WP12

Theoretical Methods for Condensed Matter

Part III

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1 Bulk Properties of NaCl

As part of this practical computational course, bulk properties of sodium chloride such as lattice parameters, atomization energies, band gaps and densities of states were computed. An experimental crystal structure of sodium chloride was taken from the Crystallography Open Database **LIT** (COD-ID: 9006369). This specific structure was chosen as experimental input because it was measured at 298 K which was closest to the optimum temperature of 0 K (temperature of the calculations).

1.1 Structural relaxation

Full structural relaxations on the LDA/VWN, PWGGA, M06L and PBE0 level of theory employing *double-ζ* basis sets developed by M. Peintinger et al. **LIT** were performed. Results are summarized in **??**. The LDA/VWN functional strongly underestimates the reference value of $a_{\text{exp}} = 5.5937\,\text{Å}$ which can be deduced to the overbinding nature of the functional. Improvement comes with the meta-GGA functional M06L which nevertheless underestimates the lattice parameter by more than 1 %. Good accuracy is reached by PWGGA and PBE0. The latter hybrid functional comes with a largely increased computation time which is about four times larger compared to the other functionals. In conclusion, it can be said that reasonable geometries do not require the use of hybrid functionals but can also be obtained from certain GGA functionals. This is also well known for geometry optimization of molecules. **LIT**

1.2 Structural relaxation

The atomization energy of sodium chloride was computed employing PBE0 and *triple-ζ* basis sets developed by M. Peintinger et al. To do so, the atomic basis sets were converged to a limit of 1 kcal/mol by adding *s, p* and *d* shells. Having reached the desired convergence, an atomization energy of 623.3 kJ/mol was obtained as displayed in **??**. This value represents an electronic energy and cannot be directly compared to an experimental quantity which is usually the atomization enthalpy $\Delta H^0_{\text{atom}}(\text{NaCl})$. Comparison is achieved according to the Born–Haber circle by adding the sublimation enthalpy of sodium $\Delta H^0_{\text{subl}}(\text{Na}) = 107.3\,\text{kJ/mol}$ and half of the dissociation enthalpy of chlorine $\Delta H^0_{\text{diss}}(\text{Cl}_2) = 121.3\,\text{kJ/mol}$ to the enthalpy of formation $\Delta_f H^0_{\text{solid}}(\text{NaCl}) = -411.1\,\text{kJ/mol}$ (all values taken from the NIST chemistry webbook **LIT**):

$$\Delta H^0_{\text{atom}}(\text{NaCl}) = \Delta_f H^0_{\text{solid}}(\text{NaCl}) + \frac{1}{2}\Delta H^0_{\text{diss}}(\text{Cl}_2) + \Delta H^0_{\text{subl}}(\text{Na}) \tag{1}$$

