



Center for Hybrid Approaches in Solar Energy to Liquid Fuels

Nuclear-Electronic Orbital Approach to Quantization of Protons in Periodic Electronic Structure Calculations

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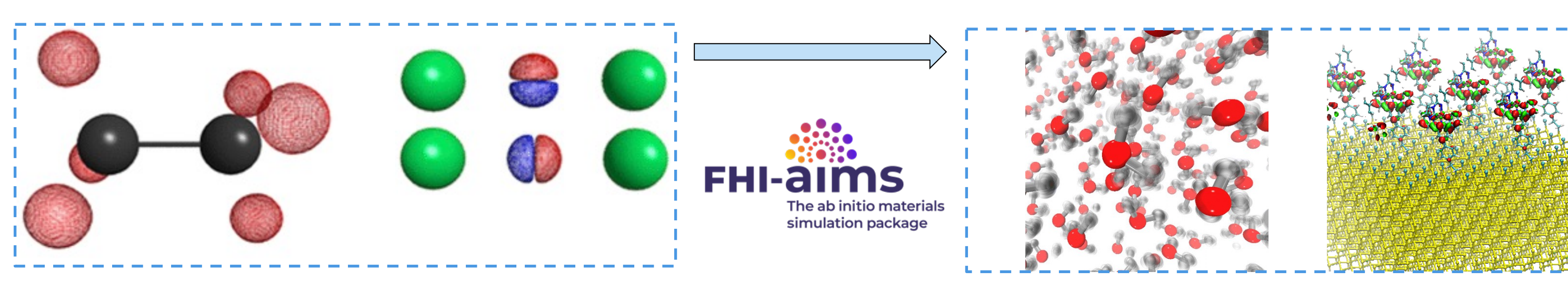
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Introduction

RESEARCH GOALS:

Accurate modeling of key processes for solar-to-fuel conversions, such as proton-coupled electron transfer in complex heterogeneous environments, requires the quantization of protons in electronic structure calculations. The nuclear-electronic orbital (NEO) method is a well-established approach for treating nuclei quantum mechanically in molecular systems beyond the usual Born-Oppenheimer approximation. This work further develops the NEO method for periodic electronic structure calculations, in the context of multicomponent density functional theory (DFT).

The NEO-DFT method is implemented in an all-electron electronic structure code, FHI-aims, using a combination of analytical and numerical integration techniques as well as a resolution of the identity scheme to enhance computational efficiency.



Theory and Method

NEO Hamiltonian

$$H_{\text{NEO}} = -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e} \sum_A^{N_c} \frac{Z_A}{|\mathbf{r}_i^e - \mathbf{r}_A^c|} + \sum_{i>j}^{N_e} \frac{1}{|\mathbf{r}_i^e - \mathbf{r}_j^e|} - \frac{1}{2m_p} \sum_l^{N_p} \nabla_l^2 + \sum_l^{N_p} \sum_A^{N_c} \frac{Z_A}{|\mathbf{r}_l^p - \mathbf{r}_A^c|} + \sum_{l>j}^{N_p} \frac{1}{|\mathbf{r}_l^p - \mathbf{r}_j^p|} - \sum_l^{N_p} \sum_i^{N_e} \frac{1}{|\mathbf{r}_l^p - \mathbf{r}_i^e|}$$

NEO Multicomponent DFT formalism

$$E[\rho^e, \rho^p] = E_{\text{ext}}[\rho^e, \rho^p] + E_{\text{ref}}[\rho^e, \rho^p] + E_{\text{exc}}[\rho^e] + E_{\text{pxc}}[\rho^p] + E_{\text{epc}}[\rho^e, \rho^p]$$

Electron-proton Kohn-Sham equations

$$\hat{H}_k^e \psi_{i,k}^e(\mathbf{r}^e) = \left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}^e(\mathbf{r}^e) \right] \psi_{i,k}^e = \epsilon_{i,k}^e \psi_{i,k}^e(\mathbf{r}^e) \quad \text{Electron: k-points sampling}$$

$$\hat{H}_i^p \psi_i^p(\mathbf{r}^p) = \left[-\frac{1}{2M^p} \nabla^2 + v_{\text{eff}}^p(\mathbf{r}^p) \right] \psi_i^p = \epsilon_i^p \psi_i^p(\mathbf{r}^p) \quad \text{Proton: } \Gamma\text{-point approximation}$$

