

Beyond the mean field: electron correlation

Peter Reinhardt

Laboratoire de Chimie Théorique, Université Paris VI, 75252 Paris CEDEX 05,

Peter.Reinhardt@upmc.fr

- p. 1/c

- p. 3/c

What do we have: Hartree-Fock, notation

Closed-shell systems

Wavefunction:

$$\begin{aligned}
 |\Phi_0\rangle &= \Phi_0(\vec{r}_1 s_1, \vec{r}_2 s_2, \dots, \vec{r}_{n-1} s_{n-1}, \vec{r}_n s_n) \\
 &= \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\vec{r}_1) \sigma_\uparrow(s_1) & \dots & \phi_{n/2}(\vec{r}_1) \sigma_\downarrow(s_1) \\ \vdots & \ddots & \vdots \\ \phi_1(\vec{r}_n) \sigma_\uparrow(s_n) & \dots & \phi_{n/2}(\vec{r}_n) \sigma_\downarrow(s_n) \end{vmatrix} \\
 &= |\phi_1, \bar{\phi}_1, \dots, \phi_{n/2}, \bar{\phi}_{n/2}\rangle \text{ with } |\phi_i\rangle = \phi_i(\vec{r}) \sigma_\uparrow \text{ et } |\bar{\phi}_i\rangle = \phi_i(\vec{r}) \sigma_\downarrow
 \end{aligned}$$

Molecular orbitals

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

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

- p. 2/c

- p. 4/c

What do we have: Hartree-Fock, notation

Closed-shell systems

- Hamiltonian :

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

- Total energy: $E_{HF} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$
- Orbitals are (self-consistent) solution of $\hat{F} \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$ with the Fock operator

$$\hat{F} \phi_i(\vec{r}) = \left[-\frac{1}{2} \Delta - \sum_I \frac{Z_I}{|\vec{R}_I - \vec{r}|} \right] \phi_i(\vec{r}) + \sum_{j \in occ} \left[2 \int \frac{\phi_j(\vec{r}') \phi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' \phi_i(\vec{r}) - \int \frac{\phi_j(\vec{r}') \phi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' \phi_j(\vec{r}) \right]$$

- p. 64

- p. 74

What do we have: Hartree-Fock, notation

Closed-shell systems

At disposition

- Molecular orbitals \rightarrow density, multipolar moments
 - Orbital energies \rightarrow ionization potentials, excitation energies, band structures
 - Total energy \rightarrow geometry, dissociation energies, vibrational and rotational constants, IR spectra, polarizabilities, thermochemistry
- 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 continuously into two separated open-shell systems
 - Only high-spin states possible, no open-shell singlet for instance

- p. 64

- p. 84

What to do ?

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

$$\Psi = \Phi_0 + \sum_I c_I \Phi_I \quad (1)$$

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

Dynamical correlation

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

- bond breaking, open-shell singlets

Non-dynamical correlation

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

- p. 96

- p. 116

Treating dynamical correlation

Definition of the (dynamical) correlation energy:

$$E_{\text{Corr}} = E_{\text{total}} - E_{\text{HF}} \quad (2)$$

Remember:

$$E_{\text{HF}} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \quad (3)$$

but

$$\hat{H} | \Phi_0 \rangle \neq E_{\text{HF}} | \Phi_0 \rangle \quad (4)$$

Two basic approaches:

- Perturbation
- Variation

- p. 106

- p. 126

Perturbation theory

- Decompose \hat{H} in two parts

$$\hat{H} = \hat{H}_0 + \hat{V}$$

- Eigenfunctions of \hat{H}_0 known:

$$\hat{H}_0 \Phi_k = E_k^{(0)} \Phi_k \quad (5)$$

- \hat{V} small

-p. 134

-p. 144

Perturbation theory

- Introduce a parameter λ with $0 \leq \lambda \leq 1$:

$$\hat{H}(\lambda) = \hat{H}_0 + \lambda \hat{V}$$

- Parametrize the total energy and the wavefunction with λ in the Schrödinger equation:

$$\hat{H}(\lambda) \Psi(\lambda) = E(\lambda) \Psi(\lambda)$$

- Develop in powers of λ :

