Analog quantum simulation of chemical dynamics

arXiv:2012.01852

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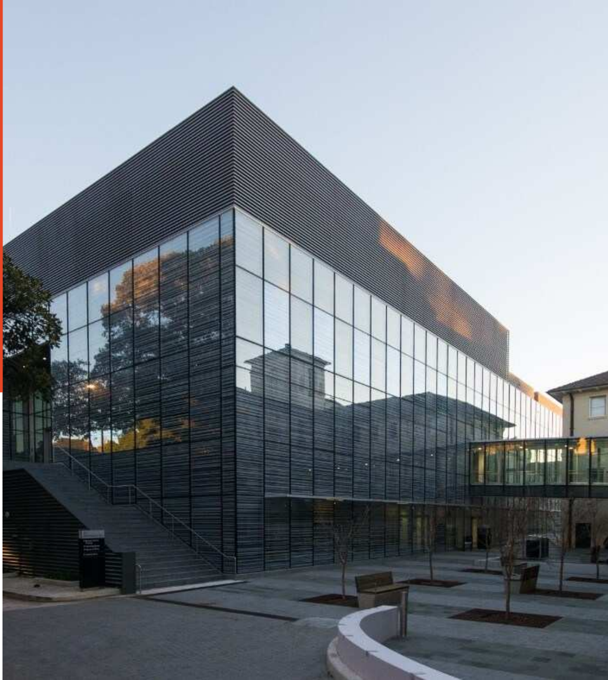
January 28, 2021

THE UNIVERSITY OF SYDNEY

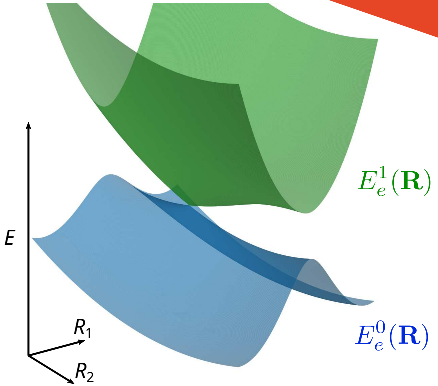


Motivation

- Chemical reactions are governed by the dynamics of electrons and nuclei
- The Born-Oppenheimer approximation:

$$|\Psi(\mathbf{r},\mathbf{R},t)\rangle = |\psi(\mathbf{r};\mathbf{R})\rangle\,|\chi(\mathbf{R},t)\rangle\,, \qquad \hat{H} = \hat{H}_e + \hat{T}_N,$$

$$\hat{H}_e\,|\psi(\mathbf{r};\mathbf{R})\rangle = E_e(\mathbf{R})\,|\psi(\mathbf{r};\mathbf{R})\rangle$$



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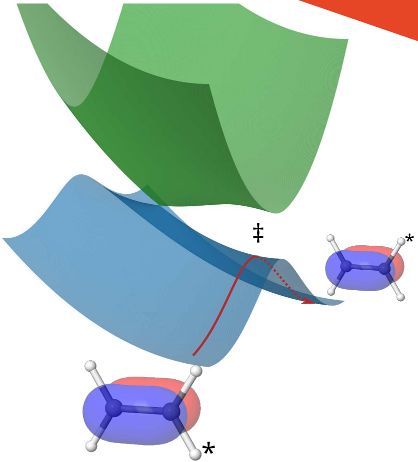
$$\hat{H}_e \left|\psi(\mathbf{r};\mathbf{R})\right\rangle = E_e(\mathbf{R}) \left|\psi(\mathbf{r};\mathbf{R})\right\rangle$$

- Sufficient for many reactions



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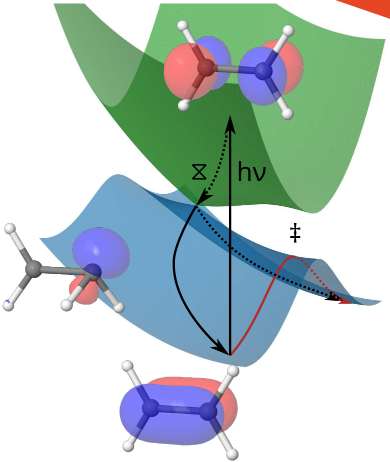
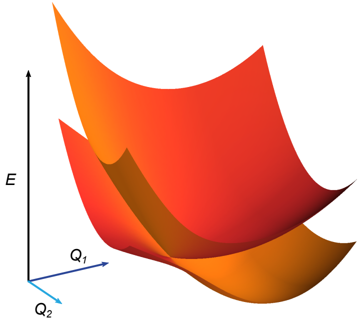
- Sufficient for many reactions
- ... but fails catastrophically for others
- Accurate simulation requires quantum mechanical treatment of nuclei



