# Green's function approach to *ab initio* band structures

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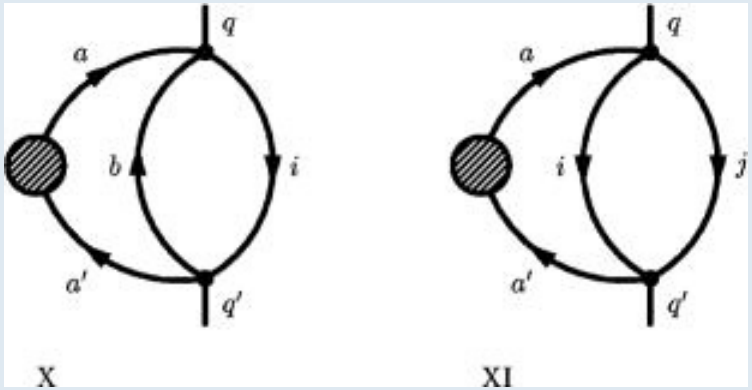


# Contents

# 1.1 First principles methods

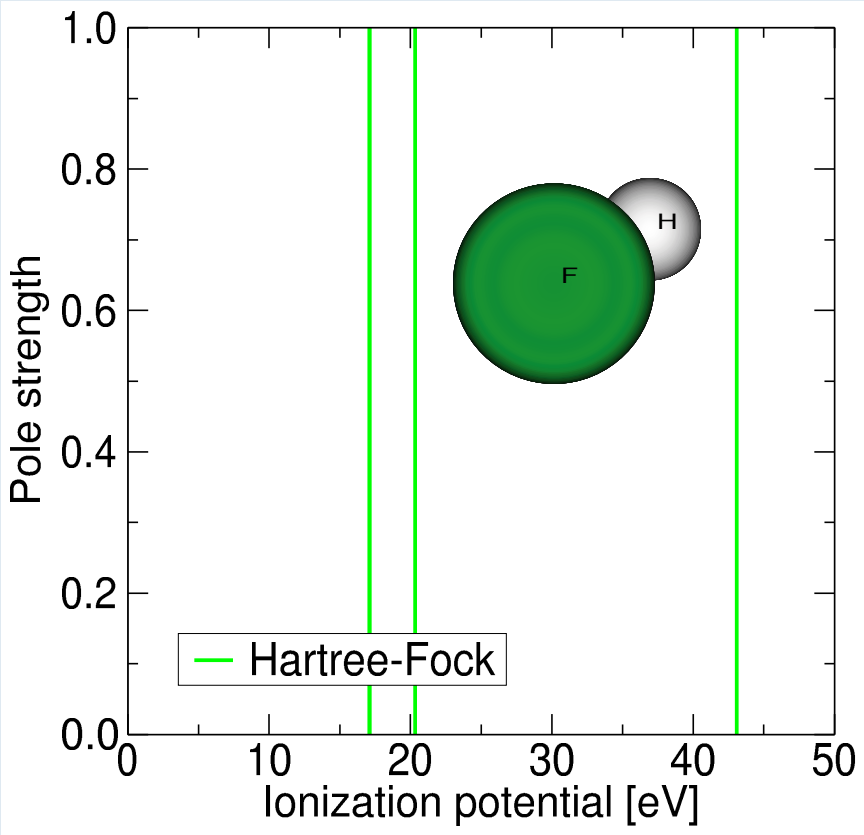
- Schrödinger equation with the *full* electronic Hamiltonian

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

- Independent particle/quasi-particle theories:
  - *Ab initio* (wavefunction based): Hartree-Fock
  - Density functional theory: time-*in*dependent DFT
- **But** there are many-body effects beyond the one-particle picture!

