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 $G_{pq}(\vec{k},t,t')$.
- **But** $G_{pq}(\vec{k},\omega)$ is 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.

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

- Self-energy can be represented in terms of Wannier orbitals and subsequently transformed to the crystal momentum representation.
- Three schemes:
  - *Supercell form*, i.e., a supercell is taken and treated like a large molecule.
  - *Semi-transformed form*, i.e., invariance of $\boldsymbol{\Sigma}(\vec{k},\omega)$ under lattice translations is exploited.
  - *Fully translational symmetry adapted form*, i.e., the invariance under lattice translations of the individual terms constituting the self-energy is exploited.

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 correlated band structure is determined by solving the Hermitian eigenvalue problem:

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

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

- The stable formulation of ADC in terms of a Hermitian eigenvalue problem facilitates to investigate strong correlation and electronic resonances in molecules [3, 4].

Configuration selection:

- The problem of assembling $\boldsymbol{\Sigma}(\vec{k},\omega)$ is still *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*!

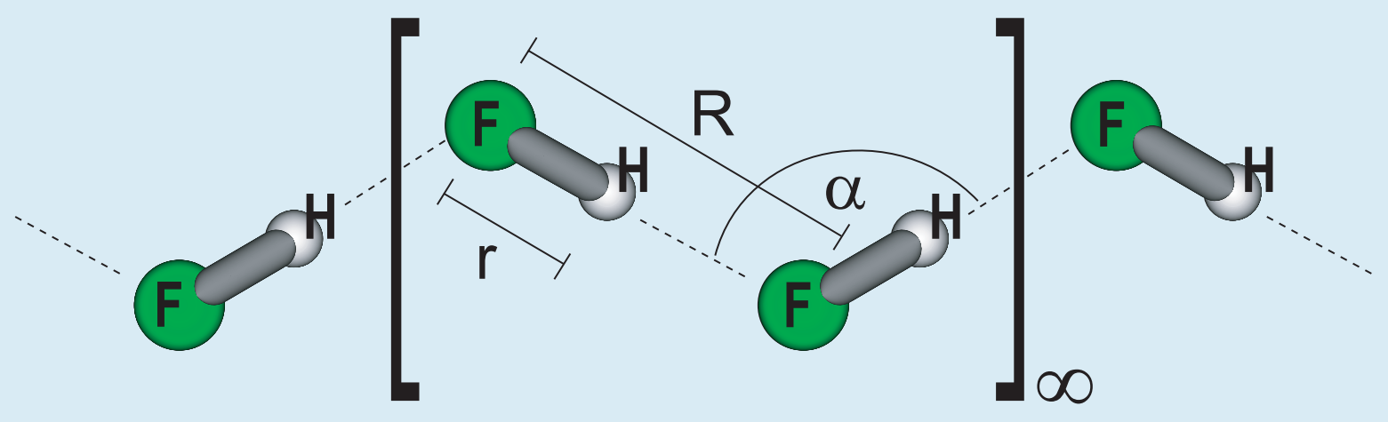
References:

