

QUANTUM COMPUTING FOR QUANTUM CHEMISTRY

COMPOUND INTEREST

Practical uses for quantum computers are emerging in chemistry, promising to speed the development of materials, catalysts, and drugs

30 MAY 2024 • 12:00 PM ET • BY [ROBERT F. SERVICE](#)



doi: [10.1126/science.zlxq0ls](https://doi.org/10.1126/science.zlxq0ls)

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Advanced User Computing Day (AUCD)
12th December 2024

ACKNOWLEDGEMENTS



Prof. Dr. Lucas Visscher,
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Dr. Sachin Kinge,
Advanced Materials Research Center, Toyota Motor Europe, Belgium



Dr. Carlos Rocha,
Netherlands eScience center, Amsterdam, The Netherlands

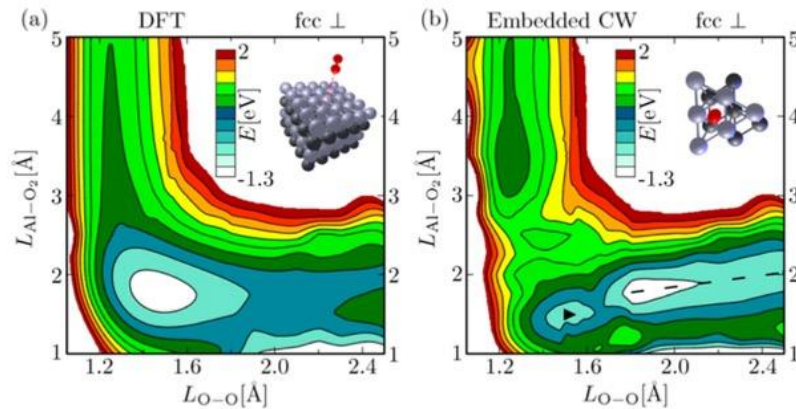
**Toyota Motor Europe
Quantum Delta NL**

Dr. Nicolaus Renaud,
Netherlands eScience center, Amsterdam, The Netherlands



STRONG CORRELATION IN CATALYSIS

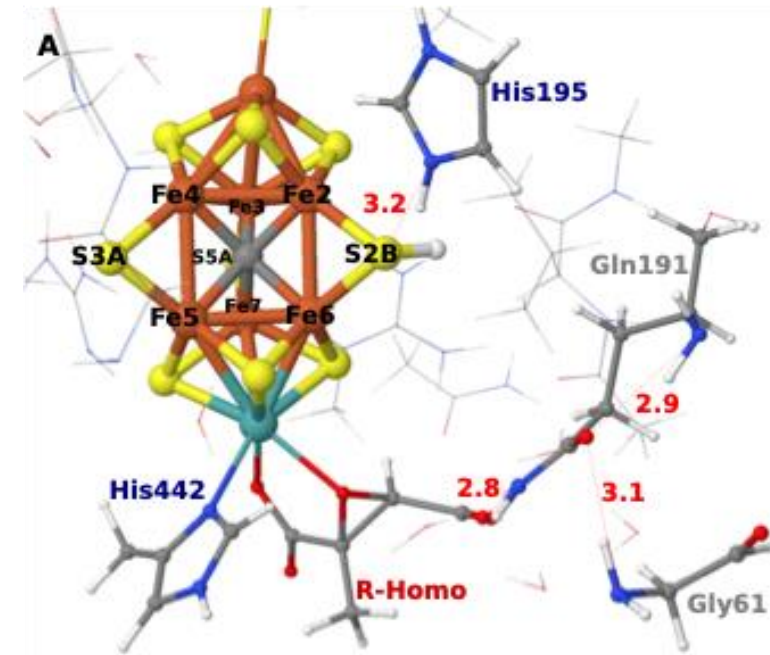
Heterogeneous catalysis



O₂ dissociation on Al(111)

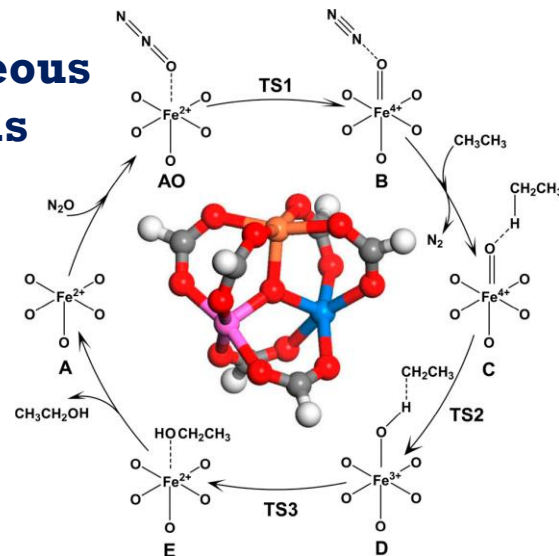
Enzyme catalysis

Nitrogen to ammonia conversion on nitrogenase enzyme
FeMo-cofactor – much-debated system in
quantum computing



M Montemore et al., Chem. Rev. 118, 2816–2862 (2018)
CA Gaggoli et al, ACS Catal. 9, 8481–8502 (2019).
VJ Bukas, JK Nørskov, <https://doi.org/10.26434/chemrxiv.10029224.v1> (2019)

Homogeneous catalysis



Ethane to
ethanol
conversion

Model cluster $M_1(\text{III})M_2(\text{III})\text{Fe}(\text{II})(\mu_3\text{-O})(\text{HCOO})_6$

