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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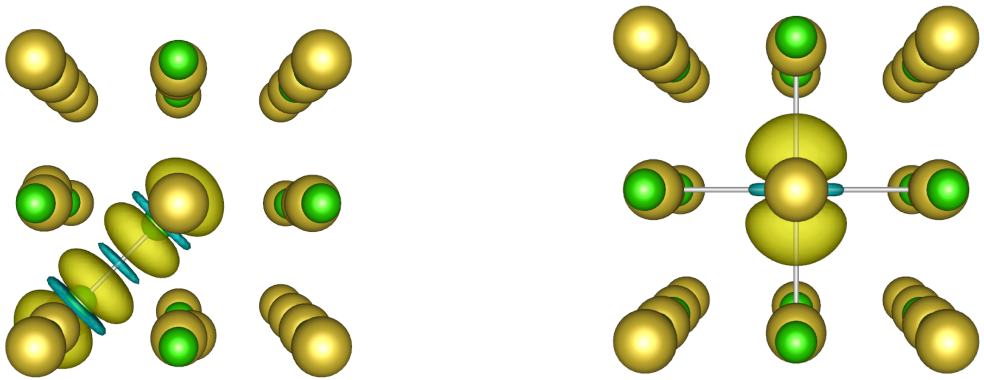

25th International Conference on the Jahn-Teller Effect
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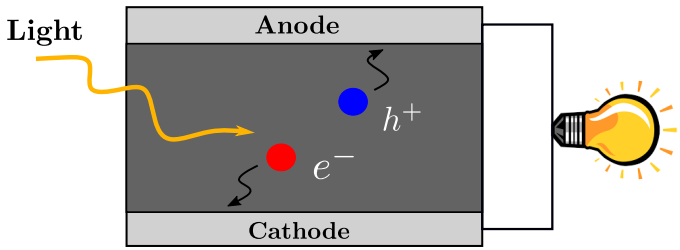
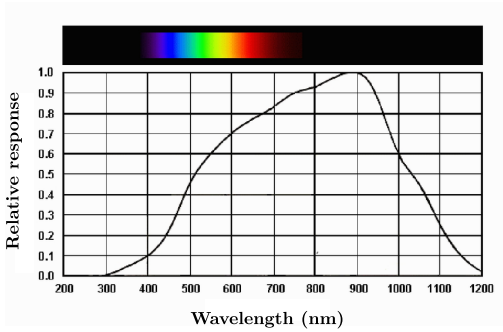
Optical Properties and EXCITONS

- Developing modern optoelectronic devices $\longrightarrow$ Interpretation of optical spectra

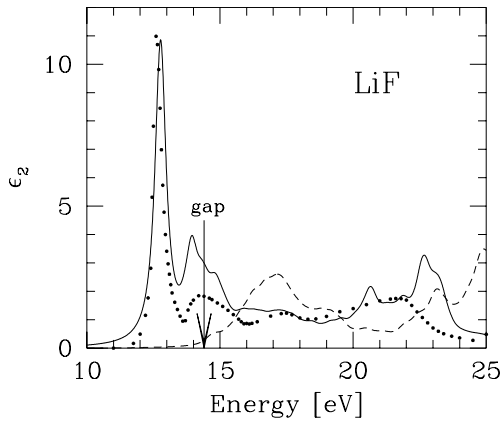


Photovoltaic cell

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 ...



