FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

DFT+U+V: Ground State and Real-Time Dynamics

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MOTIVATION

- Goal:
  - Accurate excited-state simulations in large systems
  - Low-cost alternative to hybrid functionals
- Method: Real-time time-dependent DFT+U+V (RT-TDDFT+U+V)
  - RT-TDDFT: Excited state dynamics
  - +U: Improves description of localized states
  - +V: To improve description of delocalized states

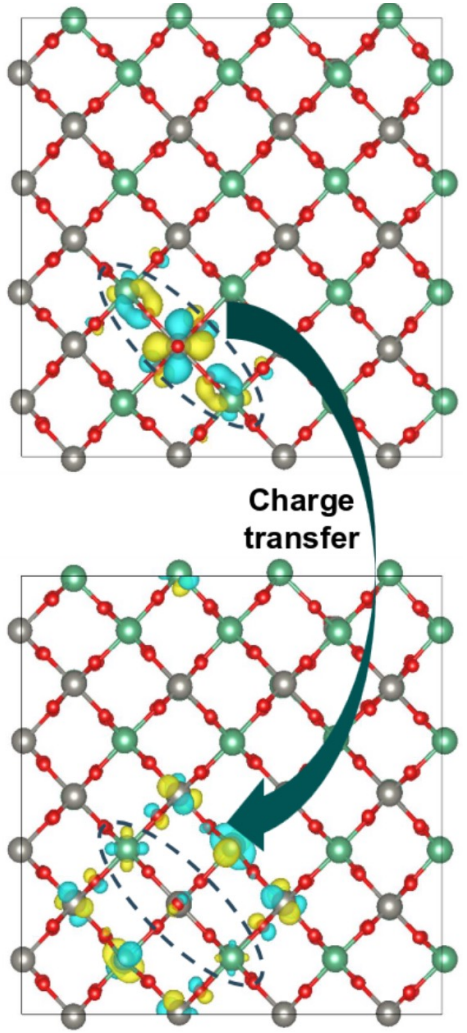


Figure created by Leon M. Müller

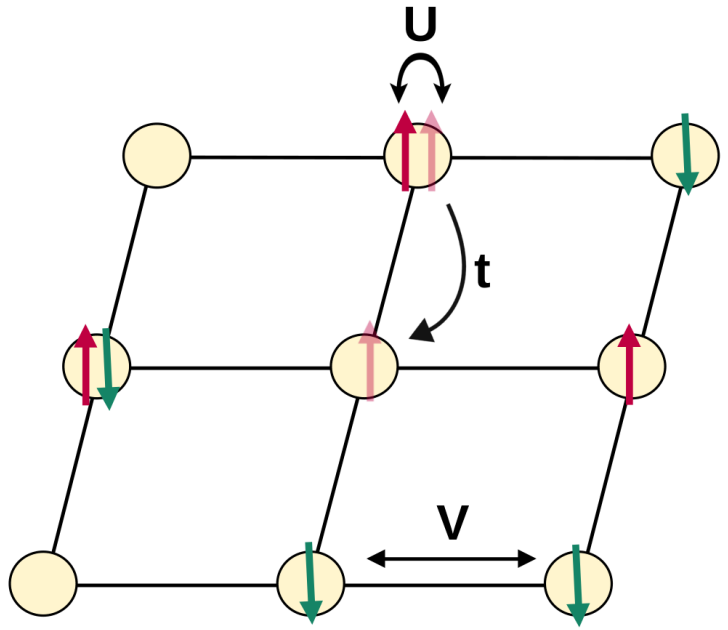
INSPIRATION FROM EXTENDED HUBBARD MODEL

$$H_{\mathrm{Hub}} = t \sum_{<i,j>,\sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + c^{\dagger}_{j,\sigma} c_{i,\sigma}) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow} + V \sum_{<i,j>} n_i n_j$$

