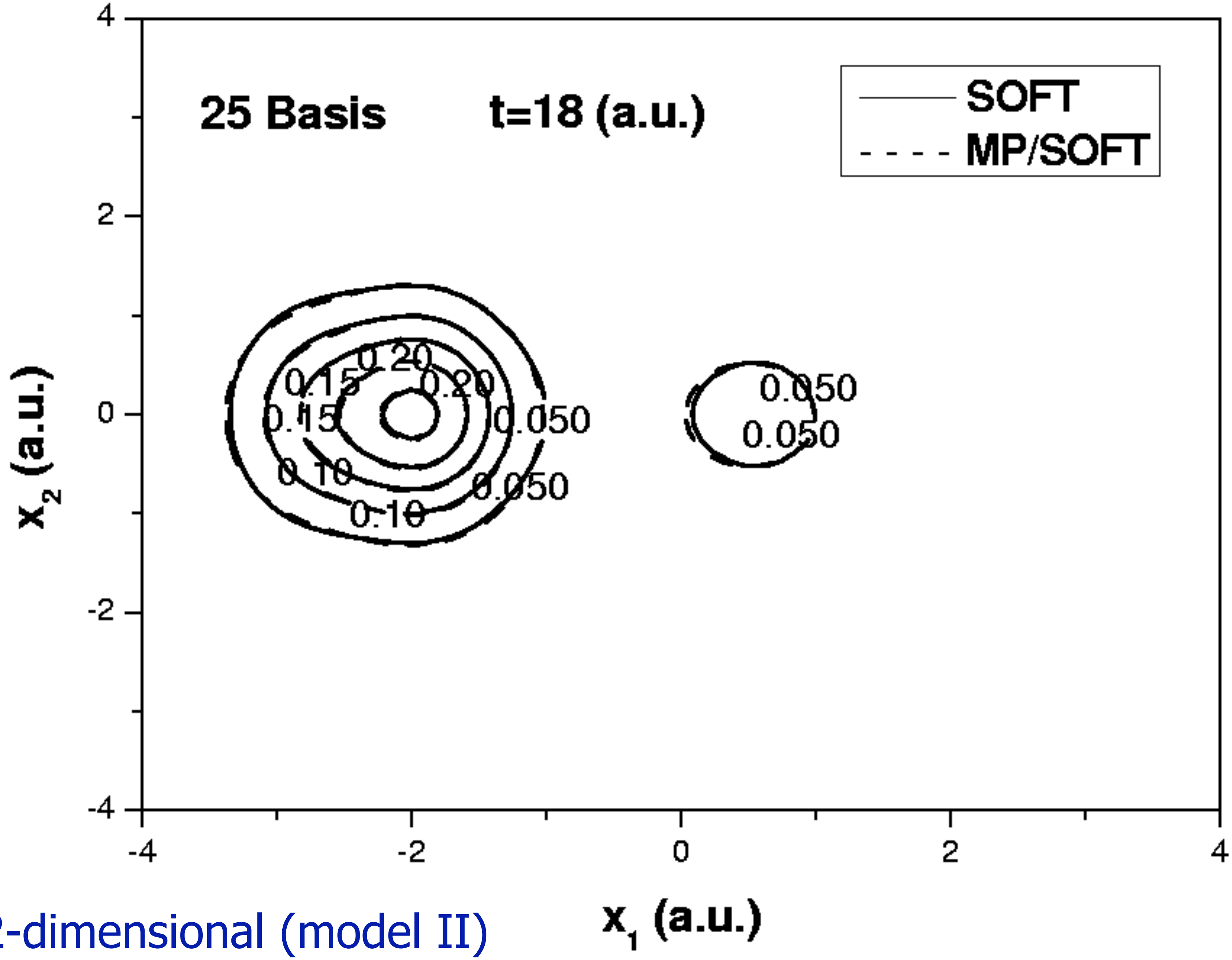
where $\mathrm{m}_j = 1.0$ a.u., $\omega_j = 1.0$ a.u. and $c_j = 0.1$ a.u. for $j = 1$—N with N = 1—20.

$$V_1(\hat{x}_1) = \frac{1}{16\eta} \hat{x}_1^4 - \frac{1}{2} \hat{x}_1^2,$$

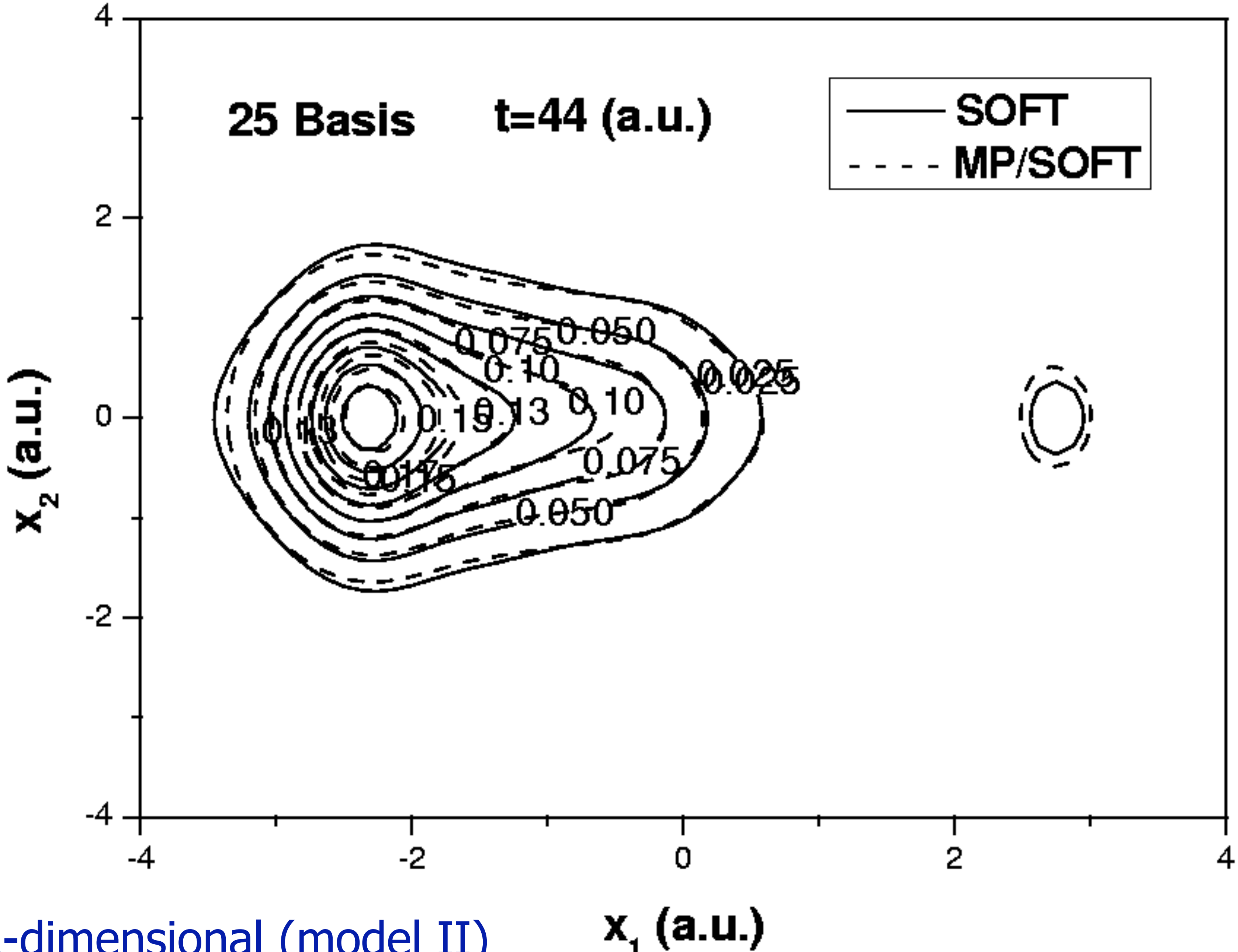
with $\eta = 1.3544$.



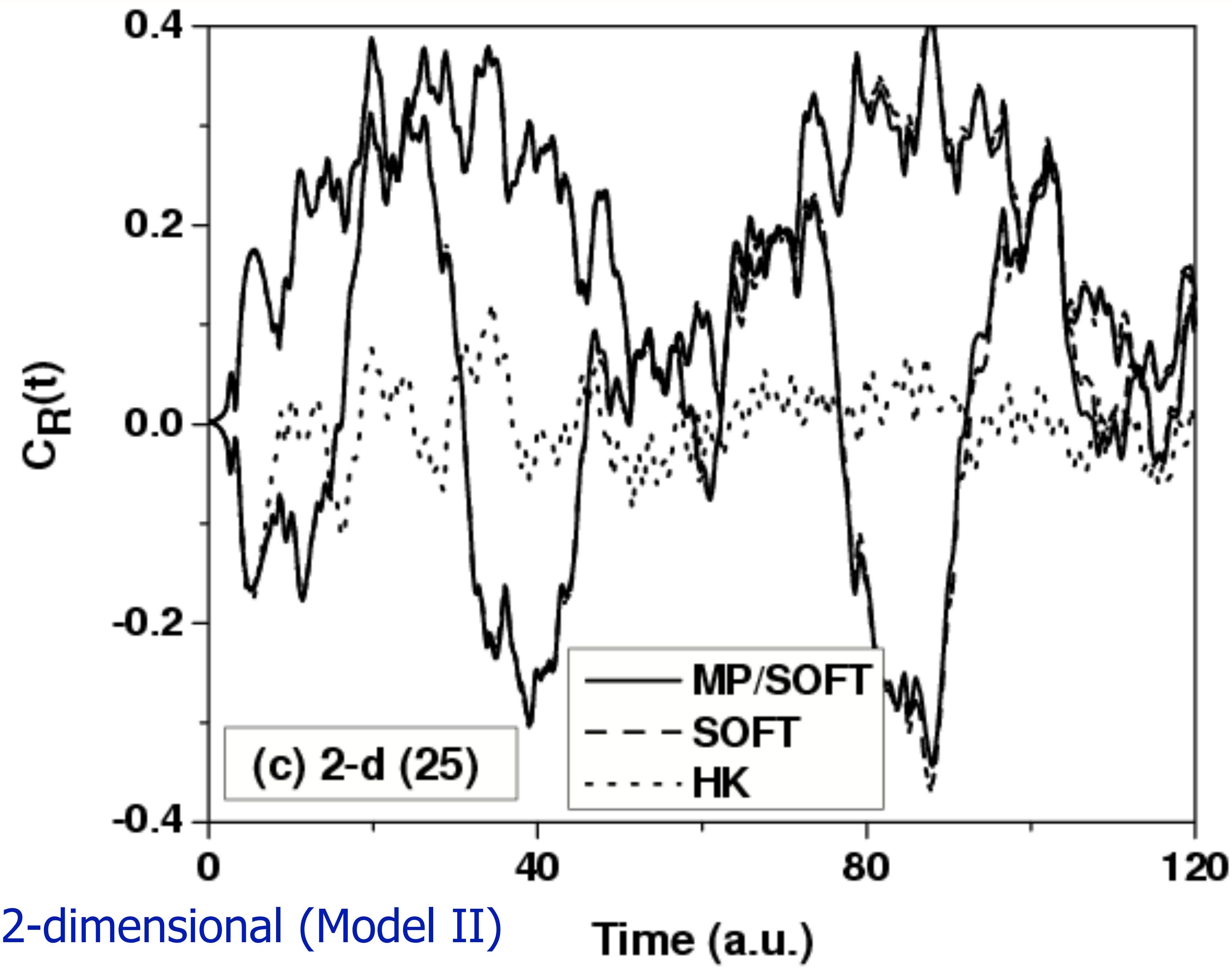

(2-dimensional Model II)




2-dimensional (model II)

