Roscoff 2018 – Theoretical chemistry

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Organisation

Wednesday 3 h lecture + 3 h application; Thursday + 3 h practical work; Friday 3 h lecture

- Schrödinger's equation and simple systems
  - Bohr model
  - 1D box, harmonic oscillator
  - Hydrogen atom and orbitals
- polyelectronic systems
  - Simplified models: LCAO, hybrids, Hückel theory
  - Wavefunctions: Slater determinants
  - Hartree-Fock
  - Atomic basis functions
- Bond breaking: Configuration Interaction, multi-determinantal wavefunctions
- Dynamical correlation: DFT, CI, perturbation, Coupled-Cluster
- Localized orbitals: what changes?

Organisation

- Applications, wednesday afternoon
  - Slater rules, Hartree-Fock calculations, bond breaking
  - some calculations with commercial programs, Gaussian, Molpro, GAMESS, Dalton

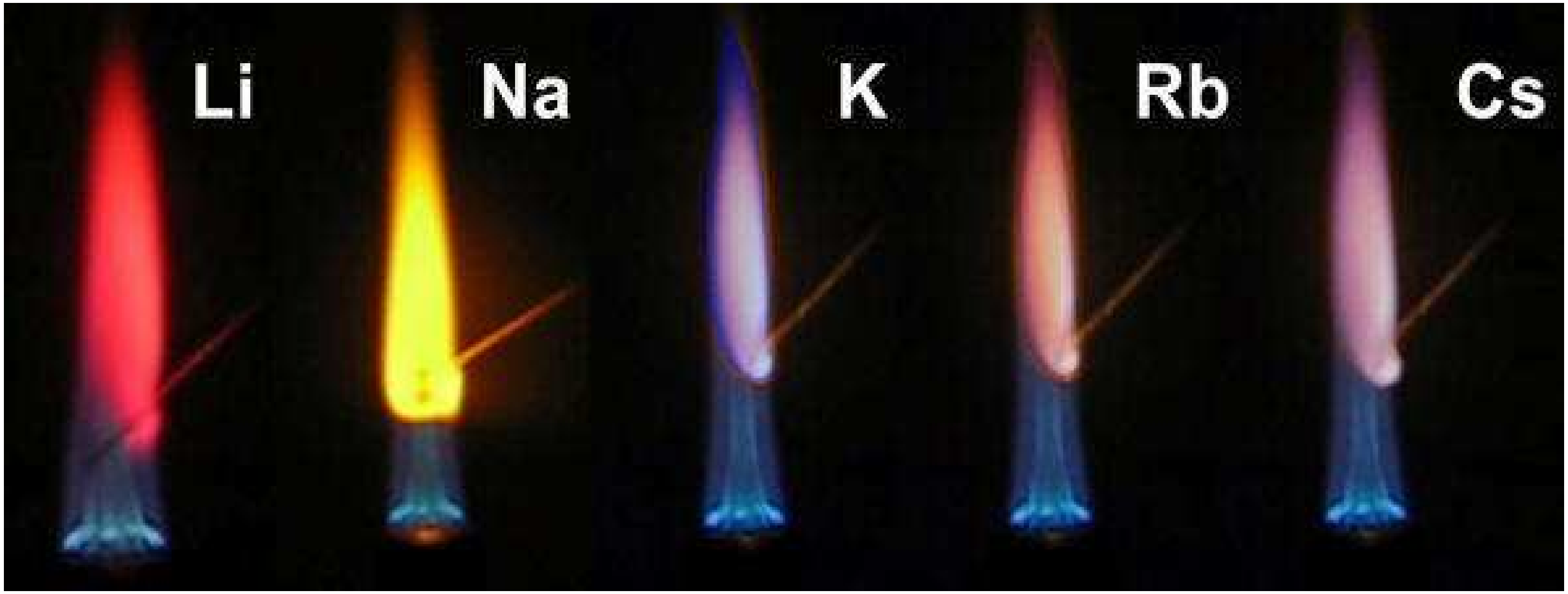
  All this for calculating the dissociation energy of the F_2 molecule.
- Practical work Thursday afternoon
  - NCI - non-covalent interactions
  - Mathematics with Mathematica

Spectroscopy

Hydrogen spectrum in the sun light - Joseph Fraunhofer

German stamp, 1987

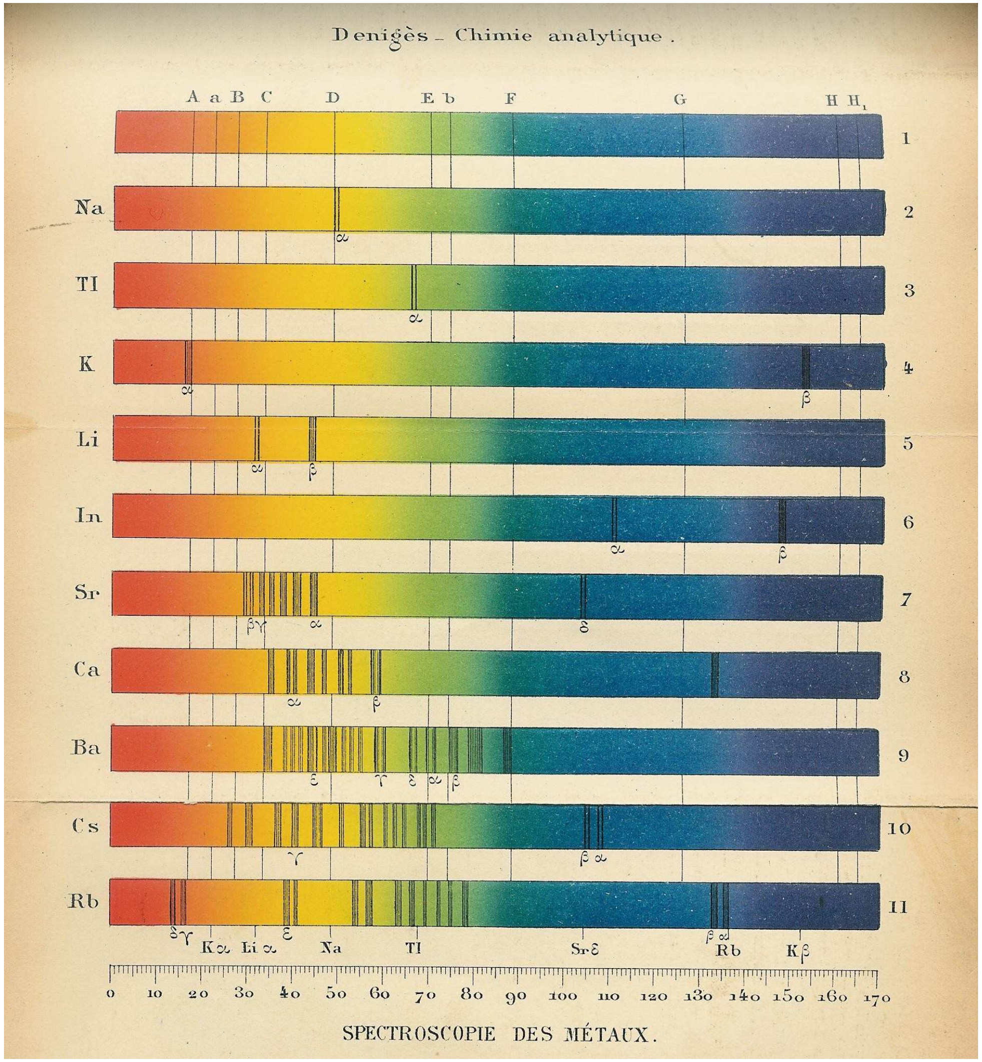
Spectroscopy

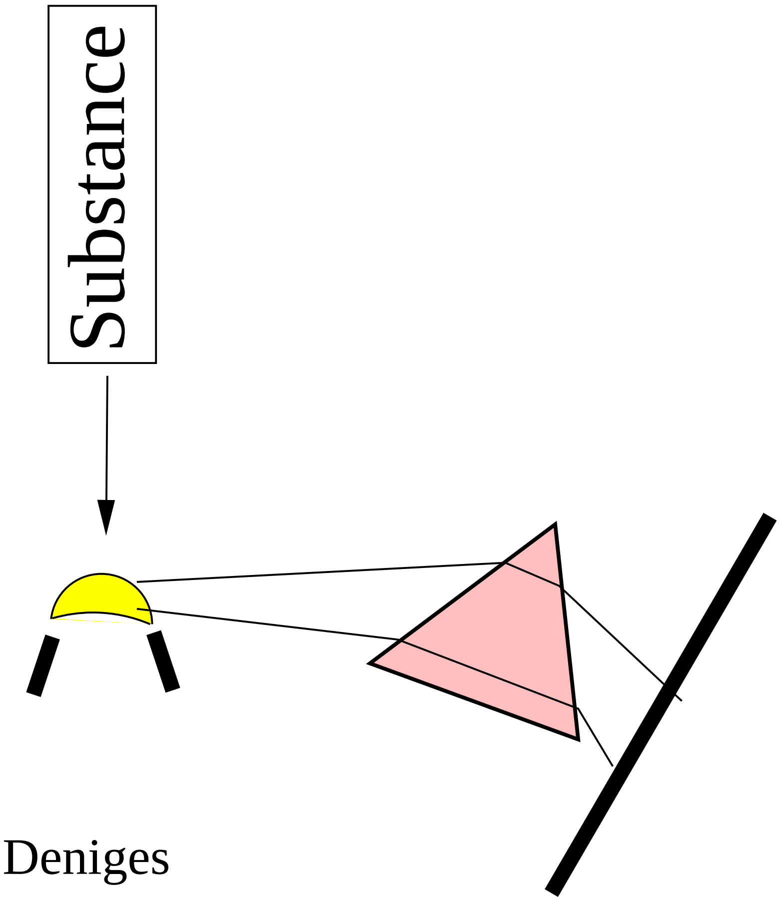


Flame coloration from atomic spectra

Spectroscopy

Atomic emission spectra, helping to identify elements





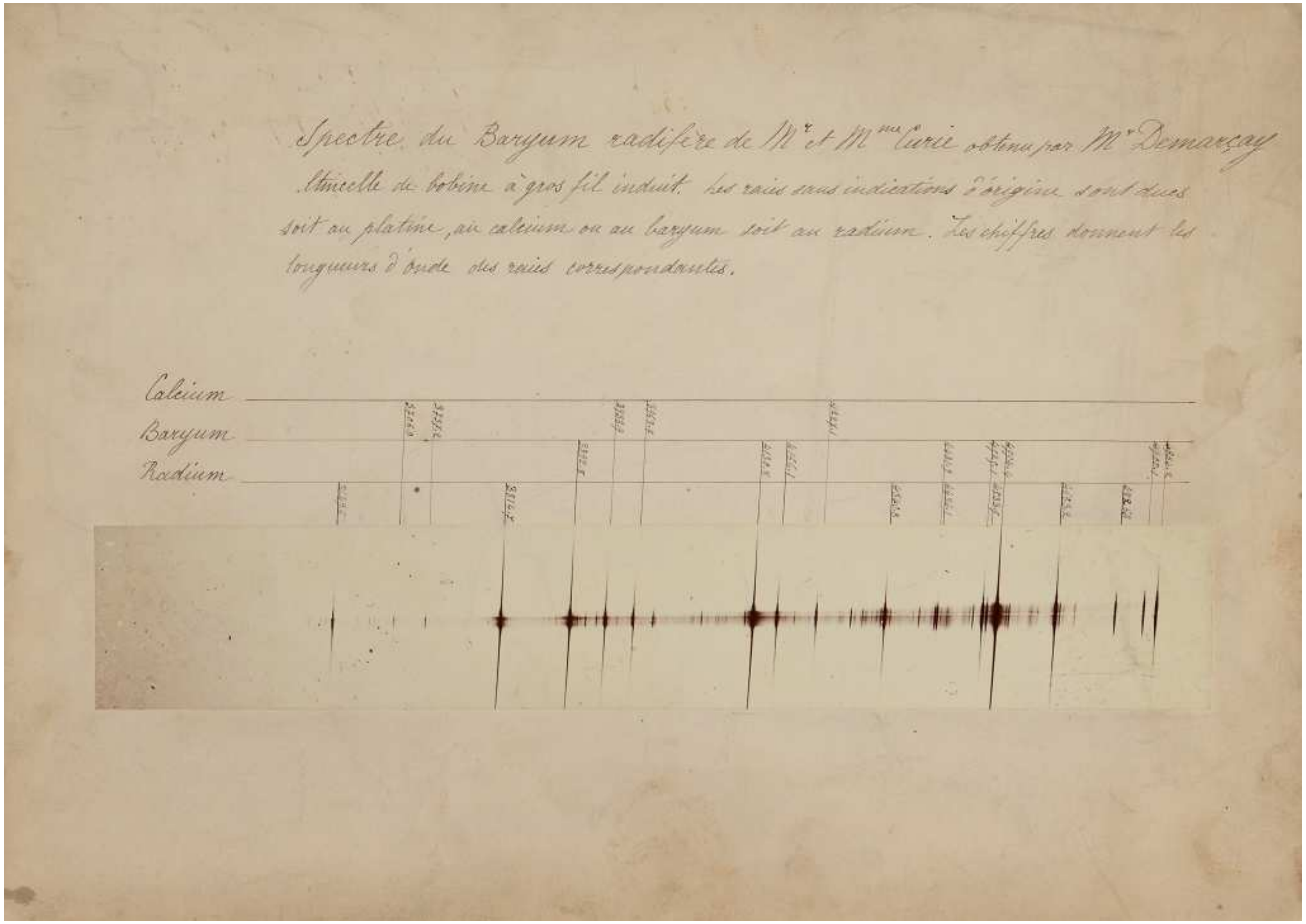
Deniges

Chimie analytique

Paris 1913

Spectroscopy

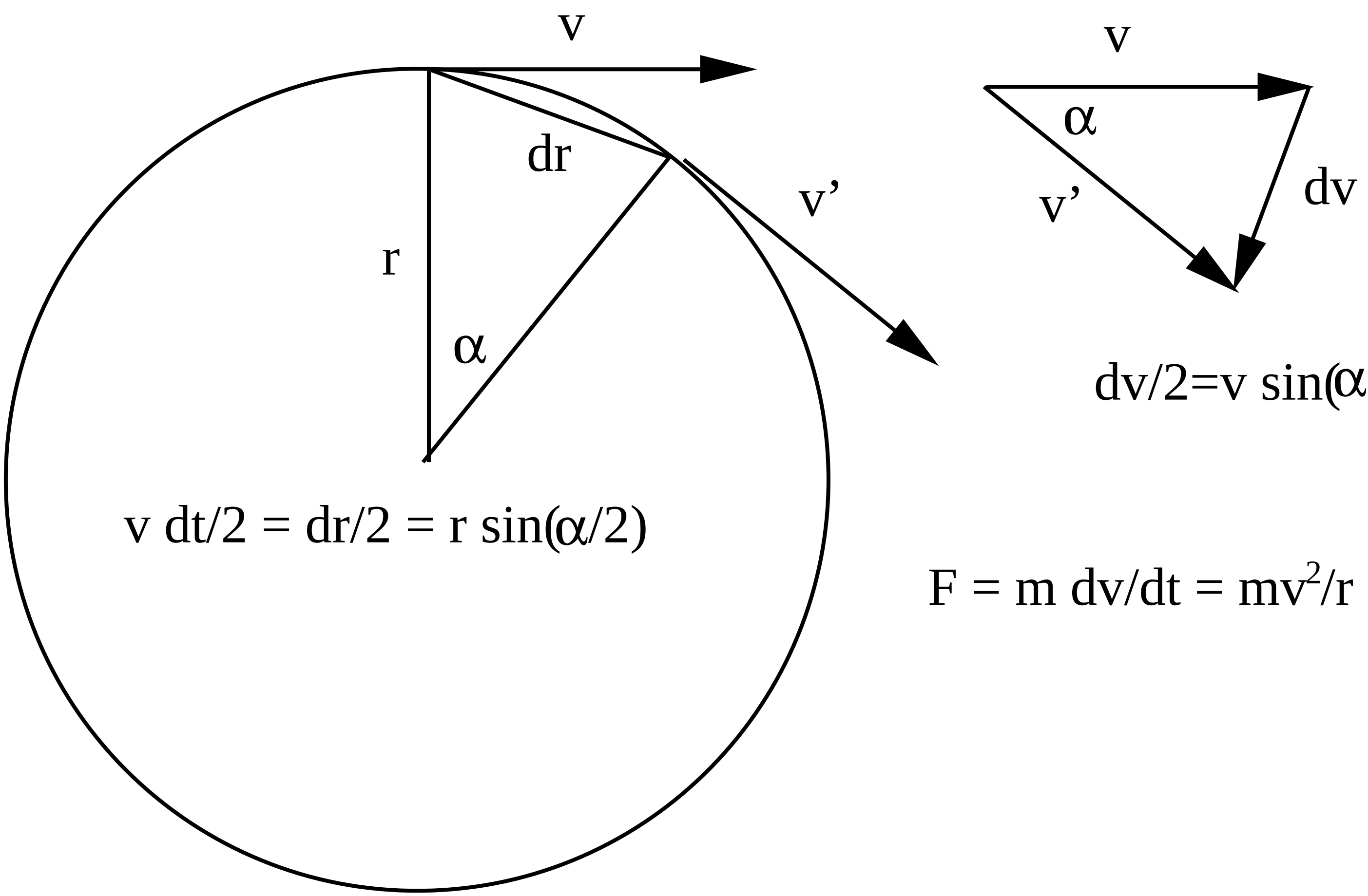
Identification of radium, 1898



Spectre du Baryum radifère de Mr et Mme Curie obtenu par Mr Demarçay
Étincelle de bobine à gros fil induit. Les raies sans indications d'origine sont dues
soit au platine, au calcium ou au baryum soit au radium. Les chiffres donnent les
longueurs d'onde des raies correspondantes.