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} ; |\Psi\rangle = \sum_{n=0}^{\infty} \lambda^n |\Psi^{(n)}\rangle ; E_0 = \sum_{n=0}^{\infty} \lambda^n E_0^{(n)} .$$

- Develop $|\Psi^{(n)}\rangle$ in eigenfunctions of \hat{H}_0 (excited determinants):

$$|\Psi^{(n)}\rangle = \sum_{k=1}^{\infty} |\Phi_k\rangle \langle \Phi_k | \Psi^{(n)} \rangle = \sum_{k=1}^{\infty} c_k^{(n)} |\Phi_k\rangle$$

- Rayleigh-Schrödinger perturbation theory

-p. 134

-p. 154

Perturbation theory

Schrödinger equation $\mathbf{H}|\Psi\rangle = E_0|\Psi\rangle$:

$$(\hat{H}_0 + \lambda \hat{V}) \sum_{n=0}^{\infty} \lambda^n |\Psi^{(n)}\rangle = \sum_{m=0}^{\infty} \lambda^m E_0^{(m)} \sum_{k=0}^{\infty} \lambda^k |\Psi^{(k)}\rangle$$

Energies:

$$E_0^{(n)} = \langle 0 | \hat{V} | n-1 \rangle$$

Coefficients:

$$c_k^{(n)} = \langle \Phi_k | \Psi^{(n)} \rangle = \frac{1}{E_0^{(0)} - E_k^{(0)}} \left[\langle k | \hat{V} | n-1 \rangle \right.$$

$$\left. - E_0^{(1)} c_k^{(n-1)} - E_0^{(2)} c_k^{(n-2)} - \dots - E_0^{(n-1)} c_k^{(1)} \right]$$

Perturbation theory

Schrödinger equation $\mathbf{H}|\Psi\rangle = E_0|\Psi\rangle$:

$$(\hat{H}_0 + \lambda \hat{V}) \sum_{n=0}^{\infty} \lambda^n |\Psi^{(n)}\rangle = \sum_{m=0}^{\infty} \lambda^m E_0^{(m)} \sum_{k=0}^{\infty} \lambda^k |\Psi^{(k)}\rangle$$

- We always have

$$E_0^{(0)} + E_0^{(1)} = \langle \Phi_0 | \hat{H}_0 + \hat{V} | \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = E_{HF}$$

-

$$c_k^{(1)} = \langle \Phi_k | \Psi^{(1)} \rangle = \frac{1}{E_0^{(0)} - E_k^{(0)}} \langle k | \hat{V} | 0 \rangle$$

$$E_0^{(2)} = \langle \Phi_0 | \hat{V} | \Psi^{(1)} \rangle = \sum_{k \neq 0} \frac{\langle 0 | \hat{V} | k \rangle^2}{E_0^{(0)} - E_k^{(0)}} < 0$$

Perturbation theory

$$\begin{aligned}
 E_0^{(1)} &= \langle \Phi_0 | \hat{V} | \Phi_0 \rangle = \langle 0 | \hat{V} | 0 \rangle \\
 E_0^{(2)} &= \langle \Phi_0 | \hat{V} | \Psi^{(1)} \rangle = \sum_{k \neq 0} \langle 0 | \hat{V} \frac{|k\rangle\langle k|}{E_0^{(0)} - E_k^{(0)}} \hat{V} | 0 \rangle \\
 E_0^{(3)} &= \langle \Phi_0 | \hat{V} | \Psi^{(2)} \rangle \\
 &= \sum_{k,l \neq 0} \langle 0 | \hat{V} \frac{|k\rangle\langle k|}{E_0^{(0)} - E_k^{(0)}} \hat{V} \frac{|l\rangle\langle l|}{E_0^{(0)} - E_l^{(0)}} \hat{V} | 0 \rangle \\
 &\quad - E_0^{(1)} \sum_{k \neq 0} \left(\frac{\langle 0 | \hat{V} | k \rangle}{E_0^{(0)} - E_k^{(0)}} \right)^2
 \end{aligned} \tag{6}$$