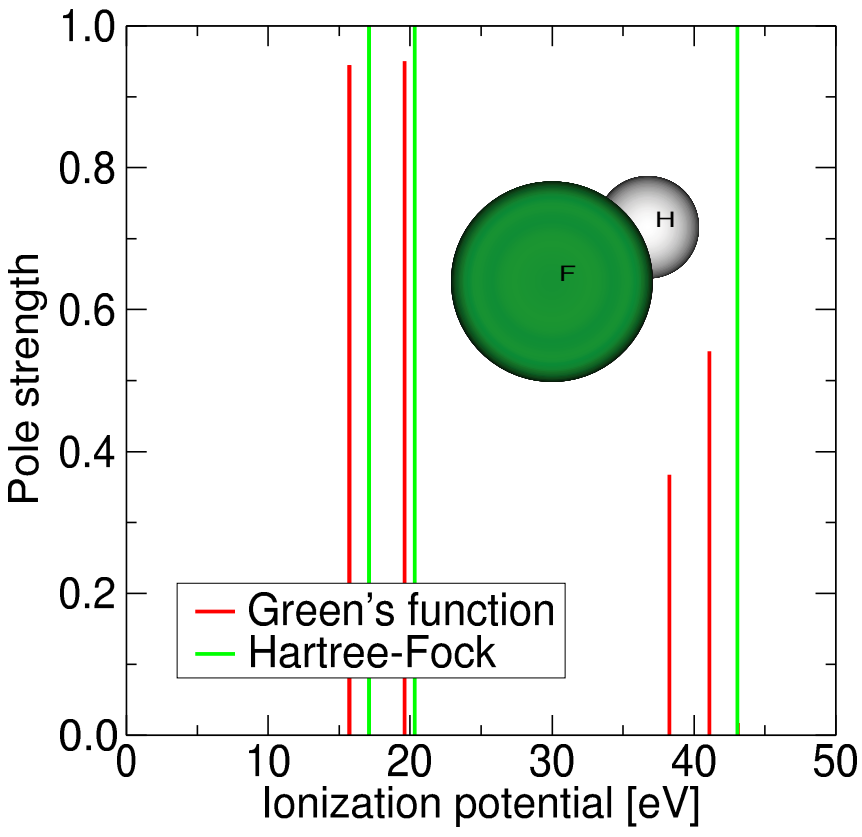
# 1.2a Hydrogen fluoride molecule

- The Hartree-Fock approximation yields ionization potentials (Koopmans' theorem)
- Many-body effects are neglected



# 1.2b Hydrogen fluoride molecule

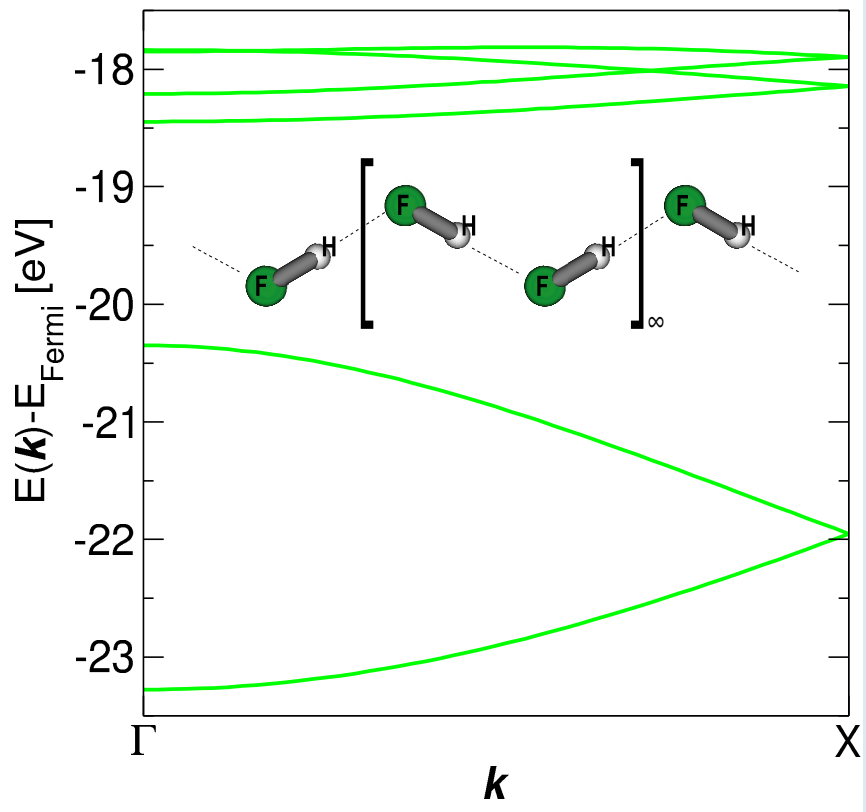
- Many-body effects are dominant for the inner valence region in molecules
- Electronic resonances like the Auger effect can be understood more deeply for molecules




