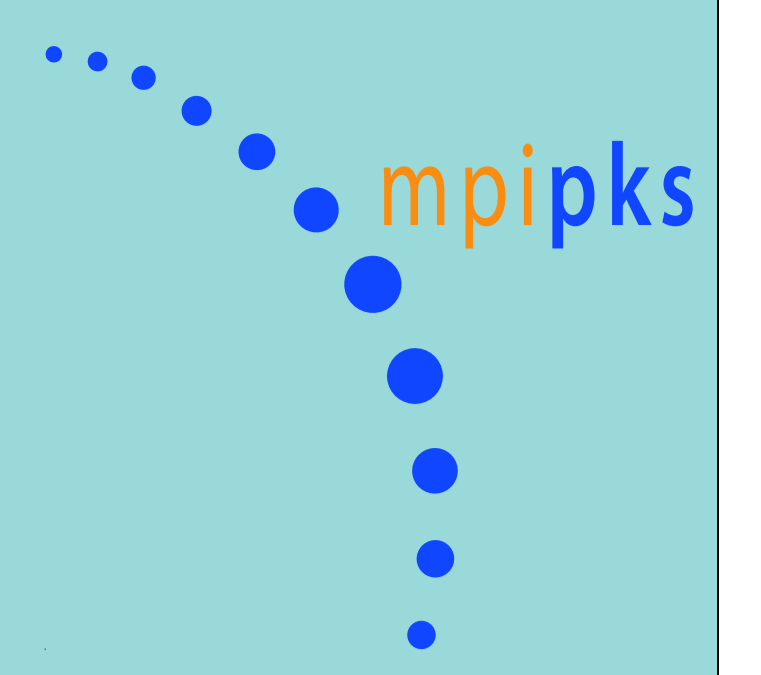




Green's function approach to ab initio band structures

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Crystal orbital algebraic diagrammatic construction (CO-ADC)

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

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

- 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 $\Sigma(\vec{k}, \omega)$ by the Dyson equation.

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

- 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].

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

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

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

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

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

- 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 $\mathbf{\Sigma}(\vec{k}, \omega)$ 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:

$$\frac{V_{\bar{0}\bar{2}\bar{g}_1\kappa|\bar{g}_2\alpha\bar{g}_3\beta} V_{\bar{R}\alpha\bar{g}_1\kappa|\bar{g}_2\alpha\bar{g}_3\beta}^*}{\omega - \varepsilon_{\bar{g}_2\alpha} - \varepsilon_{\bar{g}_3\beta} + \varepsilon_{\bar{g}_1\kappa}} n_{\bar{g}_1\kappa} \bar{n}_{\bar{g}_2\alpha} \bar{n}_{\bar{g}_3\beta}$$

- Truncation of the configuration space implies a finite-range of the Coulomb interaction.
- Only a certain number of non-degenerate states are described.
- 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!*

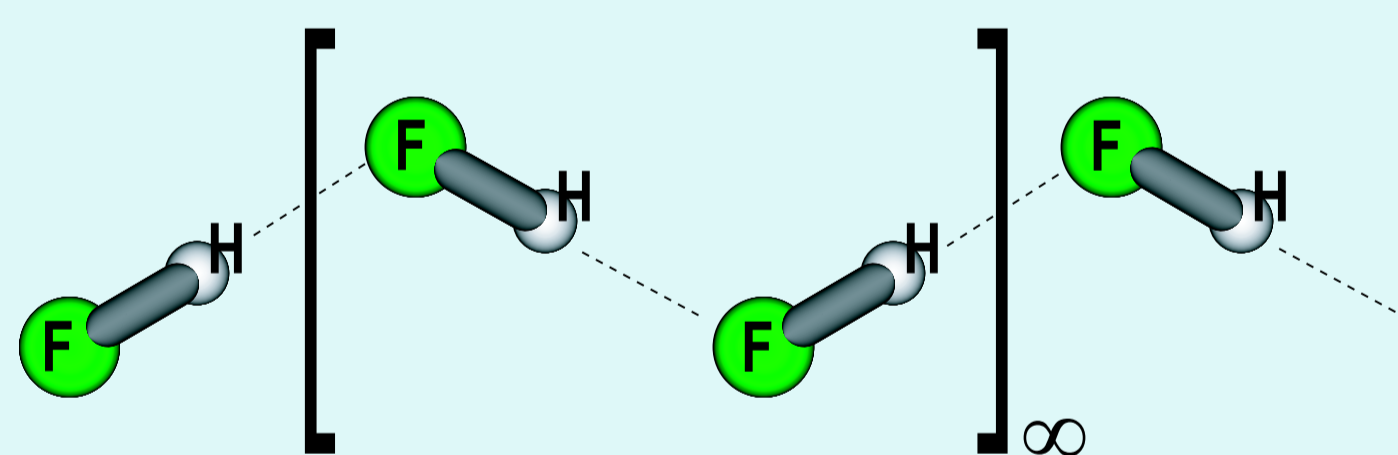
References:

- [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

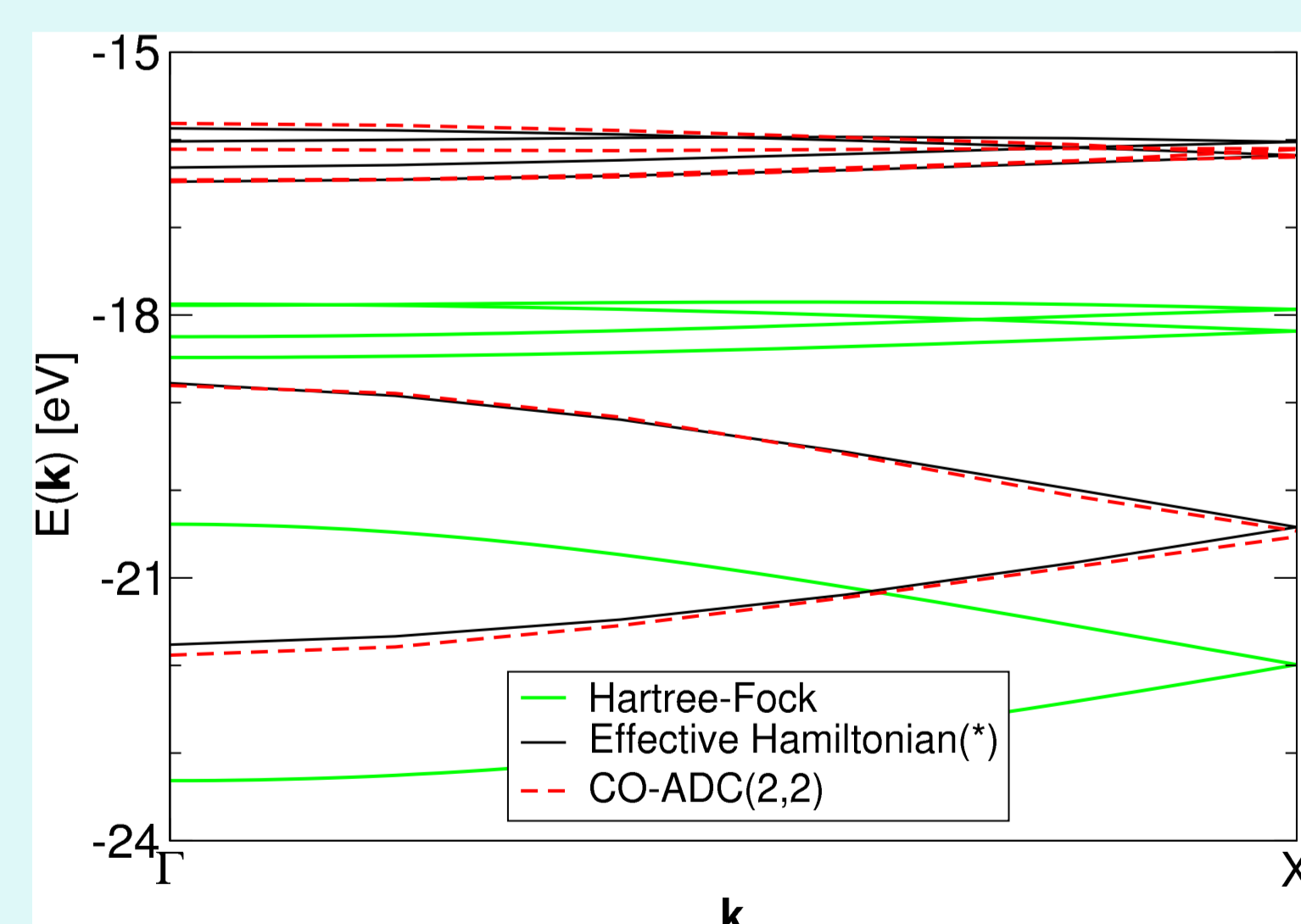
Ab initio quasi-particle band structures of a $(\text{HF})_\infty$ chain and a bulk LiF crystal

Band structure of $(\text{HF})_\infty$ 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.

