Beyond the mean field: electron correlation

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What do we have: Hartree-Fock, notation

Closed-shell systems

What do we have: Hartree-Fock, notation

Closed-shell systems

Wavefunction: 1 single Slater determinant

$$|\Phi_0\rangle \quad = \quad \Phi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{n-1}, \vec{r}_n)$$

$$= \quad \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\vec{r}_1)\sigma_\uparrow & \cdots & \phi_{n/2}(\vec{r}_1)\sigma_\downarrow \\ \vdots & \ddots & \vdots \\ \phi_1(\vec{r}_n)\sigma_\uparrow & \cdots & \phi_{n/2}(\vec{r}_n)\sigma_\downarrow \end{vmatrix}$$

$$= \quad |\phi_1, \bar{\phi}_1, \ldots, \phi_{n/2}, \bar{\phi}_{n/2}\rangle \text{ with } |\phi_i\rangle = \phi_i(\vec{r})\,\sigma_\uparrow \text{ and } |\bar{\phi}_i\rangle = \phi_i(\vec{r})\,\sigma_\downarrow$$

Molecular orbitals

$$\phi_i(\vec{r}) = \sum_{\alpha=1}^{N} c_{\alpha\,i}\,\chi_\alpha(\vec{r})$$

Normalized wavefunction : $\langle \Phi_0 | \Phi_0 \rangle = 1$

What do we have: Hartree-Fock, notation

Extension to periodic systems:

- Born-von Karman cyclic boundary conditions in 1, 2 or 3 dimensions

- Symmetry index $\vec{k}$ with $\vec{k}\,\vec{g}_i = 2\,\pi/n_i$ for real space cell indices $\vec{g}_i$

- "Molecular orbitals" for each k point

$$\phi_i^{\vec{k}}(\vec{r}) = \sum_{\alpha=1}^{N} c_{\alpha\,i}^{\vec{k}}\, u_\alpha^{\vec{k}}(\vec{r}) \qquad \text{with} \qquad u_\alpha^{\vec{k}}(\vec{r}) = \sum_{\vec{g}} e^{i\,\vec{k}\cdot\vec{g}}\, \chi_\alpha^{\vec{g}}(\vec{r})$$

- Alternative representation: Wannier orbitals, localized in each cell $\vec{g}$

$$w_i^{\vec{g}}(\vec{r}) = \sum_\alpha \sum_{\vec{h}} c_{\alpha\,i}^{\vec{h}} \chi_\alpha^{\vec{g}+\vec{h}}(\vec{r})$$

(occupied and virtual orbitals in real space) with orthogonality condition

$$\langle w_i^{\vec{g}} | w_j^{\vec{h}} \rangle = \delta_{ij}\delta_{\vec{g},\vec{h}}$$

What do we have: Hartree-Fock, notation

Closed-shell systems

- Hamiltonian :

$$\hat{H} = E_{NN} - \frac{1}{2}\sum_i^n \Delta_i - \sum_I \sum_i \frac{Z_I}{|\vec{R}_I - \vec{r}_i|} + \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

- Orbitals are (self-consistent) solution of $\hat{F}\phi_i(\vec{r}) = \epsilon_i\,\phi_i(\vec{r})$ with the Fock operator

$$\hat{F}\,\phi_i(\vec{r}) = \left[-\frac{1}{2}\Delta - \sum_I \frac{Z_I}{|\vec{R}_I - \vec{r}|}\right]\phi_i(\vec{r}) +$$

$$+ \sum_{j\in occ}\left[2\int \frac{\phi_j(\vec{r}')\phi_j(\vec{r}')}{|\vec{r} - \vec{r}'|}d^3r'\,\phi_i(\vec{r}) - \int \frac{\phi_j(\vec{r}')\phi_i(\vec{r}')}{|\vec{r} - \vec{r}'|}d^3r'\,\phi_j(\vec{r})\right]$$

- Total energy:

$$E_{HF} = \langle\Phi_0|\hat{H}|\Phi_0\rangle = \sum_{i\in occ}\langle\phi_i|\hat{h}|\phi_i\rangle + \sum_{i,j\in occ}\left[2\,(ii|jj) - (ij|ij)\right]$$

What do we have: Hartree-Fock, notation

<div align="center" style="color:blue">Closed-shell systems</div>

Solids: Fourier transformations for matrix elements
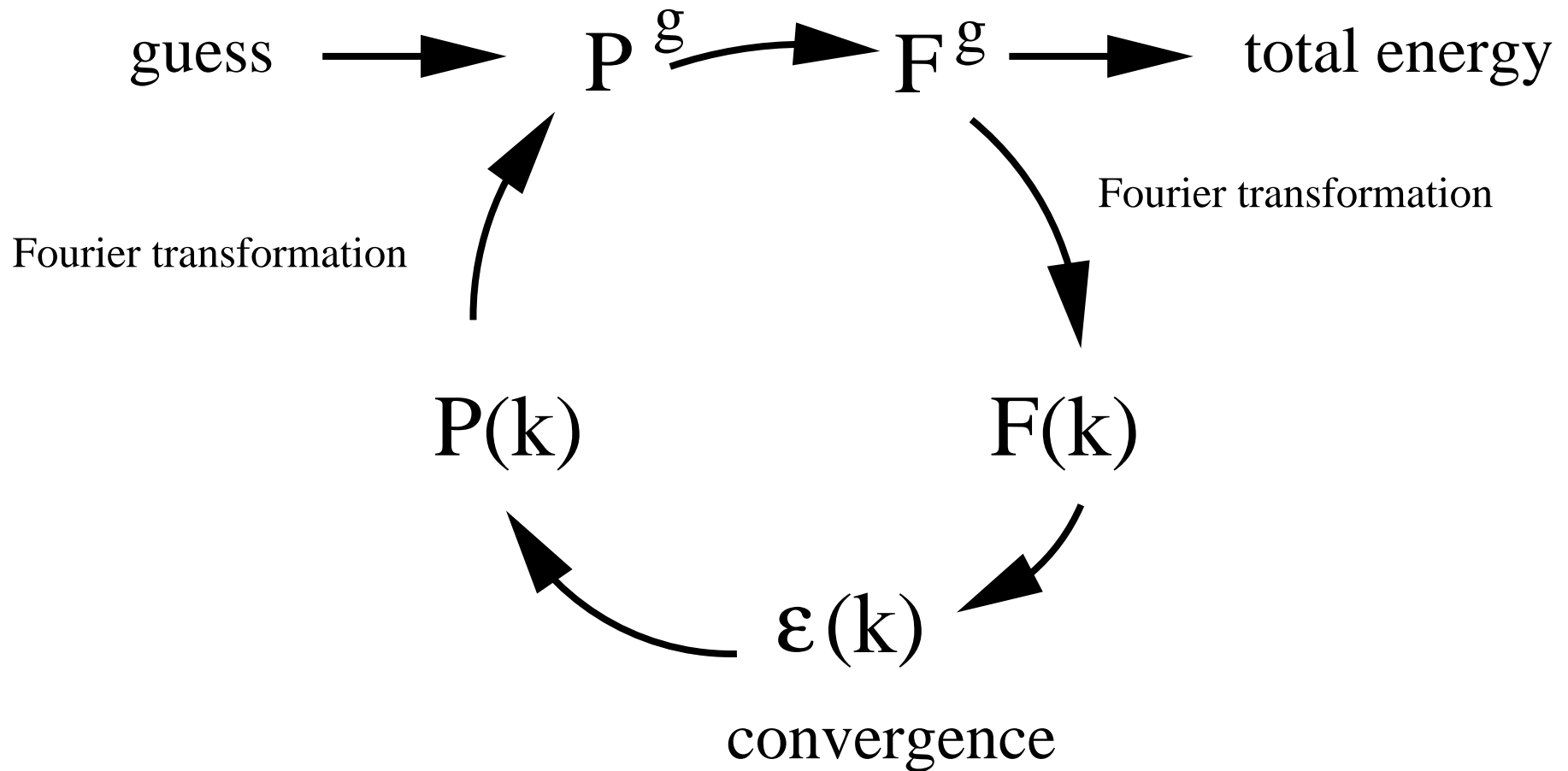
$$
\begin{aligned}
F_{ij}^{\vec{g}} &= \langle w_i^{\vec{h}} | \hat{F} | w_j^{\vec{h}+\vec{g}} \rangle = \frac{1}{V_B} \int_{BZ} e^{-i\vec{k}\cdot\vec{g}}\, F_{ij}(\vec{k})\, d^3k \\
F_{ij}(\vec{k}) &= \langle \phi_i(\vec{k}) | \hat{F} | \phi_j(\vec{k}) \rangle = \sum_{\vec{g}} e^{i\vec{k}\cdot\vec{g}}\, F_{ij}^{\vec{g}}
\end{aligned}
$$

