Quantum-chemical molecular-dynamics study of polaron formation in perovskite $NaTaO_3$ as a water-splitting photocatalyst

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DETAILS OF DFTB PARAMETER FITTING

In the framework of DFTB, total energy of the system is written as[1]

$$E = \sum_{i}^{N_{\mathrm{MO}}} n_i \left\langle \psi_i \middle| \hat{H}_0 \middle| \psi_i \right\rangle + +\frac{1}{2}\sum_{I,J}^{N_{\mathrm{atom}}} \Delta q_I \Delta q_J \gamma_{IJ} + \frac{1}{2}\sum_{A}^{N_{\mathrm{atom}}} \sum_{l,l' \in A} p_{Al} p_{Al'} W_{All'} + E_{\mathrm{rep}}(\mathbf{R}) \tag{S1}$$

where the second and third terms in the right hand side represent the contributions from charge and spin polarization, respectively. ψ_i is i-th molecular orbital (MO), n_i is its occupation number, Δq_I is difference in Mulliken charge of atom I from that for the isolated neutral atom, and E_{rep} is an ad hoc correction term for interatomic repulsion potential. γ_{IJ} is a function of the interatomic distance, whose explicit form is provided in ref. 1. p_{Al} is spin population of shell l in atom A, and $W_{All'}$, which denotes the spin-spin interaction between p_{Al} and $p_{Al'}$, is an element-dependent constant.[2] The matrix elements of $\hat{H}_0$ are described as

$$H^0_{\mu\nu} = \begin{cases} \epsilon^0_\mu & \mu = \nu \\ \left\langle \phi_\mu \middle| \hat{T} + V_{\mathrm{eff}}\left[\rho_A + \rho_B\right] \middle| \phi_\nu \right\rangle & A \neq B \;\&\; \mu \neq \nu \\ 0 & \text{otherwise} \end{cases} \tag{S2}$$

where ϕ_μ is a pseudo-atomic one-electron orbital as defined later, $\hat{T}$ is the kinetic energy operator, and V_{eff} is the exchange–correlation potential in the GGA-PBE functional.[3] ρ_A is the electron density of isolated atom A. The pseudo-atomic orbital ϕ_μ and the orbital energy ϵ^0_μ are obtained by solving the following Kohn–Sham-like equation.

$$\left[\hat{T} + V_{\mathrm{eff}}\left[\rho_A\right] + V_{\mathrm{conf}}\right]\phi_\mu = \epsilon_\mu \phi_\mu \tag{S3}$$

In general, the atomic orbitals in molecules or solid materials are expected to be spatially "compressed" compared to that of the isolated atom due to the presence of the neighbouring atoms. V_{conf} is an artificial atom-centered potential to take into account such confinement effect. The parameter tuning in the present context is nothing other than searching the optimal shape of V_{conf} so that the DFTB reproduces the target physical properties with a satisfactory accuracy. In the present study, the following form of V_{conf} is employed.

$$V_{\mathrm{conf}}(r) = \frac{W}{1 + \exp\left[-a\left(r - r_0\right)\right]} \tag{S4}$$

Here, W, a, and r_0 are controllable parameters subject to optimization. Practically, separate values for the set of parameters (W, a, and r_0) can be employed for obtaining the atomic electron density

(ρ_A) and for defining the pseudo-atomic orbitals (ϕ_μ) by solving eq. S3. The set of parameters can be further separately defined the pseudo-atomic orbitals for each angular momentum (s, p, and d). In practical DFTB calculations, $H^0_{\mu\nu}$ is pre-computed with scanning interatomic distance and tabulated as a function of the distance, which is given as a Slater–Koster file. Since $H^0_{\mu\nu}$ depends not only on the distance but also on the direction due to the anisotropy of ϕ_μ and ϕ_ν (unless they are s-type orbitals), the value of $H^0_{\mu\nu}$ is obtained via Slater–Koster transformation from that table.

The reference DFT calculations were performed with VASP program package[4,5] and the optimization of W, a, and r_0 parameters was conducted using ADPT program package.[6] For Na and Ta, the parameter sets were optimized to reproduce the GGA-PBE level band structures of Na metals (bcc, fcc, and sc) and Ta metals (bcc, fcc, and sc), respectively. Based on the defined parameter set for Na and Ta, the parameter set for O was tuned to reproduce the GGA-PBE level band structure of cubic $NaTaO_3$ at the cell parameters optimized at the GGA-PBE level. The values of the optimized parameters are listed in Tables S1, S2, and S3.

TABLE S1. Optimized parameters for Na.

W^{dens} / a.u.	a^{dens} / a.u.	r_0^{dens} / a.u.	W^{sp} / a.u.	a^{sp} / a.u.	r_0^{sp} / a.u.
19.835729	10.916415	6.346857	19.835729	10.916415	6.346857

TABLE S2. Optimized parameters for Ta.

W^{dens} / a.u.	a^{dens} / a.u.	r_0^{dens} / a.u.	W^{spd} / a.u.	a^{spd} / a.u.	r_0^{spd} / a.u.
16.879164	7.778502	15.747541	23.769435	1.601473	6.275239

Figure S1 compares the resulting DFTB band structure (orange) and the reference GGA-PBE result (blue). As shown in Figure S1, the shape of the valence and conduction bands in the DFTB band structure are reasonably agreed with the GGA-PBE result, while the curvature of the valence bands seems slightly underestimated in the DFTB. In contrast to the reasonable agreement in the band shapes, the agreement in the band gap is sacrificed; the DFTB band gap is overestimated by >

TABLE S3. Optimized parameters for O.

