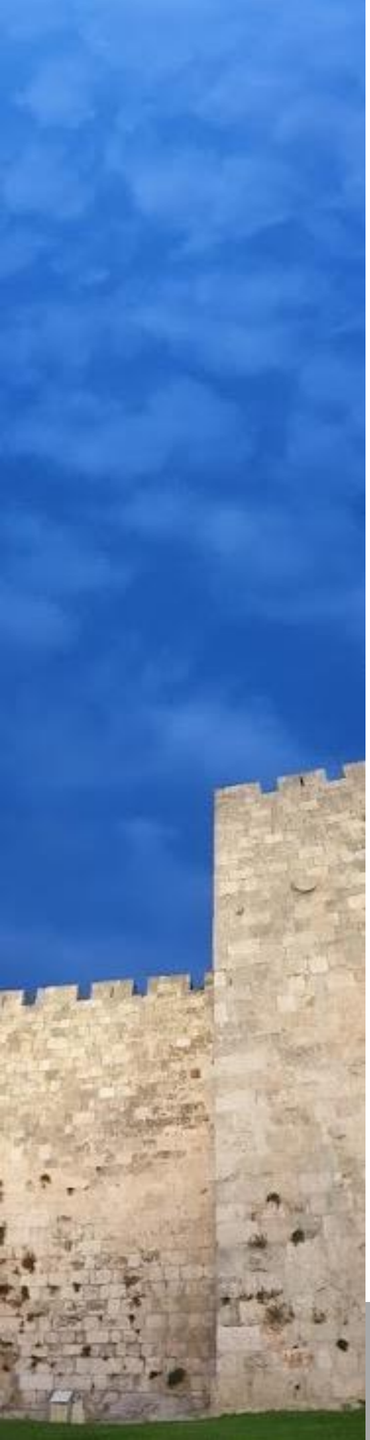
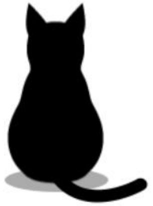


Ksenia Komarova

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

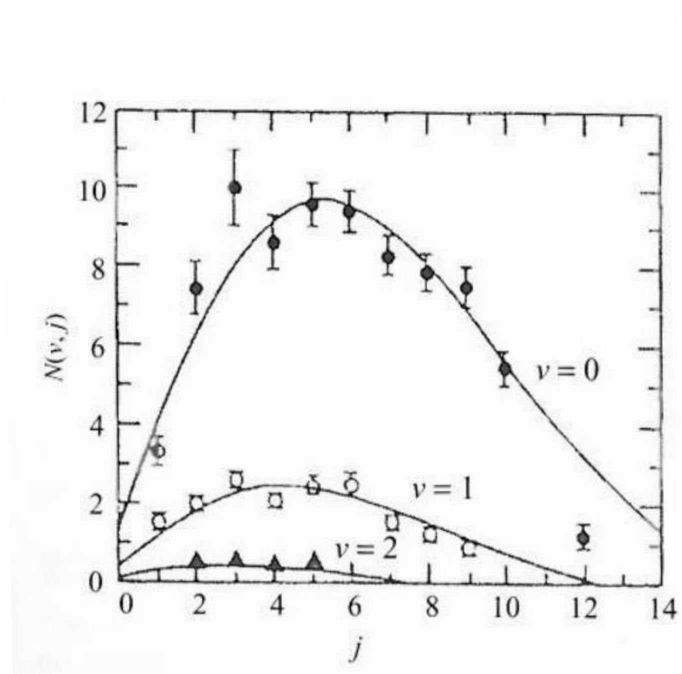
*Extensively applied in different fields:

-> 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

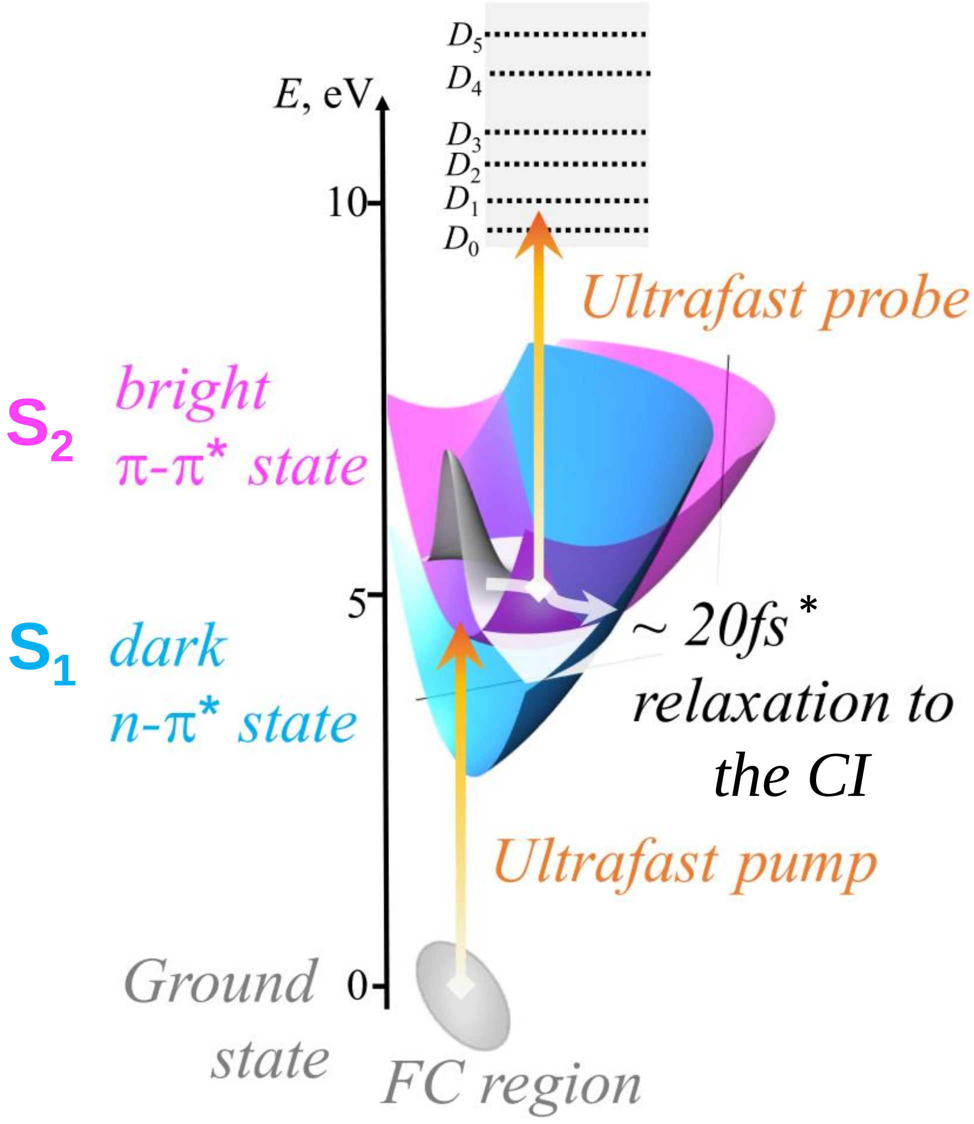
Zadran et al. Surprisal analysis characterizes the free energy time course of cancer cells undergoing epithelial-to-mesenchymal transition. PNAS, 111:13235–13240 (2014)



Experimental HD state distributions measured for H+D_2 collision

Ultrafast non-radiative relaxation

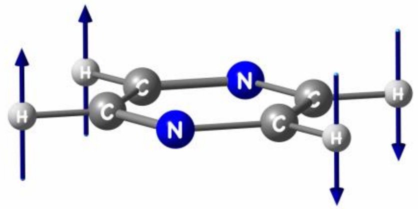
Dynamics in excited electronic states of pyrazine



