Green's function approach to ab initio band structures

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Crystal orbital algebraic diagrammatic construction (CO-ADC)

One-particle Green's function in crystal momentum representation:

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

- The one-particle Green's function contains less information than the many-particle wave function:
  - *Exact* correlated band structures are given by the poles of $G_{pq}(\vec{k},\omega)$.
  - The *exact* ground-state energy and the *exact* ground-state expectation values of one-particle operators can be expressed in terms of $G_{pq}(\vec{k},t,t')$.
- $G_{pq}(\vec{k},\omega)$ can be evaluated perturbatively in terms of Goldstone diagrams which is the central approximation employed.

Intermediate change of representation:

- Introduction of the self-energy $\boldsymbol{\Sigma}(\vec{k},\omega)$ by the Dyson equation.

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

- Electron correlations are predominantly local!
- Generalized Wannier orbitals are the conceptual equivalent to localized molecular orbitals.
- Localized orbitals have been utilized successfully in linear scaling methods to compute ground-state energies of large molecules.
- **Thus** represent self-energy in terms of Wannier orbitals.
- Full translational symmetry adaption.
- Exploitation of the invariance under lattice translations of the individual terms in the self-energy.

Algebraic diagrammatic construction (ADC) for crystal orbitals:

- Ansatz for the self-energy (ADC form) [1, 2].

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

$$\boldsymbol{M}^{\pm}(\vec{k},\omega) = \boldsymbol{U}^{\pm\dagger}(\vec{k})\,(\omega\,\mathbb{1} - \boldsymbol{K}^{\pm}(\vec{k}) - \boldsymbol{C}^{\pm}(\vec{k}))^{-1}\,\boldsymbol{U}^{\pm}(\vec{k})$$

- The Lehmann representation of the one-particle Green's function $\boldsymbol{G}(\vec{k},\omega)$ which yields the quasi-particle band structure is determined from the Hermitian eigenvalue problem:

$$\boldsymbol{B}(\vec{k})\boldsymbol{X}(\vec{k}) = \boldsymbol{X}(\vec{k})\boldsymbol{E}(\vec{k})$$

$$\boldsymbol{B}(\vec{k}) = \begin{pmatrix} (\boldsymbol{F}+\boldsymbol{\Sigma}^{\infty})(\vec{k}) & \boldsymbol{U}^{+\dagger}(\vec{k}) & \boldsymbol{U}^{-\dagger}(\vec{k}) \\ \boldsymbol{U}^{+}(\vec{k}) & (\boldsymbol{K}^{+}+\boldsymbol{C}^{+})(\vec{k}) & \boldsymbol{0} \\ \boldsymbol{U}^{-}(\vec{k}) & \boldsymbol{0} & (\boldsymbol{K}^{-}+\boldsymbol{C}^{-})(\vec{k}) \end{pmatrix}$$

- Allows a numerically stable determination of poles.
- *Non-perturbative description:* perturbation theory *only* serves to construct an intermediate state representation of the Hamiltonian which is diagonalized subsequently.
- Describes correlation effects **beyond** the quasi-particle picture: strong correlation and electronic resonances [3, 4].

Configuration selection:

- The problem of assembling $\boldsymbol{\Sigma}(\vec{k},\omega)$ is *infinite*.
- Configuration selection is needed to obtain a linear scaling configuration space.
- The summand in the analytic expression of the second order self-energy diagrams can be used as a selection criterion:

$$\frac{V_{\vec{0}\varrho\,\vec{g}_1\kappa\,[\vec{g}_2\alpha\,\vec{g}_3\beta]}\,V^{*}_{\vec{R}\sigma\,\vec{g}_1\kappa\,[\vec{g}_2\alpha\,\vec{g}_3\beta]}}{\omega-\varepsilon_{\vec{g}_2\alpha}-\varepsilon_{\vec{g}_3\beta}+\varepsilon_{\vec{g}_1\kappa}}\; n_{\vec{g}_1\kappa}\,\bar{n}_{\vec{g}_2\alpha}\,\bar{n}_{\vec{g}_3\beta}\ .$$

- Truncation of the configuration space implies a finite-range of the Coulomb interaction.
- Only a certain number of non-degenerate states are decribed.
- The computational effort to determine excited states in crystals scales linearly, if only a few a priori chosen states are considered, but, generally, the problem is a *quadratical scaling problem*!