Fig. 92. — Appareil de M. Demarçay pour produire les spectres électriques.

Bohr model and Schrödinger’s equation

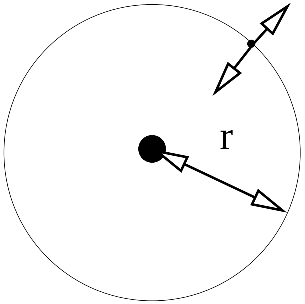


$v\,dt/2 = dr/2 = r \sin(\alpha/2)$

$dv/2 = v \sin(\alpha/2)$

$F = m\,dv/dt = mv^2/r$

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 $\hbar$: $|\vec{L}| = m\,r\,v \;=\; n\,\hbar$

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

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

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

- 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

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

Simple systems, atoms, molecules, solids

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

- 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

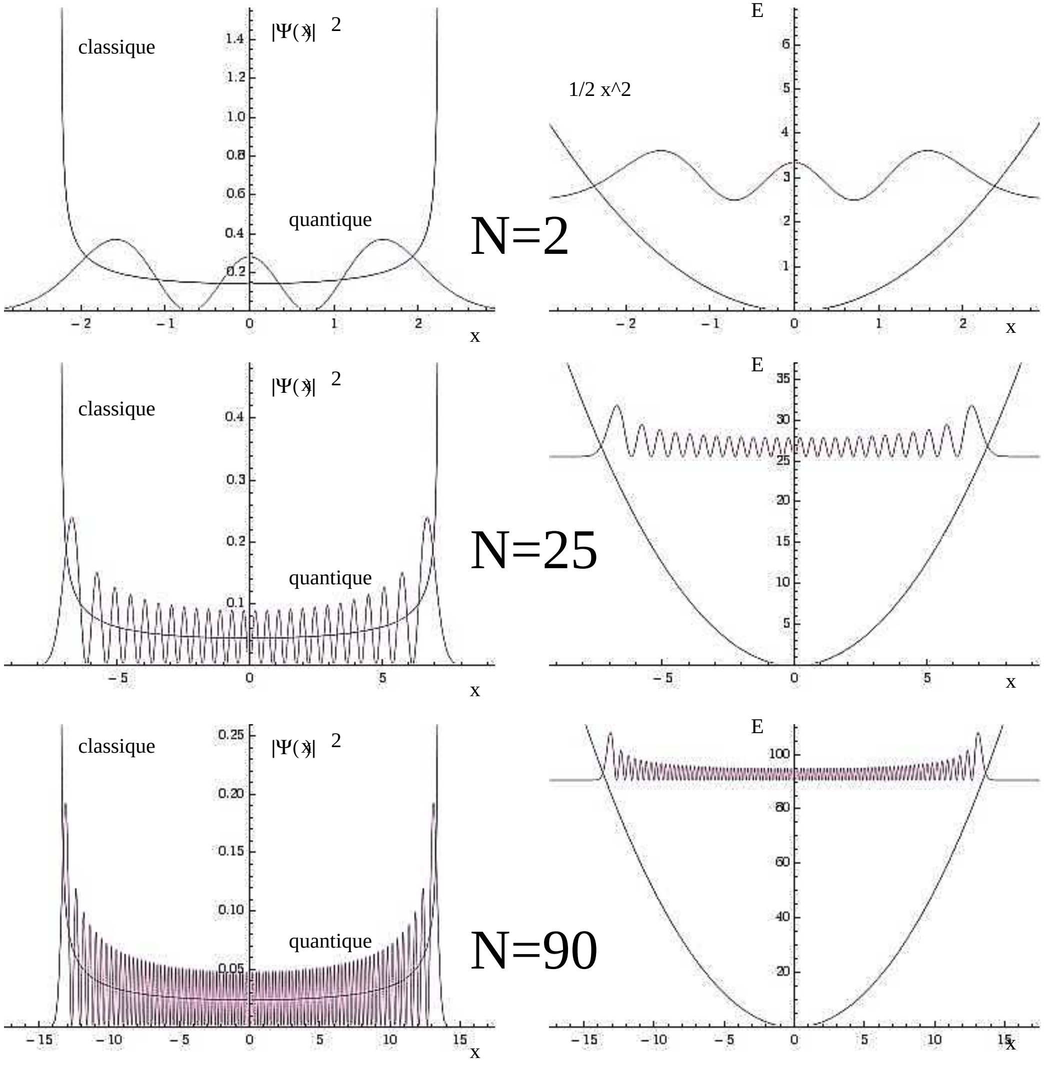
- Solution in two steps ($\alpha = \sqrt{\mu\omega/\hbar}$, $\omega = \sqrt{k/\mu}$):
  - $x \longrightarrow \infty$: $\Psi(x) \sim e^{-\frac{(\alpha x)^2}{2}}$
  - Correction as polynomial in x:

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

- Energy levels $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$
- Application: vibrational spectroscopy (IR, RAMAN)

Simple systems

Harmonic oscillator:



N=2

N=25

N=90

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 $\rho = r/n$:
  - $r \longrightarrow \infty$: $\rho\, R(\rho) \sim e^{-\rho}$; $r \longrightarrow 0$: $\rho\, R(\rho) \sim \rho^{\ell+1} e^{-\rho}$
  - Complete solution $R_{n\ell}(\rho) = N_{n\ell} L^{2\ell+1}_{n+\ell}(\rho)\rho^{\ell} e^{-\rho}$ with associated Laguerre polynomials $L^{2\ell+1}_{n+\ell}(\rho)$.
  - 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

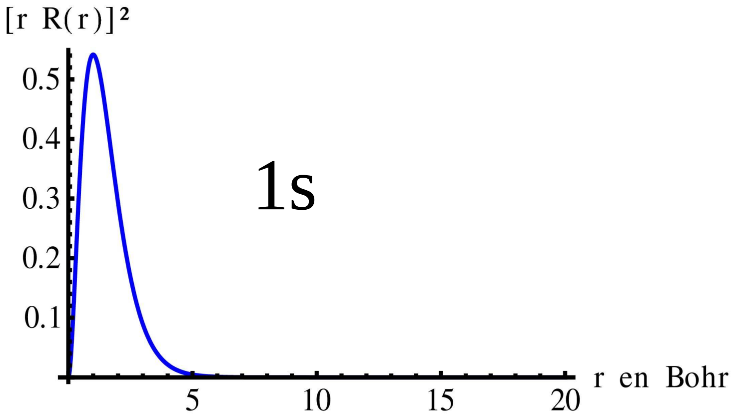
$$\Psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$$

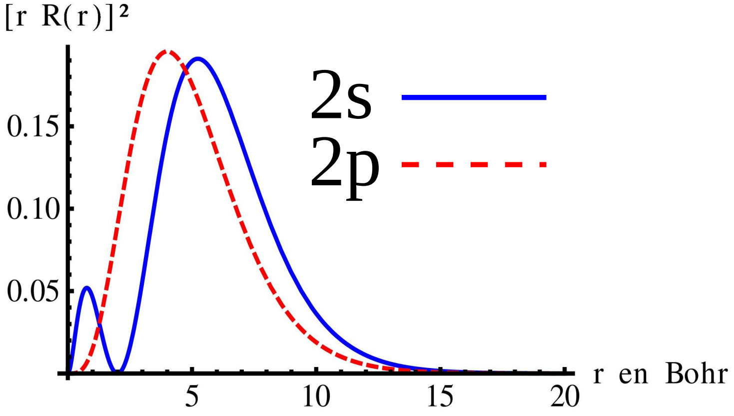
$$R_{n\ell}(r) = N_{nl} \left(\frac{2r}{n} \right)^{\ell} L_{n-\ell-1}^{2\ell+1} \left(\frac{2r}{n} \right) e^{-(r/n)}$$

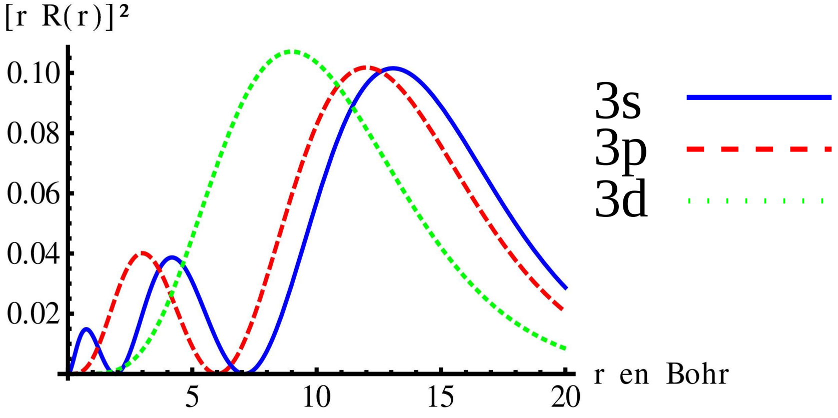
- Classification: $\ell = 0 \longrightarrow s$, $\ell = 1 \longrightarrow p$, $\ell = 2 \longrightarrow d$, $\ell = 3 \longrightarrow f$
- Spherical harmonics $Y_{\ell m}$ complex, real combinations, multiplied with r^{ℓ} = real solid harmonics = $Y_{\ell m} + Y_{\ell -m}$, $-i(Y_{\ell m} - Y_{\ell -m})$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

Simple systems

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

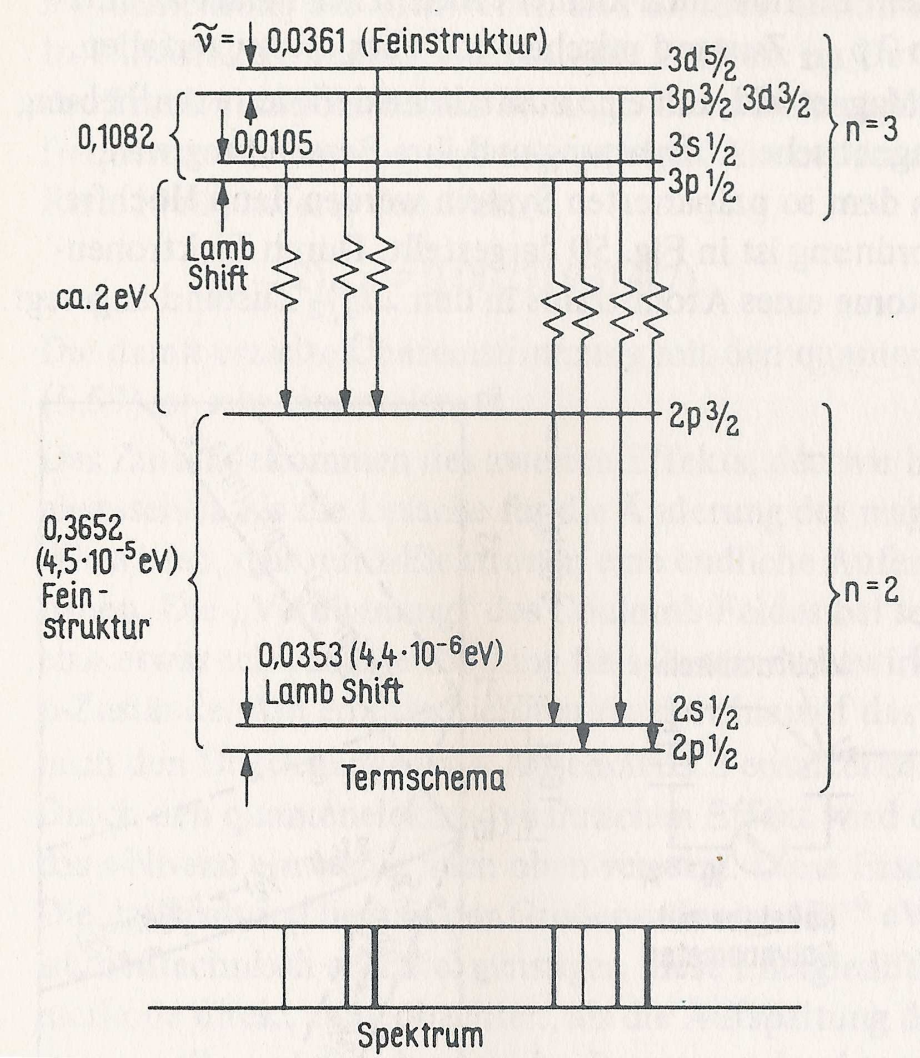






Simple systems

Complete treatment



Spin−Orbit coupling: fine structure

Relativistic effects: LS −> J

Quantum electrodynamics: Lamb shift

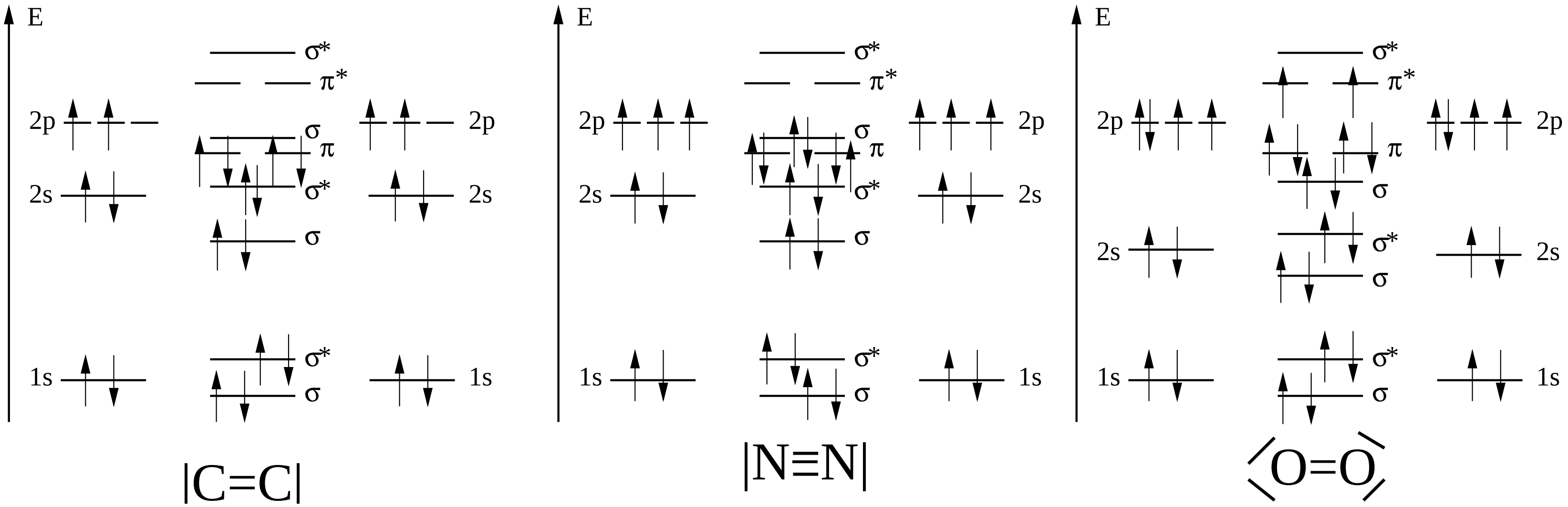
Hyperfine structure (spin−spin coupling)

