Green's Function Approach to Ab Initio Band Structures of HF and HCl Chains

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Cohesive Energy of $(\mathrm{HF})_\infty$ and $(\mathrm{HCl})_\infty$

Incremental scheme for the correlation energy:

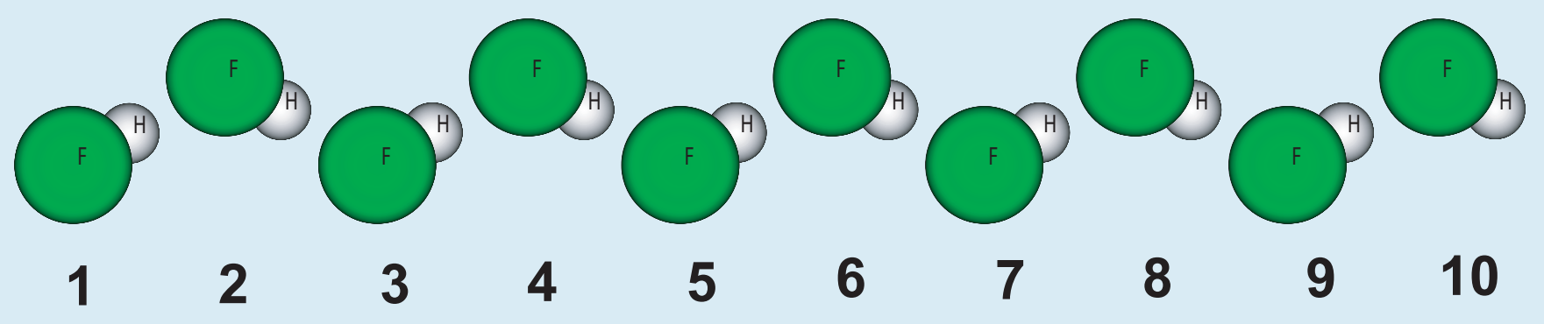
$$\mathcal{E}_{\mathrm{Corr}} = \sum_{I} \Delta\varepsilon_I + \frac{1}{2!} \sum_{I \neq J} \Delta\varepsilon_{IJ} + \dots$$

$\Delta\varepsilon_I$ is termed one-body increment. It is given by the correlation energy obtained by correlating only the electrons in the bond I. $\Delta\varepsilon_{IJ} = \mathcal{E}_{IJ} - \Delta\varepsilon_I - \Delta\varepsilon_J$ is termed two-body increment. $\mathcal{E}_{IJ}$ denotes the correlation energy obtained by correlating only the electrons in the bonds I and J [1, 2].

- Local orbital correlation method which scales linearly with the size of the unit cell in crystals (or with the number of atoms in large molecules).
- Symmetry can be exploited of which the most important for crystals is the translational symmetry, i.e. the actual number of energy increments is reduced tremendously.
- Correlation effects are classified into one-body, two-body, three-body, … contributions elucidating the amount of localization of the Wannier orbitals.
- Convergence can be checked by monitoring the decay of the incremental series.

Oligomer calculations:

- Oligomers approximate electron correlation in crystals since electron correlation is short-ranged.
- Oligomers provide a domain decomposition for the virtual orbitals.
- Localized occupied molecular orbitals (transferable orbitals) approximate Wannier orbitals.
- Virtual orbitals are canonical orbitals.



Basis sets:

- In crystals BSSE is particularly large due to the tight packing and the infinite repetition.
- Basis set effects are important in $(\mathrm{HF})_\infty$ and $(\mathrm{HCl})_\infty$ as hydrogen bonds are weak.
- The error of the counterpoise correction in $(\mathrm{HF})_\infty$ is comparable to the cohesive energy, even for aug-cc-pVDZ basis sets, therefore very flexible basis sets are required for $(\mathrm{HF})_\infty$.

Hartree-Fock contribution to the cohesive energy:

$(\mathrm{HF})_\infty$	cc-pVDZ	aug-cc-pVDZ
$\mathcal{E}_{\mathrm{coh}}^{\mathrm{SCF}}$ [a.u.]	-1.031×10^{-2}	-0.973×10^{-2}

$(\mathrm{HCl})_\infty$	cc-pVDZ	aug-cc-pVDZ
$\mathcal{E}_{\mathrm{coh}}^{\mathrm{SCF}}$ [a.u.]	-9.414×10^{-4}	-5.895×10^{-4}

- Calculations where carried out with the periodic Hartree-Fock program CRYSTAL98.
- Further investigation is necessaray concerning basis set convergence for $(\mathrm{HF})_\infty$ and $(\mathrm{HCl})_\infty$.

