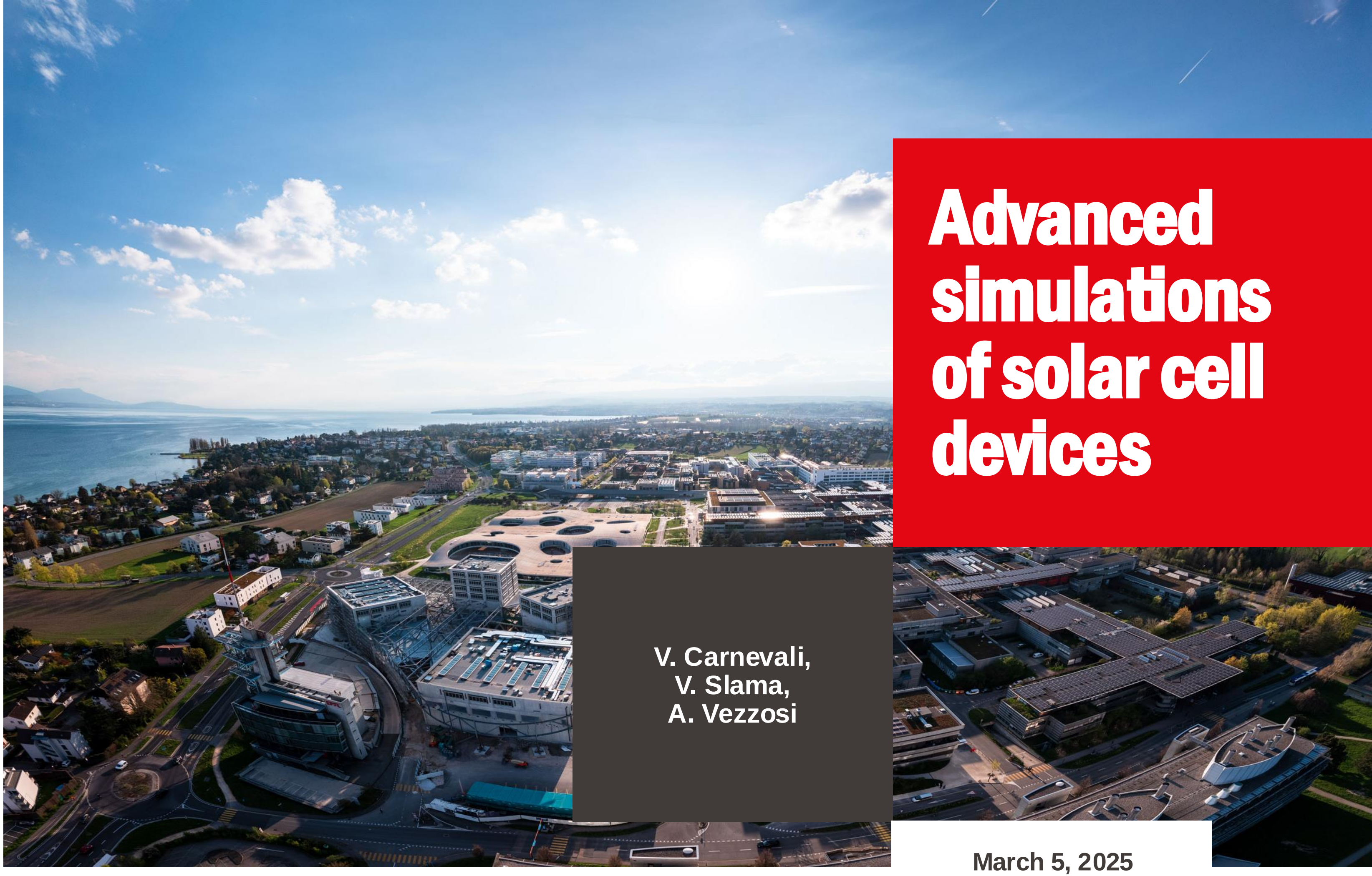
EPFL



Advanced simulations of solar cell devices

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Quasi-Fermi Level Splitting (QFLS)

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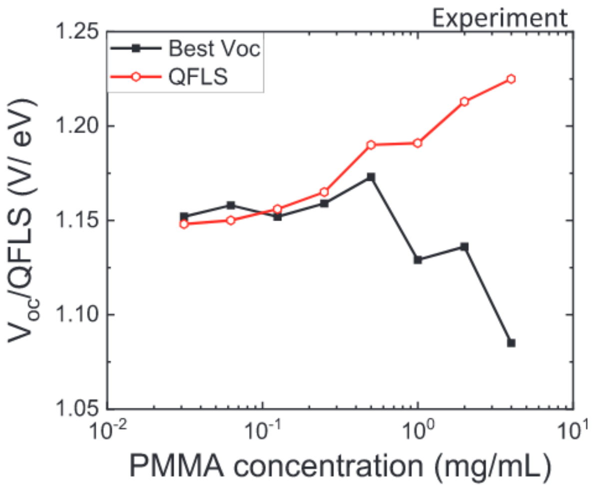
QFLS – excited e$^-$ in the CB and corresponding h$^+$ in the VB have different chemical potential.
Related to the internal potential of semiconductor.
Depends on the population of the exited e$^-$ and h$^+$.
Increasing the excited carrier population in the bands increases the difference in chemical potential between e$^-$ and h$^+$, which generates an internal voltage.

$$QFLS = k_B T \ln\left(PLQY \times \frac{\overset{\text{Generation current}}{\uparrow}\,J_G}{J_{0,rad}\,\underset{\text{Radiative current in the dark}}{\downarrow}}\right)$$



QFLS & V_{oc} are related – ideally QFLS ≈ V_{oc}
Bottlenecks are non-radiative recombination losses, non-selective charge collecting layers, resistances at the ETL/AL/HTL interfaces.