- Matrix elements decay (in general) exponentially in real space with $\vec{g}$
- Matrices F, P block-diagonal in k-space, diagonalization for each block.
- Total energy per unit cell needed.
- Total energy decomposed in different, (conditionally) converging, sums (kinetic, electrostatic, exchange).

What do we have: Hartree-Fock, notation

Closed-shell systems

guess $\longrightarrow$ P^g $\longrightarrow$ F^g $\longrightarrow$ total energy

Fourier transformation

Fourier transformation

$P(k)$

$F(k)$

$\varepsilon(k)$

convergence

What do we have: Hartree-Fock, notation

Closed-shell systems

At disposition

- Molecular orbitals $\longrightarrow$ density, multipolar moments
- Orbital energies $\longrightarrow$ ionization potentials, excitation energies, band structures
- Total energy $\longrightarrow$ geometry, dissociation energies, vibrational and rotational constants, IR spectra, polarizabilities, thermochemistry

What do we have: Hartree-Fock, notation

Closed-shell systems

At disposition

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How do they perform?

- Good geometries, slightly too short bond lengths
- Good ionization potentials (Koopmans theorem)
- Bad binding energies (50 % of experimental values)
- Bad vibrational frequencies (much too high)
- Incapable to dissociate closed-shell systems continously into two separated open-shell systems
- Only high-spin states possible, no open-shell singlets for instance

What to do ?

- Add term to total energy $\longrightarrow$ DFT
- Parametrize with experimental results $\longrightarrow$ semi-empirical methods
- Use multi-determinantal wavefunctions

$$\Psi = \Phi_0 + \sum_I c_I \, \Phi_I \tag{1}$$

- Correction to the total energy of a closed-shell system:

Dynamical correlation

Reference determinant; other determinants of minor weight ($c_I << 1$)

- bond breaking, open-shell singlets

Non-dynamical correlation

Several determinants of comparable weight (some $c_I > 0.2 \dots 0.4$)

Treating dynamical correlation

Definition of the (dynamical) correlation energy:

$$E_{\text{Corr}} = E_{total} - E_{HF} \tag{2}$$

Remember:

$$E_{HF} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \tag{3}$$

but

$$\hat{H} | \Phi_0 \rangle \neq E_{HF} | \Phi_0 \rangle \tag{4}$$

Two basic approaches:

- Variation – today

- Perturbation – J. Toulouse

Configuration interaction

Straight-forward approach to Schrödinger's equation and the variational principle:

- Add more determinants within the same HF orbitals

$$\Psi = c_0\,\Phi_0 + \sum_I c_I\,\Phi_I$$

- Minimize the total energy under the constraint $\langle\Psi|\Psi\rangle = 1$:

$$E(\{c_I\}) = \left\langle c_0\Phi_0 + \sum_I c_I\Phi_I \left| \mathbf{H} \right| c_0\Phi_0 + \sum_J c_J\Phi_J \right\rangle$$

$$\mathcal{L}(\{c_I\};\lambda) = E(\{c_I\}) - \lambda\left(\langle\Psi|\Psi\rangle - 1\right)$$

- System of linear equations

$$\frac{\partial\mathcal{L}(\{c_I\};\lambda)}{\partial c_I} = 0\;; \qquad \frac{\partial\mathcal{L}(\{c_I\};\lambda)}{\partial\lambda} = 0$$

Configuration interaction

Written as matrix equation:

$$
\begin{pmatrix}
\langle 0|\mathbf{H}|0\rangle & \ldots & \langle 0|\mathbf{H}|I\rangle & \ldots \\
\vdots & & & \\
\langle 0|\mathbf{H}|J\rangle & \ldots & \langle I|\mathbf{H}|J\rangle & \ldots \\
\vdots & & &
\end{pmatrix}
\cdot
\begin{pmatrix}
c_0 \\
\vdots \\
c_I \\
\vdots
\end{pmatrix}
= \lambda
\begin{pmatrix}
c_0 \\
\vdots \\
c_J \\
\vdots
\end{pmatrix}
$$

Identify λ with the total energy from the functional:

$$
E(\{c_I\}) = \sum_I c_I \underbrace{\sum_J c_J \langle \Phi_I|\hat{H}|\Phi_J\rangle}_{=\lambda\, c_I} = \lambda \sum_I c_I^2 = \lambda
$$

Configuration interaction

Subtract $E_{HF} = \langle \Phi_0 | \mathbf{H} | \Phi_0 \rangle$ from the diagonal:

$$
\begin{pmatrix}
0 & \cdots & \langle 0 | \hat{\mathbf{H}} | I \rangle & \cdots \\
\vdots & \ddots & & \vdots \\
\langle 0 | \hat{\mathbf{H}} | I \rangle & \cdots & \langle I | \mathbf{H} | I \rangle - E_{HF} & \cdots \\
\vdots & & & \ddots
\end{pmatrix}
\cdot
\begin{pmatrix}
c_0 \\
\vdots \\
c_I \\
\vdots
\end{pmatrix}
= E_{Corr}
\begin{pmatrix}
c_0 \\
\vdots \\
c_J \\
\vdots
\end{pmatrix}
$$

