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ELECTRONIC STRUCTURE METHODS IN QUANTUM CHEMISTRY

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ELECTRONIC STRUCTURE METHODS IN QUANTUM CHEMISTRY

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Problem to solve:

Solution of the

- electronic
- time-independent
- non relativistic

Schrödinger equation for many electron systems:

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

$$\mathcal{H} = \sum_{i}^{N}(-1/2\nabla_i^2 - \sum_{I}\frac{Z_I}{r_{iI}}) + \sum_{i}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}$$

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$$

Historical QC-Landmarks:

- 1927 H_2 **Heitler & London**
- 1955 N_2 **Scherr**
  (2 assistants, mechanical calculators: 2 years)
- 1958-59 1rst row diatomics & hydrides
- 1971 cytosine-guanine complex
  -
  -
  - 1986: full CI (DZP) H_2O ($\sim 10^7$ det)
  -
- 1996 p53 tumor supressor tetramization monomer
  (HF, 3836 basis fcts on a IBM RS6000/590)
  C_{20} DZP CCSD(T)

Overview:

- Basis Sets
- **Hartree-Fock**
  (RHF, ROHF, UHF)
- **Configuration Interaction**
  (CI, CISD, CISDT,..FCI, MRCI,
  MCSCF, CASSCF, GVB)
- **Many-Body Perturbation**
  (MP2, MP3, MP4,..MPn)
- **Coupled Cluster**
  (CCD, CCSD, QCISD, CCSDT,
  CCSD(T), CCSDTQ)
- **Applications**

Literature:

General Literature about QC Methods:

- Modern Quantum Chemistry Introduction to Advanced Electronic Structure Theory
  A. Szabo and N.S. Ostlund, McGraw-Hill Publishing Co., New York (1989) (now: new edition - as paperback!)
- Ab Initio Molecular Orbital Theory
  W.J. Here, L. Radom, P.v.R. Schleyer, and J.A. Pople, Wiley-Interscience, New York (1986)
- Exploring Chemistry with the Gaussian Quantum Chemistry Program
  J.B. Foresman and AE. Frisch, Gaussian Inc. (1993)
- Applications of Post-Hartree-Fock Methods: A Tutorial
  Rev.in Computational Chemistry, eds. K.B. Lipkowitz and D.B. Boyd, VCH Publishers New York (1990), vol 1, p.45-81

Basis Sets:

- Basis Set Selection for Molecular Calculations
  E.R. Davidson, D. Feller, Chem.Rev. **86**, 681 (1986)
- Compilation of Gaussian exponents and contraction coefficients:
  R. Poirier, R. Kari and I.G. Csizmadia, *Handbook of Gaussian Basis Sets*, Elsevier Science, NY (1985)

- Compilation of polarization exponents:
  B. Roos and P. Siegbahn, Theor. Chim. Acta, **17**, 208 (1970)

R12-Methods:

- W. Klopper and W. Kutzelnigg, Chem. Phys. Lett. **134**, 17 (1987)
  (MP2-R12)
- W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991)
  (MP2-R12, MP3-R12, CI-R12, CEPA-R12)
- J.Noga and W. Kutzelnigg, J. Chem. Phys. **101**, 7738 (1994)
  (CC-R12)

Coupled-Cluster:

- Theor. Chim. Acta **80**, 71ff (1991)

Semi-empirical Methods:

- Semi-empirical Molecular Orbital Methods
  Rev.in Computational Chemistry, eds. K.B. Lipkowitz and D.B. Boyd, VCH Publishers New York (1990), vol 5, p.65

WWW Addresses:

- The CCQC Book of Knowledge:
  http://zopyros.ccqc.uga.edu/Docs
  /Knowledge/intro.html
- Sandia National Labs, Center for Computational Engineering:
  http://midway.ca.sandia.gov/chemistry
  /index.html
- WWW Computational Chemistry Resources:
  http://lacebark.ntu.edu.au/chem_ref.html
- Quantum Chemistry Program Exchange QCPE:
  http://www.osc.edu/ccl/qcpe
  /QCPE/index.html
- Pacific Northwest Laboratory Basis set server:
  http://www.emsl.pnl.gov:2080/forms
  /basisform.html

Software Packages:

Name	Methods	Written/Distributed by	Price
ACES II	MBPT, CC, TDRHF	R.Bartlett, Florida (USA) aces2@qtp.ufl.edu http://www.qtp.ufl.edu/Aces2/	
ADF	DFT	B.te Velde, Amsterdam (NL) tevelde@chem.vu.nl http://tc.chem.vu.nl/SCM/Doc/PI/PI.html	$1800
AMPAC 5.0	MINDO/3, MNDO, AM1	M.J.S. Dewar, QCPE http://www.osc.edu/ccl/qcpe/QCPE/index.html	$100-200
CADPAC 5.1	MP4, RHF, UHF DFT	R.D. Amos, Camebridge (GB) cadpac@theor.ch.cam.ac.uk	
COLUMBUS	SCF, MCSCF MRCI	I.Shavitt, Ohio (USA) shavitt@mps.phio-state.edu	free
CRYSTAL 95	HF, DFT with pbc's	R. Dovesi, C. Roetti, Torino (Italy) V.R. Saunders, Daresbury (GB) http://wserv1.dl.ac.uk/TCS/Software/CRYSTAL/	908 000 ItL
DMOL	DFT	Molecular Simulations, Inc (MSI)	

Name	Methods	Written/Distributed by	Price
GAMESS	RHF, ROHF, UHF, GVB,MCSCF,CI,MP2	M.S.Gordon, Iowa (USA) http://www.ameslab.gov/GAMESS/GAMESS.html	free
Gaussian 94	all	Gaussian Inc info@gaussian.com http://www.gaussian.com	$2000
MOLCAS_4	CASSCF, RASSCF, CASPT2, MRCISD	University of Lund, Sweden http://garm.teokem.lu.se/MOLCAS/	
MOPAC 6.0	MNDO, MINDO/3, AM1, PM3	J.J.P. Stewart, QCPE http://iti2.net.jstewart	(free)
TURBOMOLE 4.0	SCF, MP2	R. Ahlrichs, Karslruhe (D) MSI	
VAMP 6.0	MNDO, AM1, PM3	T. Clark, Erlangen (D) Oxford Molecular Products	

ACES	Advanced Concepts in Electronic Structure
ADF	Amsterdam Density Functional Program
AMPAC	Austin Method Package
CADPAC	Camebridge Analytical Derivatives PACkage
GAMESS	General Atomic and Molecular Electronic Structure System
MOPAC	Molecular Orbital Package

Basis Sets (BSs)

Which basis set??

- **$>$ 100 different basis sets!**
- **no universal basis set**

'Golden Rules':

- balanced basis sets
- 'better' method needs 'better' basis!

Types of Basis Functions:

Slater-type Orbitals (STO's):

$\zeta = (Z-s)/n^*$

$$\Phi_{nlm} = N r^{n-1} e^{-\xi r} Y_{lm}(\theta, \phi)$$

Gaussian-type Orbitals (GTO's):
(Boys 1950, McWeeny 1953)

Cartesian Gaussian: $x^l y^m z^n e^{-\alpha r^2}$

$$G_{1s}(r) = (\frac{8\alpha^3}{\pi^3})^{1/4} e^{-\alpha r^2}$$

$$G_{2px} = (\frac{128\alpha^5}{\pi^3})^{1/4} x e^{-\alpha r^2}$$

$$G_{3dxy} = (\frac{2048\alpha^7}{\pi^3})^{1/4} xy e^{-\alpha r^2}$$

Redundancy for $l \geq 2$:

Ex: 3d orbitals: $x^2 - y^2, r^2 - z^2, xy, xz, yz$ →5
cartesian $x^2, y^2, z^2, xy, xz, yz$ →6

$x^2 + y^2 + z^2 = r^2$: "3s" →redundant!

Contracted Gaussian (CGTO's):

(Clementi & Whitten) 1965, 1966

fixed LC of primitive Gaussian functions:

$$\phi_{lmn} = x^l y^m z^n \sum_{p=1}^{L} d_i e^{-\alpha_i r^2}$$

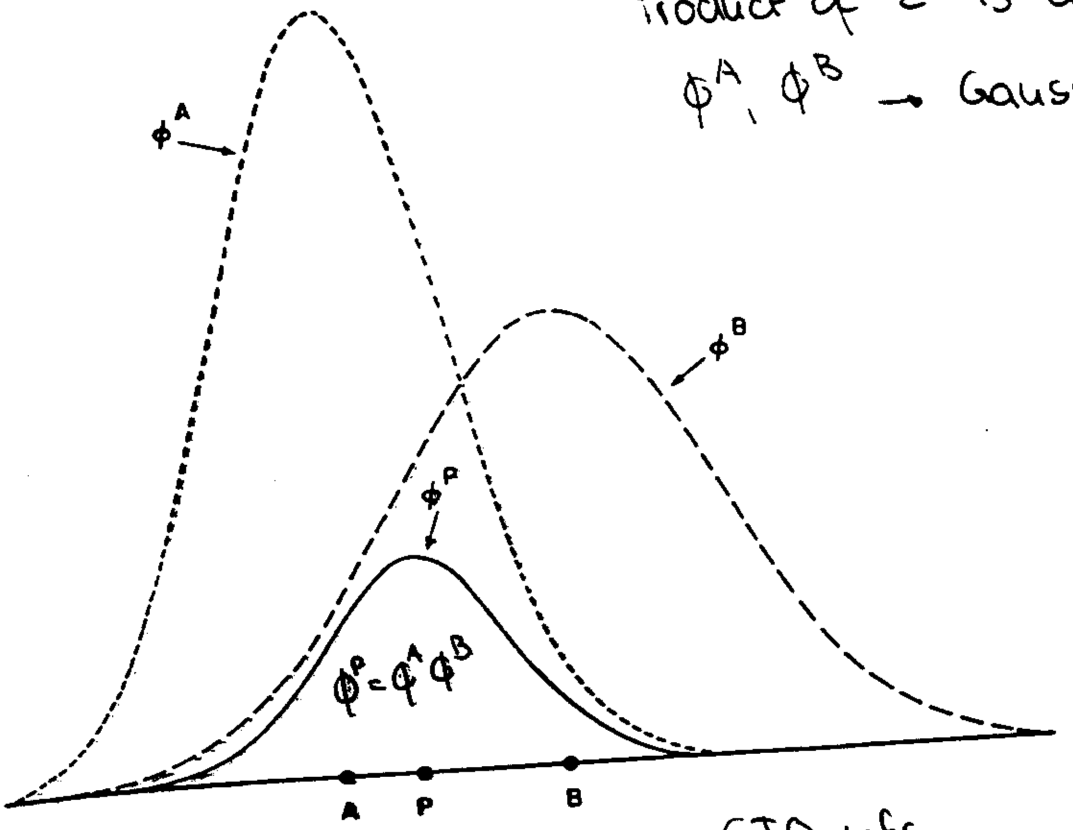
L: length of contraction (segmented or general)
d_i, α_i: **fixed (determined once)**

'Exotics'

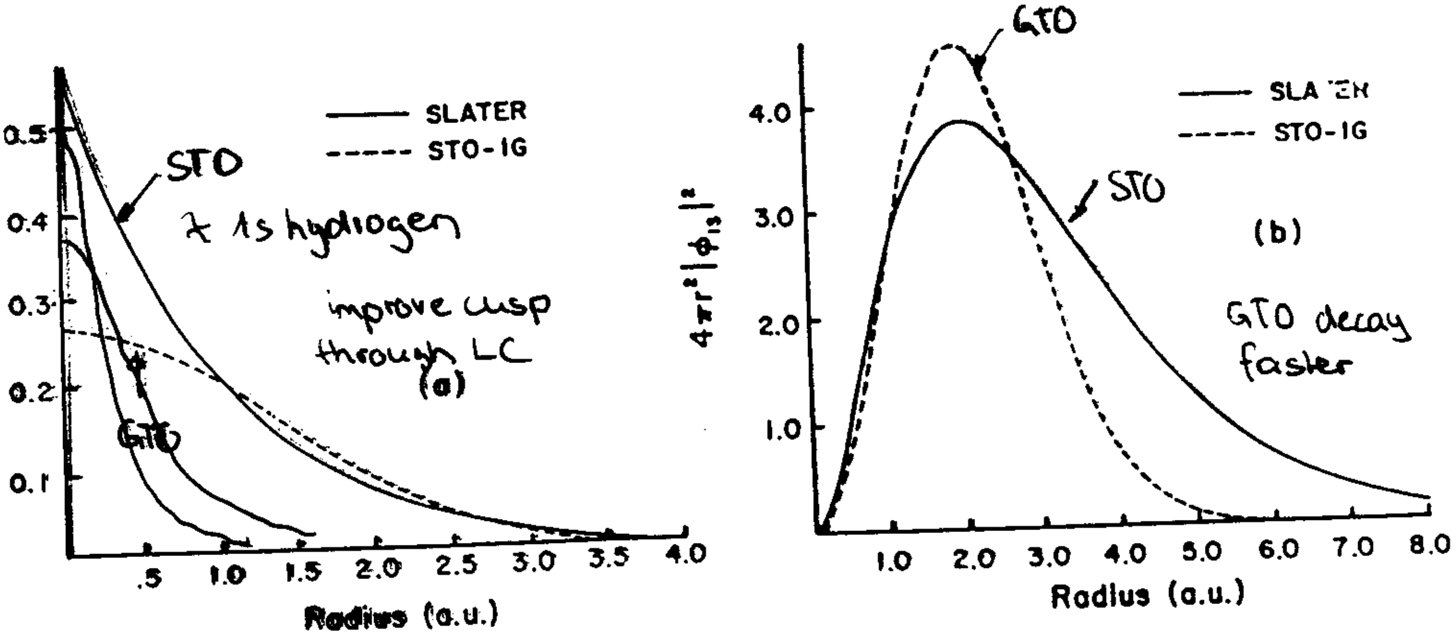
- lobe functions
- floating spherical GTO's
- (gaussian) geminals
- r12-dependent basis fcts

Product of 2 1s Gaussians

$\phi^A, \phi^B \rightarrow$ Gaussian ϕ^P



Comparison STO vs GTO wfc



Gaussian Product Theorem:

(product of 2 Gaussian on two different centers is 1 Gaussian at a third center)

Ex. unormalized 1s GTO's:

$$g_{1s}(\vec{r}-\vec{R}_A)g_{1s}(\vec{r}-\vec{R}_B)$$

$$= exp[-\alpha(\vec{r}-\vec{R}_A)^2]exp[-\beta(\vec{r}-\vec{R}_B)^2]$$

$$= exp[-\frac{\alpha\beta}{\alpha+\beta}(\vec{R}_A-\vec{R}_B)^2]exp[-(\alpha+\beta)(\vec{r}-\vec{R}_p)^2]$$

$$R_p = \frac{\alpha R_A + \beta R_B}{\alpha+\beta}$$

→4-center integrals (for 1s Gaussians) reduce to two-center integrals

Laplace transform

(Gaussian integral transform)

$$\frac{1}{r} = \frac{1}{\sqrt{\pi}}\int_0^{\infty} e^{-sr^2}\sqrt{s}ds$$

→nuclear attraction integral and electron repulsion integral transform to

$$I = \sum_0^L C_m F_m(\omega) \qquad F_m(\omega) = \int_0^1 t^{2m}e^{-\omega t^2}dt$$

Types of Basis Sets

Nomenclature

- contractions: (9s5p) →[4s 2p]

  $(\underbrace{9s5p}_{\text{heavy element}}/\underbrace{3s2p}_{\text{hydrogen}}) \rightarrow [4s2p/2s1p]$

- minimum, double zeta, triple zeta...