Vibronic coupling Hamiltonians

- The Born-Oppenheimer approximation yields adiabatic potential energy surfaces



$$\hat{H}_{ad} = \begin{pmatrix} V_{00} & 0 \\ 0 & V_{11} \end{pmatrix} + \begin{pmatrix} T_{00} & T_{01} \\ T_{10} & T_{11} \end{pmatrix}$$

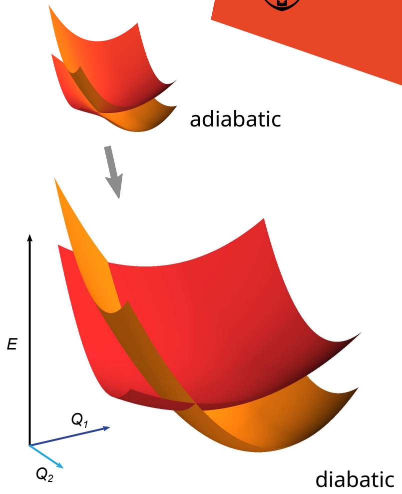
Vibronic coupling Hamiltonians

- The Born-Oppenheimer approximation yields adiabatic potential energy surfaces
- Can transform to diabatic picture with smooth (analytical) potentials and couplings

$$\hat{H} = \sum_{nm} \left(h_0(\mathbf{Q})\delta_{nm} + P_{nm}(\mathbf{Q}) \right) |n\rangle\langle m|$$

$$h_0(\mathbf{Q}) = \frac{1}{2}\hbar \sum_j \omega_j \left(Q_j^2 - \partial^2/\partial Q_j^2 \right)$$

$$P_{nm}(\mathbf{Q}) = p_0^{(nm)} + \sum_j p_j^{(nm)} Q_i + \sum_{jk} p_{jk}^{(nm)} Q_j Q_k + \cdots$$



$$\hat{H}_{di} = \begin{pmatrix} V_{00} & V_{01} \\ V_{10} & V_{11} \end{pmatrix} + \begin{pmatrix} T_{00} & 0 \\ 0 & T_{11} \end{pmatrix}$$

Vibronic coupling Hamiltonians

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"LVC"

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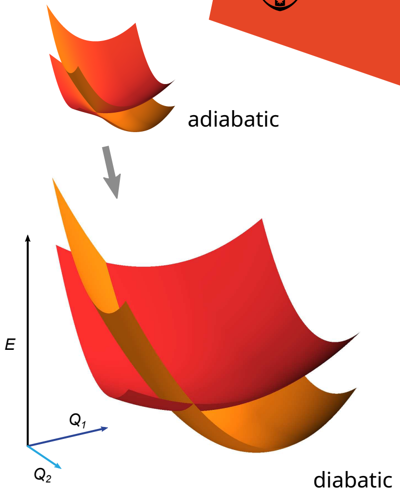
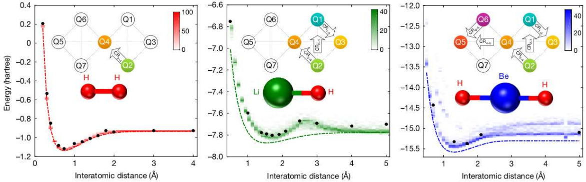


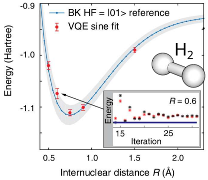
$$\hat{H}_{di} = \begin{pmatrix} V_{00} & V_{01} \\ V_{10} & V_{11} \end{pmatrix} + \begin{pmatrix} T_{00} & 0 \\ 0 & T_{11} \end{pmatrix}$$

Universal QC for chemistry

- Time-independent properties



Kandala, A. et al. *Nature* **2017**, *549*, 242–246.



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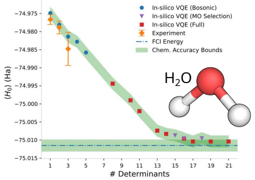
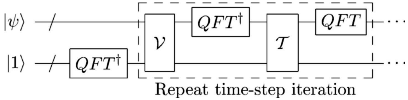


Nam, Y. et al. *npj Quantum Inf.* **2020**, *6*, 33.

- Time-dependent simulation



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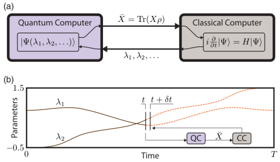

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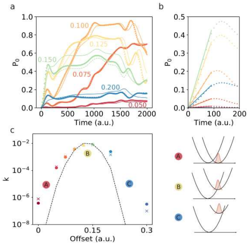


Ollitrault, P.J. et al. *Phys. Rev. Lett.* **2020**, *125*, 260511.