- Intermediate norm: $c_0 = 1$:

$$
E_{total} = \langle \Phi_0 | \hat{\mathbf{H}} | \Psi \rangle = E_{HF} + \sum_{I \neq 0} c_I \langle 0 | \hat{\mathbf{H}} | \Phi_I \rangle
$$

$$
E_{Corr} = \sum_{I \neq 0} c_I \langle 0 | \hat{\mathbf{H}} | \Phi_I \rangle
$$

- The correlation energy is entirely determined by the coefficients of the di-excitations

Calculate with Slater determinants

"Problem": how to calculate a matrix element $H_{IJ} = \langle \Psi_I | \hat{H} \, \Psi_J \rangle$ when Ψ_I and Ψ_J are Slaterdeterminants

$$|\Psi\rangle = \frac{1}{\sqrt{(2n)!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_1(\vec{r}_2) & \ldots & \phi_1(\vec{r}_{2n}) \\ \vdots & & \ddots & \vdots \\ \phi_n(\vec{r}_1) & & \ldots & \phi_n(\vec{r}_{2n}) \\ \bar{\phi}_n(\vec{r}_1) & & \ldots & \bar{\phi}_n(\vec{r}_{2n}) \end{vmatrix} = |1\bar{1}2\bar{2}\ldots n\bar{n}\rangle$$

and $\hat{H}$ the molecular Hamilton operator

$$\hat{H} = \sum_i \left(-\frac{1}{2}\Delta_i - \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}_i|} \right) + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

with a one-electron part and a two-electron part

Calculate with Slater determinants

One-electron operator $\hat{O}_1 = \sum_{i=1}^{2n} \hat{h}_i$:

$$\langle 1\bar{1}2\bar{2}\ldots i \ldots n\bar{n}|\hat{O}_1|1\bar{1}2\bar{2}\ldots j \ldots n\bar{n}\rangle$$

$$= \quad \frac{1}{(2n)!} \left\langle \underbrace{\det}_{(2n)! \text{ terms}} \Bigg| \underbrace{\sum}_{2n \text{ terms}} \Bigg| \underbrace{\det}_{(2n)! \text{ terms}} \right\rangle$$

$$= \quad \frac{1}{(2n)!} \int \ldots \int f(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_{2n}) \left(\sum_k \hat{h}(\vec{r}_k) \right) g(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_{2n}) \, d^3 r_1 \ldots d^3 r_{2n}$$

$$= \quad \langle \phi_1|\phi_1\rangle\langle\bar{\phi}_1|\bar{\phi}_1\rangle \ldots \langle\phi_i|\hat{h}|\phi_j\rangle \ldots \langle\phi_n|\phi_n\rangle\langle\bar{\phi}_n|\bar{\phi}_n\rangle$$

$$= \quad \langle\phi_i|\hat{h}|\phi_j\rangle$$

- as each of the $(2n)!$ terms has to appear in the same ordering on the left and on the right,

- as each of $2n$ operators acts equally on each electron,

- as the integration factorizes,

- as orbitals are orthogonal, e.g. $\langle\phi_1|\hat{h}|\phi_1\rangle \ldots \langle\phi_i|\phi_j\rangle \ldots \langle\bar{\phi}_n|\bar{\phi}_n\rangle = 0$.

Calculate with Slater determinants

One-electron operator $\hat{O}_1 = \sum_i \hat{h}_i$, other cases

$$\langle 1\bar{1}2\bar{2}\ldots i \ldots k \ldots n\bar{n}|\hat{O}_1|1\bar{1}2\bar{2}\ldots j \ldots \ell \ldots n\bar{n}\rangle = 0$$

$$\langle 1\bar{1}2\bar{2}\ldots i \ldots n\bar{n}|\hat{O}_1|1\bar{1}2\bar{2}\ldots j \ldots n\bar{n}\rangle = \langle \phi_i|\hat{h}|\phi_j\rangle$$

$$\langle 1\bar{1}2\bar{2}\ldots n\bar{n}|\hat{O}_1|1\bar{1}2\bar{2}\ldots n\bar{n}\rangle = 2\sum_{i=1}^{n}\langle \phi_i|\hat{h}|\phi_i\rangle$$

Useful:

- Hartree-Fock energy:

$$E_{HF} = 2 \sum_{i \in occ.} \langle \phi_i|\hat{h}|\phi_i\rangle + \sum_{i,j \in occ.} \left(2\,(ii|jj) - (ij|ji)\right)$$

- Fock matrix

$$F_{ij} = \langle \phi_i|\hat{h}|\phi_j\rangle + \sum_{k \in occ.} \left(2\,(ij|kk) - (ik|kj)\right)$$

Calculate with Slater determinants

Two-electron operator $\hat{O}_2 = \sum_{i<j} \hat{g}_{ij}$:

$$\langle 1\bar{1}2\bar{2}\ldots i\ldots j\ldots k\ldots n\bar{n}|\hat{O}_2|1\bar{1}2\bar{2}\ldots p\ldots q\ldots r\ldots n\bar{n}\rangle = 0$$

$$\langle 1\bar{1}2\bar{2}\ldots i\ldots \bar{j}\ldots n\bar{n}|\hat{O}_2|1\bar{1}2\bar{2}\ldots p\ldots \bar{q}\ldots n\bar{n}\rangle = \langle \phi_i\phi_j|\hat{g}|\phi_p\phi_q\rangle$$

$$\langle 1\bar{1}2\bar{2}\ldots i\ldots j\ldots n\bar{n}|\hat{O}_2|1\bar{1}2\bar{2}\ldots p\ldots q\ldots n\bar{n}\rangle = \langle \phi_i\phi_j|\hat{g}|\phi_p\phi_q\rangle$$
$$-\langle \phi_i\phi_j|\hat{g}|\phi_q\phi_p\rangle$$

$$\langle 1\bar{1}2\bar{2}\ldots i\bar{i}\ldots n\bar{n}|\hat{O}_2|1\bar{1}2\bar{2}\ldots p\bar{i}\ldots n\bar{n}\rangle = \sum_{k\neq i}^{n} 2\langle \phi_k\phi_i|\hat{g}|\phi_k\phi_p\rangle - \langle \phi_k\phi_i|\hat{g}|\phi_p\phi_k\rangle$$

$$+\langle \phi_i\phi_i|\hat{g}|\phi_p\phi_i\rangle$$

$$\langle 1\bar{1}2\bar{2}\ldots n\bar{n}|\hat{O}_2|1\bar{1}2\bar{2}\ldots n\bar{n}\rangle = \sum_{i=1}^{n}\sum_{j=1}^{n} 2\langle \phi_i\phi_j|\hat{g}|\phi_i\phi_j\rangle - \langle \phi_i\phi_j|\hat{g}|\phi_j\phi_i\rangle$$