Quasi-Fermi Level Splitting (QFLS)

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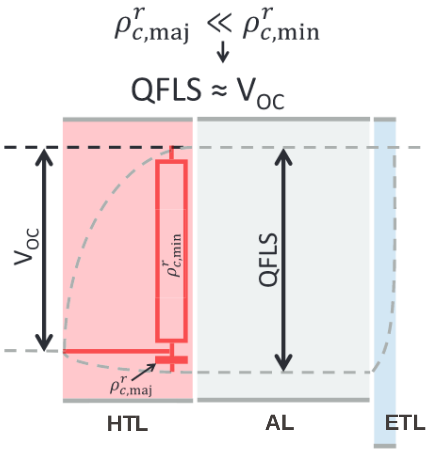
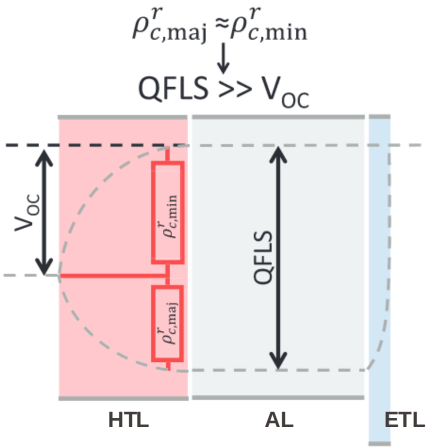
Metallic electrodes / degenerated doped semiconductors – QFL has to collapse





$$\frac{V_{oc}}{QFLS} = \frac{\rho^r_{c,min}}{\rho^r_{c,min} + \rho^r_{c,maj}} = S_{e,maj}$$

$\rho^r_{c,min} / \rho^r_{c,maj}$

Device contact resistances for majority and minority carries

$S_{e,maj} \in \{0,1\}$

Selectivity for majority carries

e$^-$/h$^+$ electrical current density at each point in the devices

$$J_{e/h} = J_{e/h,drift} + J_{e/h,diff} = -/+ \frac{\sigma_{e/h} \nabla E_{f,e/h}}{e}$$

V_{oc} steady state

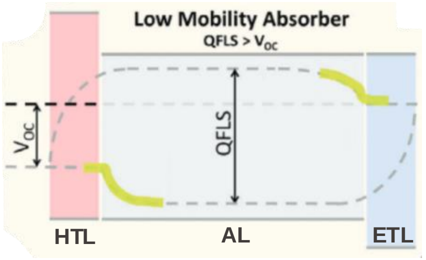
$$J = J_e + J_h = 0 \rightarrow J_h = -J_e = \boxed{J_R}$$ Recombination current

$$\frac{\sigma_h}{\sigma_e} = -\frac{\nabla E_{f,e}}{\nabla E_{f,h}}$$

At V_{oc}, e- and h+ QFL gradients are inversely proportional to the ratio of the carriers' conductivities.

V_{oc}-QFLS mismatch in PSC

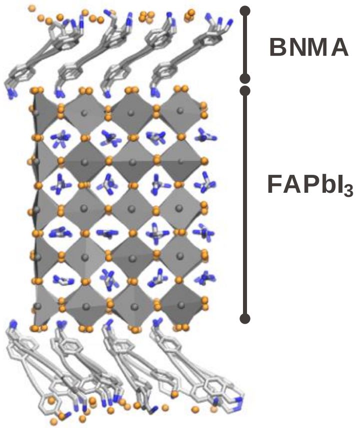
https://doi.org/10.1002/aenm.202303135
https://doi.org/10.1002/ange.202417432

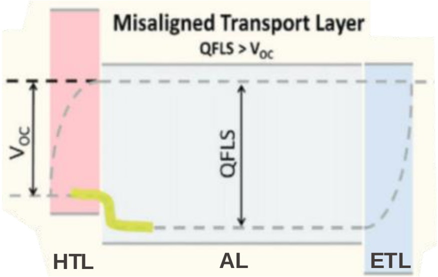


3D perovskite mobility ~1 $cm^2V^{-1}s^{-2}$

2D/3D perovskites

Very low out-of-plane mobility: carriers do not diffuse fast enough to the interface, and rapid non-radiative recombination





Large offset for the majority carriers

Contact region without energetic selectivity

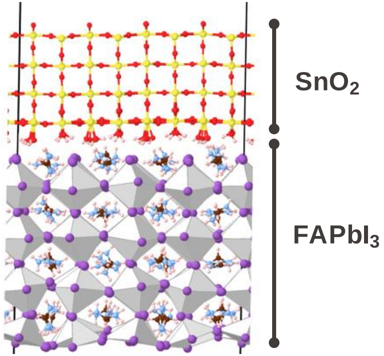
Passivator layer with strong dipole

Reducing of QFLS-V_{oc} mismatch

Energy injection barrier formation

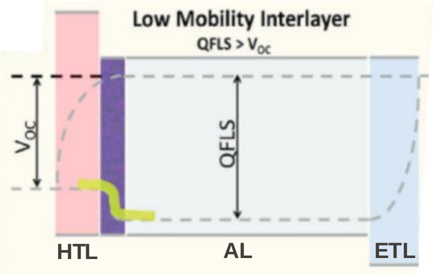
The majority carriers go back into perovskites