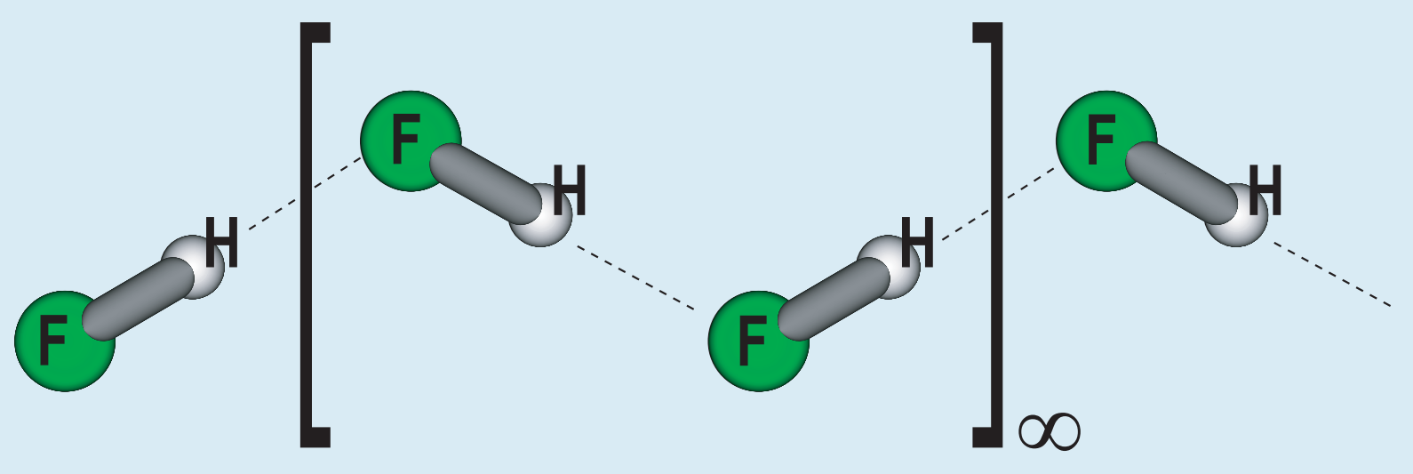
References:

[1] J. Schirmer, L. S. Cederbaum, and O. Walter, Phys. Rev. A **28** 1237 (1983)
[2] C. Buth, U. Birkenheuer, M. Albrecht, and P. Fulde, submitted to Phys. Rev. B., arXiv: cond-mat/0409078
[3] C. Buth, R. Santra, and L. S. Cederbaum, J. Chem. Phys., **119** 7763 (2003), arXiv: physics/0306123
[4] C. Buth, R. Santra, and L. S. Cederbaum, J. Chem. Phys., **119** 10575 (2003), arXiv: physics/0303100