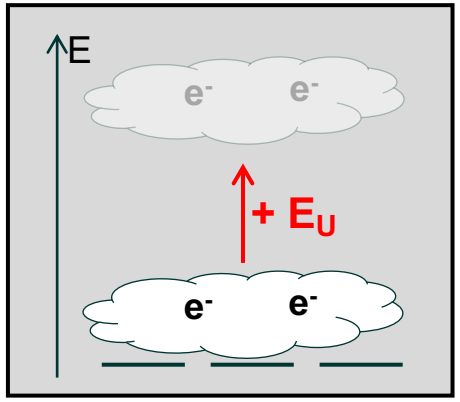
$$E_{tot} = E_{DFT} + E_U + E_V$$

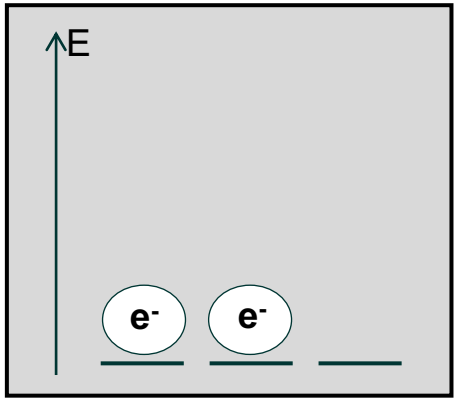
$$E_{\mathrm{U}} = \sum_{I,\sigma} \frac{U^I}{2} \mathrm{Tr}[\boldsymbol{n}^{I\sigma}(1 - \boldsymbol{n}^{I\sigma})]$$

$$E_{\mathrm{V}} = -\sum_{\sigma} \sum_{I,J}^{*} \frac{V^{IJ}}{2} \mathrm{Tr}(n^{\sigma}_{IJ} n^{\sigma}_{JI})$$

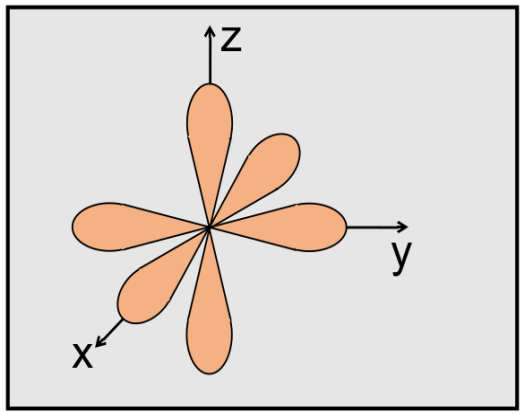


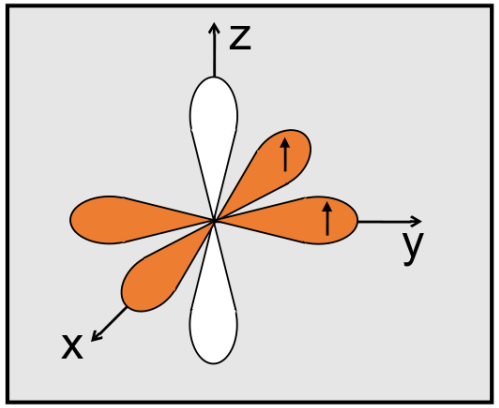
+U: ENERGY PENALTY FOR FRACTIONAL OCCUPATION



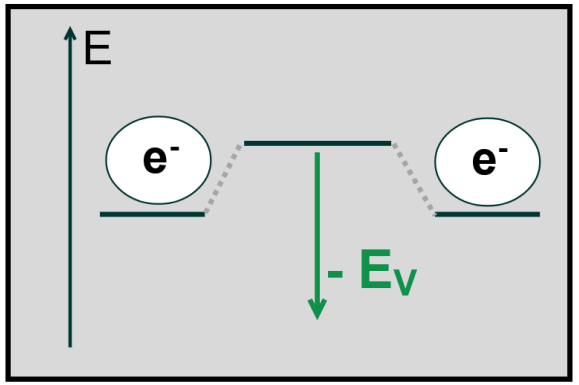


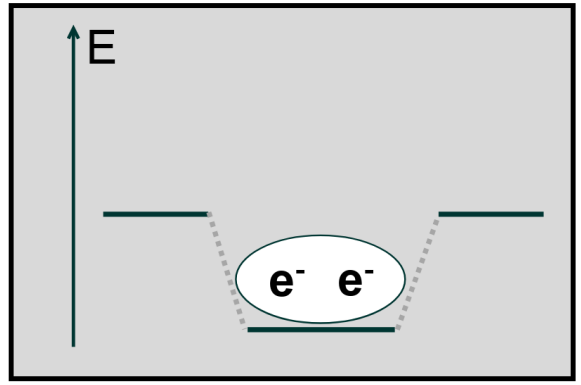
$$E_{\mathrm{U}} = \sum_{I,\sigma} \frac{U^I}{2} \mathrm{Tr}[\boldsymbol{n}^{I\sigma}(1 - \boldsymbol{n}^{I\sigma})]$$



