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

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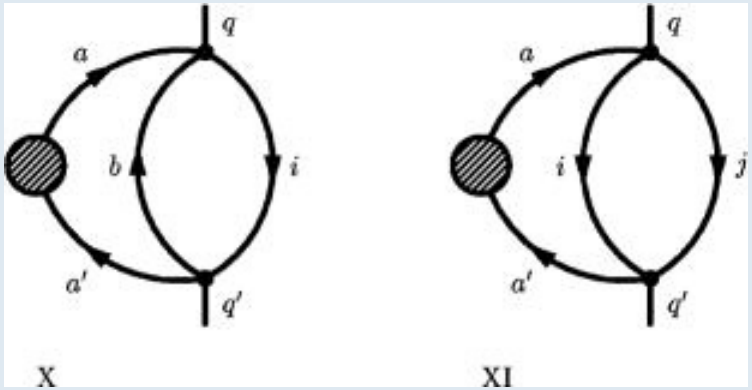
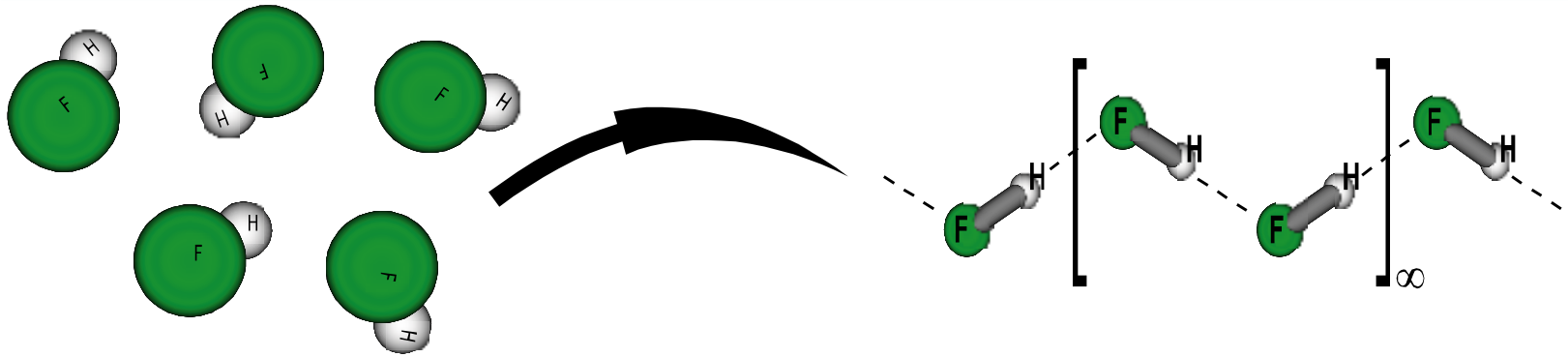


# Contents

# 1.1 From molecules to crystals

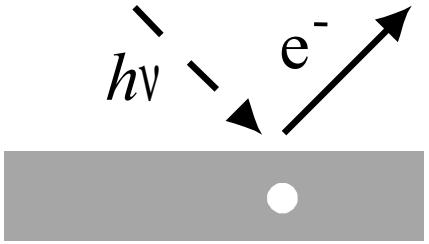
- Crystallization



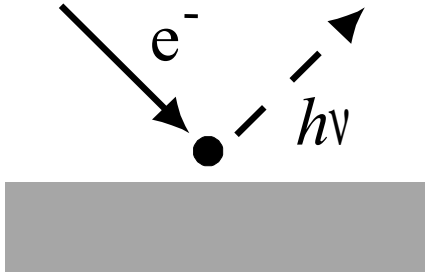

- Crystals are huge molecules
- Periodic repetition (translational symmetry)
- **Usual model:** crystals extend to infinity

