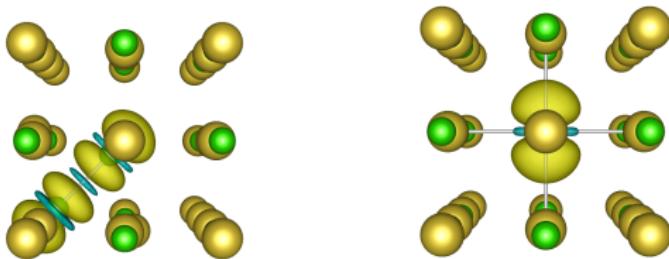


# Interpretation of self-trapped excitons in rock salt halides from a vibronic coupling perspective: A first step to simulate real-time diffusion

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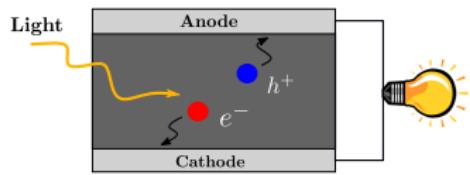


25th International Conference on the Jahn-Teller Effect  
14th - 18th of February 2023



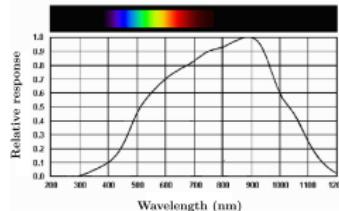
# Optical Properties and EXCITONS

- Developing modern optoelectronic devices → Interpretation of optical spectra

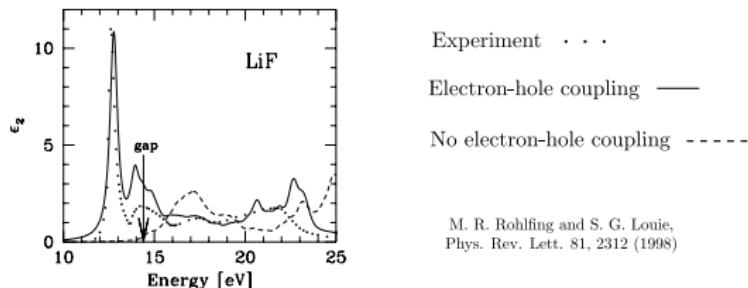


**Photovoltaic cell**

1. Light absorption
2. Electron-hole formation
3. Charge transport to electrodes
4. Generation of electricity



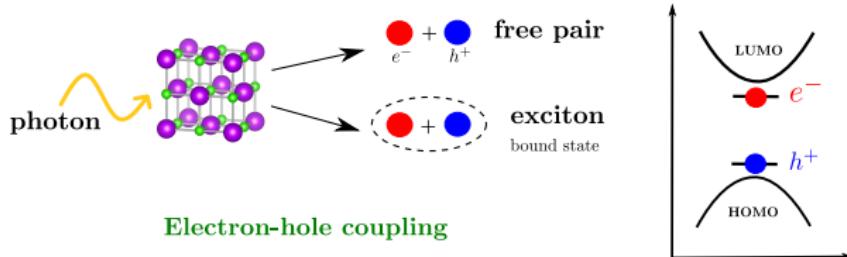
- Difficult task as influenced by multiple effects: impurities, geometry distortions (electron-phonon coupling), strain, temperature, electron-hole coupling ...
- Interesting example: **Alkali-Halides**: AX, A = Li, Na, K, ..., X = F, Cl, Br, I ...



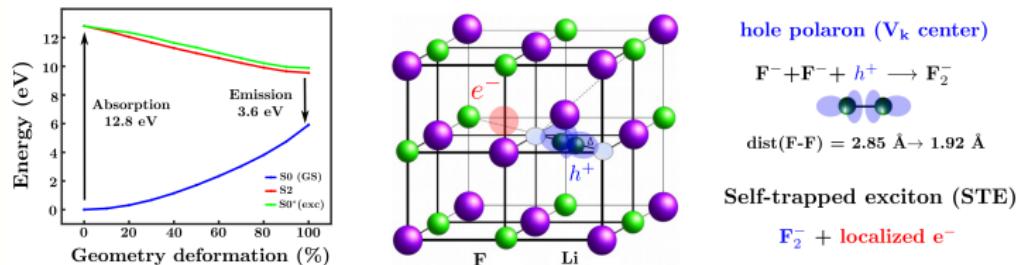
Absorption in LiF below energy gap due to an EXCITON (electron-hole coupling)