Built-in field reduction across the device



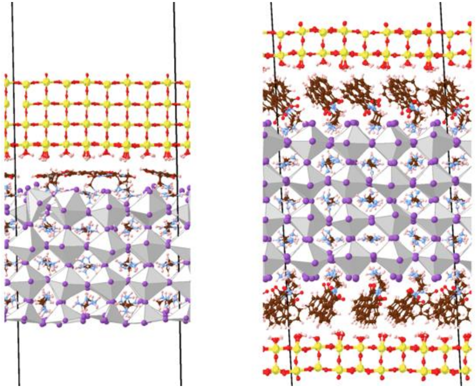
V_{oc}-QFLS mismatch in PSC

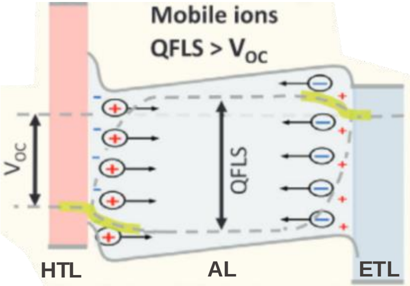
https://doi.org/10.1002/aenm.202303135
https://doi.org/10.1016/j.isci.2020.101415



Passivator layer thickness

Carriers' density at the interface become more similar, increasing the interface recombination





Light soaking and ion migrations

Charge accumulation that is detrimental for the internal functioning of the device; charges' resistivities become more similar

Charge carriers

Free electron model – free e$^-$ confined into a cubic box of side L

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2$$

Hamiltonian

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = Ae^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

Solution

$$\boldsymbol{k} = \left(\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L}\right)$$

Boundary conditions

$$\epsilon_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m}$$

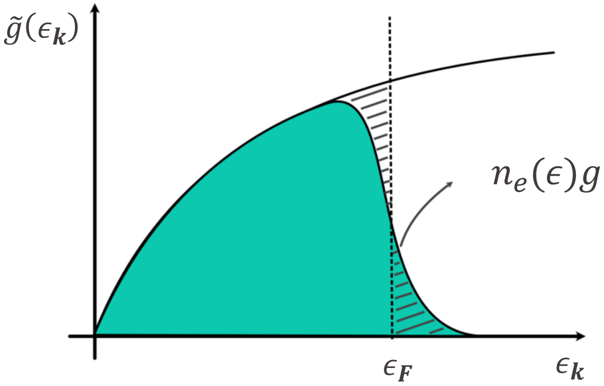
Energy eigenvalues

$$N(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{\frac{3}{2}} \quad \rightarrow$$

orbitals up to $\epsilon_{\boldsymbol{k}}$

$$g(\epsilon) = \frac{dN(\epsilon)}{d\epsilon} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\epsilon}$$

orbitals / $\epsilon_{\boldsymbol{k}}$ (Density of states)

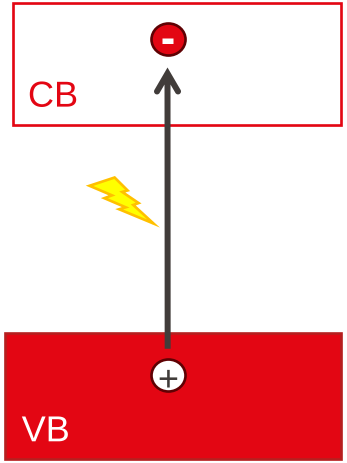


$$n_e(\epsilon)g(\epsilon) = n$$

$$n_e(\epsilon) = \frac{1}{e^{\frac{\epsilon-\epsilon_F}{k_B T}}}$$

Fermi-Dirac
distribution

Charge carriers



Low-temperature regime

$$\epsilon - \epsilon_F \gg k_B T$$

$$\epsilon_c = E_c + \frac{\hbar^2 k^2}{2m_e}$$

$$\epsilon_v = E_v - \frac{\hbar^2 k^2}{2m_h}$$

$$g_e(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\epsilon - E_c} \qquad g_h(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E_v - \epsilon}$$

Carriers' density at equilibrium:

$$n = \int_{E_c}^{\infty} g_e(\epsilon) n_e(\epsilon) = N_c e^{\frac{\epsilon_F - E_c}{k_B T}} \qquad p = \int_{-\infty}^{E_v} g_h(\epsilon) n_h(\epsilon) = N_h e^{\frac{E_v - \epsilon_F}{k_B T}}$$

$$n \cdot p = N_c N_v \, e^{\frac{-E_g}{k_B T}} = n_i^2 \qquad \epsilon_F = \frac{E_g}{2} + \frac{3}{4} k_B T \ln\left(\frac{m_h}{m_e}\right)$$

