Ecole thématique Roscoff – chimie théorique

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Organisation

Cours : mardi 3 h + 1 h, mercredi 1 h 30 + 1 h, jeudi 1 h 30

- Equation de Schrödinger et systèmes simples
  - Modèle de Bohr
  - Boîte 1D, oscillateur harmonique
  - Atome d'hydrogène et ses orbitales

- Systèmes polyélectroniques
  - Modèles simplifiés : LCAO, hybrides, Hückel
  - Fonctions d'onde : déterminants et règles de Slater
  - Hartree-Fock
  - Bases de fonctions atomiques

- Rupture de liaison : fonctions multidéterminantales

- Corrélation électronique : perturbation, IC, CC

- DFT et couplage avec perturbation

Organisation

Travaux pratiques.

- Mardi AM 1 h : règles de Slater, calcul HF, rupture de liaison

- Mercredi AM 2 h : calcul pertubation, IC, logiciels "grand public"
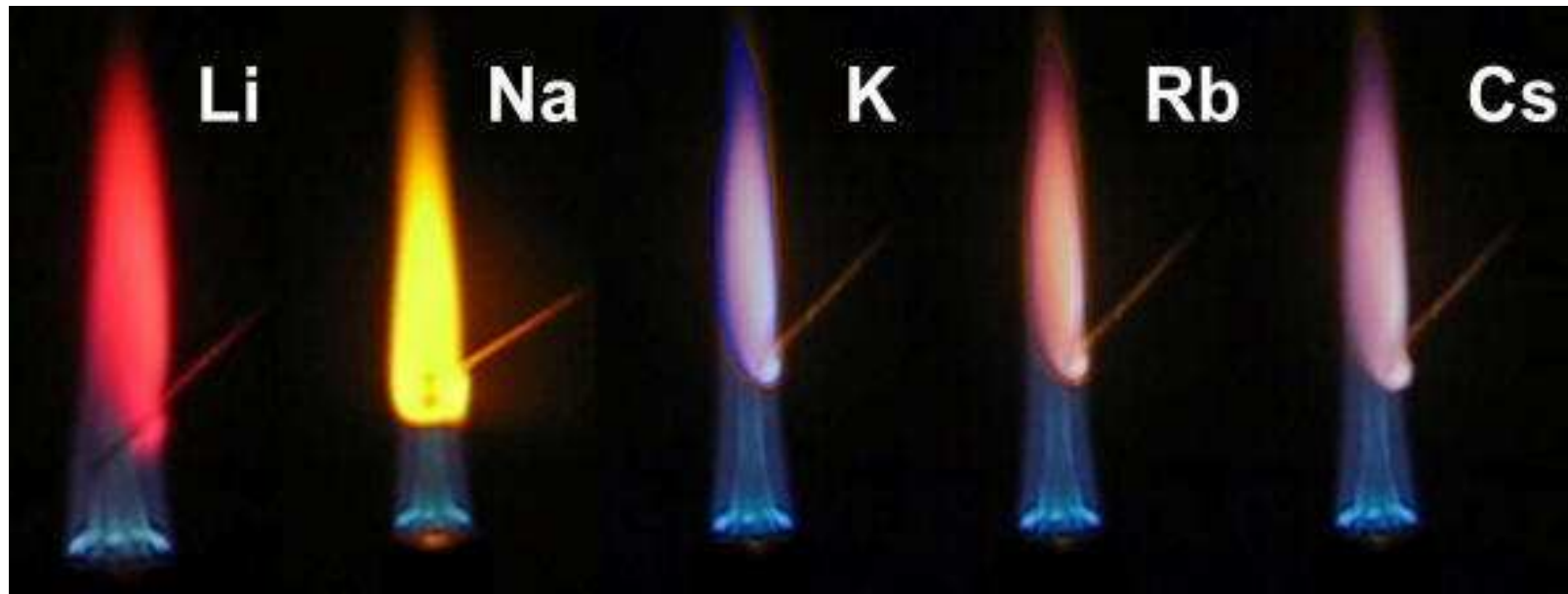 Gaussian, Molpro, GAMESS, Dalton

Spectroscopy

Hydrogen spectrum in the sun light - Joseph Fraunhofer
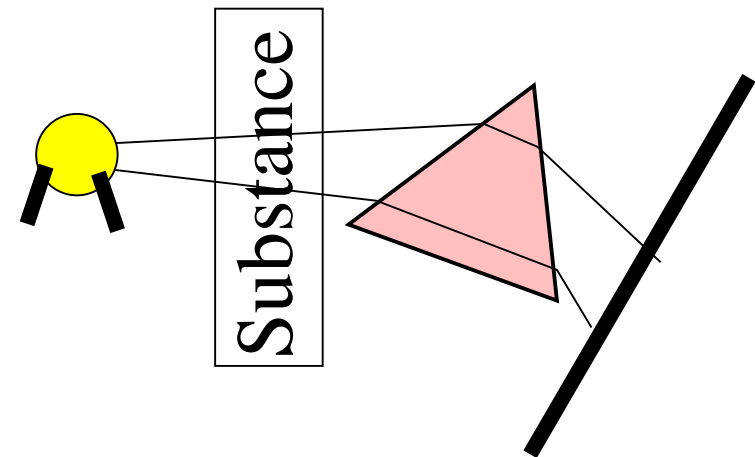

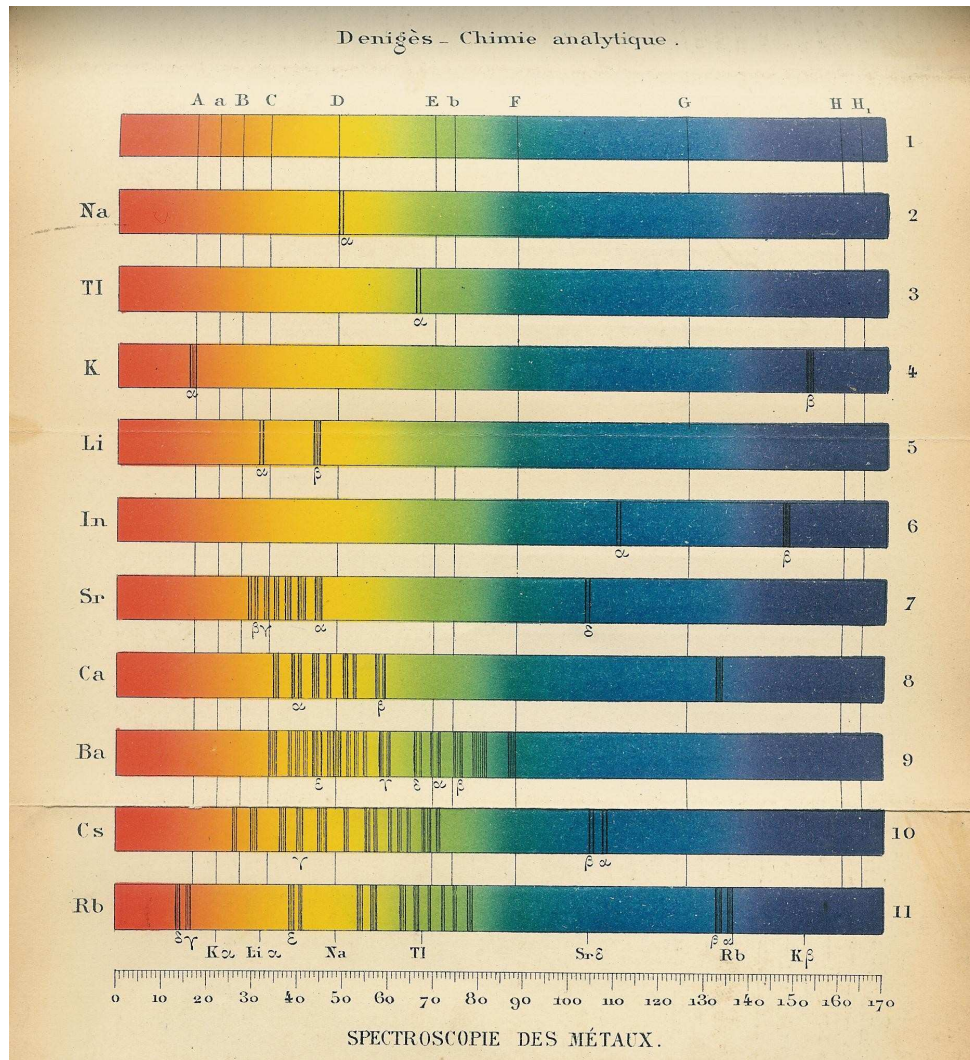German stamp, 1987

Spectroscopy

Flame coloration from atomic spectra

Spectroscopy
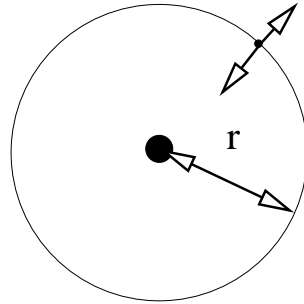
Atomic emission spectra, helping to identify elements

Deniges

Chimie analytique

Paris 1913

Bohr model and Schrödinger's equation

$$\frac{mv^2}{r} = \left(\frac{e^2}{4\pi\,\epsilon_0}\right)\frac{1}{r^2}$$

Angular momentum $\vec{L} = \vec{r} \times \vec{p} = m\vec{r} \times \vec{v}$ in units of h: $|\vec{L}| = m\,r\,v = n\hbar$

$$\longrightarrow \quad r_n = \frac{\hbar^2\,4\pi\epsilon_0}{e^2\,m}\,n^2, \qquad v_n = \frac{e^2}{4\pi\epsilon_0\,\hbar}\,\frac{1}{n}$$

$$T_n = \frac{1}{2}mv_n^2 = +\frac{m}{2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{\hbar^2\,n^2}$$

$$V_n = \int_{r_n}^{\infty} F(r)\,dr = -\left(\frac{e^2}{4\pi\,\epsilon_0}\right)\frac{1}{r_n} = -\frac{m\,e^4}{(4\pi\epsilon_0)^2\hbar^2}\,\frac{1}{n^2}$$

- Works for the hydrogen atom and nothing else ...

Bohr model and Schrödinger's equation

Photoelectric effect shows for light quanta of energy:

$$E = h\,\nu = \frac{h\,c}{\lambda}$$

- Compton scattering confirms the equivalence of light and matter.
- Heisenberg: 2-index quantities needed for describing energy differences
- Schrödinger: one differential equation with a Hamilton operator

$$i\hbar\frac{\partial}{\partial t}\,\Psi = \hat{H}\,\Psi$$

with $|\Psi^2|$ as probability distribution to find a particle in space and time.

- Time-independent problem: $\hat{H}\,\Psi = E\,\Psi$ with total energy E.
- No movement, but average over many experiments to localize a particle (e.g. photographic film)
- Average over operator: $E = \langle\,\Psi\,|\,\hat{H}\,|\,\Psi\,\rangle$

Bohr model and Schrödinger's equation

Contributions to the Hamiltonian:

- Kinetic energy $p^2/(2m)$ of each particle, with $\vec{p} = -i\hbar\vec{\nabla}$
- Potential energy: electrostatics
- External fields: electromagnetic waves, static fields

Solve thus Schrödinger's equations for many particles

$$\left(-\frac{1}{2}\sum_i \Delta_i + V(\vec{r}_1, \vec{r}_2, \ldots) \right) \Psi(\vec{r}_1, \vec{r}_2, \ldots) = E\,\Psi(\vec{r}_1, \vec{r}_2, \ldots)$$

Simple systems, atoms, molecules, solids

$\longrightarrow$ physics and chemistry through mathematics

Simple systems

1D rectangular potential:

-
$$V = \begin{cases} 0 & \text{for } 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

- Solve

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) = E\,\Psi(x)$$

  with boundary conditions $\Psi(0) = \Psi(L) = 0$

- Unique solution:

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\,\pi x}{L}$$

  with prefactor to respect $\int_0^L |\Psi_n(x)|^2\,dx = 1$.

- Energy $E_n = \langle\,\Psi_n\,|\,\hat{H}\,|\,\Psi_n\,\rangle = \int_0^L \Psi_n(x)\hat{H}\Psi_n(x)\,dx = \dfrac{n^2 h^2}{8mL^2}$

- Applications: dyes, acid-base indicators, nano-structured lasers

Simple systems

Harmonic oscillator:

- Potential: $V(r) = \frac{1}{2}kx^2$ from Hooke's law $F(x - x_0) = -k(x - x_0)$

- Solve

$$\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 \right) \Psi(x) = E\,\Psi(x)$$
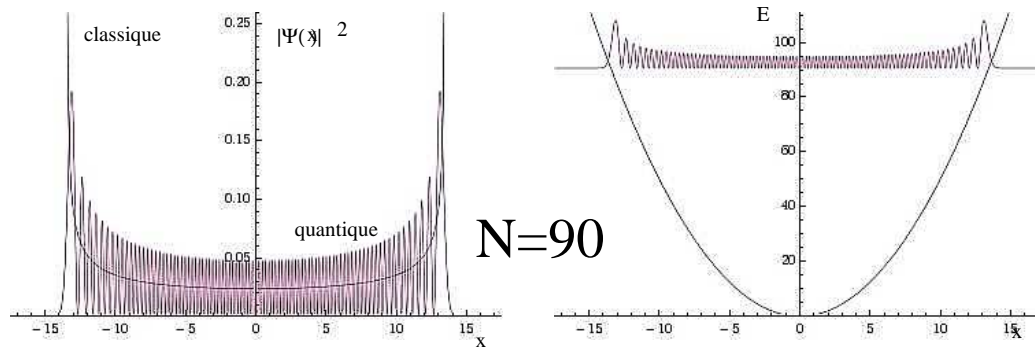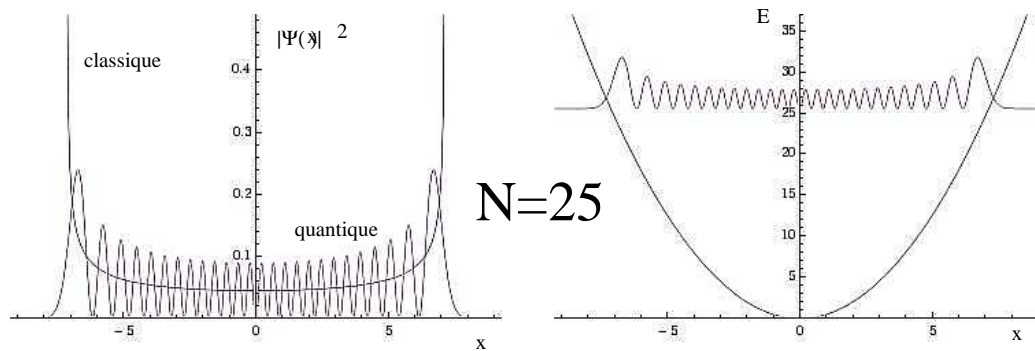
  with reduced mass μ

- Solution in two steps ($\alpha = \sqrt{\mu\omega/\hbar}$, $\omega = \sqrt{k/\mu}$):

  - $x \to \infty$: $\Psi(x) \sim e^{-\frac{(\alpha x)^2}{2}}$

  - Correction as polynomial in x:

$$\Psi_n(x) = \sqrt{\frac{\alpha}{\sqrt{\pi}}}\left(\frac{1}{\sqrt{2^n n!}} \right) H_n(\alpha x)\, e^{-\frac{(\alpha x)^2}{2}}$$

- Energy levels $E_n = \hbar\omega\left(n + \frac{1}{2} \right)$

- Application: vibrational spectroscopy (IR, RAMAN)

Simple systems

Harmonic oscillator:
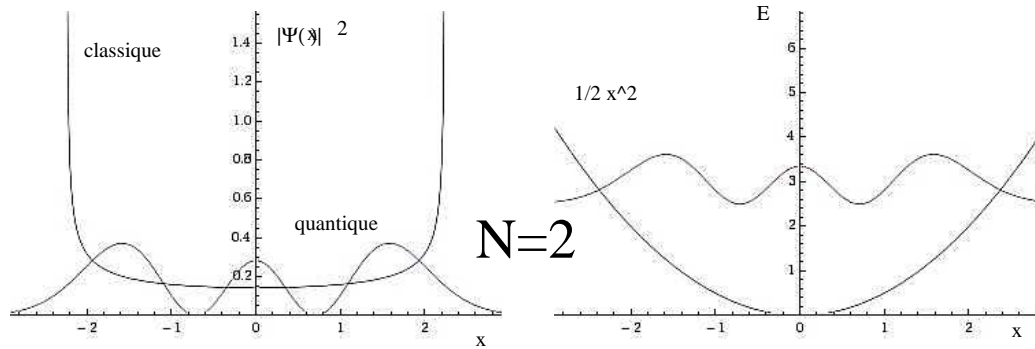
Simple systems

Hydrogen atom:

- Potential: $V(r) = -1/r$ spherically symmetric

- Spherical harmonics $Y_{\ell m}(\theta, \phi)$ solution of

  $$\hat{\vec{L}}^2 \, Y_{\ell m}(\theta, \phi) = \hbar^2 \ell(\ell+1) \, Y_{\ell m}(\theta, \phi)$$

- Laplacian in spherical co-ordinates $\Delta = \frac{1}{r^2} \frac{\partial}{\partial r}(r^2 \frac{\partial}{\partial r}) + \frac{L^2}{r^2}$

- Hamiltonian in spherical co-ordinates:

  $\hat{H} = -\frac{1}{2}\Delta - \frac{1}{r} = \frac{1}{r^2} \frac{\partial}{\partial r}(r^2 \frac{\partial}{\partial r}) + \frac{L^2}{2r^2} - \frac{1}{r}$

- Look for solution for the radial part (1D differential equation), in three steps $\rho = r/n$:

  - $r \to \infty$: $\rho \, R(\rho) \sim e^{-\rho}$; $\ r \to 0$: $\rho \, R(\rho) \sim \rho^{\ell+1} e^{-\rho}$

  - Complete solution $R_{n\ell}(\rho) = N_{n\ell} L_{n+\ell}^{2\ell+1}(\rho)\rho^\ell e^{-\rho}$ with associated Laguerre polynomials $L_{n+\ell}^{2\ell+1}(\rho)$.

  - Energy: $E = -\frac{1}{2}\frac{1}{n^2}$ as in the simple Bohr model.

Degeneracy n^2 via $\ell = 0, \ldots, n-1$ and $m = -\ell, \ldots, \ell$ values of secondary and magnetic quantum numbers.

Simple systems

Hydrogen atom: Laguerre polynomials

$$L_n^\alpha(x) = \frac{x^{-\alpha}}{n!} e^x \frac{d}{dx} \left[e^{-x} x^{n+\alpha} \right]$$
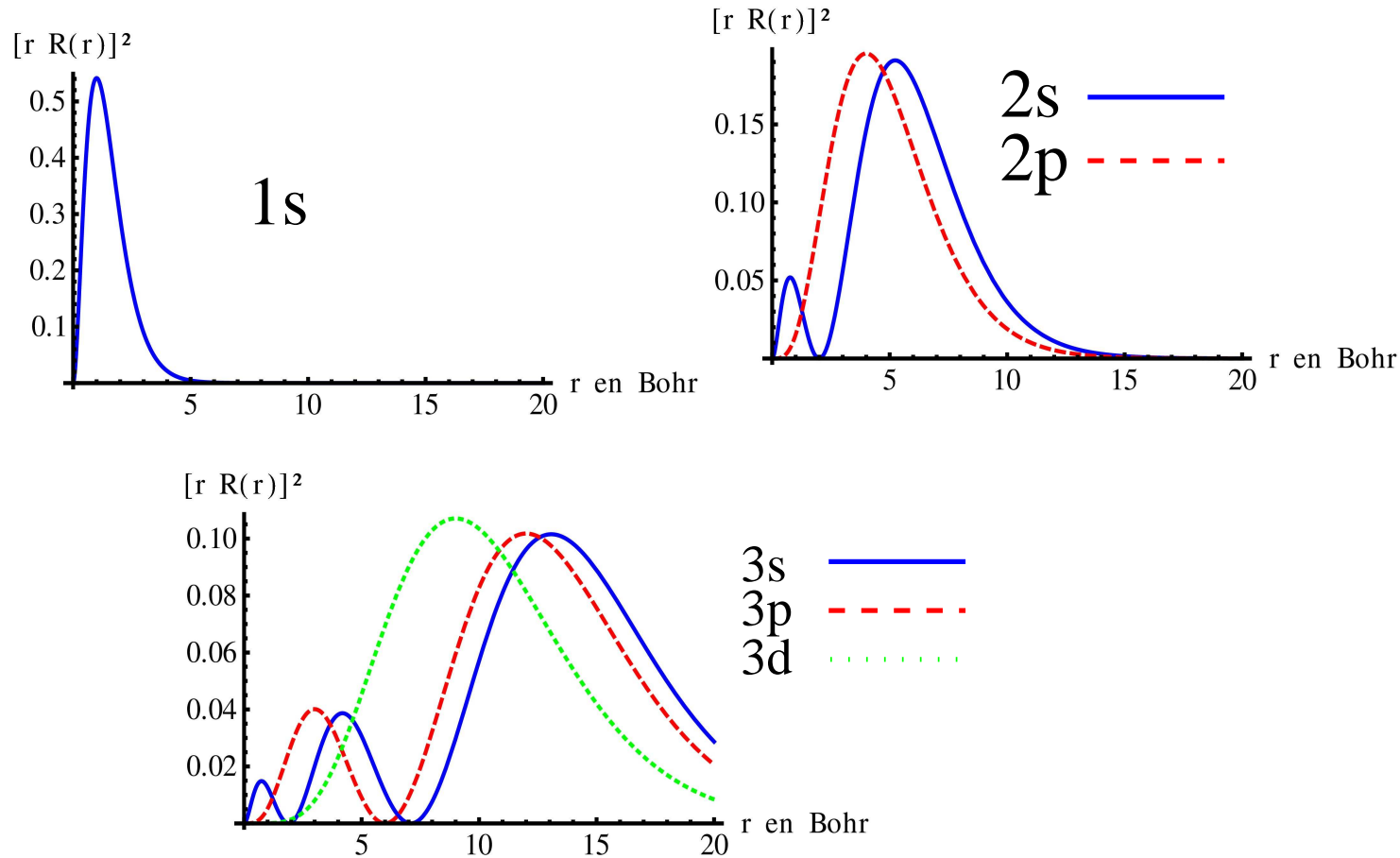
Hydrogenic functions

$$\Psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) \, Y_{\ell m}(\theta, \phi)$$

$$R_{n\ell}(r) = N_{nl} \left(\frac{2r}{n} \right)^\ell L_{n-\ell-1}^{2\ell+1} \left(\frac{2r}{n} \right) e^{-(r/n)}$$

- Classification: $\ell = 0 \to s$, $\ell = 1 \to p$, $\ell = 2 \to d$, $\ell = 3 \to f$
- Spherical harmonics $Y_{\ell m}$ complex, real combinations, multiplied with $r^\ell =$ real solid harmonics $= Y_{\ell m} + Y_{\ell - m}$, $-i(Y_{\ell m} - Y_{\ell - m})$
- $1, x, x, y, z, xy, xz, yz, x^2 - y^2, 3z^2 - r^2, ...$
- Energy levels depend only on n: $E_n = -\frac{1}{2} \frac{1}{n^2}$
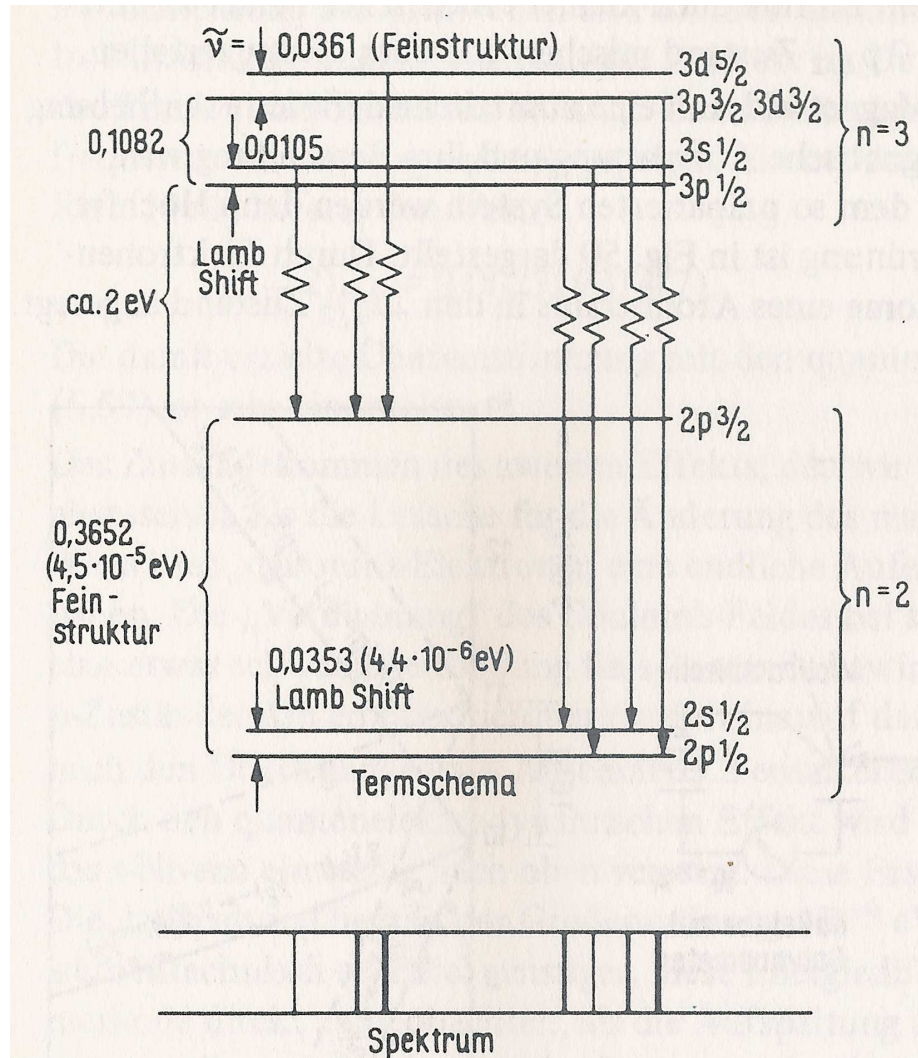
Simple systems

Hydrogen atom: radial densities $r^2 R^2(r)$

Simple systems

Complete treatment

Spin−Orbit coupling: fine structure

Relativistic effects: LS −> J

Quantum electrodynamimcs: Lamb shift

Hyperfine structure (spin−spin coupling)

Th. Mayer−Kuckuk, Atomphysik
Teubner, 1986

Small corrections, but all visible and understood for the hydrogen atom.