Slater-Condon rules (*J.C. Slater*, Phys.Rev., **34** (1929) 1293; *E.U. Condon*, Phys.Rev., **36** (1930) 1121)

Calculate with Slater determinants

Integral notations:

- Physicists:

$$\langle \phi_i \phi_j | \overbrace{\frac{1}{r_{12}}} | \phi_k \phi_\ell \rangle = \int \int \frac{\phi_i(\vec{r}_1)\phi_j(\vec{r}_2)\phi_k(\vec{r}_1)\phi_\ell(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2$$

- Chemists:

$$(ij|k\ell) = \int \int \frac{\phi_i(\vec{r}_1)\phi_j(\vec{r}_1)\phi_k(\vec{r}_2)\phi_\ell(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2$$

- Symmetry:

$$
\begin{aligned}
(ij|k\ell) &= (ji|k\ell) = (ji|\ell k) = (ij|\ell k) \\
&= (k\ell|ij) = (\ell k|ij) = (\ell k|ji) = (k\ell|ji)
\end{aligned}
$$

CI of Singles and Doubles

Number of configurations: N orbitals, n electrons α, β

$$N_{\text{Det}} = \binom{N}{n}^2 = \left(\frac{N!}{n!(N-n)!} \right)^2$$

Example: H_2O, 10 electrons, 40 orbitals (small basis) $n = 5$, $N = 40$:

$$432974528064 = 4.6 \times 10^{11} \text{ determinants}$$

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Possible solution: limit the number of excitations

- only doubly excited determinants in the expression for the correlation energy
- Contribution of triples and quadruples small in MP4

Spin conservation during an excitation:

$$\longrightarrow 78225 = \underbrace{(5 \times 4) \times 2 \times 35 \times 34}_{\text{same spin}} + \underbrace{(5 \times 5) \times 35 \times 35}_{\text{opposite spin}} \text{ determinants}$$

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Additional reduction of the number of determinants:

- by spatial symmetry
- by spin combination: 4 open shells $\rightarrow$ 1 quintet, 3 triplets, 2 singlets

CI of Singles and Doubles

Nevertheless: too many determinants to hold the matrix of all $\langle \Phi_I | \hat{H} | \Phi_J \rangle$
Iterative solution of the eigenvalue problem, we are only interested in the **best** wavefunction (Davidson procedure):

- Starting wavefunction (Φ_{HF} or $\Phi_{\mathrm{HF}} + \Psi^{(1)}$)

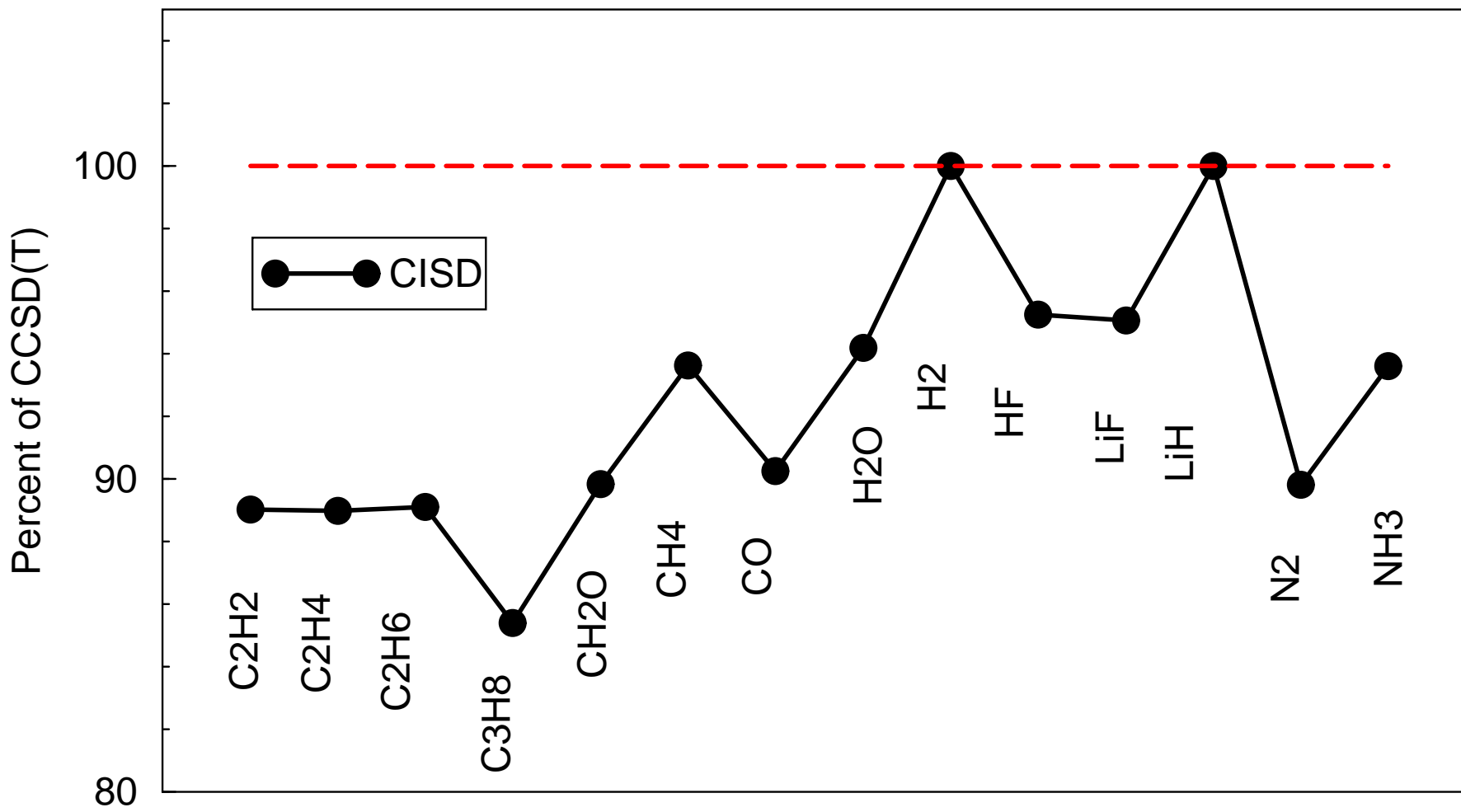- Form $|\tilde{\Psi}'\rangle = \hat{H}|\Psi\rangle$, construct the 2×2 matrix

$$
\begin{pmatrix}
\langle \Psi | \hat{H} | \Psi \rangle & \langle \Psi | \hat{H} | \tilde{\Psi}' \rangle \\
\langle \tilde{\Psi}' | \hat{H} | \Psi \rangle & \langle \tilde{\Psi}' | \hat{H} | \tilde{\Psi}' \rangle
\end{pmatrix}
$$

diagonalize it; eigenvector is a better WF Ψ'

- Construct $|\tilde{\Psi}''\rangle = \hat{H}|\Psi'\rangle$, augment the 2×2 matrix by one line and column: 3×3 matrix

