Algebraic diagrammatic construction for band structures

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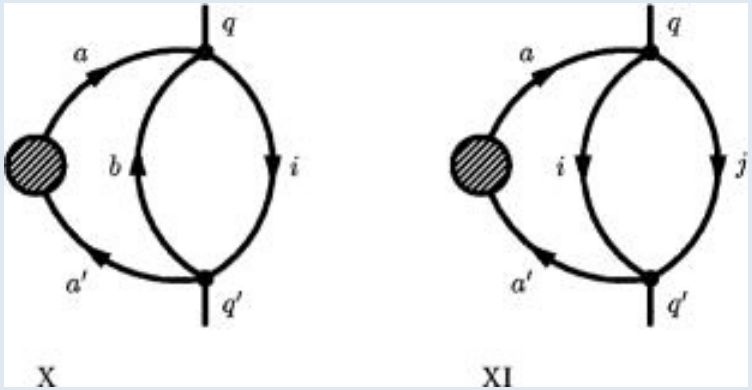
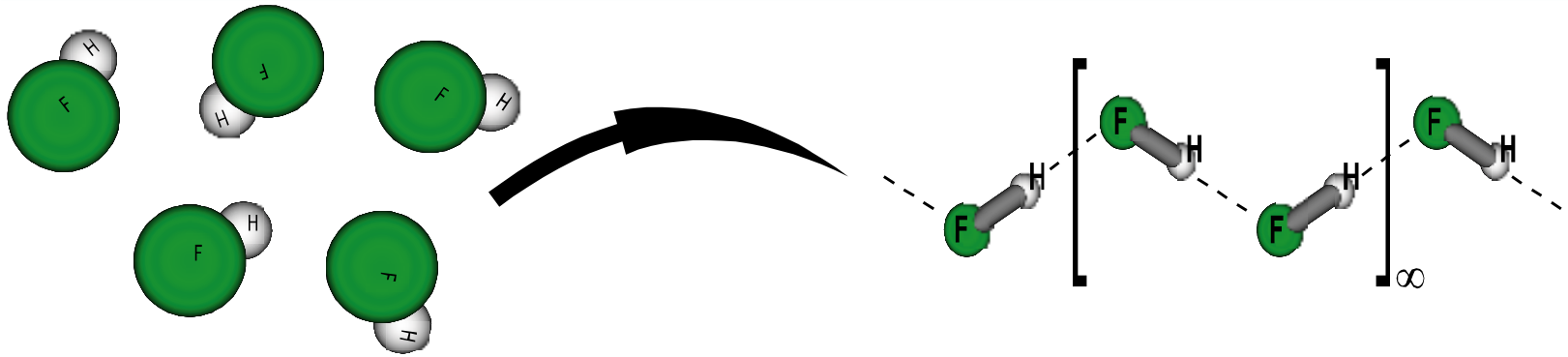


Contents

1.1 From molecules to crystals

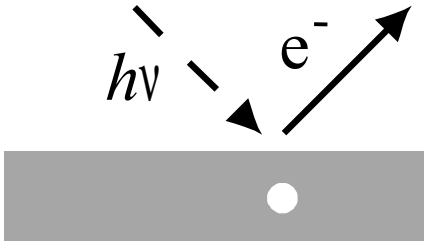
- Crystallization



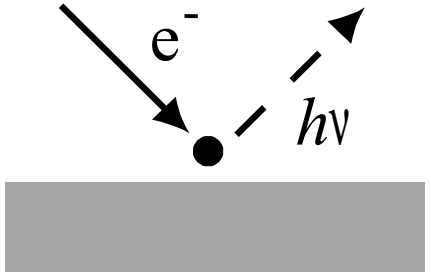
- Crystals are huge molecules
- Periodic repetition (translational symmetry)
- **Model:** crystals extend to infinity