Working with atomic orbitals

- Multi-electron system (atom) may be described by hydrogen-like orbitals
- Diatomics: combine atomic orbitals of same symmetry and near energy to molecular orbitals with simple rules: correlation diagrams

|C=C| |N≡N| ⟨O=O⟩
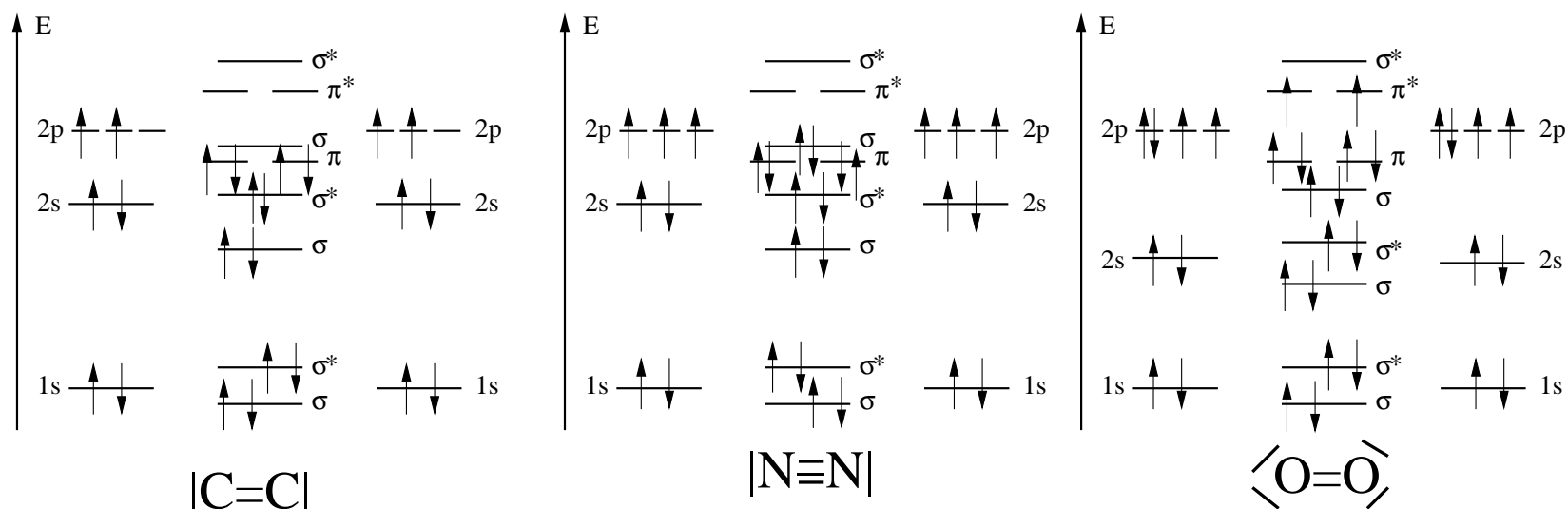
- Bonding, anti-bonding and non-bondig orbitals, stability of diatomics
- Spin ground states, reactivity

Working with atomic orbitals

Works even for solids, TiO_2

OM octaèdre TiO_6

Structure de bandes attendues
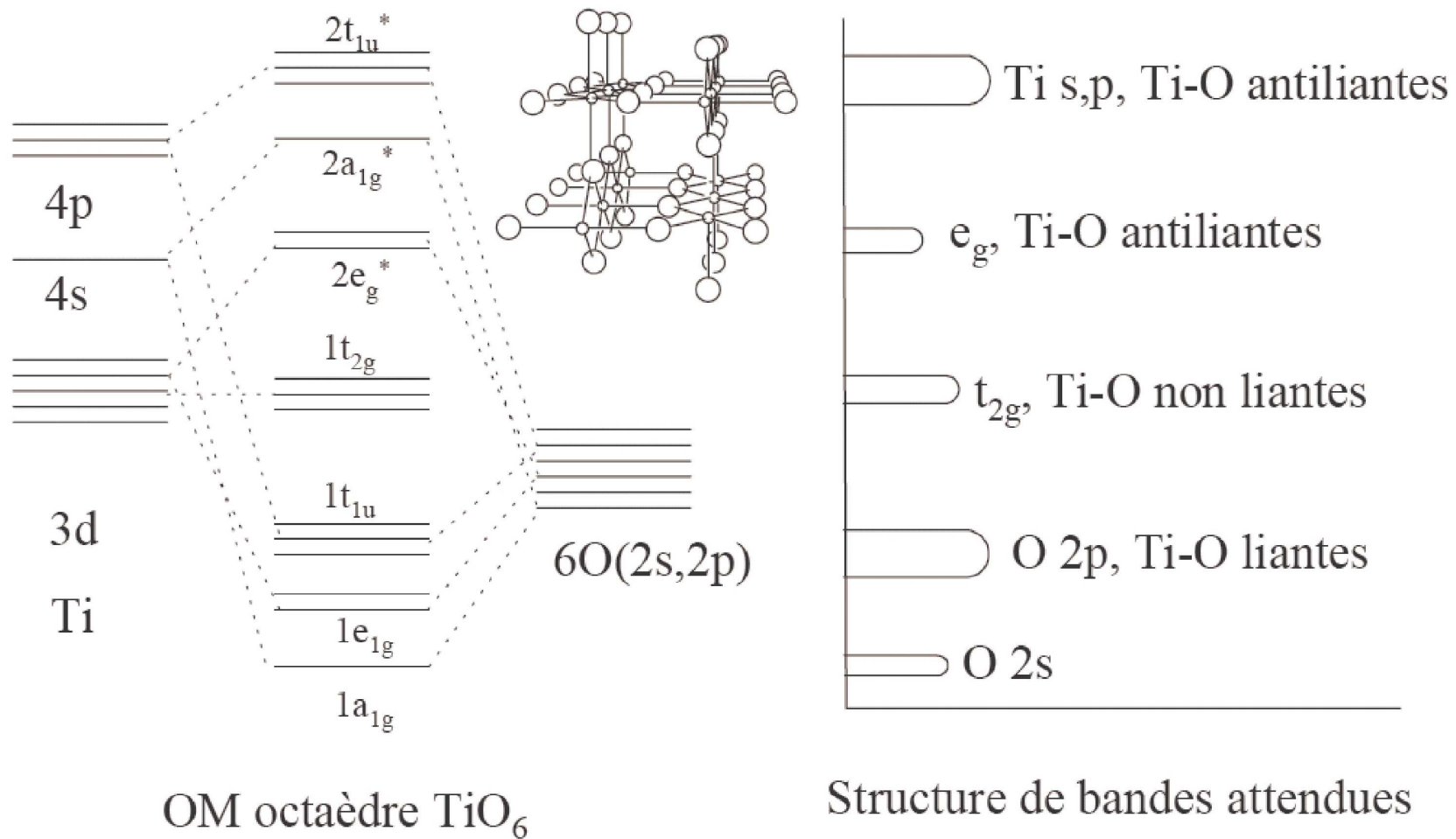
Diagram: Monica Calatayud, LCT, after R. Hoffmann, Solids and surfaces, Wiley-VCH, 1989

Working with atomic orbitals

More than 2 centers: hybridization of atomic orbitals
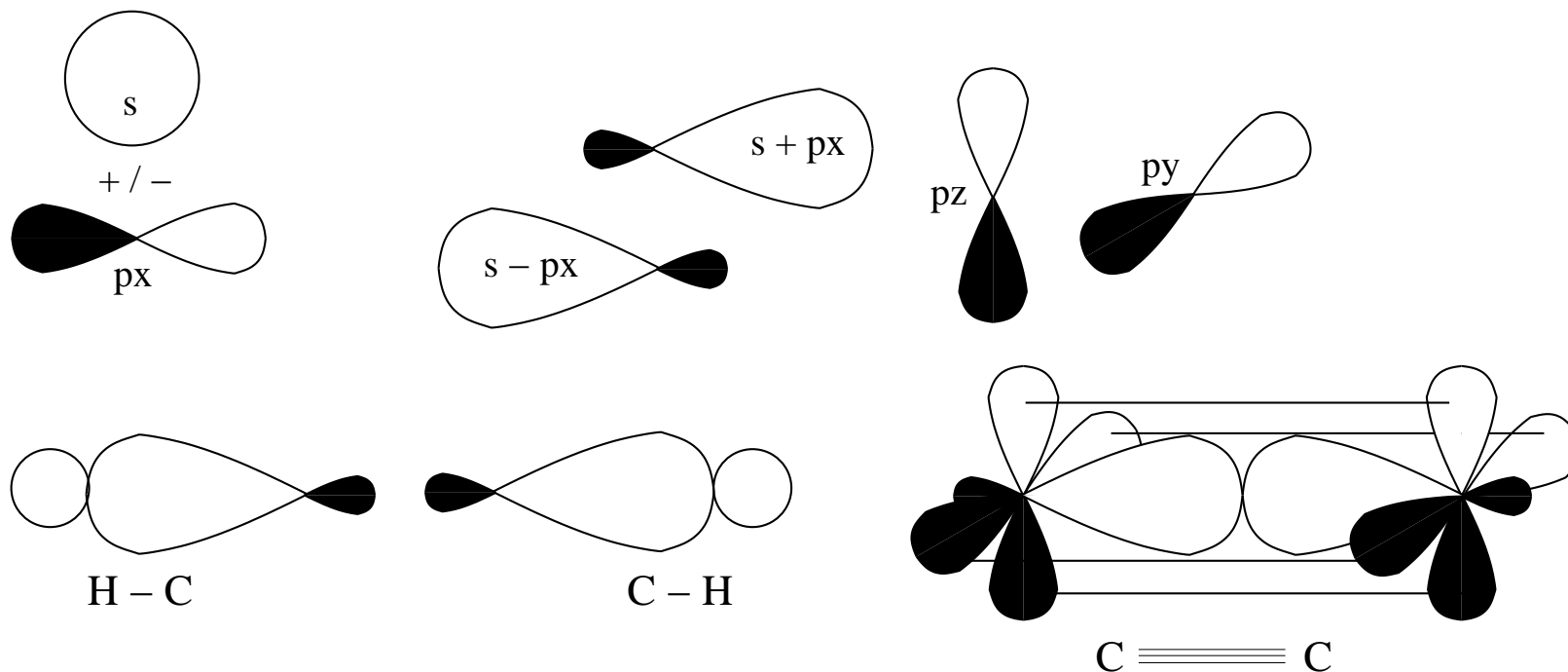
Series sp, sp^2, sp^3 for describing H–C≡C–H, H_2C=CH_2, H_3C—CH_3

$$\phi_{1,2}^{sp} = s \pm p_z \qquad \text{sp hybrid}$$

$$\phi_3 = p_x$$

$$\phi_4 = p_y$$

Working with atomic orbitals

Triangular situation: sp^2 hybrids

$$\phi_1^{sp^2} = \frac{1}{\sqrt{6}}\,s + \sqrt{\frac{2}{3}}\,p_x \qquad \text{sp}^2 \text{ hybrid}$$

$$\phi_{2,3}^{sp^2} = \frac{1}{\sqrt{3}}\,s - \frac{1}{\sqrt{6}}\,p_x \pm \frac{1}{\sqrt{2}}\,p_y \qquad \text{sp}^2 \text{ hybrid}$$

$$\phi_4 = p_z$$

Tetrahedral situation (4 bonds)

$$\phi_{1,2} = \frac{1}{2}\left(s + p_x \pm p_y \pm p_z\right)$$

$$\phi_{3,4} = \frac{1}{2}\left(s - p_x \pm p_y \mp p_z\right)$$

Very idealized situations — qualitatively correct, intuitive chemistry

Working with atomic orbitals

Bond lengths may as well be explained with sp^3 hybrids only

Fig. 109. Double bonds as bent sigma bonds.
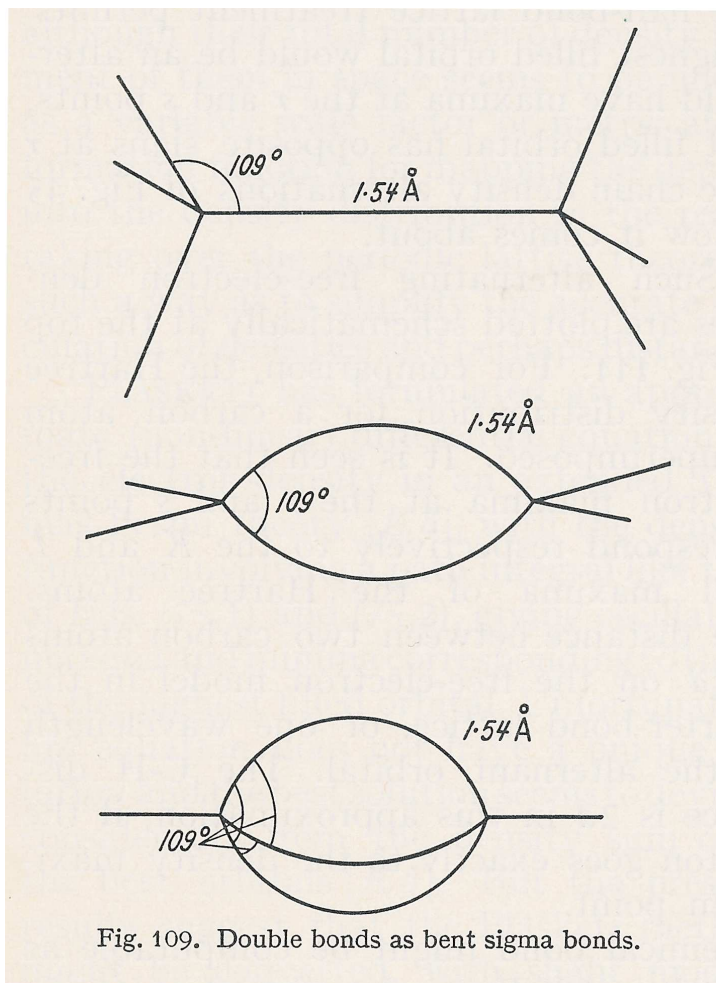
Single bond 154 pm

Double bond 133 pm

Triple bond 121 pm

H.J. Bernstein, J.Chem.Phys., **15** (1947) 284, 339, 688

The variational principle

Theorem: any approximate (normalized) wavefunction for the ground state of the Hamiltonian $\hat{H}$ is higher in energy than the true ground state Ψ_0 :

$$\langle \Psi_{approx} | \hat{H} | \Psi_{approx} \rangle \geq \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E_0$$

with $\hat{H} | \Psi_0 \rangle = E_0 | \Psi_0 \rangle$

Proof: $\hat{H}$ is hermitian, thus

- the eigenvalues of $\hat{H}$ are real.

- the eigenvectors of $\hat{H}$ are orthogonal.

- any approximate wavefunction can be expressed in the eigenfunctions of $\hat{H}$

$$
\begin{aligned}
E_{approx} &= \langle \Psi_{approx} | \hat{H} | \Psi_{approx} \rangle \\
&= \sum_i c_i^2 \langle \Phi_i | \hat{H} | \Phi_i \rangle = \sum_i c_i^2 E_i \geq E_0 \sum_i c_i^2 = E_0
\end{aligned}
$$

Hückel theory

Ernst Hückel, 1930: admit a simple

- product wavefunction $\Psi = \phi_1(1)\phi_2(2)\ldots\phi_n(n)$ and an

- one-electron Hamiltonian $\hat{H} = \hat{h}_1 + \hat{h}_2 + \ldots \hat{h}_n$ acting on electrons $1\ldots n$.

If

$$\hat{h}\,\phi_i(\vec{r}) = \epsilon_i\,\phi_i(\vec{r})$$

then

$$\hat{H}\,|\Psi\rangle = \left(\sum_i \hat{h}_i\right)|\Psi\rangle = \left(\sum_i \epsilon_i\right)|\Psi\rangle = E\,|\Psi\rangle$$

satisfying Schrödinger's equation.

- Valence atomic orbitals χ (or only π system) for each atom

- On-site interaction $\langle\chi_\alpha|\hat{h}|\chi_\alpha\rangle = a < 0$

- Next-neighbour interaction $\langle\chi_\alpha|\hat{h}|\chi_\beta\rangle = b < 0$

- Parametrized matrix elements

Hückel theory

Example butadiene CH_2=CH–CH=CH_2:

$$\hat{H} = \begin{pmatrix} a & b & 0 & 0 \\ b & a & b & 0 \\ 0 & b & a & b \\ 0 & 0 & b & a \end{pmatrix}$$

- 4 eigenvalues $\frac{1}{2}\left(2a \pm b \pm \sqrt{5}b\right)$

- Corresponding eigenvectors: $+ + + +, + + - -, + - - +, + - + -$

- $4\,\pi$ electrons to be inserted into the two lowest orbitals

a + 1.62 b   a + 0.62 b   a − 0.62 b   a − 1.62 b
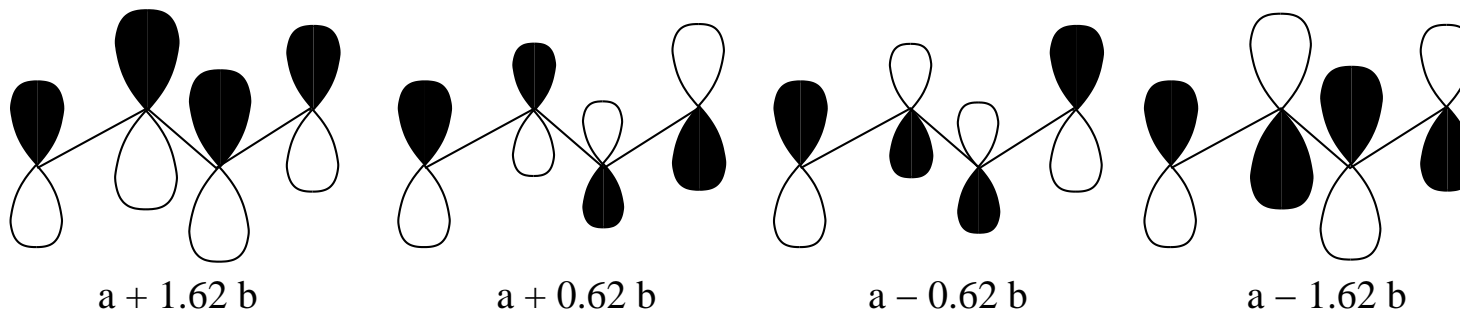
Hückel theory

Example cyclo-butadiene -CH=CH–CH=CH-:

$$\hat{H} = \begin{pmatrix} a & b & 0 & b \\ b & a & b & 0 \\ 0 & b & a & b \\ b & 0 & b & a \end{pmatrix}$$

- 3 different eigenvalues $a - 2b$, a, a, $a + 2b$
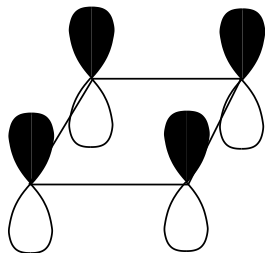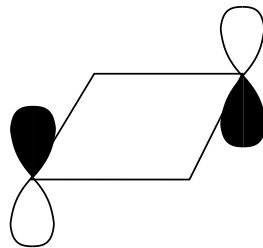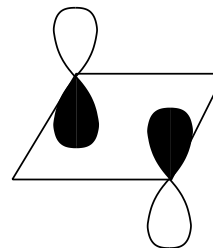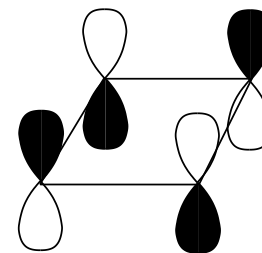
| $a + 2b$ | a | a | $a - 2b$ |

- Where to put the 4 electrons ? Unstable molecule.
- $4n + 2$ rule for cyclic hydrocarbons.

Many-electron wavefunctions

Many-electron systems: atomic Hamiltonian

$$\hat{H} = -\frac{1}{2}\left(\sum_{i=1}^{n}\Delta_i\right) - Z\left(\sum_{i=1}^{n}\frac{1}{r_i}\right) + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Wavefunction contains as well spin $\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n, s_1, s_2, \ldots, s_n)$

- Should be antisymmetric

$$\Psi((\vec{r}_1, s_1), (\vec{r}_2, s_2), \ldots) = -\Psi((\vec{r}_2, s_2), (\vec{r}_1, s_1), \ldots)$$

- Electron density

$$\rho(\vec{r}) = n \underbrace{\int \ldots \int}_{3n-3 \text{ integrals}} |\Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_n)|^2 \, d^3r_2 \ldots d^3r_n$$

Many-electron wavefunctions

Case of 2 electrons, same spatial orbital ϕ, different spins:

$$
\begin{aligned}
\Psi(\vec{r}_1, s_1, \vec{r}_2, s_2) &= \phi(\vec{r}_1)\phi(\vec{r}_2) \frac{1}{\sqrt{2}} \left[\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1) \right] \\
&= \Phi_S(\vec{r}_1, \vec{r}_2) \times \Theta_A(s_1, s_2)
\end{aligned}
$$

Energy depends only on the spatial part

$$
\langle \Phi_S \Theta_A | \hat{H} | \Phi_S \Theta_A \rangle = \langle \Phi_S | \hat{H} | \Phi_S \rangle \times \langle \Theta_A | \Theta_A \rangle = \langle \Phi_S | \hat{H} | \Phi_S \rangle
$$

Many-electron wavefunctions

Two different orbitals, two different spins

$$\Psi^I(\vec{r}_1, s_1, \vec{r}_2, s_2) = \Phi_S(\vec{r}_1, \vec{r}_2) \times \Theta_A(s_1, s_2)$$
$$= [\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)] \, [\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)] \, /2$$

Other possibility

$$\Psi^{II}(\vec{r}_1, s_1, \vec{r}_2, s_2) = [\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)] \, \alpha(s_1)\alpha(s_2)$$
$$= \Phi_A(\vec{r}_1, \vec{r}_2) \times \Theta_S(s_1, s_2)$$

3 possibilities for symmetric spin parts

$$\alpha(s_1)\alpha(s_2) \qquad \frac{1}{\sqrt{2}}(\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)) \qquad \beta(s_1)\beta(s_2)$$

Conclusion: one singlet wavefunction, 3 triplet wavefunctions, different in energy, even with equal orbitals.