Carriers' density at out-of-equilibrium:

$$n = N_c e^{\frac{E_{Fc} - E_c}{k_B T}} \qquad p = N_h e^{\frac{E_v - E_{Fv}}{k_B T}}$$

$$n \cdot p = N_c N_v \, e^{\frac{\boxed{E_{Fc}} - E_c}{k_B T}} \, e^{\frac{E_v - \boxed{E_{Fv}}}{k_B T}}$$

Related to V_{oc}

How to simulate a material

Material – collection of interacting atoms

Nucleus: neutrons, protons (+)

Electrons (-)

$$H = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r})$$

Many-body Schrödinger equation

$$H\,\psi(\{\boldsymbol{r}\},\{\boldsymbol{R}\}) = E\psi(\{\boldsymbol{r}\},\{\boldsymbol{R}\})$$

→

Ab initio – no need of any empirical parameters

Nucleus: number (N_I), charge ($Z_I e$), mass (M_I)

Electrons: number (N), charge ($- e$), mass (m)

The Hamiltonian of a generical physical system is:

$$H = T_e(\{\boldsymbol{p}\}) + T_N(\{\boldsymbol{P}\}) + V_{ee}(\{\boldsymbol{r}\}) + V_{NN}(\{\boldsymbol{R}\}) + V_{eN}(\{\boldsymbol{r}\},\{\boldsymbol{R}\})$$

$$T_e(\{\boldsymbol{p}\}) = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m}$$

$$V_{ee}(\{\boldsymbol{r}\}) = \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

$$T_N(\{\boldsymbol{P}\}) = \sum_{I=1}^{N_I} \frac{\boldsymbol{P}_I^2}{2M_I}$$

$$V_{NN}(\{\boldsymbol{R}\}) = \frac{1}{2}\sum_{I\neq J} \frac{Z_I Z_J e^2}{|\boldsymbol{R}_i - \boldsymbol{R}_j|}$$

$$V_{eN}(\{\boldsymbol{r}\},\{\boldsymbol{R}\}) = -\sum_{i=1}^{N}\sum_{I=1}^{N_I} \frac{Z_I e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_I|}$$

How to simulate a material

Born-Oppenheimer approximation – $M_I \gg m$ ⟶

$$\psi(\{\boldsymbol{r}\},\{\boldsymbol{R}\}) = \psi(\{\boldsymbol{r}\};\{\boldsymbol{R}\})\,\phi(\{\boldsymbol{R}\})$$

$$H_e = T_e + V_{ee} + V_{eN} + V_{NN}$$

Many-body Schrödinger equation

$$H\,\psi(\{\boldsymbol{r}\},\{\boldsymbol{R}\}) = E\psi(\{\boldsymbol{r}\},\{\boldsymbol{R}\})$$

⟶

$$H_e\,\psi(\{\boldsymbol{r}\};\{\boldsymbol{R}\}) = E(\{\boldsymbol{R}\})\psi(\{\boldsymbol{r}\};\{\boldsymbol{R}\})$$

$\{\boldsymbol{R}\}$ is a parameter: fix potential energy surface

Using the Hellmann-Feynman theorem we can compute the force $\boldsymbol{F}_I$ acting on the nuclei

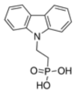
$$\begin{aligned}\frac{dE_\lambda}{d\lambda} = \frac{d}{d\lambda}\langle\psi_\lambda|H_\lambda|\psi_\lambda\rangle &= \left\langle\frac{d\psi_\lambda}{d\lambda}\middle|H_\lambda\middle|\psi_\lambda\right\rangle + \left\langle\psi_\lambda\middle|H_\lambda\middle|\frac{d\psi_\lambda}{d\lambda}\right\rangle + \left\langle\psi_\lambda\middle|\frac{dH_\lambda}{d\lambda}\middle|\psi_\lambda\right\rangle\\ &= E_\lambda\left\langle\frac{d\psi_\lambda}{d\lambda}\middle|\psi_\lambda\right\rangle + E_\lambda\left\langle\psi_\lambda\middle|\frac{d\psi_\lambda}{d\lambda}\right\rangle + \left\langle\psi_\lambda\middle|\frac{dH_\lambda}{d\lambda}\middle|\psi_\lambda\right\rangle = E_\lambda\frac{d}{d\lambda}\langle\psi_\lambda|\psi_\lambda\rangle + \left\langle\psi_\lambda\middle|\frac{dH_\lambda}{d\lambda}\middle|\psi_\lambda\right\rangle\\ &= \left\langle\psi_\lambda\middle|\frac{dH_\lambda}{d\lambda}\middle|\psi_\lambda\right\rangle\end{aligned}$$

$$\boldsymbol{F}_I = -\frac{dE(\{\boldsymbol{R}\})}{d\boldsymbol{R}_I} = -\left\langle\psi(\{\boldsymbol{r}\};\{\boldsymbol{R}\})\middle|\frac{dH_e}{d\boldsymbol{R}_I}\middle|\psi(\{\boldsymbol{r}\};\{\boldsymbol{R}\})\right\rangle = -\langle\psi(\{\boldsymbol{r}\};\{\boldsymbol{R}\})|\nabla_{\boldsymbol{R}_I}H_e|\psi(\{\boldsymbol{r}\};\{\boldsymbol{R}\})\rangle$$

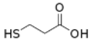
Molecular dynamics (MD)