  (No. of basis fct per occupied orbital)

  (ex. C: 1s,2s,2p) ⚠ H,He: 1s
  Li,Be: 1s 2s 2p! Li-Ne

- **split-valence basis sets**

  1 basis fct per inner shell orbital, 2 (3) basis fct per valence shell orbital

  example: 6-31G

  1s : **6 primitive GTO's contracted to 1 CGTO**
  2s/2p: 3 GTO →1 CGTO, 1 GTO uncontracted

- **diffuse functions: 6-31$^+$G, 6-31^{++}G**

  (1 more s and p function)

  (anions, weak interactions, lone pairs, highly excited states)

- polarization fcts: 6-31*G, 6-31**G
  6-311G(3df,2p)

  (set of basis fcts with $l = l_{max}^{occ}$+1)

  but: Li: d-fcts!

```
Carbon 6-311G
----------------------------------------
  alpha          contraction
                 coefficient
----------------------------------------
S    6 1.00
 0.456324D+04  0.196665D-02
 0.682024D+03  0.152306D-01
 0.154973D+03  0.761269D-01
 0.444553D+02  0.260801D+00
 0.130290D+02  0.616462D+00
 0.182773D+01  0.221006D+00
SP   3 1.00
 0.269642D+02  0.114660D+00  0.402487D-01
 0.480331D+01  0.919999D+00  0.237594D+00
 0.145933D+01 -0.303068D-02  0.815854D+00
SP   1 1.00
 0.483456D+00  0.100000D+01  0.100000D+01
SP   1 1.00
 0.145585D+00  0.100000D+01  0.100000D+01
----------------------------------------
Diffuse function => 6-311G+

SP   1 1.00
 0.438000D-01  0.100000D+01  0.100000D+01

----------------------------------------
Polarisation function => 6-311G*

D    1 1.00
 0.626000D+00  0.100000D+01
----------------------------------------
```

"SP shells"
α is the same
for s and p(x,y,z)
contraction coeff.
is different

dz   Fri Apr 29 18:59:08 1994   1

(4s 5p) → (4s 2p)

Carbon Huzinaga-Dunning DZ

```
-----------------------------
  alpha          contraction
                 coefficient
-----------------------------
S    6 1.00
 0.423261E+04   0.202900E-02
 0.634882E+03   0.155350E-01
 0.146097E+03   0.754110E-01
 0.424974E+02   0.257121E+00
 0.141892E+02   0.596555E+00
 0.196660E+01   0.242517E+00
S    1 1.00
 0.514770E+01   0.100000E+01
S    1 1.00
 0.496200E+00   0.100000E+01
S    1 1.00
 0.153300E+00   0.100000E+01
P    4 1.00
 0.181557E+02   0.185340E-01
 0.398640E+01   0.115442E+00
 0.114290E+01   0.386206E+00
 0.359400E+00   0.640089E+00
P    1 1.00
 0.114600E+00   0.100000E+01
-----------------------------
```

contracted "1s"

3 uncontracted

contracted

uncontracted

Often used Basis Sets:

Origin:

- **least square fit to STO's** (Pople: **STO-nG)**
- **optimize HF energy atoms:**
  - **Individually optimized:**
    Huzinaga **(9s,5p) (H-Ne)** →(Dunning: **DZ)**
    Van Duijneveldt **(14s,9p)** →**Davidson (C,O)**
  - **additional contraints:**
    - **primitives of the same shell constraint to share exponents):** (Pople: **n-ijG)** $\zeta_i = \alpha\beta^{k-1} \times [1+\gamma(k/K)^\delta]$
      4 parameter form
    - even-tempered, well tempered BSs: **(exponents form geometric progression):**

$\zeta_i = \alpha\beta^i$ for s,p,d...

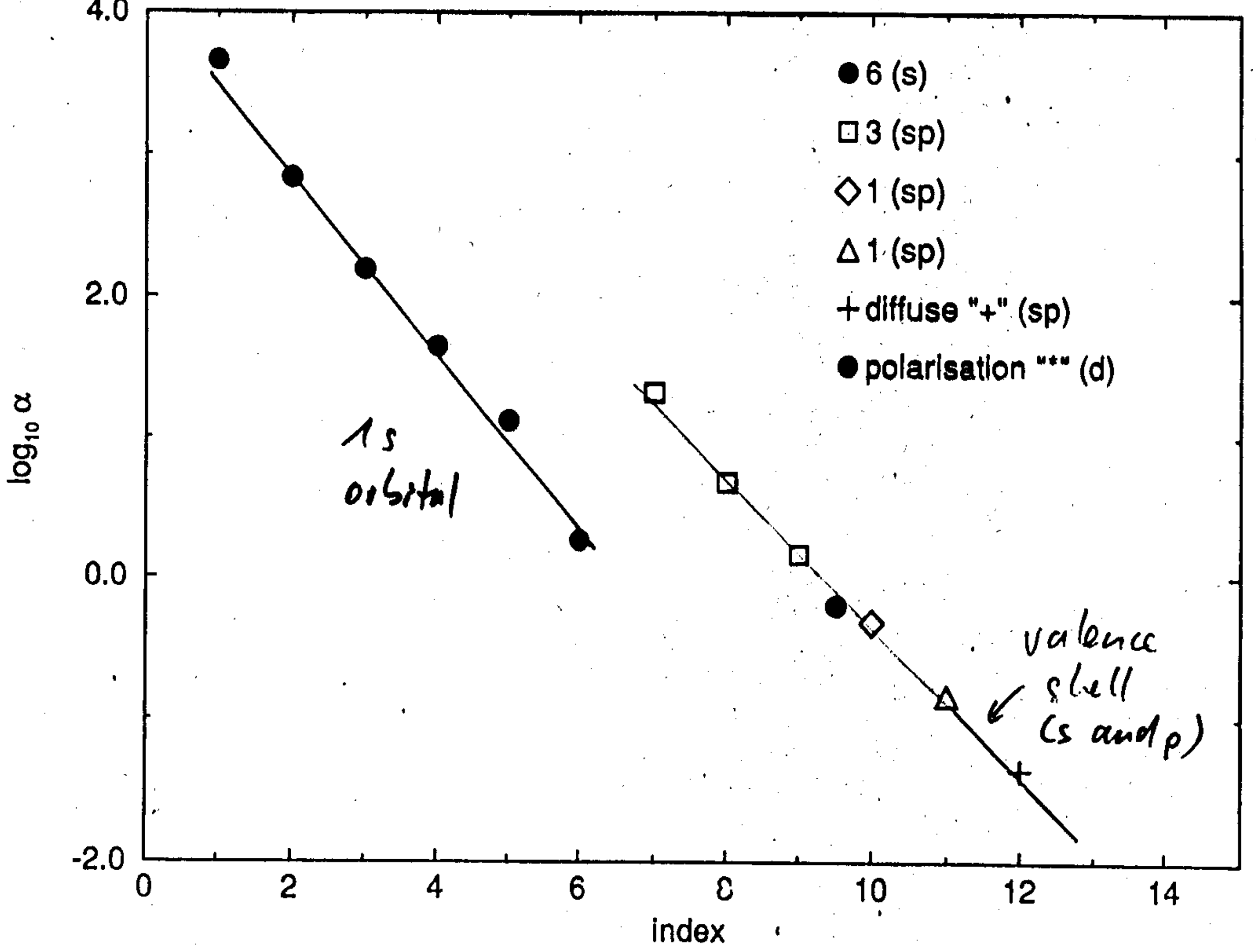
$$\alpha_i/\alpha_{i+1} = \beta \approx const$$

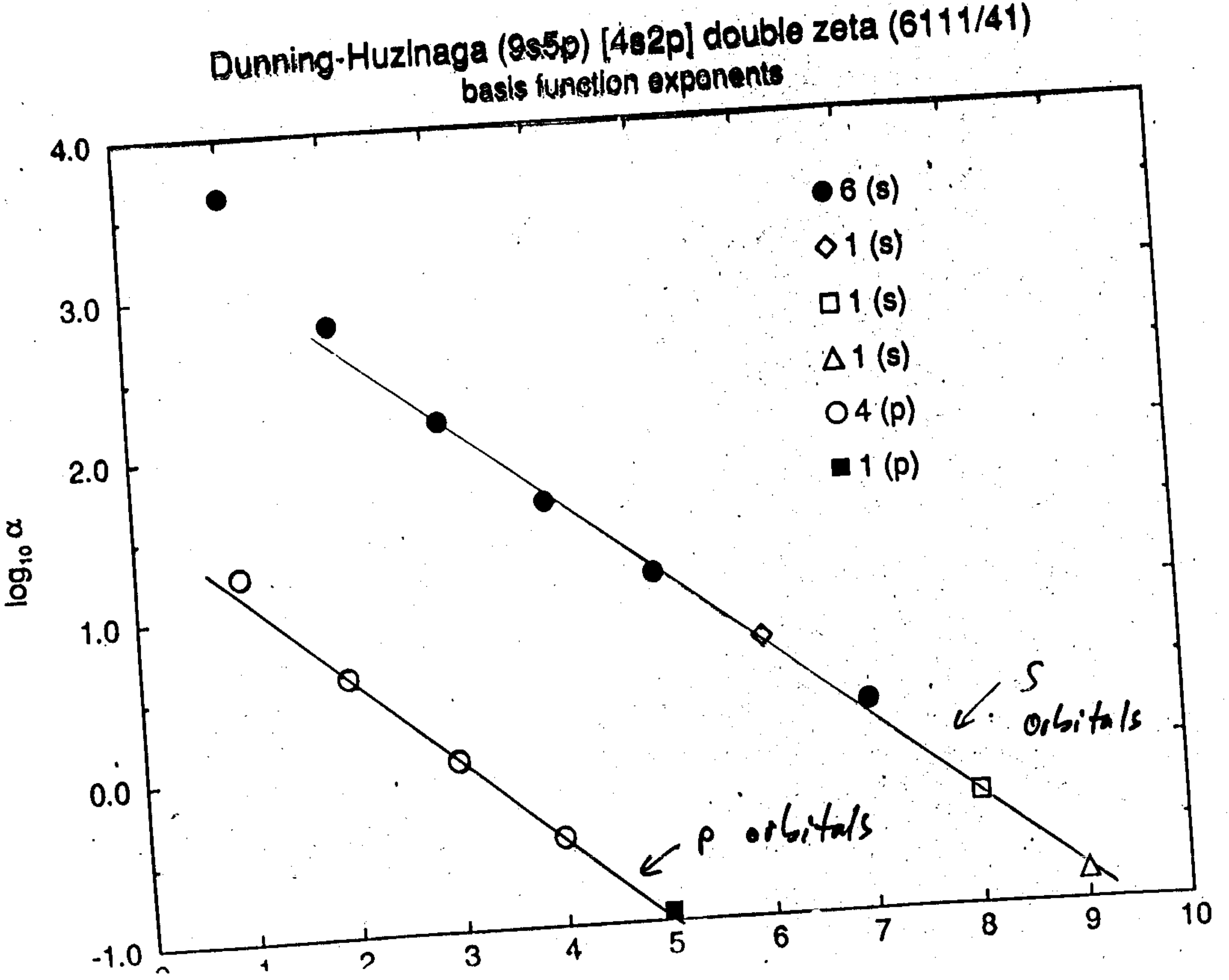
Huzinaga: (14s,9p) first row elements
(16s,11p) second row

STO-3G, STO-4G..	STO-ng **(Pople)** **(minimal basis sets)**
3-21G, 4-21G	n-ijG **(Pople)**
4-31G, 5-31G, 6-31G	**split valence BS**
6-311G**	**(optimized at MP2 level)**
6-311++G(3df,3pd)	**(optimized at UMP4)**
DZP	**Dunning Double Zeta with Polarization**
MINI-i, MIDI-i, MAXI-i (i=1-4)	**Tatewaki and Huzinaga (minimal and split valence)**

Gaussian 6-311 basis set (carbon)

basis function exponents





Dunning-Huzinaga (9s5p) [4s2p] double zeta (6111/41)
basis function exponents

Special BSs for Correlated Methods:

- even-tempered, well tempered BSs →can be used to 'continue' basis set
- ANO's
- cc (correlation consistent BSs)

	1st row
ccPVDZ	3s2p1d
ccPVTZ	4s3p2d1f
ccPVQZ	5s4p3d1fg

Basis-Set Superposition Error (BSSE)

Calculation of binding energies:
$E_{bind} = E_{AB} - E_A - E_B$
To be consistent E_{AB}, E_A and E_B have to be calculated with the same basis set

Problem:

If basis at A is incomplete, Basis at B will improve wf at A →artificially better basis set for molecule AB than for isolated A,B →lower E_{AB} →too high binding energy

Especially severe for the case weak interactions:

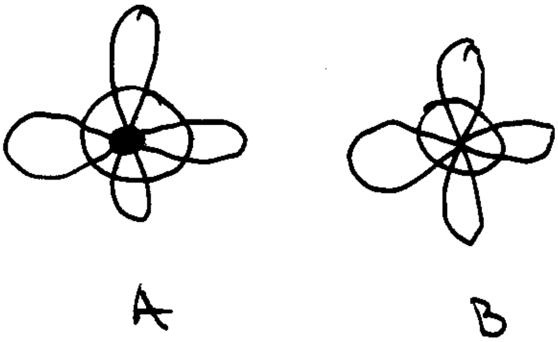
$$E_{bind} >> E_{AB}, E_A, E_B$$

Example: Water dimer

	Δ E (SCF) [kJ/mol]	BSSE [kJ/mol]
STO-4G	**-26.4**	**-24**
4-31G	**-32.2**	$\sim$ **4**
[541/31]	**-19.8**	$\sim$ **3**
HF$_{limit}$	**-15.4**	

Remedy:

- **'complete' basis set**
- Counterpoise Correction
  (Boys and Bernardi 1970)
  Calculate A with its own basis and with B's basis (without B), do the analogous for B



→ $A(BS_A \cup BS_B)$

Hartree-Fock Method

Ansatz for Wave Function

Hartree (1927), Fock (1930):

$$\Psi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\ldots.\psi_N(\vec{r}$$

$$= \prod_{i=1}^{N} \psi_i(\vec{r}_i) \xrightarrow{\text{Fock}} \text{[illegible]}$$

→effective 1-particle model

Substituting into Schrödinger Eq.