# 1.2 Experiments

- Excited states of solids




Ionization potentials
Valence bands




Electron affinities
Conduction bands

# 1.3 First principles methods

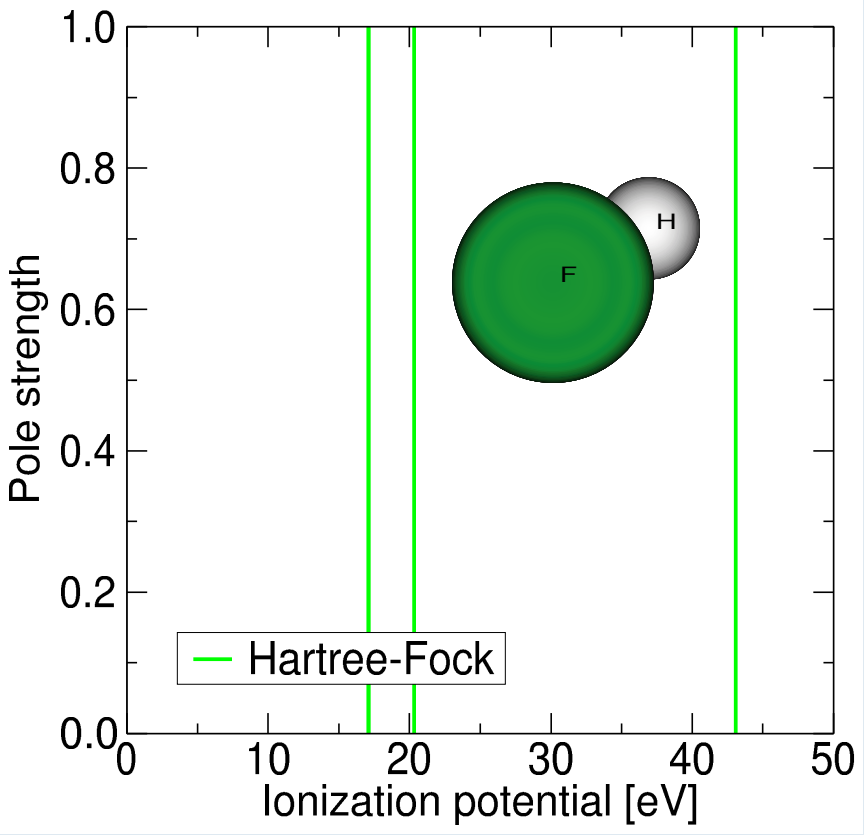
- Schrödinger equation with the *full* electronic Hamiltonian

