Fundamentals of quantum chemistry

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Simulating Correlations with Computers
Jülich

Contents

- Schrödinger equation
- Hartree-Fock
- Basis sets
- Correlation: mainly „traditional“ post-Hartree-Fock with CI, CCSD… ,

  a bit about DFT
- Examples

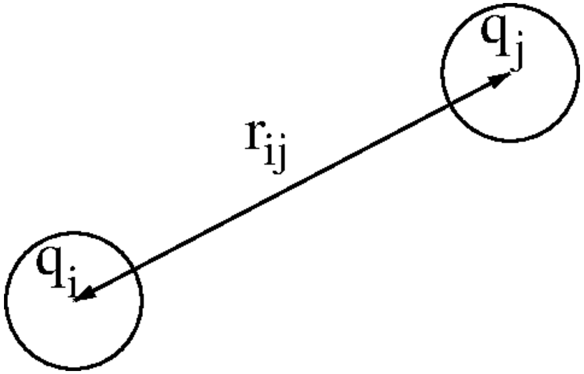
- *many equations: mainly serve as reference, for derivations: see cited text books in Lecture Notes, especially [1-4]*

Computed properties

- Total energy, usually only energy differences relevant:
  - binding energy as energy difference
  - good error cancellation necessary (i.e. treat atom, molecule, various geometries on equal footing)!
- Geometry: via minimum of total energy, saddle point of energy …
- Vibrational frequencies
- Spectroscopy: IR, Raman, NMR …

Set up the Hamiltonian

- initial geometry (here: 2 atoms):



- Coulomb interaction of nuclei :

$$\boxed{V_{ij} = V(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} := \frac{q_i q_j}{r_{ij}}}$$

- Coulomb interaction of nuclei with electrons, electron-electron

- Kinetic energy:

$$\boxed{E = \frac{1}{2} M_i \vec{v}_i^2 + \frac{1}{2} M_j \vec{v}_j^2 + \sum_{k=1}^{N_{el}} \frac{1}{2} m_{el} \vec{v}_k^2}$$

Total energy: Hamiltonian

$$E = E_{kinetic} + E_{Coulomb} \left(+ E_{external\,fields} + E_{relativistic\ corrections} \right)$$

$$= \frac{1}{2} \sum_{j=1}^{n} \frac{\vec{p}_j^{\,2}}{M_j} + \frac{1}{2} \sum_{i=1}^{N} \frac{\vec{p}_{el,i}^{\,2}}{m_{el}} + \sum_{j=1}^{n} \sum_{\substack{j'=1 \\ j'>j}}^{n} \frac{Z_j Z_{j'}}{|\vec{R}_j - \vec{R}_{j'}|} + \sum_{i=1}^{N} \sum_{\substack{i'=1 \\ i'>i}}^{N} \frac{1}{|\vec{r}_i - \vec{r}_{i'}|} - \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{Z_j}{|\vec{r}_i - \vec{R}_j|}$$

kinetic energy: nuclei, electrons

Coulomb energy: nucl.-nucl., electron-electron, nucl.-elec.

nuclei much heavier than electrons
=> neglect kinetic energy of nuclei
(Born-Oppenheimer approximation)

Hamiltonian: from classical to quantum mechanical

- Classical

$$E = E_{kinetic} + E_{Coulomb}$$

$$= \frac{1}{2}\sum_{j=1}^{n}\frac{\vec{p}_j^{\,2}}{M_j} + \frac{1}{2}\sum_{i=1}^{N}\frac{\vec{p}_{el,i}^{\,2}}{m_{el}} + \sum_{\substack{j,j'=1\\ j'>j}}^{n}\frac{Z_j Z_{j'}}{|\vec{R}_j-\vec{R}_{j'}|} + \sum_{\substack{i,i'=1\\ i'>i}}^{N}\frac{1}{|\vec{r}_i-\vec{r}_{i'}|} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_j}{|r_i-R_j|}$$

$$\text{(B.-O. Approx.)} \approx \frac{1}{2}\sum_{i=1}^{N}\frac{\vec{p}_{el,i}^{\,2}}{m_{el}} + \sum_{\substack{j,j'=1\\ j'>j}}^{n}\frac{Z_j Z_{j'}}{|\vec{R}_j-\vec{R}_{j'}|} + \sum_{\substack{i,i'=1\\ i'>i}}^{N}\frac{1}{|\vec{r}_i-\vec{r}_{i'}|} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_j}{|\vec{r}_i-\vec{R}_j|}$$

- quantum mechanical, replace:

$$p_{x,i}, p_{y,i}, p_{z,i} \qquad \text{with} \qquad -i\hbar\frac{\partial}{\partial x_i}, -i\hbar\frac{\partial}{\partial y_i}, -i\hbar\frac{\partial}{\partial z_i}$$

- => Schrödinger equation is obtained: a differential equation
- atomic units: $\boxed{\hbar = m_{el} = e = 1}$

Schrödinger equation

$$\boxed{H=-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2+\sum_{\substack{j,j'=1\\ j'>j}}^{n}\frac{Z_j Z_{j'}}{|\vec{R}_j-\vec{R}_{j'}|}+\sum_{\substack{i,i'=1\\ i'>i}}^{N}\frac{1}{|\vec{r}_i-\vec{r}_{i'}|}-\sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_j}{|\vec{r}_i-\vec{R}_j|}}$$

Schrödinger equation: $\boxed{H\Psi(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N)=E\Psi(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N)}$

many-body problem: $\boxed{\Psi(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N)}$

usually no analytical solution possible (few exceptions, e.g. H-atom)

remember: even classical 3-body problem can not be solved exactly

approximations (some known from quantum mechanics lectures), e.g.:

- (non)variational wave function
- perturbation theory

numerical approximations: finite basis set

Quantum chemical approach

Focus is here:

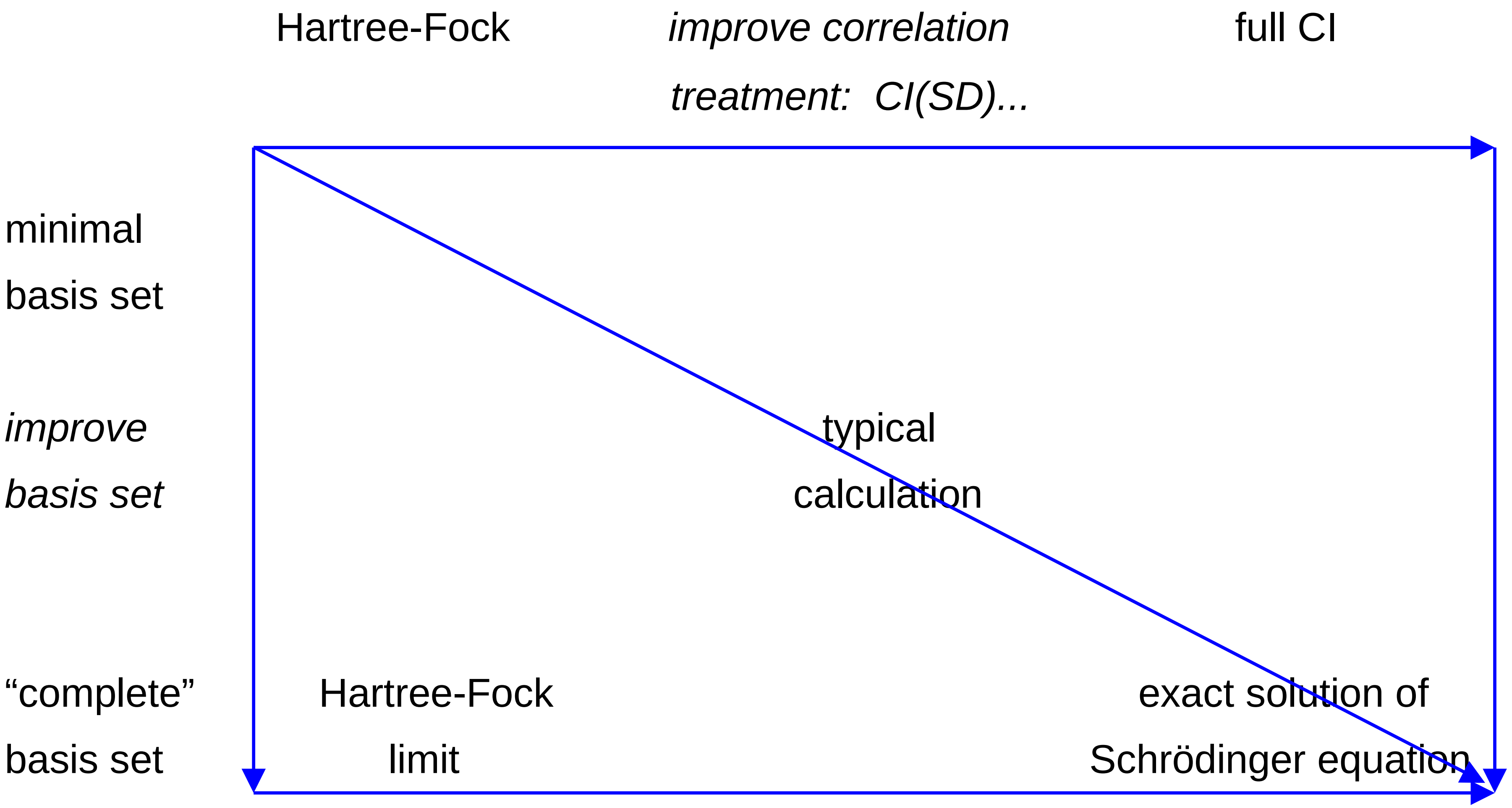
- Hartree-Fock, followed by “correlation” calculation, “post-Hartree-Fock” methods
- finite basis set, usually Gaussian basis set
- molecules and periodic systems (bulk, surfaces, nanotubes ...)

