Computers have transformed chemistry
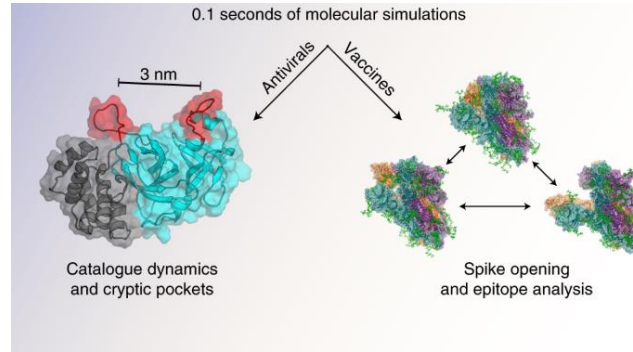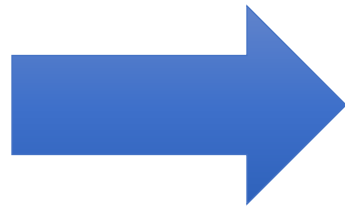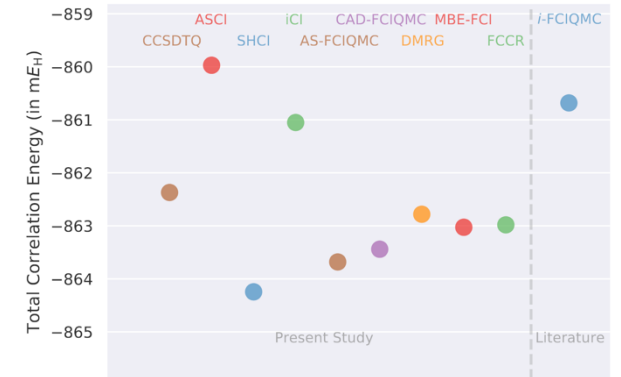
Electronic energy of LiH and BH⁺
J. Chem. Phys. (1957)

Exa-scale SARS-CoV-2
Nat. Chem. (2021)

but

Benzene (C_6H_6) challenge
J. Phys. Chem. Lett. (2020)
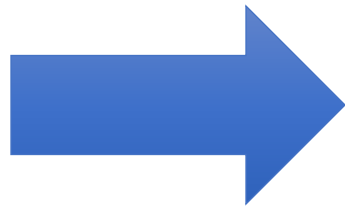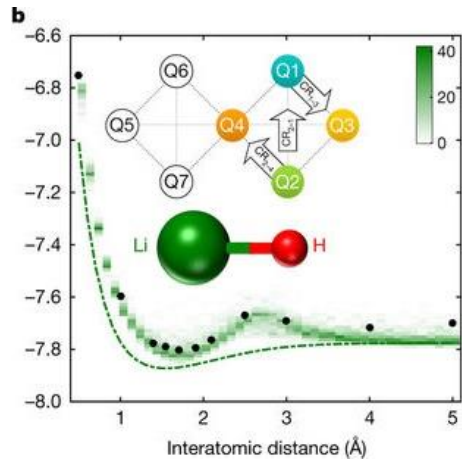
Electronic energy of LiH
Nature (2017)
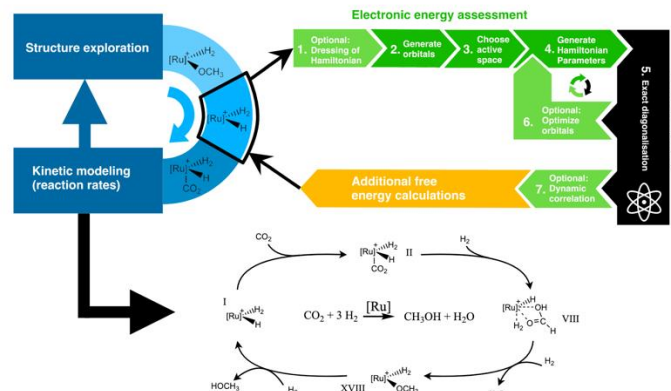
Quantum computing for catalysis
Phys. Rev. Res. (2022)
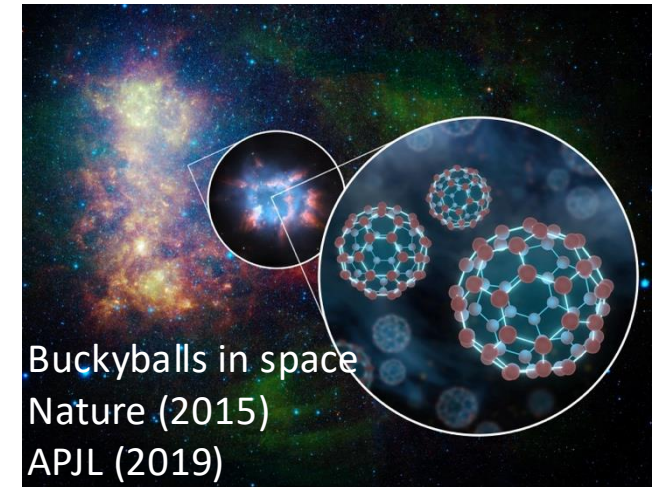
Buckyballs in space
Nature (2015)
APJL (2019)

Where is my QPU?
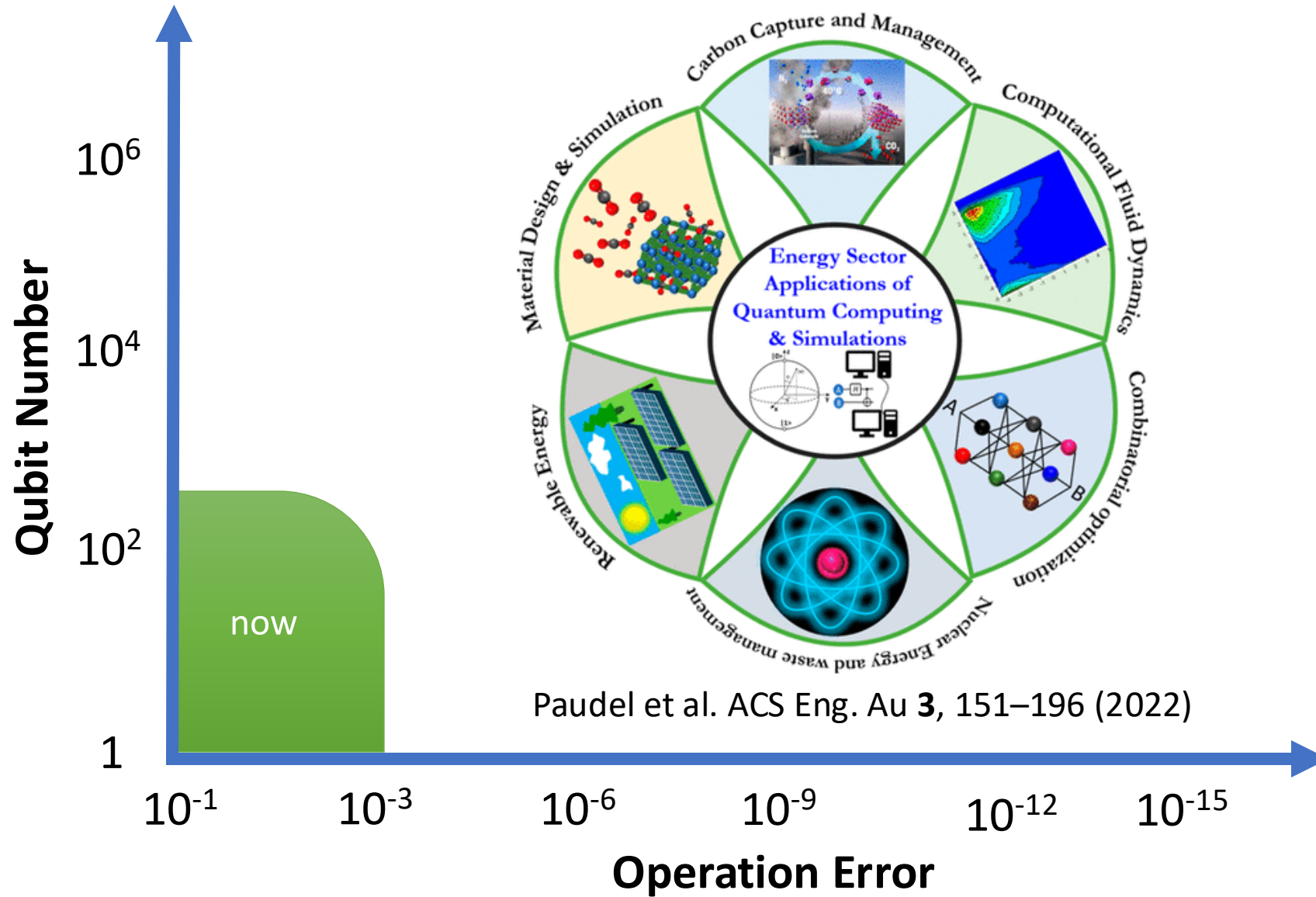
Paudel et al. ACS Eng. Au **3**, 151–196 (2022)

Solar cell optimization depends on vibronic dynamics

| System	# Qubits	# Toffoli Gates	Parameters
$(NO)_4$-Anth [60]	148	8.9×10^8	$N=5, M=19, K=16,$ $t=100\text{fs}, \epsilon=10\%$
	154	2.9×10^9	$N=5, M=19, K=16,$ $t=100\text{fs}, \epsilon=1\%$
$(NO)_4$-Anth Dimer [129]	160	1.8×10^9	$N=6, M=21, K=16,$ $t=100\text{fs}, \epsilon=1\%$
	164	2.0×10^{10}	$N=6, M=21, K=16,$ $t=500\text{fs}, \epsilon=1\%$
Anth/C_{60} [63]	117	1.5×10^7	$N=4, M=11, K=16,$ $t=100\text{fs}, \epsilon=1\%$
	1065	2.7×10^9	$N=4, M=246, K=16,$ $t=100\text{fs}, \epsilon=1\%$

Quantum Algorithm for Vibronic Dynamics:
Case Study on Singlet Fission Solar Cell Design
D. Motlagh arXiv:2411.13669

Cost is driven by mapping bosons to qubits
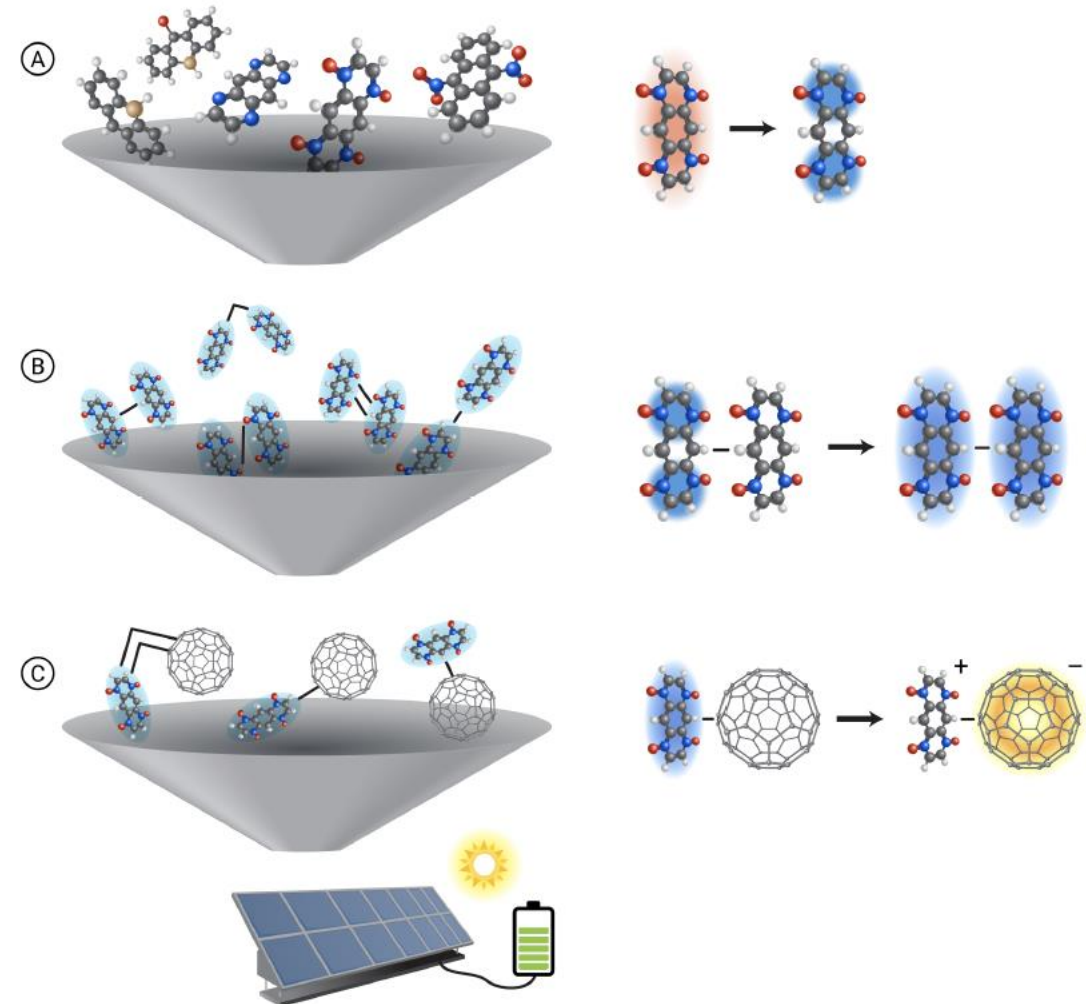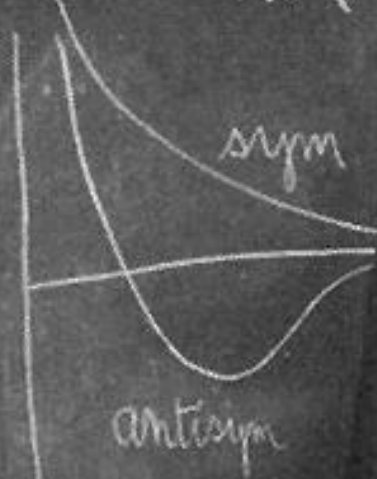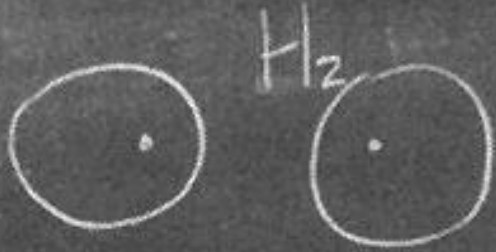
- The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