1.2 Experiments

- Excited states of solids



Ionization potentials
Valence bands



Electron affinities
Conduction bands

1.3 First principles approach

- *Full* electronic Hamiltonian

$$\hat{H}_{\mathrm{el}} = -\frac{1}{2}\sum_{n} \Delta_n - \sum_{n,\vec{R}A} \frac{Z_{\vec{R}A}}{\left|\vec{r}_n - \vec{r}_{\vec{R}A}\right|} + \frac{1}{2}\sum_{n \neq m} \frac{1}{\left|\vec{r}_m - \vec{r}_n\right|}$$

- Wave functions and canonical orbitals of crystals obey Bloch's theorem

$$\psi_{\vec{k}\,n}(\vec{r} + \vec{R}) = \mathrm{e}^{\mathrm{i}\vec{k}\,\vec{R}}\,\psi_{\vec{k}\,n}(\vec{r})$$

- Crystal momentum quantum number $\vec{k}$

1.4 Hartree-Fock approximation

- Canonical crystal orbitals
  - Characterized by band index n and crystal momentum $\vec{k}$
  - Expansion in terms of quasi-periodic Gaussians

$$\psi_{\vec{k}n}(\vec{r}) = \sum_{\mu} C_{\mu n}(\vec{k})\,\phi_{\vec{k}\mu}(\vec{r})$$

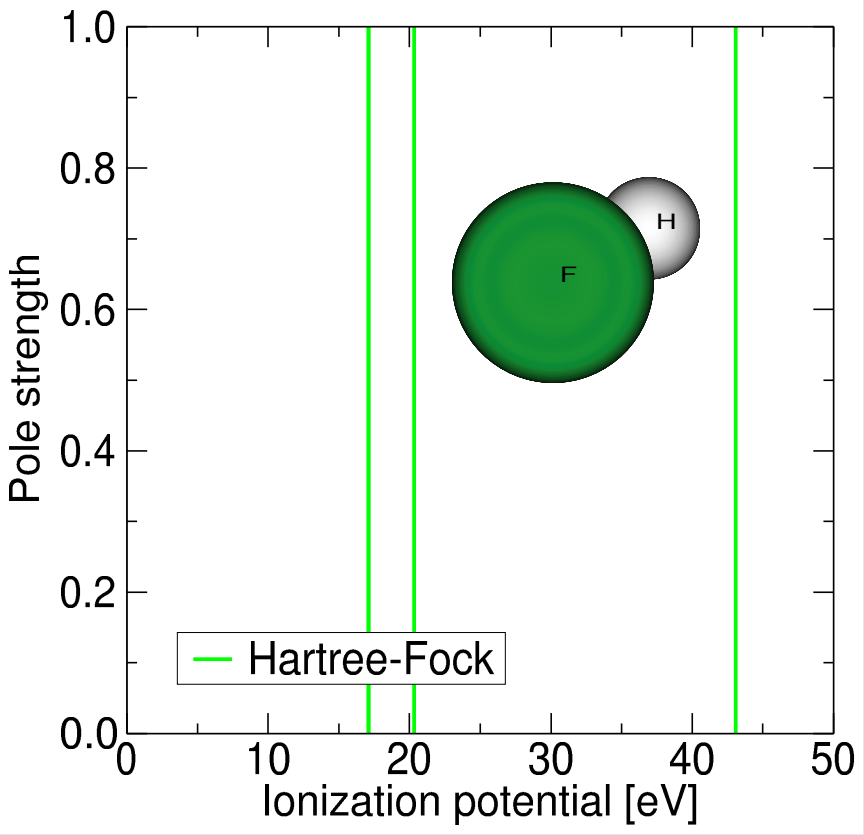
$$\phi_{\vec{k}\mu}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\vec{R}}\,\chi_{\mu}(\vec{r} - \vec{g}_{\mu} - \vec{R})$$

- Self-consistent solution of

$$\mathbf{F}(\vec{k})\mathbf{C}(\vec{k}) = \mathbf{S}(\vec{k})\mathbf{C}(\vec{k})\mathbf{E}(\vec{k})$$