Th. Mayer−Kuckuk, Atomphysik
Teubner, 1986

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

Working with atomic orbitals

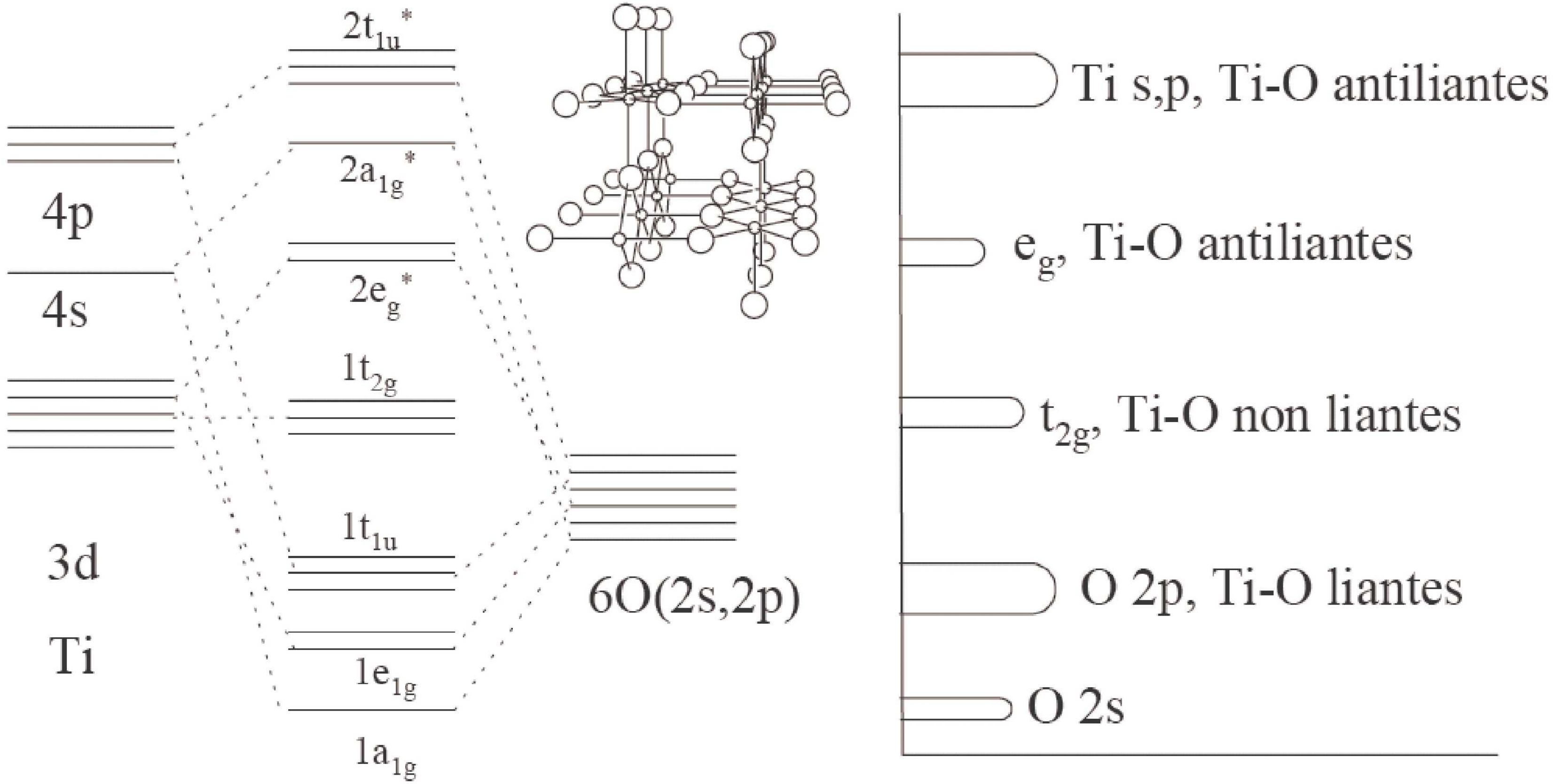
- Multi-electron system (atom) may be described by hydrogen-like orbitals
- Diatomics: combine atomic orbitals of same symmetry and near energy to molecular orbitals with simple rules: correlation diagrams



- Bonding, anti-bonding and non-bondig orbitals, stability of diatomics
- Spin ground states, reactivity

Working with atomic orbitals

Works even for solids, TiO_2



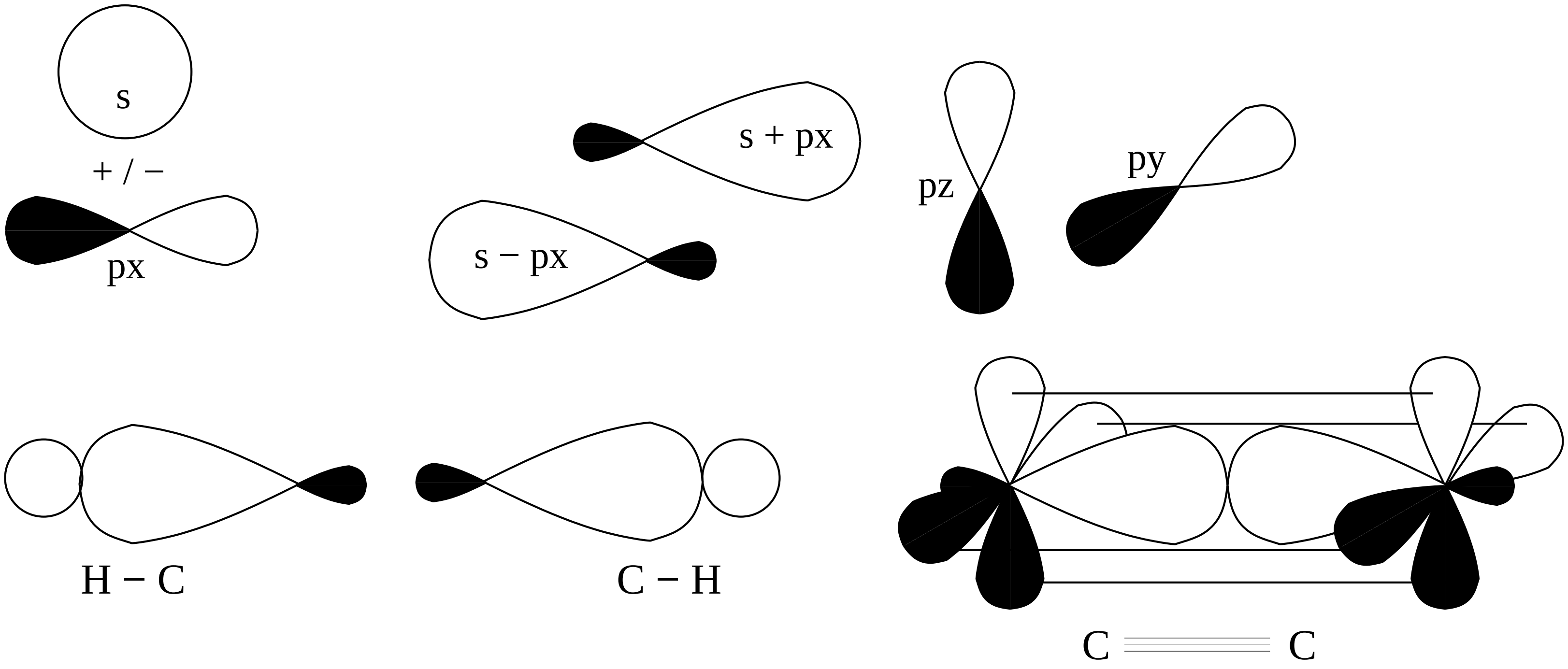
OM octaèdre TiO_6

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, $H_2C{=}CH_2$, $H_3C{-}CH_3$

$$\begin{aligned} \phi^{sp}_{1,2} &= s \pm p_z \qquad \text{sp hybrid} \\ \phi_3 &= p_x \\ \phi_4 &= p_y \end{aligned}$$

Working with atomic orbitals

Triangular situation: sp^2 hybrids

$$\begin{aligned}
\phi_1^{sp^2} &= \frac{1}{\sqrt{6}}\,s + \sqrt{\frac{2}{3}}p_x && \text{sp}^2\text{ hybrid} \\
\phi_{2,3}^{sp^2} &= \frac{1}{\sqrt{3}}\,s - \frac{1}{\sqrt{6}}\,p_x \pm \frac{1}{\sqrt{2}}p_y && \text{sp}^2\text{ hybrid} \\
\phi_4 &= p_z
\end{aligned}$$

Tetrahedral situation (4 bonds)

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

Very idealized situations — qualitatively correct, intuitive chemistry

Working with atomic orbitals

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

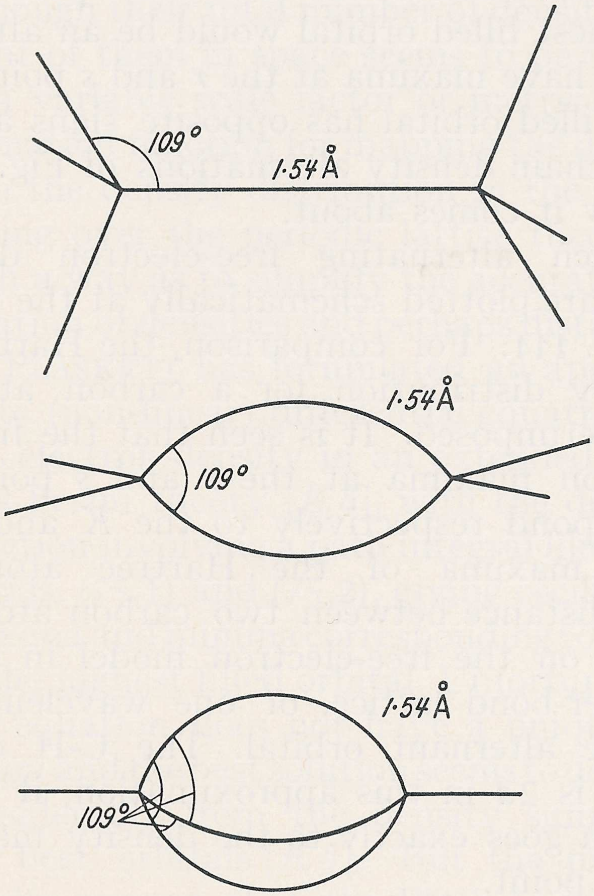


Fig. 109. Double bonds as bent sigma bonds.

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

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

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 $\langle\chi_\alpha|\hat{h}|\chi_\beta\rangle = b < 0$
- Overlap zero between different atoms
- Parametrized matrix elements

Hückel theory

How to satisfy $\hat{h}\,\phi_i(\vec{\mathrm{r}}) = \epsilon_i\,\phi_i(\vec{\mathrm{r}})$?
Develop into the atomic basis functions

$$\begin{aligned}
\hat{h}\sum_\alpha c_{\alpha i}\chi_\alpha(\vec{\mathrm{r}}) &= \epsilon_i\sum_\gamma c_{\gamma i}\chi_\gamma(\vec{\mathrm{r}}) \\
\sum_\alpha c_{\alpha i}\underbrace{\langle\chi_\beta|\hat{h}|\chi_\alpha\rangle}_{:=h_{\alpha\gamma}} &= \epsilon_i\sum_\gamma c_{\gamma i}\underbrace{\langle\chi_\beta|\chi_\gamma\rangle}_{=\delta_{\beta\gamma}} \\
\sum_\alpha h_{\alpha\gamma}c_{\alpha i} &= \epsilon_i\,c_{\gamma i}
\end{aligned}$$

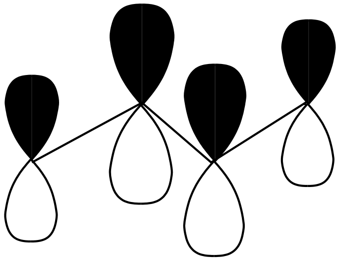
Simple eigenvalue problem

Hückel theory

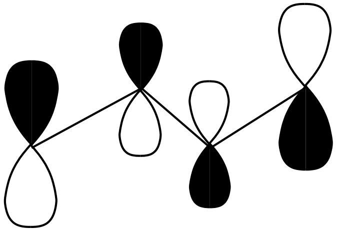
Example butadiene $CH_2{=}CH{-}CH{=}CH_2$:

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

- 4 eigenvalues $\frac{1}{2}\left(2a \pm b \pm \sqrt{5}b\right)$
- Corresponding eigenvectors: + + + +, + + - -, + - - +, + - + -
- 4 π electrons to be inserted into the two lowest orbitals



a + 1.62 b



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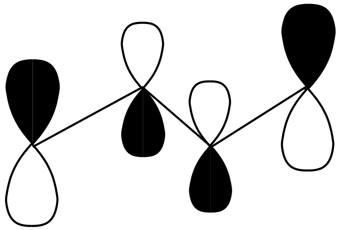
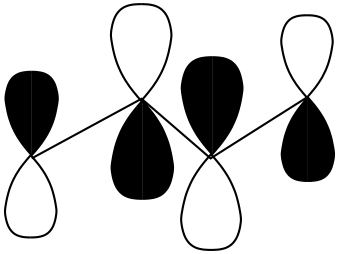


a − 0.62 b



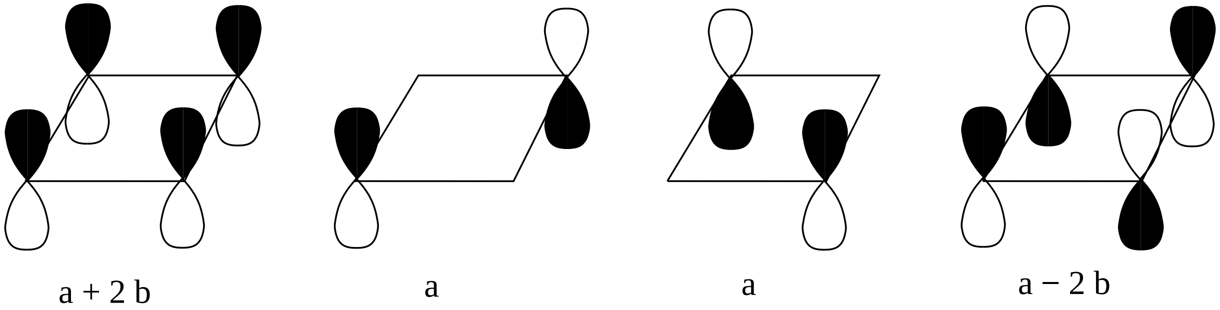
a − 1.62 b

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, $a + 2b$



- 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

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

Many-electron wavefunctions

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

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

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

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

Other possibility

$$\begin{aligned}\Psi^{II}(\vec{r}_1, s_1, \vec{r}_2, s_2) &= \left[\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)\right]\alpha(s_1)\alpha(s_2) \\ &= \Phi_A(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2) \times \Theta_S(s_1, s_2)\end{aligned}$$

3 possibilities for symmetric spin parts

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

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)

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

Many-electron wavefunctions

However:

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

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 for instance a total energy $E \;=\; \langle\Psi|\hat{H}\,\Psi\rangle$ or only $\hat{H}\,\Psi\rangle$ when Ψ is a Slaterdeterminant

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

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

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

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

Calculate with Slater determinants

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

$$\begin{aligned}
& \langle 1\bar{1}2\bar{2}\ldots i\ldots n\bar{n}|\hat{O}_1|1\bar{1}2\bar{2}\ldots j\ldots n\bar{n}\rangle \\
= \quad & \frac{1}{(2n)!}\left\langle \underbrace{\det}_{(2n)!\text{ terms}} \;|\; \underbrace{\sum}_{2n\text{ terms}} \;|\; \underbrace{\det}_{(2n)!\text{ terms}} \right\rangle \\
= \quad & \frac{1}{(2n)!}\int\ldots\int f(\vec{r}_1,\vec{r}_2\ldots\vec{r}_{2n})\left(\sum_k \hat{h}(\vec{r}_k)\right) g(\vec{r}_1,\vec{r}_2\ldots\vec{r}_{2n})\, d^3r_1\ldots d^3r_{2n} \\
= \quad & \langle\phi_1|\phi_1\rangle\langle\bar{\phi}_1|\bar{\phi}_1\rangle\ldots\langle\phi_i|\hat{h}|\phi_j\rangle\ldots\langle\phi_n|\phi_n\rangle\langle\bar{\phi}_n|\bar{\phi}_n\rangle \\
= \quad & \langle\phi_i|\hat{h}|\phi_j\rangle
\end{aligned}$$

- as each of the $(2n)!$ terms has to appear in the same ordering on the left and on the right,
- as each of $2n$ operators acts equally on each electron,
- as the integration factorizes,
- as orbitals are orthogonal, e.g. $\langle\phi_1|\hat{h}|\phi_1\rangle\ldots\langle\phi_i|\phi_j\rangle\ldots\langle\bar{\phi}_n|\bar{\phi}_n\rangle = 0$.