- P.A.M. Dirac, Proc. R. Soc. A **123**, 714 (1929)

Molecular Hamiltonian

$$\hat{H} = -\sum_A^{\text{nuc}} \frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2m} \sum_i^{\text{elec}} \nabla_i^2 - \sum_A^{\text{nuc}} \sum_i^{\text{elec}} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B}^{\text{nuc}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j}^{\text{elec}} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$
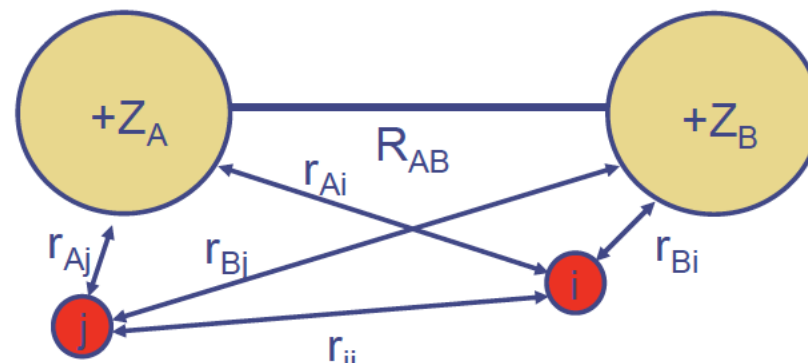
Nuclei Kinetic Energy   Nuclei-Electron Attraction   Electron-Electron Repulsion

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r})$$

Electron Kinetic Energy   Nuclei-Nuclei Repulsion

Born-Oppenheimer Approximation

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_k \underset{\text{electronic}}{\Psi_k(\mathbf{r}; \mathbf{R})} \underset{\text{nuclear}}{\chi_k(\mathbf{R})}$$

Separate variables based on $M_N/m_e > 1$

Electronic wavefunction for fixed nuclei

$$\hat{H}_{el} = \hat{T}_e(\mathbf{r}) + V_{eN}(\mathbf{r}; \mathbf{R}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r})$$

$$\hat{H}_{el}(\mathbf{r}; \mathbf{R})\Psi(\mathbf{r}; \mathbf{R}) = E_{el}(\mathbf{R})\Psi(\mathbf{r}; \mathbf{R})$$

Nuclei wavefunction based on distinct electronic states

$$\left[\hat{T}_N(\mathbf{R}) + T''_{kk}(\mathbf{R}) + E_{el}(\mathbf{R})\right]\chi_k(\mathbf{R}) = E\chi_k(\mathbf{R})$$

Kinetic   Potential

Electronic Structure Problem

$$\hat{H}_{el} = \hat{T}_e(\mathbf{r}) + V_{eN}(\mathbf{r}; \mathbf{R}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r})$$

Second quantize

$$\hat{H}_e = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r,$$

Map to qubits
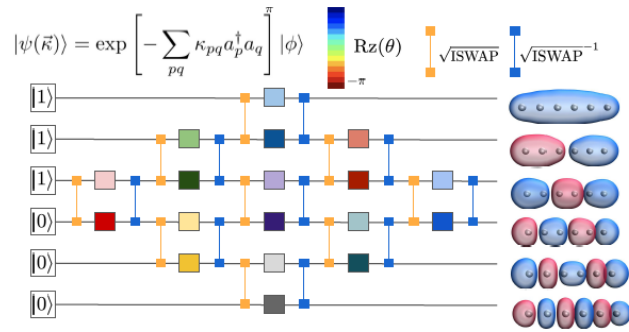Jordan-Wigner, Bravyi-Kitaev,
Superfast, etc.

$$\widehat{H}_{el} = \sum_j P_j$$
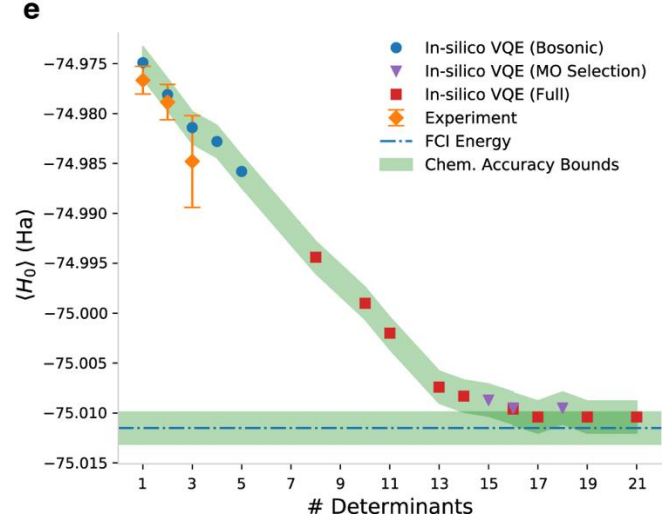
Phase Estimation
Abrams & Lloyd, PRL (1999)
Aspuru-Guzik, Dutoi, Love & Head-Gordon Science (2005)
VQE
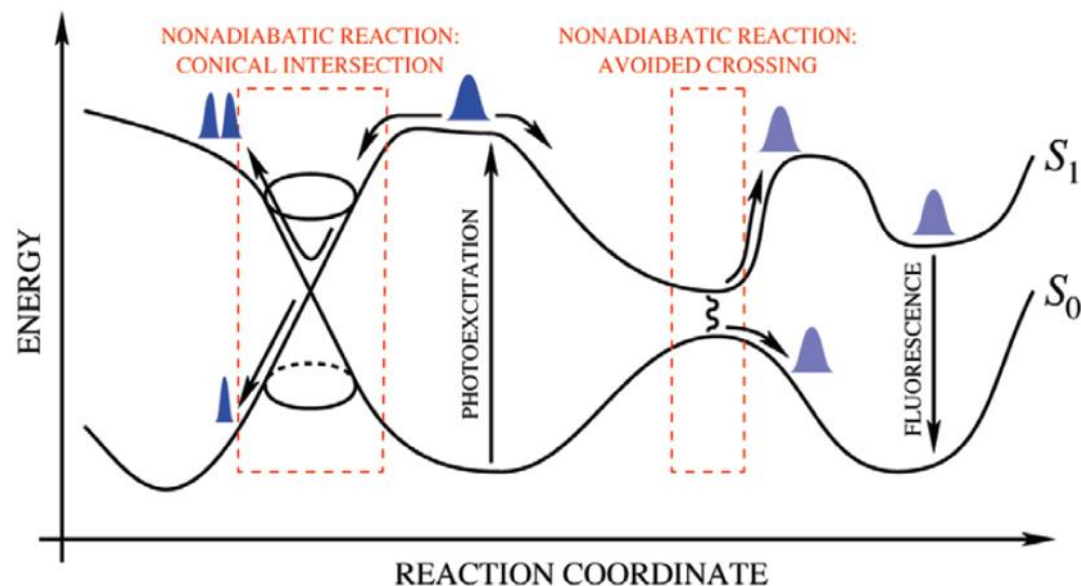Peruzzo et al. Nat. Commun. (2014)


Arute et al. Science (2020)

Nam et al. njp Quantum Information (2020)

Conical intersections and quantum simulation

Conical intersections are ubiquitous in photochemistry.
Quantum simulation allows us to probe quantum effects that may be inaccessible to pump-probe spectroscopy
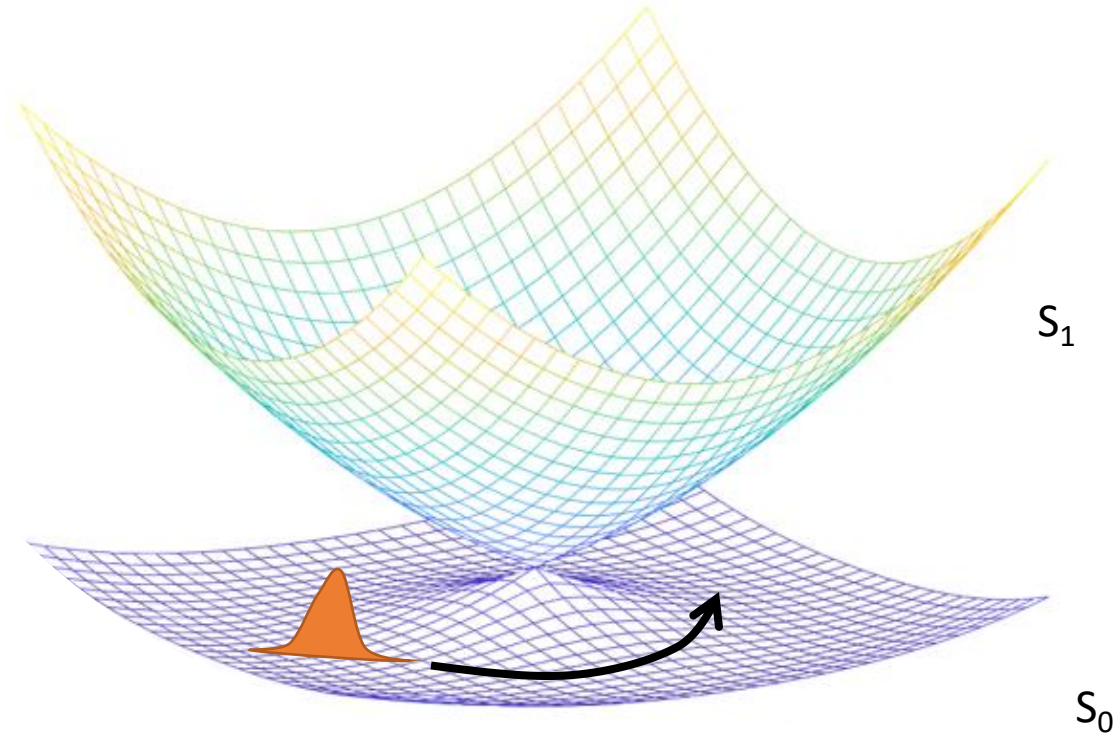

Photoexcited Vibrational Dynamics in Vicinity of Conical Intersections
A. Piryatinski, S. Tretiak, M. Stepanovv, and V. Chernyak, LALP-06-100 (2006)
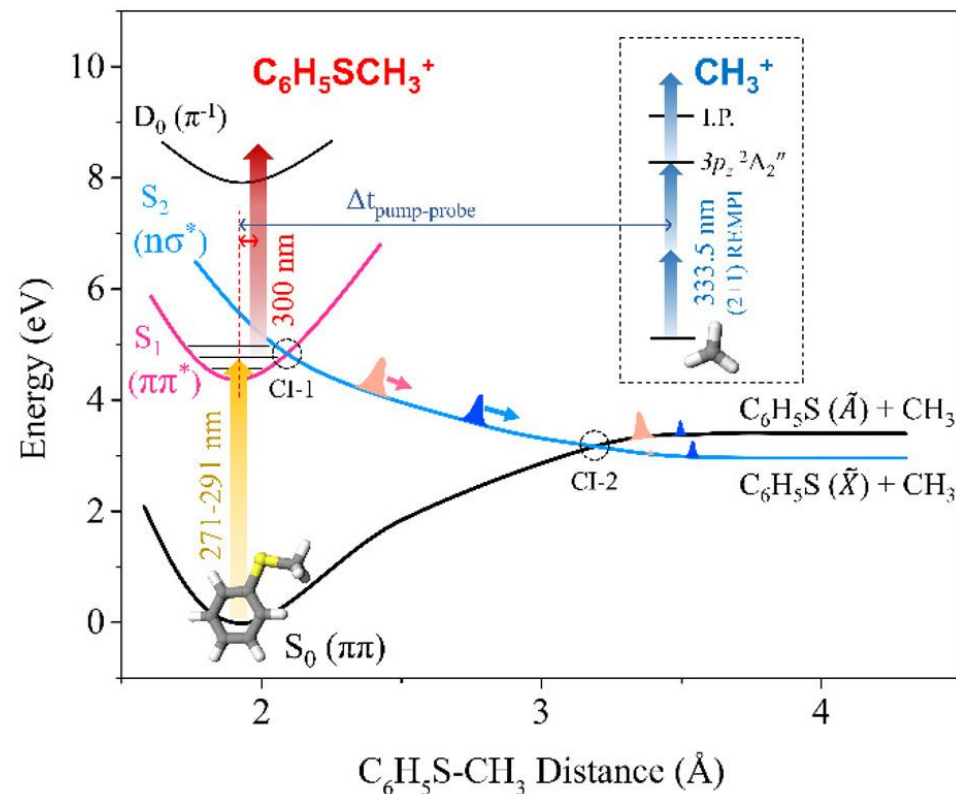
Real-Time Observation of Nonadiabatic Bifurcation Dynamics at a Conical Intersection
K.C. Woo, D.H. Kang, and S.K. Kim JACS **139**, 17152 (2017)

Geometric phase on the ground state

S_1

S_0

Quantum mechanics predicts a geometric phase on the ground state potential

Femtosecond molecule

TIME-RESOLVED OPTICAL TESTS FOR ELECTRONIC GEOMETRIC PHASE DEVELOPMENT

JEFFREY A. CINA* and TIMOTHY J. SMITH, JR.