STRONG (STATIC) CORRELATION

- **Correlation energy, E_c**

- $E_c = E_{\text{exact}} - E^{\text{HF}}$; $E_{\text{exact}} = E_{\text{FCI}}$; Rigorously defined
- Dynamic and non-dynamic (static) correlation – not rigorously defined

- **Dynamic correlation:**

- Simple correlation – easy to model using perturbation theory.
- $E_c^{\text{LYP}}[\rho]$ or $E_c^{\text{PBE}}[\rho]$ in DFT

- **Non-dynamic (static) correlation:**

- Appears in situations where multiple configurations associated with degeneracy or near degeneracy are needed.
- Classic example: H_2 dissociation

MULTI-CONFIGURATIONS AND CONICAL INTERSECTION

Single configuration:

For two electrons in molecular orbitals χ_1 and χ_2 :

$$\Psi_{\text{single}} = \frac{1}{\sqrt{2!}} \begin{vmatrix} \chi_1(1) & \chi_1(2) \\ \chi_2(1) & \chi_2(2) \end{vmatrix}$$

Where $\chi_1(i)$ denotes the orbital χ_1 occupied by electron i .

Multi-configuration:

1. Configuration 1: Both electrons in χ_1 .

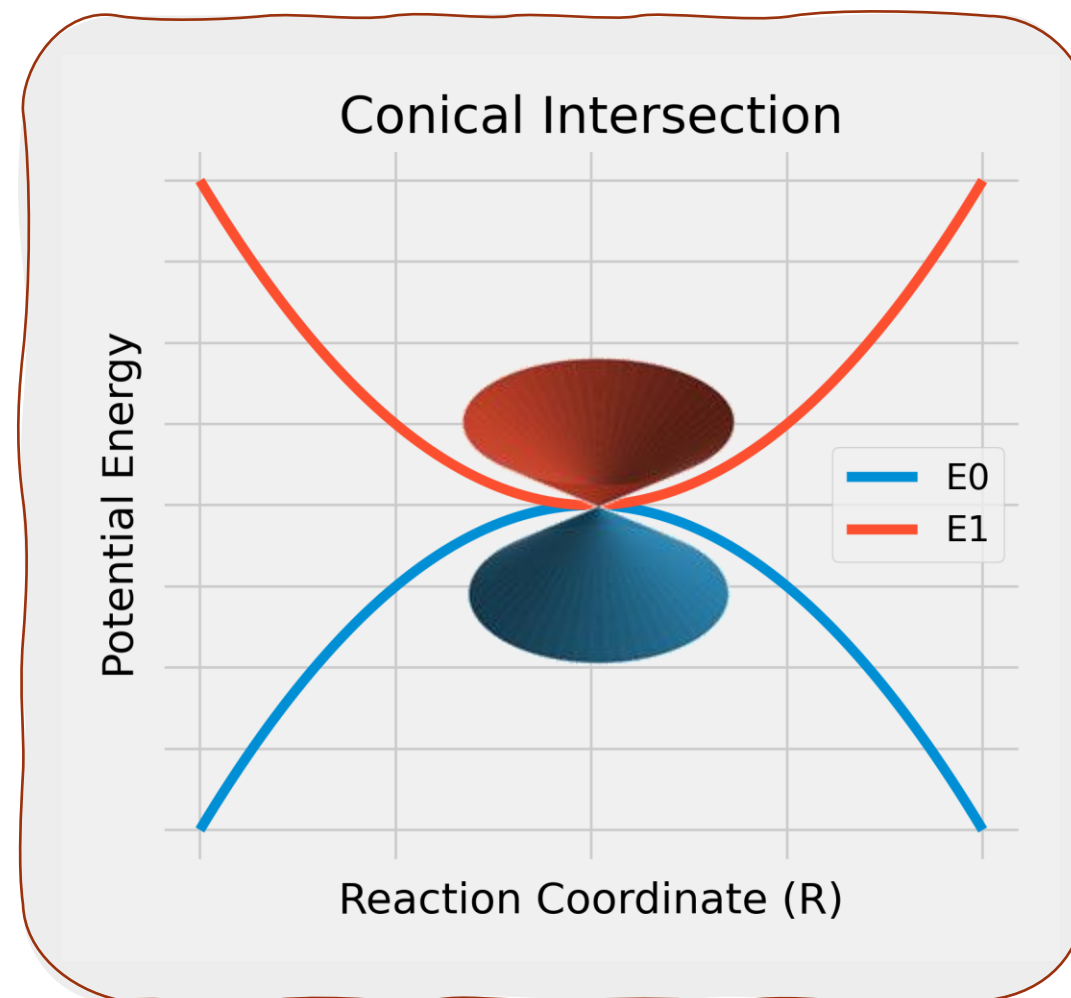
$$\Psi_{\text{config 1}} = \frac{1}{\sqrt{2!}} \begin{vmatrix} \chi_1(1) & \chi_1(2) \\ \chi_1(1) & \chi_1(2) \end{vmatrix}$$

2. Configuration 2: One electron in χ_1 and the other in χ_2 .

$$\Psi_{\text{config 2}} = \frac{1}{\sqrt{2!}} \begin{vmatrix} \chi_1(1) & \chi_1(2) \\ \chi_2(1) & \chi_2(2) \end{vmatrix}$$

