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Matching-Pursuit Representations for Simulations of Quantum Processes

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OZONE-WATER CLUSTERS: NBO ANALYSIS OF STEREOELECTRONIC INTERACTIONS **(PHYS 391)**

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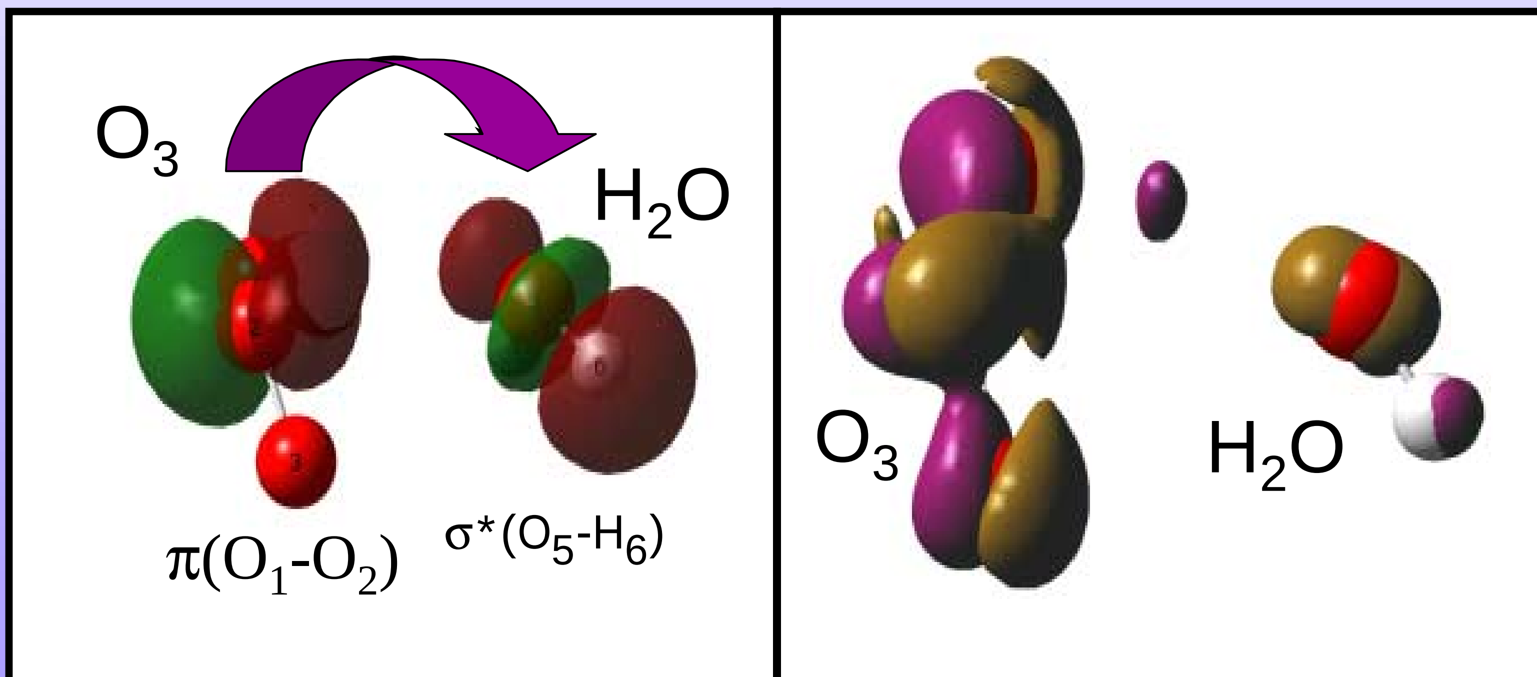

QM/MM Studies of Protein Polarization due to Proton Transfer in GFP (COMP 197)

Jose A. Gascon, Siegfried Leung, and Victor S. Batista

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Influence of Bound Water Molecules in hydroxylation and epoxydation reactions in cytochrome P450cam wild type and T252A mutant (PHYS 465)

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Coherent-Control of Excited State Intramolecular Proton Transfer in 2-(2'-hydroxyphenyl)-oxazole

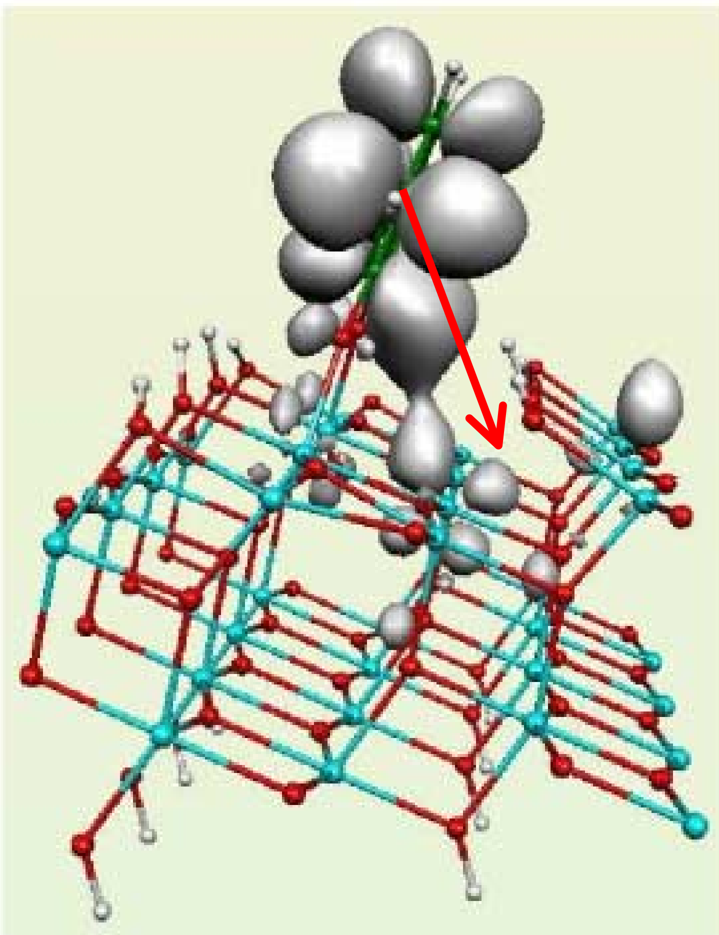
Victor S. Batista and Paul Brumer *Phys. Rev. Lett.* **89**,5889 (2003);
ibid. **89**,28089 (2003)

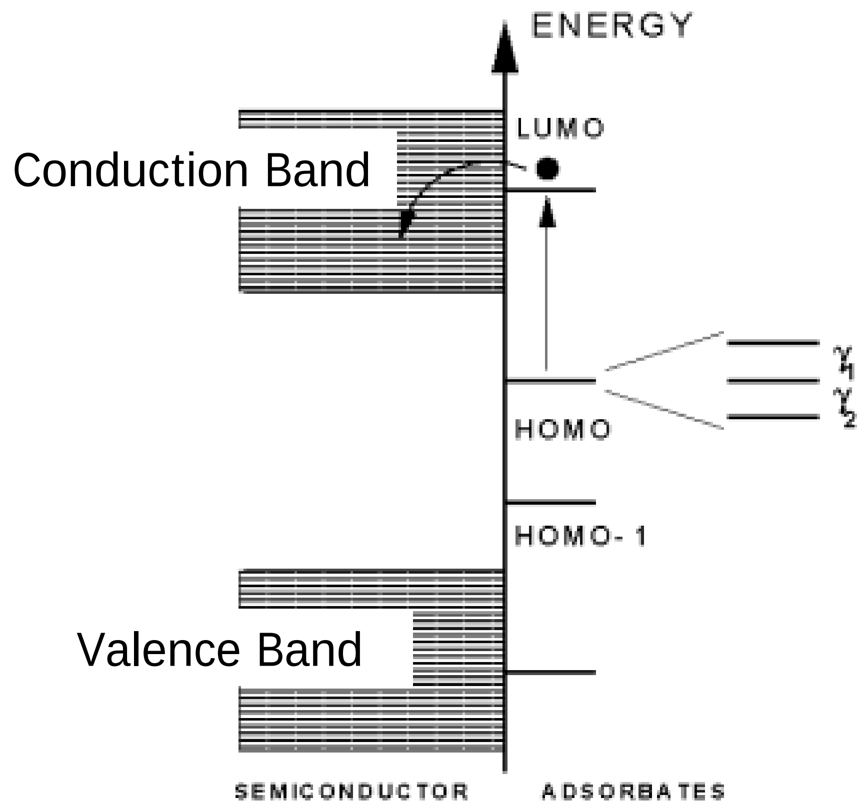
Model Study of Coherent-Control of Rhodopsin Photo-isomerization: The Primary Step in Vision

Samuel Flores and Victor S. Batista *Phys. Chem. B* (in press) (2004)

Interfacial Electron Transfer in Functionalized Semiconductors

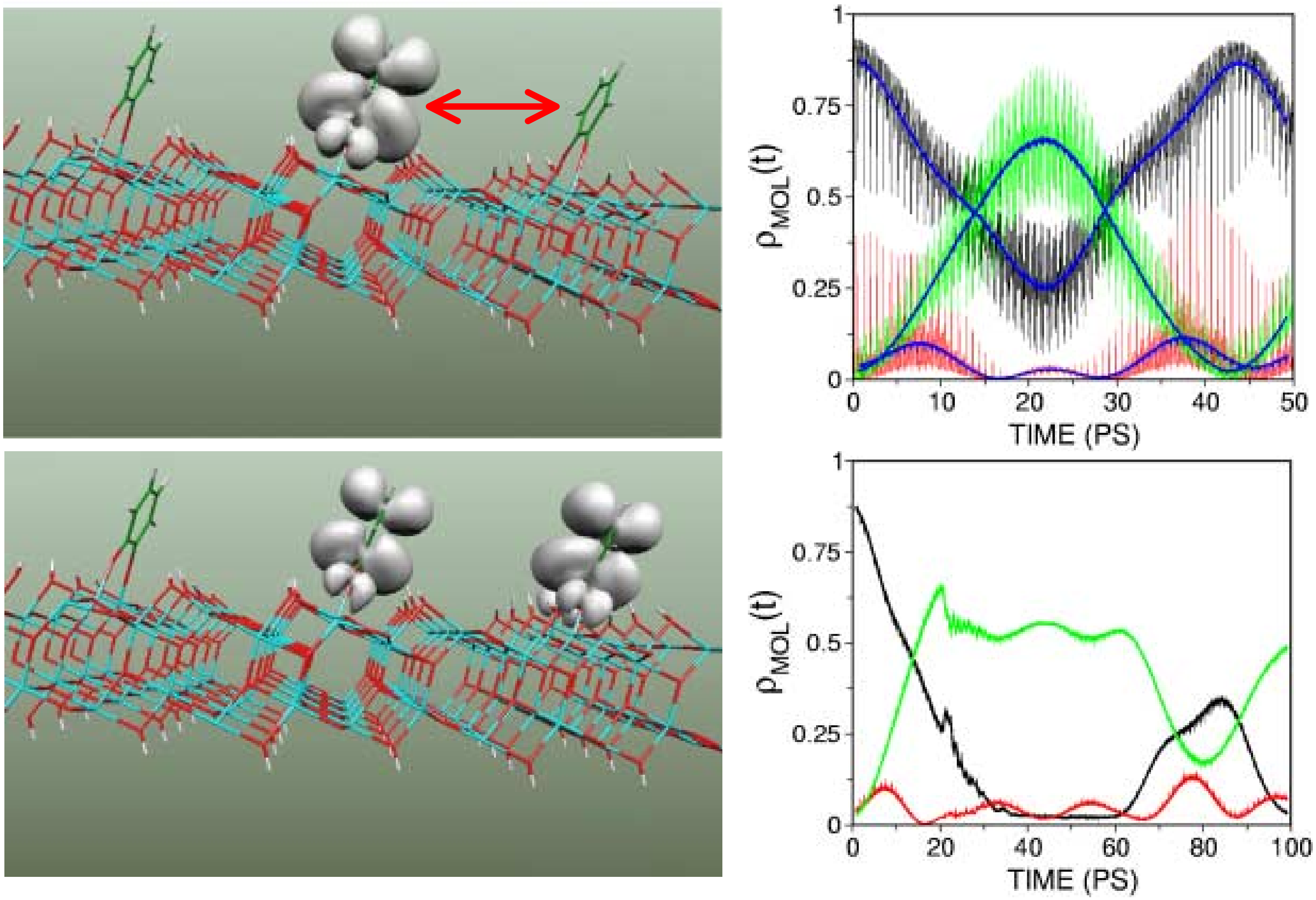
Luis G.C. Rego and Victor S. Batista *J. Am. Chem. Soc.* **125**,7989 (2003)





Quantum-Entanglement and Coherent-Control of Hole Relaxation Dynamics Localized Deep in the Semiconductor Band Gap

Luis G.C. Rego and Victor S. Batista *(submitted to Phys. Rev. Lett.)*



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).

MP/SOFT Method (Trotter Expansion)

Wu, Y. and Batista, V.S. *J. Chem. Phys*. **118**, 6720 (2003); *ibid*. **118**, 6720 (2003); *ibid*. **submitted** (2004).

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

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

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** $A_j(k) \equiv (a_j(k)/\pi)^{1/4}\text{exp}[-\frac{1}{2}a_j(k)d_j(k)^2 - d_j(k)g_j(k) - (b_j(k)d_j(k) + f_j(k))^2/(2a_j(k))]$.

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 ϵ,

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

Norm conservation is maintained within a desired precision.