[Buth, Santra, Cederbaum, J. Chem. Phys. **119** 10575 (2003)]

# 1.3 Hartree-Fock band structure

- Hydrogen fluoride polymer
- Calculations are routine
- CRYSTAL03 or WANNIER98



# 2.1 Many-Body Green's Functions

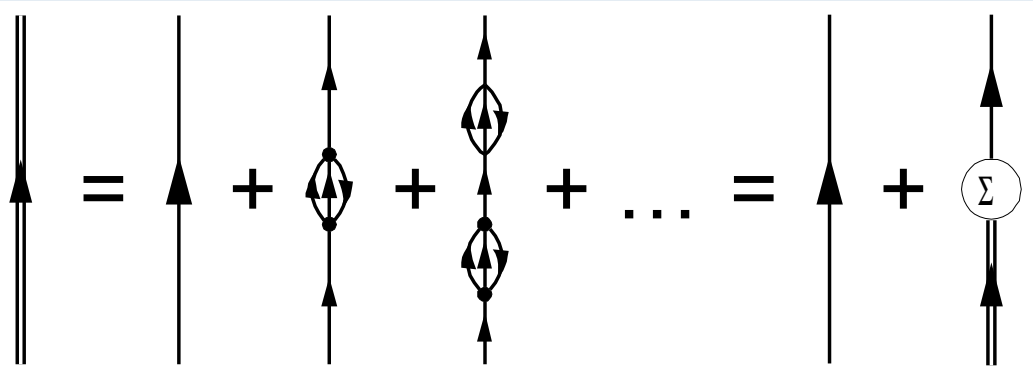
- Particle propagator

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

- Ground state energy
- Ground state expectation values of one-particle operators
- Excitation energies, i.e. the band structure

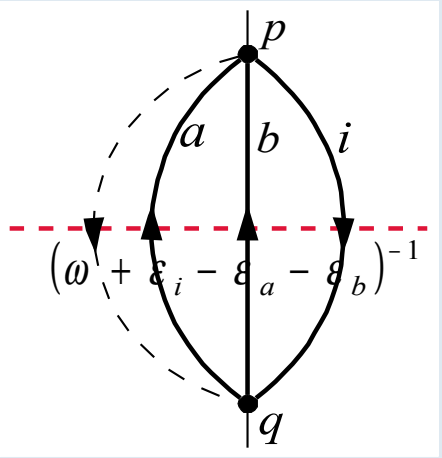
# 2.2 Feynman diagrams

- Time-dependent perturbation theory for residual interaction
- Explicit $n$-th order expressions for the Green's function
- Sum of Feynman diagrams to $\infty$ order by the Dyson equation