Effective potential

$$v_{\text{eff}}^e(\mathbf{r}^e) = v_{\text{ext}}(\mathbf{r}^e) + v_{\text{es}}^e(\mathbf{r}^e) - v_{\text{es}}^p(\mathbf{r}^e) + \frac{\delta E_{\text{xc}}^e[\rho^e]}{\delta \rho^e} + \frac{\delta E_{\text{epc}}[\rho^e, \rho^p]}{\delta \rho^e} \quad \text{Electron terms}$$

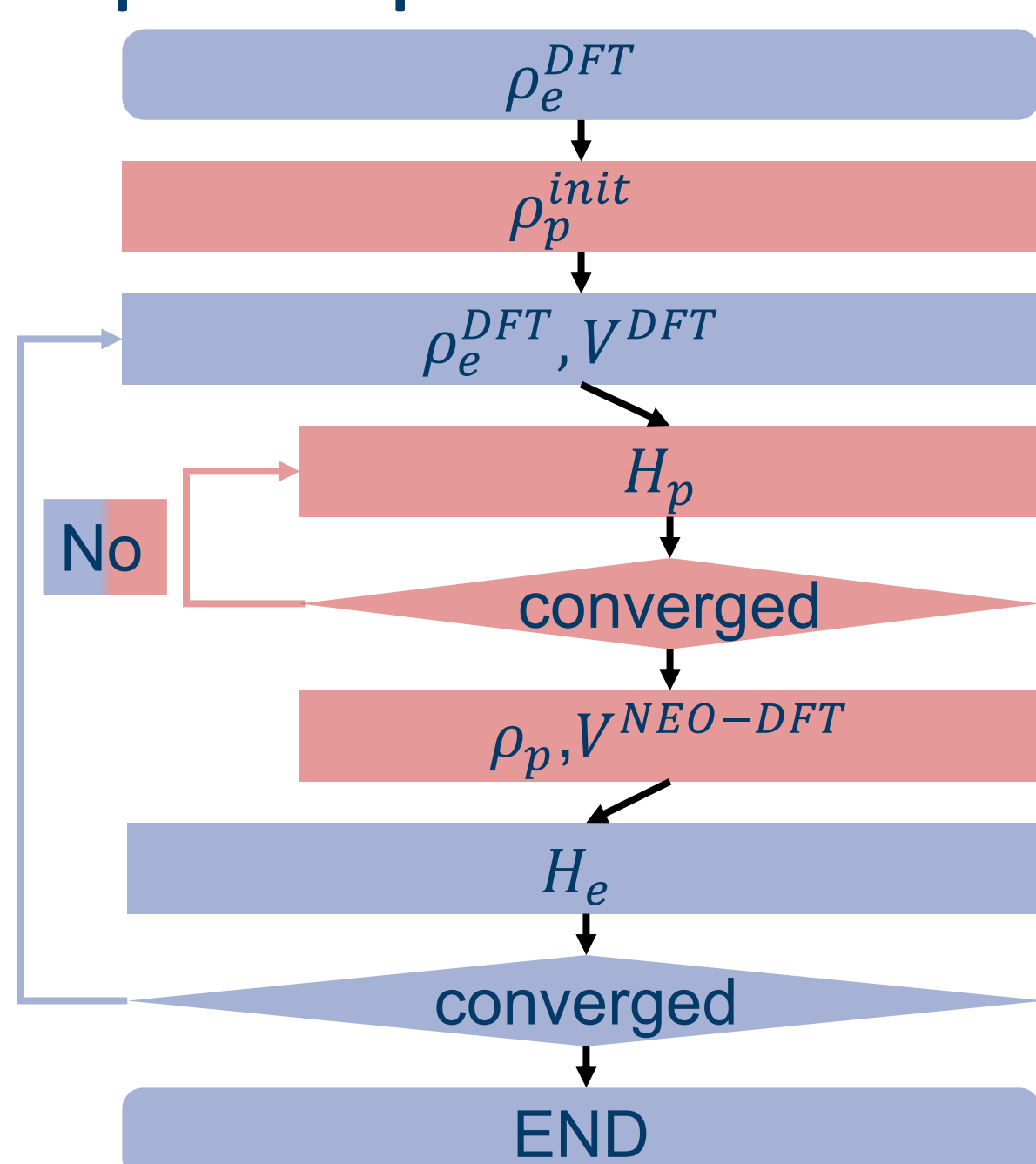
$$v_{\text{eff}}^p(\mathbf{r}^p) = -v_{\text{ext}}(\mathbf{r}^p) - v_{\text{es}}^p(\mathbf{r}^p) + v_{\text{es}}^e(\mathbf{r}^p) + \frac{\delta E_{\text{xc}}^p[\rho^p]}{\delta \rho^p} + \frac{\delta E_{\text{epc}}[\rho^e, \rho^p]}{\delta \rho^p} \quad \text{Proton terms}$$