Experiment · · ·

Electron-hole coupling ——

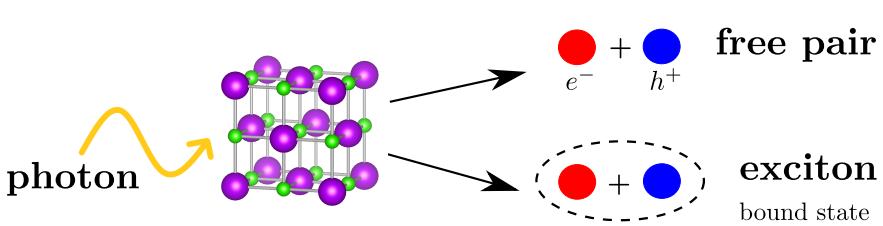
No electron-hole coupling - - - - -

M. R. Rohlfing and S. G. Louie,
Phys. Rev. Lett. 81, 2312 (1998)

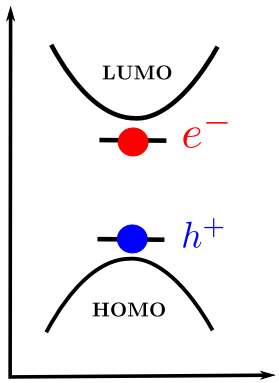
Absorption in **LiF** below energy gap due to an EXCITON (electron-hole coupling)

Optical Properties and EXCITONS

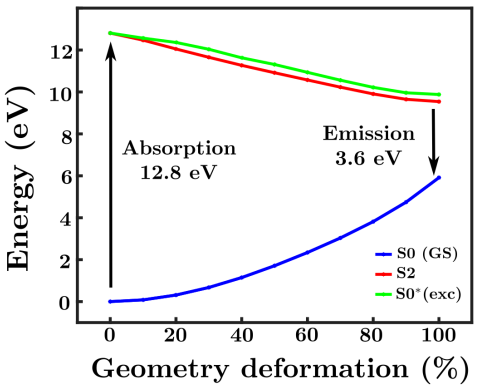
- **EXCITONS:** bound state formed by excited electron + valence hole
- Interacting charged particles $\longrightarrow$ $E_{\text{exciton}} < E_{\text{gap}}$ **(exciton footprint)**

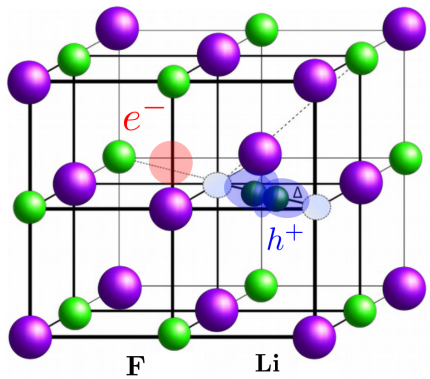


Electron-hole coupling



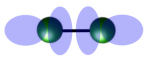
- **Self-trapped exciton** stabilized due to geometry deformation (elect-phon)





hole polaron (V_k center)

$\mathbf{F^- + F^- + h^+ \longrightarrow F_2^-}$



dist(F-F) = 2.85 Å→ 1.92 Å

Self-trapped exciton (STE)

$\mathbf{F_2^-}$ + **localized e$^-$**

Electron-phonon influence the spectra $\longrightarrow$ **red-shift**

Method to simulate STE: Second-Principles DFT

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

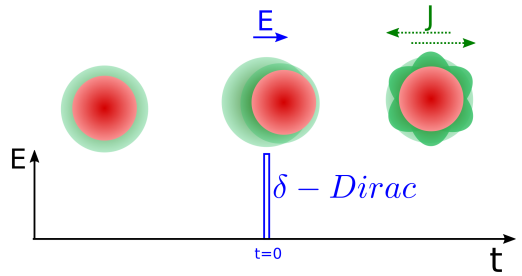
$$h^s_{ab} = \underbrace{\gamma^{\text{RAG,sr}}_{ab}}_{\substack{\text{short-range}\\ \text{tight-binding}}} + \underbrace{\delta\gamma^{\text{el-lat-sr}}_{ab}(\{\vec{u}_\lambda\})}_{\substack{\text{electron-lattice}\\ \text{(out of RAG)}}} + \sum_{a'b'}(D^U_{a'b'}\underbrace{U_{aba'b'}}_{\text{Hubbard}} \pm D^I_{a'b'}\underbrace{I_{aba'b'}}_{\text{Stoner}}) + \underbrace{\gamma^{\text{lr}}_{ab}}_{\substack{\text{long-range}\\ \text{electrostatic}}}$$

$$\delta\gamma^{\text{el-lat}}_{ab} = \sum_{\lambda v}[\underbrace{\vec{f}^T_{ab,\lambda v}}_{\substack{\text{linear}\\ \text{coupling}}}\delta\vec{r}_{\lambda v} + \delta\vec{r}^T_{\lambda v}\underbrace{\overleftrightarrow{g}_{ab,\lambda v}}_{\substack{\text{quadratic}\\ \text{coupling}}}\delta\vec{r}_{\lambda v}] \quad \text{(restricted to a single bond)}$$

