MANY-BODY POST-PROCESSING OF DFT CALCULATIONS USING VQE

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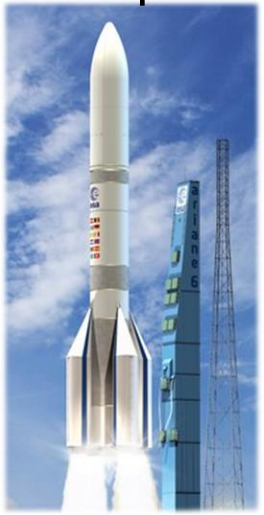
From Quantum Mechanics to Material Science and Engineering

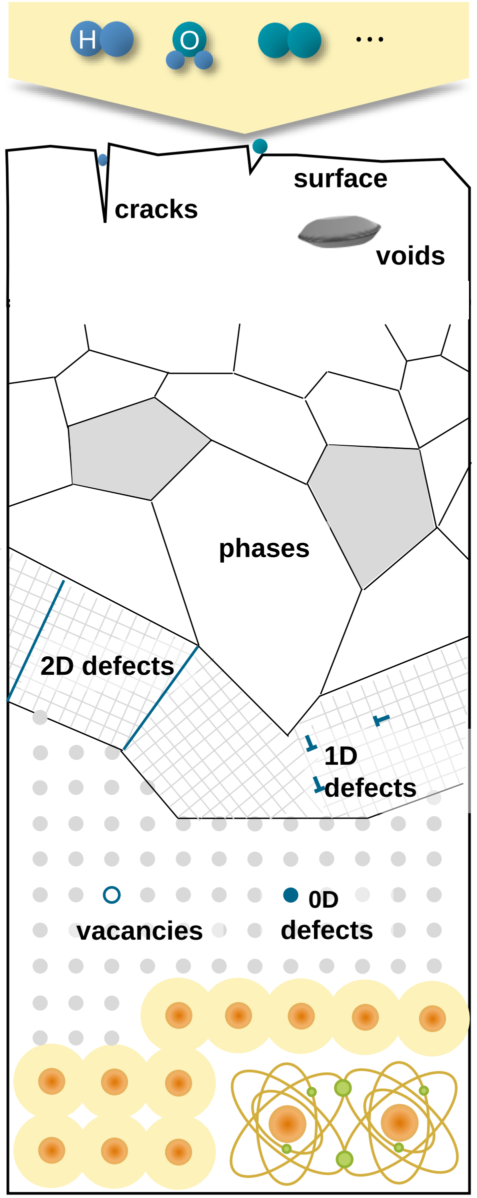
Applications

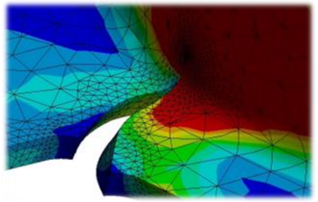
Aeronautics

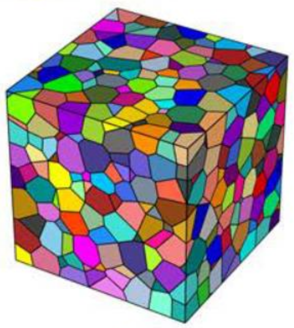
Energy

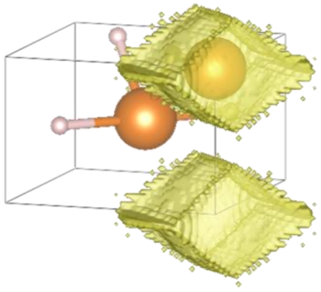
Aerospace











Simulation

$\sim 0.1 - 1m$
Continuum model: Fatigue life, ductility

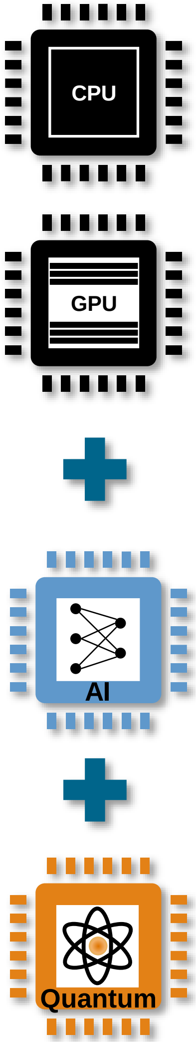
$\sim 1 - 10mm$
Finite element method: Fracture toughness, Creep Strength

$\sim 50nm - 1\mu m$
Molecular dynamics: Dislocation dynamics, diffusion, phase diagram

