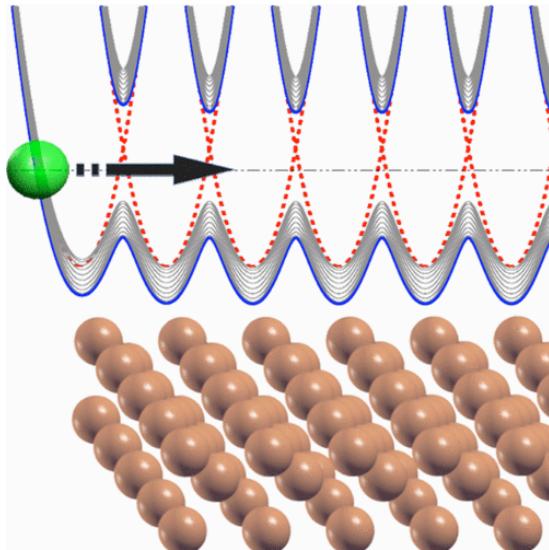
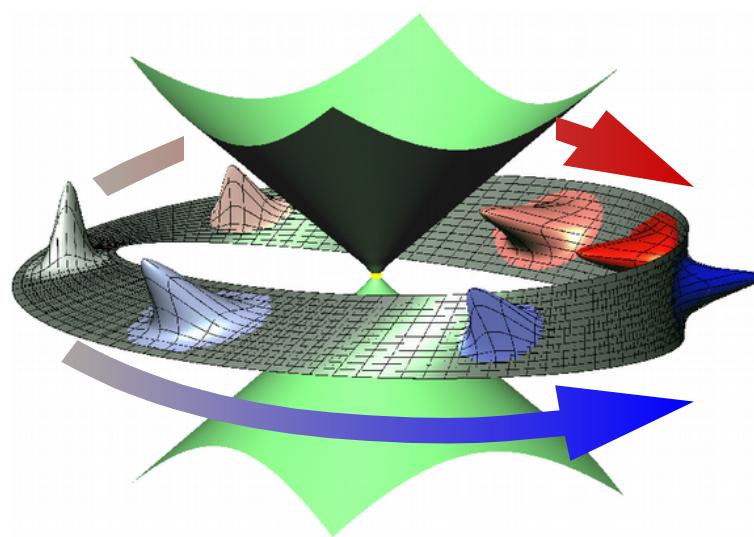


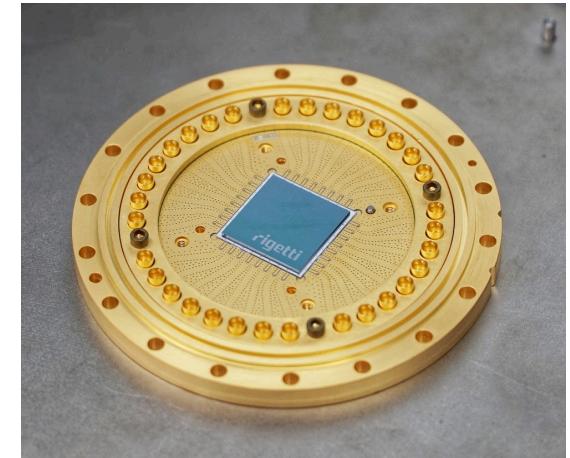
Nonadiabatic dynamics of molecules on surfaces using collective electronic variables



quantum-classical



fully quantum



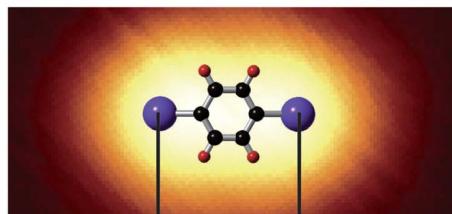
quantum-quantum

Artur Izmaylov

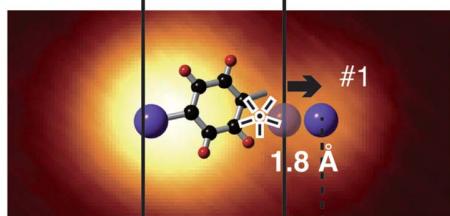


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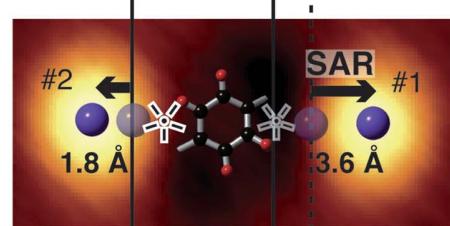
a) INITIAL STATE; pDIB



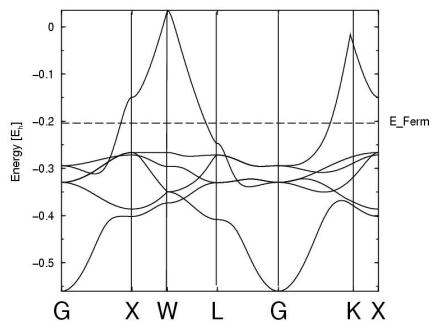
b) FINAL STATE; FIRST C-I BOND



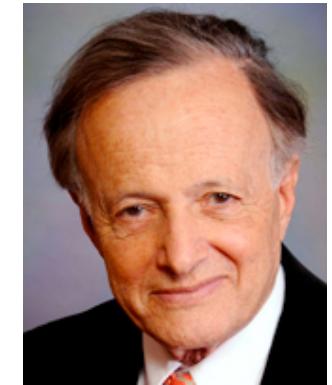
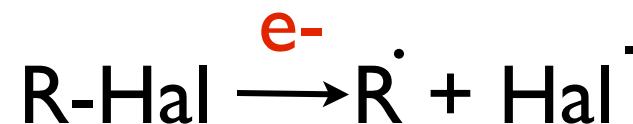
c) FINAL STATE; SECOND C-I BOND



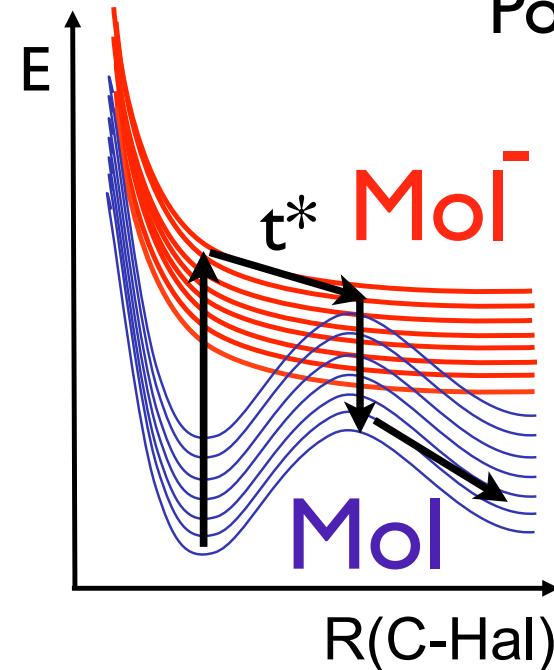
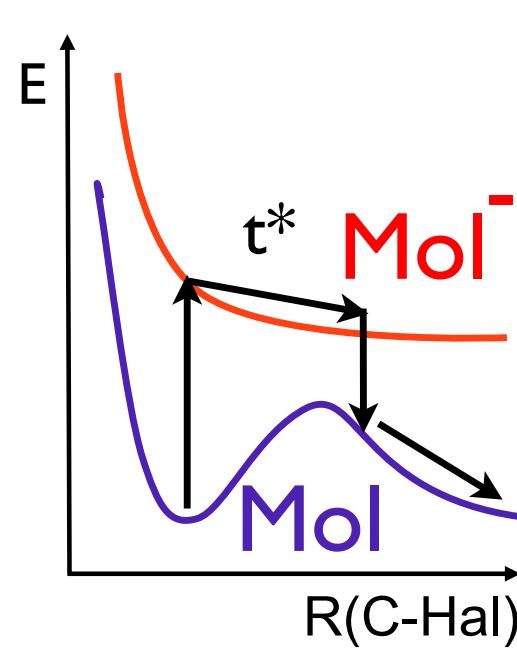
A Eisenstein, L Leung, T Lim,
Z Ning, and J C Polanyi
Faraday Disc. (2012)



STM experiments



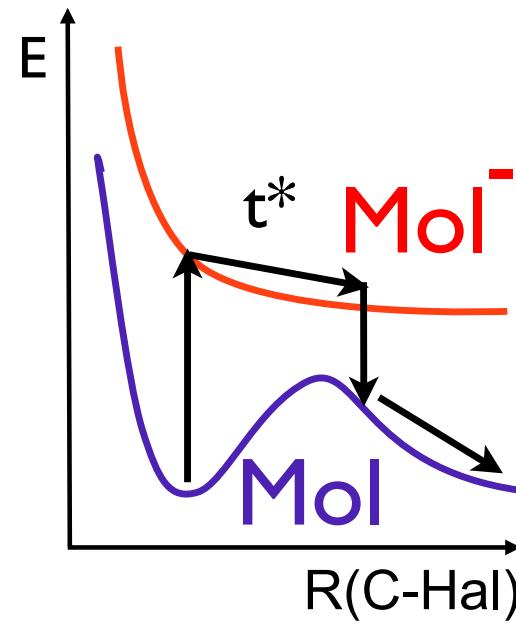
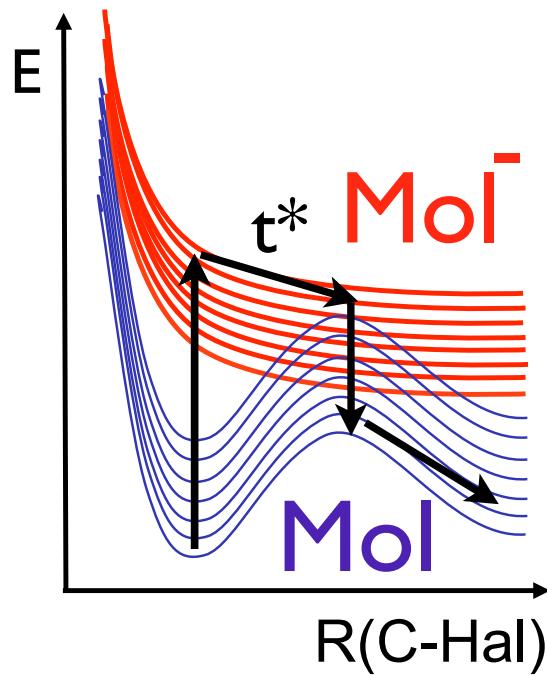
John
Polanyi