The multi-configuration wavefunction is a linear combination of these determinants:

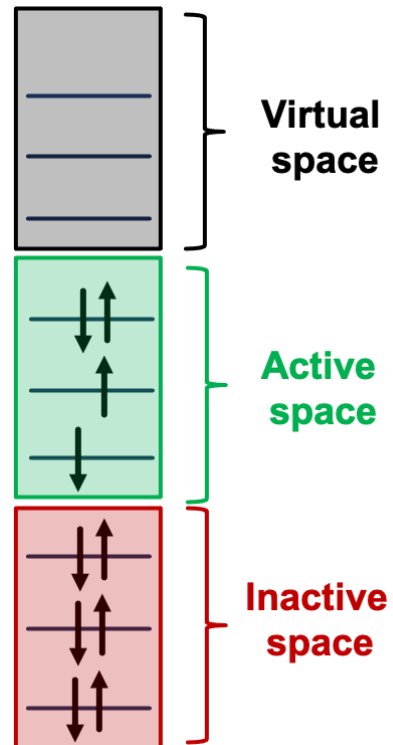
$$\Psi_{\text{multi}} = c_1 \Psi_{\text{config 1}} + c_2 \Psi_{\text{config 2}}$$



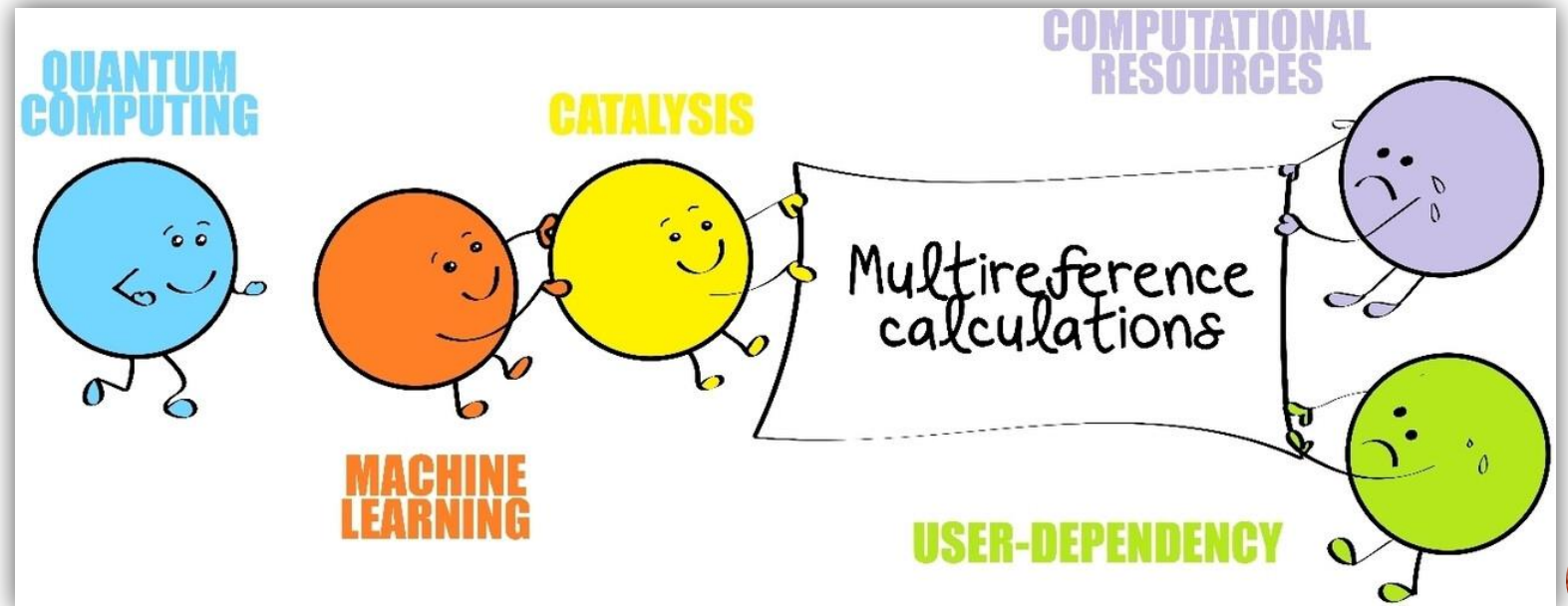
EXPONENTIAL SCALING IS CHALLENGING; ACTIVE SPACE METHODS ARE USED, AND QUANTUM COMPUTING AIDS BEYOND CAS(24,24)

Active Space approach **MCSCF approach; CASSCF approach most successful**

CAS(m, n):
 m electrons in n orbitals



- **Exact CASSCF:** CAS(20, 20) on HPCs
- **CASCI:** CAS(44, 44) with (loads of) approximations
- **DMRG:** CAS (84, 84)