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

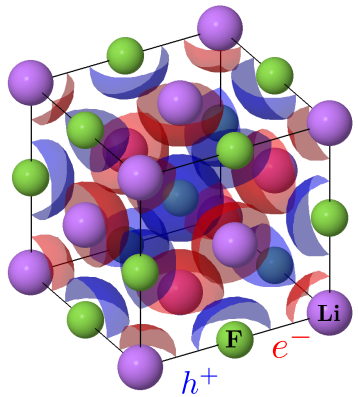
Real-Time Second-Principles TDDFT: Absorption of LiF

Perturbation by an instant pulse



electrons start moving

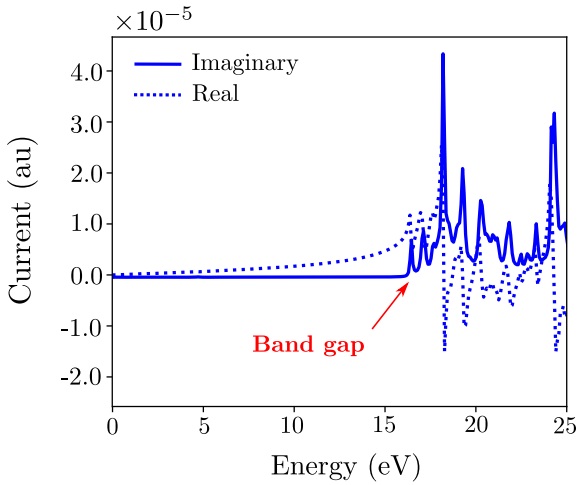
Electron density difference right after pulse - ground state

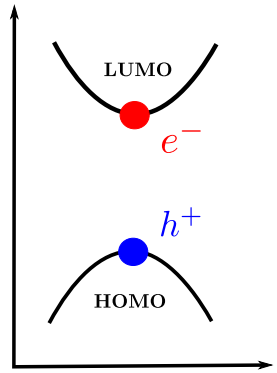


electron in **conduction band** $\longrightarrow$ **Li character**

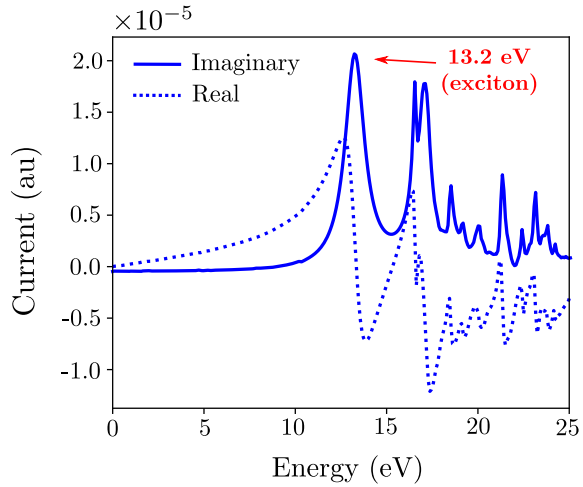
hole in **valence band** $\longrightarrow$ **F character**