# 2.3 Evaluation of diagrams

- Evaluation of diagrams with a Fourier transformation to energy variables




$$\Sigma^{(2)}_{pq}(\omega) = \sum_{\substack{i,a,b \\ a<b}} \frac{V_{p\,i[a\,b]}\, V^{*}_{q\,i[a\,b]}}{\omega + \varepsilon_i - \varepsilon_a - \varepsilon_b}$$

$$= \underbrace{\begin{pmatrix} \cdots & V_{p\,i[a\,b]} & \cdots \end{pmatrix}}_{\vec{U}^{+}_{p}} \underbrace{\begin{pmatrix} \ddots & & \\ & \omega + \varepsilon_i - \varepsilon_a - \varepsilon_b & \\ & & \ddots \end{pmatrix}^{-1}}_{(\omega\,\mathbf{1} - \mathbf{K})^{-1}} \underbrace{\begin{pmatrix} \vdots \\ V^{*}_{q\,i[a\,b]} \\ \vdots \end{pmatrix}}_{\vec{U}_{q}}$$

$$= \vec{U}^{+}_{p}\,(\omega\,\mathbf{1} - \mathbf{K})^{-1}\,\vec{U}_{q}$$

[Cederbaum, Domcke: Adv. Chem. Phys. **36** 205 (1977)]

# 2.4a Algebraic diagrammatic construction

- Static and dynamic self-energy

$$\mathbf{\Sigma}(\omega) = \mathbf{\Sigma}^{\infty} + \mathbf{M}_{\mathrm{I}}(\omega) + \mathbf{M}_{\mathrm{II}}(\omega)$$

- Analytic structure of $\mathbf{M}(\omega)$ [Schirmer, Cederbaum, Walter: Phys. Rev. A, **28** 1237 (1983)]

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

- *n*-th order approximation to ADC matrices

$$\mathbf{U}(\vec{k}) = \mathbf{U}^{(1)}(\vec{k}) + \mathbf{U}^{(2)}(\vec{k}) + \mathbf{U}^{(3)}(\vec{k}) + \ldots$$

$$\mathbf{C}(\vec{k}) = \mathbf{C}^{(1)}(\vec{k}) + \mathbf{C}^{(2)}(\vec{k}) + \ldots$$

# 2.4b Algebraic diagrammatic construction

- Geometric series expansion

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

$$= \mathbf{U}^{+} \sum_{n=0}^{\infty} \left[ (\omega \mathbf{1} - \mathbf{K})^{-1} \mathbf{C} \right]^{n} (\omega \mathbf{1} - \mathbf{K})^{-1} \mathbf{U}$$

- Pole search by diagonalizing $\mathbf{K} + \mathbf{C}$
- *Infinite* partial summation of diagrams

# 2.5 Correlated band structures

- Band structures are calculated 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 eigenvalue solver

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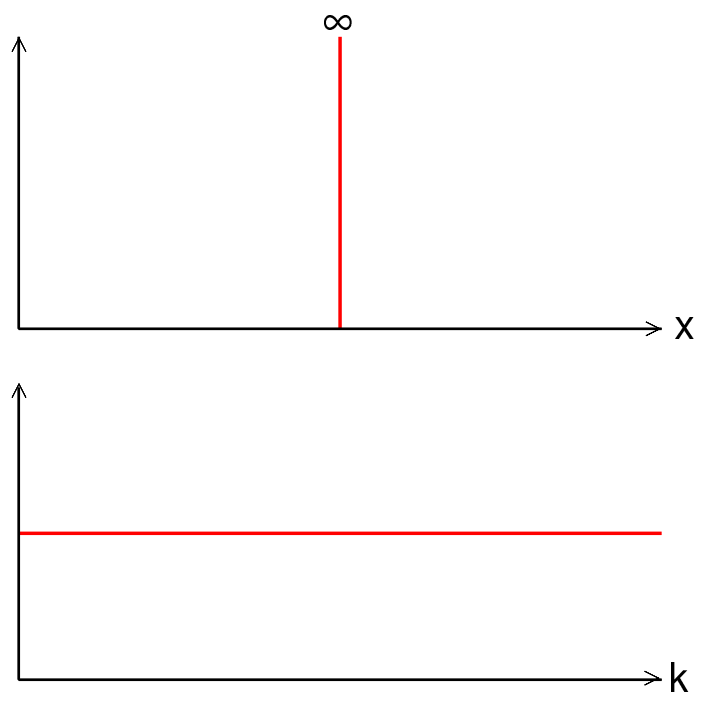
# 3.1 Wannier transformation