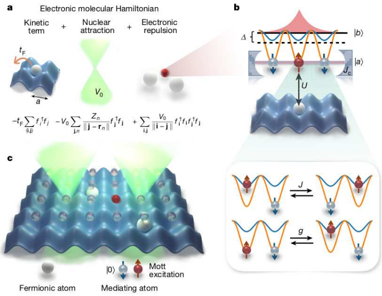
Analog simulation

- Classical: model a complex system with a controllable system

Analog simulation

- Classical: model a complex system with a controllable system
- Quantum: map a desired Hamiltonian onto a controllable quantum system

electronic structure



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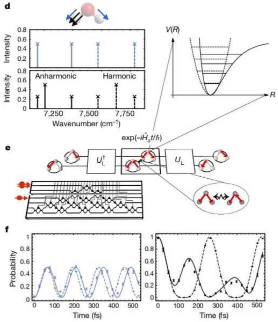
vibrational structure



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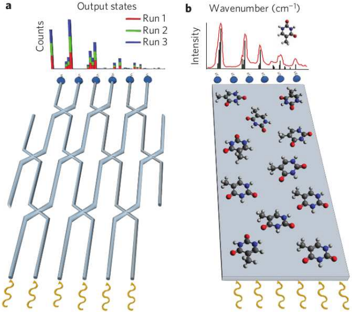
Franck-Condon spectra



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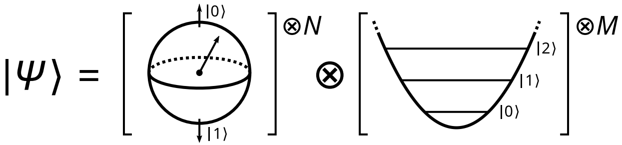
Mixed qudit-boson quantum simulators

- Architectures with internal (qudit) and bosonic degrees of freedom



mapping:
electronic → internal
vibrational → bosonic

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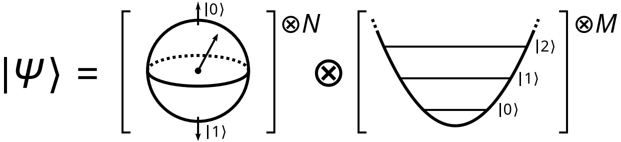

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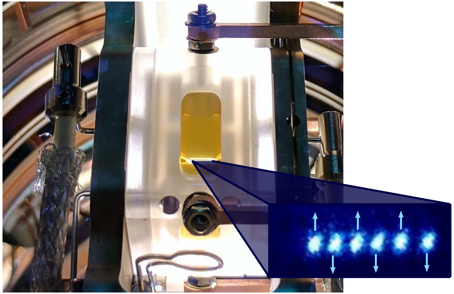
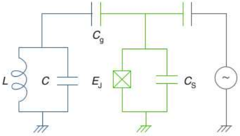
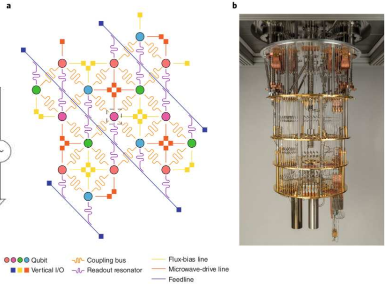
- Ion traps



- Circuit quantum electrodynamics (cQED)

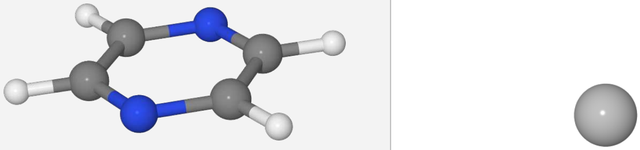




Blais, A. et al. *Nature Phys.* **2020**, *574*, 247–256.

2D LVC model (pyrazine) on a trapped ion

$$\hat{H}_{\mathrm{mol}} = \frac{1}{2}\sum_j \omega_j \left(\hat{Q}_j^2 + \hat{P}_j^2\right) - \frac{1}{2}\Delta E \hat{\sigma}_z + \sum_n c_1^{(n,n)} |n\rangle\langle n| \hat{Q}_1 + c_2^{(0,1)} \hat{\sigma}_x \hat{Q}_2$$



$$\hat{H}_{\mathrm{sim}} = \sum_j \omega_j^{ion} \hat{a}_j^\dagger \hat{a}_j - \frac{1}{2}\omega_0 \hat{\sigma}_z + \sum_j (\delta_j - \omega_j^{ion}) \hat{a}_j^\dagger \hat{a}_j - \frac{1}{2}(\Delta\chi/2 - \omega_0)\hat{\sigma}_z + \sum_n \Theta_n' |n\rangle\langle n| \left(\hat{a}_1^\dagger + \hat{a}_1\right) + \Omega' \hat{\sigma}_x \left(\hat{a}_2^\dagger + \hat{a}_2\right)$$