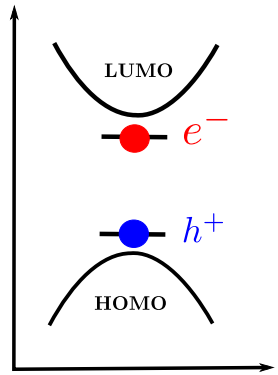
No electron-hole coupling





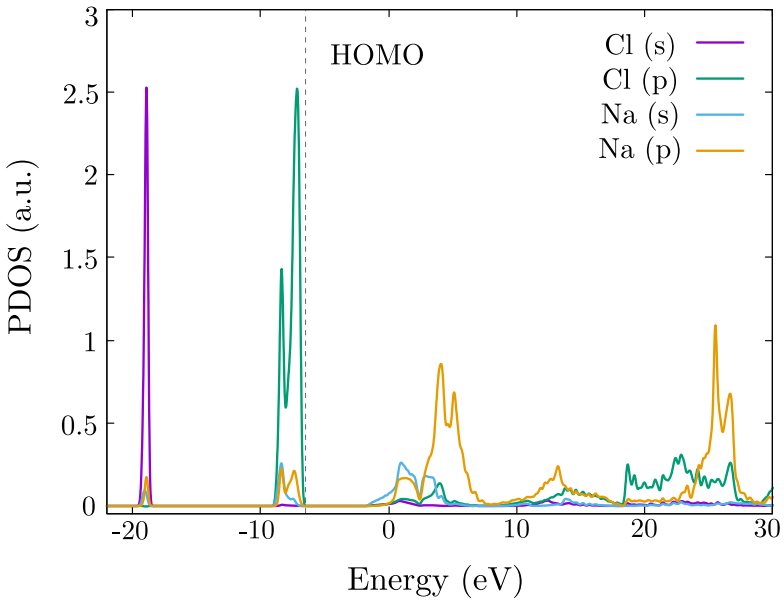
Electron-hole coupling





STH in Alkali Halides: Vk center vs octahedral distortion

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



Q mode reduces symmetry (vibronic coupling)

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

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

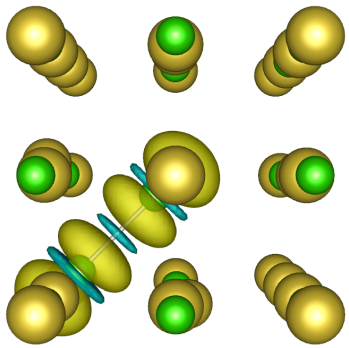
h^+ localized (STH) and degeneration disappears

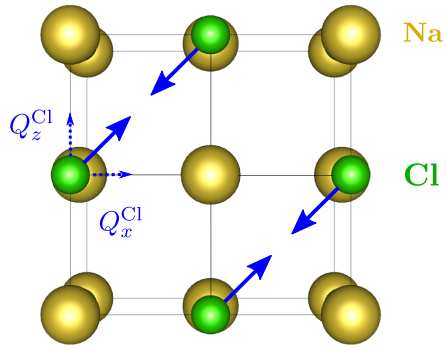
[1] STE: Self-Trapped Exciton. STH: Self-Trapped Hole

STH in Alkali Halides: Vk center vs octahedral distortion

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

Vk center
(σ^* orbital of Cl_2^-)

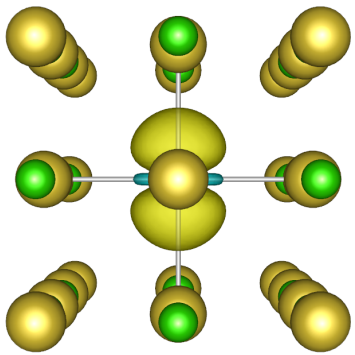


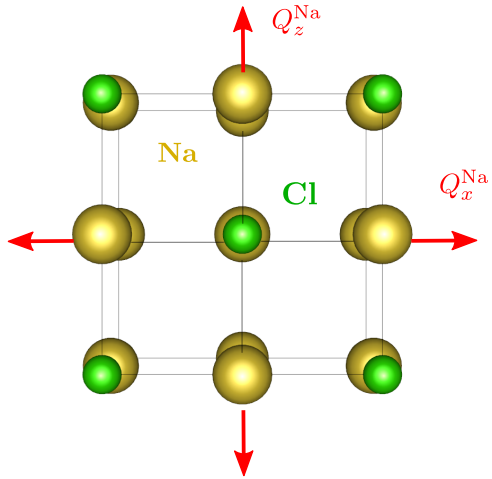


$\Delta Q_z^{Cl} = -0.49$Å

$\Delta Q_x^{Cl} = -0.49$Å

Octahedral expansion
(p_z orbital of Cl)