- diagonalize, best vector gives $|\Psi''\rangle$

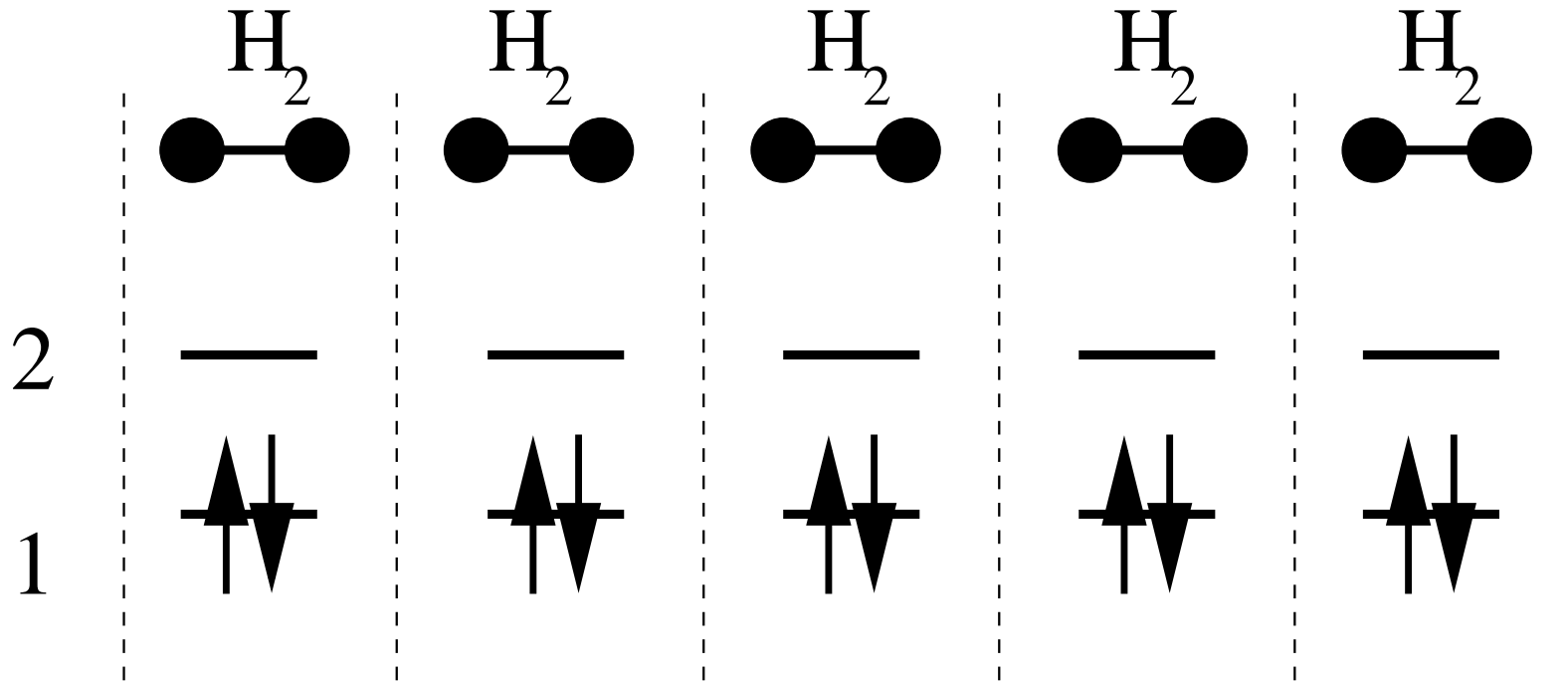- Continue until convergence

- Convergence in ca. 10 iterations

CI of Singles and Doubles

HF opt, pvtz basis set

Wrong scaling property of SD-CI

Model of N hydrogen molecules in minimal basis, without interaction

Wrong scaling property of SD-CI

- One single H_2 molecule:

$$\begin{aligned}
\langle \Phi_{1\bar{1}} | \mathbf{H} | \Phi_{1\bar{1}} \rangle &= E_{HF} = 2\,h_{11} + (11|11) \\
\langle \Phi_{2\bar{2}} | \mathbf{H} | \Phi_{2\bar{2}} \rangle &= E_{2\bar{2}} = 2\,h_{22} + (22|22) \\
\langle \Phi_{1\bar{1}} | \mathbf{H} | \Phi_{2\bar{2}} \rangle &= (12|12) = K_{12}
\end{aligned}$$

-

$$\begin{pmatrix} E_{HF} & K_{12} \\ K_{12} & E_{2\bar{2}} \end{pmatrix} \begin{pmatrix} 1 \\ c_{2\bar{2}} \end{pmatrix} = E \begin{pmatrix} 1 \\ c_{2\bar{2}} \end{pmatrix}$$

with eigenvalues

$$E_{\pm} = E_{HF} + \underbrace{\frac{E_{2\bar{2}} - E_{HF}}{2}}_{\Delta} \pm \sqrt{\left(\frac{E_{2\bar{2}} - E_{HF}}{2} \right)^2 + K_{12}^2}$$

$$= E_{HF} + \underbrace{\Delta \pm \sqrt{\Delta^2 + K_{12}^2}}_{E_{Corr}}$$

Wrong scaling property of SD-CI

N independent molecules ($(N-1)E_{HF}$ subtracted):

$$
\begin{pmatrix}
E_{HF} & K_{12} & \dots & \dots & K_{12} \\
K_{12} & E_{2\bar{2}} & 0 & \dots & 0 \\
\vdots & 0 & \ddots & \ddots & \vdots \\
\vdots & \vdots & \ddots & \ddots & 0 \\
K_{12} & 0 & \dots & 0 & E_{2\bar{2}}
\end{pmatrix}
\begin{pmatrix}
1 \\
\vdots \\
c_{2\bar{2},I} \\
\vdots \\
\vdots
\end{pmatrix}
= E
\begin{pmatrix}
1 \\
\vdots \\
c_{2\bar{2},I} \\
\vdots \\
\vdots
\end{pmatrix}
$$

In fact only two equations:

$$
K_{12} + c_{2\bar{2}}\, E_{2\bar{2}} = c_{2\bar{2}}(E_{HF} + E_{Corr}) \;\longrightarrow\; c_{2\bar{2}} = \frac{K_{12}}{E_{Corr} - 2\Delta}
$$

$$
E_{HF} + N\, K_{12}\, c_{2\bar{2}} = E_{HF} + E_{Corr} \;\longrightarrow\; E_{Corr} = N\, c_{2\bar{2}}\, K_{12} = \frac{N K_{12}^2}{E_{Corr} - 2\,\Delta}
$$

Wrong scaling property of SD-CI

Solution of the quadratic equation

$$E_{Corr}^2 - 2\,\Delta\,E_{Corr} - N\,K_{12}^2 \;=\; 0$$

$$E_{Corr} \;=\; \Delta - \sqrt{\Delta^2 + N\,K_{12}^2} \;\sim\; \sqrt{N}$$

Default of the size consistence !