TWO ALGORITHMS FOR TWO ERAS

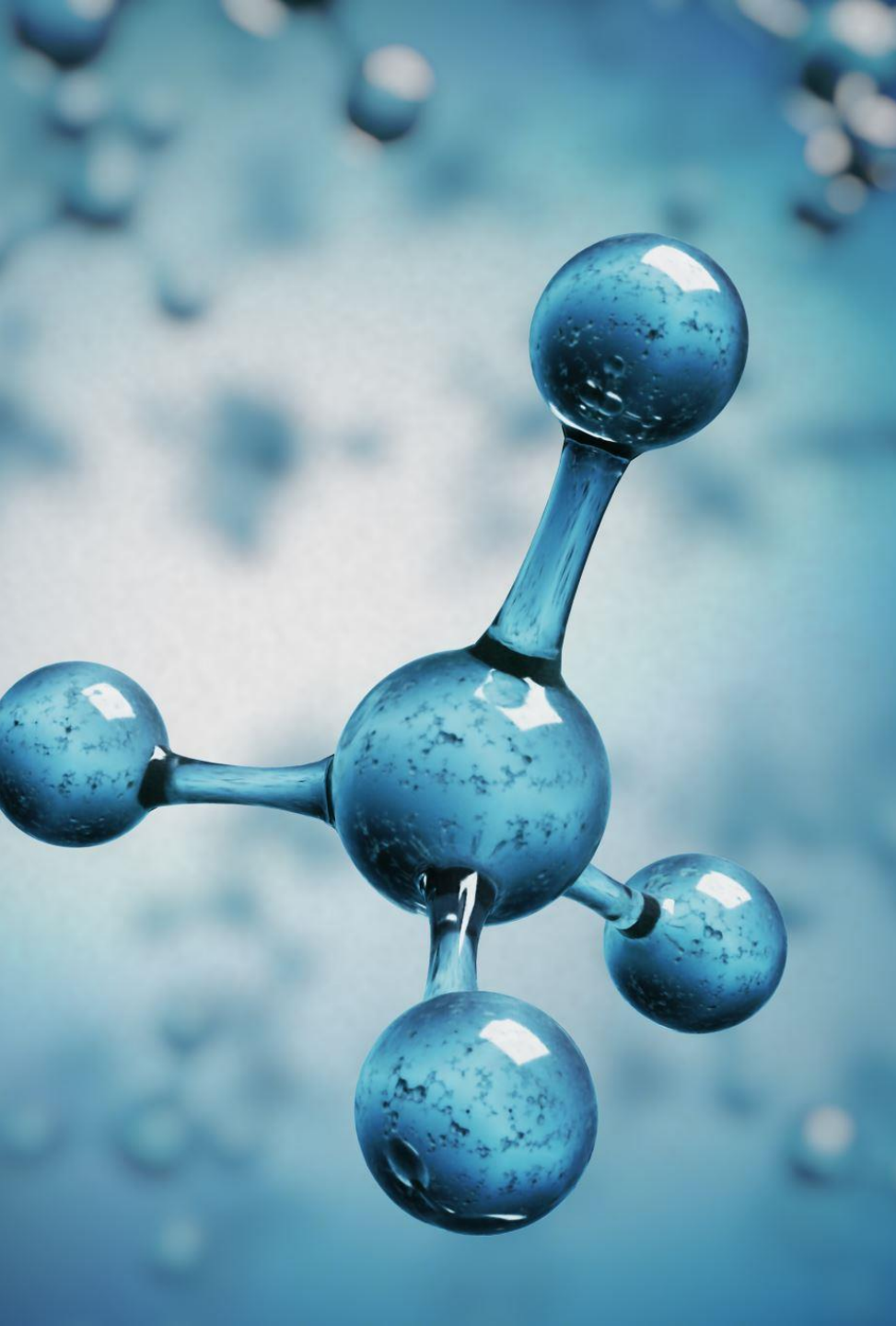
	NISQ Era	FTQC Era
Qubit Quality & Quantity	Moderate number of noisy qubits	High-quality qubits with error correction
Application Scope	Heuristic algorithms (e.g., Variational Quantum Eigensolver - VQE)	Large-scale algorithms (e.g., Quantum Phase Estimation - QPE)
Error Management	Limited error suppression and mitigation	Full fault-tolerant error correction
Objective	Ground state energy (VQE)	Eigenvalue estimation (QPE)
Algorithm Type	Hybrid quantum-classical (VQE)	Purely quantum (QPE)
Resource Requirements	Fewer qubits, suited for NISQ	Many qubits, suited for FTQC
Error Sensitivity	Resilient due to classical optimization loop	Sensitive, requiring robust error correction

POTENTIAL APPLICATIONS

Table 1 Overview of potential application areas for quantum algorithms alongside with information about relevant physical target quantities, underlying theoretical foundations, and some of the traditional algorithms to compete with

Applications	Molecular structure prediction & exploration	Biochemical processes (e.g. drug-molecule protein docking)	Ground state chemistry (e.g. catalysis)	Photochemistry (e.g. photosynthesis)	Complex dynamics (e.g. charge dynamics)	Cheminformatics
Chemical physics	Forces on atom	Thermodynamics	Kinetics	Spectroscopy	Electronic & nuclear dynamics	Data-driven, physics-inspired, cost-function optimization
Physical quantity to be calculated	Energy gradient	Free energy (difference)	Reaction & activation energies	Excitation energies	Autocorrelation functions	Universal applicability
Accuracy (Hartree atomic units)	$10^{-3} \sim 10^{-4}$	$10^{-3} \sim 10^{-4}$	$10^{-3} \sim 10^{-4}$	10^{-3}	purpose dependent	purpose dependent
Mechanical theory	Effectively classical dynamics of nuclei/ions	Effectively classical dynamics of nuclei/ions	Electronic Schrödinger equation for ground states	Electronic Schrödinger equation for excited states	Time-dependent electronic and nuclear Schrödinger equations	Agnostic to the underlying mechanical theory
State-of-the-art traditional competitors	DFT, QM/MM	FF,DFT,QM/MM	CCSD(T), CASSCF, DMRG-CI/SCF, FCIQMC/SCF, MR-PT2, MRCI+Q	EOM-CC/LR-CC, DMRG-CI/SCF, MR-PT2, MRCI+Q,	MCTDH	Neural Network
Routine traditional competitor	DFT, FF	FF	DFT, MP2	TD-DFT, ADC(2)	Surface hopping	
Quantum algorithms	Quantum search	Quantum Metropolis-Hastings	QPE, VQE	QPE, VQE	Hamiltonian simulation	Quantum Machine Learning
Quantum speedup	Quadratic	Polynomial	Exponential	Exponential	Exponential	Unknown