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

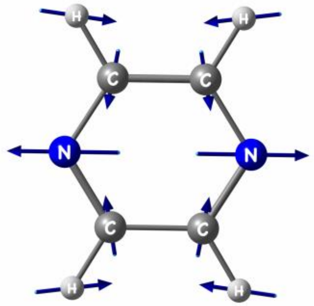
Ultrafast non-radiative relaxation

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

* 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

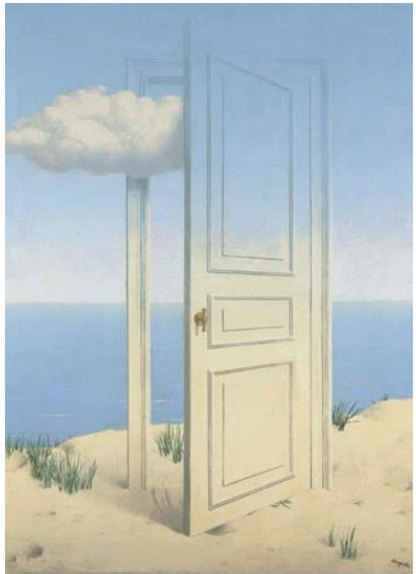
Challenge

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

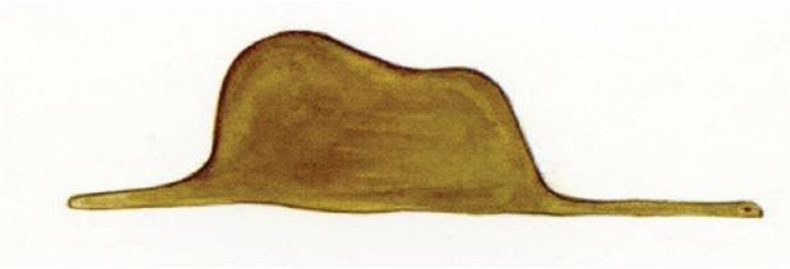
'Quantum' features

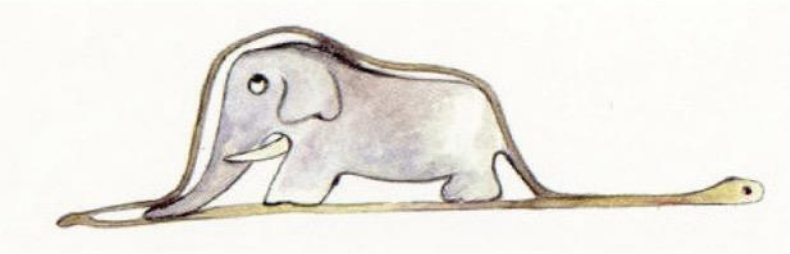
- Branching of the wave packets in configurational space
- Coherence effects on the vibrational and/or electronic dynamics
- Electronic energy redistribution for the coherent dynamics on multiple electronic states

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



Algebraic approach in chemical dynamics





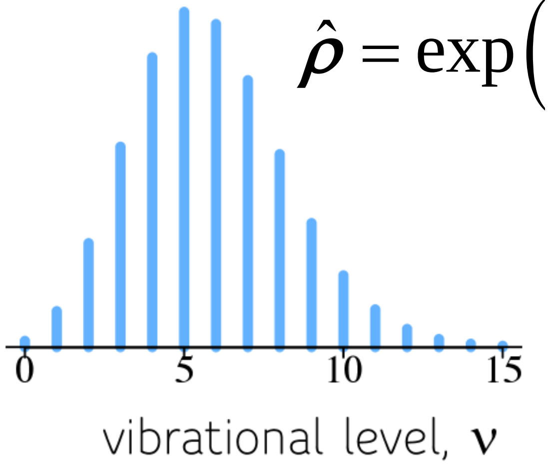
The state of the system, the density matrix:

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

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

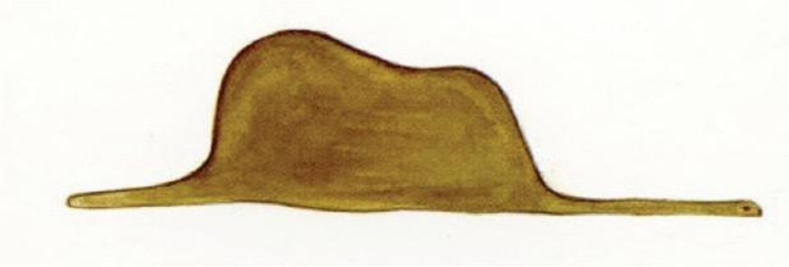
\- constraints*

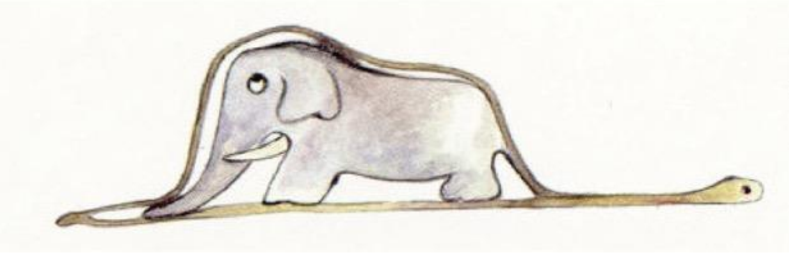
*More examples of different algebras:
Dynamical symmetry, C.E. Wulfman (2010



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

Algebraic approach in chemical dynamics





The state of the system, the density matrix:

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

$$\hat{A}_k : \; \hat{R}, \hat{P}, \hat{H}, \ldots \quad \hat{a}, \hat{a}^{\dagger}, \hat{a}^{\dagger}\hat{a}, \ldots$$

- 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**

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

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

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:

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

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

ormation about the time evolution is **compressed** to just a **vector** **λ(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:

$$I_{nm}(t=0)=\left\langle \varphi_n \middle| \hat{I}(t=0) \middle| \varphi_m \right\rangle = \sum_k \lambda_k(t=0) A_{nm}^{k}$$