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

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

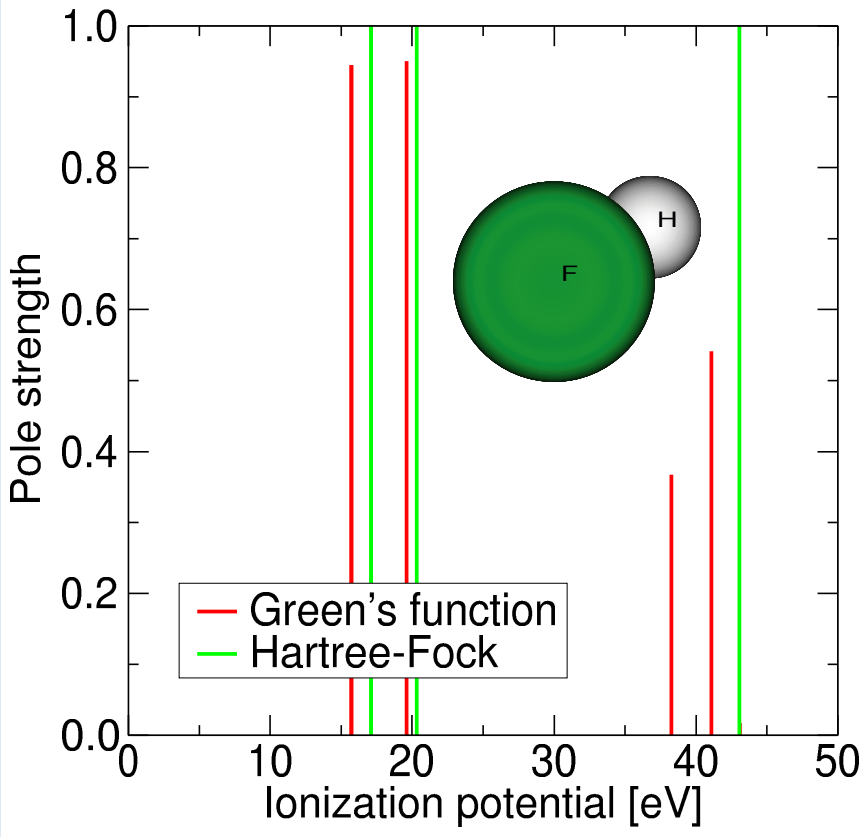
# 1.4a Hydrogen fluoride molecule

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



# 1.4b Hydrogen fluoride molecule

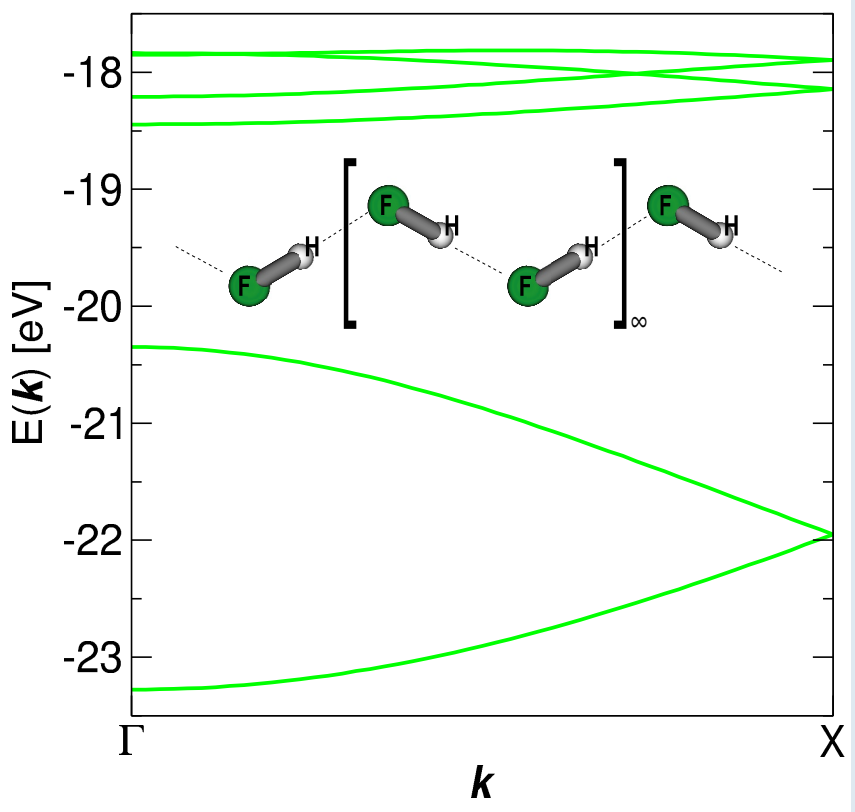
- Strong many-body effects govern the inner valence region
- Electronic resonances like the Auger effect can be understood




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

# 1.5 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

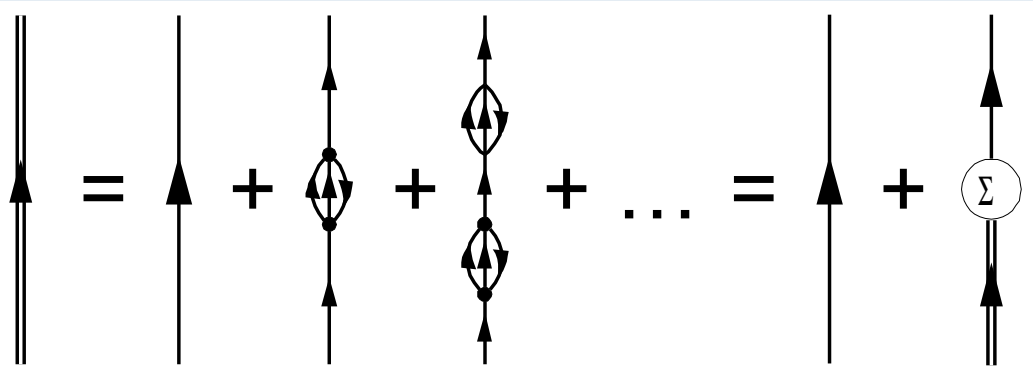
- Green's function (particle propagator)

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

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

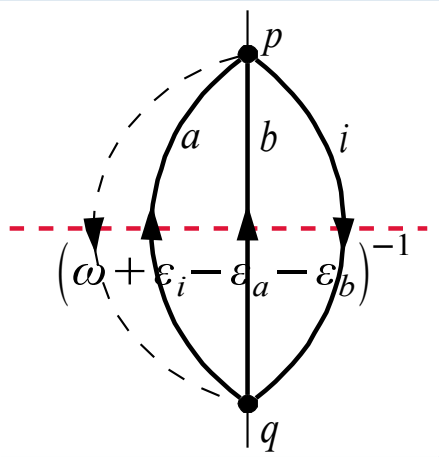
# 2.2 Feynman diagrams

- 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 ($2p1h$ contribution)