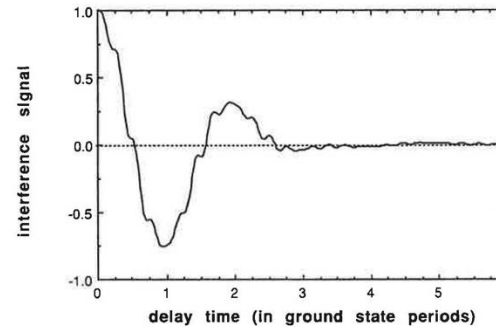*Department of Chemistry and the James Franck Institute, The University of Chicago, Chicago, Illinois*

VÍCTOR ROMERO-ROCHÍN

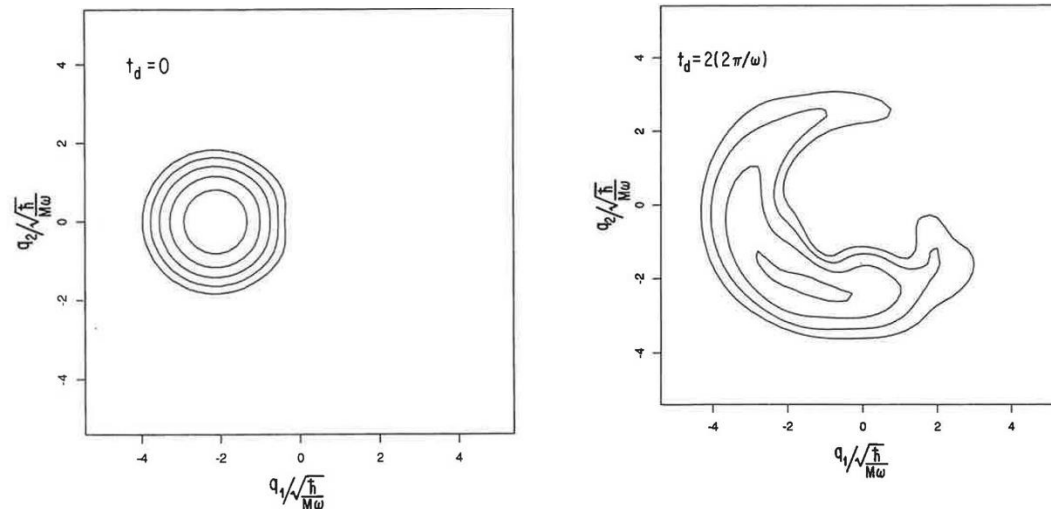*Instituto de Física, Universidad Nacional Autónoma de México, México, D.F.*

Adv. Chem. Phys (1992)

Example predicted experimental signal

Computational view of the wave packet

Experiment in molecules never happened
Timing challenging
Orientation of molecules in condensed phase
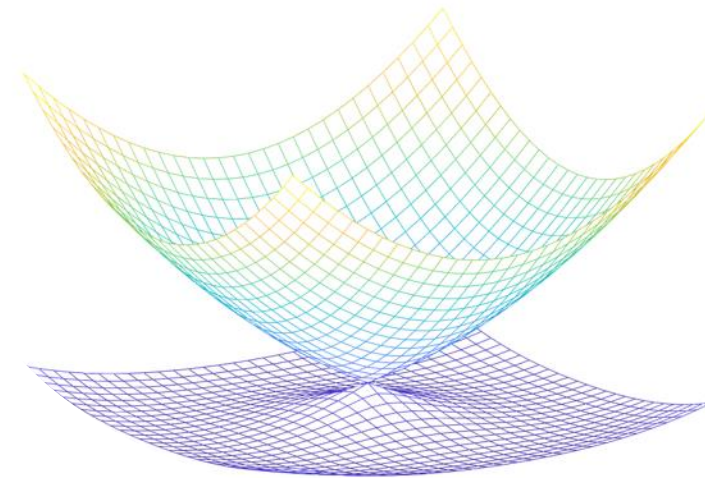**More complicated potentials**
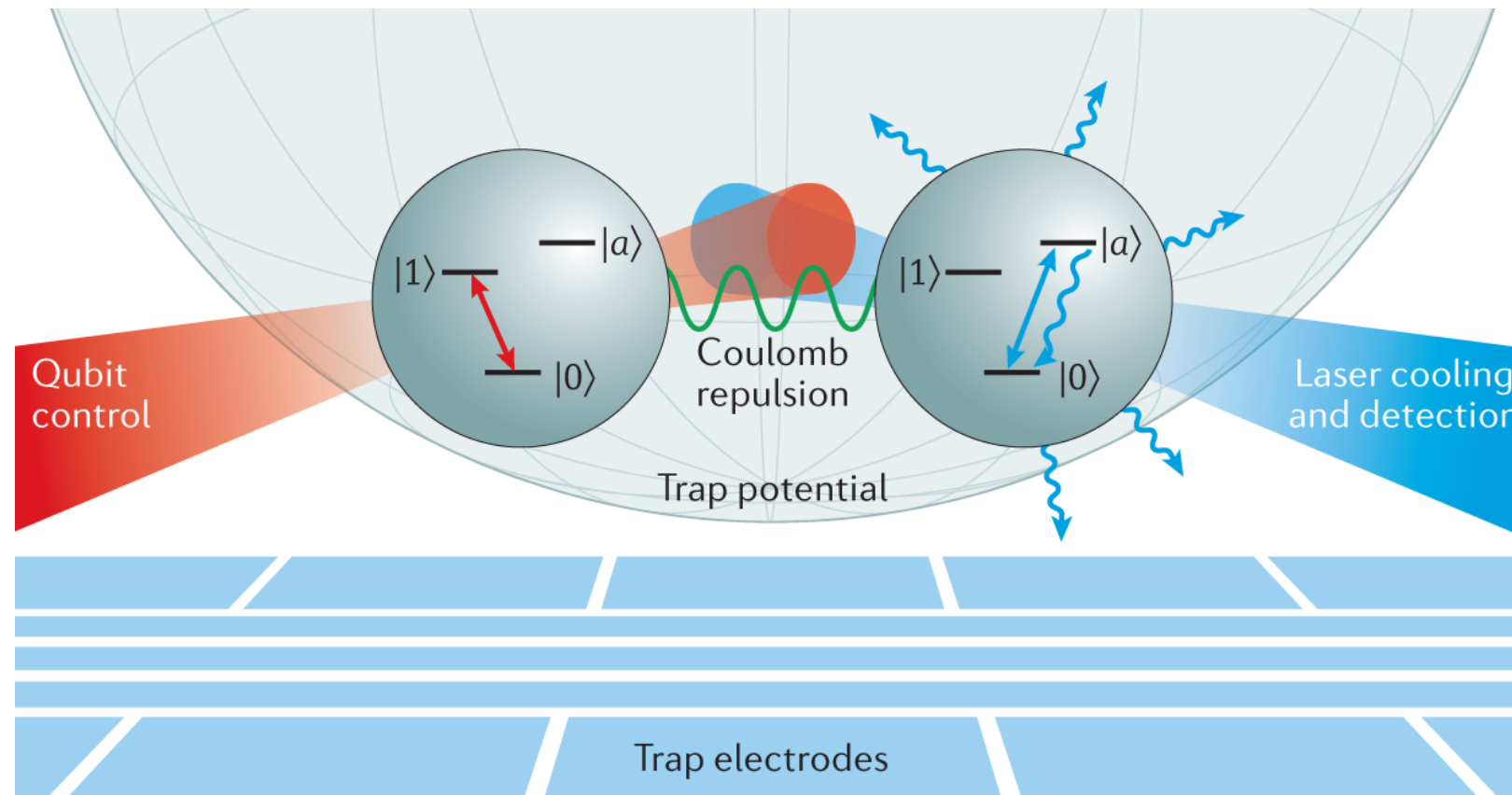
Simple conical intersection

- A two-dimensional harmonic oscillator with two spin-dependent displacements.

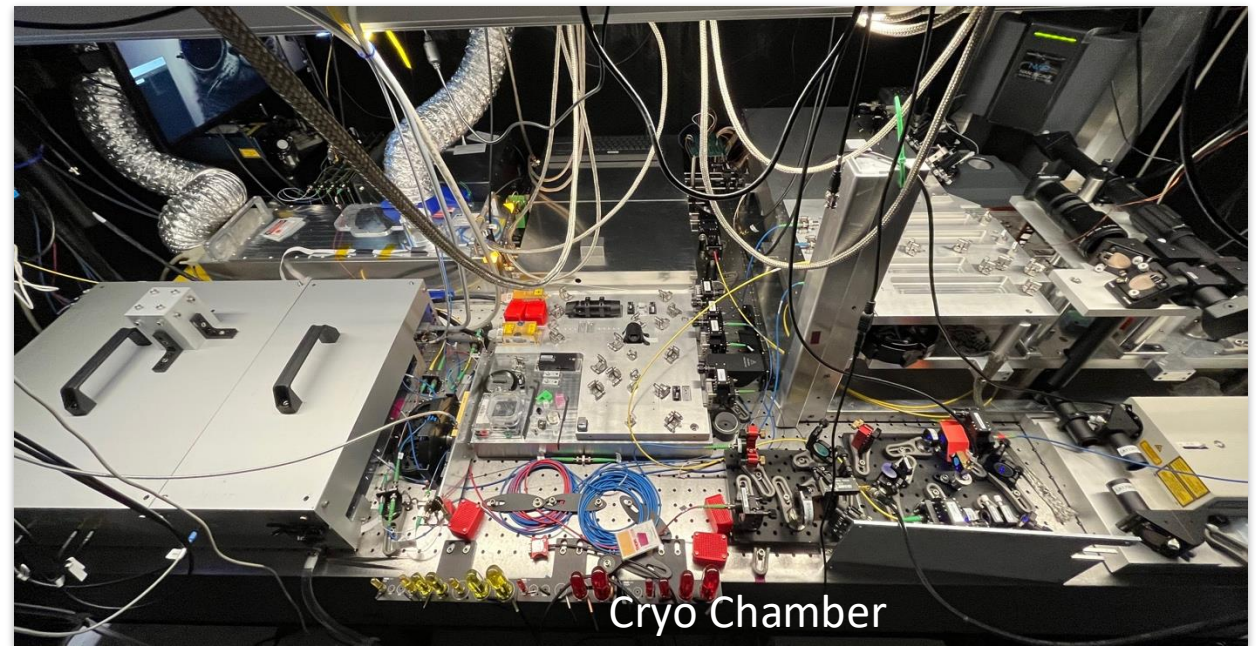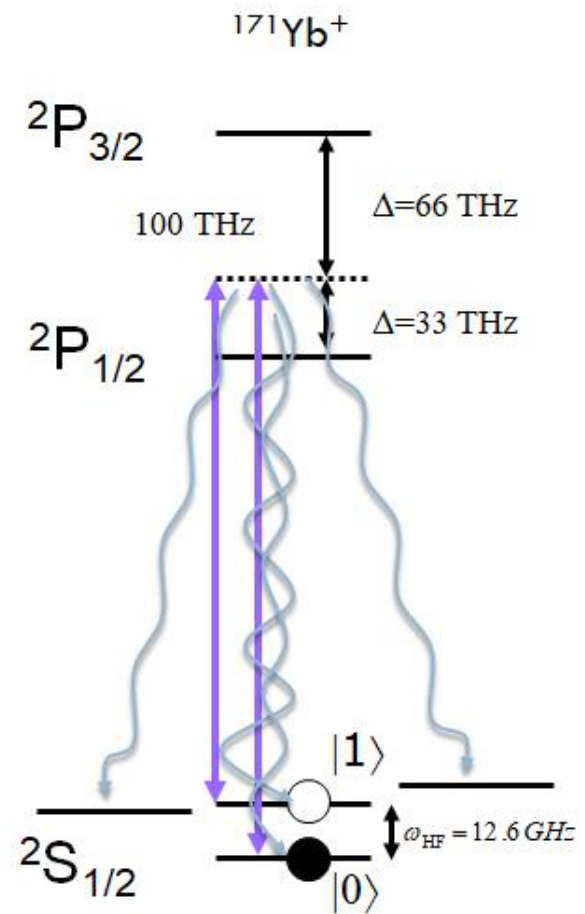$$H = \sum_{q=\{x,y\}} \frac{p_q^2}{2m} + \frac{mq^2}{2} + F_q \sigma_q q$$

- Adiabatic potential energy surfaces where the spin is the eigenstate of

$$F_x \sigma_x x + F_y \sigma_y y$$
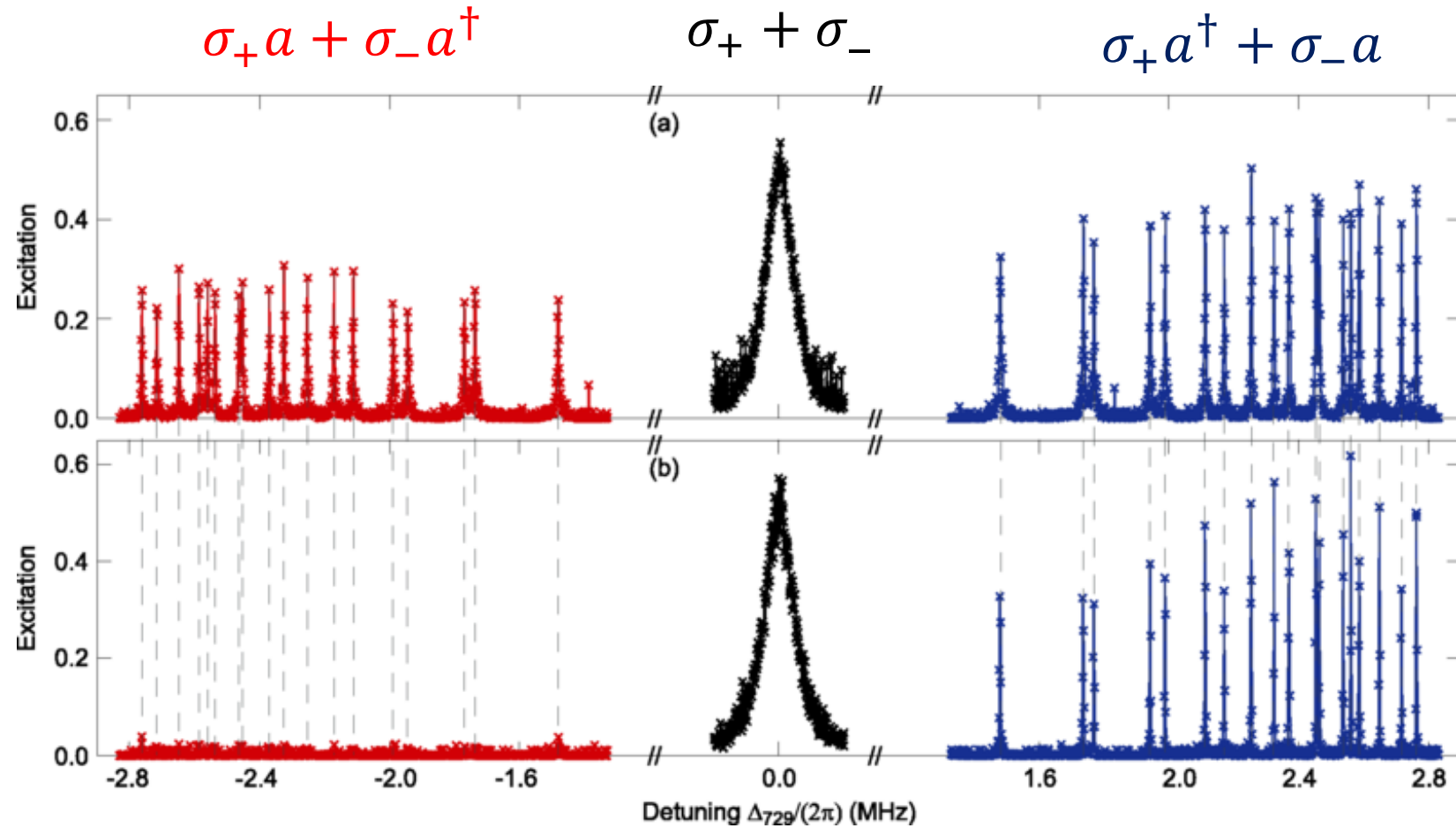
Controlling trapped ions