Equation of motion for the surprisal:

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

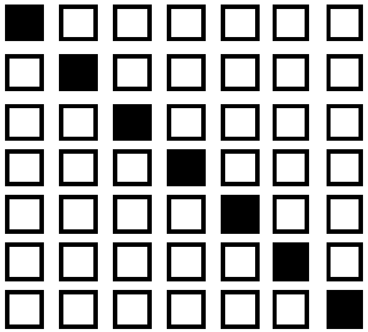
Compact representation via **dominant constraints**:

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

Straightforward transformation between them via the spectral decomposition:

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

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



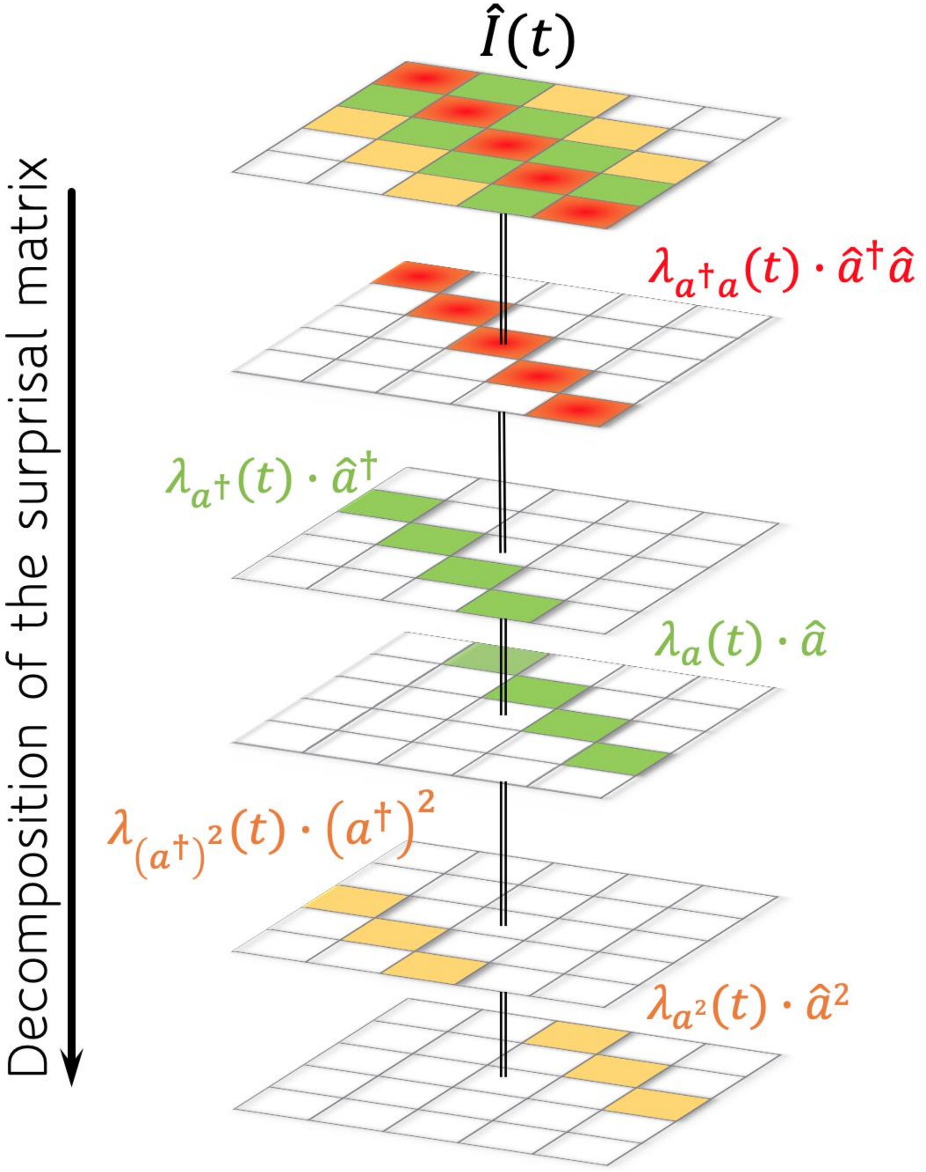
K. Komarova, F. Remacle, R.D. Levine, *J Chem Phys*, 2020, accepted.
ChemRxiv: https://doi.org/10.26434/chemrxiv.12981857.v1