Periodic Basis sets

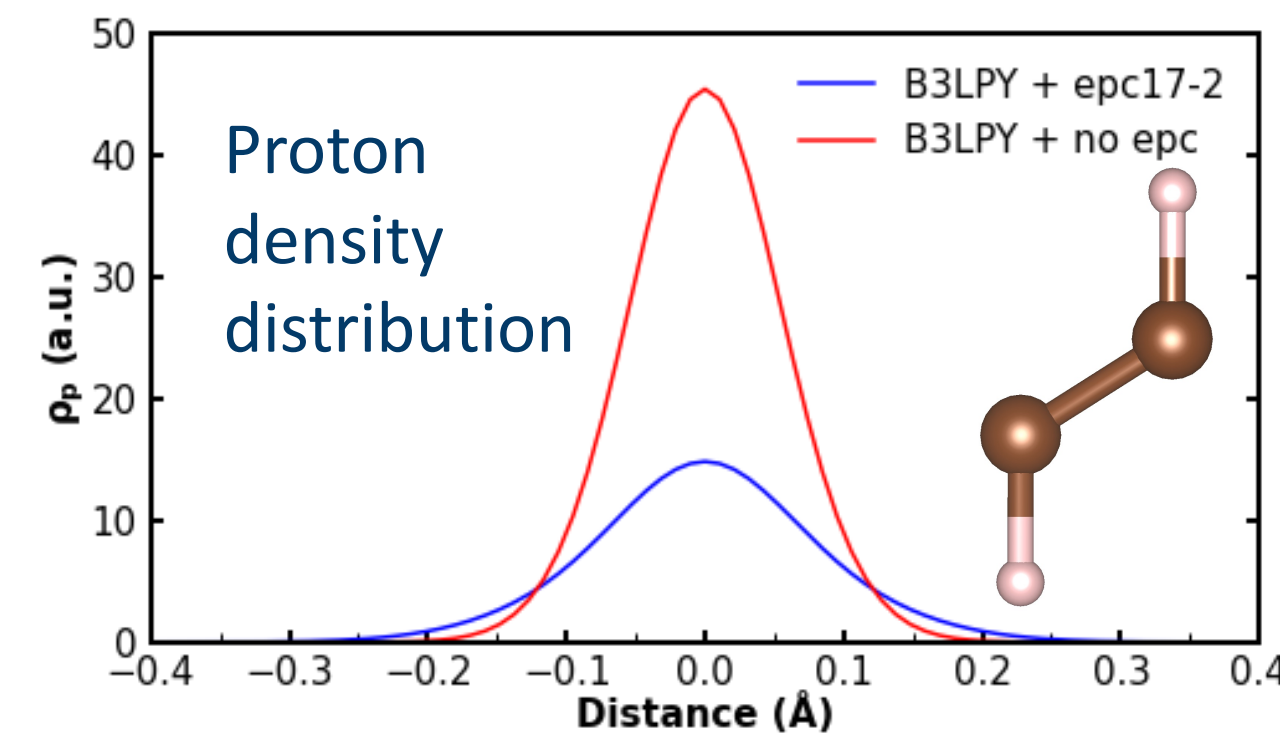
$$\psi_{i,k}^e(\mathbf{r}^e) = \sum_{N,\mu} c_{\mu i k} e^{i\mathbf{k} \cdot \mathbf{T}(N)} \phi_{\mu,N}^{e:\text{NAO}}(\mathbf{r}^e) \quad \phi_{\mu,N}^{e:\text{NAO}}(\mathbf{r}^e) = \phi_{\mu}^{e:\text{NAO}}(\mathbf{r}^e - \mathbf{R}_{\mu} + \mathbf{T}(N))$$

$$\psi_i^p(\mathbf{r}^p) = \sum_{N,m} c_{m i} \phi_{m,N}^{p:\text{GTO}}(\mathbf{r}^p) \quad \phi_{m,N}^{p:\text{GTO}}(\mathbf{r}^p) = \phi_m^{p:\text{GTO}}(\mathbf{r}^p - \mathbf{R}_m + \mathbf{T}(N))$$

Coupled SCF procedure



Benchmark



System	$E_{\text{tot}}^{\text{NEO-DFT}}$ (eV)	$E_{\text{tot}}^{\text{DFT}}$ (eV)
Q-Chem, molecule	-2102.5128	-2103.1777
FHI-aims, molecule	-2102.5129	-2103.1777
FHI-aims, 10 Å box	-2102.5208	-2103.1770
FHI-aims, 20 Å box	-2102.5161	-2103.1777
FHI-aims, 30 Å box	-2102.5129	-2103.1777

Electron exchange-correlation functional

Within the NEO framework, the electron-electron exchange-correlation functional is defined identically to the conventional electronic functionals. Any electronic XC functional can be used in NEO calculations.