Many-electron wavefunctions

General case with more than 2 electron: Slater determinant (J.C. Slater 1929)

$$\Psi(\vec{r}_1 \ldots, \vec{r}_n, s_1 \ldots s_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\vec{r}_1)\sigma_1(s_1) & \ldots & \phi_1(\vec{r}_n)\sigma_1(s_n) \\ \vdots & \ddots & \vdots \\ \phi_n(\vec{r}_1)\sigma_n(s_1) & \ldots & \phi_n(\vec{r}_n)\sigma_n(s_n) \end{vmatrix}$$

Completely antisymmetric upon exchange of electrons

Many-electron wavefunctions

General case with more than 2 electron: Slater determinant (J.C. Slater 1929)

$$\Psi(\vec{r}_1 \ldots, \vec{r}_n, s_1 \ldots s_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\vec{r}_1)\sigma_1(s_1) & \ldots & \phi_1(\vec{r}_n)\sigma_1(s_n) \\ \vdots & \ddots & \vdots \\ \phi_n(\vec{r}_1)\sigma_n(s_1) & \ldots & \phi_n(\vec{r}_n)\sigma_n(s_n) \end{vmatrix}$$

Completely antisymmetric upon exchange of electrons
The triplet wavefunctions (un-normalized)

$$\begin{aligned} \Psi_{\alpha\alpha}^{II} &= [\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)] \left(\alpha(1)\alpha(2) + \alpha(1)\alpha(2)\right) \\ &= \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(2)\alpha(2) \\ \phi_2(1)\alpha(1) & \phi_2(2)\alpha(2) \end{vmatrix} = |\phi_1\phi_2\rangle \\ \Psi_{\beta\beta}^{II} &= \begin{vmatrix} \phi_1(1)\beta(1) & \phi_1(2)\beta(2) \\ \phi_2(1)\beta(1) & \phi_2(2)\beta(2) \end{vmatrix} = |\bar{\phi}_1\bar{\phi}_2\rangle \end{aligned}$$

Many-electron wavefunctions

However:

$$\Psi^{II}_{\alpha\beta} = \phi_1\bar{\phi}_2 + \bar{\phi}_1\phi_2 - \phi_2\bar{\phi}_1 - \bar{\phi}_2\phi_1$$

$$= \begin{vmatrix} \phi_1(1) & \phi_1(2) \\ \bar{\phi}_2(1) & \bar{\phi}_2(2) \end{vmatrix} + \begin{vmatrix} \bar{\phi}_1(1) & \bar{\phi}_1(2) \\ \phi_2(1) & \phi_2(2) \end{vmatrix} = |\phi_1\bar{\phi}_2\rangle + |\bar{\phi}_1\phi_2\rangle$$

$$\Psi^{I}_{\alpha\beta} = \phi_1\bar{\phi}_2 - \bar{\phi}_1\phi_2 + \phi_2\bar{\phi}_1 - \bar{\phi}_2\phi_1$$

$$= \begin{vmatrix} \phi_1(1) & \phi_1(2) \\ \bar{\phi}_2(1) & \bar{\phi}_2(2) \end{vmatrix} - \begin{vmatrix} \bar{\phi}_1(1) & \bar{\phi}_1(2) \\ \phi_2(1) & \phi_2(2) \end{vmatrix} = |\phi_1\bar{\phi}_2\rangle - |\bar{\phi}_1\phi_2\rangle$$

Two determinants necessary
Single-determinant situations:

- Closed-shell systems (for every occupied ϕ there is an occupied $\bar{\phi}$)
- High-spin systems (singly occupied orbitals have all the same spin)
- Combinations of both: $|1\bar{1}2\bar{2}\ldots5\bar{5}\,6\,8\,7\,9\rangle$

Calculate with Slater determinants

"Problem": how to calculate $\hat{H}\,\Psi$ or

$$\langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi|\hat{H}\Psi\rangle = \langle\hat{H}^\dagger\Psi|\Psi\rangle = \langle\hat{H}\Psi|\Psi\rangle$$

when Ψ is a Slaterdeterminant, 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

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

Calculate with Slater determinants

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

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

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

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

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

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

- 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 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

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

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

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

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:

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

- 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:

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

Hartree-Fock equations

Total energy for one single determinant (closed shell case):

$$
\begin{aligned}
E &= 2 \sum_{i \in occ.} h_{ii} + \sum_{i,j \in occ.} \left(2(ii|jj) - (ij|ij) \right) \\
&= \sum_{\alpha,\beta} P_{\alpha\beta} h_{\alpha\beta} + \frac{1}{4} \sum_{\alpha,\beta} P_{\alpha\beta} \left(\sum_{\gamma,\delta} P_{\gamma\delta} \left(2(\alpha\beta|\gamma\delta) - (\alpha\delta|\gamma\beta) \right) \right)
\end{aligned}
$$

- Density matrix $P_{\alpha\beta} = 2 \sum_{i \in occ.} c_{\alpha i} \, c_{\beta i}$ in a (finite) basis $\phi_i(\vec{r}) = \sum_{\alpha} c_{\alpha i} \chi_{\alpha}(\vec{r})$.

- We have to derive E wrt the $c_{\alpha i}$ under the condition

$$
\delta_{ij} = \langle \phi_i | \phi_j \rangle = \sum_{\alpha\beta} c_{\alpha i} \, c_{\beta j} \, S_{\alpha\beta}
$$

$$
\frac{\partial}{\partial c_{\gamma i}} \sum_{\alpha\beta} P_{\alpha\beta} h_{\alpha\beta} = 4 \, c_{\gamma i} h_{\gamma\gamma} + 2 \sum_{\beta \neq \gamma} c_{\beta i} h_{\beta\gamma} + 2 \sum_{\beta \neq \gamma} c_{\beta i} h_{\gamma\beta} = 4 \sum_{\beta} c_{\beta i} h_{\gamma\beta}
$$

Hartree-Fock equations

Lagrange multipliers ϵ :

$$\mathcal{L} = E - 4 \sum_{ij} \epsilon_{ij} \left(\sum_{\alpha\beta} c_{\alpha i} c_{\beta j} S_{\alpha\beta} - \delta_{ij} \right)$$

leads to equations

$$
\begin{aligned}
0 &= \frac{\partial}{\partial c_{\alpha i}} \mathcal{L} \\
&= 4 \sum_{\beta} c_{\beta i} \underbrace{\left(h_{\alpha\beta} + \sum_{\gamma\delta} P_{\gamma\delta} \left(2(\alpha\beta|\gamma\delta) - (\alpha\delta|\gamma\beta) \right) \right)}_{\text{Fock matrix } F_{\alpha\beta}} - 4 \sum_{j} \sum_{\beta} \epsilon_{ij} c_{\beta j} S_{\alpha\beta}
\end{aligned}
$$

Hartree-Fock equations

In matrix form:

$$F\,C\ =\ S\,C\,\epsilon$$

or

$$F\,\phi_i\ =\ \sum_j \epsilon_{ij}\,\phi_j$$

beyond the limitations of a (finite) basis set to express molecular orbitals ϕ_i

- Self-consistent (F contains the occupied orbitals ϕ_i) eigenvalue problem
- Orbitals for lowest energy within single-determinant wavefunction
- Unitary rotations ($U^\dagger = U^{-1}$) within the occupied or the virtual orbital space do not change the energy of wavefunction.
- Transform orbitals for ϵ diagonal: canonical orbitals

$$F\,\phi_i\ =\ \epsilon_i\,\phi_i$$

- Brillouin's theorem: occupied and virtual orbital do not mix: $F_{ia} = 0$ for any set of Hartree-Fock orbitals (canonical or not).

Basis sets

Hydrogen atom: spans not all possible space of one-electron functions.

- Nodeless Slater functions

$$\phi_{n\ell m}^{\mathrm{STF}}(r, \theta, \varphi; \alpha) \;=\; Y_{\ell m}(\theta, \varphi) \times r^{n-1} \times e^{-\beta\, r} \qquad \ell \le n - 1$$

- Gaussian functions

$$\phi_{\ell m}^{\mathrm{GTF}}(r, \theta, \varphi; \alpha) \;=\; Y_{\ell m}(\theta, \varphi) \times r^{\ell} \times e^{-\alpha\, r^2}$$

Why Gaussians ? Try to calculate a four-center bielectronic integral

$$\int \int \frac{e^{-\alpha|\vec{r}_1 - \vec{R}_A|} e^{-\beta|\vec{r}_1 - \vec{R}_B|} e^{-\gamma|\vec{r}_2 - \vec{R}_C|} e^{-\delta|\vec{r}_2 - \vec{R}_D|}}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2$$

Possible with Gaussians due to product formula

$$e^{-a(\vec{r} - \vec{R}_A)^2} e^{-b(\vec{r} - \vec{R}_B)^2} = e^{-\frac{ab}{a+b}(\vec{R}_A - \vec{R}_B)^2} e^{-(a+b)(\vec{r} - \frac{a\vec{R}_A + b\vec{R}_B}{a+b})^2}$$

transforming a 4-center integral into a 2-center integral.

Basis sets

- Minimal basis sets: for each atomic occupied level a set of basis functions
  (H $1s$, C $1s2s2p$, Ti $1s2s2p3s3p3d4s$ etc.)

- Split-valence basis sets: multiple basis functions for each valence orbital
  (6-31G, double or triple ζ etc.)

- Even-tempered basis sets: Gaussian exponents obey geometrical law
  $\alpha_i = \alpha_0 \times \tau^i$

- add polarization functions of higher angular momentum

- add diffuse functions with small exponents for bond formation

- add correlation functions

- ... ... toward complete basis set.

Basis set libraries: `https://bse.pnl.gov/bse/portal` Basis Set
Exchange with ≈ 500 basis sets.

- Nearly every quantum chemistry program has its library

Basis set extrapolations

- Larger basis set = lower energy

- Hartree-Fock limit: still 1 determinant

- Systematic constructions ?

Example: He atom in series of basis sets aug-cc-pvXz, X=2..6

X	HF energy (a.u.)	correlated energy (Full CI, a.u.)	# basis functions
2	-2.855704	-2.88955	11
3	-2.861183	-2.90060	28
4	-2.861522	-2.90253	58
5	-2.861627	-2.90320	108
6	-2.861673	-2.90346	186

Extrapolation: empirically $E(X) = A + \frac{B}{X^3}$

$$E(\infty) = A = E(X) - \frac{Y^3}{X^3 - Y^3}\left(E(X) - E(Y)\right)$$

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Extrapolation

	A	B
HF	-2.86228	0.0509344
Full CI	-2.90431	0.1168

What do we have already: Hartree-Fock

<p style="text-align:center">Closed-shell systems</p>

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 already: Hartree-Fock

<p style="text-align:center">Closed-shell systems</p>

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- Total energy $\longrightarrow$ 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 continously into two separated open-shell systems

- Only high-spin states possible, no open-shell singlet for instance

Bond dissociation

Calculation for H_2 in a minimal basis for different bond lengths

$$\sigma = s_A + s_B \qquad\qquad \sigma^* = s_A - s_B$$
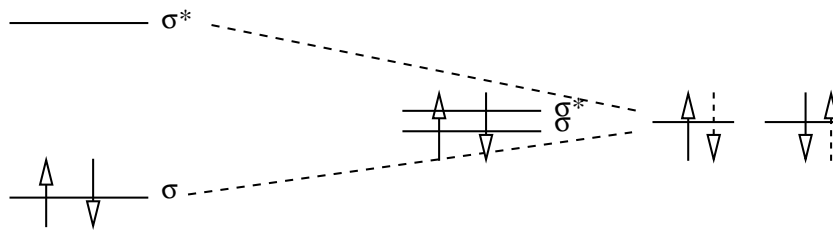
- Equilibrium distance:
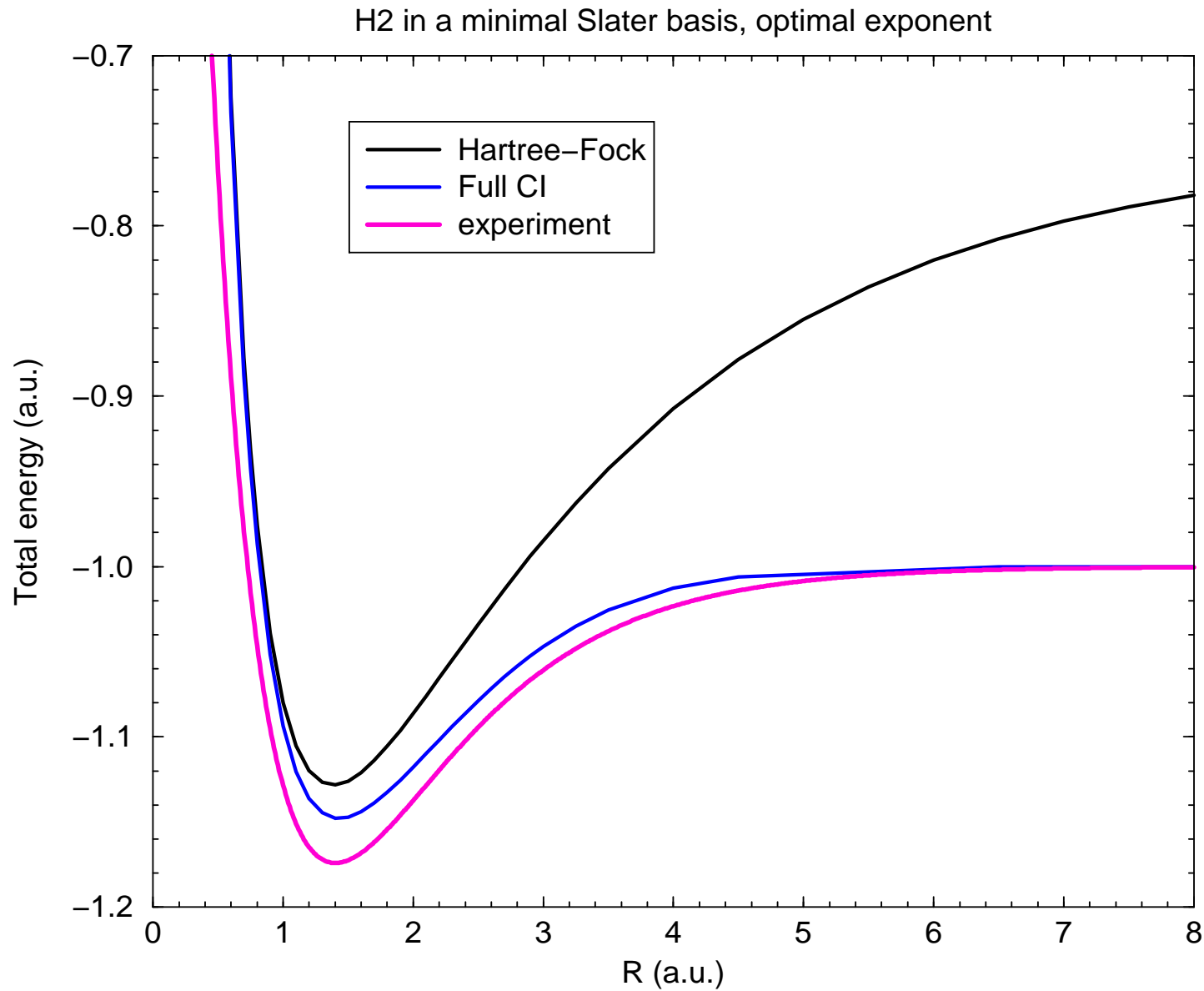 - Hartree-Fock $|\Phi_0\rangle = |\sigma\bar{\sigma}\rangle$
  - 2-determinant wavefunction: $|\Psi\rangle = \sqrt{1-\epsilon^2}|\sigma\bar{\sigma}\rangle + \epsilon|\sigma^*\bar{\sigma}^*\rangle$

Long distance:

$$|\Psi\rangle = a|\sigma\bar{\sigma}\rangle + b|\sigma^*\bar{\sigma}^*\rangle \text{ with } |a| \approx |b| \approx 1/\sqrt{2}$$

in order to have $|s_A\bar{s}_B\rangle + |s_B\bar{s}_A\rangle$ without the ionic configurations $|s_A\bar{s}_A\rangle$ and $|s_B\bar{s}_B\rangle$

Bond dissociation

H2 in a minimal Slater basis, optimal exponent

Bond dissociation

Hartree-Fock:

$$|\Psi\rangle = \begin{vmatrix} \sigma(1) & \sigma(2) \\ \bar{\sigma}(1) & \bar{\sigma}(2) \end{vmatrix} = \begin{vmatrix} (s_A + s_B)(1) & (s_A + s_B)(2) \\ (\bar{s}_A + \bar{s}_B)(1) & (\bar{s}_A + \bar{s}_B)(2) \end{vmatrix}$$

$$= |s_A \bar{s}_A\rangle + |s_B \bar{s}_B\rangle + |s_A \bar{s}_B\rangle + |s_B \bar{s}_A\rangle$$

Two regimes of deviation from experiment:

- $R \approx R_{eq}$: small, but significant contribution, dynamical electron correlation
- $R \to \infty$: $c_0 = c_1$, nondynamical electron correlation
- Electron correlation = insufficiency of "1 electron = 1 orbital"

Definition of the correlation energy

$$E_{Corr} = E - E_{HF}$$

Two common approaches to dynamical correlation:

1. Perturbation theory
2. Configuration Interaction

Electron Correlation

Treat it in a mixed order:

- Configuration Interaction

- MCSCF and bond breaking

- Dynamical correlation

  - Configuration Interaction of Single and Double excitations

  - Perturbation theory

  - Coupled-Cluster Theory

Configuration interaction

- Add additional determinants

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

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

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

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

- 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:

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

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

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

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

- Intermediate norm: $c_0 = 1$:

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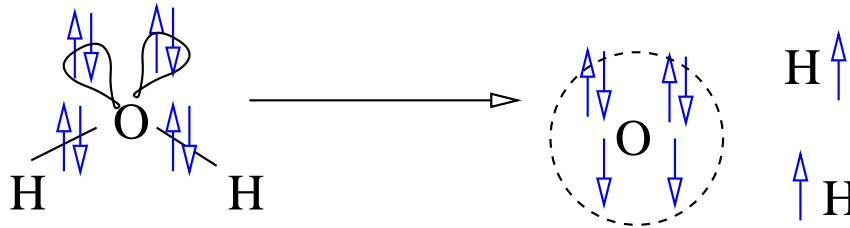$$

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

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

MCSCF: general considerations

Few electrons in a few orbitals to consider

- H_2O: 4 electrons in 4 orbitals to start with

- Better: 8 electrons in 6 orbitals (s on H, $2sp$ on O)
- Full CI in this subspace

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Other example:

- Triple bond in N_2: 6 electrons of the 14 possible in 6 atomic $2p$ orbitals

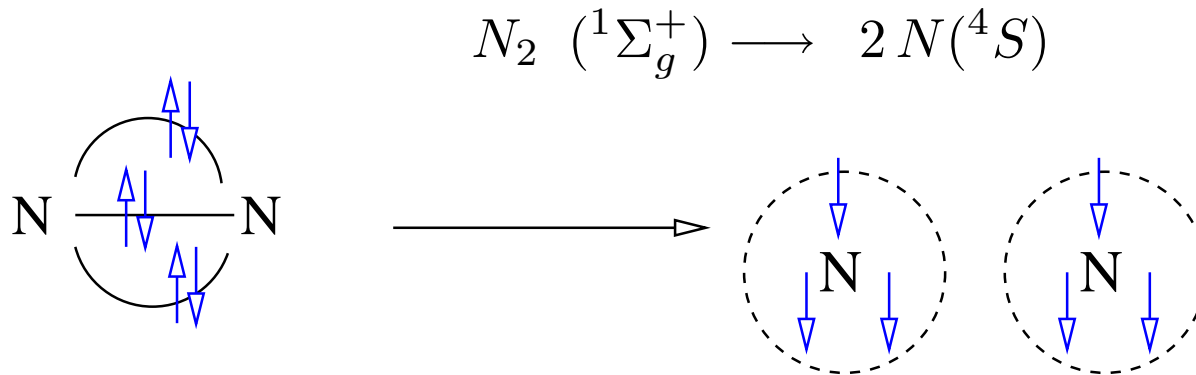$$N_2 \ (^1\Sigma_g^+) \longrightarrow \ 2\,N(^4S)$$

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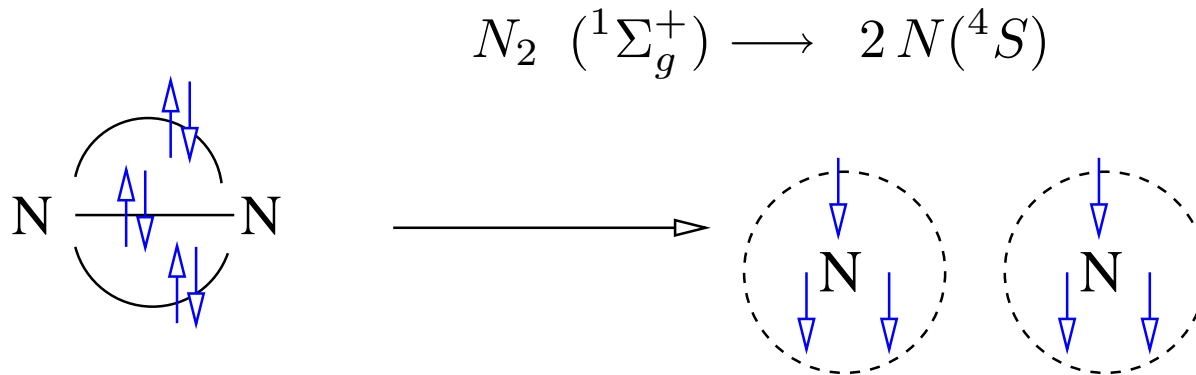- Triple bond in N_2: 6 electrons of the 14 possible in 6 atomic $2p$ orbitals

$$N_2 \ (^1\Sigma_g^+) \longrightarrow \ 2\,N(^4S)$$

Need for multiconfigurational wavefunctions

Non-dynamical correlation

General considerations

2 ingredients needed:

- Where to look for orbitals?

- Which determinants to take?

Hartree-Fock orbitals optimized for one single determinant.

- Average over different occupations?

- But how to treat open-shell determinants? No spin eigenfunctions!

Simultaneous optimization of orbitals and wavefunctions:

Multiconfigurational Self-Consistent Field (M C S C F)

Super-CI method

Alternative to the diagonalization of the Fock matrix

1. Starting orbitals

2. Orthonormalize the orbitals

3. Construct Fock matrix, calculate total energy

4. Construct CI matrix of single excitations

$$\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle \approx F_{ab}\delta_{ij} - F_{ij}\delta_{ab}$$

5. Use the CI coefficients of

$$|\Psi\rangle = |\Phi_0\rangle + \frac{1}{\sqrt{2}} \sum_{ia} c_i^a \left(|\Phi_i^a\rangle + |\Phi_{\bar{i}}^{\bar{a}}\rangle \right)$$

to correct the orbitals (occupied and virtual ones) through

$$\phi_i' = \phi_i + \sum_a c_i^a \phi_a \; ; \qquad \phi_a' = \phi_a - \sum_i c_i^a \phi_i$$

6. Go to step 2

Super-CI method

If canonical orbitals are required, then diagonalize once the converged Fock matrix

- Orbitals change through mono-excitations
- Excitation operator

$$
\begin{aligned}
\hat{E}_{ia} &= \frac{1}{\sqrt{2}} \left(\hat{a}^{\dagger}_{a,\alpha} \hat{a}_{i,\alpha} + \hat{a}^{\dagger}_{a,\beta} \hat{a}_{i,\beta} \right) \\
\hat{E}_{ia} \left| \Phi_0 \right\rangle &= \frac{1}{\sqrt{2}} \left(\left| \Phi_i^a \right\rangle + \left| \Phi_{\bar{i}}^{\bar{a}} \right\rangle \right) \\
\left| \Psi \right\rangle &= \left(1 + \sum_{ia} c_i^a \, \hat{E}_{ia} \right) \left| \Phi_0 \right\rangle
\end{aligned}
$$

- Convergence achieved if Brillouin's theorem is satisfied

$$
\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = F_{ia} \longrightarrow 0
$$

or total energy changes smaller than a given threshold

Super-CI method

If canonical orbitals are required, then diagonalize once the converged Fock matrix

- Orbitals change through mono-excitations
- Excitation operator
  - Creation/destruction operators obey anti-commutator rules:
    - Creation operators $\hat{a}_i^\dagger$, destruction operators $\hat{a}_i$
    - Definition for an antisymmetric wavefunction:

$$\hat{a}_i |n_1 \ldots n_i \ldots\rangle = (-1)^{\sum_{k<i} n_k} n_i |n_1 \ldots 0_i \ldots\rangle = \theta_i\, n_i\, |n_1 \ldots 0_i \ldots\rangle$$
$$\hat{a}_i^\dagger |n_1 \ldots n_i \ldots\rangle = \theta_i\, (1 - n_i)\, |n_1 \ldots 1_i \ldots\rangle$$

  - Wavefunction is antisymmetric: the order of creation is important
  - $\hat{a}_i^\dagger \hat{a}_j^\dagger = -\hat{a}_j^\dagger \hat{a}_i^\dagger$, or $\hat{a}_i^\dagger \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i^\dagger = 0$
  - the same holds for the destruction operators: $\hat{a}_i \hat{a}_j = -\hat{a}_j \hat{a}_i$
  - We may destroy an existing particle or hole and recreate it, or create a non-existing particle or hole and destroy it: $\hat{a}_i^\dagger \hat{a}_i + \hat{a}_i \hat{a}_i^\dagger = 1$

$$\hat{E}_{ia} = \frac{1}{\ } \left(\hat{a}_{a,\alpha}^\dagger \hat{a}_{i,\alpha} + \hat{a}_{a,\beta}^\dagger \hat{a}_{i,\beta} \right)$$

Super-CI method

If canonical orbitals are required, then diagonalize once the converged Fock matrix

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\begin{aligned}
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\hat{E}_{ia} \left| \Phi_0 \right\rangle &= \frac{1}{\sqrt{2}} \left(\left| \Phi_i^a \right\rangle + \left| \Phi_{\bar{i}}^{\bar{a}} \right\rangle \right) \\
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\end{aligned}
$$

- Convergence achieved if Brillouin's theorem is satisfied

$$
\left\langle \Phi_0 \right| \hat{H} \left| \Phi_i^a \right\rangle = F_{ia} \longrightarrow 0
$$

or total energy changes smaller than a given threshold

Generalization

Matrix elements between determinants $|\Phi_m\rangle$ and $|\Phi_n\rangle$

- Monoelectronic operator $\hat{h}$:

$$\langle\,\Phi_m\,|\,\hat{h}\,|\,\Phi_n\,\rangle \;=\; \sum_{ij} h_{ij}\langle\,\Phi_m\,|\,\hat{E}_{ij}\,|\,\Phi_n\,\rangle$$

$$=\; \sum_{ij} h_{ij}\, D^{mn}_{ij}$$

- Bi-electronic operator $\hat{G}$:

$$\langle\,\Phi_m\,|\,\hat{G}\,|\,\Phi_n\,\rangle \;=\; \frac{1}{2}\sum_{ijkl} g_{ijkl}\langle\,\Phi_m\,|\,\hat{E}_{ij}\hat{E}_{kl} - \delta_{jk}\hat{E}_{il}\,|\,\Phi_n\,\rangle$$

$$=\; \sum_{ij} g_{ijkl}\, P^{mn}_{ijkl}$$

Generalization

$$|\Psi\rangle = |\Phi_0\rangle + \sum_n c_n |\Phi_n\rangle$$

- First-order density matrix (or 1-particle density matrix)

$$D_{ij} = \langle\,\Psi\,|\,\hat{E}_{ij}\,|\,\Psi\,\rangle = \sum_{mn} c_m^* c_n \, D_{ij}^{mn}$$

- Second-order density matrix (or 2-particle density matrix)

$$P_{ijkl} = \frac{1}{2}\langle\,\Psi\,|\,\hat{E}_{ij}\hat{E}_{kl} - \delta_{jk}\hat{E}_{il}\,|\,\Psi\,\rangle = \sum_{mn} c_m^* c_n \, P_{ijkl}^{mn}$$

Generalization

$$|\Psi\rangle = |\Phi_0\rangle + \sum_n c_n |\Phi_n\rangle$$

- First-order density matrix (or 1-particle density matrix)

$$D_{ij} = \langle \Psi | \hat{E}_{ij} | \Psi \rangle = \sum_{mn} c_m^* c_n D_{ij}^{mn}$$

- Second-order density matrix (or 2-particle density matrix)

$$P_{ijkl} = \frac{1}{2} \langle \Psi | \hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} | \Psi \rangle = \sum_{mn} c_m^* c_n P_{ijkl}^{mn}$$

- Total energy

$$E_{\text{tot}} = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{ij} h_{ij} D_{ij} + \sum_{ijkl} g_{ijkl} P_{ijkl}$$

- h_{ij} and g_{ijkl} depend only on the molecular orbitals
- D_{ij} and P_{ijkl} depend only on the wavefunction expansion coefficients c_n.