Dominant constraints in the vibrational basis

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

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

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



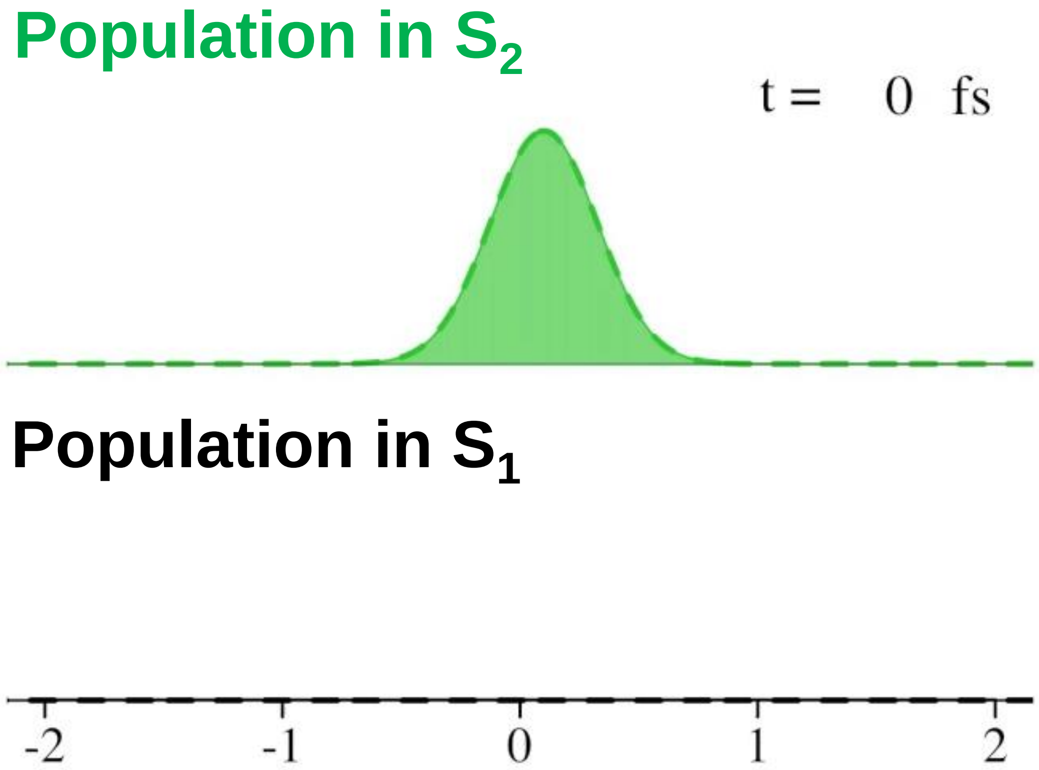
Compact representation of the non-adiabatic transfer in pyrazine

$$\left\{I_N, \hat{a}, \hat{a}^\dagger, \hat{a}^\dagger\hat{a}\right\} \otimes \left\{I_e, \hat{\boldsymbol{\sigma}}_x, \hat{\boldsymbol{\sigma}}_y, \hat{\boldsymbol{\sigma}}_z\right\}$$

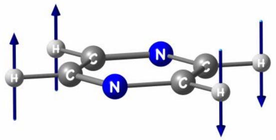
$$\hat{H} = \hat{H}_0 + \hat{V}$$

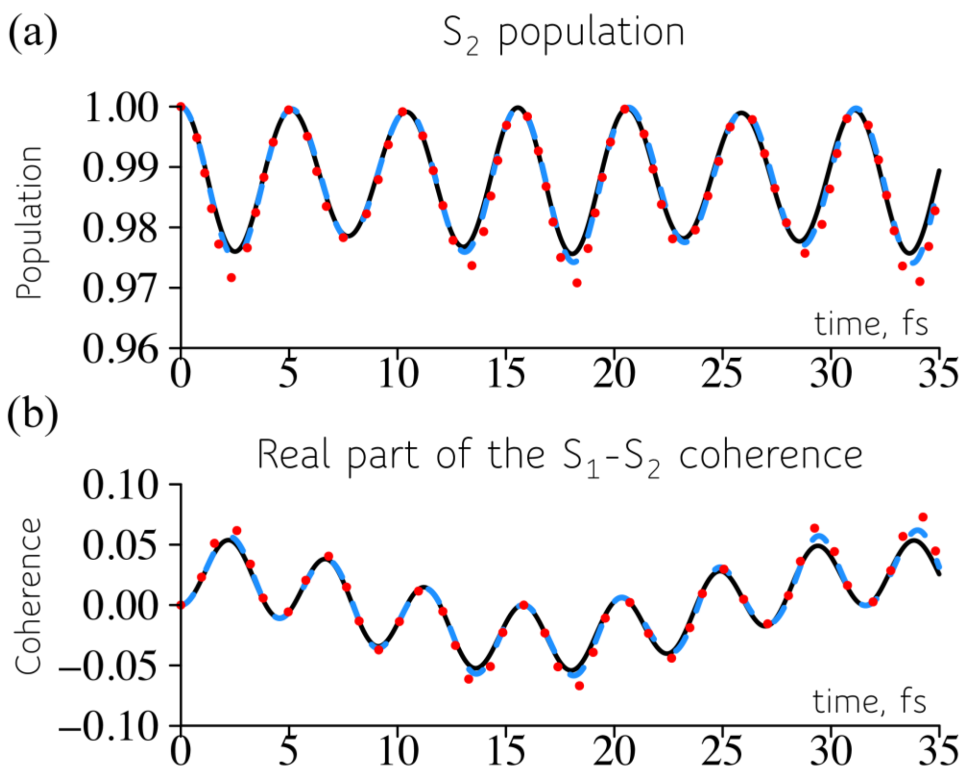
$$\hat{H}_0 = \hbar\omega \cdot I_e \otimes \left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) + V_0 \cdot \hat{\sigma}_z \otimes I_N$$