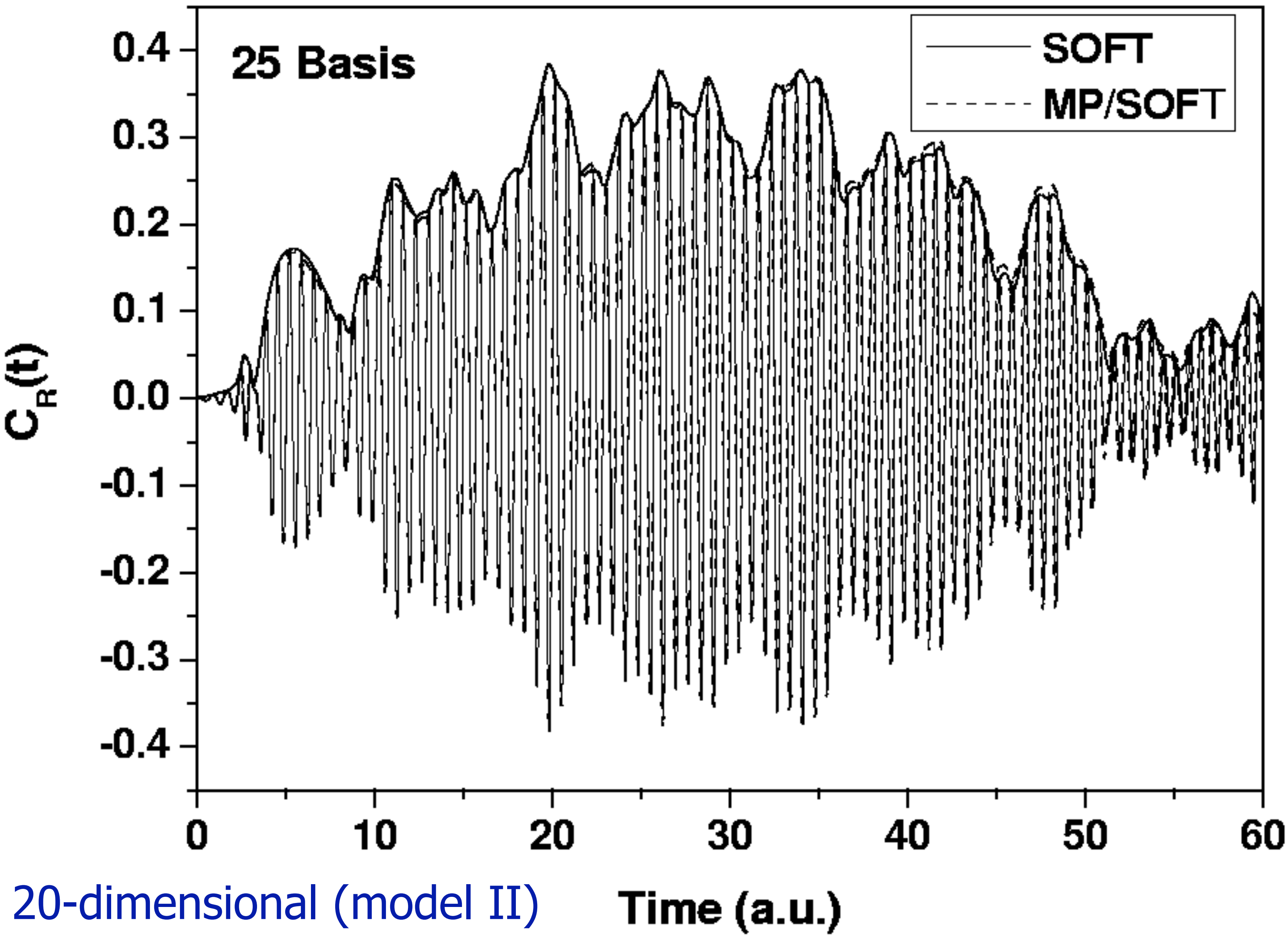



2-dimensional (model II)



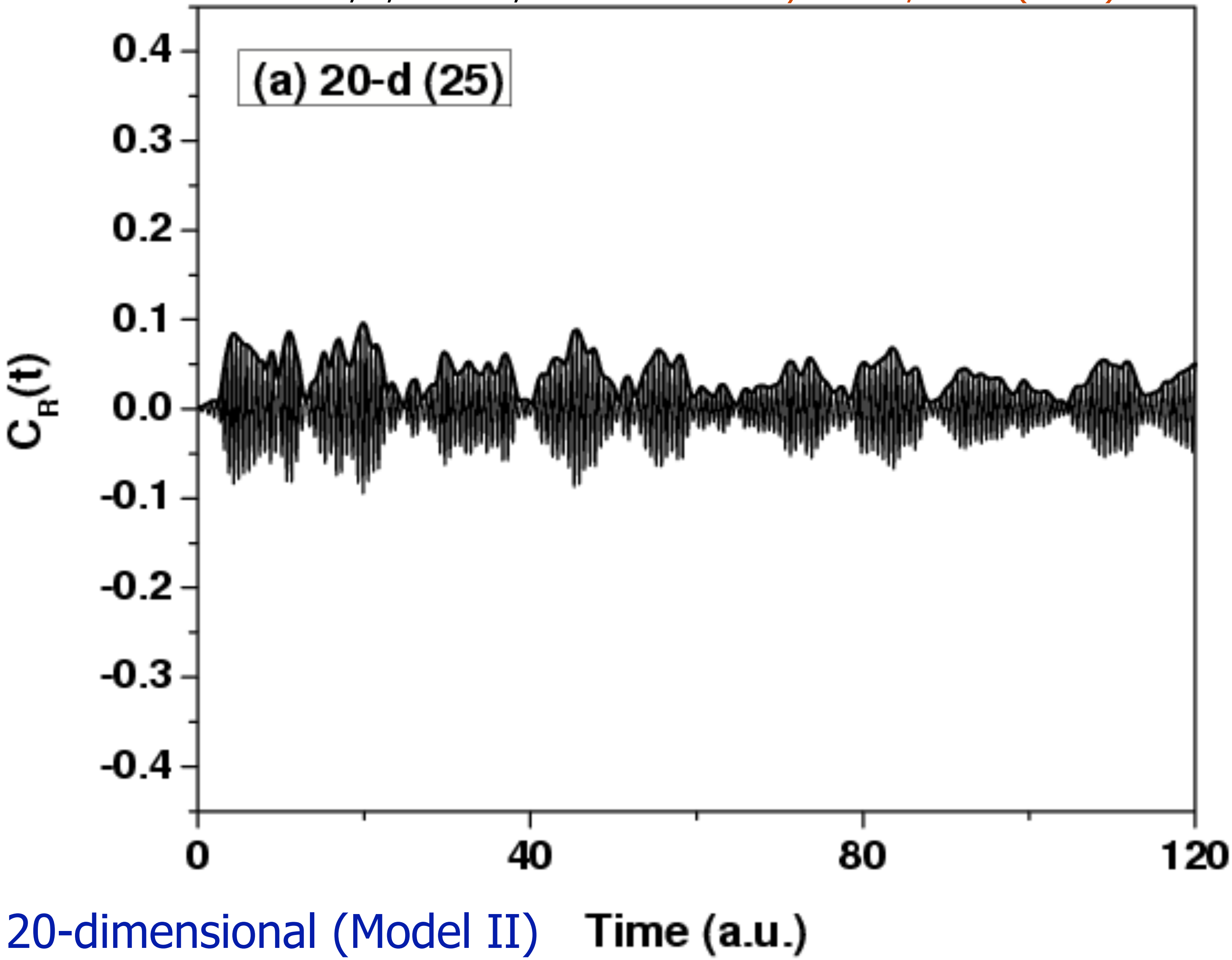

2-dimensional (Model II)

Benchmark calculation: Wu,Y.; Batista, V.S. *J. Chem. Phys.* **121**, 1676 (2004)




20-dimensional (model II)

Wu,Y.; Batista, V.S. *J. Chem. Phys.* **121**, 1676 (2004)




20-dimensional (Model II)

# Thermal Correlation Functions

Chen, X., Wu,Y.; Batista, V.S. *J. Chem. Phys.* **122**, 64102 (2005)

$$C(t) = Z^{-1}\mathrm{Tr}[e^{-\beta\hat{H}_0}\hat{A}e^{i\hat{H}_1 t}\hat{B}e^{-i\hat{H}_1 t}],$$

$$\hat{H}_j = \hat{\mathbf{p}}^2/(2m) + V_j(\hat{\mathbf{x}}).$$

## Time-Dependent Boltzmann Ensemble Averages

$$\langle B(t)\rangle = Z^{-1}\mathrm{Tr}[e^{-\beta\hat{H}_0}e^{i\hat{H}_1 t}\hat{B}e^{-i\hat{H}_1 t}],$$

$$\langle B(t)\rangle = Z^{-1}\int d\mathbf{x}\int d\mathbf{x}'\int d\mathbf{x}''\langle\mathbf{x}|e^{-\frac{\beta}{2}\hat{H}_0}|\mathbf{x}'\rangle\langle\mathbf{x}'|e^{i\hat{H}_1 t}\hat{B}e^{-i\hat{H}_1 t}|\mathbf{x}''\rangle\langle\mathbf{x}''|e^{-\frac{\beta}{2}\hat{H}_0}|\mathbf{x}\rangle.$$

Chen, X., Wu,Y.; Batista, V.S. *J. Chem. Phys.* **122**, 64102 (2005)

# Bloch Equation: MP/SOFT Integration

$$\frac{\partial \langle \mathbf{x}|\hat{\rho}_\beta|\mathbf{x}'\rangle}{\partial \beta} = -\hat{H}_0 \langle \mathbf{x}|\hat{\rho}_\beta|\mathbf{x}'\rangle,$$

Boltzmann Matrix: $\langle \mathbf{x}|\hat{\rho}_\beta|\mathbf{x}'\rangle = \langle \mathbf{x}|e^{-\beta\hat{H}_0}|\mathbf{x}\rangle$ ⟶

Partition Function

$$Z = \mathrm{Tr}[e^{-\beta\hat{H}_0}]$$

$$\langle \mathbf{x}|\hat{\rho}_\beta|\mathbf{x}'\rangle = \int d\mathbf{x}'' \langle \mathbf{x}|e^{-(\beta-\epsilon)\hat{H}_0}|\mathbf{x}''\rangle\langle \mathbf{x}''|\hat{\rho}_\epsilon|\mathbf{x}'\rangle,$$

$$\langle \mathbf{x}|\hat{\rho}_\epsilon|\mathbf{x}'\rangle = \left(\frac{m}{2\pi\epsilon}\right)^{1/2} e^{-\frac{\epsilon}{2}[V_0(\mathbf{x})+V_0(\mathbf{x}')]} e^{-\frac{m}{2\epsilon}(\mathbf{x}-\mathbf{x}')^2},$$

$$\hat{\mathbf{1}} = \int d\mathbf{x}_j|\mathbf{x}_j\rangle\langle \mathbf{x}_j|,$$

yielding

$$\langle \mathbf{x}|e^{-(\beta-\epsilon)\hat{H}_0}|\mathbf{x}''\rangle = \int d\mathbf{x}_{n-1}\dots\int d\mathbf{x}_1 \langle \mathbf{x}\,|\,e^{-i\hat{H}_0\tau}\,|\,\mathbf{x}_{n-1}\rangle \times \dots \langle \mathbf{x}_1\,|\,e^{-i\hat{H}_0\tau}\,|\mathbf{x}''\rangle,$$

where $\tau \equiv -i(\beta-\epsilon)/n$.