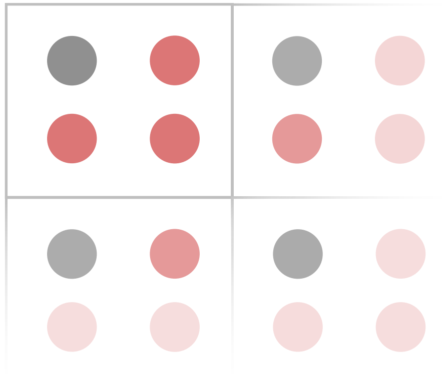
$\sim 1 - 10nm$
Density Functional Theory: Total energy, band gap, alloy free-energy

$\sim 0.01 - 1nm$
Quantum Chemistry: Wave-function, orbital occupancy

Methods



Simulation of periodic systems: DFT



- Density functional theory:
  - Formally exact reformulation of the Schrödinger equation
  - Everything is a functional of the electronic density: $H\psi = E\psi \rightarrow E[\rho]$
  - $E[\rho]$ unknown, has to be approximated

$$E[\rho] = E_{\text{kin}}[\rho] + E_{\text{pp}}[\rho] + E_{n-n} + E_{\text{Hartree}}[\rho] + E_{\text{XC}}[\rho]$$

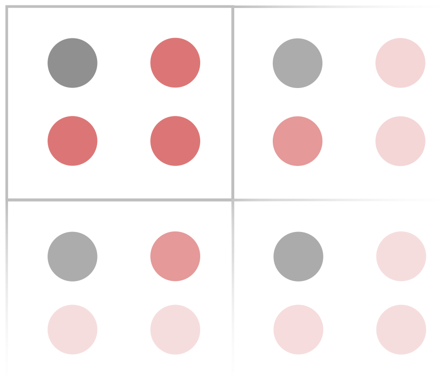
  - Kohn-Sham DFT: Calculate density by solving artificial one-body Hamiltonian:

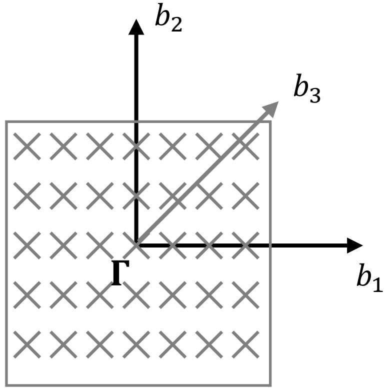
$$\left[-\frac{\nabla^2}{2} + V_{\text{pp}}(r) + E_{n-n} + V_{\text{Hartree}}[\rho](r) + V_{\text{XC}}[\rho](r)\right]\phi_i(r) = \epsilon_i \phi_i(r)$$

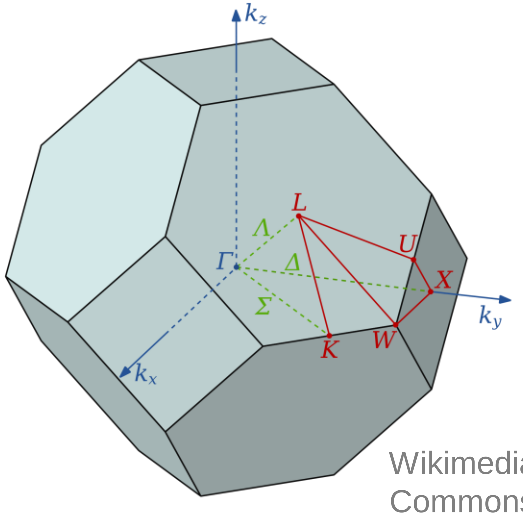
- Periodic orbitals as sum over plane waves $\phi_i^{(k)}(r) = \sum_{G,\, G \leq G_{\text{cut}}} c_{G,i}^{(k)}\, e^{i(k+G)\cdot r}$
- Electronic density $\rho(r) = \sum_{i,k} f_i^{(k)} \left|\phi_i^{(k)}(r)\right|^2$

Simulation of periodic systems: k-point sampling

- Simulating computational cell with periodic boundary conditions
  - Introduces finite size errors
  - Supercell approach:
    Include **periodic images explicitly** in the computational cell
  - k-point sampling:
    Equivalent to supercell approach but in **reciprocal space**. Average over calculations on different k-points