# Optical Properties and EXCITONS

- **EXCITONS:** bound state formed by **excited electron** + **valence hole**
- Interacting charged particles  $\rightarrow E_{\text{exciton}} < E_{\text{gap}}$  (**exciton footprint**)



- **Self-trapped exciton** stabilized due to geometry deformation (**elect-phon**)



Electron-phonon influence the spectra  $\rightarrow$  red-shift

# Method to simulate STE: Second-Principles DFT

- Proposal to simulate EXCITONS → Second-Principles (**model** based on DFT)
- **One-electron** hamiltonian (extension TB model) in **Wannier** functions basis

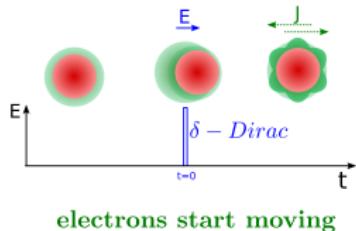
$$h_{ab}^s = \underbrace{\gamma_{ab}^{\text{RAG,sr}}}_{\begin{array}{l} \text{short-range} \\ \text{tight-binding} \end{array}} + \underbrace{\delta\gamma_{ab}^{\text{el-lat-sr}}(\{\vec{u}_\lambda\})}_{\begin{array}{l} \text{electron-lattice} \\ \text{(out of RAG)} \end{array}} + \sum_{a'b'} (D_{a'b'}^U \underbrace{U_{aba'b'}}_{\text{Hubbard}} \pm D_{a'b'}^I \underbrace{I_{aba'b'}}_{\text{Stoner}}) + \underbrace{\gamma_{ab}^{\text{lr}}}_{\begin{array}{l} \text{long-range} \\ \text{electrostatic} \end{array}}$$

$$\delta\gamma_{ab}^{\text{el-lat}} = \sum_{\lambda v} \left[ \underbrace{f_{ab,\lambda v}^T}_{\begin{array}{l} \text{linear} \\ \text{coupling} \end{array}} \delta\vec{r}_{\lambda v} + \delta\vec{r}_{\lambda v}^T \underbrace{\overleftrightarrow{g}_{ab,\lambda v}}_{\begin{array}{l} \text{quadratic} \\ \text{coupling} \end{array}} \delta\vec{r}_{\lambda v} \right] \quad (\text{restricted to a single bond})$$

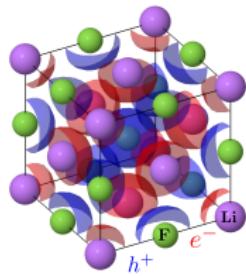
- **Electron-electron** (Hubbard-Stoner) → Electron-hole coupling
- **Electron-lattice** (vibronic) → geometry deformation + charge localization
- **Real-Time TDDFT** → Exciton formation (absorption)  
→ Study STE dynamics (polaron diffusion)

# Real-Time Second-Principles TDDFT: Absorption of LiF

Perturbation by an instant pulse



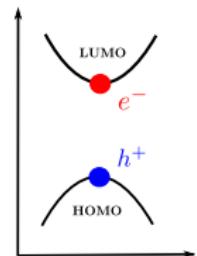
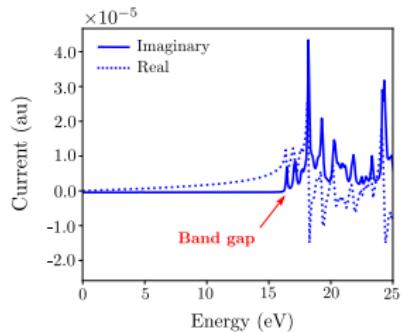
Electron density difference  
right after pulse - ground state