→Hartree-Fock equations:

$$\hat{f}(i)\psi_i = \epsilon_i \psi_i \qquad i = 1, 2, \ldots, N$$

Fock operator $\hat{f}(i)$:

$$\hat{f}(1) = \hat{h}(1) - \sum_{j=1}^{N} \mathcal{J}_j(1) - \mathcal{K}_j(1)$$

$\hat{h}(1)$: exact one-electron operator:

$$\hat{h}(1) = -1/2\nabla_1^2 + \sum_A \frac{Z_I}{r_{1I}}$$

$\mathcal{J}_j(1)$: Coulomb operator

$$\mathcal{J}_j(1) = \int \psi_j^*(2)\frac{1}{r_{12}}\psi_j(2)d\vec{r}_2$$

Coulomb integral $\mathbf{J}_{ij} = [ii|jj] = <ij|ij>$:

$$J_{ij} = <\psi_i(1)|\mathcal{J}_j(1)|\psi_i(1)>$$

$$= \int\int \psi_i^*(1)\psi_i(1)\frac{1}{r_{12}}\psi_j(2)^*\psi_j(2)d\vec{r}_1 d\vec{r}_2$$

→mean field approximation: 1 electron moves independently in the average field of all the other (n-1) electrons

$\mathcal{K}_j(1)\psi_i(1)$: (non-local) exchange operator:

$$\mathcal{K}_j(1)\psi_i(1) = [\int \psi_j^*(2)\frac{1}{r_{12}}\psi_i(2)d\vec{r}_2]\psi_j(1)$$

Exchange integral $\mathsf{K}_{ij} = [ij|ji] = <ij|ji>$:

$$K_{ij} = < \psi_i(1)|\mathcal{K}_j(1)|\psi_i(1) >$$

$$= \int\int \psi_i^*(1)\psi_j(1)\frac{1}{r_{12}}\psi_j(2)^*\psi_i(2)d\vec{r}_1 d\vec{r}_2$$

Fock operator depends implicitly on wf → solution has to be done iteratively until a self-consistent field (SCF) is reached → "SCF method"

Some Remarks:

- **Solution of the HF eqs.**
  → gives "the best" [illegible] determinant wf **i.e. the Slater determinant with the lowest possible energy (for this basis)**
- **motions of electrons with the same spin are** partially **correlated (Fermi hole)**
- exchange is exact
- **electrons with different spins move independently →** no electron correlation
- **HF is** variational **(HF energy > true energy)**

Short-hands for 2-electron integrals:

"physicist's notation":

$$<\mathrm{ij}|\mathrm{kl}>=\int\int \chi_{\mathrm{i}}^*(\vec{\mathrm{x}}_1)\chi_{\mathrm{j}}^*(\vec{\mathrm{x}}_2)\frac{1}{\mathrm{r}_{12}}\chi_{\mathrm{k}}(\vec{\mathrm{x}}_1)\chi_{\mathrm{l}}(\vec{\mathrm{x}}_2)\mathrm{d}\vec{\mathrm{x}}_1\mathrm{d}\vec{\mathrm{x}}_2$$

"chemist's notation":

$$[\mathrm{ij}|\mathrm{kl}]=\int\int \chi_{\mathrm{i}}^*(\vec{\mathrm{x}}_1)\chi_{\mathrm{j}}(\vec{\mathrm{x}}_1)\frac{1}{\mathrm{r}_{12}}\chi_{\mathrm{k}}^*(\vec{\mathrm{x}}_2)\chi_{\mathrm{l}}(\vec{\mathrm{x}}_2)\mathrm{d}\vec{\mathrm{x}}_1\mathrm{d}\vec{\mathrm{x}}_2$$

$$[\mathrm{ij}|\mathrm{kl}]=<\mathrm{ik}|\mathrm{jl}>$$

"antisymmetrized" 2-el integrals:

$$\begin{aligned}<ij||kl> &=<ij|kl>-<ij|lk>\\ &=[ik|jl]-[il|jk]\end{aligned}$$

formulation for spatial orbitals:

$$\begin{aligned}(\mathrm{ij}|\mathrm{kl}) &=\int\int \psi_{\mathrm{i}}^*(\vec{\mathrm{r}}_1)\psi_{\mathrm{j}}(\vec{\mathrm{r}}_1)\frac{1}{\mathrm{r}_{12}}\psi_{\mathrm{k}}^*(\vec{\mathrm{r}}_2)\psi_{\mathrm{l}}(\vec{\mathrm{r}}_2)\mathrm{d}\vec{\mathrm{r}}_1\mathrm{d}\vec{\mathrm{r}}_2\\ &=\int\int \psi_{\mathrm{i}}^*(1)\psi_{\mathrm{j}}(1)\frac{1}{\mathrm{r}_{12}}\psi_{\mathrm{k}}^*(2)\psi_{\mathrm{l}}(2)\mathrm{d}\vec{\mathrm{r}}_1\mathrm{d}\vec{\mathrm{r}}_2\end{aligned}$$

index permutation symmetries:

$<ij\|kl>=<ji\|lk>$	complex orbitals
$<ij\|kl>=<kl\|ij>^*$	complex
$[ij\|kl]=[kl\|ij]$	real or complex
$[ij\|kl]=[ji\|kl]=[ij\|lk]=[ji\|lk]$	real

II. Electron Correlation and Single Determinant wf

Example:

(a) 2 electrons with anti parallel spin

$$\Phi(\vec{x}_1, \vec{x}_2) = ||\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\alpha(1)\beta(2)||$$

Probability of finding electrons in $d\vec{x}_1 d\vec{x}_2$:

$$|\Phi|^2 d\vec{x}_1 d\vec{x}_2 = 1/2[\phi_1(\vec{r}_1)\alpha(1)\phi_2(\vec{r}_2)\beta(2)$$

$$-\phi_1(\vec{r}_2)\alpha(2)\phi_2(\vec{r}_1)\beta(1)]^2 d\vec{x}_1 d\vec{x}_2$$

$$= 1/2[|\phi_1(\vec{r}_1)|^2\alpha(1)^2|\phi_2(\vec{r}_2)|^2\beta(2)^2$$

$$+|\phi_1(\vec{r}_2)|^2\alpha(2)^2|\phi_2(\vec{r}_1)|^2\beta(1)^2$$

$$-2\phi_1(\vec{r}_1)\alpha(1)\phi_2(\vec{r}_2)\beta(2)\phi_1(\vec{r}_2)\alpha(2)\phi_2(\vec{r}_1)\beta(1)]d\vec{x}_1 d\vec{x}_2$$

$$\alpha(1)\alpha(1) = 1 \qquad \alpha(1)\beta(1) = 0$$

$$= 1/2[|\phi_1(\vec{r}_1)|^2|\phi_2(\vec{r}_2)|^2 + |\phi_1(\vec{r}_2)|^2|\phi_2(\vec{r}_1)|^2]d\vec{r}_1 d\vec{r}_2$$

$$|\Psi(\vec{r}_1, \vec{r}_2)|^2 = |\phi_1(\vec{r}_1)|^2|\phi_2(\vec{r}_2)|^2(+e - exchange)$$

$$\Longleftrightarrow p(A, B) = p(A)p(B)$$

—positions of electrons are uncorrelated!

Special case:

$\phi_1 = \phi_2$ (two electrons in the same orbital)

$$|\Psi(\vec{r}_1, \vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 = |\phi_1(\vec{r}_1)|^2|\phi_1(\vec{r}_2)|^2$$

for $\vec{r}_1 = \vec{r}_2$:

$$|\Psi(\vec{r}_1, \vec{r}_1)|^2 d\vec{r}_1 d\vec{r}_1 = (|\phi_1(\vec{r}_1)|^2)^2 \neq 0$$

→electrons can be at the same point in space (mean-field interaction avoids $1/r_{12}$ singularity)

(b) 2 electrons with parallel spin

$$\Phi(\vec{x}_1, \vec{x}_2) = ||\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\alpha(1)\alpha(2)||$$

$$= 1/2[|\phi_1(\vec{r}_1)|^2\alpha(1)^2|\phi_2(\vec{r}_2)|^2\alpha(2)^2$$

$$+|\phi_1(\vec{r}_2)|^2\alpha(2)^2|\phi_2(\vec{r}_1)|^2\alpha(1)^2$$

$$-2\phi_1(\vec{r}_1)\alpha(1)\phi_2(\vec{r}_2)\alpha(2)\phi_1(\vec{r}_2)\alpha(2)\phi_2(\vec{r}_1)\alpha(1)]d\vec{x}_1 d\vec{x}_2$$

$$= 1/2[|\phi_1(\vec{r}_1)|^2|\phi_2(\vec{r}_2)|^2 + |\phi_1(\vec{r}_2)|^2|\phi_2(\vec{r}_1)|^2]d\vec{r}_1 d\vec{r}_2$$

$$-2\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\phi_1(\vec{r}_2)\phi_2(\vec{r}_1)]d\vec{r}_1 d\vec{r}_2$$

for $\vec{r}_1 = \vec{r}_2$:

$$= 1/2[2|\phi_1(\vec{r}_1)|^2|\phi_2(\vec{r}_1)|^2 - 2|\phi_1(\vec{r}_1)|^2|\phi_2(\vec{r}_1)|^2]d\vec{r}_1 d\vec{r}_2 = 0$$

—electrons with parallel spins [illegible] at the same point in space (Fermi [illegible])

Solution of the HF Eqs:

- set of coupled integro-differential eqs
- basis set expansion →matrix eqs

Hartree-Fock-Roothaan Eqs.

(closed shell systems, singlets)

$$\hat{f}(i)\psi_i(i) = \epsilon_i\psi_i(i) \quad i = 1, 2, \ldots N/2$$

$$\hat{f}(i) = \overset{\text{1el or core hamiltonian}}{\overset{\downarrow}{\hat{h}(i)}} + \sum_{j=1}^{N/2} 2\overset{\text{coulomb operator}}{\overset{\downarrow}{\mathcal{J}_j(i)}} - \underset{\text{exchange operator}}{\underset{\uparrow}{\mathcal{K}_j(i)}}$$

Expansion in basis set:

$$\psi_i = \sum_q c_{iq}\phi_q$$

$$\hat{f}(i)\sum_q c_{iq}\phi_q = \epsilon_i \sum_q c_{iq}\phi_q$$

$$\int \phi_p^* \hat{f}(i) \sum_q c_{iq}\phi_q dV = \epsilon_i \int \phi_p^* \sum_q c_{iq}\phi_q dV$$

$$\sum_q c_{iq} \int \phi_p^* \hat{f}(i)\phi_q dV = \epsilon_i \sum_q c_{iq} \int \phi_p^* \phi_q dV$$

invariant under
unitary transformation
$\Phi T = \Phi$ $\quad f(1)\Phi(1)$
$= \Phi(1) T \varepsilon T^{+}$

$$\sum_q c_{iq} F_{pq} = \epsilon_i \sum_q c_{iq} S_{pq}$$

energy matrix
(diag: orbital energies)
↳ canonical HF orb

$$\text{Fock matrix} \longrightarrow \boldsymbol{F}\underset{\uparrow\ \text{coefficient matrix}}{\boldsymbol{C}} = \underset{\text{overlap matrix}}{\boldsymbol{S}}\boldsymbol{C}\boldsymbol{E} \longleftarrow$$

transformation yields eigenvalue problem:

$$\boldsymbol{F}'\boldsymbol{C}' = \boldsymbol{C}'\boldsymbol{E}$$

with

$$\boldsymbol{F}' = \boldsymbol{S}^{-1/2}\boldsymbol{F}\boldsymbol{S}^{-1/2}\cancel{-1/2}$$
$$\boldsymbol{C}' = \boldsymbol{S}^{-1/2}\boldsymbol{C}$$