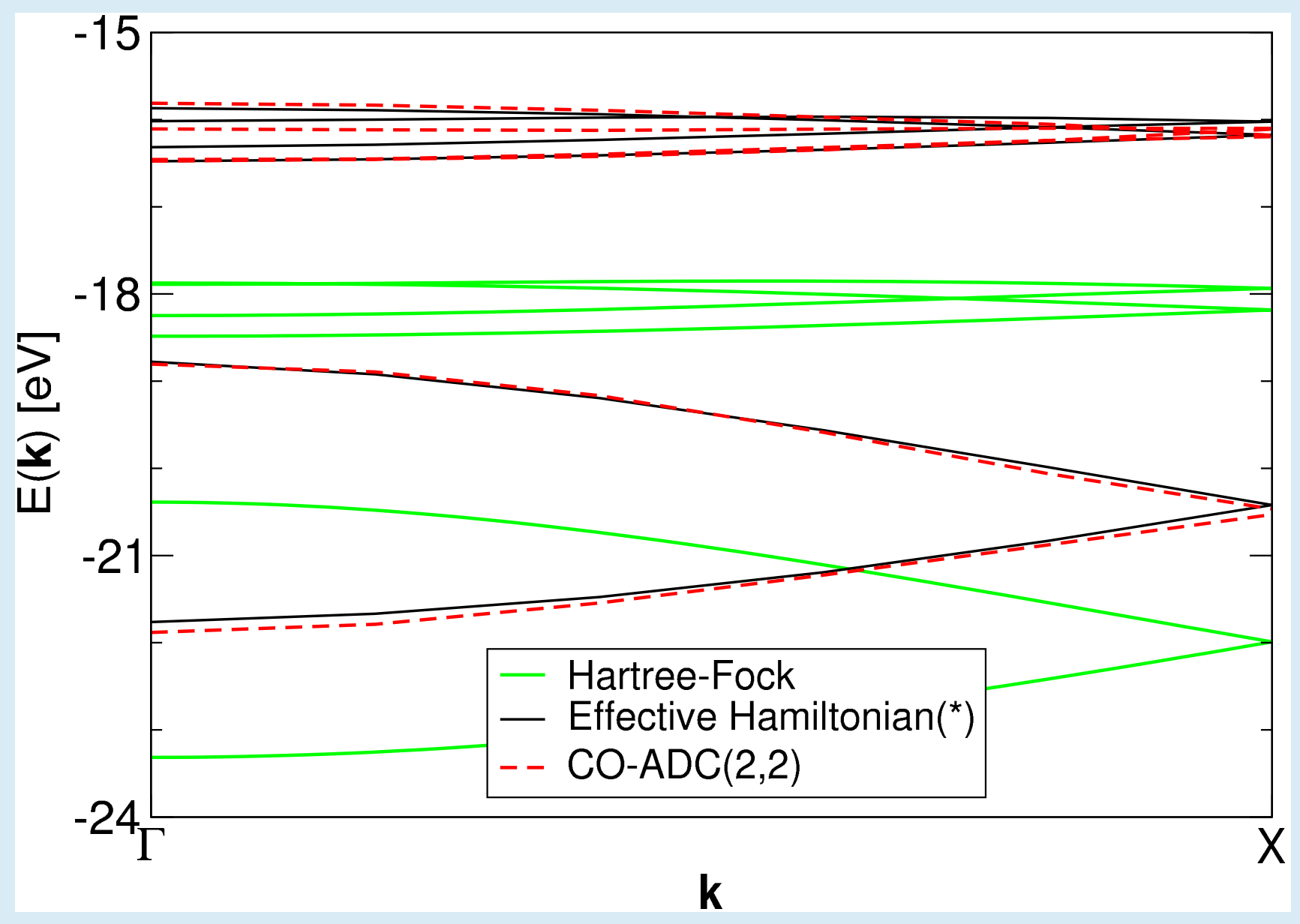
Ab initio quasi-particle band structures of a $(\mathrm{HF})_\infty$ chain and a bulk LiF crystal

Band structure of $(\mathrm{HF})_\infty$ chains:

- Zig-zag chain, basis set cc-pVDZ.



- Excitations from the valence orbitals of the origin unit cell plus the nearest and next nearest neighbour unit cells.

