Constrained DFT to mimick thermalized photo-excited carriers

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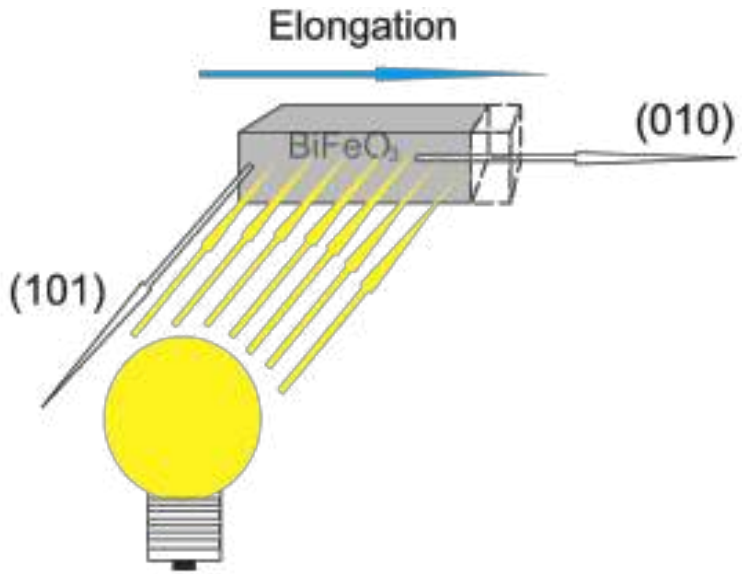
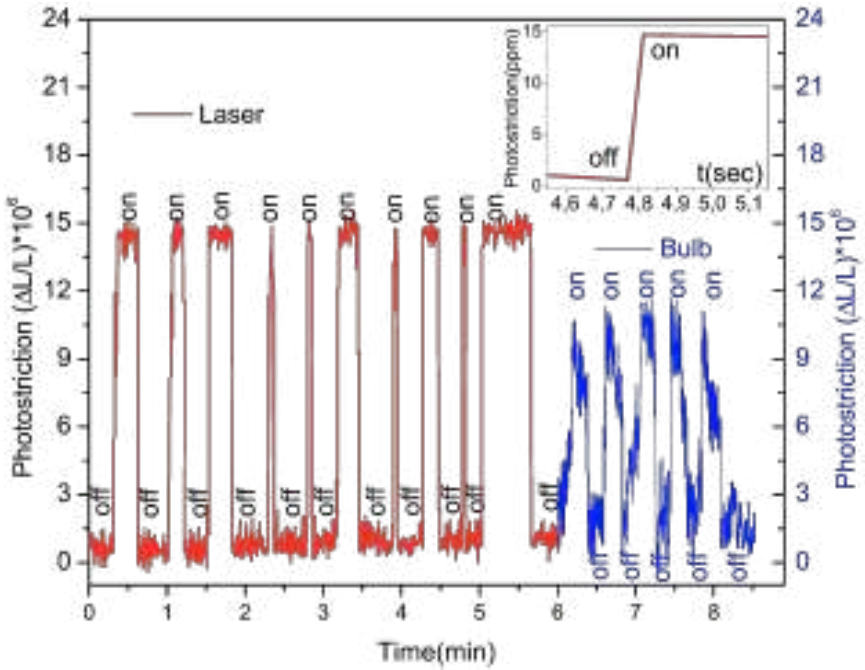
Outline

Photostriction in ferroelectrics

- Ferroelectric = functional material with switchable electrical polarization
- Photostriction= change of shape under illumination.
- BFO: longitudinal distortion of $\approx 1.5 \times 10^{-3}$ % [1].

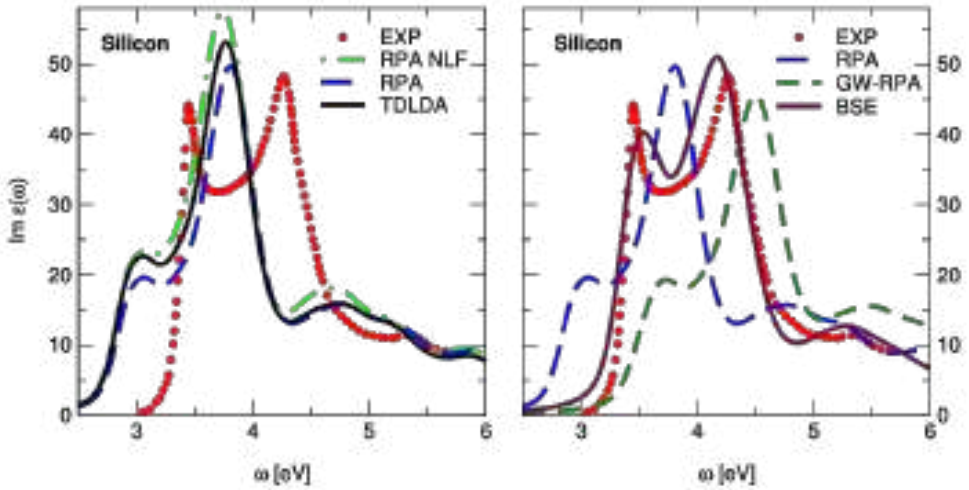




[1] Kundys *et al.*, *Nat. Mater.* **9**, 803 (2010).

Modelling light-matter interaction

- Most light-matter *ab-initio* methods focus on describing optical absorption spectra.
  - Independent Particle Approximation (IPA)
  - Random Phase Approximation (RPA)
  - Time-Dependent Density Functional Theory (TD-DFT)
  - Bethe-Salpether Equation (BSE)

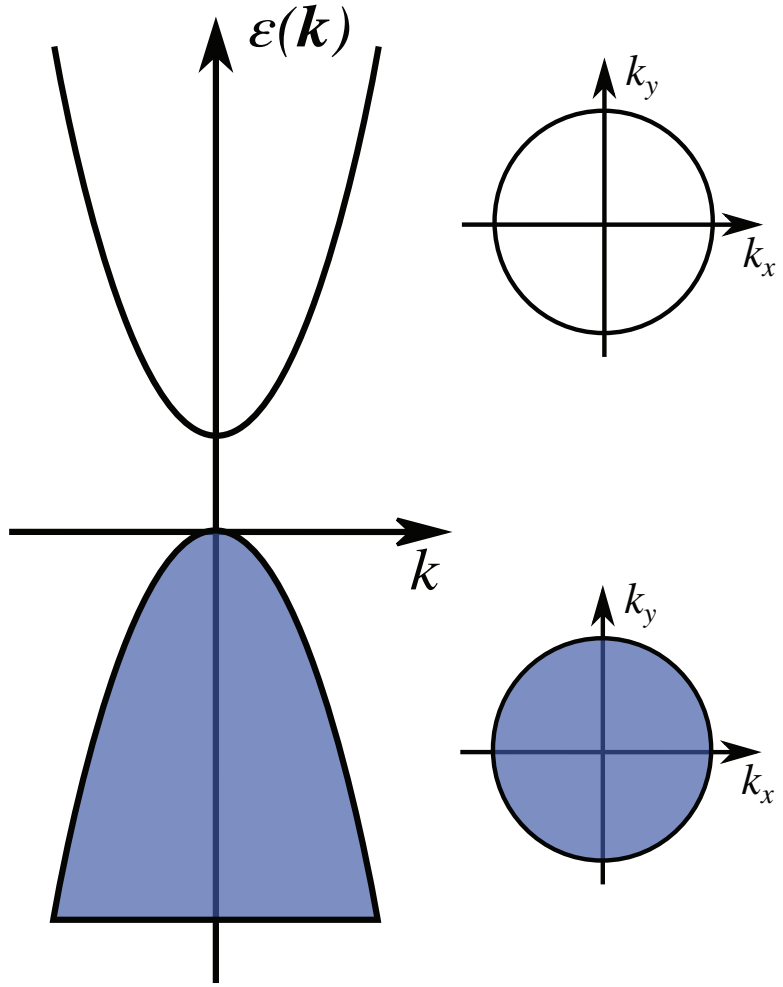


- But difficult to relax structure!

Olevani, *Structures on Different Time Scales*, vol. 1

Electronic processes during optical excitation

- Absorption of photon $\hbar\omega > E_g$ and electron-hole pair creation.
- "Isotropification" of momenta through $e - e$ elastic scattering.
- "Thermalization" (relaxation to band edges) through e-phonon inelastic scattering.
- Recombination (radiative or non-radiative), *i.e.* destruction of $e - h$ pairs.



