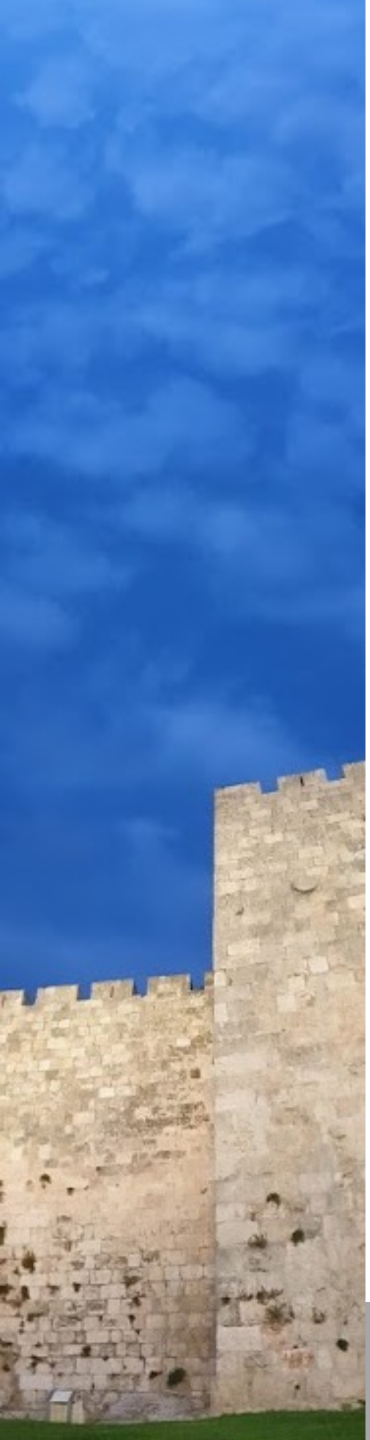


Ksenia Komarova

The Fritz Haber Center for Molecular Dynamics
The Hebrew University of Jerusalem

Surprisal of a quantum state: Dynamics, compact representation and coherence effects

Why surprisal?

$$\hat{I} = -ln\hat{\rho}$$

- Effective computational method*
- High degree of the data compaction
- Novel insights

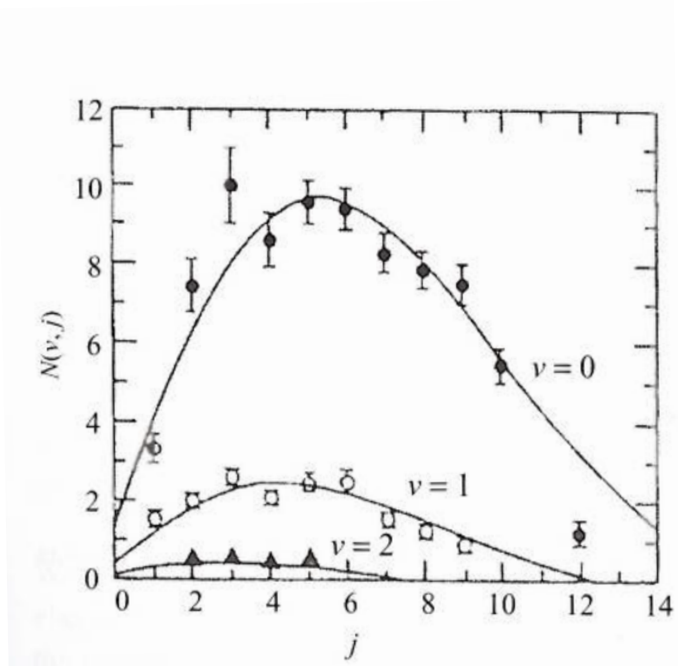
*Extensively applied in different fields:

-> to analyse the energy disposal in reaction dynamics

R. B. Bernstein and R. D. Levine, "Entropy and Chemical Change. I. Characterization of Product (and Reactant) Energy Distributions in Reactive Molecular Collisions: Information and Entropy Deficiency," J. Chem. Phys. **57**, 434-449 (1972)