$t^* = 20-80$ fs were empirically found for various compounds

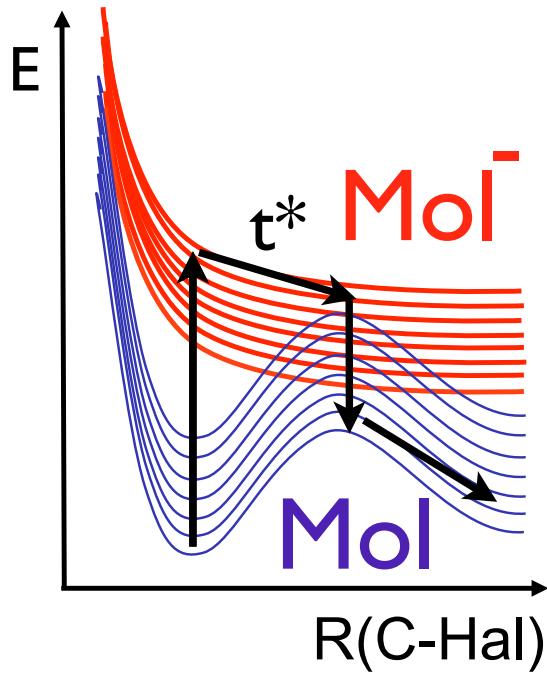
Motivation

Rationalizations of *ad hoc* 2-state model from first-principles



Building a framework that removes empirical times

Mixed quantum-classical methods



$$\psi_e(\mathbf{r}; \mathbf{R}, t) = \sum_{j=1}^2 c_j(t) \phi_j^{\text{adi}}(\mathbf{r}; \mathbf{R}(t))$$

$$i\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix} = \begin{pmatrix} W_1(\mathbf{R}) & -i\hbar \mathbf{d}_{12} \cdot \dot{\mathbf{R}} \\ -i\hbar \mathbf{d}_{21} \cdot \dot{\mathbf{R}} & W_2(\mathbf{R}) \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\mathbf{d}_{ij} = \langle \phi_i^{\text{adi}} | \nabla \phi_j^{\text{adi}} \rangle$$

Large number of states becomes a challenge

Friction: perturbative Ehrenfest

Perturbative treatment of nonadiabatic couplings

N

$$\psi_e(\mathbf{r}; \mathbf{R}, t) = \sum_{j=1} c_j(t) \phi_j^{\text{adi}}(\mathbf{r}; \mathbf{R}(t))$$

Electrons:

$$i\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix} = \begin{pmatrix} W_1(\mathbf{R}) & -i\hbar \mathbf{d}_{12} \cdot \dot{\mathbf{R}} \\ -i\hbar \mathbf{d}_{21} \cdot \dot{\mathbf{R}} & W_2(\mathbf{R}) \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Nuclei:

$$\ddot{R}_\alpha = -\mathbf{c}^\dagger \frac{\partial \mathbf{H}_{\text{adi}}^{(e)}}{\partial R_\alpha} \mathbf{c} + \mathbf{c}^\dagger [\mathbf{H}_{\text{adi}}^{(e)}, \mathbf{d}_\alpha] \mathbf{c}$$

Friction eq

$$\ddot{R}_\alpha = -\frac{\partial E_0}{\partial R_\alpha} - \sum_\beta \int_0^t dt' \Lambda_{\alpha\beta}(t, t') \dot{R}_\beta + \mathcal{R}_R(t)$$

M. Head-Gordon and J.C. Tully. *J. Chem. Phys.* **103** 10137 (1995)

Super-adiabatic treatment

$$i\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix} = \begin{pmatrix} W_1(\mathbf{R}) & -i\hbar \mathbf{d}_{12} \cdot \dot{\mathbf{R}} \\ -i\hbar \mathbf{d}_{21} \cdot \dot{\mathbf{R}} & W_2(\mathbf{R}) \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Diagonalization of nonadiabatic couplings

$$\psi_e(\mathbf{r}; \mathbf{R}, t) = \sum_{j=1}^2 \tilde{c}_j(t) \phi_j^{(s)}(\mathbf{r}; \mathbf{R}(t), \dot{\mathbf{R}}(t))$$

R. Lim and M. Berry. *J. Phys. A: Math. Gen.* **24** 3255 (1991)

N. Shenvi *J. Chem. Phys.* **130** 124117 (2009)

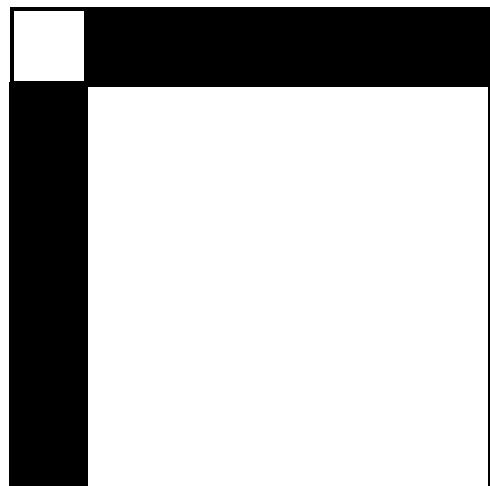
R. Gherib, L. Ye, I.G. Ryabinkin, and AFI, *J. Chem. Phys.* **144**, 154103 (2016)

New “super-nonadiabatic” couplings

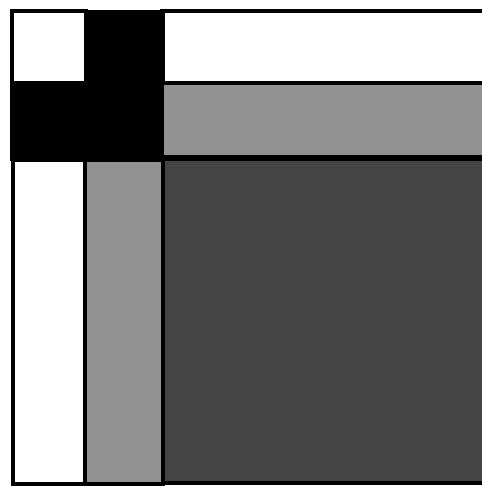
Diagonalization needs to be done analytically