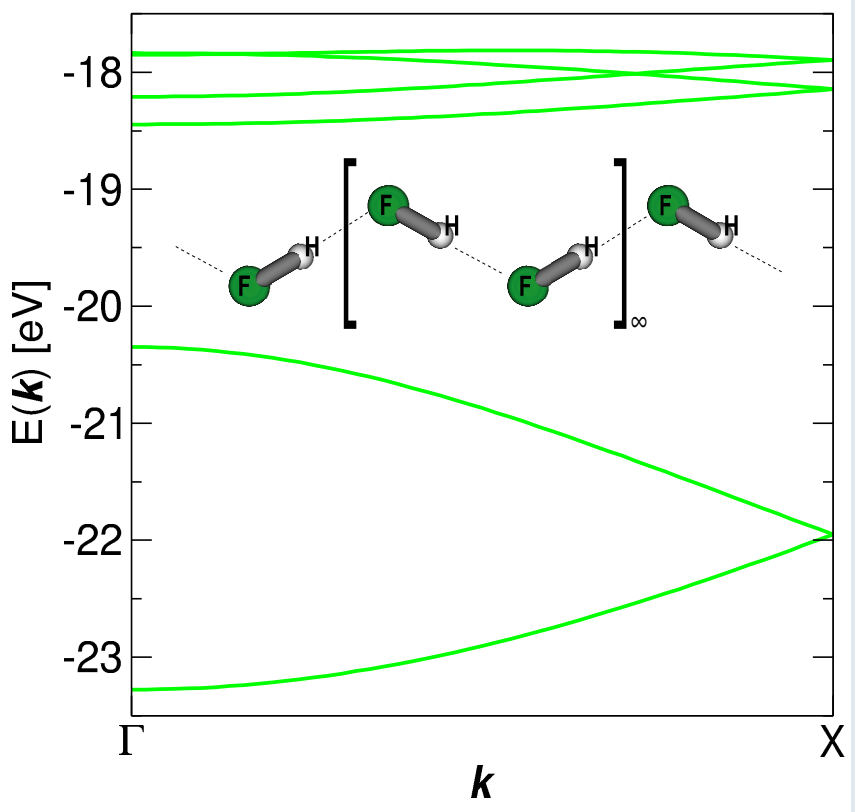
1.5 Hydrogen fluoride molecule

- HF molecule
- Hartree-Fock approximation
- IPs and EAs via Koopmans' theorem
- Basis set cc-pVDZ



1.6 Hydrogen fluoride chain

- $(HF)_\infty$ chain
- Hartree-Fock approximation
- Energy levels
- Translational symmetry classified
- Calculations are routine
- Basis set cc-pVDZ



2.1 Many-Body Green's Functions

- Particle propagator

$$i G_{pq}(\vec{k}, t - t') = \left\langle \Psi_0^N \middle| \hat{T}[\hat{c}_{\vec{k}p}(t)\, \hat{c}^{+}_{\vec{k}q}(t')] \middle| \Psi_0^N \right\rangle$$

- Poles are band structure
- Dyson equation

$$\mathbf{G}(\vec{k}, \omega) = \mathbf{G}^0(\vec{k}, \omega) + \mathbf{G}^0(\vec{k}, \omega)\boldsymbol{\Sigma}(\vec{k}, \omega)\mathbf{G}(\vec{k}, \omega)$$

- Static and dynamic self-energy

$$\boldsymbol{\Sigma}(\vec{k}, \omega) = \boldsymbol{\Sigma}^{\infty}(\vec{k}) + \mathbf{M}(\vec{k}, \omega)$$

2.2 Crystal orbital ADC

- Molecular ADC

$$\mathbf{M}(\omega) = \mathbf{U}^{+} \, (\omega \, \mathbf{1} - \mathbf{K} - \mathbf{C})^{-1} \, \mathbf{U}$$