Calculate with Slater determinants

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

$$\begin{aligned}
\langle 1\bar{1}2\bar{2}\ldots i\ldots k\ldots n\bar{n}|\hat{O}_1|1\bar{1}2\bar{2}\ldots j\ldots \ell\ldots n\bar{n}\rangle &= 0 \\
\langle 1\bar{1}2\bar{2}\ldots i\ldots n\bar{n}|\hat{O}_1|1\bar{1}2\bar{2}\ldots j\ldots n\bar{n}\rangle &= \langle\phi_i|\hat{h}|\phi_j\rangle \\
\langle 1\bar{1}2\bar{2}\ldots n\bar{n}|\hat{O}_1|1\bar{1}2\bar{2}\ldots n\bar{n}\rangle &= 2\sum_{i=1}^{n}\langle\phi_i|\hat{h}|\phi_i\rangle
\end{aligned}$$

Useful:

- Hartree-Fock energy:

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

- Fock matrix

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

Calculate with Slater determinants

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

$$\begin{aligned}
\langle 1\bar{1}2\bar{2}\ldots i\ldots j\ldots k\ldots n\bar{n}|\hat{O}_2|1\bar{1}2\bar{2}\ldots p\ldots q\ldots r\ldots n\bar{n}\rangle &= 0 \\
\langle 1\bar{1}2\bar{2}\ldots i\ldots \bar{j}\ldots n\bar{n}|\hat{O}_2|1\bar{1}2\bar{2}\ldots p\ldots \bar{q}\ldots n\bar{n}\rangle &= \langle \phi_i\phi_j|\hat{g}|\phi_p\phi_q\rangle \\
\langle 1\bar{1}2\bar{2}\ldots i\ldots j\ldots n\bar{n}|\hat{O}_2|1\bar{1}2\bar{2}\ldots p\ldots q\ldots n\bar{n}\rangle &= \langle \phi_i\phi_j|\hat{g}|\phi_p\phi_q\rangle \\
&\quad -\langle \phi_i\phi_j|\hat{g}|\phi_q\phi_p\rangle
\end{aligned}$$

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

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

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

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:

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

- Chemists:

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

- 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 $\phi_i(\vec{\mathrm{r}}) = \sum_\alpha c_{\alpha i}\, \chi_\alpha(\vec{\mathrm{r}})$.
- 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).

Hartree-Fock equations

Where does Brillouin's theorem come from?

- Total energy: $E = \sum_{i\in occ} h_{ii} + f_{ii}$
- Trace of a symmetric matrix invariant upon unitary transformations
- Here: as well part of the trace invariant
- No mixing of occupied and virtual orbitals allowed
- Thus

$$\begin{aligned} F\,\phi_i &= \sum_{j\in occ} \epsilon_{ij}\,\phi_j \\ F\,\phi_a &= \sum_{b\in virt} \epsilon_{ab}\,\phi_b \end{aligned}$$

- Fock matrix in molecular orbitals is block-diagonal, block occ-virt is strictly zero.

Basis sets

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

- Nodeless Slater functions

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

- Gaussian functions

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

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

$$\int\!\!\int \frac{e^{-\alpha|\vec{\mathrm{r}}_1-\vec{\mathrm{R}}_A|}e^{-\beta|\vec{\mathrm{r}}_1-\vec{\mathrm{R}}_B|}e^{-\gamma|\vec{\mathrm{r}}_2-\vec{\mathrm{R}}_C|}e^{-\delta|\vec{\mathrm{r}}_2-\vec{\mathrm{R}}_D|}}{|\vec{\mathrm{r}}_1-\vec{\mathrm{r}}_2|}d^3r_1d^3r_2$$

Possible with Gaussians due to product formula

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

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 $\approx$ 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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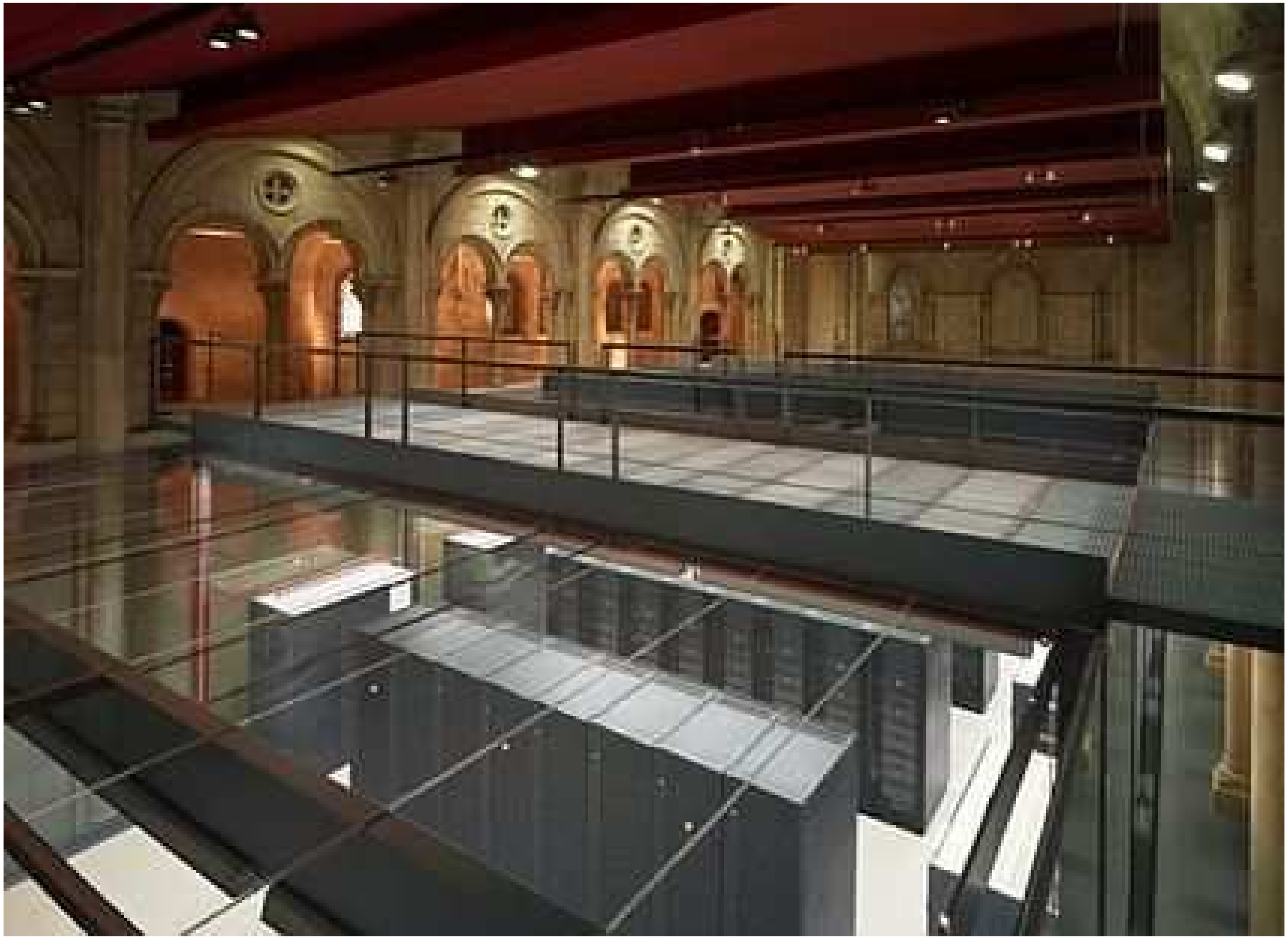
Extrapolation

	A	B
HF	−2.86228	0.0509344
Full CI	−2.90431	0.1168



Marenostrum Computer Center, Barcelona

What do we have already: Hartree-Fock

Closed-shell systems

At disposition

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

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

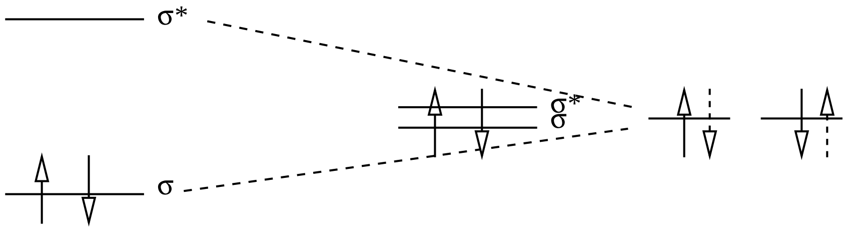
How do they perform?

- 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

$$\sigma \;=\; s_A + s_B \qquad\qquad \sigma^* \;=\; s_A - s_B$$



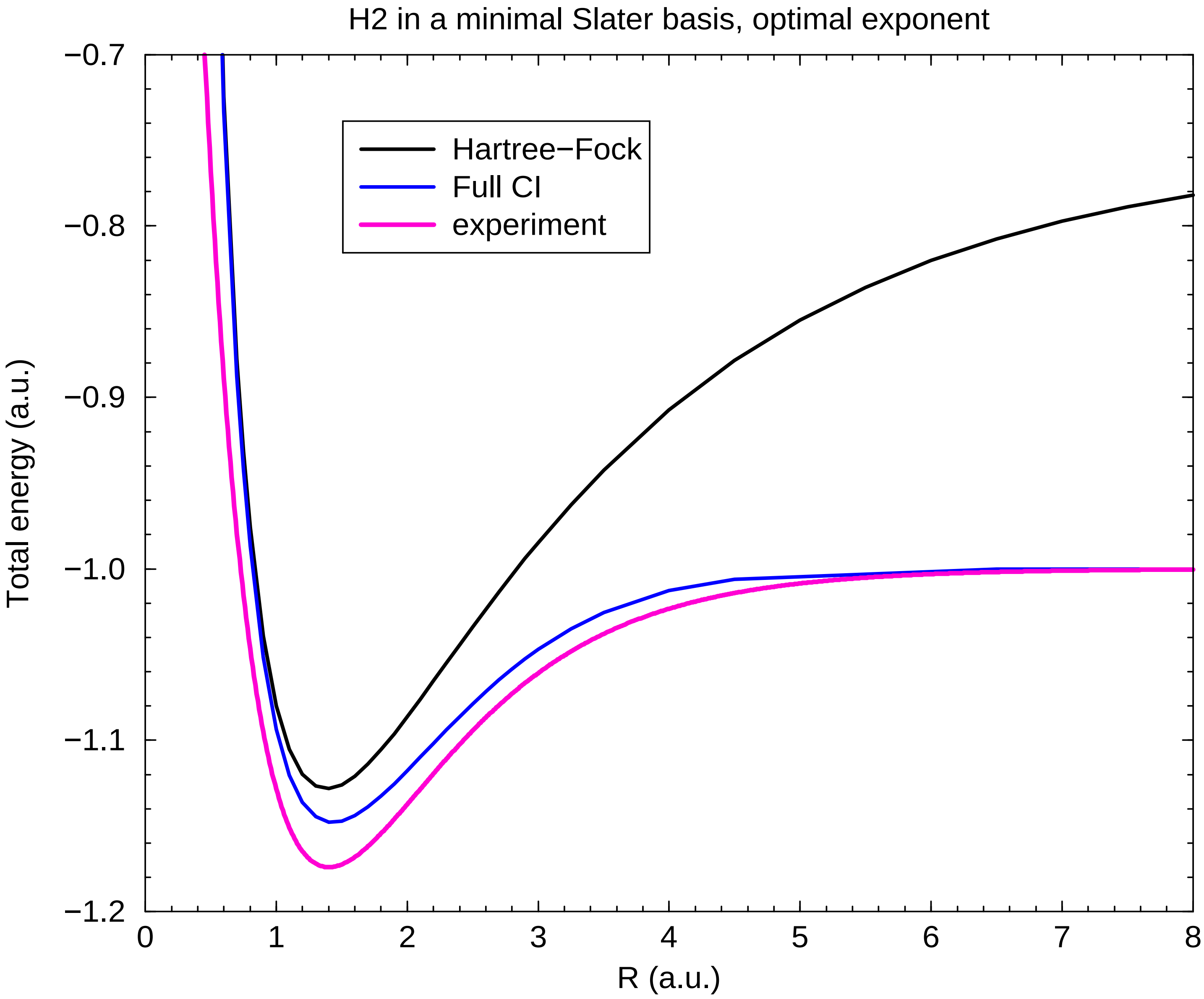
- Equilibrium distance:
  - Hartree-Fock $|\Phi_0\rangle \;=\; |\sigma\bar{\sigma}\rangle$
  - 2-determinant wavefunction: $|\Psi\rangle \;=\; \sqrt{1-\epsilon^2}|\sigma\bar{\sigma}\rangle + \epsilon|\sigma^*\bar{\sigma}^*\rangle$

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



Bond dissociation

Hartree-Fock:

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

Two regimes of deviation from experiment:

- $R \approx R_{eq}$: small, but significant contribution, dynamical electron correlation
- $R \longrightarrow \infty$: $c_0 = c_1$, 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

and Density Functional Theory

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 $\langle\Psi|\Psi\rangle = 1$:

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

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

- System of linear equations

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

Configuration interaction

Written as matrix equation:

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

Identify λ with the total energy from the functional:

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

Configuration interaction

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 ($c_0 = 1$):

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

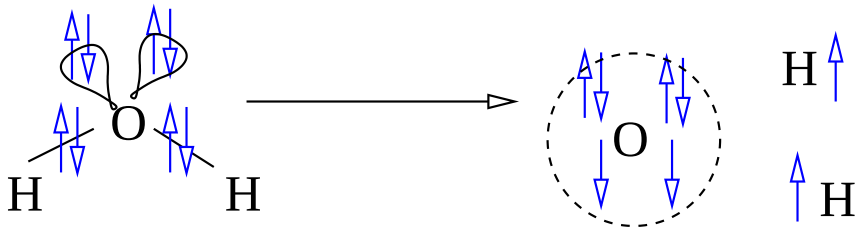
$$E_{Corr} = \sum_{I \neq 0} c_I \langle 0 | \mathbf{H} | \Phi_I \rangle$$