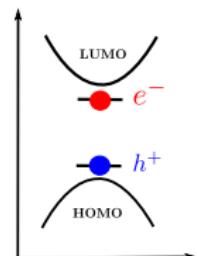
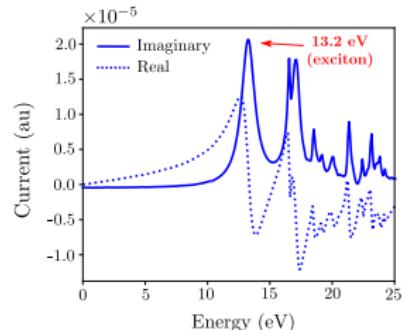
electron in conduction band  $\rightarrow$  Li character

hole in valence band  $\rightarrow$  F character

No electron-hole coupling

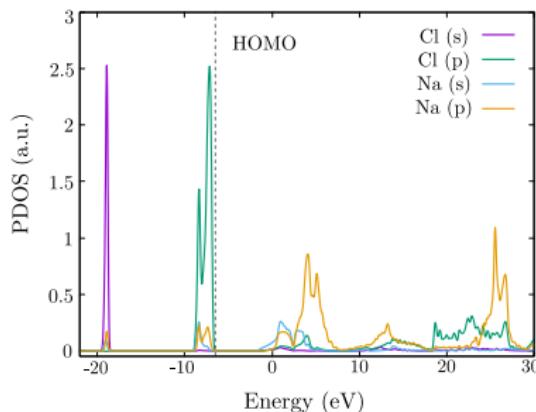


Electron-hole coupling



# STH in Alkali Halides: Vk center vs octahedral distortion

- In Alkali Halides the **STE**<sup>1</sup> is formed by a **STH ( $h^+$ )** and a **localized  $e^-$** .
- The **STH** has ***p* character of Cl** in **NaCl** (studied example).
- **Cl** has ***O<sub>h</sub>* coordination** in NaCl  $\longrightarrow p \in T_{1u}$  in ***O<sub>h</sub>*** (degenerate,  **$h^+$  unstable**).



$Q$  mode reduces symmetry (vibronic coupling)

$$h(r, Q) = h^0(r) + fQ; \quad f = \langle T_{1u} | \frac{dh}{dQ} | T_{1u} \rangle$$

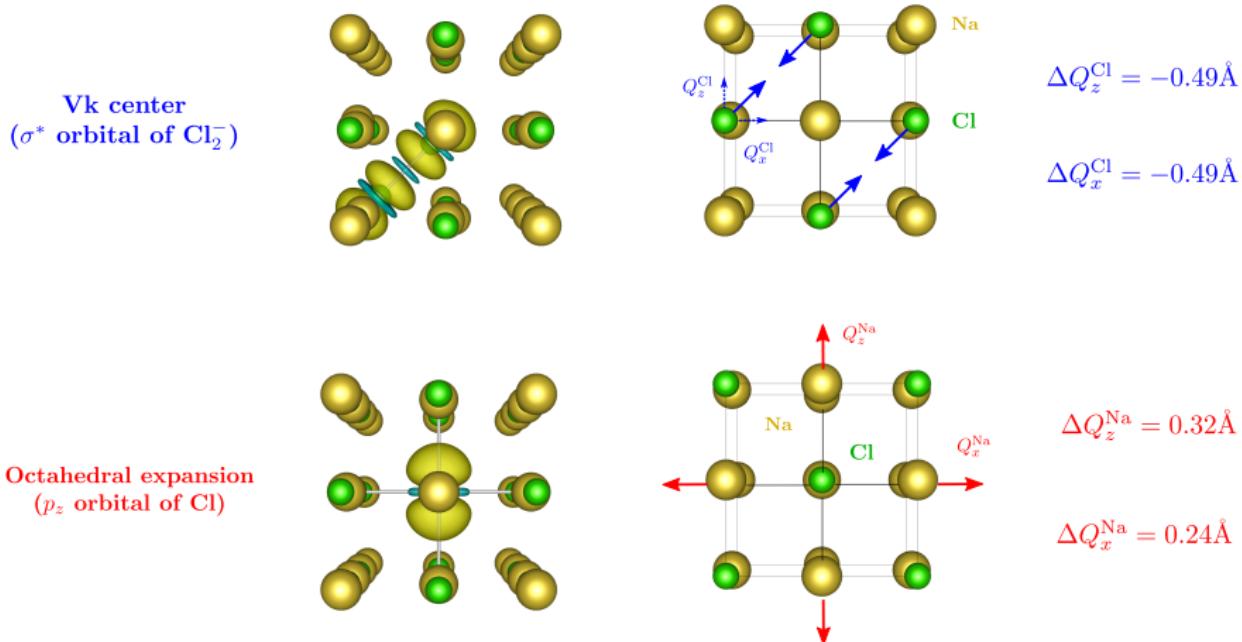
$$Q \in T_{1u} \otimes T_{1u} = \underbrace{A_{1g} + E_g}_{\text{main ones}} + [T_{1g}] + T_{2g}$$