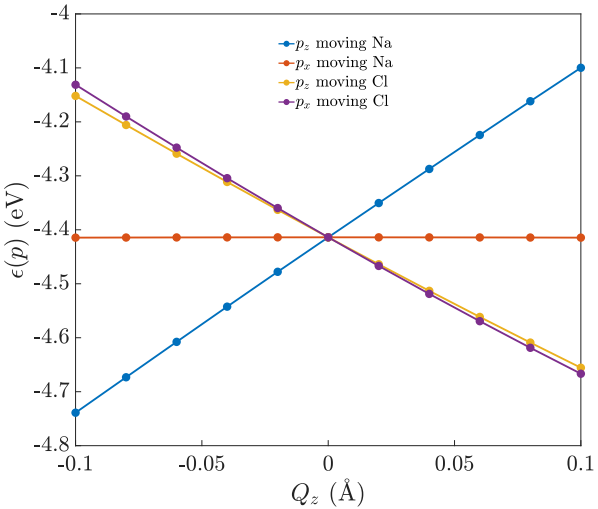
$\Delta Q_z^{Na} = 0.32$Å

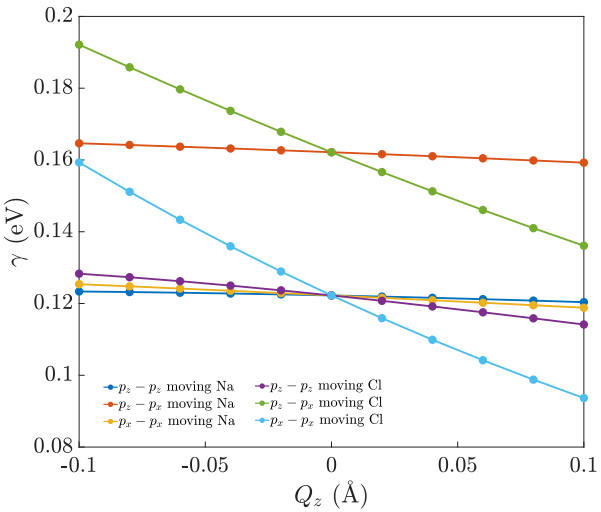
$\Delta Q_x^{Na} = 0.24$Å

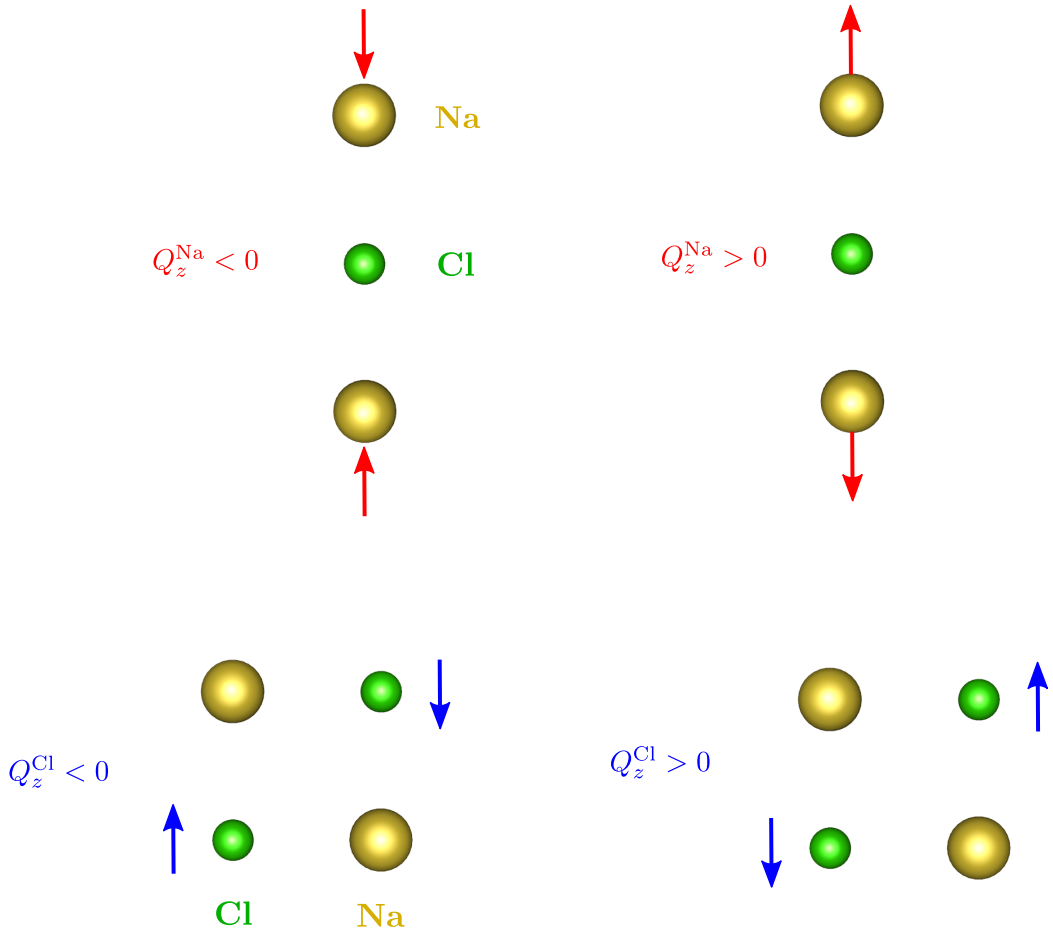
- Let's **analyze the origin** with a simple model based on **wannier functions**.