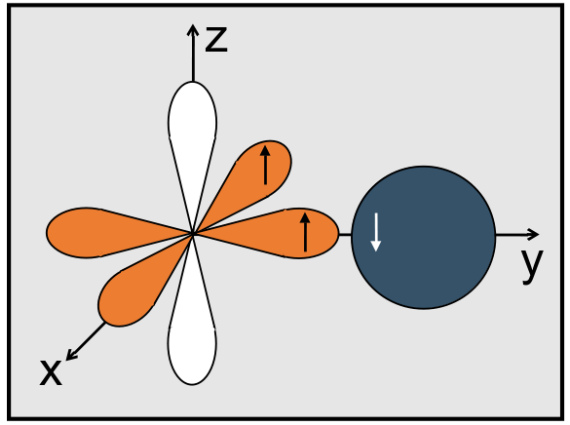


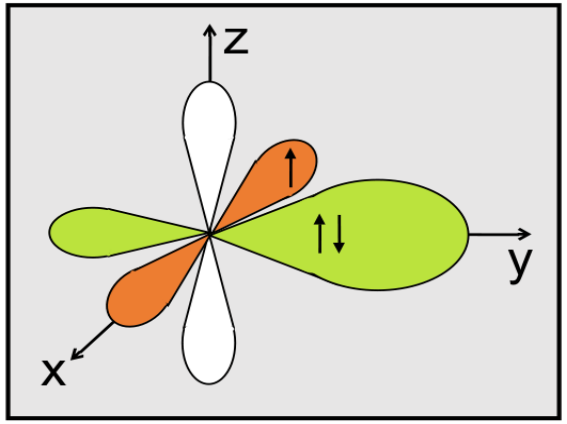
+V: ENERGETIC ENCOURAGEMENT OF BONDING





$$E_{\mathrm{V}} = -\sum_{\sigma}\sum_{I,J}^{*}\frac{V^{IJ}}{2}\mathrm{Tr}(n^{\sigma}_{IJ}n^{\sigma}_{JI})$$





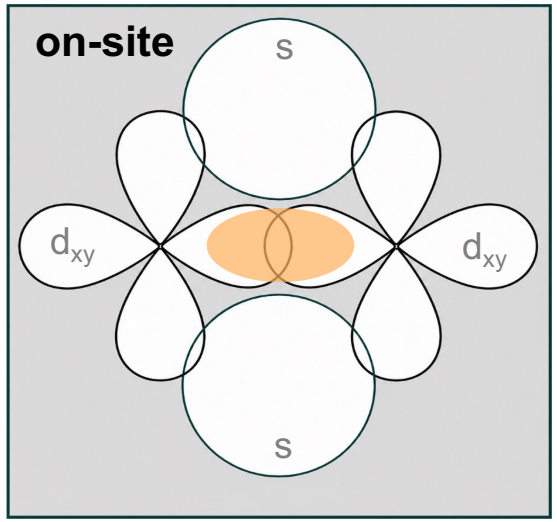
DEFINITION OF OCCUPATIONS

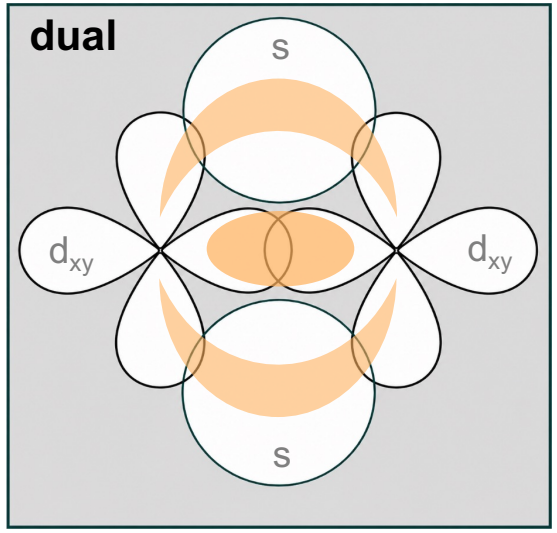
$$E_{\mathrm{V}} = -\sum_{\sigma}\sum_{I,J}^{*}\frac{V^{IJ}}{2}\mathrm{Tr}(n^{\sigma}_{IJ}n^{\sigma}_{JI})$$

$$n^{\sigma}_{ab} = \sum_{\gamma} f^{\sigma}_{\gamma} \left\langle \Phi^{\sigma}_{\gamma} \right| \hat{P}_{ab} \left| \Phi^{\sigma}_{\gamma} \right\rangle$$

$$n^{\sigma}_{ab}(\text{on-site}) = D^{\sigma}_{ab}$$

$$n^{\sigma}_{ab}(\text{dual}) = \frac{1}{2}\sum_{c}(S_{ac}D^{\sigma}_{cb} + D^{\sigma}_{ac}S_{cb})$$





