University of Amsterdam

NWO

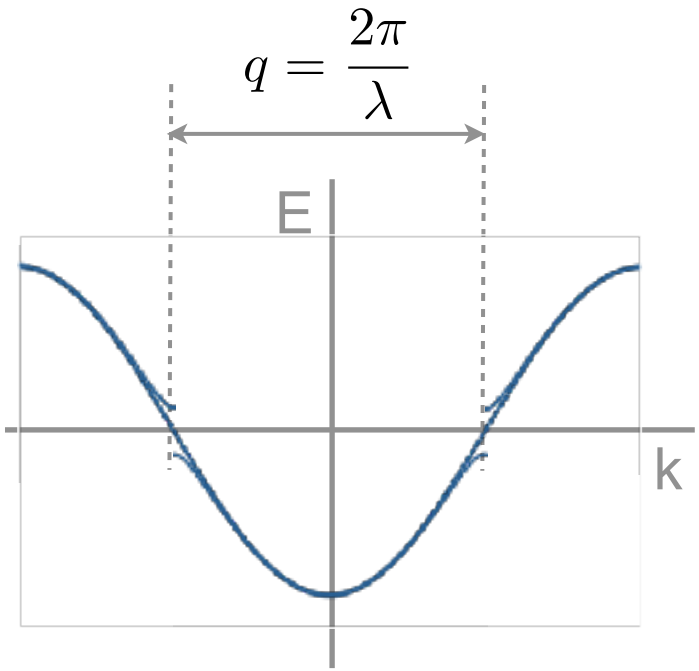
Multipole charge density waves causing Orbital order

Yingying Peng, Felix Flicker, Jans Henke, …, Jasper van Wezel

Charge Order

Prototype CDW

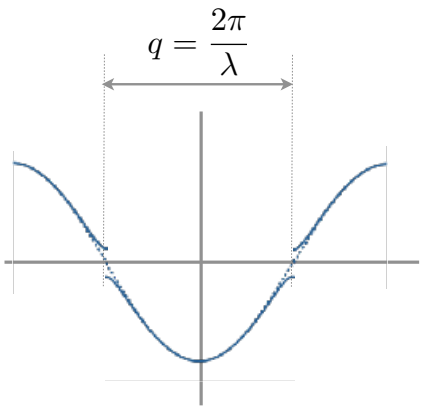
1D



$\Delta \propto u \qquad \epsilon \propto u^2$

Sir Rudolf Peierls

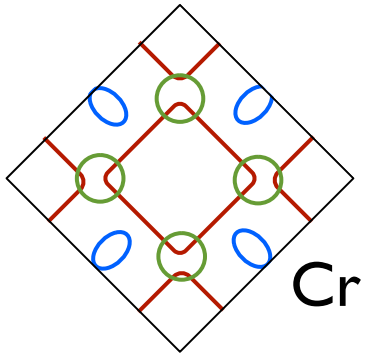
Prototype CDW



$\Delta \propto u \qquad \epsilon \propto u^2$

Oversimplified picture

- (absence of) nesting in 2 and 3D



A. W. Overhauser, Phys Rev 128, 1437 (1962).

- Coulomb (and other) interactions

$$\frac{1}{\chi_q} \leq \frac{4\eta_q^2}{\hbar\omega_q} - (2U_q - V_q)$$

Chan & Heine, J. Phys. F **3**, 795 (1973)
Johannes & Mazin, PRB **77**, 165135 (2008)

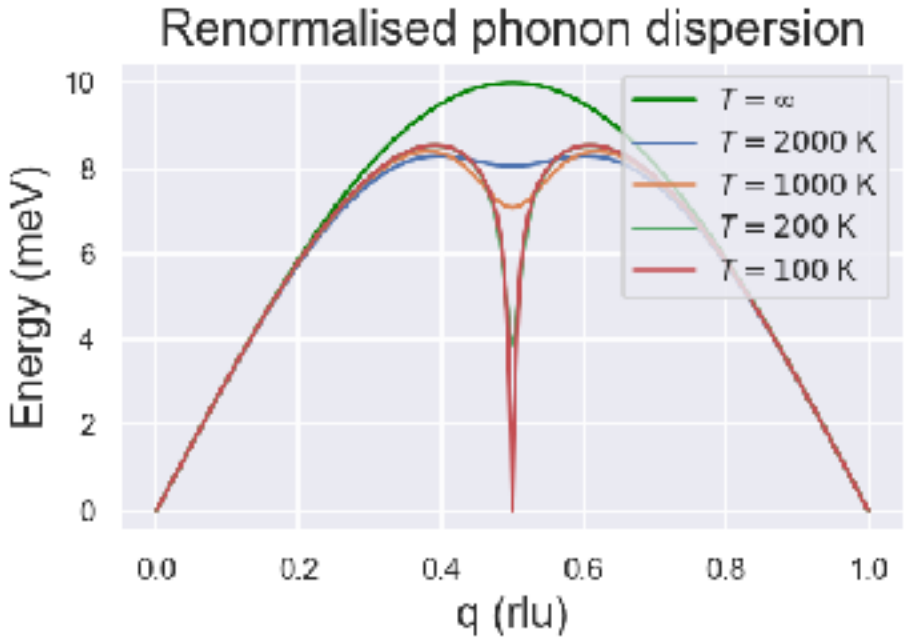
- Structured coupling

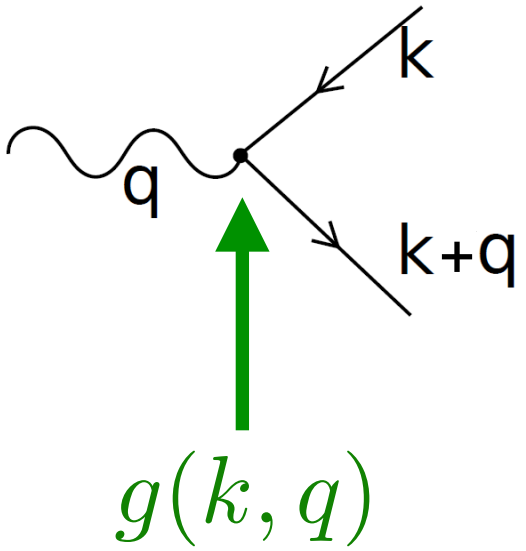
- Orbital structure

Structured coupling

Kohn anomaly

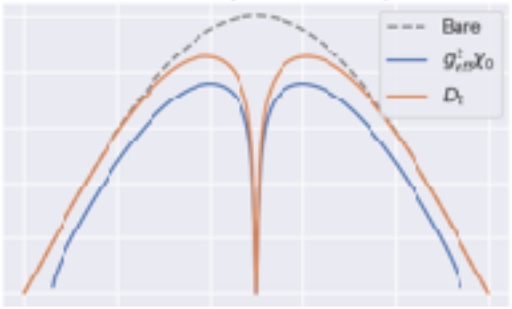
$$\tilde{\omega_q}^2 = \omega_q \left(\omega_q - \sum_k |g(k,q)|^2 \chi(k,q) \right)$$





Structured e-ph coupling

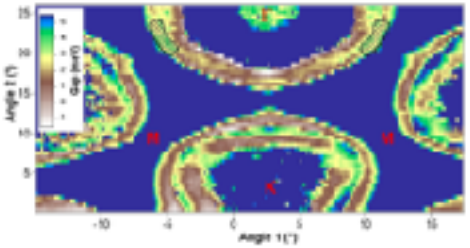
Peierls: prevent unphysical instability



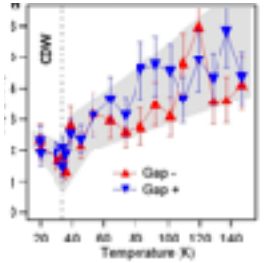
Crucial for understanding:

- Peierls model
- CDW in TMDC
  - *2H*-$NbSe_2$
  - *1T*-VSe_2
  - …
- Superconductors
  - Sr_2RO_4
  - *2H*-$NbSe_2$
  - …

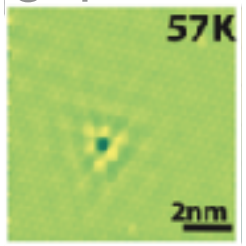
NbSe2: Fermi arcs, pseudogap, strain effects

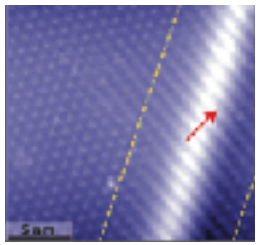


PRL 102, 166402 (2009)