Closely related:

- Density functional theory
- Monte-Carlo methods
- Empirical methods, force fields, QM/MM

“ab inito” , “first principles” …: notions not unambiguously used

Quantum chemical approach



Hartree-Fock

improve correlation

treatment: CI(SD)...

full CI

minimal

basis set

improve

basis set

typical

calculation

“complete”

basis set

Hartree-Fock

limit

exact solution of

Schrödinger equation

In addition: numerical accuracy (integration, $\vec{k}$-point number...)

Schrödinger equation: Hartree-Fock approximation

Hamiltonian assumed to be without spin-dependence

=>Single electron: described by spin orbital: $\chi(\vec{x}) = \psi(\vec{r})\,\alpha(s)$; spatial part **ψ**, spin part **α**

Hartree-Fock approximation: **single determinant** as ansatz for wavefunction (variational ansatz)

$$\Psi_{HF}(1,2,3,\ldots N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \ldots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \ldots & \chi_N(2) \\ \ldots & \ldots & \ldots & \ldots \\ \chi_1(N) & \chi_2(N) & \ldots & \chi_N(N) \end{vmatrix}$$

Fermions => antisymmetric (determinant gives sign; Pauli principle of two columns are identical)

minimise Hartree-Fock energy:

$$E_{total,HF} = <\Psi_{HF}(1,2,3,\ldots,N)|H|\Psi_{HF}(1,2,3,\ldots,N)>$$

variational principle: energy of exact solution is lower bound

$$E_{total,HF} \geq E_{exact\ solution}$$

Hartree-Fock approximation: how to solve

$$E_{total,HF} = <\Psi_{1,2,3,\ldots,N}|H|\Psi_{1,2,3,\ldots,N}>$$

- spin orbitals must be normalised (one electron per spin orbital)
- orthogonalise

$$\Big\} \quad <\chi_i|\chi_j> = \delta_{ij}$$

Constrained minimisation:

$$L = E_{total,HF} - \sum_{a,b=1}^{N} \epsilon_{ba}\left(<\chi_a|\chi_b> - \delta_{ab}\right)$$

$\boldsymbol{\varepsilon}_{ab}$: Lagrange multiplier

Closed-shell or open-shell case depending whether all orbitals are doubly occupied or not; in the following: closed-shell case only

Hartree-Fock approximation: how to solve

$$L = E_{total,HF} - \sum_{a,b=1}^{N} \epsilon_{ba} \left(<\chi_a | \chi_b> - \delta_{ab} \right)$$

With:

$$\Psi_{HF}(1,2,3,\ldots N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \ldots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \ldots & \chi_N(2) \\ \ldots & \ldots & \ldots & \ldots \\ \chi_1(N) & \chi_2(N) & \ldots & \chi_N(N) \end{vmatrix}$$

after some calculation (see e.g. *Szabo, Ostlund, Modern Quantum Chemistry*), we obtain:

$$\boxed{\begin{aligned} E_{total,HF} &= E_{NN} + \sum_{a=1}^{N} \int \chi_a^*(\vec{x}) (H_{kin} + H_{el-nuc}) \chi_a(\vec{x})\, d\vec{x} \\ &+ \frac{1}{2} \sum_{a,b=1}^{N} \int \int \frac{\chi_a^*(\vec{x}_1) \chi_a(\vec{x}_1) \chi_b^*(\vec{x}_2) \chi_b(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_1 d\vec{x}_2 \\ &- \frac{1}{2} \sum_{a,b=1}^{N} \int \int \frac{\chi_a^*(\vec{x}_1) \chi_b(\vec{x}_1) \chi_b^*(\vec{x}_2) \chi_a(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_1 d\vec{x}_2 \end{aligned}}$$

Nuclear repusion+ contribution due to one-electron integrals

kinetic energy + nuclear attraction

bi-electronic integrals:

Coulomb

Exchange

missing: contributions due to more than one Slater determinant: **Correlation**

Hartree-Fock approximation: how to solve

$$\boxed{\chi \to \chi + \delta\chi \quad \Rightarrow \quad \delta L}$$

$$\Downarrow$$

left hand side:

$$\boxed{(H_{kin} + H_{el-nuc})\chi_a(\vec{x}_1) + \sum_{b\neq a}^{N} \int \frac{\chi_b^*(\vec{x}_2)\chi_b(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_2 \chi_a(\vec{x}_1) - \sum_{b\neq a}^{N} \int \frac{\chi_b^*(\vec{x}_2)\chi_a(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_2 \chi_b(\vec{x}_1)}$$

$$\boxed{(H_{kin} + H_{el-nuc})\chi_a(x_1) + \sum_{b\neq a}^{N} J_b(\vec{x}_1)\chi_a(\vec{x}_1) - \sum_{b\neq a}^{N} K_b(\vec{x}_1)\chi_a(\vec{x}_1)}$$

Coulomb (local):
potential defined
at a local point $\vec{r}_1$
multiplied with $\chi_a(\vec{r}_1)$

Exchange: depends on $\chi_a(\vec{x}_2)$ in whole space
(non-local)
no simple potential defined at local point $\vec{r}_1$

$$\boxed{K_b(\vec{x}_1)\chi_a(\vec{x}_1) = \int \frac{\chi_b^*(\vec{x}_2)\chi_a(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_2 \chi_b(\vec{x}_1)}$$

after variation: Hartree-Fock equations

$$\boxed{(H_{kin} + H_{el-nuc})\chi_a(x_1) + \sum_{b\neq a}^{N} J_b(\vec{x}_1)\chi_a(\vec{x}_1) - \sum_{b\neq a}^{N} \int K_b(\vec{x}_1)\chi_a(\vec{x}_1) = \epsilon_a \chi_a(\vec{x}_1)}$$

Transformation was made so that $\epsilon_{ab} \to \epsilon_a$ becomes diagonal: “canonical” orbitals; other than canonical orbitals possible, e.g. localised orbitals

Hartree-Fock approximation: how to solve

Hartree-Fock equations

$$\boxed{\left(H_{kin}+H_{el-nuc}\right)\chi_a(\vec{x}_1)+\sum_{b\neq a}^{N} J_b(\vec{x}_1)\,\chi_a(\vec{x}_1)-\sum_{b\neq a}^{N}\int K_b(\vec{x}_1)\,\psi_a(\vec{x}_1)=\epsilon_a\chi_a(\vec{x}_1)}$$

$$\boxed{f(\vec{x}_1)\,\chi_a(\vec{x}_1)=\epsilon_a\chi_a(\vec{x}_1)}$$

f: Fock operator acting on spin orbital $\chi_a(\vec{r})$ (depends on spin orbitals $\chi_j(\vec{r})$!)

- Eigenvalue equation: spin orbitals as eigenfunctions, orbital energy as eigenvalue
- ϵ_i must be negative, otherwise electron would not bind
- Integro-differential equation, practically always only numerical solution possible

Hartree-Fock approximation:

Hartree-Fock equations

$$\boxed{f(\vec{x}_1)\chi_a(\vec{x}_1) = \epsilon_a \chi_a(\vec{x}_1)}$$

Numerical solution:
expand spatial orbitals ψ in linear combination of K basis functions, $c_{\nu i}$ unknown:

$$\boxed{\psi_i(\vec{r}) = \sum_{\nu=1}^{K} c_{\nu i}\, \phi_\nu(\vec{r})}$$

Multiply on the left, integrate: $\int d^3r\, \phi_\mu^*$

Fock matrix:

$$\boxed{F_{\mu\nu} = \int \phi_\mu^*(\vec{r})\, f(\vec{r})\, \phi_\nu(\vec{r})\, d^3r}$$

Overlap matrix:

$$\boxed{S_{\mu\nu} = \int \phi_\mu^*(\vec{r})\, \phi_\nu(\vec{r})\, d^3r}$$

$c_{\nu i}$, $\boldsymbol{\epsilon}_i$ to be determined

$$\boxed{\sum_{\nu=1}^{K} F_{\mu\nu} c_{\nu i} = \epsilon_i \sum_{\nu=1}^{K} S_{\mu\nu} c_{\nu i}}$$

Hartree-Fock-Roothaan equations

periodic systems:

$$\boxed{\sum_{\nu=1}^{K} F_{\mu\nu}(\vec{k})\, c_{\nu i}(\vec{k}) = \epsilon_i(\vec{k}) \sum_{\nu=1}^{K} S_{\mu\nu}(\vec{k})\, c_{\nu i}(\vec{k})}$$