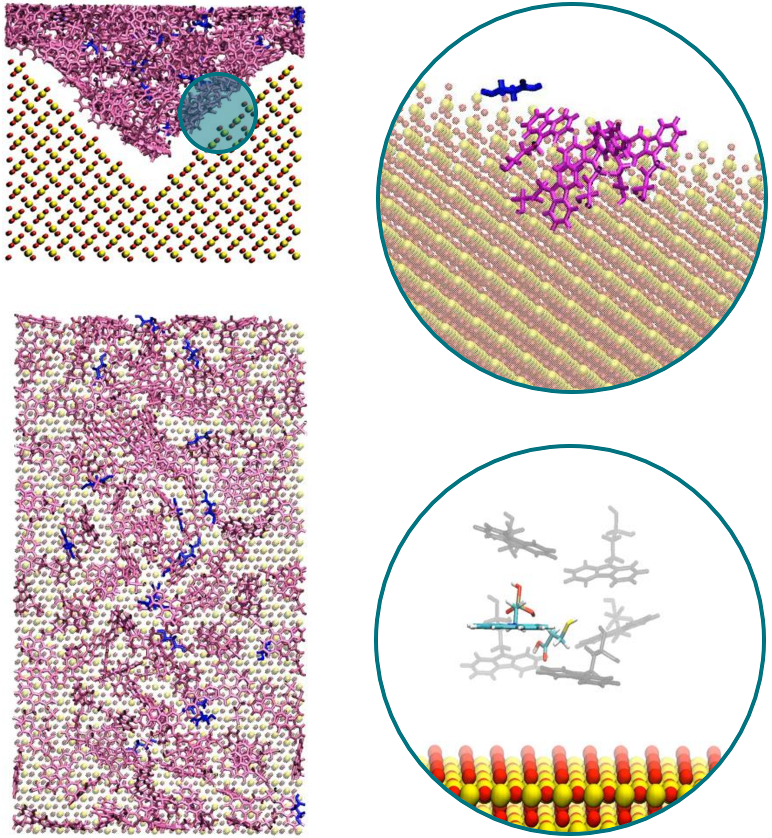
Deterministic trajectories that sample the phase space according to statistical mechanics.

2PACz



MPA





Classical MD – atoms are classical spheres that are moved according the Newton equation.

$$\boldsymbol{F}_I = -\nabla_{\boldsymbol{R}_I} U(\{\boldsymbol{R}_I\})$$

$U(\{\boldsymbol{R}_I\})$ **–** classical potential: all the physics is embedded in the potential. No quantum mechanics is involved (no charge transfer, tunnelling, charge hopping…).

Ab initio MD – atoms are quantum objects with electron density and nuclei.

$$\boldsymbol{F}_I = -\left\langle \psi(\{\boldsymbol{r}\};\{\boldsymbol{R}\}) \middle| \nabla_{\boldsymbol{R}_I} H_e \middle| \psi(\{\boldsymbol{r}\};\{\boldsymbol{R}\}) \right\rangle$$

$\nabla_{\boldsymbol{R}_I} H_e$ **–** ground state for the electrons is computed at each step of the MD in the Born-Oppenheimer approximation after moving the nuclei.

Density Functional Theory (DFT)

DFT – ground state method to solve the many-body Schrödinger equation
From 3N (N = # electrons) variable to 3 (electron density in 3D).
Based on the two Höhenberg-Kohn theorems.

Theorem I – For any system of interacting particles in an external potential V_{ext}, V_{ext} is determined uniquely, apart from a constant, by the ground state density $n_0(\boldsymbol{r})$.

$$\begin{tikzcd}
V_{ext} \arrow[d] & n_o(\boldsymbol{r}) \arrow[l, "\text{H-K}"'] \\
\psi_i(\{\boldsymbol{r}\}) \arrow[r] & \psi_o(\{\boldsymbol{r}\}) \arrow[u]
\end{tikzcd}$$

Theorem II – For any external potential V_{ext}, it is possible to define the energy of the system as a functional of the density $n(\boldsymbol{r})$: $E = E[n]$. The ground state energy of the system is the minimum value of this functional and the density that minimizes $E[n]$, keeping the # of electrons *N* constant, is the ground state density $n_0(\boldsymbol{r})$.

Density Functional Theory (DFT)

B-O approximation – $H_e = T_e + V_{ee} + V_{eN} + V_{NN}$

DFT – $V_{eN} = V_{ext} = \sum_i v_{ext}(\boldsymbol{r}_i)$

$$E[n] = T_e[n] + V_{ee}[n] + \int d\boldsymbol{r}\, v_{ext}(\boldsymbol{r})n(\boldsymbol{r}) + E_{NN} = \bigcirc\!\!\!\!\!\!F[n] + \int d\boldsymbol{r}\, v_{ext}(\boldsymbol{r})n(\boldsymbol{r}) + E_{NN}$$

no explicit universal functional form

Kohn-Sham approach – one-to-one correspondence between electronic density of the interacting system and that of some non-interacting system with an opportune fictitious potential.

$$E[n] = T_s[n] + \int d\boldsymbol{r}\, v_{ext}(\boldsymbol{r})n(\boldsymbol{r}) + E_{Hartree}[n] + E_{NN} + E_{xc}[n]$$

$$E_{Hartree}[n] = \frac{e^2}{2}\int d\boldsymbol{r}d\boldsymbol{r}'\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