There is a systematic structure in the equations ...

e.g. $2n + 1$ rule:

$$E_0^{(3)} = \langle \Psi^{(1)} | \hat{V} | \Psi^{(1)} \rangle - E_0^{(1)} \langle \Psi^{(1)} | \Psi^{(1)} \rangle$$

- p. 19f

- p. 21f

Møller-Plesset perturbation theory

C.Møller, M.S.Plesset, Phys.Rev., 46 (1934) 618

What should we take for \hat{H}_0 ?

We know the eigenfunctions of the Fock operator: orbitals

We know the eigenvalues of these functions: orbital energies ϵ_i

$$\hat{H}_0 = \sum_i \epsilon_i \hat{a}_i^\dagger \hat{a}_i \tag{7}$$

Apply this to a Slater determinant : $\hat{H}_0 \Phi_k = \left(\sum_{i \in \text{occ}(k)} \epsilon_i \right) \Phi_k$ (8)

Matrix element $\langle 0 | \hat{V} | k \rangle$: k must be a di-excited determinant, otherwise zero.

$$\begin{aligned}
 \langle 0 | \hat{V} | k \rangle &= \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle - \underbrace{\langle \Phi_0 | \hat{H}_0 | \Phi_{ij}^{ab} \rangle}_{=0} = \langle 0 | \hat{H} | k \rangle \\
 &= (ia|jb) - (ib|ja) \delta_{\sigma_i \sigma_j} \quad \text{bi-electronic integrals}
 \end{aligned} \tag{9}$$

- p. 20f

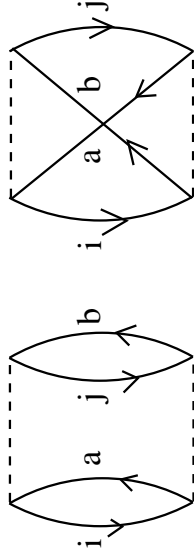
- p. 22f

Møller-Plesset perturbation theory

Second-order energy:

$$E^{(2)} = \sum_{ijab} \frac{2(ia|jb) - (ib|ja)(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (11)$$

And higher-order formulas can be derived as well ... but become more and more complex



$$2 \frac{(ia|jb)(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} - \frac{(ia|jb)(ib|ja)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

-p. 284

-p. 284

Diagrammatic language

The rules of the game

1. For a nth-order diagram draw 2 vertical rows of n linked points
2. Link all the points (one line in, one line out)
3. Sum over all internal lines
4. A horizontal link between 2 points gives a bi-electronic integral
5. Draw a horizontal line between two pairs of points. Every of these results in a factor in the denominator with the orbital energies of the vertical lines encountered. Holes are positive, particles negative.

$$\sum_{i \in occ} \epsilon_i - \sum_{a \in virt} \epsilon_a$$

6. The overall sign is given by the number of closed loops and the number of holes

$$(-1)^{\text{closed loops} + \text{holes}}$$

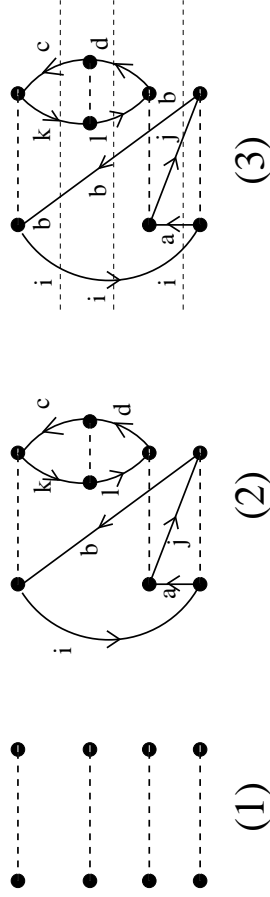
7. If a symmetry plane is present, multiply by 1/2
8. The diagram has to be multiplied by $2^{\text{closed loops}}$