Chen, X., Wu,Y.; Batista, V.S. *J. Chem. Phys.* **122**, 64102 (2005)

- Step [1]: Decompose $\langle \mathbf{x}|\tilde{\rho}_\epsilon|\mathbf{x}'\rangle \equiv e^{-iV_0(\mathbf{x})\tau/2}\langle \mathbf{x}|\rho_\epsilon|\mathbf{x}'\rangle$ in a matching-pursuit coherent-state expansion:

$$\langle \mathbf{x}|\tilde{\rho}_\epsilon|\mathbf{x}'\rangle \approx \sum_{j=1}^{n} c_j \langle \mathbf{x}|\phi_j\rangle\langle \phi'_j|\mathbf{x}'\rangle,$$

where

$$c_j \equiv \begin{cases} \langle \phi_1|\overline{\rho}_\epsilon|\phi'_1\rangle, & \text{when } j=1, \\ \phi_j|\overline{\rho}_\epsilon|\phi'_j\rangle - \sum_{k=1}^{j-1} c_k \langle \phi_j|\phi_k\rangle\langle \phi'_k|\phi'_j\rangle, & \text{otherwise.} \end{cases}$$

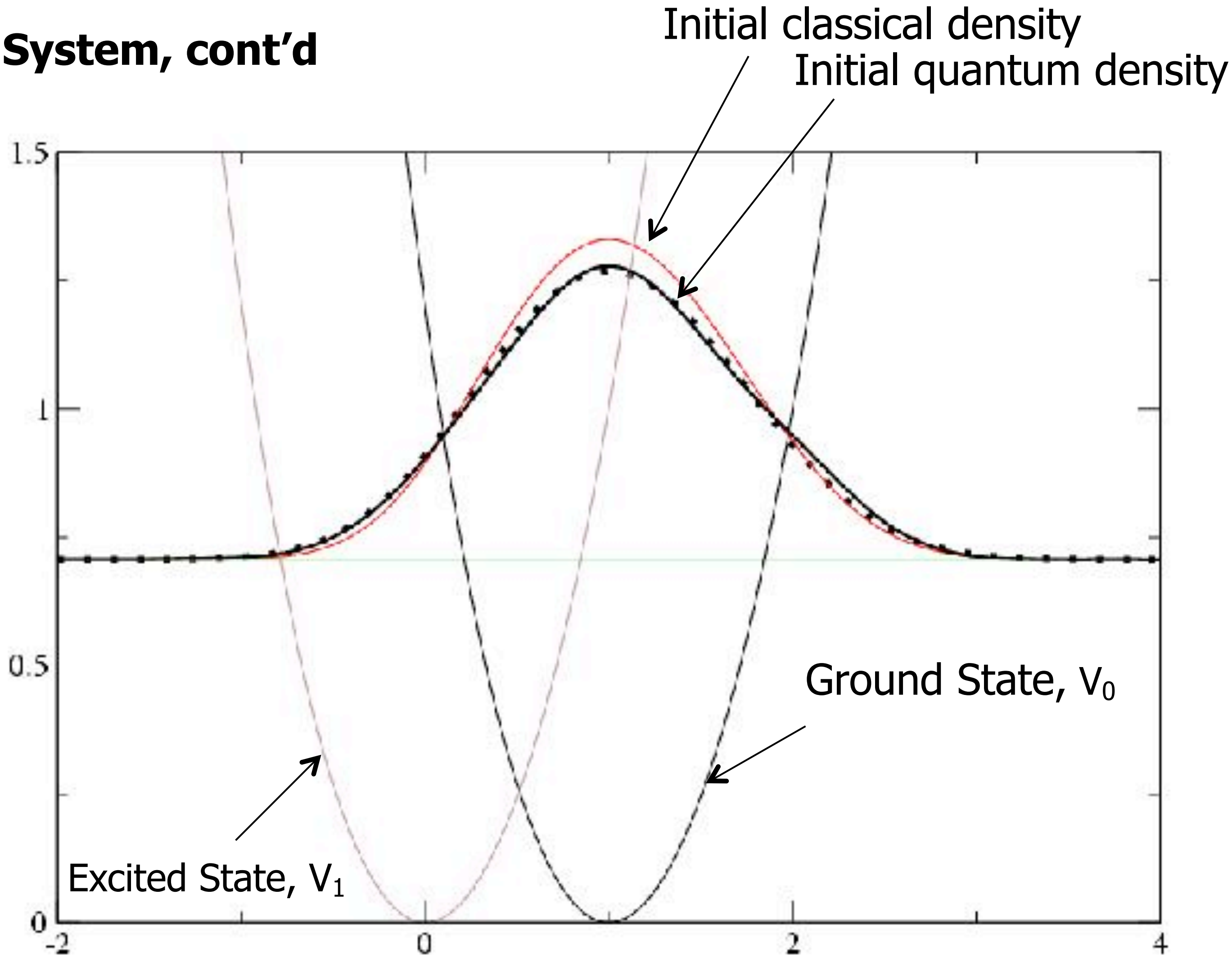
Here $\langle \mathbf{x}|\phi_j\rangle$ are N-dimensional coherent-states,

$$\langle \mathbf{x}|\phi_j\rangle \equiv \prod_{k=1}^{N} A_{\phi_j}(k) e^{-\gamma_{\phi_j}(k)\left(x(k)-x_{\phi_j}(k)\right)^2/2} \times e^{i p_{\phi_j}(k)\left(x(k)-x_{\phi_j}(k)\right)},$$

with complex-valued coordinates $x_{\phi_j}(k) \equiv r_{\phi_j}(k)+id_{\phi_j}(k)$, momenta $p_{\phi_j}(k) \equiv g_{\phi_j}(k) + if_{\phi_j}(k)$ and scaling parameters $\gamma_{\phi_j}(k) \equiv a_{\phi_j}(k) + ib_{\phi_j}(k)$. The normalization constants are $A_{\phi_j}(k) \equiv (a_{\phi_j}(k)/\pi)^{1/4}\exp[-\frac{1}{2}a_{\phi_j}(k)d_{\phi_j}(k)^2 - d_{\phi_j}(k)g_{\phi_j}(k) - \left(b_{\phi_j}(k)d_{\phi_j}(k) + f_{\phi_j}(k)\right)^2/(2a_{\phi_j}(k))]$.

Chen, X., Wu,Y.; Batista, V.S. *J. Chem. Phys.* **122**, 64102 (2005)

**Model System, cont'd**



Chen, X., Wu,Y.; Batista, V.S. *J. Chem. Phys.* **122**, 64102 (2005)

# Calculations of Thermal Correlation Functions

**Position-Position Correlation Function:**

$$C(t) = Z^{-1} \int d\mathbf{x} \int d\mathbf{x}' \int d\mathbf{x}'' \langle \mathbf{x}| e^{-\frac{\beta}{2}\hat{H}_0} |\mathbf{x}'\rangle A(\mathbf{x}') \, \langle \mathbf{x}'| e^{i\hat{H}_1 t} \hat{B} e^{-i\hat{H}_1 t} |\mathbf{x}''\rangle \, \langle \mathbf{x}''| e^{-\frac{\beta}{2}\hat{H}_0} |\mathbf{x}\rangle,$$

$A(\mathbf{x}') = \mathbf{x}'$ and $\hat{B} = \hat{x}$.

**Time-Dependent Position Ensemble Average**

$A(\mathbf{x}') = 1$ and $B = \hat{x}$

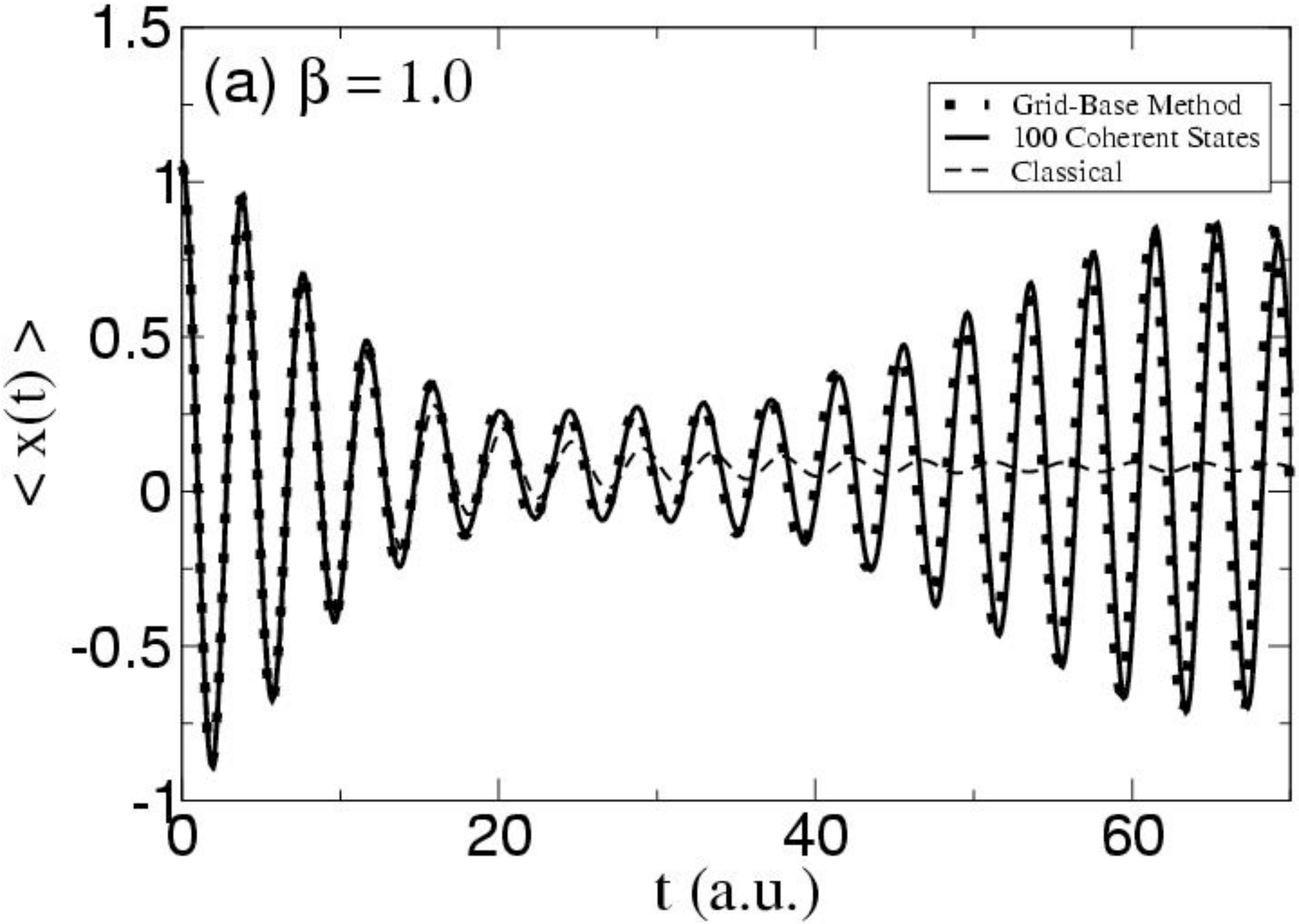
**Model System:**

$$V_0(x) = \frac{1}{2} m\omega^2 (x-a)^2 - c(x-a)^3 + c(x-a)^4,$$

$$V_1(x) = \frac{1}{2} m\omega^2 x^2 - cx^3 + cx^4,$$

Chen, X., Wu,Y.; Batista, V.S. *J. Chem. Phys.* **122**, 64102 (2005)

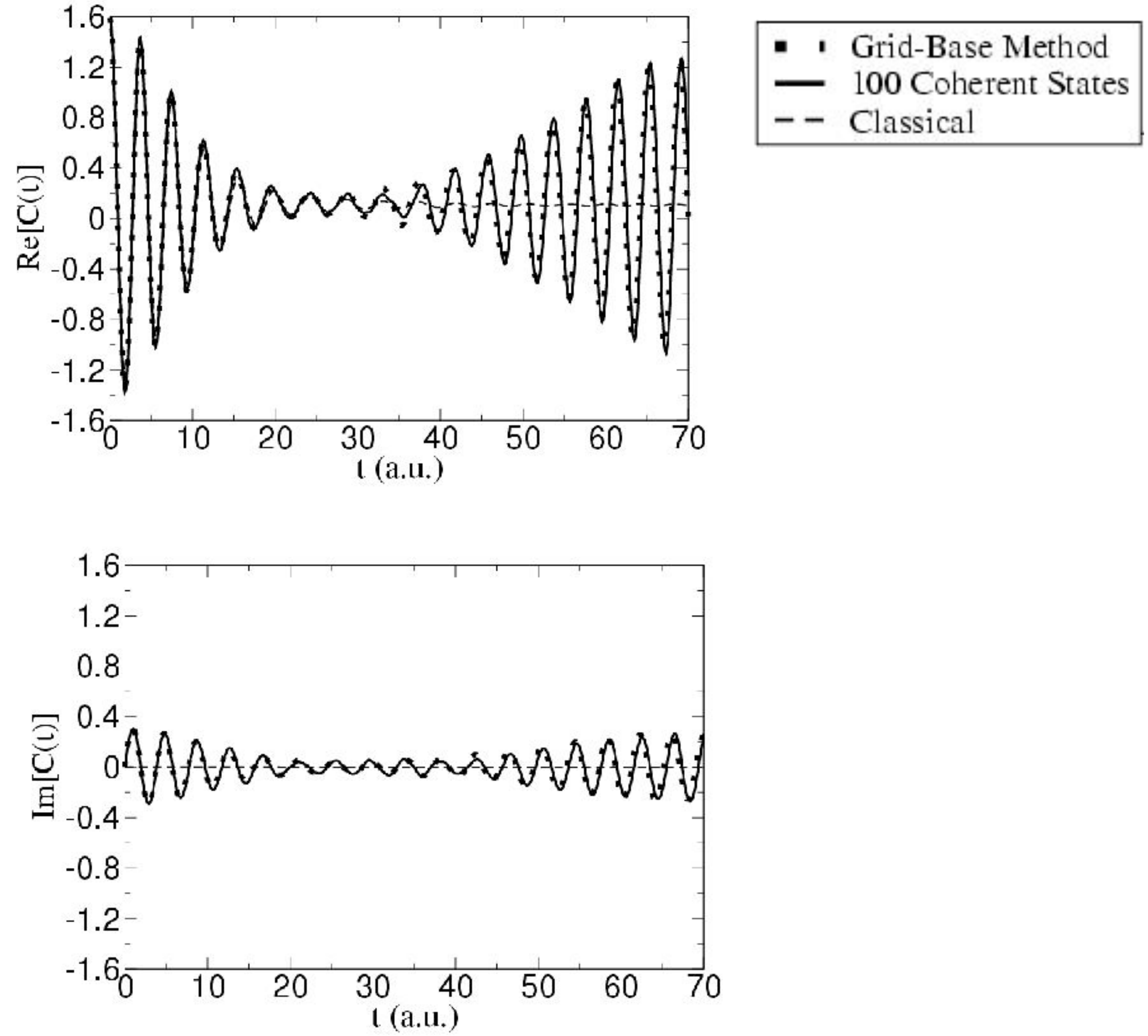
**Time-Dependent Position Ensemble Average**