- Electron correlation is local
  - Bloch orbitals are delocalized
  - Wannier orbitals are local
- Generalized Wannier transformation



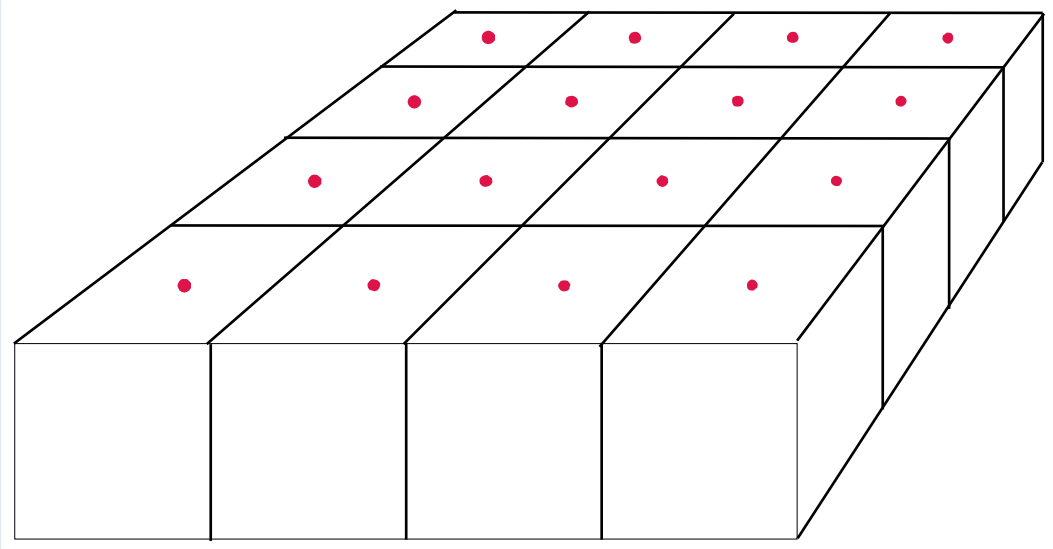

$$\left|\vec{R}\sigma\right\rangle = \frac{1}{\sqrt{N_0}} \sum_{\vec{k}} \sum_{p} U_{p\sigma}(\vec{k})\, e^{-i\vec{k}\vec{R}} \left|\vec{k}p\right\rangle$$

# 3.2 CO-ADC in Wannier orbitals

- Self-energy depends on a single crystal momentum vector $\mathbf{\Sigma}(\vec{k},\omega)$
- Express the $\vec{k}$ -dependent self-energy in terms of Wannier orbitals
  - Three schemes are customary in Literature
  - Differ by the degree of exploitation of translational symmetry

# 3.3 Large cluster

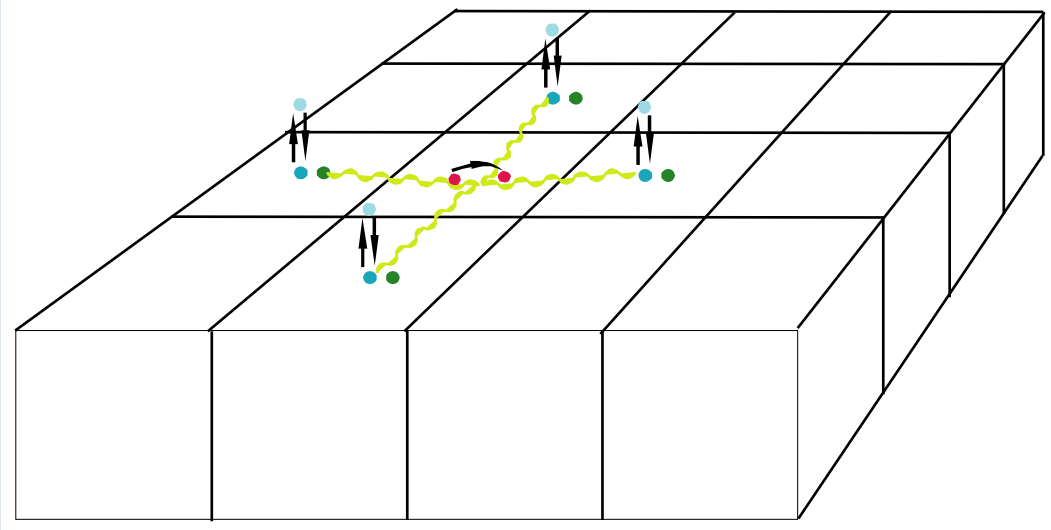
- Parallelepiped of $N_0^3$ unit cells
- “Molecular” calculation