Wrong scaling property of SD-CI

Solution of the quadratic equation

$$E_{Corr}^2 - 2\,\Delta\,E_{Corr} - N\,K_{12}^2 \;=\; 0$$

$$E_{Corr} \;=\; \Delta - \sqrt{\Delta^2 + N\,K_{12}^2} \;\sim\; \sqrt{N}$$

Default of the size consistence !

- Siegbahn's correction

$$E_{\mathrm{Corr}} \longrightarrow (1 - c_0^2)/c_0^2\,E_{\mathrm{Corr}}$$

P.E.M.Siegbahn, Chem.Phys.Lett., **55** (1978) 386
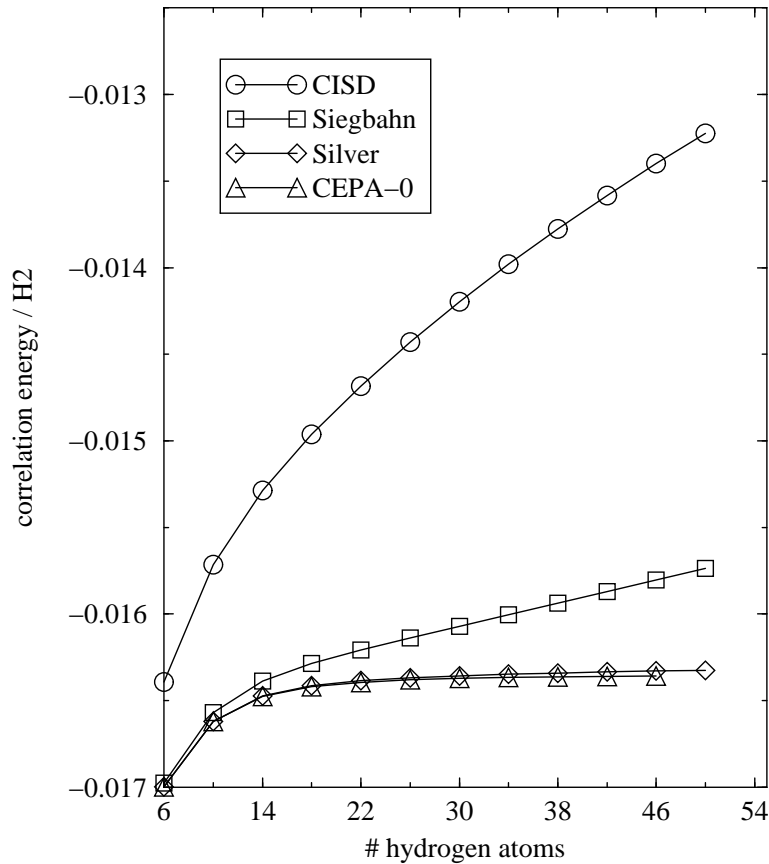
- Correction of Davidson and Silver

$$E_{\mathrm{Corr}} \longrightarrow (1 - c_0^2)/(2c_0^2 - 1)\,E_{\mathrm{Corr}}$$