Classical Coulomb
$n(\boldsymbol{r})$ self-interaction

$$E_{xc}[n] = T[n] - T_s[n] + V_{ee}[n] - E_{Hartree}[n]$$

Exchange-correlation:
many-body effects

Density Functional Theory (DFT)

***N* –** # of electrons in the system

$$n(\boldsymbol{r}) = \sum_{i=1}^{N} |\psi_i(\boldsymbol{r})|^2$$

$$T_s[n] = \frac{1}{2}\sum_{i=1}^{N} |\nabla\psi_i(\boldsymbol{r})|^2$$

$$H_{KS} = -\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(\boldsymbol{r}) + e^2\int d\boldsymbol{r}'\frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \boxed{v_{xc}(\boldsymbol{r})} = -\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(\boldsymbol{r})$$

non-classical electron interaction

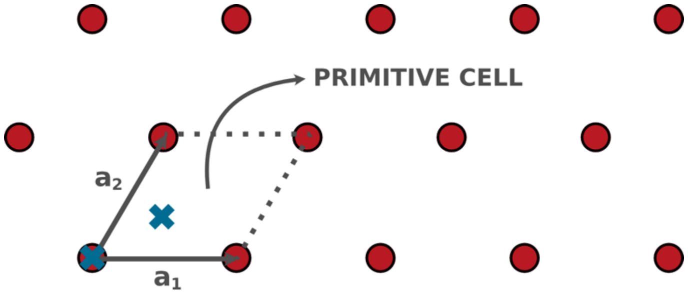
$$v_{xc}[n] = \frac{\delta E_{xc}[n]}{\delta n(\boldsymbol{r})}$$

Many-body interaction problem has been reduced to the computation of independent-particle equation to be resolved self-consistently with the resulting $n(\boldsymbol{r})$.

$$H_{KS}\,\psi_i(\boldsymbol{r}) = \epsilon_i\,\psi_i(\boldsymbol{r})$$

Up to now, no approximation has been done.

Plane wave (PW) basis set



Crystal

$$\boldsymbol{R} = n_1\boldsymbol{r_1} + n_2\boldsymbol{r_2} + n_3\boldsymbol{r_3}\,,\ n_i \in \mathbb{Z}$$

Reciprocal lattice

$$\boldsymbol{G} = l_1\boldsymbol{k_1} + l_2\boldsymbol{k_2} + l_3\boldsymbol{k_3}\,,\ l_i \in \mathbb{Z}$$

$$\boldsymbol{r_i} \cdot \boldsymbol{k_j} = 2\pi\delta_{ij}$$

Bloch vector in the first Brillouin zone

$$\psi_{i,\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} c_{i,\,\boldsymbol{k}+\boldsymbol{G}}\ \phi_{i,\,\boldsymbol{k}+\boldsymbol{G}} = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{G}} c_{i,\,\boldsymbol{k}+\boldsymbol{G}}\ e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}}$$

band index

generic vector of the reciprocal lattice

PW are the simplest basis set for the H_{KS} eigenstates expansion that allows to transform the KS equations in a matrix diagonalization problem:

$$\sum_{\boldsymbol{G}} \left(\langle\, \phi_{i,\,\boldsymbol{k}+\boldsymbol{G}} | \nabla_{\boldsymbol{R}_I} H_{KS} |\, \phi_{i,\,\boldsymbol{k}+\boldsymbol{G'}} \rangle - \epsilon_{i,\boldsymbol{k}} \delta_{\boldsymbol{G},\boldsymbol{G'}} \right) c_{i,\,\boldsymbol{k}+\boldsymbol{G'}} = 0$$

SOC

k • p approach for III-V semiconductors

One-electron Sch. equation

$$\left[-\frac{\hbar^2}{2m_0}\nabla^2+\underbrace{\frac{\hbar}{4m_0^2c^2}(\boldsymbol{\sigma}\times\boldsymbol{\nabla}V)\cdot(-i\hbar\boldsymbol{\nabla})}_{\text{Pauli SOC}}+\underbrace{V(\boldsymbol{r})}_{\text{Crystalline + ext. potential}}\right]\overbrace{\Psi(\boldsymbol{r})}^{\text{2 components spinor}}=E\Psi(\boldsymbol{r})$$

$$\Psi(\boldsymbol{r})=\sum_{\mu}\underbrace{\psi_\mu(\boldsymbol{r})}_{\text{Envelope functions}}\underbrace{U_\mu(\boldsymbol{r})}_{\text{Bravais lattice periodic functions}}$$

$$-\frac{\hbar^2}{2m_0}\boldsymbol{\nabla}^2\psi_\mu(\boldsymbol{r})-\frac{i\hbar}{m_0}\sum_\nu\boldsymbol{\pi}_{\mu\nu}(\boldsymbol{r})\cdot\boldsymbol{\nabla}\psi_\nu(\boldsymbol{r})+\sum_\nu H_{\mu\nu}(\boldsymbol{r})\psi_\nu(\boldsymbol{r})=E\psi_\mu(\boldsymbol{r})$$

$$H_{\mu\nu}(\boldsymbol{r})=T_{\mu\nu}+H^{SO}_{\mu\nu}(\boldsymbol{r})+V_{\mu\nu}(\boldsymbol{r})$$

