

# Analytical and numerical study of polarons

## A DFT calculation of a small polaron in rutile TiO<sub>2</sub>

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Laurea in Fisica  
Università di Bologna

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# Overview

## ① Introduction

Intuitive notion of a Polaron  
Polarons properties

## ② Small and Large Polarons

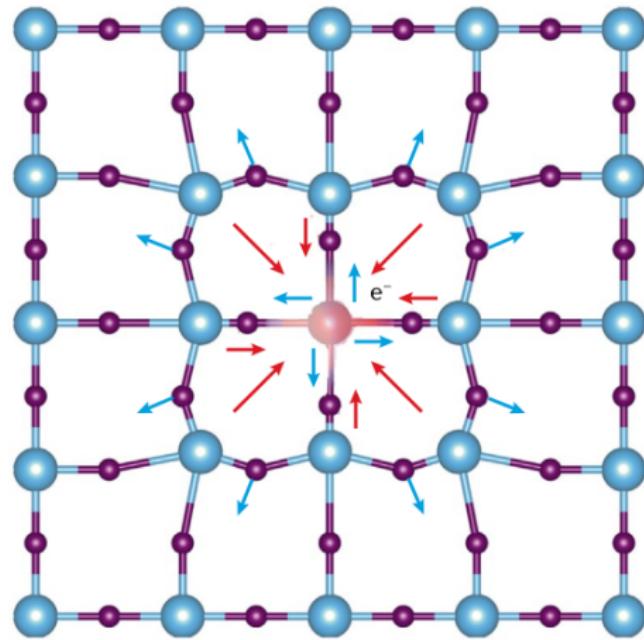
## ③ Density Functional Theory

## ④ Simulation of a small polaron

Employed procedure  
Results

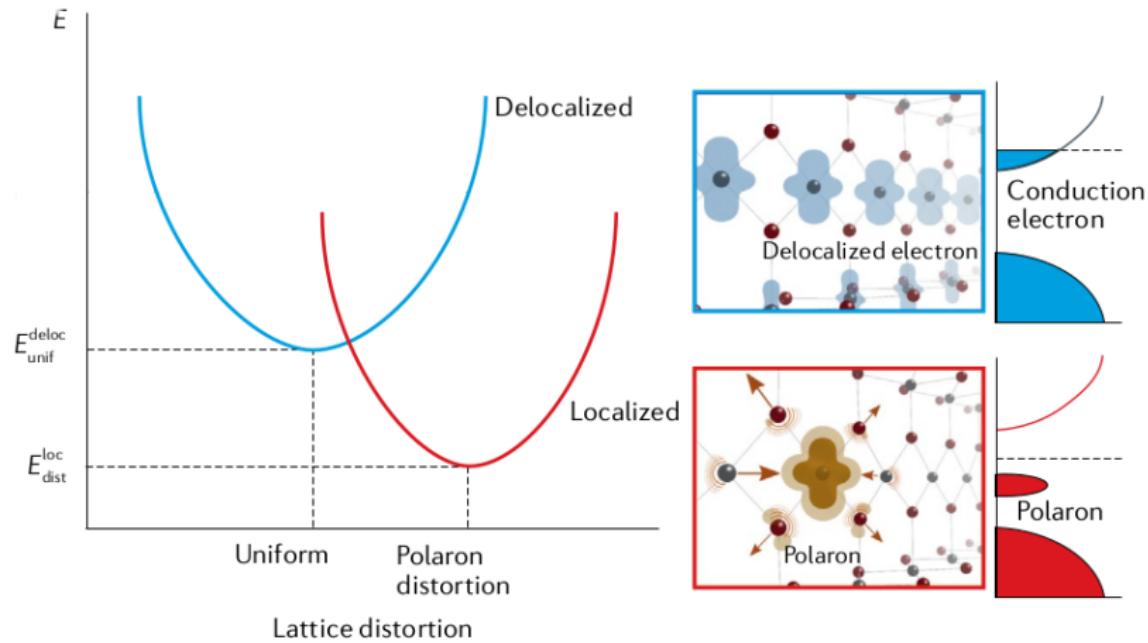
## ⑤ Conclusions

# Intuitive notion of a polaron



**Figure 1:** Figure from Franchini et al. 'Polarons in materials', Nature Reviews Materials, Jul. 2021, doi: 10.1038/s41578-021-00289-w.