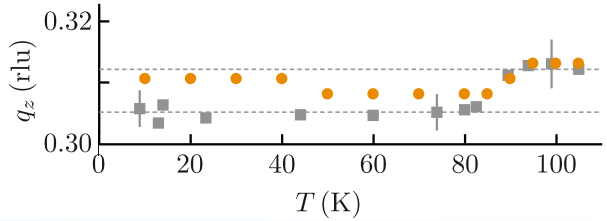
PRB 89, 235115 (2014)

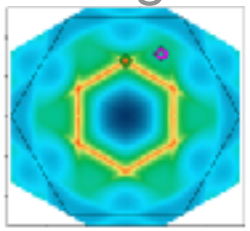




PNAS 110, 1623 (2013)

VSe2: thermal evolution, coexisting CDWs





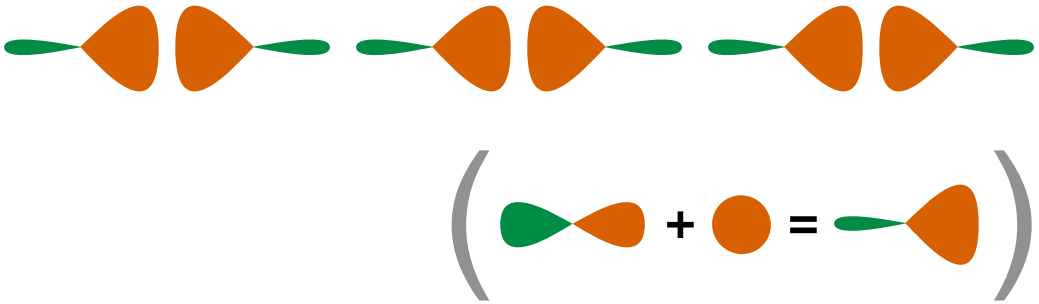
Nat Comm 6, 7034 (2015)
PRB 94, 235135 (2016)
PRR 1, 033108 (2019)
SciPost Phys. 9, 056 (2020)
Science 372, 6549 (2021)
ACS Nano 16, 783 (2022)

Orbital structure

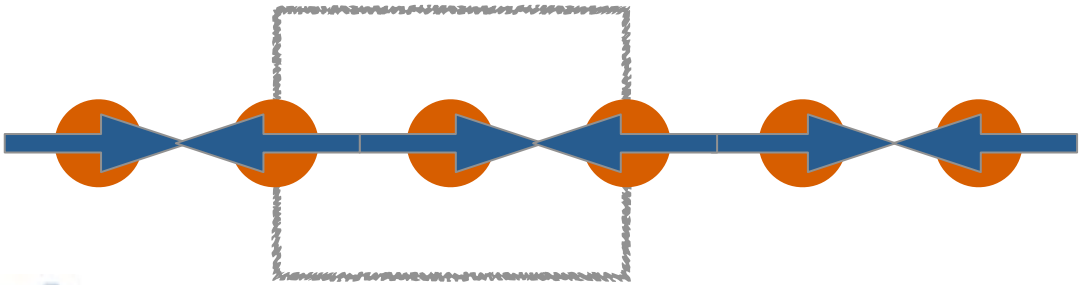
I: quantum chemistry

Atomic displacement:

Orbital structure:

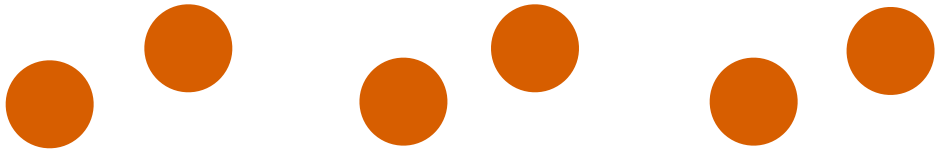


Charge redistribution:

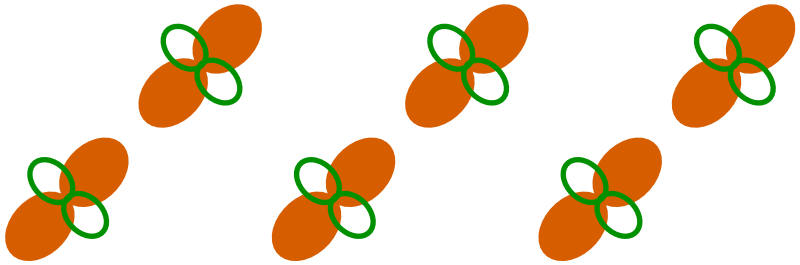


II: degenerate orbitals

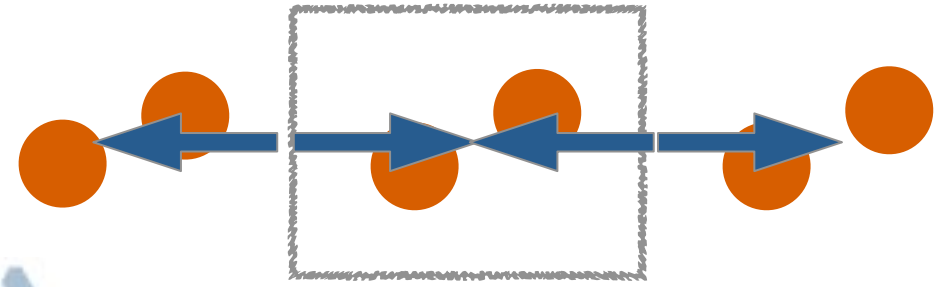
Atomic displacement:



Orbital structure:



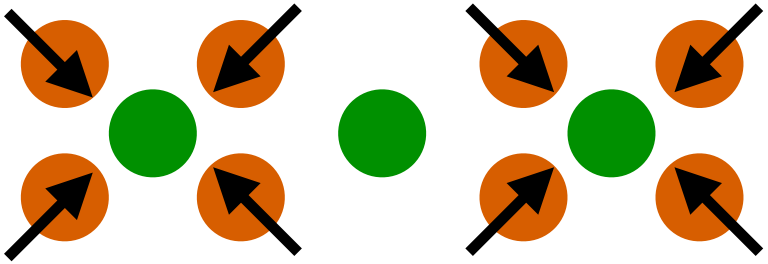
Charge redistribution:



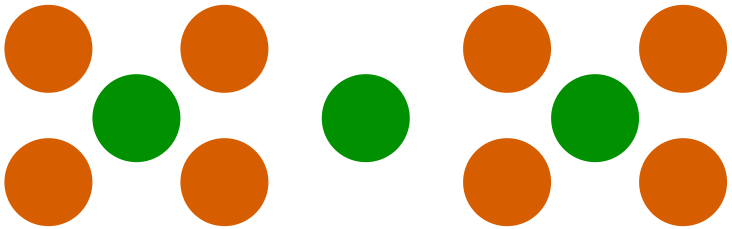
in SDW: JMMM 290, 318 (2005)

III: multipole expansion

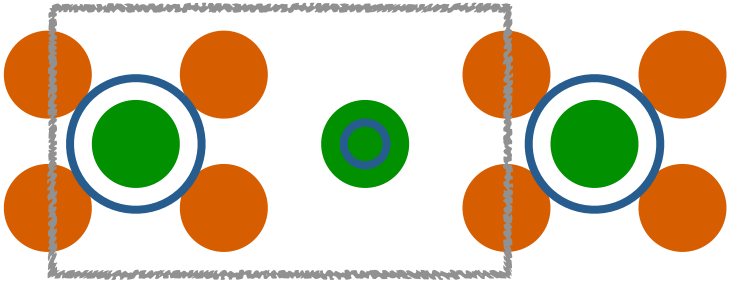
Atomic displacement:



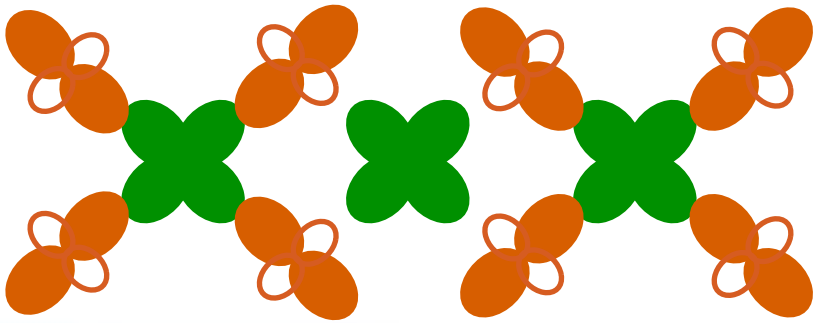
Monopole



Charge redistribution:



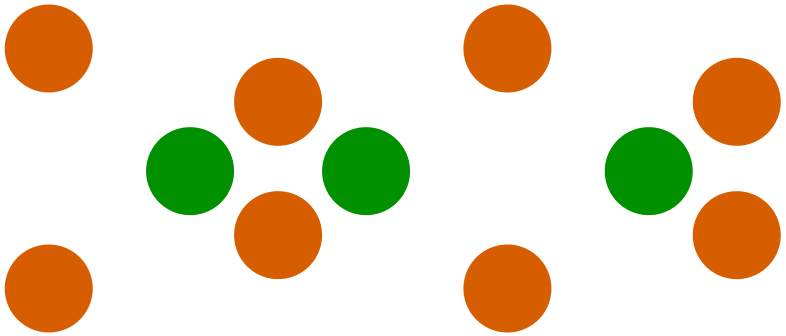
Orbital structure:



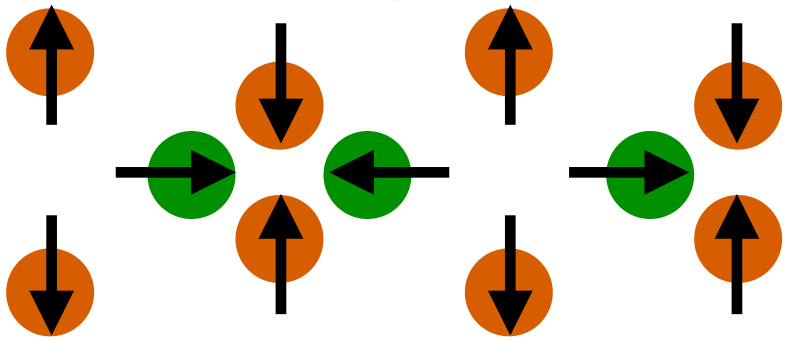
Henke, PhD thesis (2022)

III: multipole expansion

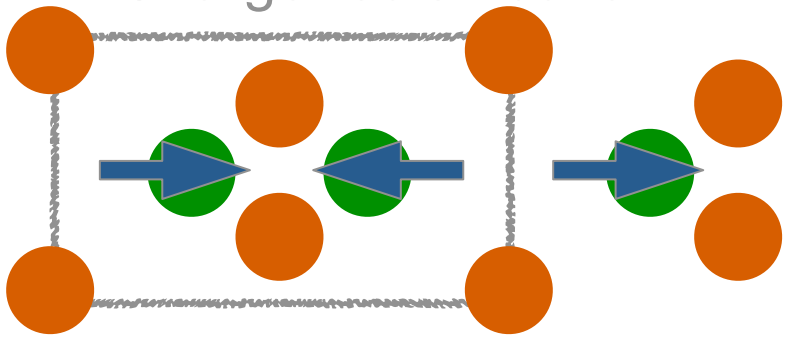
Longitudinal dipole



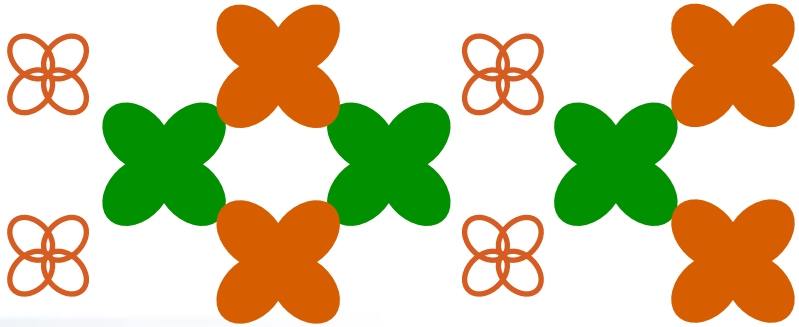
Atomic displacement:



Charge redistribution:



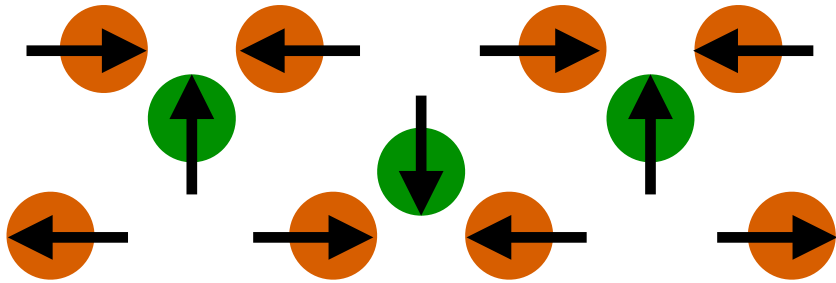
Orbital structure:



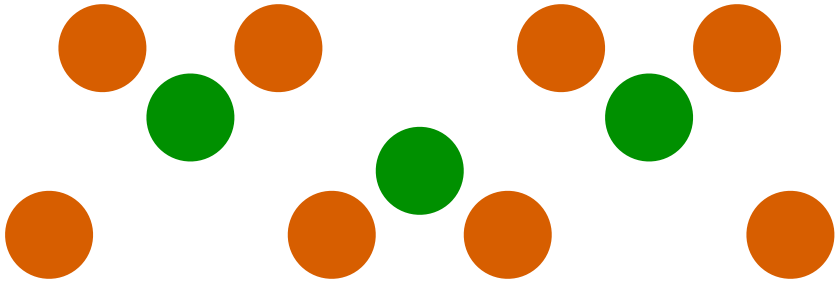
Henke, PhD thesis (2022)

III: multipole expansion

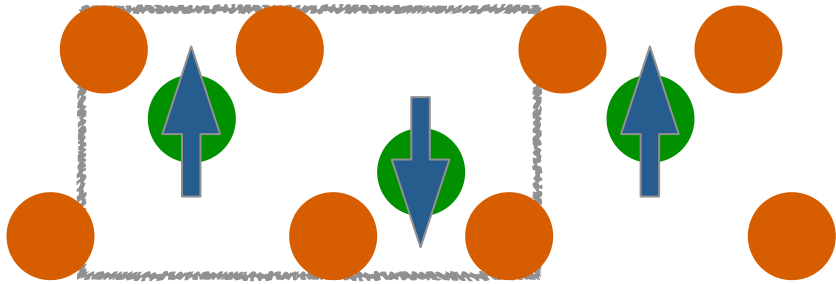
Atomic displacement:



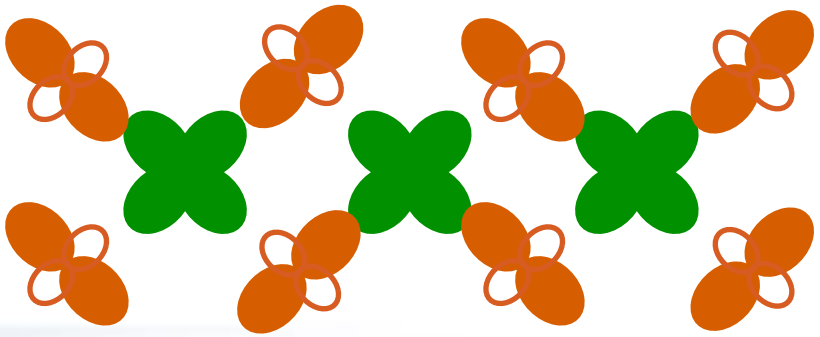
Transverse dipole



Charge redistribution:



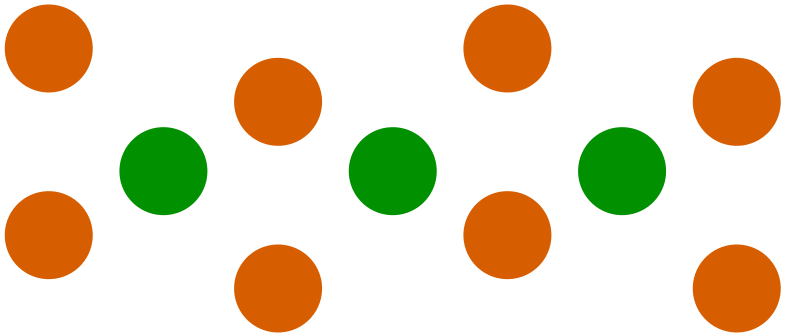
Orbital structure:



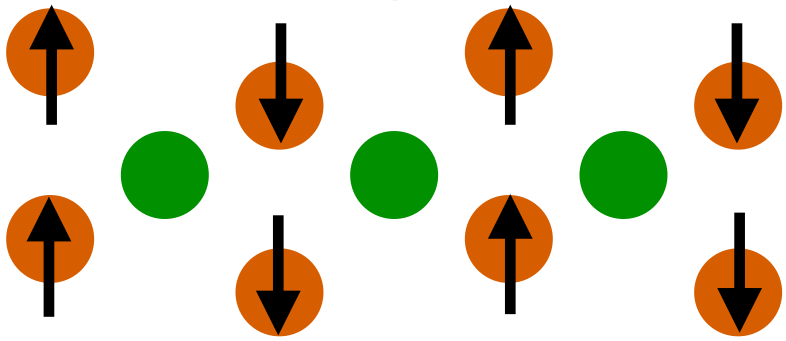
Henke, PhD thesis (2022)