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

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

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

[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)]

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

- Geometric series expansion

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

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

# 2.4b Algebraic diagrammatic construction

- $n$-th order approximation to ADC matrices

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

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

- Determination of $\mathbf{U}^{(i)}, \mathbf{C}^{(i)}$ by comparison with the Feynman diagrams for $\mathbf{M}(\omega)$
- Pole search by diagonalizing $\mathbf{K} + \mathbf{C}$
- *Infinite* partial summation of diagrams

# 2.5 Crystal orbital ADC

- Molecular ADC equations for $\mathbf{U}, \mathbf{K}, \mathbf{C}$
- Replace MO by CO $i \rightarrow \vec{k}i$
- Exploit translational symmetry of $\mathbf{U}, \mathbf{K}, \mathbf{C}$

# 2.6 Quasi-particle band structures

- Band structures are calculated by means 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

# Contents

# 3.1 Views on independent electrons

- Views on independent 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

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

- Hartree-Fock wave function unchanged

# 3.2 CO-ADC with local orbitals

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

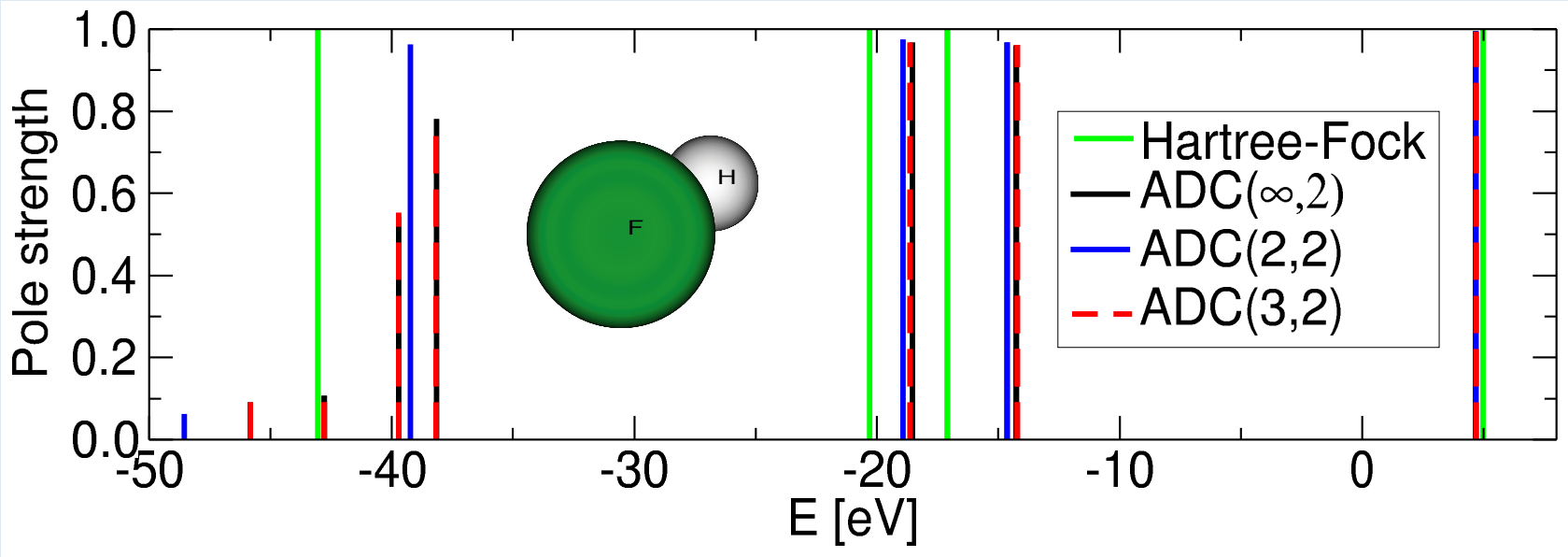
$$\mathbf{M}(\vec{k},\omega) = \mathbf{U}^{+} (\omega\, \mathbf{1} - \mathbf{K} - \mathbf{C})^{-1} \mathbf{U}$$