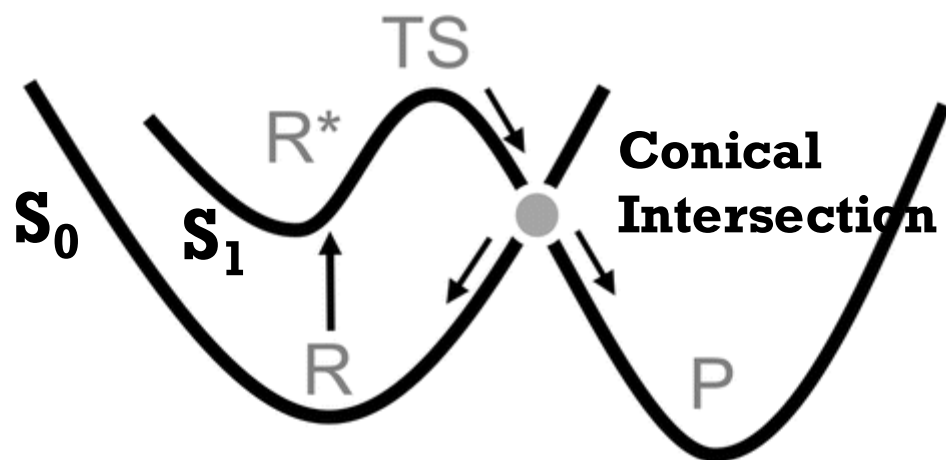
H. Liu , G. H. Low, D. S. Steiger, T. Häner, M. Reiher, M. Troyer,
 Prospects of quantum computing for molecular sciences,
 Materials Theory (2022) 6:11 <https://doi.org/10.1186/s41313-021-00039-z>.



QUANTUM COMPUTING FOR QUANTUM CHEMISTRY: VU, LEIDEN, UvA (QUSOFT)

- SA-OO-VQE implementation
- Gradients and non-adiabatic coupling (NAC)
- Detection of conical intersection (CI)
- Photocatalysis/heterogeneous catalysis
- Non-adiabatic dynamics
- Vibrational Circular Dichroism (VCD)
- Adiabatic state preparation (ASP)
- Embedding Methods (FragPT2)

THE GENERAL MECHANISM OF PHOTOCHEMICAL CATALYTIC REACTIONS OFTEN INVOLVES A CONICAL INTERSECTION



S_0 – ground electronic state* (singlet)

S_1 – excited electronic state (singlet)

**electronic state – specific arrangement of electrons in a molecule*

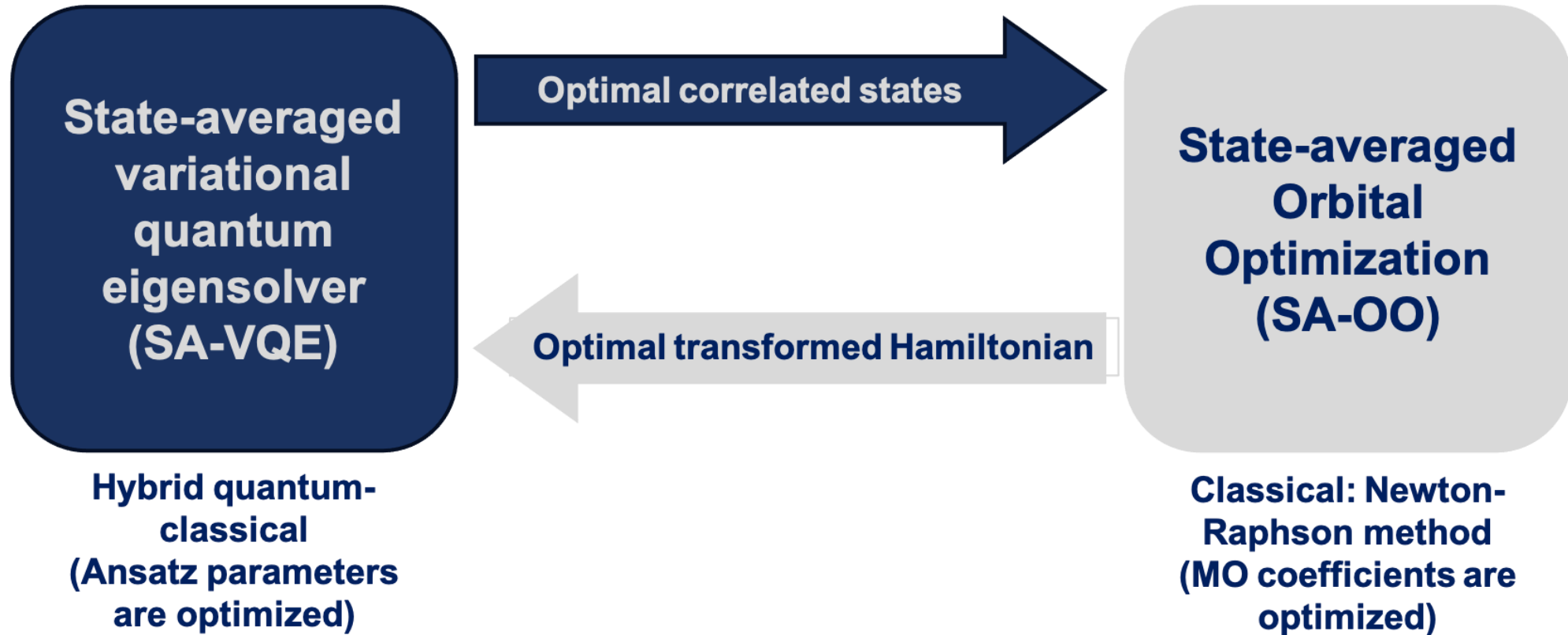
State-averaged algorithms offer a democratic description of two states simultaneously