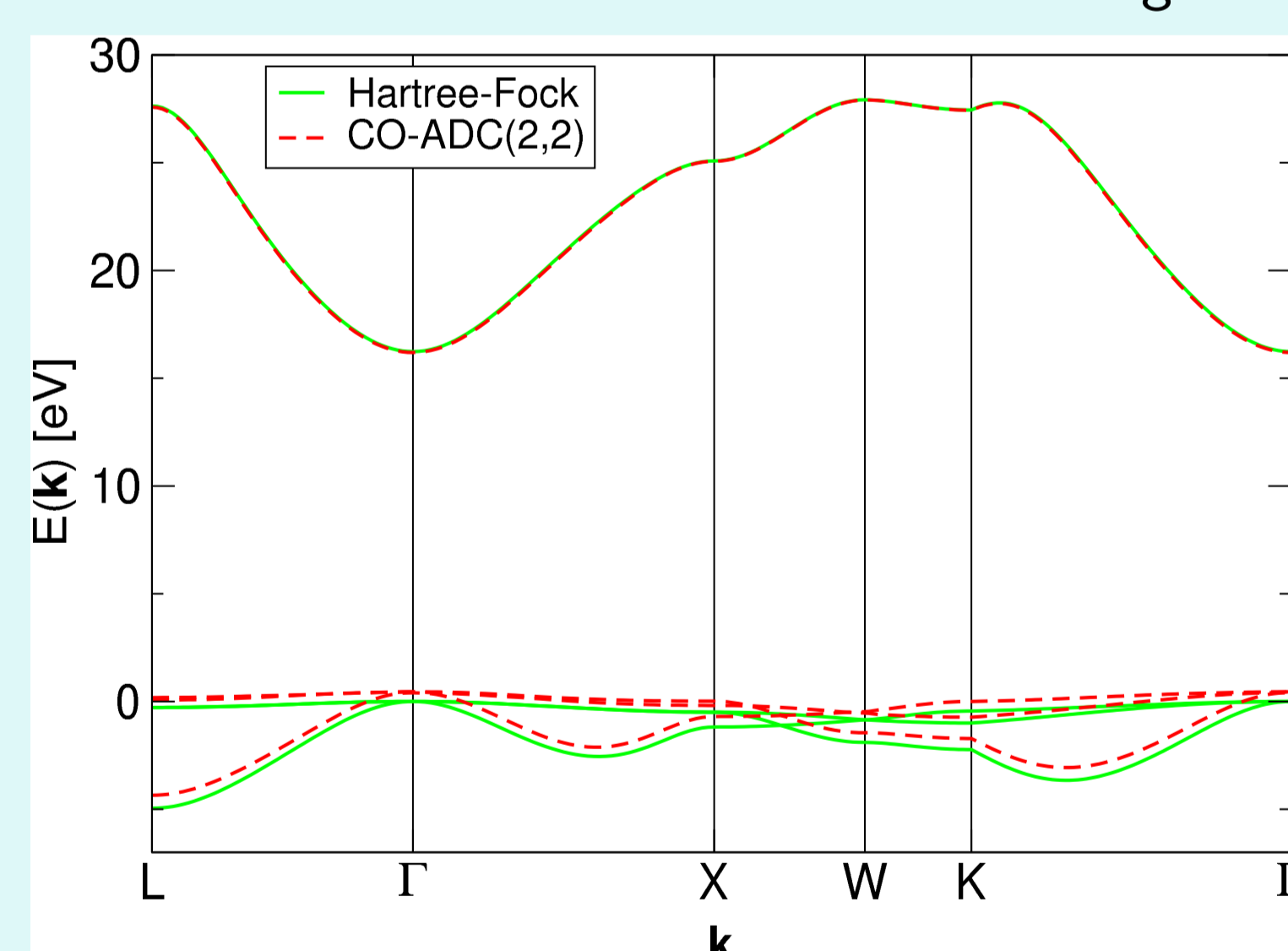


(*) Quasi-particle band structure obtained with an effective Hamiltonian approach by BEZUGLY and BIRKENHEUER.