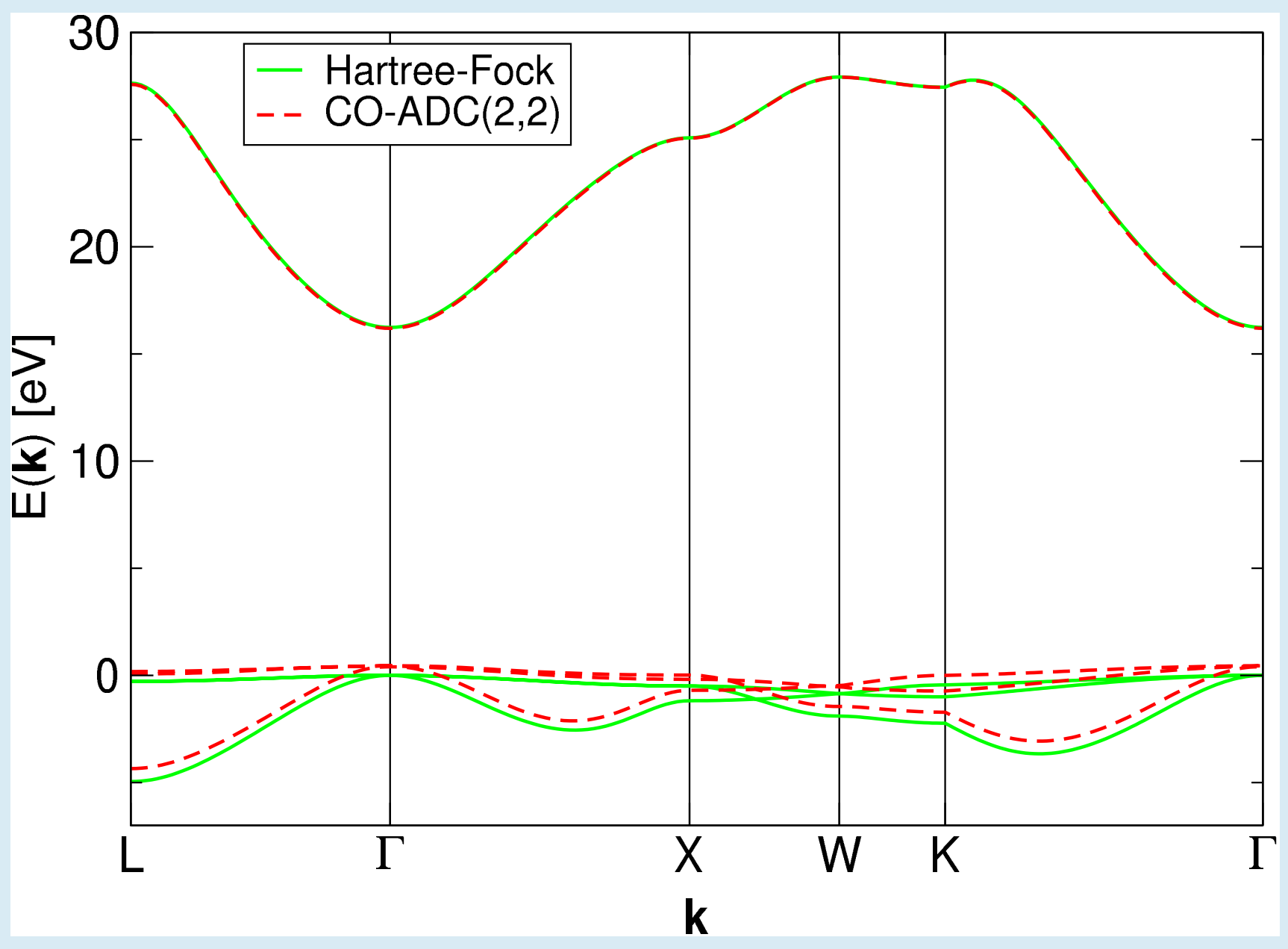


(*) Quasi-particle band structure obtained with an effective Hamiltonian approach by Bezugly and Birkenheuer.