Density matrices

Hartree-Fock:

$$E_{HF} = 2 \sum_{i \in occ} h_{ii} + \sum_{ij \in occ} 2(ii|jj) - (ij|ji)$$

fits in the same expression as above with the density matrices

$$D_{ij} = \begin{cases} 2 & i = j; \ i \in occ. \\ 0 & \text{otherwise} \end{cases}$$

$$P_{ijkl} = \begin{cases} 2 & i = j, \ k = l, \ i \neq k; \ all \ \in \ occ. \\ 1 & i = j = k = l; \ i \in occ. \\ -1 & i = l, \ j = k, \ i \neq j; \ i, j \in occ. \\ 0 & \text{otherwise} \end{cases}$$

Only entries 0, 1, 2 or -1 in these matrices in the 1-determinant case.

$$E_{HF} = \sum_{ij \in all} D_{ij} \, h_{ij} + \sum_{ijkl \in all} P_{ijkl} \, (ij|kl)$$

Density matrices

- One-electron properties:

  Multipolar moments, electrostatic potentials as $\sum_{ij} D_{ij} \langle \phi_i | \hat{O} | \phi_j \rangle$

- Integrals of the operator in molecular orbitals

- Alternative: integrals and density matrix in atomic orbitals

$$F_{\alpha\beta} = h_{\alpha\beta} + \sum_{\gamma\delta} D_{\gamma\delta} \left[2(\alpha\beta|\gamma\delta) - (\alpha\delta|\gamma\beta) \right]$$

- Mulliken population analysis

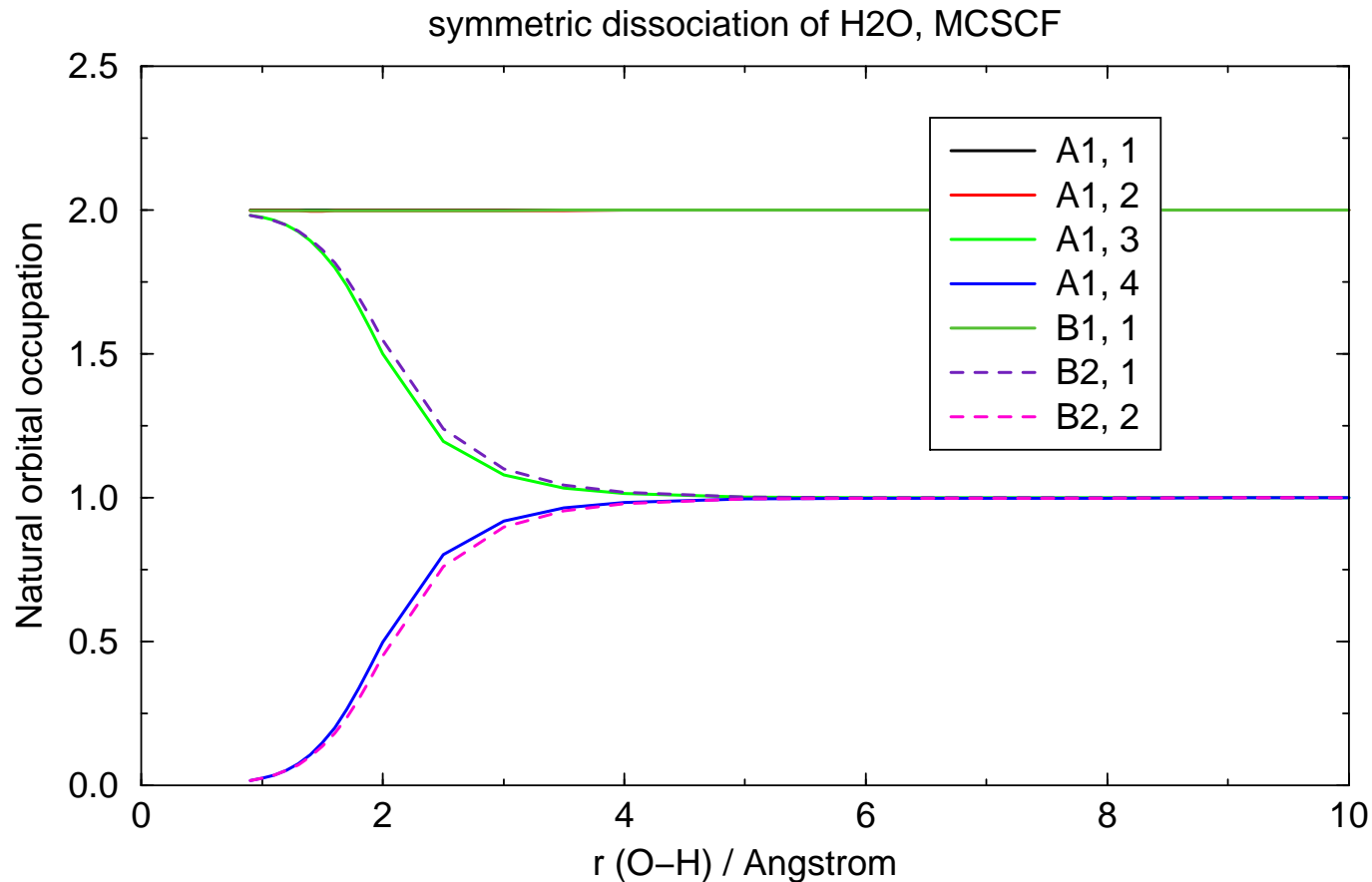$$N_A = \sum_{\alpha\beta \in A} D_{\alpha\beta} S_{\alpha\beta}$$

- Dipole moment

$$\vec{\mu} = \sum_{\alpha\beta} D_{\alpha\beta} \langle \chi_\alpha | \hat{\vec{r}} | \chi_\beta \rangle = \sum_{i \in occ} D_{ii} \langle \phi_i | \hat{\vec{r}} | \phi_i \rangle$$

Natural orbitals

We may diagonalize the multi-determinantal 1-particle matrix D_{ij}: orbitals with fractional occupation numbers.

- ≈ 2 electrons: closed shell

- ≈ 1 electron : singly occupied orbital

- ≈ 0 electrons: virtual orbitals

symmetric dissociation of H2O, MCSCF

Legend:
- A1, 1
- A1, 2
- A1, 3
- A1, 4
- B1, 1
- B2, 1
- B2, 2

x-axis: r (O–H) / Angstrom
y-axis: Natural orbital occupation

Remains to work

Derivatives of the total energy with respect to orbitals and CI coefficients:

- Derivatives of h_{ij} and g_{ijkl} wrt orbital expansion coefficients
- Derivatives of the density matrices wrt to WF expansion coefficients
- Alternate between orbital and WF optimization steps

Orbitals

Ψ
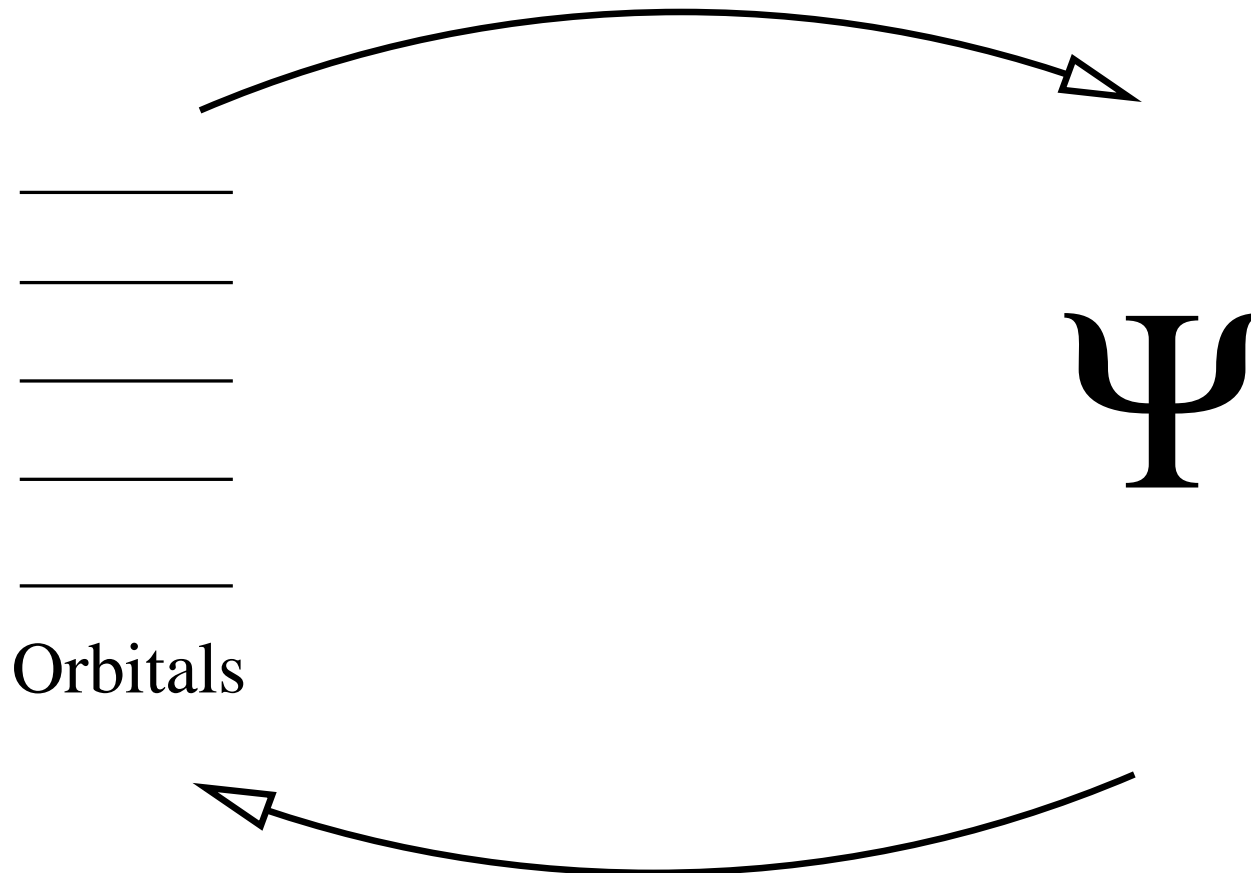
Remains to work

Rotations in the parameter space via unitary matrices U with $U^\dagger U = UU^\dagger = 1$.

- Conserves orthonormality

- Can be expressed as exponential of an anti-hermitian matrix T,

$$T^\dagger = -T \quad : \qquad U = e^{\hat{T}}$$

- Orbital rotations (parameters are the matrix elements T_{ij}):

$$\hat{T} = \sum_{i>j} T_{ij} \left(\hat{E}_{ij} - \hat{E}_{ji} \right)$$

- Wavefunction rotations: $\hat{S} = \sum_{K \neq 0} S_{K0} \left(|\Psi_K\rangle\langle\Psi_0| - |\Psi_0\rangle\langle\Psi_K| \right)$

- Transformation of a general multireference state $|\Psi_0\rangle$ into another

$$|\Psi\rangle = e^{\hat{T}} e^{\hat{S}} |\Psi_0\rangle$$

Finally the optimization

- Total energy after application of the rotations on an initial multi-configurational state $|\Psi_0\rangle$:

$$E_{\text{tot}} \;=\; \langle\,\Psi_0\,|\,e^{-\hat{S}}e^{-\hat{T}}\hat{H}e^{\hat{T}}\,e^{\hat{S}}\,|\,\Psi_0\,\rangle$$

- Expansion of the exponentials to 2nd order:

$$
\begin{aligned}
E_{\text{tot}} \;=\;& \langle\,\Psi_0\,|\,\hat{H}\,|\,\Psi_0\,\rangle + \langle\,\Psi_0\,|\,\big[\hat{H},\hat{T}\big]\,|\,\Psi_0\,\rangle + \langle\,\Psi_0\,|\,\big[\hat{H},\hat{S}\big]\,|\,\Psi_0\,\rangle + \\
&+ \frac{1}{2}\langle\,\Psi_0\,|\,\big[\big[\hat{H},\hat{T}\big],\hat{T}\big]\,|\,\Psi_0\,\rangle + \frac{1}{2}\langle\,\Psi_0\,|\,\big[\big[\hat{H},\hat{S}\big],\hat{S}\big]\,|\,\Psi_0\,\rangle \\
&+ \langle\,\Psi_0\,|\,\big[\big[\hat{H},\hat{T}\big],\hat{S}\big]\,|\,\Psi_0\,\rangle + \;\ldots
\end{aligned}
$$

- Taylor expansion in the rotational parameters T_{ij} and S_{K0}

Finally the optimization

- Newton-Raphson procedure:

$$
\begin{aligned}
E(\mathbf{x}) &= E(0) + \mathbf{a}^\dagger . \mathbf{x} + \frac{1}{2}\mathbf{x}^\dagger \mathbf{B} \mathbf{x} \\
\mathbf{a} + \mathbf{B}.\mathbf{x} &= 0 \\
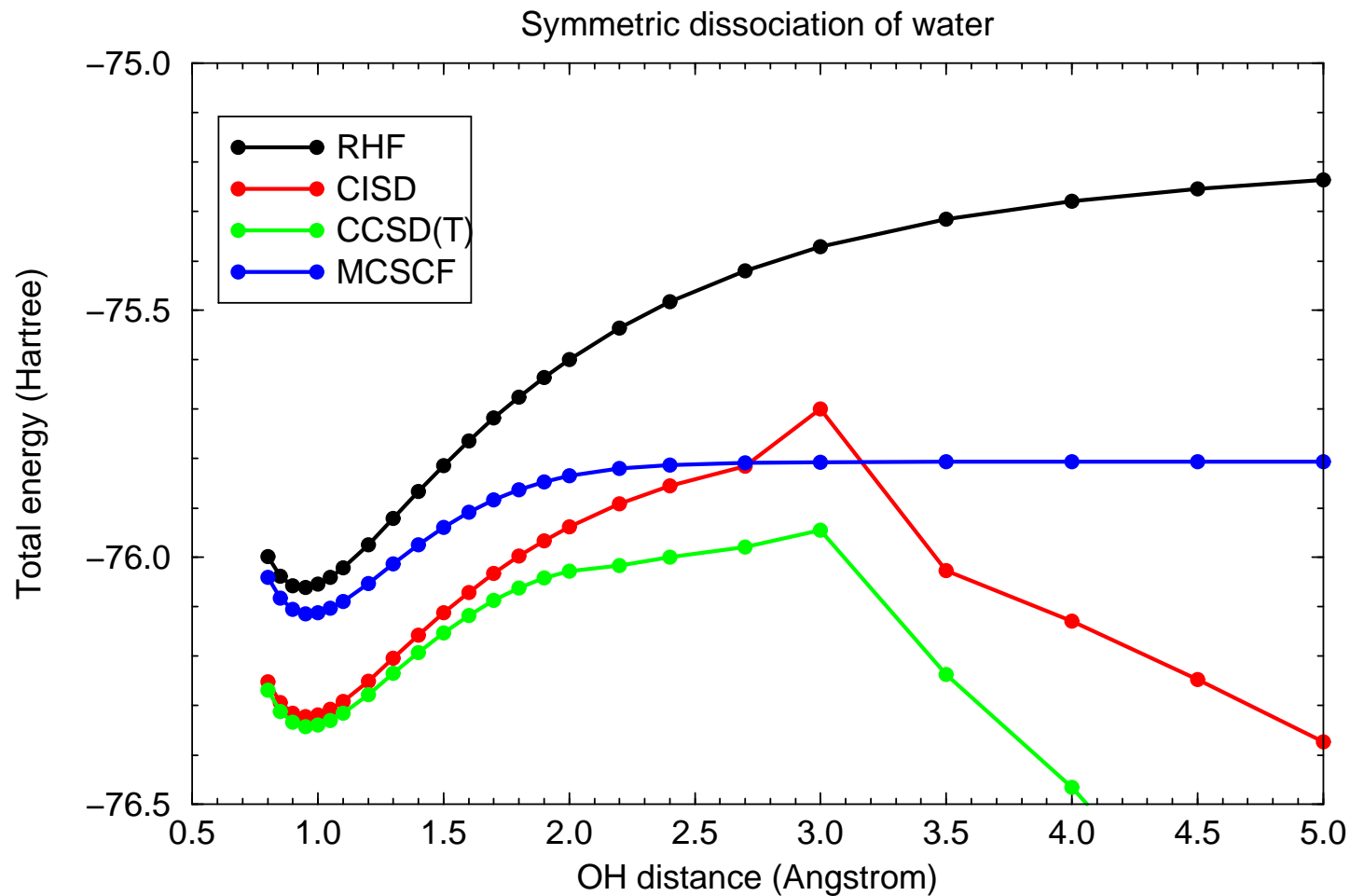\mathbf{x} &= -\mathbf{B}^{-1}.\mathbf{a}
\end{aligned}
$$

- Identify:

$$
\begin{aligned}
\mathbf{a}_{T_{ij}} &= \left(\frac{\partial E}{\partial T_{ij}} \right) = \langle \Psi_0 | \left[\hat{H}, \hat{E}_{ij} - \hat{E}_{ji} \right] | \Psi_0 \rangle \\
\mathbf{a}_{S_{K0}} &= \left(\frac{\partial E}{\partial S_{K0}} \right) = 2 \langle \Psi_0 | \hat{H} | \Psi_K \rangle
\end{aligned}
$$

Three types of 2nd derivatives: orbital–orbital, WF–orbital, WF–WF

Has to be implemented ....

Symmetric dissociation of water

Symmetric dissociation of water

Practical aspects

- Much more expensive than RHF

- Grows exponentially with number of active orbitals

- Definition of active space not straightforward: all valence electrons in all valence atomic orbitals may be too large

- Convergence not assured

- Active space may change for different points on a potential surface

- Starting point for calculations on

  - Open-shell systems

  - Electronically excited states

  - Resonant singlet systems

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:

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

CI of Singles and Doubles

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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

Too many determinants to hold the matrix of all $\langle\, \Phi_I \mid H \mid \Phi_J \,\rangle$

Iterative solution of the eigenvalue problem, we are only interested in the **best** wavefunction (Davidson procedure):
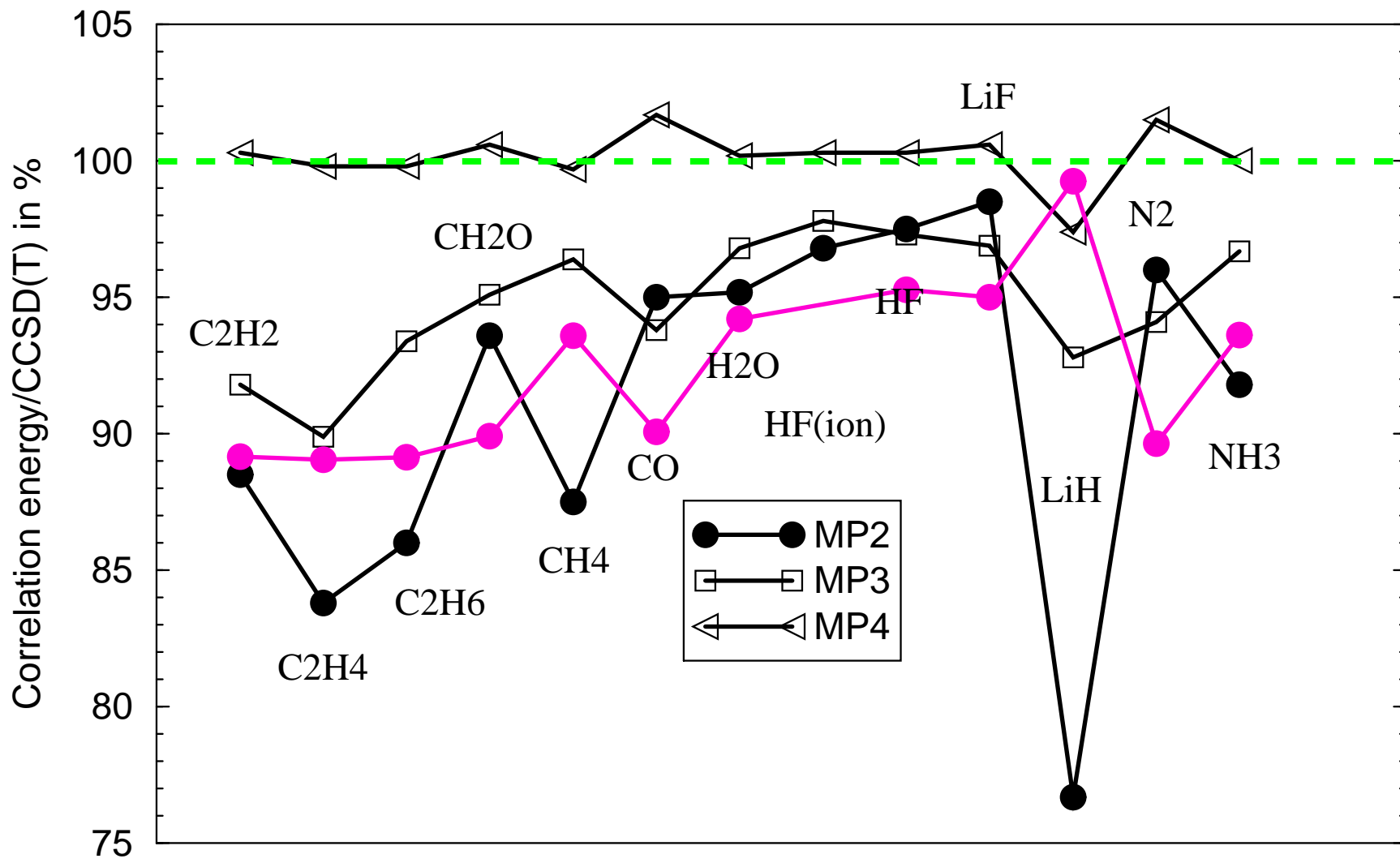
- Starting wavefunction (Φ_{HF} or $\Phi_{\mathrm{HF}} + \Psi^{(1)}$)