E.R.Davidson, D.W.Silver, Chem.Phys.Lett., **52** (1977) 403

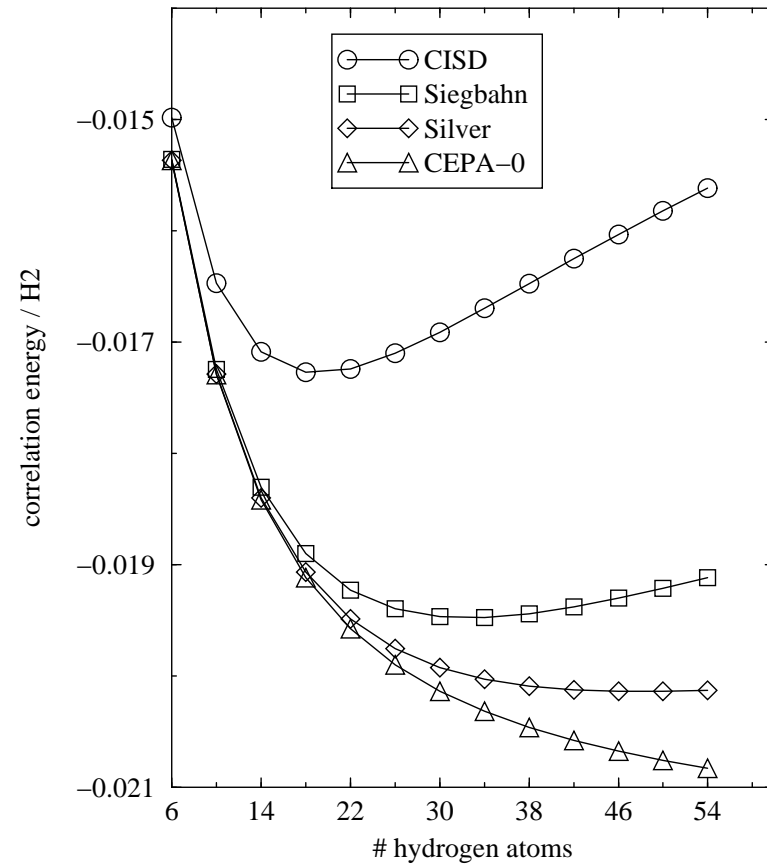# Wrong scaling property of SD-CI

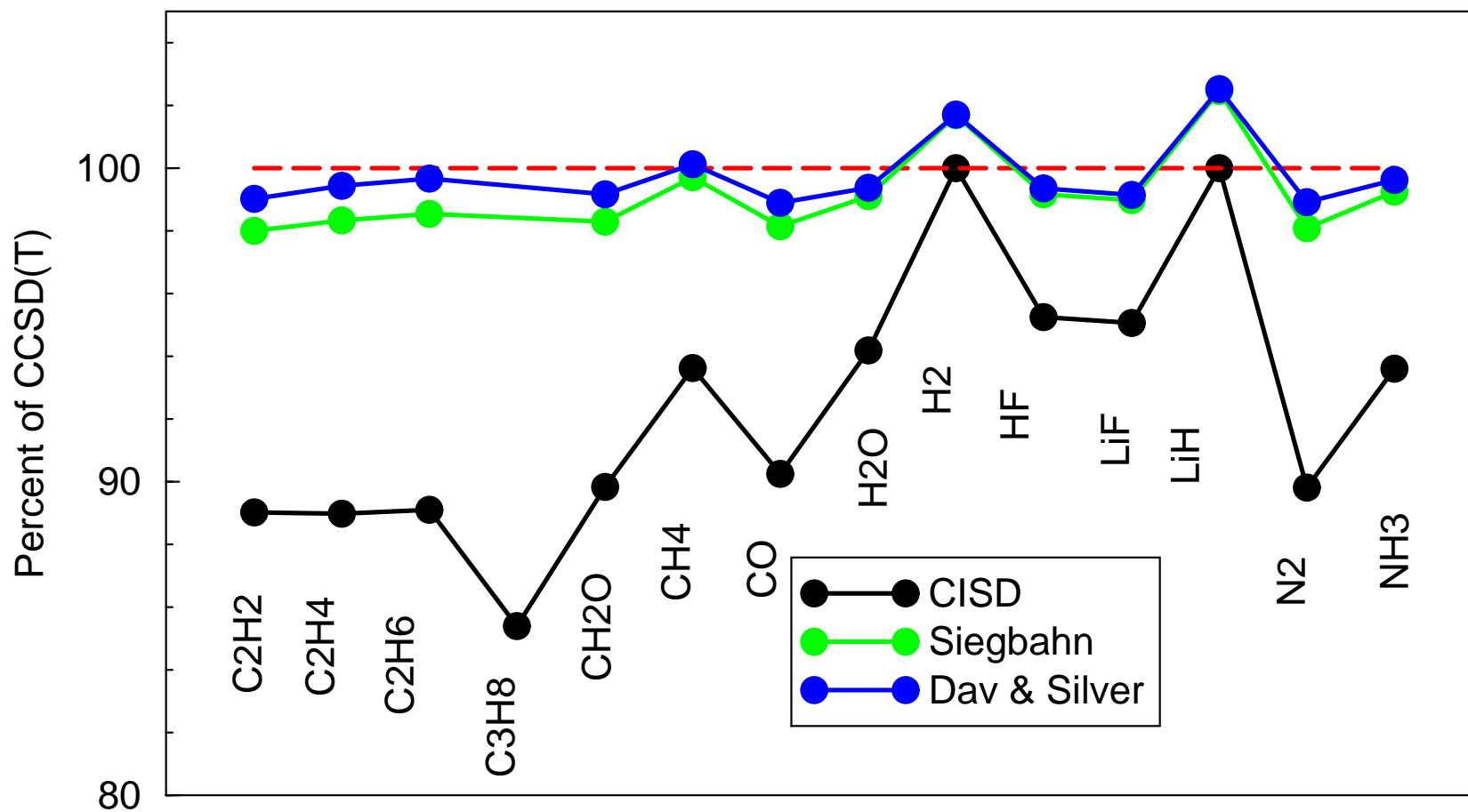Result for $(H_2)_n$ rings :

molecular case

metal-like case

Wrong scaling property of SD-CI

HF opt, pvtz basis set

Size-consistent methods

CISD eigenvalue problem

$$
\begin{pmatrix}
0 & \cdots & H_{0I} & & \cdots \\
\vdots & \ddots & & & \\
\vdots & & H_{II} - E_{\mathrm{HF}} & & \\
\vdots & & & & \ddots \\
\vdots & & & &
\end{pmatrix}
\begin{pmatrix}
1 \\
\vdots \\
\\
c_I \\
\vdots
\end{pmatrix}
= E_{\mathrm{Corr}}
\begin{pmatrix}
1 \\
\vdots \\
\\
c_I \\
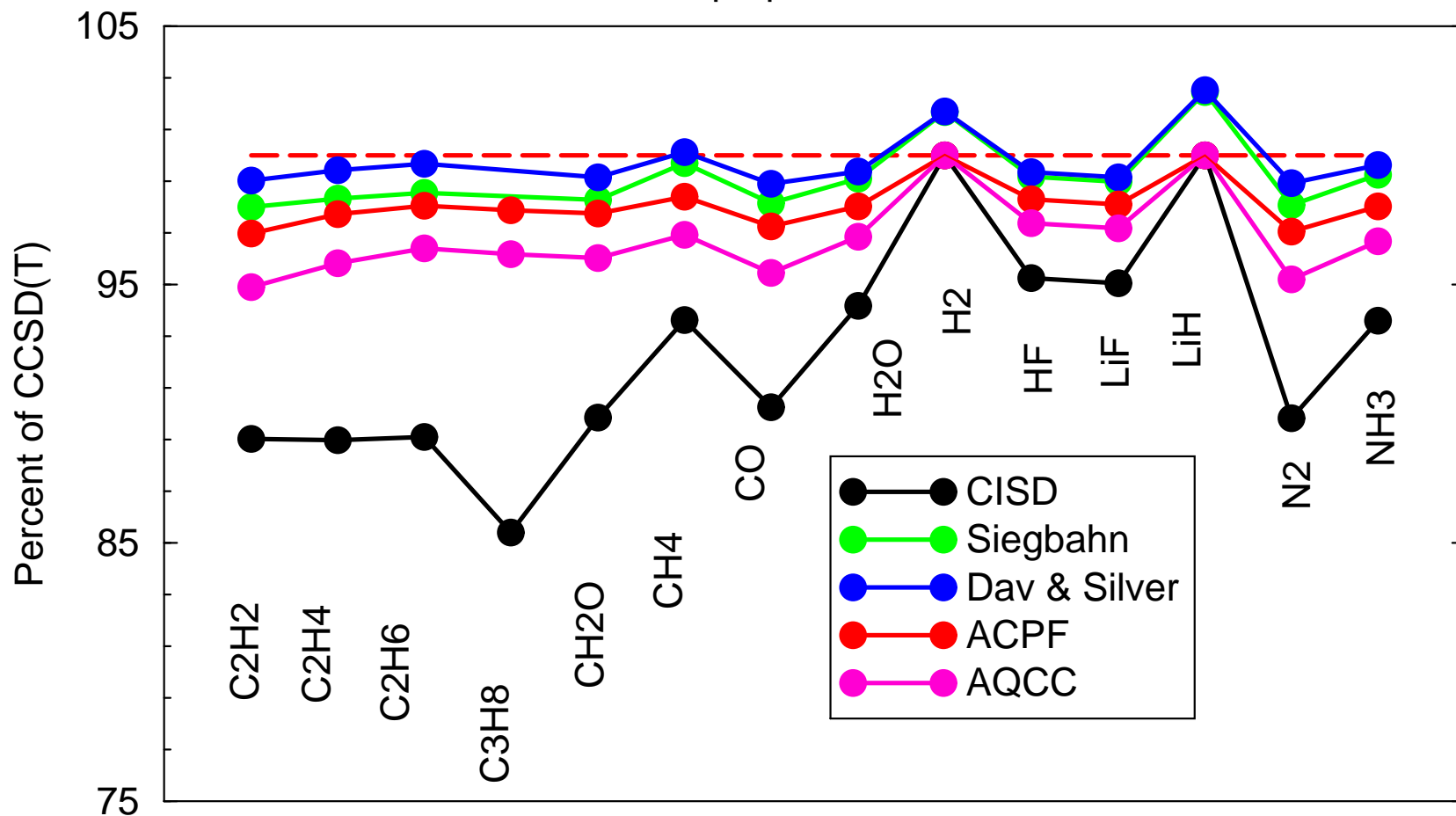\vdots
\end{pmatrix}
$$