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



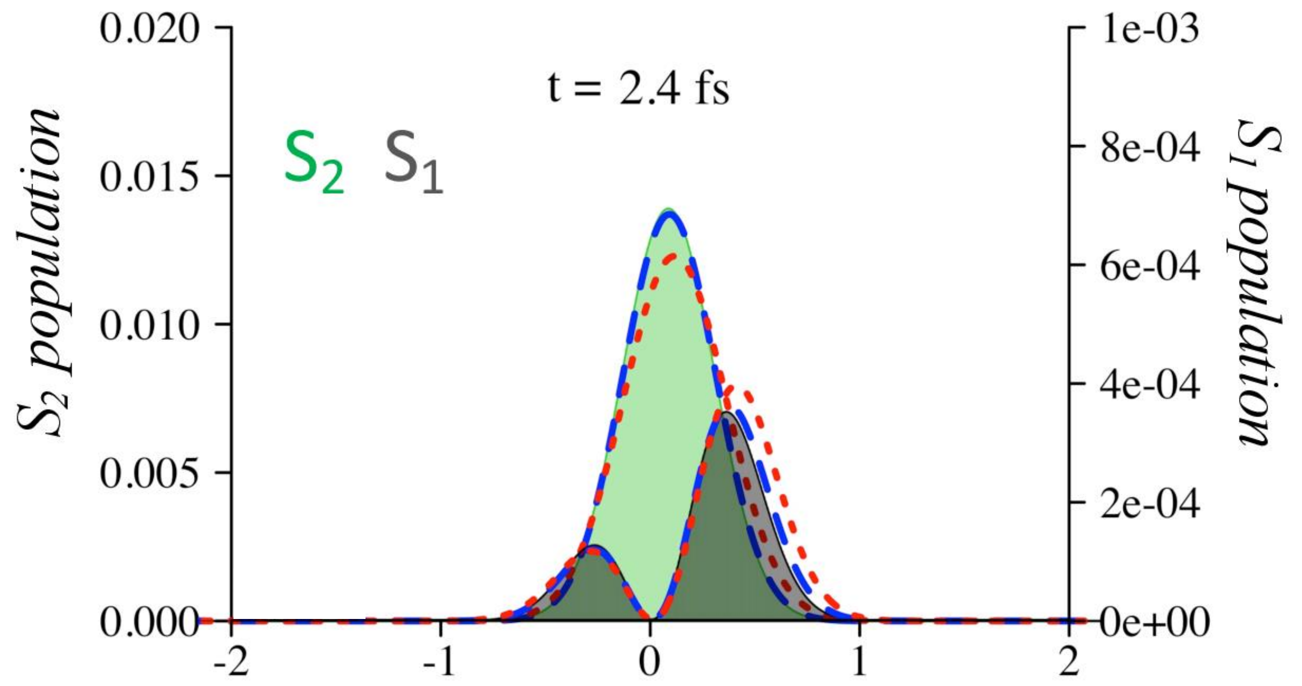
Coupling mode





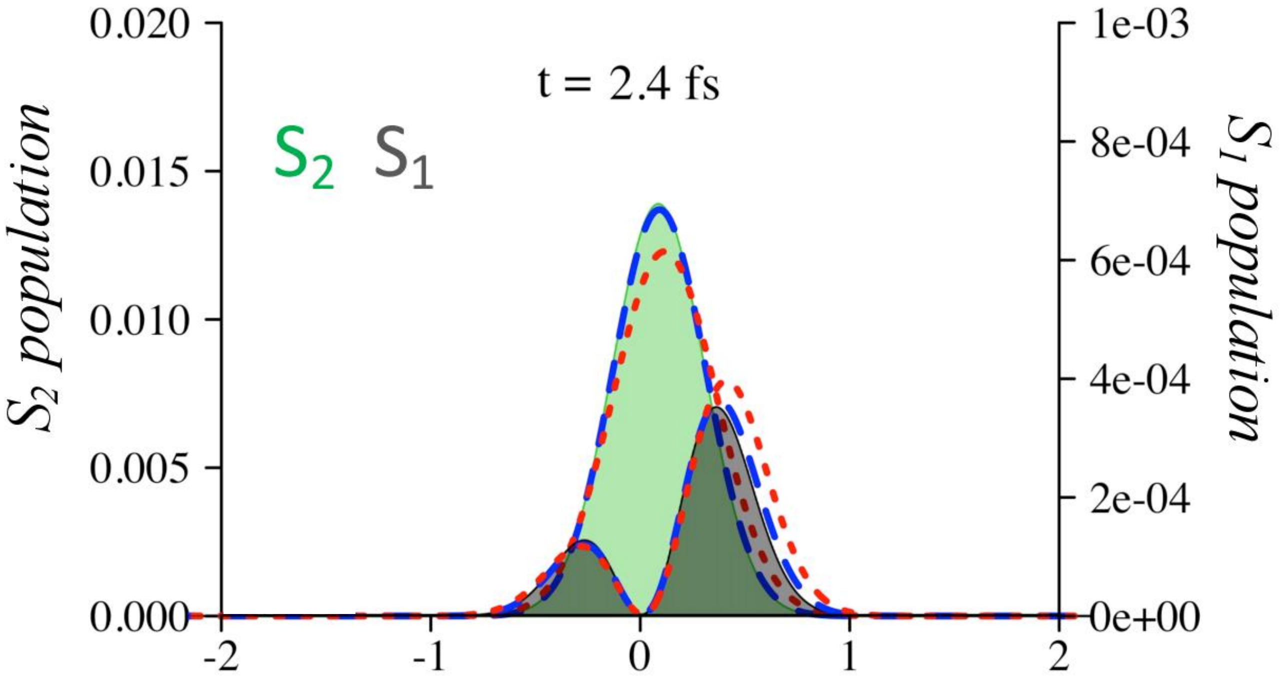
Dominant constraints

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



Dominant constraints

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

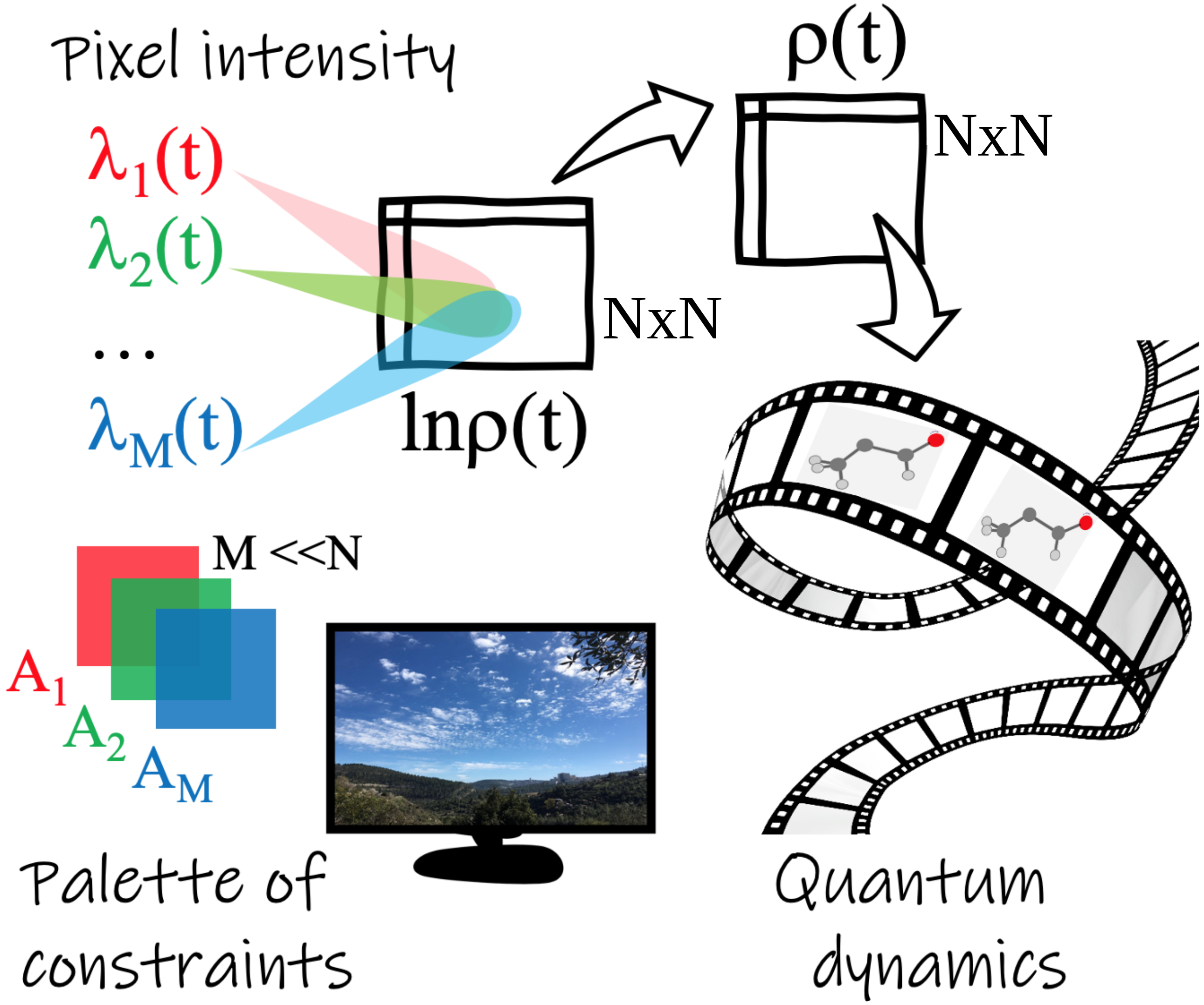


Constraints responsible for the bi-gaussian shape of the S_1 wave packet

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

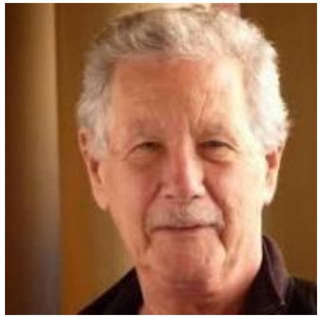