Collective electronic variables

We ignore excited-excited NACs

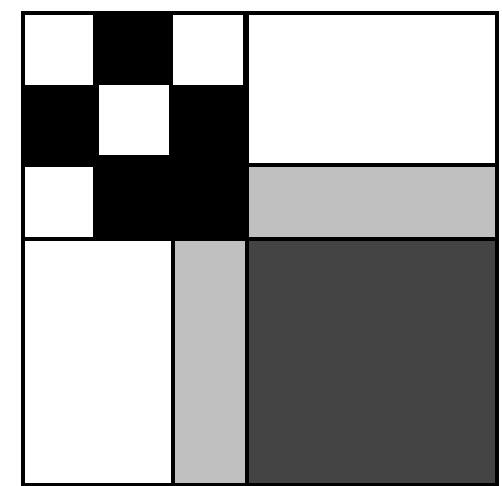


$$\xrightarrow{U_1}$$



2 modes

$$\xrightarrow{U_2}$$



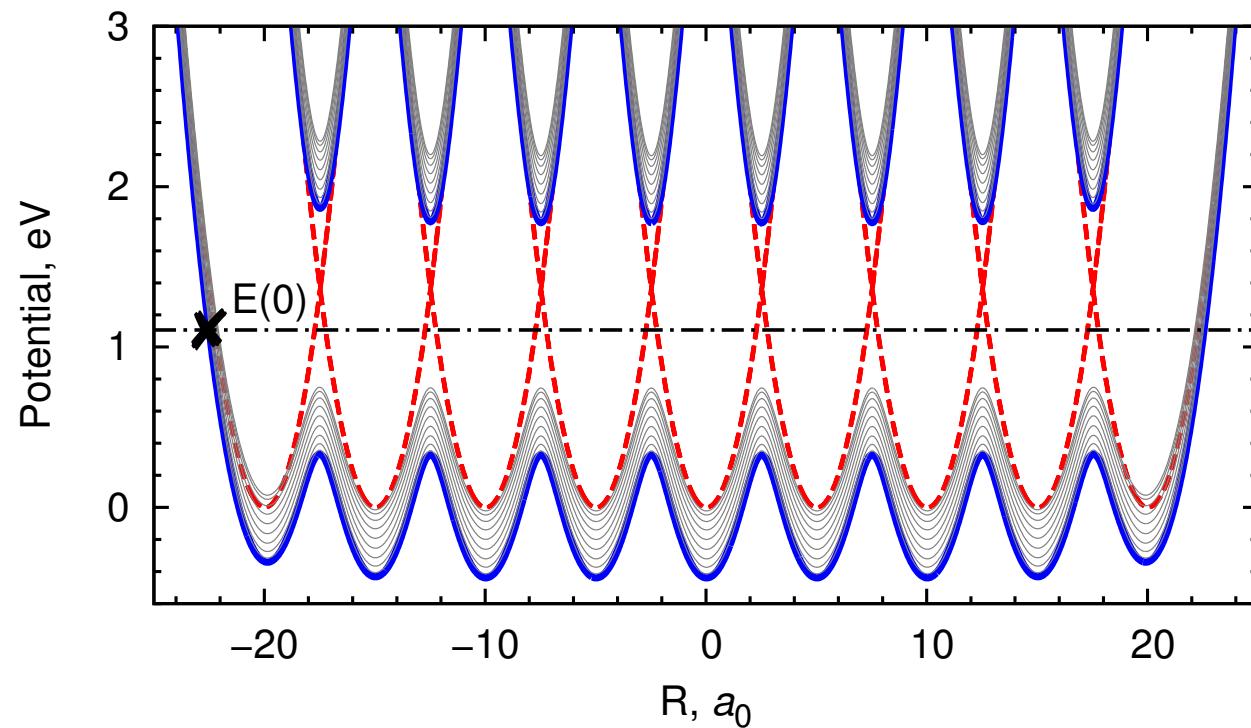
3 modes

$$\dot{\mathbf{c}} = \mathbf{T}\mathbf{c}$$

$$\dot{\mathbf{c}}^{(2)} = \mathbf{T}_{2 \times 2}^{(2)} \mathbf{c}^{(2)}$$

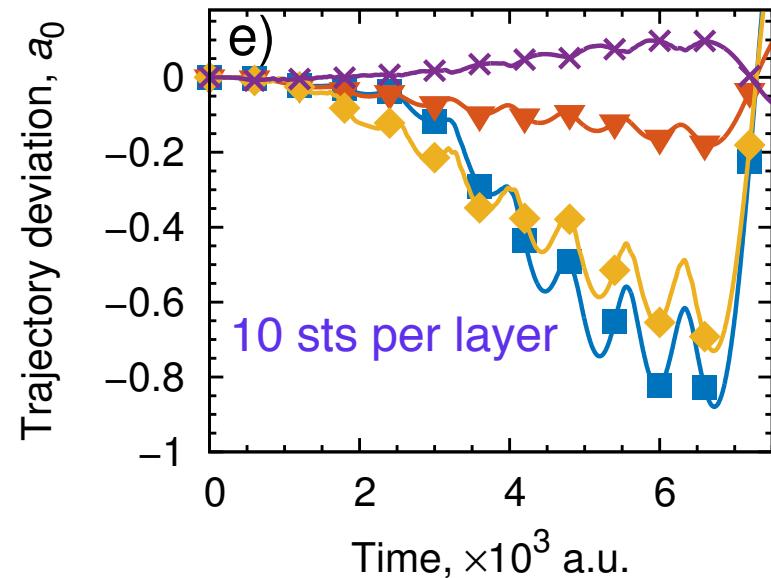
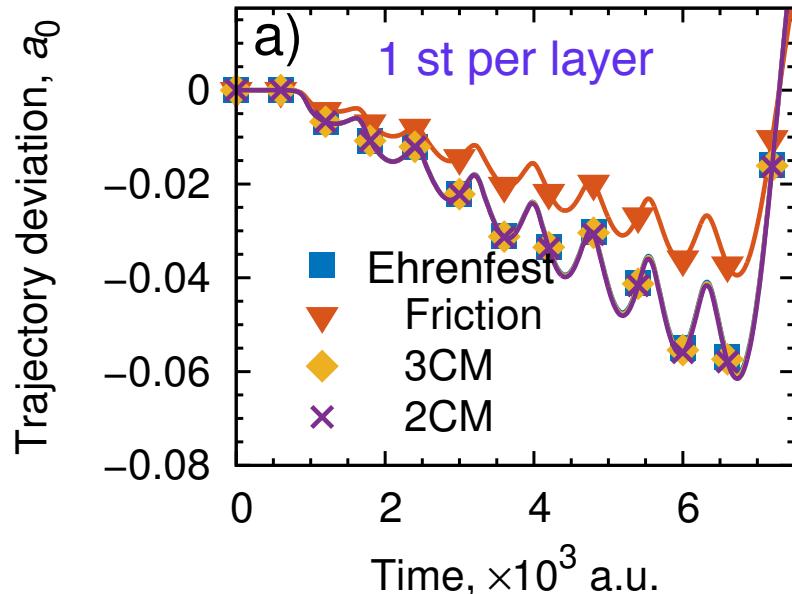
$$\dot{\mathbf{c}}^{(3)} = \mathbf{T}_{3 \times 3}^{(3)} \mathbf{c}^{(3)}$$

Model results

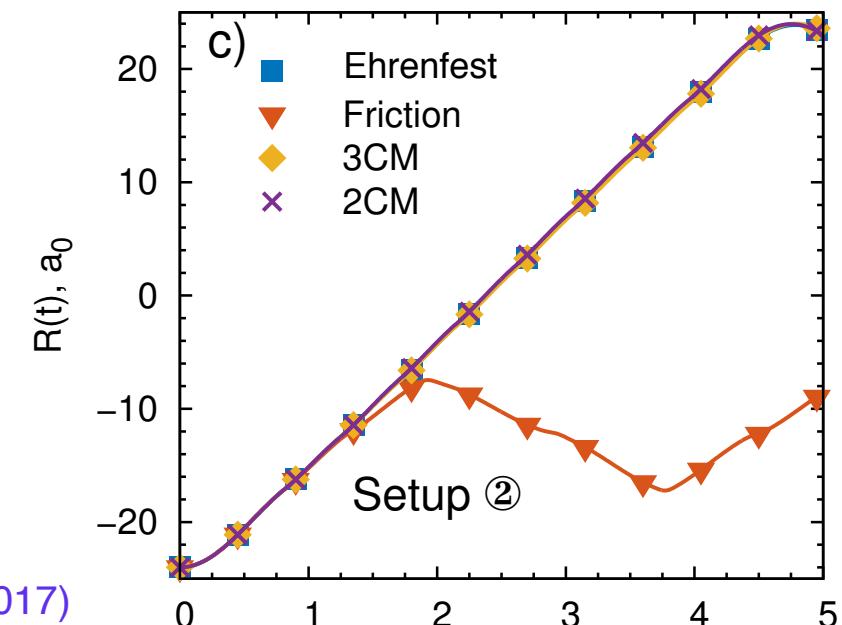
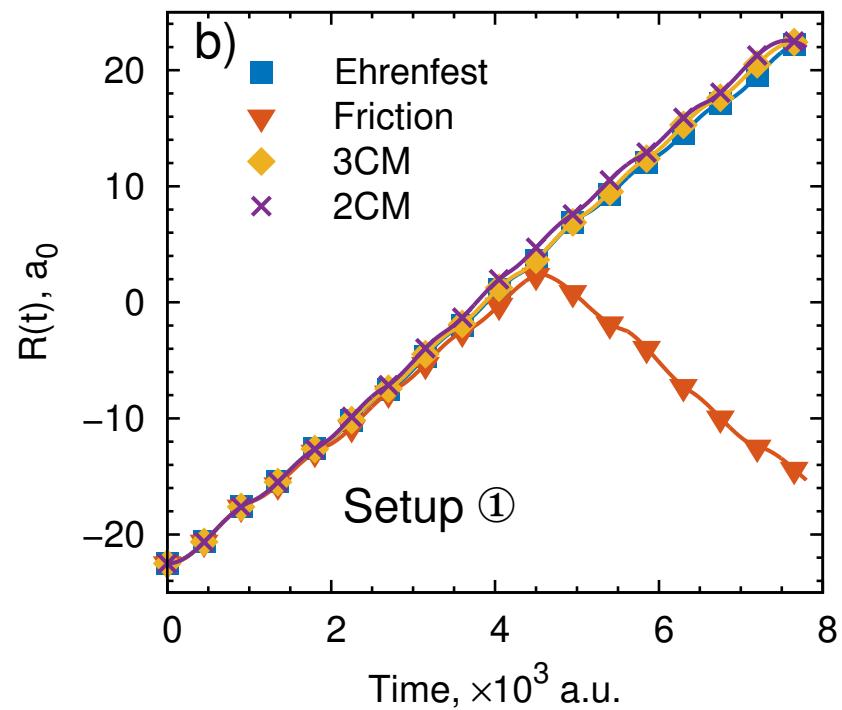
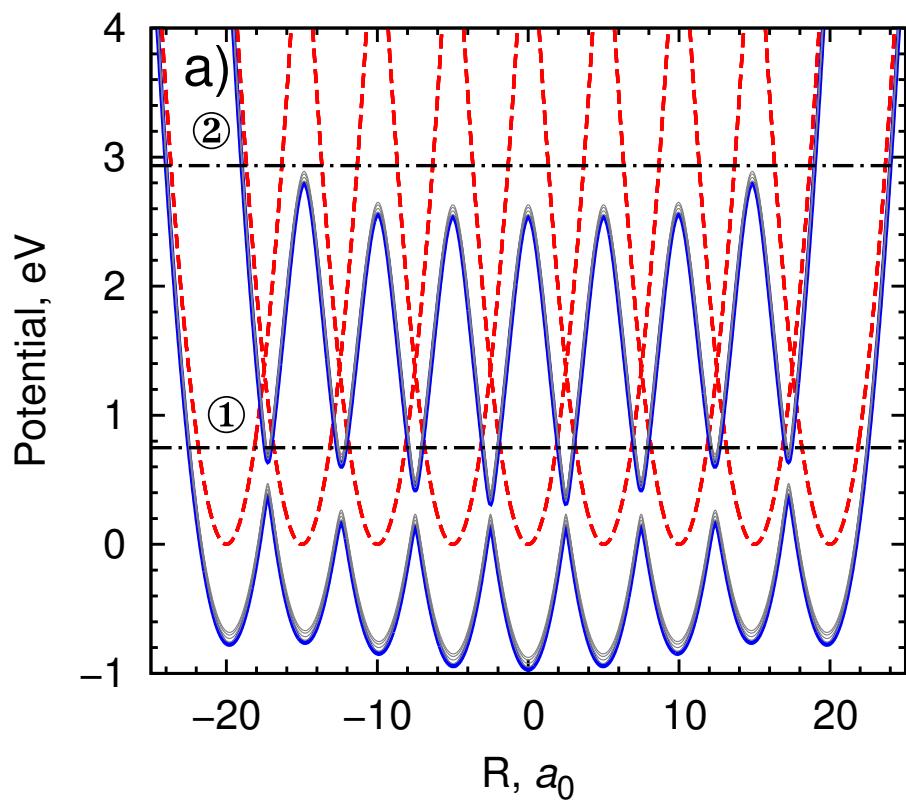