2 Calculating surfaces of Rutile

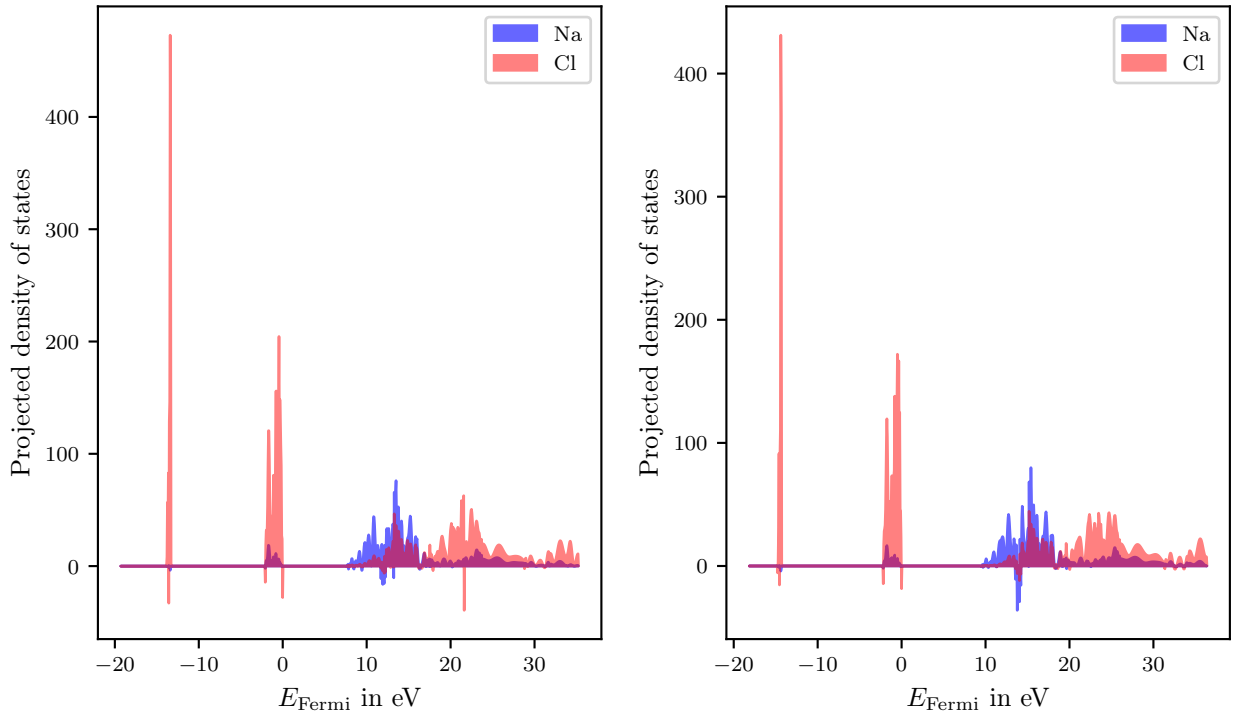

Figure 1: Projected density of states of NaCl on a PBE0/POB-TZVP level of theory with standard (left) and optimal Fock exchange fraction (right).