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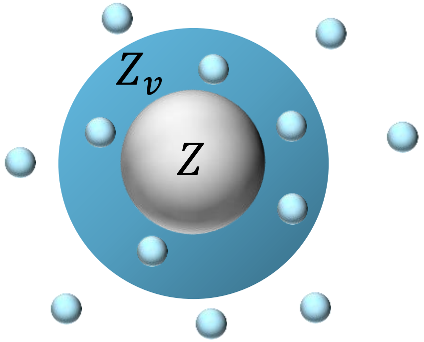
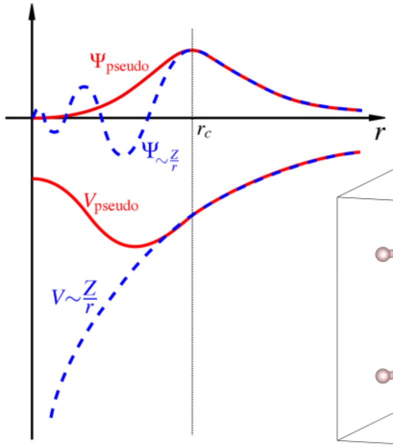
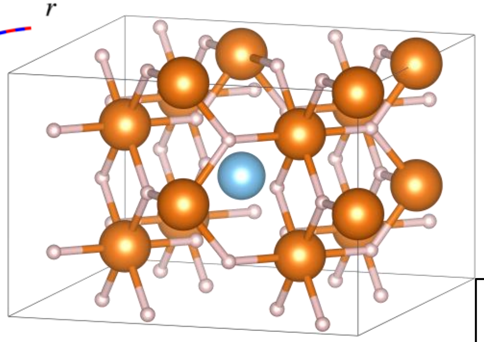
Simulation of periodic systems: Many-body approach

$$H = \boxed{-\frac{1}{2}\sum_{T,i}\nabla^2_{r_i+T}} + \boxed{\sum_{T,I,i} V_{\mathrm{pp}}(r_i - R_I - T, r'_i - R_I - T)} + \boxed{\sum_{T,I,J}\frac{Z_I Z_J}{|R_I + T - R_J|}} + \boxed{\sum_{T,i,j}\frac{1}{|r_i + T - r_j|}}$$

$$\hat{H} = \boxed{\text{kin. energy}} + \boxed{\text{pseudopot.}} + \boxed{\text{nuclear int.}} + \boxed{\text{electron int.}}$$







Kinetic energy of electrons (Born-Oppenheimer Approximation)