- Replace MO by CO $i \rightarrow \vec{k} i$

- Exploit translational symmetry of $\mathbf{U}, \mathbf{K}, \mathbf{C}$

2.3 Correlated band structures

- Band structures in terms of a Hermitian eigenvalue problem

$$\mathbf{B}(\vec{k})\mathbf{X}(\vec{k}) = \mathbf{X}(\vec{k})\mathbf{E}(\vec{k}), \qquad \mathbf{X}(\vec{k})^{\dagger}\mathbf{X}(\vec{k}) = \mathbf{1}$$

$$\mathbf{B}(\vec{k}) = \begin{pmatrix} \boldsymbol{\varepsilon} + \boldsymbol{\Sigma}^{\infty} & \mathbf{U}_{\mathrm{I}}^{\dagger} & \mathbf{U}_{\mathrm{II}}^{\dagger} \\ \mathbf{U}_{\mathrm{I}} & \mathbf{K}_{\mathrm{I}} + \mathbf{C}_{\mathrm{I}} & \mathbf{0} \\ \mathbf{U}_{\mathrm{II}} & \mathbf{0} & \mathbf{K}_{\mathrm{II}} + \mathbf{C}_{\mathrm{II}} \end{pmatrix}$$

- Band structure matrix $\mathbf{B}(\vec{k})$
- Sparse large-scale eigenvalue problem
- Lanczos algorithm

Contents

3.1 Canonical molecular orbitals

- Canonical molecular orbitals
  - Fock matrix $\boldsymbol{\varepsilon}$ is diagonal
  - Koopmans' theorem holds
  - Not local!

3.2 Local molecular orbitals

- Hartree-Fock wave function invariant under unitary transformation of orbitals

$$\Psi = \det\left|U(\psi_1 \cdots \psi_N)\right| = e^{i\varphi} \det\left|\psi_1 \cdots \psi_N\right|$$

- Choose orbitals to maximize interorbital distances (Foster-Boys)

3.3 Localized molecular orbitals

- Localized molecular orbitals
  - Block-diagonal Fock matrix (occupied and virtual blocks)
  - **No** Koopmans' theorem
  - Local!

3.4 ADC with local orbitals

- Fock matrix is no longer diagonal
- Unitary matrix: canonical → localized
- *Exact:*

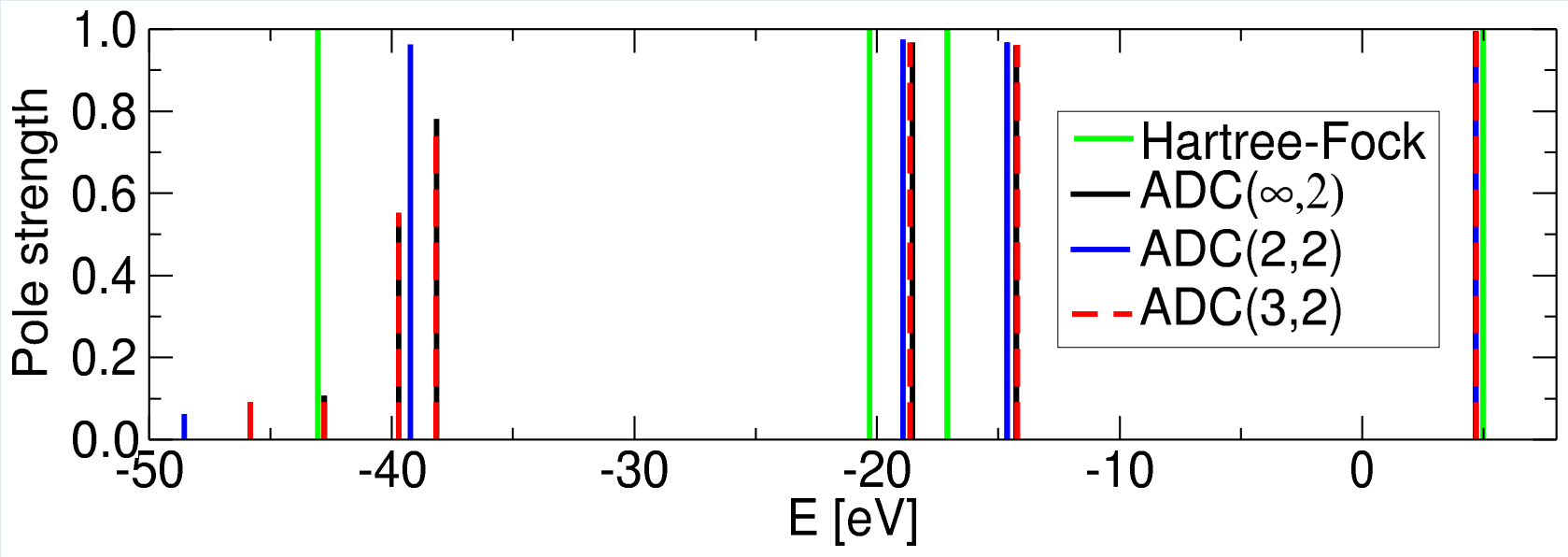
$$\mathbf{M}(\omega) = \mathbf{U}^{+} (\omega \mathbf{1} - \mathbf{K} - \mathbf{C})^{-1} \mathbf{U}$$