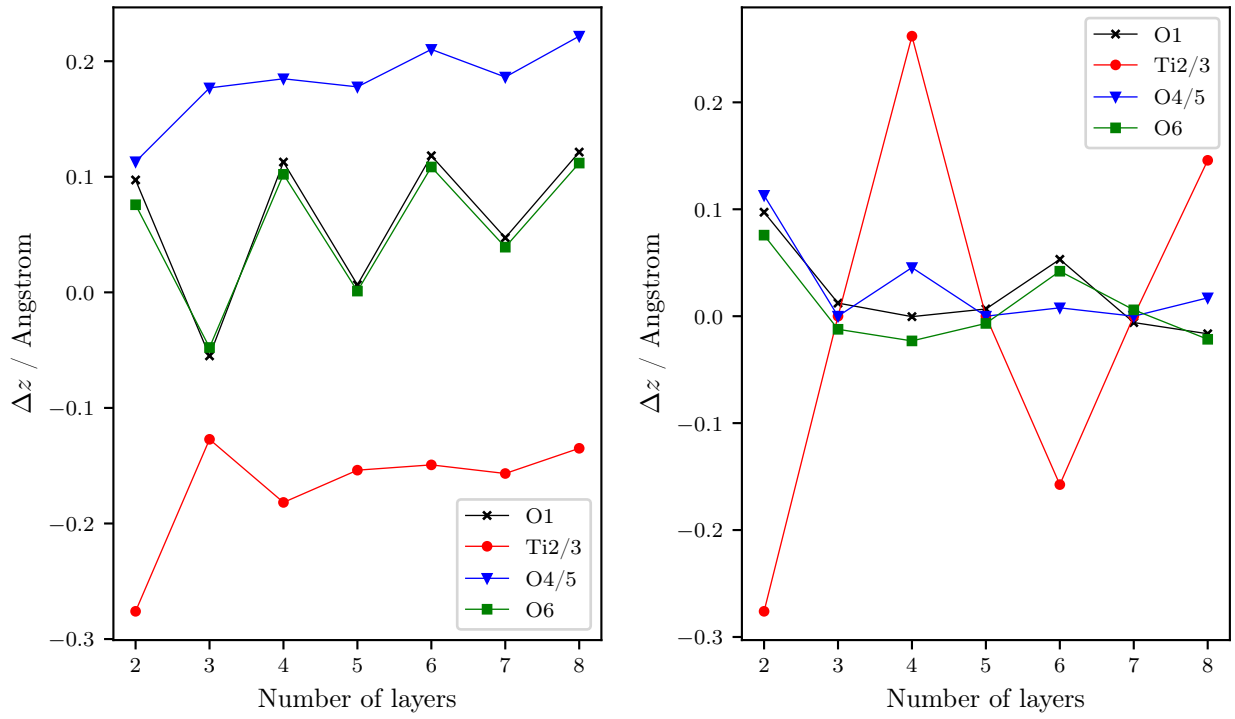

Figure 2: Relaxation of symmetry-inequivalent atoms in TiO_2 (110) surfaces of different thickness: Atoms in the topmost layer (left) are compared to bulk-like atoms in middle layers (right).

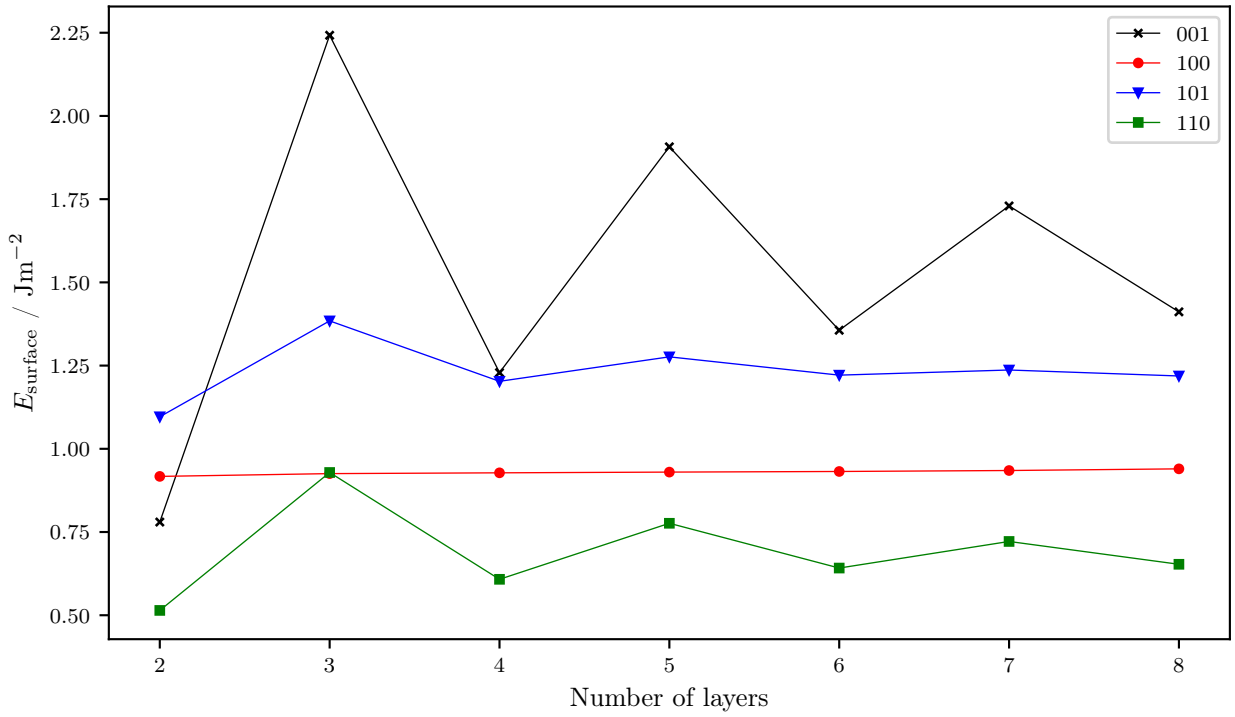

Figure 3: Calculated surface energies for different TiO_2 surfaces.