- 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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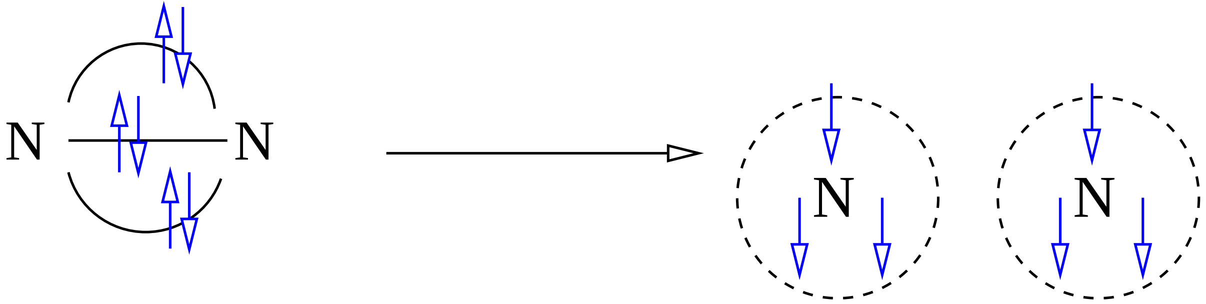
Other example:

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

$$N_2 \ \left({}^1\Sigma_g^+\right) \longrightarrow \ 2\,N\left({}^4S\right)$$



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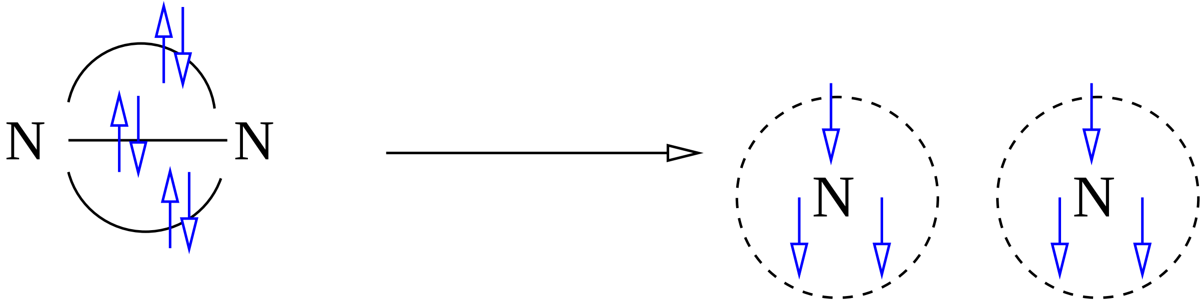

Need for multiconfigurational wavefunctions

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
- Spin-adapted excitation operator

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

- 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
- Spin-adapted 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:

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

    - 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:

$$\hat{a}_i^\dagger \hat{a}_i + \hat{a}_i \hat{a}_i^\dagger = 1$$

Super-CI method

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

- Orbitals change through mono-excitations
- Spin-adapted excitation operator

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

- 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

Generalization

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

- Monoelectronic operator $\hat{h}$:

$$\begin{aligned}\langle\, \Phi_m \,|\, \hat{h} \,|\, \Phi_n \,\rangle &= \sum_{ij} h_{ij} \langle\, \Phi_m \,|\, \hat{E}_{ij} \,|\, \Phi_n \,\rangle \\ &= \sum_{ij} h_{ij}\, D_{ij}^{mn}\end{aligned}$$

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

$$\begin{aligned}\langle\, \Phi_m \,|\, \hat{G} \,|\, \Phi_n \,\rangle &= \frac{1}{2} \sum_{ijkl} g_{ijkl} \langle\, \Phi_m \,|\, \hat{E}_{ij}\hat{E}_{kl} - \delta_{jk}\hat{E}_{il} \,|\, \Phi_n \,\rangle \\ &= \sum_{ij} g_{ijkl}\, P_{ijkl}^{mn}\end{aligned}$$

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

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- 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

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

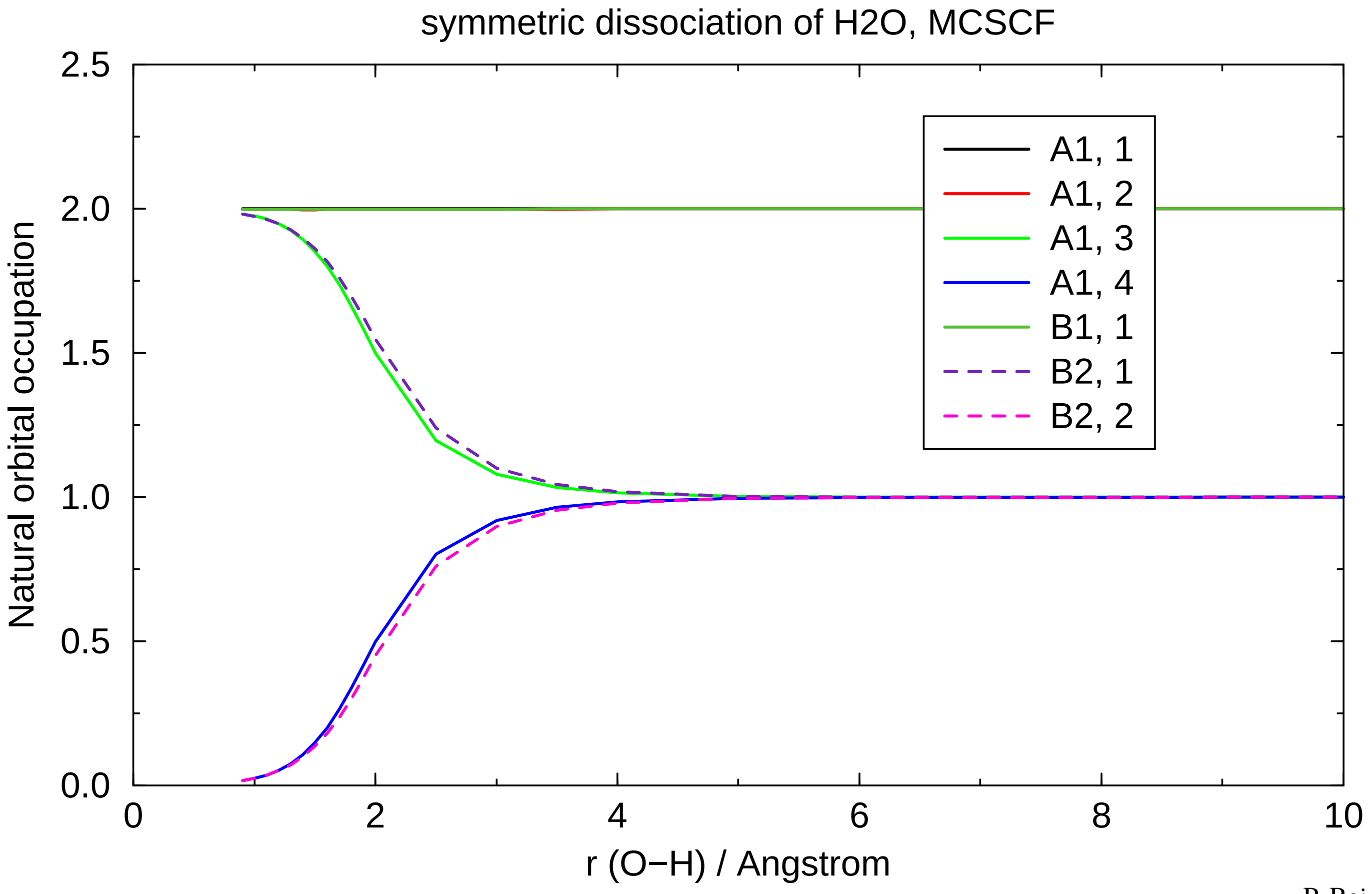
- Dipole moment

$$\vec{\mu} \;=\; \sum_{\alpha\beta} D_{\alpha\beta} \langle \chi_\alpha \,|\, \hat{\vec{r}} \,|\, \chi_\beta \rangle = \sum_{ij} D_{ij} \langle \phi_i \,|\, \hat{\vec{r}} \,|\, \phi_j \rangle$$

Natural orbitals

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

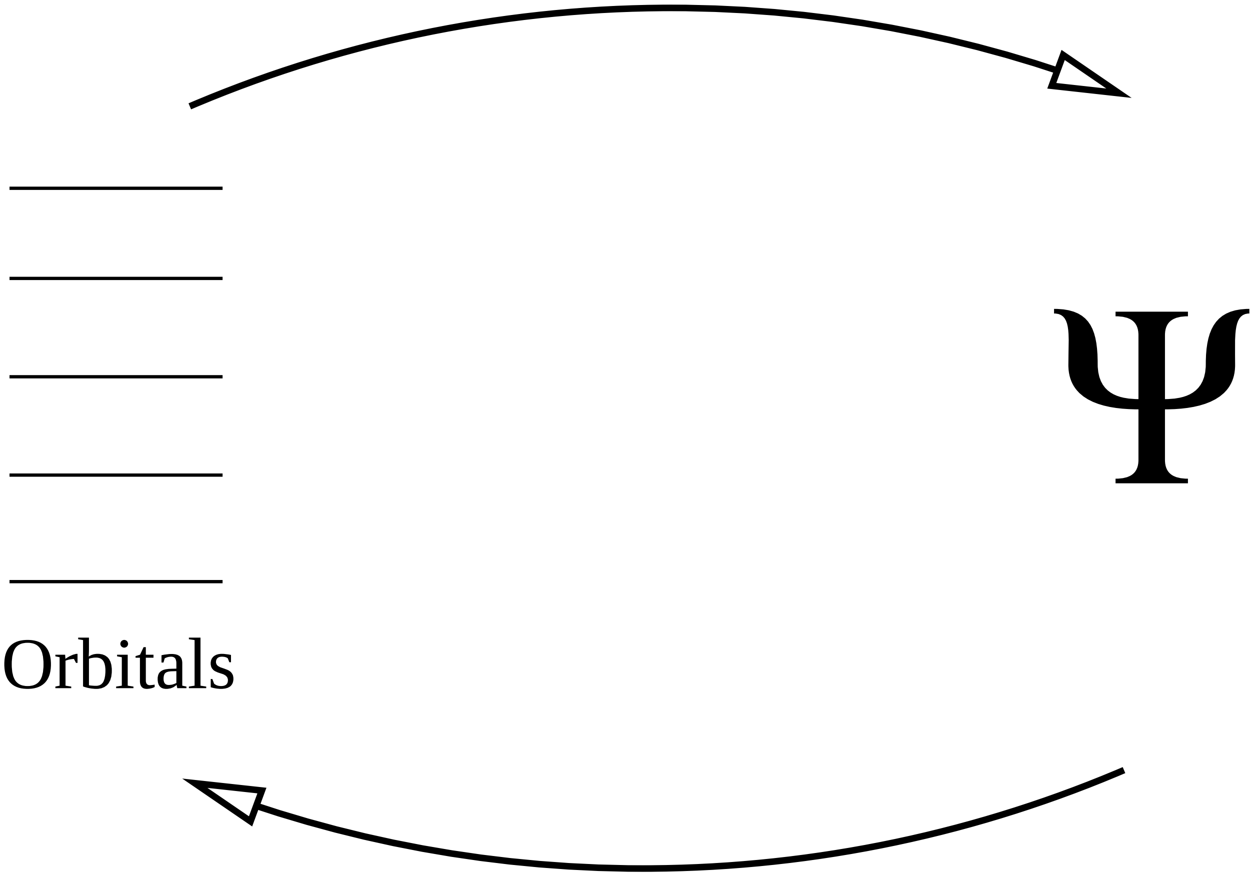
- $\approx$2 electrons: closed shell
- $\approx$1 electron : singly occupied orbital
- $\approx$0 electrons: virtual orbitals



Remains to work

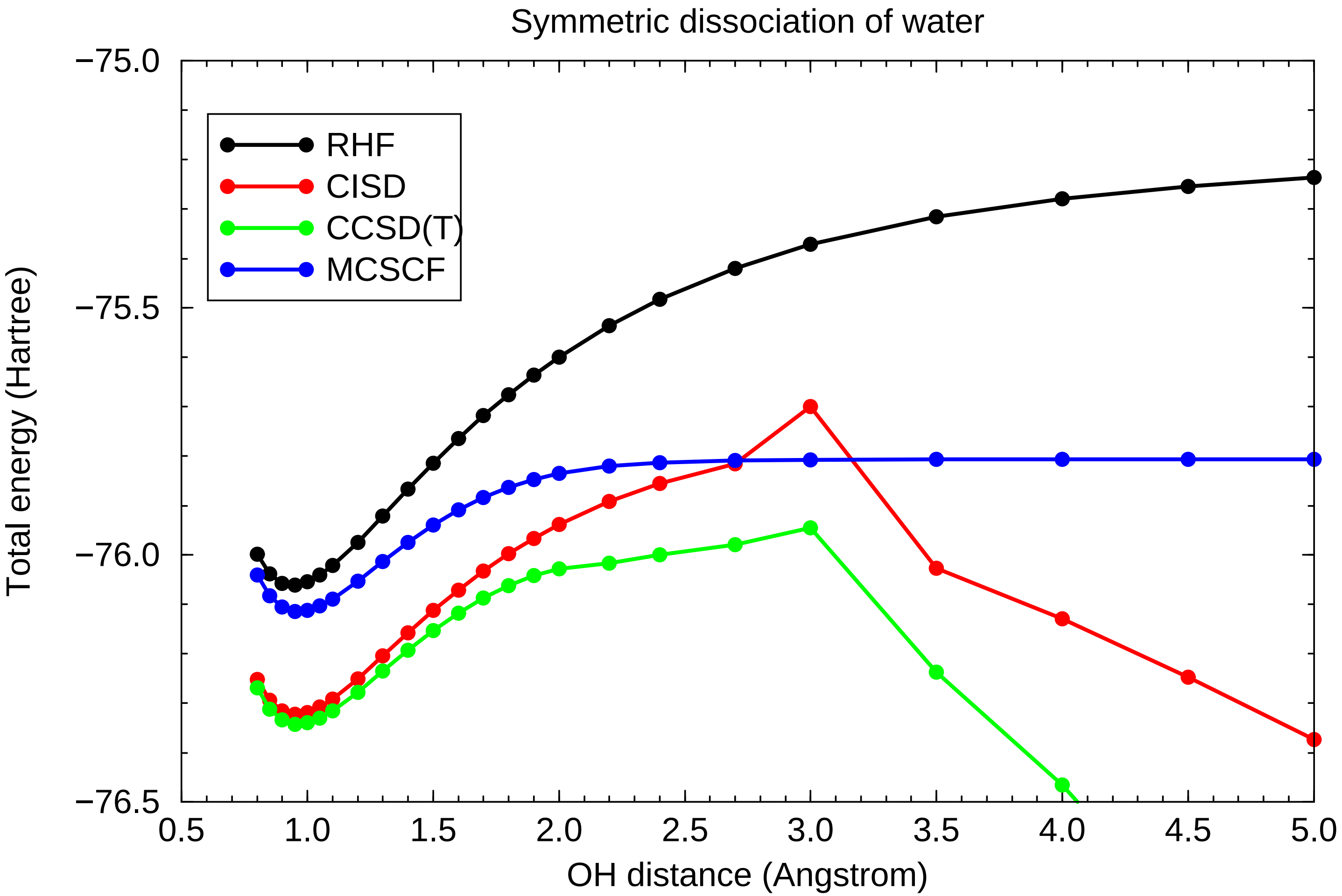
Derivatives of the total energy with respect to orbitals and CI coefficients:

- 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

Symmetric dissociation of water



Practical aspects of MCSCF

- 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 to handle
- 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

That’s it for today

We hopefully saw

- How all started
- Why we speak about orbitals
- Why chemists like orbitals
- That orbitals are not all
- What we mean when we speak of Hartree-Fock
- That a variational principle is exploited
- What we have to do for a Configuration Interaction
- How to optimize orbitals through single excitations
- How to break a bond correctly

Electron correlation – what to do ?