- **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

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

Equilibrium Density Matrix

$$\langle \mathbf{x}|\hat{\rho}_\beta|\mathbf{x}_0\rangle = \langle \mathbf{x}|e^{-\beta\hat{H}}|\mathbf{x}_0\rangle$$

$$\langle \mathbf{x}|\hat{\rho}_\beta|\mathbf{x}_0\rangle = \int d\mathbf{x}_{n-1}\ldots\int d\mathbf{x}_2\langle \mathbf{x}|e^{-(\beta_n-\beta_{n-1})\hat{H}}|\mathbf{x}_{n-1}\rangle$$
$$\ldots\langle \mathbf{x}_2|e^{-(\beta_2-\beta_1)\hat{H}}|\mathbf{x}_1\rangle\langle \mathbf{x}_1|\rho_\epsilon|\mathbf{x}_0\rangle,$$

where $\beta = \beta_n - \beta_0$ and $\epsilon = \beta_1 - \beta_0$

$$\langle \mathbf{x}_1|\rho_\epsilon|\mathbf{x}_0\rangle = \sqrt{\frac{m}{2\pi\hbar^2\epsilon}}e^{-\epsilon V(\mathbf{x}_0)/2}e^{-\frac{m}{2\hbar^2\epsilon}(\mathbf{x}_1-\mathbf{x}_0)^2}e^{-\epsilon V(\mathbf{x}_1)/2}$$

$$Z = \int d\mathbf{x}_0\langle \mathbf{x}_0|\hat{\rho}_\beta|\mathbf{x}_0\rangle$$

$$\langle A\rangle = Z^{-1}\int d\mathbf{x}_0\int d\mathbf{x}\langle \mathbf{x}|\hat{\rho}_\beta|\mathbf{x}_0\rangle\langle \mathbf{x}_0|\hat{A}|\mathbf{x}\rangle$$

Electron Tunneling in Multidimensional Systems

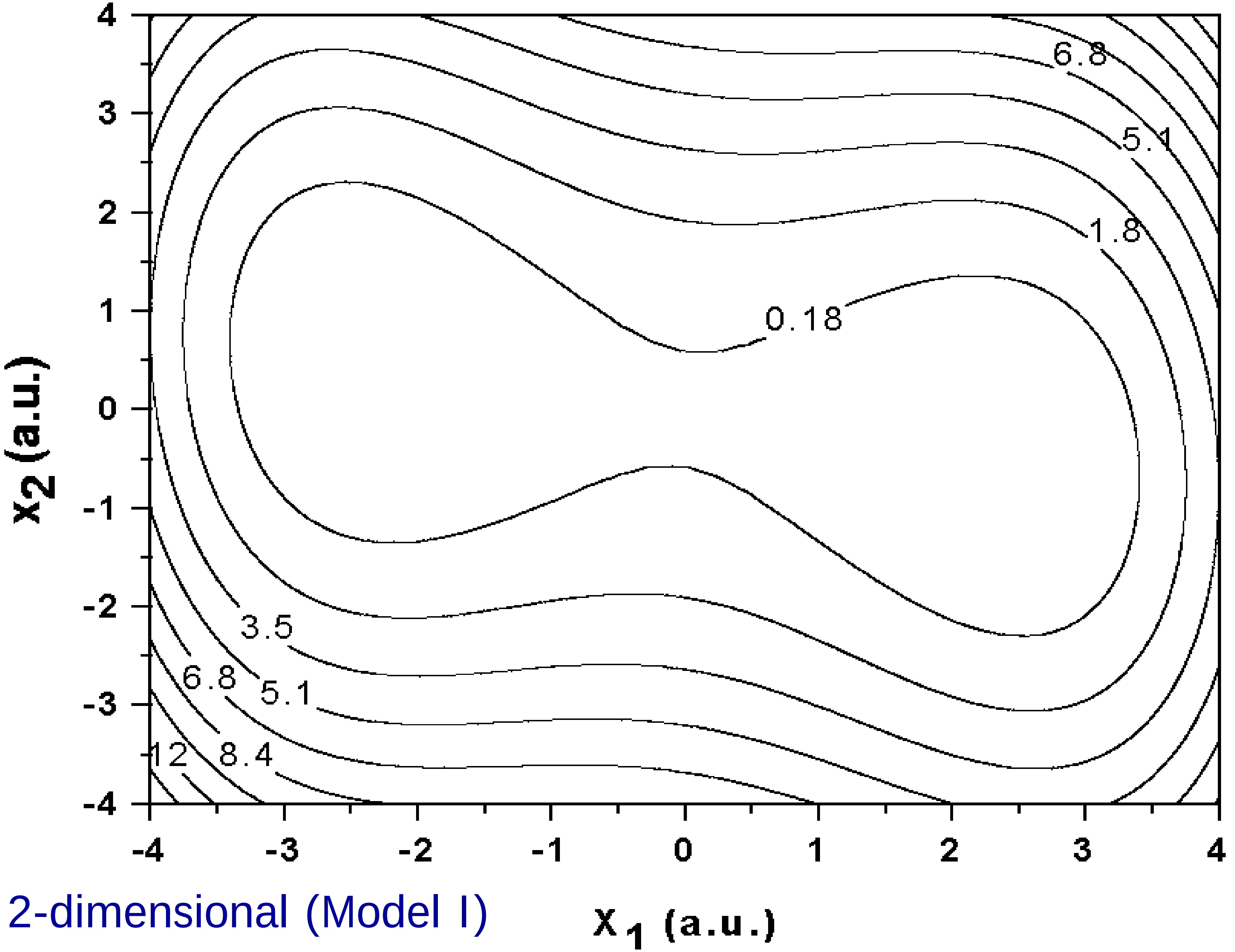
Model I:

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

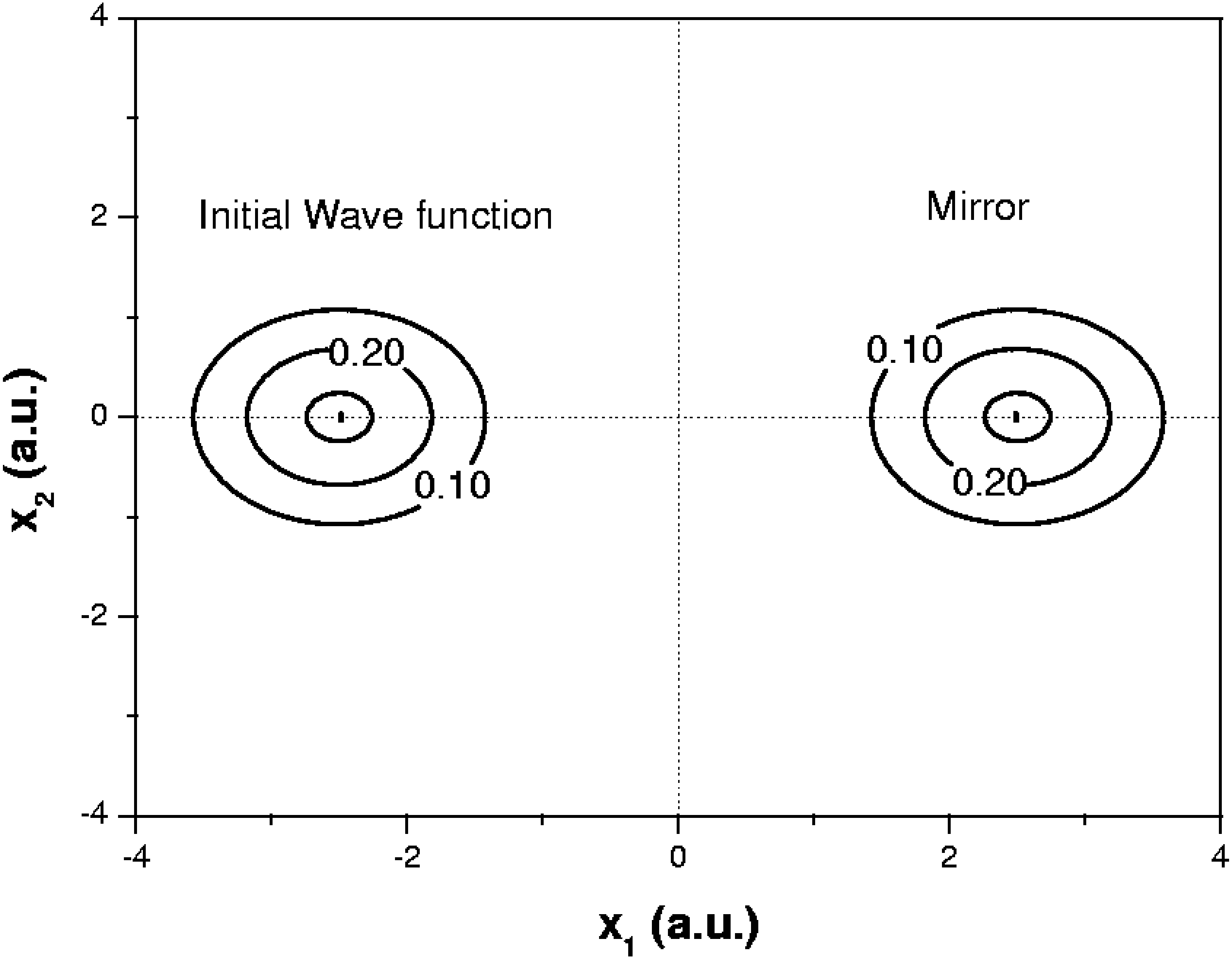
where $\mathrm{m}_j = 1.0$ a.u., $\omega_j = 1.0$ a.u. and $c_j = 0.2$ a.u. for $j = 1$—N, with N = 1—10

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

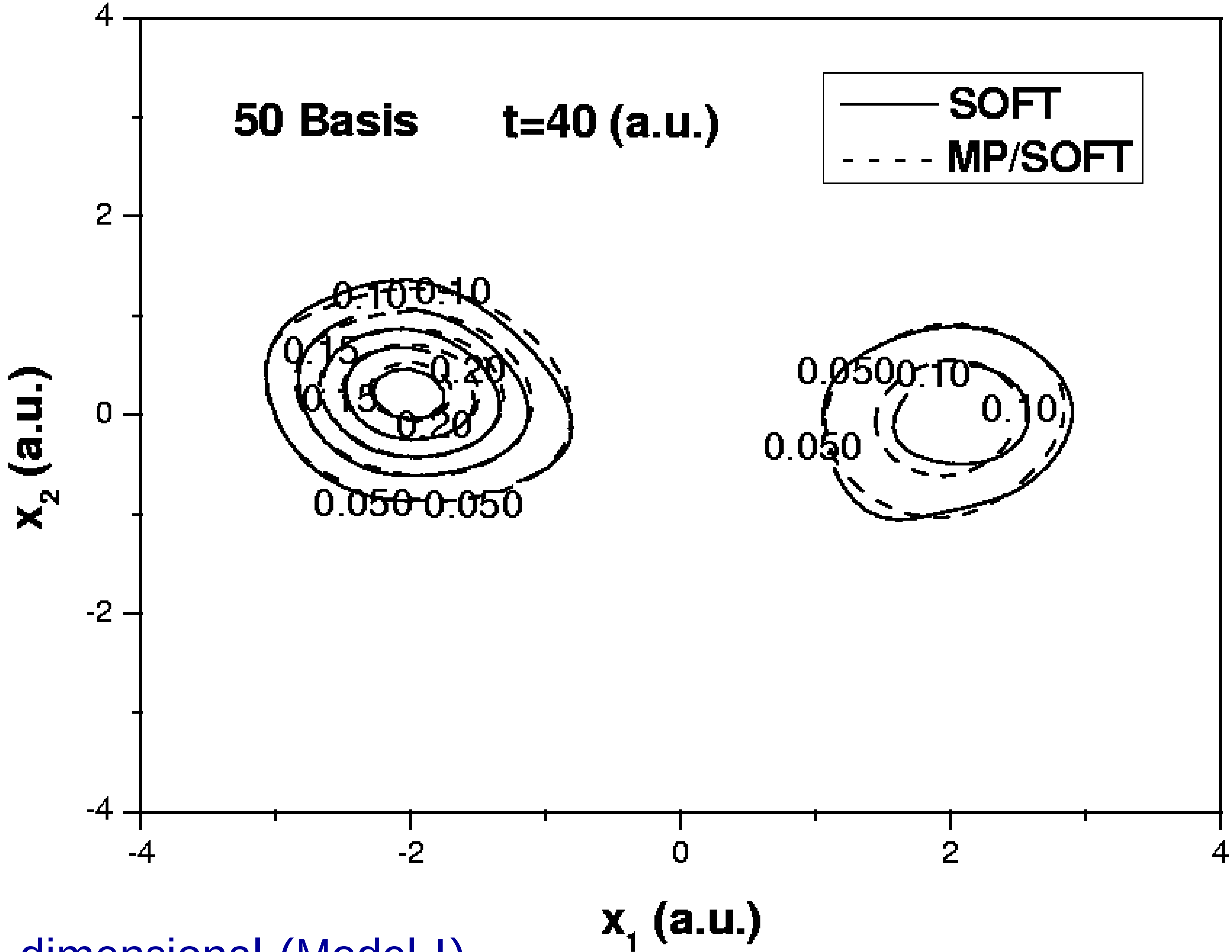
with $\eta = 1.3544$.



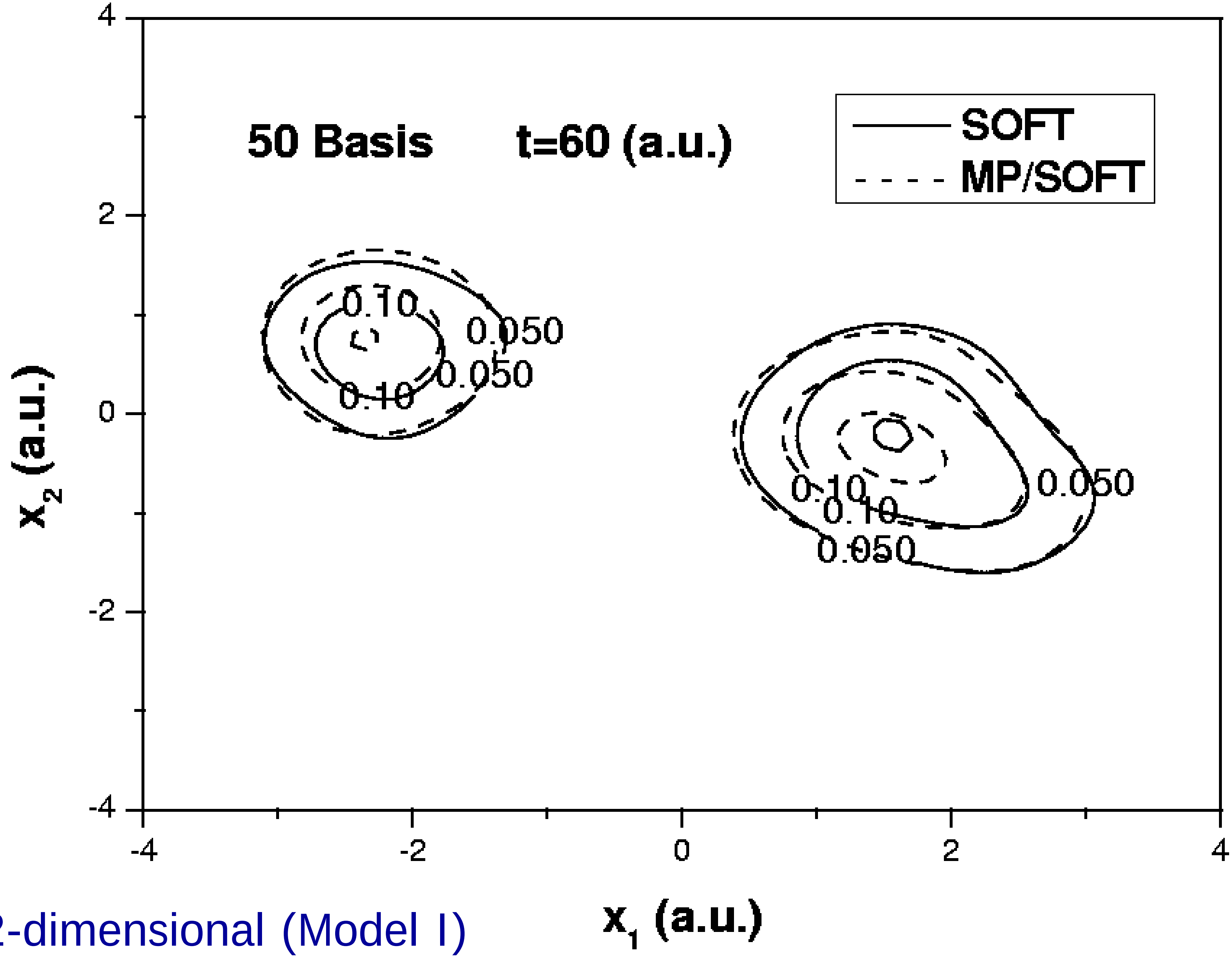
2-dimensional (Model I)