Gates with Raman Lasers

$^{171}\text{Yb}^+$

$^2P_{3/2}$

100 THz

$\Delta = 66$ THz

$^2P_{1/2}$

$\Delta = 33$ THz

$|1\rangle$

$|0\rangle$

$^2S_{1/2}$

$\omega_{HF} = 12.6\ GHz$

Cryo Chamber

Duke
PRATT SCHOOL of
ENGINEERING

Ion and Motion

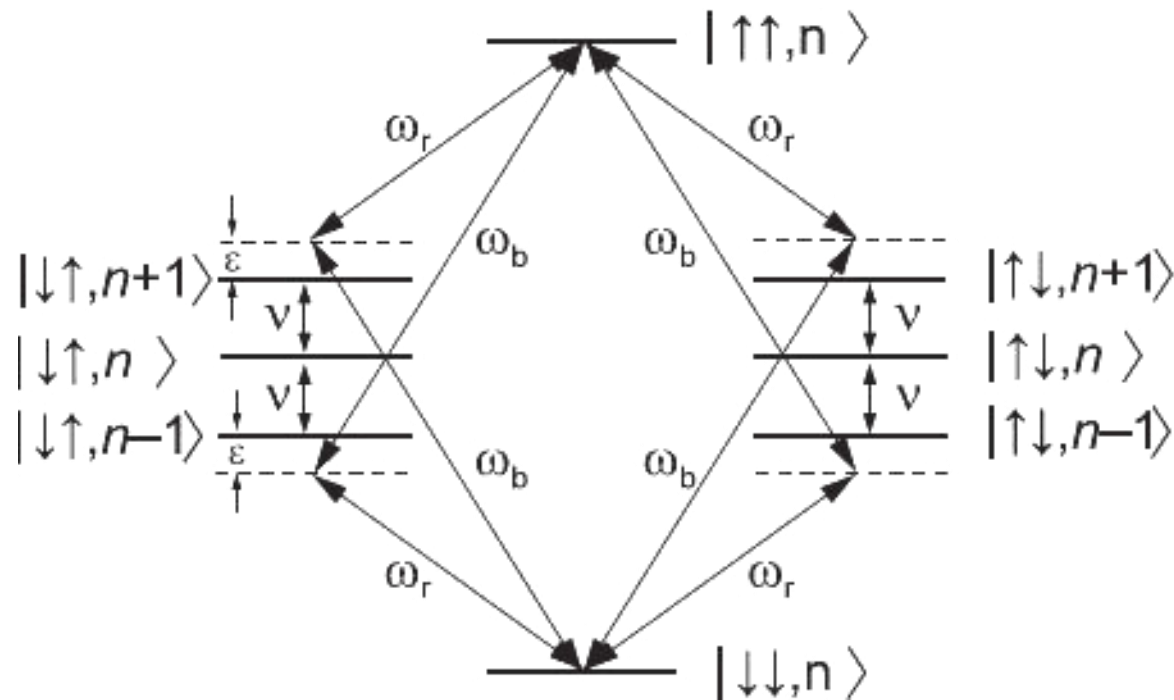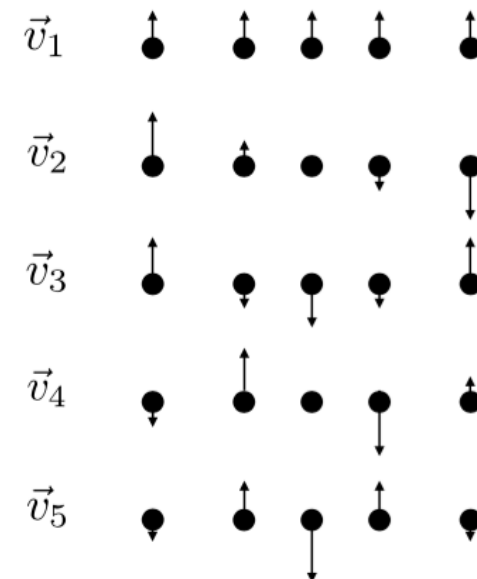$$\sigma_+ a + \sigma_- a^\dagger \qquad \sigma_+ + \sigma_- \qquad \sigma_+ a^\dagger + \sigma_- a$$

R. Lechner et al. PRA (2016)
Innsbruck

Two Qubit Pulse Sequences

Ion internal states entangled via shared motional modes

$$U = \exp(-i\,\theta/2\;XX)$$

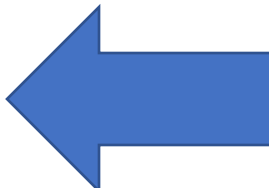A . Sorensen and K. Molmer PRL (1999)   Similar ideas: Solano and Milburn

Mølmer-Sørensen gate

- Ion Trap Hamiltonian for sideband transitions:

$$H = \sum_{i,k=1}^{N} \frac{1}{2} \eta_{ik} \sigma_x^i \Omega_i(t) (a_k^\dagger e^{i\theta_k(t)} + a_k e^{-i\theta_k(t)})$$

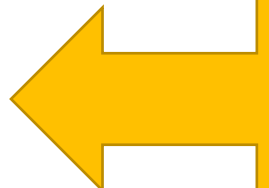$$\theta_k(t) = \int_0^t \delta_k(t') dt', \; \delta_k(t) = \mu(t) - \omega_k$$

Hamiltonian in interaction picture coupling ion internal state with motional modes

- After solving TDSE by Magnus expansion, unitary:

$$U_{MS} = \exp(\sum_{k=1}^{N} \hat{\alpha}_k(t) a_k^\dagger - \hat{\alpha}_k^\dagger(t) a_k) \exp(-i\beta(t)\sigma_x^i \sigma_x^j)$$

$$\hat{\alpha}_k(t) = \frac{1}{2}(\eta_{ik}\sigma_x^i + \eta_{jk}\sigma_x^j) \int_0^t \Omega(t') e^{i\theta_k(t')} dt'$$
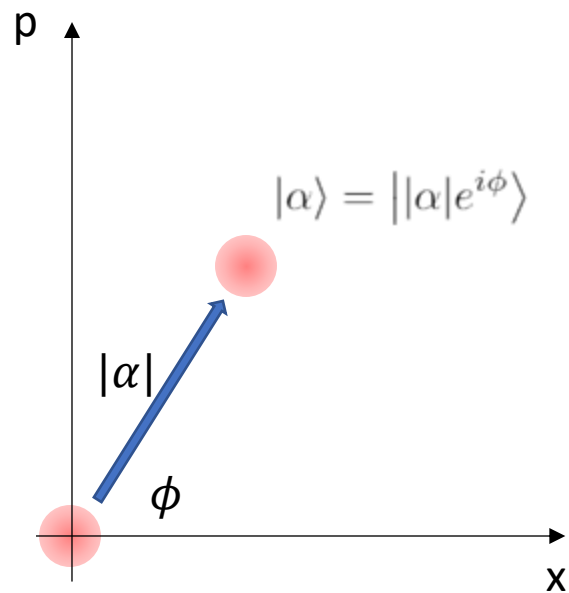
$$\beta(t) = \sum_{k=1}^{N} \frac{1}{2} \eta_{ik}\eta_{jk} \int_0^t \int_0^{t'} \Omega(t')\Omega(t'') \sin(\theta_k(t') - \theta_k(t'')) dt'' dt'$$
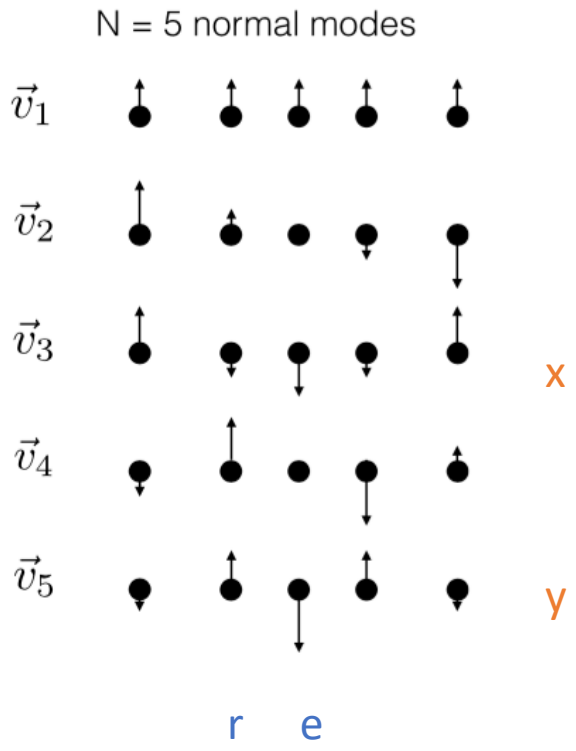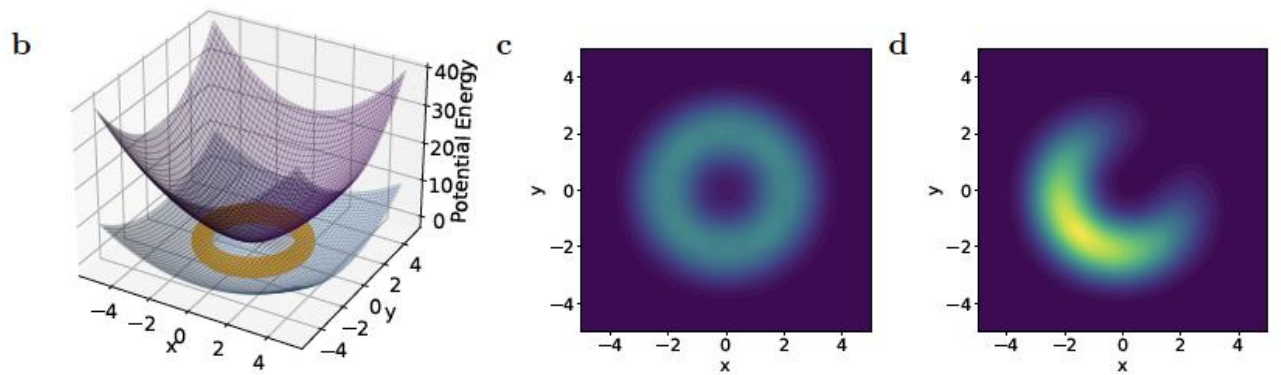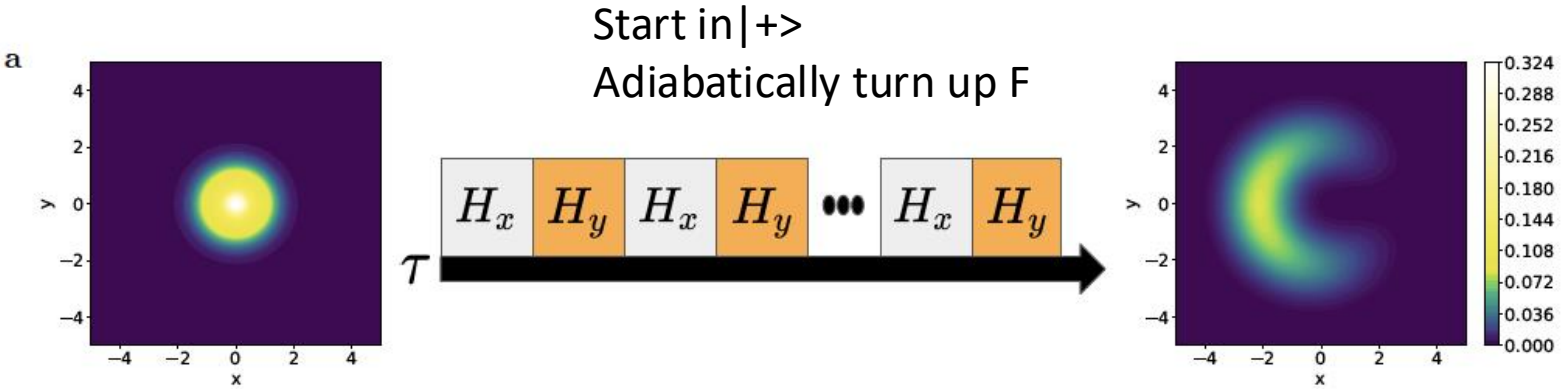
Dynamics can be described by by a second-order Magnus expansion