Chen, X., Wu,Y.; Batista, V.S. *J. Chem. Phys.* **122**, 64102 (2005)

## Position-Position Correlation Function

(a) $\beta = 1.0$



Chen, X., Wu,Y.; Batista, V.S. *J. Chem. Phys.* (2005) **122**, 64102

Chen, X.; Batista, V.S. *J. Chem. Phys.* (2006) **125**, 124313

# Nonadiabatic Propagation

$$\hat{H} = \hat{H}_0 + \hat{V}_c,$$

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} + \sum_{k=1}^{n} V_k(\mathbf{x})|k\rangle\langle k|,$$

$$\hat{V}_c = \sum_{k=1}^{n}\sum_{j\neq k}^{n} V_c(\mathbf{x})|j\rangle\langle k|,$$

$$e^{-i\hat{H}2\tau} \approx e^{-i\hat{H}_0(\hat{\mathbf{x}})\tau} e^{-i\hat{V}_c 2\tau} e^{-i\hat{H}_0(\hat{\mathbf{x}})\tau}.$$

# MP/SOFT Nonadiabatic Propagation

- Step [I]. Propagate the wave-packets $\varphi_1(\mathbf{x};t)$ and $\varphi_2(\mathbf{x};t)$ adiabatically for time $\tau$,

$$\begin{pmatrix} \varphi_1'(\mathbf{x};t+\tau) \\ \varphi_2'(\mathbf{x};t+\tau) \end{pmatrix} = \begin{pmatrix} e^{-i[\frac{\hat{\mathbf{p}}^2}{2m}+V_1(\hat{\mathbf{x}})]\tau} & 0 \\ 0 & e^{-i[\frac{\hat{\mathbf{p}}^2}{2m}+V_2(\hat{\mathbf{x}})]\tau} \end{pmatrix} \begin{pmatrix} \varphi_1(\mathbf{x};t) \\ \varphi_2(\mathbf{x};t) \end{pmatrix} \tag{1}$$

- Step [II]. Mix the two wave-packet components $\varphi_1'(\mathbf{x};t+\tau)$ and $\varphi_2'(\mathbf{x};t+\tau)$,

$$\begin{pmatrix} \varphi_1''(\mathbf{x};t+\tau) \\ \varphi_2''(\mathbf{x};t+\tau) \end{pmatrix} = \begin{pmatrix} cos(2V_c(\hat{\mathbf{x}})\tau) & -sin(2V_c(\hat{\mathbf{x}})\tau) \\ -sin(2V_c(\hat{\mathbf{x}})\tau) & cos(2V_c(\hat{\mathbf{x}})\tau) \end{pmatrix} \begin{pmatrix} \varphi_1'(\mathbf{x};t+\tau) \\ \varphi_2'(\mathbf{x};t+\tau) \end{pmatrix} \tag{2}$$

- Step [III]. Propagate the mixed wave-packet components $\varphi_1''(\mathbf{x};t+\tau)$ and $\varphi_2''(\mathbf{x};t+\tau)$ adiabatically for time $\tau$,

$$\begin{pmatrix} \varphi_1(\mathbf{x};t+2\tau) \\ \varphi_2(\mathbf{x};t+2\tau) \end{pmatrix} = \begin{pmatrix} e^{-i[\frac{\hat{\mathbf{p}}^2}{2m}+V_1(\hat{\mathbf{x}})]\tau} & 0 \\ 0 & e^{-i[\frac{\hat{\mathbf{p}}^2}{2m}+V_2(\hat{\mathbf{x}})]\tau} \end{pmatrix} \begin{pmatrix} \varphi_1''(\mathbf{x};t+\tau) \\ \varphi_2''(\mathbf{x};t+\tau) \end{pmatrix} \tag{3}$$

Step [III] is, however, combined with step [I] of the next propagation time sliced for all but the last propagation time increment.

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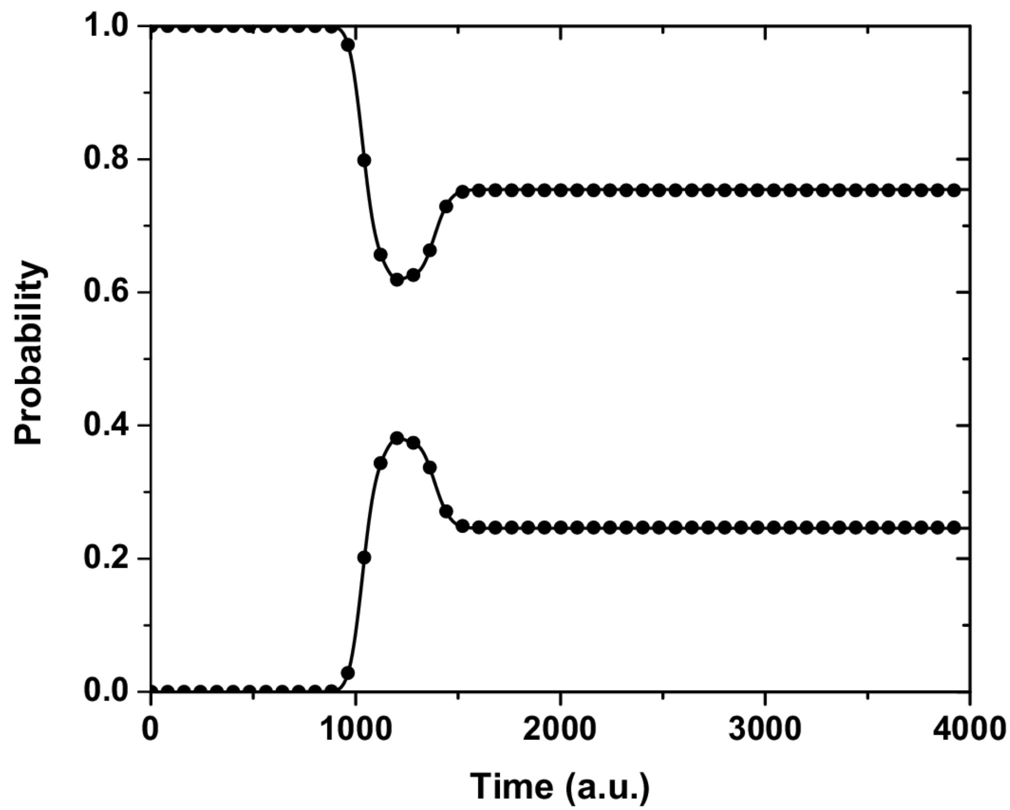
# Embedded Strang Splitting Expansion

$$e^{-i\hat{H}\tau} \approx \overbrace{e^{-i\frac{\hat{p}^2}{2m}\tau/2} e^{-iV(\hat{\mathbf{x}})\tau} e^{-i\frac{\hat{p}^2}{2m}\tau/2}} \approx \overbrace{e^{-i\frac{\hat{p}^2}{2m}\tau/2} \underbrace{e^{-iV_0(\hat{\mathbf{x}})\tau/2} e^{-iV_c(\hat{\mathbf{x}})\tau} e^{-iV_0(\hat{\mathbf{x}})\tau/2}} e^{-i\frac{\hat{p}^2}{2m}\tau/2}}$$

$$\begin{pmatrix} \varphi_1(\mathbf{x}; t+\tau) \\ \varphi_2(\mathbf{x}; t+\tau) \end{pmatrix} \approx \begin{pmatrix} \cos(V_c(\hat{\mathbf{x}})\tau) e^{-i\hat{H}_{11}\tau} & -i\sin(V_c(\hat{\mathbf{x}})\tau)\, e^{-i\frac{\hat{H}_{11}+\hat{H}_{22}}{2}\tau} \\ -i\sin(V_c(\hat{\mathbf{x}})\tau)\, e^{-i\frac{\hat{H}_{11}+\hat{H}_{22}}{2}\tau} & \cos(V_c(\hat{\mathbf{x}})\tau)\, e^{-i\hat{H}_{22}\tau} \end{pmatrix} \begin{pmatrix} \varphi_1(\mathbf{x}; t) \\ \varphi_2(\mathbf{x}; t) \end{pmatrix}$$

Wu,Y.; Herman, M.F.; Batista, V.S. *J. Chem. Phys.* **122**, 114114 (2005)

# Single Avoided Crossing
## Time-Dependent Populations



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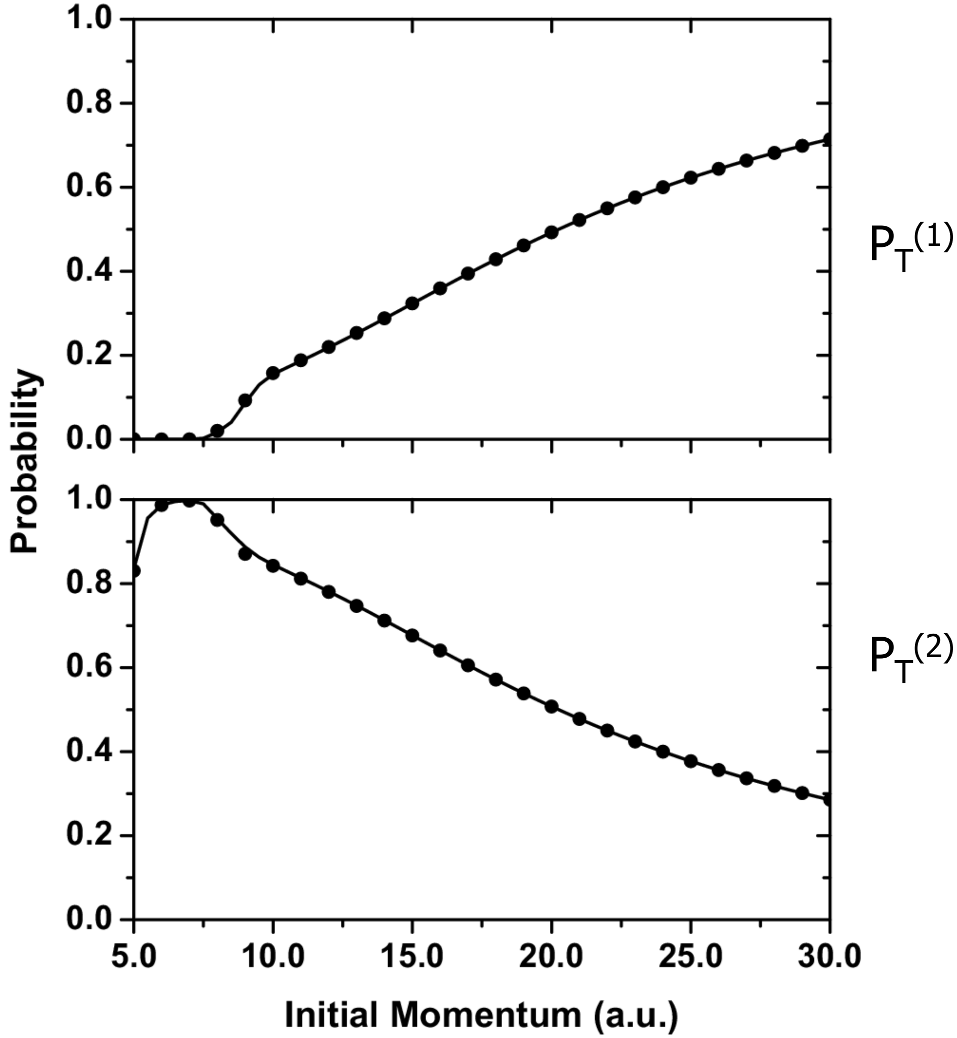
# Single Avoided Crossing