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

  - Drawback: $\mathbf{B}(\vec{k})$ is no longer sparse!
- *Perturbative:* Fock matrix partitioning

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

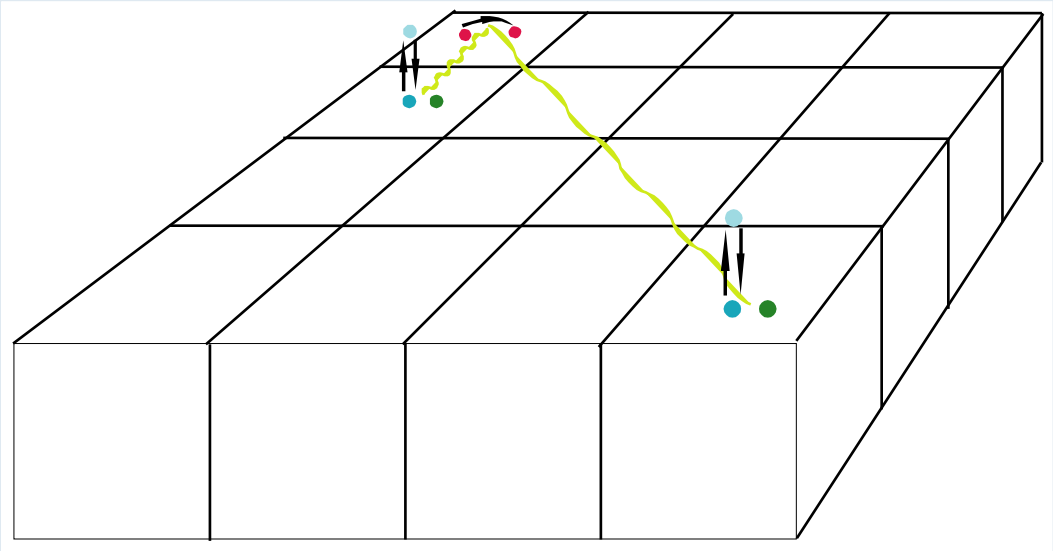
# 3.3 Treatment of off-diagonal Fock matrix




- Perturbative treatment of $\mathbf{F}^{\text{off}}(\vec{k})$ for a HF molecule, basis set cc-pVDZ
  - Second order satisfactory
  - Third order excellent

# 3.4 Configuration Selection

- Crystals are infinite
  $\Rightarrow$ select excited configurations
- Dynamical selection for each crystal anew