W^{dens} / a.u.	a^{dens} / a.u.	r_0^{dens} / a.u.	W^{s} / a.u.	a^{s} / a.u.	r_0^{s} / a.u.	W^{p} / a.u.	a^{p} / a.u.	r_0^{p} / a.u.
0.000000	-	-	50.000000	1.300000	5.000000	3.000000	12.000000	0.600000

1 eV compared to the GGA-PBE result. Note that in our simulations the polaron was modelled by cationic (for hole) and anionic (for electron) systems, instead of explicit consideration of electronic excitation from the valence to conduction bands. For this reason, the error in the band gap is not likely to influence the simulation result substantially, and the shapes of valence and conduction bands should be prioritized in the DFTB parameterization.

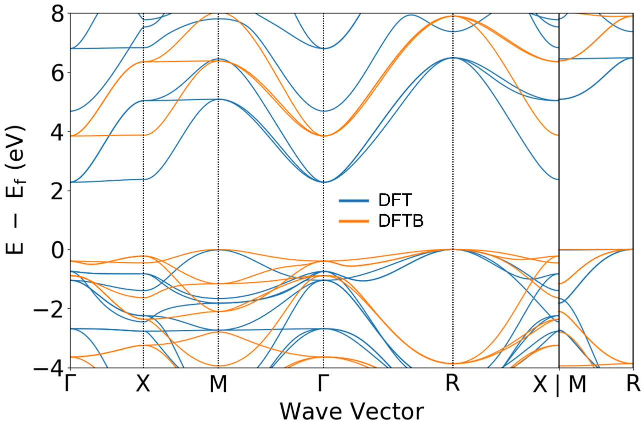

FIG. S1. Band structures of cubic $NaTaO_3$ calculated using GGA-PBE (blue) and DFTB with the optimized parameter set (orange).

The last term in the right-hand side of eq. S1, E_{rep}, is a function of the interatomic distance and its shape is also optimized to reproduce the structural and dynamical properties of the system. In the present study, E_{rep} was defined for each pair of elements and expressed as fourth-order spline, which is a smooth polynomial curve connecting fixed points $\{R_n\}$ called knots.

$$E_{\mathrm{rep}}(R) = c_0^n + c_1^n (R - R_n) + c_2^n (R - R_n)^2 + c_3^n (R - R_n) + c_4^n (R - R_n)^4 \quad (R_n \leq R < R_{n+1}) \qquad \text{(S5)}$$

The number and positions of knots are defined in advance. The coefficients $\left\{c_i^n\right\}$ $(0 \leq i \leq 4)$ are subject to optimization. In the present study, $\left\{c_i^n\right\}$ for Ta-O pair were optimized. The snapshot structures of $NaTaO_3$ were sampled from DFT-MD simulation using the $2 \times 2 \times 2$ orthorhombic supercell (Figure S2) with the GGA-PBE functional. The DFT-MD simulations were conducted at 298 and 900 kelvins and 200 snapshots were sampled from each condition.

The resulted values of $\left\{c_i^n\right\}$ are present in *.skf files, which are also provided as Supporting Information. The optimized unit cell parameters for cubic $NaTaO_3$ are listed in Table S4, indicating that the DFTB result with the optimized parameters reproduce the DFT (GGA-PBE) result well. In addition, to check the agreement in dynamical properties, the vibrational density of states

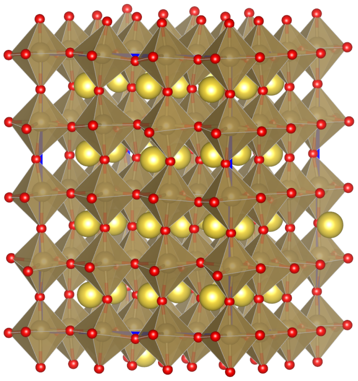

FIG. S2. 2 × 2 × 2 supercell of $NaTaO_3$.

are plotted in Figure S3. The VDOSs were calculated by Fourier transformation of velocity autocorrelation functions obtained from molecular dynamics simulations with DFT (GGA-PBE) and DFTB. The DFTB result qualitatively reproduced the tendency that the VDOS has a broad peak around $200\,\mathrm{cm}^{-1}$, while the detailed spectral shape was not perfectly reproduced.

TABLE S4. Optimized cell parameters for cubic $NaTaO_3$ (in Å).

DFT (GGA-PBE)	DFTB	Δ[%]
3.980	4.006	0.7

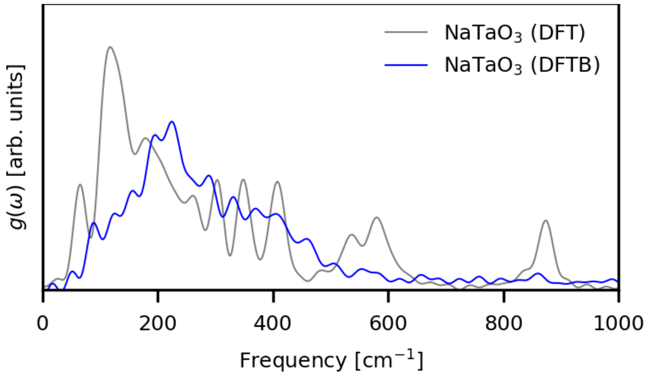

FIG. S3. Vibrational density of states calculated with DFT and DFTB.

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