## Transmission Probabilities



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# Dual Avoided Crossings with quantum interferences between the crossings

## Stuckelberg oscillations in Transmission Probabilities

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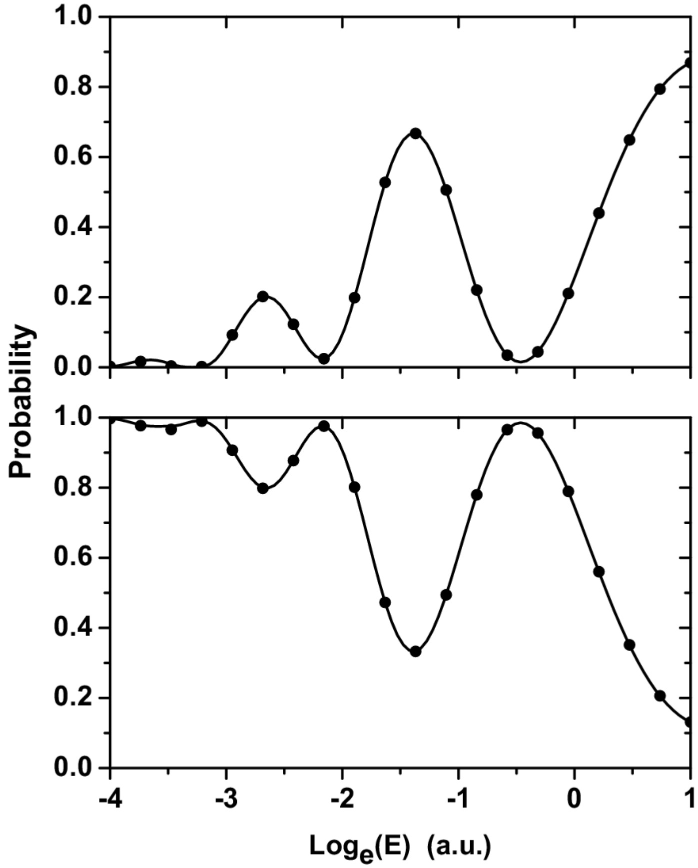