Classical: SA-CASSCF

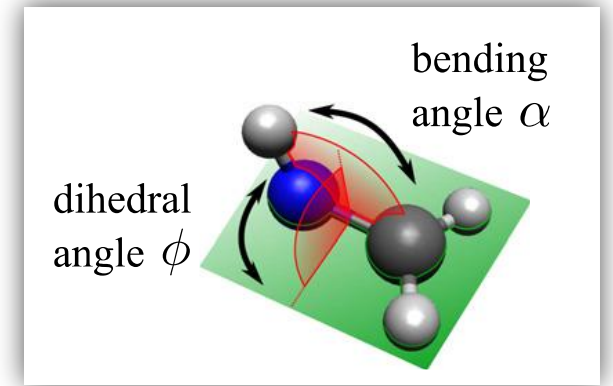
Quantum: SA-OO-VQE

Requires democratic description of multiple electronic states

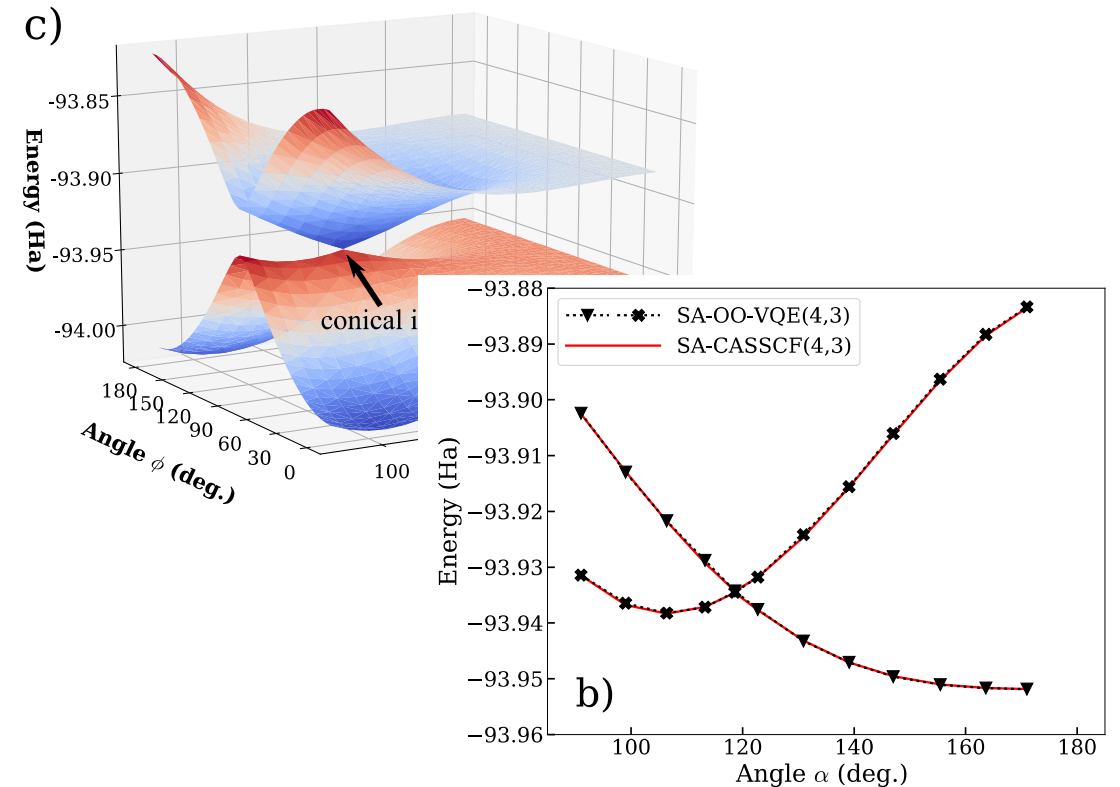
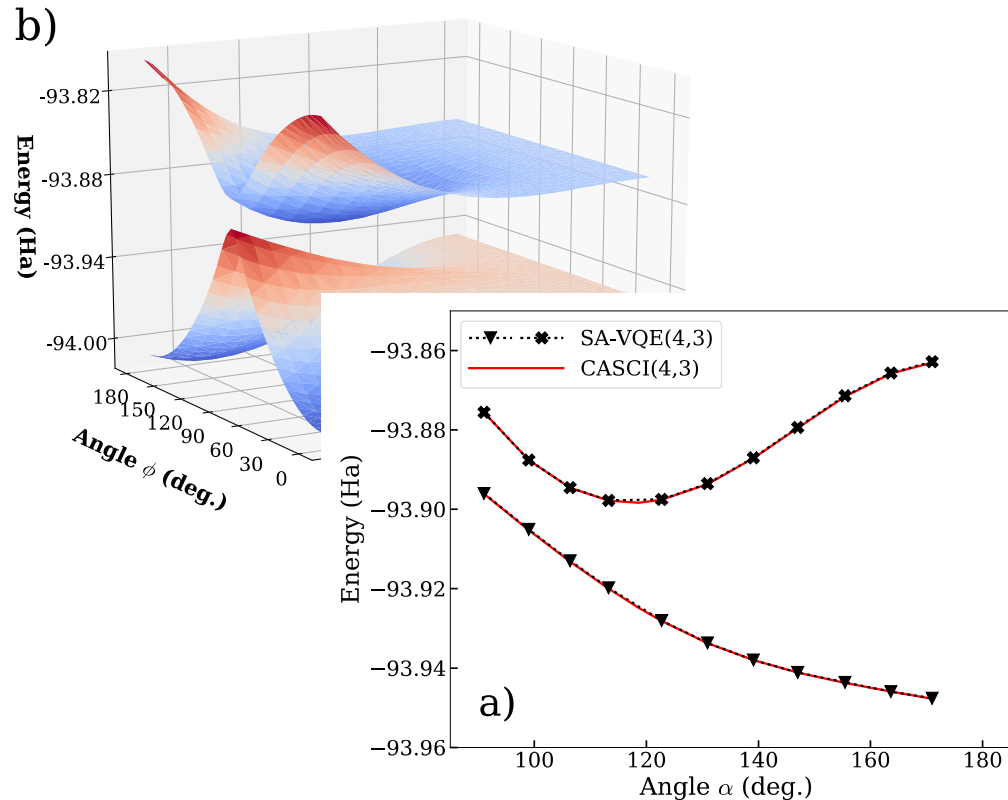
SA-OO-VQE: THE ALGORITHM