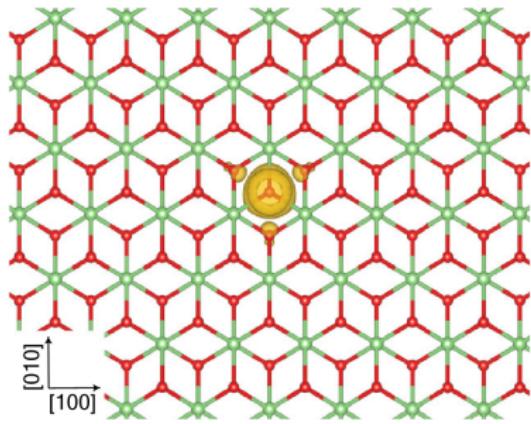
# Band structure and DOS



**Figure 2:** Figures from Franchini et al. 'Polarons in materials', Nature Reviews Materials, Jul. 2021, doi: 10.1038/s41578-021-00289-w.

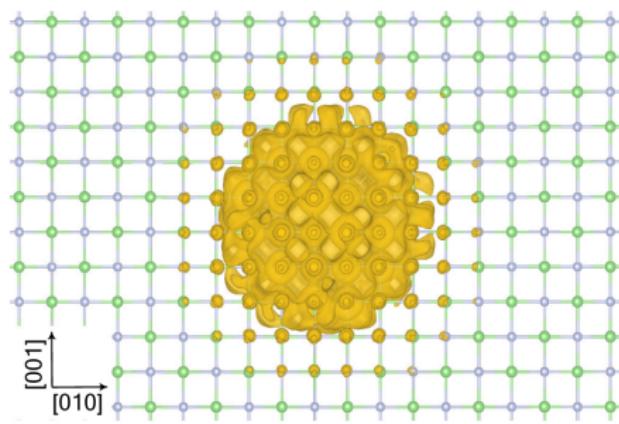
# Small and Large Polarons

$$\hat{H}_{\text{el-ph}} = \frac{g}{\sqrt{N}} \sum_{k,q} \hat{c}_{k+q}^\dagger \hat{c}_k (\hat{b}_{-q}^\dagger + \hat{b}_q)$$



(a) Small (Holstein) polaron

$$\hat{H}_{\text{el-ph}} = C \sum_{k,q} |\mathbf{q}|^{-1} \hat{c}_{k+q}^\dagger \hat{c}_k (\hat{b}_q + \hat{b}_{-q}^\dagger)$$



(b) Large (Fröhlich) polaron

**Figure 3:** Figures from W. H. Sio et al., ‘Polarons from First Principles, without Supercells’, Jun. 2019, doi: 10.1103/PhysRevLett.122.246403

# Density Functional Theory

Basic assumption: the ground-state energy of the system  $E_g$  is a functional  $E_g[\rho]$  of the sole charge density  $\rho$ , where

$$\rho(\mathbf{r}) = \sum_i \langle \Psi | \delta^3(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle$$

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$$\rho(\mathbf{r}) = \sum_i \langle \Psi | \delta^3(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle$$

Given the Hamiltonian

$$\hat{H} = \sum_i v(\mathbf{r}_i) + \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} = V + T + U$$

the charge density is found **minimizing**

$$E_g[\rho] = \langle \Psi[\rho] | V + T + U | \Psi[\rho] \rangle = \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + F[\rho]$$

# Kohn-Sham equations

To solve the problem, we consider a fictitious system of non-interacting particles with the same density  $\rho(\mathbf{r})$

$$U_{\text{KS}} = \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$
$$T_{\text{KS}} = -\frac{\hbar^2}{2m} \sum_i \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r}$$

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The difference with the real system is encoded in the exchange-correlation energy term  $E_{\text{xc}}$

$$F[\rho] = T_{\text{KS}}[\rho] + U_{\text{KS}}[\rho] + E_{\text{xc}}[\rho]$$

which has no exact known expression, and it is therefore parametrized.