$P_T^{(1)}$

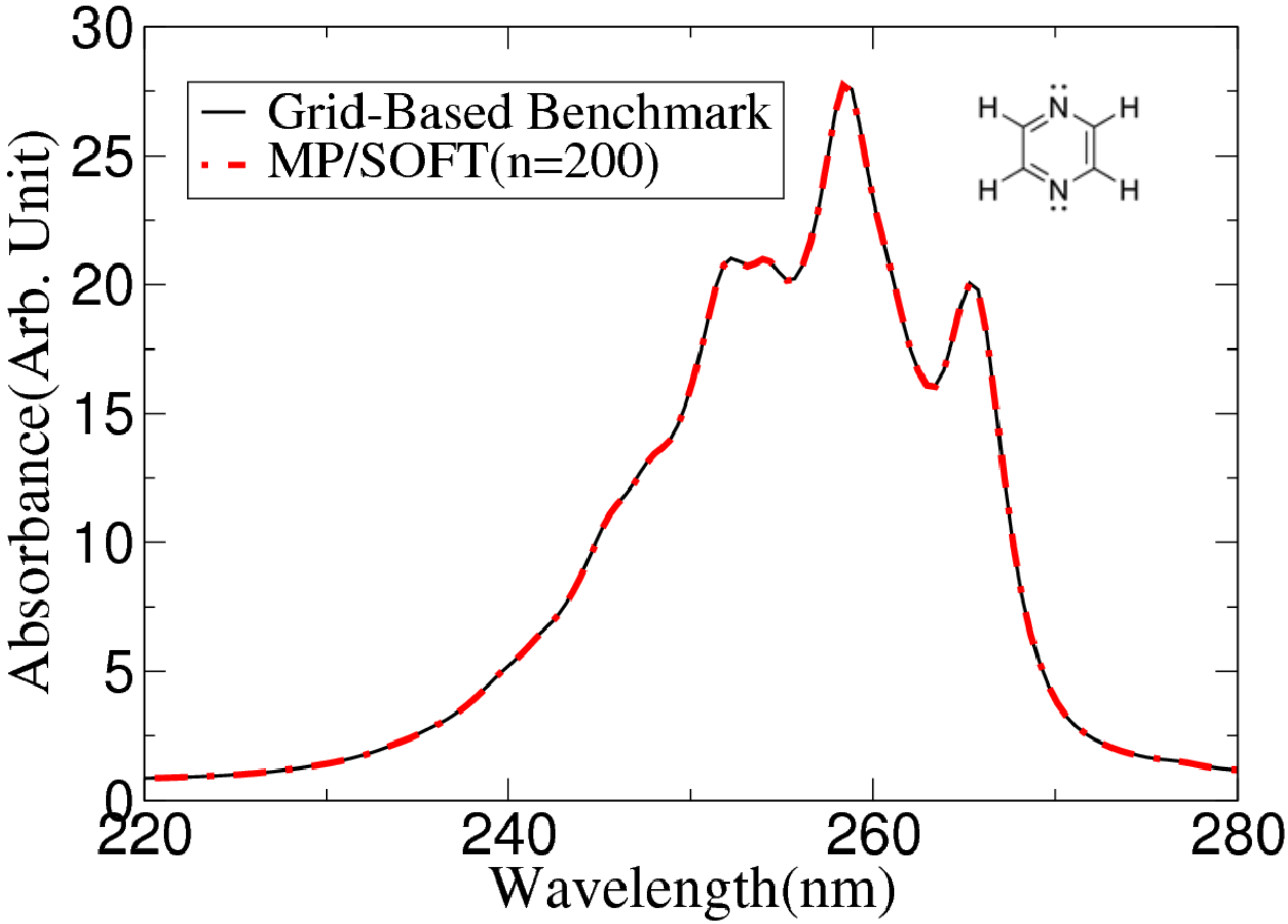
$P_T^{(2)}$

Chen,X.; Batista, V.S. *J. Chem. Phys.* (2006) **125**, 124313

# Nonadiabatic Dynamics of Pyrazine

## $S_1/S_2$ Conical Intersection

Benchmark Calcs.: 4-mode model

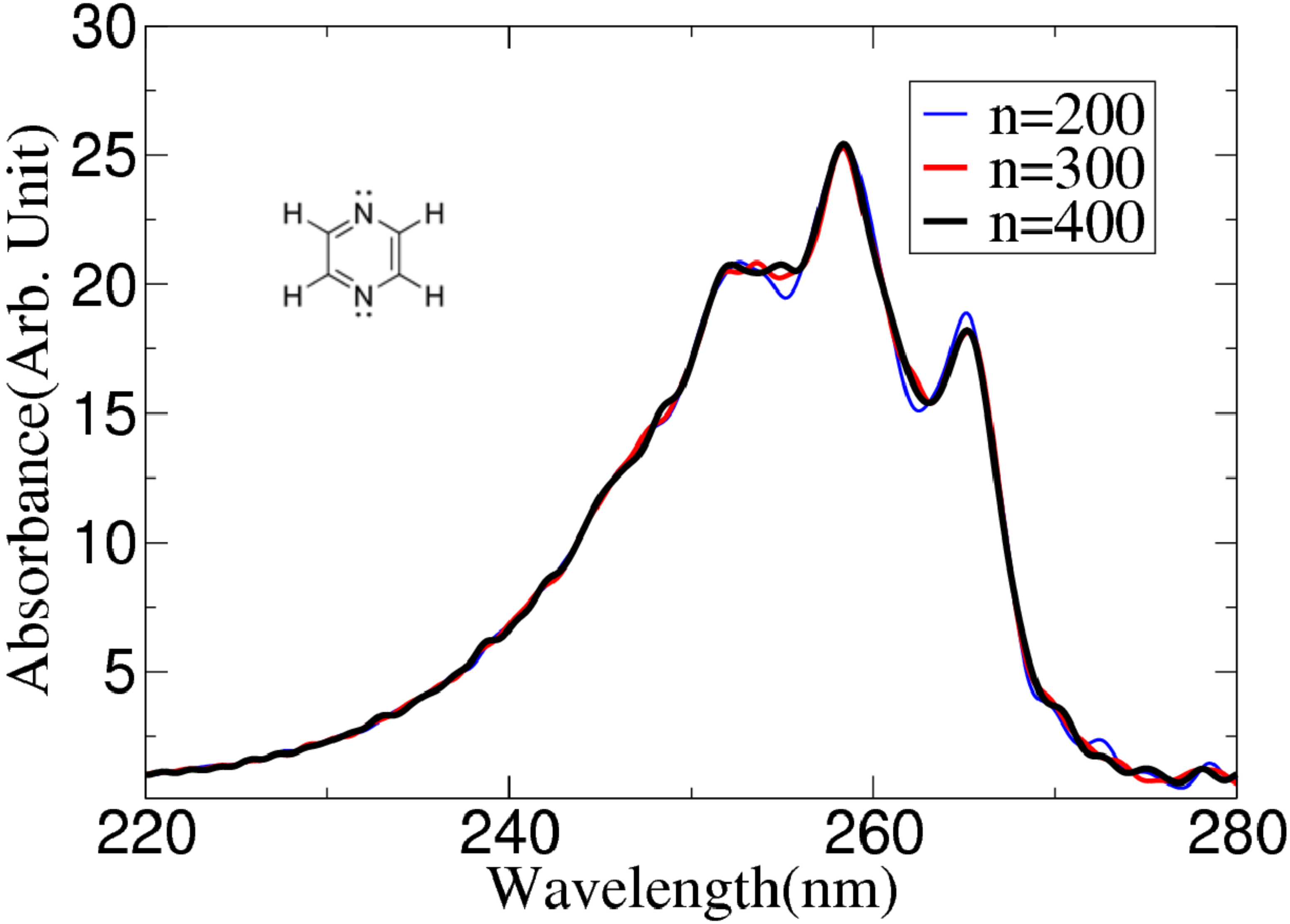


Chen,X.; Batista, V.S. *J. Chem. Phys.* (2006) **125**, 124313

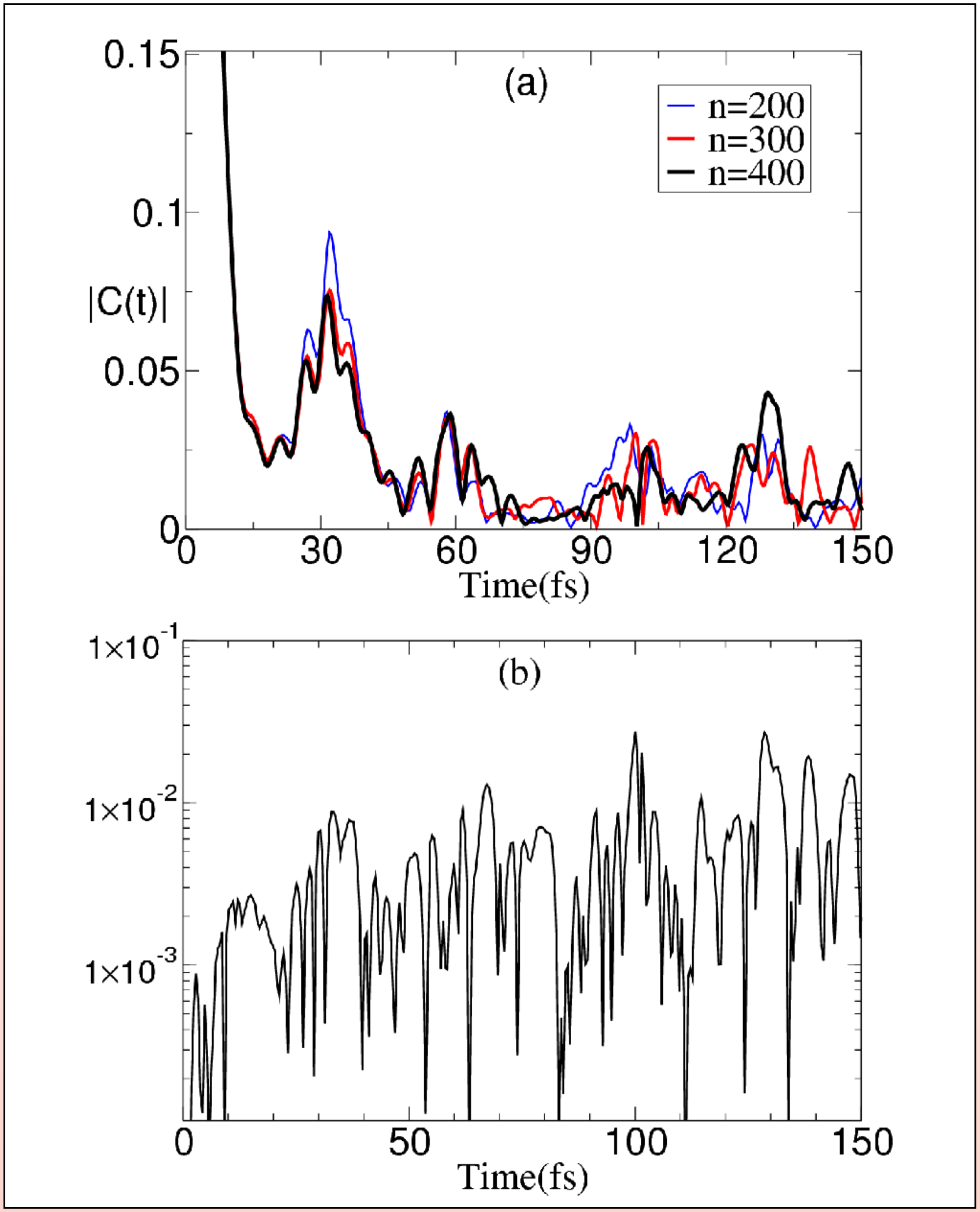
# Nonadiabatic Dynamics of Pyrazine

## $S_1/S_2$ Conical Intersection

### Benchmark Calcs.: 24-mode model



Benchmark Calcs.:
24-mode model



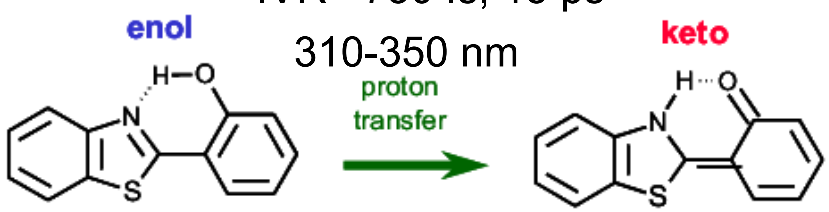
E. T. J. Nibbering, H. Fidder and E. Pines *Annu. Rev. Phys. Chem.* (2005) **56**:337-67

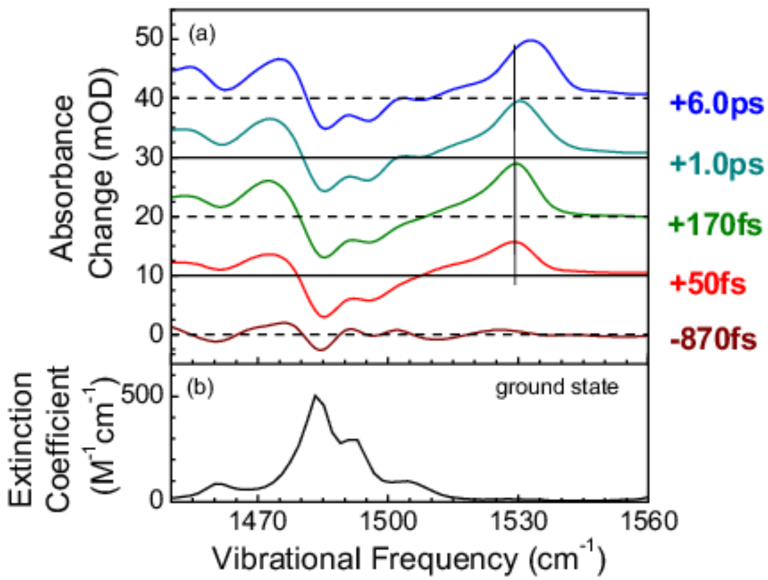
## Ultrafast Excited State Intramolecular Proton Transfer in HBT

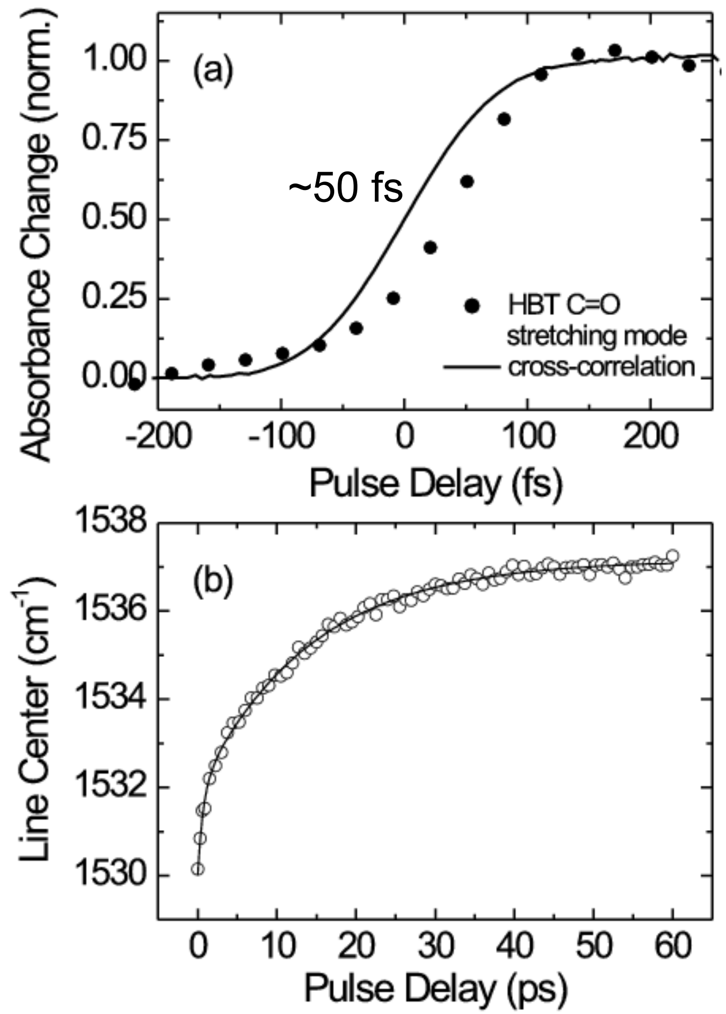
*Transient appearance of the C=O stretching mode of the keto*-state of HBT after excitation of the enol → enol* transition.*