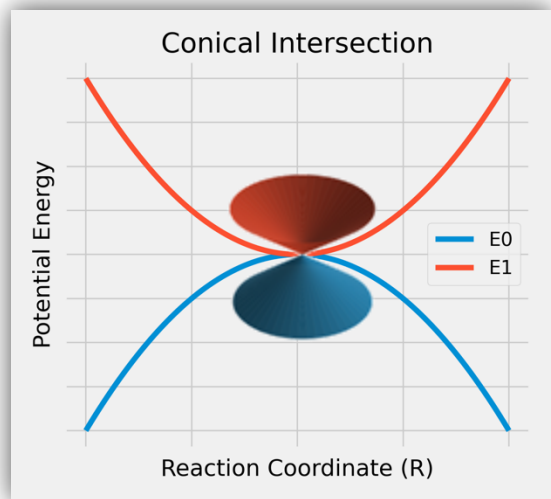
CONICAL INTERSECTIONS DURING ROTATION ALONG THE DOUBLE BOND IN FORMALDIMINE (CH_2NH)



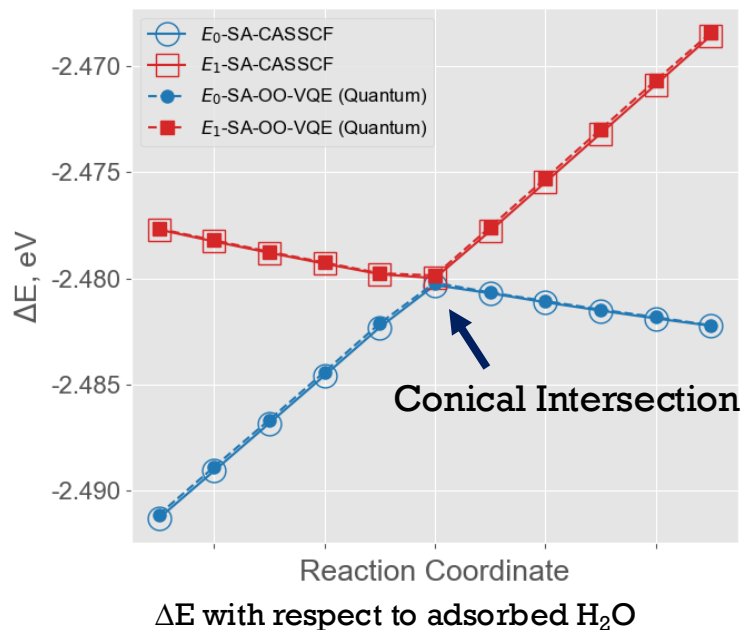
CASCI: Biased towards the ground state (SA-VQE) **SA-CASSCF:** Democratic description of states (SA-OO-VQE)



HETEROGENEOUS PHOTOCATALYSIS



Schematic – conical intersection



Beyond Born-Oppenheimer Approximation (BOA):

BOA assumes rapid electron adjustment to nuclei

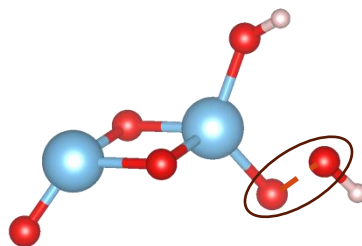
Goes beyond the separation of electron and nuclear motions e.g., conical intersection (CI)