Matrix elements

overlap matrix:

$$S_{pq} = \int \phi_p^* \phi_q dV = <p|q>$$

Fock matrix:

$$F_{pq} = \int \phi_p^* \hat{f} \phi_q dV = <p|\hat{f}|q>$$

$$F_{pq} = \int \phi_p^*(1)[\hat{h}(1) + \sum_j (2\mathcal{J}_j(1) - \mathcal{K}_j(1)]\phi_q(1) dV$$

$$= h_{pq} + 2\int \phi_p^*(1)[\sum_j \psi_j^*(2)\frac{1}{r_{12}}\psi_j(2)]\phi_q(1) dV$$

$$-\int \phi_p^*(1)\Big[\sum_j \psi_j^*(2)\frac{1}{r_{12}}\psi_j(1)\Big]\phi_q(2)\,dV$$

$$= h_{pq} - 2\sum_j \int \phi_p^*(1)\psi_j^*(2)\frac{1}{r_{12}}\psi_j(2)\phi_q(1)\,dV$$

$$-\sum_j \int \phi_p^*(1)\psi_j^*(2)\frac{1}{r_{12}}\psi_j(1)\phi_q(2)\,dV$$

$$\psi = \sum c\ \phi$$

$$= h_{pq} + 2\sum_j\sum_r\sum_s c_{jr}^* c_{js}$$

$$x\int \phi_p^*(1)\phi_r^*(2)\frac{1}{r_{12}}\phi_s(2)\phi_q(1)\,dV$$

$$-\sum_j\sum_r\sum_s c_{jr}^* c_{js}\int \phi_p^*(1)\phi_r^*(2)\frac{1}{r_{12}}\phi_s(1)\phi_q(2)\,dV$$

density matrix $R = C^{-}C$ $R = \sum \ ^*$

(j **runs** over occupied orbitals

$$= h_{pq} + \sum_r\sum_s R_{rs}[2(pq|rs) - (ps|rq)]$$

	A=5	A=16
1-el integrals: p_1=A/2(A+1)	15	120
2-el integrals: q_2=p_1/2(p_1+1)	55	1540

iterative scheme:

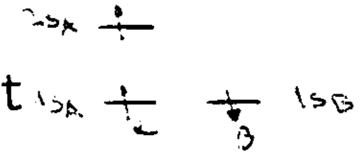
initial guess $\underbrace{[\text{illegible}] \xrightarrow{\text{diag}} [\text{illegible}] \longrightarrow [\text{illegible}]}_{30} \xrightarrow{\text{convergence}}$ [illegible]

Different types of HF methods

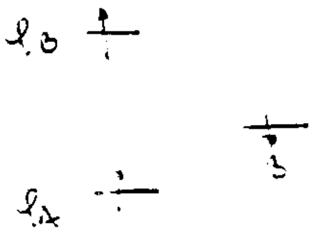
- **Restricted Hartree-Fock (RHF)**
  (Roothaan 1951, Hall 1951)
  closed-shell systems (spatial MO's doubly occupied with one spin α and one spin β electron) (non degenerate singlet ground state)

- restricted open-shell Hartree-Fock (ROHF
  (Roothaan 1951)
  spatial MO's are singly or doubly occupied

- unrestricted Hartree-Fock (UHF)
  [illegible]
  (Pople-Nesbet 195[illegible] [illegible]
  different spatial MO's for α and β spins
  Wavefunctions no longer eigen functions of spin operator $\hat{\mathcal{S}}^2 \rightarrow$ occurrence of 'spin contaminated' states: Example: Li atom



ROHF $|1s^2 2s|$ doublet
UHF $|1s_\alpha 1s_\beta 2s_\alpha|$ lower energy
but not pure doublet



(Almlöf, Faegri, Korsell 1982)

Conventional SCF Direct SCF

(1) **calculate integrals** $\underbrace{S_{pq}, h_{pq},}_{\text{keep in memory}} (pq|rs) \rightarrow$ **disk**

(2) **calculate** $S^{-1/2}$

(3) **initial guess for MO coefficients C**

- ← **semiempirical cal**
- ← $\hat{h}$**(i) only**
- ← **calc with smaller basis set**

→(4) **construct** density matrix $R=C^{+}C$

(5) **construct** Fock matrix

("integral-driven": read batch of integrals from disk, sum all their contributions into F: S,S$^{-1/2}$,C,R,F

(6) transform **Fock matrix** $F' = S^{-1/2}FS^{-1/2}$

(7) diagonalize **Fock matrix**

$C'^{+}F'C' = \varepsilon \rightarrow C = S^{-1/2}C'$

(8) converged?

- **energy change < tol**
- **density matrix change < tol**

Yes? → stop (compute HF energy)

No? → (4)

Speed up techniques for HF

- **make use of symmetry:**
  transform AO basis to symmetry-adapted basis

  → S, F factorize into blocks

  → many integrals zero

- convergence acceleration techniques:
  minimization problem min(E(C)) → DIIS (direct inversion of the iterative subspace: extrapolate C^{n+1} from C^{n}, C^{n-1}..

- integral cutoff
  - **neglect $(ij|kl)$ if $< 10^{-5}$-10^{-7} E_H**
  - **ignore whole batches based on 1 comparison, e.g. i,j,k,l d-orbitals**

$-\mathcal{O}(N^4)$ formally
$\rightarrow \mathcal{O}(N^2)$ direct SCF
density-weighted thresholding

- O(N) HF

Performance of HF

Relative good performance:

- structural properties:
  (bond distances ~0.05Å, bond angles ~ 5°, torsional angles ~ 10°
- enthalpies for isodesmic reactions:
  (error ~ 2-4 kcal/mol)
- **barriers for** internal rotations

Relative bad performance:

- **whole PES**
- vibrational frequencies:
  systematically too high (10-12 %)
- reaction energies:
  homolytic bond breaking ($\sim$ 25-40 kcal/mol off), protonations ($\sim$ 10 kcal/mol off)
- transition states
- excited states
- alkali metals **(e.g. Li_2, Na_2..)**
  transition metal complexes **(e.g. ferrocene**
- **systems with low lying excited states**

Wrong results

- dissociation to open-shell fragments
- dispersion interactions:
  e.g. Ar_2 not bound
- F_2

Correlated Methods

Electron Correlation

Probability distribution of a system with 2 electrons is not given by the product $\rho(1)\rho(2)$ only:

$$\rho_2(\vec{r}_1, \vec{r}_2) = \frac{1}{2}\rho(\vec{r}_1)\rho(\vec{r}_2)[1 + h(\vec{r}_1, \vec{r}_2)]$$

$h(\vec{r}_1, \vec{r}_2)$: **pair correlation function**

The presence of electron(1) modifies the probability distribution for electron(2):

→exchange-correlation hole

$$\rho_{xc}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_2)h(\vec{r}_1, \vec{r}_2)$$

(exchange-correlation hole created by an electron at $\vec{r}_1$).

→correlated motion of electrons

→HF_{limit} is higher than the true total energy of the system

1.9 *The radial distribution function* $g(r)$

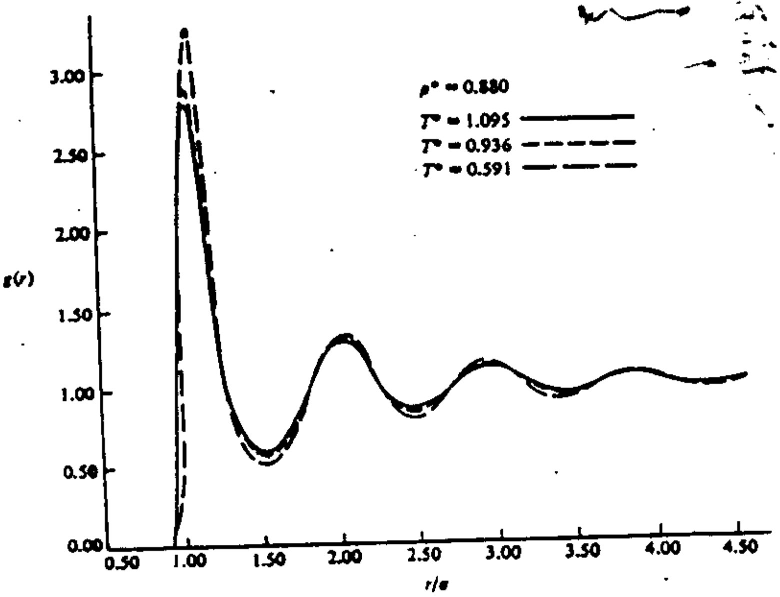
The *radial distribution function* $g(r)$ is defined such that the quantity $\rho g(r)dr$ is the "probability" of observing a second atom in the spherical shell between r and r+dr given that there is an atom at the origin of r. The quantity

$$\rho = N / V \qquad (1.9.1)$$

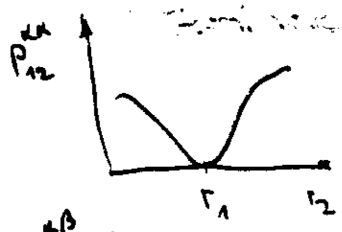
is the number density. This "probability" is not normalised to unity, but we have instead

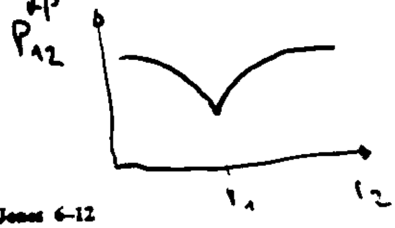
$$\int_0^\infty \rho \, g(r) \, 4\pi r^2 \, dr = N-1 \qquad (1.9.2)$$

In fact, (1.9.2) shows that $\rho g(r) 4\pi r^2 dr$ is really the number of atoms between r and r+dr about a central atom. The function g(r) can be thought of as the factor that multiplies the bulk density ρ to give a local density $\rho(r) = \rho g(r)$ about some fixed atom. Of course $g(r) \to 0$ when $r \to 0$, since atoms can not completely overlap. When r becomes large, the central atom "sees" a uniform distribution, so when $r \to \infty$ then $g(r) \to 1$. The radial distribution function contains structural information on the liquid, and can be determined from X-ray diffraction experiments.



The radial distribution function of a fluid of molecules obeying a Lennard-Jones 6–12 potential from molecular dynamics calculations. $T^* = kT/\varepsilon$ and $\rho^* = \sigma^3\rho$.

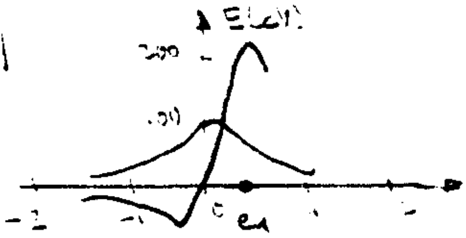




Single-determinant wf:

- (partially) 'correlates' electrons **with** the same spin
- does not correlate electrons **with** opposite spins
- does not correlate electrons within doubly occupied orbitals

Be



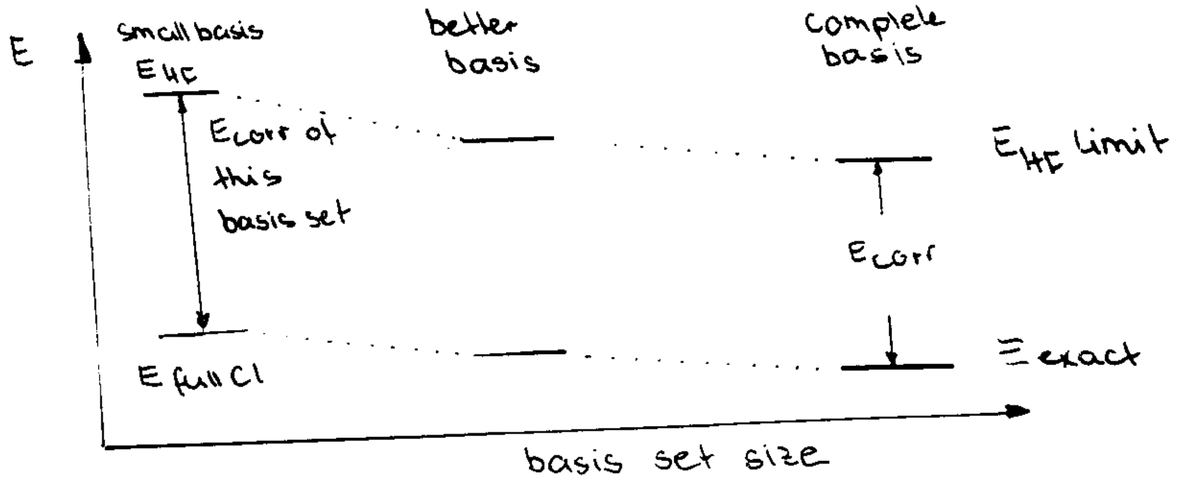
- SCF potential
- fluctuation potential $V_{exact} - V_{HF}$

pair correlation energies:

	$1s\alpha 1s\beta$	$1s\alpha 2s\alpha$	$1s\alpha 2s\beta$	$2s\alpha 2s\beta$
eV	1.126	0.022	0.658	1.234

Chemist's definition of E_{corr} (Lowdin)

$$E^{nonrel}_{exact} = E_{HF_{limit}} - E_{corr}$$



→E_{corr} is basis set dependent!

– **More intuitive:**

How is electron correlation introduced via configuration mixing?