$$U U^{+} = \mathbf{1} \qquad U^{+} U = \mathbf{1}$$

  - Drawback: $\mathbf{B}$ is no longer sparse!
- *Perturbative:* partition Fock matrix

$$\mathbf{F}(\vec{k}) = \mathbf{F}^{\mathrm{diag}}(\vec{k}) + \mathbf{F}^{\mathrm{off}}(\vec{k})$$

3.5 Treatment of off-diagonal Fock matrix



- Perturbative treatment of off-diagonal Fock matrix elements
  - Second order satisfactory
  - Third order excellent

3.6 CO-ADC with Wannier orbitals

- Views on electrons in crystals
  - Bloch orbitals are delocalized

$$\psi_{\vec{k}\,p}(\vec{r}+\vec{R}) = \mathrm{e}^{\mathrm{i}\vec{k}\vec{R}}\,\psi_{\vec{k}\,p}(\vec{r})$$

  - Wannier orbitals are local

$$w_{\vec{R}\sigma}(\vec{r}) = w_{\vec{0}\sigma}(\vec{r}-\vec{R})$$

- Generalized Wannier transformation

$$w_{\vec{R}\sigma}(\vec{r}) = \frac{1}{\sqrt{N_0}}\sum_{\vec{k}}\sum_{p} U_{p\sigma}(\vec{k})\,\mathrm{e}^{-\mathrm{i}\vec{k}\vec{R}}\,\psi_{\vec{k}\,p}(\vec{r})$$

3.7 CO-ADC with Wannier orbitals

- ADC for Wannier orbitals

$$\mathbf{M}(\vec{k},\omega) = \mathbf{U}^{+}(\vec{k})\,(\omega\,\mathbf{1} - \mathbf{K}(\vec{k}) - \mathbf{C}(\vec{k}))^{-1}\,\mathbf{U}(\vec{k})$$

$$\mathbf{U}(\vec{k}) = \sum_{\vec{R}} e^{i\vec{k}\vec{R}}\;\mathbf{U}(\vec{R})$$

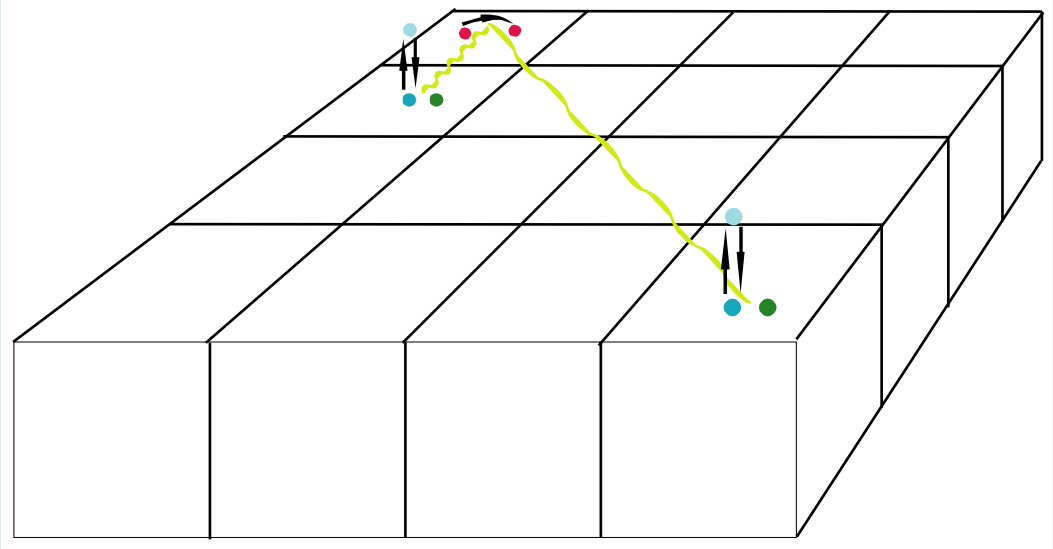
$$(\mathbf{K}+\mathbf{C})(\vec{k}) = \sum_{\vec{R}} e^{i\vec{k}\vec{R}}\;(\mathbf{K}+\mathbf{C})(\vec{R})$$