$$|1\rangle\hat{a}^\dagger\langle 2|, |2\rangle\hat{a}^\dagger\langle 1|$$

Surprisal based quantum dynamics



Acknowledgements

COPAC
Coherent Optical PArallel Computing



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Yale University

Prof. N. Tishby
Hebrew University

Prof. S. Kais
Purdue University

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

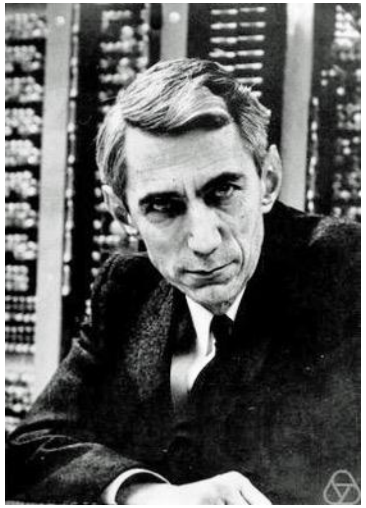
	$\hat{\mathbb{I}}_N$	$\hat{a}$	$\hat{a}^\dagger$	$\hat{a}^\dagger\hat{a}$
$\|1\rangle\langle 1\|$	$\|1\rangle\hat{\mathbb{I}}_N\langle 1\|$	$\|1\rangle\hat{a}\langle 1\|$	$\|1\rangle\hat{a}^\dagger\langle 1\|$	$\|1\rangle\hat{a}^\dagger\hat{a}\langle 1\|$
$\|2\rangle\langle 2\|$	$\|2\rangle\hat{\mathbb{I}}_N\langle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

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

Surprisal analysis and maximal entropy formalism

1948

Information Theory



Claude Shannon

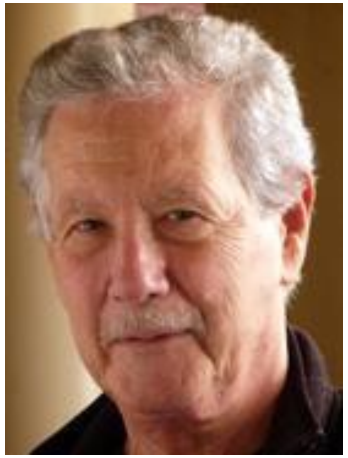
1957

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 surprisa

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

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