Duke
PRATT SCHOOL of ENGINEERING

Controlling Motion Modes

In phase space:

$$|\alpha\rangle = ||\alpha|e^{i\phi}\rangle$$

$|\alpha|$

ϕ

p

x

Experimental method and expected results

Start in|+>
Adiabatically turn up F

$$H = \sum_{q=\{x,y\}} \frac{p_q^2}{2m} + \frac{mq^2}{2} + F_q \sigma_q q$$

Whitlow et al. Nature Chem. (2023)
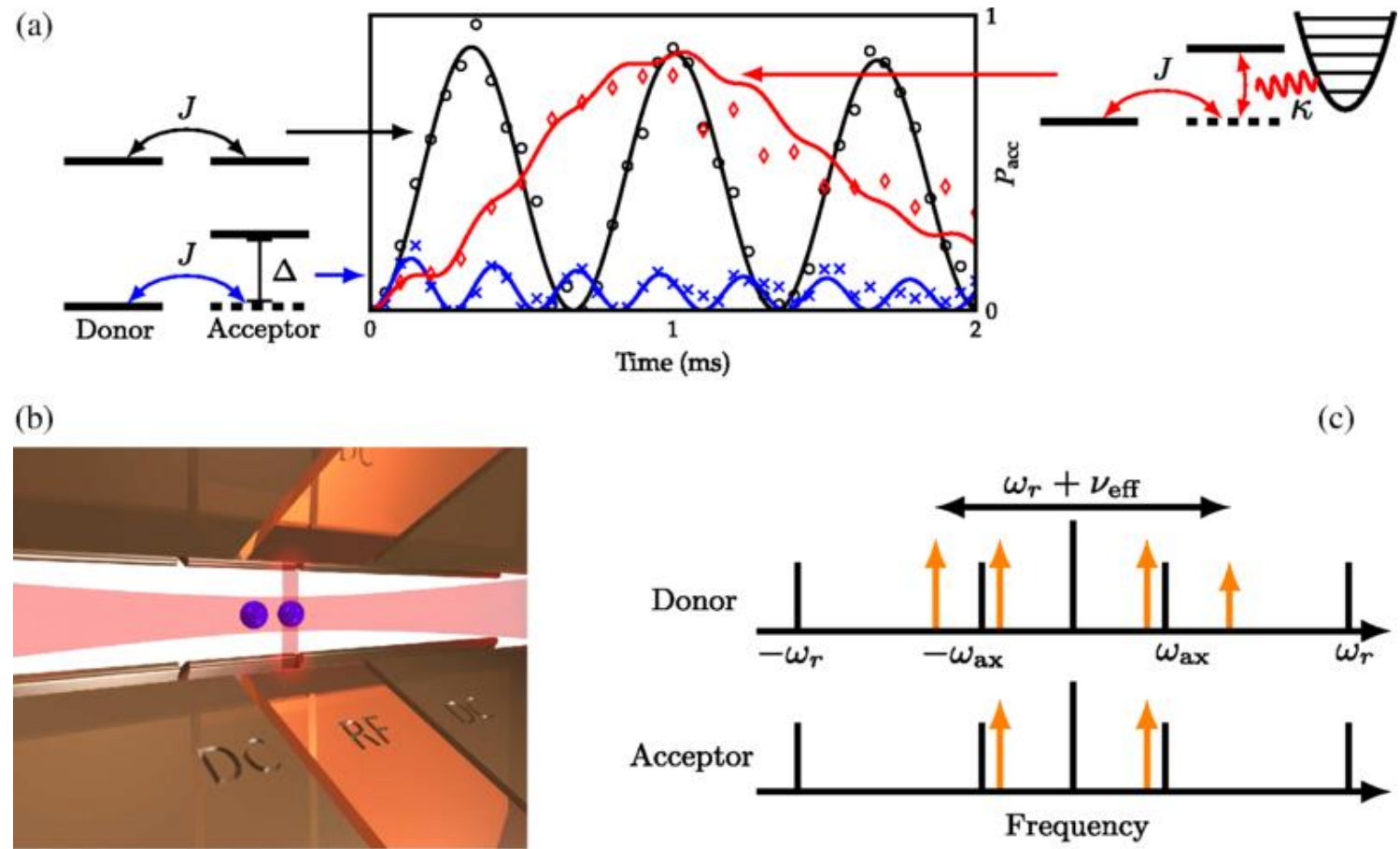
Robust feature
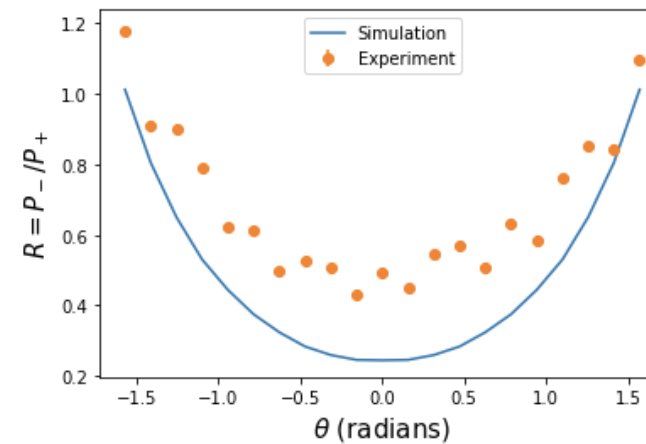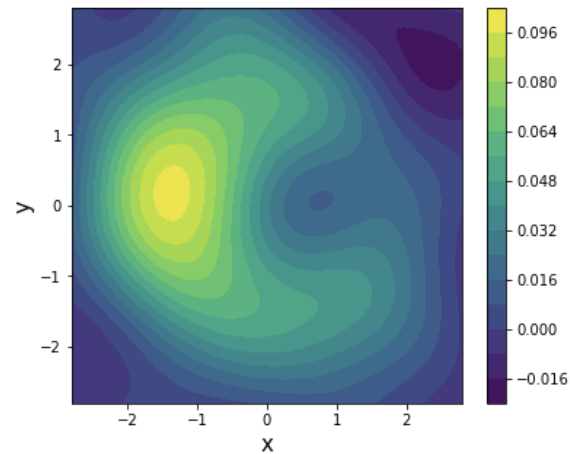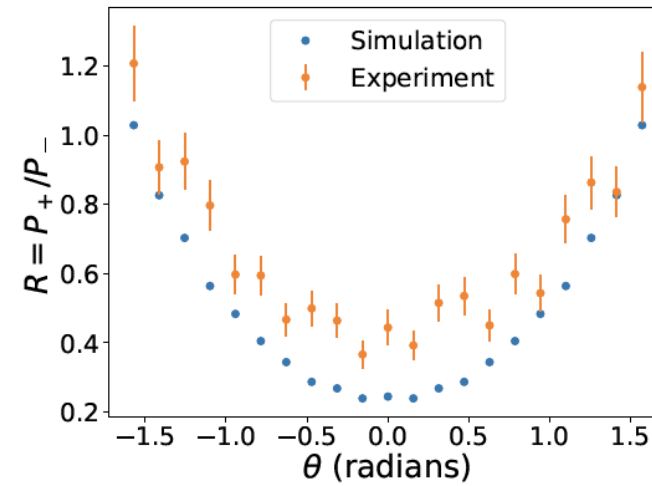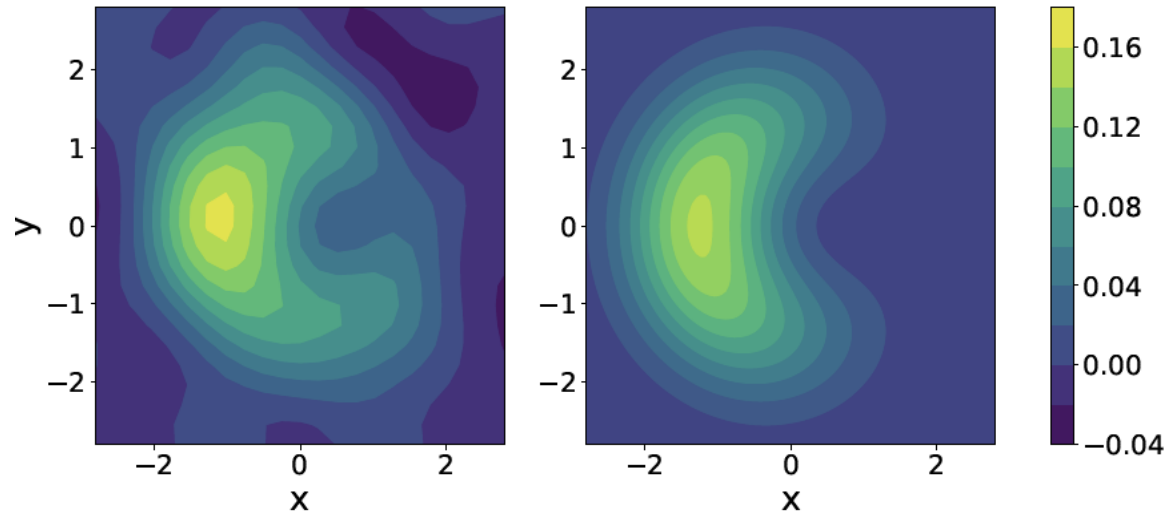
Whitlow et al. Nature Chem. (2023)

Similar work: Valahu et al. Nature Chem. 2023 (Kassal, Tan, Sydney)

Engineering Vibrationally Assisted Energy Transfer in a Trapped-Ion Quantum Simulator

Dylan J Gorman, Boerge Hemmerling, Eli Megidish, Soenke A. Moeller, Philipp Schindler, Mohan Sarovar, and Hartmut Haeffner
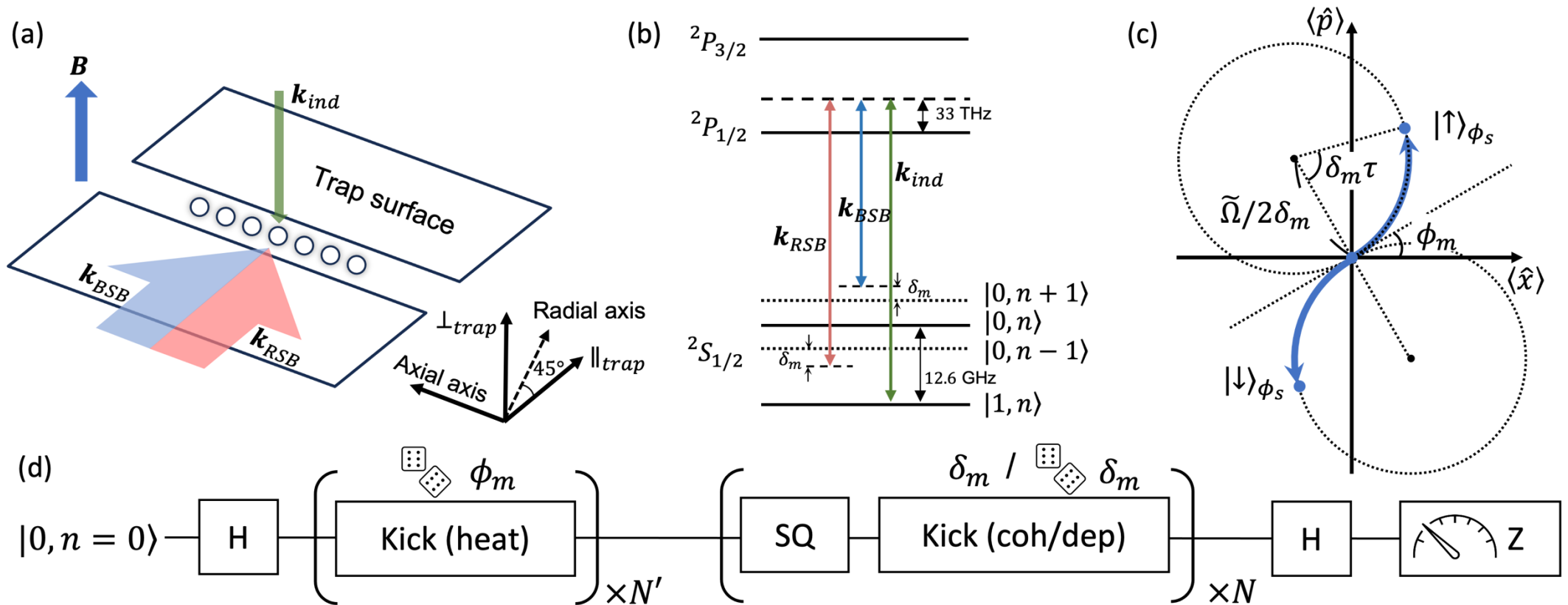
Physics See Synopsis: Quantum Simulators Tackle Energy Transfer

Ion Traps for Chemical Dynamics

(a)

Vibrational mode

Donor

Acceptor

(b)