APPLICATION TO DFT

$$v_{\mathrm{V},ij} = \sum_{\sigma} \sum_{Im,Jn}^{*} \frac{\partial E_V}{\partial D^{\sigma}_{ji}}$$

$$= -\sum_{\sigma} \sum_{Im,Jn}^{*} \langle \varphi^{\sigma}_{i} | \, \hat{P}^{\dagger}_{\mathrm{V}} \, | \varphi^{\sigma}_{j} \rangle \, V^{IJ} n^{\sigma}_{ImJn}$$

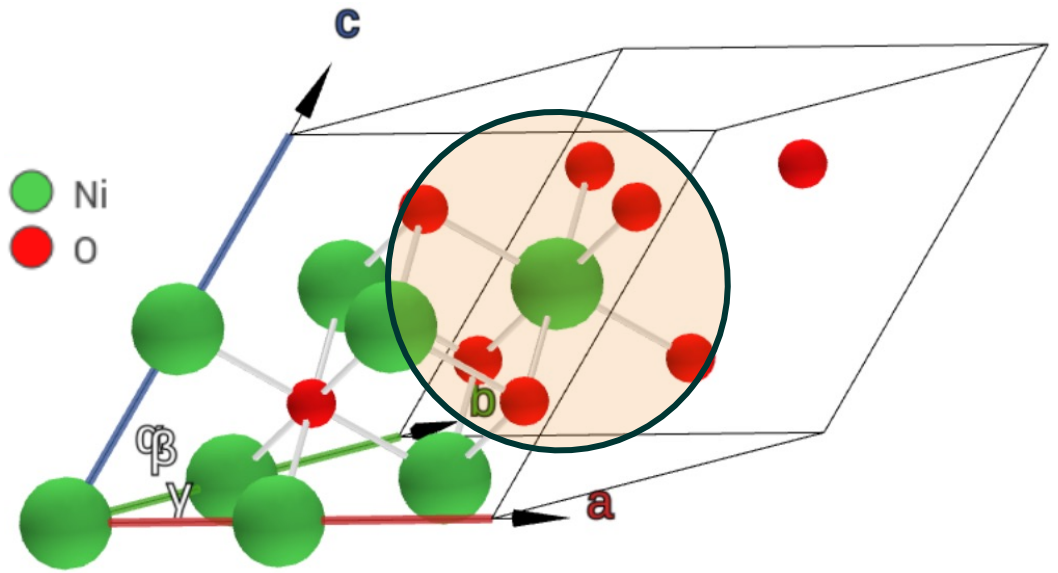
$$h_{ij} = h^{\mathrm{KS}}_{ij} + v_{U,ij} + v_{V,ij}$$

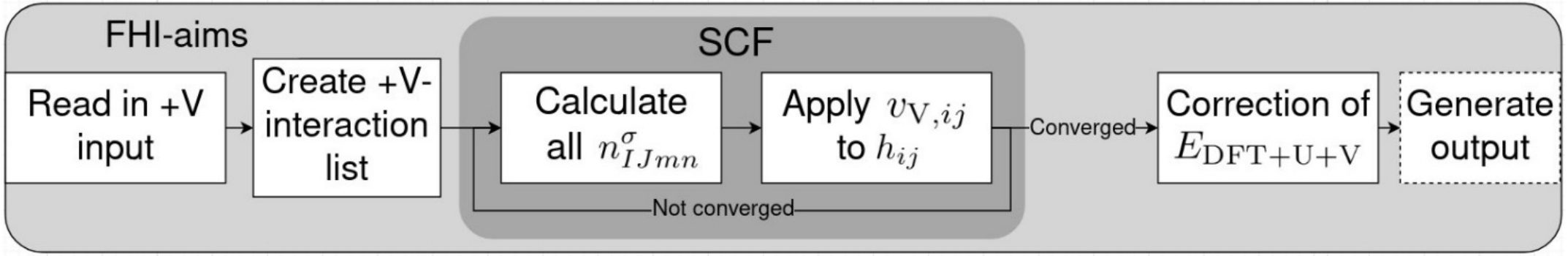
$$\boldsymbol{hc} = \boldsymbol{\epsilon S c}$$