III: multipole expansion

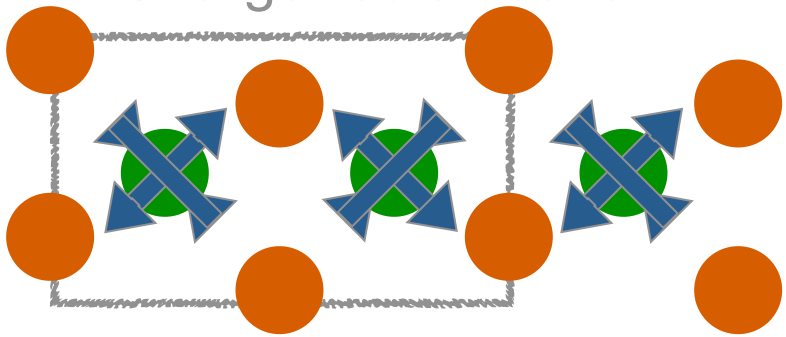
Quadrupole



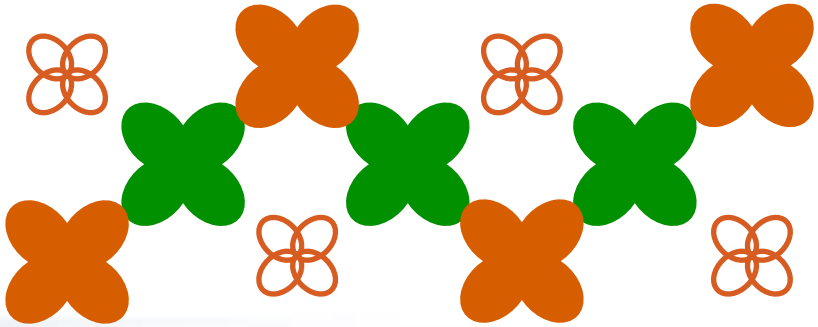
Atomic displacement:



Charge redistribution:



Orbital structure:

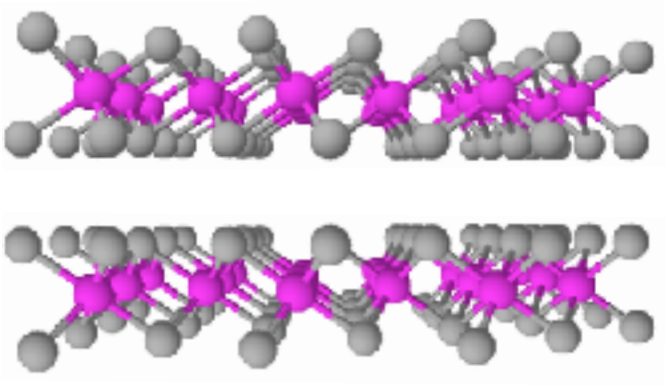


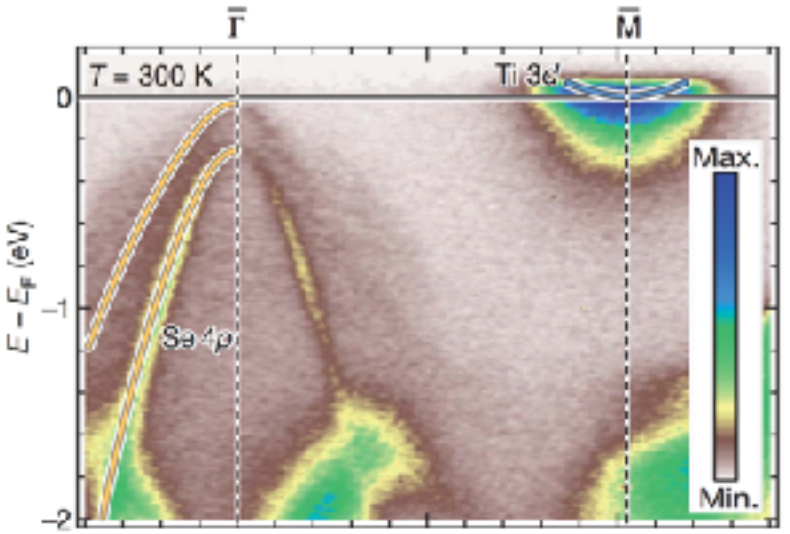
Henke, PhD thesis (2022)

Titanium di-Selenide

(orbital structure)

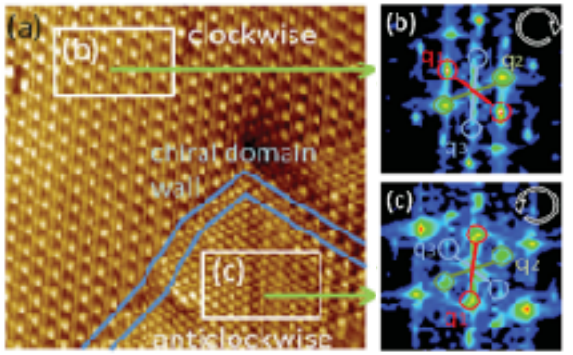
$TiSe_2$





Nature 471, 490 (2011)

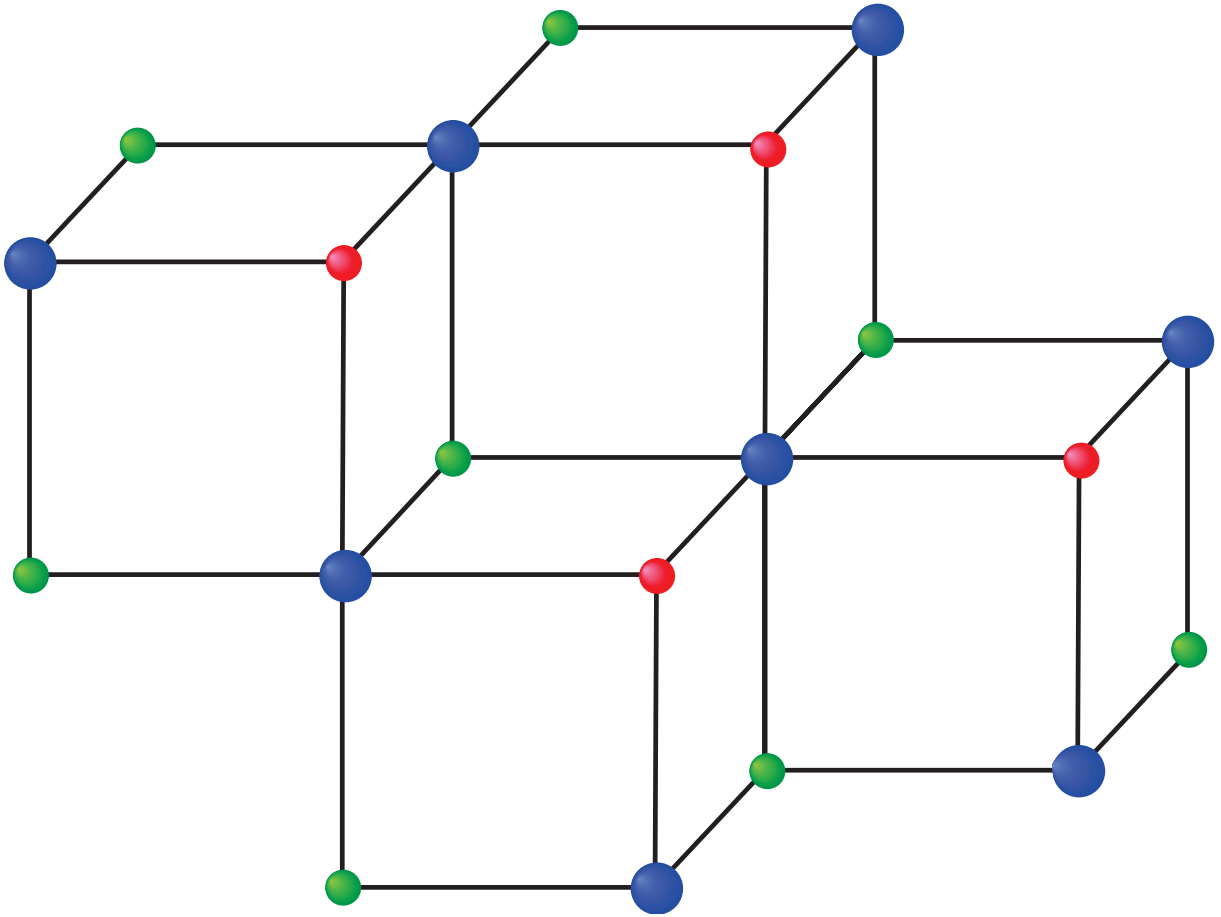
- Quasi 2D, layered material
- Commensurate charge density wave transition at 202 K
  - charge transfer from Se $4p^6$ to Ti $3d^0$
- Suggested chiral CDW phase
  - debated: no *direct* evidence