M. Kang et al. Nature Rev. Chem. (2024) arXiv:2305.03156
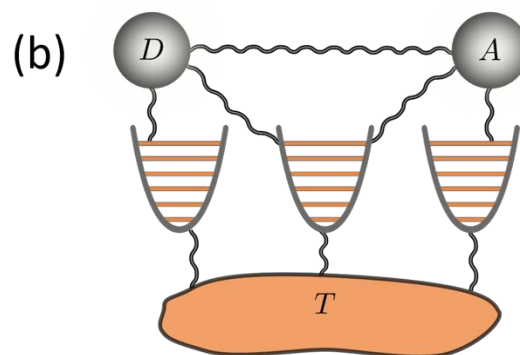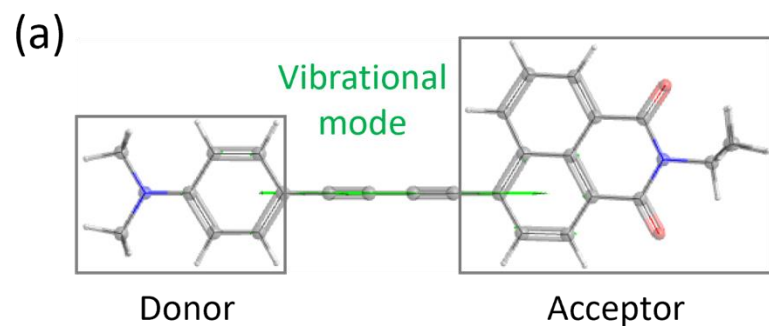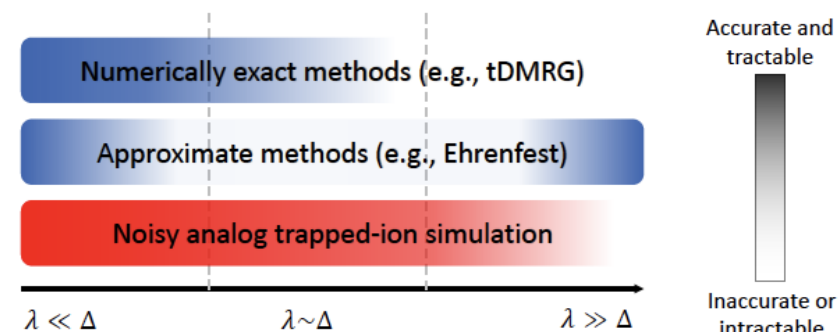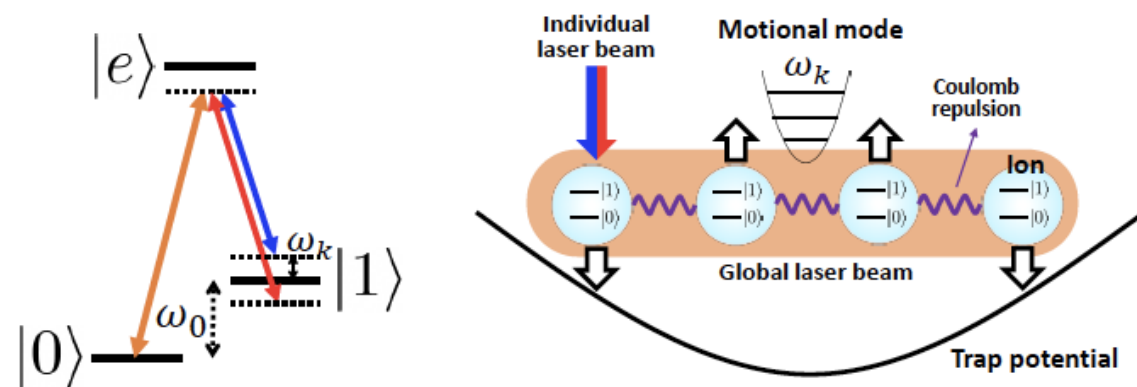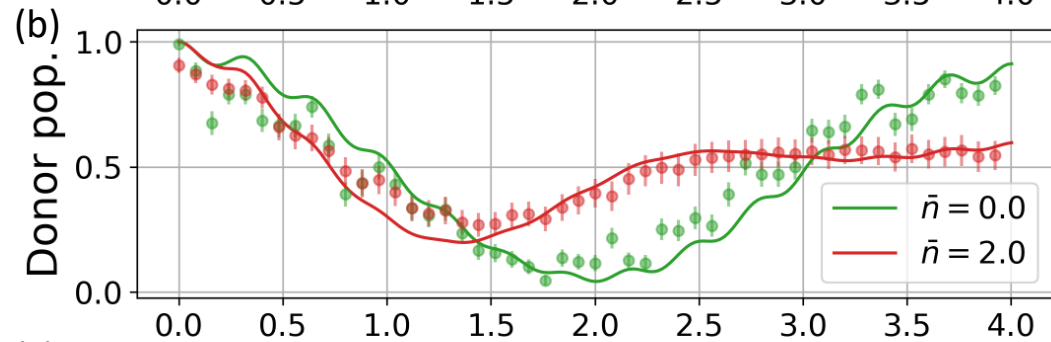
Structured Bath

Vibrational Assisted Energy Transfer
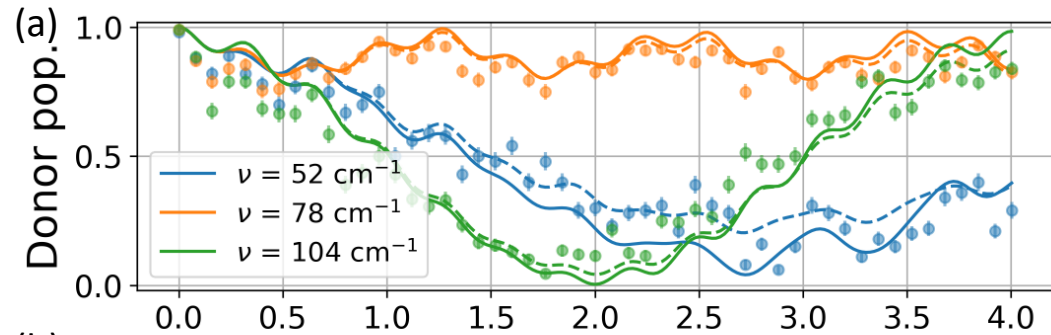
(a) Observe resonant and harmonic enhancement

(b) Wash out oscillations with higher temperature bath
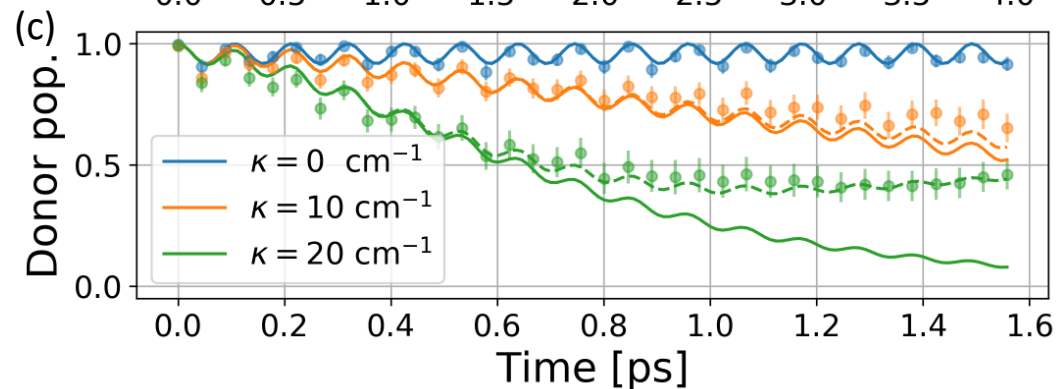
(c) Emulate a T_1 process with a T_2 process

Related Work with Tunable Dissipation:
V. So et al. arXiv:2405.10368 (Pagano)

High energy physics and nuclear physics
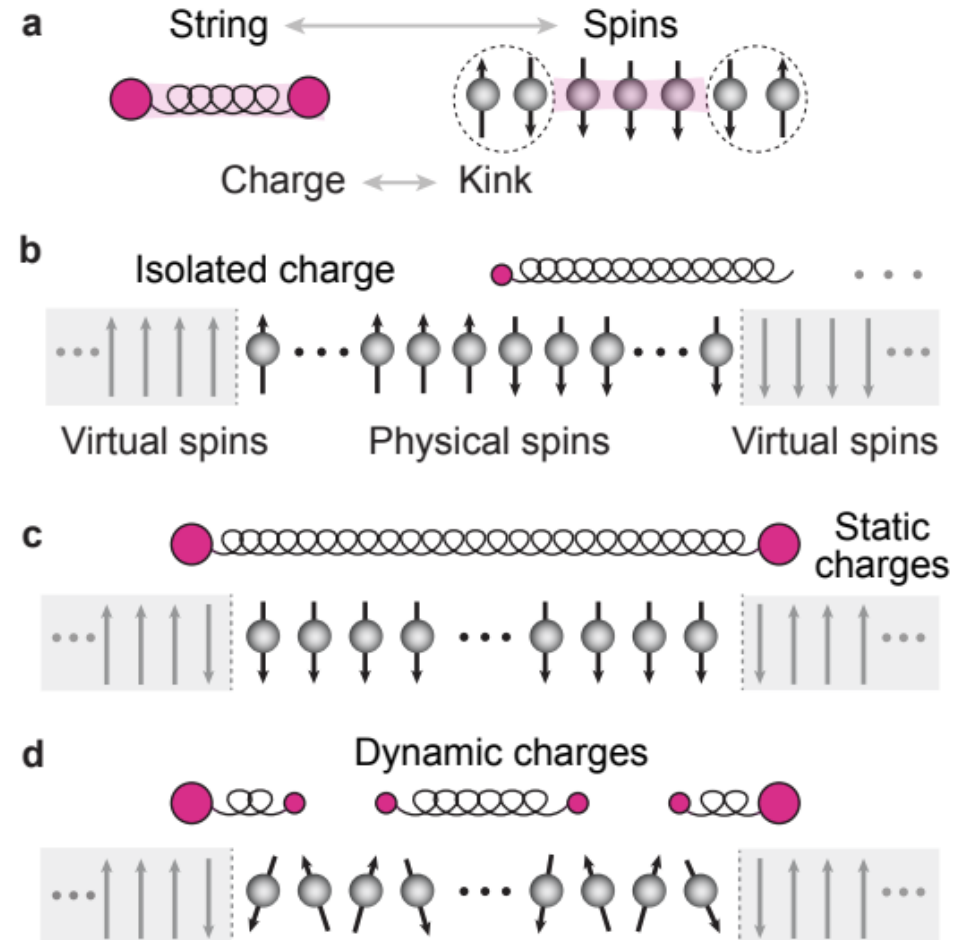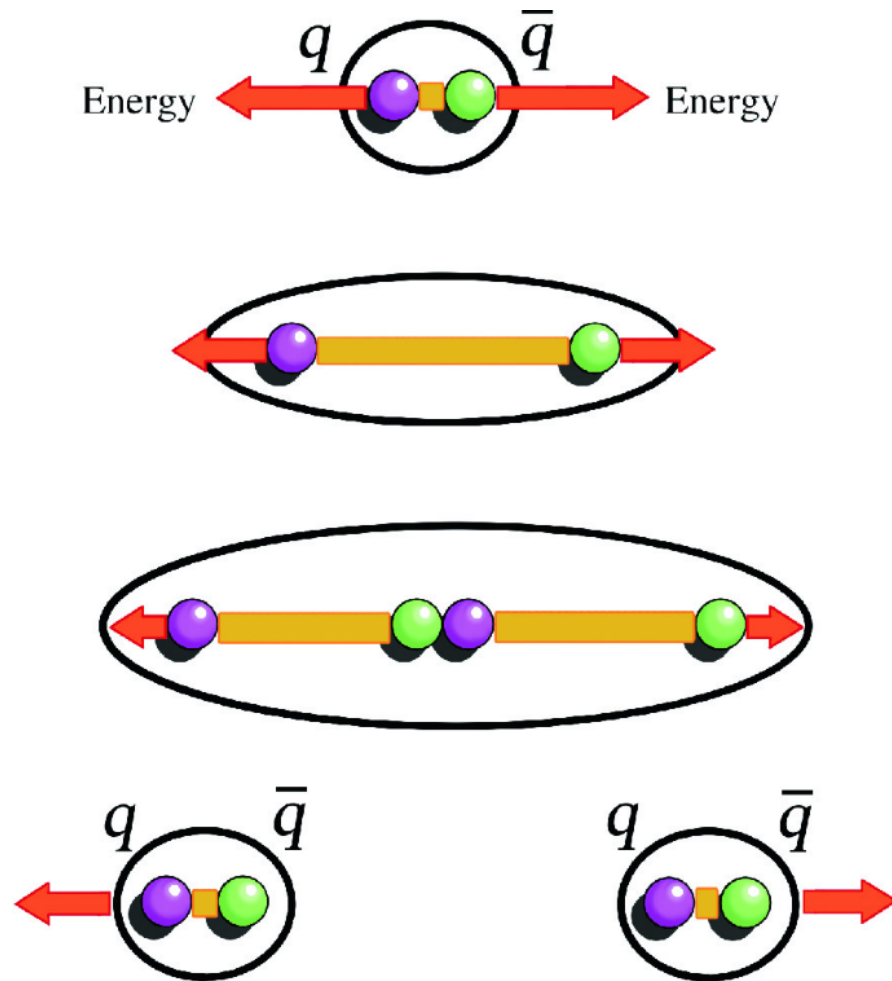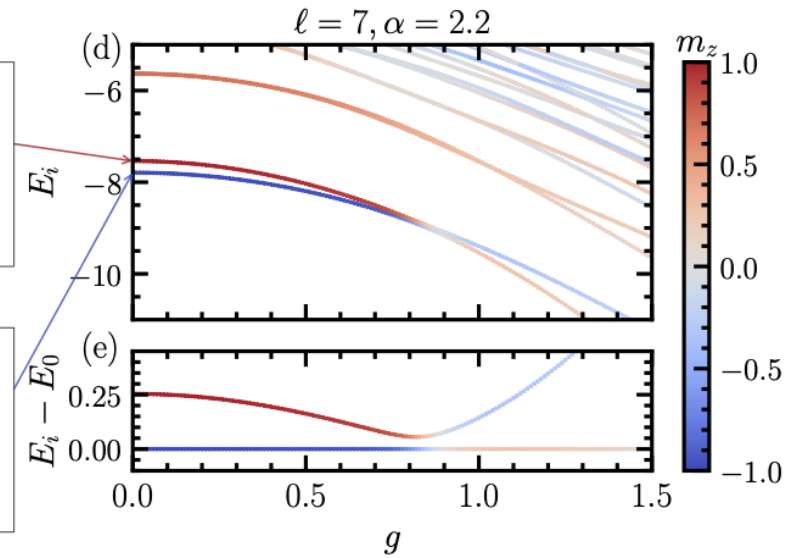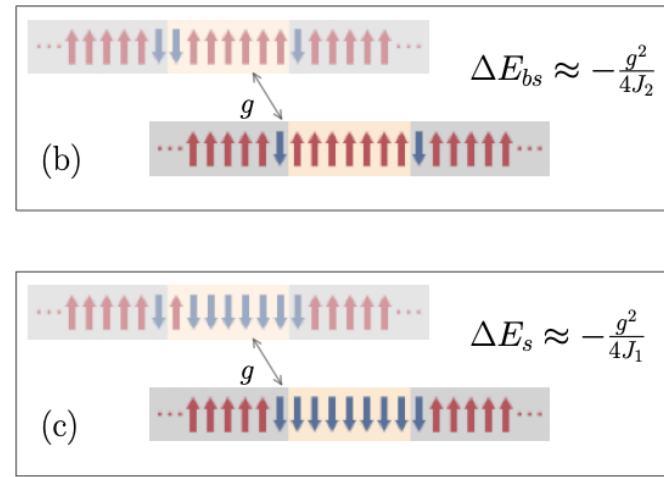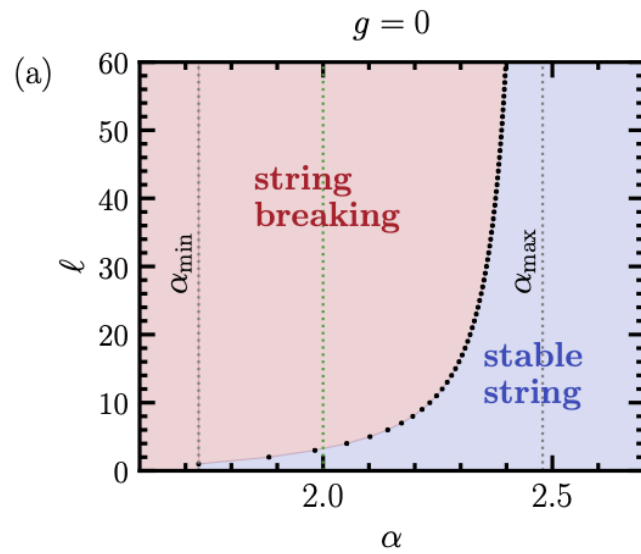
String-Breaking Dynamics in Quantum Adiabatic and Diabatic Processes