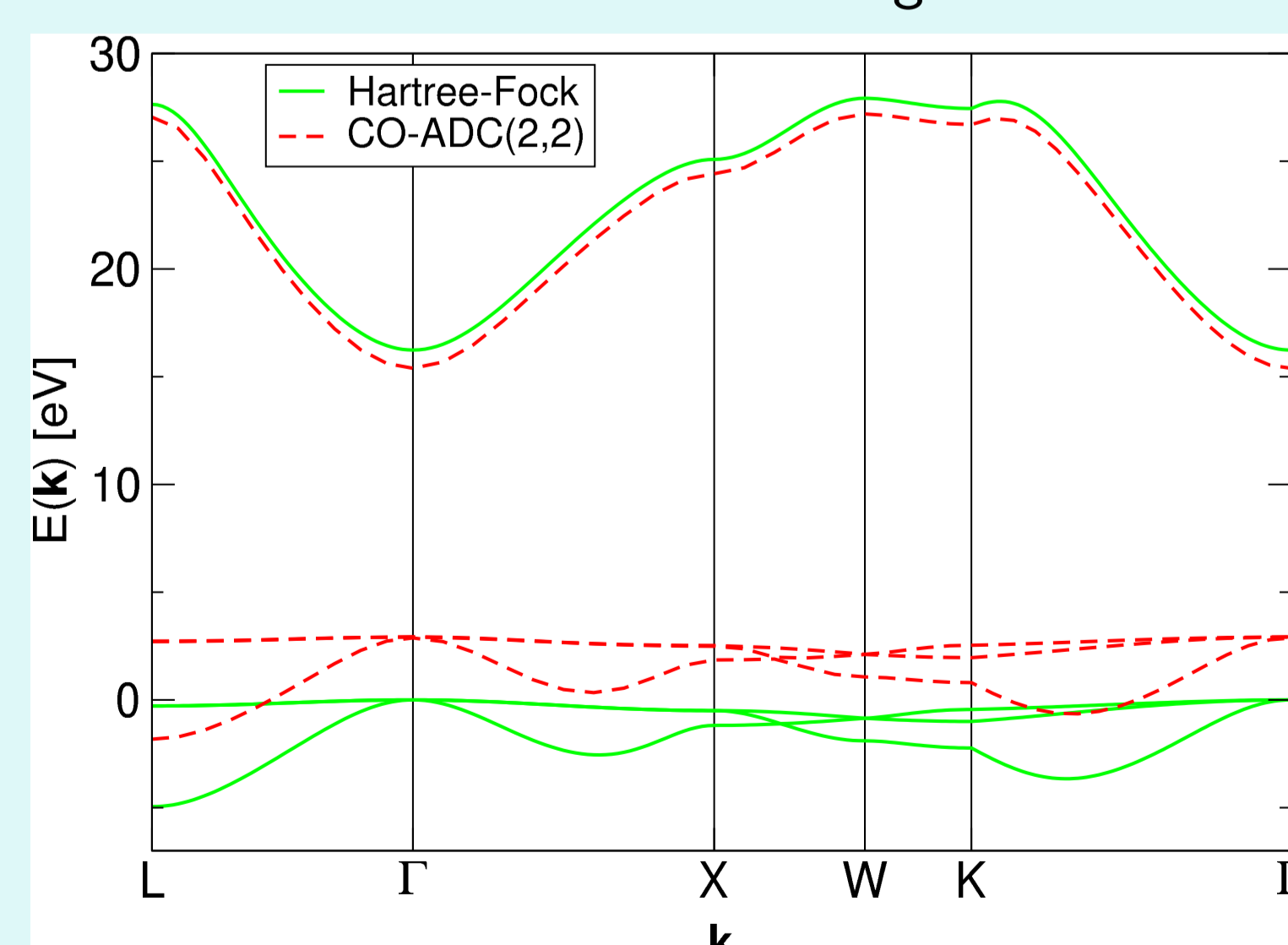
- Valence bands shift significantly upwards.
- Slight increase of the width of the isolated band complexes.
- Excitations from the origin unit cell alone already describes the band structure of $(\text{HF})_\infty$ satisfactorily.
- The inclusion of excitations in the nearest neighbour cells has only 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.