- Brillouin zone is discretized by only $N_0^3$ points
- Finite size effects

# 3.4 Translational symmetry of self-energy

- Choose a unit cell to be origin cell
- Excitations relative to origin cell



- Excitations are still redundant
- Successfully applied in Dresden

# 3.5 Full use of translational symmetry

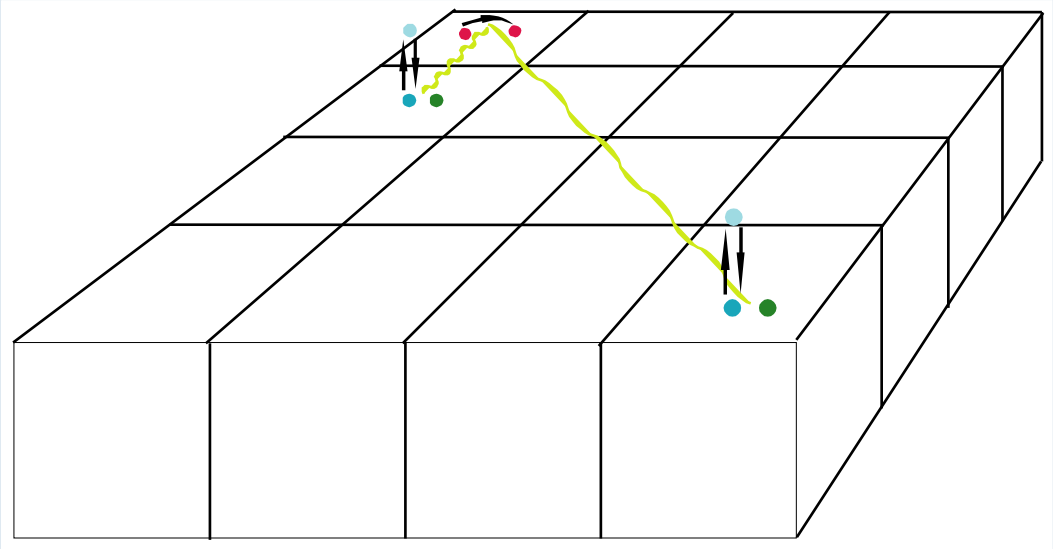
- Exploit translational symmetry of all matrices in

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

- Only excitations not related by translational symmetry are included
- No redundancy left

