

Simulation of defect complex

- (1) The supercell approach is employed to simulate the energetics of defect complexes in a crystalline host. To simulate a charged defect, a uniform background charge shall be added.
- (2) Optimize all internal structural parameters of the super cell by minimizing total energy.
- (3) Band in different super cell simulations can be aligned using appropriate atomic core levels or average potential energy.

The following key descriptors can be derived to reveal the defect properties with the super cell approach:

1. Defect Formation Energy $\Delta E_f(\alpha, q)$

$$\begin{aligned}\Delta H_f(\alpha, q) &\simeq \Delta E_f(\alpha, q) \\ &= E_{tot}(\alpha, q) - E_{tot}(host) + \sum_i n_i [E_{tot}(i) + \Delta\mu_i] + q(E_f + E_{VBM} + \Delta V), \text{ and}\end{aligned}$$

2. Transition Energy of Defect

$$\mathcal{E}_\alpha(0 | q) = I + II = [\mathcal{E}_\alpha^\Gamma(0) - \mathcal{E}_{VBM}^\Gamma(host)] + [E_{tot}(\alpha, q) - E_{tot}(\alpha, 0) + q\mathcal{E}_\alpha^k(0)]/(-q).$$

The first term I is the single-electron energy of the neutral defect at Γ point, and II denotes the U -energy parameter of the charged defect, which is the extra energy cost needed to add $+q$ charge to the neutral defect at the energy level $\mathcal{E}_\alpha^k(0)$.

For a monovalent acceptor with $q = -1$

$$\mathcal{E}_\alpha(0 | -1) = [\mathcal{E}_\alpha^\Gamma(0) - \mathcal{E}_{VBM}^\Gamma(host)] + [E_{tot}(\alpha, -1) - E_{tot}(\alpha, 0) - \mathcal{E}_\alpha^k(0)] \text{ and}$$

for a donor with $q = +1$

$$E_g^\Gamma(host) - \mathcal{E}_\alpha(0 | +1) = [\mathcal{E}_{CBM}^\Gamma(host) - \mathcal{E}_\alpha^\Gamma(0)] + [E_{tot}(\alpha, +1) - E_{tot}(\alpha, 0) + \mathcal{E}_\alpha^k(0)].$$

Simulation Procedure:

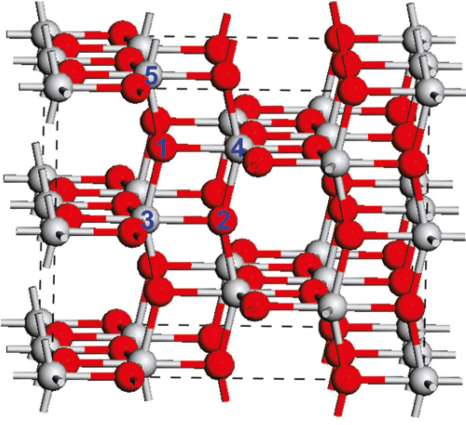
To simulate the formation of defects in anatase TiO_2 , we first prepare

- (1) a unit cell of the anatase TiO_2 (tetragonal 4/mmm) and optimize the cell structure, which yields

$$a = 3.7954\text{\AA}, c = 9.8396\text{\AA} \quad \text{and} \quad \alpha = \beta = \gamma = 90^\circ.$$

- (2) Using the optimized cell structure, construct a $2 \times 2 \times 1$ supercell. Optimize the internal structural parameters of the supercell (48 ions in the supercell $\text{T}_{16}\text{O}_{32}$), we can obtain a total energy of

$$E_{tot}(host) = -39703.9777 \text{ eV}.$$



- (3) Replace one oxygen atom (@position 1) with nitrogen in the $2 \times 2 \times 1$ supercell. After geometry optimization, we obtain a minimum energy of $E_{tot}(N_O) = -39535.1576$ eV.

After that, we calculate the defect formation energy using the equation

$$\Delta E_f(N_O) = E_{tot}(N_O) - E_{tot}(host) - \mu_N + \mu_O.$$

The chemical potentials for the bulk substances can be obtained as the total energy per unit chemical formula $\mu_{X(bulk)} = E_{tot}(X)$. The typical compounds needed to estimate the defect formation are listed in the following:

$$\mu_O = \frac{1}{2} \mu_{O_2(g)} = \frac{1}{2} E_{tot}(O_2, P1) = -433.7043 eV, \mu_N = \frac{1}{2} \mu_{N_2(g)} = \frac{1}{2} E_{tot}(N_2, P1) = -270.5850 eV. \text{ Thus,}$$

we have $\Delta E_f(N_O) = -39535.1576 + 39703.9777 + 270.5850 - 433.7043 = 5.701$ eV under the oxygen-rich condition.

- (4) Replace the Ti ion @position 1 with V in the $2 \times 2 \times 1$ supercell. After geometry optimization, we have

$E_{tot}(V_{Ti}) = -40074.4891$ eV. We use $\Delta E_f(V_{Ti}) = E_{tot}(V_{Ti}) - E_{tot}(host) - \mu_V + \mu_{Ti}$ to calculate the defect formation energy. Note that to estimate the defect formation the following chemical potentials for the bulk substances are needed: $\mu_V = E_{tot}(V \text{ metal}, IM\bar{3}M) = -1967.6045$ eV and

$$\mu_{Ti} = \frac{1}{2} E_{tot}(Ti \text{ metal}) = -1603.0650 eV. \text{ Therefore, we have}$$

$$\Delta E_f(V_{Ti}) = E_{tot}(V_{Ti}) - E_{tot}(host) - \mu_V + \mu_{Ti} = -5.9719 \text{ eV.}$$

- (5) Replace the oxygen ion @position 1 with nitrogen and the Ti ion @position 1 with V in the

$2 \times 2 \times 1$ supercell. After geometry optimization, we have $E_{tot}(V_{Ti} - N_O) = -39907.2665$ eV. We calculate the defect formation energy using

$$\Delta E_f(V_{Ti} - N_O) = E_{tot}(V_{Ti} - V_O) - E_{tot}(host) - \mu_V - \mu_N + \mu_{Ti} + \mu_O = -1.7144 \text{ eV.}$$

- (6) For a defect complex of $V_{Ti}-N_O$, we can use $E_b = E_{tot}(V_{Ti}) + E_{tot}(N_O) - E_{tot}(V_{Ti} - N_O) - E_{tot}(host) =$

-1.598 eV, which reveals the binding energy of the defect pair. Here $E_b < 0$ indicates the defect pair is unstable in the bound state and will split into V_{Ti} and N_O .