IVR~ 750 fs, 15 ps

310-350 nm

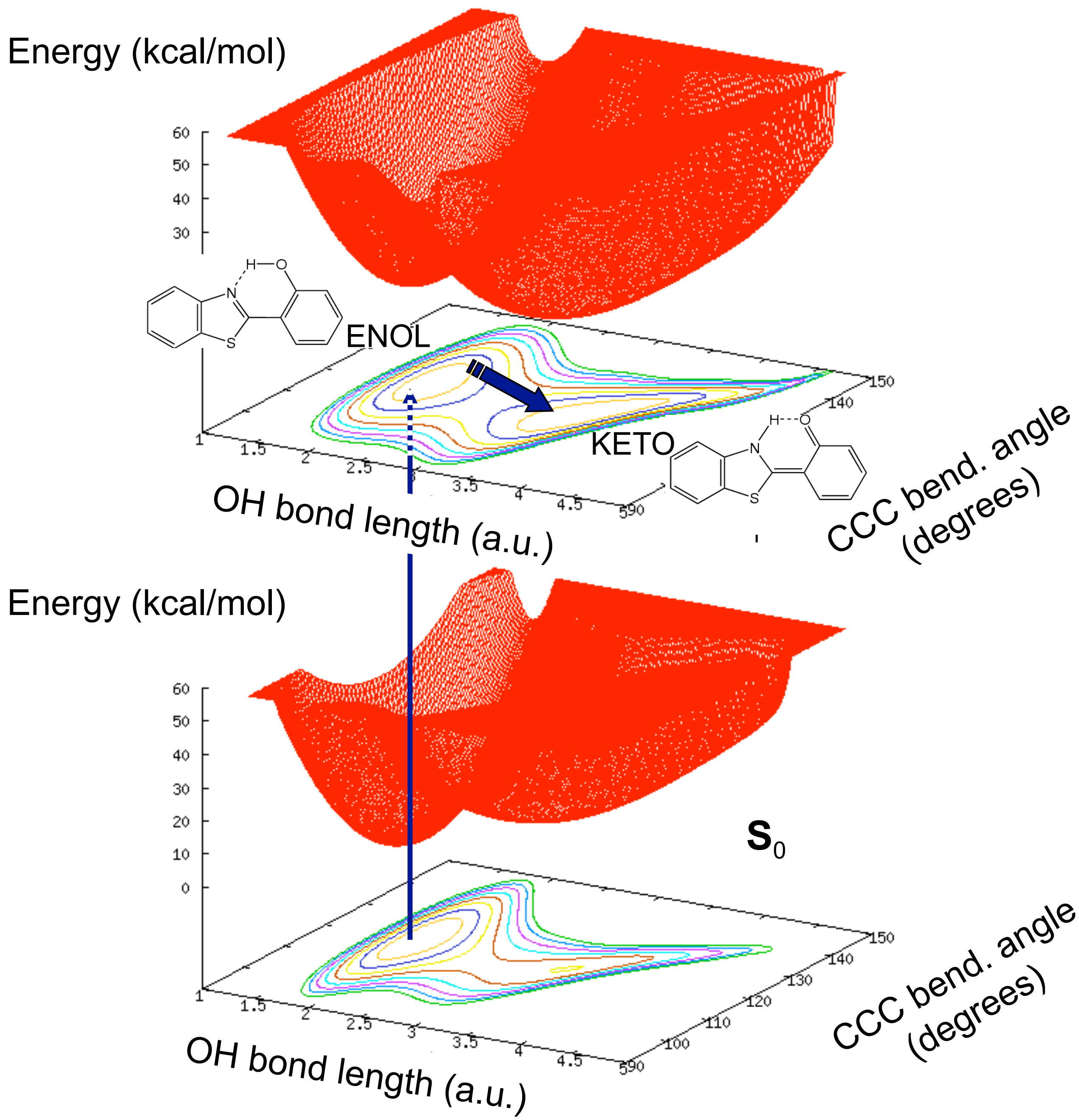


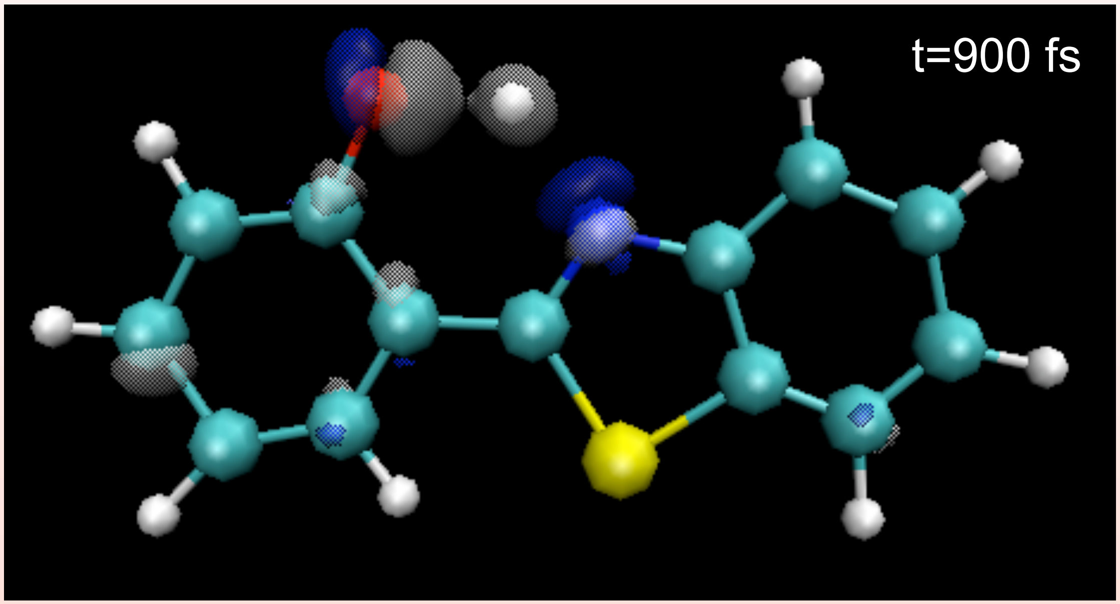

Kim, J.; Wu, Y.; Batista, V.S. *Israel J. Chem.* (2009) **49**, 187

# Reaction Surface $V_0(r_1,r_2)$

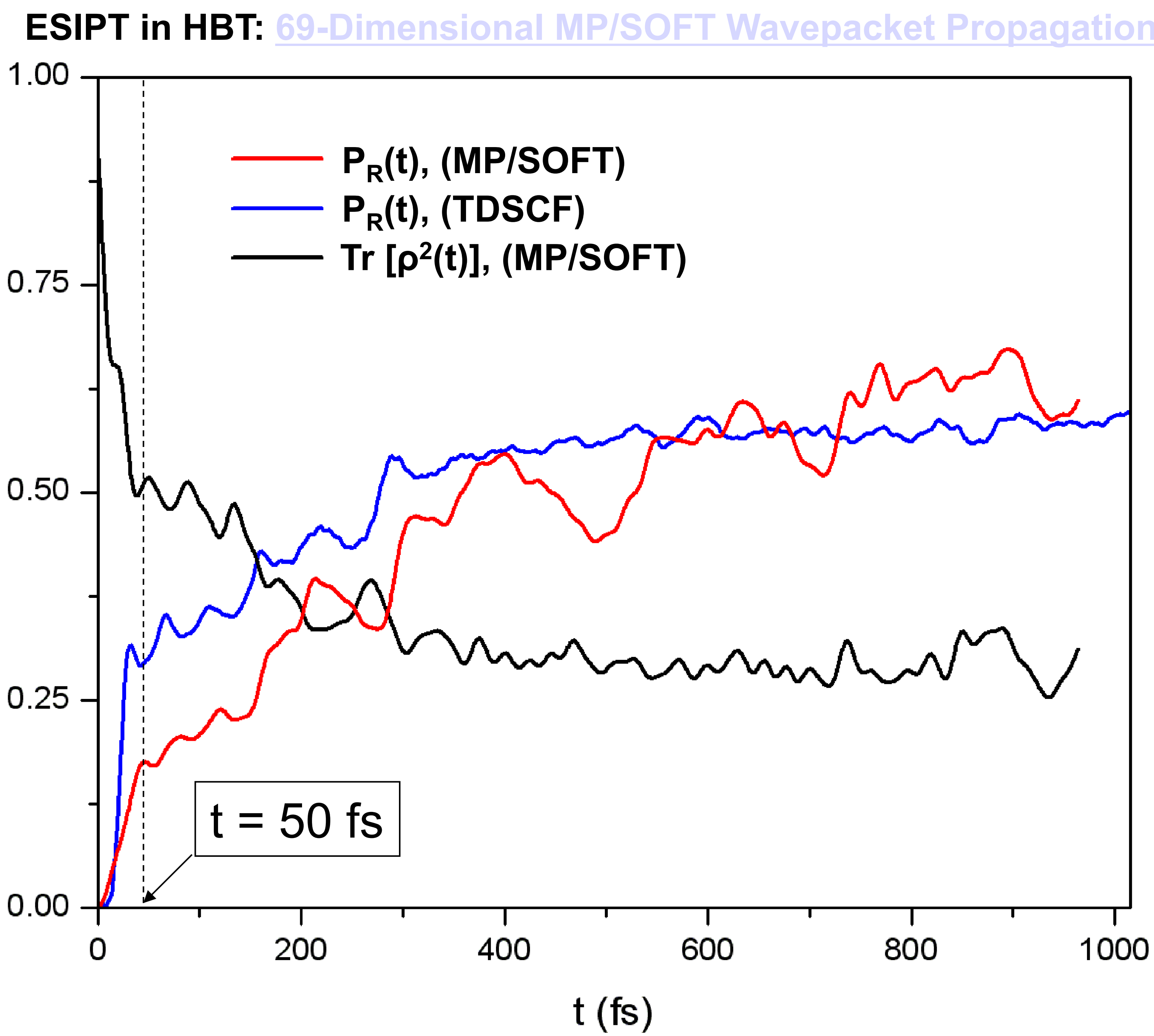


## ESIPT or ESIHT ?

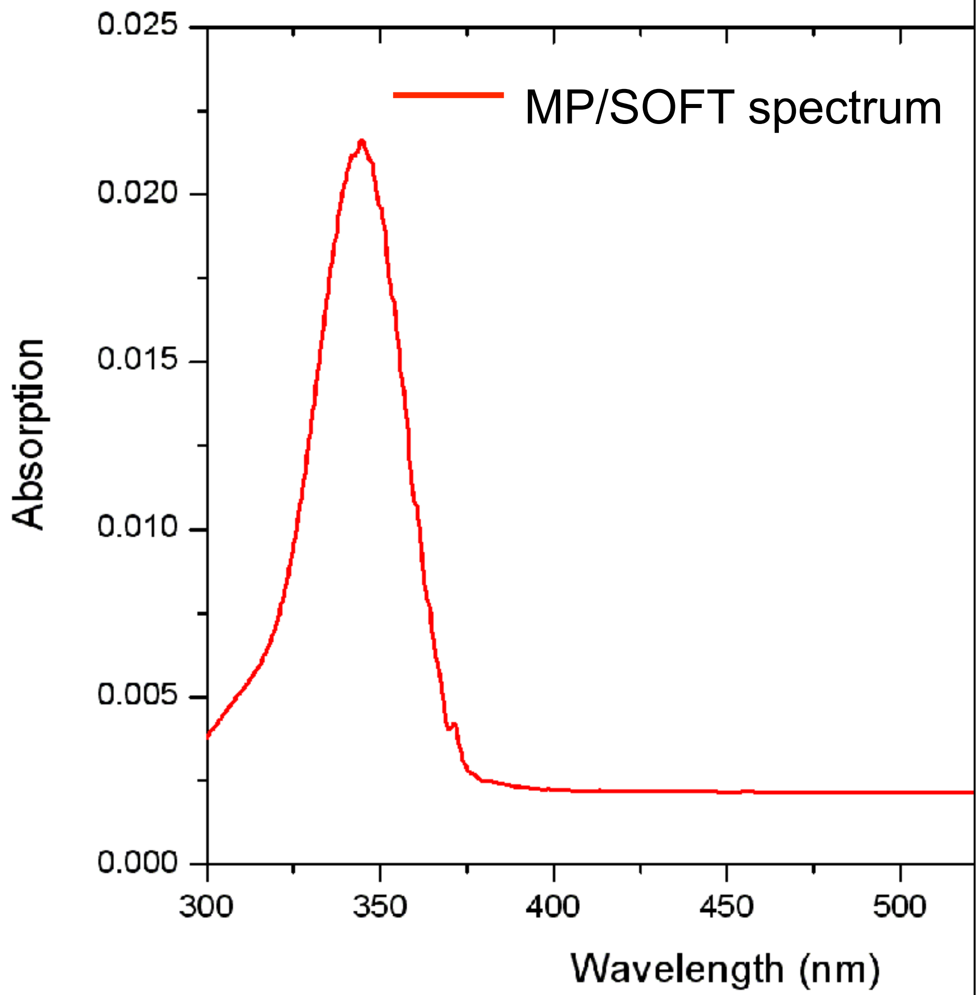
## Ultrafast Charge Redistribution in HBT

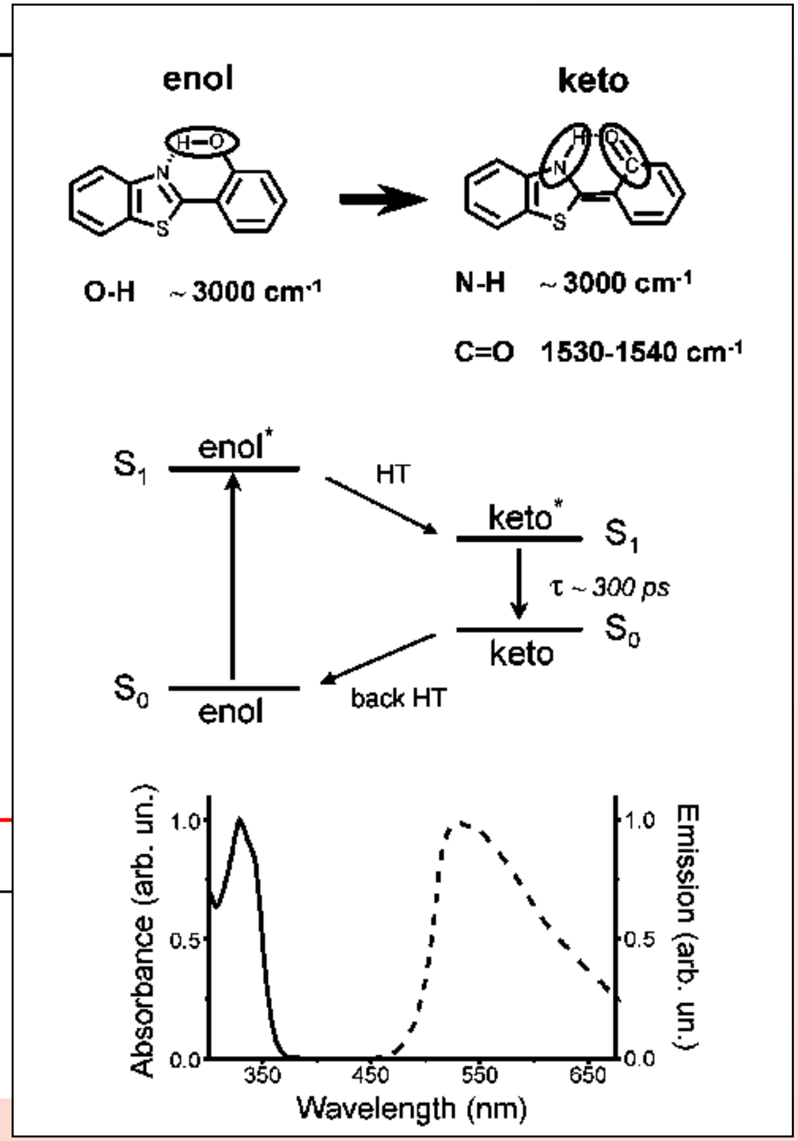



Kim, J.; Wu, Y.; Batista, V.S. *Israel J. Chem.* (2009) **49**, 187


ESIPT in HBT: 69-Dimensional MP/SOFT Wavepacket Propagation
$P_R(t)$, (MP/SOFT)
$P_R(t)$, (TDSCF)
Tr $[\rho^2(t)]$, (MP/SOFT)
t = 50 fs
1.00
0.75
0.50
0.25
0.00
0
200
400
600
800
1000
t (fs)