- $2p1h/2h1p$ configurations in Wannier orbitals

[Theory: Buth, Birkenheuer, Albrecht, Fulde: arXiv:cond-mat/0409078]

3.8 Configuration Selection

- Crystals are infinite => select excited configurations
- Dynamical selection for each crystal anew

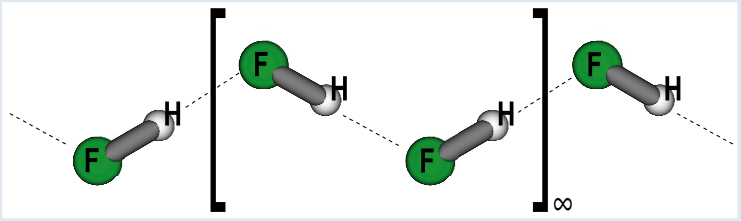


- Second order self-energy to select configurations
- Definition of degeneracy

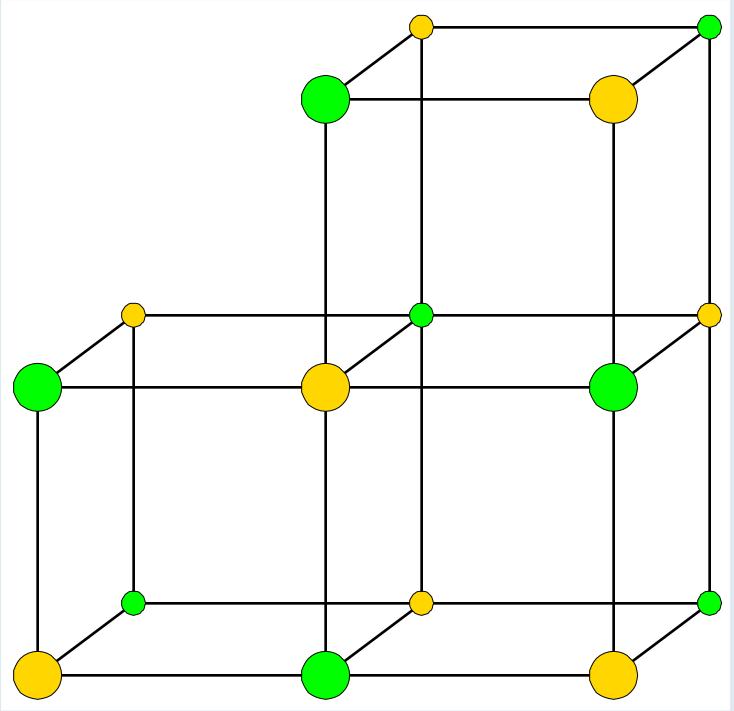