- Form $|\tilde{\Psi}'\rangle = -(H_0 - \langle\Psi|\hat{H}|\Psi\rangle)^{-1}(\hat{H} - \langle\Psi|\hat{H}|\Psi\rangle)|\Psi\rangle$, construct the 2×2 matrix

$$\begin{pmatrix} \langle\, \Psi \mid H \mid \Psi \,\rangle & \langle\, \Psi \mid H \mid \tilde{\Psi}' \,\rangle \\ \langle\, \tilde{\Psi}' \mid H \mid \Psi \,\rangle & \langle\, \tilde{\Psi}' \mid H \mid \tilde{\Psi}' \,\rangle \end{pmatrix}$$

  diagonalize it; eigenvector is a better WF Ψ'
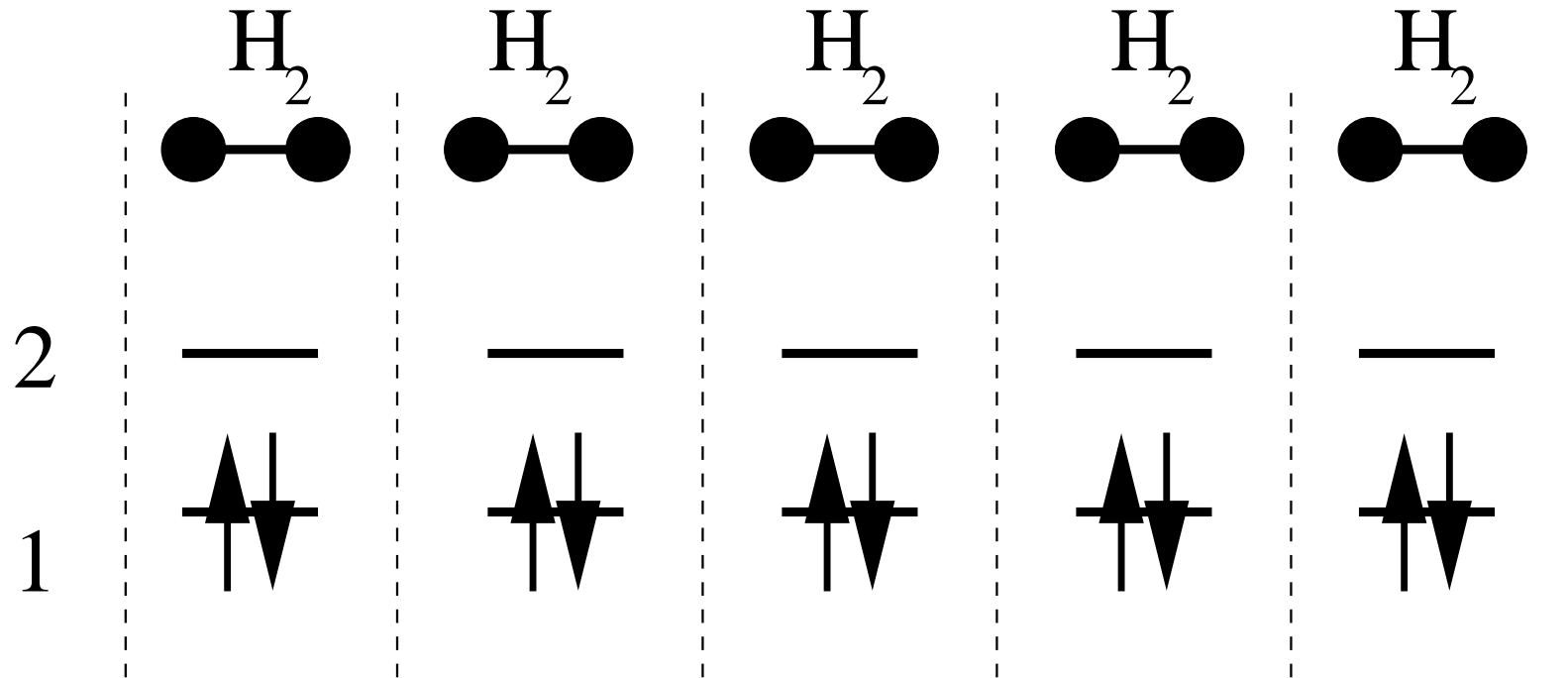
- Construct $|\tilde{\Psi}''\rangle = -(H_0 - \langle\Psi'|\hat{H}|\Psi'\rangle)^{-1}(\hat{H} - \langle\Psi'|\hat{H}|\Psi'\rangle)|\Psi'\rangle$, augment the 2×2 matrix by one line and column: 3×3 matrix

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

- Continue until convergence

- Convergence in ca. 10 iterations

CI of Singles and Doubles

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:

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

-

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

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
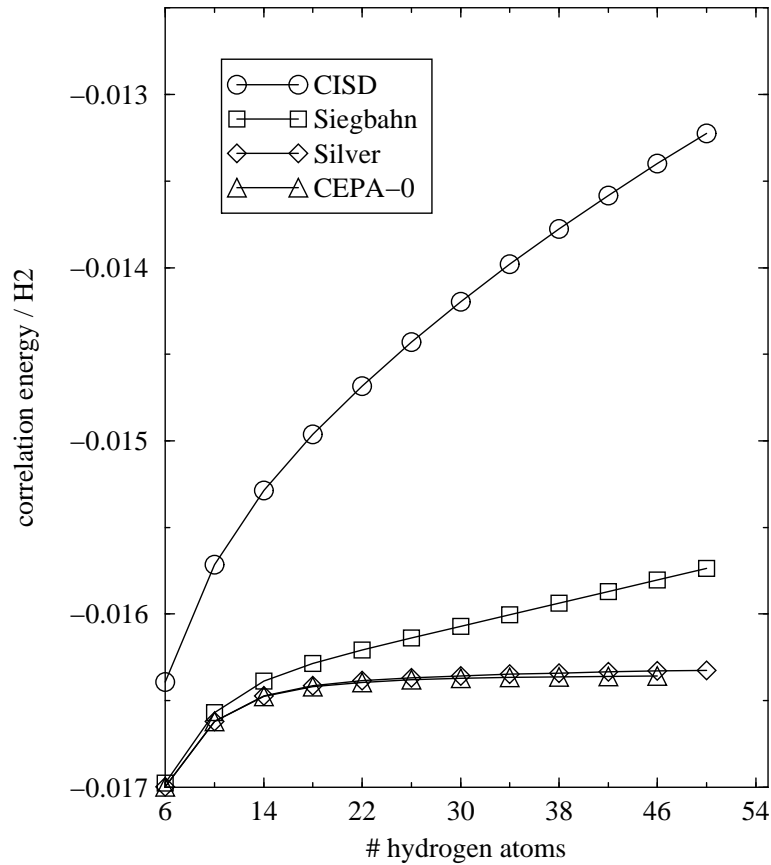
- Correction of Davidson and Silver

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

E.R.Davidson, D.W.Silver, Chem.Phys.Lett., **52** (1977) 403
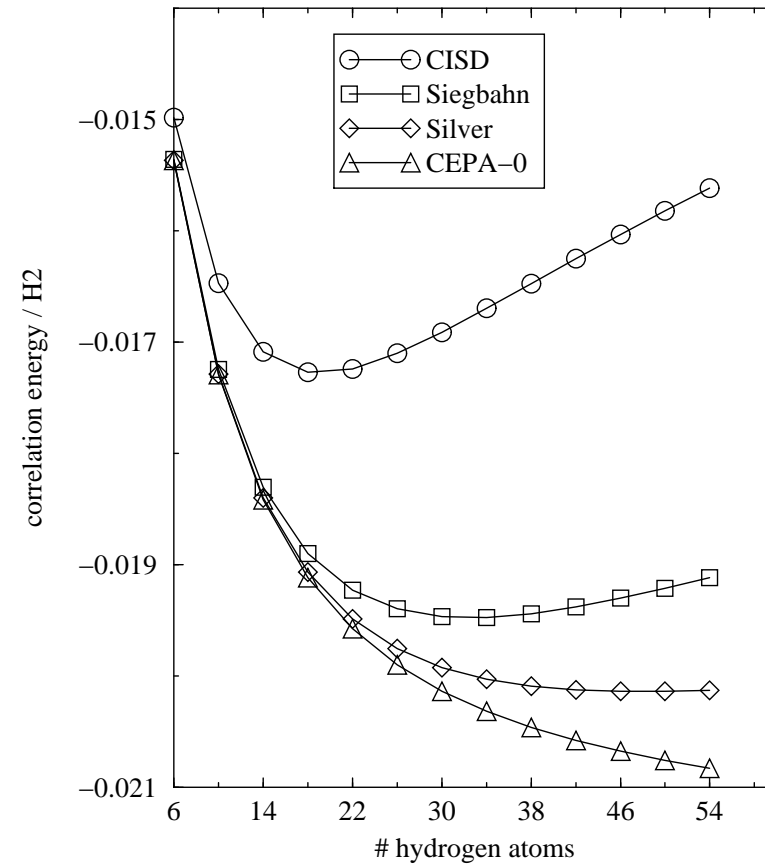
Wrong scaling property of SD-CI

Result for $(H_2)_n$ rings :


molecular case

metal-like case

Size-consistent methods

CISD eigenvalue problem

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

Size-consistent methods

Dressed CISD eigenvalue problem

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

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

Size-consistent methods
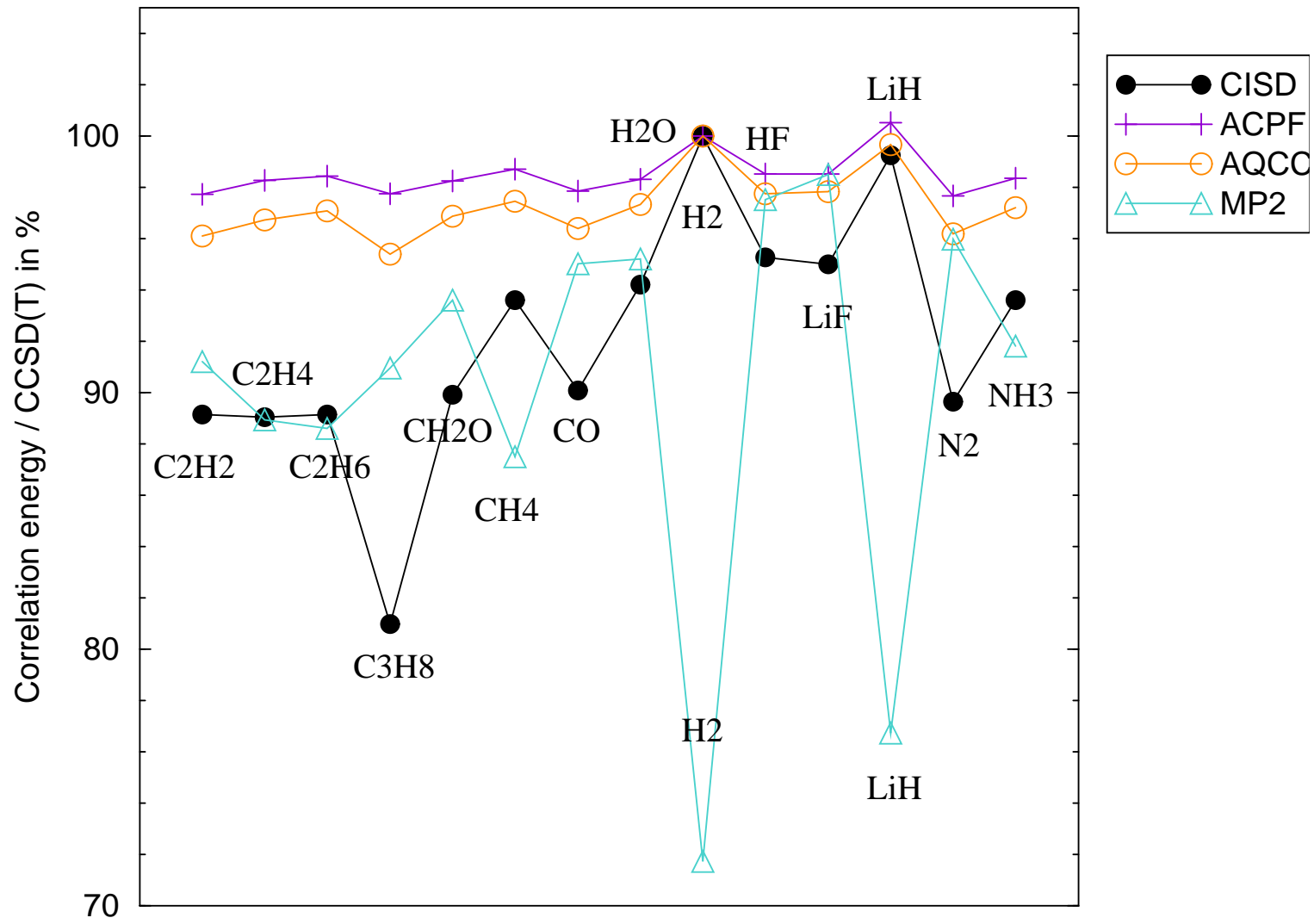
Perturbation theory

- Decompose $\hat{H}$ in two parts

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

- Eigenfunctions of $\hat{H}_0$ known:

$$\hat{H}_0\,\Phi_k \;=\; E_k^{(0)}\,\Phi_k$$

In particular

$$\hat{H}_0\,\Phi_0 \;=\; E_0^{(0)}\,\Phi_0$$

with the Hartree-Fock reference determinant Φ_0

- But not necessarily $\hat{H}_0\,\Phi_0 \;=\; E_{HF}\,\Phi_0$
- $\hat{V}$ small

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:

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

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:

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

- 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

Perturbation theory

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

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

Perturbation theory

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

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

Energies:

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

Coefficients:

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

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

Perturbation theory

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

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

- We <u>always</u> have

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

-

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

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

Perturbation theory

$$E_0^{(1)} = \langle\, \Phi_0 \,|\, V \,|\, \Phi_0 \,\rangle = \langle 0|\hat{V}|0\rangle$$

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

$$E_0^{(3)} = \langle\, \Phi_0 \,|\, V \,|\, \Psi^{(2)} \,\rangle$$

$$= \sum_{k,l\neq 0}\langle 0|\hat{V}\,\frac{|k\rangle\langle k|}{E_0^{(0)} - E_k^{(0)}}\,\hat{V}\,\frac{|l\rangle\langle l|}{E_0^{(0)} - E_l^{(0)}}\hat{V}|0\rangle$$

$$-E_0^{(1)}\sum_{k\neq 0}\left(\frac{\langle\, 0 \,|\, V \,|\, k \,\rangle}{E_0^{(0)} - E_k^{(0)}}\right)^2 \tag{1}$$

There is a systematic structure in the equations ...

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

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

Møller-Plesset perturbation theory

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

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

Møller-Plesset perturbation theory

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

- Creation/destruction operators obey anti-commutator rules:

  - Creation operators $\hat{a}_i^\dagger$, destruction operators $\hat{a}_i$

  - Definition for an antisymmetric wavefunction:

$$\hat{a}_i |n_1 \ldots n_i \ldots\rangle = (-1)^{\sum_{k<i} n_k} n_i |n_1 \ldots 0_i \ldots\rangle = \theta_i \, n_i \, |n_1 \ldots 0_i \ldots\rangle$$
$$\hat{a}_i^\dagger |n_1 \ldots n_i \ldots\rangle = \theta_i \, (1 - n_i) \, |n_1 \ldots 1_i \ldots\rangle$$

  - Wavefunction is antisymmetric: the order of creation is important
  - $\hat{a}_i^\dagger \hat{a}_j^\dagger = -\hat{a}_j^\dagger \hat{a}_i^\dagger$, or $\hat{a}_i^\dagger \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i^\dagger = 0$
  - the same holds for the destruction operators: $\hat{a}_i \hat{a}_j = -\hat{a}_j \hat{a}_i$
  - We may destroy an existing particle or hole and recreate it, or create a non-existing particle or hole and destroy it: $\hat{a}_i^\dagger \hat{a}_i + \hat{a}_i \hat{a}_i^\dagger = 1$

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

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

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

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

$$\langle \, 0 \, | \, \hat{V} \, | \, k \, \rangle \;\; = \;\; \langle \, \Phi_0 \, | \, \hat{H} \, | \, \Phi_{ij}^{ab} \, \rangle - \underbrace{\langle \, \Phi_0 \, | \, \hat{H}_0 \, | \, \Phi_{ij}^{ab} \, \rangle}_{=0} = \langle \, 0 \, | \, \hat{H} \, | \, k \, \rangle$$

$$= \;\; (ia|jb) - (ib|ja)\delta_{\sigma_i \sigma_j} \qquad \text{bi-electronic integrals}$$

Møller-Plesset perturbation theory

Second-order energy:

$$E^{(2)} = \sum_{ijab} \frac{\left(2(ia|jb) - (ib|ja)\right)(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$
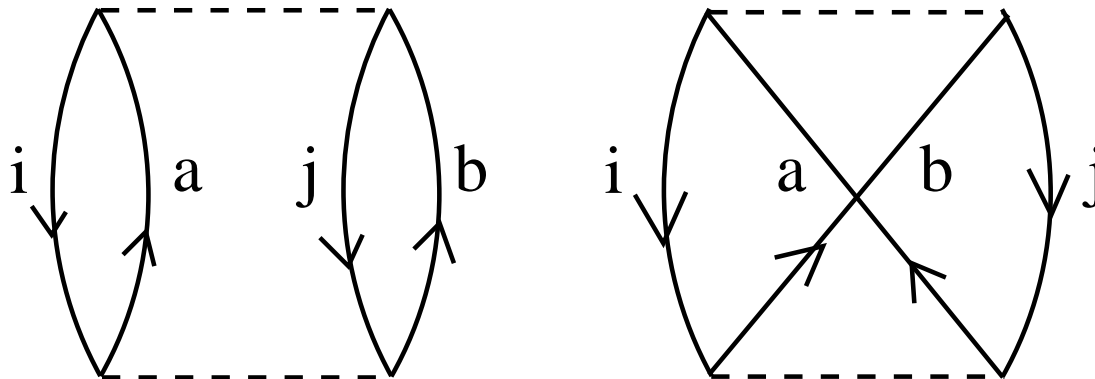
And higher-order formulas can be derived as well ... but become more and more complex

Møller-Plesset perturbation theory

Second-order energy:

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

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

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

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 $\longrightarrow$ 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 $\Psi^{(n)}$; $0 \to 1, 1 \to 3, 2 \to 5$

- Commonly used: MP2, MP4

Performance
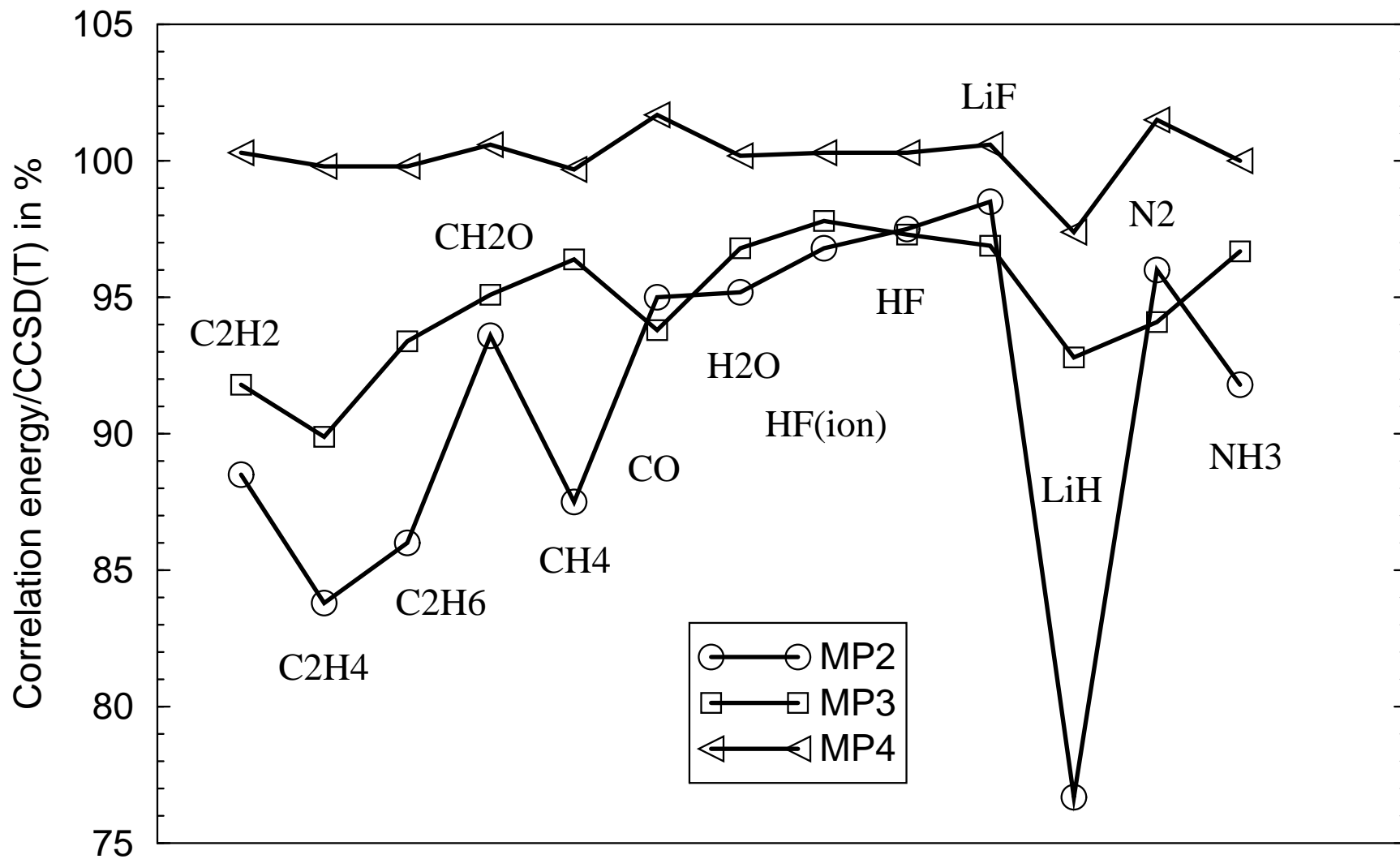
Basis aug-cc-pvtz, fixed geometry

Performance

Geometry parameters

molecule	Hartree-Fock		2nd order Møller-Plesset	
	Δ r (pm)	Δ ang (deg.)	Δ r (pm)	Δ ang (deg.)
H_2O	-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

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_2O	4121	597	3821	917	3657	918
N_2	2726	472	2187	952	2359	942
CH_4	3147	1260	3069	1607	2917	1642
CO	2421	716	2110	1099	2170	1072
HF	4465	380	4125	576	4138	567
NH_3	3686	754	3503	1128	3337	1158
P_2	909	150	726	451	781	486
SO_2	1371	393	1106	—	1151	1063

Source: NIST database `http://www.nist.org`

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 $\langle\,\Phi_{ij}^{ab}\,|\,H\,|\,\Phi_{ij}^{cd}\,\rangle$

- MP3: one iteration of CISD

- adding dressings to CISD: no additional cost

- MP4:

  - exploit: $\langle\,\Phi_{ij}^{ab}\,|\,H\,|\,\Phi_{ijkl}^{abcd}\,\rangle = \langle\,\Phi_0\,|\,H\,|\,\Phi_{kl}^{cd}\,\rangle$

  - treatment of Singles, Doubles, and Quadruples $\sim\ N^6$

  - Triples: excitation sequence

    $\langle\,0\,|\,H\,|\,D\,\rangle\langle\,D\,|\,H\,|\,T\,\rangle\langle\,T\,|\,H\,|\,D\,\rangle\langle\,D\,|\,H\,|\,0\,\rangle$

    $\langle\,\Phi_{ij}^{ab}\,|\,H\,|\,\Phi_{klm}^{cde}\,\rangle\ =\ \langle\,a\,b\,k\,l\,\underline{\mathrm{m}}\,|\,H\,|\,i\,j\,c\,d\,\underline{\mathrm{e}}\,\rangle\ \longrightarrow\ N^7$

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

Coupled Cluster Theory

Finally the Coupled-Cluster ....

- Wavefunction

$$|\Psi\rangle \;=\; e^{\hat{S}}\,|\Phi_0\rangle$$

- $\hat{S}$ excitation operator

$$\hat{T}_1 \;=\; \sum_{i,a} t_i^a\, \hat{a}_a^\dagger\, \hat{a}_i$$

$$\hat{T}_2 \;=\; \sum_{ij,ab} t_{ij}^{ab}\, \hat{a}_a^\dagger\, \hat{a}_b^\dagger\, \hat{a}_i\, \hat{a}_j \qquad \text{etc.}$$

- Schrödinger's equation $\hat{H}|\Psi\rangle = E\,|\Psi\rangle$

- Energy through projection against $\langle\Phi_0|$ or $\langle\Phi_0|e^{-\hat{S}}$

$$\langle\Phi_0|e^{-\hat{S}}\hat{H}e^{\hat{S}}|\Phi_0\rangle \;=\; \langle\Phi_0|\hat{H}e^{\hat{S}}|\Phi_0\rangle$$

$$=\; \langle\Phi_0|e^{-\hat{S}}Ee^{\hat{S}}|\Phi_0\rangle = E = E_{HF} + E_{Corr}$$

General approach

Projection of $e^{-\hat{S}}\hat{H}e^{\hat{S}}$:

$$\langle\Phi_i^a|e^{-S}\hat{H}e^{S}|\Phi_0\rangle = 0$$
$$\langle\Phi_{ij}^{ab}|e^{-\hat{S}}\hat{H}e^{\hat{S}}|\Phi_0\rangle = 0 \qquad (2)$$

Exponential

$$e^{\hat{S}} = 1 + \hat{S} + \frac{1}{2}\hat{S}^2 + \frac{1}{6}\hat{S}^3 + \dots$$

leads to the (exact) Baker-Campbell-Hausdorff expansion

$$e^{-\hat{S}}\hat{H}e^{\hat{S}} = \hat{H}+[\hat{H},\hat{S}]+\frac{1}{2}[[\hat{H},\hat{S}],\hat{S}]+\frac{1}{6}[[[\hat{H},\hat{S}],\hat{S}],\hat{S}]+\frac{1}{24}[[[[\hat{H},\hat{S}],\hat{S}],\hat{S}],\hat{S}] \quad .$$

Remains to insert $\hat{S} = \hat{T}_1 + \hat{T}_2$, regroup and evaluate.
We may use

$$e^{-\hat{S}}\hat{H}e^{\hat{S}} = e^{-\hat{T}_1-\hat{T}_2}\hat{H}e^{\hat{T}_1+\hat{T}_2} = e^{-\hat{T}_2}\left(e^{-\hat{T}_1}\hat{H}e^{\hat{T}_1}\right)e^{\hat{T}_2} = e^{-\hat{T}_2}\hat{H}_{eff}e^{\hat{T}_2}$$

General approach

Projection of $\hat{H}e^{\hat{S}}$:

$$\langle\,\Phi^a_i\,|\,\hat{H}e^{\hat{T}_1+\hat{T}_2}\,|\,\Phi_0\,\rangle \;=\; \langle\,\Phi^a_i\,|\,\hat{H}\left(\hat{T}_1+\hat{T}_2+\hat{T}_1\hat{T}_2+\frac{1}{2}\hat{T}_1^2+\frac{1}{6}\hat{T}_1^3\right)|\,\Phi_0\,\rangle$$

$$\langle\Phi^{ab}_{ij}|\hat{H}e^{\hat{T}_1+\hat{T}_2}|\Phi_0\rangle \;=\; \langle\Phi^{ab}_{ij}|\hat{H}\left(1+\hat{T}_1+\hat{T}_2+\hat{T}_1\hat{T}_2+\right.$$

$$\left.+\frac{1}{2}\hat{T}_1^2+\frac{1}{2}\hat{T}_1^2\hat{T}_2+\frac{1}{2}\hat{T}_2^2+\frac{1}{6}\hat{T}_1^3+\frac{1}{24}\hat{T}_1^4|\Phi_0\rangle\right)$$

Equation of degree 4 to solve, via iterative methods.