$h^+$  localized (STH) and degeneration disappears

<sup>1</sup>STE: Self-Trapped Exciton. STH: Self-Trapped Hole

# STH in Alkali Halides: Vk center vs octahedral distortion

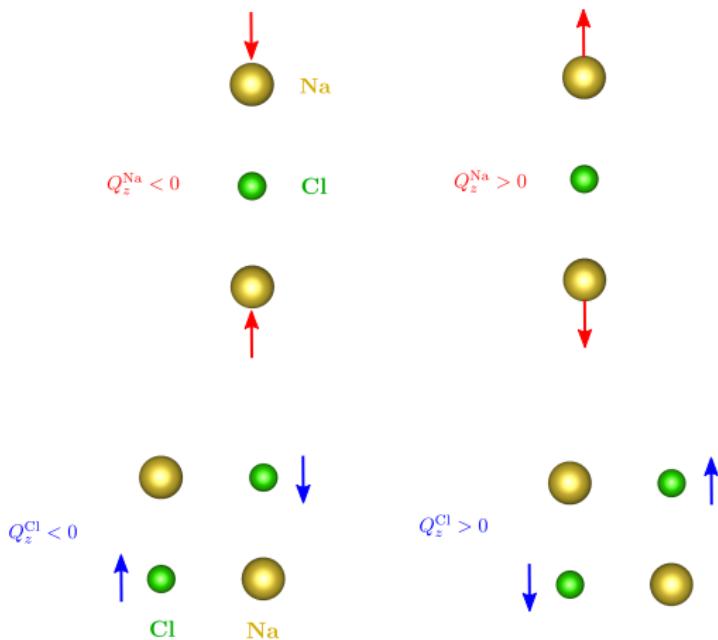
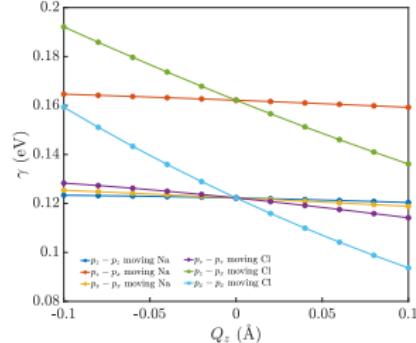
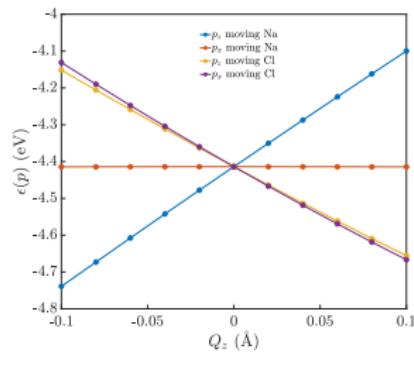
- However, this is not the distortion observed in nature (**Vk center** instead).



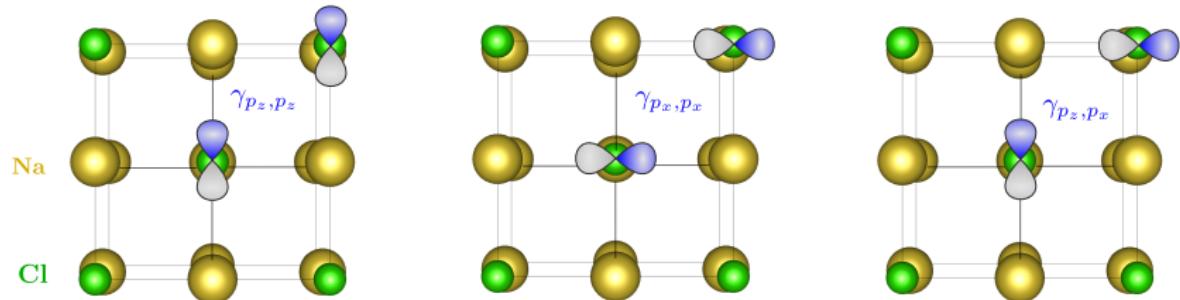
- Let's analyze the origin with a simple model based on wannier functions.