Potential of nuclei + core-electrons

Fully non-local norm-conserving **pseudopotential**

Energy between all nuclei and their (infinitely many) periodic images

Calculated via Ewald summation

Exact coulomb interaction between electrons

Calculated via pair densities

All calculated with KS-orbitals in plane-wave basis

$$|\psi_i\rangle = \sum_p c_{p,i}\,|p\rangle$$

plane-wave

DFT Hamiltonian is discarded

Periodicity through sum over lattice translation vectors T

Schultheis et al., arXiv:2510.12887

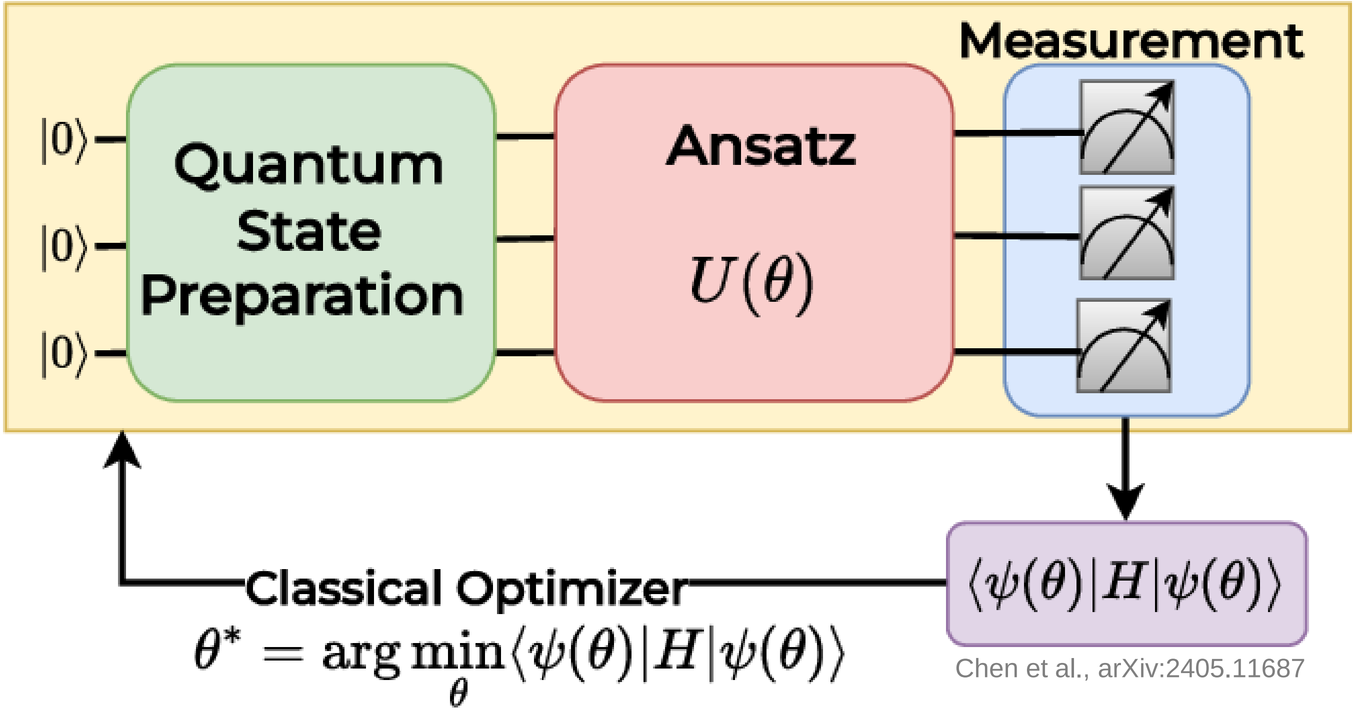
Second Quantization

- Rewrite Hamiltonian in 2nd quant. to use on a quantum computer

$$\hat{H}^{(k)}_{\text{elec}} = \sum_{tu} h^{(k)}_{tu} \hat{a}^\dagger_t \hat{a}_u + \frac{1}{2} \sum_{tuvw} h^{(k)}_{tuvw} \hat{a}^\dagger_t \hat{a}^\dagger_u \hat{a}_v \hat{a}_w + E_{\text{n-n}} + E_{\text{e-self}}$$

- One-electron terms $h_{tu} = \langle \psi_t | \, \hat{T} + \hat{V}_{\text{pp}} \, | \psi_u \rangle$
- Two-electron terms $h_{tuvw} = \frac{4\pi}{V} \sum_{\mathbf{G}, \mathbf{G} \neq \mathbf{0}} \frac{\tilde{\rho}^*_{tw}(\mathbf{G}) \tilde{\rho}_{uv}(\mathbf{G})}{G^2}$
- Constant terms $E_{\text{n-n}} = \frac{1}{2} \sum_{I,J}^{N} \sum_{\mathbf{T}}{}' \frac{Z_I Z_J}{|\mathbf{R_I} - \mathbf{R_J} - \mathbf{T}|}$ and $E_{\text{e-self}} = N_e \sum_{\mathbf{T} \neq \mathbf{0}} \frac{1}{|\mathbf{T}|}$
- Now: Compute the ground state!

VQE: Finding the ground state



Chen et al., arXiv:2405.11687

$$\hat{H}^{(k)}_{\text{elec}} = \sum_{tu} h^{(k)}_{tu} \hat{a}^\dagger_t \hat{a}_u + \frac{1}{2} \sum_{tuvw} h^{(k)}_{tuvw} \hat{a}^\dagger_t \hat{a}^\dagger_u \hat{a}_v \hat{a}_w + E_{\text{n-n}} + E_{\text{e-self}}$$

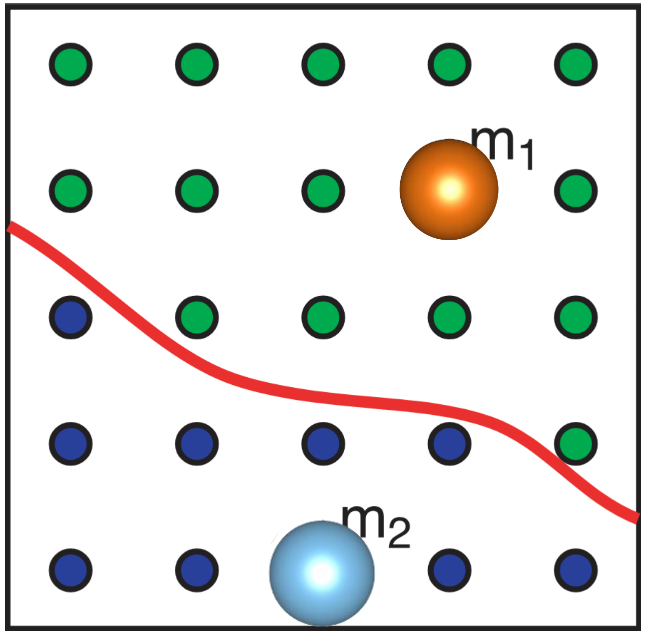
Calculating charges on atoms: Bader charges