-p. 284

-p. 284

Diagrammatic language

A 4-th order diagram as example



(1)

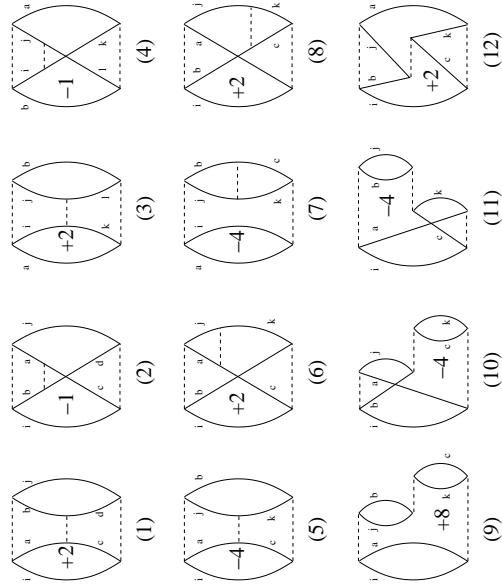
(2)

(3)

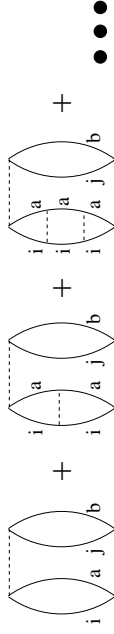
$$\sum_{ijklabcd} (-1)^{2+4} 2^2 \frac{(ib|kc)(kl|cd)(ja|ld)(ia|jb)}{(\epsilon_i + \epsilon_k - \epsilon_b - \epsilon_c)(\epsilon_i + \epsilon_l - \epsilon_b - \epsilon_d)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)}$$

Diagrammatic language

All third-order diagrams



Infinite summations



MP2

Geometrical series: $a(1 + q + q^2 + q^3 + \dots) = \frac{a}{1 - q}$

Here:

$$q = -\frac{(ii|aa)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

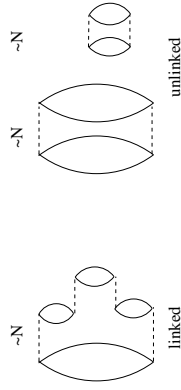
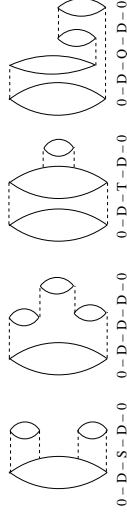
All possible same-index repetitions lead to

$$E^{(2)}(\infty) = \sum_I \frac{\langle \Phi_0 | \hat{H} | \Phi_I \rangle}{\langle \Phi_I | \hat{H} - E_{HF} | \Phi_I \rangle}$$

Different decomposition of \hat{H} in \hat{H}_0 and \hat{V} : Epstein-Nesbet

Other use of diagrams

Which excitations contribute to which order



Only linked diagrams: correlation energy grows as the size of the system (Linked-Cluster Theorem 1957)