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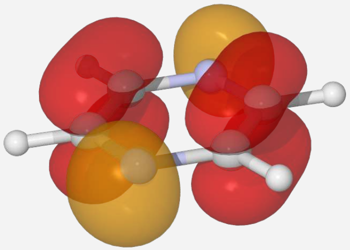
energy difference



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internal energy

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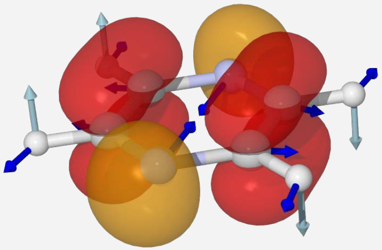
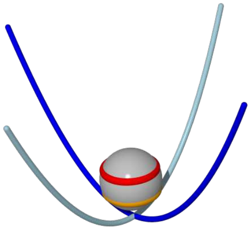
harmonic energy difference





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ion vibration internal energy

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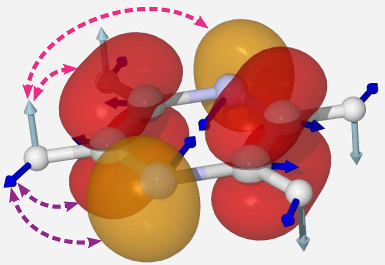
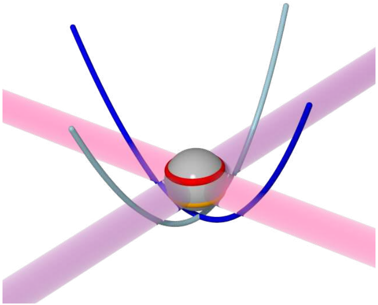
harmonic | energy difference | tuning | coupling





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ion vibration | internal energy | laser detuning | AC Stark shift | σ_z gate | MS gate

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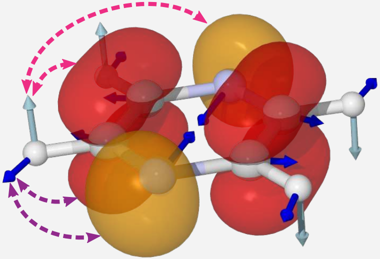

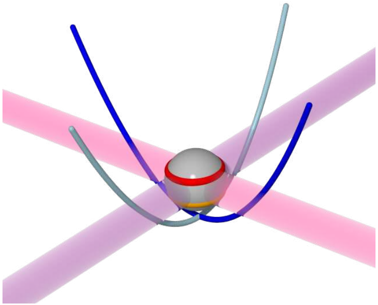

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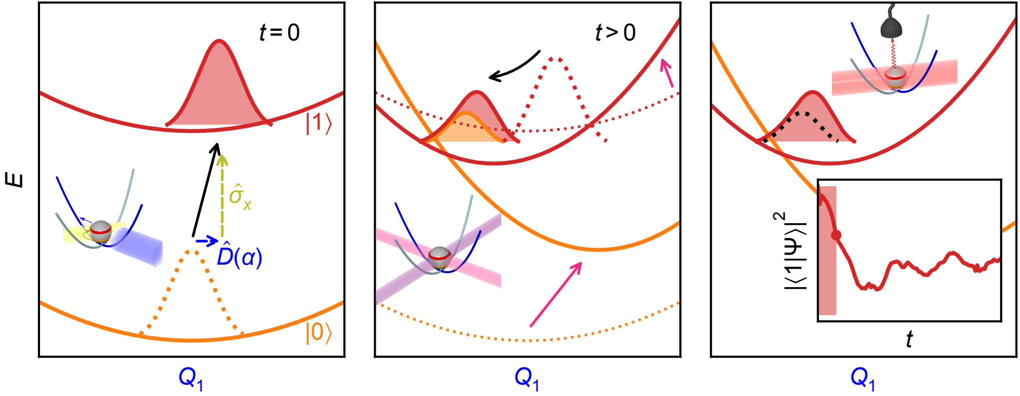
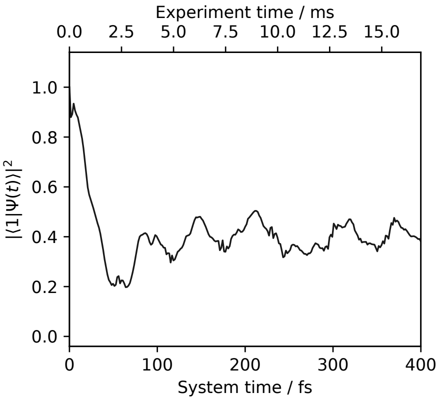
Steps for a 2D LVC model

- Simulation consists of initialization, evolution and measurement



Steps for a 2D LVC model

- Simulation consists of initialization, evolution and measurement
- Difference in simulator and system frequencies (kHz, THz) leads to simulation time scaled by a known factor (fs → ms)



