Simulation of quantum molecular dynamics with analog quantum computers

Ryan J. MacDonell, Ivan Kassal

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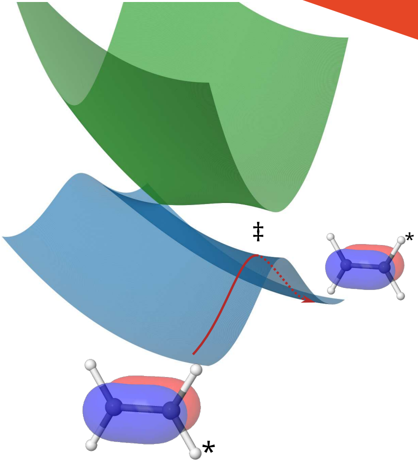
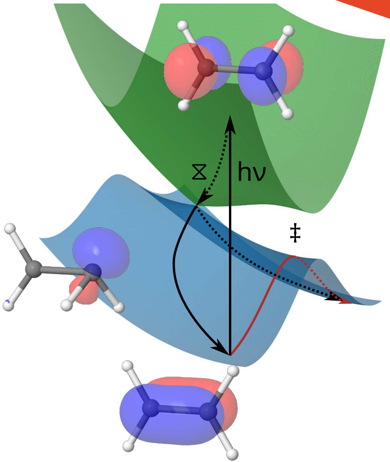
Motivation

- Chemical reactions are governed by the dynamics of molecules



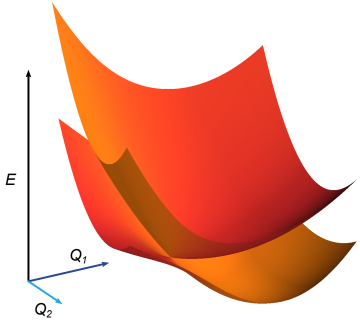
Motivation

- Chemical reactions are governed by the dynamics of molecules
- Ultrafast photochemistry requires a dynamical, quantum mechanical treatment
- Classical computing cost of exact simulation scales exponentially number of degrees of freedom
- Simulation with a quantum system significantly reduces the cost



Vibronic coupling Hamiltonians

- The Born-Oppenheimer approximation yields adiabatic potential energy surfaces



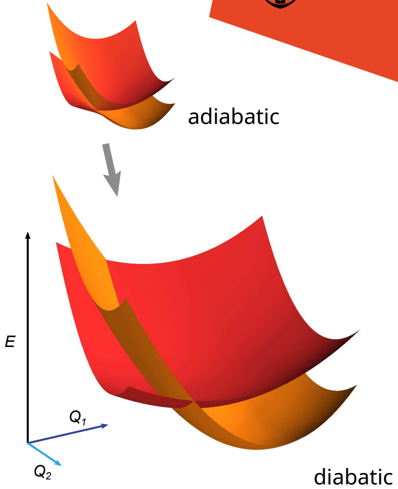
$$\hat{H}_{ad} = \begin{pmatrix} V_{00} & 0 \\ 0 & V_{11} \end{pmatrix} + \begin{pmatrix} T_{00} & T_{01} \\ T_{10} & T_{11} \end{pmatrix}$$

Vibronic coupling Hamiltonians

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

$$\hat{H} = \frac{1}{2}\sum_j \omega_j \left(\hat{Q}_j^2 + \hat{P}_j^2\right) + \sum_{n,m} \hat{C}_{n,m} \left|n\right\rangle \left\langle m\right| ,$$

$$\hat{C}_{n,m} = c_0^{(n,m)} + \sum_j c_j^{(n,m)} \hat{Q}_j + \sum_{j,k} c_{j,k}^{(n,m)} \hat{Q}_j \hat{Q}_k + \cdots$$