# Kohn-Sham equations

The charge density that minimize the energy of the real system  $E_g[\rho]$  is found solving the **Kohn-Sham equations**

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

where

$$v_H(\mathbf{r}) = e^2 \int \frac{\rho'(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho'(\mathbf{r})}$$

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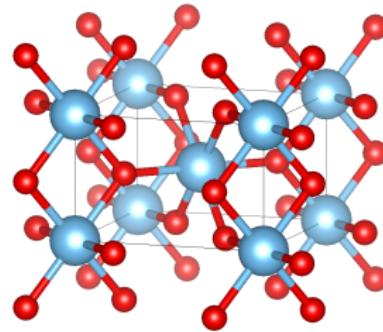
The energy of the real system is given by

$$E_g[\rho] = \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + T_{KS}[\rho] + U_{KS}[\rho] + E_{xc}[\rho]$$

# DFT on Rutile TiO<sub>2</sub>

## Unit cell

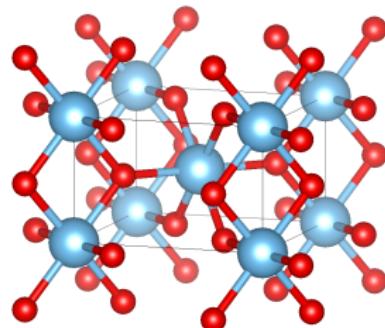
- ① Structure relaxation
- ② Standard DFT calculation
- ③ DFT+U calculation with  
 $U = 3.9 \text{ eV}$



# DFT on Rutile TiO<sub>2</sub>

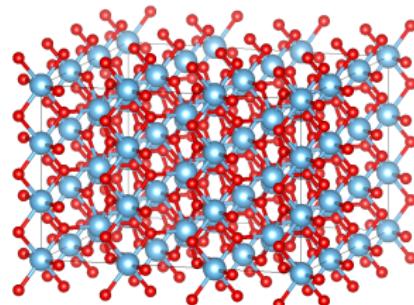
## Unit cell

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- ② Standard DFT calculation
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## Supercell

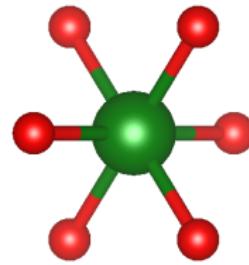
- ④ DFT calculation with  
 $U = 3.9 \text{ eV}$
- ⑤ Extra electron localization



# Polaron in Rutile TiO<sub>2</sub>

## Electron localization

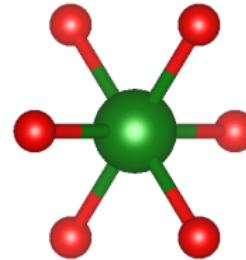
- ⑥ Vanadium,  $U = 9 \text{ eV}$



# Polaron in Rutile TiO<sub>2</sub>

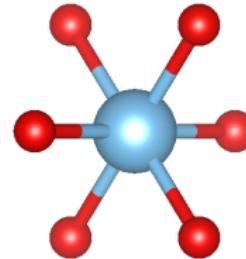
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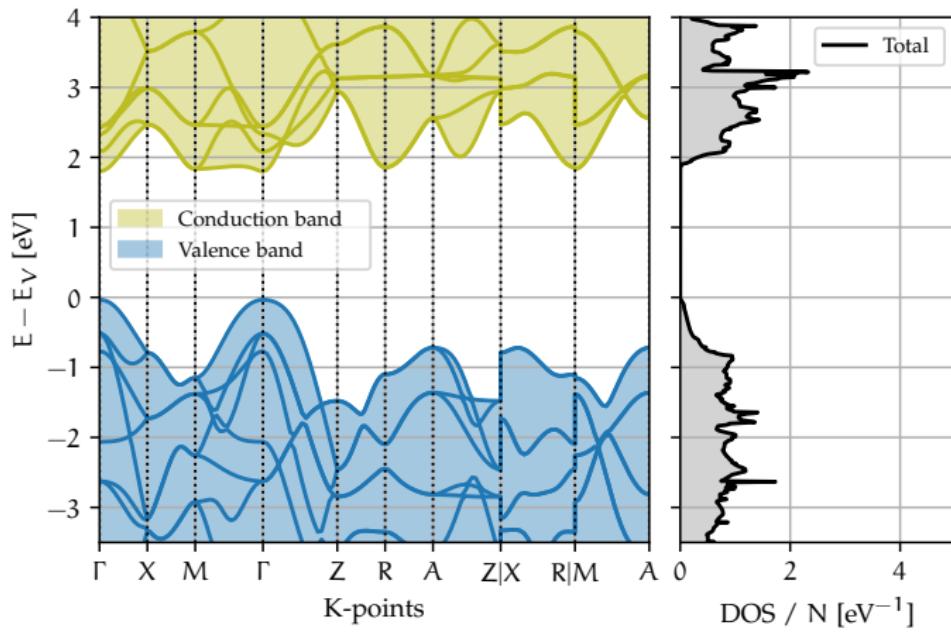