Ehrenfest
method

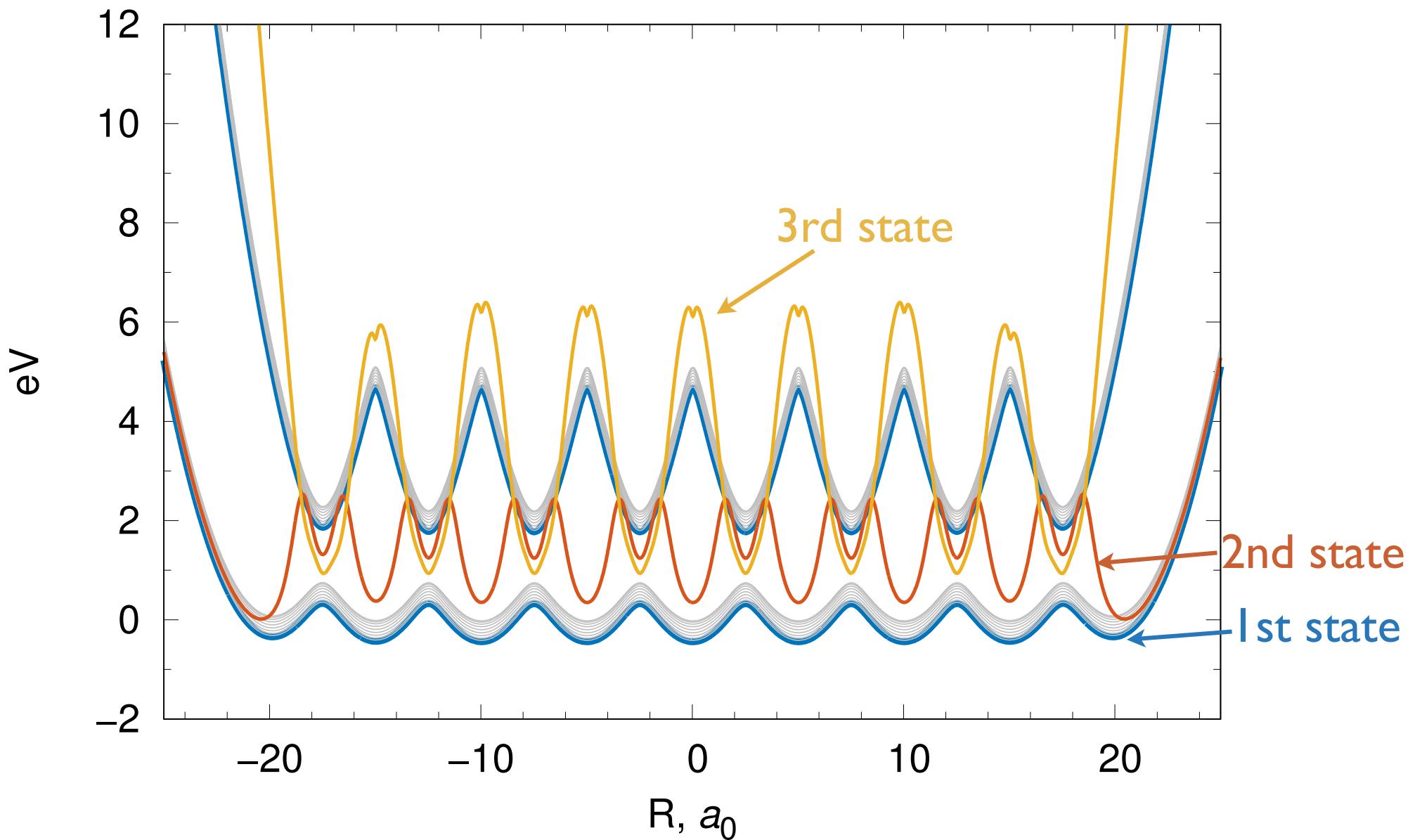
$$M = 2000m_e$$



Friction failure



Collective PESs



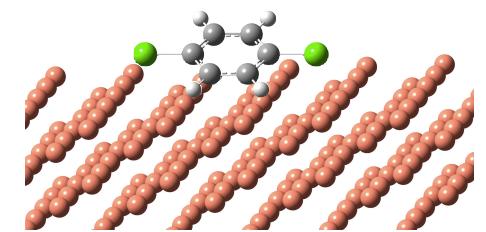
Implementation with DFT

Practical approximation: Using Kohn-Sham determinant as a wave-function

Collective method requires the same elements as the Ehrenfest method

Electrons: $i\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix} = \begin{pmatrix} W_1(\mathbf{R}) & -i\hbar \mathbf{d}_{12} \cdot \dot{\mathbf{R}} \\ -i\hbar \mathbf{d}_{21} \cdot \dot{\mathbf{R}} & W_2(\mathbf{R}) \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$

$$\mathbf{d}_{12} \cdot \mathbf{R} = \left\langle \phi_1[\mathbf{R}(t)] \mid \dot{\phi}_2[\mathbf{R}(t)] \right\rangle$$



I.G. Ryabinkin, J. Nagesh, AFI, *J. Phys. Chem. Lett.* **6**, 4200 (2015)

Nuclei:

$$\ddot{R}_\alpha = -\mathbf{c}^\dagger \frac{\partial \mathbf{H}_{\text{adi}}^{(e)}}{\partial R_\alpha} \mathbf{c} + \mathbf{c}^\dagger [\mathbf{H}_{\text{adi}}^{(e)}, \mathbf{d}_\alpha] \mathbf{c}$$

Full energy dissipation $\sim \sum_{ia} |\langle \Phi_0 | \partial_t \Phi_i^a \rangle|^2$

Effective-**M**ode **E**lectronic **R**educed-dimensin**AL**ity **D**ynamics
EMERALD patch for Quantum Espresso

Summary and outlook

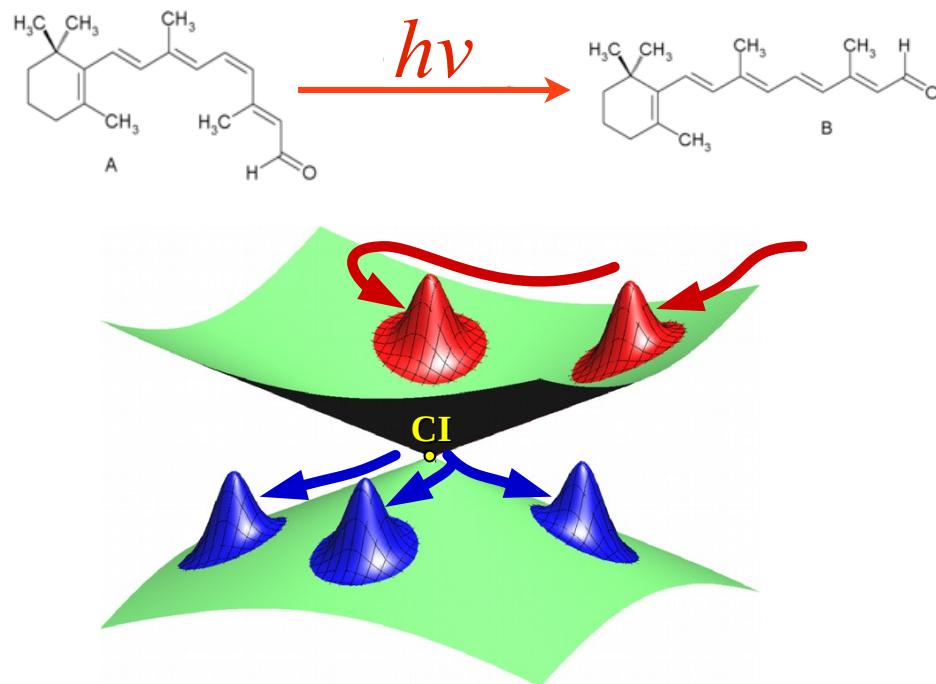
Friction theories can be **problematic**

Collective electronic variable approach:

- *accounts for necessary electronic states on-the-fly
- *more careful account for the “friction”
- *has been implemented within Ehrenfest-light
in Quantum Espresso

Surface hopping implementation is on its way

2. Fully quantum nonadiabatic dynamics



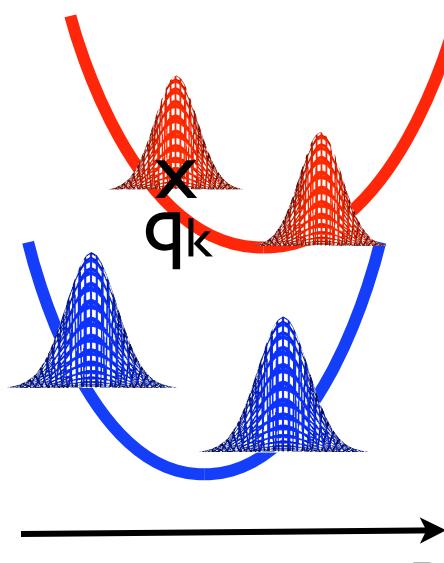
Nonadiabatic Quantum Dynamics with Frozen-Width Gaussians

[Loic Joubert-Doriol](#) and [Artur F. Izmaylov](#)
Feature Article

THE JOURNAL OF
PHYSICAL CHEMISTRY A

1. Decoherence (e.g., charge-transfer processes)
2. Zero Point Energy and Tunnelling: barriers on excited state (e.g., NH₃, pyrrole)
3. Quantum interference: from geometric phase (e.g., phenol)

Quantum nuclei with on-the-fly electronic structure



$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_s \chi_s(\mathbf{R}, t) \Phi_s(\mathbf{r}|\mathbf{R})$$

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{k,s} C_k^{(s)}(t) g_k(\mathbf{R}|\mathbf{p}_k^{(s)}, \mathbf{q}_k^{(s)}) \Phi_s(\mathbf{r}|\mathbf{R})$$

$$i\hbar \frac{\partial \Psi(\mathbf{r}, \mathbf{R}, t)}{\partial t} \underset{\textcolor{red}{\approx}}{=} \hat{H}\Psi(\mathbf{r}, \mathbf{R}, t)$$

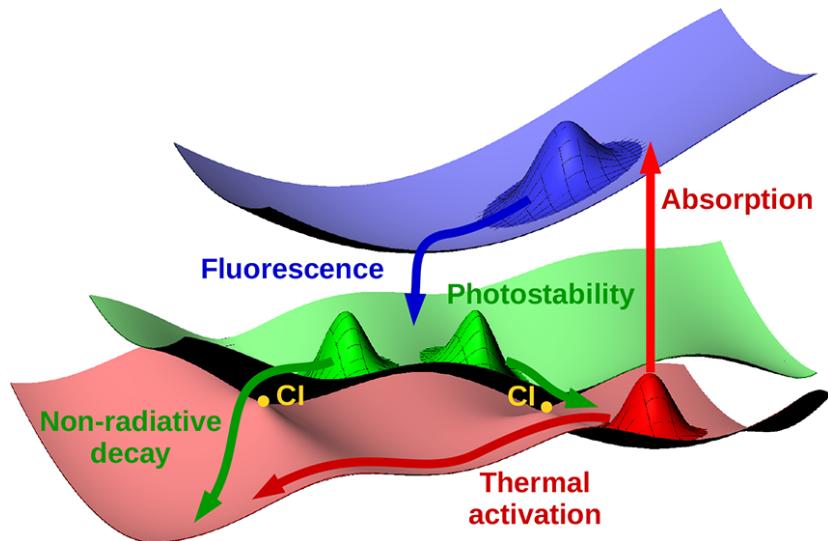
Time-Dependent Variational Principle

$$\begin{aligned}\dot{C}_k^{(s)}(t) &= f(\{C_{k'}^{(s')}\}, \{\mathbf{p}_{k'}\}, \{\mathbf{q}_{k'}\}) \\ \dot{\mathbf{q}}_k(t) &= \tilde{f}(\{C_{k'}^{(s')}\}, \{\mathbf{p}_{k'}\}, \{\mathbf{q}_{k'}\}) \\ \dot{\mathbf{p}}_k(t) &= \dots\end{aligned}$$