Correlation contribution to the cohesive energy:

$$\mathcal{E}_{(\mathrm{HF})_\infty,\mathrm{coh}} \approx \Delta\varepsilon_4 + \Delta\varepsilon_{45} + \Delta\varepsilon_{46} - \mathcal{E}_{\mathrm{HF,corr}}$$

- Only one-body and two-body increments are essential.
- $\mathcal{E}_{\mathrm{HF,corr}}$ correlation energy of a single HF molecule.

$(\mathrm{HF})_\infty$	$\mathcal{E}_{\mathrm{coh}}^{\mathrm{CCSD}}$ [a.u.]	$\mathcal{E}_{\mathrm{coh}}^{\mathrm{CCSD(T)}}$ [a.u.]
cc-pVDZ	0.000450	0.000383
aug-cc-pVDZ	-0.000223	-0.000242
cc-pVTZ	-0.000596	-0.000612
aug-cc-pVTZ	-0.001007	-0.001007

$(\mathrm{HCl})_\infty$	$\mathcal{E}_{\mathrm{coh}}^{\mathrm{CCSD}}$ [a.u.]	$\mathcal{E}_{\mathrm{coh}}^{\mathrm{CCSD(T)}}$ [a.u.]
cc-pVDZ	-0.000850	-0.000946
aug-cc-pVDZ	-0.001852	-0.002015
cc-pVTZ	-0.001871	-0.001927

- The cohesive energy of $(\mathrm{HF})_\infty$ converges slowly with basis set quality and has to be investigated further.
- The cohesive energy of $(\mathrm{HCl})_\infty$ converges reasonably with basis set quality.

References:

[1] H. Stoll, Chem. Phys. Lett. **191** 548 (1992)
[2] B. Paulus, Chem. Phys. Lett. **371** 7 (2003); P. Fulde, Adv. Phys. **51** 909 (2002)

Ab Initio Correlated Band Structures

Electronic Hamiltonian:

$$\hat{H} = \sum_{n=1}^{N_0\,N} \left[-\frac{1}{2}\Delta_n - \sum_{j=1}^{N_0} \sum_{A=1}^{M} \frac{Z_{\vec{R}_j A}}{r_{n,\,\vec{R}_j A}} \right] + \frac{1}{2} \sum_{m,n=1}^{N_0\,N} \frac{1}{r_{m,\,n}}$$

- *Ab initio* electronic structure theory.
- Based on non-relativistic electronic Hamiltonian.
- Starting point periodic Hartree-Fock approximation.

One-particle Green's function:

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

- Well-suited for a correlated treatment of band structures.
- Bands are given by the poles of $G_{pq}(\vec{k}, \omega)$.
- There are various approximation schemes for $G_{pq}(\vec{k}, \omega)$, eg. the approximation of Igarashi used in [1].

Direct space versus reciprocal space:

- Numerous reciprocal space integrations are necessary to evaluate the Goldstone diagrams, eg. for second order self-energy diagrams, two integrations are required, …
- The Brillouin zone is discretized using hundreds of $\vec{k}$-points that have to be considered.
- One is urged to minimize the number of integrations!
- Correlation effects turn out to be local in direct space.
- Physically motivated cutoff criteria can be applied in direct space.

Dilemma: On the one hand we want to use direct space quantities to describe electron correlation. On the other hand band structures are defined with respect to reciprocal space.

Semitransformed quantities:

- Transform a suitable quantity (should not depend on more than two external orbital indices) to reciprocal space after evaluation in direct space [1].
- The self-energy fulfills this requirement. We call this property semitransformability.
- A crystal orbital formulation of the algebraic diagrammatic construction scheme [2] can be derived to approximate the self-energy.