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

Vibronic coupling Hamiltonians

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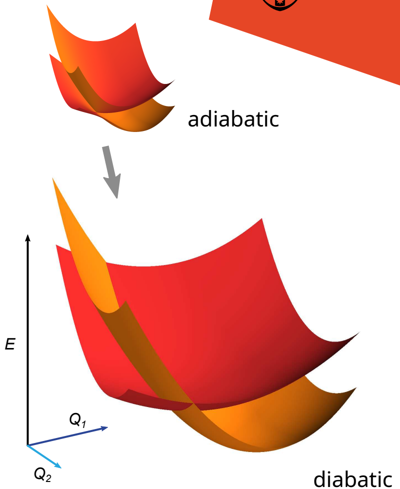
$$\hat{C}_{n,m} = c_0^{(n,m)} + \sum_j c_j^{(n,m)} \hat{Q}_j \cancel{+ \sum_{j,k} c_{j,k}^{(n,m)} \hat{Q}_j \hat{Q}_k + \cdots}$$

"LVC"



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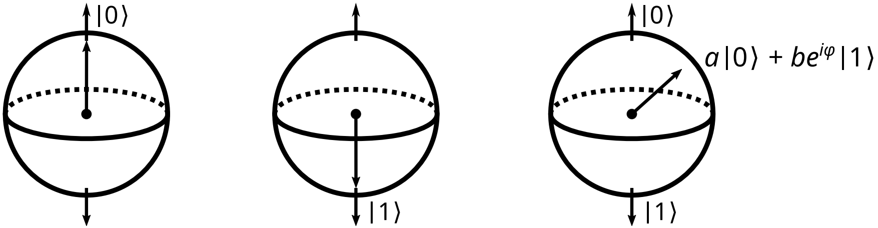
Universal quantum computing

- Information is represented by quantum bits (qubits)



Universal quantum computing

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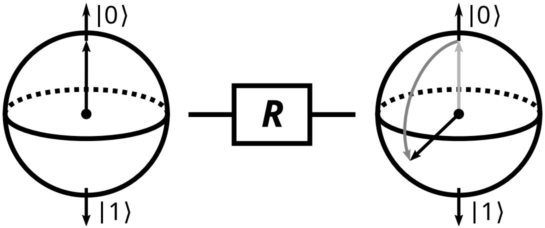
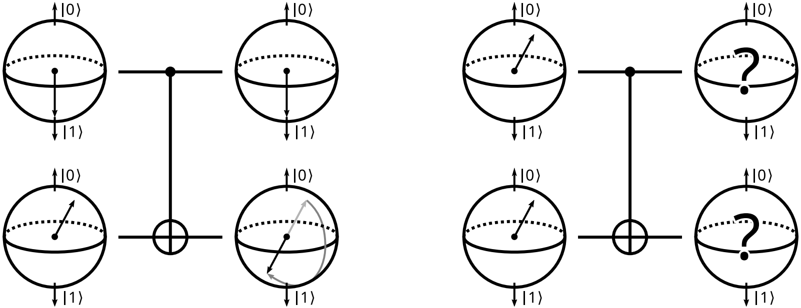
- Single-qubit gates rotate the qubit state (superposition)



Universal quantum computing

- Information is represented by quantum bits (qubits)
- Single-qubit gates rotate the qubit state (superposition)
- Multi-qubit gates change target qubit states based on the states of control qubits (entanglement)



Universal QC for chemistry

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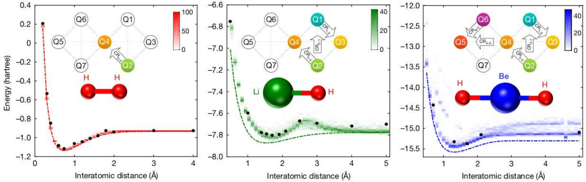
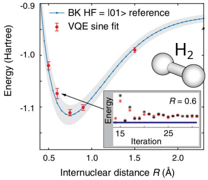
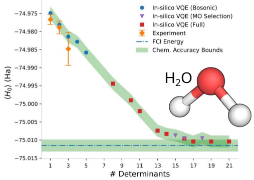
- Time-independent properties



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

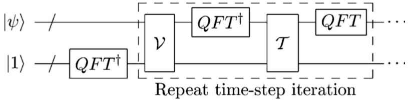


Hempel, C. et al. *Phys. Rev X* **2018**, *8*, 031022.