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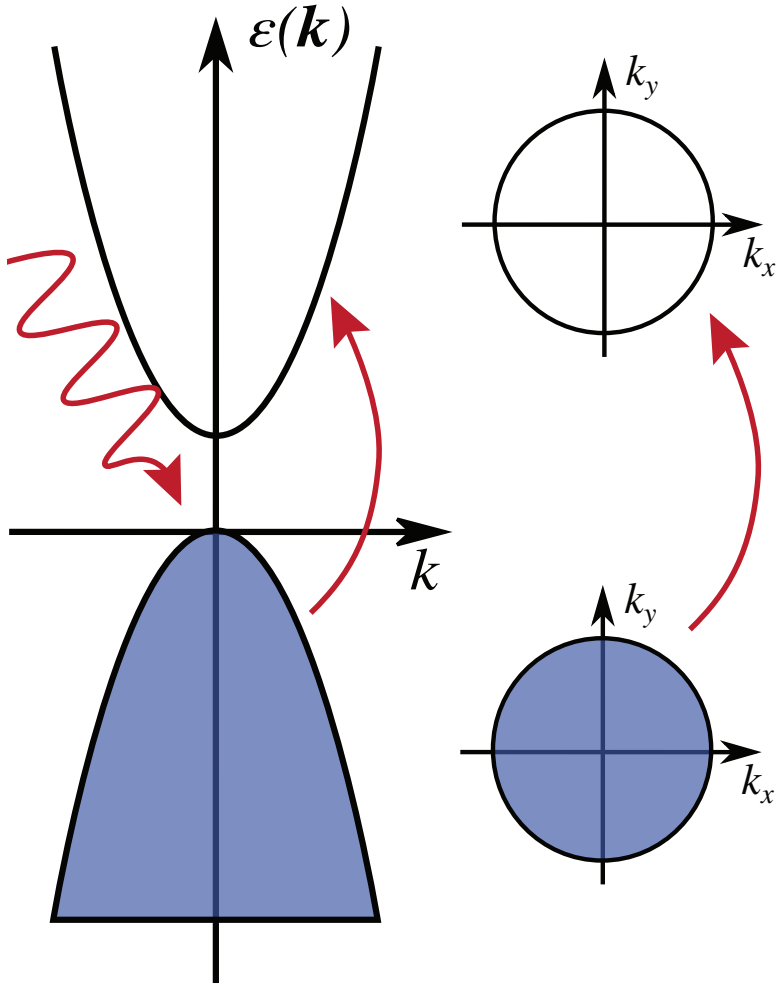

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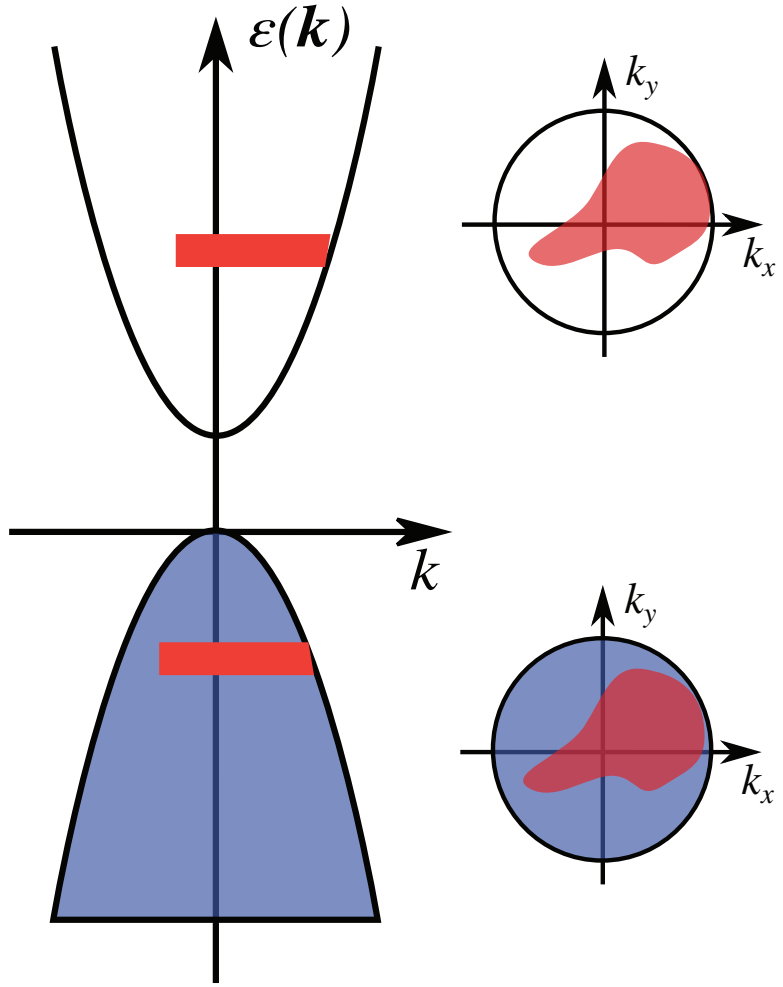

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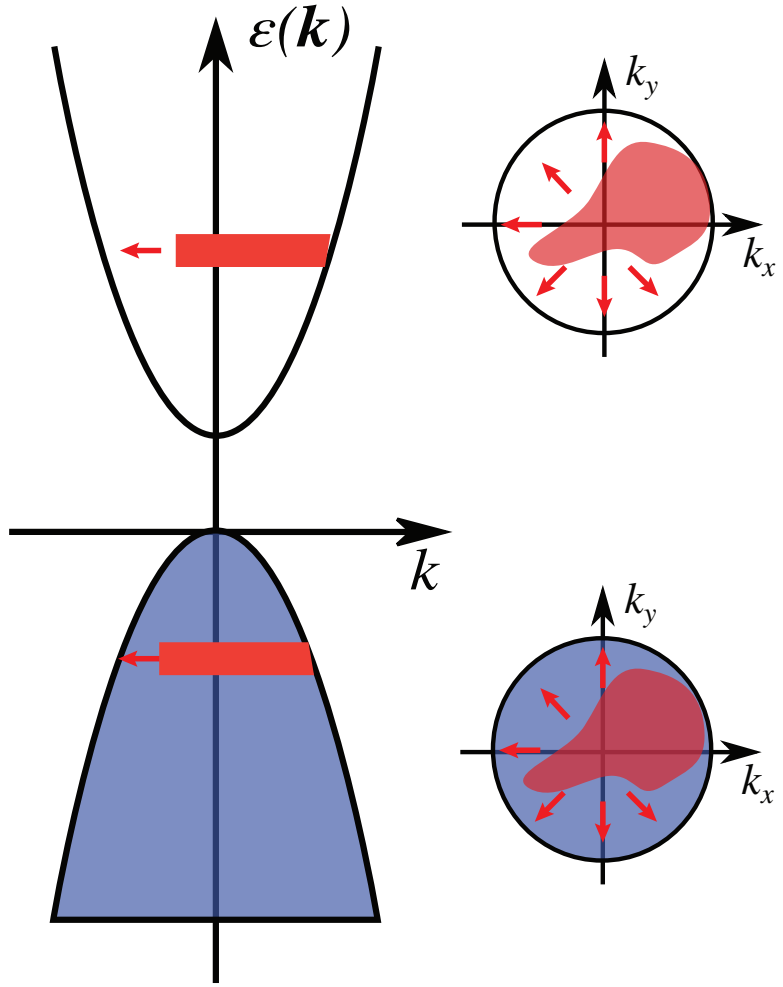

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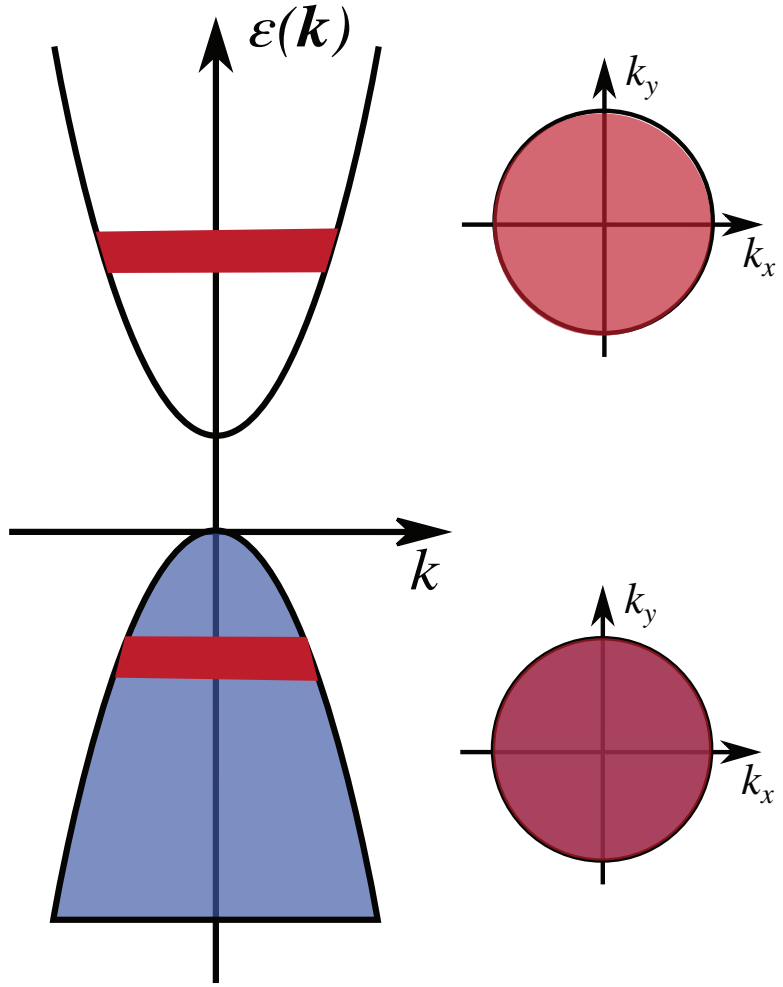