[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

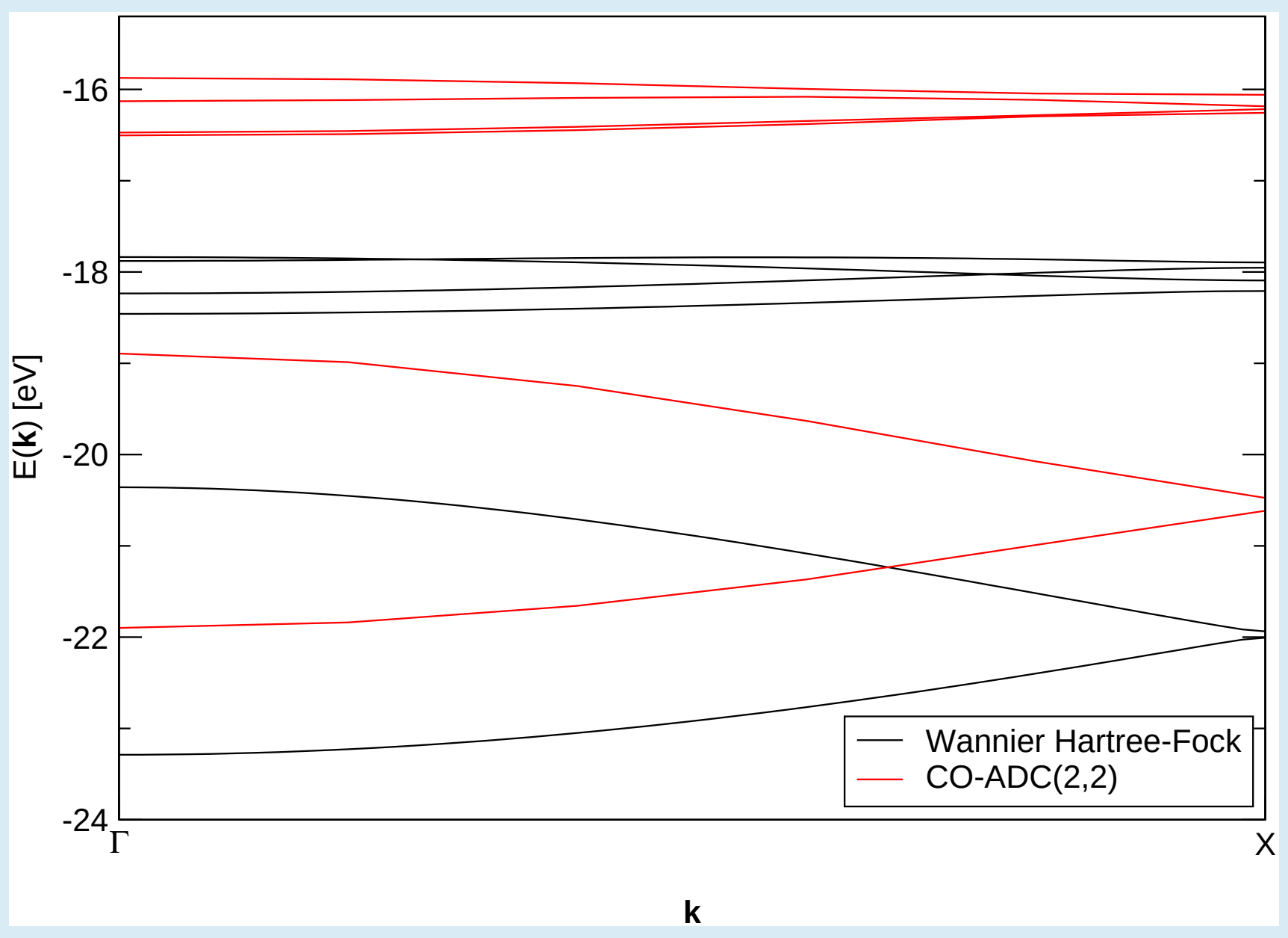
Ab initio correlated band structures of $(\mathrm{HF})_\infty$ chains and bulk LiF

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

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



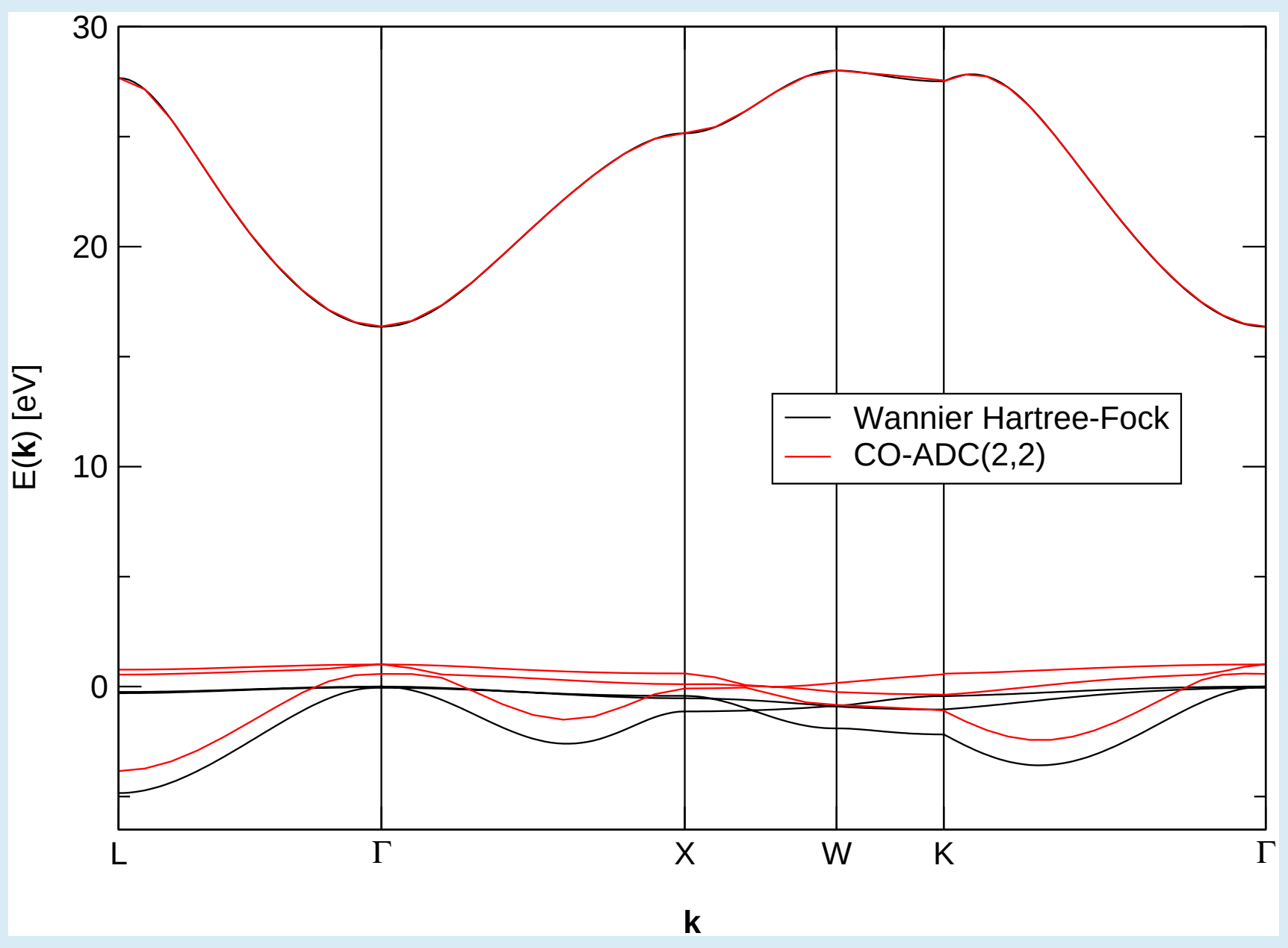
- Excitations from the valence orbitals of a single unit cells.