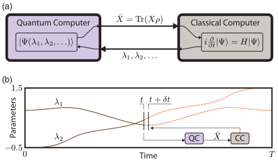


Nam, Y. et al. *npj Quantum Inf.* **2020**, *6*, 33.

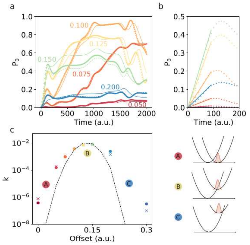
- Time-dependent simulation



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



Li, Y.; Benjamin, S.C. *Phys. Rev. X* **2017**, *7*, 021050.



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

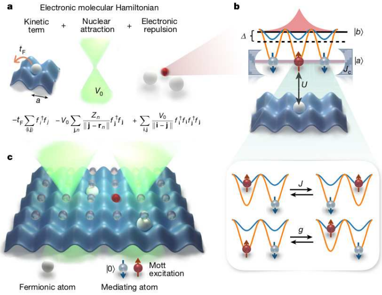
Analog simulation

- Classical: model a complex system with a controllable system

Analog simulation

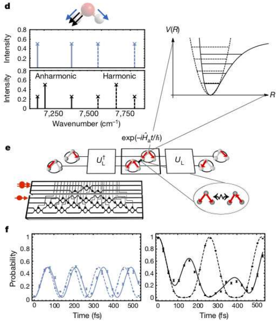
- Classical: model a complex system with a controllable system
- Quantum: map a desired Hamiltonian onto a controllable quantum system

electronic structure



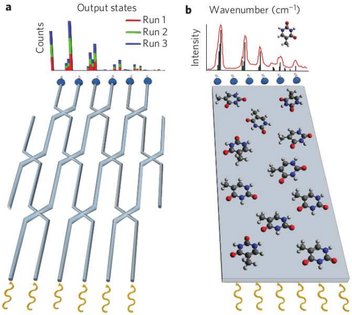
Arguello-Luengo, J. et al. *Nature* **2019**, *574*, 215–218.

vibrational structure



Sparrow, C. et al. *Nature* **2018**, *557*, 660–667.

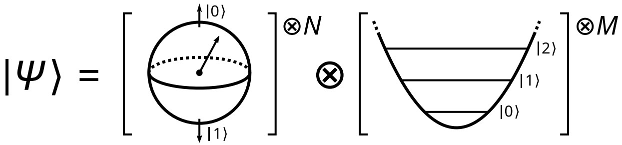
Franck-Condon spectra



Huh, J. et al. *Nat. Photonics* **2015**, *9*, 615–620.

Mixed qudit-boson quantum simulators

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



mapping:
electronic → internal
vibrational → bosonic

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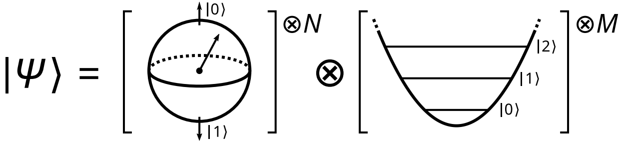

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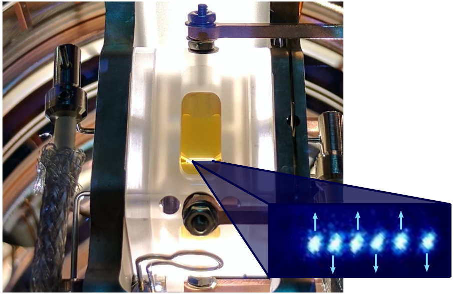
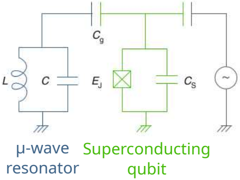
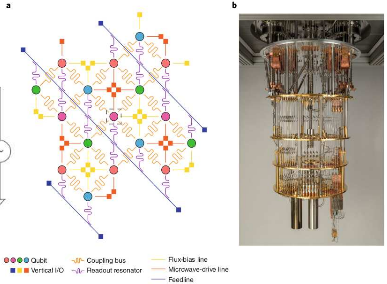
- Ion traps



- Circuit quantum electrodynamics (cQED)

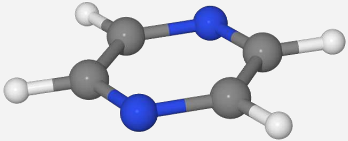




Blais, A. et al. *Nature Phys.* **2020**, *574*, 247–256.