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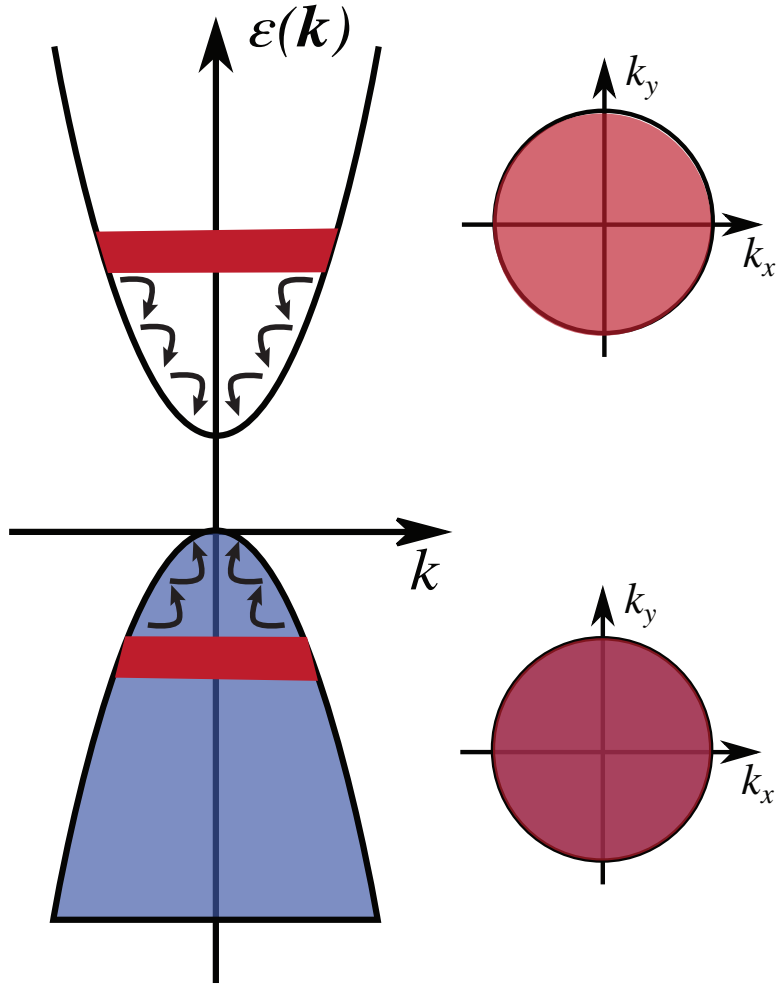

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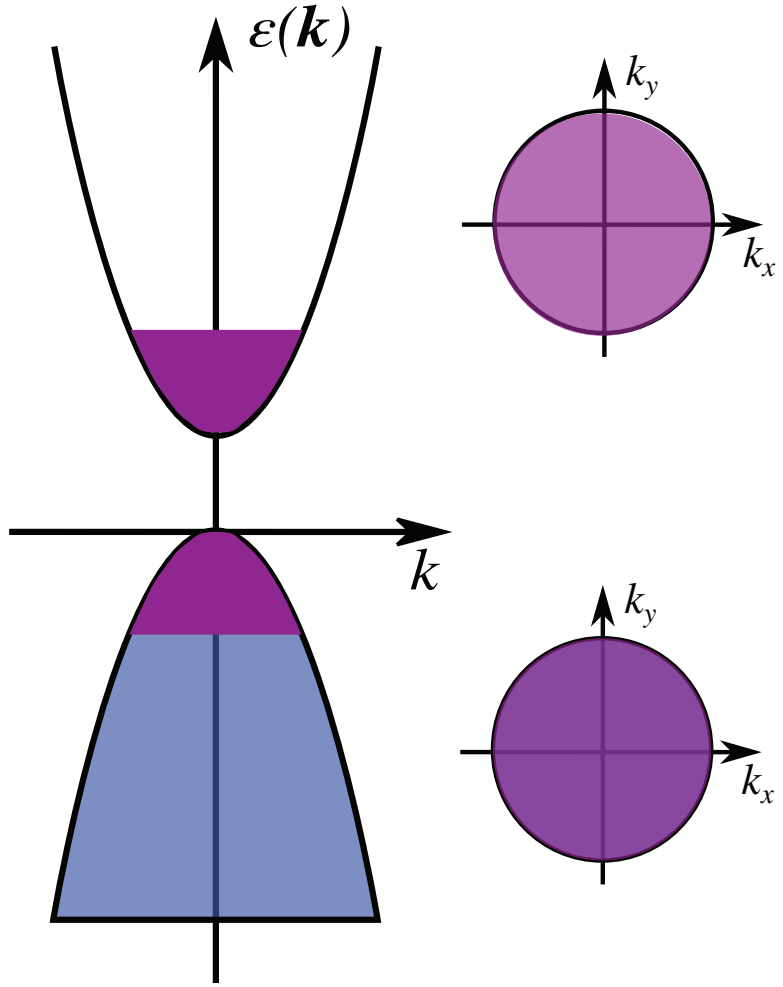

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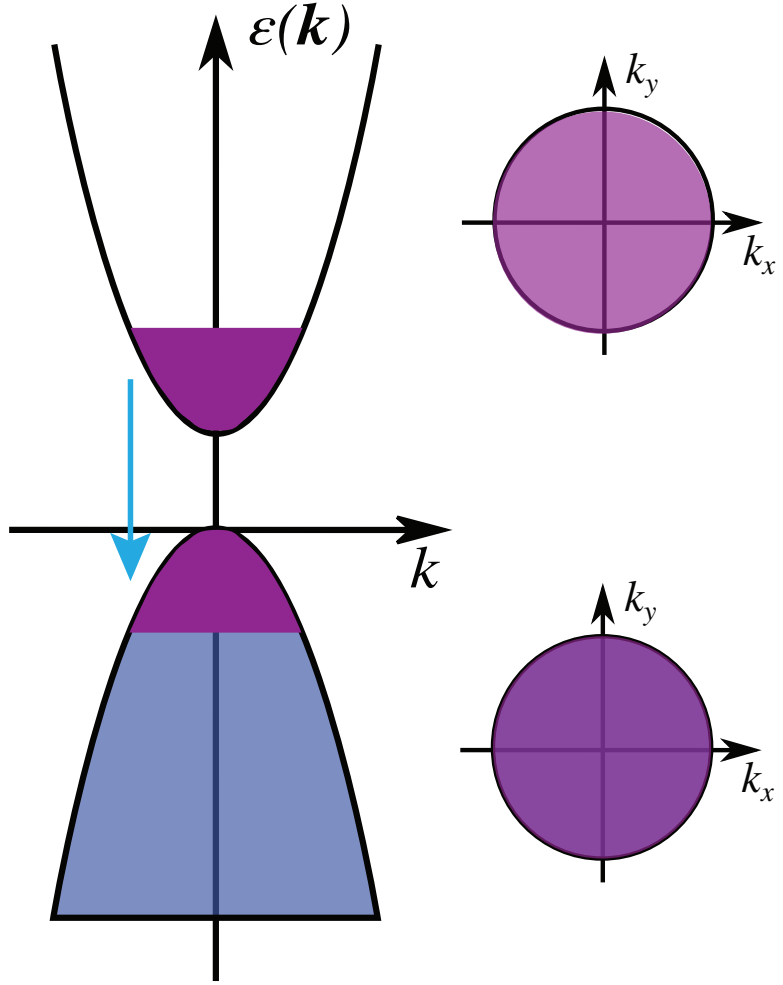