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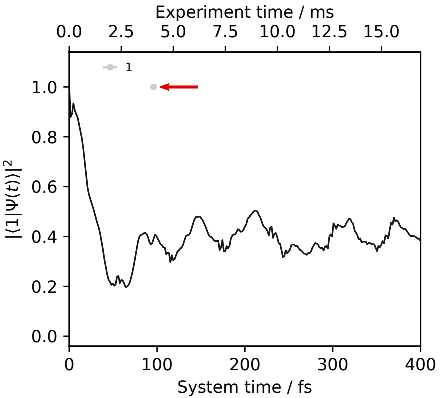

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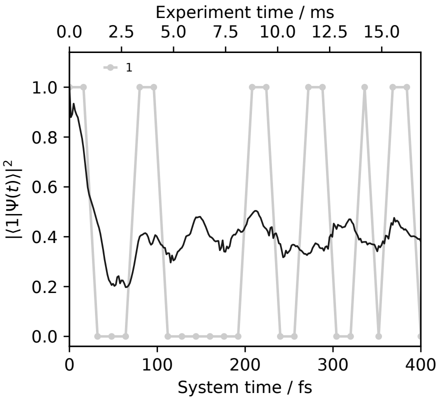

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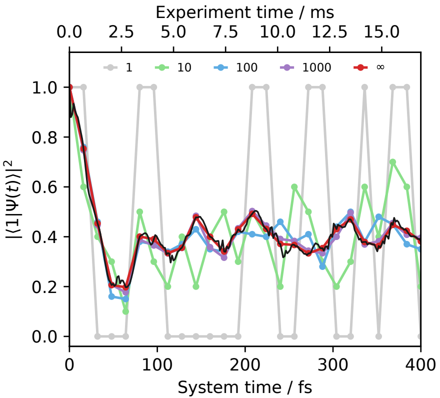
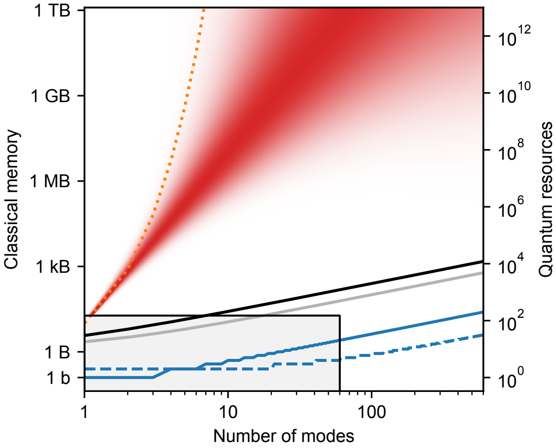
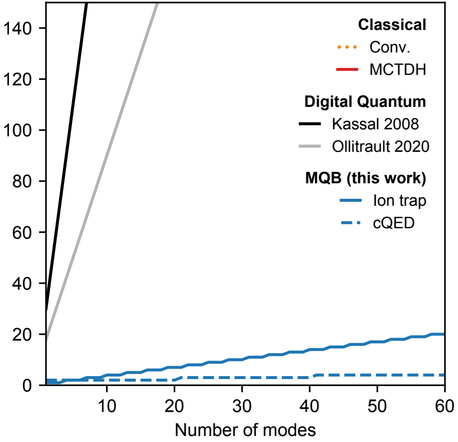


Going beyond the 2D LVC model





Wang, H. *J. Phys. Chem. A* **2015**, *119*, 7951–7965.

Kassal, I. et al. *Proc. Natl. Acad. Sci.* **2008**, *105*, 18681–18686.

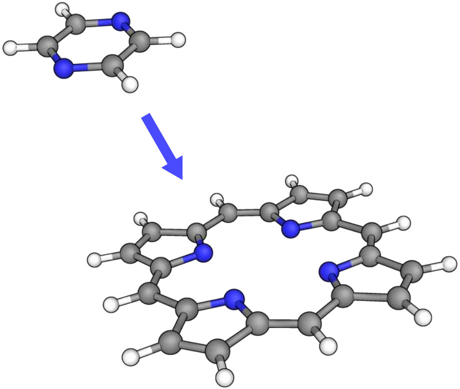
Ollitrault, P.J. et al. *Phys. Rev. Lett.* **2020**, *125*, 260511.