$\epsilon_i(\vec{k})$: band structure

Solution technique

- Specify molecule /periodic system

  => Schrödinger equation $\boxed{H\Psi = E\Psi}$
- Hartree-Fock approximation: end up with Hartree-Fock equations: must be solved numerically
- Initial guess of the solution $c_{\mu\nu} \Rightarrow \Psi_{guess}(\vec{x}_1, \vec{x}_2, \vec{x}_3, \ldots, \vec{x}_N)$
- Compute Fock matrix
- Set up Hartree-Fock-Roothaan equations: $\boxed{\sum_{\nu=1}^{K} F_{\mu\nu} c_{\nu i} = \epsilon_i \sum_{\nu=1}^{K} S_{\mu\nu} c_{\nu i}}$
- Solve equations, compute total energy
- Insert new $c_{\mu\nu}$ as guess in Hartree-Fock $\Psi_{guess}(\vec{x}_1, \vec{x}_2, \vec{x}_3, \ldots, \vec{x}_N)$
- Repeat until $\psi_{new\ guess} = \psi_{previous\ guess}$ or energy difference between iterations below threshold

“SELF CONSISTENT FIELD (SCF)” method

Density functional theory

Energy is functional of electron density $\rho(\vec{r})$,
one-to-one correspondence between potential and ground state density (Hohenberg, Kohn) ; text book: *Richard M. Martin, Electronic Structure*

$$\boxed{E_{total} = E[\rho] = E_{nn} + E_{kin}[\rho] + E_{ee}[\rho] + E_{ne}[\rho]}$$

Variational principle: exact density minimises E_{total}
But: functional unknown

Kohn, Sham strategy: use density of non-interacting reference system, put all corrections in E_{XC}

$$\rho(\vec{r}) = \sum_{i=1}^{N} \chi_i^*(\vec{r}) \chi_i(\vec{r})$$

$$E_{kin}[\rho] = -\frac{1}{2} \sum_{i=1}^{N} \int d^3 r \, \chi_i^*(\vec{r}) \;\Delta\; \chi_i(\vec{r})$$

$$E_{ne}[\rho] = -\sum_{j=1}^{n} Z_j \int d^3 r \frac{\rho(\vec{r})}{|\vec{r} - \vec{R}_j|}$$

$$E_{ee}[\rho] = E_{Coulomb}[\rho] + E_{XC}[\rho] = \frac{1}{2} \int\int d^3 r \, d^3 r' \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} + E_{XC}[\rho]$$

Density functional theory

Variation gives Kohn-Sham equations:

$$\boxed{\begin{gathered}\left(-\frac{1}{2}\Delta+V_{eff}(\vec{r})\right)\chi_i(\vec{r})=\epsilon_i\chi_i(\vec{r})\\ V_{eff}(\vec{r})=\sum_{j=1}^{n}\frac{Z_j}{|\vec{r}-\vec{R}_j|}+\int\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r'+\frac{\delta E_{XC}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\end{gathered}}$$

E_{XC} unknown, numerous functionals have been suggested

note the similarity of Kohn-Sham and Hartree-Fock equations
=> similar computer codes used
=> effort:
systems which can be studied on the Hartree-Fock level can usually/always be studied on the DFT level as well

HF vs DFT use:
today, rarely pure HF is used, usually DFT (e.g. compare various functionals for one system, to have a bandwidth of results; e.g. gaps)

Basis sets

Basis set types

Hartree-Fock/Kohn-Sham equations can in general not be solved analytically
=> expand molecular/crystalline orbitals in basis functions

- local basis sets (linear combination of atomic orbitals, LCAO):

  - Slater type orbitals (STO):

    $$\phi_{STO}(\vec{r}) = N\, x^a y^b z^c \exp(-\zeta r)$$

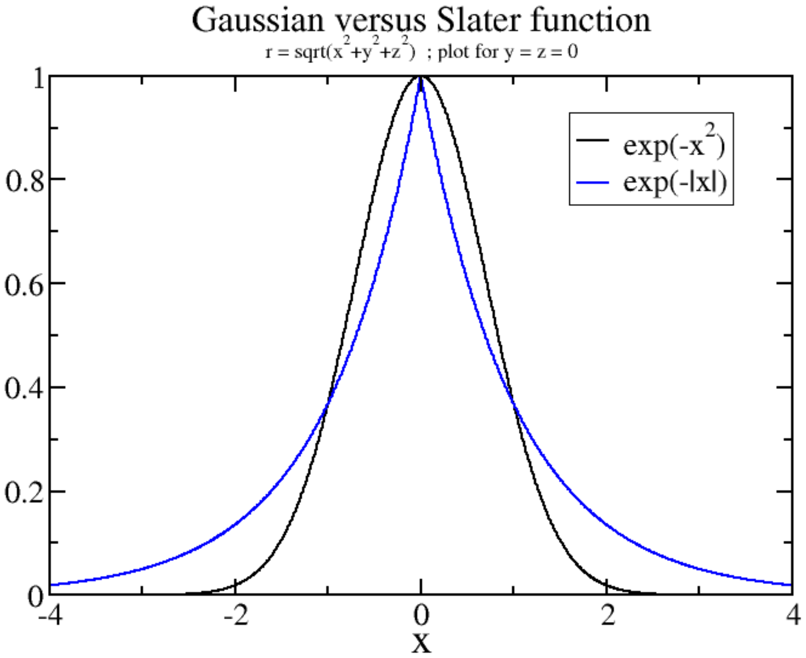
    solve H-atom exactly

    core region correct (cusp)

  - Gaussian type orbitals (GTO):

    $$\phi_{GTO}(\vec{r}) = N\, x^a y^b z^c \exp(-\zeta r^2)$$

    integrals easier than for STOs



Gaussian basis sets

$$\phi_{primitive}(\vec{r}) = N(x-A_x)^a(y-A_y)^b(z-A_z)^c \exp(-\zeta(\vec{r}-\vec{A})^2)$$

a,b,c: integer numbers

primitive basis function, atom-centered, atom at $\vec{A}$

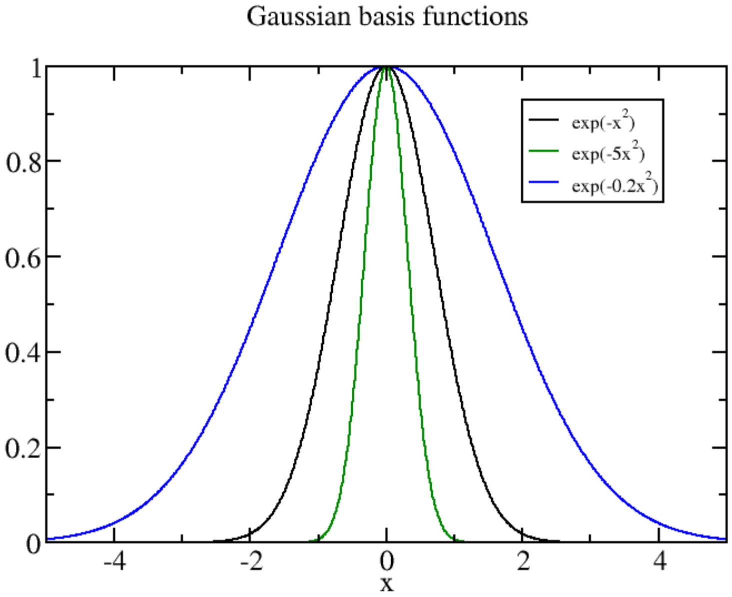
Exponent: ζ:

unit: 1/bohr^2
1 bohr =0.5291772 Å

large ζ: tight
important for core region

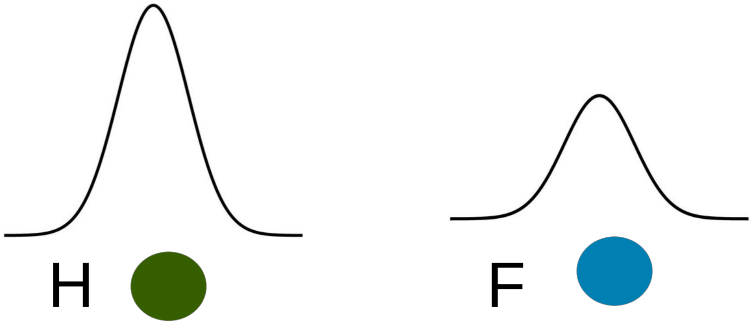
small ζ (< 1) :

diffuse, important for valence region, chemical bond

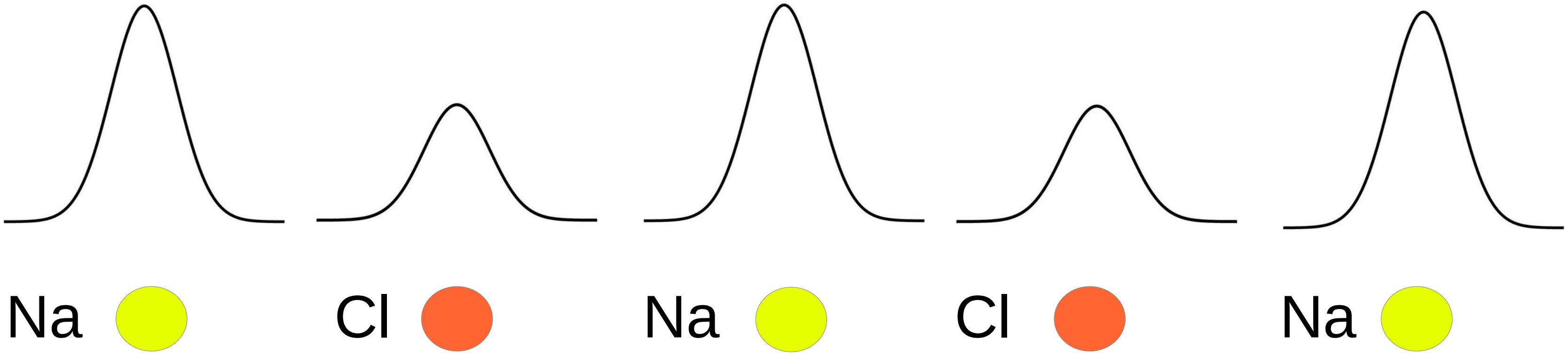


Gaussians placed at position of atoms

molecule:



periodic system:



Contraction

Idea: the core region does not change very much when a chemical bond is formed

=> make linear combination which describes core region well:
"contraction":

$$\phi(\vec{r}) = N \sum_{i=1}^{n} d_i \underbrace{x^a y^b z^c \exp(-\zeta_i r^2)}_{\text{primitive Gaussian}}$$

d_i: contraction coefficients (fixed numbers)

Total basis set: set of various $\phi_\mu(\vec{r})$ with different exponents,
contractions coefficients

Orbitals

Molecular orbital: $\Psi_i(\vec{r}) = \sum_{\mu} c_{i\mu} \phi_{\mu}(\vec{r})$

Crystalline orbital: $\Psi_i(\vec{r}, \vec{k}) = \sum_{\mu} c_{i\mu}(\vec{k}) \Phi_{\mu}(\vec{r}, \vec{k})$

with: $\Phi_{\mu}(\vec{r}, \vec{k}) = \sum_{\vec{g}} \phi_{\mu}(\vec{r} - \vec{A}_{\mu} - \vec{g}) \exp(\mathrm{i} \vec{k} \vec{g})$

The orbitals are obtained when the Hartree-Fock/Kohn-Sham equations are solved.

All basis functions contribute to each orbital.

Angular part, 1

$Y_{lm}(\theta,\varphi)$: spherical harmonics, eigenstates of operators L^2 and L_z

$r^l\ Y_{lm}(\theta,\varphi)$: solid harmonics

Y_{lm} are complex, but can be combined to real functions (=> not L_z eigenstates any more; but L_z eigenstate anyway only in atom or linear molecule)

=> real combinations are preferably used (Condon-Shortley convention, normalisation ignored in the following!):

$l=0$: Y_{00} => 1

$l=1$: $Y_{11} - Y_{1-1}$ => x

$Y_{11} + Y_{1-1}$ => y

Y_{10} => z

Angular part, 2

l=2 : Y_{20} => $3z^2-r^2 = 2z^2-x^2-y^2$

$Y_{21} – Y_{2-1}$ => xz

$Y_{21} + Y_{2-1}$ => yz

$Y_{22} + Y_{2-2}$ => x^2-y^2

$Y_{22} – Y_{2-2}$ => xy

Exponents: where from?

Easiest: even tempered: exponents separated by common factor

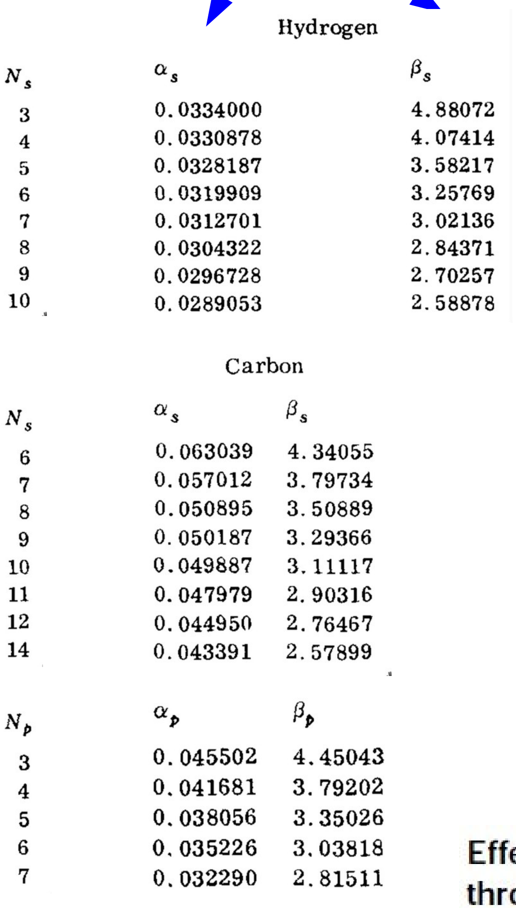
Example: factor 4, start from 0.25, stop at 4096:
0.25, 1, 4, 16, 64, 256, 1024, 4096

general: $\alpha\beta^k$ here: $\alpha=0.25$ $\beta=4$ $k=0...7$

must be done for the different angular momenta:
α_s, β_s, α_p, β_p, α_d, β_d …
Optimise α, β (lowest total energy of the respective atom)

Even tempered basis sets: optimise parameters α, β

$\alpha\beta^k$



Hydrogen

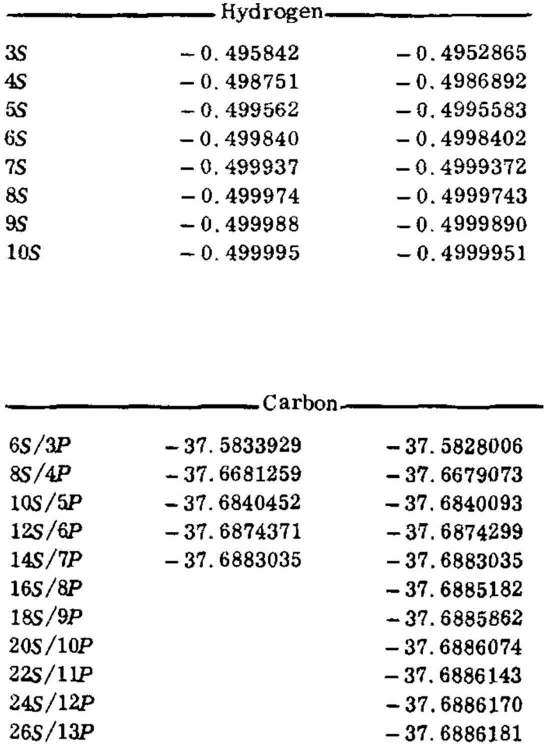
N_s	α_s	β_s
3	0.0334000	4.88072
4	0.0330878	4.07414
5	0.0328187	3.58217
6	0.0319909	3.25769
7	0.0312701	3.02136
8	0.0304322	2.84371
9	0.0296728	2.70257
10	0.0289053	2.58878

Carbon

N_s	α_s	β_s
6	0.063039	4.34055
7	0.057012	3.79734
8	0.050895	3.50889
9	0.050187	3.29366
10	0.049887	3.11117
11	0.047979	2.90316
12	0.044950	2.76467
14	0.043391	2.57899

N_p	α_p	β_p
3	0.045502	4.45043
4	0.041681	3.79202
5	0.038056	3.35026
6	0.035226	3.03818
7	0.032290	2.81511

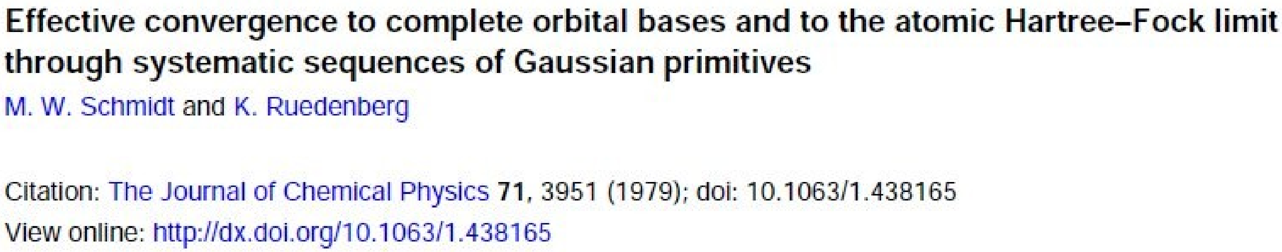
Energy in Hartree units,
1 Hartree = 27.2114 eV



Hydrogen		
3S	−0.495842	−0.4952865
4S	−0.498751	−0.4986892
5S	−0.499562	−0.4995583
6S	−0.499840	−0.4998402
7S	−0.499937	−0.4999372
8S	−0.499974	−0.4999743
9S	−0.499988	−0.4999890
10S	−0.499995	−0.4999951

Carbon		
6S/3P	−37.5833929	−37.5828006
8S/4P	−37.6681259	−37.6679073
10S/5P	−37.6840452	−37.6840093
12S/6P	−37.6874371	−37.6874299
14S/7P	−37.6883035	−37.6883035
16S/8P		−37.6885182
18S/9P		−37.6885862
20S/10P		−37.6886074
22S/11P		−37.6886143
24S/12P		−37.6886170
26S/13P		−37.6886181

- Hartree-Fock limit can be reached with more and more basis functions
- **For practical purposes: use exponents separated by factors of 2-4**



Effective convergence to complete orbital bases and to the atomic Hartree–Fock limit through systematic sequences of Gaussian primitives