2D LVC model (pyrazine) on a trapped ion

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



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

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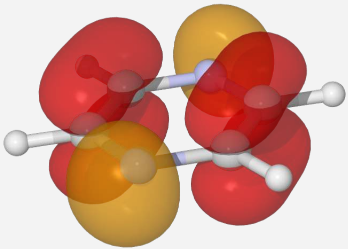
energy difference



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internal energy

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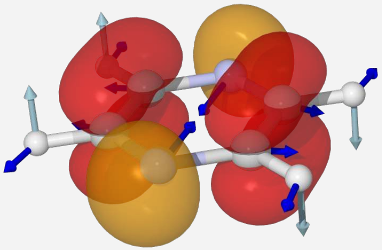
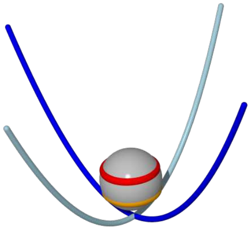
harmonic energy difference





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ion vibration internal energy

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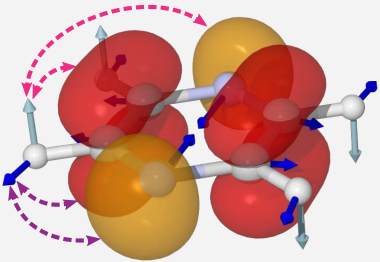
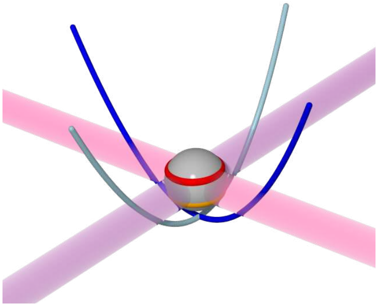
harmonic | energy difference | tuning | coupling





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

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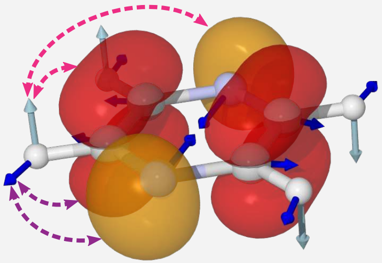