Going beyond the 2D LVC model

1. Including additional states/modes

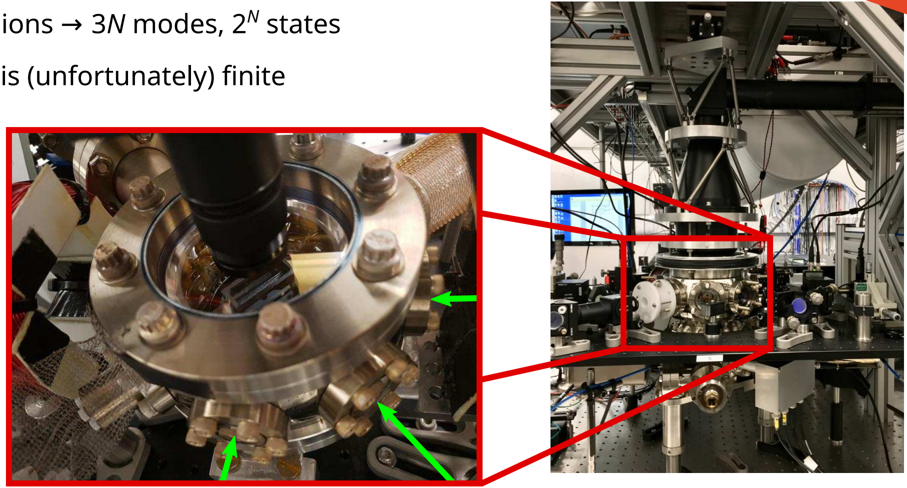
2. System-bath interactions

3. Higher-order terms



1. Including additional states/modes

- N trapped ions → $3N$ modes, 2^N states
- Lab space is (unfortunately) finite

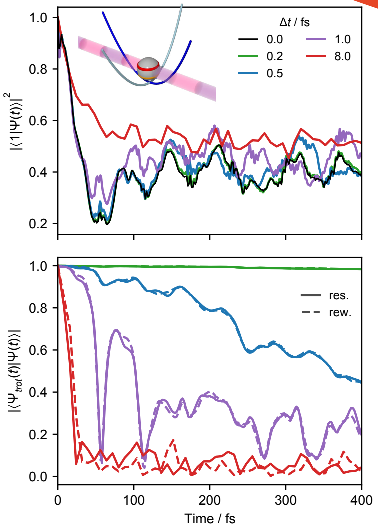


1. Including additional states/modes

- N trapped ions → $3N$ modes, 2^N states
- Lab space is (unfortunately) finite
- Suzuki-Trotter expansion

$$\exp\left(-\frac{i}{\hbar}\sum_j \hat{H}_j t\right) \approx \left(\prod_{j=1}^{M} \exp(-i\hat{H}_j t/n\hbar)\right)^n$$

  - Split terms of the Hamiltonian into multiple short timesteps
  - Terms corresponding to different modes from a single laser source

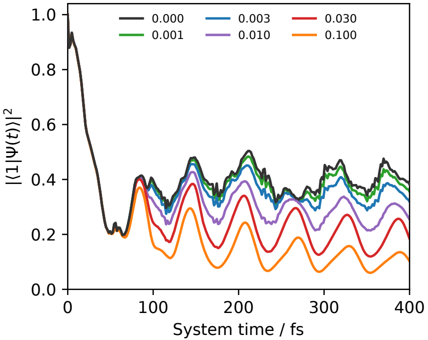


2. System-bath interactions

- Exact simulation involves solving a master equation
- Weak vibrational coupling to an infinite bath with Linblad superoperator

$$\mathcal{L}_j^-[\hat{\rho}] = \hat{a}_j \hat{\rho} \hat{a}_j^\dagger - \frac{1}{2}\{\hat{a}_j^\dagger \hat{a}_j, \hat{\rho}\}, \quad \mathcal{L}_j^+[\hat{\rho}] : \hat{a}_j^\dagger \leftrightarrow \hat{a}_j$$

$$\partial \hat{\rho}/\partial t = -i[\hat{H}, \hat{\rho}] + \sum_j \gamma_j \left[(\langle n_j \rangle + 1)\mathcal{L}_j^-[\hat{\rho}] + \langle n_j \rangle \mathcal{L}_j^+[\hat{\rho}]\right]$$



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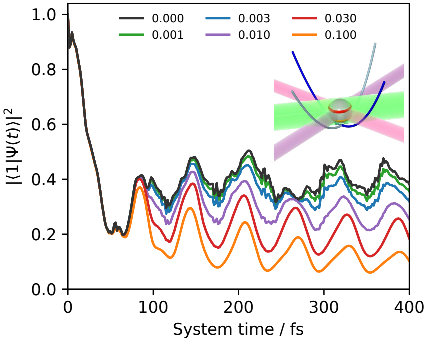
- Exact simulation involves solving a master equation
- Weak vibrational coupling to an infinite bath with Linblad superoperator

$$\mathcal{L}_j^-[\hat{\rho}] = \hat{a}_j\hat{\rho}\hat{a}_j^\dagger - \frac{1}{2}\{\hat{a}_j^\dagger\hat{a}_j, \hat{\rho}\}, \quad \mathcal{L}_j^+[\hat{\rho}] : \hat{a}_j^\dagger \leftrightarrow \hat{a}_j$$

$$\partial\hat{\rho}/\partial t = -i[\hat{H}, \hat{\rho}] + \sum_j \gamma_j \left[(\langle n_j\rangle + 1)\mathcal{L}_j^-[\hat{\rho}] + \langle n_j\rangle\mathcal{L}_j^+[\hat{\rho}]\right]$$