M. W. Schmidt and K. Ruedenberg

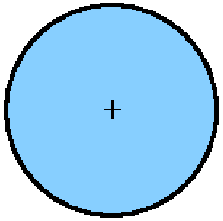
Citation: The Journal of Chemical Physics **71**, 3951 (1979); doi: 10.1063/1.438165
View online: http://dx.doi.org/10.1063/1.438165

Polarisation functions

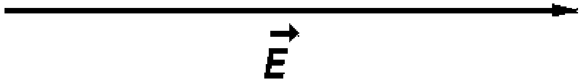
- Even if only s-orbitals are occupied, higher angular momenta usually necessary in the basis set (s occupied → p ...
  p occupied → d …)

- Higher angular momenta in basis set also necessary when doing correlation calculations, to describe excitations to these orbitals

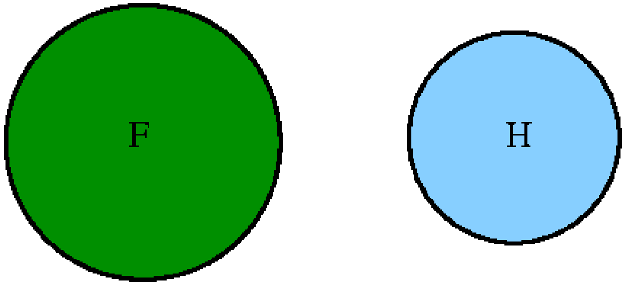
Hydrogen atom:
proton + spherically symmetric charge distribution;
only s–function necessary



external electric field will polarise the charge distribution



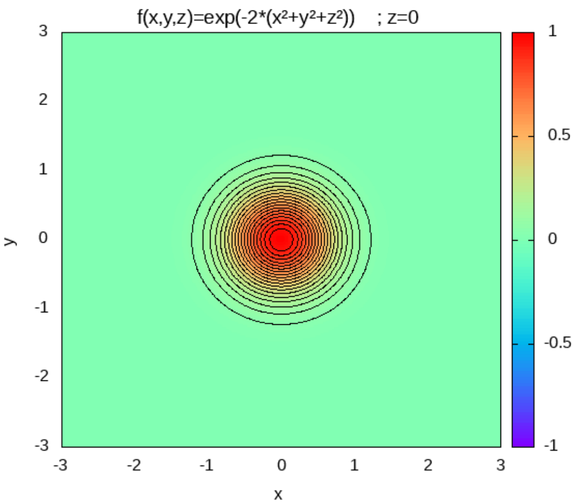
another atom will also polarise the H atom

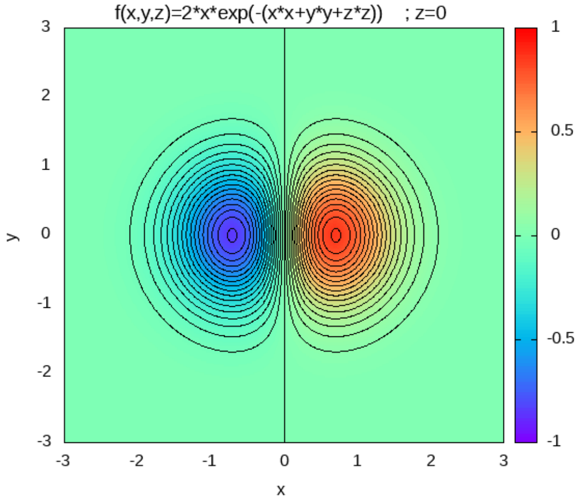


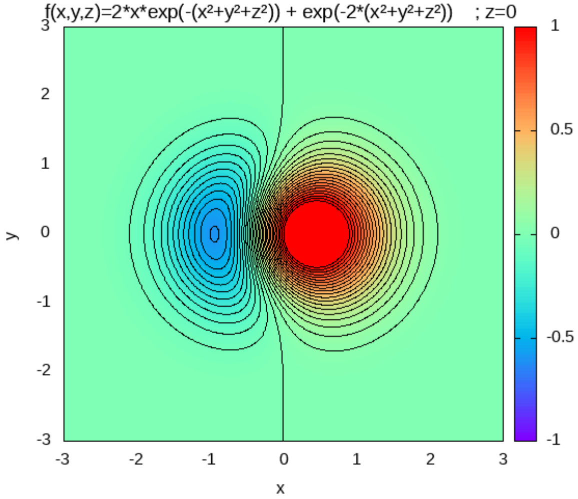
Polarisation functions

s **p** **s + p**

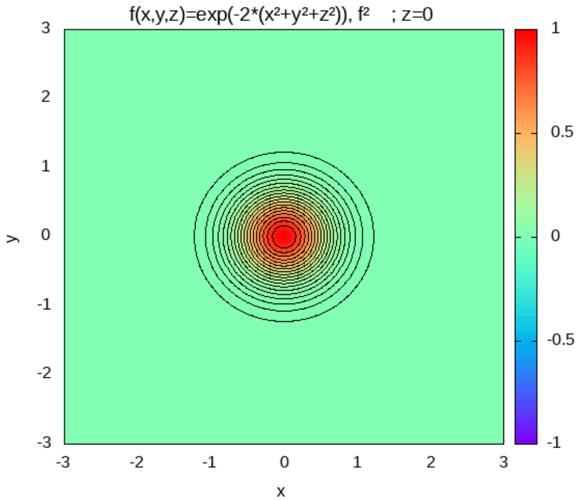
wave function:

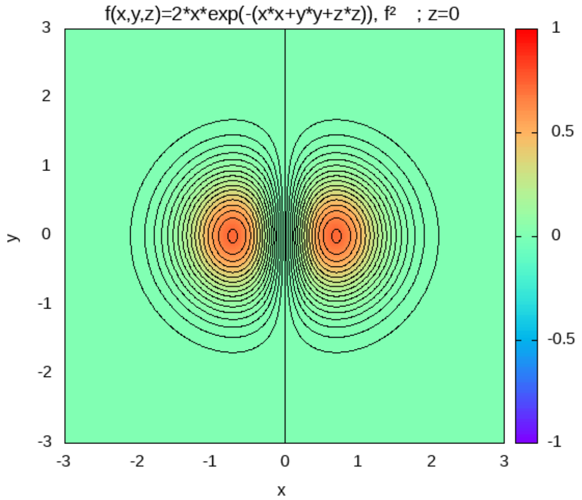


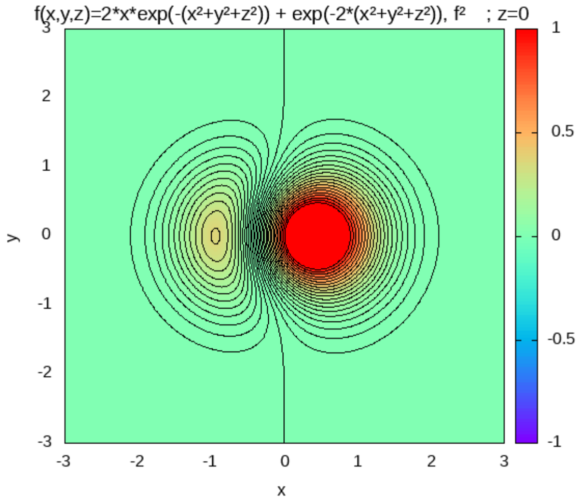




density:







Basis set choice: general recommendations; important also when applying a standard program package

- Hartree-Fock or DFT: relatively small basis set is sufficient
- wave-function based correlation (CCSD, CI, MP2 …): larger basis set necessary, e.g. “correlation-consistent” basis sets

- depends on charge state (0, -1, +1 … ?): negative ions have larger radius than positive ions
  => extra diffuse exponents required for negatively charged atoms (and metals in the periodic case)

- usually good to include polarisation function

- which property:
  - (hyper)polarisability (→ higher angular momenta)
  - excited states (→ higher angular momenta, diffuse functions ...)
  - core levels, electron density near core (→ tight functions)

- effective core potentials may be advantageous from 1st row transition metals on (to reduce calculational effort + include scalar-relativistic effects) – but you can still do all-electron calculations even for heavy atoms (e.g. to look at core-levels)

Basis set choice: databases

Molecular case: databases available

Basis set exchange: https://www.basissetexchange.org/

MOLPRO code:

http://www.molpro.net/info/basis.php?portal=user&choice=Basis+library

Huge number of basis sets available

Periodic systems: CRYSTAL website

http://www.crystal.unito.it/basis-sets.php

Problems of Hartree-Fock

- electronic correlation missing (description needs more than 1 Slater determinant)
  though this is only a small fraction of the total energy, it
  is crucial for
  - energy differences
    (binding energy, electron affinities, ionisation potentials ….)
  - excited states (solids: band gaps)

- Proper description of near-degeneracies

- Solids: vaninshing density of states at the Fermi level, for metals !
  see e.g. N. W. Ashcroft + N. D. Mermin, Solid State Physics

Is Hartree-Fock useless? NO!