Contents

4.1 Periodic systems

- $(HF)_\infty$ simple model for HF crystal
- Hydrogen-bonded

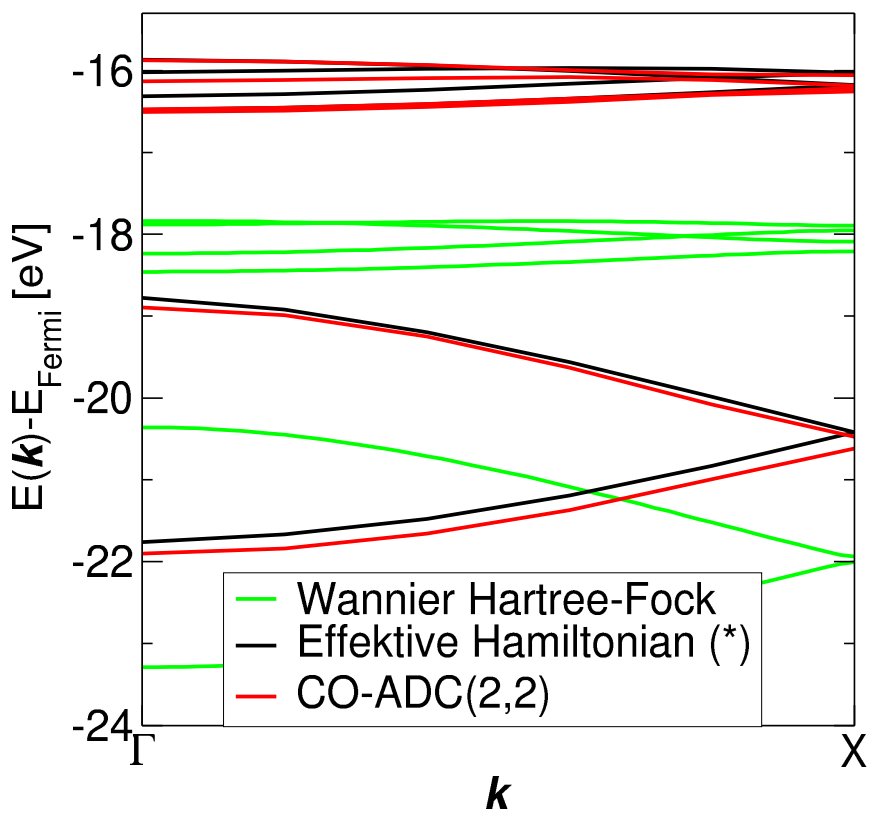


- LiF crystal
- Rock salt structure (fcc)
- Ionic



4.2 Correlated band structure of $(HF)_\infty$

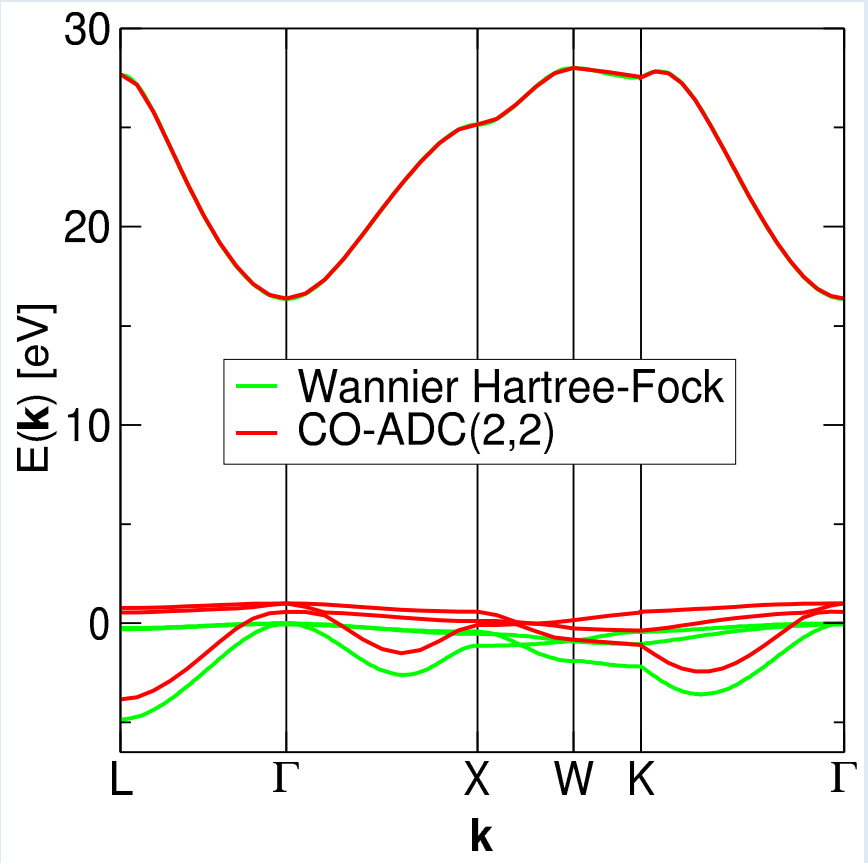
- Excitations from origin cell only
- Band widths are increased by electron correlation
- Basis set cc-pVDZ