PRL 105, 176401 (2010)

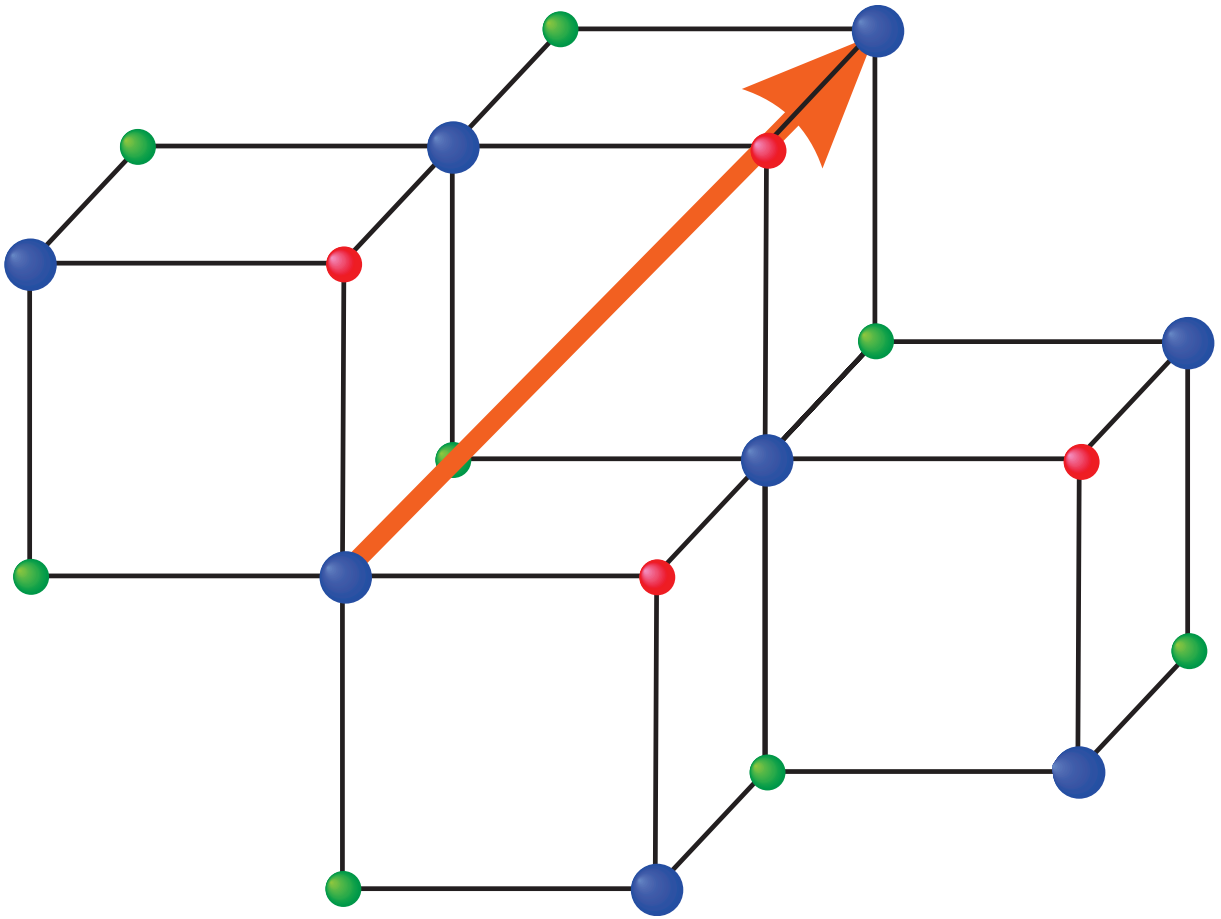
EPL 96, 67011 (2011)
PRL 110, 196404 (2013)
PRL 120., 136404 (2018)
PRL 122, 229701 (2019)
Nature 578, 545 (2020)

Charge and orbital order



van Wezel, *EPL* **96**, 67011 (2011)
Whangbo & Canadell, *J. Am. Chem. Soc.* **114**, 9587 (1992)

Charge and orbital order



van Wezel, *EPL* **96**, 67011 (2011)
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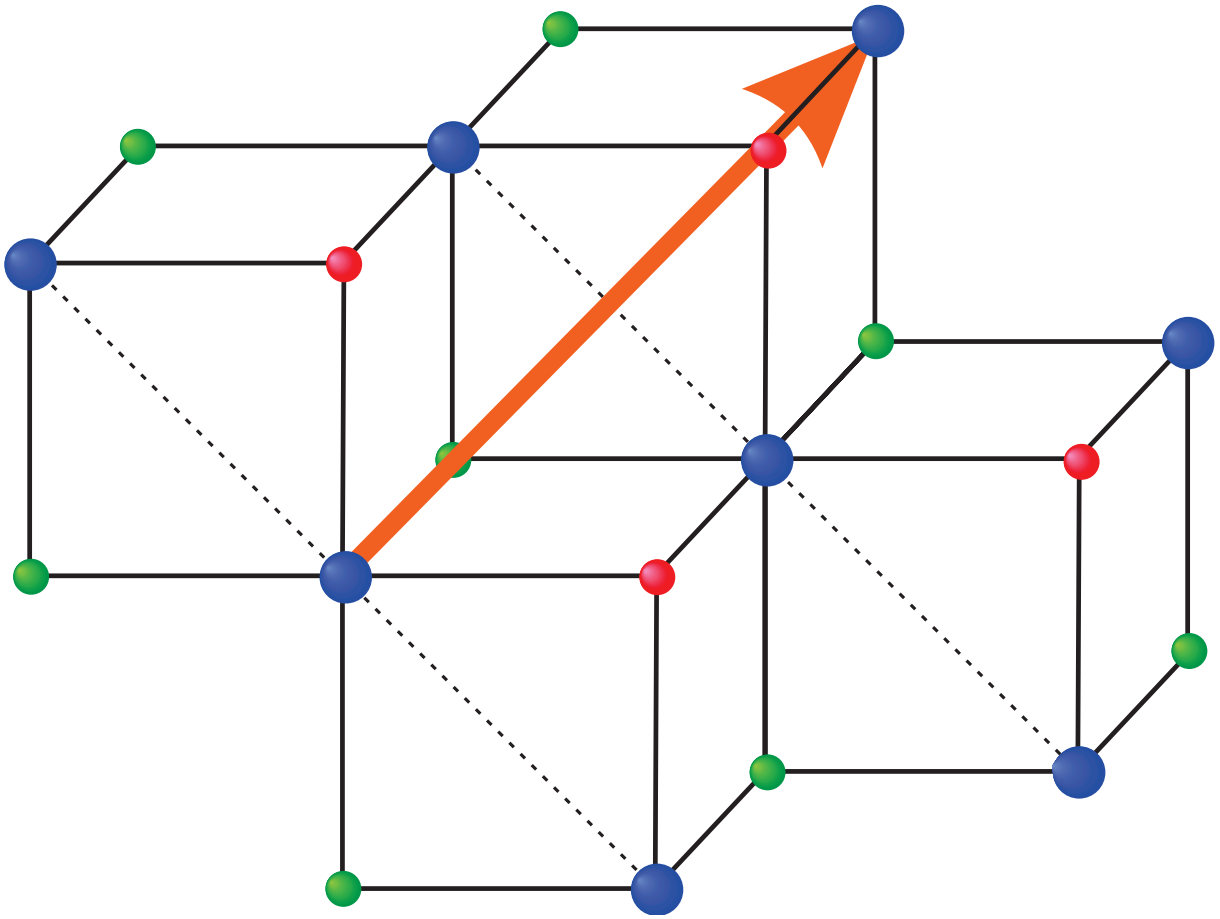
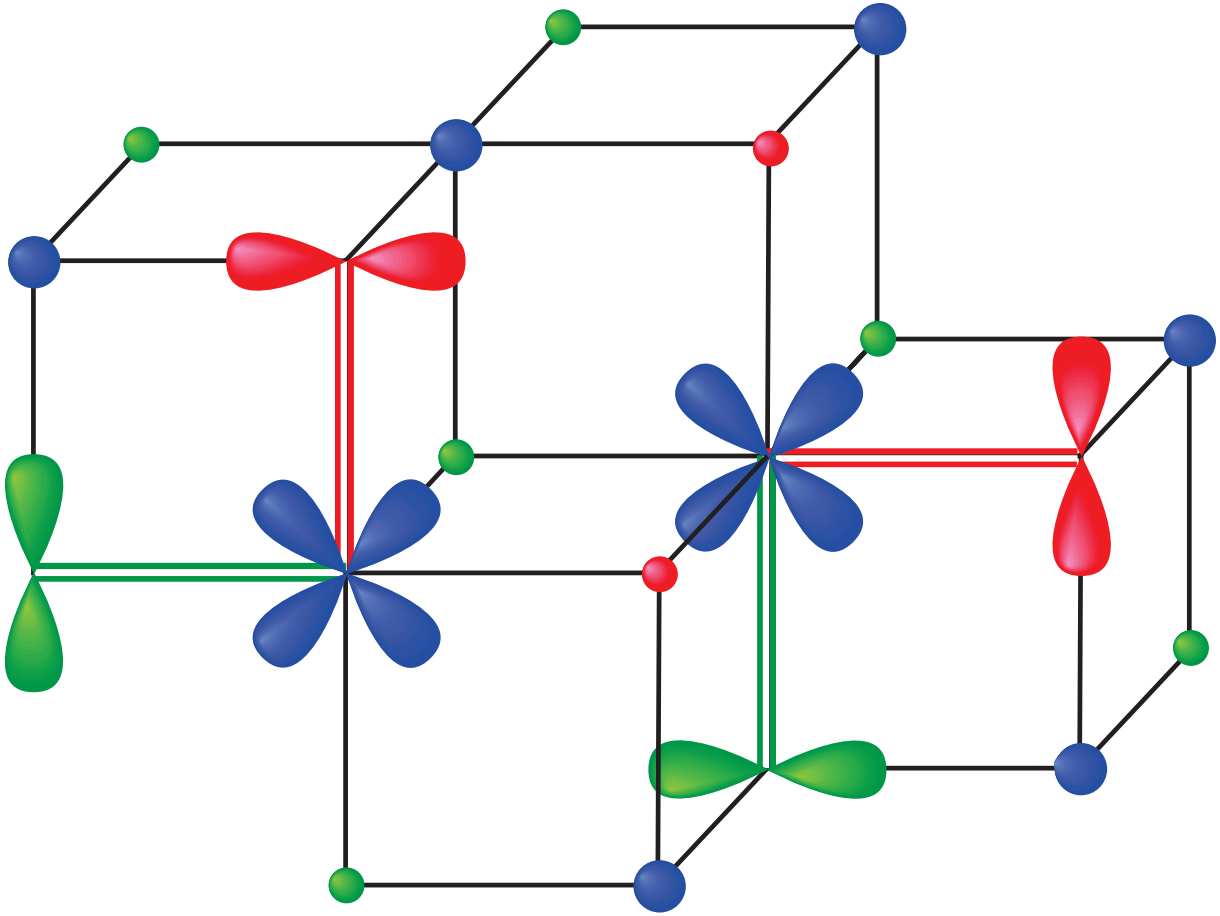
Charge and orbital order