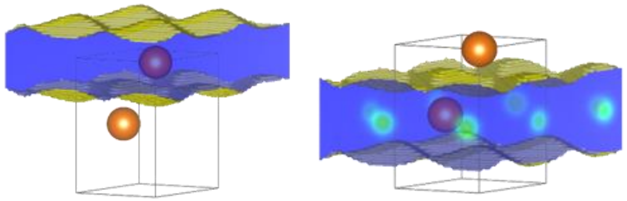
- Quantifying charges on atoms
  - Bonding
  - Oxidation states
  - Charge locality and charge transfer
- Bader regions
  - Real-space is divided into regions
    bound by zero-flux surfaces
    running through minima of the charge density
- Bader (excess) charge:

$$Q_I = \int_{B_I} \rho(r)\,\mathrm{d}^3 r \qquad\qquad Q_I \to Q_I - Z_I$$

- From density:

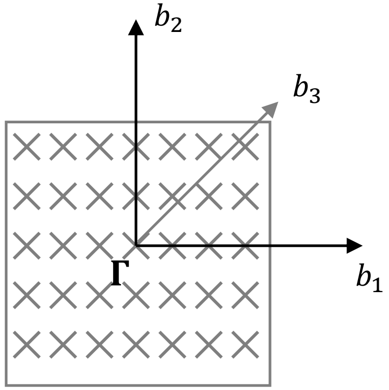
$$\rho(r) = \sum_{i,k} f_i^{(k)} \left|\phi_i^{(k)}(r)\right|^2 \qquad\qquad f_{i,\mathrm{MB}}^{(k)} = \left\langle \Psi_{\mathrm{MB}}^{(k)} \middle| \hat{n}_i \middle| \Psi_{\mathrm{MB}}^{(k)} \right\rangle$$

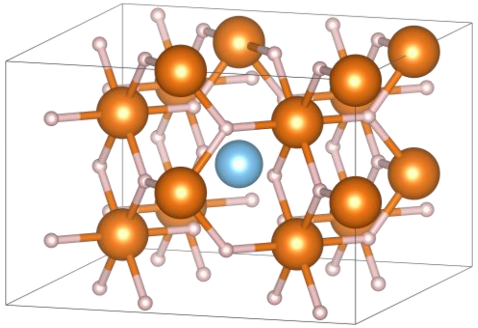


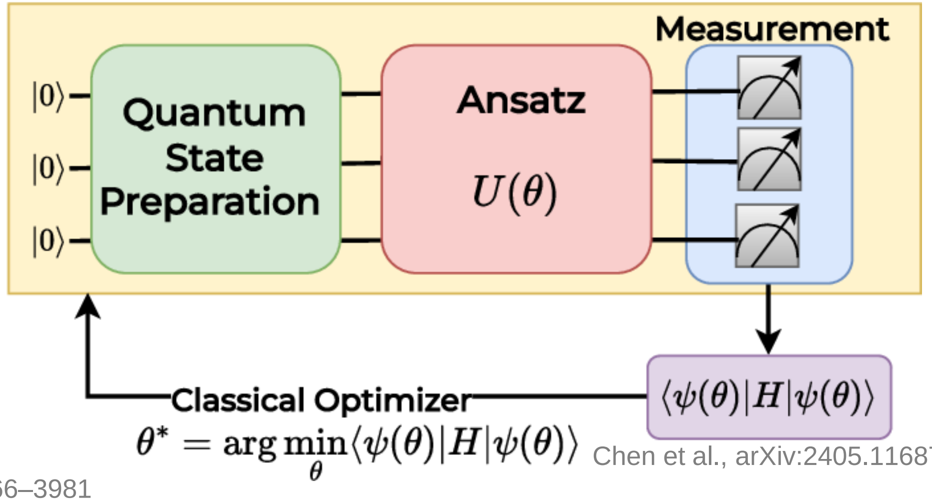


Computational details

- Spin-unpolarized, Γ-only DFT calculations
- Active space with frozen core approximation
- UCCSD ansatz
  - Two Trotter steps for CrO_2, RhO_2, RuO_2
- L-BFGS optimizer
- Simulation using TenCirChem[1]
- References are k-mesh calculations