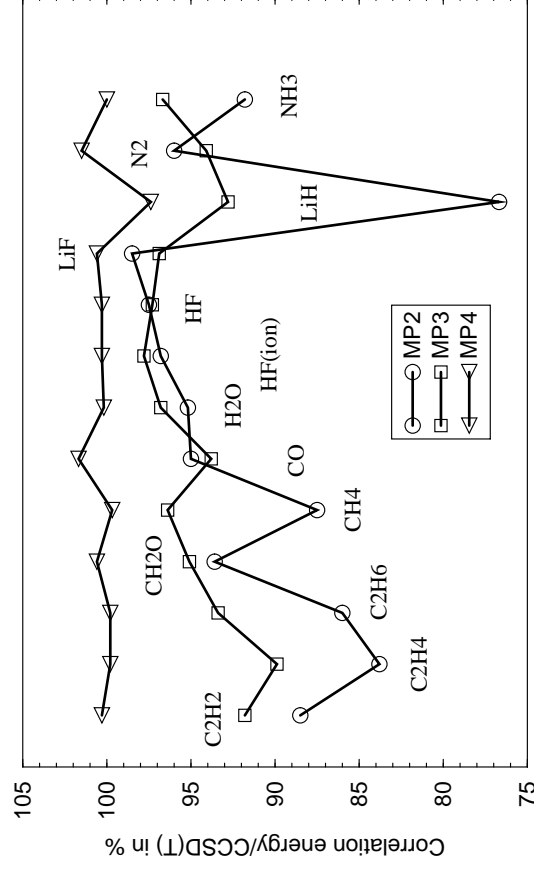
Summary

- Development order-by-order to improve **total energy**
- Straight-forward evaluation, term by term, diagram by diagram
- Only **infinite order** satisfies Schrödinger's equation
- Zeroth+first order is the **Hartree-Fock energy**
- 1st-order wavefunction \rightarrow natural orbitals, density
- Second-order **always** lowers the total energy
- Higher orders become rapidly more and more complex
- $2n + 1$ rule: $E^{(2n+1)}$ known from $\Psi^{(n)}$; $0 \rightarrow 1, 1 \rightarrow 3, 2 \rightarrow 5$
- Commonly used: **MP2, MP4**

- p. 346c

- p. 360c

Performance



Basis aug-cc-pvtz, fixed geometry

- p. 350c

- p. 370c

Performance

Geometry parameters

molecule	Hartree-Fock		2nd order Møller-Plesset	
	Δr (pm)	Δ ang (deg.)	Δr (pm)	Δ ang (deg.)
H ₂ O	-1.7	+1.8	+0.1	-0.4
N ₂	-3.1		+1.6	
CH ₄	-0.5		-0.1	
CO	-2.4		+1.1	
HF	-1.8		+0.5	
NH ₃	-1.4	+1.5	0.0	+0.5
P ₂	-3.6		+3.4	
SO ₂	-2.7	-1.3	+2.7	-1.1

Source: NIST database <http://www.nist.org>

-p. 38t

-p. 38t

Performance

Vibrational constants, atomization energies

molecule	Hartree-Fock		2nd order Møller-Plesset		Experiment	
	ν (cm ⁻¹)	at.ener. (kJ/mol)	ν (cm ⁻¹)	at.ener. (kJ/mol)	ν (cm ⁻¹)	at.ener. (kJ/mol)
H ₂ O	4121	597	3821	917	3657	918
N ₂	2726	472	2187	952	2339	897
CH ₄	3147	1260	3069	1607	3028	1617
CO	2421	716	2110	1099	2144	1040
HF	4465	380	4125	576	4128	557
NH ₃	3686	754	3503	1128	3464	1131
P ₂	909	150	726	451	768	437
SO ₂	1371	393	1106	—	1136	968

Source: NIST database <http://www.nist.org>

-p. 38t

-p. 38t

Configuration interaction

Different approach to Schrödinger's equation:

- Add additional determinants

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

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

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

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

- System of linear equations

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

- p. 416

- p. 426

Configuration interaction

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

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

- Intermediate norm: $c_0 = 1$:

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

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

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

- p. 416

- p. 436

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: H₂O, 10 orbitals, 40 orbitals (small basis):

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

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:

$$\longrightarrow 107100 = 10 \times 9 \times 35 \times 34 \text{ determinants}$$

Additional reduction of the number of determinants:

- by spatial symmetry
 - by spin combination: 4 open shells \rightarrow 1 quintet, 4 triplets, 2 singlets
- Resulting wavefunction has same spin and space symmetry as Hartree-Fock

- p. 464

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 $\Phi_{\text{HF}} + \Psi^{(1)}$)
- Form $|\Psi'\rangle = \hat{H}|\Psi\rangle$, construct the 2×2 matrix

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

diagonalize it; eigenvector is a better WF Ψ'