(*) Calculation by **Viktor Bezugly**
[Theory: Bezugly, Birkenheuer: Chem. Phys. Lett. **399** 57 (2004)]

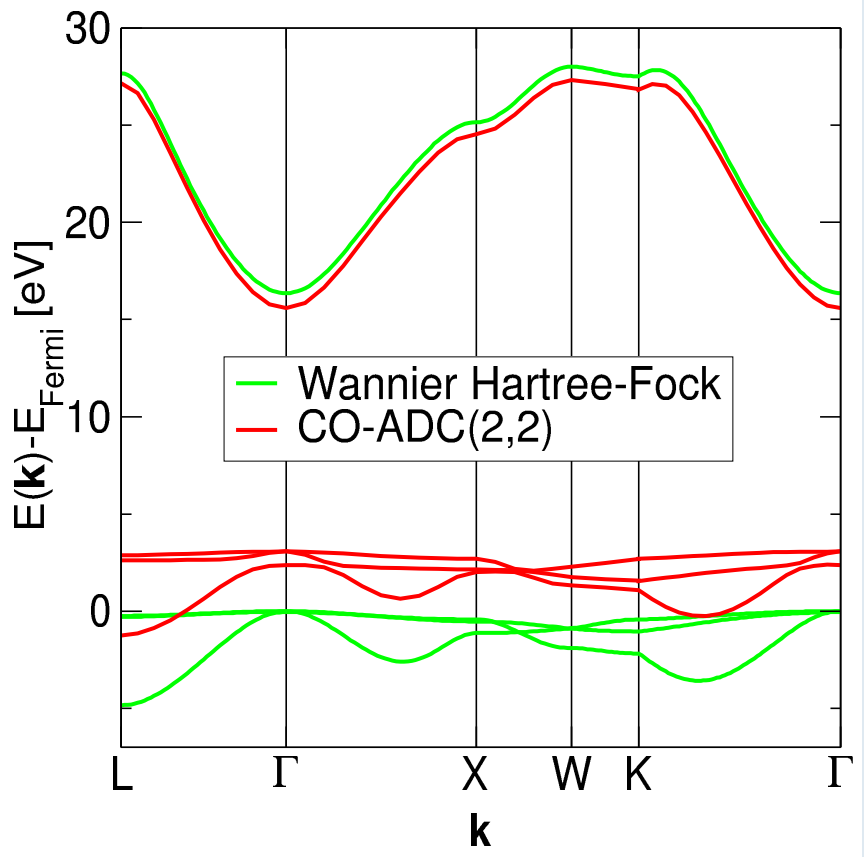
4.3 Correlated band structure of LiF

- Excitations from origin cell only
- Upwards shift of valence bands
- Conduction band unchanged
- Minimal basis set STO-6G



4.4 Correlated band structure of LiF

- Excitations from 19 unit cells
- Shift of conduction and valence bands increased
- Band widths are increased by electron correlation
- Good agreement with experiments



5.1 Conclusion

- *Ab initio* methods enable to predict properties of solids
- Electron correlation plays a significant role
- Translational symmetry
- Configuration selection
- ADC with local orbitals
- Systematically improvable CO-ADC(2), CO-ADC(3), …

5.2 Outlook

- Strong correlation
- Electronic resonances (Auger effect)
- No metals!
  - Wannier orbitals decay extremely slowly
  - Occupation numbers dependent on crystal momentum
  - Need to exchange the one-particle orbitals

5.3 Acknowledgement

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