-> in system biology to characterize dominant behavior patterns

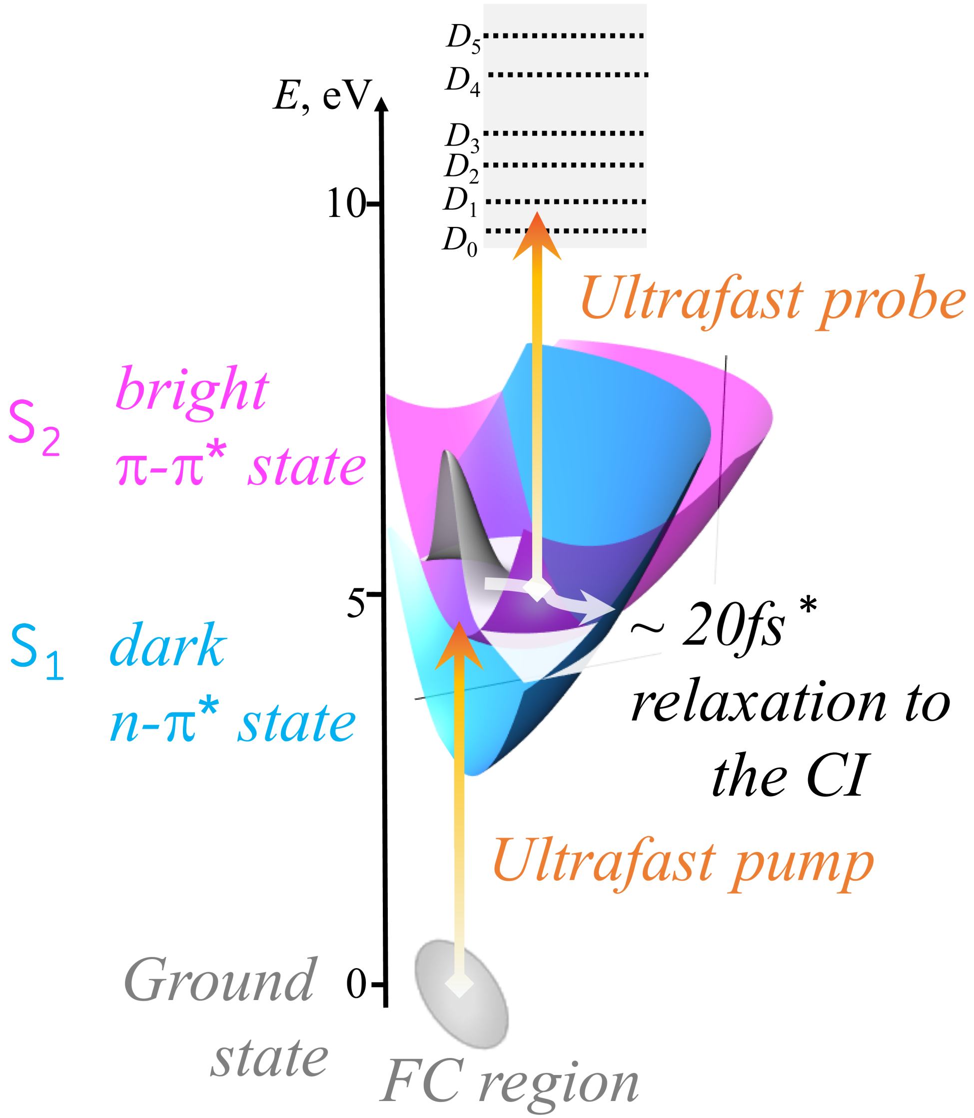
Zadran S et al. Surprisal analysis characterizes the free energy time course of cancer cells undergoing epithelial-to-mesenchymal transition. PNAS, 111:13235-13240 (2014)



Experimental HD state distributions measured for $H+D_2$ collision

Ultrafast non-radiative relaxation

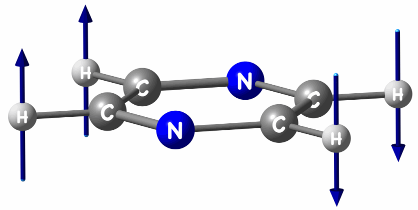
Dynamics in excited electronic states of pyrazine



*Real-time resolved pump-probe photoelectron spectroscopy experiment: Y.-I. Suzuki et al, *J Chem Phys*, 2010, 132, 174302

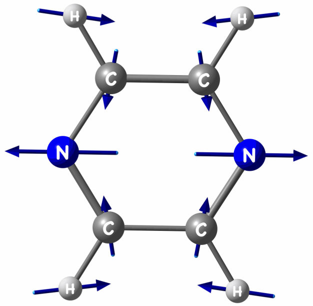
Ultrafast non-radiative relaxation

Dynamics in excited electronic states of pyrazine



Coupling mode Q_1*

->Diabatic coupling between S_2 and S_1: $\boldsymbol{\kappa}Q_1$



Tuning mode Q_2

-> Nuclear motion towards CI

MCTDH: 24-modes diabatic picture for the dynamics**

* R. Schneider, W. Domcke, Chem Phys Lett, 1988, 150, 235

** I. Burghardt et al, Phys. Scr. 2006, 73, C42

Non-adiabatic quantum dynamics on multiple electronic states

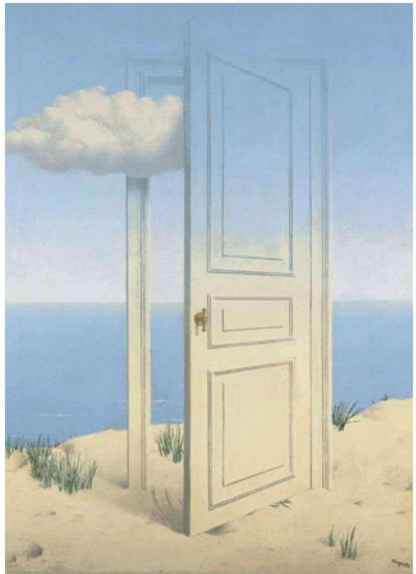
Challenge

Can we have a compact representation
for the **quantum treatment** of the dynamics?

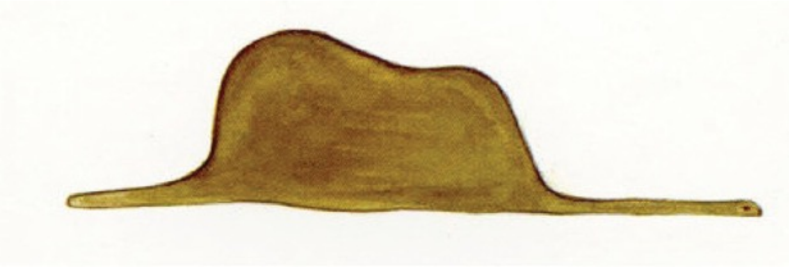
'Quantum' features

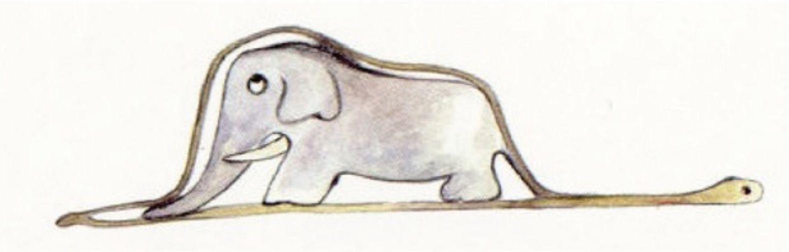
- Branching of the wave packets in configurational space
- Coherence effects on the vibrational and/or electronic dynamics
- Electronic energy redistribution for the coherent dynamics on multiple electronic states

Let us try to address the problem
from a fresh perspective!