WORKFLOW FHI-aims

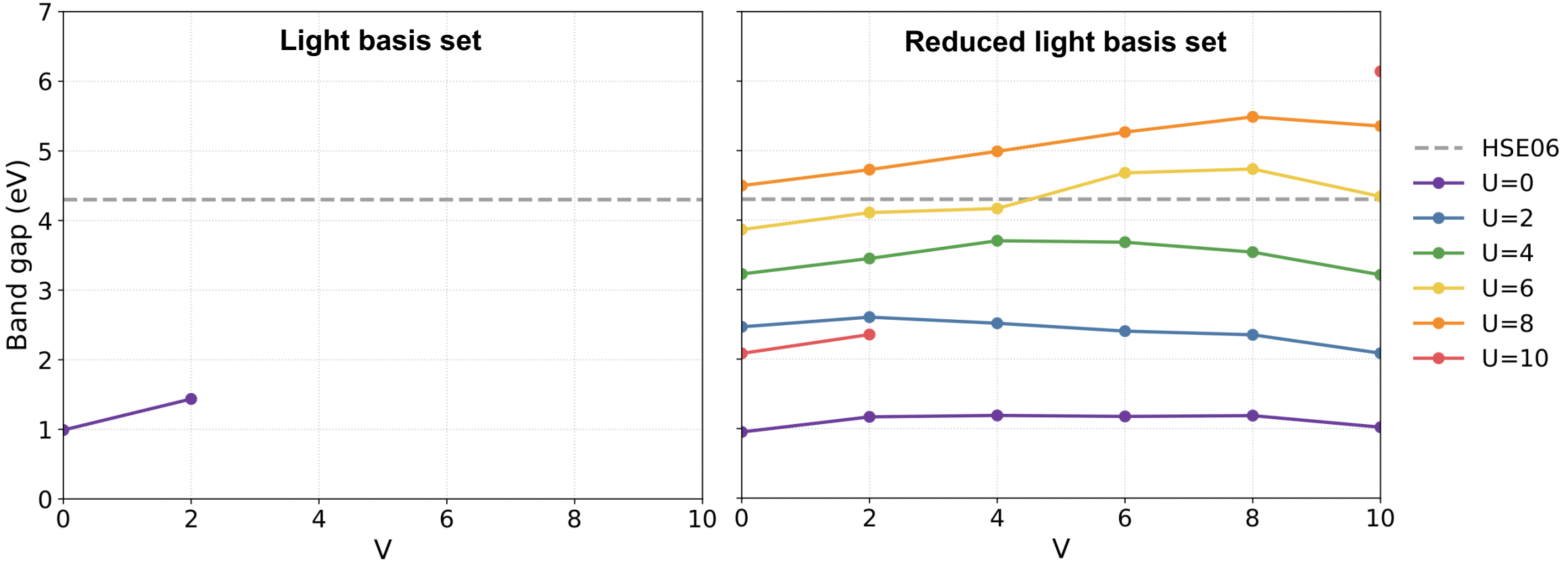
The ab initio materials simulation package

- **control.in:**
  - **plus_v Ni 3 d O 2 p 1 3**
  - **plus_v_use_mulliken**
  - **plus_v_matrix_control**