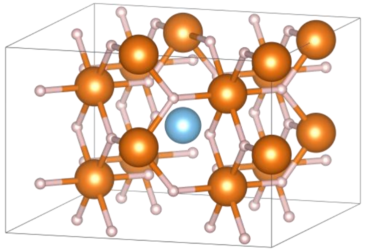


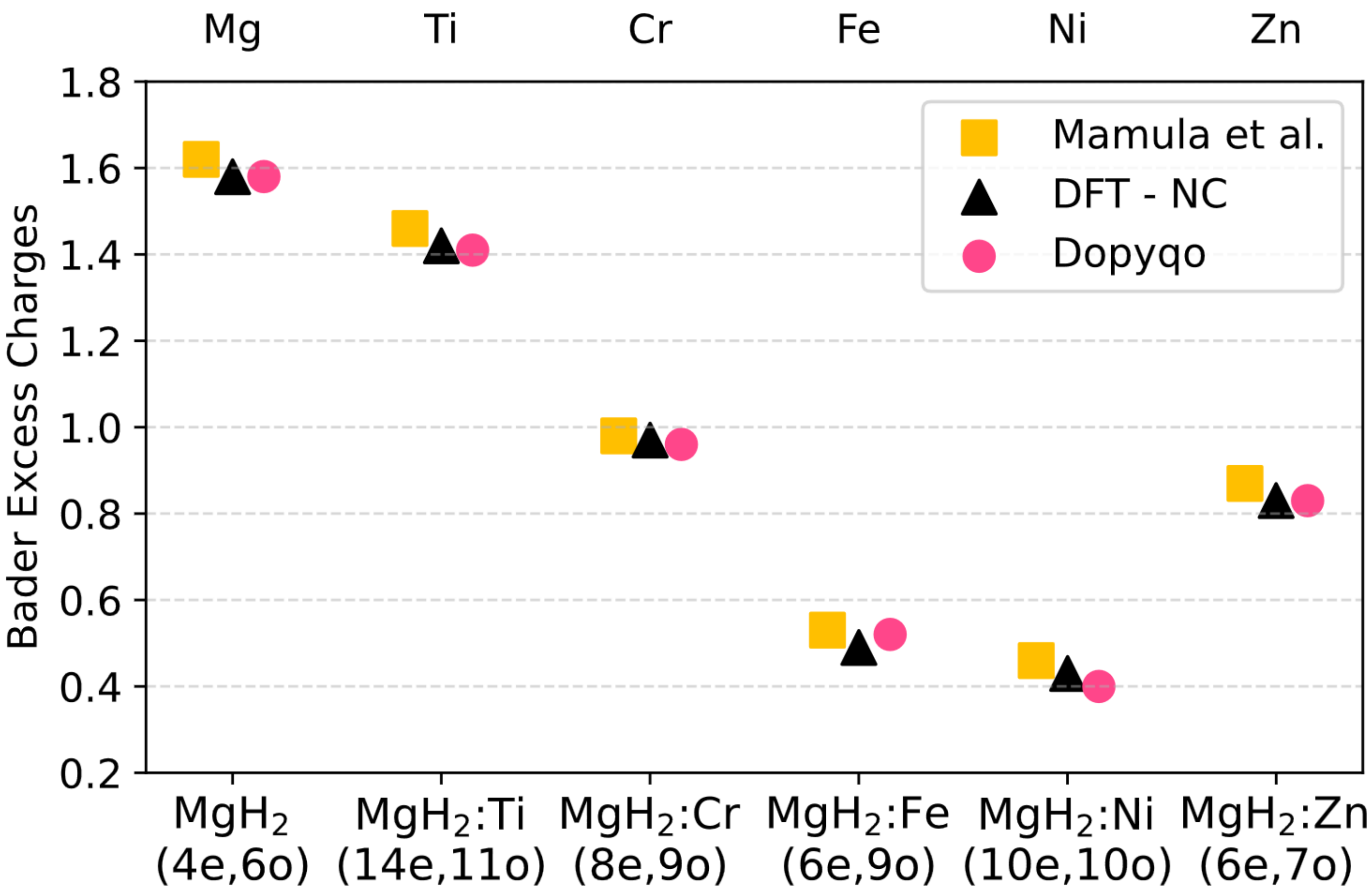


Chen et al., arXiv:2405.11687

[1] *J. Chem. Theory Comput.* 2023, 19, 13, 3966–3981

Bader charges: MgH_2-TM

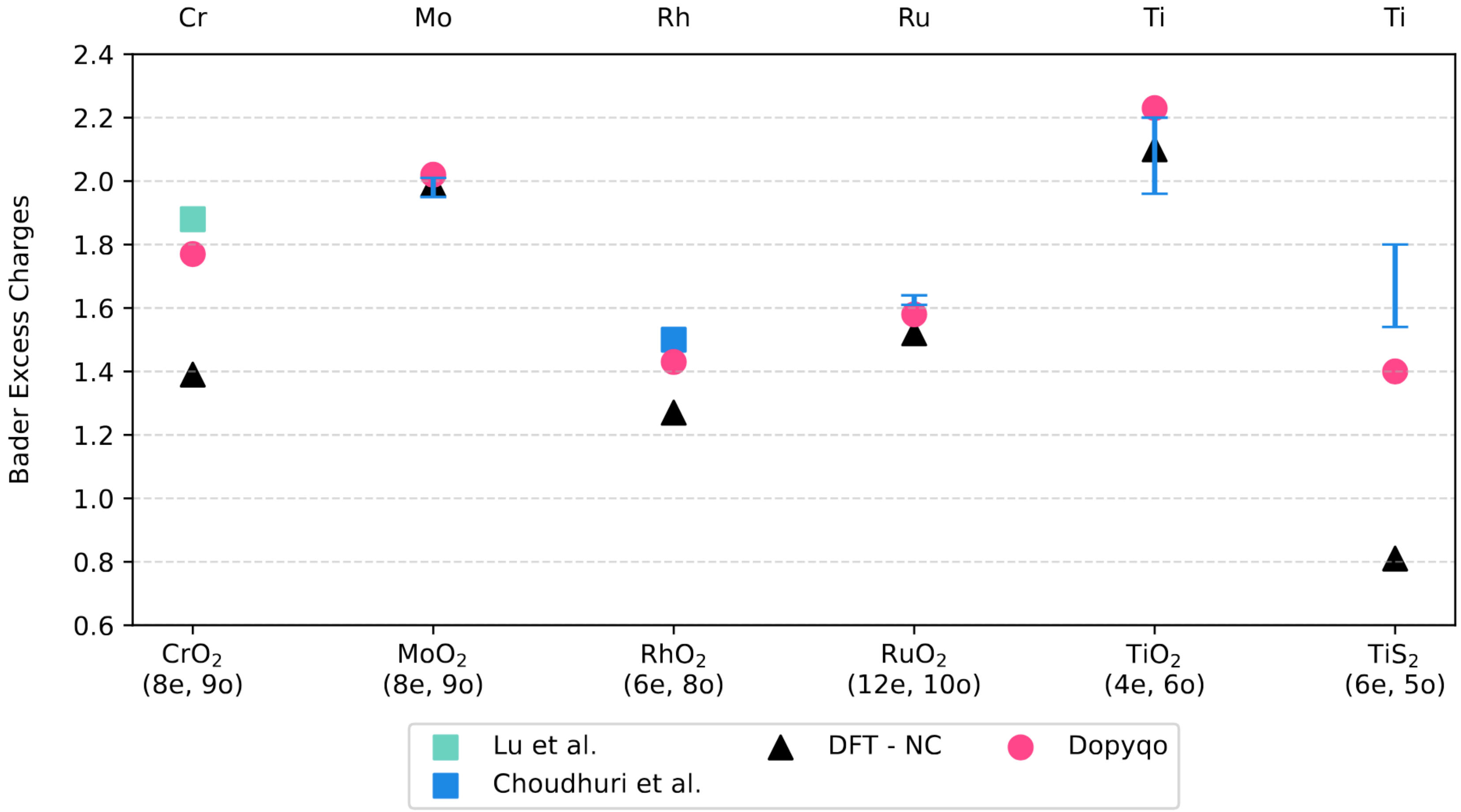




- Weakly correlated systems: Bader charges match DFT and DFT literature values

Schultheis et al., arXiv:2510.12887

Bader charges: Transition metal oxides

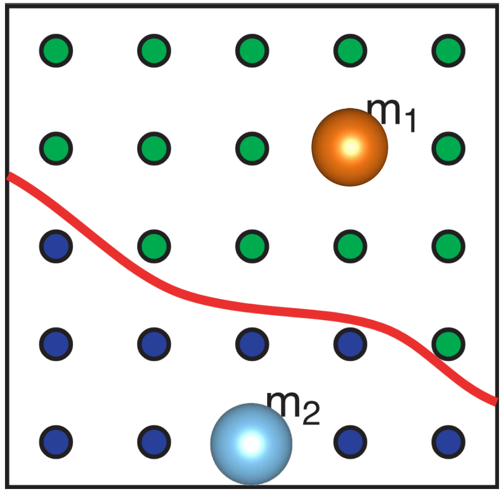


Two Trotter steps for CrO_2, RhO_2, RuO_2

- Strongly correlated systems: Bader charges different and improves towards k-mesh spin-polarized DFT+U values