- Hartree-Fock is a mathematically clear theory
- Hartree-Fock can be systematically improved
- In the following, wave-function based correlation, “post Hartree-Fock” : start from Hartree-Fock (use Hartree-Fock orbitals and energy)

Beyond Hartree-Fock: correlation

- Configuration interaction: CI(SD) ...
- Coupled cluster: CCSD ...
- Perturbation theory: MP2 …
- Multi-configuration/multi-reference methods: MCSCF, MRCI ...

advantage: well controlled, can be systematically improved

disadvantage: demanding (CPU time, memory)

Second quantisation

Instead of Slater determinant:

$$\Psi_{HF}(1,2,3,\ldots N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\chi_1(1) & \chi_2(1) & \ldots & \chi_N(1)\\ \chi_1(2) & \chi_2(2) & \ldots & \chi_N(2)\\ \ldots & \ldots & \ldots & \ldots\\ \chi_1(N) & \chi_2(N) & \ldots & \chi_N(N)\end{vmatrix}$$

use creation a^+_i and annihilation a_i operators:

$$|\Psi>=a_1^+a_2^+\ldots a_N^+|0>$$

e.g. with canonical orbitals, we obtain: $|\Psi_{HF}>=a_1^+a_2^+\ldots a_N^+|0>$

Fermions => anticommuting: $\boxed{\{a_i^+,a_j\}=a_i^+a_j+a_ja_i^+=\delta_{ij}}$

Second quantisation

Slater determinant of singly excited state (excitation from orbital i → a):

$$\Psi_i^a = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \dots & \chi_a(\vec{x}_1) & \dots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \dots & \chi_a(\vec{x}_2) & \dots & \chi_N(\vec{x}_2) \\ \dots & \dots & \dots & \dots & \dots \\ \chi_1(\vec{x}_N) & \dots & \chi_a(\vec{x}_N) & \dots & \chi_N(\vec{x}_N) \end{vmatrix}$$

use creation a^{+}_{a} and annihilation a_i operators: $|\Psi_i^a> = a_a^+ a_i |\Psi_{HF}>$

Slater determinant of doubly excited state:

$$\Psi_{ij}^{ab} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \dots & \chi_a(\vec{x}_1) & \dots & \chi_b(\vec{x}_1) & \dots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \dots & \chi_a(\vec{x}_2) & \dots & \chi_b(\vec{x}_2) & \dots & \chi_N(\vec{x}_2) \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \chi_1(\vec{x}_N) & \dots & \chi_a(\vec{x}_N) & \dots & \chi_b(\vec{x}_N) & \dots & \chi_N(\vec{x}_N) \end{vmatrix}$$

$$|\Psi_{ij}^{ab}> = a_b^+ a_a^+ a_j a_i |\Psi_{HF}>$$

Second quantisation: Operators

H_1 : sum of one electron operators *h* for each electron
(kinetic energy, nuclear-electron attraction)
H_2 : two electron operator (electron-electron interaction)
H_{nn} : nuclear-nuclear repulsion

$$|\Psi> = a_1^+ a_2^+ \dots a_N^+ |0>$$

$$|\Psi_i^a> = a_a^+ a_i |\Psi>$$

$$<\Psi_i^a|h|\Psi> = \langle \chi_a | h | \chi_i \rangle$$

$$H_1 = \sum_{pr} \langle \chi_p | h | \chi_r \rangle a_p^+ a_r$$

$$H_2 = \frac{1}{2} \sum_{pqrs} \langle \chi_p \chi_q | \frac{1}{r_{12}} | \chi_r \chi_s \rangle a_p^+ a_q^+ a_s a_r$$

$$H = H_1 + H_2 + H_{nn}$$

see also previous talk by E. Koch

Correlation: full configuration interaction (full CI)

Include single, double, triple …. substitutions:

$$\boxed{\begin{aligned} |\Psi_{\text{full CI}}> = (1 + \sum_{\substack{a\\ i}} t_a^i a_a^+ a_i + \sum_{\substack{a<b\\ i<j}} t_{ab}^{ij} a_b^+ a_a^+ a_i a_j \\ + \sum_{\substack{a<b<c\\ i<j<k}} t_{abc}^{ijk} a_c^+ a_b^+ a_a^+ a_i a_j a_k + \ldots) |\Psi_{HF}> = \sum_I c_I |\Psi_I> \end{aligned}}$$

Energy:

$$E_{\text{full CI}} = \frac{<\Psi_{\text{full CI}}|H|\Psi_{\text{full CI}}>}{<\Psi_{\text{full CI}}|\Psi_{\text{full CI}}>}$$

normalised, variational

enormous matrix to be diagonalised:

$$\boxed{\begin{gathered} H|\Psi_{\text{full CI}}> = E|\Psi_{\text{full CI}}> \\ \Rightarrow \left\langle \Psi_I \middle| H - E_{\text{full CI}} \middle| \Psi_{\text{full CI}} \right\rangle = 0 \end{gathered}}$$

scales factorially with system size

Correlation: configuration interaction (CI)

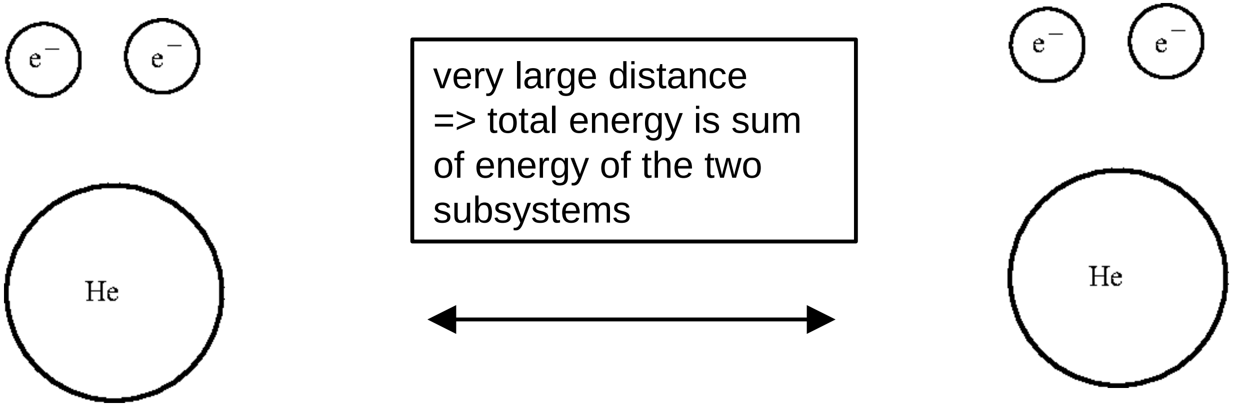
Include single and double substitutions: CI(SD)

$$|\Psi_{\mathrm{CI(SD)}}> = \left(1 + \sum_{ai} t_a^i a_a^+ a_i + \sum_{abij} t_{ab}^{ij} a_b^+ a_a^+ a_i a_j\right) |\Psi_{HF}>$$

Energy: $$E_{CI(SD)} = \frac{<\Psi_{CI(SD)}|H|\Psi_{CI(SD)}>}{<\Psi_{CI(SD)}|\Psi_{CI(SD)}>}$$

variational, scales with N^6 , with system size N

CI(SD): not size-consistent



very large distance
=> total energy is sum of energy of the two subsystems

Subsystem 1, He atom
CI(SD) includes all excitations

Subsystem 2, He atom
CI(SD) includes all excitations

Supersystem: CI(SD) does not include all excitations => not size consistent!
Here: energy of supersystem $\neq$ energy of subsytem 1 + subsystem 2

Correlation: coupled cluster (CC)

Coupled cluster with single and double substitutions: CCSD

$$|\Psi_{\mathrm{CCSD}}> = \exp\left(\sum_{ai} t_a^i a_a^+ a_i + \sum_{abij} t_{ab}^{ij} a_b^+ a_a^+ a_i a_j\right) |\Psi_{HF}> = \exp(T) |\Psi_{HF}>$$

intermediate normalisation: $\langle \Psi_{HF} | \Psi_{\mathrm{CCSD}} \rangle = 1$

Energy *E*:

$$H|\Psi_{CCSD}> = E|\Psi_{CCSD}>$$
$$\Rightarrow <\Psi_{HF}|H|\Psi_{CCSD}> = E<\Psi_{HF}|\Psi_{CCSD}>$$
$$\Rightarrow <\Psi_{HF}|H-E|\Psi_{CCSD}> = 0$$

Coefficients:

$$<\Psi_i^a|H-E|\Psi_{CCSD}> = 0$$
$$<\Psi_{ij}^{ab}|H-E|\Psi_{CCSD}> = 0$$

not variational, but size-consistent
scales like N^6

Perturbation theory, second order: text book

Start from:

$$H|\Psi> = E|\Psi>$$

Expand:

$$H = H_0 + \lambda H_1$$

$$\Psi = \Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \lambda^3 \Psi_3 + \ldots$$

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \lambda^3 E_3 + \ldots$$

Insert in Schrödinger equation:

$$(H_0 + \lambda H_1)|\Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \lambda^3 \Psi_3 + \ldots > =$$

$$(E_0 + \lambda E_1 + \lambda^2 E_2 + \lambda^3 E_3 + \ldots)|\Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \lambda^3 \Psi_3 + \ldots >$$