2 Examples: (a) Be atom

Ab initio calculations show that the following 4 configurations contribute mainly to the gs wf:

$$\Psi = C_1|1s^2 2s^2| - C_2\{|1s^2 2p_x^2| + |1s^2 2p_y^2| + |1s^2 2p_z^2|\}$$

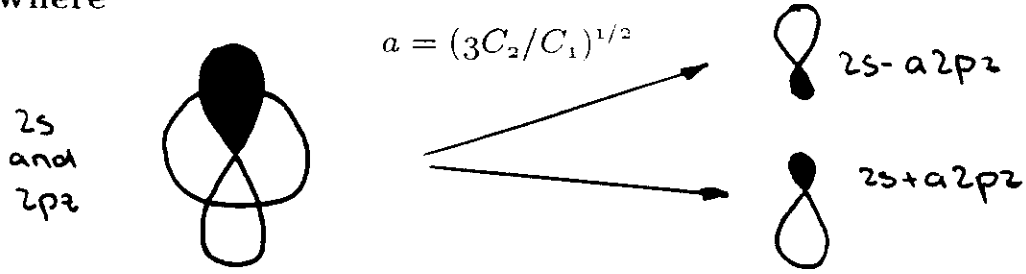
This function can be expressed equivalently:

$$\Psi = 1/6 C_1 |1s^2$$

$$\cdot\{[(2s - a2p_x)\alpha(2s + a2p_x)\beta - (2s - a2p_x)\beta(2s + a2p_x)\alpha] +$$
$$[(2s - a2p_y)\alpha(2s + a2p_y)\beta - (2s - a2p_y)\beta(2s + a2p_y)\alpha] +$$
$$[(2s - a2p_z)\alpha(2s + a2p_z)\beta - (2s - a2p_z)\beta(2s + a2p_z)\alpha]\}$$

where

$$a = (3C_2/C_1)^{1/2}$$



→polarized orbitals pairs (2s ± a2p$_{x,y,z}$) →electrons reduce mutual Coulomb repulsion by occupying different regions of space, they undergo angular correlation

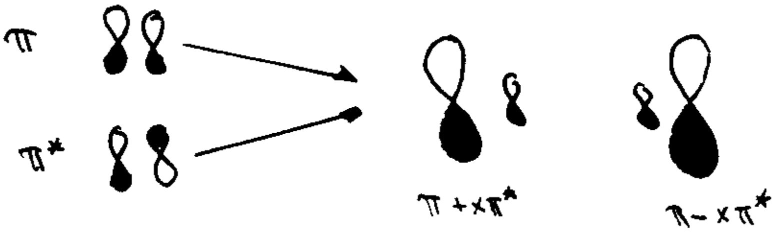
(b) π^2 **electron pair of an olefin**

Main contribution from other configurations: doubly excited configurations $(\pi^*)^2$ **,like above:**

$$C_1|\ldots\phi\alpha\phi\beta\ldots| - C_2|\ldots\phi'\alpha\phi'\beta| =$$

$$1/2C_1\ldots(\phi - a\phi')\alpha(\phi + a\phi'\beta\ldots| - \ldots(\phi - a\phi')\beta(\phi + a\phi'\alpha\ldots|$$

→π^2 **electrons undergo left-right correlation**



Different Types of Correlation:

dynamic correlation

'real' correlation effects due to the correlated motion of the electrons

'non-dynamic' (static) correlation:

'everything for which the single-determinant approximation is inappropriate:

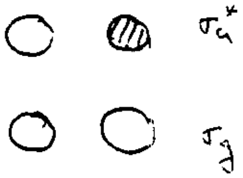
- **nearly degenerate states**
- **RHF: wrong dissociation of (singlet) molecules into open-shell fragments**

Can be put right by:

- **2 determinants**
- **valence bond**

$$\Psi = \frac{1}{\sqrt{2}}[\boldsymbol{\sigma}_A(1)\boldsymbol{\sigma}_B(2) + \boldsymbol{\sigma}_A(2)\boldsymbol{\sigma}_B(1)]$$

$\times (\alpha(1)\beta(2) - \alpha(2)\beta(2))$



- **UHF**

is to be contrasted with the potential energy curve obt order many-body perturbation theory (Chapter 6) usi function as the starting point (see Fig. 6.3). Second-theory gives a larger fraction of the correlation energy c rium bond length than GVB. However, as R increases

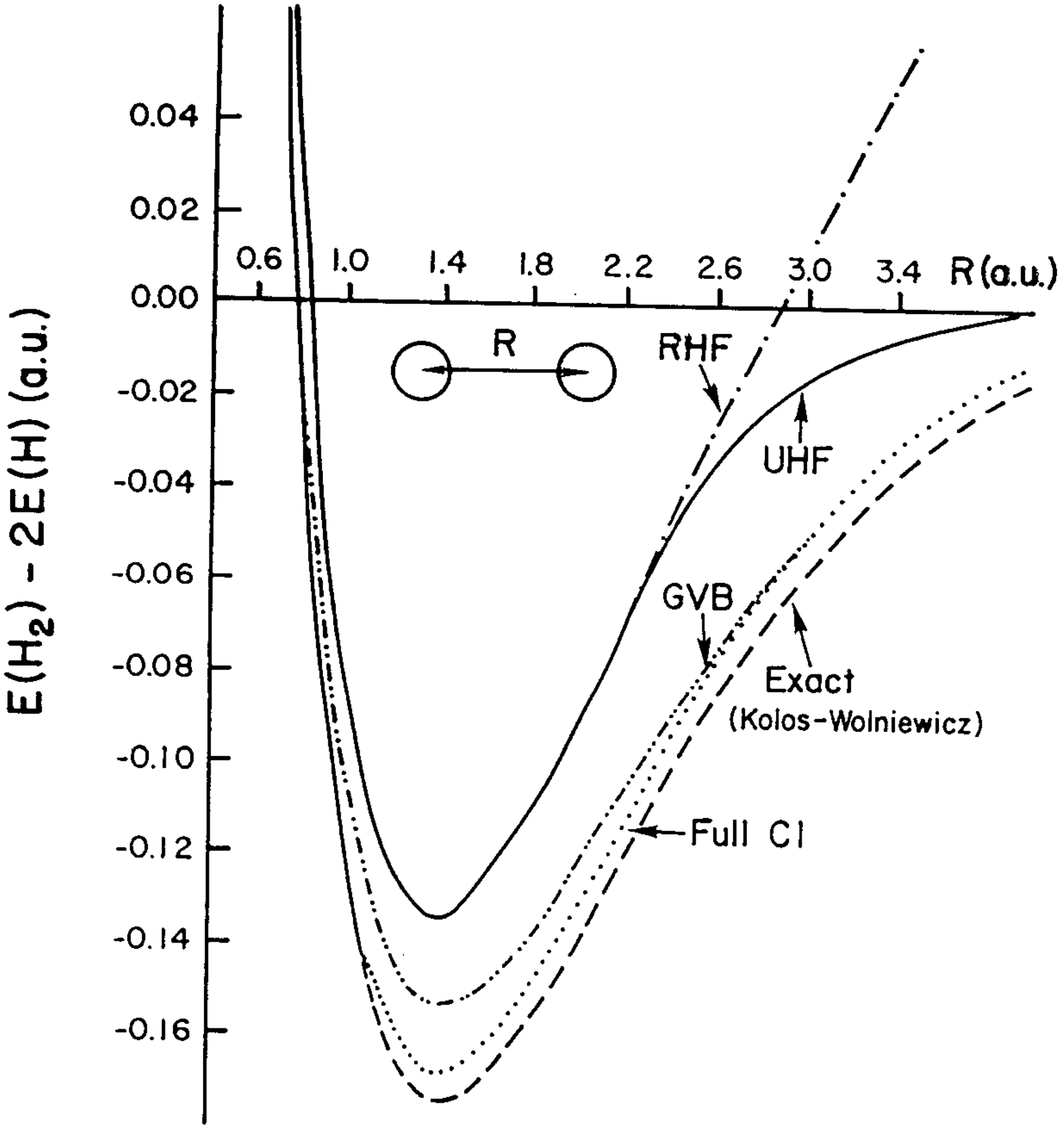


Figure 4.4 6-31G** potential energy curves for H_2.

Configuration Interaction

$$\Psi_{CI} = \sum_K C_K \Phi_K$$

many-electron basis fcts (Slater dets)

expansion coefficients

$$\psi_i = \sum_q c_{iq} \phi_q$$

1-el basis fcts (AO's)

molecular orbitals

expansion coefficient

$$HC = SCE$$

many electron state energies

in SD basis

if MO's are orthogonal:

$$< \phi_i | \phi_j >= \delta_{ij}$$

SD's are orthogonal:

$$< \Psi_K | \Psi_L >= \delta_{KL}$$

$$HC = CE$$

CI is trivial!

CI is not so trivial!

(2) number of possible determinants:

$$\approx \begin{pmatrix} N_{SO} \\ N_{electrons} \end{pmatrix} = \frac{N_{SO}!}{N_{el!(N_{SD}-N_{el})!}}$$

Ex.: Benzene with 6-311G basis:**

$$\begin{pmatrix} \mathbf{288} \\ \mathbf{42} \end{pmatrix} \approx \mathbf{10^{52}}$$

→slow convergence, critically dependent on quality of basis

(3) calculate a $10^{52} x 10^{52}$ matrix??

→$\approx 10^{93}$ **TByte**

→10000x10000 $\sim$ **0.8 Gbyte**

(4) diagonalize such a large matrix?

In practice:

(2) large number of determinants

- full CI (FCI) **possible for small systems only (e.g. double-zeta H_2O)**
  →exact result for this basis set
- **For all other systems:**
  →choose ways to restrict No. of SD's

(1) AO(ϕ_p) →MO(ψ_i) →SD(Ψ_i)

(2) construct all Slater determinants

$$\Phi_K = ||\psi_1\psi_2\psi_3 \ldots \Psi_i\psi_j \ldots \Psi_n||$$

N-electron basis functions Φ_K can be written as 'excitations' from the HF reference determinant into virtual orbitals:

$$|\Psi_0 >= C_0|\Phi_0 > + \sum_a \sum_r C_a^r |\Phi_a^r >$$

$$+ \sum_a \sum_b \sum_r \sum_s C_{ab}^{rs} |\Phi_{ab}^{rs} > + \ldots$$

Φ_0 : **HF ground-state determinant**

Φ_a^r : **singly-excited determinant**

Φ_{ab}^{rs} : **doubly-excited determinant**

r,s: indices for virtual orbital

a,b: indices for occupied orbitals

(3) calculate Hamiltonian matrix

$$H_{KL} =< \Phi_K|H|\Phi_L >$$

(4) diagonalize H

→energies and wf's of all states which can be described by chosen basis

- do CI for valence electrons only (or for 'active' electrons)
- consider only all single-, double-, triple..excitati from a reference determinant (HF) →(CIS, CISD,....CISDTQ...)
- multi reference CI (MRCI)
  HF →a few important determinants →CISD from all these determinants
- selected CI:
  determine approximate energy contribution of every determinant (via perturbation theory) and include only those > threshold
- use symmetry where possible
- Slater determinants →configuration state functions (CSF's)
  CSF: linear combination of a small number of SD's which are spin eigen functions

→10^3-10^9 determinants (or CSF's)

(3) storage of matrix
Direct CI:
(recalculate H matrix elements as needed in the diagonalization, store only coefficient vectors (CI vectors)

(4) diagonalization: no full diagonalization

instead: find only the lowest eigenvalues and eigenvectors (gs + first few excited states) →O(N^2) algorithm (Shavitt, Davidson)

Properties of the CI expansion

Wf ansatz for the ground-state:

$$|\Psi_0> = C_0|\Phi_0> + \sum_a \sum_r C_a^r|\Phi_a^r>$$

$$+ \sum_a \sum_b \sum_r \sum_s C_{ab}^{rs}|\Phi_{ab}^{rs}> + \cdots$$

Matrix elements between Slater determinant

Expectation:
singly-excited determinants are closest in energy →will contribute most to gs wf...doubles next...etc..

Consider CI expansion of 2 terms:

- **HF + 1 singly-excited determinant**

$$|\Psi_o> = C_0|\Phi_0> + C_a^r|\Phi_a^r>$$

CI eqs:

$$\begin{pmatrix} <\Phi_0|H|\Phi_0> & <\Phi_0|H|\Phi_a^r> \\ <\Phi_a^r|H|\Phi_0> & <\Phi_a^r|H|\Phi_a^r> \end{pmatrix} \begin{pmatrix} C_0 \\ C_a^r \end{pmatrix} = E_o \begin{pmatrix} C_0 \\ C_a^r \end{pmatrix}$$

mixing is determined by off-diagonal elements:

$$<\Phi_0|H|\Phi_a^r> = <a|h|r> + \sum_b^{occ} <ab|rb> - <ab|br$$

$$<a|\hat{h} + \sum_b^{occ} (\mathcal{J}_b - \mathcal{K}_b)|r> = <a|f|r> = \epsilon_a \delta_{ar} = 0$$

Brillouin theorem:

no direct interaction between HF determinant and singly-excited determinan

- Doubly excited configurations do have a direct interaction with HF determinant
- triply- and higher excited **determinants do** not

General rules: Slater-Condon rules

matrix elements of any 1-el and 2-el operator between pairs of anti symmetrized spin-orbital products (arranged with maximal coincidence)

Table 2.3 Matrix elements between determinants for one-electron operators in terms of spin orbitals

$$\mathscr{O}_1 = \sum_{i=1}^{N} h(i)$$

Case 1: $|K\rangle = |\cdots mn \cdots\rangle$

$$\langle K|\mathscr{O}_1|K\rangle = \sum_m^N [m|h|m] = \sum_m^N \langle m|h|m\rangle$$

Case 2: $|K\rangle = |\cdots mn \cdots\rangle$
$|L\rangle = |\cdots pn \cdots\rangle$

$$\langle K|\mathscr{O}_1|L\rangle = [m|h|p] = \langle m|h|p\rangle$$

Case 3: $|K\rangle = |\cdots mn \cdots\rangle$
$|L\rangle = |\cdots pq \cdots\rangle$

$$\langle K|\mathscr{O}_1|L\rangle = 0$$

Table 2.4 Matrix elements between determinants for two-electron operators in terms of spin orbitals

$$\mathscr{O}_2 = \sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij}^{-1}$$

Case 1: $|K\rangle = |\cdots mn \cdots\rangle$

$$\langle K|\mathscr{O}_2|K\rangle = \frac{1}{2}\sum_m^N \sum_n^N [mm|nn] - [mn|nm] = \frac{1}{2}\sum_m^N \sum_n^N \langle mn||mn\rangle$$

Case 2: $|K\rangle = |\cdots mn \cdots\rangle$
$|L\rangle = |\cdots pn \cdots\rangle$

$$\langle K|\mathscr{O}_2|L\rangle = \sum_n^N [mp|nn] - [mn|np] = \sum_n^N \langle mn||pn\rangle$$

Case 3: $|K\rangle = |\cdots mn \cdots\rangle$
$|L\rangle = |\cdots pq \cdots\rangle$

$$\langle K|\mathscr{O}_2|L\rangle = [mp|nq] - [mq|np] = \langle mn||pq\rangle$$

where

$$|\Psi_1\rangle = |abcd\rangle$$

$$|\Psi_2\rangle = |crds\rangle$$

r s d   r s c d
= – < [illegible] > = . a >

At first glance, it might appear that the two determinants differ in all four columns; however, by interchanging columns of $|\Psi_2\rangle$ and keeping track of

CI Hamiltonian matrix (blocks)

$$\begin{pmatrix}
<\Phi_0|H|\Phi_0> & 0 & <\Phi_0|H|D> & 0 & 0 & \cdots \\
 & <S|H|S> & <S|H|D> & <S|H|T> & 0 & \cdots \\
 & & <D|H|D> & <D|H|T> & <D|H|Q> & \cdots \\
 & & & <T|H|T> & <T|H|Q> & \cdots \\
 & & & & <Q|H|Q> & \cdots \\
 & & & & & \vdots
\end{pmatrix}$$