Size-consistent methods

Dressed CISD eigenvalue problem

$$
\begin{pmatrix}
0 & \cdots & H_{0I} & & \cdots \\
\vdots & \ddots & & & \\
\vdots & & H_{II} - E_{\mathrm{HF}} + \Delta & & \\
\vdots & & & & \ddots
\end{pmatrix}
\begin{pmatrix}
1 \\
\vdots \\
c_I \\
\vdots
\end{pmatrix}
= E_{\mathrm{Corr}}
\begin{pmatrix}
1 \\
\vdots \\
c_I \\
\vdots
\end{pmatrix}
$$

- $\Delta = E_{\mathrm{Corr}}$ decouples the equations: CEPA-0, too severe
- Δ should go to E_{Corr} asymptotically, but be zero for 2 electrons (Full CI !)
- ACPF: $\Delta = E_{\mathrm{Corr}} \left(1 - \dfrac{2}{N} \right)$ Averaged Coupled Pair Functional
- AQCC: $\Delta = E_{\mathrm{Corr}} \dfrac{(N-2)(N-3)}{N(N-1)}$ Averaged Quadratic Coupled Cluster
- Self-consistent solution of the dressed equations

Size-consistent methods

HF opt, pvtz basis set

Diagonal approximation

$$\sum_J \langle 0 | \hat{\mathbf{H}} | J \rangle \, c_J \;\; = \;\; E_{Corr}$$

$$\mathbf{H}_{0I} + \langle \Phi_I | \mathbf{H} - E_{HF} + \underbrace{E_{corr} + \Delta'_I}_{=\Delta_I} | \Phi_I \rangle \, c_I + \sum_{J \neq I} \mathbf{H}_{IJ} \, c_J \;\; = \;\; E_{Corr} \, c_I$$
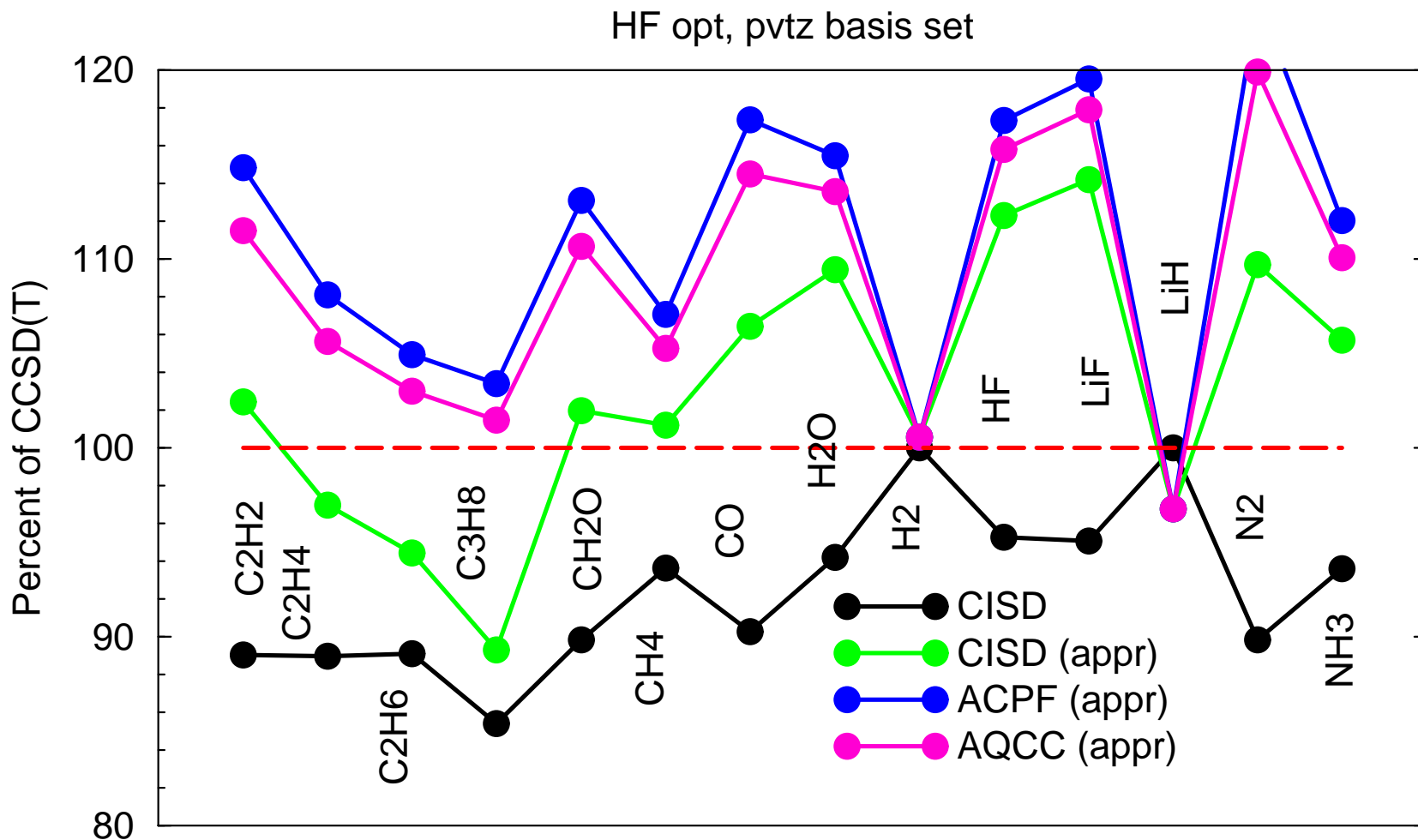
Diagonal approximation

$$\sum_J \langle\, 0\, |\, \hat{\mathbf{H}}\, |\, J\,\rangle\, c_J \;=\; E_{Corr}$$

$$\mathbf{H}_{0I} + \langle\Phi_I|\mathbf{H} - E_{HF} + \Delta'_I|\Phi_I\rangle\, c_I \;=\; 0$$

or

$$c_I = -\frac{\langle\, 0\, |\, \hat{\mathbf{H}}\, |\, I\,\rangle^2}{\langle\, I\, |\, \hat{\mathbf{H}}\, |\, I\,\rangle - E_{HF} + \Delta'_I}$$

- Cheap method: perturbation !!

- No integrals $(vv|vv)$ needed, only integrals $(oo|vv)$ and $(ov|ov)$.

- Iterative solution for c_I: Δ'_I depends on it

- No matrix diagonalization of $\mathbf{H}$.

Diagonal approximation

HF opt, pvtz basis set

How much does it cost ?

- At least N^5 due to integral transformation $(\alpha\beta|\gamma\delta) \longrightarrow (ia|jb)$

- CISD: N^6, form matrix elements $\langle\, \Phi_{ij}^{ab} \mid \hat{H} \mid \Phi_{ij}^{cd} \,\rangle$

- adding Davidson correction or dressings to CISD: no additional cost

- for comparison: HF or DFT $\sim\ N^3$

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