Proton exchange-correlation functional

In most cases, exchange and correlation effects among protons are negligibly small. The proton-proton correlation functional is approximated with the Hartree-Fock exchange. In practice, one can even use only the diagonal terms of the exchange matrix, which counteracts self-interaction.

$$K_{ij} = - \sum_{MN,kl} D_{kl} (\phi_i \phi_k^M | \phi_j \phi_l^N)$$

Electron-proton correlation functional

Several electron-proton correlation functionals based on a multicomponent extension of the Colle-Salvetti formalism have been developed. In this work, a local density approximation (LDA) type of functional, epc17, is used

$$E_{\text{epc}}^{17} = - \int \frac{\rho^e(\mathbf{r}) \rho^p(\mathbf{r})}{a + b \rho^e(\mathbf{r})^{\frac{1}{2}} \rho^p(\mathbf{r})^{\frac{1}{2}} + c \rho^e(\mathbf{r}) \rho^p(\mathbf{r})} d\mathbf{r}$$

- Analytical & numerical atomic integrals:

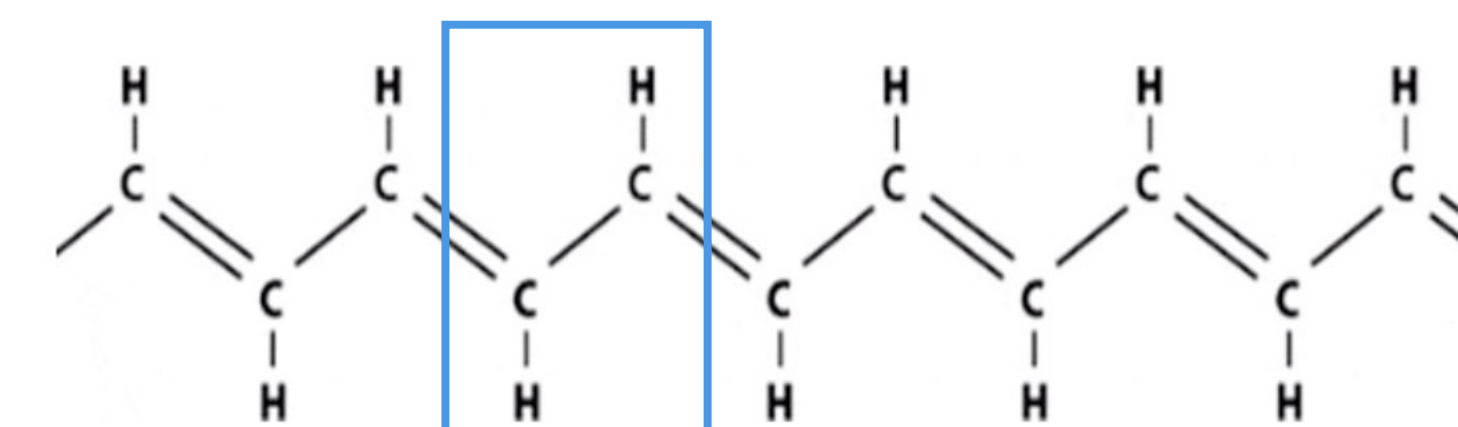
$$h_{ij} = \sum_{N-M} \langle \phi_{i,0}^p | \hat{h} | \phi_{j,N-M}^p \rangle = \sum_{M,N} \int_{\text{unit cell}} \phi_{i,M}^p(\mathbf{r}) \hat{h} \phi_{j,N}^p(\mathbf{r}) d\mathbf{r}$$

- Resolution of identity (Density fitting):

$$\phi_i(\mathbf{r}) \phi_j(\mathbf{r}) = \sum_{\mu} C_{ij}^{\mu} P_{\mu}(\mathbf{r})$$