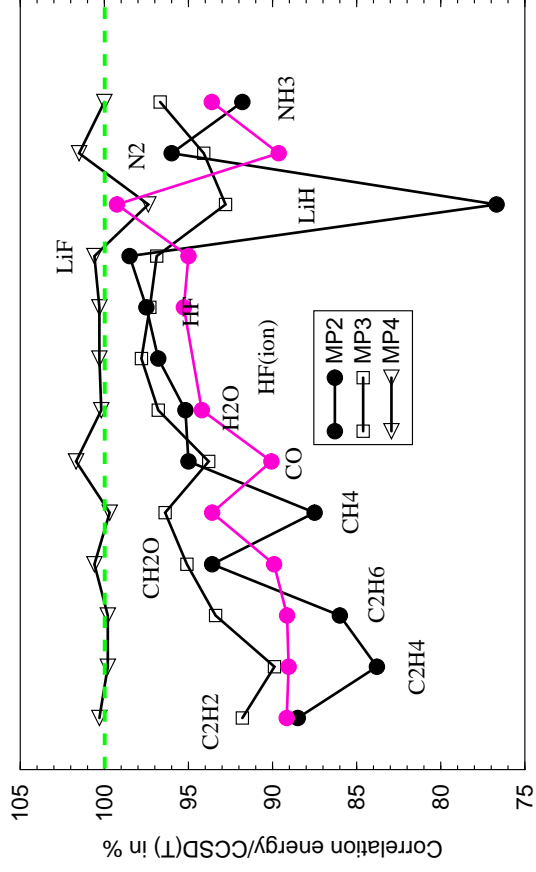
- Construct $|\Psi''\rangle = \hat{H}|\Psi'\rangle$, augment the 2×2 matrix by one line and column: 3×3 matrix
- diagonalize, best vector gives $|\Psi''\rangle$
- Continue until convergence
- Convergence in ca. 10 iterations

- p. 464

- p. 464

- p. 474

CI of Singles and Doubles

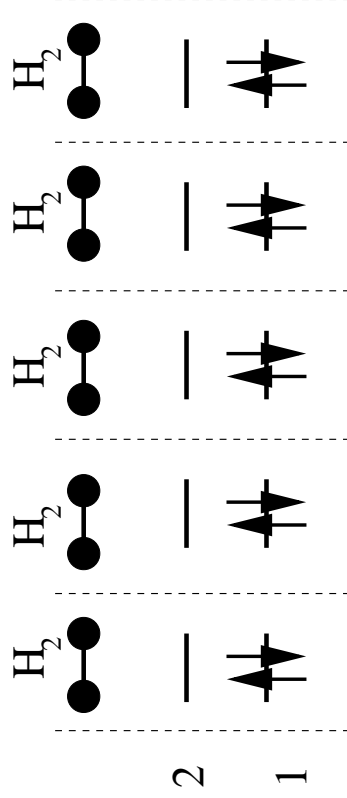


-p. 48/c

-p. 50/c

Wrong scaling property of SD-CI

Model of N hydrogen molecules in minimal basis, without interaction



-p. 48/c

-p. 51/c

Wrong scaling property of SD-CI

- One single H₂ molecule:

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

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

with eigenvalues

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

-p. 58t

Wrong scaling property of SD-CI

N independent molecules:

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

In fact only two equations:

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

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

-p. 58t

Wrong scaling property of SD-CI

Solution of the quadratic equation

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

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

Default of the size consistence !