Algebraic approach in chemical dynamics





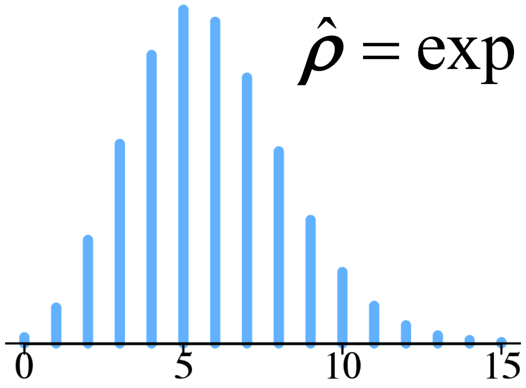
The state of the system, the density matrix:

$$\hat{\rho} = \exp\left(-\sum_k \lambda_k \hat{A}_k\right)$$

$$\hat{A}_k : \; \hat{R}, \hat{P}, \hat{H}, \ldots \qquad \text{- constraints*}$$
$$\hat{a}, \hat{a}^\dagger, \hat{a}^\dagger \hat{a}, \ldots$$

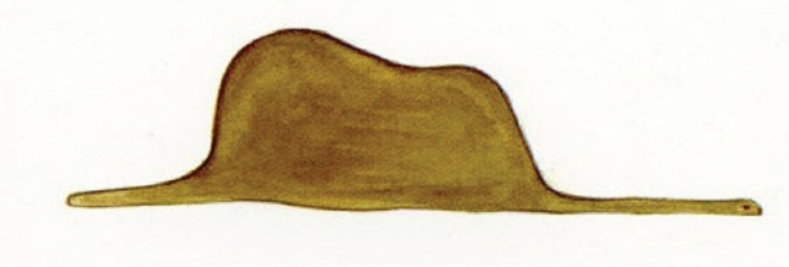
*More examples of different algebras: *Dynamical symmetry*, C.E. Wulfman (2010)

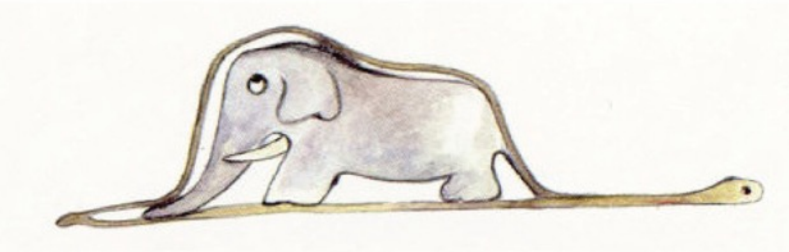
$$\hat{\rho} = \exp\left(-\beta \hat{H}\right)$$



vibrational level, ν

Algebraic approach in chemical dynamics





The state of the system, the density matrix:

$$\hat{\rho} = \exp\left(-\sum_k \lambda_k \hat{A}_k \right)$$

$$\begin{aligned} \hat{A}_k :\ & \hat{R}, \hat{P}, \hat{H}, \ldots \\ & \hat{a}, \hat{a}^\dagger, \hat{a}^\dagger \hat{a}, \ldots \end{aligned}$$

- constraints*

$$\hat{\rho}(t=0) = \exp\left(-\sum_k \lambda_k (t=0) \hat{A}_k \right) \qquad \hat{U}(t) = \exp\left\{ -\frac{i}{\hbar} \hat{H} t \right\}$$

Time evolution of the **density** via the evolution of the constraints

$$\begin{aligned} \hat{\rho}(t) &= \hat{U}(t) \hat{\rho}(t=0) \hat{U}^\dagger(t) \\ &= \exp\left[-\sum_k \lambda_k (t=0) \left\{ \hat{U}(t) \hat{A}_k \hat{U}^\dagger(t) \right\} \right] \end{aligned}$$

Y. Alhassid, R.D. Levine, *J Chem Phys*, 1977, 67, 4321

Density and its surprisal

$$\hat{\rho} = \exp\left(-\sum_k \lambda_k \hat{A}_k\right)$$

$$\hat{I} = -\ln\hat{\rho}$$

Surprisal

$$\hat{I} = \sum_k \lambda_k \hat{A}_k$$

$$\hat{I}(t=0) = \sum_k \lambda_k (t=0) \hat{A}_k$$

When time evolution of the constraints is closed:

$$i\hbar \frac{d\hat{I}}{dt} = \left[\hat{H}, \hat{I}\right] \qquad \left[\hat{H}, \hat{I}\right] = \sum_k \lambda_k \left[\hat{H}, \hat{A}_k\right] \qquad \left[\hat{H}, \hat{A}_k\right] = \sum_s g_{ks} \hat{A}_s$$

$$\hat{I}(t) = \sum_k \lambda_k (t) \hat{A}_k$$

Information about the time evolution is **compressed** to just a **vector $\boldsymbol{\lambda}(\mathbf{t})$**

Y. Alhassid, R.D. Levine, *J Chem Phys*, 1977, 67, 4321

Surprisal of a quantum state in the general case

In a given finite basis representation:

$$I_{nm}(t=0) = \langle \varphi_n | \hat{I}(t=0) | \varphi_m \rangle = \sum_k \lambda_k(t=0) A^k_{nm}$$

Equation of motion for the surprisal:

$$i\hbar \frac{d\mathbf{I}}{dt} = \left(\mathbf{H} \cdot \mathbf{I} - \mathbf{I} \cdot \mathbf{H} \right)$$