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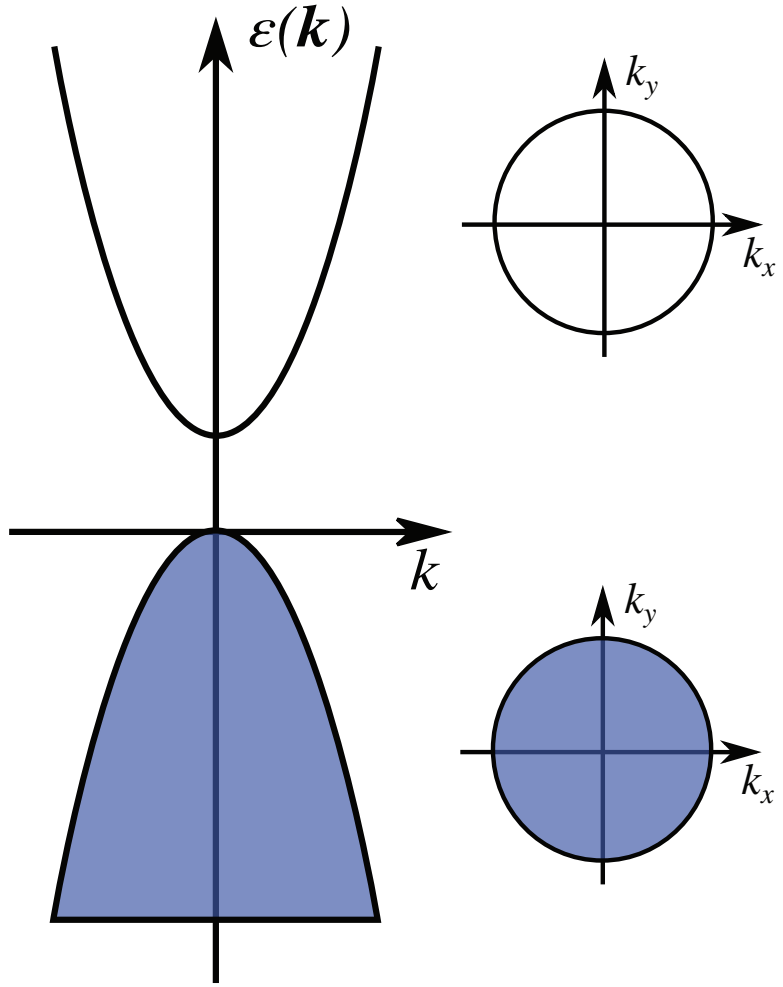
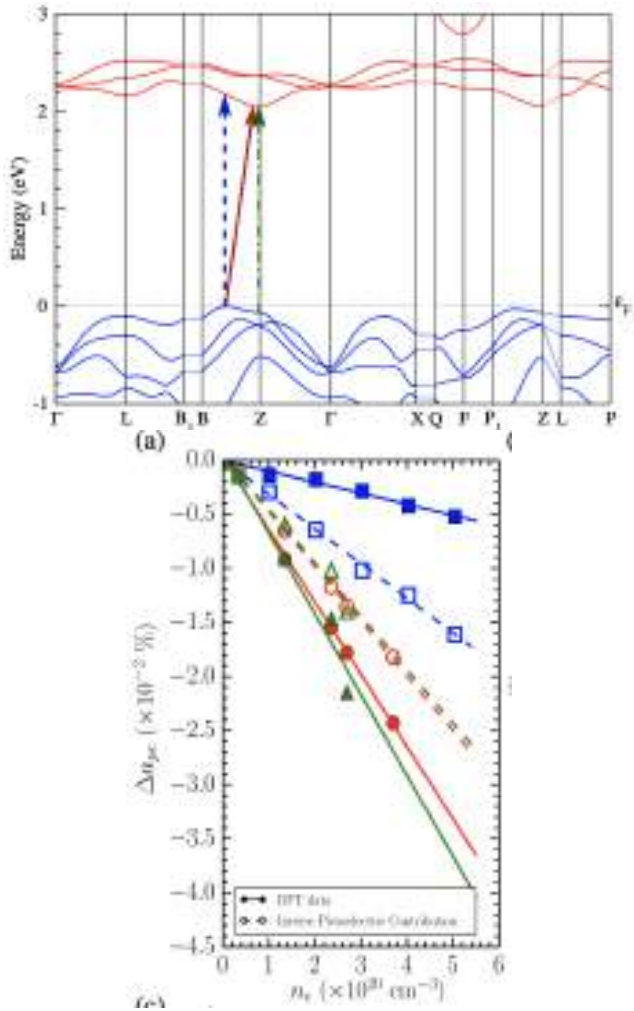


The ΔSCF method

- One possibility to relax structure while "mimicking" photo-excitation: ΔSCF method.
- Basically, fix occupation number by hand. Already doable in abinit using occopt 2 and occ.



C. Paillard *et al.*, *Phys. Rev. Lett.* **116**, 247401 (2016).

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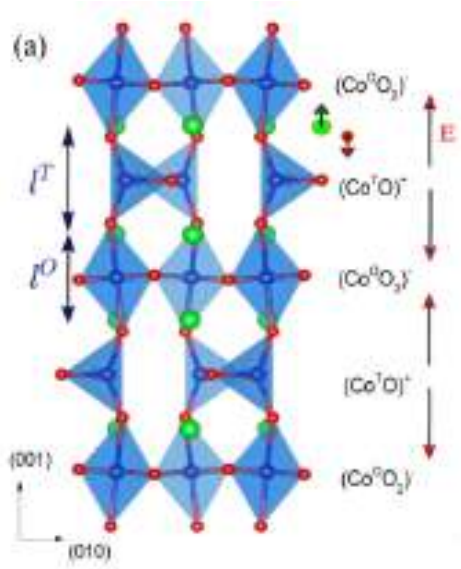

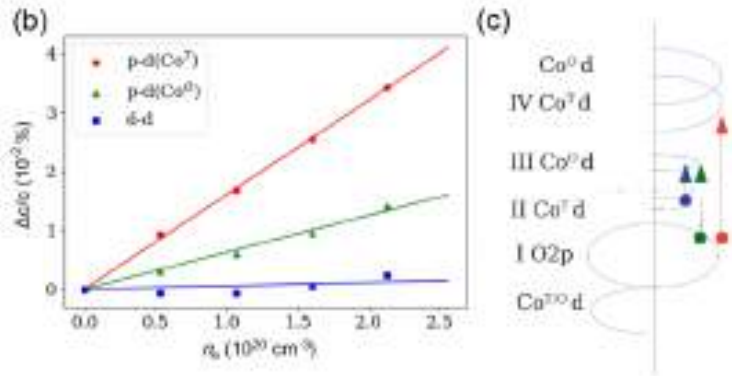

B. Zhang *et al.*, *Phys. Rev. B* **100**, 144201 (2019).

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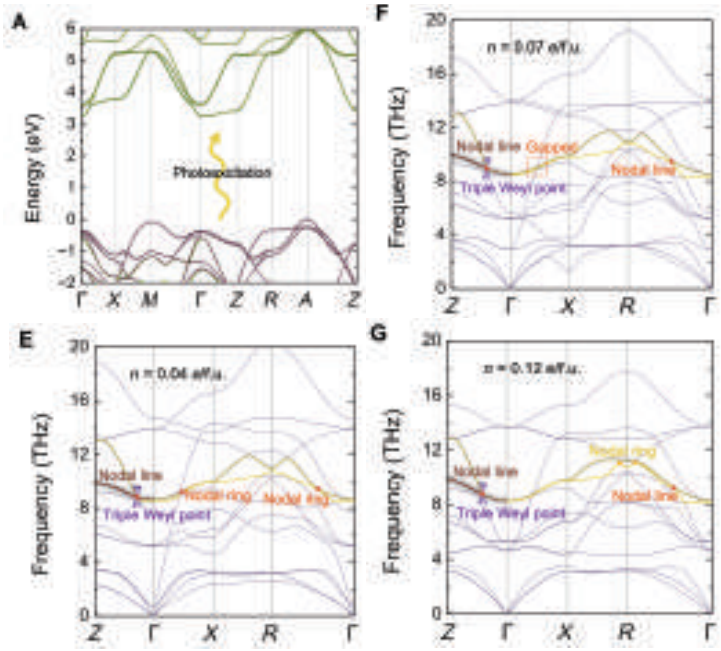
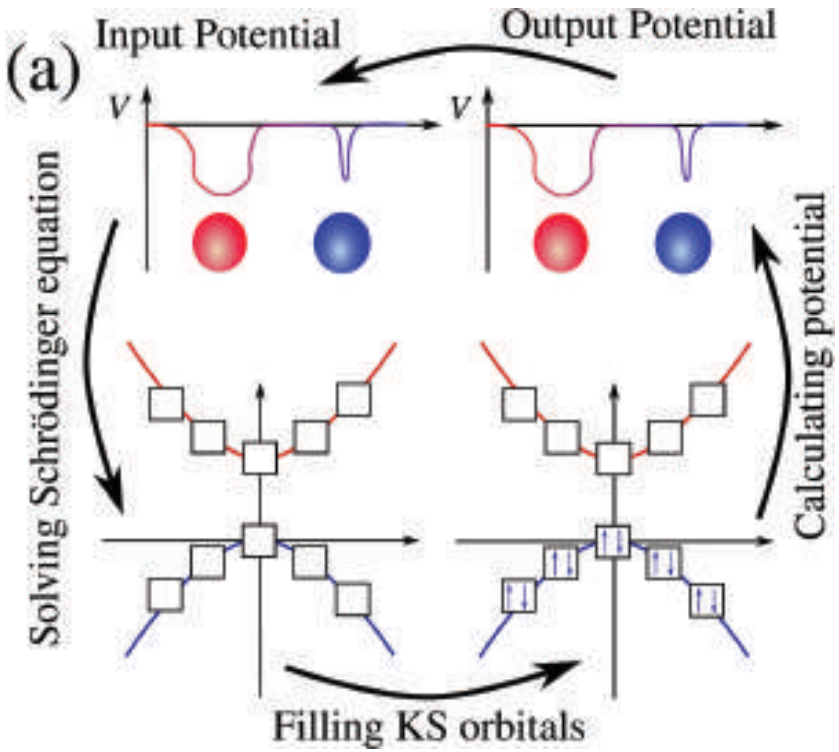


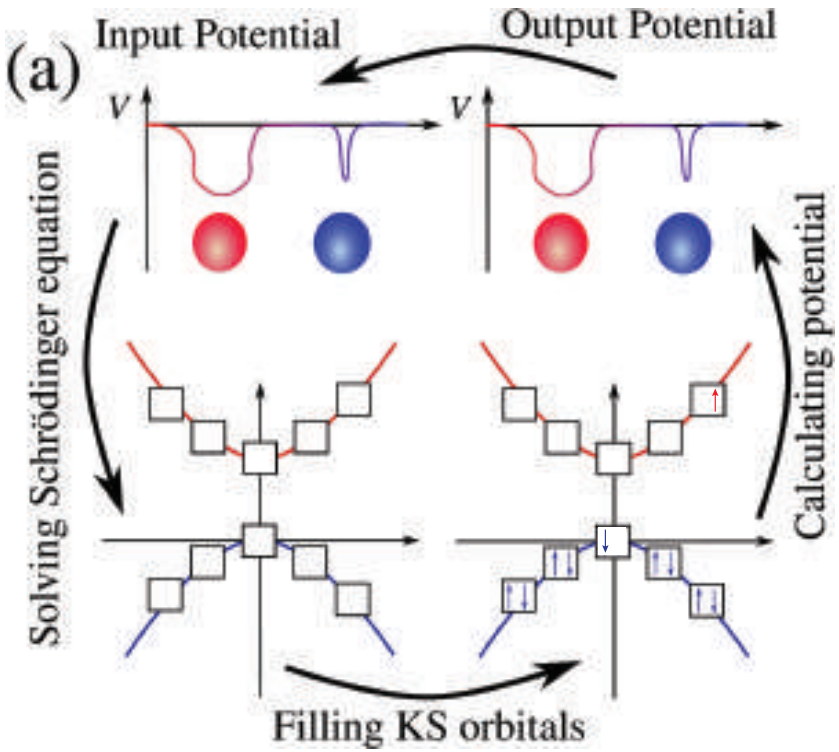
B. Peng *et al.*, *Sci. Adv.* **6**, eabd1618 (2020).