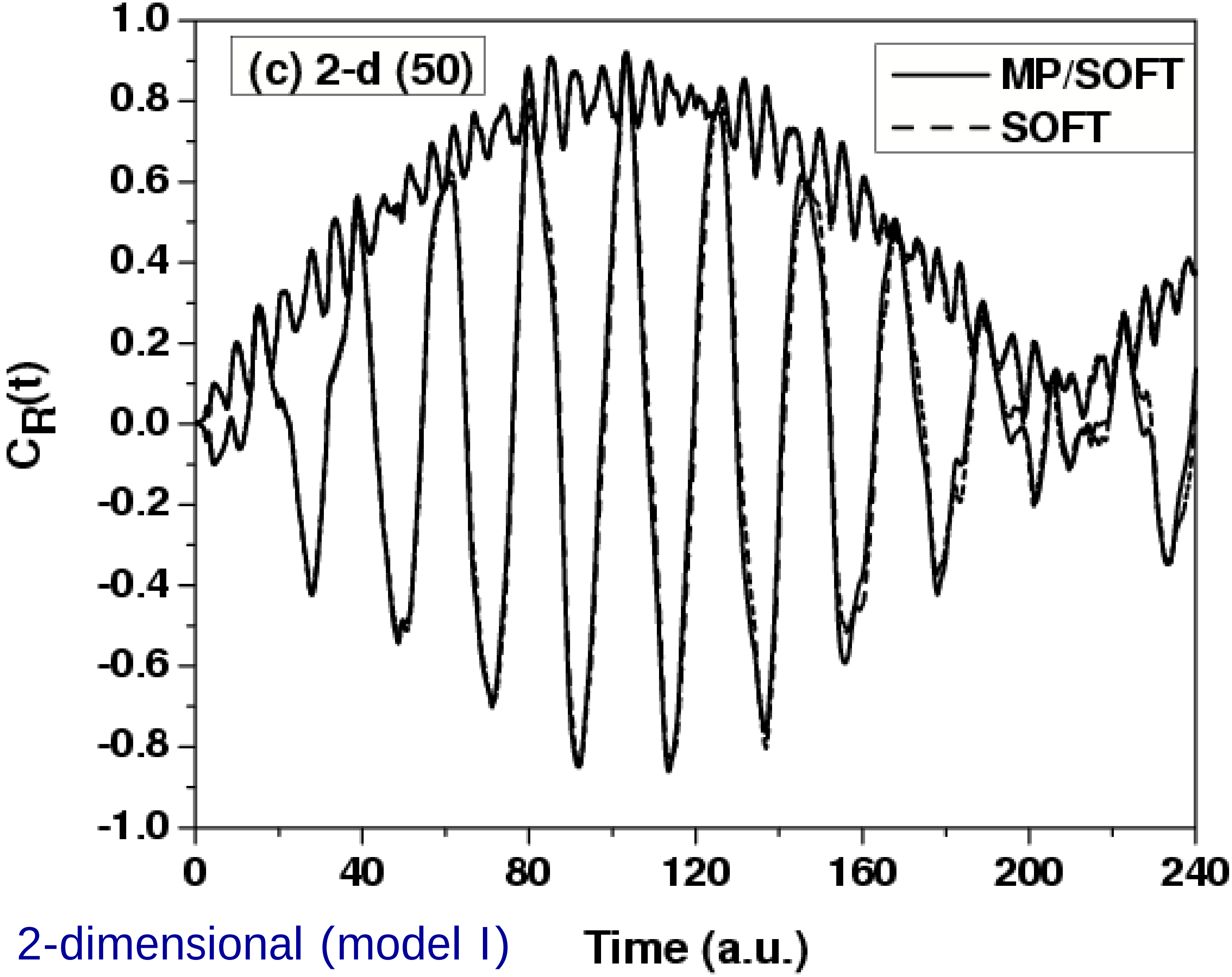
Initial Wave function
Mirror
0.20
0.10
0.10
0.20
x2 (a.u.)
x1 (a.u.)
4
2
0
-2
-4
-4
-2
0
2
4



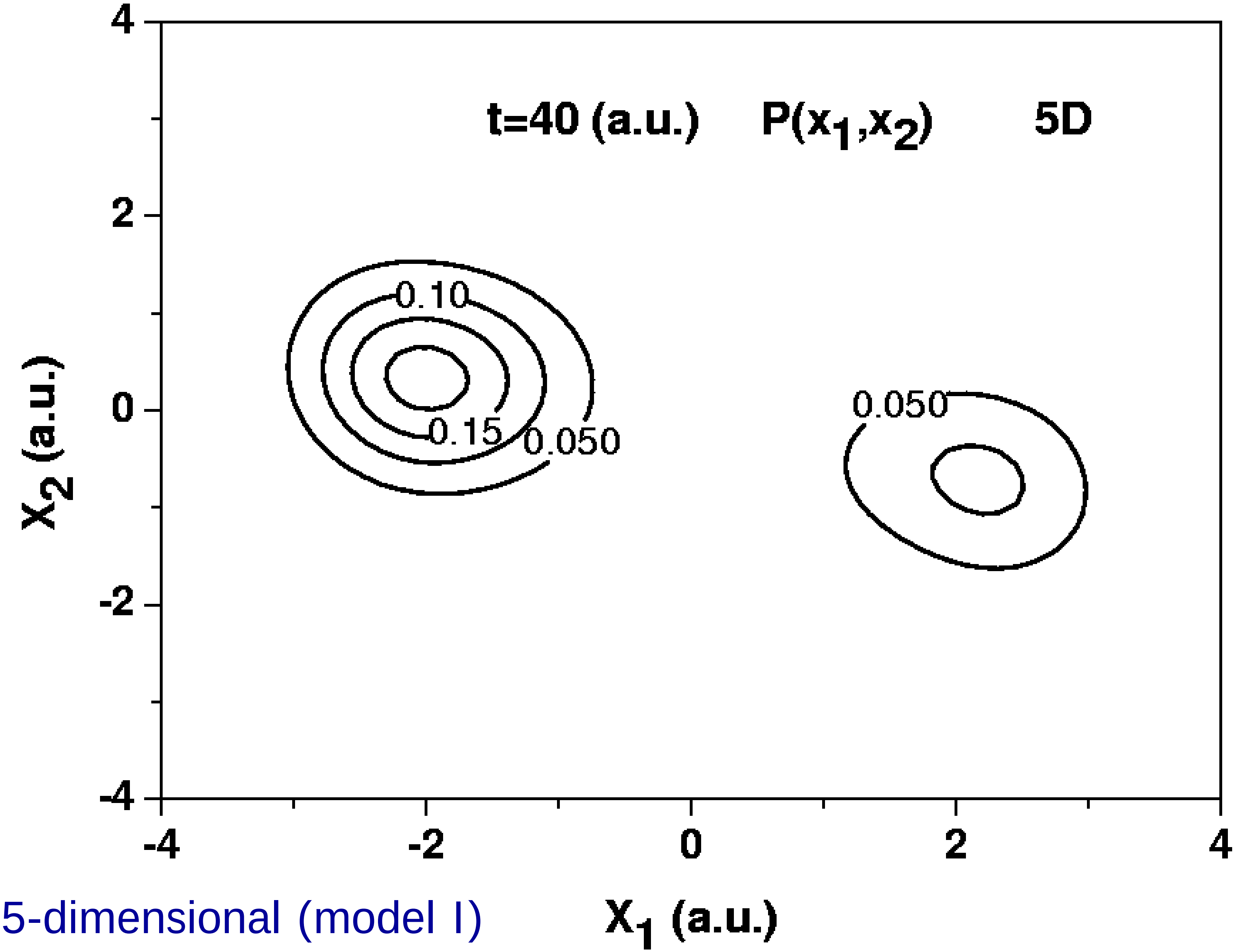
2-dimensional (Model I)



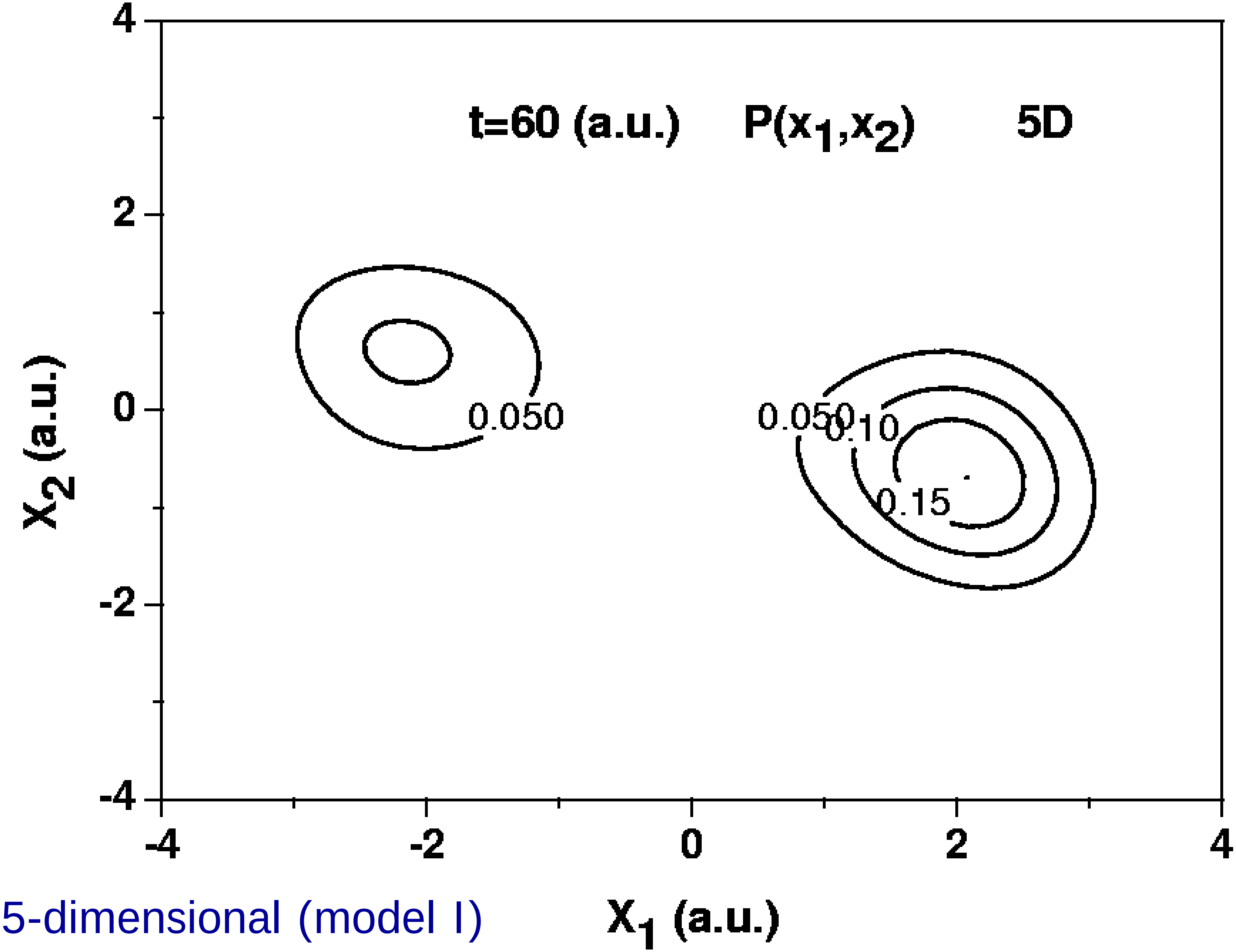
2-dimensional (Model I)



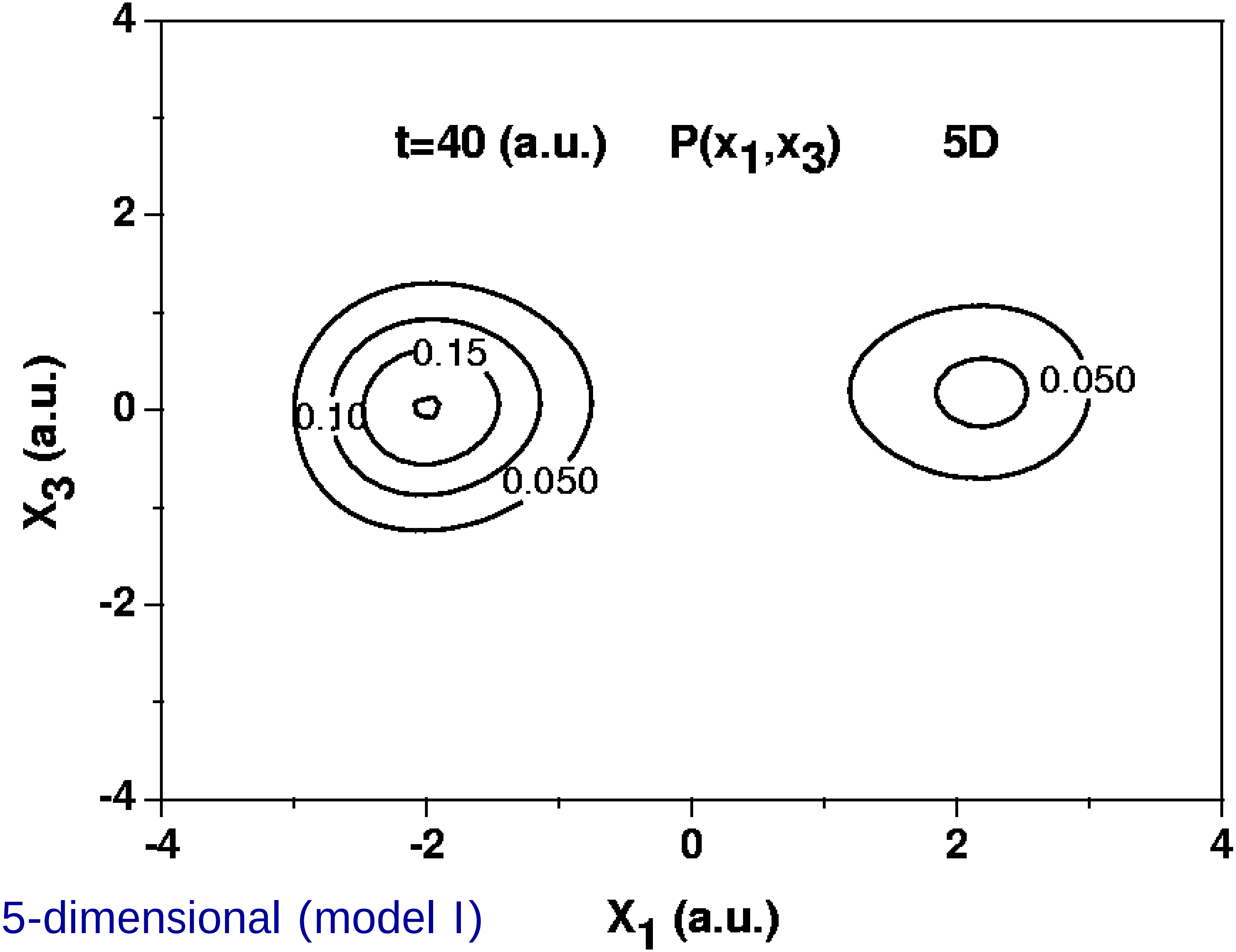
2-dimensional (model I)