# UV-Vis Photoabsorption Spectrum of HBT



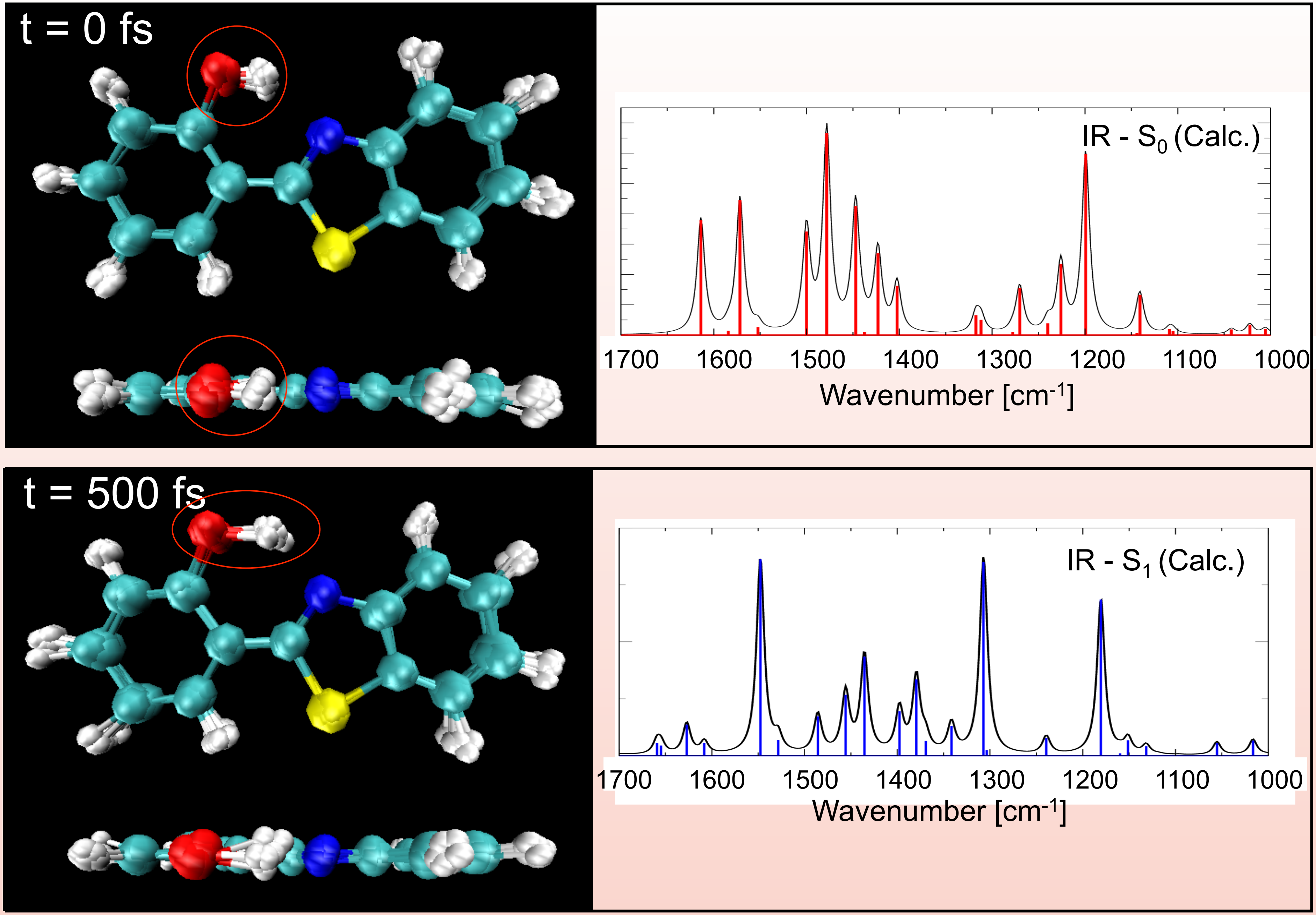




**Experiments:**

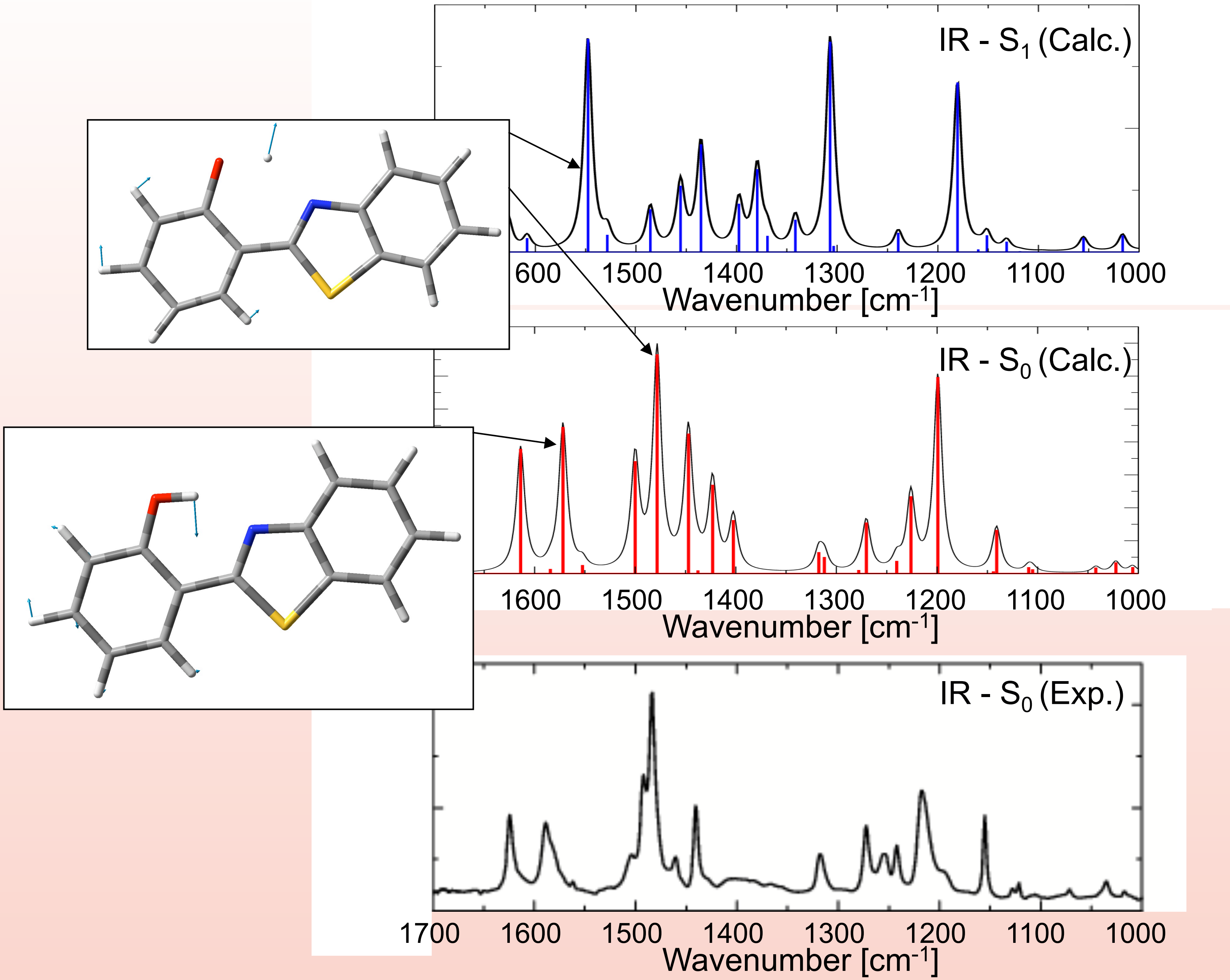
Rini M,KummrowA, Dreyer J, Nibbering ETJ, Elsaesser T. 2003. *Faraday Discuss*. **122**:27–40

Rini M, Dreyer J, Nibbering ETJ, Elsaesser T. 2003. *Chem. Phys. Lett*. **374**:13–19

## Ultrafast Excited State Intramolecular Proton Transfer in HBT

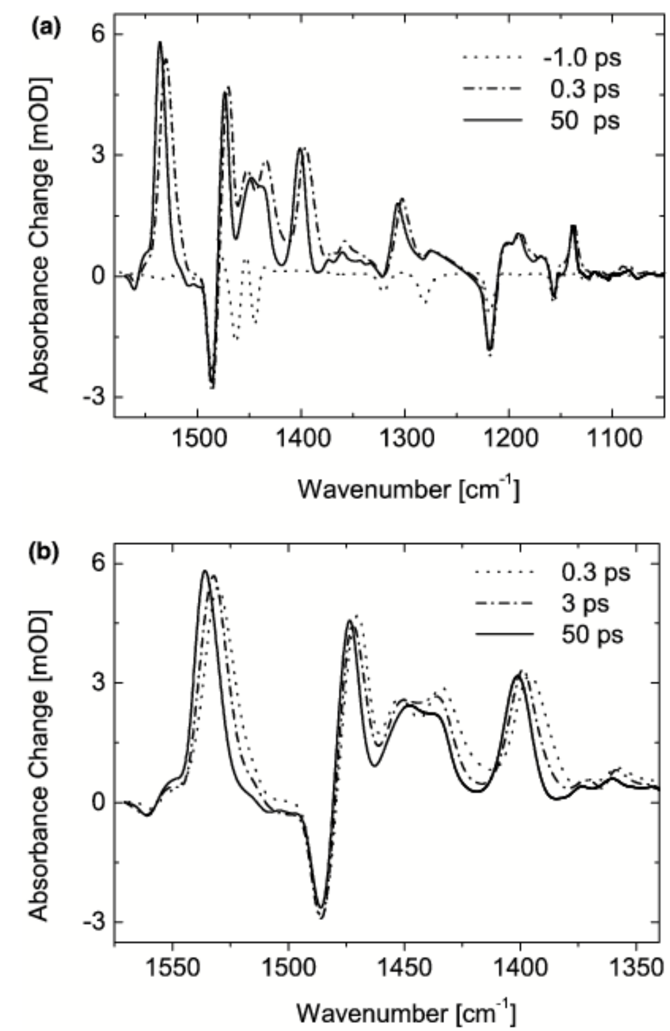


# Infrared spectra of HBT

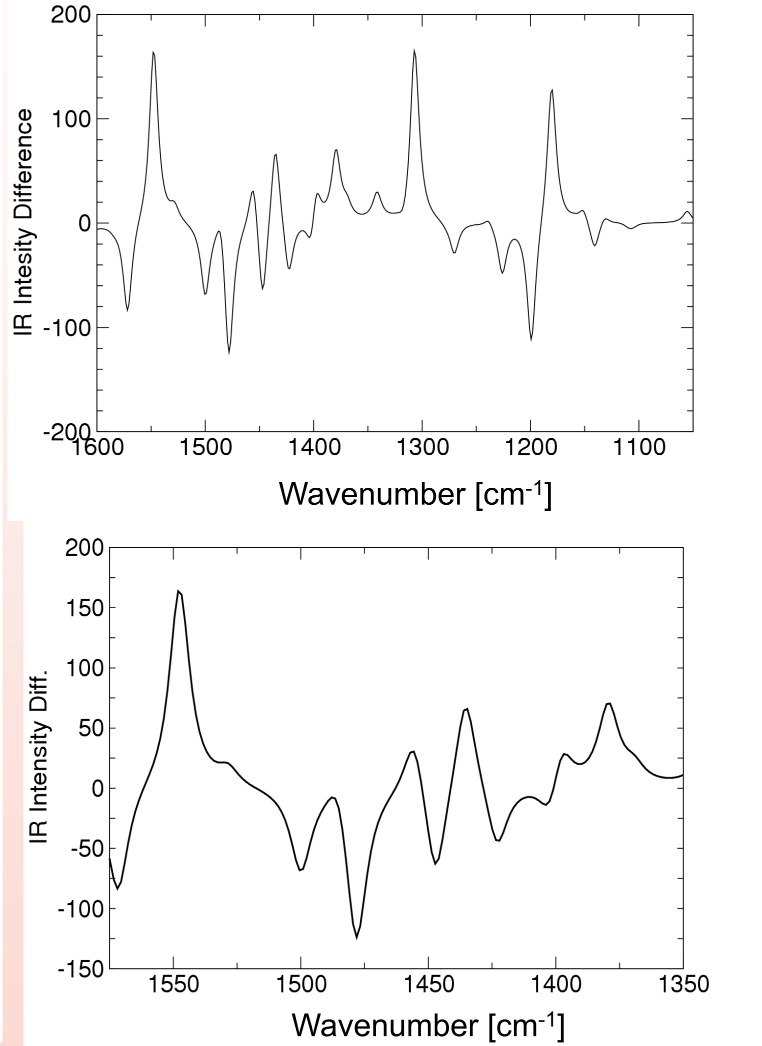


# Transient infrared spectra of HBT

Experimental




Theoretical




**Experiments:**

Rini M,KummrowA, Dreyer J, Nibbering ETJ, Elsaesser T. 2003. *Faraday Discuss*. **122**:27–40

Rini M, Dreyer J, Nibbering ETJ, Elsaesser T. 2003. *Chem. Phys. Lett*. **374**:13–19

# Conclusions

- We have introduced the MP/SOFT method for time-sliced simulations of quantum processes in systems with many degrees of freedom. The MP/SOFT method generalizes the grid-based SOFT approach to non-orthogonal and dynamically adaptive coherent-state representations generated according to the matching-pursuit algorithm.
- The accuracy and efficiency of the resulting method were demonstrated in simulations of excited-state intramolecular proton transfer in 2-(2'-hydroxyphenyl)-oxazole (HPO), as modeled by an *ab initio* 35-dimensional reaction surface Hamiltonian, as well as in benchmark simulations of nonadiabatic quantum dynamics in pyrazine.
- Further, we have extended the MP/SOFT method for computations of thermal equilibrium density matrices (equilibrium properties of quantum systems), finite temperature time-dependent expectation values and time-correlation functions. The extension involves solving the Bloch equation via imaginary-time propagation of the density matrix in dynamically adaptive coherent-state representations, and the evaluation of the Heisenberg time-evolution operators through real-time propagation.

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