Continuing

Take only diexcitations ($t_{ij}^{ab} = c_{ij}^{ab}$):

$$E = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle = E_{HF} + \sum_I c_I \langle \Phi_0 | \hat{H} | \Phi_I \rangle$$

$$\langle \Phi_{ij}^{ab} | \hat{H} \left(1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 \right) | \Phi_0 \rangle = E \underbrace{\langle \Phi_{ij}^{ab} | \hat{T}_2 | \Phi_0 \rangle}_{= c_{ij}^{ab}}$$

Look at the contributions from $\hat{T}_2 \hat{T}_2 | \Phi_0 \rangle = 2 \sum_{klcd} (c_{ij}^{ab} * c_{kl}^{cd}) | \Phi_{ijkl}^{abcd} \rangle$

with all the possibilities

$$
\begin{aligned}
c_{ij}^{ab} * c_{kl}^{cd} &= c_{ij}^{ab} c_{kl}^{cd} - \langle c_{ij}^{ab} * c_{kl}^{cd} \rangle \\
&= c_{ij}^{ab} c_{kl}^{cd} - c_{ik}^{ab} c_{jl}^{cd} + c_{il}^{ab} c_{jk}^{cd} - c_{ij}^{ac} c_{kl}^{bd} + c_{ik}^{ac} c_{jl}^{bd} - c_{il}^{ac} c_{jk}^{bd} \\
&\quad + c_{ij}^{ad} c_{kl}^{bc} - c_{ik}^{ad} c_{jl}^{bc} + c_{il}^{ad} c_{jk}^{bc} + c_{ij}^{cd} c_{kl}^{ab} - c_{ik}^{cd} c_{jl}^{ab} + c_{il}^{cd} c_{jk}^{ab} \\
&\quad - c_{ij}^{bd} c_{kl}^{ac} + c_{ik}^{bd} c_{jl}^{ac} - c_{il}^{bd} c_{jk}^{ac} + c_{ij}^{bc} c_{kl}^{ad} - c_{ik}^{bc} c_{jl}^{ad} + c_{il}^{bc} c_{jk}^{ad}
\end{aligned}
$$

Continuing

Assembly :

$$\hat{H}_{0I} + \sum_J \hat{H}_{IJ}\, c_J +$$

$$+ \sum_J \langle\Phi_I|\hat{H}|\Phi_{I+J}\rangle (c_I\, c_J - \langle c_I * c_J\rangle)$$

$$- \underbrace{\left(E_{HF}\, c_I + \sum_J \hat{H}_{0J}\, c_I\, c_J \right)}_{E\, c_I} \qquad = \qquad 0$$

With $\langle\, \Phi_I\, |\, \hat{H}\, |\, \Phi_{I+J}\, \rangle = \langle\, \Phi_0\, |\, \hat{H}\, |\, \Phi_J\, \rangle$

$$\sum_J \langle\Phi_I|\hat{H}|\Phi_{I+J}\rangle c_I\, c_J - \sum_J \hat{H}_{0J}\, c_I\, c_J = 0$$

Continuing

Finally the equations to determine the coefficients :

$$\hat{H}_{0I} + \langle \Phi_I | \hat{H} - E_{HF} | \Phi_I \rangle \, c_I + \sum_{J \neq I} \hat{H}_{IJ} \, c_J = \sum_J \hat{H}_{0J} \, \langle c_I \ast c_J \rangle$$

- Still quadratic in the coefficients
- Only di-excited determinants to consider
- We had for the variational CISD correlation energy:

$$E_{Corr} = \sum_I c_I \langle \Phi_0 | \hat{H} | \Phi_I \rangle$$

- Equations ressemble the CISD equations !
- To be solved iteratively

Including triple excitations

- CCSD: only di-excited determinants needed

- Cost as CISD or MP4 (SDQ): $\sim N^6$

- Triples may be important:
  - Orbital corrections for di-excitations
  - Much better performance for intermolecular interactions

- Full triples step costs $\sim N^8$:

$$\langle i\,j\,k\,a\,b\,c|\hat{H}|l\,m\,n\,d\,e\,f\rangle$$

6 indices $ijkabc$ and 2 differences $\longrightarrow N^8$

- Needs much more memory for coefficients t_{ijk}^{abc}, etc.

- Perturbative treatment: straightforward, no need for iterations $\longrightarrow$ CCSD(T) as triples in MP4: $\sim N^7$

- Nowadays reference method for closed-shell systems

Example: NH$_3$—NH$_3$

NH3 – NH3

Energie d'interaction (mH) vs distance N – N (Ångstrøm)

Data points: B–LYP, B3LYP, CEPA–0, ACPF, CCSD, MP2, MP4, CCSD(T), SAPT(hybrid)
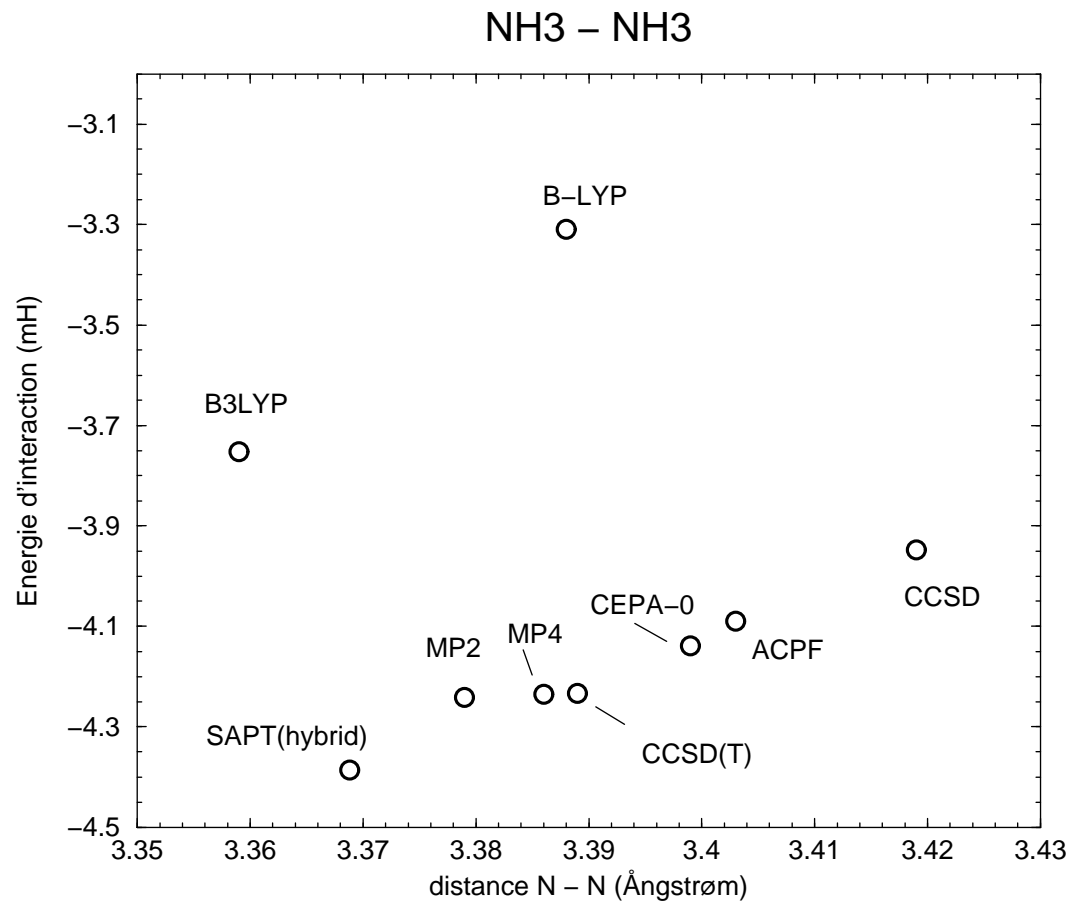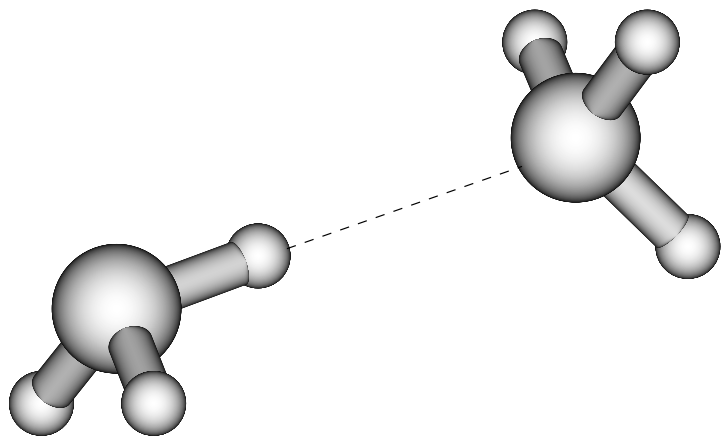
Performance

Geometry parameters

molecule	Hartree-Fock		MP2		CCSD(T)	
	$\Delta\,r$ (pm)	Δ ang (°)	$\Delta\,r$ (pm)	Δ ang (°)	$\Delta\,r$ (pm)	Δ ang (°)
H_2O	−1.7	+1.8	+0.1	−0.4	−0.1	−0.3
N_2	−3.1		+1.6		+0.6	
CH_4	−0.5		−0.1		+0.3	
CO	−2.4		+1.1		+0.8	
HF	−1.8		+0.5		+0.4	
NH_3	−1.4	+1.5	0.0	+0.5	+2.3	−0.3
P_2	−3.6		+3.4		+2.3	
SO_2	−2.7	−1.3	+2.7	−1.1	+0.3	−1.1

Source: NIST database `http://www.nist.org`

Performance

Vibrational constants, atomization energies

molecule	2nd order Møller-Plesset		CCSD(T)		Experiment	
	ν (cm^{-1})	at.ener. (kJ/mol)	ν (cm^{-1})	at.ener. (kJ/mol)	ν (cm^{-1})	at.ener. (kJ/mol)
H_2O	3821	917	3811	899	3657	918
N_2	2187	952	2339	897	2359	942
CH_4	3069	1607	3028	1617	2917	1642
CO	2110	1099	2144	1040	2170	1072
HF	4125	576	4128	557	4138	567
NH_3	3503	1128	3464	1131	3337	1158
P_2	726	451	768	437	781	486
SO_2	1106	—	1136	968	1151	1063

Source: NIST database `http://www.nist.org`

Adding dynamical correlation to MCSCF

- Add excitations
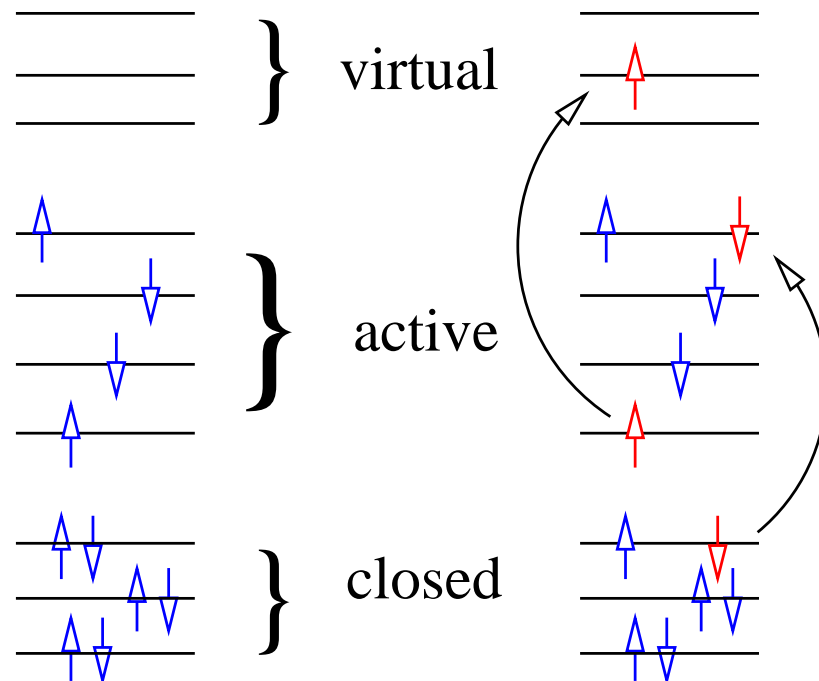
- CISD like in the mono-reference case
- Dressing techniques available: MR–CEPA, MR–ACPF, MR–AQCC
- Same size-consistence problems as for mono-reference case

Adding dynamical correlation to MCSCF

H2O – symmetric bond stretching
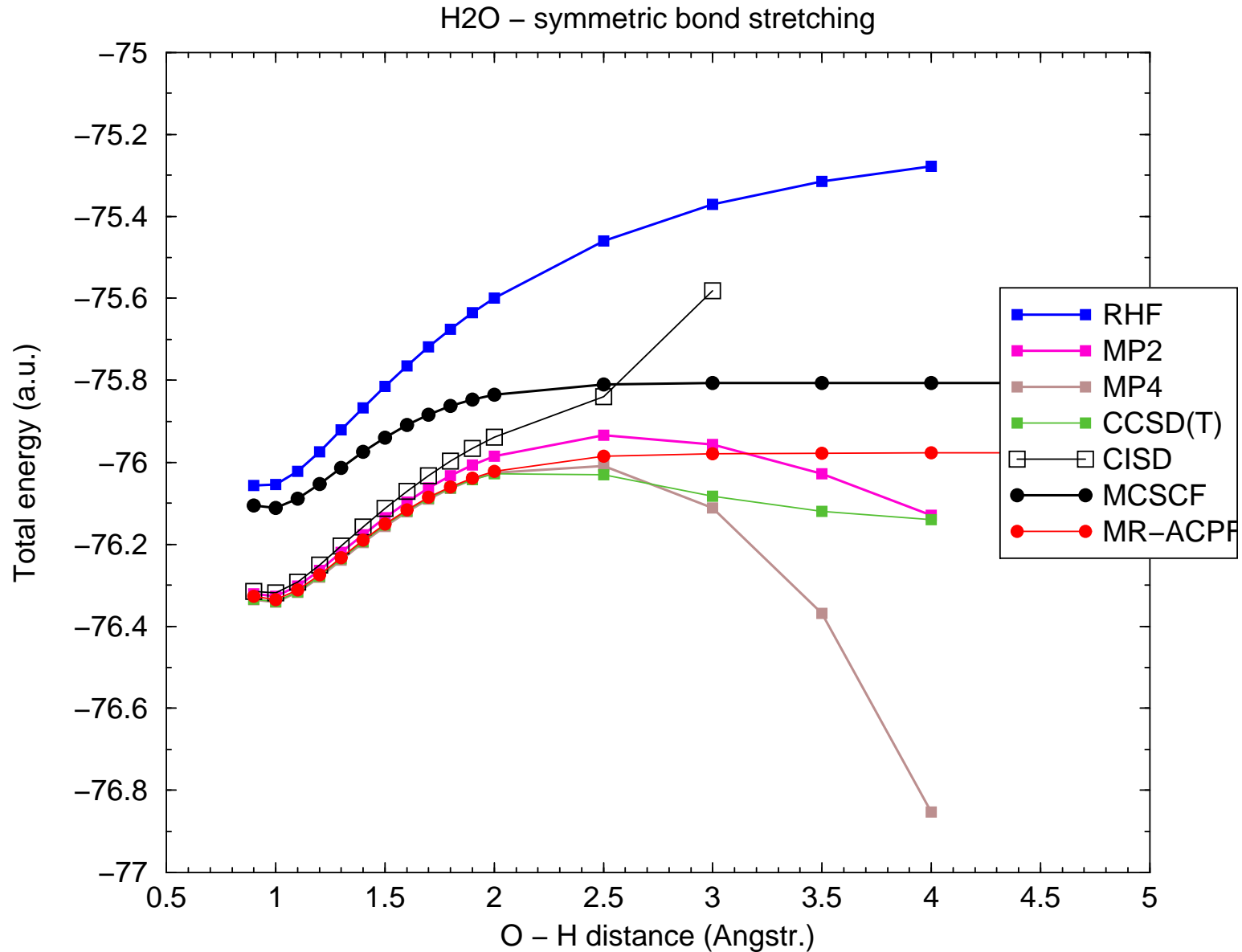
Range-separated DFT

- Common Kohn-Sham procedure

$$E_{\text{exact}} = \min_{\Phi} \left\{ \langle \Phi | T + V_{\text{ne}} | \Phi \rangle + E_{\text{Hxc}} \left[n_{\Phi} \right] \right\}$$

Range-separated DFT

- Range-separated hybrid approach (RSH):

$$E^{\mathrm{RSH}} = \min_{\Phi} \left\{ \langle \Phi | T + V_{\mathrm{ne}} + W_{\mathrm{ee}}^{\mathrm{lr}} | \Phi \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr}} \left[n_{\Phi} \right] \right\}$$

with long-range part $\langle \Phi | W_{\mathrm{ee}}^{\mathrm{lr}} | \Phi \rangle$ as Hartree term (electrostatics) and Hartree-Fock exchange

Range-separated DFT

- Range-separated hybrid approach (RSH):

$$E^{\mathrm{RSH}} = \min_\Phi \left\{ \langle \Phi | T + V_{\mathrm{ne}} + W_{\mathrm{ee}}^{\mathrm{lr}} | \Phi \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr}} [n_\Phi] \right\}$$

Range separation via the error function and a parameter μ

$$\frac{1}{r_{ij}} = w_{ee}^{\mathrm{lr}} + \left(\frac{1}{r_{ij}} - w_{ee}^{\mathrm{lr}} \right) \text{ with } w_{ee}^{\mathrm{lr}}(r_{ij}) = \mathrm{erf}(\mu\, r_{ij})/r_{ij}$$
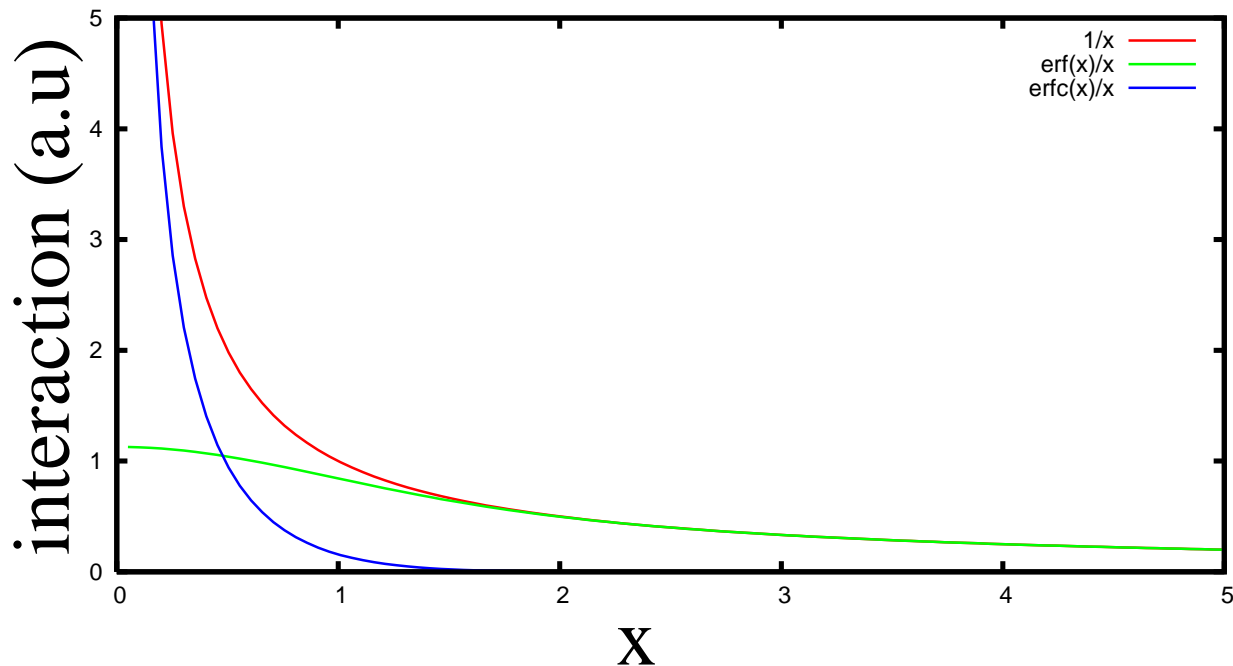
Range-separated DFT

Kohn-Sham-like RSH equations

$$\left(T + V_{\text{ne}} + V_{\text{H}} + V_{\text{x}}^{\text{lr}} + V_{\text{xc}}^{\text{sr}}\right) |\phi_i^{\text{RSH}}\rangle = \epsilon_i |\phi_i^{\text{RSH}}\rangle$$

- Long-range HF exchange part V_{x}^{lr} ("erf" part of the e-e interaction)
- Specific short-range exchange and correlation functionals $V_{\text{xc}}^{\text{sr}}(\mu)$

Total energy E^{RSH} does not include long-range correlation.