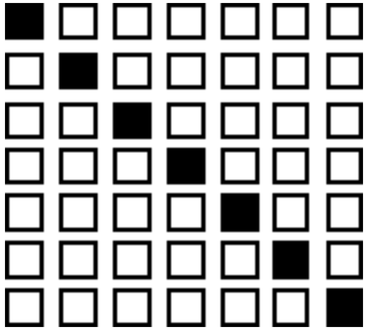
Compact representation via **dominant constraints**:

$$\hat{I}(t) \approx \sum_k \lambda_k(t) \hat{A}_k$$

Straightforward transformation between them via the spectral decomposition:

$$\hat{I} = -\ln \hat{\rho} = \sum_{s=0}^{N} \mu_s |s\rangle\langle s|$$

$$\hat{\rho} = \sum_{s=0}^{N} \exp(-\mu_s) |s\rangle\langle s|$$



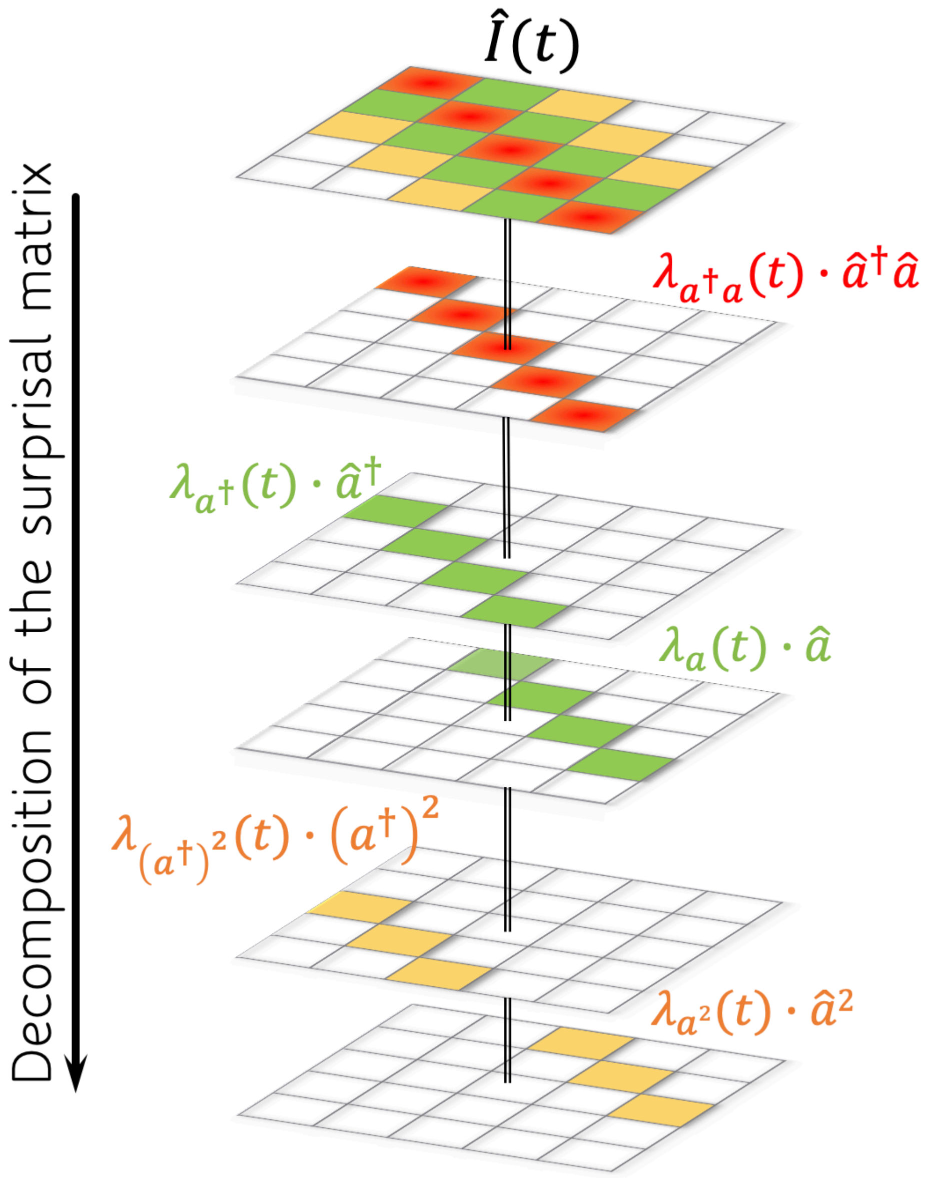
K. Komarova, F. Remacle, R.D. Levine, *J Chem Phys*, 2020, accepted.
ChemRxiv: https://doi.org/10.26434/chemrxiv.12981857.v1

Dominant constraints in the vibrational basis

$$i\hbar \frac{d\mathbf{I}}{dt} = \left(\mathbf{H}\cdot\mathbf{I} - \mathbf{I}\cdot\mathbf{H}\right)$$