Programs: MCTDH and Quantics

Adiabatic representation

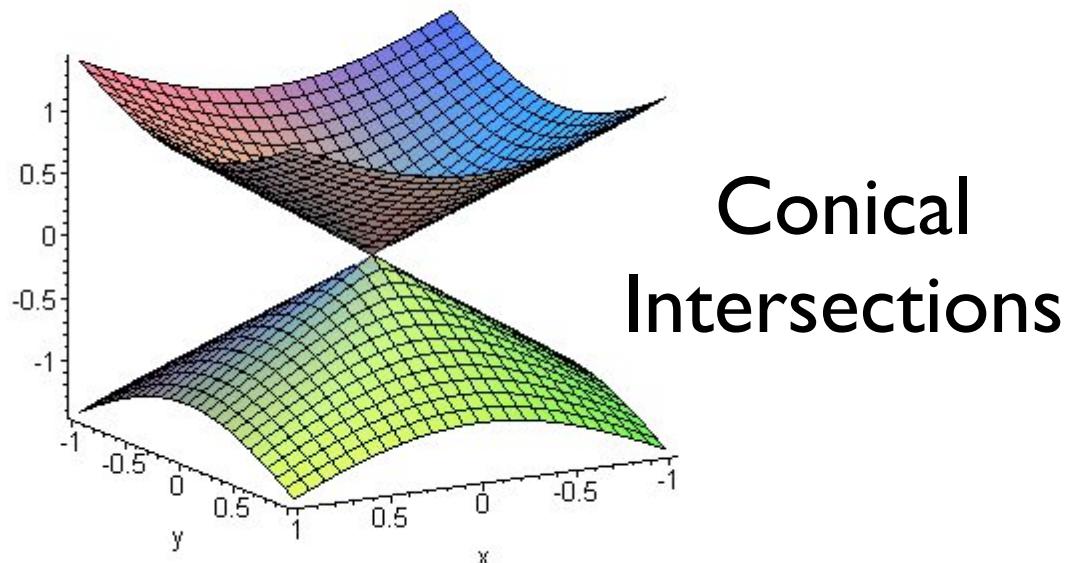
$$\Psi(r,R,t) = \sum_i \Phi_i(r|R) X_i(R,t)$$



Difficulties:

Great things:

1. Comes from electronic structure, unambiguously defined
2. PES are generally well separated, couplings are localized



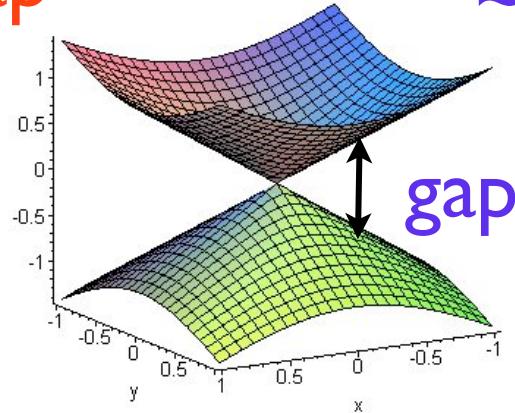
Problem#1: Nonadiabatic couplings

$$\Psi(r, R, t) = \sum_i X_i(R, t) \Phi_i(r|R)$$

$$\hat{H}(r, R) = \hat{T}_N(R) + \hat{H}_e(r|R)$$

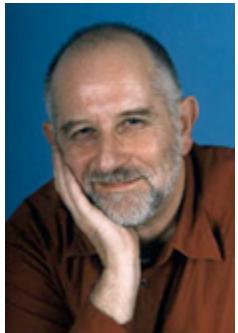
$$\hat{\tau}_{kj} = -\langle \Phi_k(R) | \nabla^2 \Phi_j(R) \rangle / 2 - \langle \Phi_k(R) | \nabla \Phi_j(R) \rangle \nabla$$

$$\sim 1/\text{gap}^2 \quad \quad \quad \sim 1/\text{gap}$$



Divergencies derail our equations for $X_i(R, t)$
 $\Phi_i(r|R)$'s R-dependence to blame!

Problem#2: Geometric Phase

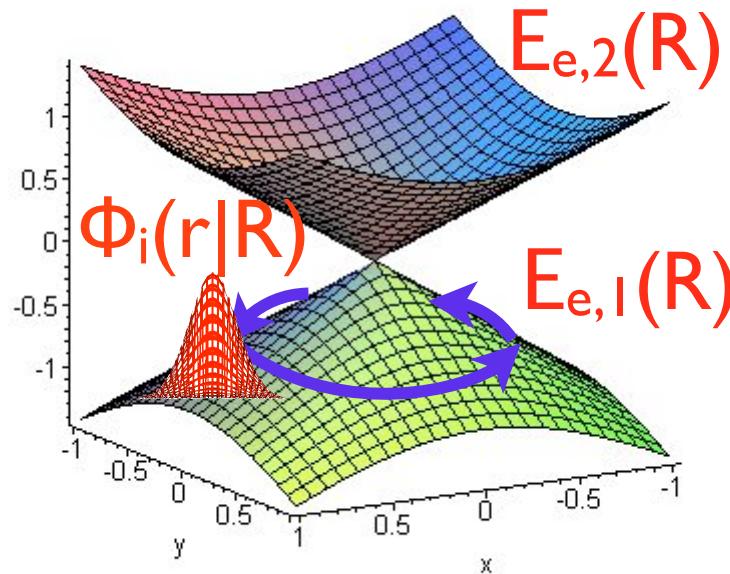


M. Berry
(1984)

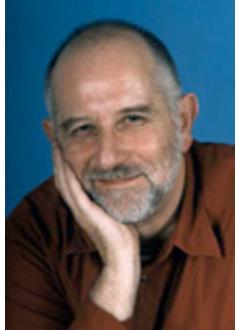
$$\Psi(r, R, t) = \sum_i \Phi_i(r|R) X_i(R, t)$$



H. C. Longuet-
Higgins
(1958-1963)



Problem#2: Geometric Phase

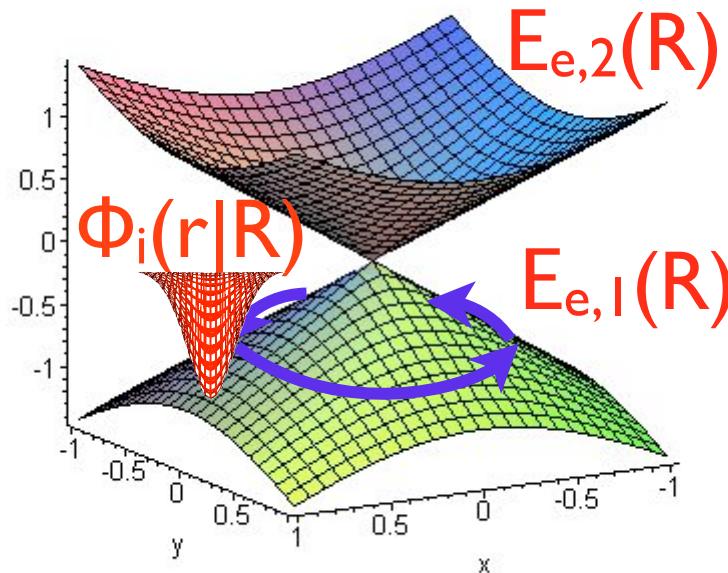


M. Berry
(1984)

$$\Psi(r, R, t) = \sum_i \Phi_i(r|R) X_i(R, t)$$



H. C. Longuet-
Higgins
(1958-1963)

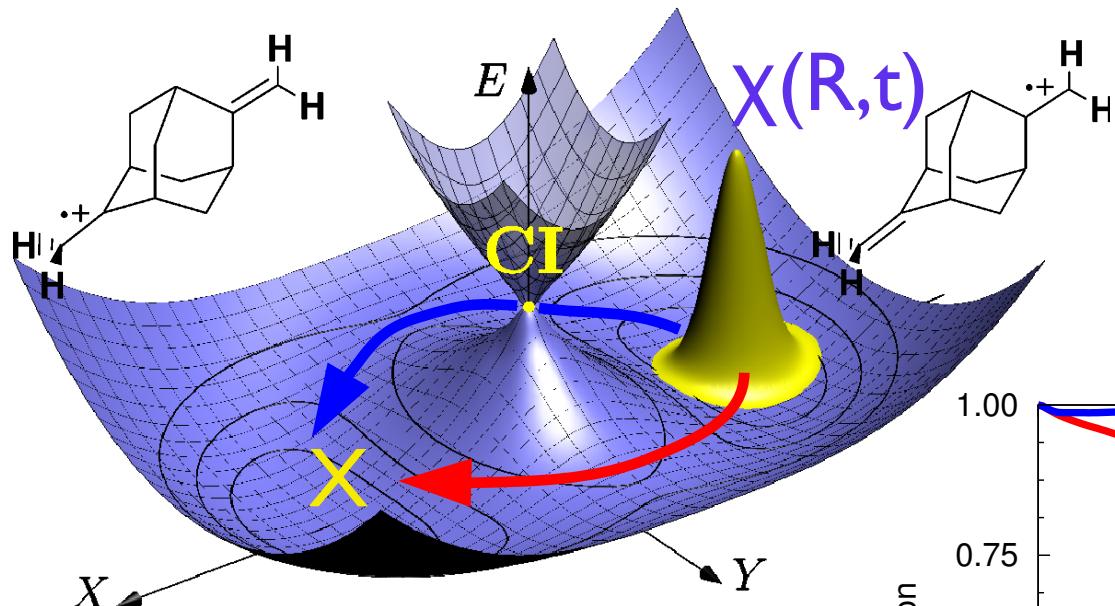


Electronic functions are double-valued

Both wave-functions $\Phi_i(r|R)$ and $X_i(R, t)$ must be double-valued!

How does this affect dynamics?