The ΔSCF method

SCF cycle



ΔSCF cycle



Yang *et al.*, *J. Phys.: Cond. Matt.* **30**, 073001 (2018).

Outline

Implementation

KS-DFT SCF cycle

1. Initialize potential from density
2. Diagonalize Hamiltonian and find Kohn-Sham orbitals and energies $\varepsilon_{n\boldsymbol{k}\sigma}$.
3. Determine occupancy of orbitals: find μ such

$$\sum_{n,\boldsymbol{k},\sigma} w_{\boldsymbol{k}} f(\varepsilon_{n\boldsymbol{k}\sigma}, \mu, T_{smear}) = n_{elec}$$

   using bi-section algorithm.
4. Deduce the electronic density. Go back to 1) if not converged.

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Implementation

KS "c"-DFT SCF cycle

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2. Diagonalize Hamiltonian and find Kohn-Sham orbitals and energies $\varepsilon_{n\boldsymbol{k}\sigma}$.
3. Determine occupancy of orbitals: find μ_e, μ_h such

$$\sum_{n\in\text{conduction},\boldsymbol{k},\sigma} w_{\boldsymbol{k}} f(\varepsilon_{n\boldsymbol{k}\sigma}, \mu_e, T_{smear}) = n_{ph}$$

AND

$$\sum_{n\in\text{valence},\boldsymbol{k},\sigma} w_{\boldsymbol{k}} f(\varepsilon_{n\boldsymbol{k}\sigma}, \mu_h, T_{smear}) = n_{elec} - n_{ph}$$

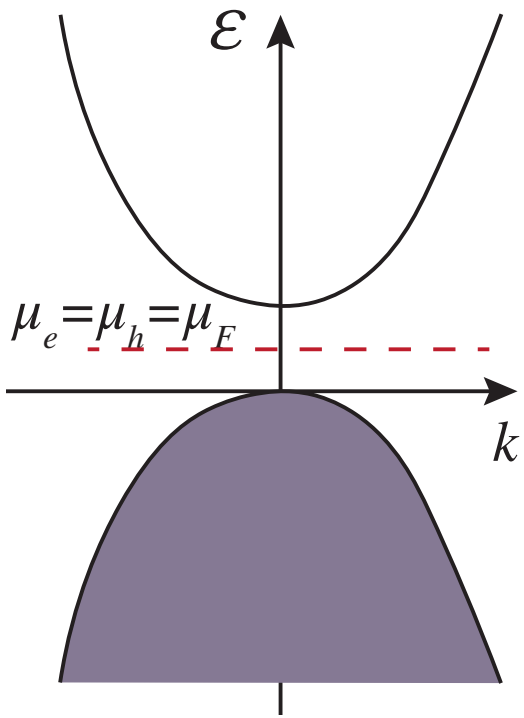
using bissection algorithm.

4. Deduce the electronic density. Go back to 1) if not converged.

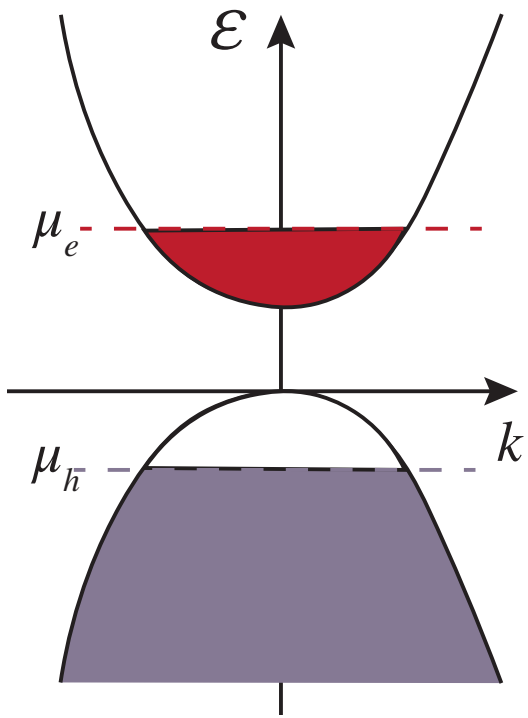
Physical picture

μ_e and $\mu_h \equiv$ quasi-equilibrium Fermi-Dirac chemical potentials for electrons in CB (holes in VB).

Normal SCF



constrained SCF



Inputs

Fermi-Dirac DFT

```
occopt 3
tsmear 0.004
```

Constrained DFT

```
occopt 9
ival 88
nqFD 0.10
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index last valence band

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```

index last valence band

number of excited e^- in CB and h^+ in VB

Outputs

```
Fermi energy for thermalized electrons
and holes (hartree) =    0.28525,     0.17012
Average Vxc (hartree)=  -0.34726
```

μ_e, μ_h