STH in Alkali Halides: Vk center vs octahedral distortion

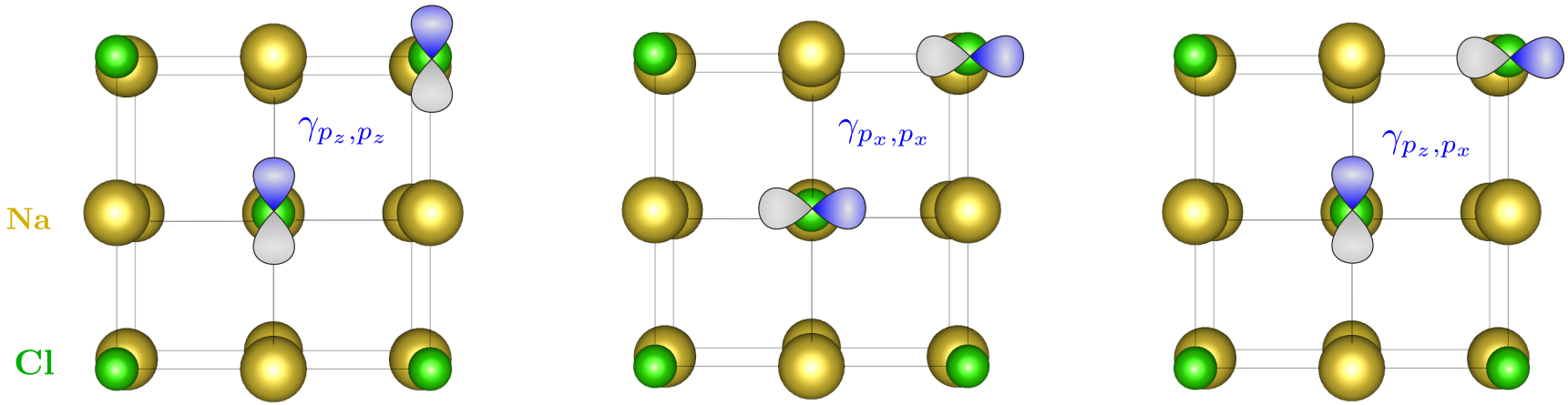
- Dependence (**linear**) of the **self-interaction** energy (ϵ) and the first neighbour **hopping** (γ) of **Cl** $2p$ wannier orbitals with **movements in** z (Q_z) of **Na** and **Cl**.