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

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

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

Dynamical correlation

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

- bond breaking, open-shell singlets, strong correlations

Non-dynamical correlation

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

Kato's theorem

$$\frac{1}{2}\left(\frac{\left|\vec{\nabla}\rho(\vec{\mathrm{r}})\right|}{\rho(\vec{\mathrm{r}})}\right)_{av.} \quad = \; Z$$

(*T.Kato*, Comm.Pure.Appl.Math., **10** (1957) 151)

- Knowledge of the density gives position and charge of nuclei
- Write down a Schrödinger equation
- Solve it

  Everything is in the density .... Nobel prize Walther Kohn 1998

Kohn-Sham equations

$$E[\rho] = T_s[\rho] + \int d\mathbf{r}\; v_{\mathrm{ext}}(\mathbf{r})\rho(\mathbf{r}) + E_H[\rho] + E_{\mathrm{xc}}[\rho]$$

$$T_s[\rho] = \sum_{i=1}^{N} \int d\mathbf{r}\; \phi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \phi_i(\mathbf{r})$$

$$E_H = \frac{1}{2}\int d\mathbf{r} \int d\mathbf{r}'\; \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$v_{\mathrm{eff}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r})}$$

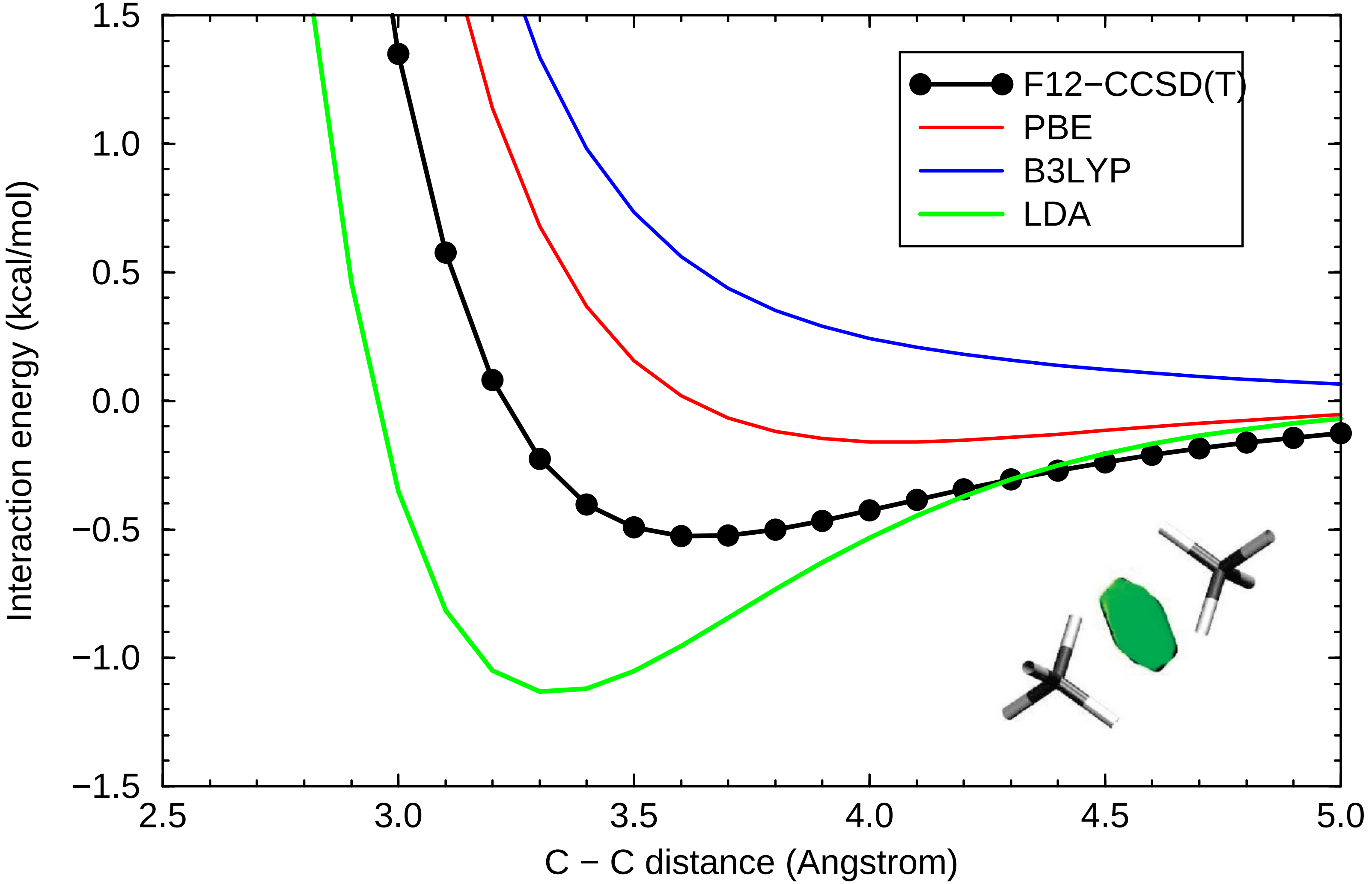
$$v_{\mathrm{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r})}$$

Minimization of $E[\rho]$ should lead to E_{exact}

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\mathrm{eff}}(\mathbf{r})\right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

But ...

The methane dimer:



CI of Singles and Doubles

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

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

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

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

Possible solution: limit the number of excitations

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

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

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

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

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

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

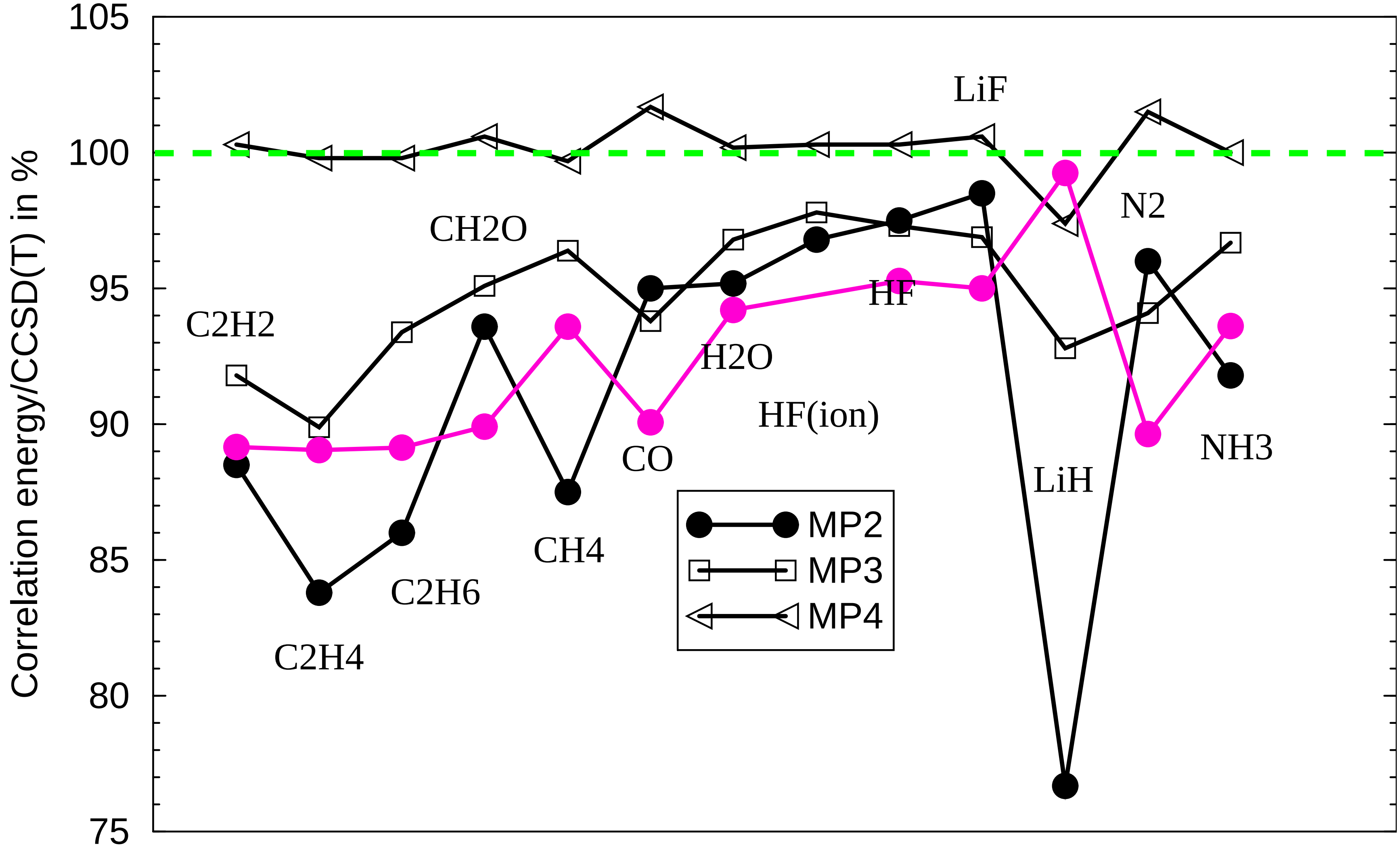
Possible solution: limit the number of excitations

Additional reduction of the number of determinants:

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

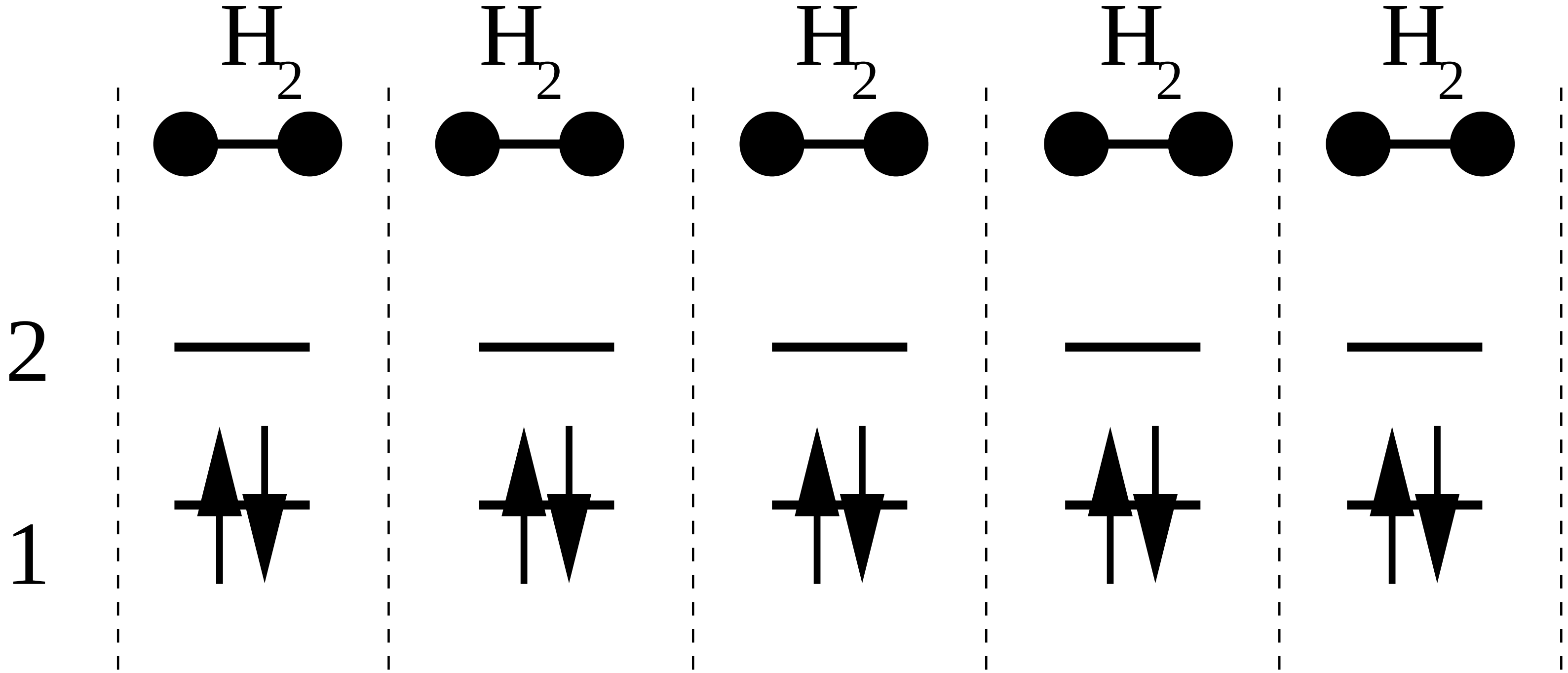
Resulting wavefunction has same spin and space symmetry as Hartree-Fock reference.

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:

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

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

  with eigenvalues

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

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:

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

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

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

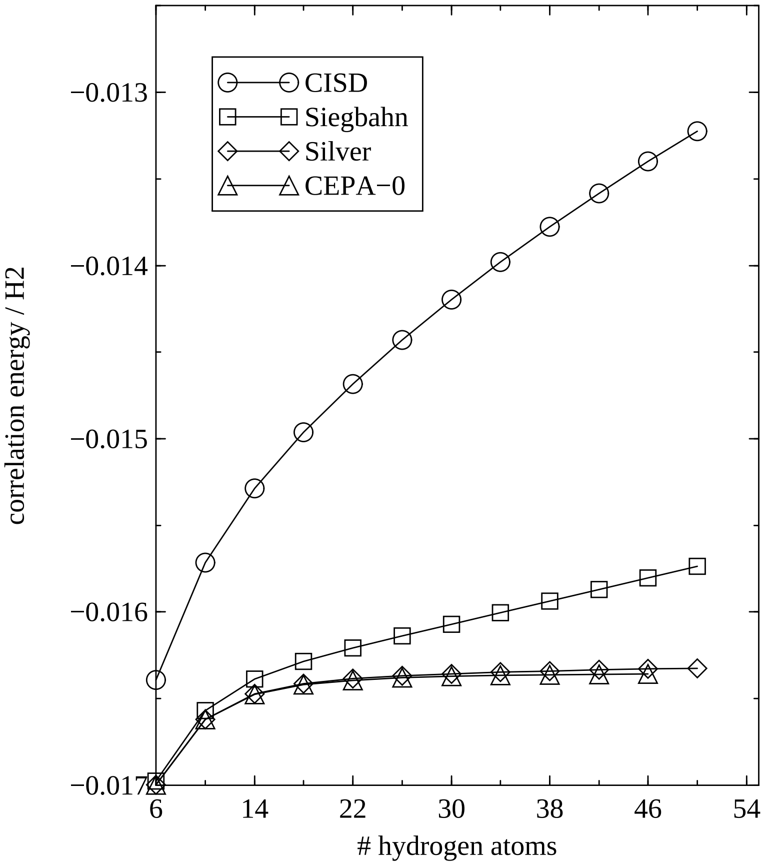
$$E_{\mathrm{Corr}} \longrightarrow (1 - c_0^2)/(2c_0^2 - 1)\; E_{\mathrm{Corr}}$$