$$\hat{I}(t) \approx \sum_k \boldsymbol{\lambda}_k(t)\hat{A}_k$$

$$\hat{A}_k : \ \hat{a}, \hat{a}^\dagger, \hat{a}^\dagger\hat{a}, \ldots$$



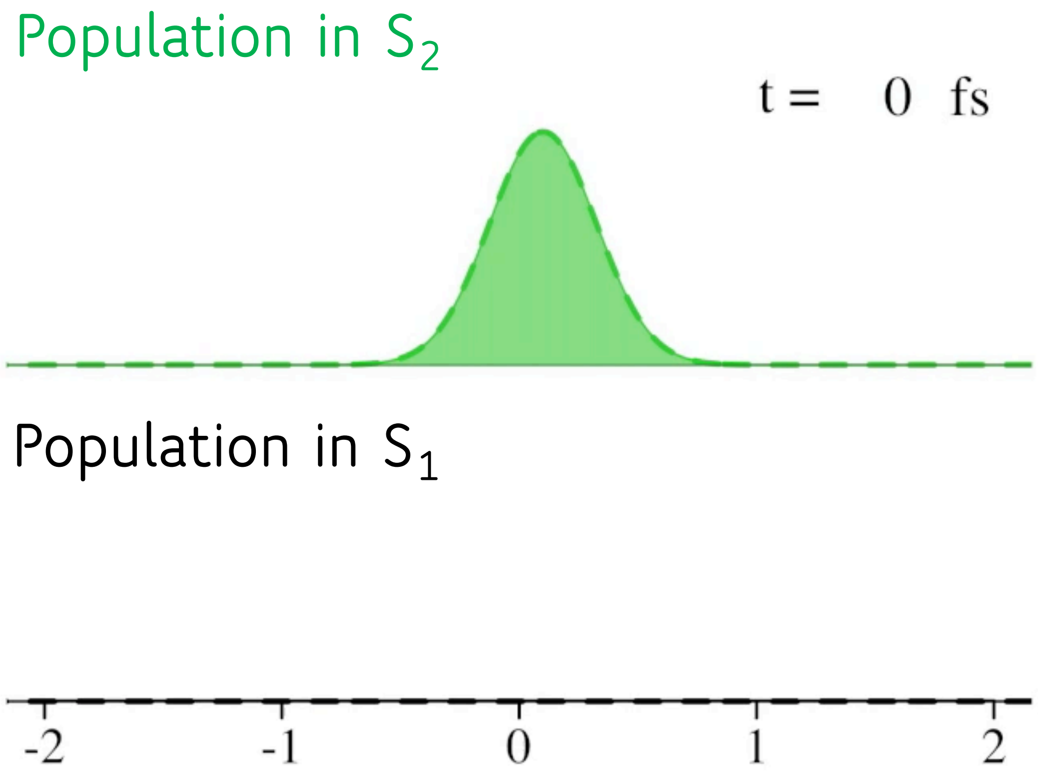
Compact representation of the non-adiabatic transfer in pyrazine

$$\left\{\hat{\mathbb{I}}_N, \hat{a}, \hat{a}^\dagger, \hat{a}^\dagger\hat{a}\right\} \otimes \left\{\hat{\mathbb{I}}_e, \hat{\boldsymbol{\sigma}}_x, \hat{\boldsymbol{\sigma}}_y, \hat{\boldsymbol{\sigma}}_z\right\}$$

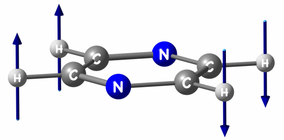
$$\hat{H} = \hat{H}_0 + \hat{V}$$

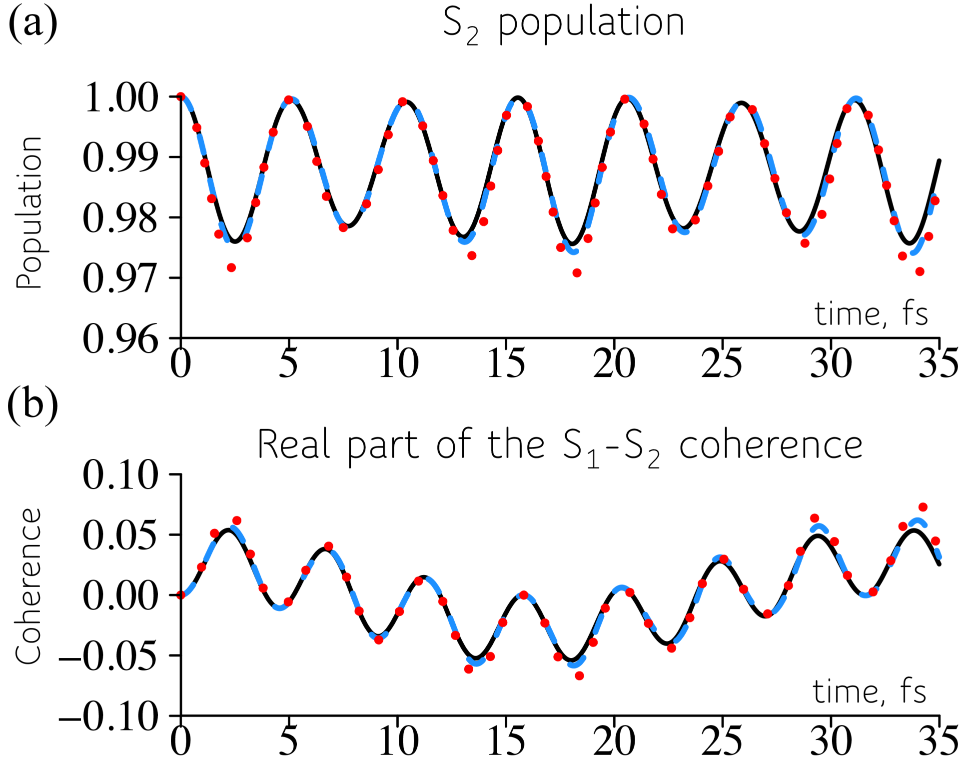
$$\hat{H}_0 = \hbar\omega \cdot \hat{\mathbb{I}}_e \otimes \left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) + V_0 \cdot \hat{\sigma}_z \otimes \hat{\mathbb{I}}_N$$

$$\hat{V} = \hat{\sigma}_x \otimes \kappa\left(\hat{a} + \hat{a}^\dagger\right)$$