STH in Alkali Halides: Vk center vs octahedral distortion



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

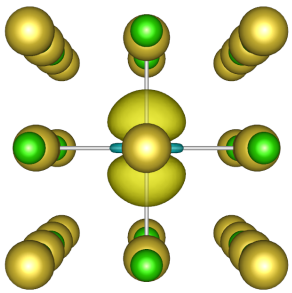
Table: First order vibronic-coupling (electron-lattice) terms in eV/Å

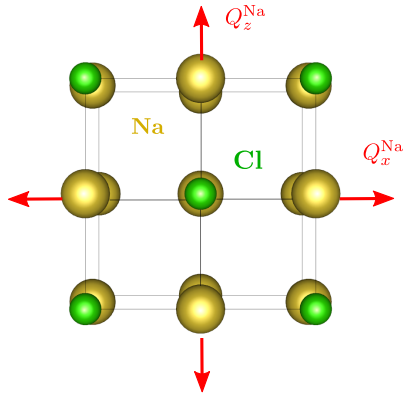
- **Octahedral distortion** (Na movement) dominated by $f^{\epsilon}_{p_z}$(Na).
- **Vk distortion** (Cl movement) dominated by $f^{\epsilon}_{p_z}$(Cl) and $f^{\epsilon}_{p_x}$(Cl).

Conclusions

- $f^{\epsilon}_{p_z}(\mathrm{Na}) > 0 \longrightarrow Q_z^{\mathrm{Na}} > 0$ favours localization (**elongated octahedron**).

Octahedral expansion
(p_z orbital of Cl)





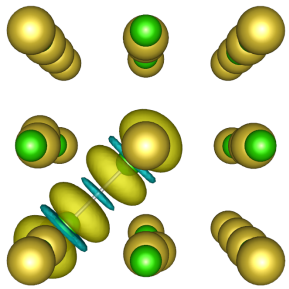
$\Delta Q_z^{\mathrm{Na}} = 0.32$Å

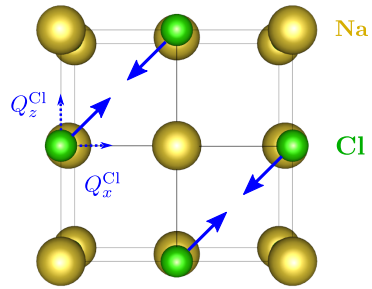
$\Delta Q_x^{\mathrm{Na}} = 0.24$Å

$$\Delta\epsilon_{p_z} = 2 f^{\epsilon}_{p_z}(\mathrm{Na})\ \Delta Q_z^{\mathrm{Na}} = 2 \cdot 3.1950 \cdot 0.32 = 2.0448 \text{ eV}$$

- $f^{\epsilon}_{p_z}(\mathrm{Cl}) < 0 \longrightarrow Q_z^{\mathrm{Cl}} < 0$ favours localization (**Cl_2^- dimer, Vk center**).

Vk center
(σ^* orbital of Cl_2^-)





$\Delta Q_z^{\mathrm{Cl}} = -0.49$Å

$\Delta Q_x^{\mathrm{Cl}} = -0.49$Å

$$\Delta\epsilon_{\mathrm{Vk}} = \Delta\epsilon^{Q_z}_{p_z} + \Delta\epsilon^{Q_x}_{p_z} = f^{\epsilon}_{p_z}(\mathrm{Cl})\ \Delta Q_z^{\mathrm{Cl}} + f^{\epsilon}_{p_z}(\mathrm{Na})\ \Delta Q_x^{\mathrm{Na}} = 2.5411 \text{ eV}$$

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