F. N. Surace et al. arXiv:2411.10652

Observation of string-breaking dynamics in a quantum simulator

A. De et al. arXiv:2410.13815
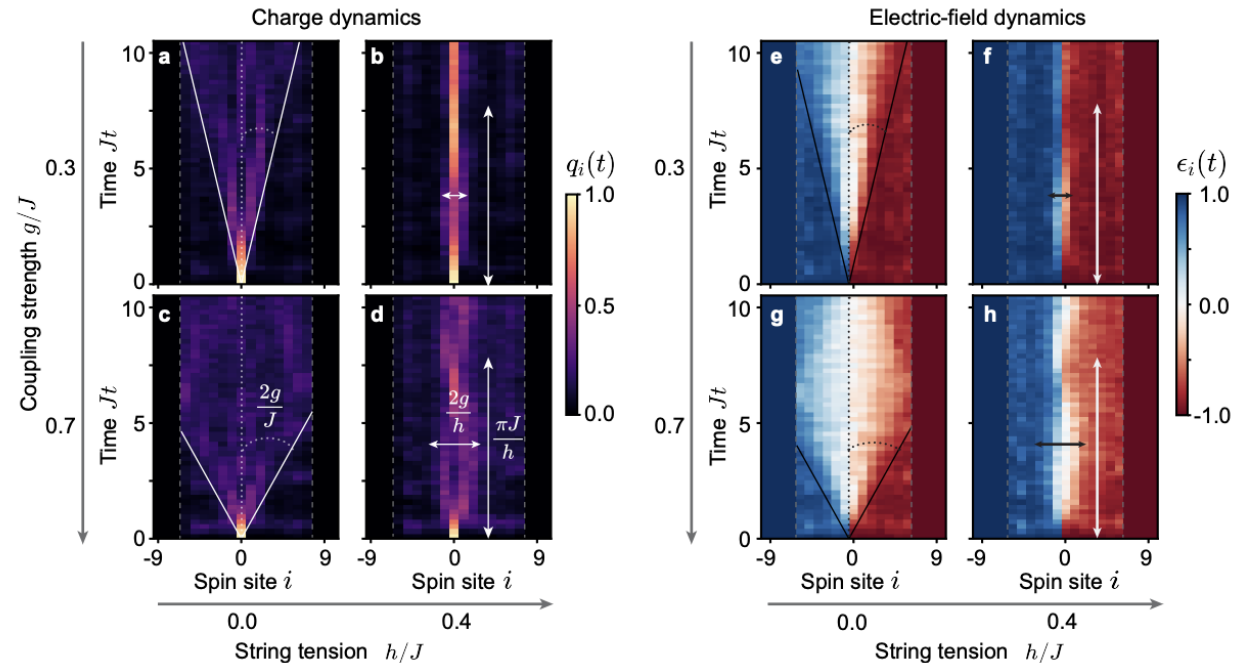
Schwinger Model. 1+1D QED
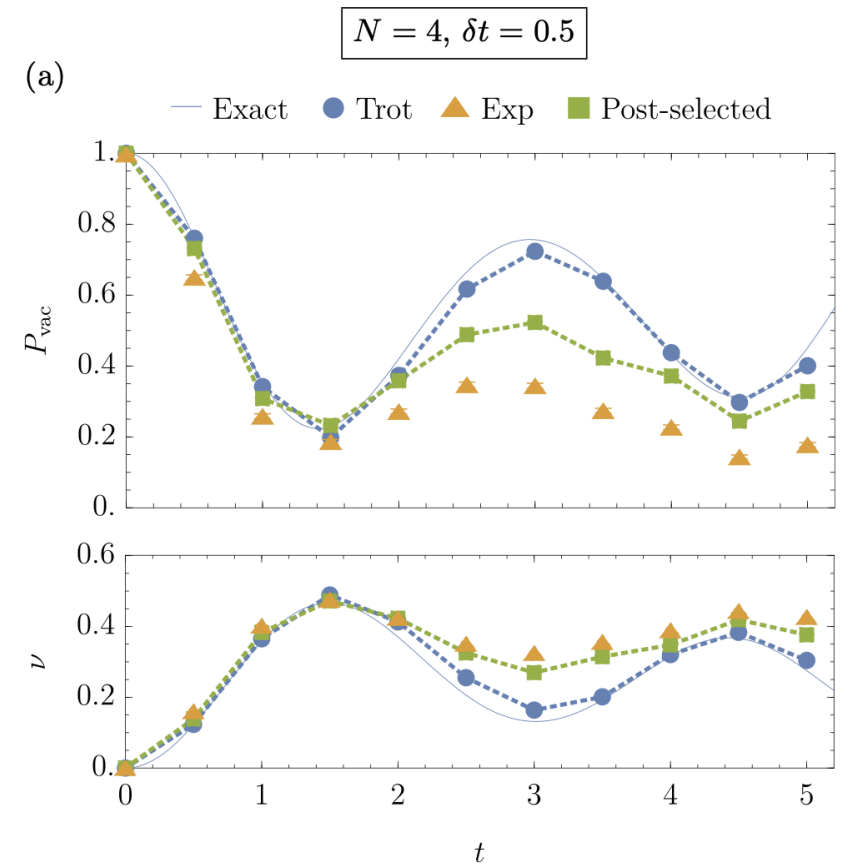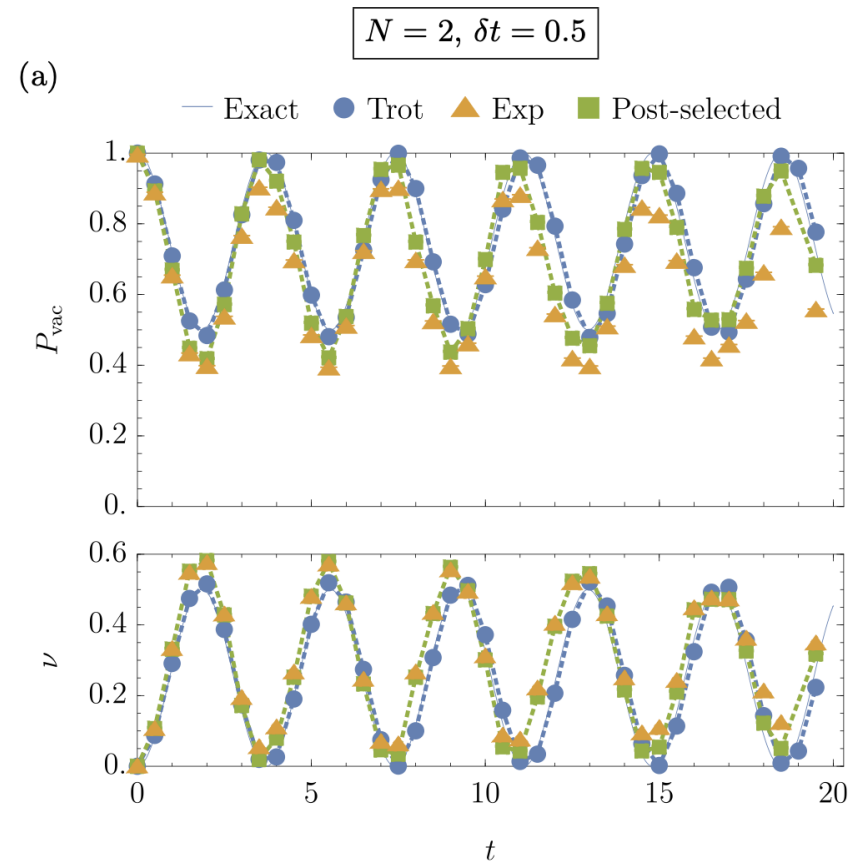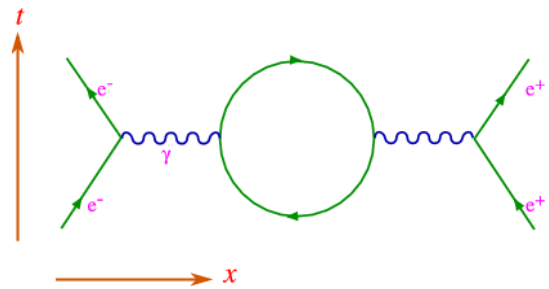
N. Nguyen et al. PRX Quantum **3**, 020324 (2022)

Hybrid Oscillator-Qubit Quantum Processors: Simulating Fermions, Bosons, and Gauge Fields
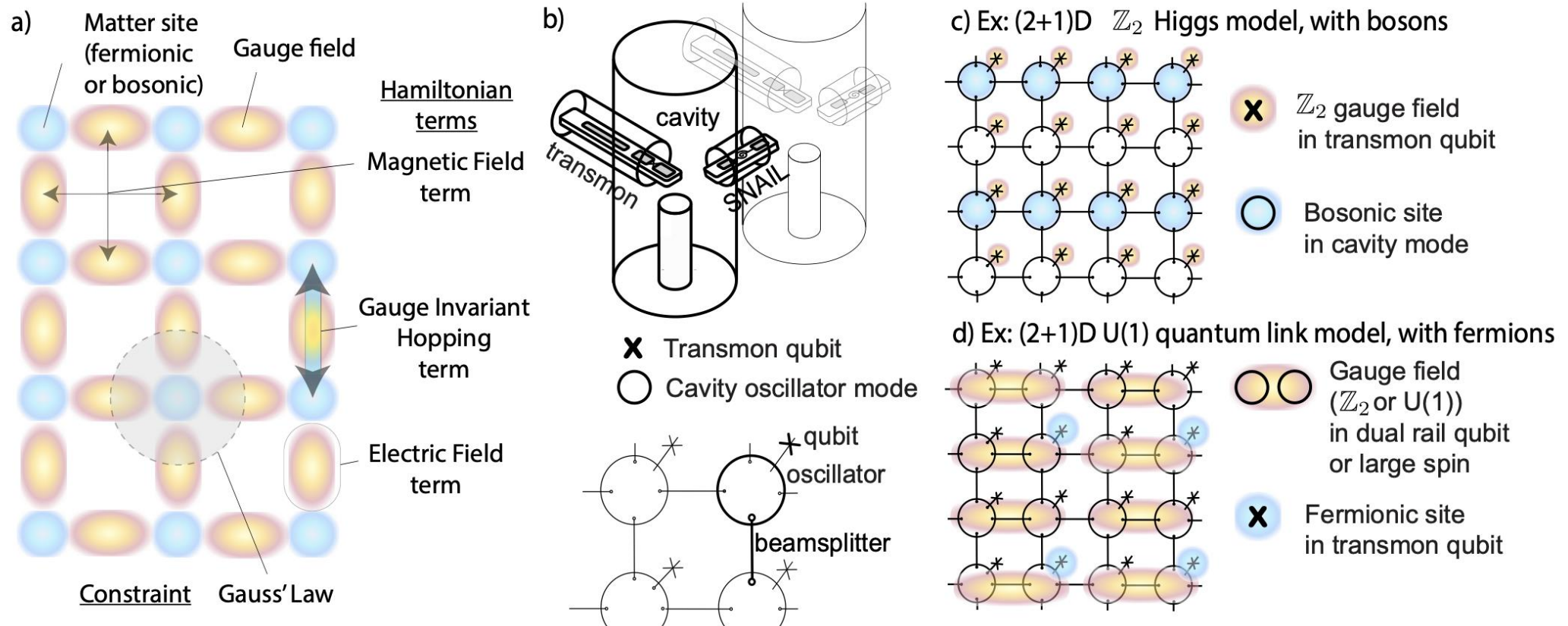
E. Crane et al. arXiv:2409.03747