- Furnishes orbital energies ϵ_i
- Molecular orbitals $\phi_i(\vec{\text{r}})$
- Long-range correlation energy, e.g. MP2

$$E_{\mu,\text{MP2}}^{(2)} = \sum_{ijab} \frac{(ia|jb)_{lr,\mu}\left(2(ia|jb)_{lr,\mu} - (ib|ja)_{lr,\mu}\right)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

Range-separated DFT
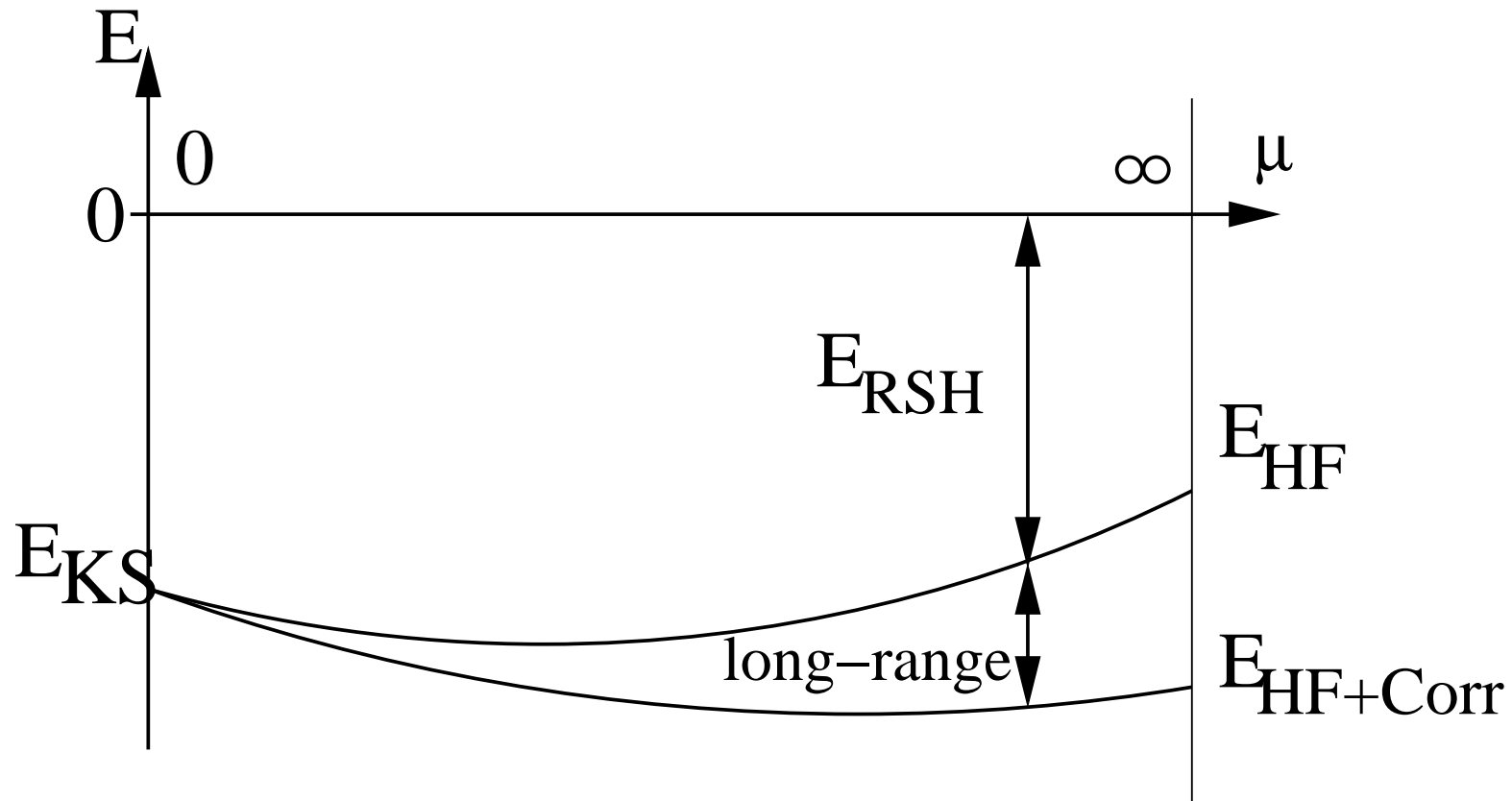
- $\mu = 0 \quad \longrightarrow$ standard Kohn-Sham theory
- $\mu \to \infty \quad \longrightarrow$ Hartree-Fock + correlation

Range-separated DFT

- Asymptotic behaviour for $\mu \longrightarrow 0$: standard LDA or PBE functionals, long-range exchange part exactly zero

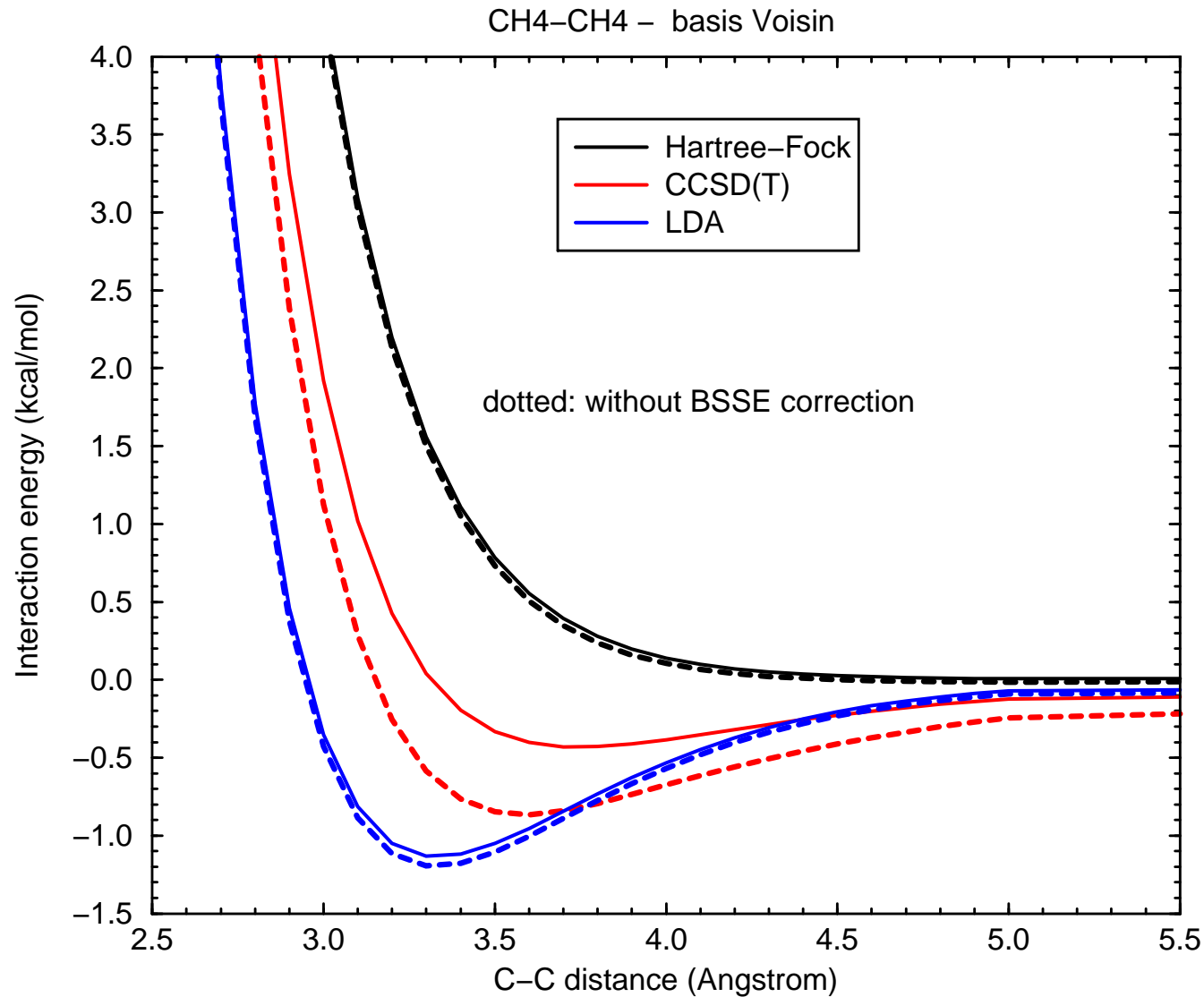- Functionals go to zero with $\mu \longrightarrow \infty$, and $E^{\text{RSH}} \longrightarrow E_{HF}$

CH4 – basis Voisin

$E(\text{HF}) = -39.914$ a.u.
$E(\text{LDA}) = -39.822$ a.u.
$E(\text{PBE}) = -40.162$ a.u.

RSH–LDA
RSH–PBE

Range-separated DFT

- Asymptotic behaviour for $\mu \longrightarrow 0$: standard LDA or PBE functionals, long-range exchange part exactly zero

- Functionals go to zero with $\mu \longrightarrow \infty$, and $E^{\mathrm{RSH}} \longrightarrow E_{HF}$

CH4 – basis Voisin

$E(CCSD(T)) = -40.116$ a.u.

Legend:
- RSH–LDA
- RSH–PBE
- RSHLDA+CCSD(T)
- RSHPBE+CCSD(T)

total energy (a.u.)

separation parameter mu (a.u.)
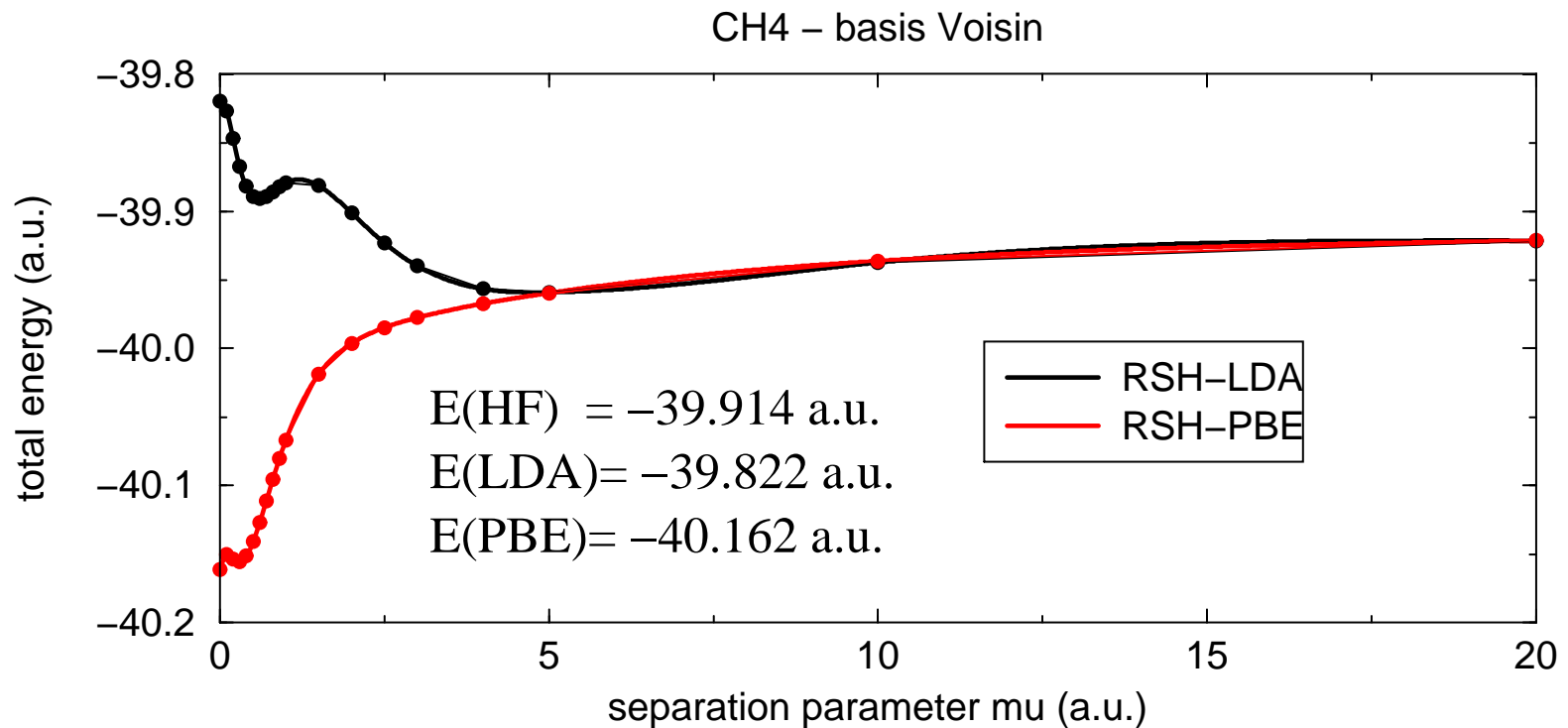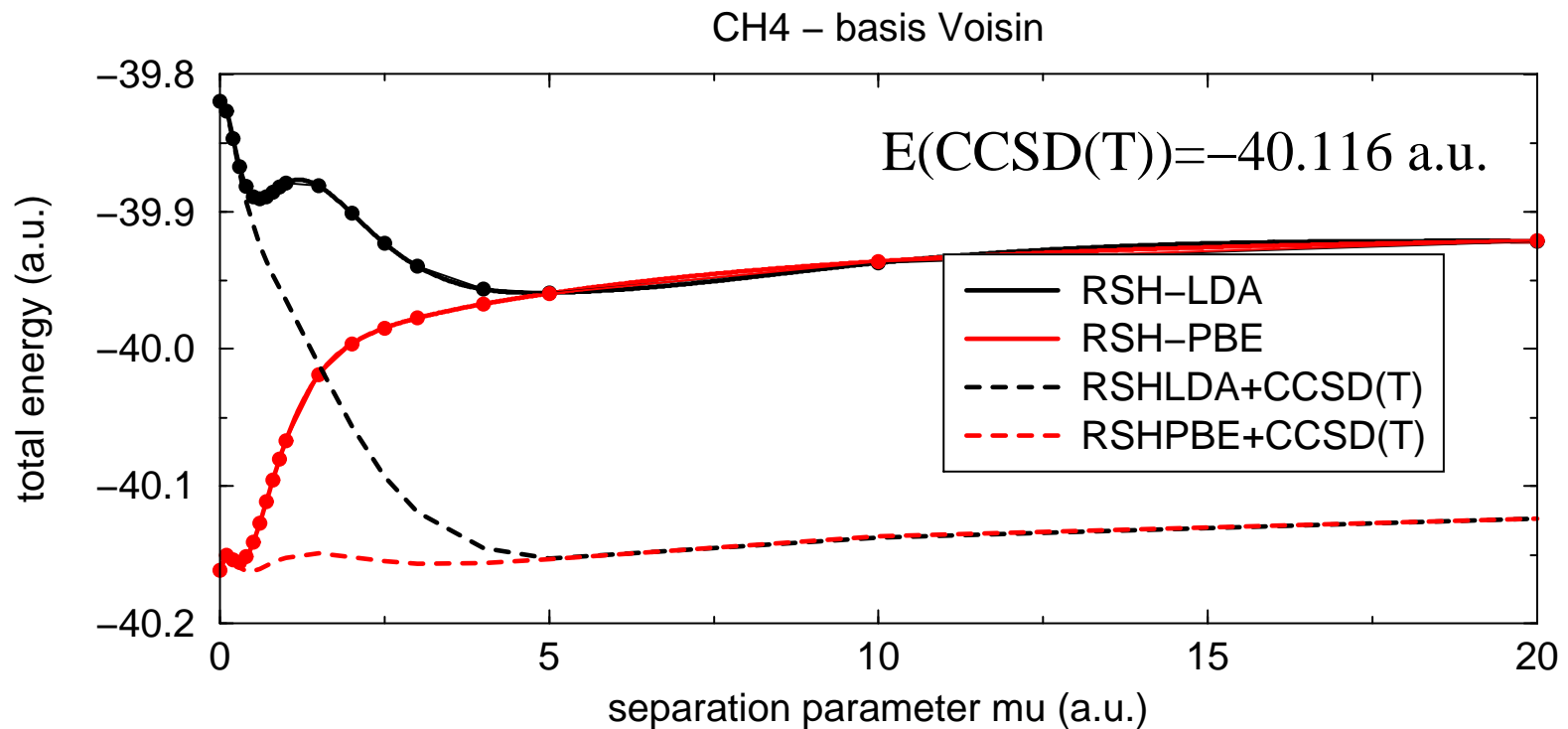
Expected advantages

- Computationally advantageous

  - HF/DFT: $\sim N^3$

  - CCSD(T) $\sim N^7$

  - RPA $\sim N^4$ (dRPA); MP2 $\sim N^5$; RPAx, CISD $\sim N^6$

  - long-range AO integrals not numerous for small μ, as well MO integrals

    in localized orbitals

Expected advantages

- Computationally advantageous

- Should describe long-range correlation effects correctly

- BSSE less important

- Less basis set dependent than "standard methods"

Expected advantages

- Computationally advantageous

CH4–CH4 – basis Voisin

dotted: without BSSE correction

Legend: Hartree–Fock (black), CCSD(T) (red), LDA (blue)

Axis labels: Interaction energy (kcal/mol) vs C–C distance (Angstrom)

Expected advantages

- Computationally advantageous

- Should describe long-range correlation effects correctly
- BSSE less important
- Less basis set dependent than "standard methods"

Choose μ as small as possible

Long-range correlation, RPA

MP2, CISD, CCSD etc.: $E_{Corr.} = \sum_{ijab} t_{ij}^{ab} \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle$

different classes of diexcitations
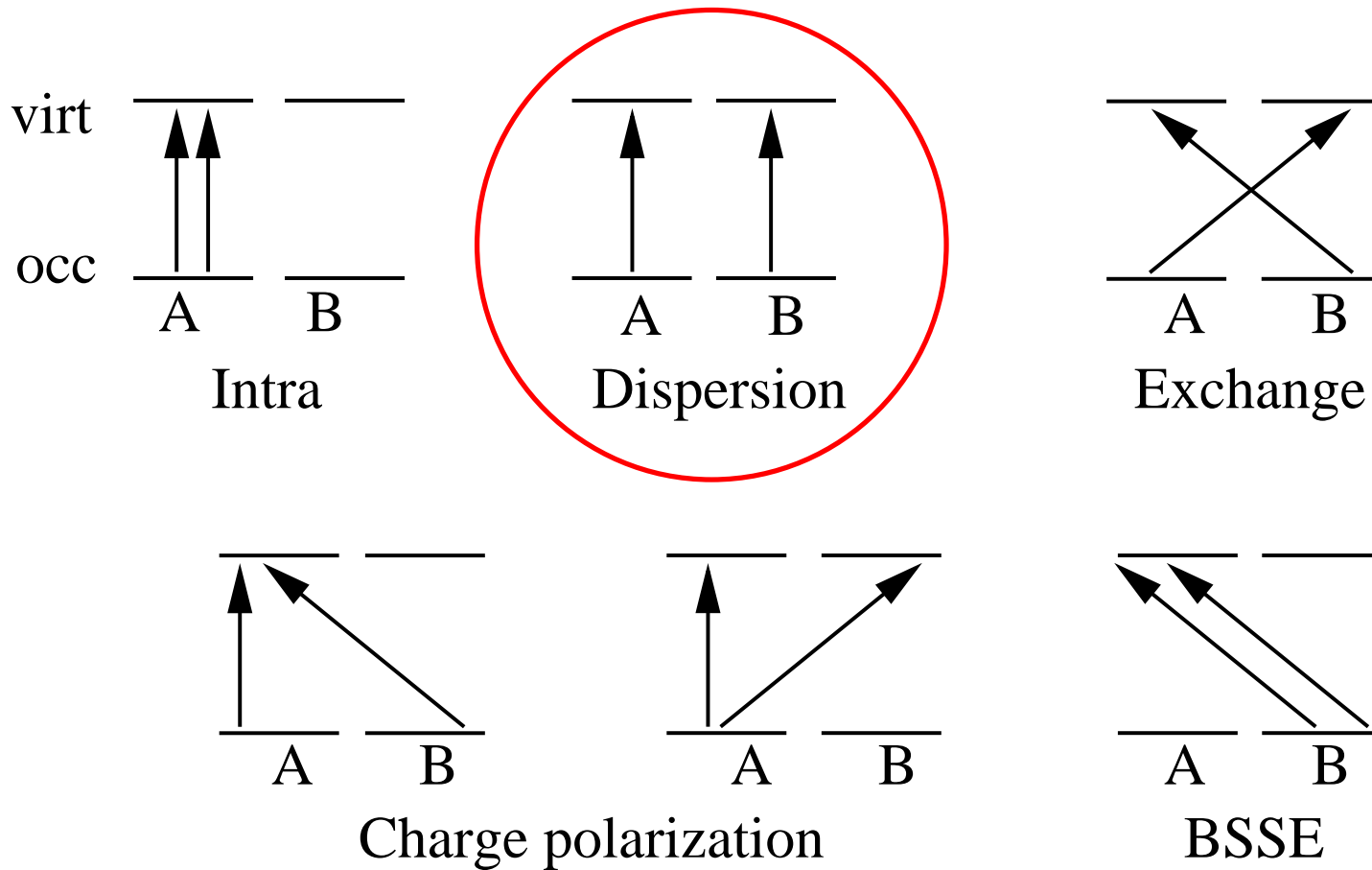
Long-range correlation, RPA

En vogue: Random Phase Approximation (RPA)

- Coupling of singlet mono-excitations

- Equations from excited states $\langle \Psi_0 | [\hat{H}, F] | \Psi_q \rangle = \Delta E_{0q} \langle \Psi_0 | \hat{F} | \Psi_q \rangle$ and

$$
\begin{aligned}
\Psi_0 &= \Phi_0 + \frac{1}{4} \sum_{ia,jb} D_{ia,jb} \Phi_{ij}^{ab} \\
\Psi_q &= \sum_{ia} c_i^a \Phi_i^a
\end{aligned}
$$

- Ground state: ring-CCD equations, infinite summation of ring diagrams in perturbation theory

- Different flavours tested and implemented recently

- Formulation via an adiabatic connection used here

Long-range correlation, RPA

RPA, some elements:

- Matrix equations of type

$$E_{Corr} = \frac{1}{2} \int_0^1 \sum_{ia,jb} (ia|jb)^{lr} (P_{\lambda,c})_{ia,jb} \, d\lambda$$

$$P_{c,\lambda} = 2[(A_\lambda - B_\lambda)^{1/2} M_\lambda^{-1/2} (A_\lambda - B_\lambda)^{1/2} - 1]$$

with matrices A, B and M

$$M_\lambda = (A_\lambda - B_\lambda)^{1/2}(A_\lambda + B_\lambda)(A_\lambda - B_\lambda)^{1/2}$$

$$(A_\lambda)_{ia,jb} = \langle \Phi_i^a | \hat{H}_\lambda | \Phi_j^b \rangle = F_{ab}\delta_{ij} - F_{ij}\delta_{ab} + 2\lambda(ia|jb)^{lr} - \lambda(ij|ab)^{lr}$$

$$(B_\lambda)_{ia,jb} = \langle \Phi_0 | \hat{H}_\lambda | \Phi_{ij}^{ab} \rangle = 2\lambda(ia|jb)^{lr} - \lambda(ib|ja)^{lr}$$

- Dimension only $n_{occ} \times n_{virt}$.

- Energy through a linear functional in the amplitudes

- Correlation energy invariant to orbital rotations

- Size consistent

Orbital localization

- SCF of monomers in monomer basis (canonical or localized orbitals)
- Keep virtual orbitals
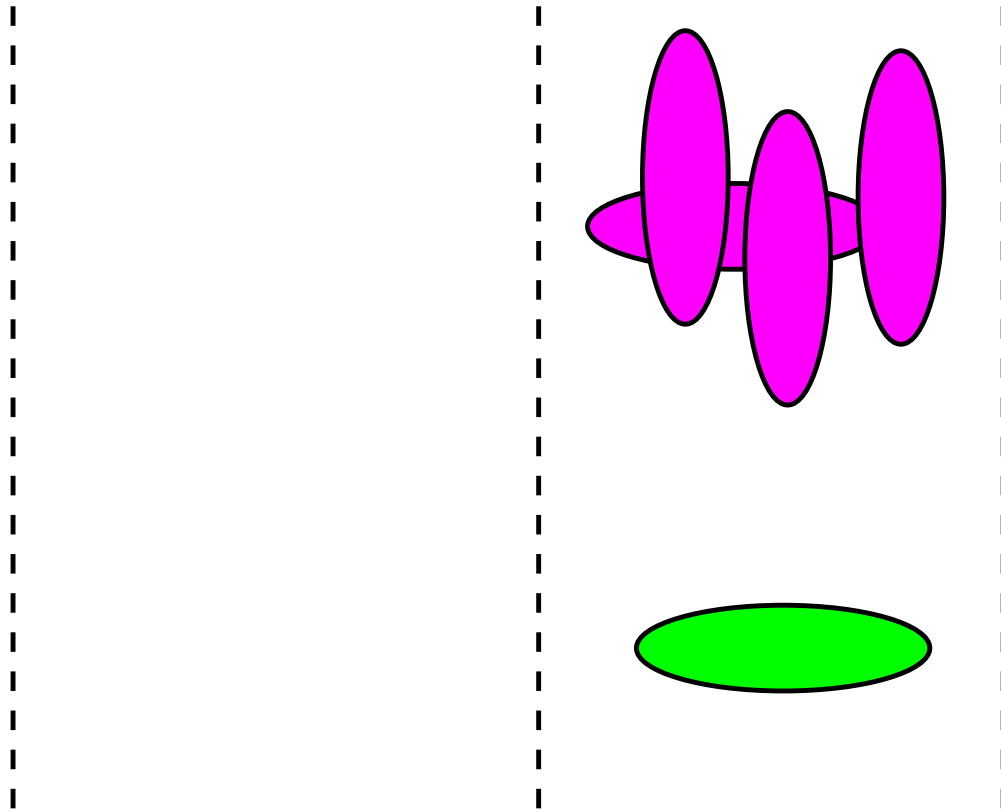
Orbital localization

- SCF of monomers in the dimer basis

- Keep occupied orbitals
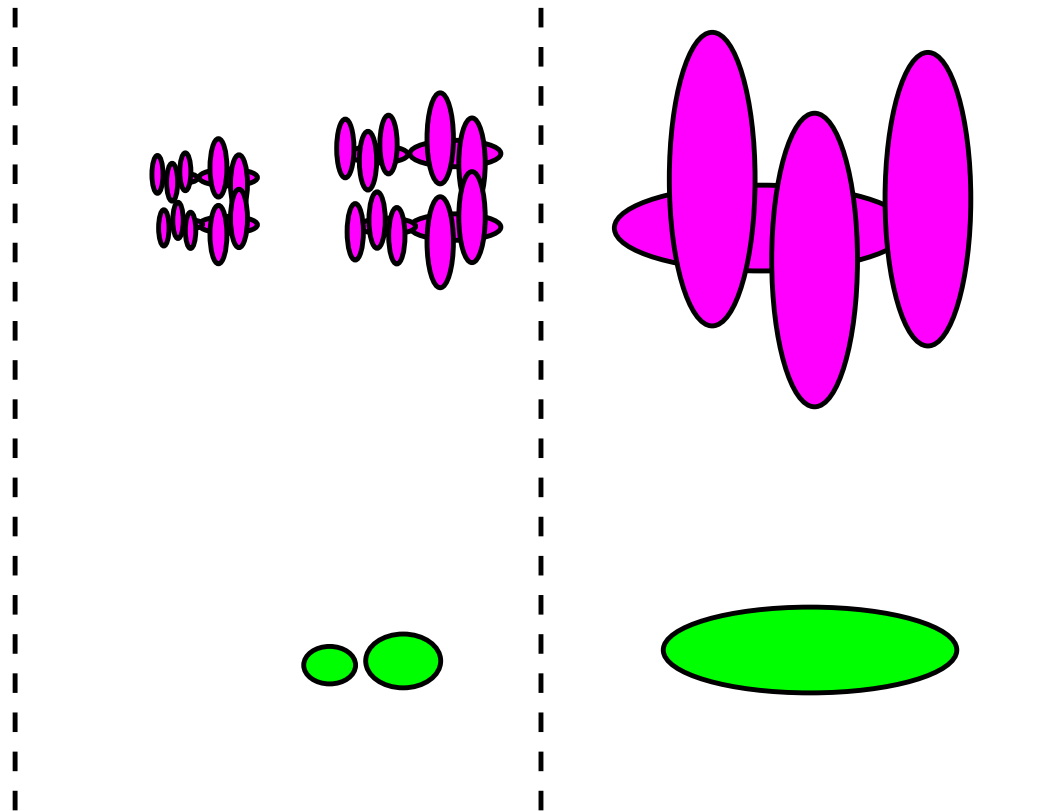
Orbital localization
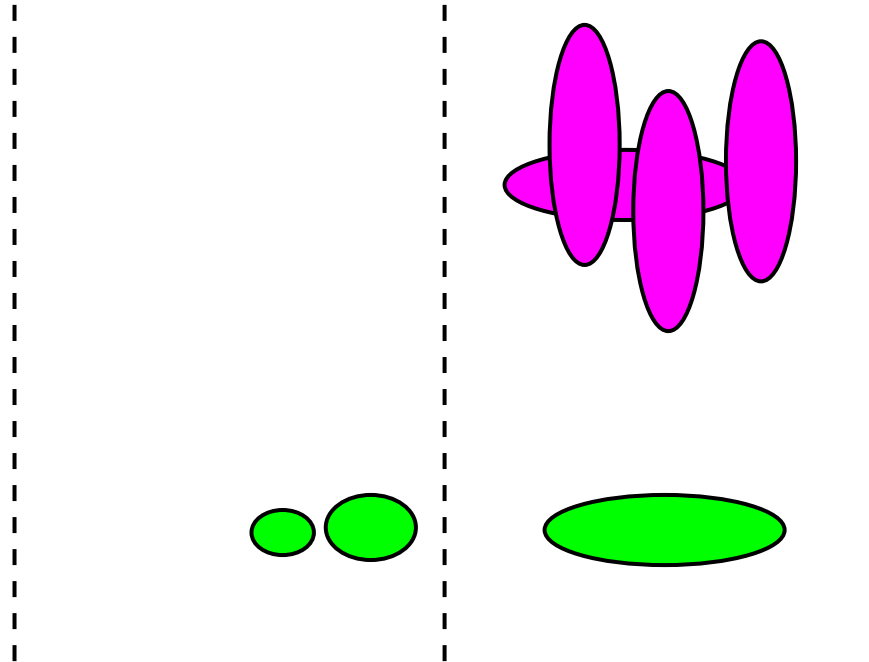
- Occupied orbitals : symmetrical orthogonalisation $\mathbf{S}^{-1/2}$
- Occupied/virtual ones : projection
- Virtuals : symmetric orthogonalisation $\mathbf{S}^{-1/2}$