⑦ Titanium,  $U = 9 \text{ eV}$

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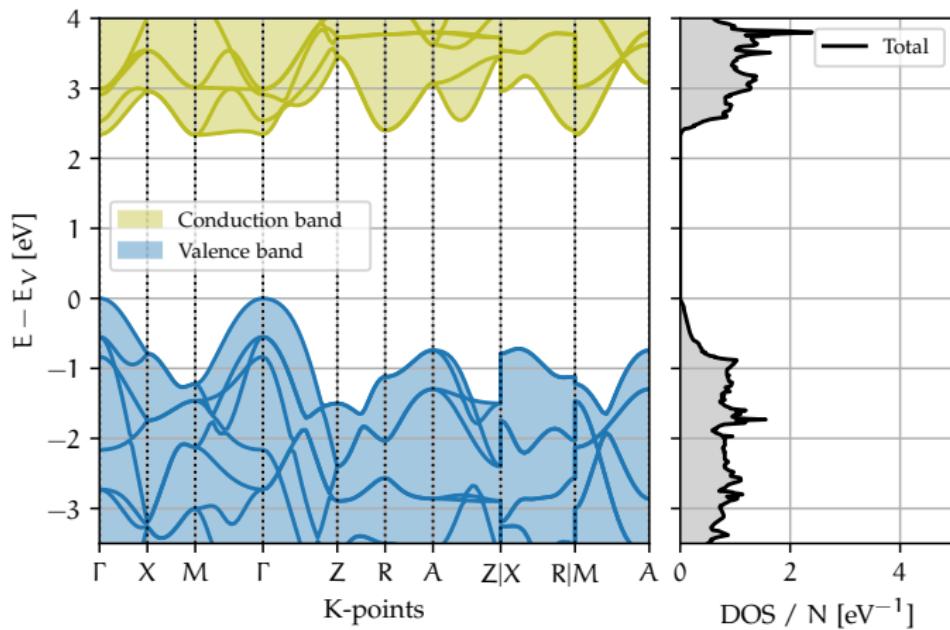


# Rutile TiO<sub>2</sub> band structure



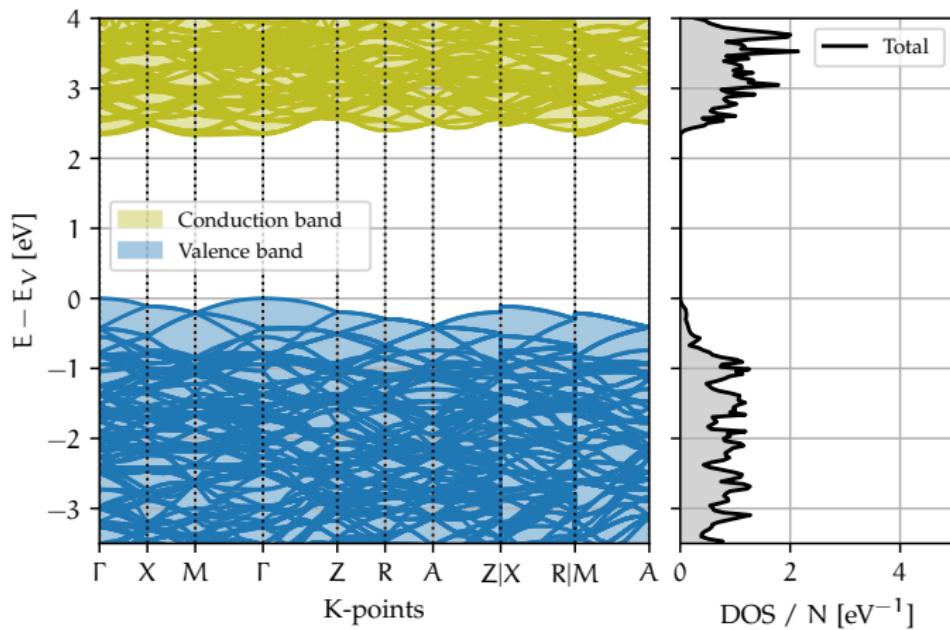
**Figure 4:** Band structure and DOS of the rutile unit cell (standard DFT). The direct  $\Gamma - \Gamma$  energy gap is of 1.83 eV.