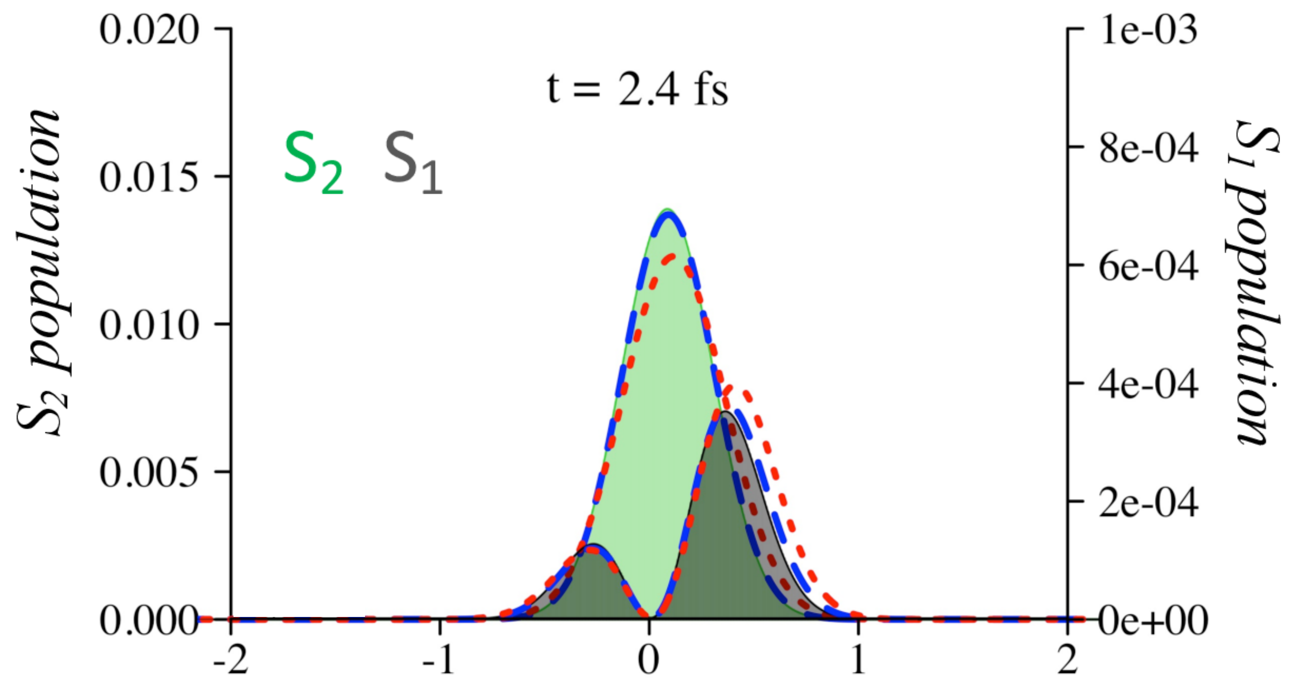
Coupling mode





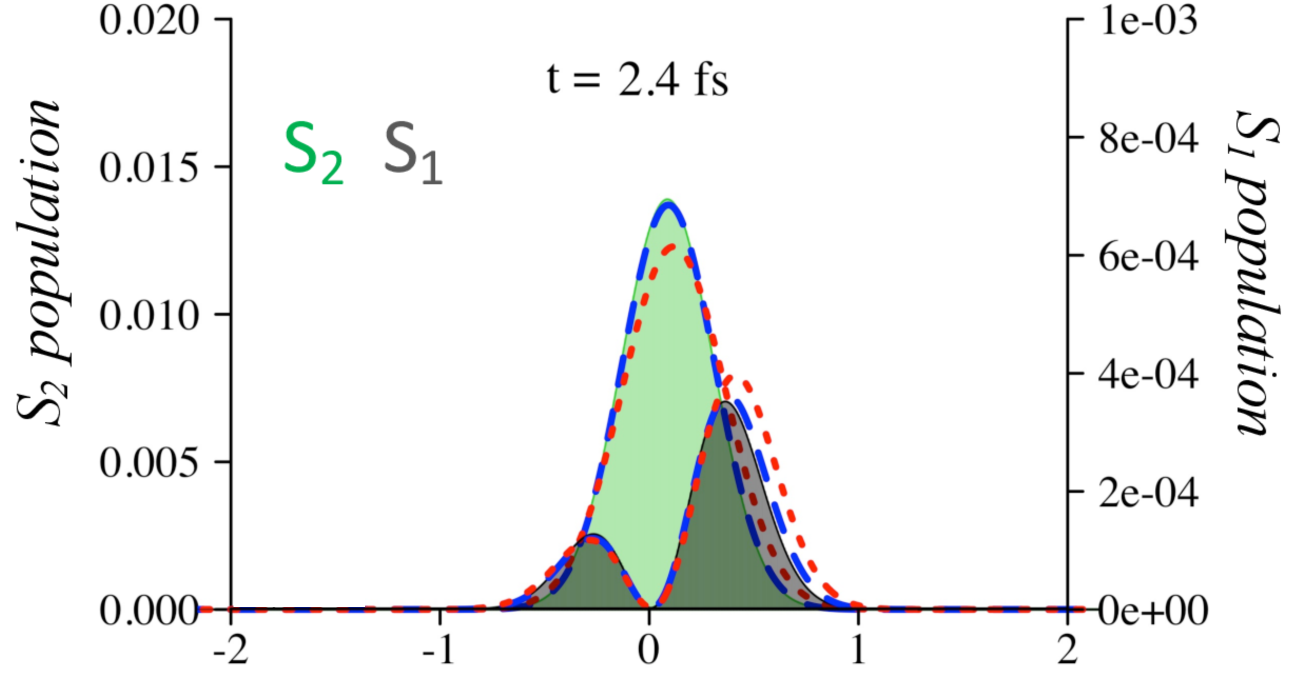
Dominant constraints

	Gelfand basis	Dominant constraints $\hat{I}(t) \approx \sum_k \boldsymbol{\lambda}_k(t) \hat{A}_k$
Small initial shift	400	16 $\left\{\hat{\mathbb{I}}_N, \hat{a}, \hat{a}^\dagger, \hat{a}^\dagger\hat{a}\right\} \otimes \left\{\hat{\mathbb{I}}_e, \hat{\boldsymbol{\sigma}}_x, \hat{\boldsymbol{\sigma}}_y, \hat{\boldsymbol{\sigma}}_z\right\}$
Large initial shift	1600	24 $\left\{\hat{\mathbb{I}}_N, \hat{a}, \hat{a}^\dagger, \hat{a}^2, (\hat{a}^\dagger)^2 \hat{a}^\dagger\hat{a}\right\} \otimes \left\{\hat{\mathbb{I}}_e, \hat{\boldsymbol{\sigma}}_x, \hat{\boldsymbol{\sigma}}_y, \hat{\boldsymbol{\sigma}}_z\right\}$



Dominant constraints