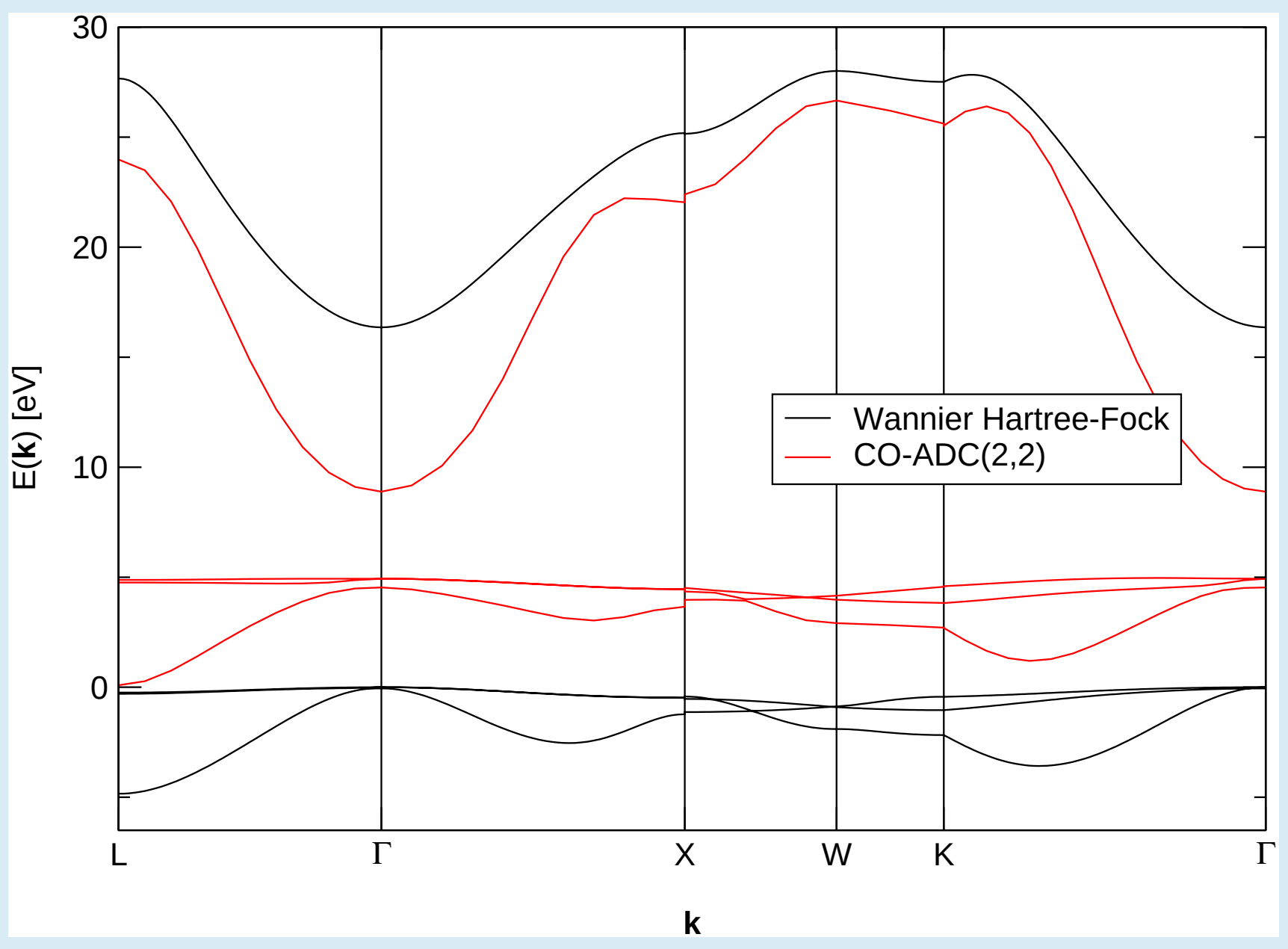
- Valence bands shift significantly upwards.
- Slight increase in band width.
- Excitations from the origin cell already turn out to describe the band structure of $(\mathrm{HF})_\infty$ satisfactorily. The inclusion of excitations in the nearest neighbour cells has only a minor influence on the band structure, ≈ 0.1–$0.3\,\mathrm{eV}$, at the Γ point.
- A comparison of this CO-ADC(2,2) band structure to results obtained with the effective Hamiltonian approach can be found on the poster of Victor Bezugly. Their *excellent* agreement is encouraging.