Order according to **λ**:

$$H_0|\Psi_0> = E_0|\Psi_0>$$

$$H_1|\Psi_0> + H_0|\Psi_1> = E_1|\Psi_0> + E_0|\Psi_1>$$

$$H_1|\Psi_1> + H_0|\Psi_2> = E_0|\Psi_2> + E_1|\Psi_1> + E_2|\Psi_0>$$

$$\ldots$$

Perturbation theory, second order: text book

$$\begin{aligned}
&(1) \quad H_0|\Psi_0> &&= E_0|\Psi_0> \\
&(2) \quad H_1|\Psi_0> + H_0|\Psi_1> &&= E_1|\Psi_0> + E_0|\Psi_1> \\
&(3) \quad H_1|\Psi_1> + H_0|\Psi_2> &&= E_0|\Psi_2> + E_1|\Psi_1> + E_2|\Psi_0>
\end{aligned}$$

use $(i \geq 1)$: $<\Psi_0|\Psi_0> = 1$; $<\Psi_i|\Psi_0> = 0$ (intermediate normalisation)

multiply with $<\Psi_0|$

$$<\Psi_0|H_0|\Psi_i> = (<\Psi_i|H_0|\Psi_0>)^+ = (<\Psi_i|E_0|\Psi_0>)^+ = 0$$

$$\begin{aligned}
&(1) <\Psi_0|H_0|\Psi_0> = E_0 \\
&(2) <\Psi_0|H_1|\Psi_0> + 0 = E_1 + 0 \\
&(3) <\Psi_0|H_1|\Psi_1> + 0 = 0 + 0 + E_2
\end{aligned}$$

Perturbation theory: Møller-Plesset, 2nd order (MP2)

Perturbation theory: $\boxed{H = H_0 + H_1}$

0th order:

$$H_0 = \sum_{i=1}^{N} f(i) \qquad \text{(Fock operator)}$$

$$|\Psi_0\rangle = |\Psi_{HF}\rangle$$

$$H_0|\Psi_{HF}\rangle = E_0|\Psi_{HF}\rangle$$

$$E_0 = \sum_{i=1}^{N} \epsilon_i$$

1st order:

$$E_1 = \langle\Psi_0|H_1|\Psi_0\rangle = \langle\Psi_0|H - H_0|\Psi_0\rangle = E_{HF} - E_0$$

$$E_0 + E_1 = E_{HF}$$

2nd order

$$E_2 = \langle\Psi_0|H_1|\Psi_1\rangle = \langle\Psi_0|H - H_0|\Psi_1\rangle = \langle\Psi_0|H|\Psi_1\rangle$$

Perturbation theory: Møller-Plesset, 2nd order (MP2)

2nd order:

$$|\Psi_1> = \sum_{a,k} t_a^k \psi_k^a + \sum_{ab,kl} t_{ab}^{kl} \psi_{kl}^{ab} + \ldots$$

$$E_2 = <\Psi_0|H_1|\Psi_1> = <\Psi_0|H - H_0|\Psi_1> = <\Psi_0|H|\Psi_1>$$

Single substitutions have vanishing matrix elements (Brillouin’s theorem):

$$<\psi_k^a|H|\Psi_{HF}> = 0$$

Triply and higher excited states have vanishing matrix elements (look at H in second quantisation):

$$<\psi_{klm}^{abc}|H|\Psi_{HF}> = 0$$

Left with:

$$|\Psi_1> = \sum_{ab,kl} t_{ab}^{kl} \psi_{kl}^{ab}$$

Coefficients:

$$t_{ab}^{kl} = -\frac{\int d^3 r_1 d^3 r_2 \frac{\chi_a^*(\vec{r}_1)\chi_k(\vec{r}_1)\chi_b^*(\vec{r}_2)\chi_l(\vec{r}_2) - \chi_a^*(\vec{r}_1)\chi_l(\vec{r}_1)\chi_b^*(\vec{r}_2)\chi_k(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}}{\epsilon_a + \epsilon_b - \epsilon_k - \epsilon_l}$$

Energy:

$$E_2 = -\sum_{k>l} \sum_{a>b} \frac{\left(\int d^3 r_1 d^3 r_2 \frac{\chi_a^*(\vec{r}_1)\chi_k(\vec{r}_1)\chi_b^*(\vec{r}_2)\chi_l(\vec{r}_2) - \chi_a^*(\vec{r}_1)\chi_l(\vec{r}_1)\chi_b^*(\vec{r}_2)\chi_k(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\right)^2}{\epsilon_a + \epsilon_b - \epsilon_k - \epsilon_l}$$

not variational, but size-consistent

scales roughly like N^4 with system size N

Multi-configuration SCF (MCSCF)

Wavefunction: $$\boxed{|\Psi_{MCSCF}> = \sum_I C_I |\Psi_I>}$$

$$|\Psi_I> \quad \in \quad \{ c_0 |\Psi_{HF}>, \ c_a^k |\psi_k^a> \ , \ c_{ab}^{kl} |\psi_{kl}^{ab}> \ , \ c_{abc}^{klm} |\psi_{klm}^{abc}>, \ \ldots \ \} : \quad \text{active space}$$

Optimize coefficients AND orbitals

Multi-reference CI (MRCI)

Wavefunction:

$$|\Psi_{\mathrm{MRCI(SD)}}> = \left(1 + \sum_{ai} t_a^i a_a^+ a_i + \sum_{abij} t_{ab}^{ij} a_b^+ a_a^+ a_i a_j\right) |\Psi_{MCSCF}>$$

used in case of near-degeneracies, low-lying excited states
(usually strongly correlated systems)
optimise coefficients

Explicit correlation

Additionally include terms in CI with r_{12} dependence, such as :

$$\left(1-\frac{1}{\gamma}\exp\left(-\gamma\left|\vec{r}_1-\vec{r}_2\right|\right)\right)\Psi_{HF}$$

local correlation

start from localised orbitals instead of canonical orbitals

Properties

Expressed as derivatives with respect to nuclear position $\vec{R}$, external electric field $\vec{F}$, external manetic field $\vec{B}$, nuclear magnetic spin $\vec{I}$, electron magnetic spin $\vec{s}$:

Force: $-\frac{\partial E}{\partial \vec{R}}$

Vibrations: $\frac{\partial^2 E}{\partial \vec{R} \partial \vec{R}}$

Dipole: $\frac{\partial E}{\partial \vec{F}}$

IR intensity: $\frac{\partial^2 E}{\partial \vec{R} \partial \vec{F}}$

usually quite an effort to implement (Pulay-forces)

Properties

For a table of properties expressed
as derivatives, see:

F. Jensen,
Introduction to
Computational
Chemistry

Example: electron affinity of oxygen

O → O^- exp. value: 1.461 eV versus calculation (Molpro):

basis set:	HF	CI (SD)	CCSD	CCSD(T)	CCSD-F12	CCSD(T)-F12
	method					
aug-cc-pvdz	-0.493	0.941	1.086	1.188	1.294	1.394
aug-cc-pvtz	-0.525	1.016	1.185	1.335	1.299	1.445
aug-cc-pvqz-f12	-0.534	1.068	1.245	1.410	1.303	1.465
aug-cc-pv5z-f12	-0.535	1.084	1.264	1.431	1.298	1.464
numerical (MCHF code)	-0.535					

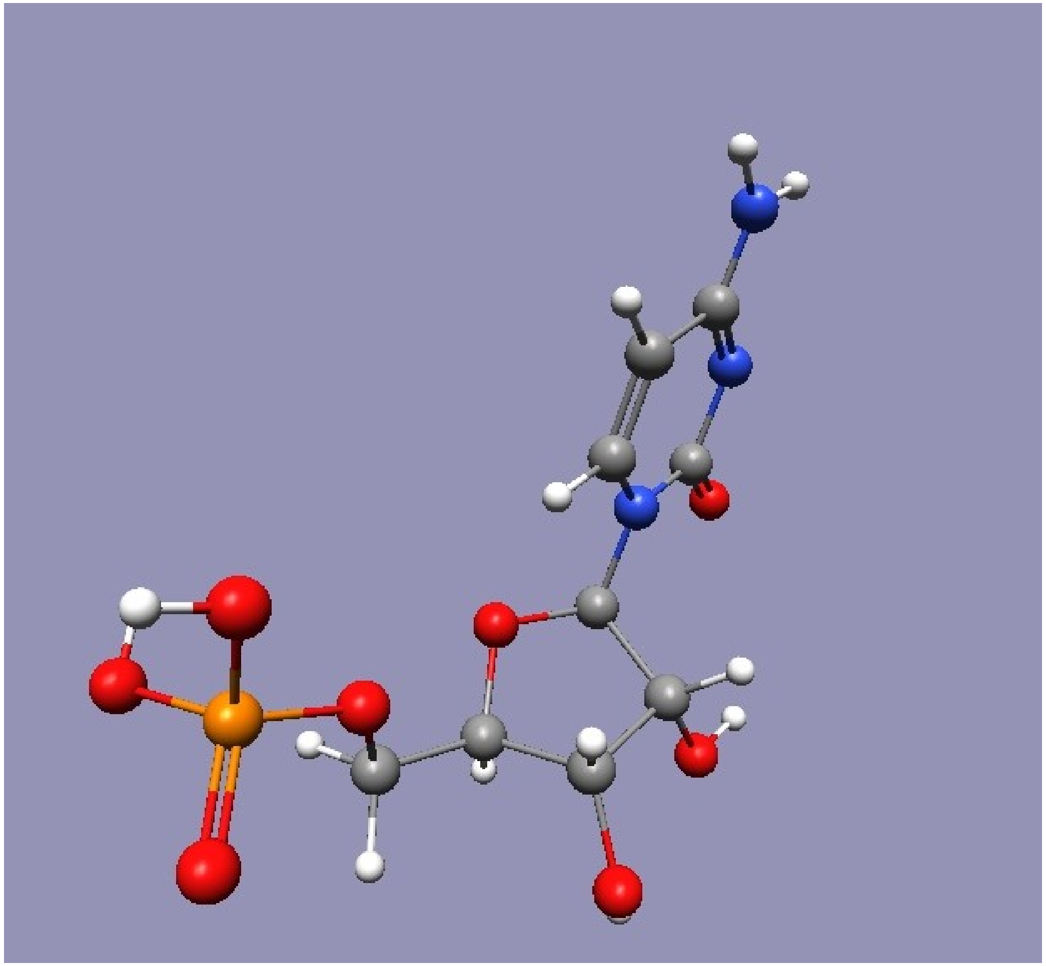
HF: even wrong sign!
imporant, correct in HF: negative orbital eigenvalues ϵ_i : otherwise unstable (may happen for some DFT functionals, e.g. LDA !)
CI(SD), CCSD …: all start from HF orbitals