Prototype 2:

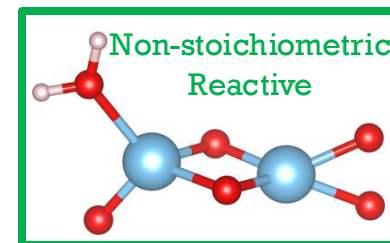
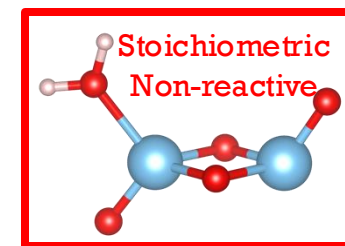
H_2O dissociation on non-stoichiometric Ti_2O_5

- Previous experiments + computations¹ compare Ti_2O_4 vs Ti_2O_5
- Used mixture of methods for calculating potential energy curves
- We calculated CI for this reaction
- Attributed the origin of CI to the additional oxygen – clarifies reaction mechanism²

Reaction coordinate is the distance between the 'additional O' and OH



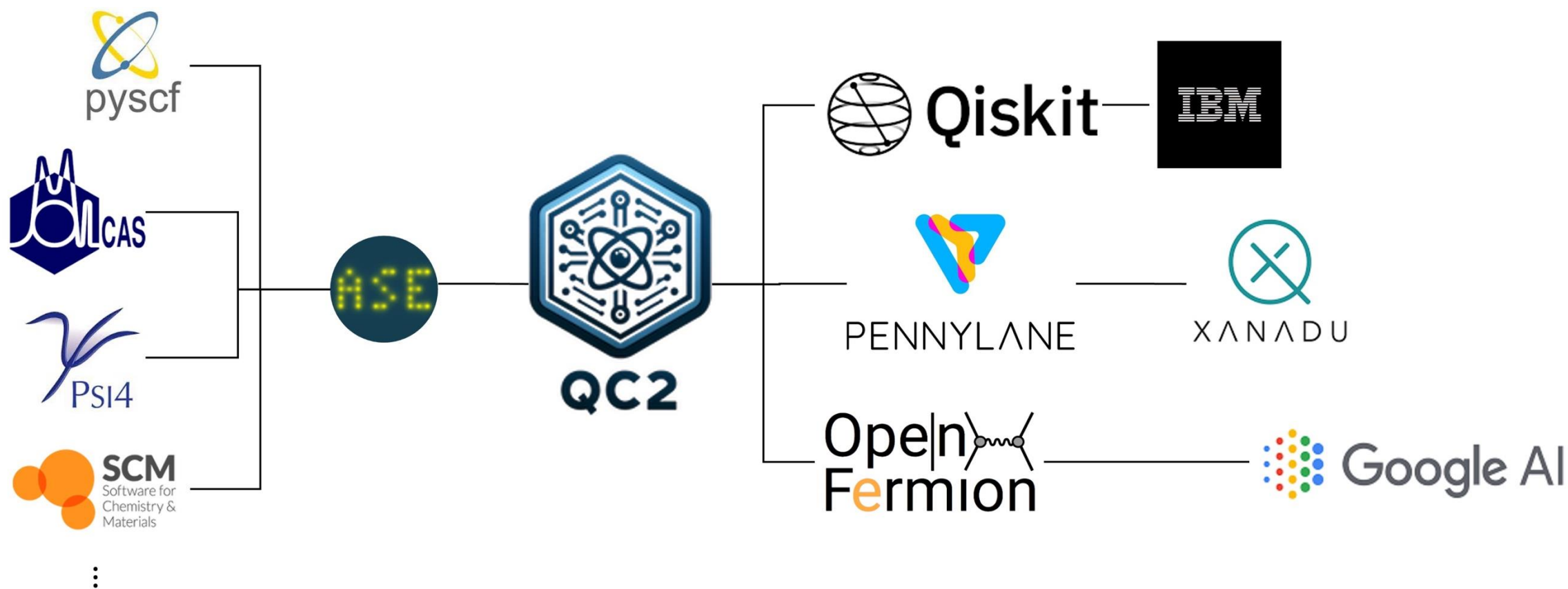
Explains why



¹S. Yin and E. R. Bernstein, Phys.Chem.Chem.Phys., 16, 13900-13908 (2014).

²S. Hariharan, S. Kinge, K. Schoutens, L. Visscher, In preparation (2024).

QC² SOFTWARE



<https://github.com/qc2nl>; <https://qc2.readthedocs.io/en/latest/>;

<https://blog.esciencecenter.nl/quantum-computing-for-quantum-chemistry-with-qc2-69ee18ef2969>

SUMMARY

Quantum chemistry

- Quantum computing is useful in quantum chemistry for strongly correlated systems
- NISQ to FTQC era – plethora of opportunities and developments
- Extract most out of VQE and ways to cut costs of QPE, Hamiltonian simulation

Developments in our group

- Our group implemented SA-OO-VQE algorithm
- Investigated a variety of problems: structure, energetics, dynamics and spectra
- Will be investigating more interesting problems in the future

Hardware developments

- Growing together with hardware developments
- Adapting software to the hardware developments
- Fault-tolerant not so far in the future

Outlook

- Quantum-centric computing, Embedding techniques, Using quantum information, Quantum multiscale modelling, Machine learning and Quantum Computing etc.