# Rutile TiO<sub>2</sub> band structure (DFT+U)



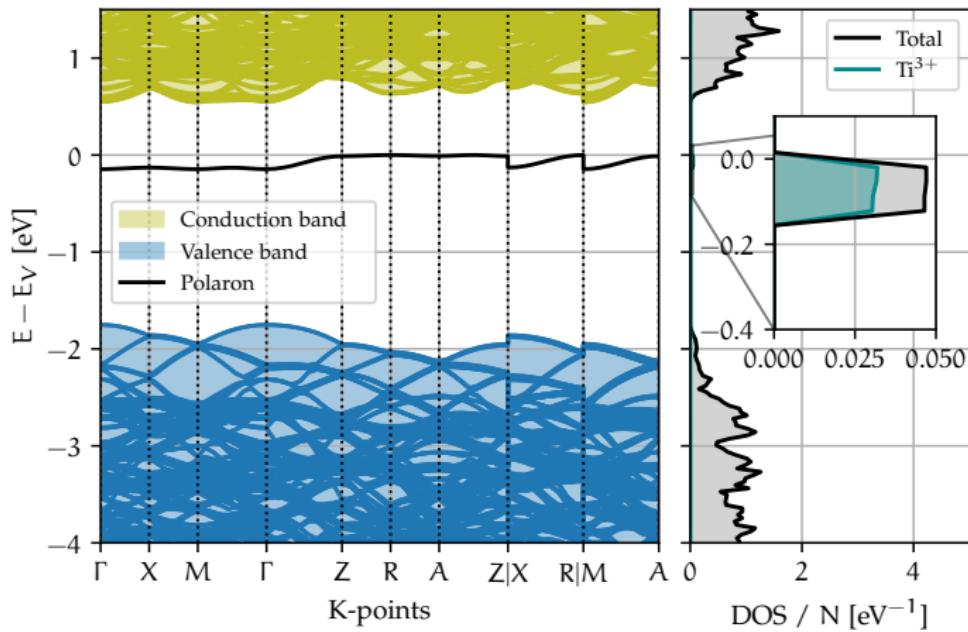
**Figure 5:** Band structure and DOS of the rutile unit cell (DFT+U,  $U = 3.9$  eV). The direct  $\Gamma - \Gamma$  energy gap is of 2.33 eV.

# Rutile TiO<sub>2</sub> supercell band structure



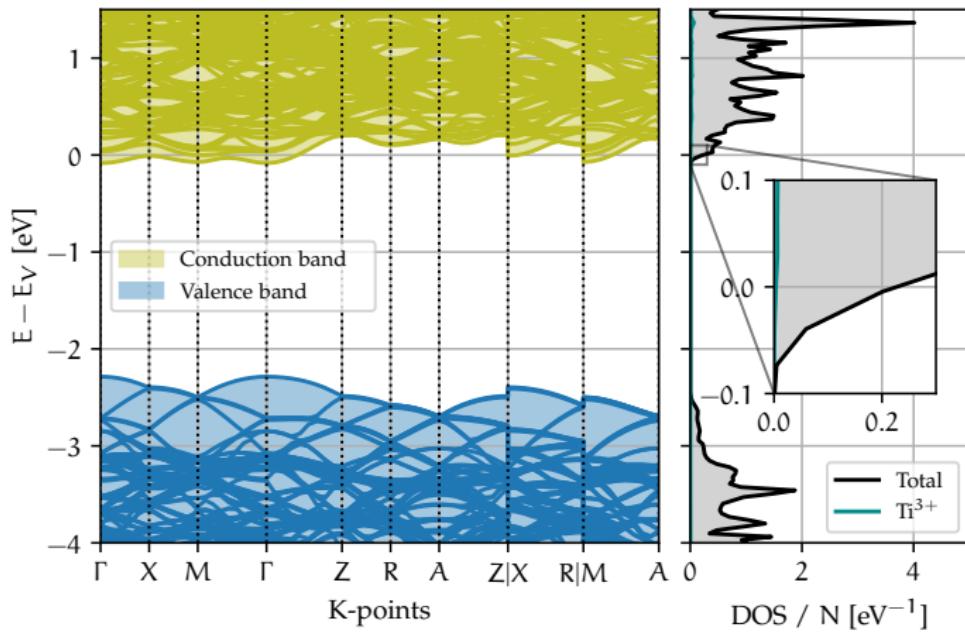
**Figure 6:** Band structure and DOS of the rutile supercell (DFT+U,  $U = 3.9$  eV). The direct  $\Gamma - \Gamma$  energy gap is of 2.33 eV.