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

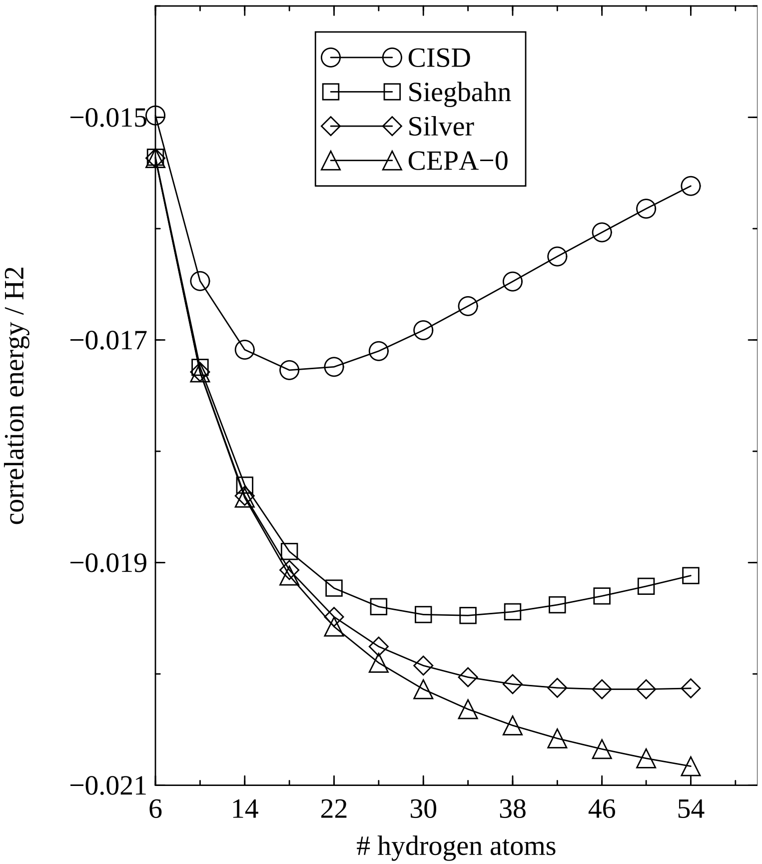
Wrong scaling property of SD-CI

Result for $(H_2)_n$ rings :

molecular case



metal-like case



Size-consistent methods

CISD eigenvalue problem

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

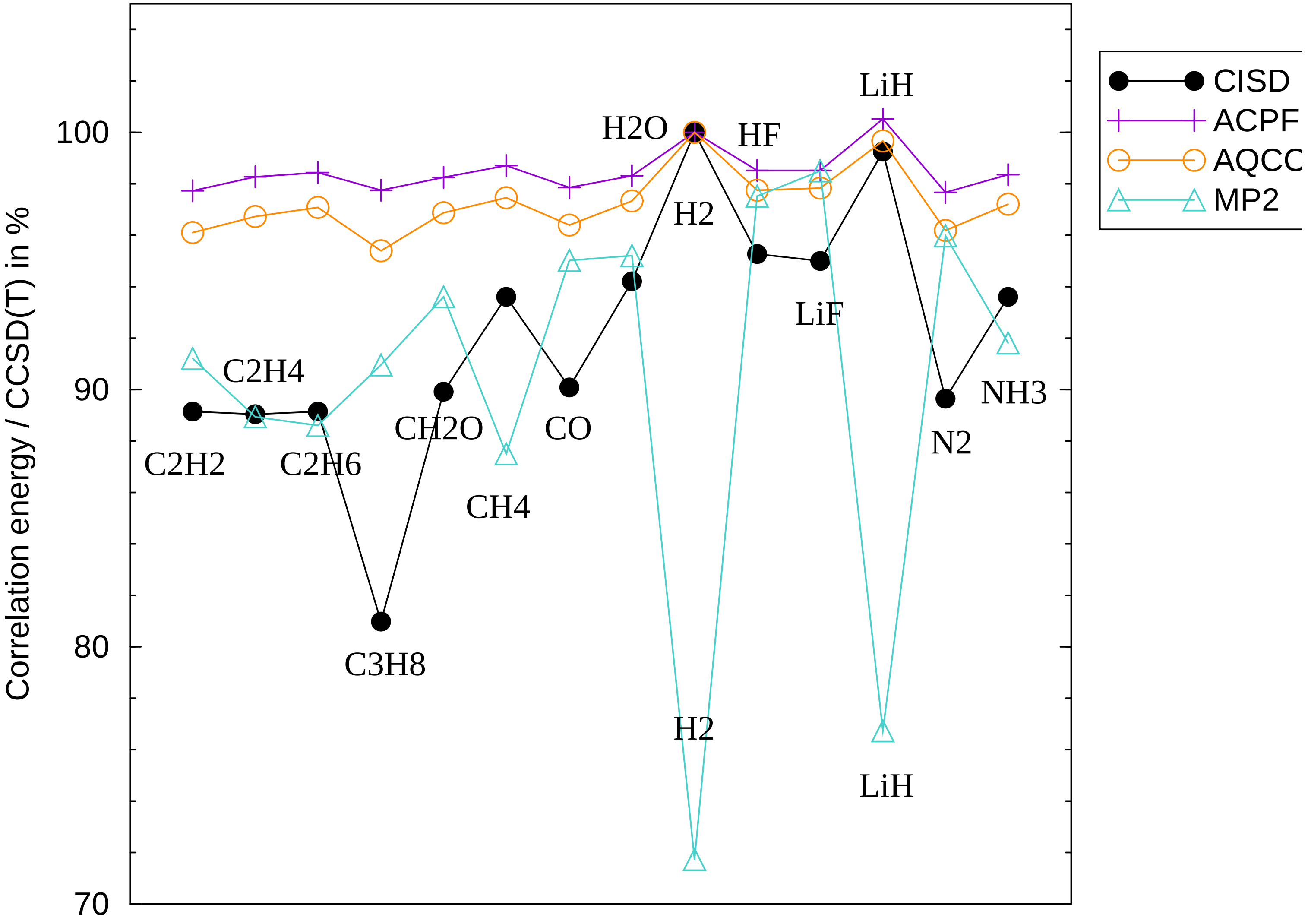
Size-consistent methods

Dressed CISD eigenvalue problem

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

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

Size-consistent methods



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
- Schrödinger equation $(\hat{H}_0 + \hat{V})|\Psi\rangle = E_0|\Psi\rangle$

Rayleigh-Schrödinger 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:

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

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

- 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:

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

- 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-Schödinger perturbation theory

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

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

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

Energies:

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

Coefficients:

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

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

Rayleigh-Schödinger 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

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

-

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

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

RS perturbation theory

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

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

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 $\epsilon_i = F_{ii}$

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

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We know the eigenvalues of these functions: orbital energies $\epsilon_i = F_{ii}$

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

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

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

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

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

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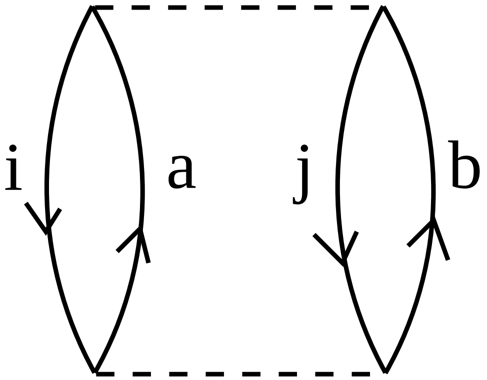
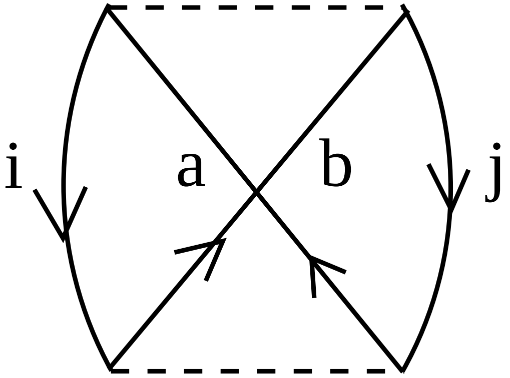
And higher-order formulas can be derived as well ... but become more and more complex





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

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

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.

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

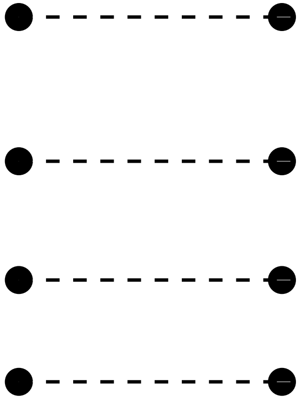
6. The overall sign is given by the number of closed loops and the number of holes

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

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

Diagrammatic language

A 4-th order diagram as example



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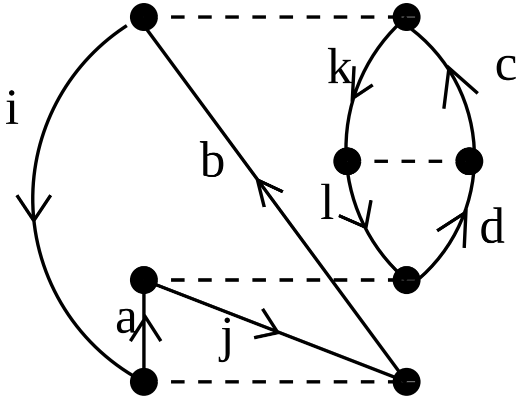

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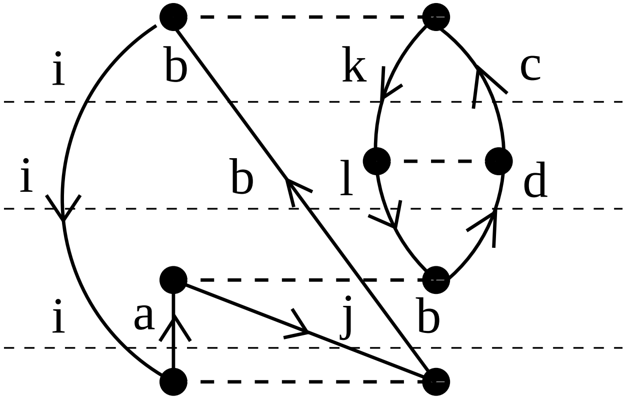
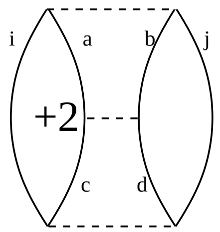


(3)

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

Diagrammatic language

All third-order diagrams



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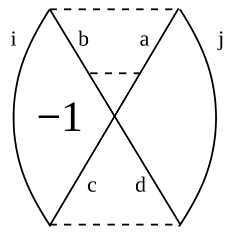

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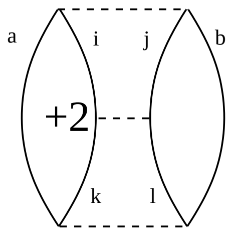

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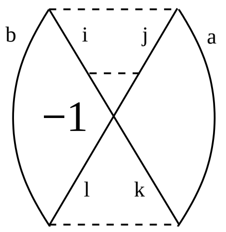

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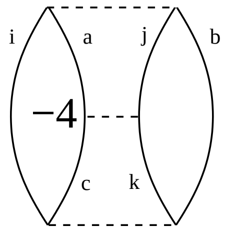

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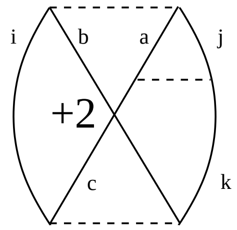

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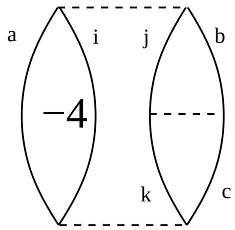

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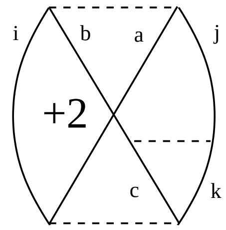

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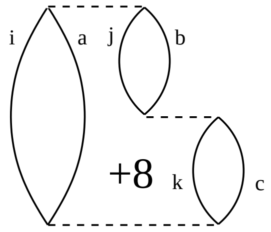

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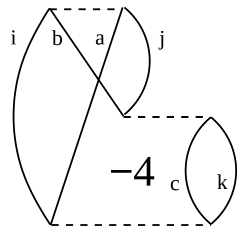

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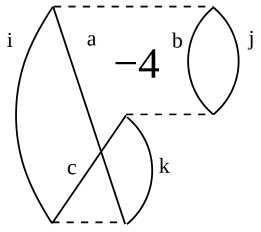

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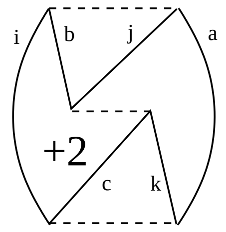
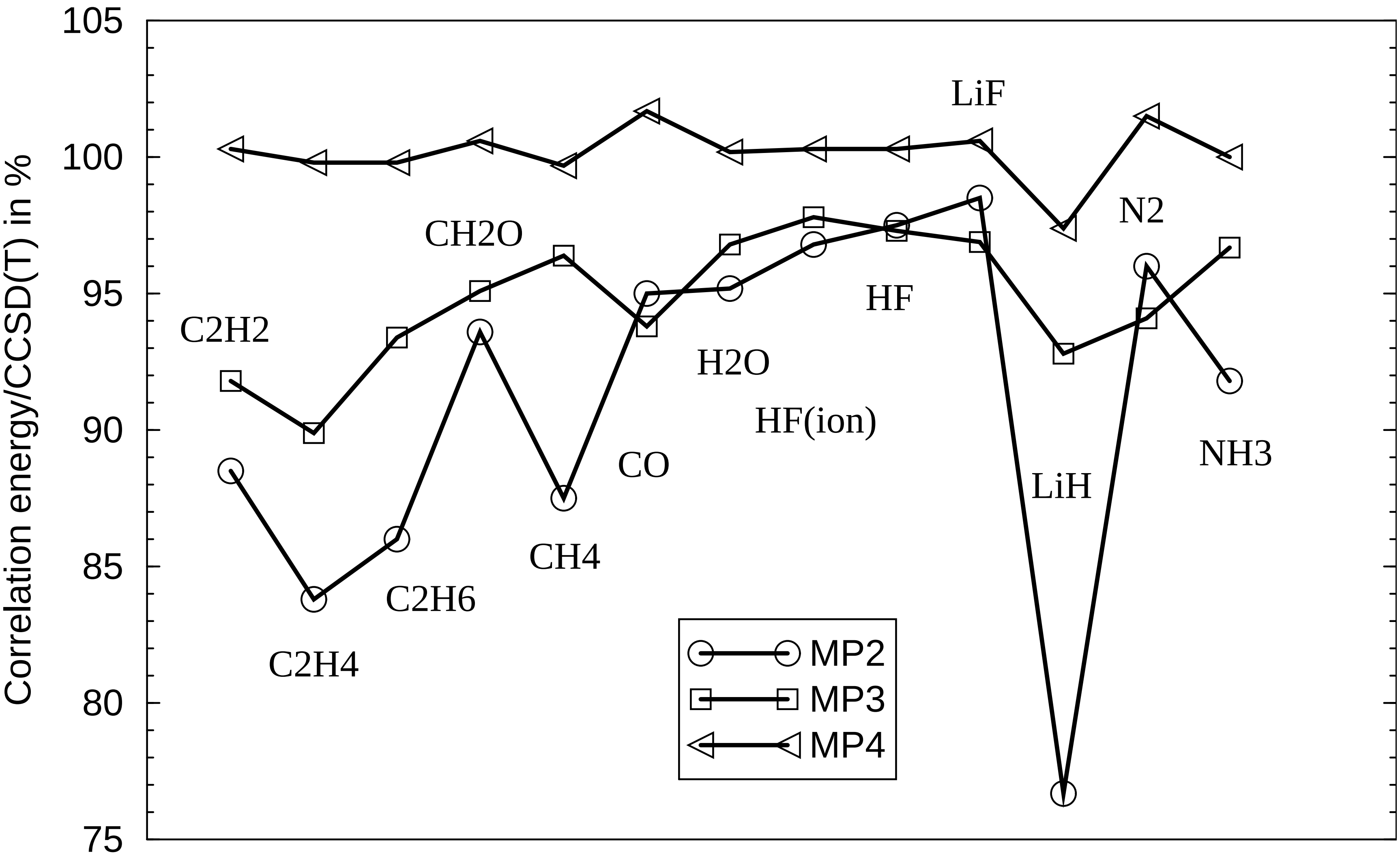


(12)

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 rapidely 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

Performance



Basis aug-cc-pvtz, fixed geometry

Performance

Geometry parameters

	Hartree-Fock		2nd order Møller-Plesset	
molecule	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

$$\begin{aligned}\hat{T}_1 &= \sum_{i,a} t_i^a\,\hat{a}_a^\dagger\,\hat{a}_i \\ \hat{T}_2 &= \sum_{ij,ab} t_{ij}^{ab}\,\hat{a}_a^\dagger\,\hat{a}_b^\dagger\,\hat{a}_i\,\hat{a}_j \qquad \text{etc.}\end{aligned}$$