```
occ      2.000000  2.000000  1.709670  1.286049  0.031578  0.000000
         0.000000  0.000000
         2.000000  2.000000  1.999997  1.984930  0.009216  0.000000
         0.000000  0.000000
         2.000000  2.000000  2.000000  1.999995  1.993200  0.000002
         0.000000  0.000000
         2.000000  2.000000  2.000000  1.999835  0.000003  0.000000
         0.000000  0.000000
         2.000000  2.000000  1.999998  0.013526  0.000012  0.000000
         0.000000  0.000000
         2.000000  2.000000  2.000000  1.999740  0.635282  0.000000
         0.000000  0.000000
         2.000000  2.000000  2.000000  2.000000  1.999974  0.207407
         0.000000  0.000000
         2.000000  2.000000  2.000000  2.000000  0.001207  0.000000
         0.000000  0.000000
         2.000000  1.983120  0.000027  0.000027  0.000247  0.000001
         0.000001  0.000000
         2.000000  2.000000  0.518049  0.518049  1.362480  0.000000
         0.000000  0.000000
```

VB CB

What it can and can't do?

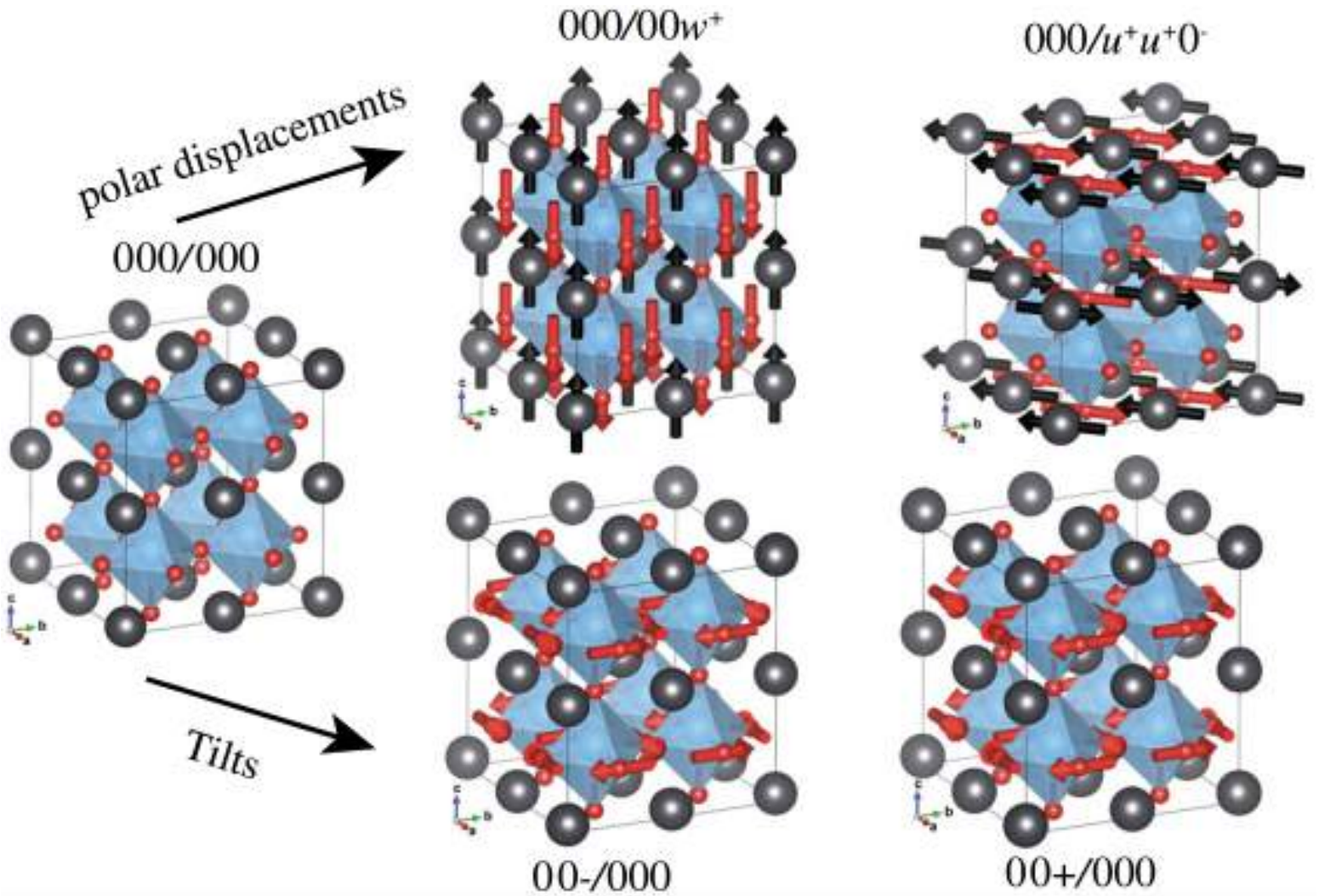
- ✓ SCF
- ✓ structural relaxation
- ✓ spin-orbit coupling
- ✗ DFPT
- ✗ Fixed magnetization (spinmagntarget)

Main modifications: 61_occeig/m_occ.F90

- getnel
  - Added fermih, ibandmin, ibandmax to the list of arguments