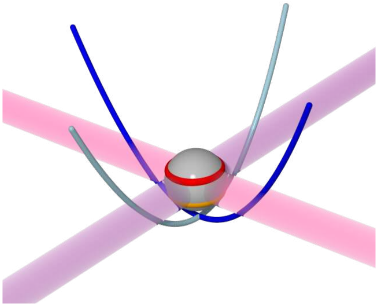

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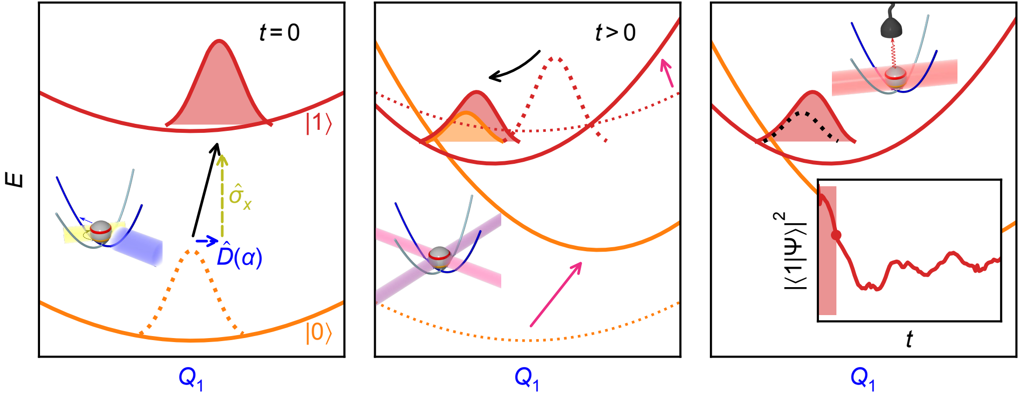
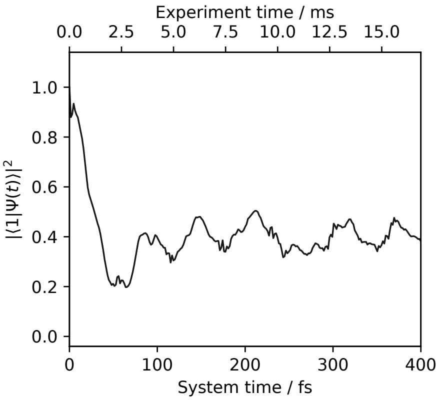
Steps for a 2D LVC model

- 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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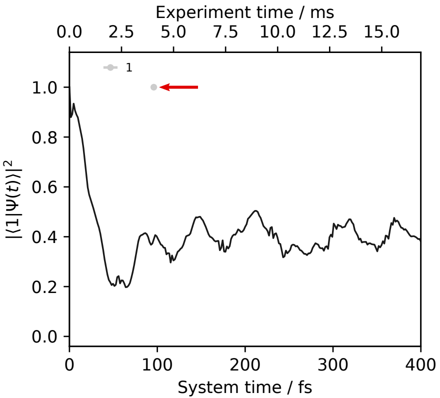

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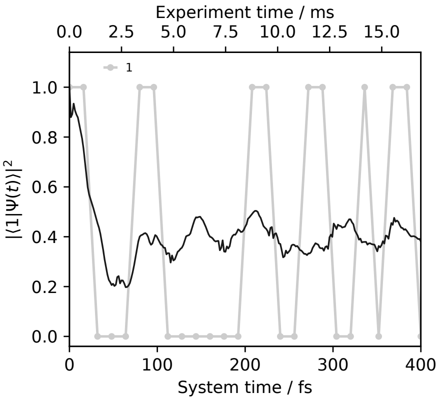

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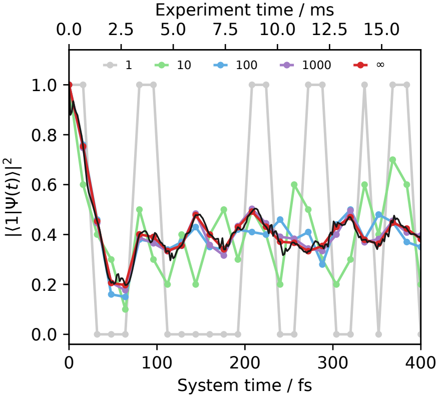
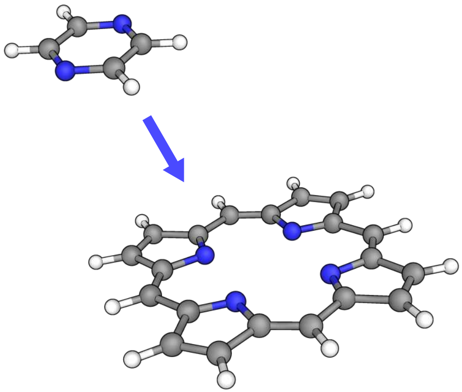