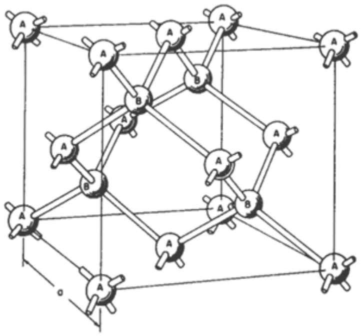
$$H^{bulk}_{\mu\nu}=\frac{1}{\Omega_0}\int \mathrm{d}^3\boldsymbol{r}\,U^{*T}_\mu(\boldsymbol{r})H^{bulk}(\boldsymbol{r})U_\nu(\boldsymbol{r})$$

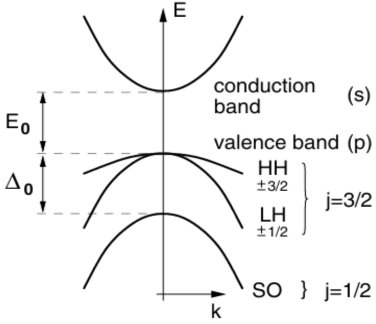
SOC

k • p approach for III-V semiconductors

- In III-V semiconductors compound like GaAs there are 8 outer electrons per unit cell which contribute to chemical bonds.
- The 8 outermost electrons hybridize to form tetrahedral bonds between one kind of atoms (Ga) and its four nearest neighbors (As).
- As a result, bonding (p-like, 6 electrons) and antibonding orbitals (s-like, 2 electrons) form the bands of the semiconductors.

- In absence of SOC the top of the valence (at Γ) band formed by the three p-like orbitals is six-fold degenerate.
- SOC splits the six-fold degenerate state and gives rise to a quadruplet (J=3/2) and a doublet (J=1/2).



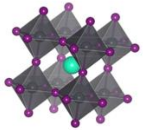


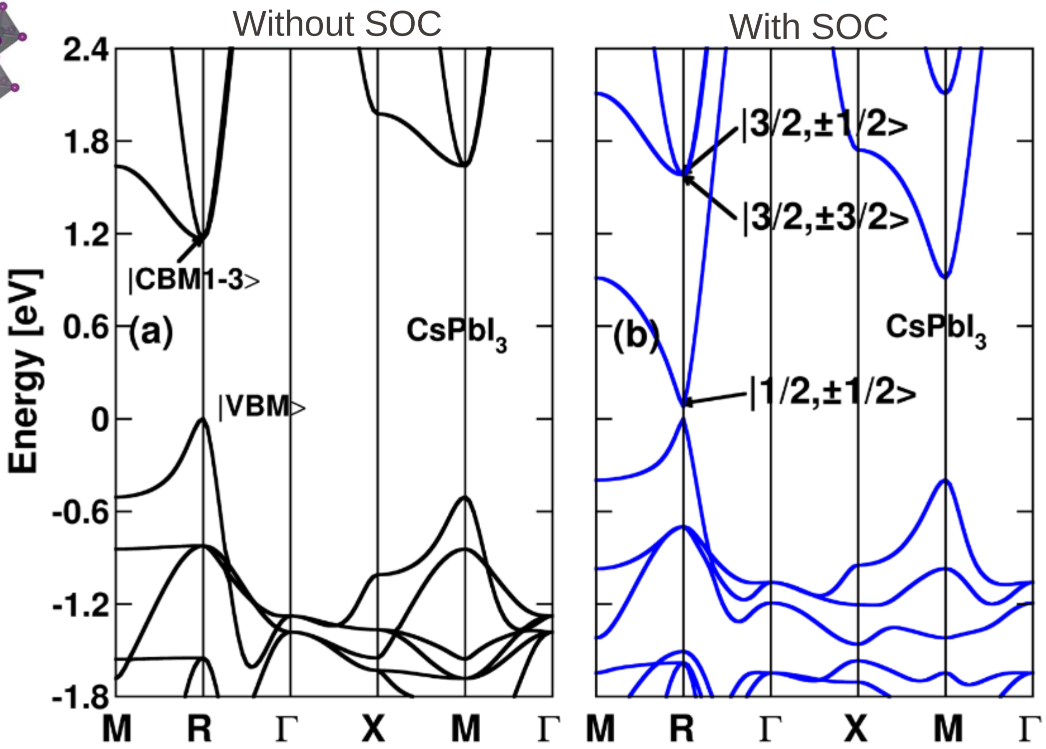
Spin-orbit gap

$$\Delta_0 = \frac{3i\hbar}{4m_0^2c^2}\langle X|\partial_x V\, p_y - \partial_y V\, p_x|Y\rangle$$