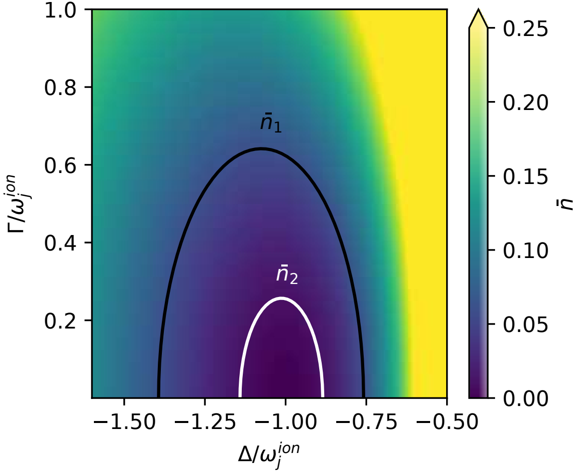
- Laser cooling + heating: $\sum_j A_j^-\mathcal{L}_j^-[\hat{\rho}] + A_j^+\mathcal{L}_j^+[\hat{\rho}]$

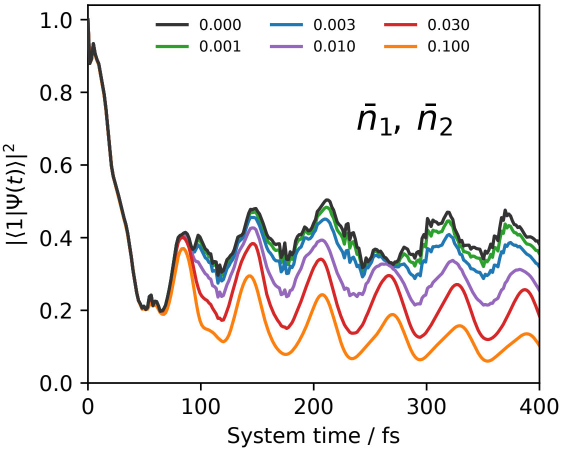
$$A_j^\pm = \eta_j^2\Gamma_j\left(P_j(\Delta \pm \omega_j^{ion}) + \alpha P_j(\Delta)\right), \qquad P_j(\Delta) = \frac{\Omega_0^2}{\Gamma_j^2 + 4\Delta^2}$$



2. System-bath interactions

$$A_j^{\pm} = \eta_j^2 \Gamma_j \left(P_j(\Delta \pm \omega_j^{ion}) + \alpha P_j(\Delta) \right), \qquad P_j(\Delta) = \frac{\Omega_0^2}{\Gamma_j^2 + 4\Delta^2}$$





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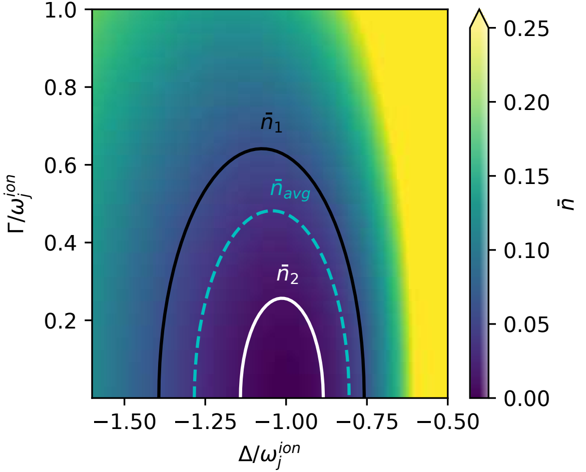
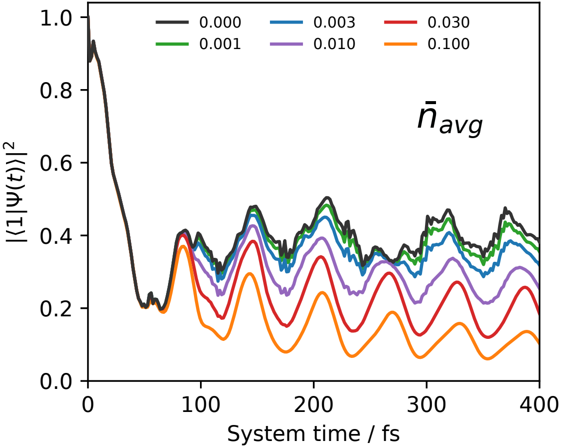




3. Higher-order terms

- Can also achieve second order terms with light-matter interactions
  - Dispersive coupling (Q_j^2)

    Pedernales, J. S. *Sci. Rep.* **2015**, *5*, 15472.