Proof-of-principle demonstrations

1D trans-polyacetylene [C₂H₂]_n



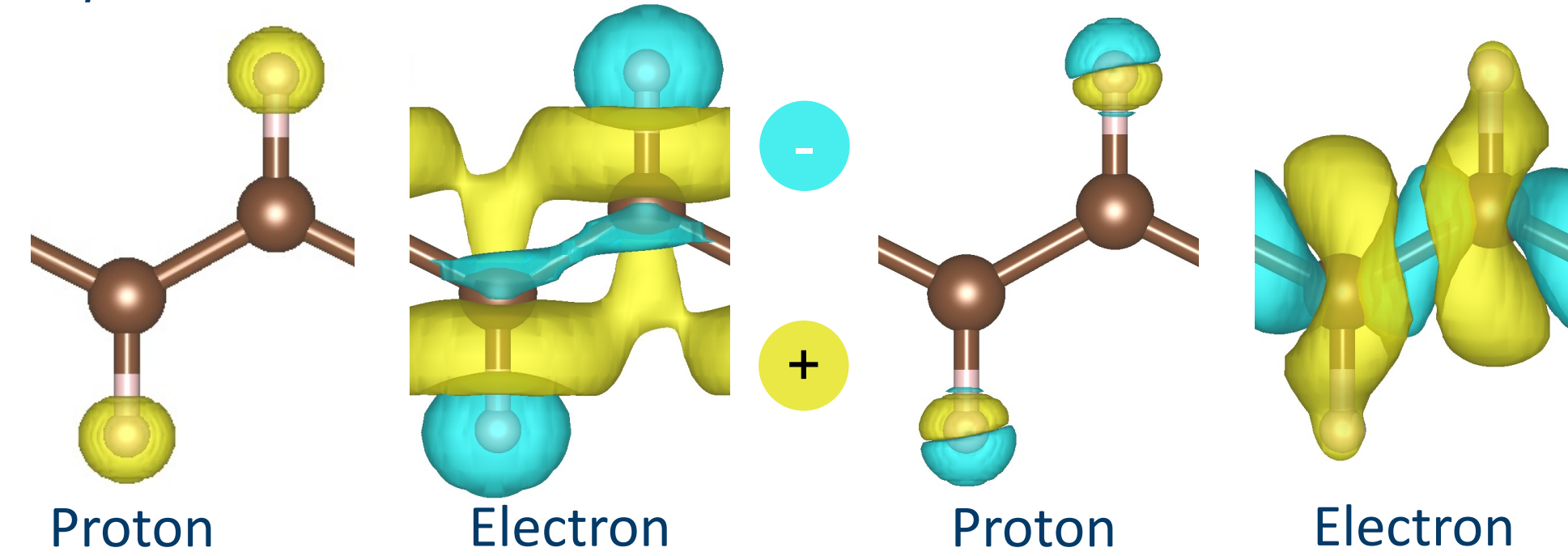
	$E_{\text{tot}}^{\text{NEO-DFT}}$ (eV)	$E_{\text{tot}}^{\text{DFT}}$ (eV)	ΔE per proton
[C ₂ H ₂] _n	-2107.244	-2106.321	0.462
HB	-1382.983	-1382.170	0.406