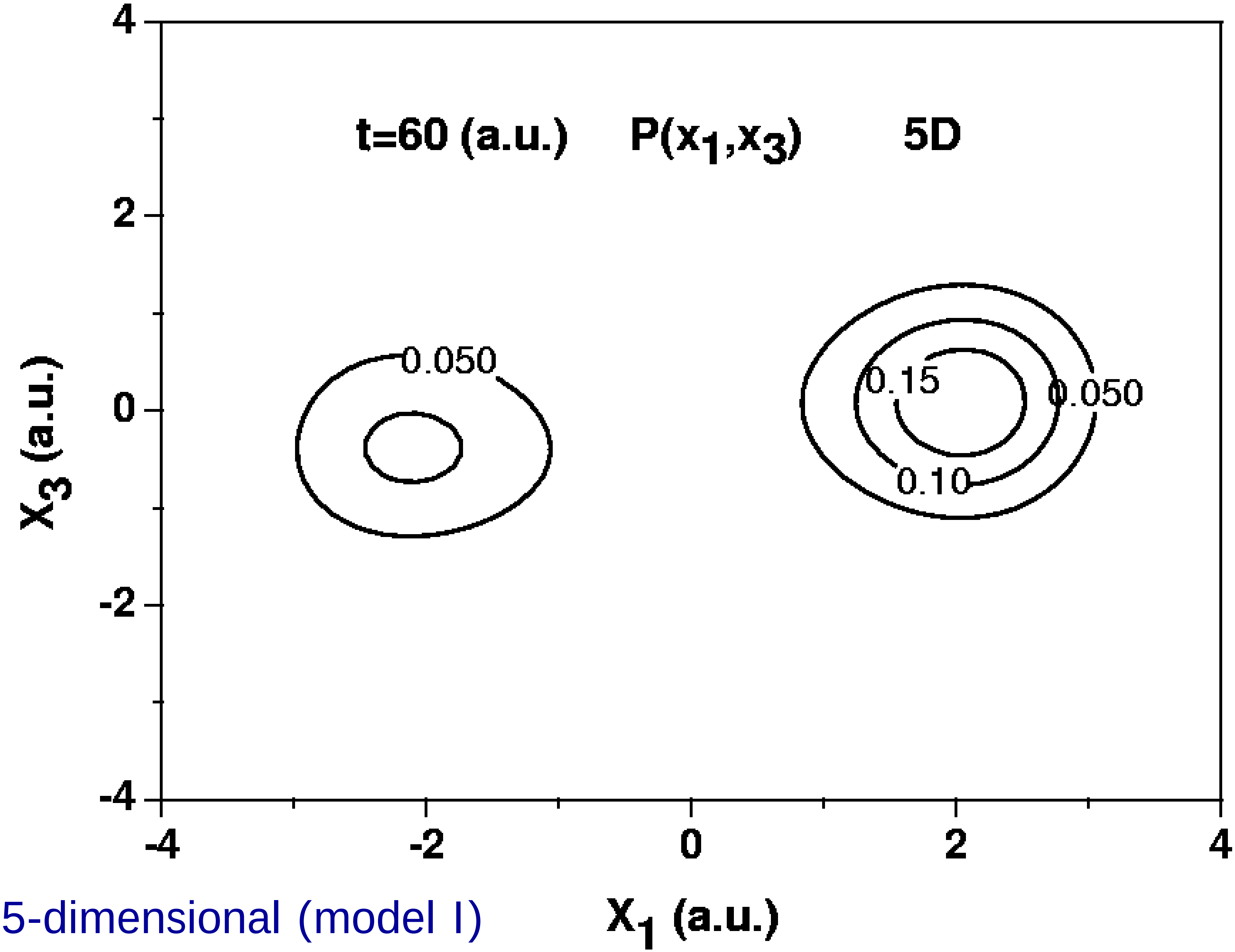
5-dimensional (model I)



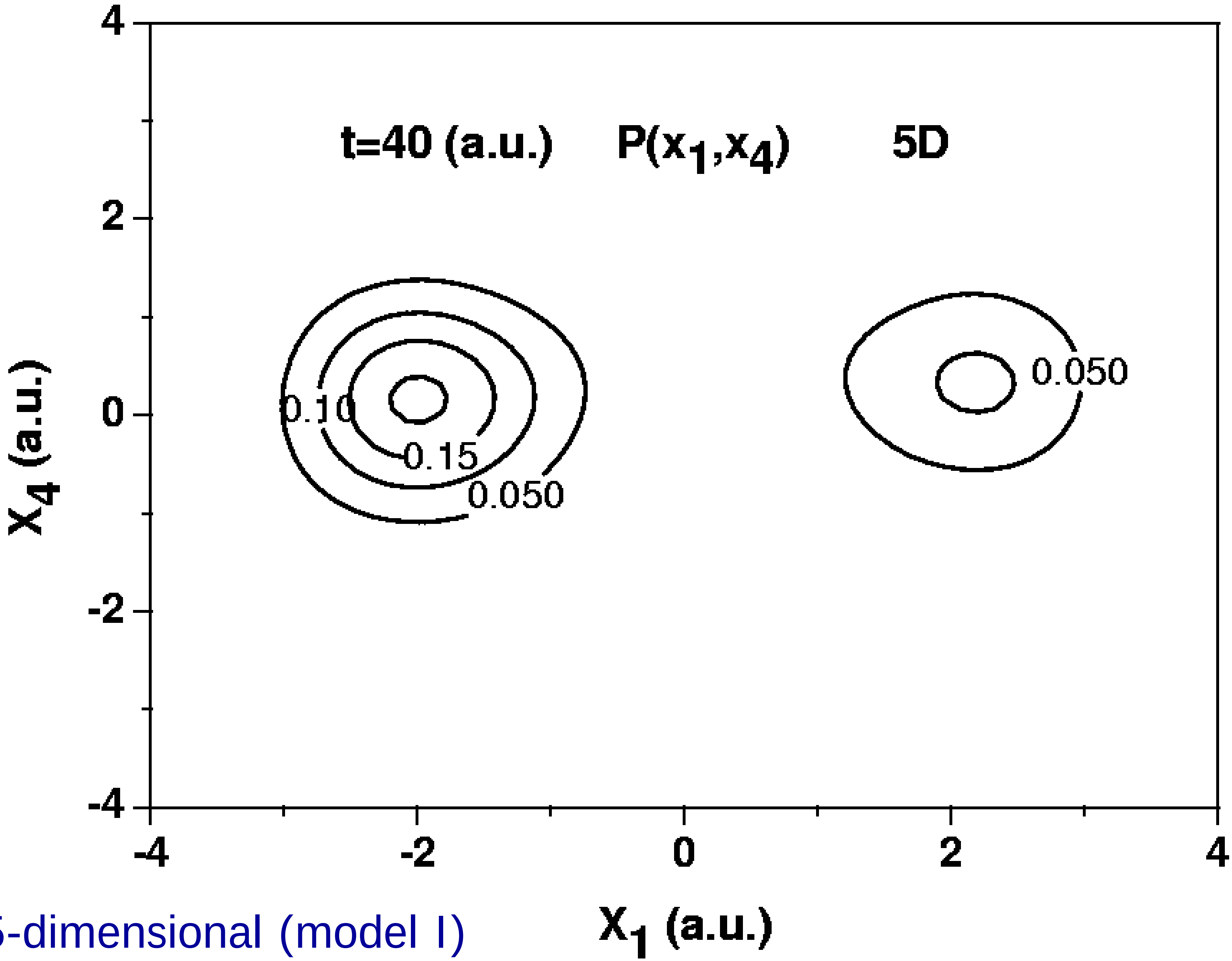
5-dimensional (model I)



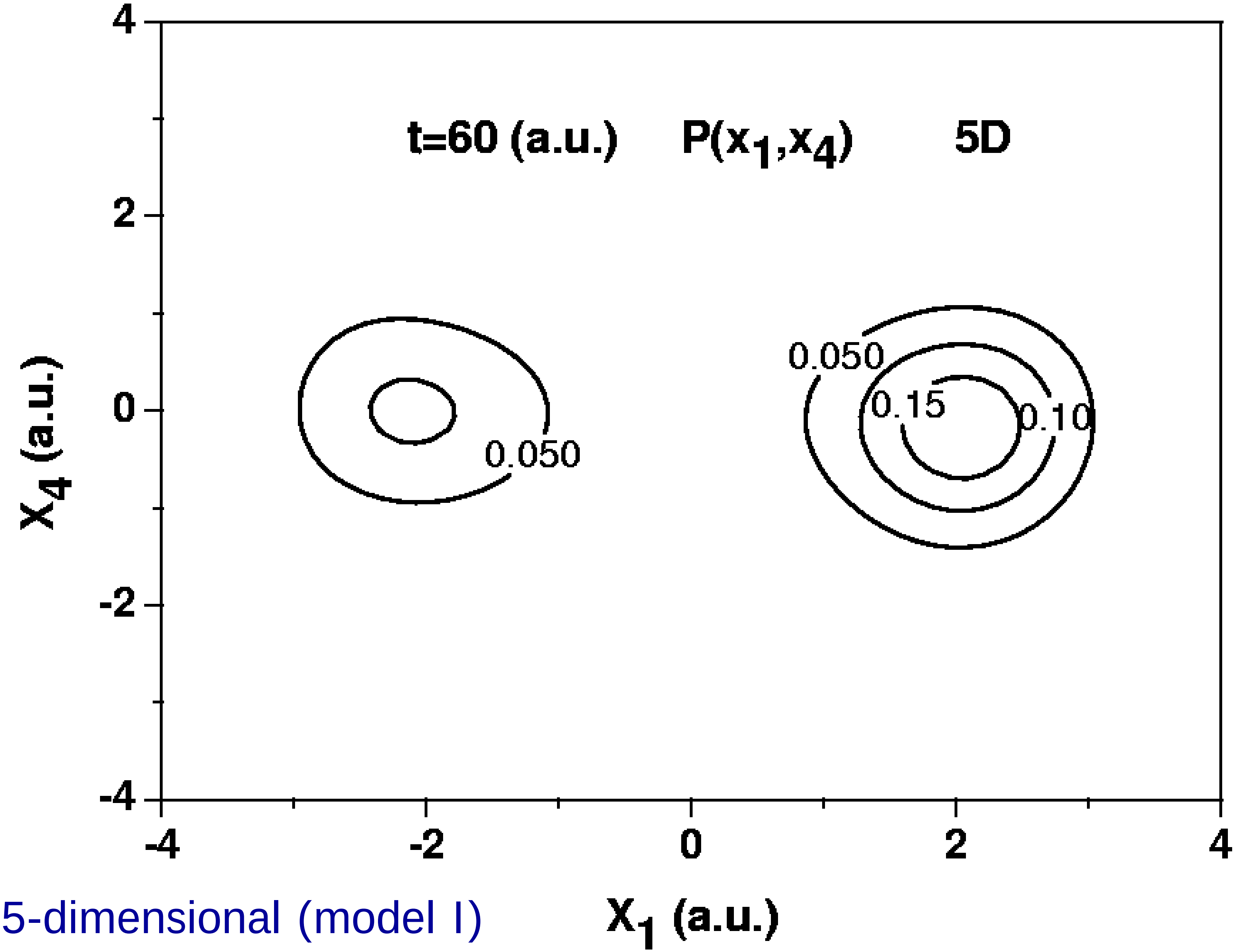
5-dimensional (model I)



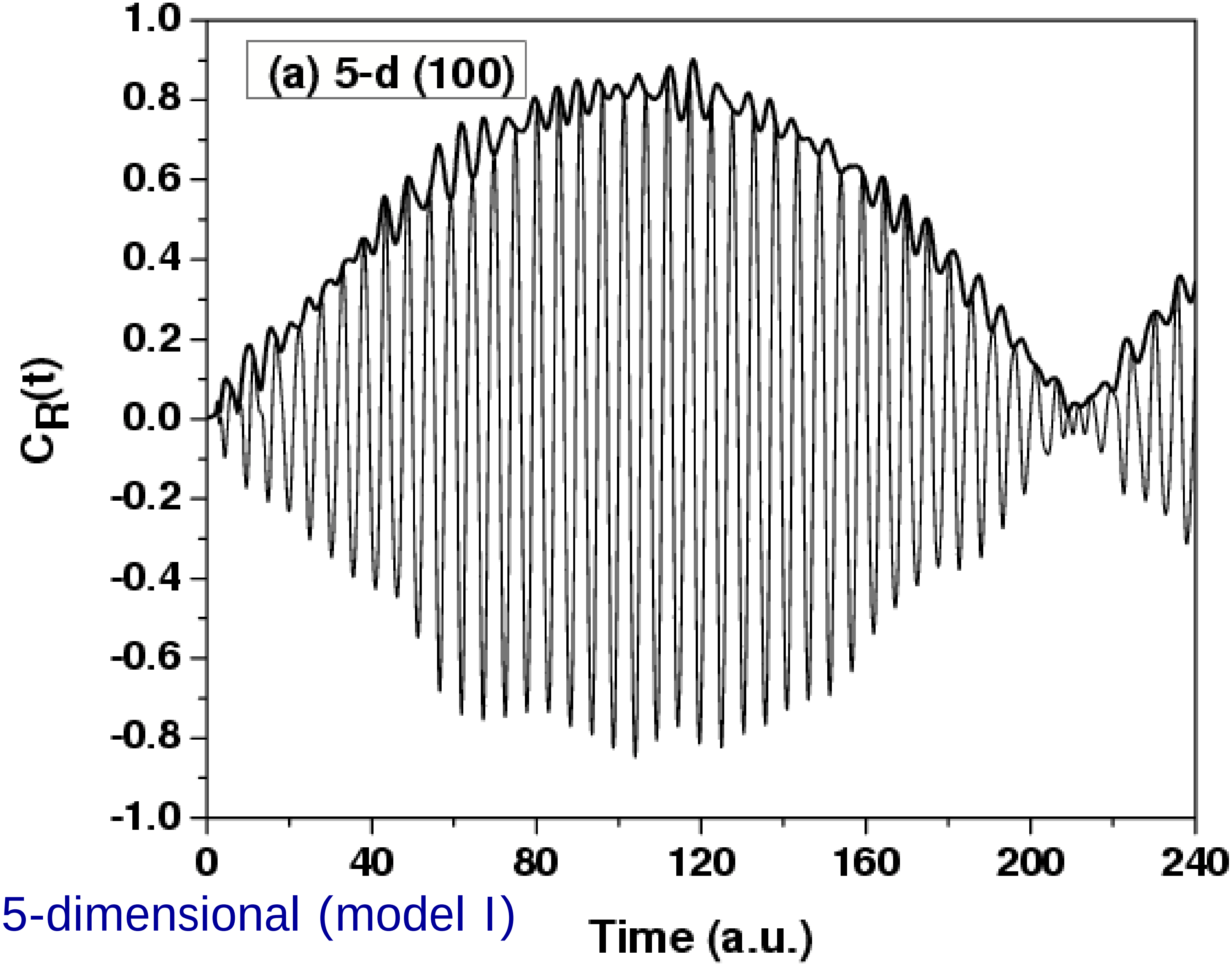
5-dimensional (model I)