- Schrödinger's equation $\hat{H}|\Psi\rangle = E\,|\Psi\rangle$
- Energy through projection against $\langle\Phi_0|$ or $\langle\Phi_0|e^{-\hat{S}}$

$$\begin{aligned}\langle\Phi_0|e^{-\hat{S}}\hat{H}e^{\hat{S}}|\Phi_0\rangle &= \langle\Phi_0|\hat{H}e^{\hat{S}}|\Phi_0\rangle \\ &= \langle\Phi_0|e^{-\hat{S}}Ee^{\hat{S}}|\Phi_0\rangle = E = E_{HF} + E_{Corr}\end{aligned}$$

General approach

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

$$\begin{aligned} \langle\Phi_i^a|e^{-S}\hat{H}e^{S}|\Phi_0\rangle &= 0 \\ \langle\Phi_{ij}^{ab}|e^{-\hat{S}}\hat{H}e^{\hat{S}}|\Phi_0\rangle &= 0 \end{aligned} \tag{3}$$

Exponential

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

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

$$\hat{T}_1 = \sum_{ia} \hat{a}_a^\dagger \hat{a}_i \qquad \hat{T}_2 = \sum_{jkbc} \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_j \hat{a}_k$$

where $\hat{a}_a^\dagger$ creates an electron in (spin-)orbital a, and $\hat{a}_i$ destroys an electron in (spin-)orbital i.
The operators obey the anti-commutation relations

$$\begin{aligned} \{\hat{a}_i^\dagger, \hat{a}_j\} &= \hat{a}_i^\dagger \hat{a}_j + \hat{a}_j \hat{a}_i^\dagger = \delta_{ij} \\ \{\hat{a}_i, \hat{a}_j\} &= \hat{a}_i \hat{a}_j + \hat{a}_j \hat{a}_i = 0 \\ \{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} &= \hat{a}_i^\dagger \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i^\dagger = 0 \end{aligned} \tag{4}$$

due to the sign-change when exchanging two fermions in a wavefunction (Pauli's principle). As a consequence we have

$$\begin{aligned} \hat{T}_1 \hat{T}_2 &= \sum_{ia} \sum_{jkbc} \hat{a}_a^\dagger \underbrace{\hat{a}_i \hat{a}_b^\dagger}_{-\hat{a}_b^\dagger \hat{a}_i} \underbrace{\hat{a}_c^\dagger \hat{a}_j}_{-\hat{a}_j \hat{a}_c^\dagger} \hat{a}_k \\ &= \sum_{ijab} \sum_{kc} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j \hat{a}_c^\dagger \hat{a}_k = \hat{T}_2 \hat{T}_1 \end{aligned} \tag{5}$$

General approach

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

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

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

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

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 :

$$
\begin{aligned}
&\hat{H}_{0I} + \sum_J \hat{H}_{IJ}\, c_J + \\
&+ \sum_J \langle \Phi_I | \hat{H} | \Phi_{I+J} \rangle (c_I\, c_J - \langle c_I * c_J \rangle) \\
&\underbrace{- \left(E_{HF}\, c_I + \sum_J \hat{H}_{0J}\, c_I\, c_J \right)}_{E\, c_I} \qquad = \qquad 0
\end{aligned}
$$

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 :

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

- 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
- For a given I we have to loop over all J: cost → N^8

Including triple excitations

- CCSD: only di-excited determinants needed
- Cost as CISD or MP4 (SDQ): $\sim\ N^6$ by precontraction
- Triples may be important:
  - Orbital corrections for di-excitations
  - Much better performance for intermolecular interactions
- Full triples step costs $\sim\ N^8$:

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

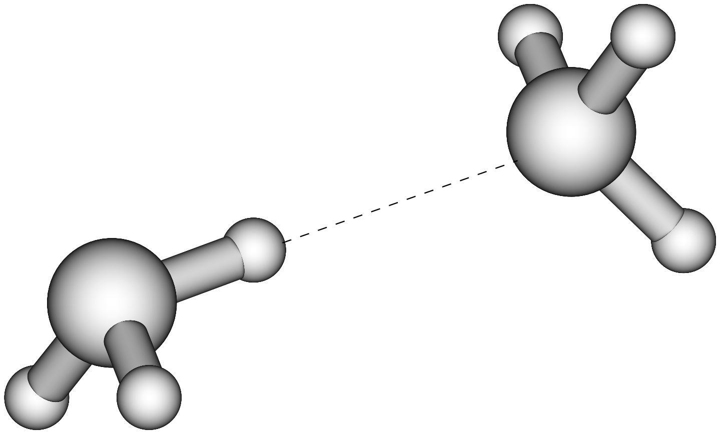
6 indices $ijkabc$ and 2 differences $\longrightarrow N^8$

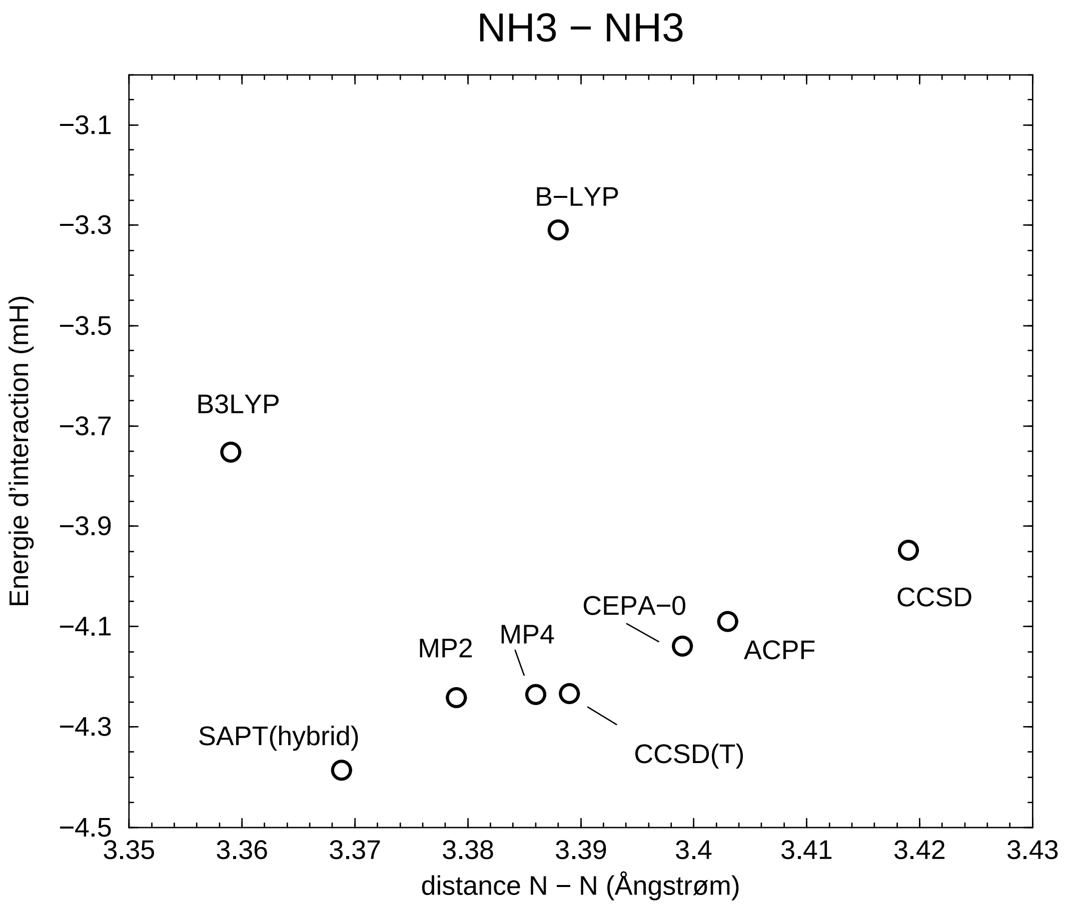
- Needs much more memory for coefficients t_{ijk}^{abc}, etc.
- Perturbative treatment: straightforward, no need for iterations $\longrightarrow$ CCSD(T)

as triples in MP4: $\sim N^7$

- Nowadays reference method for closed-shell systems

Example: NH_3—NH_3





Performance

Geometry parameters

	Hartree-Fock		MP2		CCSD(T)	
molecule	Δ r (pm)	Δ ang (^{o})	Δ r (pm)	Δ ang (^{o})	Δ r (pm)	Δ ang (^{o})
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

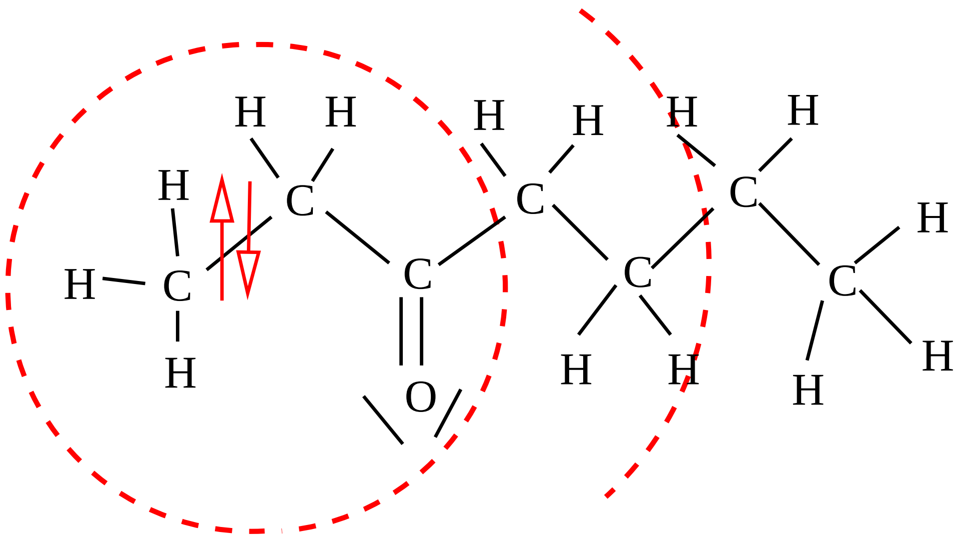
Vibrational constants, atomization energies

molecule	2nd order Møller-Plesset ν (cm^{-1})	at.ener. (kJ/mol)	CCSD(T) ν (cm^{-1})	at.ener. (kJ/mol)	Experiment 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`

Orbital localization: what does it change?

- Correlation important if electrons are close

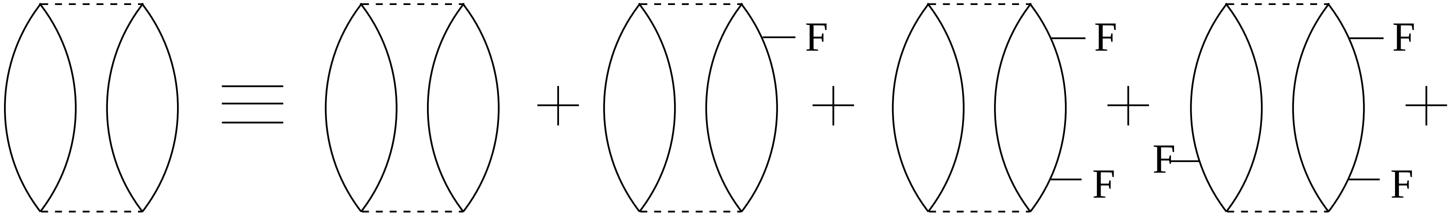


- Bielectronic integrals less important for distant orbitals
- Hartree-Fock reference invariant to orbital rotations
- CISD as well as variational procedure
- The same holds for total-energy dressings (CEPA–0, ACPF)
- CCSD projects against all excited determinants, the infinite summations of all T operators.

Orbital localization: what does it change?

Perturbation theory is different:

- The Fock matrix is not any more diagonal
- Either leave $\hat{H}_0 = \sum_i F_{ii}\hat{a}_i^\dagger\,\hat{a}_i = \sum_i \epsilon_i\hat{a}_i^\dagger\,\hat{a}_i$ and add the off-diagonal Fock-matrix elements to the perturbation $\hat{V}$ as additional series



orbitales canoniques
(MP2C)

orbitales localisées
(MP2L)

perturbation supplémentaire en F
(MP2C − MP2L)

- Or introduce the off-diagonal matrix elements in $\hat{H}_0 = \sum_{ij} F_{ij}\hat{a}_i^\dagger\,\hat{a}_j$ and leave the perturbation $\hat{V}$ as is.

Orbital localization: what does it change?

Orbital invariant MP2:

- Schrödinger equation $(\hat{H}_0 + \lambda\hat{V})\sum_i \lambda^i \Psi^{(i)} \;=\; \sum_j \lambda^j E^{(i)} \sum_k \lambda^k \Psi^{(k)}$
- First order wavefunction $\Psi^{(1)} = \sum_I \; c_I^{(1)}\,\Phi_I$, projection on Φ_K

$$\sum_I c_I^{(1)}\,\langle\Phi_K|\hat{H}_0 - E_0^0|\Phi_I\rangle + \langle\Phi_K|\hat{V}|\Phi_0\rangle \;=\; 0$$

- Define a functional (Hylleraas 1930)

$$h = 2\langle\Psi^{(1)}|\hat{V}|\Psi^{(0)}\rangle + \langle\Psi^{(1)}|\hat{H}_0 - E_0^{(0)}|\Psi^{(1)}\rangle$$

- Put derivatives to zero (minimize h)

$$\frac{\partial h}{\partial c_K} \;=\; 2\,\langle\Phi_K|\hat{V}|\Phi_0\rangle + \sum_I 2\,c_I\,\langle\Phi_K|\hat{H}_0 - E_0^{(0)}|\Phi_I\rangle = 0$$

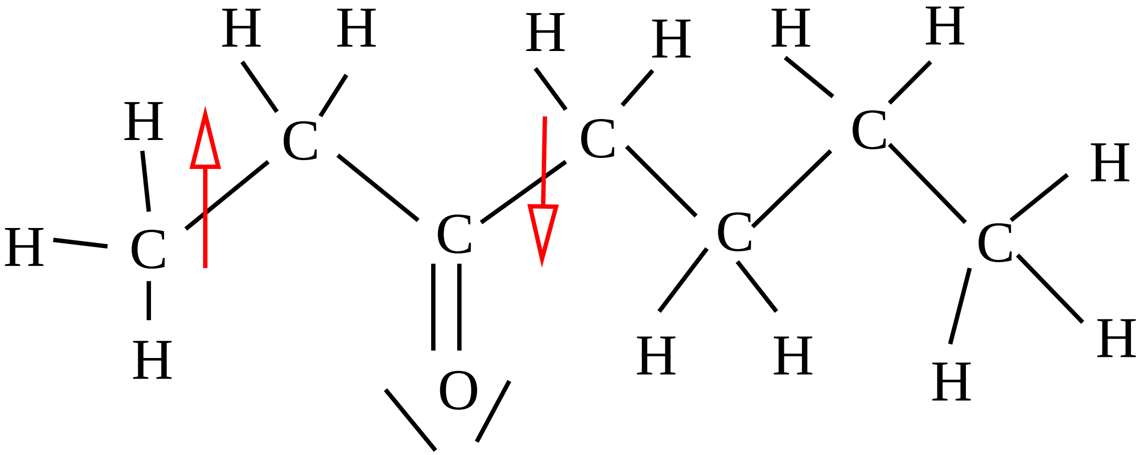
- Insert into functional: $h \;=\; \langle\Psi^{(1)}|\hat{V}|\Psi^{(0)}\rangle \;=\; E^{(2)}$

Orbital localization: what does it change?

- System of linear equations

$$\langle\Phi_K|\hat{H}|\Phi_0\rangle + \sum_{c\in virt}\left(c_{ij}^{cb}F_{ac} + c_{ij}^{ac}F_{bc}\right) - \sum_{k\in occ}\left(c_{kj}^{ab}F_{ik} + c_{ik}^{ab}F_{jk}\right) = 0$$

- Evaluate integrals and Fock matrix in any set of localized orbitals
- Energy will be always the same as the coefficients minimize a functional.
- Formulas more complicated, but hope for linear scaling



That's all

We saw today

- That a CI, although variational, is not all
- What a size-consistent method should be
- What perturbation means in quantum chemistry
- That a perturbational approach grows rapidly in cost with the order
- How to write the Coupled-Cluster equations for having a correlation energy
- That working in localized orbitals may be a way to reduce effort