Supercell vs. electron k-points

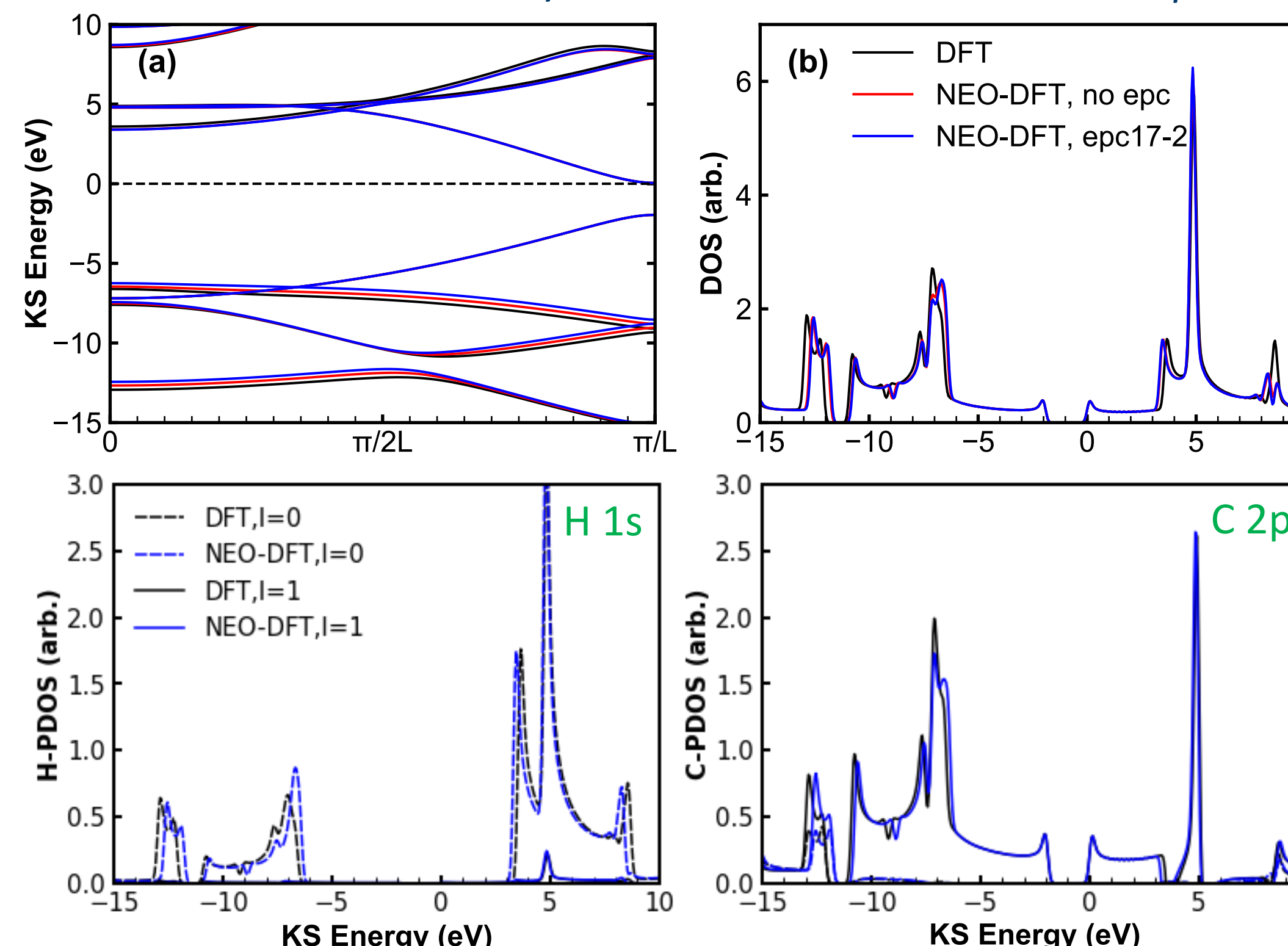
No. unit cell	1	2	4	8	16
$E_{\text{tot}}^{\text{NEO-DFT}}/n_p$ (eV)	0.361	0.459	0.464	0.462	0.462
No. k point	1	2	4	8	16
$E_{\text{tot}}^{\text{NEO-DFT}}/n_p$ (eV)	0.361	0.459	0.462	0.462	0.462

This also numerically validates the Γ -point only sampling of BZ integration for protons. Both calculations show degenerate proton eigenvalues of -27.348 eV.