# STH in Alkali Halides: $V_k$ center vs octahedral distortion

- Dependence (**linear**) of the **self-interaction energy** ( $\epsilon$ ) and the first neighbour **hopping** ( $\gamma$ ) of **Cl**  $2p$  wannier orbitals with **movements in  $z$**  ( $Q_z$ ) of **Na** and **Cl**.



# STH in Alkali Halides: Vk center vs octahedral distortion



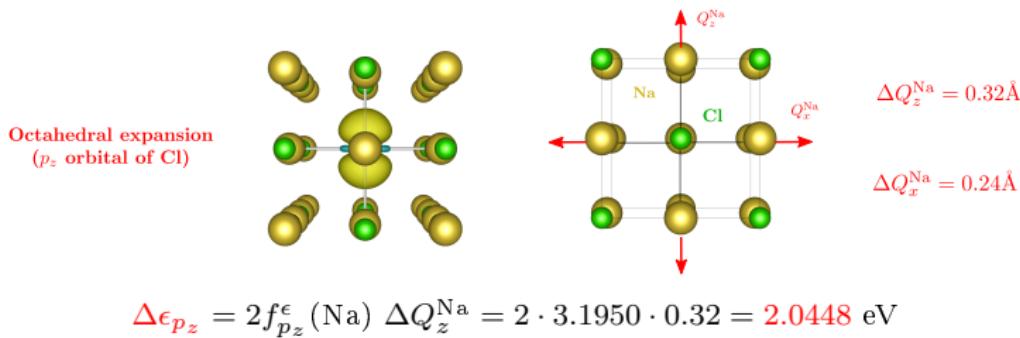
Atom moved	$f_{p_z}^\epsilon$	$f_{p_x}^\epsilon$	$f_{p_z,p_z}^\gamma$	$f_{p_z,p_x}^\gamma$	$f_{p_x,p_x}^\gamma$
Na	3.1950	0.0	-0.0149	-0.0270	-0.0329
Cl	-2.5196	-2.6785	-0.0714	-0.2802	-0.3273

Table: First order vibronic-coupling (electron-lattice) terms in eV/Å

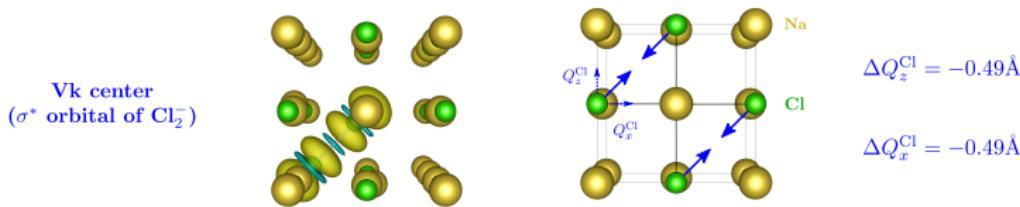
- **Octahedral distortion** (Na movement) dominated by  $f_{p_z}^\epsilon$  (Na).
- **Vk distortion** (Cl movement) dominated by  $f_{p_z}^\epsilon$  (Cl) and  $f_{p_x}^\epsilon$  (Cl).

# Conclusions

- $f_{p_z}^{\epsilon}(\text{Na}) > 0 \rightarrow Q_z^{\text{Na}} > 0$  favours localization (**elongated octahedron**).



- $f_{p_z}^{\epsilon}(\text{Cl}) < 0 \rightarrow Q_z^{\text{Cl}} < 0$  favours localization ( **$\text{Cl}_2^-$  dimer, Vk center**).



- First order vibronic coupling main effect for which **Vk center** is more stable.