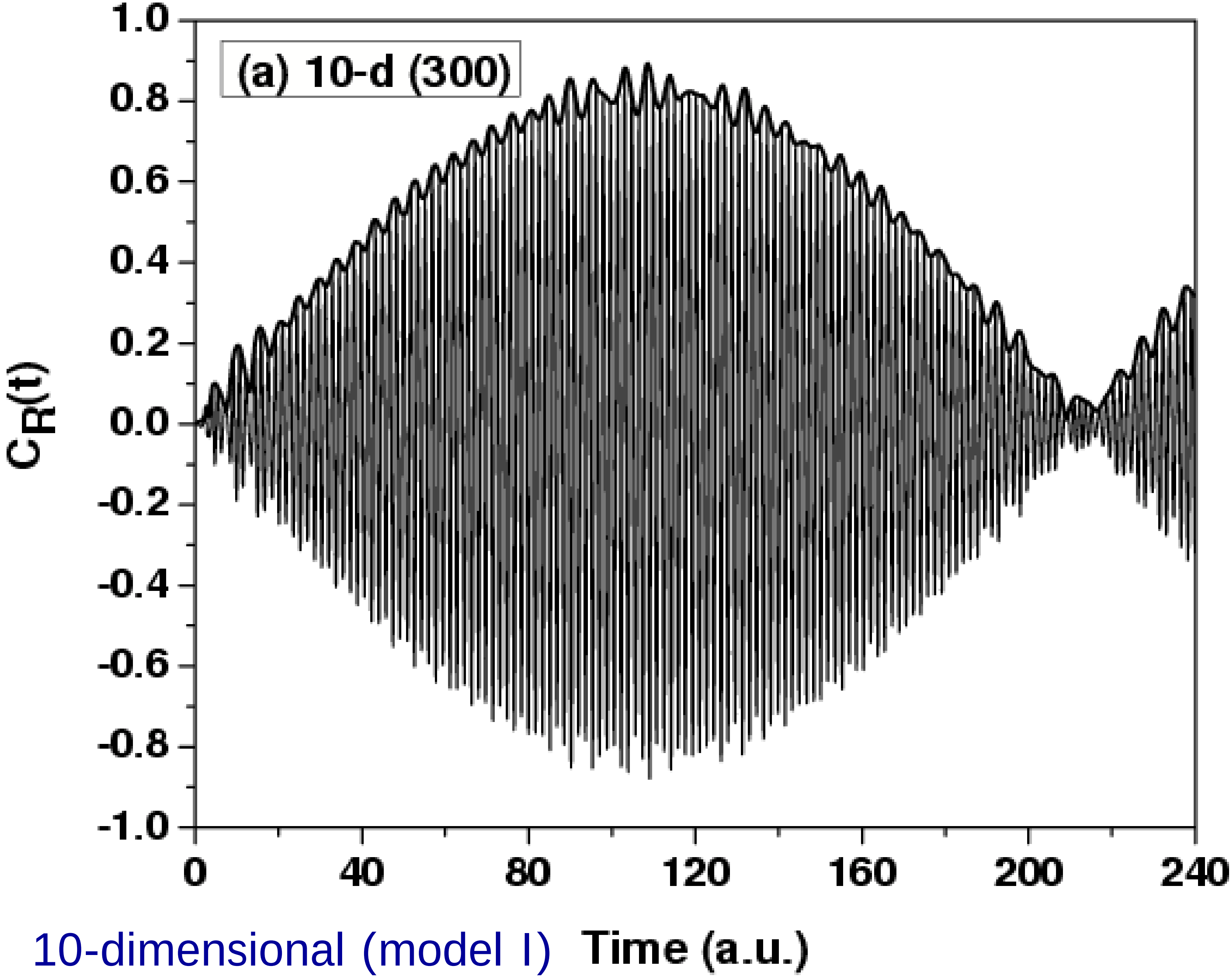
5-dimensional (model I)



5-dimensional (model I)



5-dimensional (model I)



10-dimensional (model I)

Electron Tunneling in Multidimensional Systems

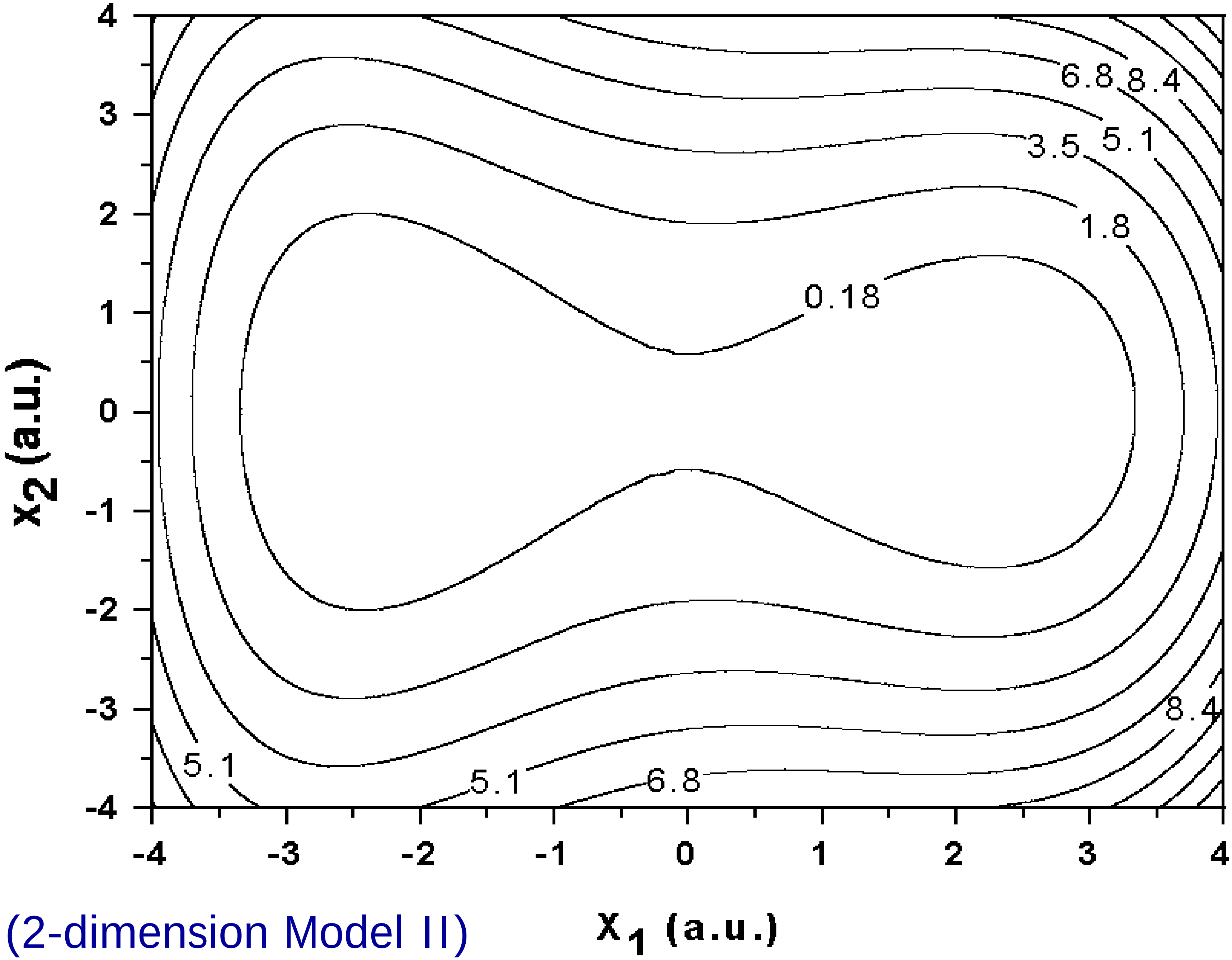
Model II

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

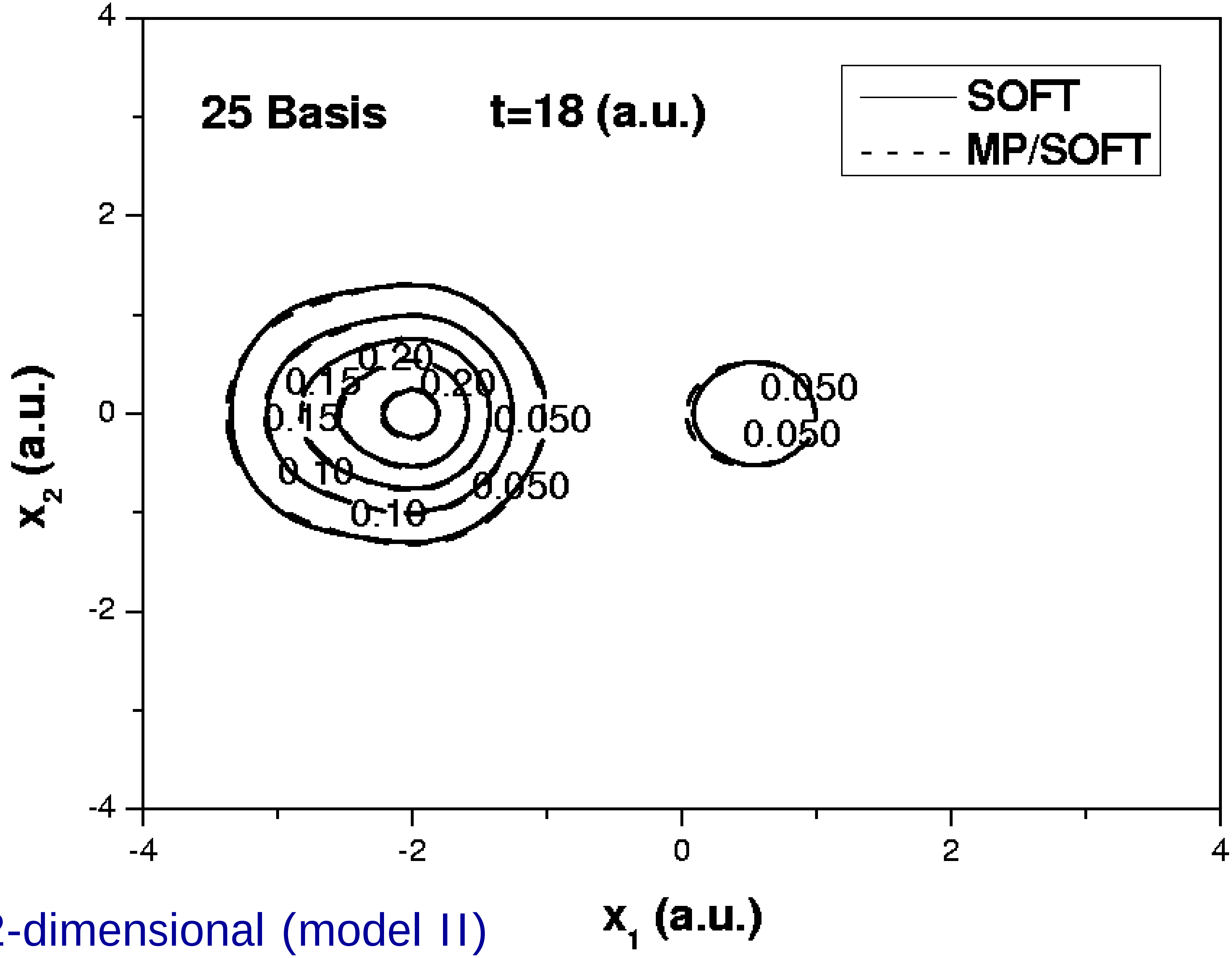
where $\mathrm{m}_j = 1.0$ a.u., $\omega_j = 1.0$ a.u. and $c_j = 0.1$ a.u. for $j = 1$—N with N = 1—20.

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

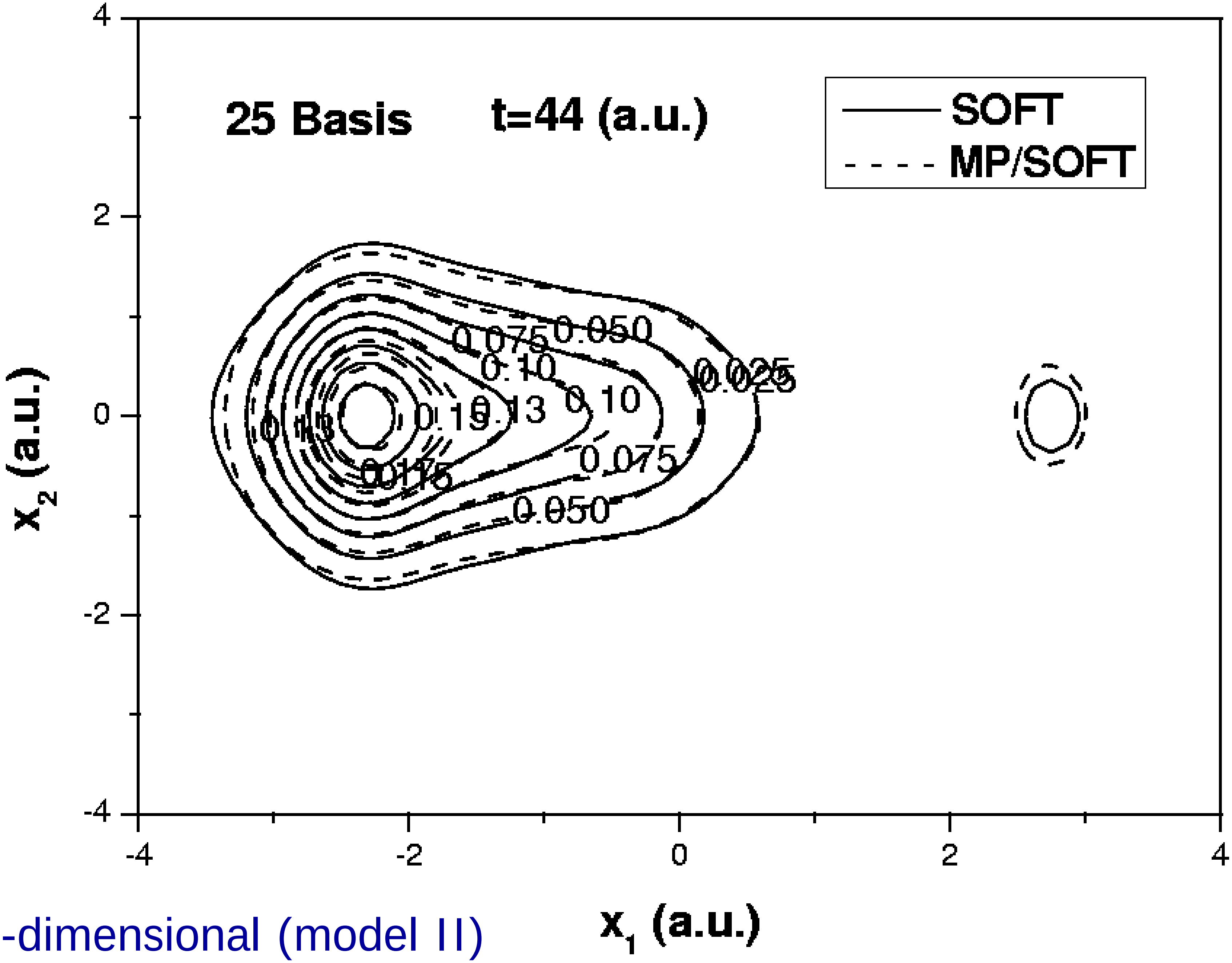
with $\eta = 1.3544$.