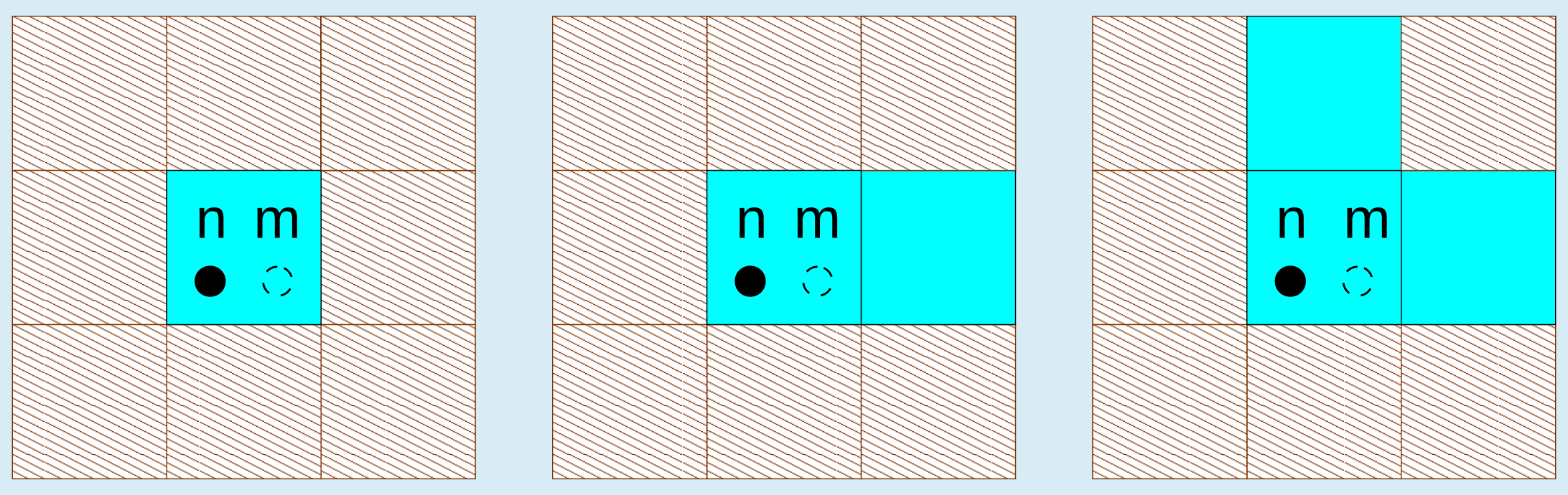
$$\begin{aligned}\boldsymbol{\Sigma}(\vec{k}, \omega) &= \sum_{\vec{R}} \mathrm{e}^{i\vec{k}\vec{R}}\, \boldsymbol{\Sigma}(\vec{R}, \omega) \\ &= \boldsymbol{\Sigma}^{\infty}(\vec{k}) + \boldsymbol{M}^{+}(\vec{k}, \omega) + \boldsymbol{M}^{-}(\vec{k}, \omega)\end{aligned}$$

$$M_{nm}^{\pm}(\vec{k}, \omega) = \vec{U}_{\vec{0}\,m}^{\pm}\, (\omega\, \mathbb{1} - \boldsymbol{K}^{\pm} - \boldsymbol{C}^{\pm})^{-1}\, \vec{U}_{n}^{\pm\dagger}(\vec{k})$$

Configuration selection:

- The problem of assembling $\boldsymbol{\Sigma}(\vec{k}, \omega)$ is still *infinite*.
- Configuration selection is needed to obtain a flat configuration space.
- The addend of the analytic expression of the second order self-energy diagrams can be used to derive a cutoff/selection criterion, eg.

$$\frac{V_{\vec{0}n\,\vec{R}_1 j\,[\vec{R}_2 k\,\vec{R}_3 l]}\, V^{*}_{\vec{R}m\,\vec{R}_1 j\,[\vec{R}_2 k\,\vec{R}_3 l]}}{\omega + \varepsilon_{\vec{R}_1 j} - \varepsilon_{\vec{R}_2 k} - \varepsilon_{\vec{R}_3 l}}\; n_{\vec{R}_1 j}\, \bar{n}_{\vec{R}_2 k}\, \bar{n}_{\vec{R}_3 l}$$



intra one−cell two−cell

Band structure:

In our new framework the *correlated ab initio* band structure of a crystal is obtained by solving the Dyson equation

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

The pole search of the Green's function $\boldsymbol{G}(\vec{k}, \omega)$ can be written in terms of the following diagonalization problem:

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

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

where the algebraic diagrammatic construction scheme [2] is extended to crystal orbitals.

Outlook:

- Further theoretical investigations: variants of CO-ADC, convergence of the eigenvalues with the number of configurations, …
- Calculation and analysis of the band structure of $(\mathrm{HF})_\infty$ with [1] is in progress.
- Program development (ADC based approach).

References:

[1] M. Albrecht and J.-I. Igarashi, J. Phys. Soc. Jpn. **70** 1035 (2001)
[2] J. Schirmer, L. S. Cederbaum, and O. Walter, Phys. Rev. A **28** 1237 (1983)