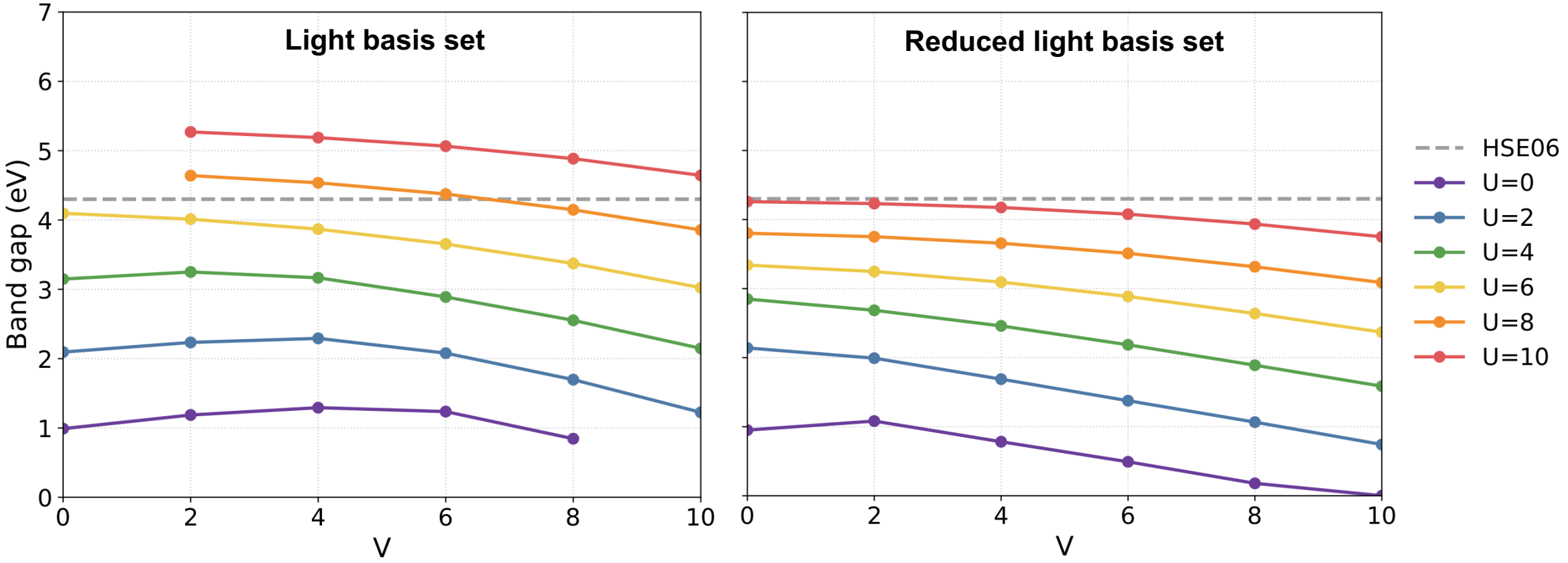




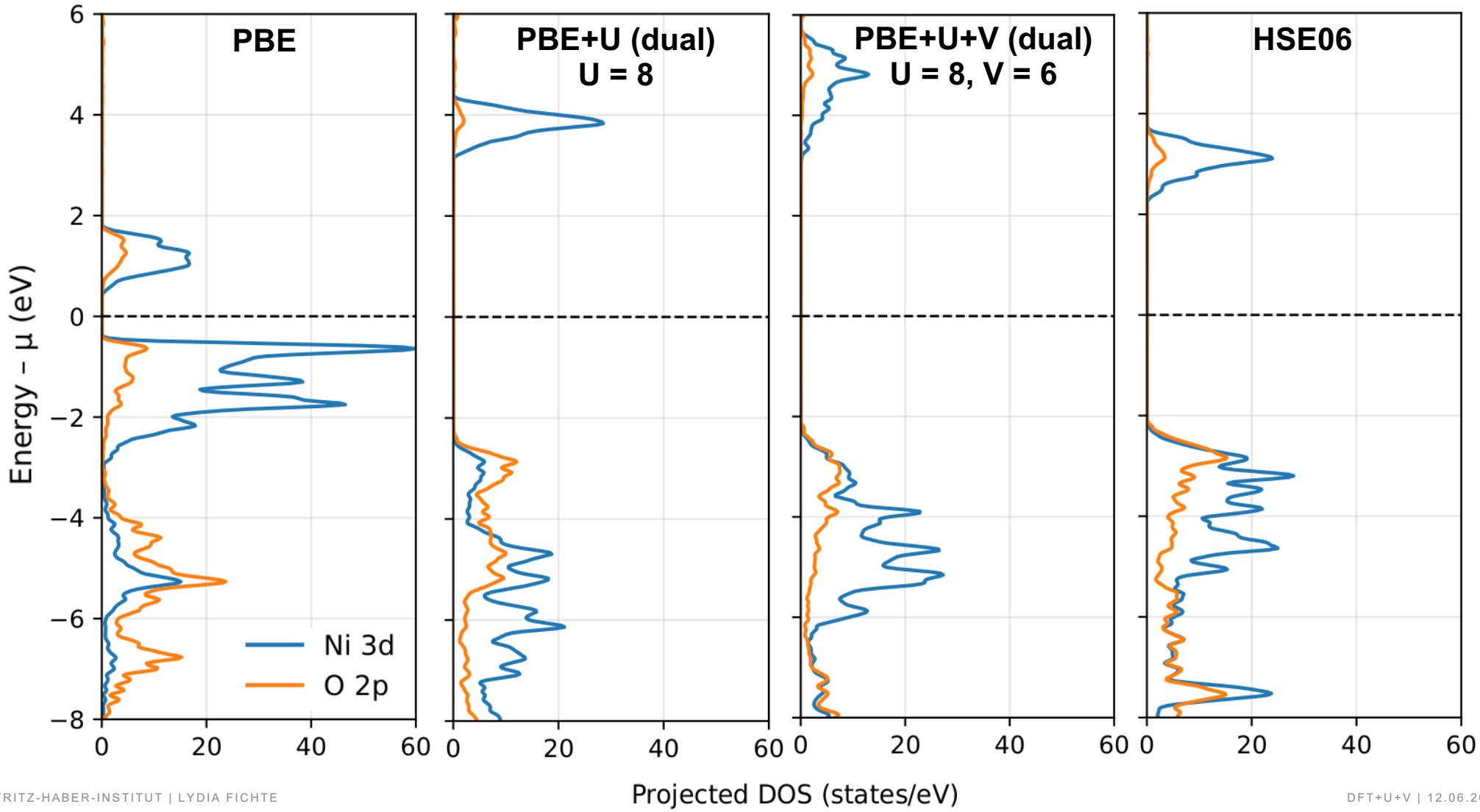
NIO BAND GAP (ONSITE)