- Siegbahn's correction

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

P.E.M. Siegbahn, Chem.Phys.Lett., **55** (1978) 386

- Correction of Davidson and Silver

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

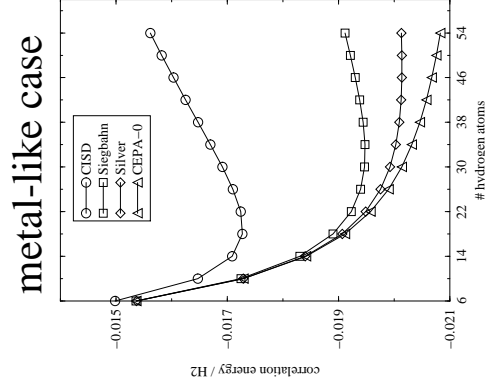
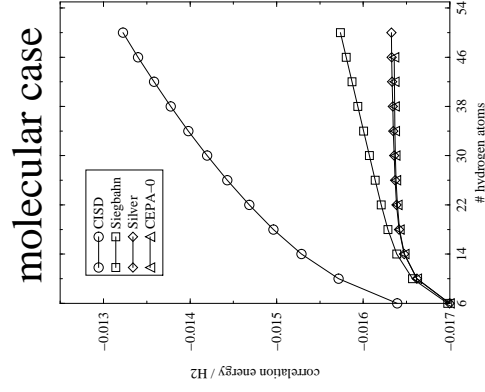
E.R. Davidson, D.W. Silver, Chem.Phys.Lett., **52** (1977) 403

-p. 56t

-p. 57t

Wrong scaling property of SD-CI

Result for $(\text{H}_2)_n$ rings :



-p. 56t

-p. 56t

Size-consistent methods

CISD eigenvalue problem

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

-p. 69f

-p. 69f

Size-consistent methods

Dressed CISD eigenvalue problem

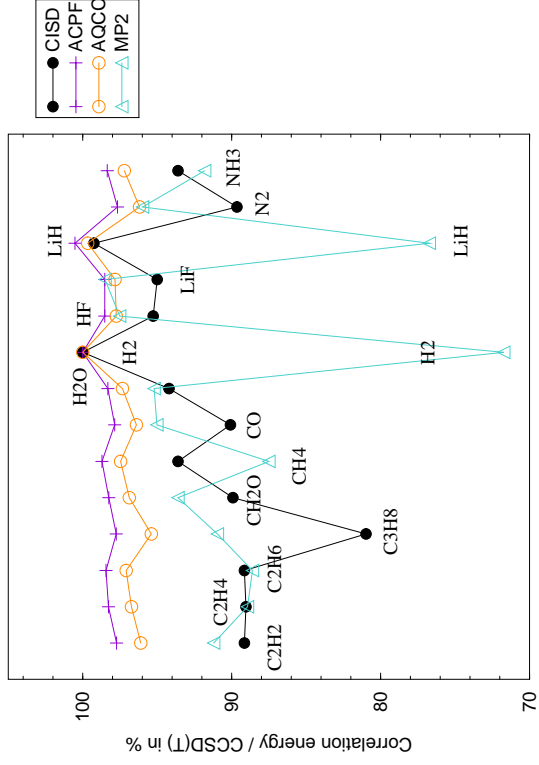
$$\begin{pmatrix} 0 & \dots & H_{0I} & \dots & \dots \\ \vdots & \ddots & \vdots & \vdots & \vdots \\ \vdots & \vdots & H_{II} - E_{\text{HF}} + \Delta & \dots & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix} \begin{pmatrix} 1 \\ \vdots \\ c_I \\ \vdots \end{pmatrix} = E_{\text{Corr}}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

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

-p. 69f

-p. 69f

Size-consistent methods



- p. 684c

- p. 684c

How much does it cost ?

- MP2: N^5 due to integral transformation $(\alpha\beta|\gamma\delta) \longrightarrow (ia|jb)$
- CISD: N^6 , form matrix elements $\langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ij}^{cd} \rangle$
- MP3: one iteration of CISD
- adding dressings to CISD: no additional cost
- MP4:
 - exploit: $\langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ijkl}^{abcd} \rangle = \langle \Phi_0 | \hat{H} | \Phi_{kl}^{cd} \rangle$
 - treatment of Singles, Doubles, and Quadruples $\sim N^6$
 - Triples: excitation sequence

$$\langle 0 | \hat{H} | D \rangle \langle D | \hat{H} | T \rangle \langle T | \hat{H} | D \rangle \langle D | \hat{H} | 0 \rangle$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{klm}^{cde} \rangle = \langle abklm | \hat{H} | ijcd \rangle \longrightarrow N^7$$
- for comparison: HF or DFT $\sim N^3$

- p. 684c

- p. 684c