Going beyond the 2D LVC model

1. Including additional states/modes

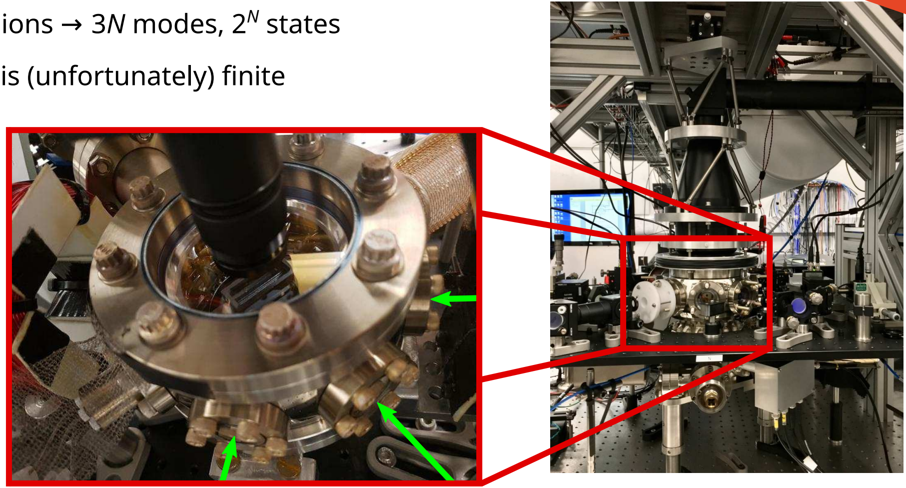
2. System-bath interactions

3. Higher-order terms



1. Including additional states/modes

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

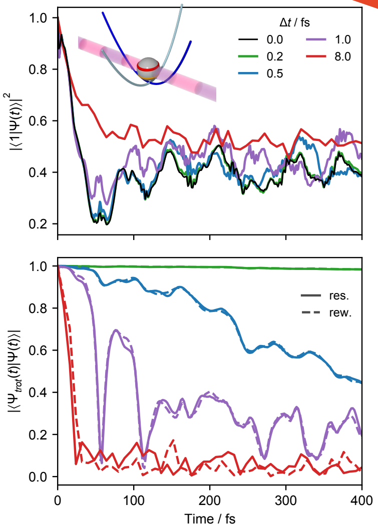


1. Including additional states/modes

- 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

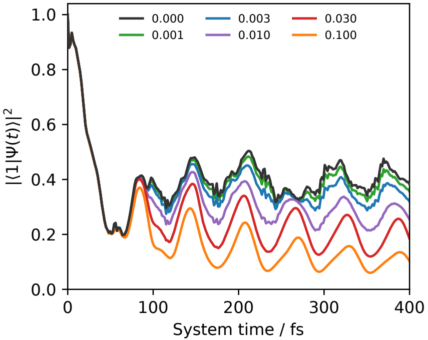


2. System-bath interactions

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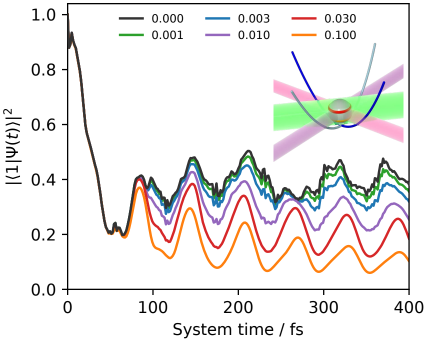
- Laser cooling + heating: $\sum_j A_j^- \mathcal{L}_j^-[\hat{\rho}] + A_j^+ \mathcal{L}_j^+[\hat{\rho}]$

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



3. Higher-order terms

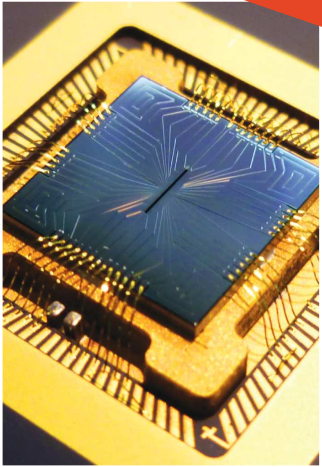
- Can also achieve second order terms with light-matter interactions
  - Dispersive coupling (Q_j^2) Pedernales, J. S. *Sci. Rep.* **2015**, *5*, 15472.