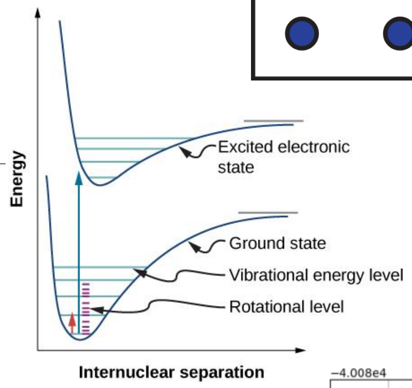
Schultheis et al., arXiv:2510.12887

Summary and future work



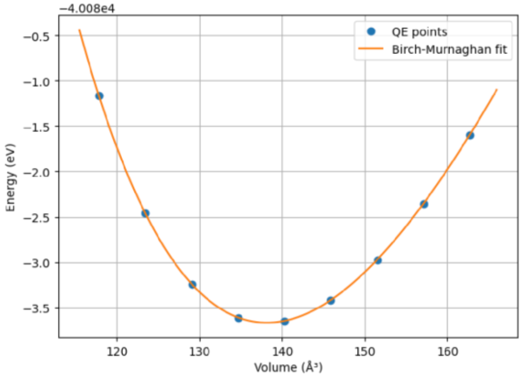
- Improvement of Bader charges towards k-mesh DFT+U for strongly correlated materials

- Software available: Dopyqo
  - Generates and solves Hamiltonians of periodic materials

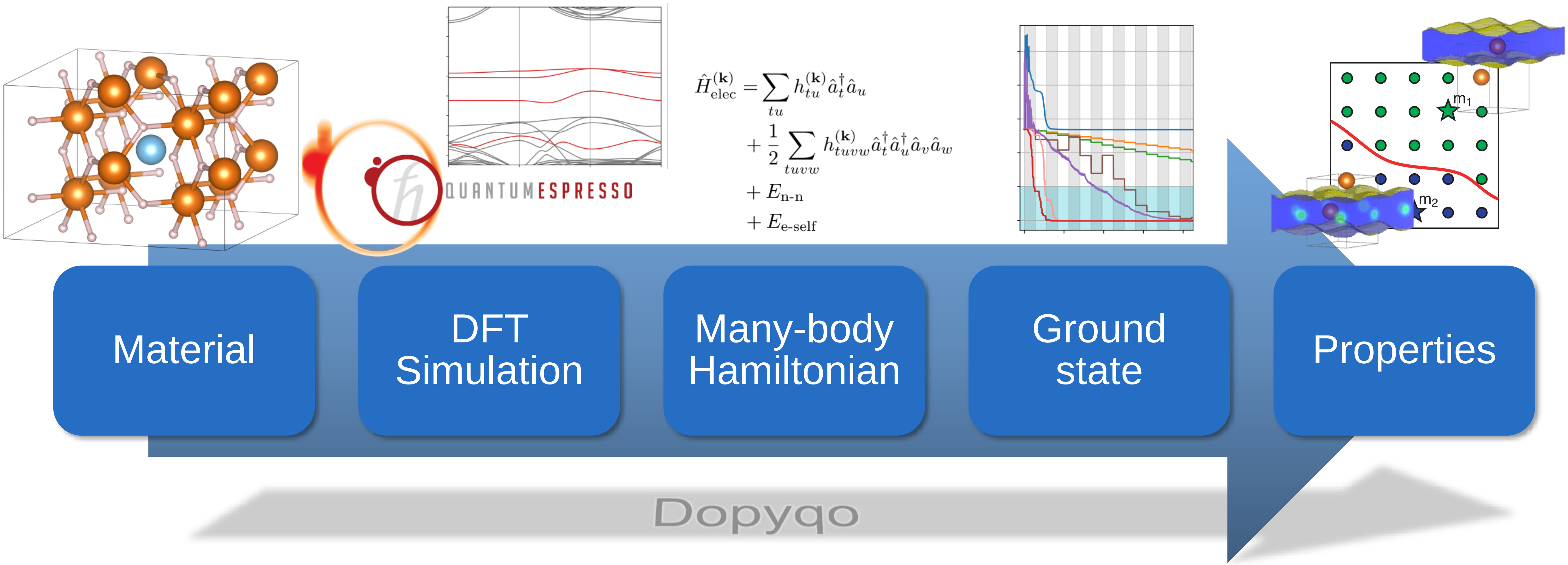


- Bader charge dependence on active space

- Investigating other properties: bulk modulus, excited states



Questions?



pip install dopyqo

DLR-WF/Dopyqo

Schultheis et al., arXiv:2510.12887