  - When occopt=9, computes the number of electron for bands located between ibandmin and ibandmax.
- newocc
  - added fermih, ivalence, ne_qFD and nh_qFD
  - occopt=9: determines fermie and fermih of electrons and holes with the constraints of having nelec - nh_qFD for bands 1 up to ivalence and ne_qFD for bands $\geq$ ivalence + 1

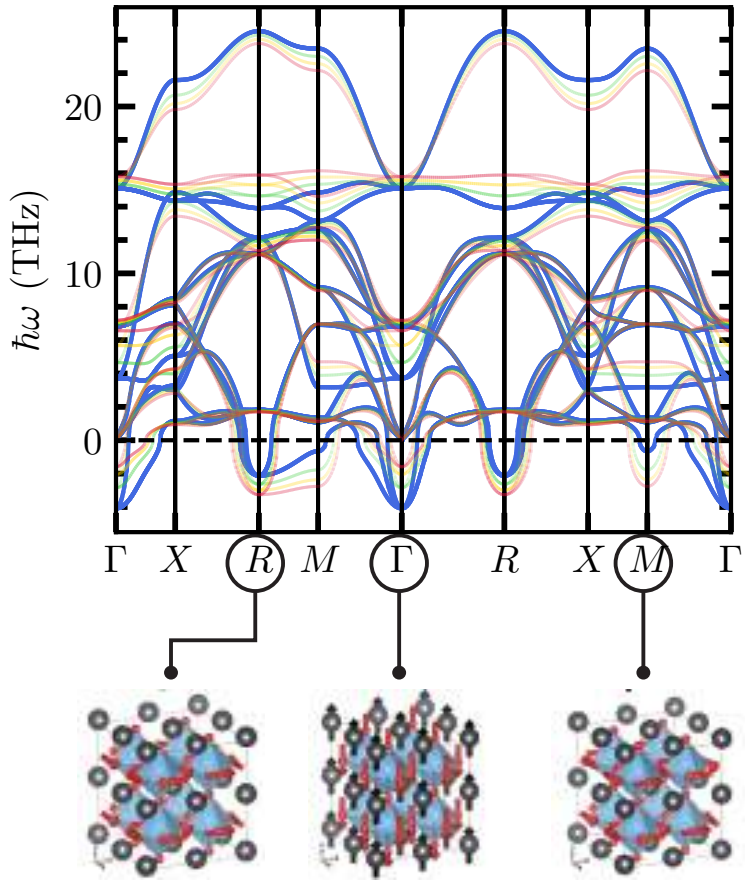
Outline

Ferroelectric instabilities in perovskite oxides



Ferroelectric instabilities in perovskite oxides

- Phonon in $PbTiO_3$ cubic phase using PHONOPY
  - $2 \times 2 \times 2$ perovskite supercell (40 atoms)
  - $8 \times 8 \times 8$ Γ-centered k-mesh.
  - PAW; 35 Ha plane wave cut-off.
- Increasing $n_{ph} \Rightarrow$
  - Γ (polar) instabilty "less" unstable.
  - $M-$, $R-$instabilities (tilts) becomes dominant instability.



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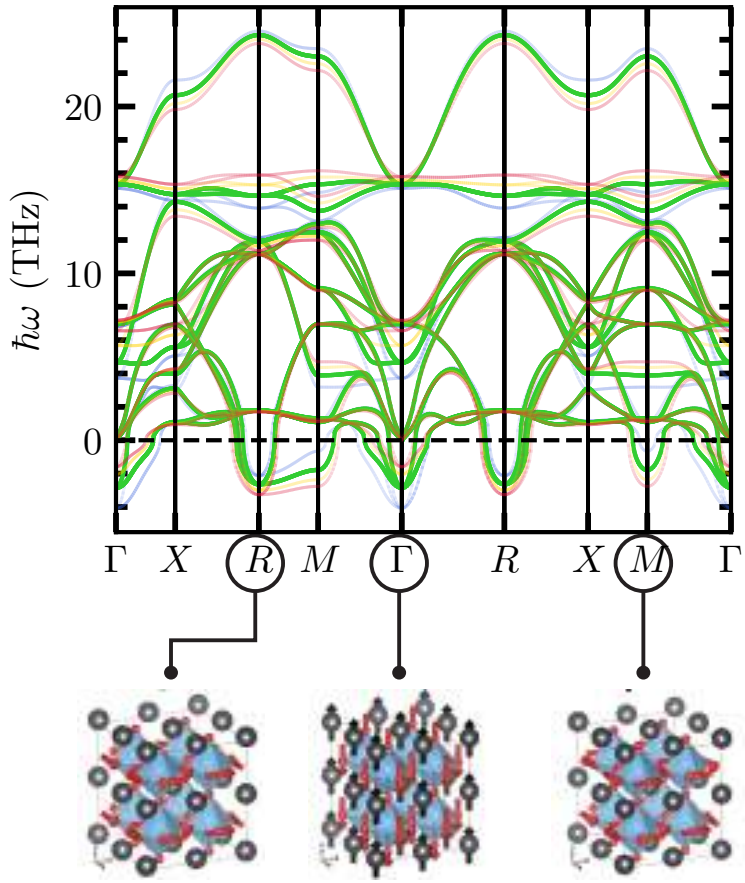

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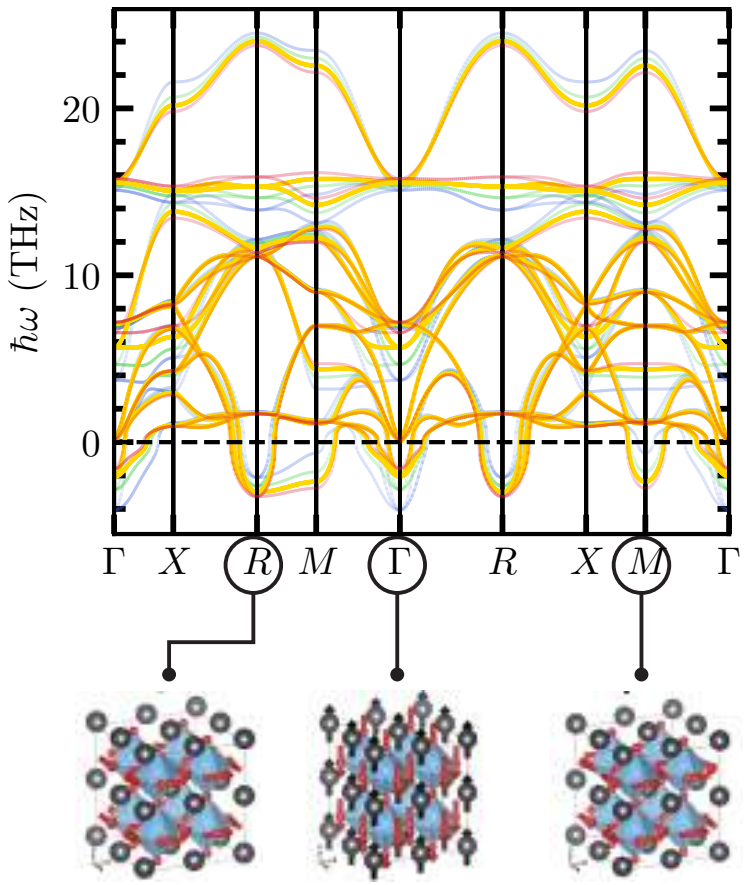

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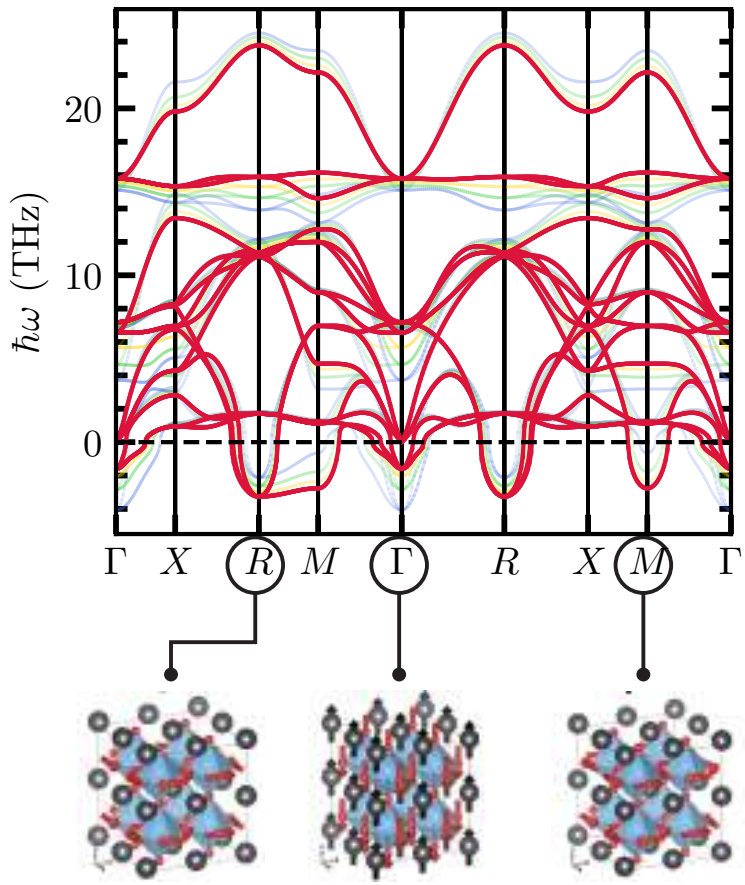

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Photo-induced phase transition

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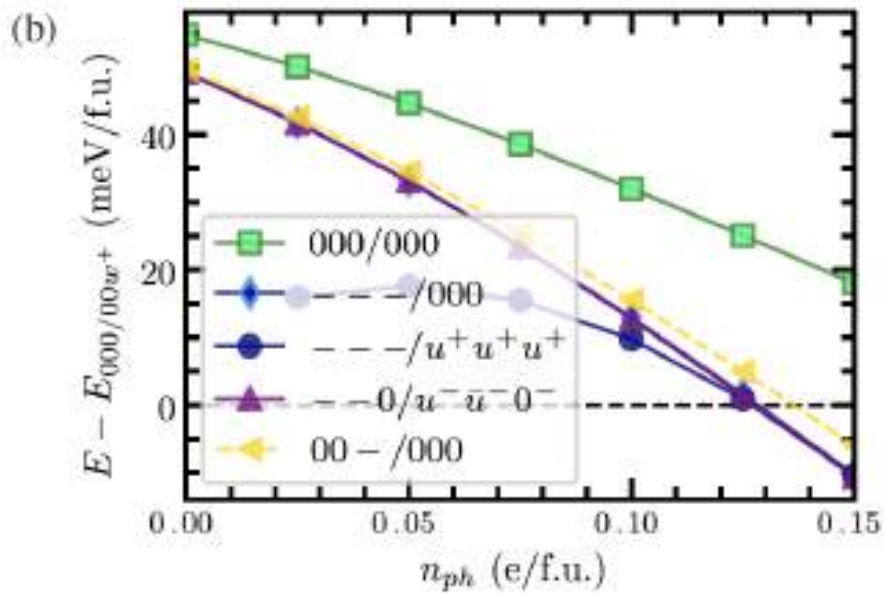