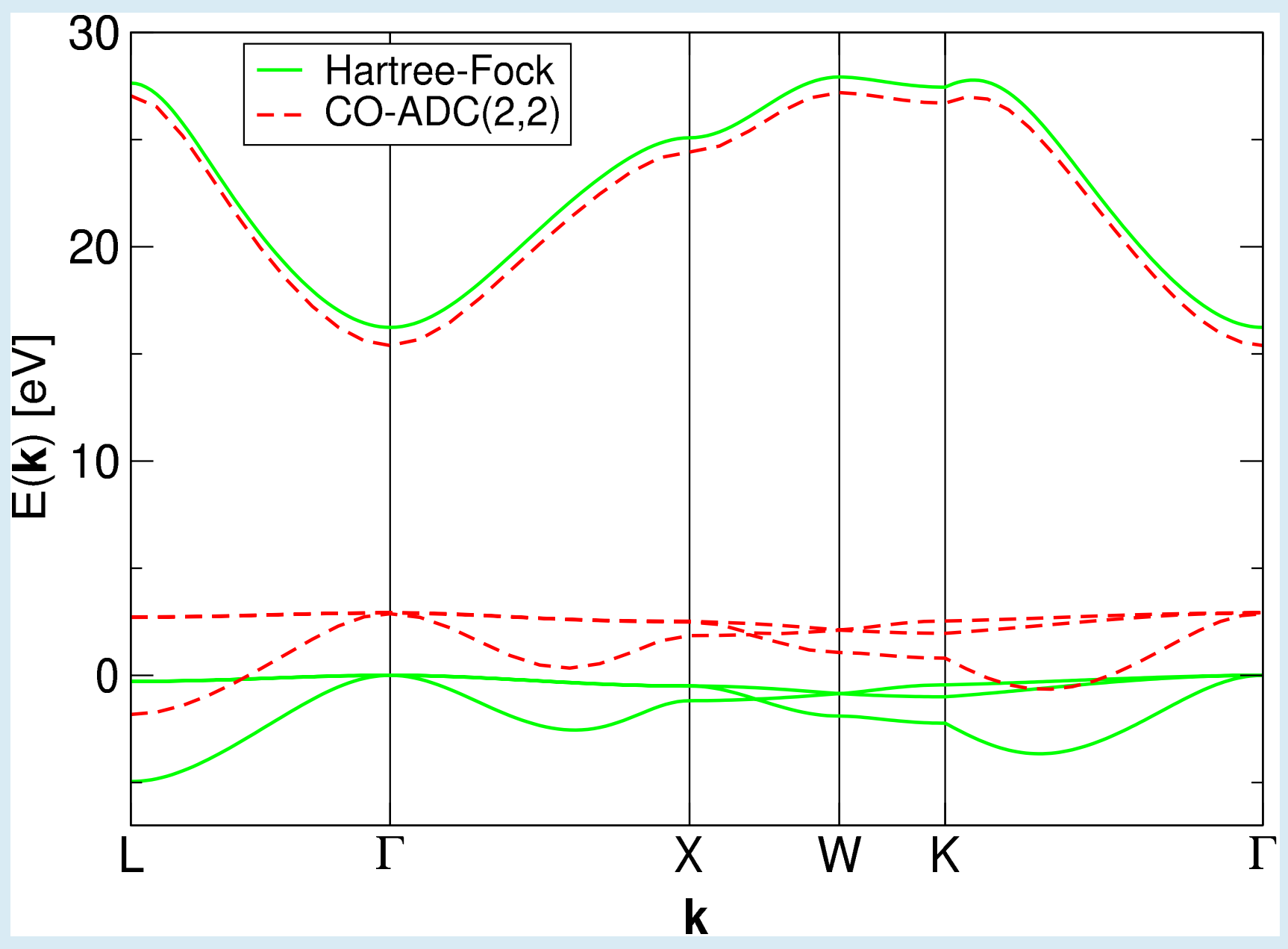
- Valence bands shift significantly upwards.
- Slight increase of the width of the isolated band complexes.
- Excitations from the origin unit cell alone already describes the band structure of $(\mathrm{HF})_\infty$ satisfactorily.
- The inclusion of excitations in the nearest neighbour cells has only a minor influence on the band structure, ≈ 0.1–0.3 eV, at the Γ point.
- *Very good* agreement between CO-ADC(2,2) and the effective Hamiltonian quasi-particle band structures.

Band structure of a LiF crystal:

- Rock-salt structure, basis set STO-6G.
- Excitations from the valence orbitals of the origin unit cell.