Orbital localization

Multi-step localization without canonical orbitals: Super-CI

- CI of mono-excited determinants

    SCF iterations

    1. Guess orbitals

    2. Orthogonalization via $\mathbf{S}^{-1/2}$

    3. Construction of the Fock matrix, total energy, convergency ?

    4. Approximate Singles-CI matrix, $\langle \Phi_i^a | \mathbf{H} | \Phi_j^b \rangle \approx F_{ab}\delta_{ij} - F_{ij}\delta_{ab}$
       Best wavefunction : $\Psi = \Phi_0 + \sum_{ia} c_i^a \Phi_i^a$

    5. Correction to first order of the orbitals through the CI coefficients

    $$\phi_i' = \phi_i + \sum_a c_i^a \phi_a \qquad (3)$$

    $$\phi_a' = \phi_a - \sum_i c_i^a \phi_i \qquad (4)$$

    6. Back to step 2

Dispersion-only approximation

Three possibilities:

1. RPA calculation for dimer and monomers, difference:

$$\Delta E_{Corr} = E_{Corr,\ multimer} - E_{Corr,\ monomers}$$

2. Only the dispersion component of the dimer RPA calculation:

$$\Delta E_{Corr} = \sum_{Disp.} t_{ij}^{ab} \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle$$

3. Include only intra and dispersion interactions in the RPA
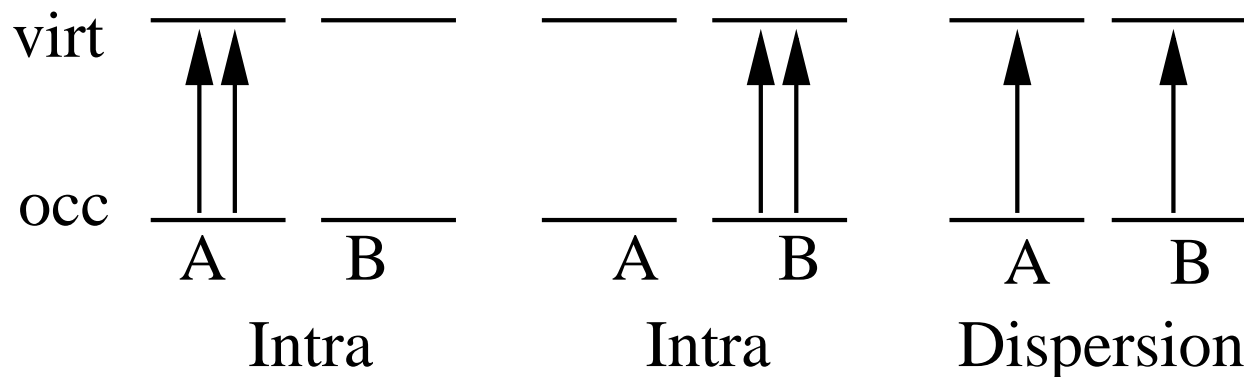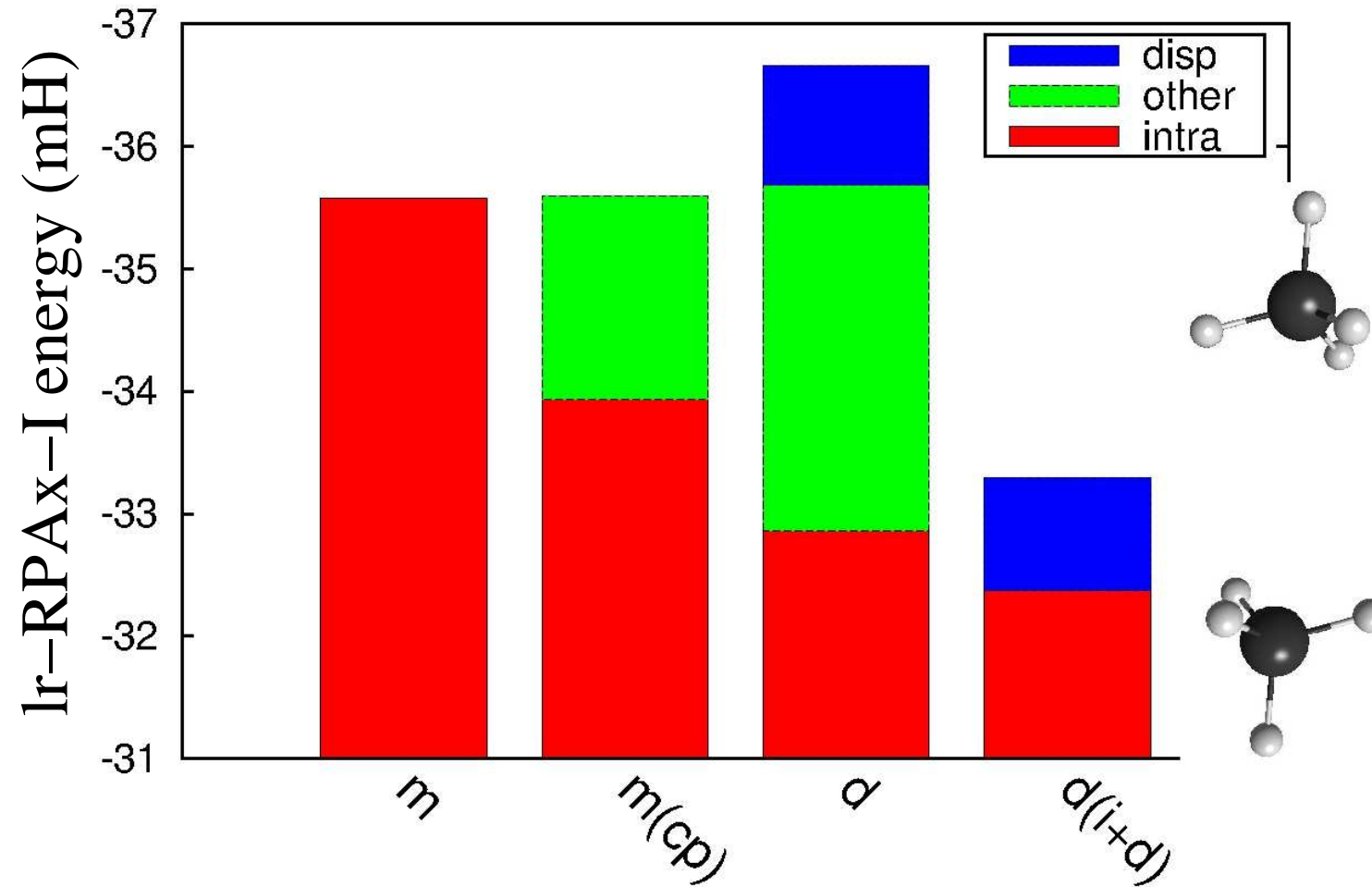
virt

occ

A   B   A   B   A   B

Intra   Intra   Dispersion

Dispersion-only approximation

$\mu = 0.5$ a.u.

Dispersion-only approximation

As a function of the separation parameter μ
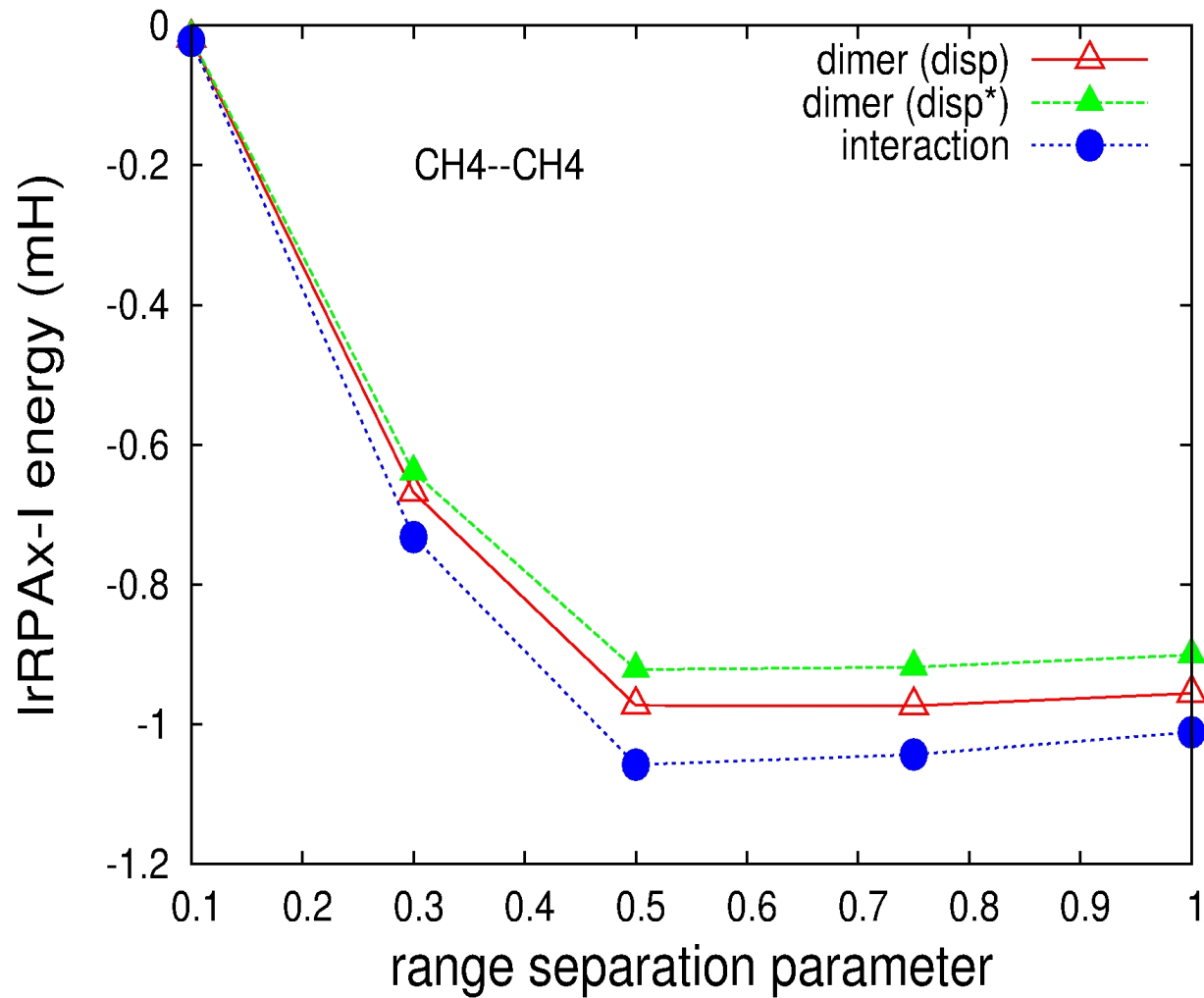
Dispersion-only approximation

$\mu = 0.5$ a.u.
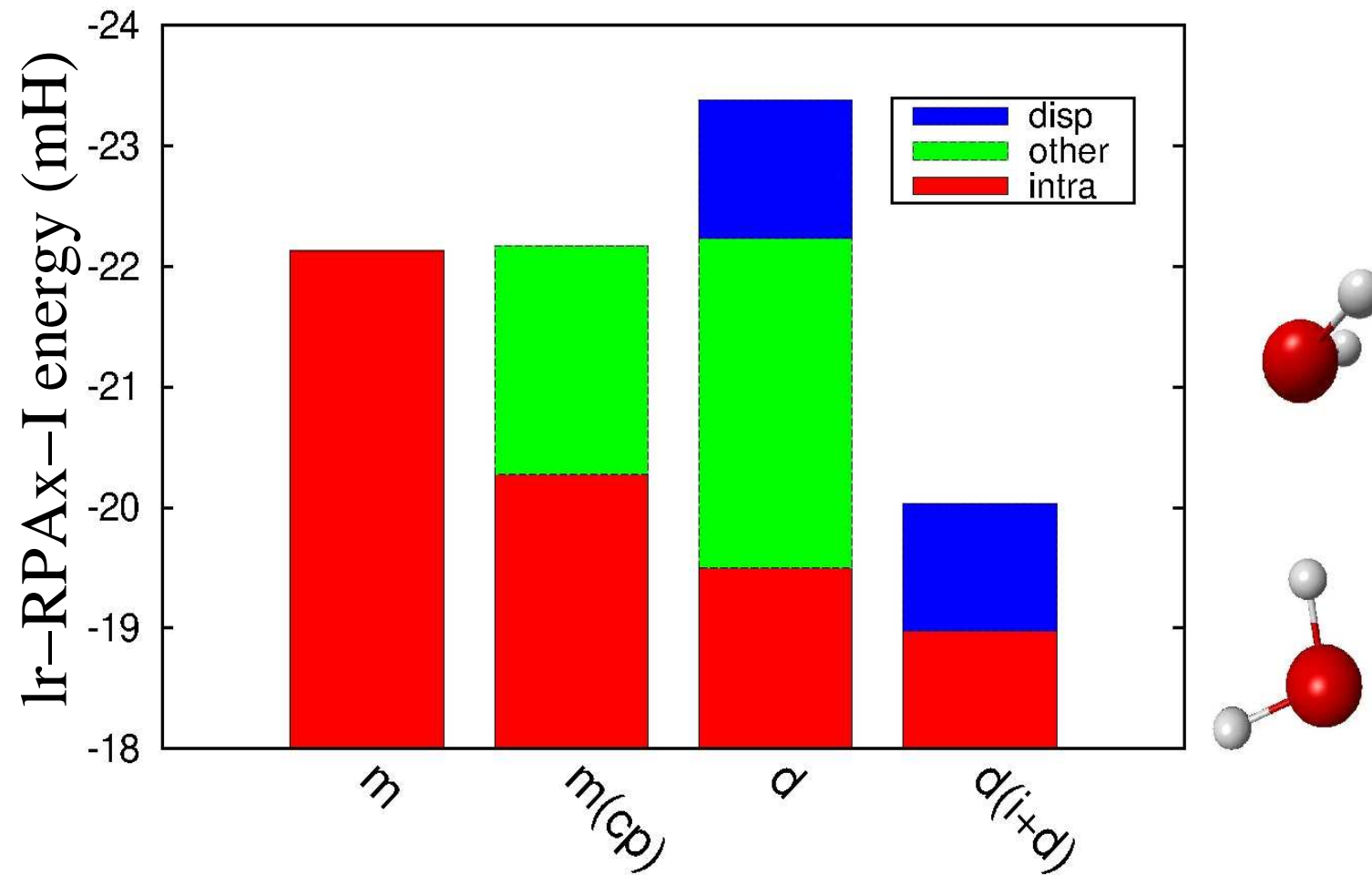
Dispersion-only approximation
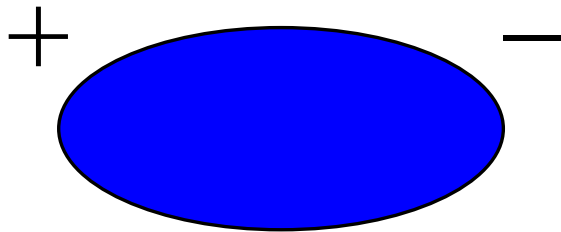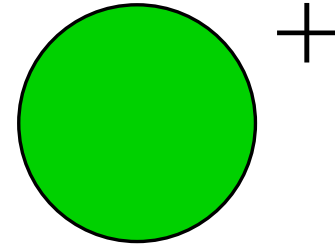
As a function of the separation parameter μ
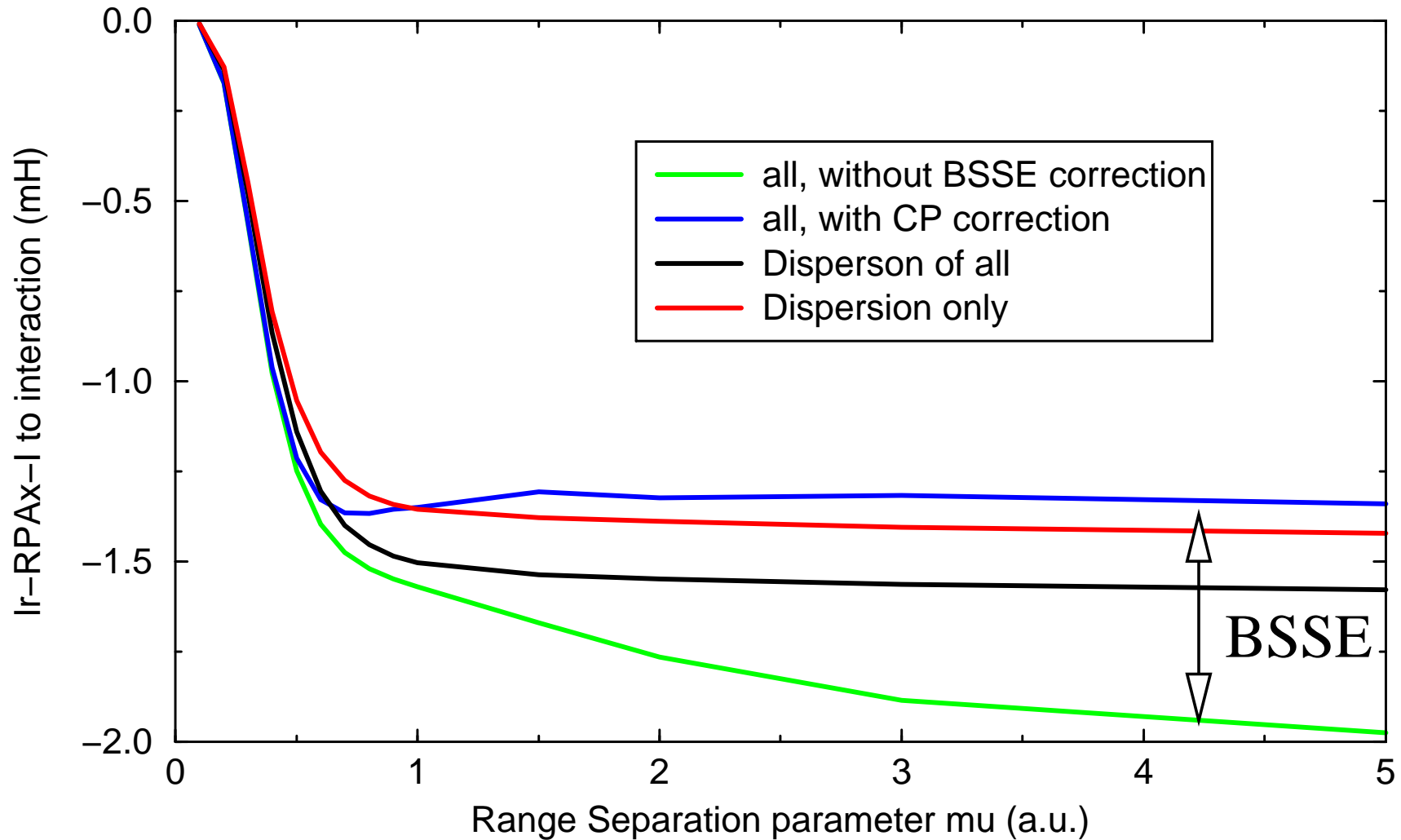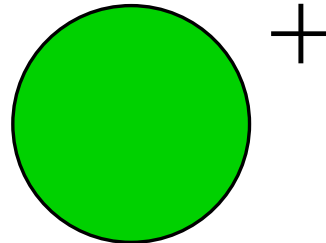
More extreme: $NH_4^+ \ldots H_2O$

Repulsive correlation contribution: monomer correlation larger than in the dimer due to polarization
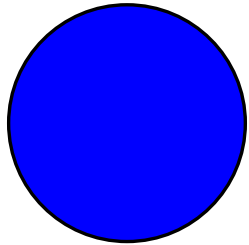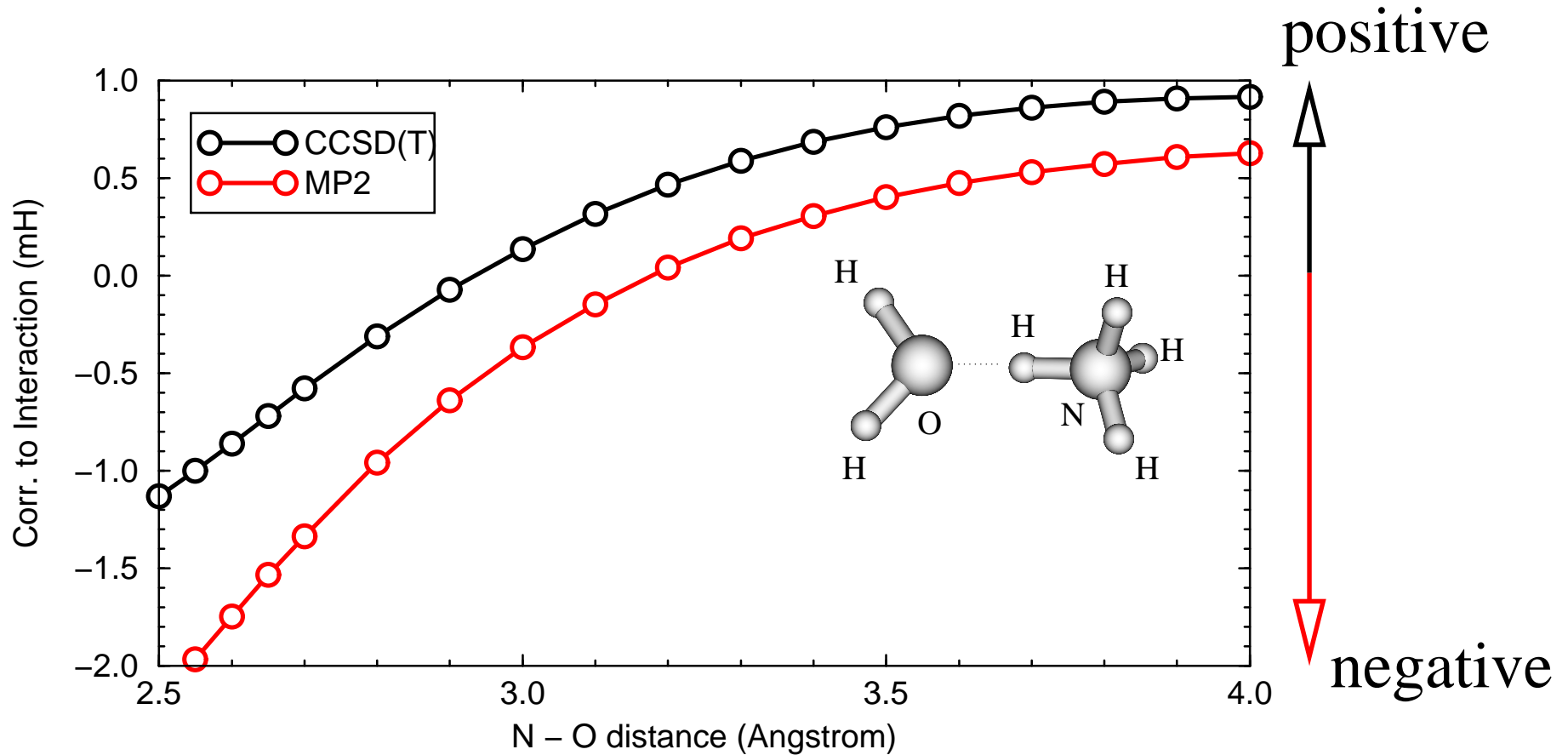

unperturbed density

polarized density

However, dispersion is ALWAYS attractive

More extreme: $NH_4^+ \ldots H_2O$

Correlation contribution to the interaction energy
$\mu \longrightarrow \infty$, i.e. Hartree-Fock wavefunction

More extreme: $NH_4^+ \ldots H_2O$

Repulsive correlation contribution ($d = 3.5\,\text{Å}$)