van Wezel, *EPL* **96**, 67011 (2011)
Whangbo & Canadell, *J. Am. Chem. Soc.* **114**, 9587 (1992)

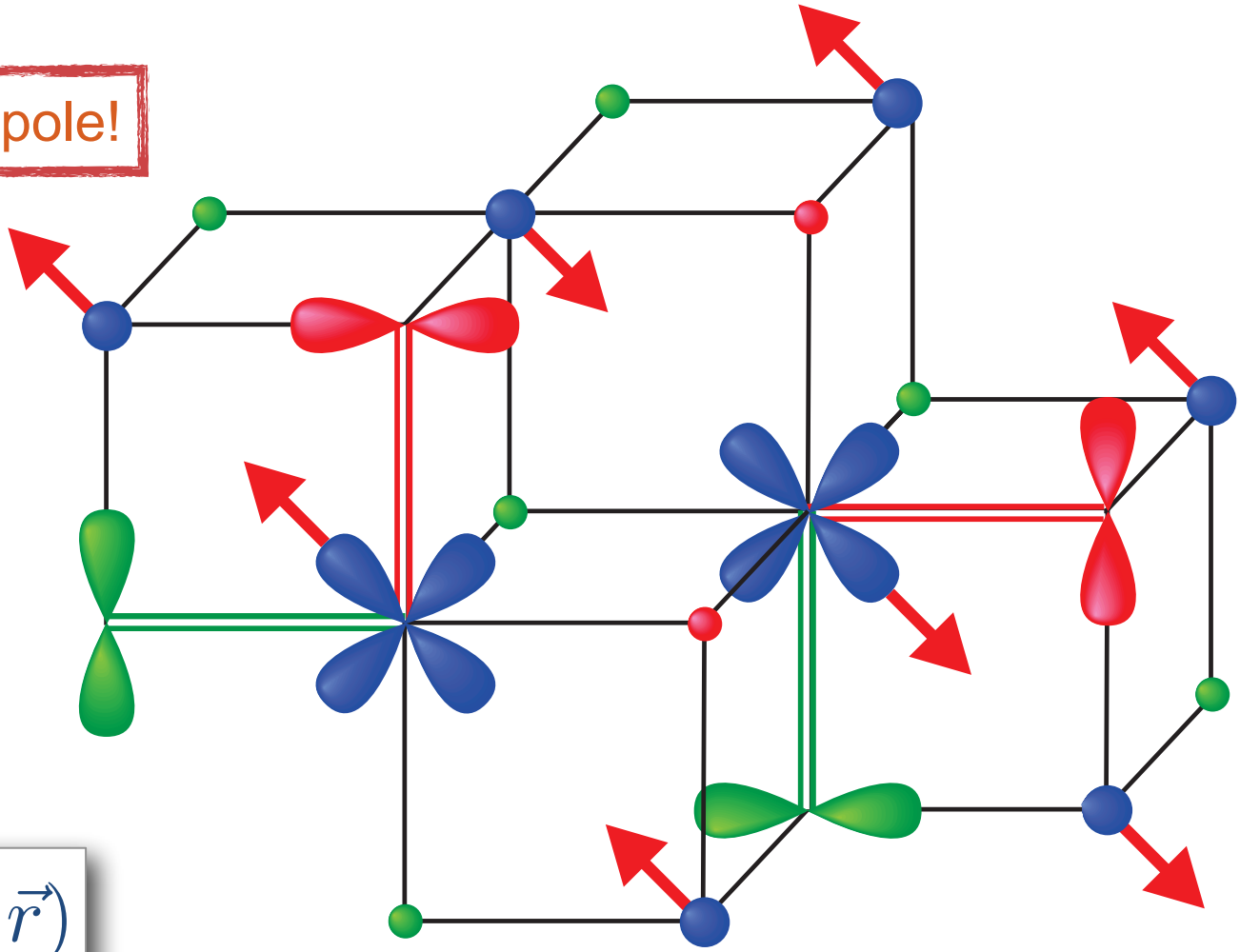
Charge and orbital order



van Wezel, *EPL* **96**, 67011 (2011)
Whangbo & Canadell, *J. Am. Chem. Soc.* **114**, 9587 (1992)

Charge and orbital order

= transverse dipole!