Example:

Percentage of Correlation energy:

Molecule	Basis Set	CISD	CISDT	CISDT
BH	DZP	94.91	n/a	99.97
H_2O (R_e)	DZ	94.70	95.47	99.82
H_2O (1.5 R_e)	DZ	89.39	91.15	99.48
H_2O (2.0 R_e)	DZ	80.51	83.96	98.60
NH_3	DZ	94.44	95.43	99.84
HF	DZP	95.41	96.49	99.86
H_7^+	DZP	96.36	96.87	99.96

- doubles **contribute most to gs correlation energy**
- quadruples **are more important than triples (at least for energy)**
- **at stretched geometries CISD and CISDT markedly poorer, CISDTQ ok**

Number of CSF's:

Molecule	Basis set	CISD	CISDT	CISDT
BH	DZP	568	n/a	28 698
H_2O	DZ	361	3 203	17 678
NH_3	DZ	461	4 029	19 925
HF	DZP	552	6 712	48 963
H_7^+	DZP	1 271	24 468	248 14

(Handy et al., CPL 95, 386 (1983)
Schaefer et al., JCP 100, 8132 (1994))

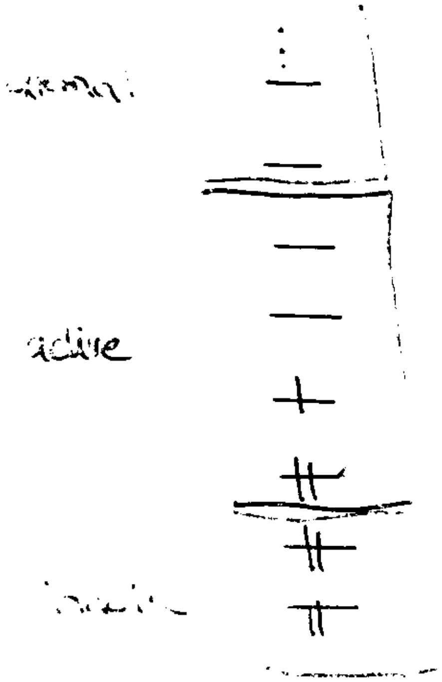
'CI'- Methods:

- Single Reference Methods:
  (optimize CI coefficients only)
  - CISD, CISDT, CISDTQ..full CI
    (max $\sim 10^9$ csf)

- Multiconfigurational Methods:
  (Multi Reference Methods)
  (optimize CI and MO coefficients)
  - MCSCF **(multi-configuration SCF)**
    (small number of determinants
    (10^3 - 10^4) ⟶ CAS
  - GVB **(generalized valence bond)**
  - MRCI **(multi reference CI)**

- **MCSCF possibly followed by CI**

Which configurations (determinants) to include?
→complete-active-space SCF (CASSCF)



never occupied

create all possible occupation patterns
"full CI"

[illegible]

Many-Body Perturbation Theory (MBPT)

General idea:

in case correlation effects are relatively small →HF solutions $|\Psi_i>_{HF}$ and $\{E_i\}_{HF}$ are already close approximations to the exact $|\Psi_i>$ and $\{E_i\}$

—correlation effects can be considered as perturbation to the HF solutions and treated via perturbation theory

Perturbation Theory:

Given: **Hamiltonian** $\mathcal{H}'$
with eigen functions $|\Psi' >$
and eigen values E'

True Hamiltonian $\mathcal{H}$ partitioned into:

$$\mathcal{H} = \mathcal{H}^0 + \lambda\mathcal{H}' = \mathcal{H}^0 + \lambda\mathcal{V} \quad (\mathcal{V} << \mathcal{H}^0)$$

[illegible] [illegible] [illegible] perturbation

Problem to be solved:

$$\mathcal{H}|\Psi_i>= E_i|\Psi_i>$$

$$(\mathcal{H}^0 + \lambda\mathcal{V})|\Psi_i>= E_i|\Psi_i>$$

- **if $(V << \mathcal{H}^0)$ and**
- **$|\Psi_i>$ and E$_i$'s involve continously as a function of λ**

→Taylor expansion of $|\Psi_i>$ and E around $\lambda = 0$:

$$E_i = \lambda^0 E_i^{(o)} + \lambda^1 E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots$$

$$|\Psi_i>= \lambda^0|\Psi_i^{(0)}> +\lambda^1|\Psi_i^{(1)}> +\lambda^2|\Psi_i^{(2)}> +$$

indices $(0), (1), (2), ...(n)$:
0th-order (unperturbed system), 1st-order, 2nd-order, ... nth-order correction

→Substitute into Schrodinger-Eqs.

nth-order correction to the energy:

$$E_i^{(n)} =< \Psi_i^{(0)}|\mathcal{V}|\Psi_i^{(n-1)} >$$

Expand $|\Psi_i^{(1)}>$ in basis of eigen functions of $\mathcal{H}^0$:

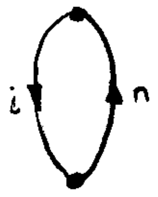
$$|\Psi_i^{(1)}>=\sum_n c_n^{(1)}|\Psi_n^{(0)}>=\sum_{n\neq i} c_n^{(1)}|\Psi_n^{(0)}>$$

1rst-order correction to the wavefunction:

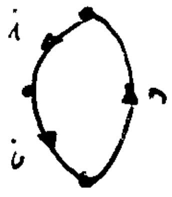
$$|\Psi_i^{(1)}>=\sum_{n\neq i}\frac{<\Psi_n^{(0)}|\mathcal{V}|\Psi_i^{(0)}>}{(E_i^{(0)}-E_n^{(0)})}|\Psi_n^{(0)}>$$

2nd-order correction to the energy:

$$E_i^{(2)}=\sum_{n\neq i}\frac{|\Psi_i^{(0)}|\mathcal{V}|\Psi_n^{(0)}|^2}{(E_i^{(0)}-E_n^{(0)})}$$



$E_i^{(3)}$:



+

Møller-Plesset Perturbation Theory

unperturbed system:

$$\mathcal{H}^0|\Psi^{(0)}>= E_0^{(0)}|\Psi^{(0)}>$$

$\mathcal{H}^0$: **Hartree-Fock Hamiltonian**

$$\mathcal{H}^0 = \sum_i^N \hat{f}(i)$$

$$E_0 = \sum_i^N \overset{<i|f|i>}{\epsilon_i} = \sum_i^N < i|\hat{h}|i > + \sum_i \sum_j < ij||ij >$$

$$\neq$$

$$E_{HF} = \sum_a \epsilon_a - 1/2 \sum_a \sum_b < ab||ab >$$

perturbation:

$$\mathcal{V}' = \mathcal{H}-\mathcal{H}^0 = (\sum_i^N \hat{h}(i)+\sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}})-\sum_i^N \hat{f}(i)$$

$$= (\sum_i^N \hat{h}(i)+\sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}})-(\sum_i^N \hat{h}(i)+\sum_i^N \hat{v}_{HF}(i))$$

$$= \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_i^N \hat{v}_{HF}(i)$$

→total e-e repulsion minus Hartree-Fock e-repulsion

Hartree-Fock ground state energy:

$$E_{HF}^{gs} = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \qquad |\Psi_0\rangle = | \dots ij \dots \rangle$$

$$= \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \langle ij || ij \rangle$$

$$\sum \varepsilon_i = \sum_i^N \langle i | \hat{h} | i \rangle + \sum_i^N \sum_j^N \langle ij || ij \rangle$$

$$\hookrightarrow \quad E_{HF}^{gs} = \sum_i^N \varepsilon_i - \frac{1}{2} \sum_i^N \sum_j^N \langle ij || ij \rangle$$

0th-order energy:

$$E_0^{(0)} = \sum_a \epsilon_a$$

1rst-order energy:

$$E_0^{(1)} = < \Psi_0|\mathcal{V}|\Psi_0 >$$

$$= < \Psi_0|\sum_{j>i}^{N}\frac{1}{r_{ij}}|\Psi_0 > - < \Psi_0|\sum_i \hat{v}_{HF}(i)|\Psi_0 >$$

$$= 1/2\sum_{ab} < ab||ab > - \sum_a < \overbrace{a|\hat{v}_{HF}\text{[illegible]}|a}^{\sum_b <ab|ab> - <ab|ba> \; = \sum_b <ab||ab>} >$$

$$= -1/2\sum_{ab} < ab||ab >$$

$$E_0 = E_0^{(0)} - E_0^{(1)} = \sum_a \epsilon_a - 1/2\sum_{ab} < ab||ab > = E_0$$

1rst-order PT restores HF solution!

→first correction to HF energy is 2nd-order perturbation correction

2nd-order energy (MP2)

$$E_0^{(2)} = \sum_{n\neq 0}\frac{|\langle\Psi_0|\mathcal{V}|\Psi_n^{(0)}\rangle|^2}{E_0^{(0)} - E_n^{(0)}}$$

What do we take for $|\Psi_n^{(0)}>$?

- Singly-excited states?

$$< \Psi^{(0)}|\mathcal{V}|\Psi_a^r > = < \Psi_0|(\mathcal{H}-\mathcal{H}_0)|\Psi_a^r >$$

$$= < \Psi_0|\mathcal{H}|\Psi_a^r > - < \Psi_0|\mathcal{H}_0|\Psi_a^r >$$

$$= - < \Psi^{(0)}|\hat{f}|\Psi_a^r > = < a|\hat{f}|r >$$

$$= \epsilon_a \delta_{ar} = 0$$

→singly-excited states don't contribute to the 2nd-order energy

$$\boxed{E_0^{(2)}} = \sum_n \frac{|\langle\Psi_0|V|\Psi_n\rangle|^2}{E_0 - E_n}$$

- doubly-excited states?

$V = H - H_0$

$\langle\Psi_0|H|\Psi_{ab}^{rs}\rangle = \langle ab$

$\langle\Psi_0|H_0|\Psi_{ab}^{rs}\rangle =$

$$|\Psi_n^{(0)} > = |\Psi_{ab}^{rs} >$$

$$E_n^{(0)} : \qquad \mathcal{H}_0|\Psi_{ab}^{rs} > = E_{abrs}^{(0)}|\Psi_{ab}^{rs} >$$

$$= (E_0^{(0)} - \epsilon_a - \epsilon_b + \epsilon_r + \epsilon_s)|\Psi_{ab}^{rs} >$$

$= E_{abrs}$

$\times \langle\Psi_0$

$= 0$

$$E_0^{(2)} = 1/4 \sum_{abrs} \frac{|< ab||rs >|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

Second-order energy $E_0^{(2)} \leftrightarrow$ pair contributions

$$E_0^{(2)} = \sum_{\substack{a<b\\ r<s}} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

$$\hookrightarrow \quad e_{ab}^{FO} = \sum_{r<s} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$ "pair contributions"

$$E_0^{(2)} = \sum_{a<b} e_{ab}^{FO}$$ sum over pair contributions

- triply- and higher-excited states do not interact directly with $|\Psi^{(0)}>$ (Slater-Condon rules)

$\Longrightarrow$ Only doubly-excited states contribute to $E_0^{(2)}$!

Contributions to correlation energy

	MP2	MP3	MP4
singles	-	-	E [illegible]
doubles	E [illegible]	E [illegible] $-$ E [illegible]	E [illegible] $-$ [illegible]
triples	-	-	E [illegible]
quadruples	-	-	E [illegible]

Example for CPU time distribution:

		CO_2 (63 bf)	CO_3^{2-} (84 bf)
AO integrals		20	62
SCF		10	30
integral transformation		27	173
MP4	**S**	1	4
	D	7	88
	T	11	216
	Q	6	45
total		1h 22 min	10h 18 min

to generate MO's:

$$\psi_i = \sum_{\mu}^{N} c_{i\mu}\phi_\mu$$

- **MO-based integrals are evaluated by transforming AO-based integrals**
  - **1-electron**

$$h_{ij} =< \psi_i|h|\psi_j >=< \sum_{\mu}^{N} c_{i\mu}\phi_\mu|h|\sum_{\nu}^{N} c_{j\nu}\phi_\nu >=$$

$$\sum_{\mu}^{N}\sum_{\nu}^{N} c_{i\mu}^{*}c_{j\nu} < \phi_\mu|\hat{h}|\phi_\nu >$$

$\rightarrow O(N^4)$ **(2-index transformation)**

  - 2-electron

$$< \psi_i\psi_k|\frac{1}{r_{12}}|\psi_j\psi_l >= \sum_{\mu}^{N}\sum_{\nu}^{N}\sum_{\lambda}^{N}\sum_{\sigma}^{N} c_{\mu i}^{*}c_{\nu j}c_{\lambda k}^{*}c_{\sigma l}(\mu\nu|\lambda\sigma)$$

$\rightarrow O(N^8)$ (4-index transformation)

- order can be reduced to $O(N^5)$ via use of an intermediate transformation:

$$< \psi_i\phi_\nu|\frac{1}{r_{12}}|\phi_\lambda\phi_\sigma >= (i\nu|\lambda\sigma) = \sum_{\mu} c_{i\mu}(\mu\nu|\lambda\sigma)$$

$$< \psi_i\psi_j|\frac{1}{r_{12}}|\phi_\lambda\phi_\sigma >= (ij|\lambda\sigma) = \sum_{\nu} c_{j\nu}(i\nu|\lambda\sigma)$$

4x O(N

$$< \psi_i\psi_j|\frac{1}{r_{12}}|\psi_k\phi_\sigma >= (ij|k\sigma) = \sum_{\lambda} c_{k\lambda}(ij|\lambda\sigma)$$

$$< \psi_i\psi_j|\frac{1}{r_{12}}|\psi_k\psi_l >= (ij|kl) = \sum_{\sigma} c_{l\sigma}(ij|k\sigma)$$

	HF	MP2	MP3	MP4	QCISD(T)	expt.
Mn $d^5s^2 \to d^6s^1$	3.19	1.76	2.60	1.98	2.24	1.97
Co $d^7s^2 \to d^8s^1$	1.61	-0.58	1.12	-0.49	0.33	0.17
Ni $d^9s^1 \to d^{10}$	4.32	-0.51	4.46	-3.42	1.70	1.57
Cu $d^9s^2 \to d^{10}s^1$	-0.29	-3.28	-0.47	-3.63	-1.85	-1.85