	Gelfand basis	Dominant constraints
Small initial shift	400	16 $\left\{\hat{\mathbb{I}}_N,\hat{a},\hat{a}^\dagger,\hat{a}^\dagger\hat{a}\right\}\otimes\left\{\hat{\mathbb{I}}_e,\hat{\boldsymbol{\sigma}}_x,\hat{\boldsymbol{\sigma}}_y,\hat{\boldsymbol{\sigma}}_z\right\}$
Large initial shift	1600	24 $\left\{\hat{\mathbb{I}}_N,\hat{a},\hat{a}^\dagger,\hat{a}^2,(\hat{a}^\dagger)^2\hat{a}^\dagger\hat{a}\right\}\otimes\left\{\hat{\mathbb{I}}_e,\hat{\boldsymbol{\sigma}}_x,\hat{\boldsymbol{\sigma}}_y,\hat{\boldsymbol{\sigma}}_z\right\}$

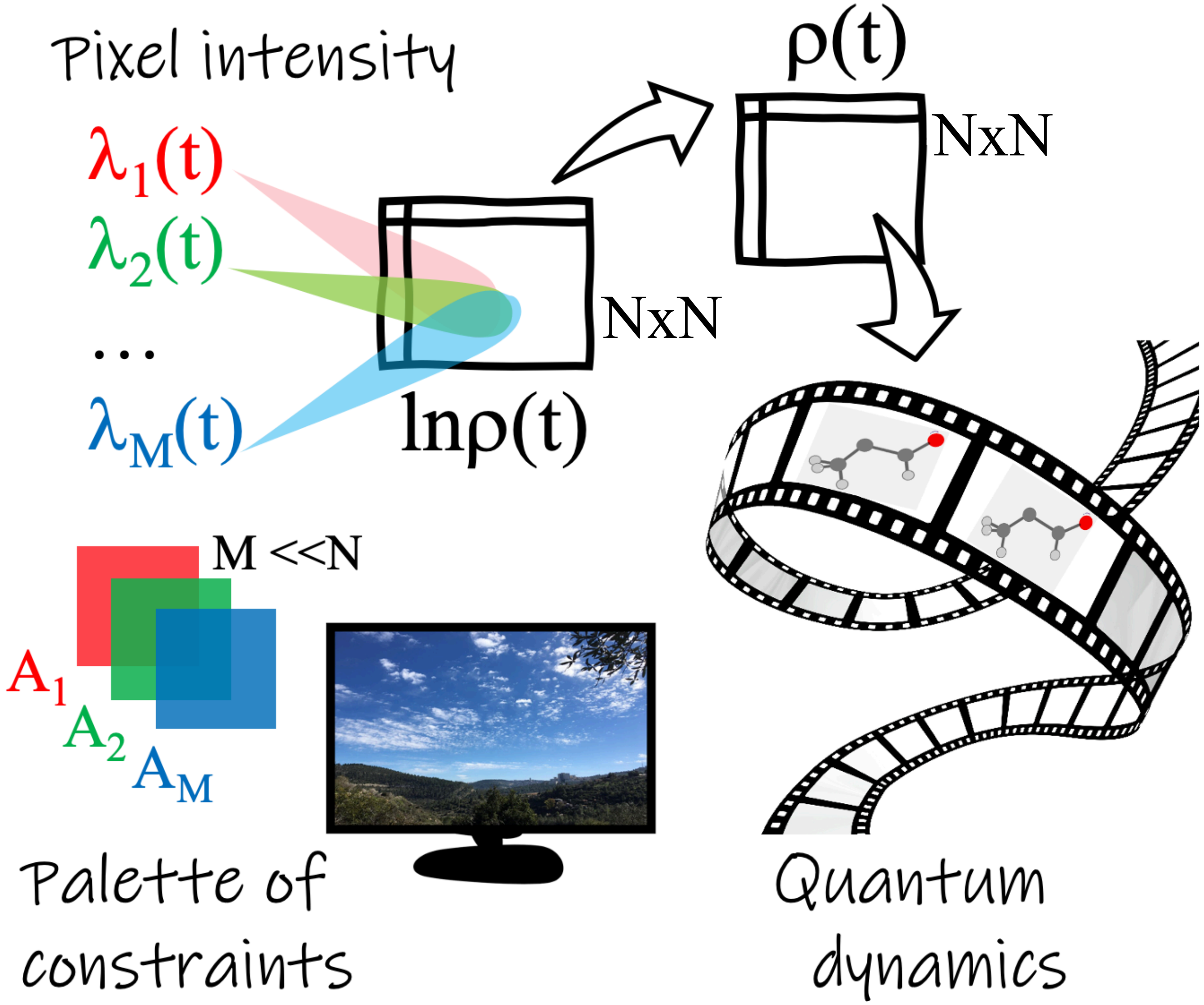


Constraints responsible for the bi-gaussian shape of the S_1 wave packet

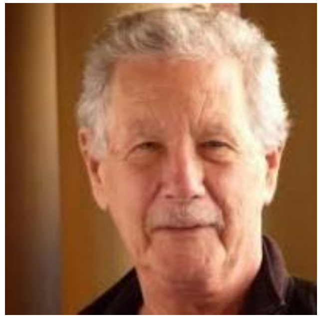
$$|1\rangle\hat{a}\langle 2|, |2\rangle\hat{a}\langle 1|$$