# 4.1 Configuration Selection

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



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

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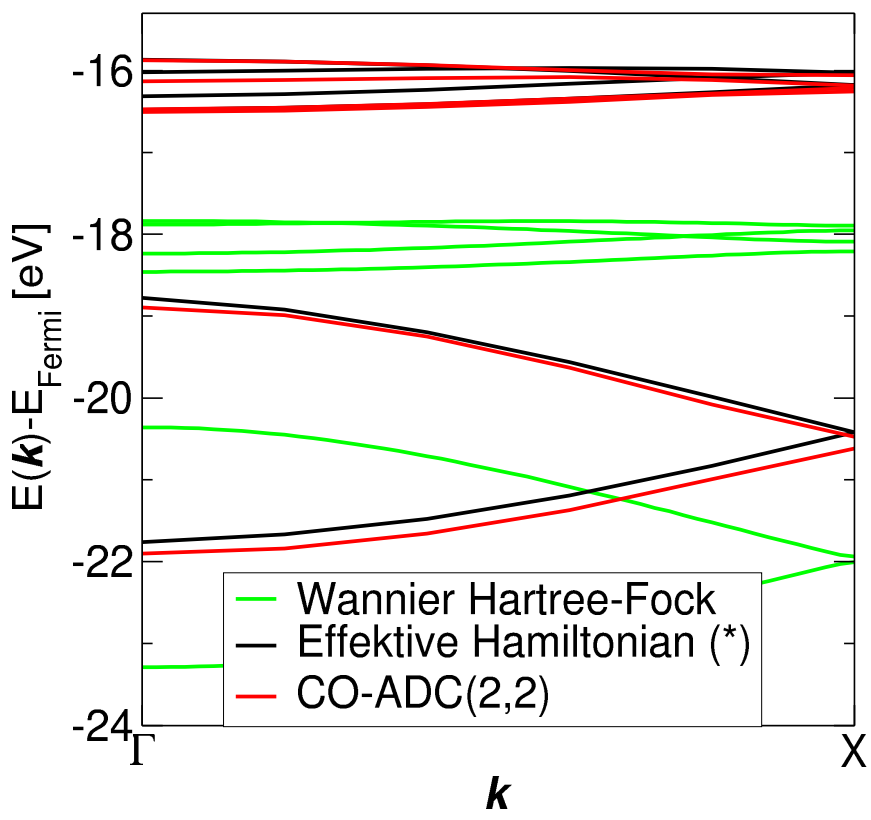
# 5.1 CO-ADC code

- CO-ADC(2) code based on Hartree-Fock calculations with WANNIER98
- Comparison with ADC(2) for molecules
- Generalized Wannier transformation => Fock matrix is no longer diagonal due to band mixing by $U(\vec{k})$
- Perturbative treatment of off-diagonal Fock matrix elements
  - Second order treatment satisfactory
  - Third order treatment excellent