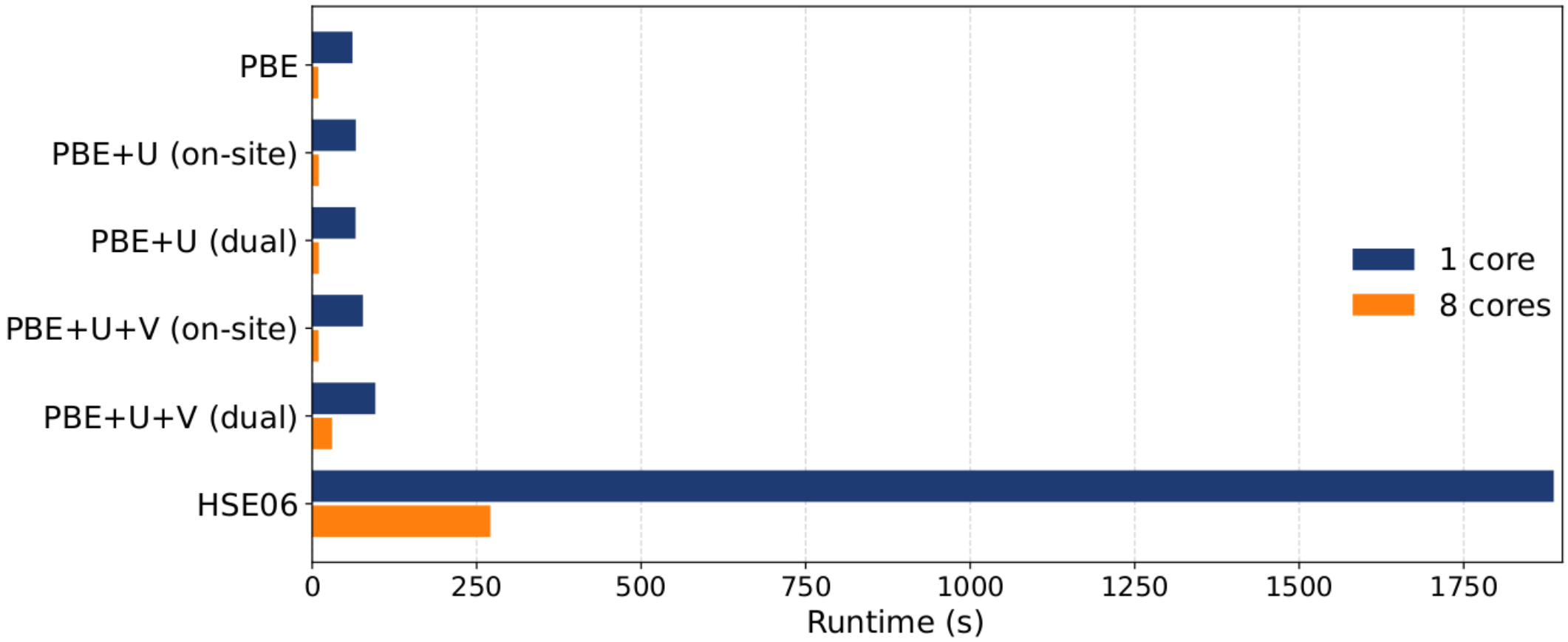
NIO BAND GAP (DUAL)



STATE-PROJECTED DENSITY OF STATES



CALCULATION TIMES PER SCF ITERATION



RT-TDDFT+U+V (LENGTH GAUGE)