$$\left|\frac{1}{2},\frac{1}{2}\right\rangle_{\mathrm{EL}} = |S'\uparrow'\rangle\,,$$
$$\left|\frac{1}{2},-\frac{1}{2}\right\rangle_{\mathrm{EL}} = i\,|S'\downarrow'\rangle\,,$$
$$\left|\frac{3}{2},\frac{3}{2}\right\rangle_{\mathrm{HH}} = \sqrt{1/2}\,|(X'+iY')\uparrow'\rangle\,,$$
$$\left|\frac{3}{2},-\frac{3}{2}\right\rangle_{\mathrm{HH}} = i\sqrt{1/2}\,|(X'-iY')\downarrow'\rangle\,,$$
$$\left|\frac{3}{2},\frac{1}{2}\right\rangle_{\mathrm{LH}} = i\sqrt{1/6}\,|(X'+iY')\downarrow'\rangle - i\sqrt{2/3}\,|Z'\uparrow'\rangle\,,$$
$$\left|\frac{3}{2},-\frac{1}{2}\right\rangle_{\mathrm{LH}} = \sqrt{1/6}\,|(X'-iY')\uparrow'\rangle + \sqrt{2/3}\,|Z'\downarrow'\rangle\,,$$
$$\left|\frac{1}{2},\frac{1}{2}\right\rangle_{\mathrm{SO}} = \sqrt{1/3}\,(|(X'+iY')\downarrow'\rangle + |Z'\uparrow'\rangle)\,,$$
$$\left|\frac{1}{2},-\frac{1}{2}\right\rangle_{\mathrm{SO}} = -i\sqrt{1/3}\,(|(X'-iY')\uparrow'\rangle - |Z'\downarrow'\rangle)\,.$$

SOC effects in CsPbI$_3$



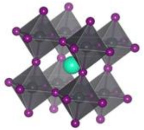


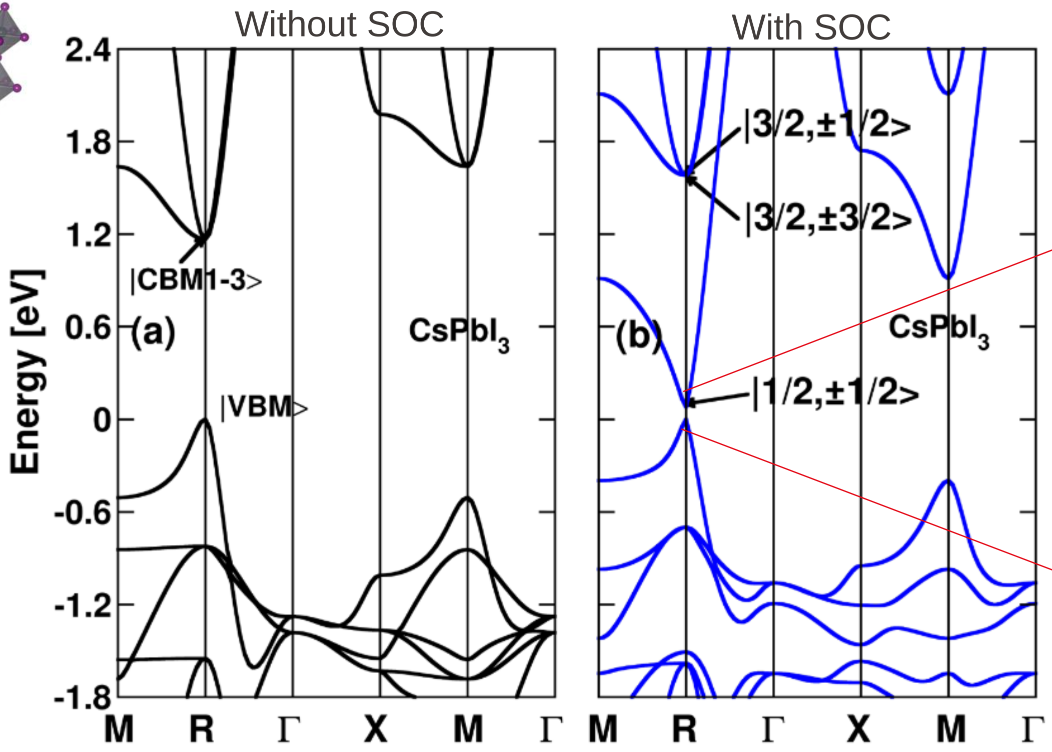
room-temperature Pm3m cubic phase

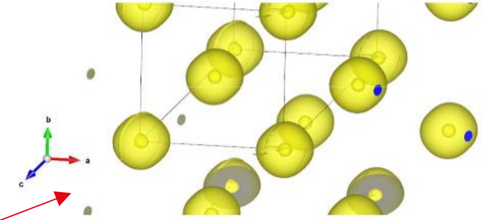
- The calculated band-gap at GGA-PBE level is in good agreement with experiments.
  SOC leads to a correction of about 1.1 eV
- Conduction band edge with SOC is the 2-fold degenerate **split-off (SO)** state. This leads to isotropic and strong optical transitions with the even s-like valence band edge states.

dx.doi.org/10.1021/jz401532q | J. Phys. Chem. Lett. 2013, 4, 2999−3005

SOC

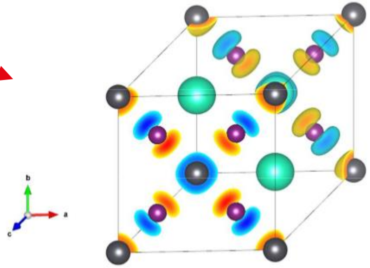






CBM $|1/2,1/2\rangle$

$$M_{\mathrm{VBM,CBM}} = \left| \left\langle \psi_{\mathrm{VBM}} \middle| -i\hbar \frac{\partial}{\partial x_i} \middle| \psi_{\mathrm{CBM}} \right\rangle \right|$$



VBM $|S\rangle$

room-temperature Pm3m cubic phase

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