# Polaron band structure



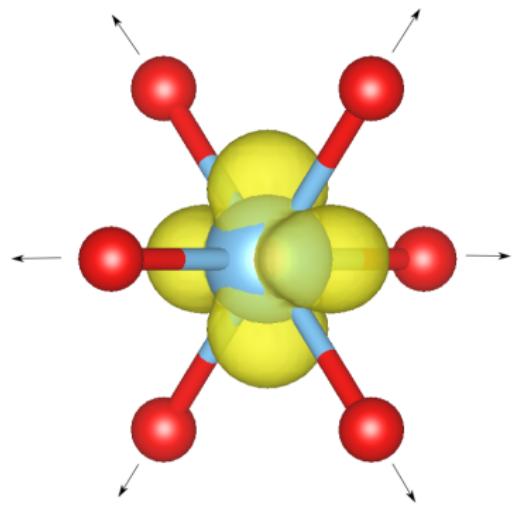
**Figure 7:** Band structure and DOS of the supercell with an extra electron localized on the central atom. An extra state is formed 0.70 eV below the conduction band.

# Delocalized electron band structure

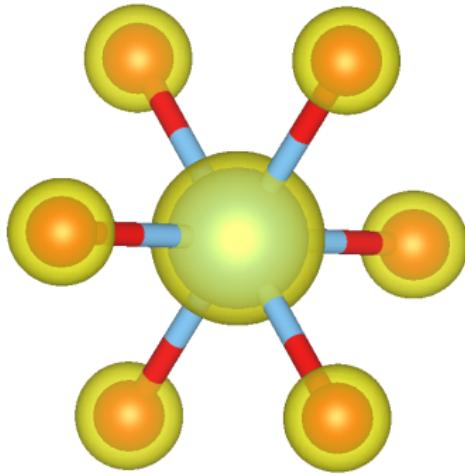


**Figure 8:** Band structure and DOS of the supercell with an extra electron delocalized in the material. The electron enters the conduction band.

# Charge isosurface



(a) Electron localized: polaron



(b) Electron delocalized

**Figure 9:** Central atom with the isosurface (10%) of the charge density projected on the extra-electron band. In (a) The four oxygen atoms closer to the titanium atom are displaced by  $0.085 \text{ \AA}$  outwards, whereas the two further oxygen atoms by  $0.023 \text{ \AA}$ .

# Take home messages

- A Polaron is formed by an electron **distorting** the lattice and creating a **potential well** in which it **localizes**

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- A Polaron is formed by an electron **distorting** the lattice and creating a **potential well** in which it **localizes**
- An **extra state** is formed below the conduction band, the effective mass is increased
- Small Polarons can be simulated using **DFT** and compared with delocalized electrons

*Thank you  
for your attention*

# DFT+U

- Fundamental problem in DFT: Hartree term

$$U_{\text{KS}} = \frac{e^2}{2} \int \frac{\rho'(\mathbf{r})\rho'(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

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$$E_{\text{xc}}^{\text{GGA}} = \int \rho(\mathbf{r}) \epsilon_{\text{xc}}(\rho, \nabla \rho) d\mathbf{r}$$

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- Correction with an Hubbard-like Hamiltonian

$$\hat{H}_{\text{Hub}} = -t \sum_{\langle i,j \rangle} \hat{c}_{j,\sigma}^\dagger \hat{c}_{j,\sigma} + U \sum_i \hat{N}_{i\uparrow} \hat{N}_{i\downarrow}$$

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- Duradev: dependency only on  $U - t$ . The greater the value assigned to  $U$  is, the more the states are localized and the more the gap broadens.