$$|1\rangle\hat{a}^\dagger\langle 2|, |2\rangle\hat{a}^\dagger\langle 1|$$

Surprisal based quantum dynamics



Acknowledgements



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Yale University

Prof. N. Tishby
Hebrew University

Prof. S. Kais
Purdue University

COPAC
Coherent Optical PArallel Computing

Thank you for your attention!

Dominant constraints in the vibrational basis

Set of 16 **time-independent constraints** for the direct product Hilbert space of electronic and nuclear degrees of freedom

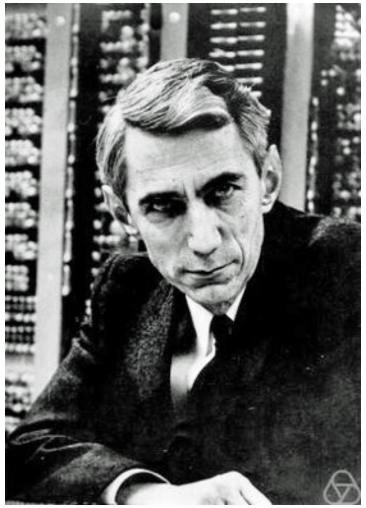
	$\hat{\mathbb{I}}_N$	$\hat{a}$	$\hat{a}^\dagger$	$\hat{a}^\dagger \hat{a}$
$\|1\rangle\langle 1\|$	$\|1\rangle \hat{\mathbb{I}}_N \langle 1\|$	$\|1\rangle \hat{a} \langle 1\|$	$\|1\rangle \hat{a}^\dagger \langle 1\|$	$\|1\rangle \hat{a}^\dagger \hat{a} \langle 1\|$
$\|2\rangle\langle 2\|$	$\|2\rangle \hat{\mathbb{I}}_N \langle 2\|$	$\|2\rangle \hat{a} \langle 2\|$	$\|2\rangle \hat{a}^\dagger \langle 2\|$	$\|2\rangle \hat{a}^\dagger \hat{a} \langle 2\|$
$\|1\rangle\langle 2\|$	$\|1\rangle \hat{\mathbb{I}}_N \langle 2\|$	$\|1\rangle \hat{a} \langle 2\|$	$\|1\rangle \hat{a}^\dagger \langle 2\|$	$\|1\rangle \hat{a}^\dagger \hat{a} \langle 2\|$
$\|2\rangle\langle 1\|$	$\|2\rangle \hat{\mathbb{I}}_N \langle 1\|$	$\|2\rangle \hat{a} \langle 1\|$	$\|2\rangle \hat{a}^\dagger \langle 1\|$	$\|2\rangle \hat{a}^\dagger \hat{a} \langle 1\|$

$$\hat{I}(t) \approx \sum_k \lambda_k(t) \hat{A}_k$$

Surprisal analysis and maximal entropy formalism

1948

Information Theory



Claude Shannon

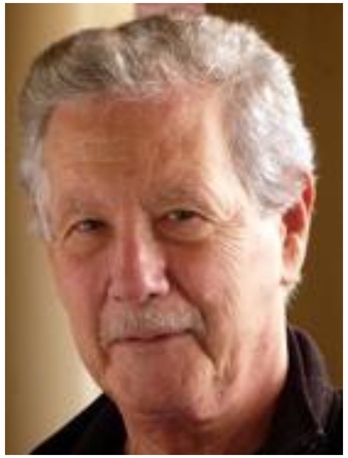
1957

Information Theory
and
Statistical Mechanics

Edwin Jaynes

1972

Information Theory
and
Chemical Change



Richard Bernstein & Raphael Levine

E.C. Kemble
A. Katz
E.H. Wichman
J.L. Kinsey
And many other..

Density and its surprisal

$$\hat{\rho} = \exp\left(-\sum_k \lambda_k \hat{A}_k \right)$$

$$\hat{I} = -ln\,\hat{\rho}$$

Surprisal

$$\hat{I} = \sum_k \lambda_k \hat{A}_k$$

$$\hat{\rho}(t) = \hat{U}(t)\hat{\rho}(t=0)\hat{U}^{\dagger}(t)$$

$$\hat{\rho}^2(t) = \hat{\rho}(t)\cdot\hat{\rho}(t) = \hat{U}(t)\hat{\rho}(t=0)\hat{U}^{\dagger}(t)\cdot\hat{U}(t)\hat{\rho}(t=0)\hat{U}^{\dagger}(t) = \hat{U}(t)\hat{\rho}^2(t=0)\hat{U}^{\dagger}(t)$$

Evolution of the surprisal

$$\hat{I}(t) = -\ln\hat{\rho}(t) = \hat{U}(t)\left[-\ln\hat{\rho}(t)(t=0)\right]\hat{U}^{\dagger}(t)$$

$$i\hbar\frac{d\hat{I}(t)}{dt} = \left[\hat{H},\hat{I}(t)\right]$$