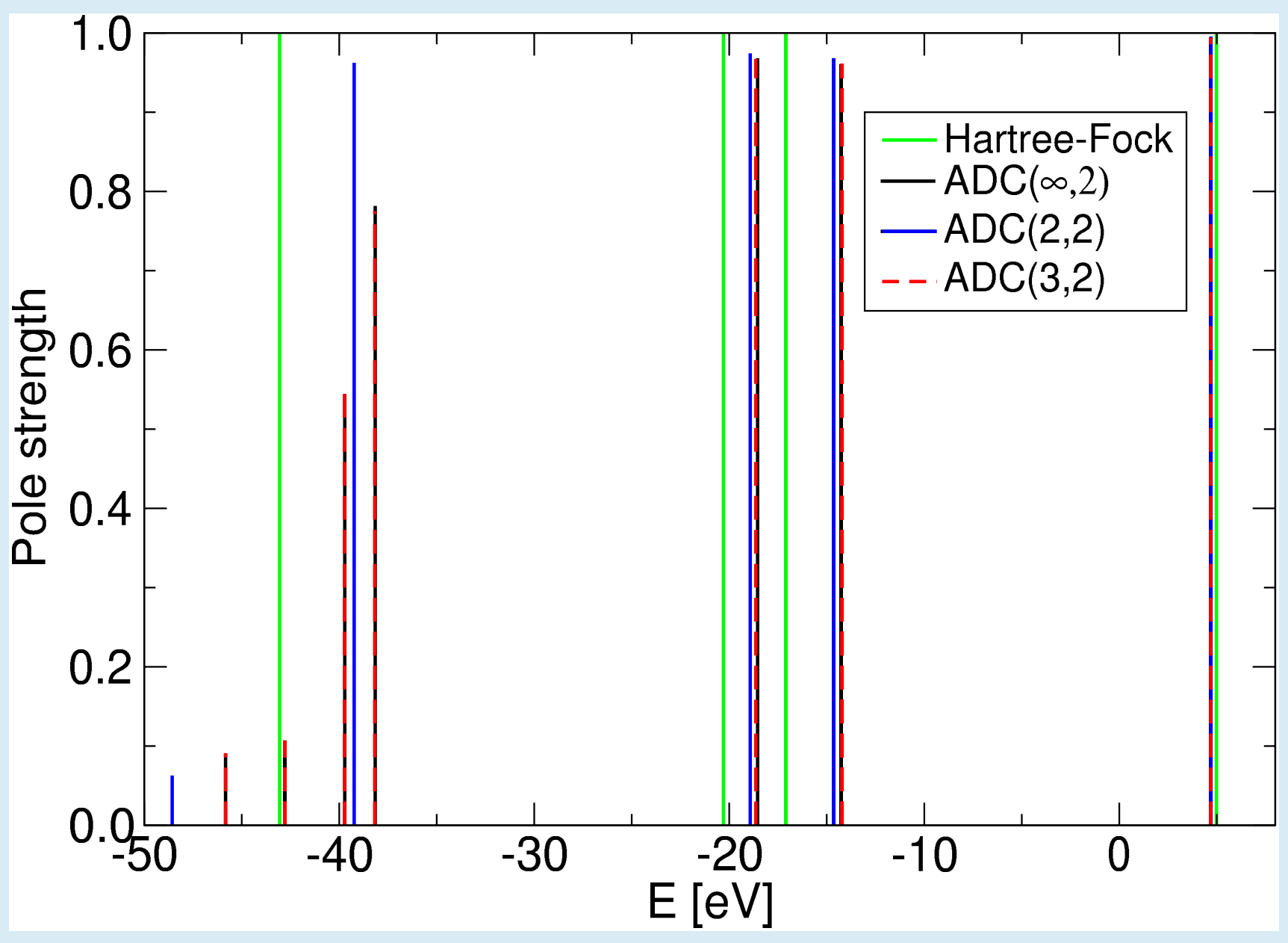
- Excitations from the valence orbitals of the origin unit cell plus the nearest and next nearest neighbour unit cells.



- The fundamental band gap is reduced significantly due to electron correlations.
- Excitations in neighbouring unit cells are essential.
- The width of the F 2*p* band complex is hardly influenced by electron correlations.
- Good agreement with experimental results.

Localized orbitals:

- The Fock matrix in terms of localized molecular or crystal orbitals is *not* diagonal.
- Exact transformation of the ADC equations leads to an ADC(∞,2) matrix with roughly 50% non-zero entries. Consequently a selective diagonalization is very expensive.
- Off-diagonal Fock matrix elements are treated perturbatively in the construction of the ADC form.
- Ionization potentials and electron affinities of a hydrogen fluoride molecule, basis set cc-pVDZ.



- Very good agreement of ADC(2,2) and ADC(∞,2) results for outer valence IPs and the lowest EA.
- Deviation of ADC(2,2) IP in the inner valence around 40 eV.
- Only ADC(3,2) and ADC(∞,2) describe strong correlation (breakdown of the molecular orbital picture of ionization) properly and are generally in excellent agreement.
- ADC(2,2) → ADC(3,2) leads to an overall improvement in accuracy of IPs and EAs by an order of magnitude with respect to ADC(∞,2).
- A more accurate treatment is *not* required!