Example: bond lengths

For various properties such as bond distances,
bond angles, atomisation energies …
as a function of basis set and method
(for 20 molecules, normal distribution of the errors),
see:

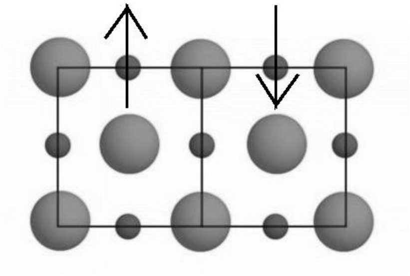
Helgaker, Jørgensen, Olsen: Molecular Electronic-Structure Theory

Example: CMP-5 (Cytidine monophosphate, nucleotide)



PNO-RCCSD(T), 35 atoms, 835 basis functions on 12 cores, single point, 174 minutes wall-clock, Molpro

Example: superexchange in NiO



only S_z Eigenstate feasible, fit Ising model

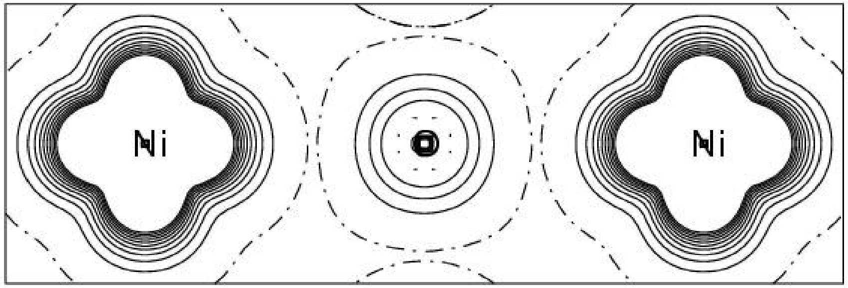
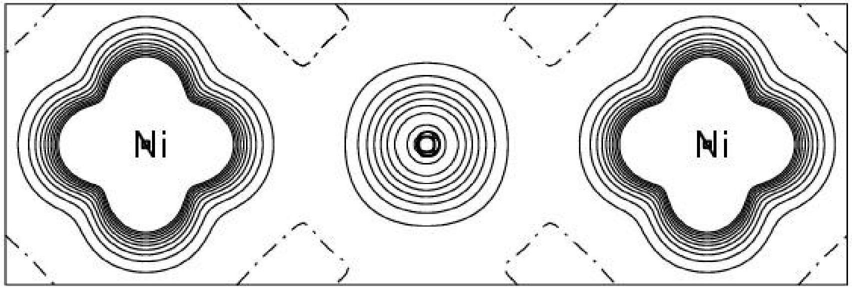
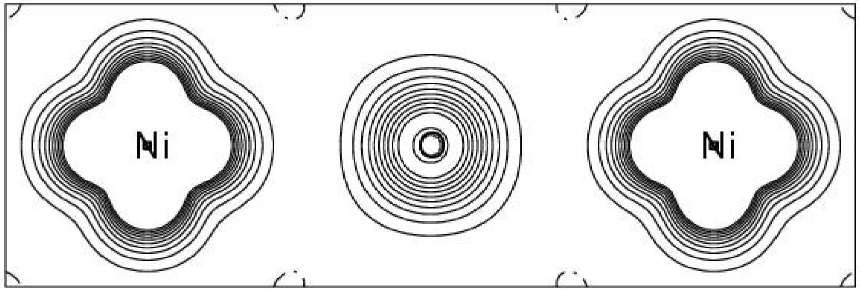
ferromagnet versus antiferromagnet:

↑↑↑↑↑↑↑↑↑ ↑↓↑↓↑↓↑↓↑

energy difference: z JS^2 (z: number of neighbours

J: superexchange coupling)

Example: superexchange in NiO

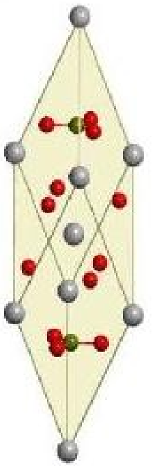
		magn. moment Ni	magn. moment O	*J*
periodic Hartree-Fock		1.9	0.1	-5.4 meV
periodic B3LYP		1.8	0.2	-29 meV
periodic LDA		1.6	0.4	-94 meV

wave-function based correlation, embedded cluster, CASPT2 *(deGraaf et al 1997, Moreira et al 2002)*: -14 … -17 meV

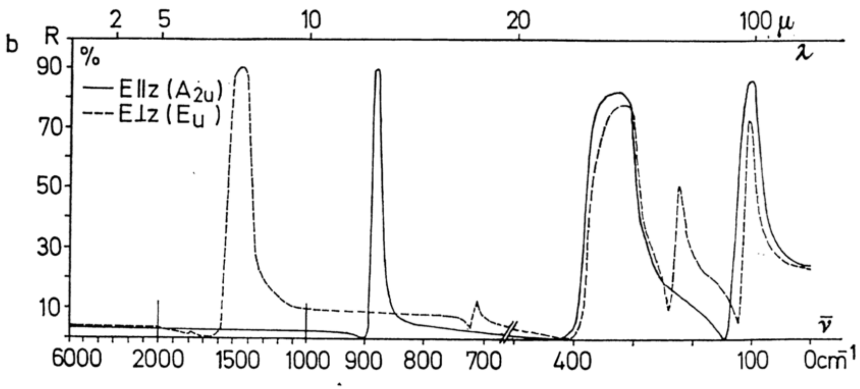
exp.: -20 meV

Example: IR spectrum of calcite

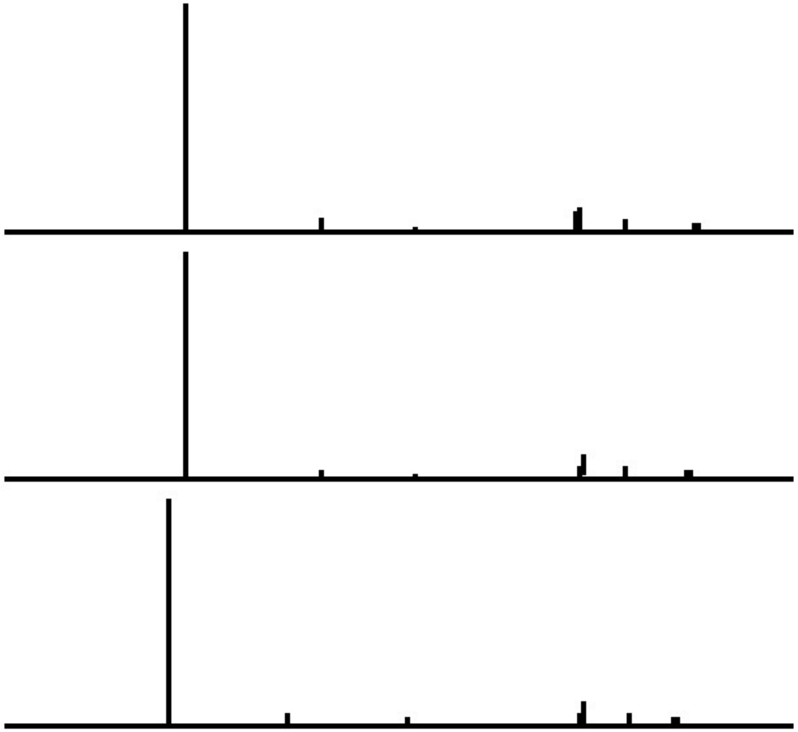
$CaCO_3$:



Frequencies,
Infrared-intensities:



Experiment:
Hellwege et al
(Z. Physik 1970)



Experiment

DFT (B3LYP)

HF

Valenzano, Torres, Doll, Pascale, Zicovich-Wilson, Dovesi (Z. Phys. Chem. 2006)

Today’s state of the art

Molecules:

- Hartree-Fock for hundreds of atoms
- wave-function based correlation for tens of atoms
- properties: mainly implemented on HF level, less for wave-function based correlation

Solids:

- Hartree-Fock for unit cell with tens/hundreds of atoms
- wave-function based correlation: some pioneering work, yet far from routine

Conclusion

- Schrödinger equation for electronic structure problem
- Hartree-Fock calculations nowadays fairly routine work
- post Hartree-Fock with wave-function based correlation:
  - demanding (computational effort, but also code implementation)
  - systematic, controlled approach to tackle Schrödinger equation

Thank you for the attention !