$\Delta\rho$ from DFT to NEO-DFT

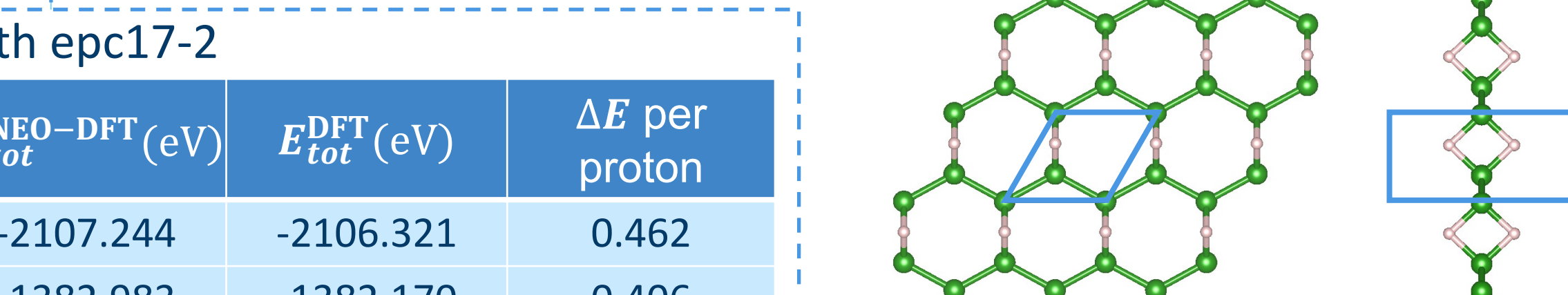


Band structures and Density of states

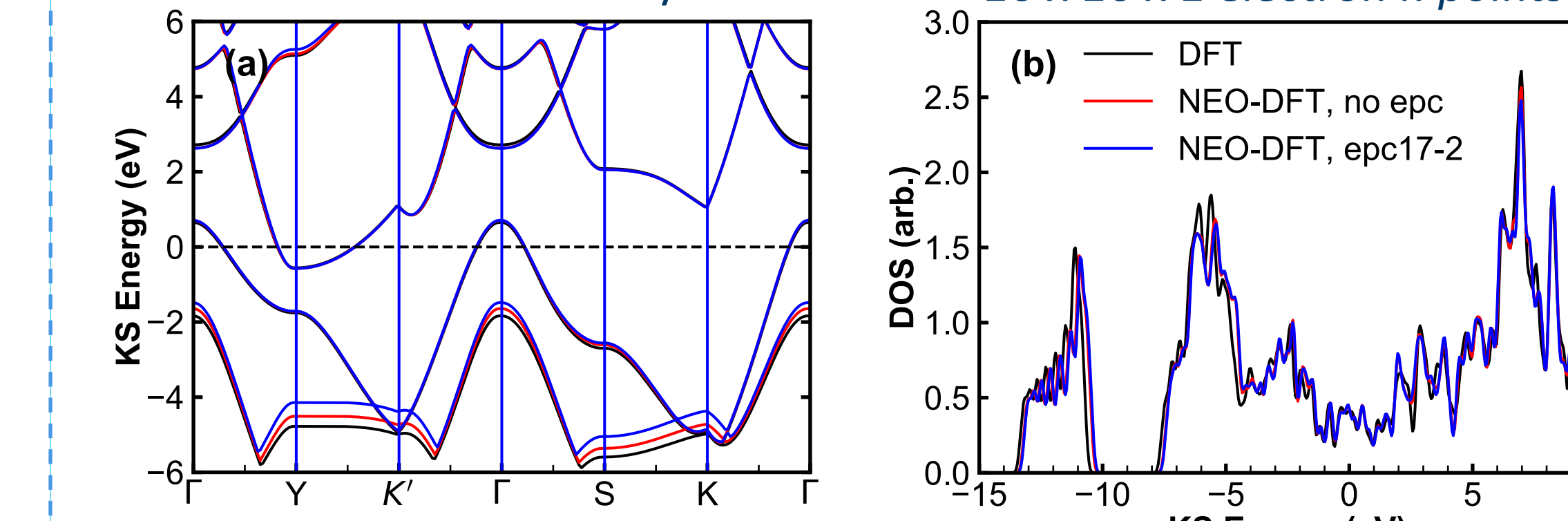


Dependence of Nuclear quantum effects (NQE) of protons on their local chemical environments can be examined.