- BTO: phase transition from rombohedral ferroelectric to cubic paraelectric.



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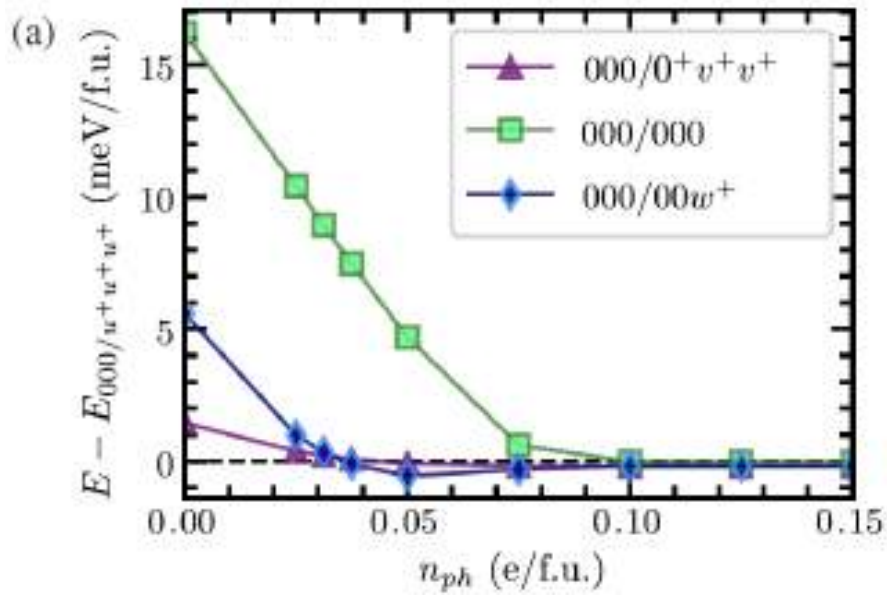

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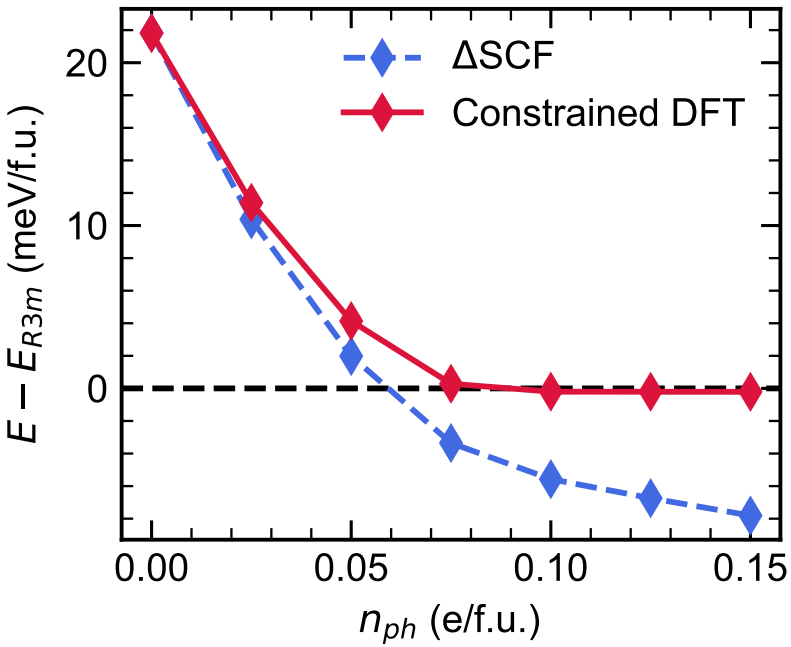
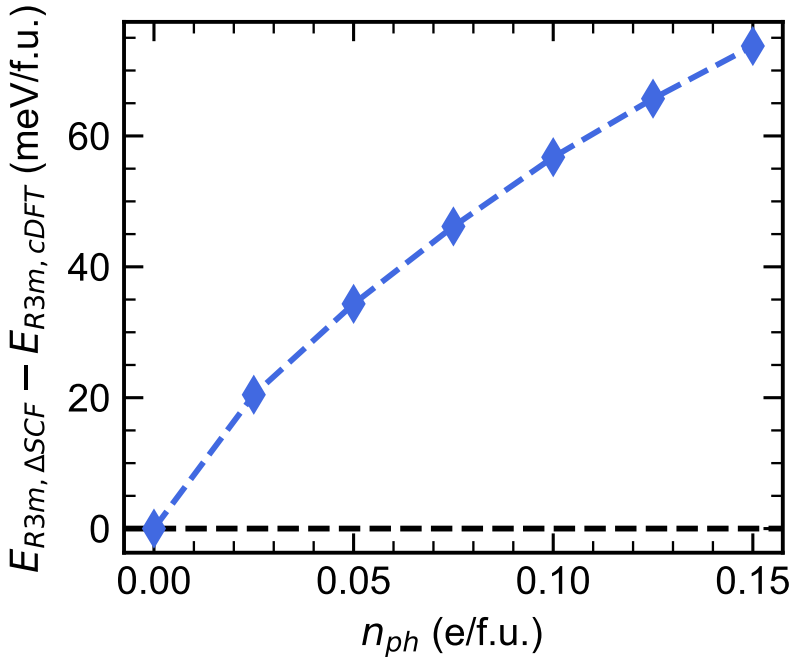
"constrained DFT" versus ΔSCF

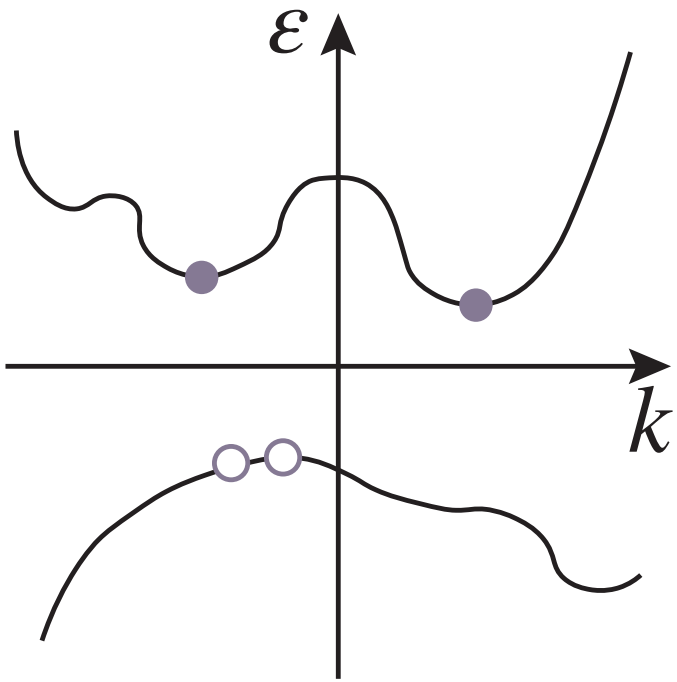




- BTO treated in ΔSCF and c-SCF.
- Final structure are similar: cubic paraelectric.

"constrained DFT" versus ΔSCF

constrained-DFT



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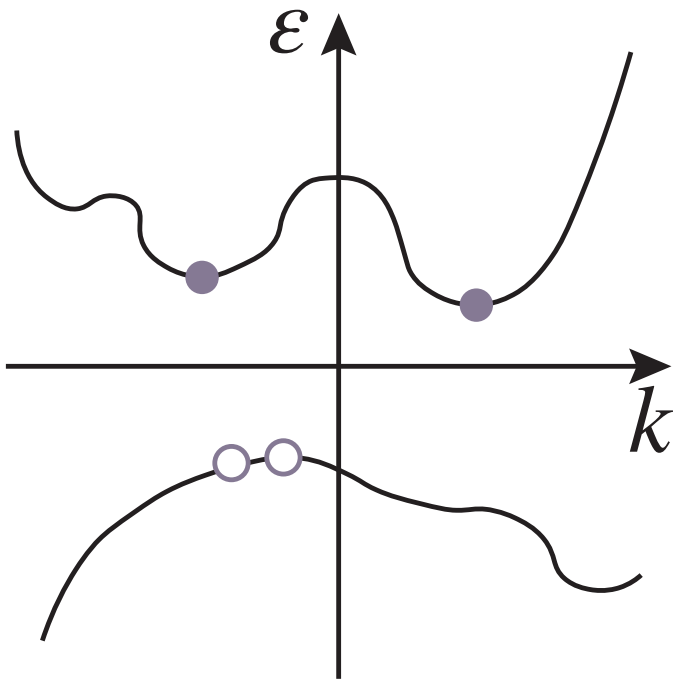
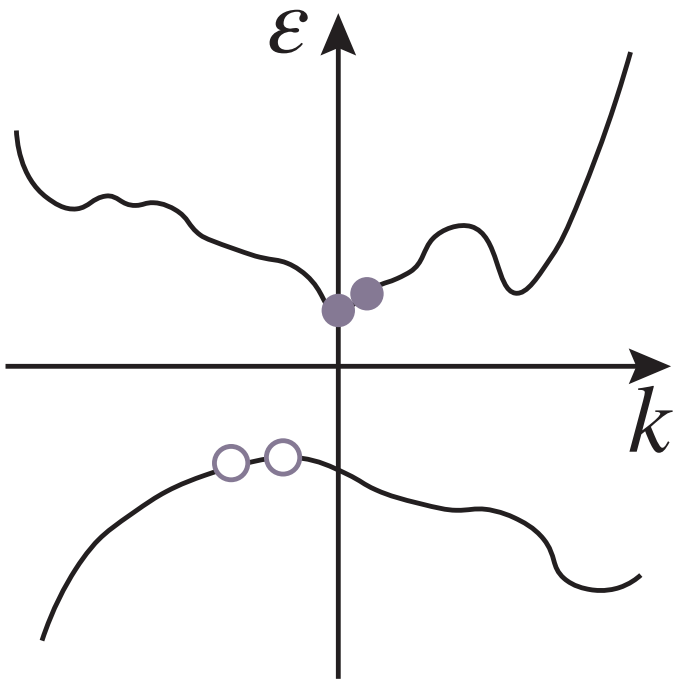
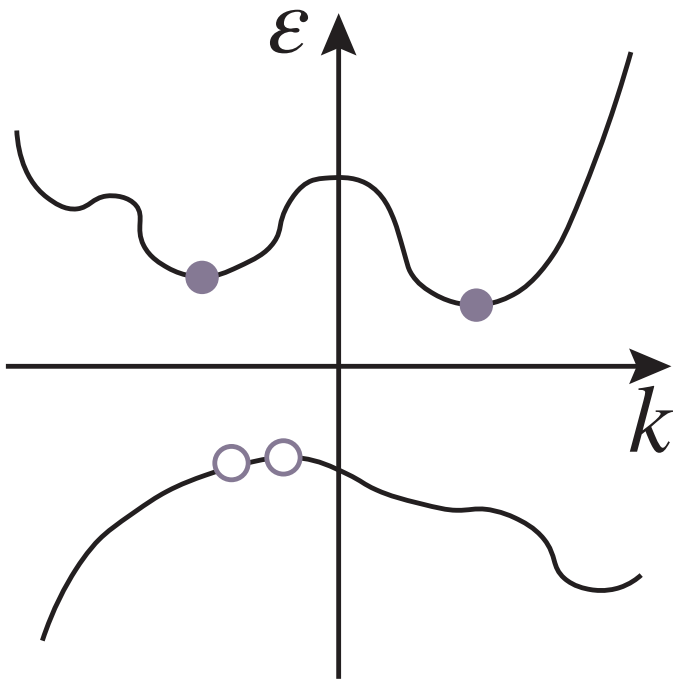


"constrained DFT" versus ΔSCF

constrained-DFT

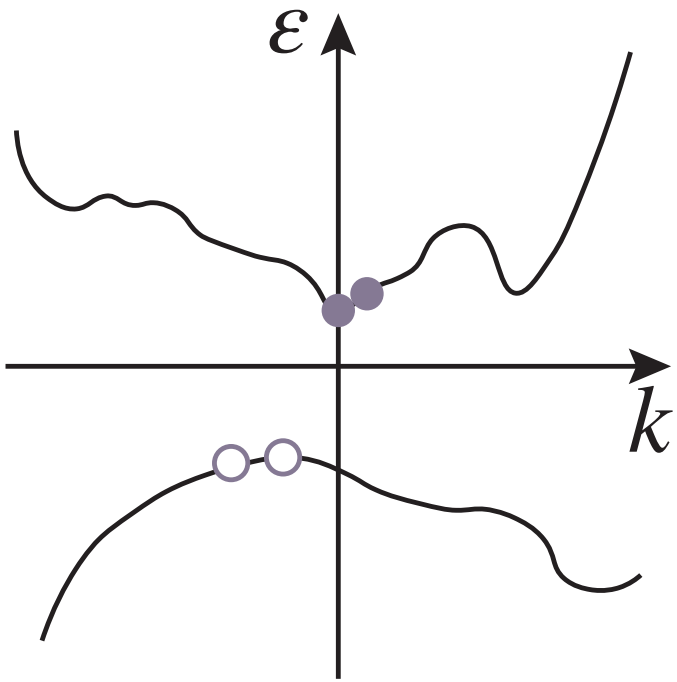


ΔSCF

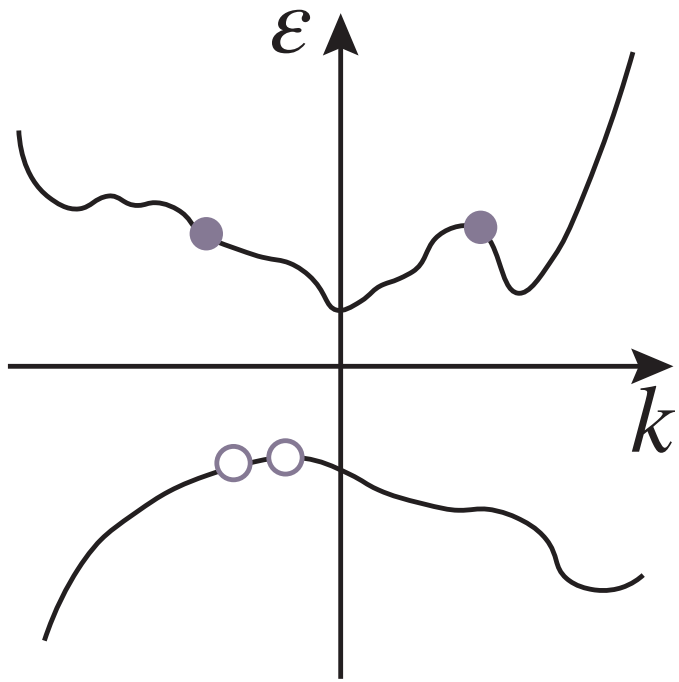


"constrained DFT" versus ΔSCF

constrained-DFT



ΔSCF



Summary

- Constrained occupation scheme: quasi-equilibrium
  - `nqFD` e^- in conduction bands with μ_e
  - `nqFD` h^+ in valence bands with μ_h
- Input: `occopt 9`, `tsmear`, `ival`,`nqfd`
- Complementary to ΔSCF method.
- Perspectives:
  - different concentrations of holes and electrons (charged system).
  - DFPT

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