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

  - Mode mixing (Q_jQ_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

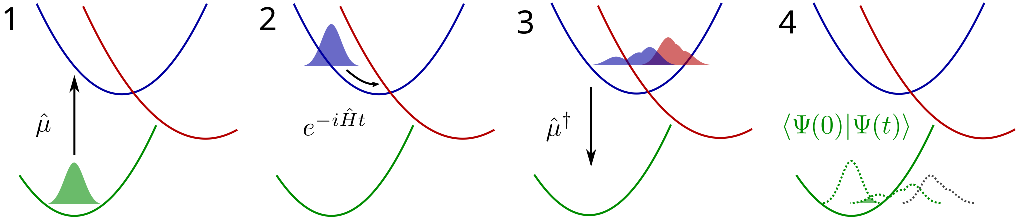


Stajic, J. *Science* **2013**, *339*, 1163.

Measuring observables

- Time-dependent observables mapped to the internal-bosonic basis
- Absorption spectra from the autocorrelation function

$$\sigma(E) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\, \exp(iEt)\, \langle \hat{\mu}\Psi(0)|\hat{\mu}\Psi(t)\rangle$$
$$\approx \frac{|\mu|^2}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\, \exp(iEt)\, \langle \Psi(0)|\Psi(t)\rangle$$



Measuring observables

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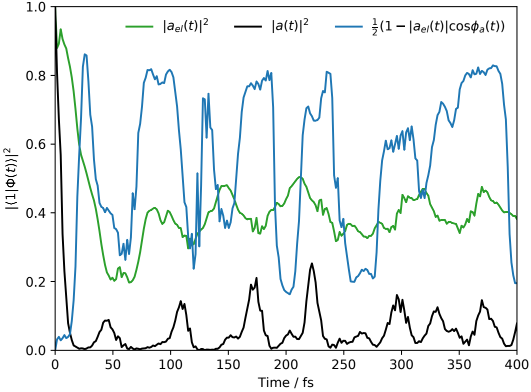
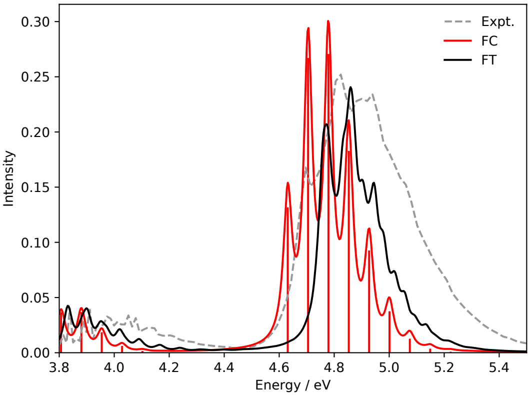
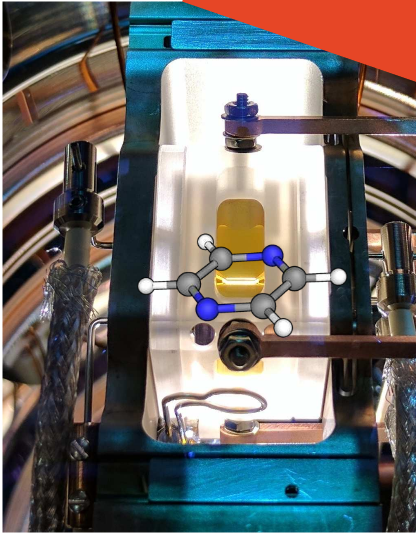




Conclusions

- Vibronic coupling models can be mapped directly onto MQB 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, system-bath couplings, other observables
- Can be achieved with **existing** quantum technology



MacDonell, R.J. et al. 2020, arXiv:2012.01852 [quant-ph].

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Light-matter interactions

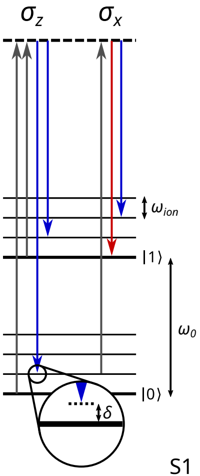
- Vibronic coupling terms in the interaction picture

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

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

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

- 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