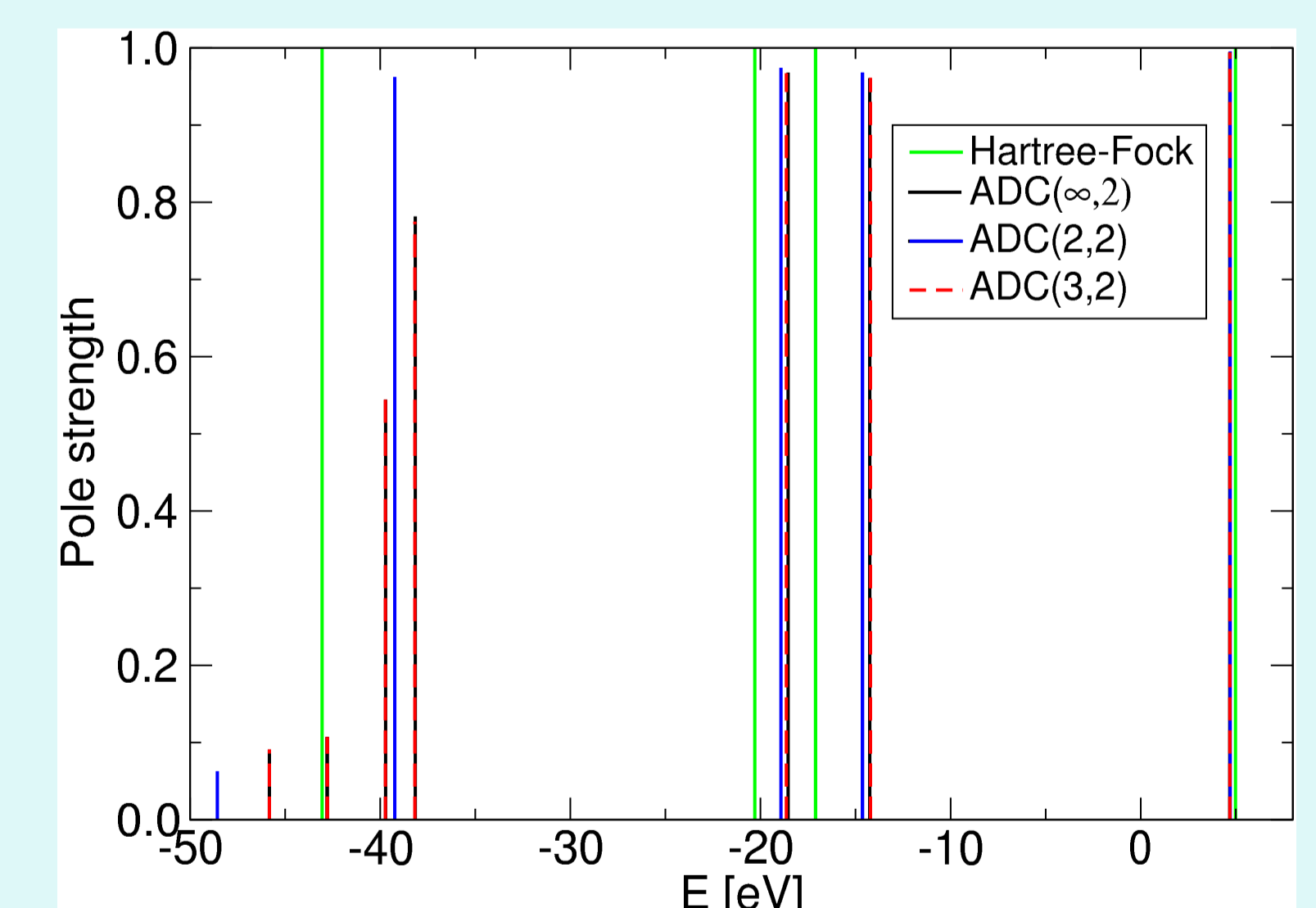
- Excitations from the valence orbitals of the origin unit cell plus the nearest and next nearest neighbour unit cells.



- The fundamental band gap is reduced significantly due to electron correlations.
- Excitations in neighbouring unit cells are essential.
- The width of the F 2p 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) \rightarrow 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!