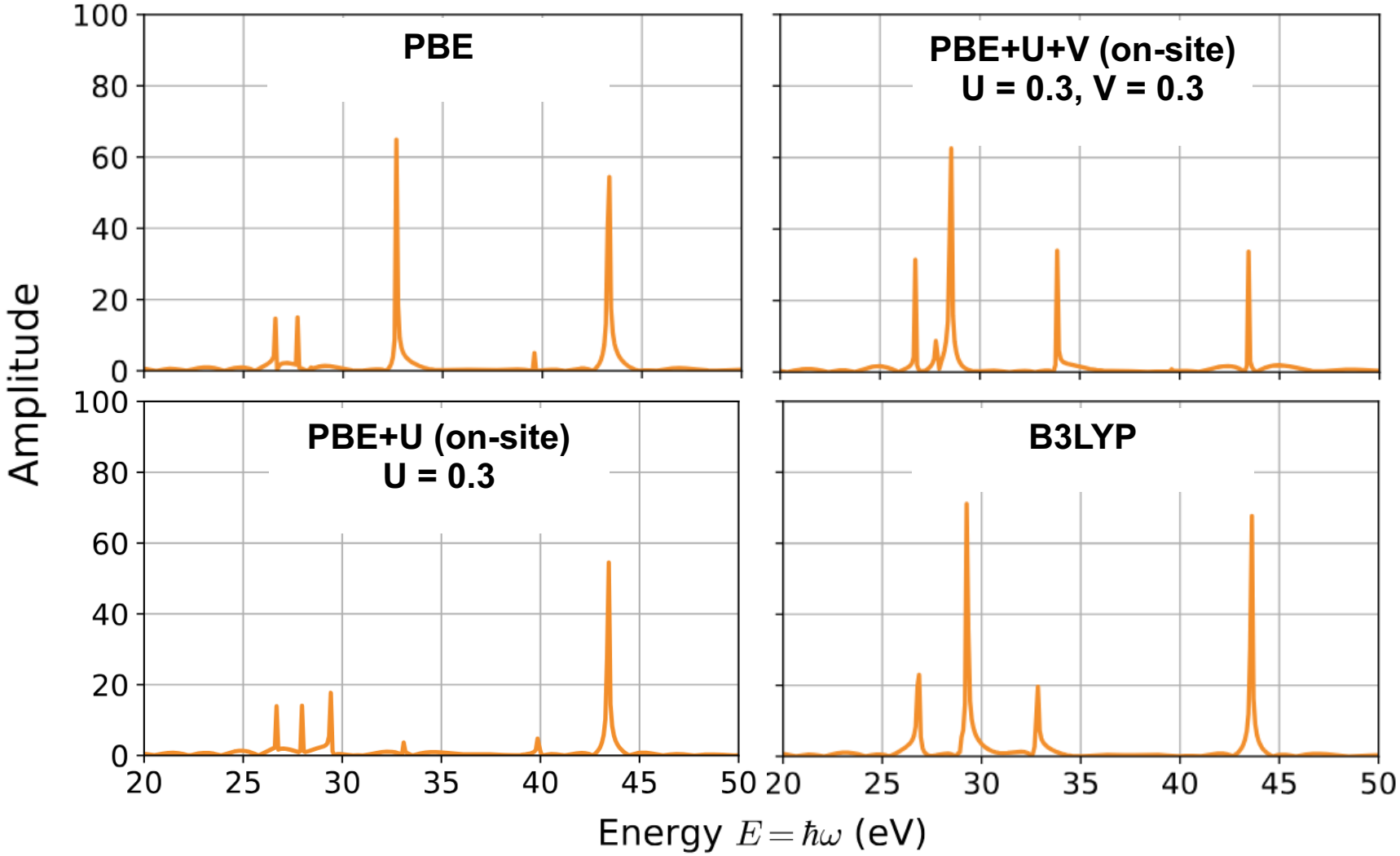
$$\frac{d}{dt}\boldsymbol{c}(t) = -i\boldsymbol{S}^{-1}\boldsymbol{h}(t)\boldsymbol{c}(t)$$

$$h_{ij}(t) = h_{ij}^{\mathrm{KS}}(t) + v_{\mathrm{U},ij}(t) + v_{\mathrm{V},ij}(t)$$

$$v_{\mathrm{U},ij}(t) = -\sum_{I,\sigma}\sum_{m,m'} \langle\varphi_i^\sigma|\,\hat{P}_{\mathrm{U}}^{\dagger}(t)\,|\varphi_j^\sigma\rangle\, U^I \left(n_{Imm'}^\sigma(t) - \frac{\delta_{mm'}}{2}\right)$$

$$v_{\mathrm{V},ij}(t) = -\sum_{\sigma}\sum_{Im,Jn}^{*} \langle\varphi_i^\sigma|\,\hat{P}_{\mathrm{V}}^{\dagger}(t)\,|\varphi_j^\sigma\rangle\, V^{IJ} n_{ImJn}^\sigma(t)$$

PRELIMINARY ABSORPTION SPECTRA: METHANE



CONCLUSION & OUTLOOK

- Similar accuracy as hybrids achievable at a fraction of the computational cost
- Results depend on parameters and projector choice
- Next steps:
  - Investigation of projector
  - RT-TDDFT+U+V in periodic systems

ACKNOWLEDGMENTS

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SOURCES

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