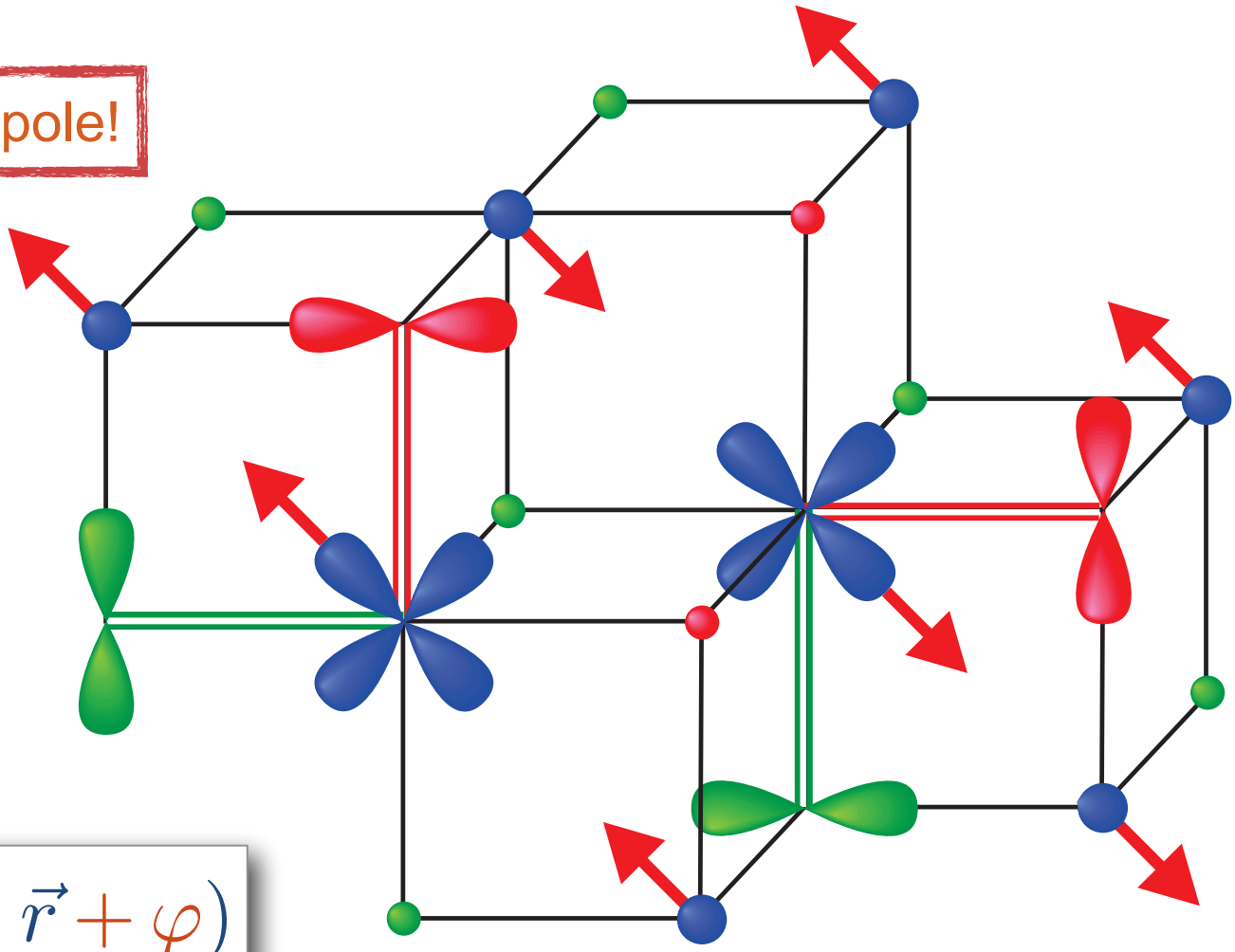
$$\hat{\epsilon} \perp \vec{Q}$$

$$\vec{u} \propto \hat{\epsilon} \sin(\vec{Q} \cdot \vec{r})$$

van Wezel, *EPL* **96**, 67011 (2011)
Whangbo & Canadell, *J. Am. Chem. Soc.* **114**, 9587 (1992)

Charge and orbital order

= transverse dipole!



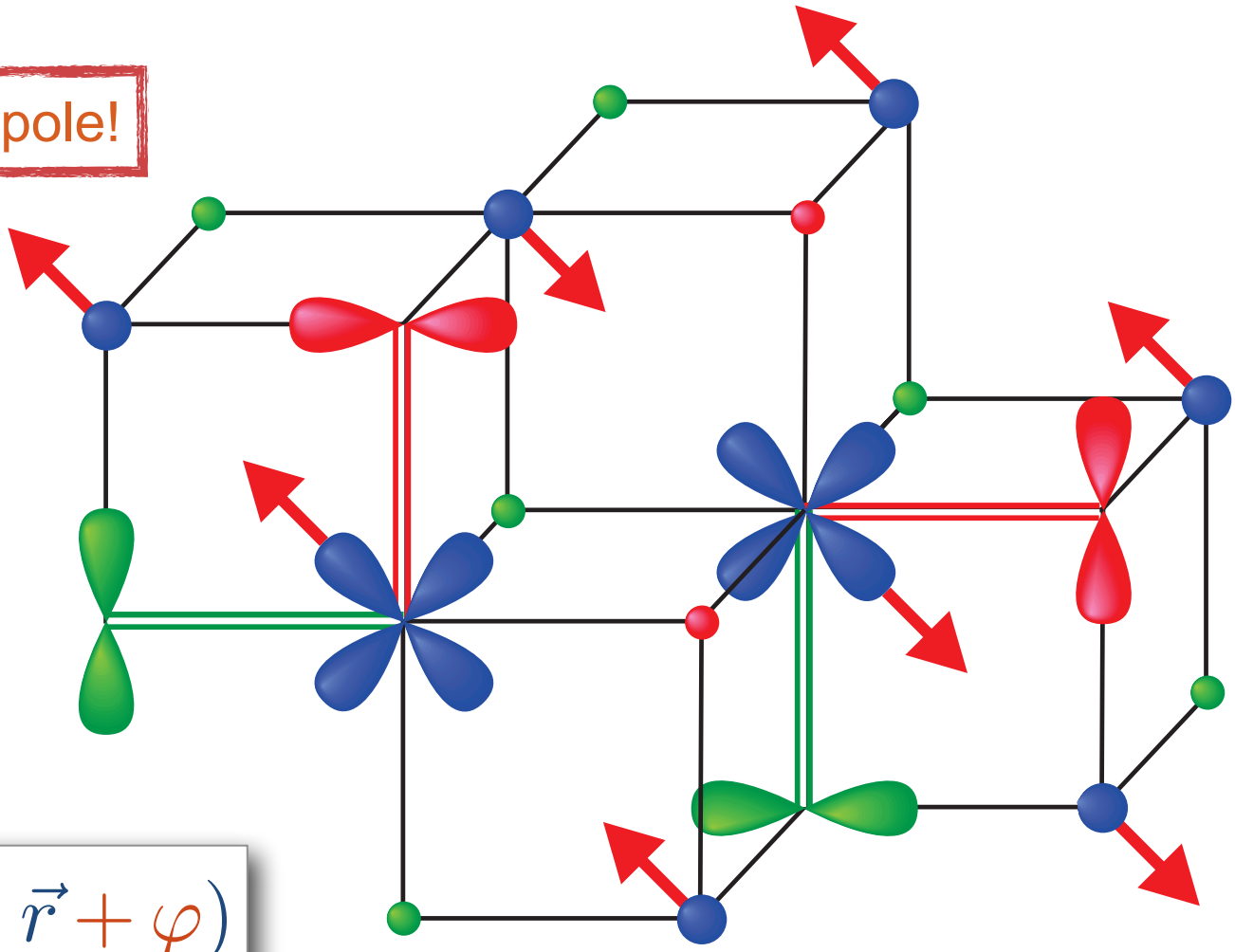
$$\hat{\epsilon} \perp \vec{Q}$$

$$\vec{u} \propto \hat{\epsilon} \sin(\vec{Q} \cdot \vec{r} + \varphi)$$

van Wezel, *EPL* **96**, 67011 (2011)
Whangbo & Canadell, *J. Am. Chem. Soc.* **114**, 9587 (1992)

Charge and orbital order

= transverse dipole!



$$\hat{\epsilon} \perp \vec{Q}$$

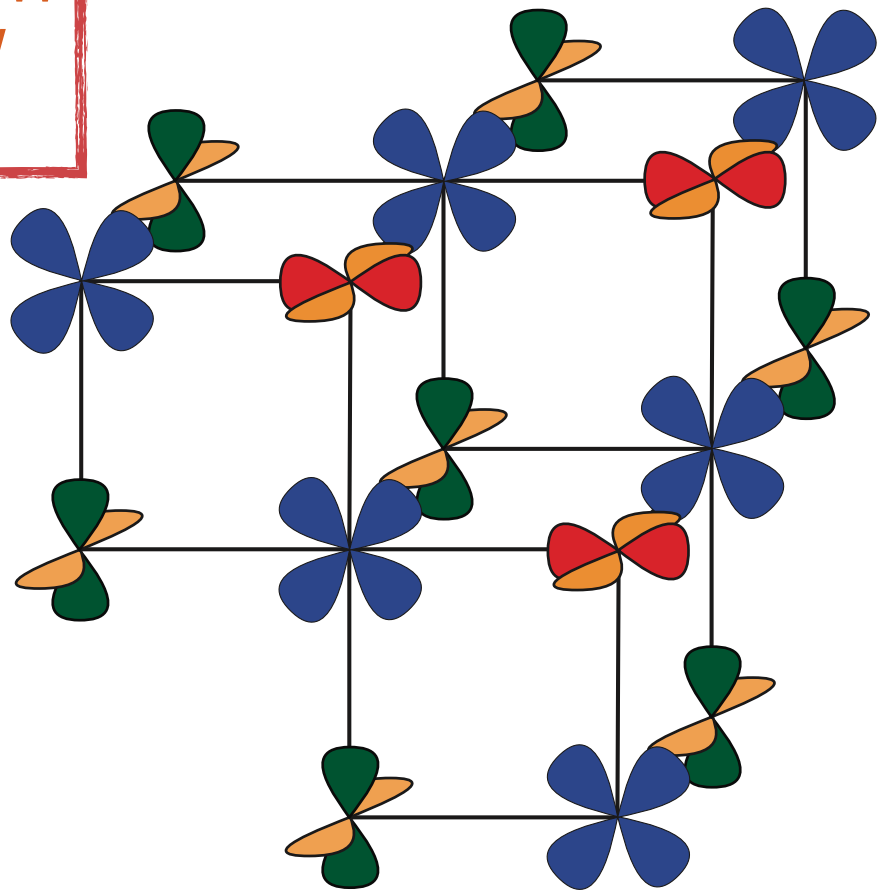
$$\vec{u} \propto \hat{\epsilon} \sin(\vec{Q} \cdot \vec{r} + \varphi)$$