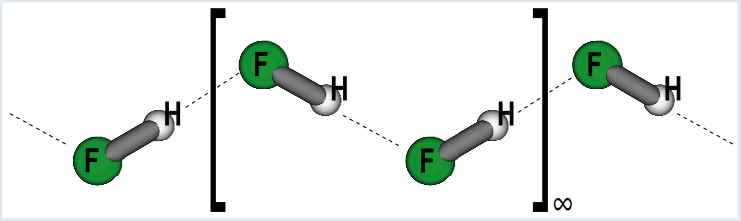


- Use 2nd order self-energy to select configurations
- Definition of degeneracy

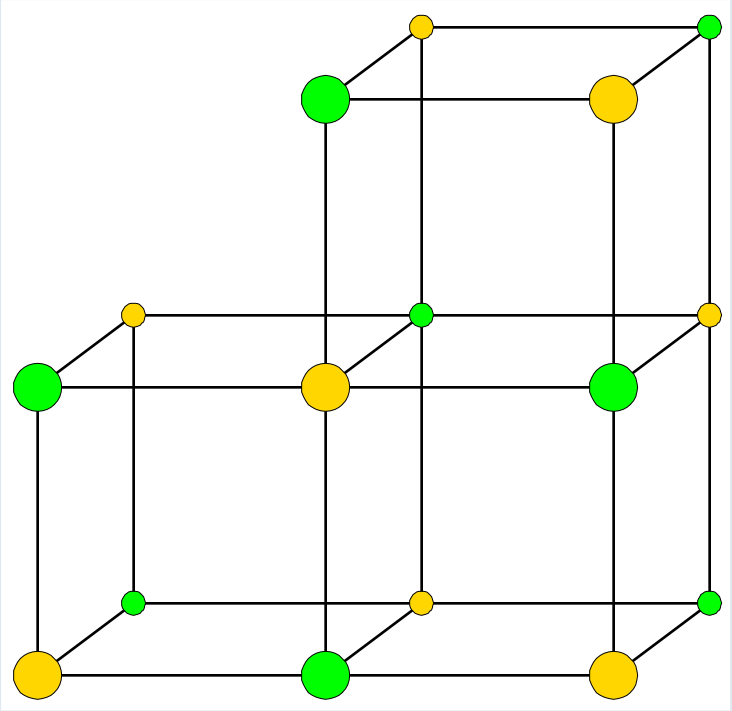
# Contents

# 4.1 Periodic systems

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

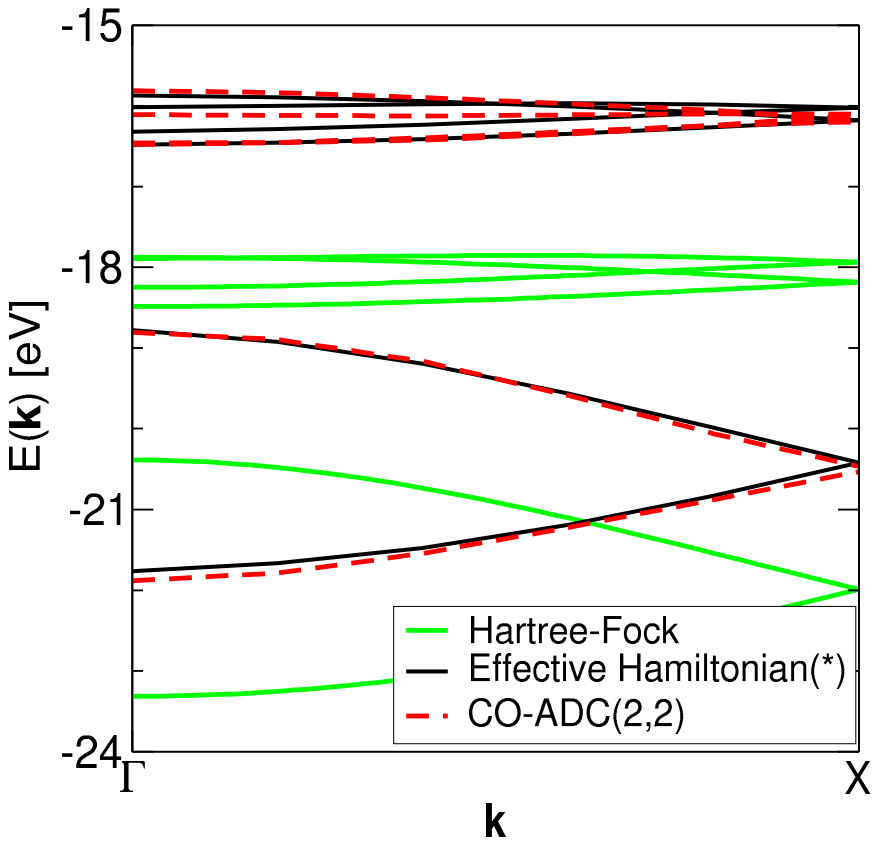



- LiF crystal
- Rock salt structure (fcc)
- Ionic



# 4.2 Quasi-particle band structure of $(HF)_\infty$

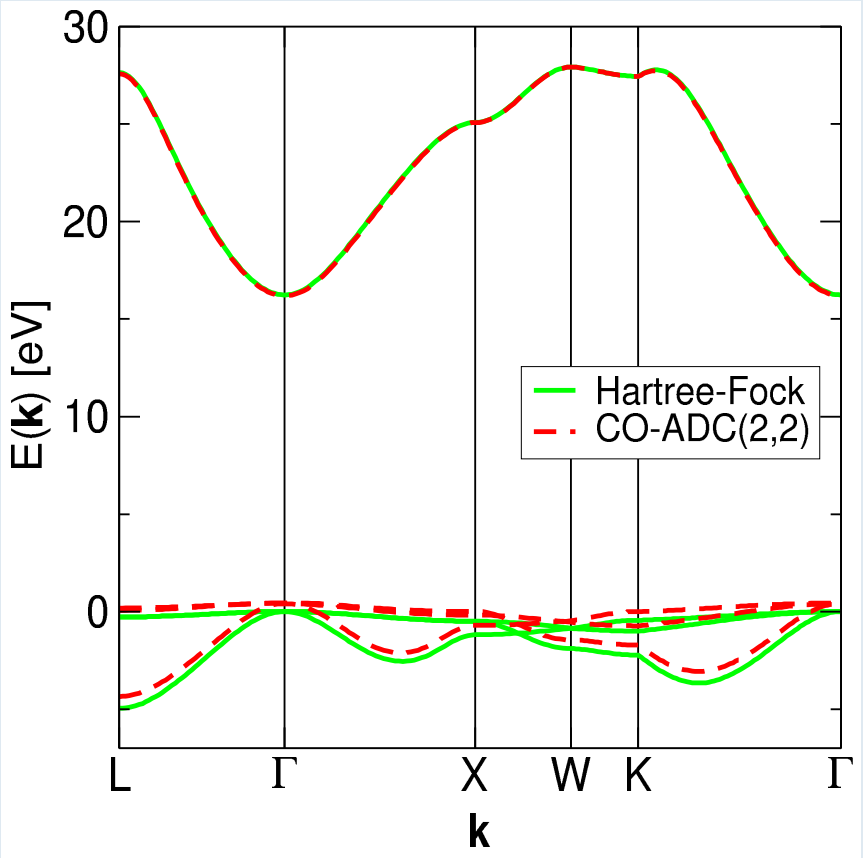
- Excitations from origin cell only
- Band widths are slightly increased by electron correlation
- Basis set cc-pVDZ




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

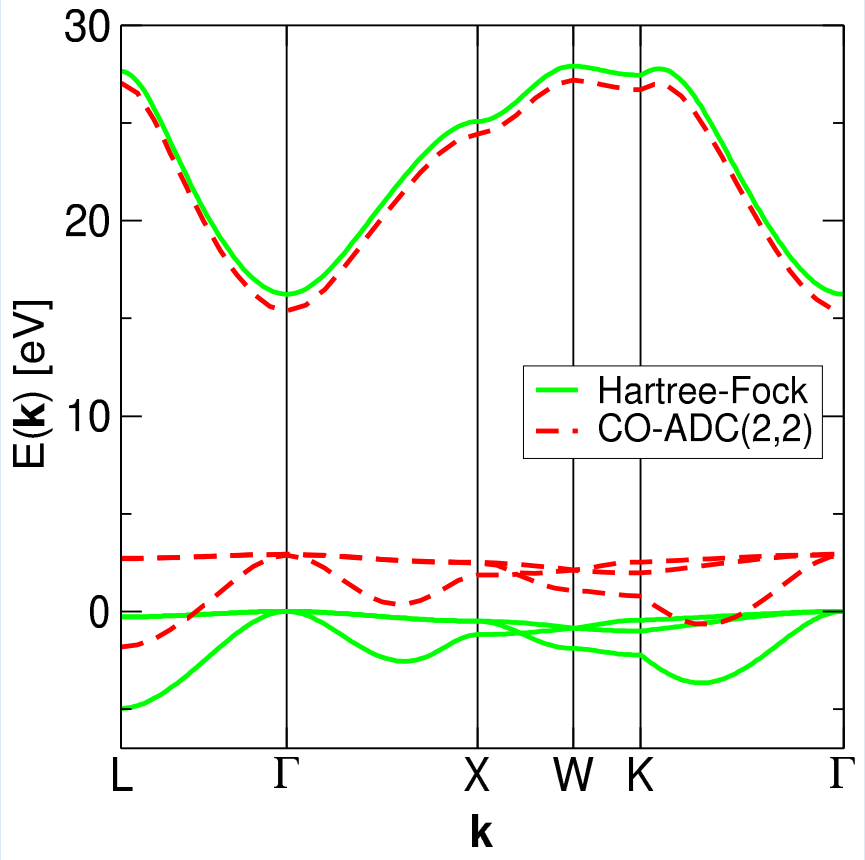
# 4.3a Quasi-particle band structure of LiF

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



# 4.3b Quasi-particle band structure of LiF

- Excitations from 19 unit cells (up to 2nd nearest neighbours)
- Shift of conduction and valence bands increased noticeably
- Band widths are hardly influenced by electron correlations
- Good agreement with experiments



# 5.1 Conclusion

- *Ab initio* methods enable to predict properties of solids
- Electron correlation plays a significant role
- Translational symmetry exploited
- Configuration selection employed
- 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 slowly
  - Occupation numbers dependent on crystal momentum

# 5.3 Acknowledgment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