Ions: J.Y. Araz, M. Grua, J. Montogomery, F. Ringer, arXiv:2410.07436

Bosons as thermal bath

A. T. Than et al. 2501.00579 Green/Muschik/Linke
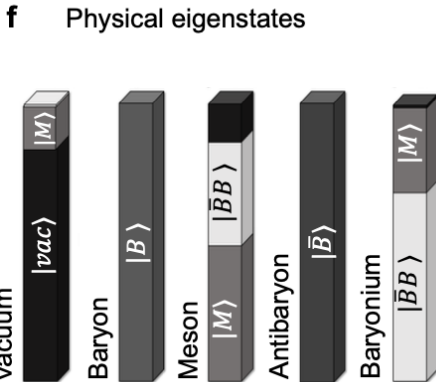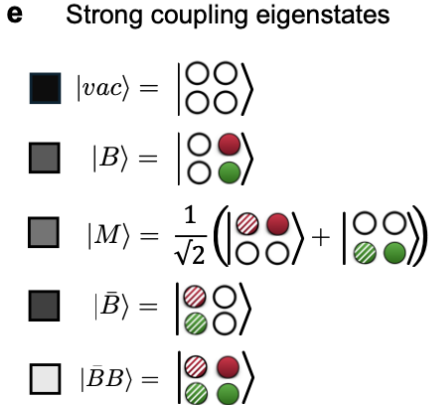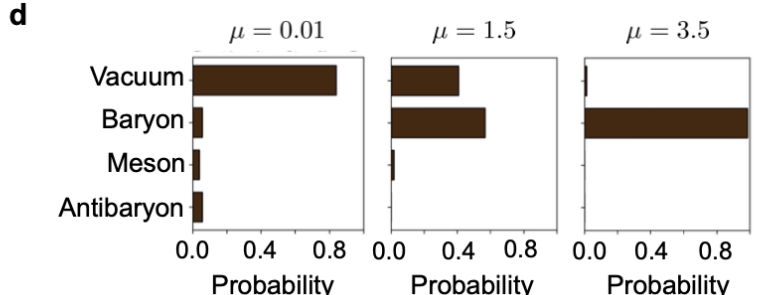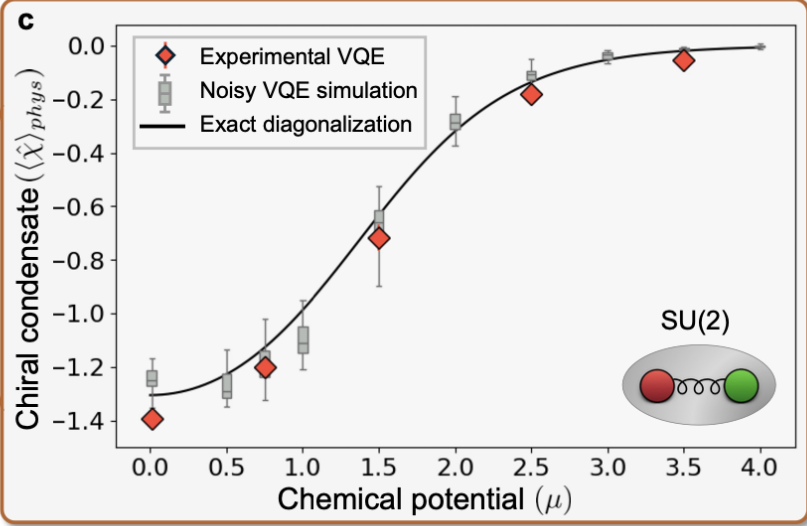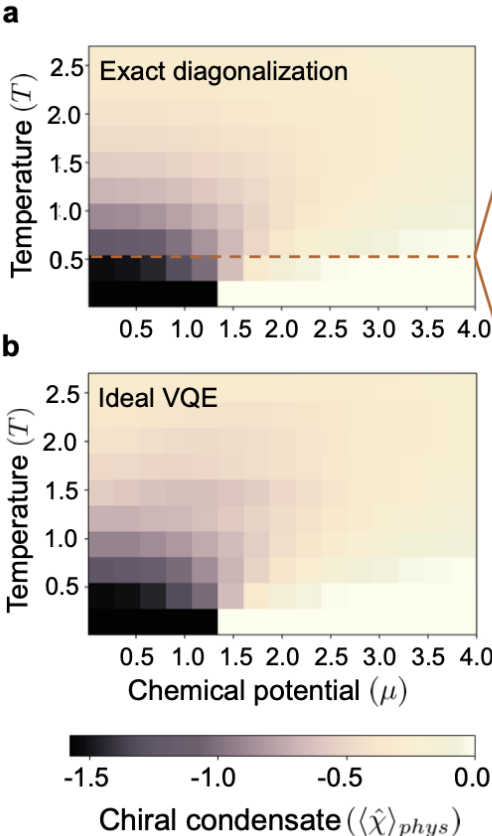
Conclusion

- Spins and bosons can be used to study chemical dynamics, nuclear physics, and particle physics

- Quantum advantage may be possible when the vibronic coupling is similar in energy scale to the electronic energy splitting

- System control allows us to include tunable dissipative effects

J. Cao et al., Sci. Adv. 6:eaaz4888 (2020)
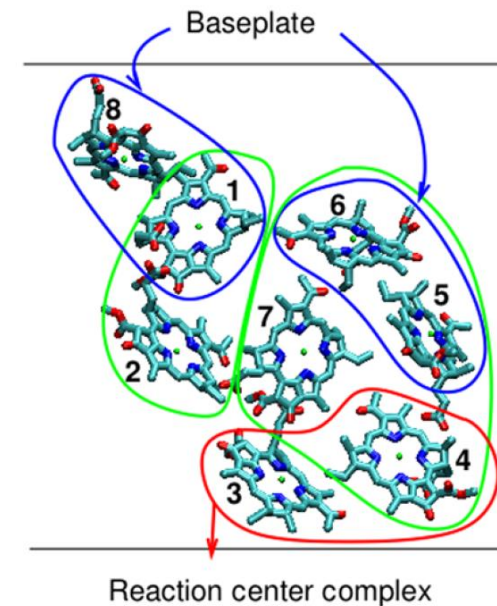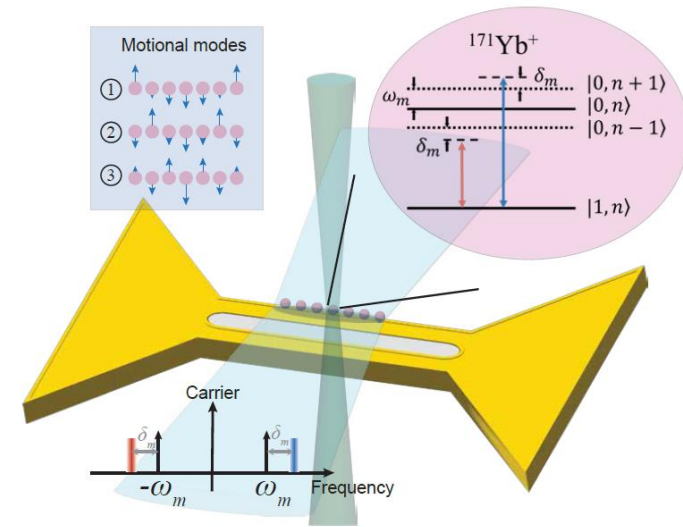
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Brown Lab and MIST Lab Fall 2023

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W. Campbell and E.R. Hudson, Phys. Rev. Lett. **125**, 120501 (2020) arXiv:1909.02668
M. Mills et al. Phys. Chem. Chem. Phys. **22**, 24964 (2020) arXiv:2008.09201
L. Qi, E. C. Reed, B. Yu, and K. R. Brown, arXiv:2411.07137

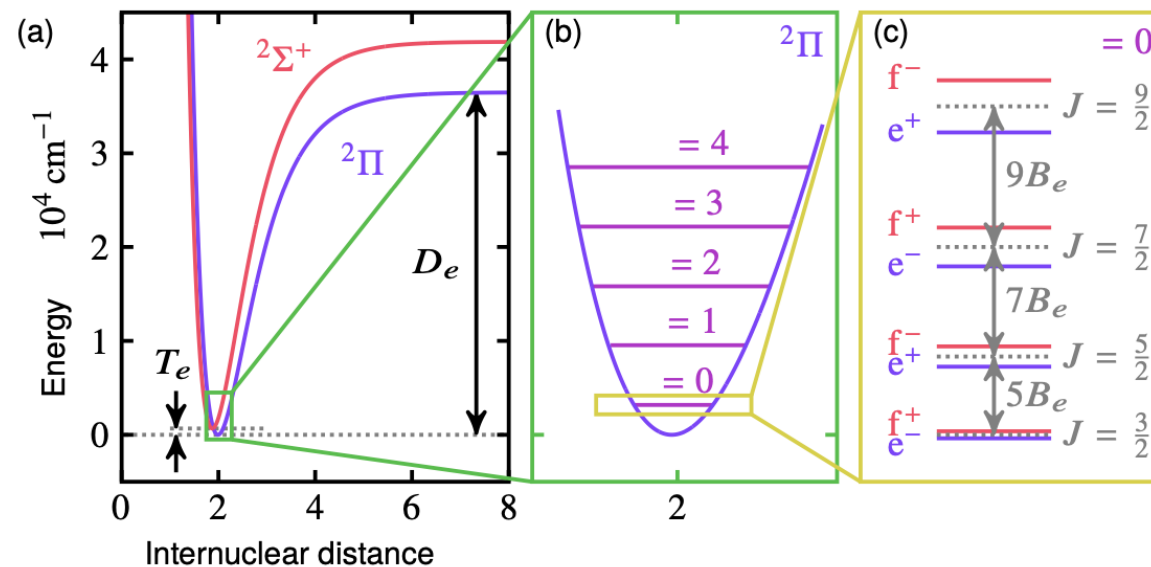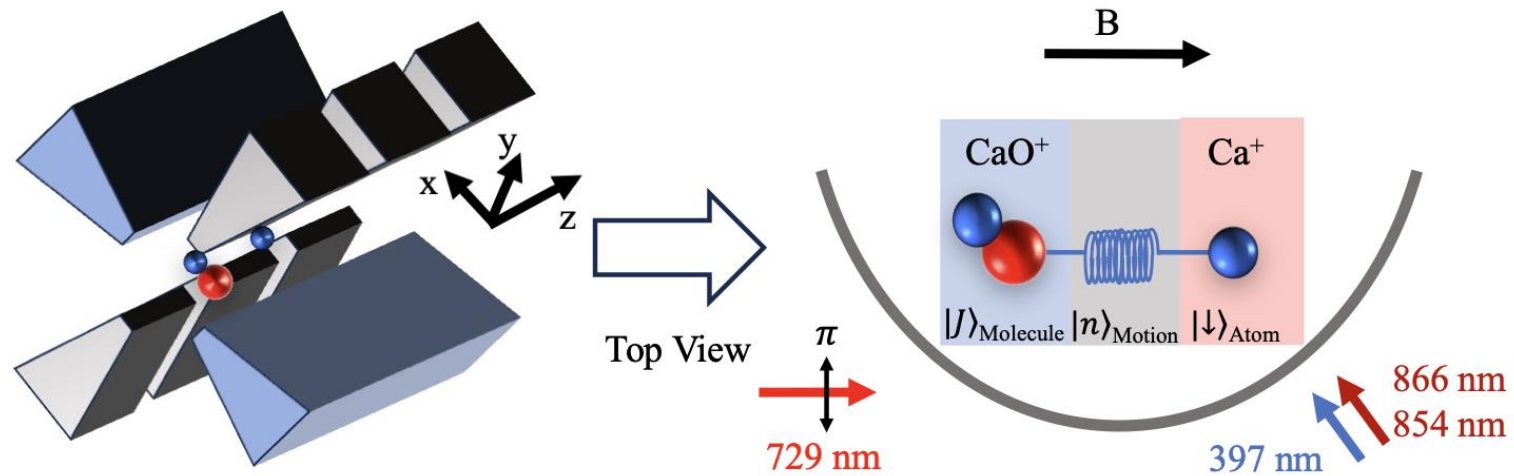|	A_{SO} (cm^{-1})	B_e (cm^{-1})	ω_e (cm^{-1})	D_e (eV)	PDM (Debye)	$10^{-3} \cdot T_e$ (cm^{-1})	Λ-doublet splitting (MHz)				4 K/300 K Population (%)			
							$J=3/2$	5/2	7/2	9/2	$J=3/2$	5/2	7/2	9/2
BeO$^+$	-117	1.44	1242	3.8	7.5	9.4	3.8	16	42	84	89/2.1	10/3.1	1/3.9	0/4.6
MgO$^+$	-130	0.53	718	2.3	8.9	7.3	0.19	0.84	2.1	4.3	54/0.8	32/1.1	11/1.5	3/1.8
CaO$^+$	-130	0.37	634	3.3	8.7	0.7	0.45	1.9	5.0	10	42/0.5	32/0.8	17/1.0	6/1.3
SrO$^+$	-147	0.31	659	4.2	7.5	0.4	0.16	0.67	1.7	3.5	0/0.1	0/0.1	0/0.1	0/0.1
BaO$^+$	-214	0.24	506	2.2	7.9	1.5	0.089	0.39	0.98	2.0	0/0	0/0	0/0	0/0
YbO$^+$	-132	0.28	601	2.2	7.0	1.0	0.14	0.59	1.5	3.0	33/0.4	30/0.6	20/0.8	10/1.0
RaO$^+$	-228	0.20	451	3.3	7.7	0.3	0.081	0.35	0.89	1.8	25/0.3	26/0.5	21/0.6	14/0.8
BeS$^+$	-310	0.71	875	3.4	7.6	15.7	0.11	0.45	1.2	2.3	66/1.2	27/1.8	6/2.3	1/2.8
MgS$^+$	-303	0.25	469	2.0	9.2	12.9	0.0051	0.022	0.056	0.11	30/0.4	29/0.6	21/0.8	12/1.0
CaS$^+$	-299	0.15	390	4.0	11.3	5.0	0.0028	0.012	0.031	0.062	19/0.3	22/0.4	20/0.5	16/0.6
SrS$^+$	-316	0.12	423	3.1	8.7	0.3	0.0086	0.036	0.094	0.19	16/0.1	20/0.2	19/0.3	16/0.4
BaS$^+$	-273	0.08	291	3.3	9.1	2.5	0.00093	0.0040	0.010	0.021	11/0.1	14/0.2	15/0.2	15/0.3
YbS$^+$	-254	0.10	345	2.2	7.8	4.6	0.0013	0.0056	0.014	0.029	13/0.1	17/0.2	18/0.3	16/0.3
RaS$^+$	-405	0.07	266	4.5	9.4	2.7	0.00043	0.0018	0.0047	0.0094	10/0.1	13/0.1	14/0.2	14/0.2

Table 1 A list of dipole-phonon quantum logic (DPQL) candidates in electronic state $^2\Pi_{3/2}$. This table includes the spin-orbital coupling constant (A_{SO}), rotational constant (B_e), vibrational constant (ω_e), dissociation energy (D_e), permanent dipole moment (PDM), energy interval between two lowest electronic states (T_e), Λ-doublet splitting and population of several low-lying rotational states. The ground electronic state of all the species in this table is $X^2\Pi_{3/2}$, except for SrO$^+$ and BaO$^+$, whose ground state is $X^2\Sigma^+$ and the first excited state is $A^2\Pi_{3/2}$.

M. Mills et al. Phys. Chem. Chem. Phys. **22**, 24964 (2020) arXiv:2008.09201

L. Qi, E. C. Reed, B. Yu, and K. R. Brown, arXiv:2411.07137