Raghavachari et al. J. Chem. Phys. 91, 1062 (1989)

Coupled Cluster Theory

- **Theory: Cizek 1966**
- **Implementation: Taylor et al 1976**

Pair and Coupled-Pair Theories

Independent Electron Pair Approximation (IEPA)

(1964: Sinanoğlu
1965 Nesbet)

$$E_{corr} = \sum_{a<b} \sum_{i<j} c_{ab}^{ij} < |\Psi_0|H|\Psi_{ab}^{ij} >$$

$$= 1/4 \sum_{ab} \sum_{ij} c_{ab}^{ij} < |\Psi_0|H|\Psi_{ab}^{ij} >$$

$$E_{corr} = \sum_{a<b} \epsilon_{ab}$$

$$\epsilon_{ab} = \sum_{i<j} c_{ab}^{ij} < \Psi_0|H|\Psi_{ab}^{ij} >$$

'pair-at-a-time CI'

⊕ ↳ size-consistent

⊖ ↳ not invariant under unitary transformations of degenerate orbitals

⇒ works reasonably well for small atoms, doesn't work for larger molecules

IEPA

'pair function' $|\Psi_{ab}\rangle$: $|\Psi_{ab}\rangle = |\Psi_0\rangle + \sum_{r<s} c^{rs}_{ab} |\Psi^{rs}_{ab}\rangle$

energy: $E_{ab} = \langle\Psi_0|\hat{H}|\Psi_0\rangle + e_{ab} = E_0 + e_{ab}$

→ substitute $|\Psi_{ab}\rangle$ into Schrödinger Eq:

$$\hat{H}|\Psi_{ab}\rangle = E_{ab}|\Psi_{ab}\rangle$$

$$\hat{H}(|\Psi_0\rangle + \sum_{t<u} c^{tu}_{ab}|\Psi^{tu}_{ab}\rangle = E_{ab}\left(|\Psi_0\rangle + \sum_{t<u} c^{tu}_{ab}|\Psi^{tu}_{ab}\rangle\right)$$

- multiply by $\langle\Psi_0|$, $\langle\Psi^{rs}_{ab}|$:

$$E_0 + \sum_{t<u} c^{tu}_{ab}\langle\Psi_0|\hat{H}|\Psi^{tu}_{ab}\rangle = E_{ab}$$

$$\langle\Psi^{rs}_{ab}|\hat{H}|\Psi_0\rangle + \sum_{t<u}\langle\Psi^{rs}_{ab}|\hat{H}|\Psi^{tu}_{ab}\rangle c^{tu}_{ab} = E_{ab} c^{rs}_{ab}$$

with $E_{ab} = \langle\Psi_0|\hat{H}|\Psi_0\rangle + e_{ab} = E_0 + e_{ab}$

$$\sum_{t<u} c^{tu}_{ab}\langle\Psi_0|\hat{H}|\Psi^{tu}_{ab}\rangle = e_{ab}$$

$$\langle\Psi^{rs}_{ab}|\hat{H}|\Psi_0\rangle + \sum_{t<u}\langle\Psi^{rs}_{ab}|\hat{H} - E_0|\Psi^{tu}_{ab}\rangle c^{tu}_{ab} = e_{ab} c^{rs}_{ab}$$

with $(D_{ab})_{rs,tu} = \langle\Psi^{rs}_{ab}|\hat{H} - E_0|\Psi^{tu}_{ab}\rangle$

$(B_{ab})_{rs} = \langle\Psi^{rs}_{ab}|\hat{H}|\Psi_0\rangle$

$(c_{ab})_{rs} = c^{rs}_{ab}$

→ matrix form: $\begin{pmatrix} 0 & B^{\dagger}_{ab} \\ B_{ab} & D_{ab} \end{pmatrix}\begin{pmatrix} 1 \\ c_{ab} \end{pmatrix} = e_{ab}\begin{pmatrix} 1 \\ c_{ab} \end{pmatrix}$

→ $E^{\text{IEPA}}_{\text{corr}} = \sum_{a<b} e_{ab}$

• Coupled Pair Theories

- consider coupling between different e-pairs $ab \leftrightarrow cd$

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{\substack{a<b\\r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c<d\\r<s<t<u}} c_{abcd}^{rstu}|\Psi_{abcd}^{rstu}\rangle + \ldots$$

- insert into Schrödinger Eq.: $(\hat{H}-E_0)|\Phi_0\rangle = E_{corr}|\Phi_0\rangle$
- project $\langle\Psi_0|$, $\langle\Psi_{ab}^{rs}|$, $\langle\Psi_{abcd}^{rstu}|$ ...

$$\sum_{\substack{c<d\\t<u}} \langle\Psi_0|\hat{H}|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} = E_{corr}$$

$$\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_0\rangle + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\hat{H}-E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{abcd}^{rstu}\rangle c_{abcd}^{rstu}$$

$$= E_{corr}\, c_{ab}^{rs}$$

Different Approximations for c_{abcd}^{rstu}:

- $c_{abcd}^{rstu} = 0 \longrightarrow$ CID variational, not size-cons.
- $c_{abcd}^{rstu} \simeq c_{ab}^{rs} * c_{cd}^{tu} \longrightarrow$ CPMET, CCD

$$\hookrightarrow \langle\Psi_{ab}^{rs}|\hat{H}|\Psi_0\rangle + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\hat{H}-E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} - \sum_{\substack{c<d\\t<u}} \langle\Psi_0|\hat{H}|\Psi_{cd}^{tu}\rangle \times \underbrace{(c_{ab}^{rs} * c_{cd}^{tu})}_{=0}$$

$\hookrightarrow$ non linear - not variational
- size consistent
- invariant towards unitary transf.

$=0$ • L-CCA

- $(c_{ab}^{rs} * c_{cd}^{tu}) = c_{ab}^{rs} c_{ab}^{tu}$ $c=a,\ d=b$

  $\hookrightarrow$ CEPA

  - [illegible]

$$c^{rs}_{ab} * c^{tu}_{cd} = c^{rs}_{ab} c^{tu}_{cd} - c^{rs}_{ac} c^{tu}_{bd} + c^{rs}_{ad} c^{tu}_{bc}$$

$$+ \ldots - \ldots$$

18 terms

Coupled-Cluster Approximation (CCA

Exponential Ansatz for wfc:

$$\Psi_{CC} = exp(T)\Psi_0$$

$$T = \sum_q T_q = T_1 + T_2 + \cdots$$

T_q generates q-fold excitations:

$$\Psi_{CCD} = exp(T_2)\Psi_0 = (1+T_2+T_2^2/2+T_2^3/3!+\ldots)\Psi$$

$$T_2\Psi_0 = \sum t_{ij}^{ab}\Psi_{ij}^{ab}$$

$$\Psi_{CCD} = \Psi_0+\sum t_{ij}^{ab}D_{ij}^{ab}+1/2\sum\sum t_{ij}^{ab}t_{kl}^{cd}D_{ijkl}^{abcd}+\cdots$$

- CCD CPMET $T = T_2$ **(1976)**
- CCSD $T = T_1 + T_2$ **(1982)** [illegible]
- CCSDT $T = T_1 + T_2 + T_3$ **(1986)**

  Approximate Schemes:
  - **QCISD(T)** Pople (1987), QCISDT (1996) + disconnected quadruples T_2^2 & triples T_1T_2
  - **CCSDT-n**
  - **CCSD+T(CCSD) (non-iterative)**
  - CCSD(T) **(1989)**

[illegible]

Coupled Cluster Eqs:

insert CC-wfc into Schrödinger-Eq. subtract reference energy $< \Psi_o|H|\Psi_o >$ from both sides:

$$H_N exp(T)\Psi_o = exp(T)\Psi_o$$

$$H_N = H - < \Psi_o|H|\Psi_o >$$

project from left by $\Psi_o >$, single, double and higher excitations:

$$\Delta E =< \Psi_o|H_N exp(T)|\Psi_o >$$

$$\Delta E < \Psi_{ij}^{ab}|e^T|\Psi_0 >=< \Psi_{ij}^{ab}|H_N exp)T)(T)|\Psi_o >$$

ΔE: correlation energy

Eqs projected by excitations →eqs for coefficients t_{ij}^{ab}:

$$\Delta E =< \Psi_o|H_N T_2|\Psi_0 >= \sum_{i>j} t_{ij}^{ab} < \Psi_{ij}^{ab}|H_N|\Psi_o$$

$$+ \sum t_{ij}^{ab} < ab||ij >$$

$$\Delta E t_{ij}^{ab} =< \Psi_{ij}^{ab}|H_N|\Psi_o > + < \Psi_{ij}^{ab}|H_N T_2|\Psi_0 >$$

$$+ < \Psi_{ij}^{ab}|H_N T_2^2|\Psi_0 >$$

For CCD eqs can be further simplified:

$$\begin{aligned}\varepsilon_{ij}^{ab} t_{ij}^{ab} = {} & \langle ab \| ij \rangle + \frac{1}{2} \sum_{cd} \langle ab \| cd \rangle t_{ij}^{cd} + \frac{1}{2} \sum_{kl} \langle ij \| kl \rangle t_{kl}^{ab} \\ & + \sum_{kc} \big(\langle ak \| jc \rangle t_{ik}^{cb} - \langle bk \| jc \rangle t_{ik}^{ca} - \langle ak \| ic \rangle t_{jk}^{cb} \\ & + \langle bk \| ic \rangle t_{jk}^{ca} + \frac{1}{4} \sum_{\substack{kl \\ cd}} \langle kl \| cd \rangle \big[t_{kl}^{ab} t_{ij}^{cd} - 2 (t_{ij}^{ac} t_{kl}^{bd} \\ & + t_{ij}^{bd} t_{kl}^{ac}) - 2 (t_{ik}^{ab} t_{jl}^{cd} + t_{ik}^{cd} t_{jl}^{ab}) + 4 (t_{ik}^{ac} t_{jl}^{bd} + t_{ik}^{bd} t_{jl}^{ac}) \big]\end{aligned}$$

→**algebraic eqs**

↳ solved iteratively with various acceleration techniques

CC ⟷ MBPT

Ex: IEPA

$$\sum_{t<u} c_{ab}^{tu} \langle \Psi_0 | \hat{H} | \Psi_{ab}^{tu} \rangle = e_{ab}$$

$$\langle \Psi_{ab}^{rs} | \hat{H} | \Psi_0 \rangle + \sum_{t<u} \langle \Psi_{ab}^{rs} | \hat{H} - E_0 | \Psi_{ab}^{tu} \rangle c_{ab}^{tu} = e_{ab} c_{ab}^{rs}$$

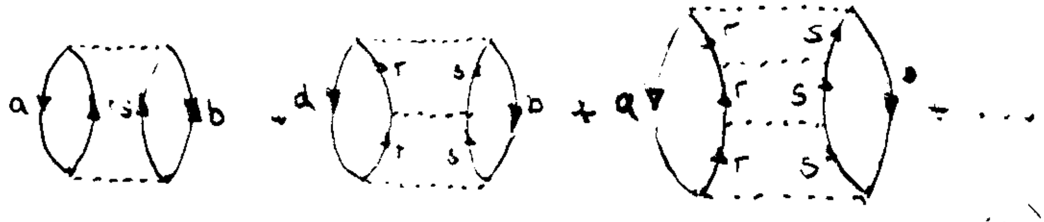
- $t=r,\ u=s$ (neglect coupling between excited dets):

$$\langle \Psi_{ab}^{rs} | \hat{H} | \Psi_0 \rangle + \langle \Psi_{ab}^{rs} | \hat{H} - E_0 | \Psi_{ab}^{rs} \rangle c_{ab}^{rs} = e_{ab} c_{ab}^{rs}$$

→ c_{ab}^{rs}

$$\hookrightarrow e_{ab} = -\sum_{r<s} \frac{|\langle \Psi_0 | \hat{H} | \Psi_{ab}^{rs} \rangle|^2}{\langle \Psi_{ab}^{rs} | \hat{H} - E_0 | \Psi_{ab}^{rs} \rangle - e_{ab}} \approx \boxed{-\sum_{r<s} \frac{|\langle \Psi_0 | \hat{H} | \Psi_{ab}^{rs} \rangle|^2}{\langle \Psi_{ab}^{rs} | \hat{H} - E_0 |}}$$

≡ Δ =



(geometric series)

→ sum over all possible diagrams

- sum all double excitation diagrams

≡ L-CCA, D-MBPT(∞)