Band structure of a LiF crystal:

- *fcc* crystal, basis set STO-6G.
- Excitations from the valence orbitals of the origin cell only.



- Excitations from the valence orbitals of the origin cell and next nearest neighbours.



- Band gap is reduced significantly due to electron correlations.
- Inclusion of excitations in the nearest neighbour cells is essential. (Also holds for richer basis sets.)
- Increase in band width.
- Good agreement with previous results.

Local orbitals:

- The Fock matrix in terms of localized molecular or crystal orbitals is *not* diagonal.
- Off-diagonal Fock matrix elements can be accounted for perturbatively.
- Exact treatment is *unessential* and very expensive as roughly one-half of the CO-ADC(2,∞) matrix elements are non-zero.

Ionization potentials and electron affinities of a hydrogen fluoride molecule:

$\mathrm{IP}_{\mathrm{Koopmans'}}$	$\mathrm{IP}_{2,2}$	$\mathrm{IP}_{2,3}$	$\mathrm{IP}_{2,\infty}$	$\mathrm{IP}^{\mathrm{ND}}_{2,\infty}$	PS
43.0593	39.2356	39.7267	39.7146	39.6975	31.2
		38.1825	38.1570	38.1421	60.4
20.3000	18.9218	18.6377	18.5494	18.5973	94.6
17.1051	14.6366	14.2165	14.2562	14.2605	92.9
17.1051	14.6365	14.2150	14.2560	14.2605	92.9

$\mathrm{EA}_{\mathrm{Koopmans'}}$	$\mathrm{EA}_{2,2}$	$\mathrm{EA}_{2,3}$	$\mathrm{EA}_{2,\infty}$	PS
-4.9851	-4.7034	-4.6854	-4.6817	0.995
-21.9623	-21.0210	-20.9216	-20.8953	0.987

$\mathbf{IP}_{\mathrm{Koopmans'}}$, $\mathbf{EA}_{\mathrm{Koopmans'}}$ – Hartree-Fock approximation.

$\mathbf{IP}_{2,2}$, $\mathbf{IP}_{2,3}$, $\mathbf{IP}_{2,\infty}$, $\mathbf{EA}_{2,2}$, $\mathbf{EA}_{2,3}$, $\mathbf{EA}_{2,\infty}$ – CO-ADC(2) approximation with off-diagonal elements of the Fock matrix treated in second or third order of perturbation theory or exactly.

$\mathbf{IP}^{\mathrm{ND}}_{2,\infty}$ – Jörg Breidbach's non-Dyson ADC(2) for ionization potentials in conjunction with GAMESS-UK (*canonical* molecular orbitals).

PS – pole strength, one-particle character of an ionized state.

Basis set – cc-pVDZ