= adding quadrupole!

van Wezel, *EPL* **96**, 67011 (2011)
Whangbo & Canadell, *J. Am. Chem. Soc.* **114**, 9587 (1992)

Charge and orbital order

Transverse dipole CDW
+ Quadrupole CDW
= Orbital order



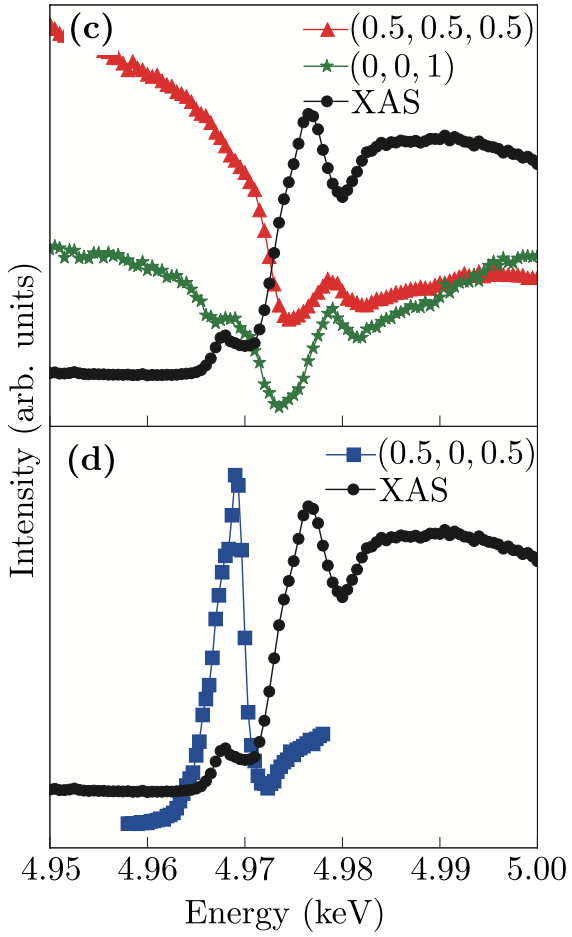
$$\hat{\epsilon} \perp \vec{Q}$$

$$\vec{u} \propto \hat{\epsilon} \sin(\vec{Q} \cdot \vec{r} + \varphi)$$

van Wezel, *EPL* **96**, 67011 (2011)

Observing orbital structure

RXS at the Ti K-edge



Two families of peaks:

1. "normal" CDW peaks
   - allowed already off-resonance
   - suppression near resonant edge: Thomson scattering from atomic cores

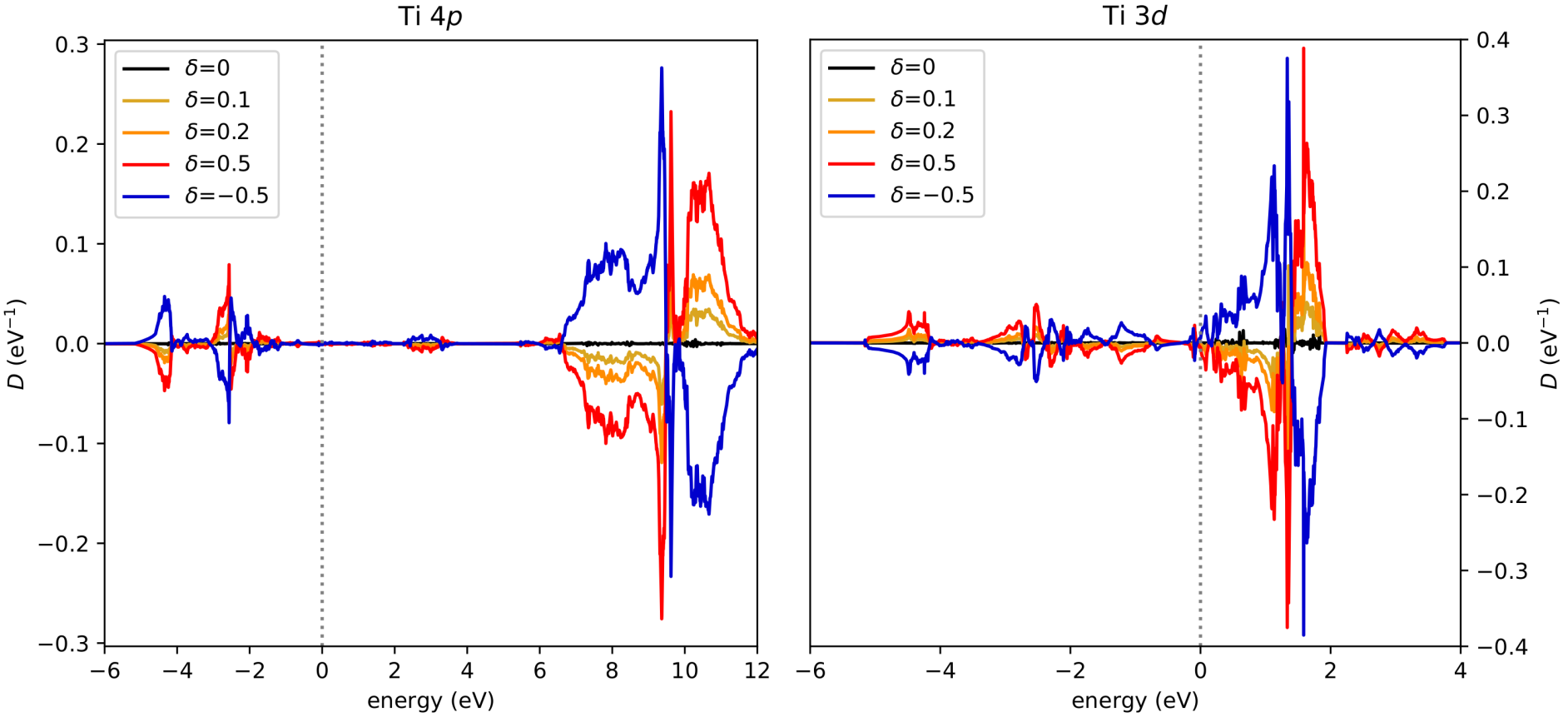
2. "anomalous" CDW peaks
   - *forbidden* off-resonance
   - peaked at pre-edge: reflections due to orbital transitions

=> Orbital occupation on Ti has lower symmetry than "normal" CDW

PRR 4, 033053 (2022)

cf. RXS at Se K-edge: PRR 3, L022003 (2021)

Consistent with broken inversion



Broken inversion: hybridization between 3d and 4p
=> yields resonant scattering at pre-edge

PRR 4, 033053 (2022)

cf. ATS at Se K-edge: PRR 3, L022003 (2021)

Conclusions

Conclusions

- Charge order can be understood *quantitatively* in real materials, if:
  - The momentum and orbital structure of the electron-phonon coupling is taken into account
  - The effects of Coulomb interactions are considered on the same level as electron-phonon coupling

- This solves many apparent mysteries:
  - Fermi arcs and pseudogap in $NbSe_2$
  - Quantum phase transitions under strain in $NbSe_2$
  - Gap structure and thermal evolution of $NbSe_2$ and VSe_2
  - Orbital order in TiSe2, as seen by recent REXS experiments
  - Orbital order in elemental chalcogens Se, Te, and Po

- The links between atomic displacements, charge redistribution, and orbital occupation can be efficiently described in terms of multipole charge order