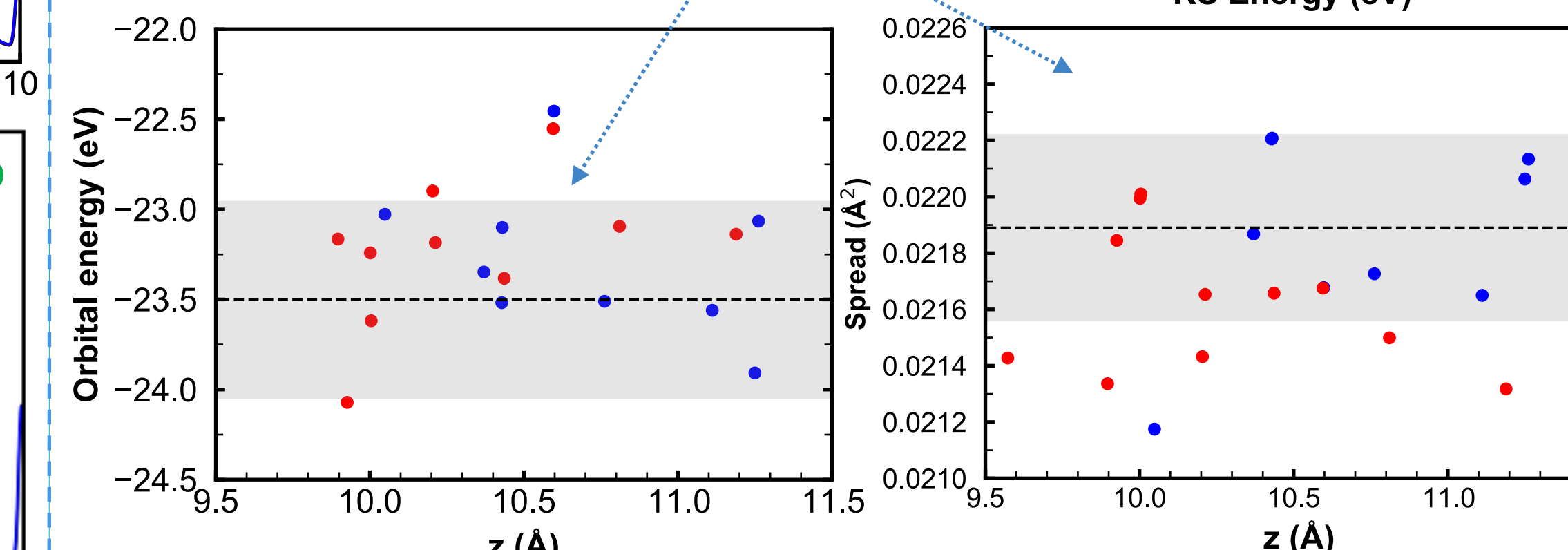
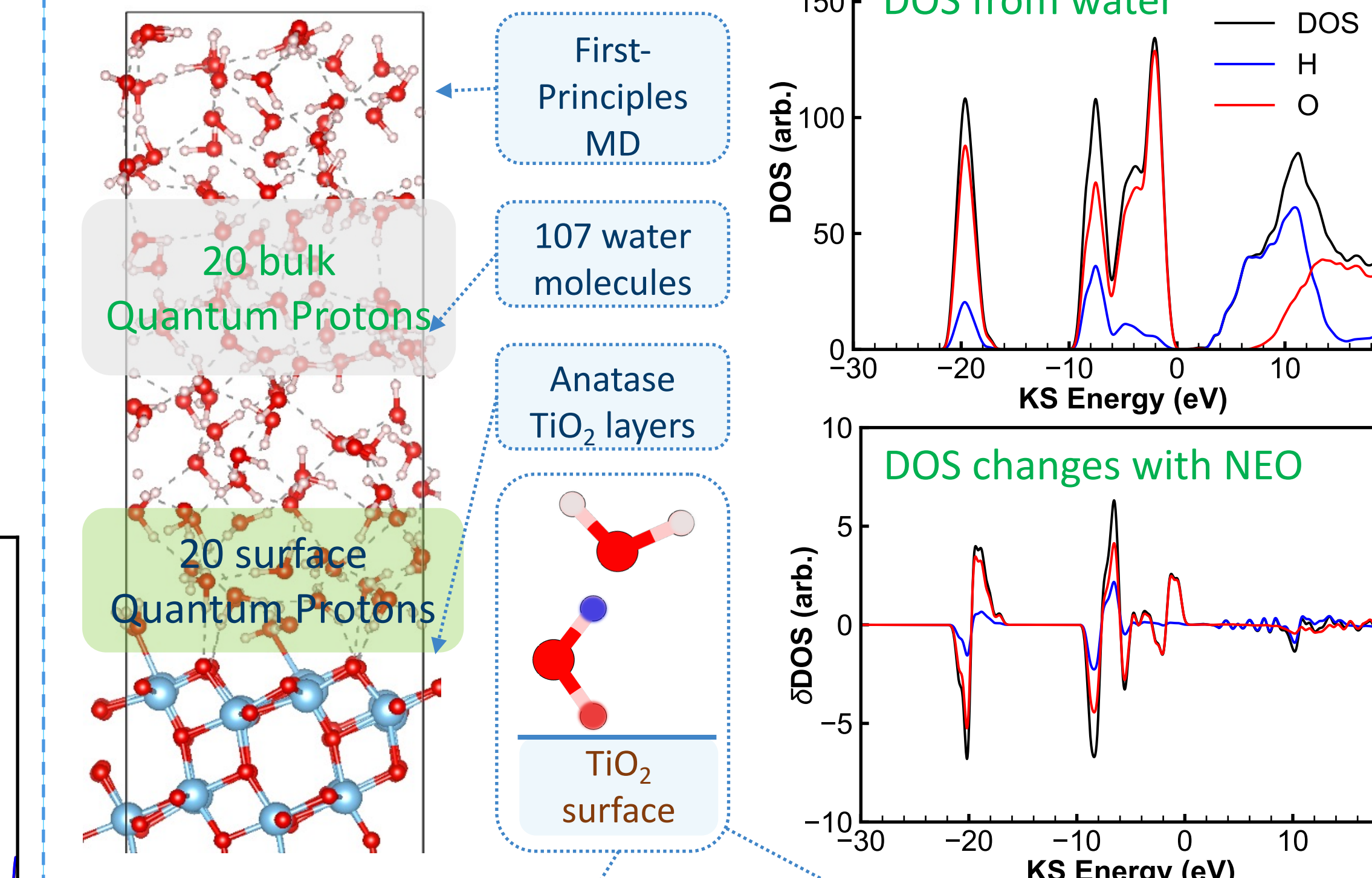
2D hydrogen boride (HB)



Band structures and Density of states



Water on TiO₂ surface



ΔE^{NEO} per proton (eV)	Surface	Bulk
epc17-2	0.33	0.31
No epc	1.07	1.06

Acknowledgments

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