# 5.2 Correlated band structure of $(HF)_\infty$

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

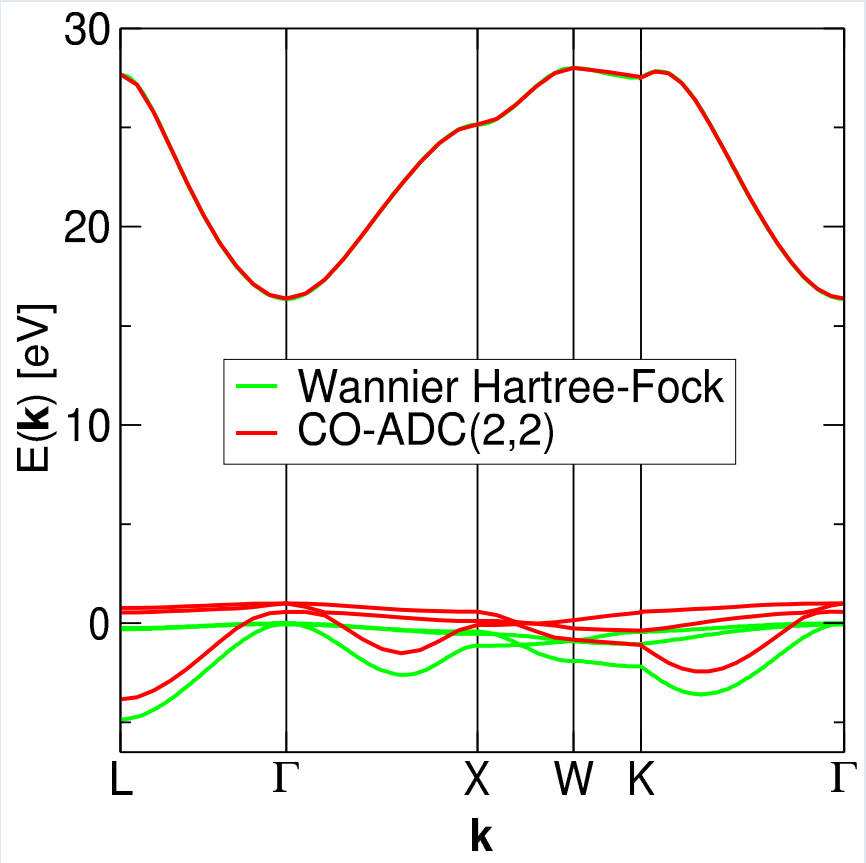



(*) Calculation by **Viktor Bezugly**

[Theory: Viktor Bezugly, Uwe Birkenheuer: arXiv:cond-mat/0407382]

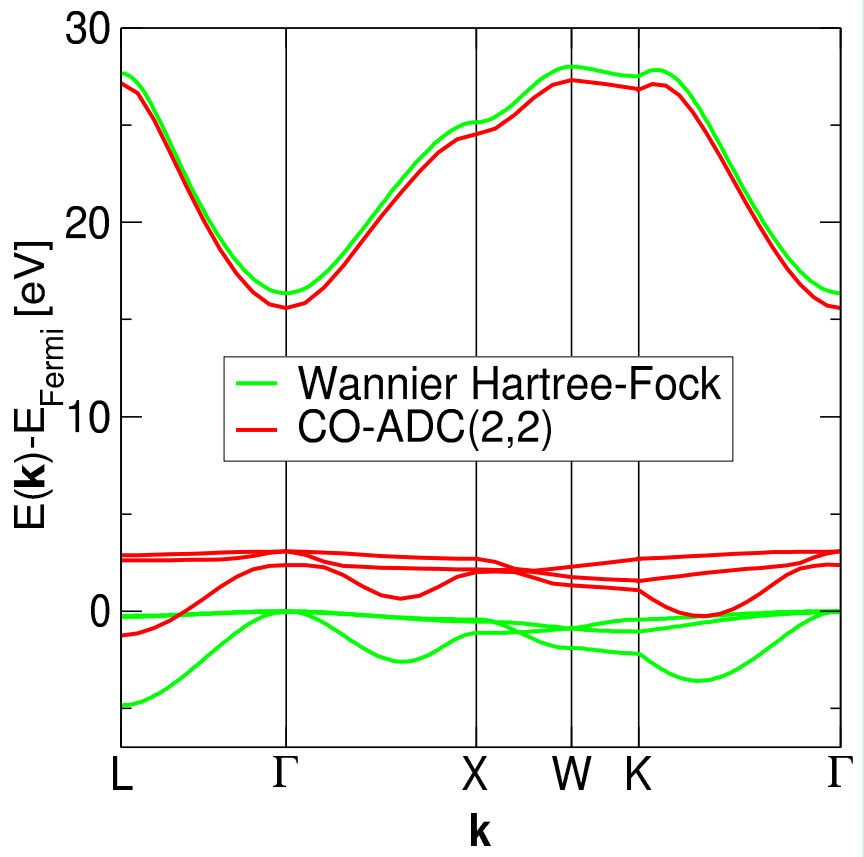
# 5.3 Correlated band structure of LiF

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



# 5.4 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



# 6.1 Conclusion

- *Ab initio* methods facilitate to predict properties of solids
- Electron correlation plays a significant role
- Translational symmetry
- Configuration selection
- CO-ADC is a simple method
- Systematically improvable CO-ADC(2), CO-ADC(3), …

# 6.2 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 basis

# 6.3 Acknowledgement


- Peter Fulde, Uwe Birkenheuer, Viktor Bezugly

Max-Planck-Institut für Physik komplexer Systeme, Dresden

- Jochen Schirmer

Theoretische Chemie, Ruprecht-Karls-Universität Heidelberg

- Martin Albrecht

Theoretische Chemie, Universität Siegen

- Alok Shukla

Indian Institute of Technology, Bombay