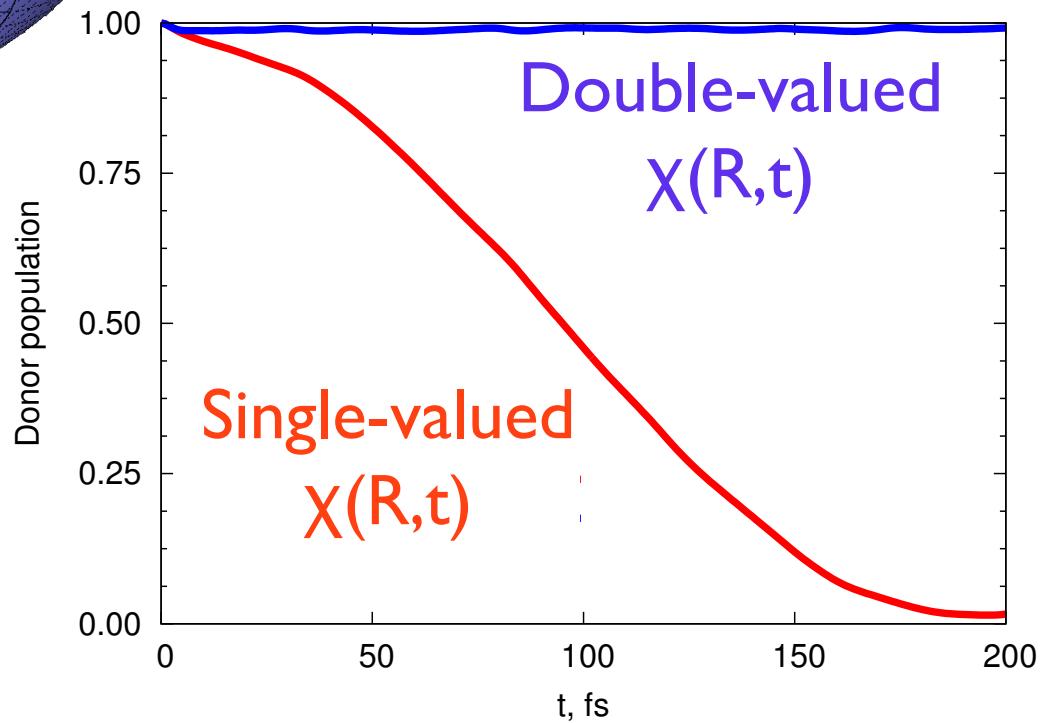
Geometric Phase Significance



**Molecular
“Topological
Insulator”**

L. Joubert-Doriol and AFI *Chem. Commun.* 53 7365 (2017)

Charge-transfer
with conical
intersection in between



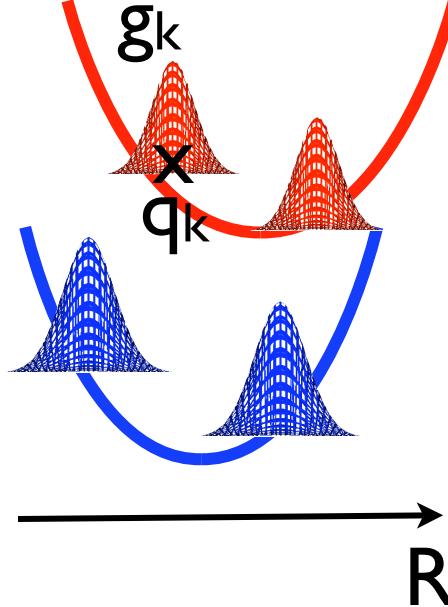
Geometric phase with Gaussians

$$\Psi(r, R, t) = \sum_s \chi_s(R, t) \Phi_s(r|R)$$

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{k,s} \boxed{C_k^{(s)}(t) g_k(\mathbf{R}|\mathbf{p}_k^{(s)}, \mathbf{q}_k^{(s)})} \Phi_s(\mathbf{r}|R)$$

Gaussians are single valued :(

Adiabatic rep.: How to fix it?



$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{k,s} C_k^{(s)}(t) g_k(\mathbf{R}|\mathbf{p}_k^{(s)}, \mathbf{q}_k^{(s)}) \Phi_s(\mathbf{r}|\mathbf{R})$$

R-dependence is the problem!

Can we reduce it? Diabatic representation?

Moving crude adiabatic representation

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{k,s} C_k^{(s)}(t) g_k(\mathbf{R}|\mathbf{p}_k^{(s)}, \mathbf{q}_k^{(s)}) \Phi_s(\mathbf{r}|\mathbf{q}_k^{(s)})$$

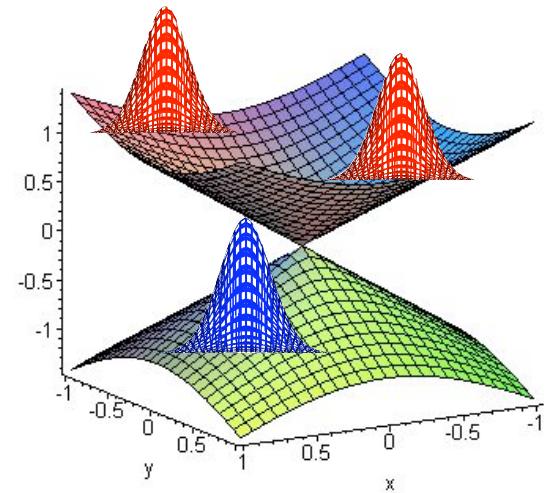
L. Joubert-Doriol et al. *J. Phys. Chem. Lett.* **8** 452 (2017)

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{k,s} C_k^{(s)}(t) g_k(\mathbf{R}|\mathbf{p}_k^{(s)}, \mathbf{q}_k^{(s)}) \Phi_s(\mathbf{r}|\mathbf{q}_k^{(s)})$$

I. Only 1st order NACs from time-derivative

$$\langle \Phi_s(\mathbf{q}_k) | \frac{\partial \Phi_{s'}(\mathbf{q}_l)}{\partial t} \rangle = \langle \Phi_s(\mathbf{q}_k) | \frac{\partial \Phi_{s'}(\mathbf{q}_l)}{\partial \mathbf{q}_l} \rangle \dot{\mathbf{q}}_l$$

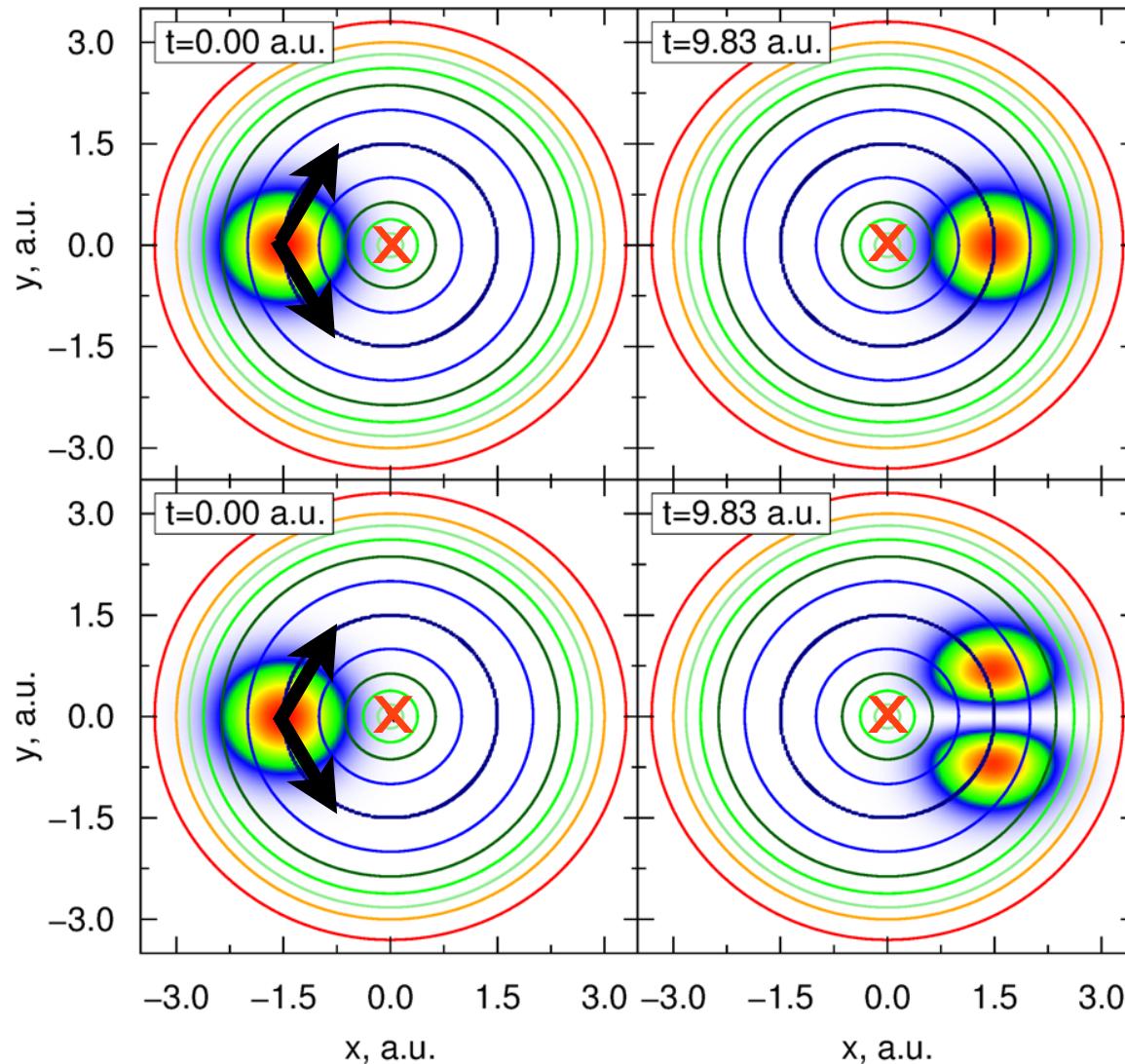
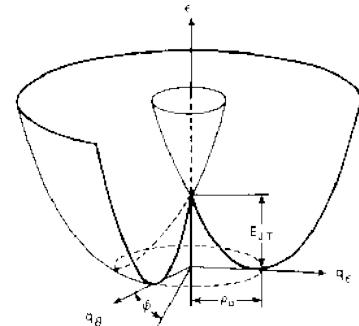
Gaussian centers will never hit CI



2. GP is taken care of, electronic functions have no **R**-dep

Geometric Phase Test

Two
Gaussians
on a
Mexican
hat



Global
adiabatic
rep (w/o GP
treatment)

Moving
crude
adiabatic
rep

Summary and Outlook #2

Global adiabatic representation: **problematic**

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{k,s} C_k^{(s)}(t) g_k(\mathbf{R}|\mathbf{p}_k^{(s)}, \mathbf{q}_k^{(s)}) \Phi_s(\mathbf{r}|\mathbf{R})$$

Moving crude adiabatic representation: **way to go**

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{k,s} C_k^{(s)}(t) g_k(\mathbf{R}|\mathbf{p}_k^{(s)}, \mathbf{q}_k^{(s)}) \Phi_s(\mathbf{r}|\mathbf{q}_k^{(s)})$$