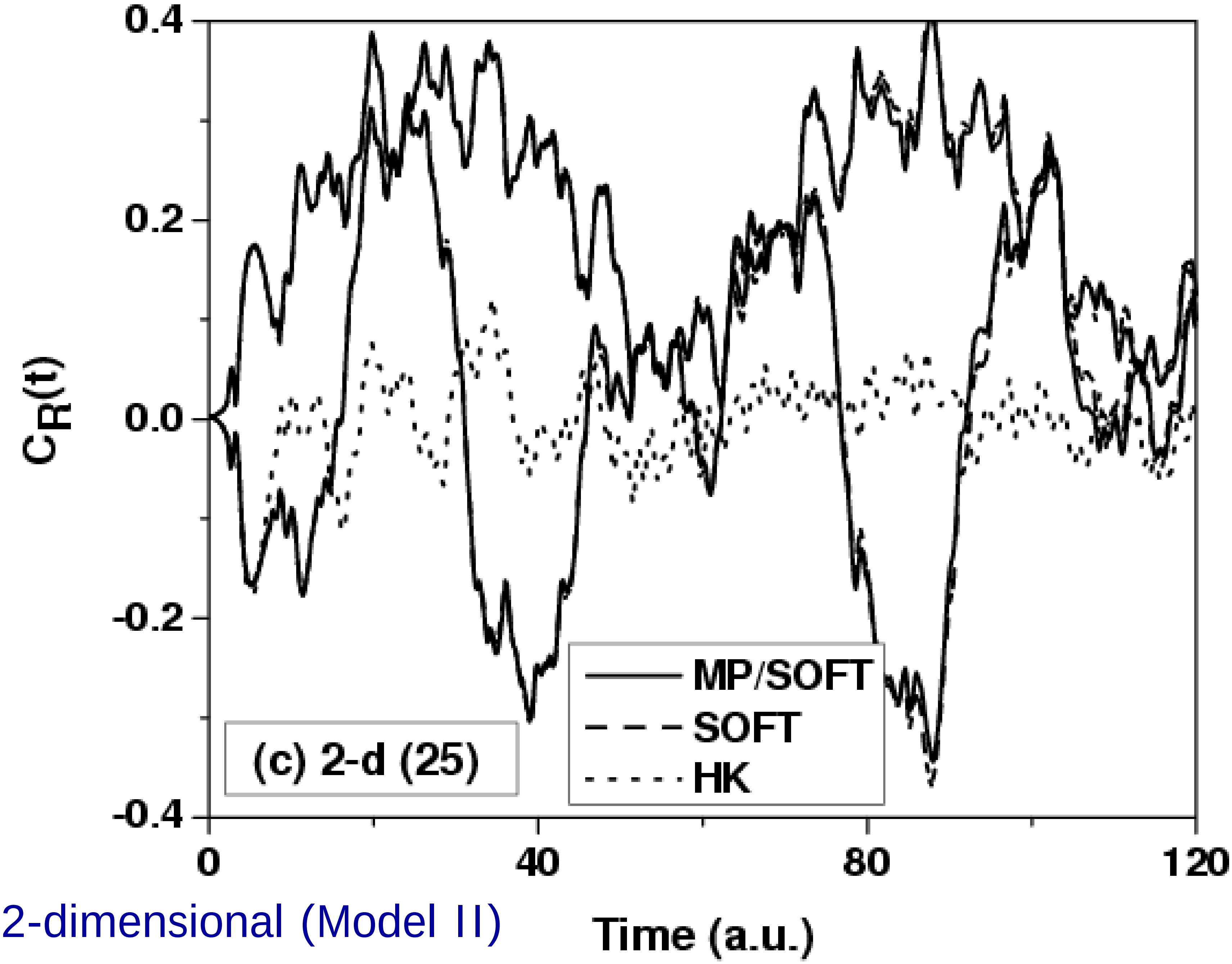
(2-dimension Model II)



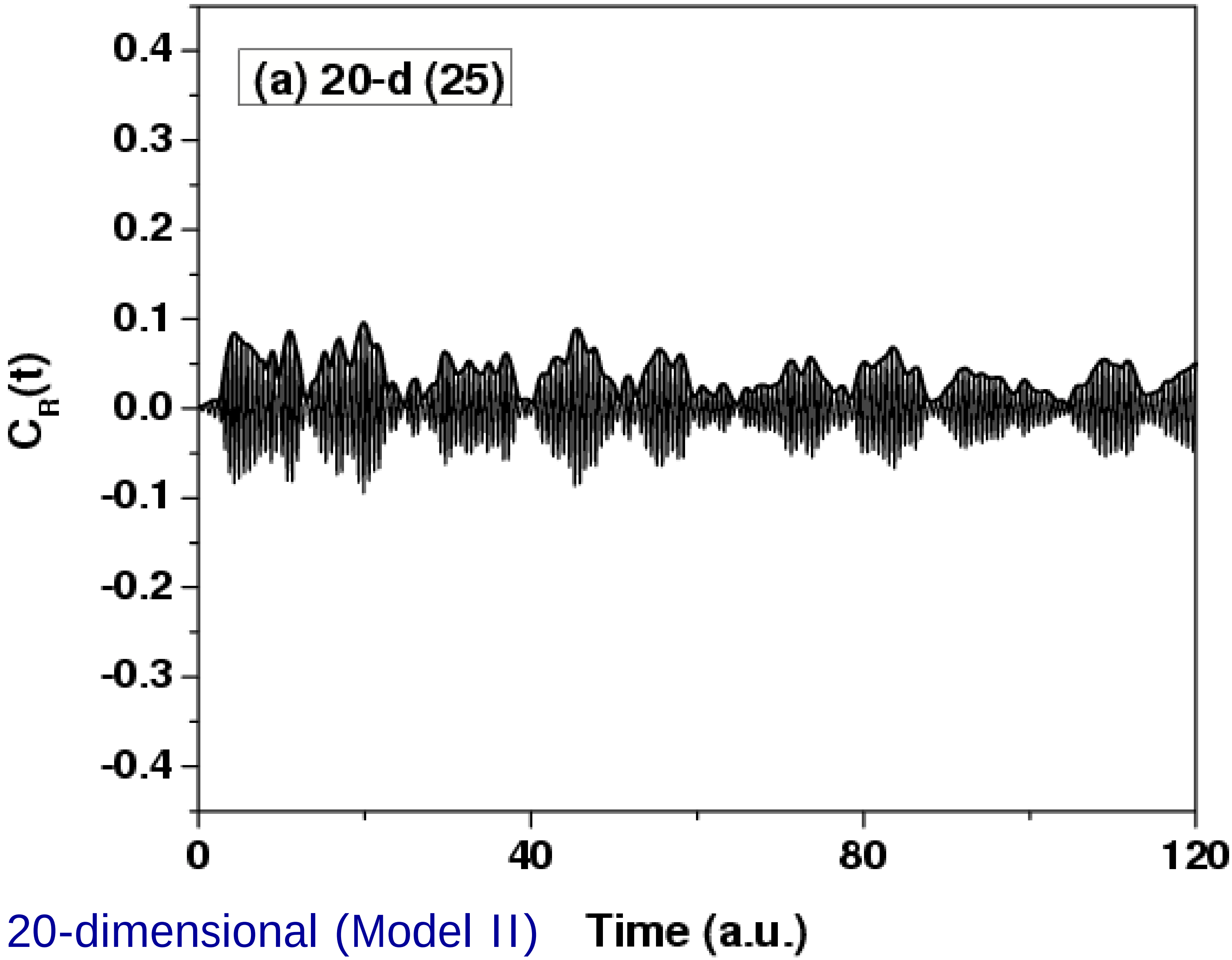
2-dimensional (model II)



2-dimensional (model II)

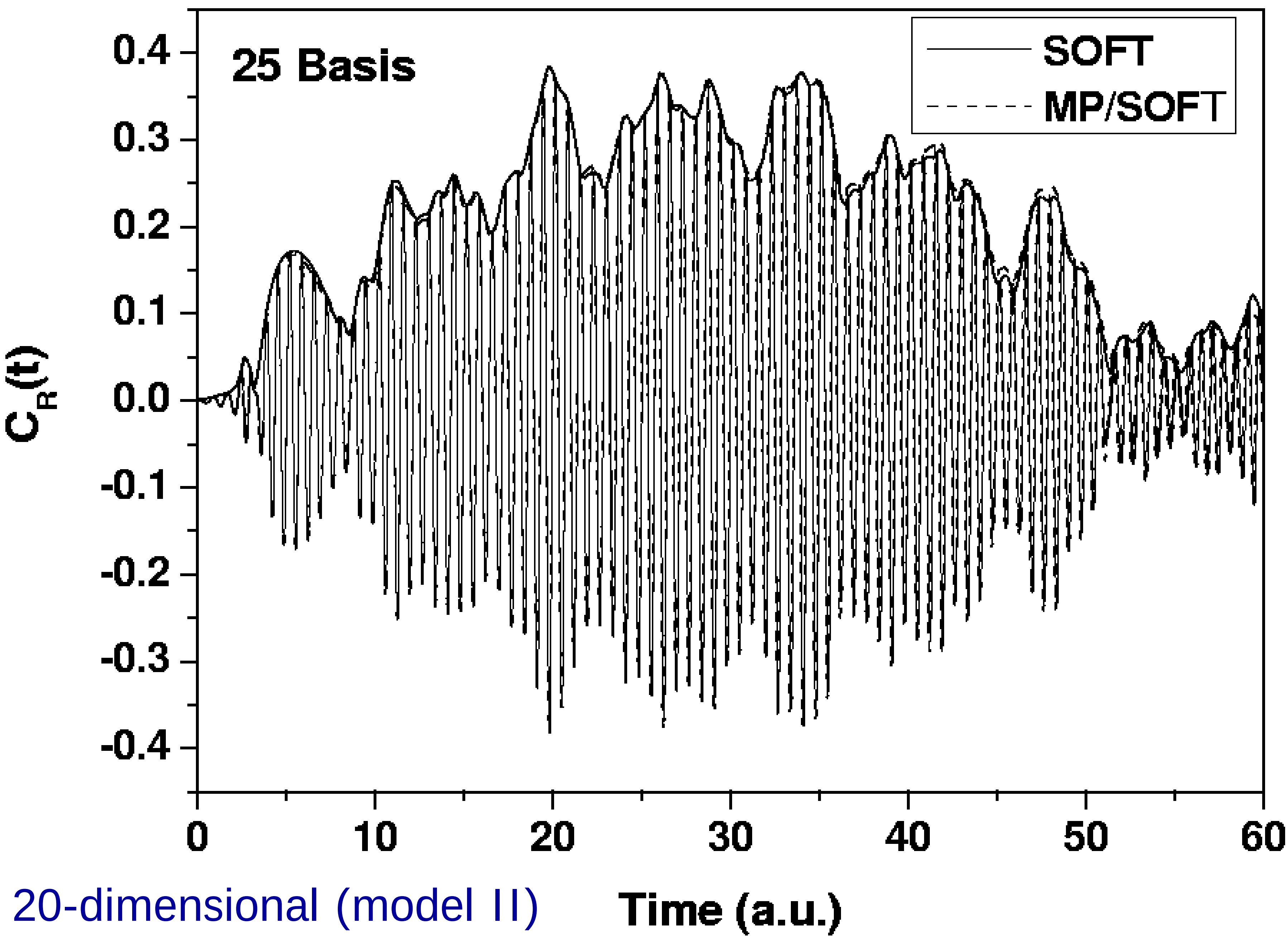


2-dimensional (Model II)



20-dimensional (Model II)

Benchmark calculation:



20-dimensional (model II)

TS/SC-IVR Approach

Burant, J. and Batista, V.S. *J. Chem. Phys.* **116**, 2748 (2002).

Wu, Y. and Batista, V.S. *J. Phys. Chem. B* **106**, 8271 (2002).

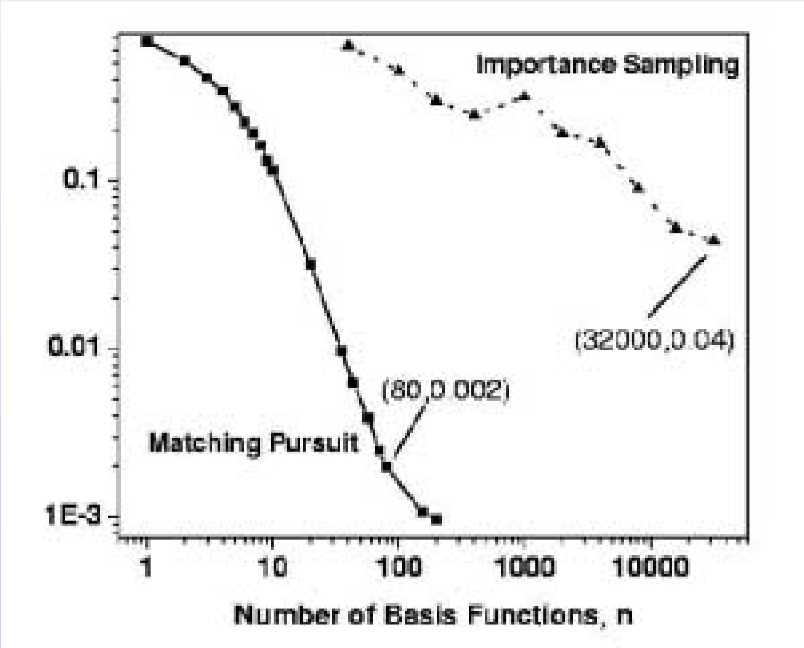
$$e^{-(i/\hbar)\hat{H}\tau} \approx (2\pi\hbar)^{-D} \int \mathbf{dp}_0 \int \mathbf{dq}_0 \mid \mathbf{p}_\tau \mathbf{q}_\tau \rangle C_\tau(\mathbf{p}_0 \mathbf{q}_0) e^{iS_\tau(\mathbf{p}_0,\mathbf{q}_0)/\hbar} \langle \mathbf{p}_0, \mathbf{q}_0 \mid,$$