# Small and Large Polarons properties

Small (Holstein) polarons	Large (Fröhlich) polarons
$\hat{H}_{\text{el-ph}} = \frac{g}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{q}} \hat{c}_{\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{\mathbf{k}} (\hat{b}_{-\mathbf{q}}^\dagger + \hat{b}_{\mathbf{q}})$	$\hat{H}_{\text{el-ph}} = C \sum_{\mathbf{k}, \mathbf{q}}  \mathbf{q} ^{-1} \hat{c}_{\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{\mathbf{k}} (\hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^\dagger)$
<ul style="list-style-type: none"> <li>• Short-range electron-phonon interaction</li> <li>• Polaron radius <math>\approx</math> lattice parameter</li> <li>• Narrow mid-gap electronic state <math>(\approx 1 \text{ eV below } E_F)</math></li> <li>• Incoherent motion (phonon assisted)</li> <li>• Thermally activated hopping mobility <math>\ll 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}</math></li> <li>• Mobility increasing with temperature</li> </ul>	<ul style="list-style-type: none"> <li>• Long-range electron-phonon interaction</li> <li>• Polaron radius <math>\gg</math> lattice parameter</li> <li>• Shallow mid-gap electronic state <math>(\approx 10 \text{ meV below } E_F)</math></li> <li>• Coherent motion</li> <li>• Free carrier mobility <math>\gg 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}</math></li> <li>• Mobility decreasing with temperature</li> </ul>

# Fröhlich Hamiltonian

$$H_{\text{Fröhlich}} = \sum_{\mathbf{k}} \frac{\hbar^2 \mathbf{k}^2}{2m} + \sum_{\mathbf{q}} \hbar \omega_{\text{LO}} \left( \hat{b}_{\mathbf{q}}^\dagger \hat{b}_{\mathbf{q}} + \frac{1}{2} \right) \\ + \sum_{\mathbf{k}\mathbf{q}} \frac{\hbar \omega_{\text{LO}}}{|\mathbf{q}|} \left( \frac{\hbar}{2m \omega_{\text{LO}}} \right)^{1/4} \left( \frac{4\pi\alpha}{\Omega} \right)^{1/2} \hat{c}_{\mathbf{k}}^\dagger \hat{c}_{\mathbf{k}-\mathbf{q}} (\hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^\dagger)$$

- Weak-coupling limit

$$E_{\mathbf{k}} = -\alpha \hbar \omega_{\text{LO}} + \left(1 - \frac{\alpha}{6}\right) \frac{\hbar^2}{2m} k^2 \quad \langle \hat{N}_{\text{ph}} \rangle = \sum_{\mathbf{q}} \langle \psi | \hat{b}_{\mathbf{q}}^\dagger \hat{b}_{\mathbf{q}} | \psi \rangle = \frac{\alpha}{2}$$

- Strong-coupling limit

$$E_{\text{var}} = -\frac{\alpha^2}{3\pi} \hbar \omega_{\text{LO}}$$

# Holstein Hamiltonian

$$\hat{H}_{\text{Holstein}} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}}^{\text{tb}} \hat{c}_{\mathbf{k}}^\dagger \hat{c}_{\mathbf{k}} + \hbar \omega_0 \sum_{\mathbf{q}} \left( \hat{b}_{\mathbf{q}}^\dagger \hat{b}_{\mathbf{q}} + \frac{1}{2} \right) + \frac{g}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{q}} \hat{c}_{\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{\mathbf{k}} (\hat{b}_{-\mathbf{q}}^\dagger + \hat{b}_{\mathbf{q}})$$

- Weak-coupling limit

$$E_k = -2t \cos(k) - \frac{1}{2\pi} \int dq \frac{\alpha \hbar \omega_0 t}{2t \cos(k) + 2t \cos(k-q) - \hbar \omega_0}$$