L. Joubert-Doriol et al. *J. Phys. Chem. Lett.* **8** 452 (2017)

also allows us to avoid introducing PES and
approximations for them

L. Joubert-Doriol and AFI *J. Chem. Phys.* **148** 114102 (2018)

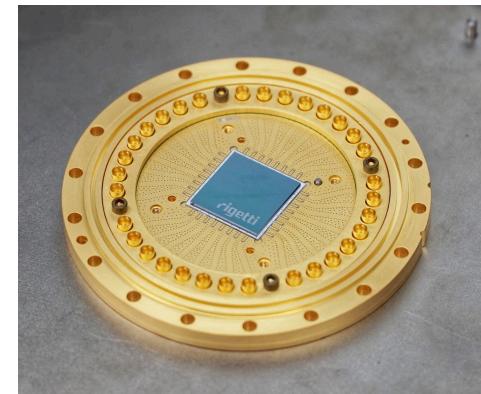
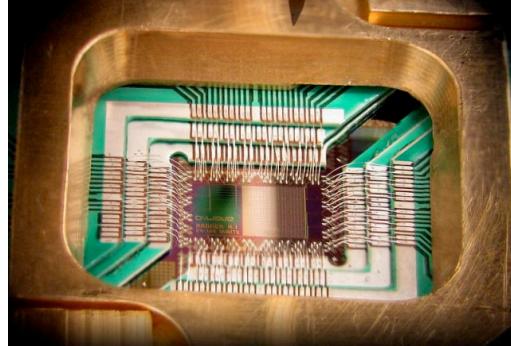
MCA will appear in Quantics package soon

3. Quantum computing

$$H_e \Phi(r|R) = E_e(R) \Phi(r|R)$$

OTI Lumionics

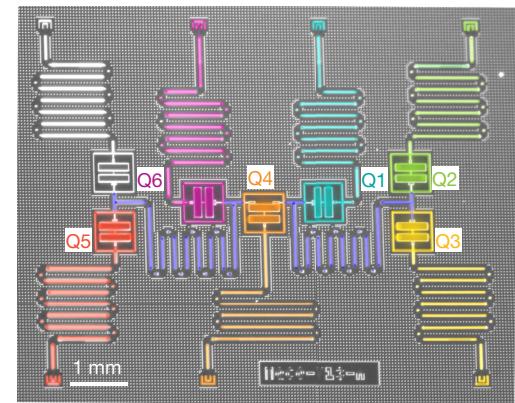
D-Wave 2000Q



Rigetti 19Q



Google 72Q



IBM 8Q

Quantum Variational Eigensolver

$$\hat{H}_e = \sum_{ij} h_{ij} \hat{a}_i^\dagger \hat{a}_j + \frac{1}{2} \sum_{ijkl} \langle ij | kl \rangle \hat{a}_i^\dagger \hat{a}_k^\dagger \hat{a}_l \hat{a}_j$$

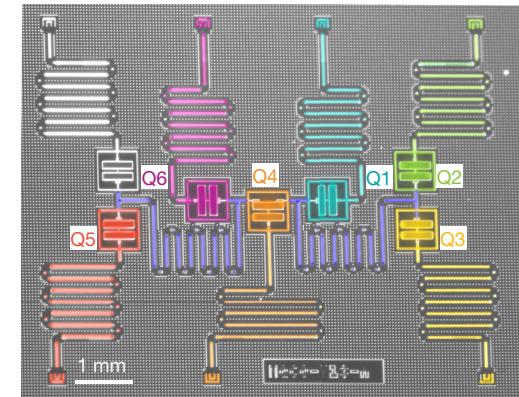
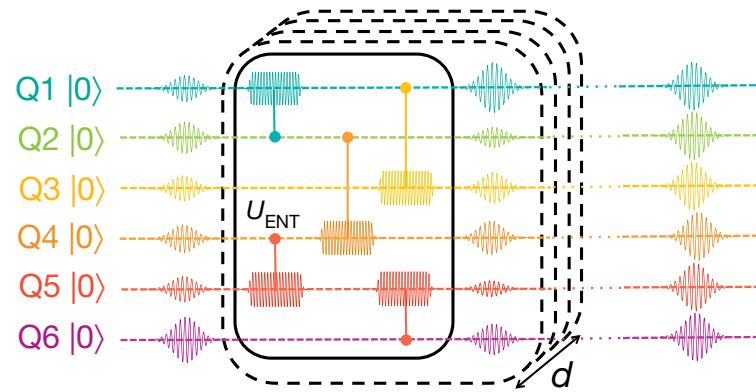
I. Exact mapping

$$\mathcal{H} = \sum_{i\alpha} h_\alpha^i \sigma_\alpha^i + \sum_{ij\alpha\beta} h_{\alpha\beta}^{ij} \sigma_\alpha^i \sigma_\beta^j + \dots$$

2. Eigenfunction in qubit space

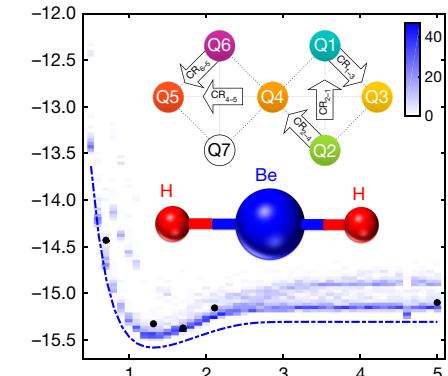
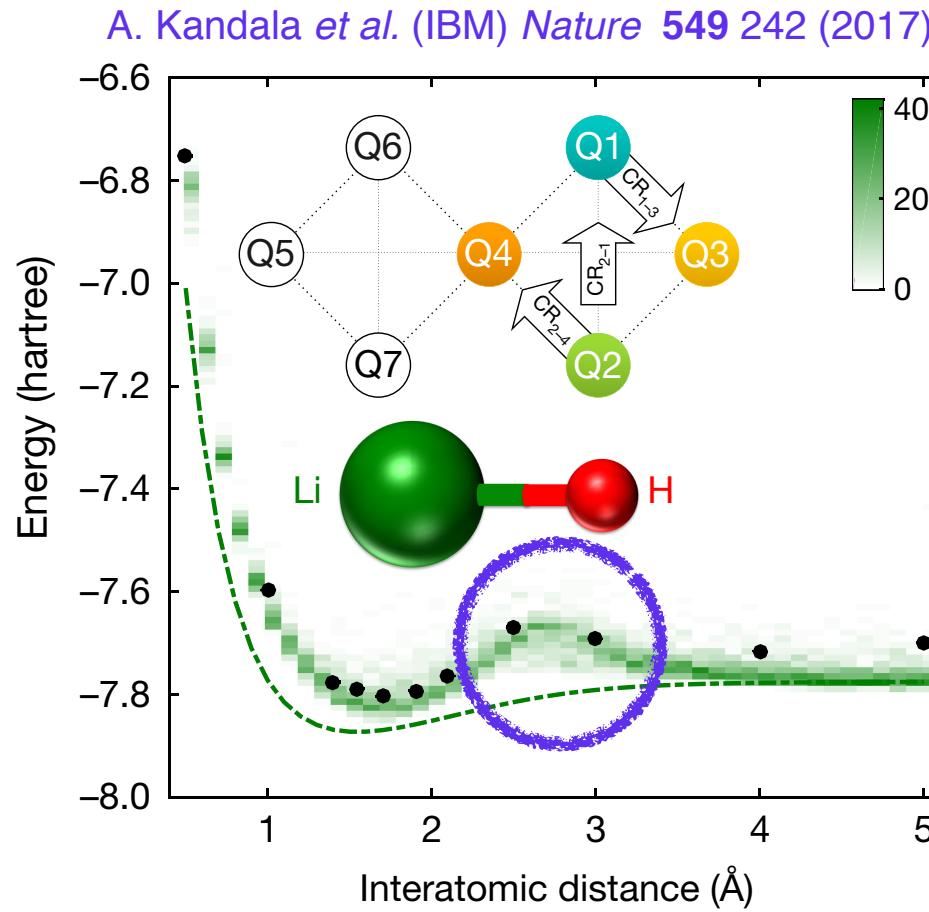
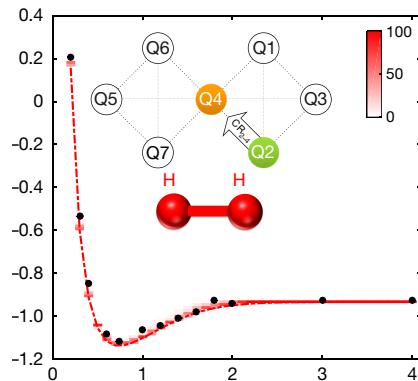
$$E_e = \min_{\theta} \langle \Phi_e(\theta) | H | \Phi_e(\theta) \rangle$$

Alan Aspuru-Guzik *et al.* *Nat. Commun.* **5**, 4213 (2014)