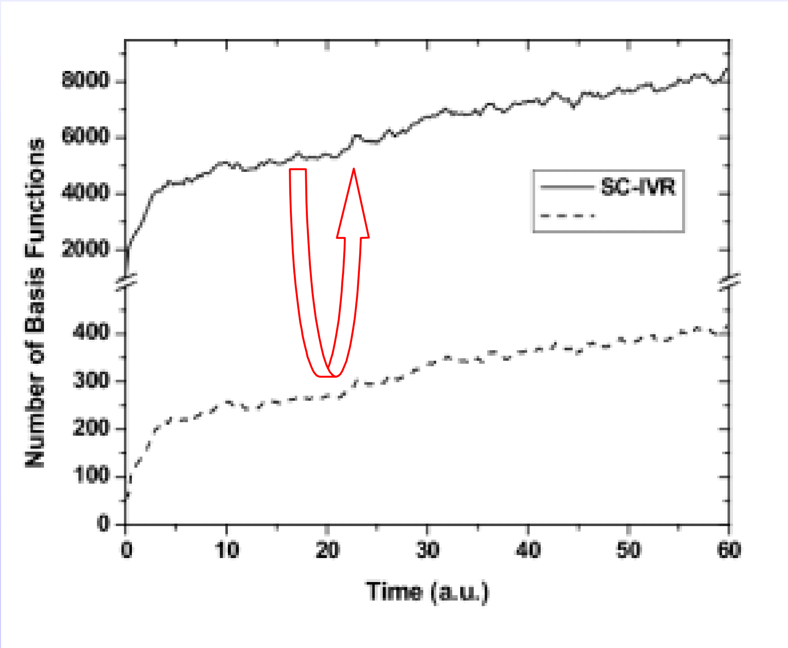
where D is the number of nuclear degrees of freedom and $\mid \mathbf{p}_\tau \mathbf{q}_\tau \rangle$ are the minimum uncertainty wavepackets, or coherent states (CS),

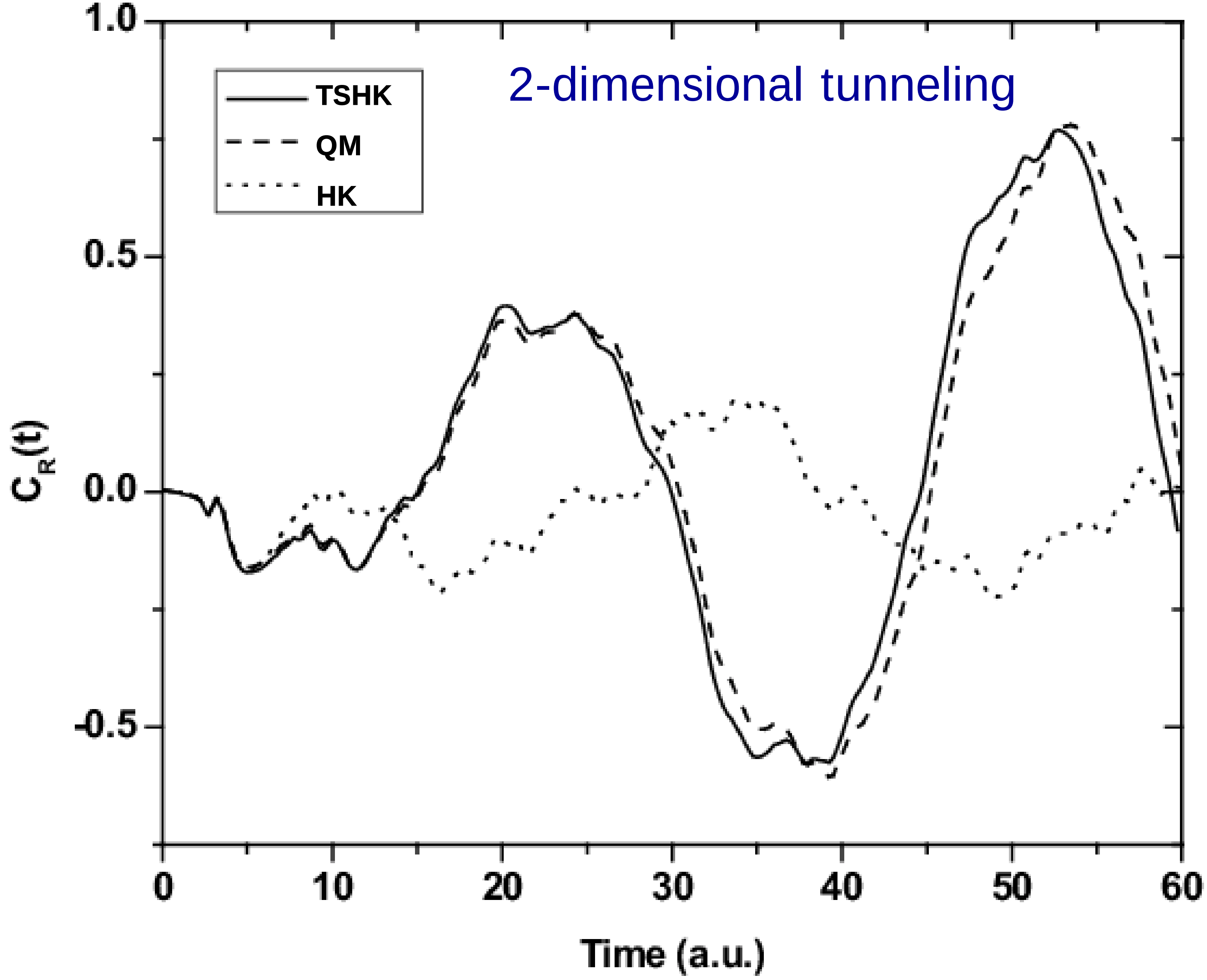
$$\langle \mathbf{x} | \mathbf{p}_\tau \mathbf{q}_\tau \rangle = \left(\frac{2\gamma}{\pi} \right)^{D/4} \exp\left[-\gamma(\mathbf{x} - \mathbf{q}_\tau)^2 + i\mathbf{p}_\tau(\mathbf{x} - \mathbf{q}_\tau)/\hbar \right],$$

The (TS) implementation avoids most of the difficulties of the standard SC-IVR, since the propagator is applied only for short time-slices while the semiclassical approximation is still accurate and efficient. However, the method introduces a new challenge: the reinitialization of the time-evolved wavefunction after each propagation time-slice.

In order to optimize the efficiency of the re-expansion procedure, the time-evolved wavefunction is represented ("compressed") at the end of each propagation time-slice according to a matching-pursuit coherent-state expansion.






2-dimensional tunneling
TSHK
QM
HK
1.0
0.5
0.0
-0.5
0
10
20
30
40
50
60
$C_R(t)$
Time (a.u.)

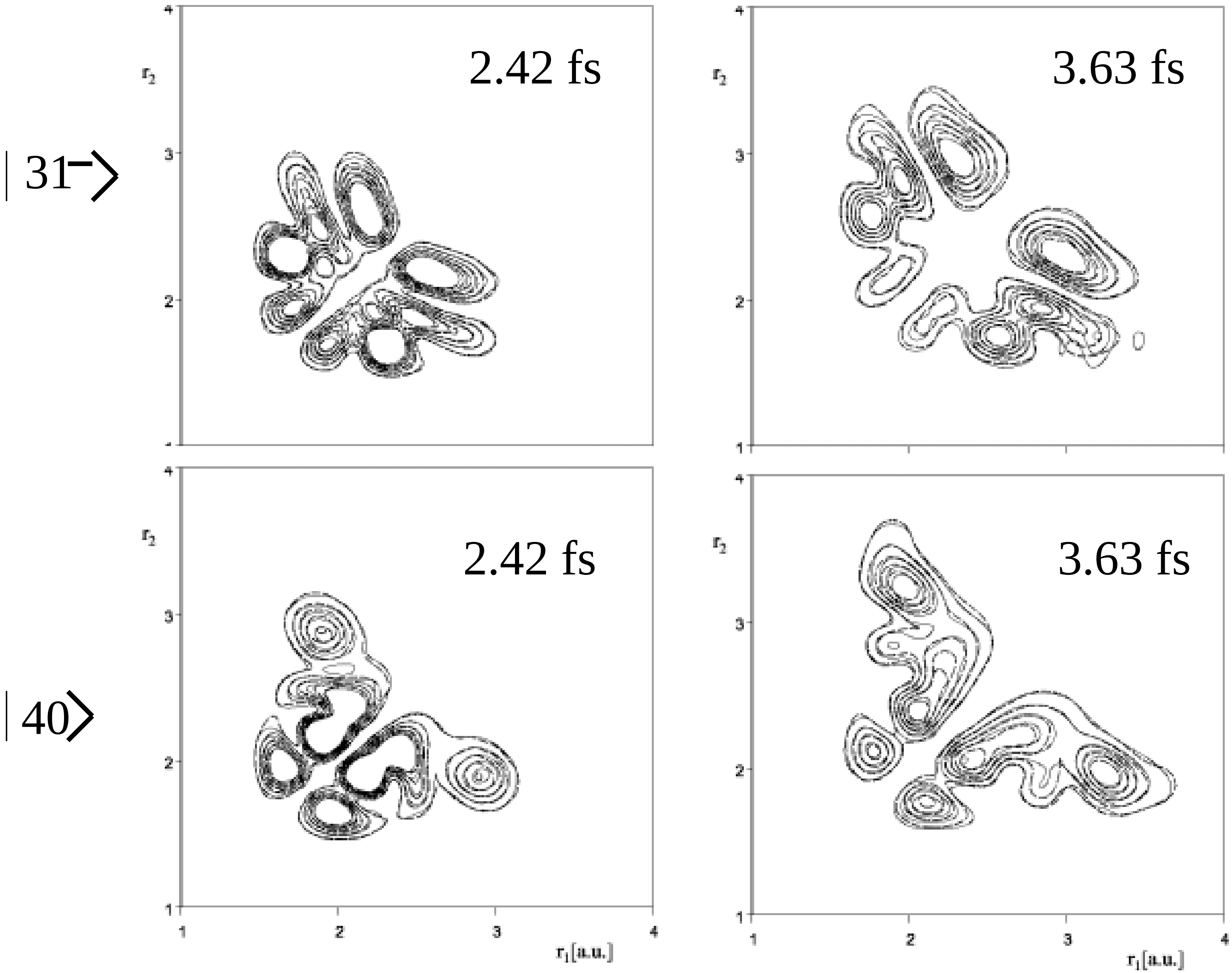
TS/SC-IVR Approach

Photodissociation of $\mathbf{H_2O}$ in the $\mathbf{A\ ^1B_1}$ Band

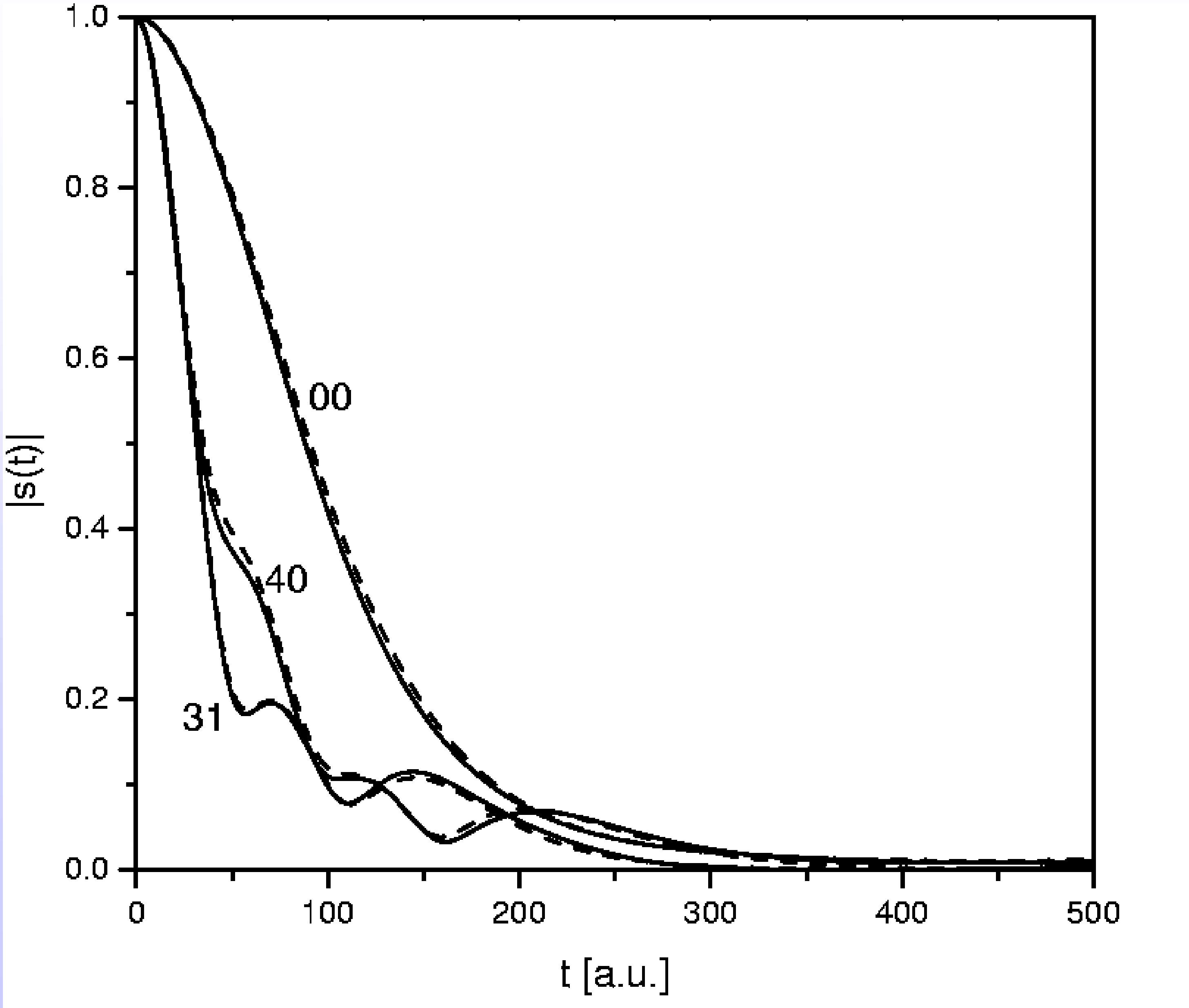
157 nm

$$H_2O(X\,^1A_1) + \hbar\omega \rightarrow H_2O(A\,^1B_1) \rightarrow H(^2S) + OH(X\,^2\Pi, n_j)$$