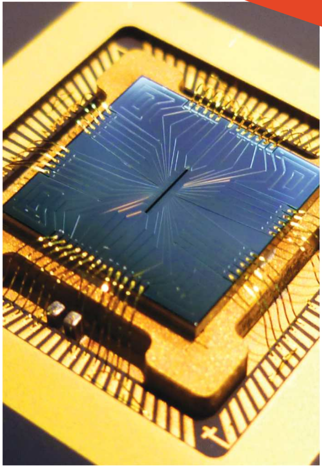
$$(a\sigma_z + b\sigma_x)\hat{a}_j^\dagger \hat{a}_j$$

  - Mode mixing ($Q_j Q_k$)

    Marshall, K.; James, D.F.V. *Appl. Phys. B* **2017**, *123*, 26.

$$(a\mathbb{1} + b\sigma_z + c\sigma_x)\left(\hat{a}_j^\dagger \hat{a}_k + h.c.\right)$$

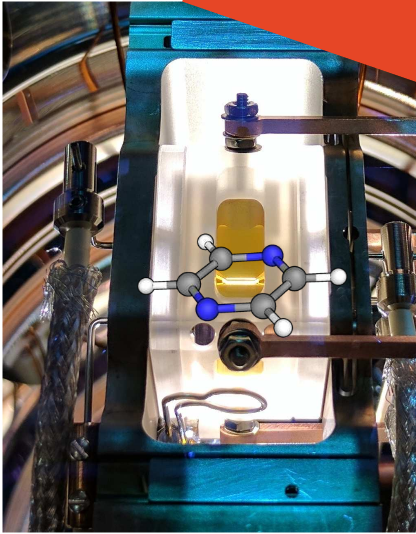
- Anharmonicity from engineered potentials
  - Surface traps
  - cQED



Stajic, J. *Science* **2013**, *339*, 1163.

Conclusions

- Vibronic coupling models can be mapped directly onto bosonic simulators
    - One-to-one correspondance of internal/bosonic with electronic/vibrational degrees of freedom
    - First order terms → common multi-qubit coupling schemes
- The model may be extended to more modes/ states and system-bath couplings
- Can be achieved with **existing** quantum technology



Acknowledgements

- Kassal group
  - Claire Dickerson
  - Clare Birch
  - Alok Kumar
- Quantum control laboratory
  - Claire Edmunds
  - Michael Biercuk
  - Cornelius Hempel

UCLA

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Light-matter interactions

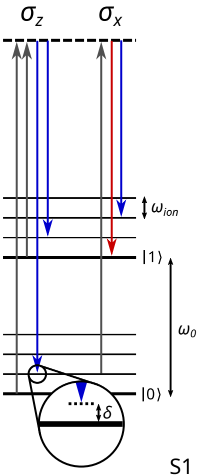
- Vibronic coupling terms in the interaction picture

$$\hat{H}_0 = \sum_n (h_0 + E_n)|n\rangle\langle n|$$

$$\hat{H}_I = \exp(i\hat{H}_0 t/\hbar)(\hat{H} - \hat{H}_0)\exp(-i\hat{H}_0 t/\hbar)$$

$$= \sum_{nm}\sum_k c_k^{(nm)} \left(|n\rangle\langle m|e^{i\Delta E_{nm}t/\hbar} + h.c.\right) \bigotimes_j \left(\hat{a}_j^\dagger e^{i\omega_j t} + h.c.\right)^{p_{jk}}$$

- First-order terms in the same form as light-matter interactions
  - σ_z gate: $$\hat{H}_I = \frac{i}{2}\hbar D_1' \eta_1 \left(\bar{\Theta}\mathbb{1} - \frac{1}{2}\Delta\Theta\sigma_z\right)\left(\hat{a}^\dagger e^{i\delta_1 t} + h.c.\right)$$
  - MS (σ_x) gate: $$\hat{H}_I = \frac{i}{2}\hbar D_1' \eta_1 \Omega \left(\sigma_+ e^{i\omega_0 t} + h.c.\right)\left(\hat{a}^\dagger e^{i\delta_1 t} + h.c.\right)$$



Lee, P.J. et al. *J. Opt. B: Quantum Semiclass. Opt.* **2005**, *7*, S371–S383.

Trotterization in the interaction picture

- Terms of the Hamiltonian are applied with respect to the "base" Hamiltonian

$$\hat{H}_0 = \sum_n (h_0 + E_n)|n\rangle\langle n|$$

$$\hat{H}'_j = \hat{H}_0 + \hat{H}_j$$

- Applying interactions in series requires rescaling

$$\sum_{j=1}^{M} \left(\hat{H}_0 + M\hat{H}_j\right) = M\hat{H}$$

- Additional phase-matching required for multiple terms from a single laser