A. Kandala *et al.* (IBM) *Nature* **549**, 242 (2017)

Quantum computer: New problems

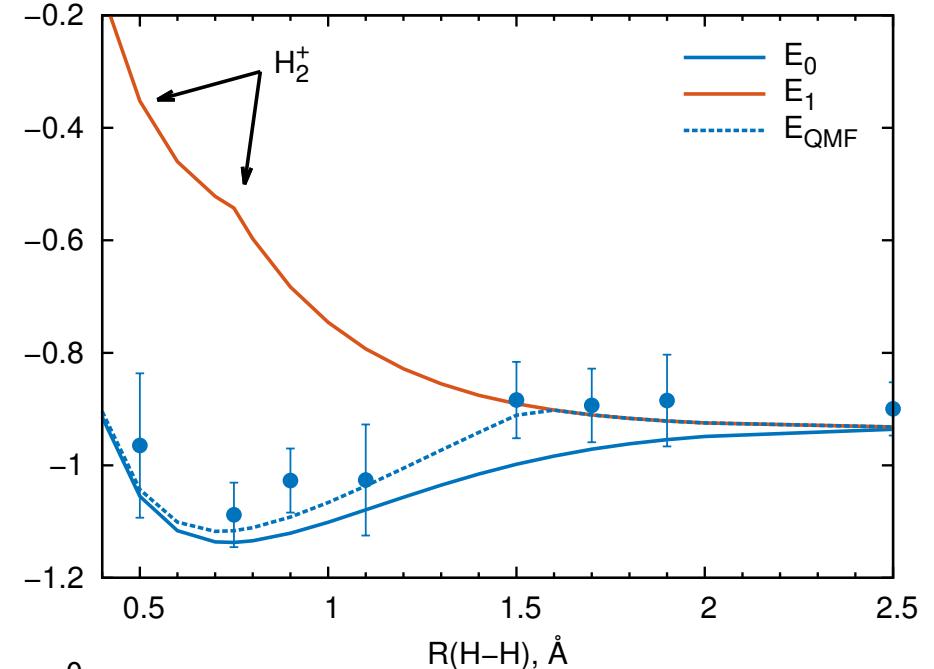
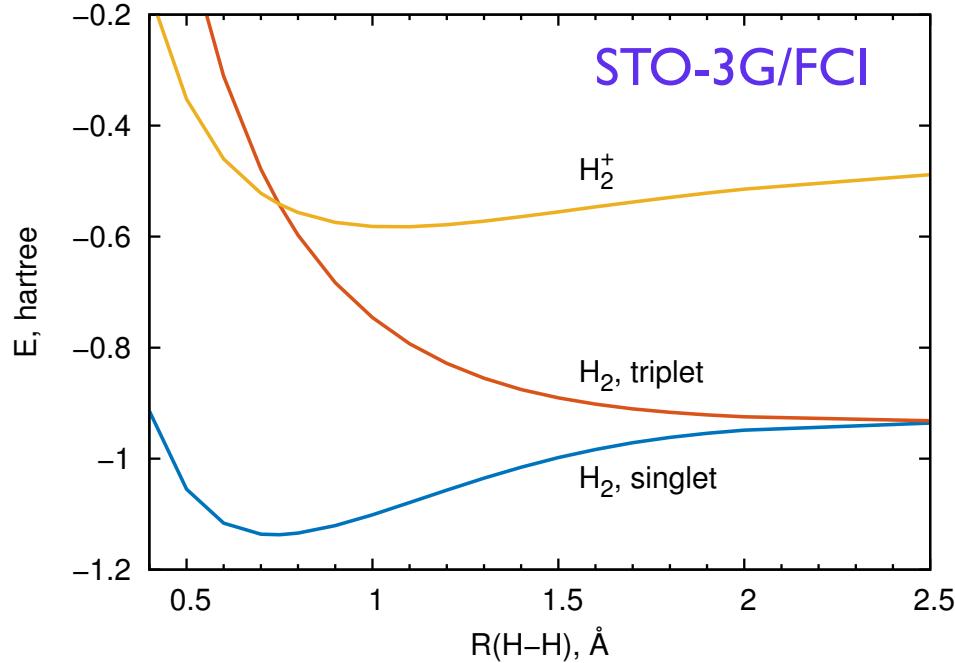


Fock space: all number of electrons and spins are present

$$\hat{H}_e = \sum_{ij} h_{ij} \hat{a}_i^\dagger \hat{a}_j + \frac{1}{2} \sum_{ijkl} \langle ij | kl \rangle \hat{a}_i^\dagger \hat{a}_k^\dagger \hat{a}_l \hat{a}_j \longrightarrow \mathcal{H} = \sum_{i\alpha} h_\alpha^i \sigma_\alpha^i + \sum_{ij\alpha\beta} h_{\alpha\beta}^{ij} \sigma_\alpha^i \sigma_\beta^j + \dots$$

Exact mapping, but eigenstate nature becomes hidden

Constrained Quantum Variational Eigensolver



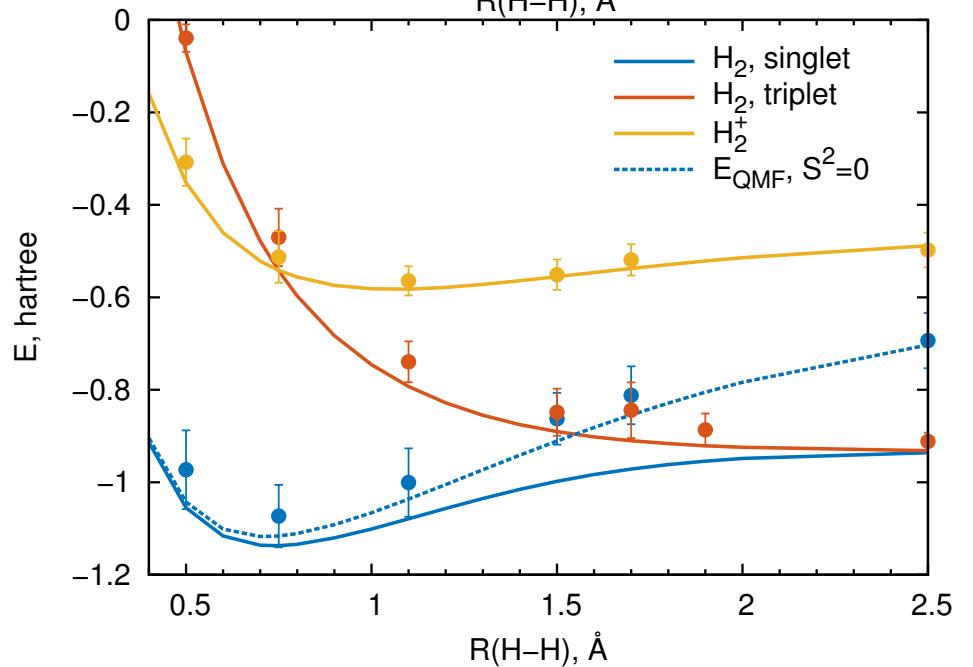
Constrained functionals:

$$\mathcal{E}_S(\Omega, \mu) = E_{QMF}(\Omega) + \mu \left[\langle \Omega | \hat{S}_{BK}^2 | \Omega \rangle - S^2 \right]^2$$

$$\mathcal{E}_N(\Omega, \mu) = E_{QMF}(\Omega) + \mu \left[\langle \Omega | \hat{N}_{BK} | \Omega \rangle - 1 \right]^2$$

Ryabinkin, Genin, AFI, arXiv: 1806:00461

arXiv: 1806:00514



Summary and Outlook #3

Variational Quantum Eigensolver (VQE) is the most used technique for Electronic Structure Problem

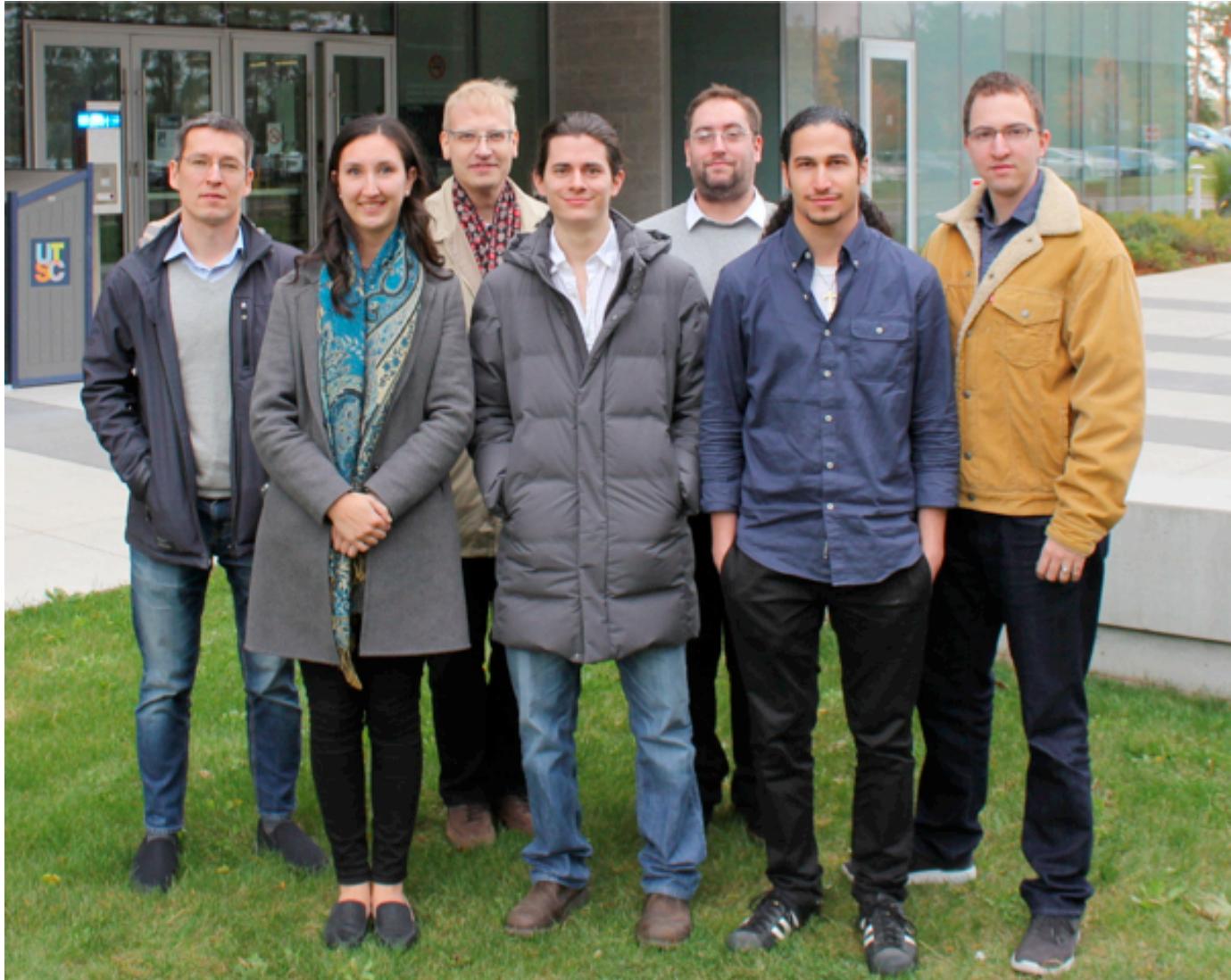
VQE effectively looks for solutions in the Fock space and needs constraints to be useful and to produce smooth PESs

Robust entanglement between qubits is required to go beyond mean-field approaches



The image shows a promotional slide for Rigetti Computing's Forest API. The background is a dark green gradient. In the top left corner, the Rigetti logo is displayed. To its right, the text "RIGETTI COMPUTING INTRODUCES" is written in a small, light font. The central feature is the word "Forest" in a large, white, sans-serif font, with a smaller "1.3" superscript to its right. Below "Forest", the text "An API for quantum computing in the cloud" is written in a light gray font. At the bottom of the slide, there are five horizontal icons with corresponding text labels: "OPEN SOURCE SOFTWARE" (represented by a cube icon), "EXAMPLE ALGORITHMS" (represented by a circuit diagram icon), "SUPERCONDUCTING QUANTUM PROCESSORS" (represented by a microchip icon), and "PYTHON DEVELOPMENT TOOLS" (represented by a laptop icon). The overall design is clean and professional.

Acknowledgments



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OTI Lumionics