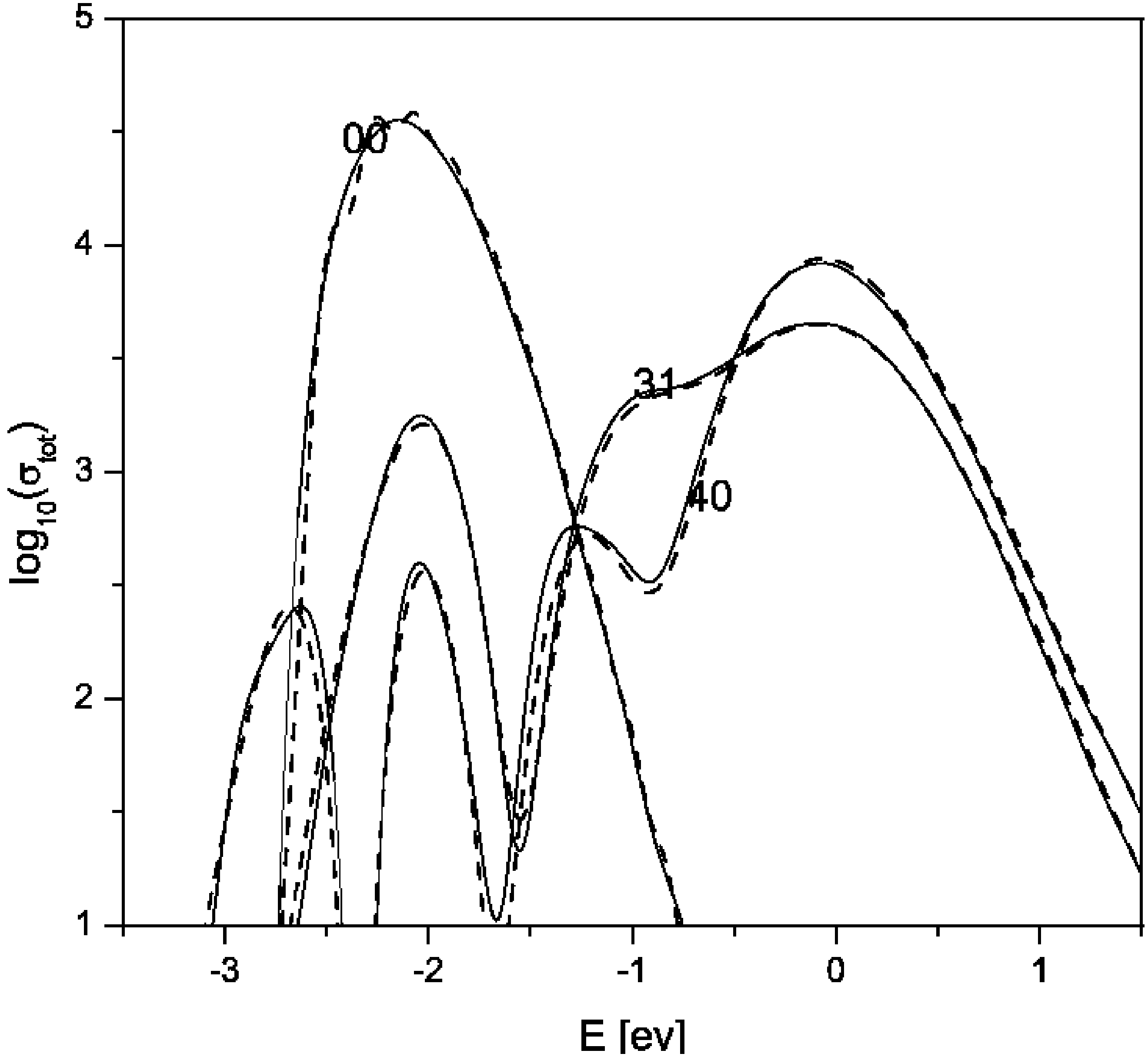
Instantaneous Time-Dependent Wavepackets



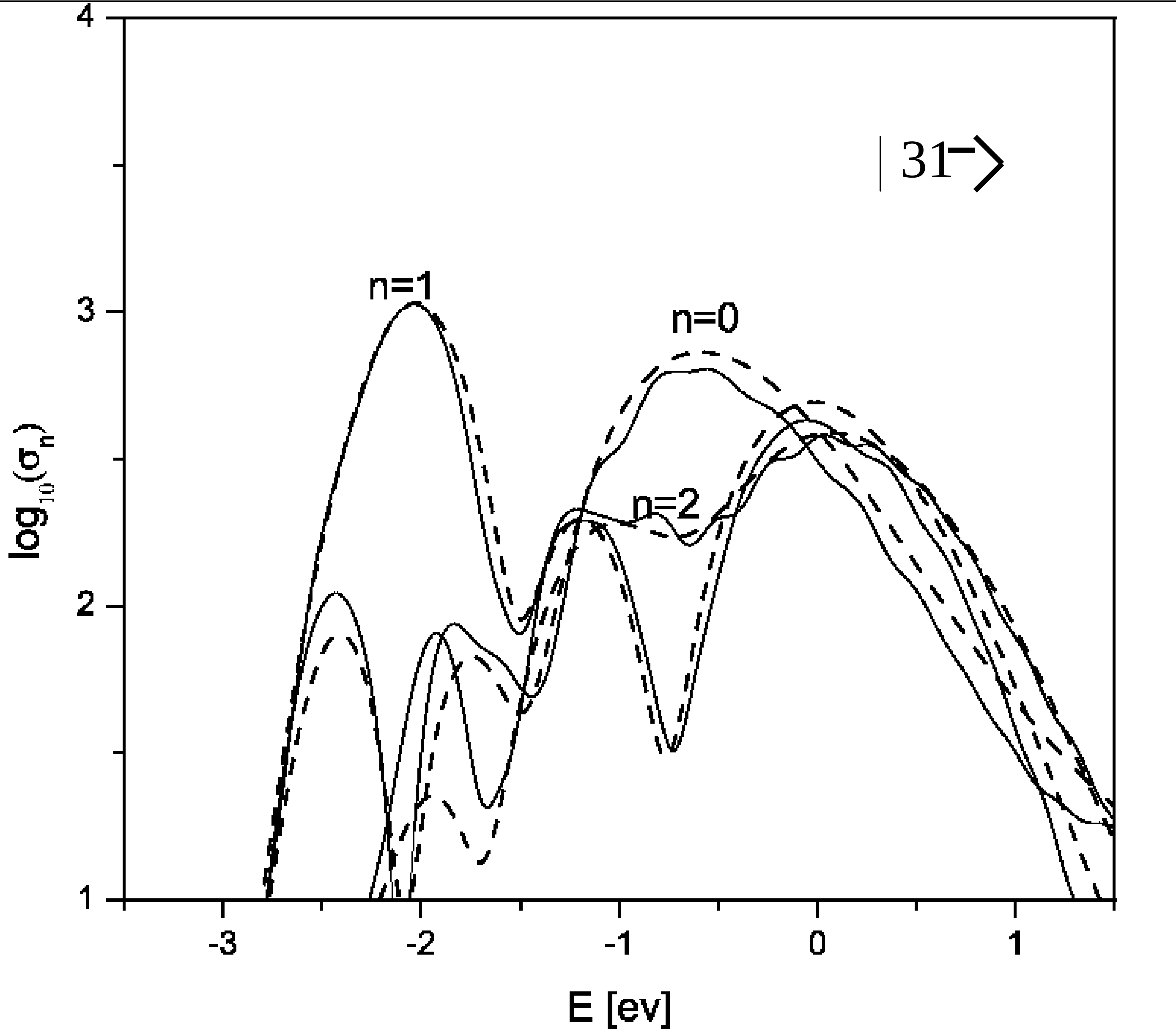
Survivial Amplitudes



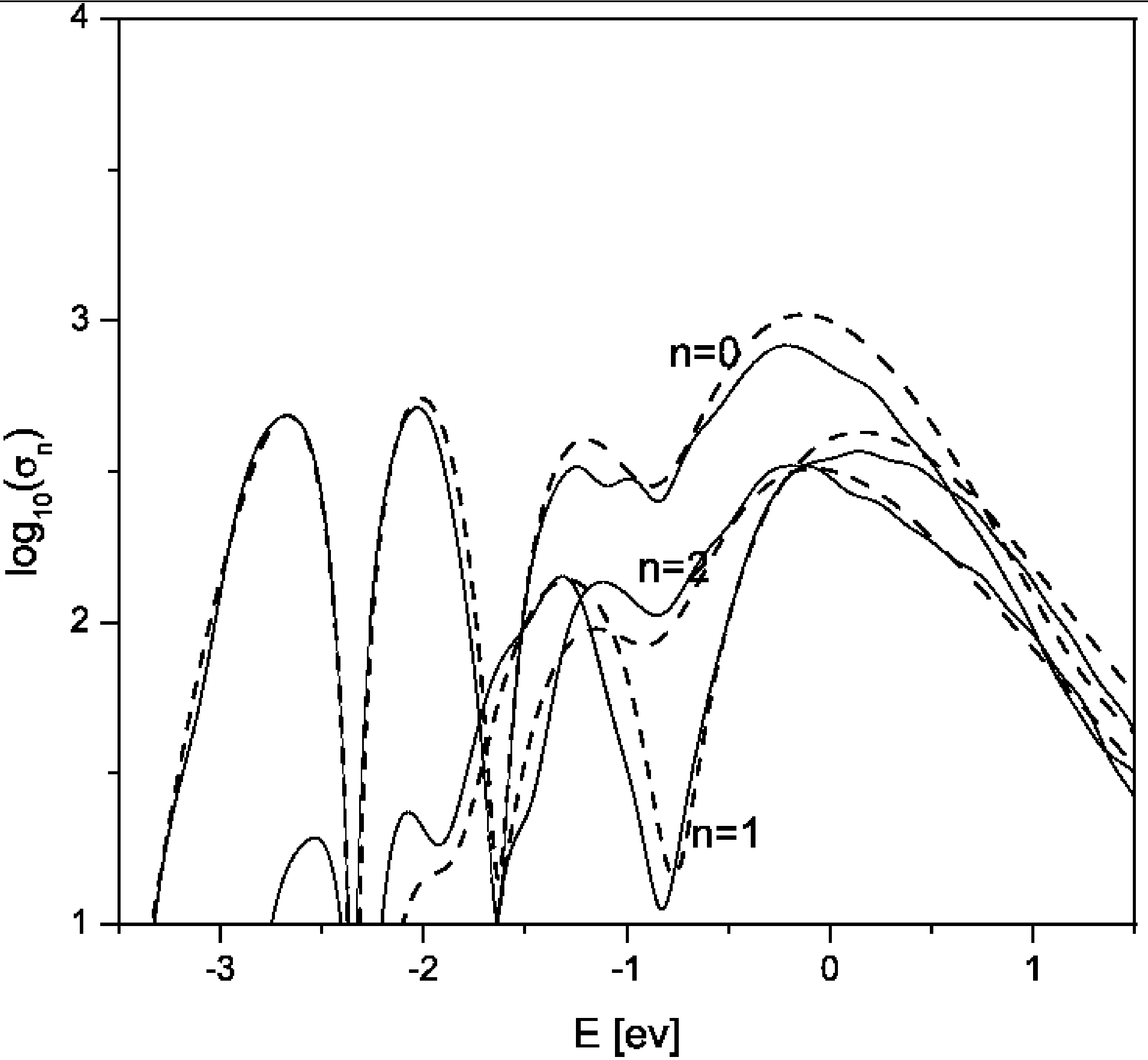
Total Photodissociation Cross Sections



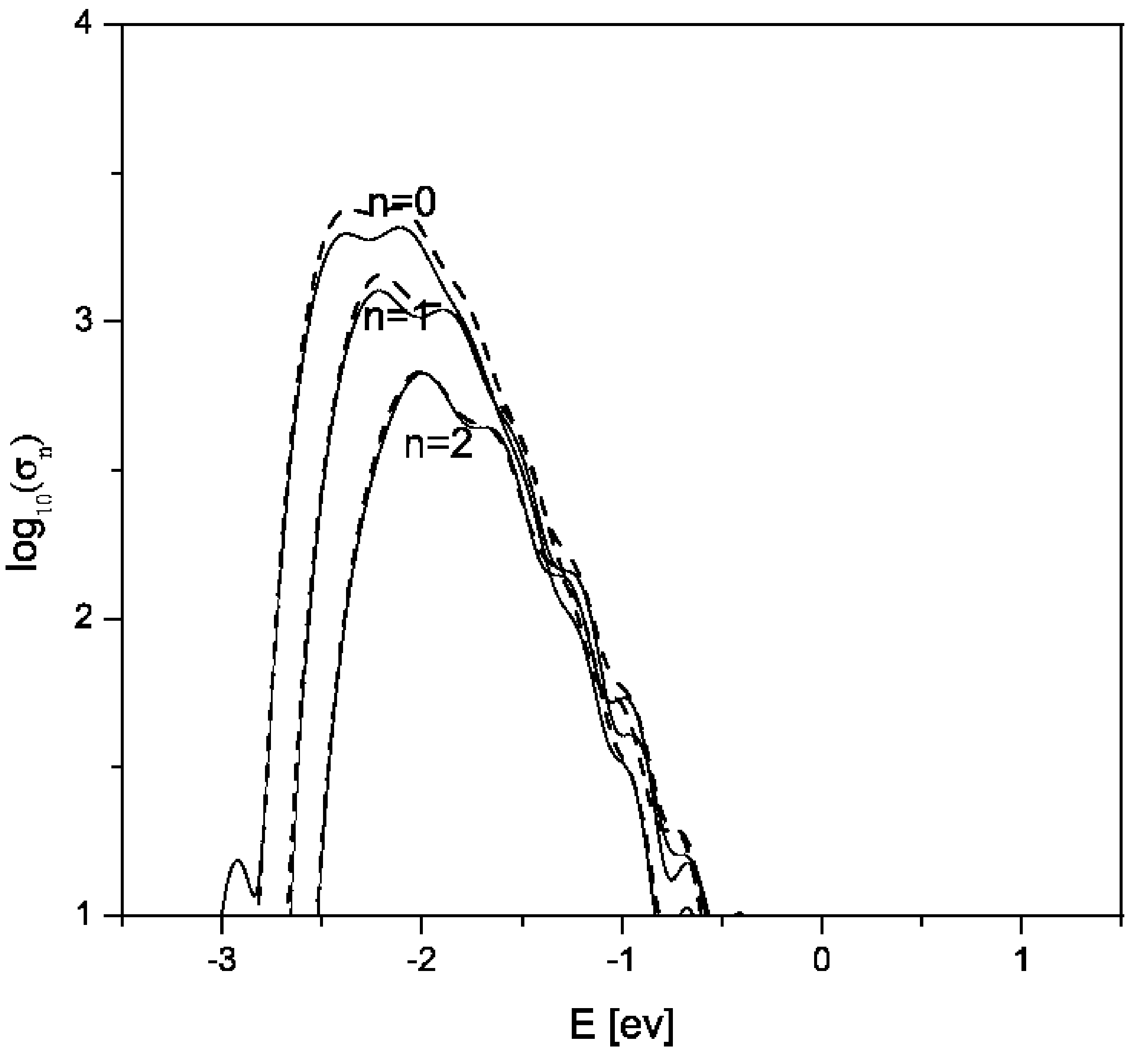
Partial Photodissociation Cross Sections



Partial Photodissociation Cross Sections



Partial Photodissociation Cross Sections



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 deep-tunneling quantum dynamics for systems with up to 20 coupled degrees of freedom.

•Work in progress involves simulations of excited-state intramolecular proton transfer in 2,2'-hydroxyphenyl-oxazole as well as calculations of the equilibrium density matrix (equilibrium properties of quantum systems).

•We have also introduced the TS/SC-IVR approach, a method that concatenates finite-time propagators and computes real-time path integrals based on the HK SC-IVR. We have shown that the approach significantly improves not only the accuracy of simulations of deep-tunneling quantum dynamics based on the HK SC-IVR but also the accuracy of computations of photo-dissociation cross sections of vibrationally hot molecules (sensitive to subtle interference effects).

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