Second-order energy $E_0^{(2)} \to$ pair contributions

$$E_0^{(2)} = \sum_{\substack{a<b \\ r<s}} \frac{|\langle ab \| rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

$$\hookrightarrow \quad e_{ab}^{FO} = \sum_{r<s} \frac{|\langle ab \| rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$ "pair contributions"

$$E_0^{(2)} = \sum_{a<b} e_{ab}^{FO}$$ sum over pair contributions

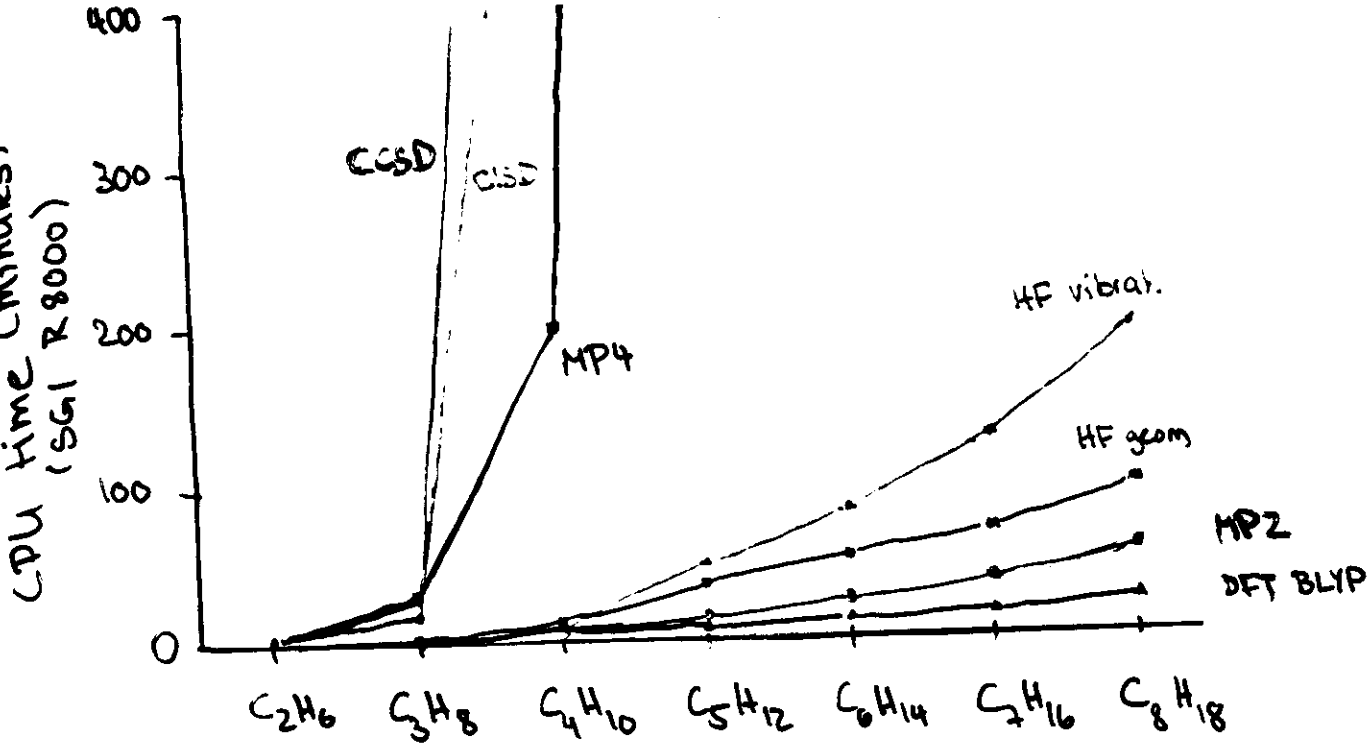
Summary QC-Methods

Approximate scaling behavior:

($\mathcal{O}(N)$ HF	$\sim N$)
HF (direct SCF, large molecules)	$\sim N^2$
HF (conventional)	$\sim N^4$
MP2	$\sim N^5$
MP3, MP4(SDQ), CISD QCISD, CCD, CCSD	$\sim N^6$
MP4, CCSD(T), QCISD(T)	$\sim N^7$
MP5, CCSDT	$\sim N^8$
CCSDTQ, CISDTQ	$\sim N^{10}$
full CI	$\sim N!/N_{el}!\,(N-N_{el})!$

HF, CIX, CCX : $\times N_{it}$

Gaussian 94


CPU time (minutes)
(SGI R8000)
400
300
200
100
0
CCSD
CISD
MP4
HF vibrat.
HF geom
MP2
DFT BLYP
C_2H_6
C_3H_8
C_4H_{10}
C_5H_{12}
C_6H_{14}
C_7H_{16}
C_8H_{18}

Comparison of Correlation Techniques in 4th Order

	S	D	T	Q
CISD	✓	✓		×
QCISD	✓	✓		✓
CCSD	✓	✓		
CCSD + T(CCSD)	✓	✓	✓	✓
QCISD(T)	✓	✓	✓	✓
CCSD(T)	✓	✓	✓	✓
CISDT	✓	✓	✓	×
QCISDT	✓	✓	✓	✓
CCSDT	✓	✓	✓	✓

✓ : included

× : only partially included

Raghavachari et al. JPC 100,
12960 (1996)

Overview

		variational	size-cons.	static correl.	dynamic correl.	Hellman-Feynman	excited states
HF	single det mean-field	+	+	only UHF	-	+	energies via Koopman's Theorem
limited CI	include explicitely selected excited dets	+	-*	-	+	-	+
MCSCF	small CI with orbitals optimized for every det	+	-	+	(-)	+	+
MBPT	evaluate contribution of excited dets consistently through given order in perturbation theory	-	+	only if based on UHF	+	-	-
CC	evaluate contribution of selected excitations through infinite order	-	+	” MR-CC	+	-	- + EOM-CC
full CI	include all possible det exact within basis set	+	+	+	+	+	+

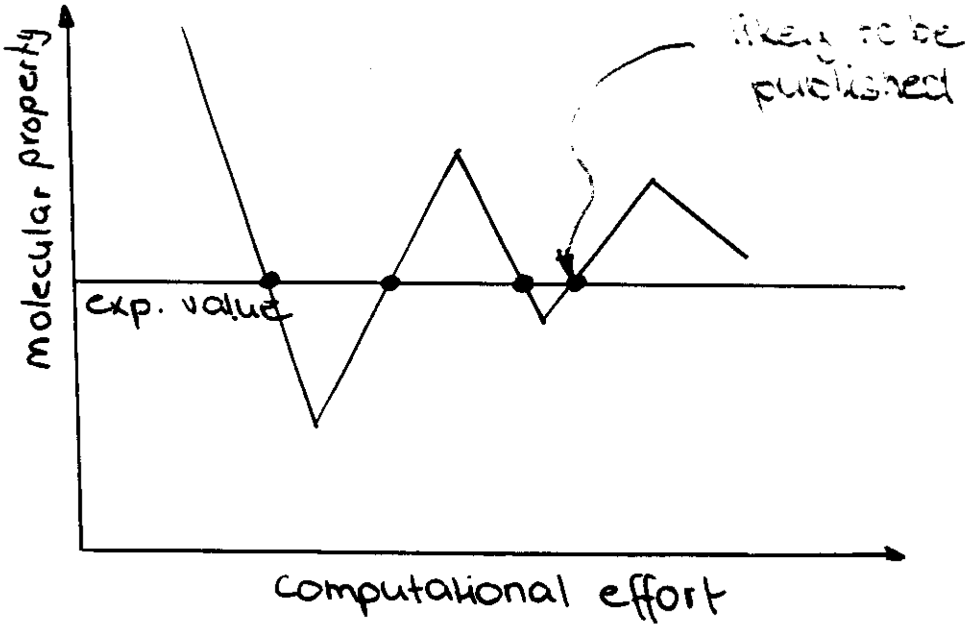
* Davidson correction for CISD: $\Delta E_{DC} = \Delta E_{CISD}(1+C_0^2)$

coeff. $|\Psi_0^{HF}\rangle$ in $|\Psi_{CISD}\rangle$ (normalized)

Applications

How to judge the quality of quantum-chemical calculations?

- direction of improvement is clear:
  ⇒ larger basis
  ⇒ more advanced computational method
- Variational Principle
  ⇒ provides quality criterion for total energy
- but:
  a lower total energy does not necessarily imply a higher accuracy for all molecular properties !!
- molecular properties may converge to 'final' result in a oscillatory way



from:
R. Janoschek
Chemie in
unserer
Zeit 29,
22 (1995)

Examples

- comparison of different methods for the same basis set
- dependence on basis set size
- some pathological cases

Average Deviation from Experiment

(set of 32 small neutral molecules, medium-sized basis set: 6-31G*)

Atomization Energies (kcal/mol)

HF	MP2	QCISD	LDA	B-GC	BLYP
86 (-)	22 (-)	29 (-)	36 (+)	4 (±)	6 (±)

Geometries

	HF	MP2	QCISD	LDA	B-GC	BLYP
r_e Å	0.020 (-)	0.014 (+)	0.013 (+)	0.021 (+)	0.018 (+)	0.020 (+)

Harmonic Vibrational Frequencies

HF	MP2	QCISD	LDA	B-GC	BLYP
168 (+)	99 (+)	42 (+)	75 (-)	61 (-)	73 (-)

Dipole Moments (Debye)

HF	MP2	QCISD	LDA	B-GC	BLYP
0.29 (+)	0.28 (+)	0.23 (±)	0.25 (±)	0.23 (±)	0.25 (±)

(Andzelm & Wimmer, J. Chem. Phys. 1995)

Reaction energies for C–H, C–C bond breaking

(DZVPP)

	CH_3-H	CH_2-H	$CH-H$	$C-H$
HF	87	88	101	55
MP2	109	110	109	73
MP4	110	112	107	76
CISD	106	109	107	74
GVB-PP	98	98	91	66
CC	111	113	102	78
LSD	124	127	122	93
BP	114	118	113	90
exp	112	116	107	84

→ average error ΔE (kcal/mol):

HF	MP2	MP4	CISD	GVB-PP	CC	LSD	BP
22	5.5	3.5	6.5	16.5	3.8	11.8	3.8

	H_3C-CH_3	$H_2C=CH_2$	$HC\equiv CH$
HF	69	122	132
CISD		154	194
CC		174	214
LSD	115	204	268
BP	95	183	235
exp	[illegible]	[illegible]	[illegible]

Average Error of H-abstraction $XH_y \rightarrow XH_{y-1} + H$

Reaction energies

$X = Li, Be, C, N, O, F, B.$

(6-31G**)

	ΔE	
MP2	7.4	kcal/mol
MP3	14.4	
MP4(SDQ)	7.1	
MP4(SDTQ)	3.7	
MP5	3.2	
CID	16.3	
CISD	13.8	
CISDT	0.5	
CISDTQ	0.7	
CCD	8.0	
CCSD	7.4	
CCSD(T)	0.7	
CCSDT-1	0.6	
CCSDT	0.5	
CCSDTQ	0.0	

DFT (Sosa & Lee)

(hydrogenation, double bond breaking, triple BB...

$-2.7 < \Delta E \leq \overset{5}{6}$ kcal/mol

BP 〃 0

3LYP 〃 4.5

Basis Set Dependence

Table 2 Representative RHF and Correlated Results Obtained with Some Commonly Used Basis Sets

Name	Contracted primitives	Functions	Elements	Average errors in geometries and other properties[a]				
				AH$_n$	A$_l$B$_m$H$_n$	Dipole	BSSE	VIP
STO-3G[b]	(3s) (6s,3p) (9s,6p) (12s,9p,3d) (15s,12p,6d)	[1s] [2s,1p] [3s,2p] [4s,3p,1d] [5s,4p,2d]	(H–He) (Li–Ne) (Na–Ar) (K–Kr) (Rb–Xe)	SCF: ±0.032 Å, ±5.6° SCF: ±0.076 Å, ±1.1° SCF: ±0.047 Å, ±1.1° SCF: ±0.089 Å, ±1.2°[c]	±0.027 Å, ±2.1°	±0.65 D	0.053	0.126
3-21G	(3s) (6s,3p) (9s,6p)	[2s] [3s,2p] [4s,3p]	(H–He) (Li–Ne) (Na–Ar)	SCF: ±0.015 Å, ±4.8° SCF: ±0.016 Å, ±3.3°	±0.017 Å, ±1.4°	±0.49 D	0.011	0.060
3-21G(*)	(9s,6p,1d)	[4s,3p,1d]	(Na–Ar)	SCF: ±0.017 Å, ±2.1°				
6-31G*	(4s) (10s,4p,1d)	[2s] [3s,2p,1d]	(H–He) (Li–Ne)	SCF: ±0.014 Å, ±2.4° MP2: ±0.011 Å, ±1.7° MP4: ±0.012 Å, ±1.7°	±0.022 Å, ±1.1° ±0.013 Å, ±0.8°	±0.30 D	0.002	0.060
	(16s,10p,1d)	[4s,3p,1d]	(Na–Ar)	SCF: ±0.014 Å, ±2.2° MP2: ±0.009 Å, ±1.2°				
6-31G**	(4s,1p) (10s,4p,1d)	[2s,1p] [3s,2p,1d]	(H–He) (Li–Ne)	SCF: ±0.014 Å, ±2.4°			0.002	0.061
6-311G**	(4s,1p) (10s,4p,1d)	[3s,1p] [4s,3p,1d]	(H–He) (Li–Ne)	SCF: ±0.012 Å, ±1.8° MP4: ±0.006 Å, ±1.9°	±0.025 Å, ±1.3° (±0.009)[d]			
DH SV[e]	(4s) (9s,5p)	[2s] [3s,2p]	(H–He) (Li–Ne)	SCF: ±0.015 Å, ±5.7°			0.010	0.055
D DZP[f]	(4s,1p) (9s,5p,1d)	[2s,1p] [4s,2p,1d]	(H–He) (Li–Ne)	SCF: ±0.009 Å, ±2.2°			0.011	0.060
	(3s)	[2s]	(H–He)					

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Table 3 Energy Differences (in kcal/mol) at Four Stationary Points on the CO_2 + H → CO + OH Potential Surface[a] exp 23 kcal/mol

	CO_2 + H	CO + OH	OCOH (SI)[b]	OC--OH (TS)[c]
STO-3G				
SCF	0.0	−34.1	−35.2	−14.4
MP2	0.0	−0.3	−2.4	11.5
MP4	0.0	−1.8		
Full CI	0.0	−4.3	−13.6	6.3
3-21G[d]				
SCF	0.0	−3.1	−1.1	13.9
MP2	0.0	29.9	13.7	31.9
Estimated full CI	0.0	20.9	−7.7	24.5
6-31G**[e]				
SCF	0.0	5.8	2.4	27.1
SD-CI	0.0	3.5		
Estimated SDQ-CI[f]	0.0	16.9		
MP2	0.0	31.8	4.4	34.3
MP4	0.0	24.0		
Estimated full CI	0.0	20.8 (25.2)[g]	14.3	28.9
Estimated HF limit[h]				
SCF	0.0	7.6		

---

[a] The difference is defined as E(arbitrary point) − E(CO_2 + H). Thus, a positive value means that CO_2 + H is lower in energy. Experimentally, the zero point vibrationally corrected ΔE for

Dependence on Basis Set

- small basis set ⇒ large variations
  (e.g. minimal basis set STO-3G:
  average deviation from experimental bond lengths for first and second row $A_lB_mH_n$:
  ± 0.03 Å
  but e.g. for
  Na_2: -0.72 Å
  F_2: -0.10 Å

- larger basis ⇒ more uniform results
  e.g. 3-21G(*):
  Na_2: 0.15 Å
  F_2: 0.01 Å

- better method ⟹ needs better basis
  - full CI for STO-G:
    not general improvement

	HF	full CI	EXP
H_2:	0.71 Å	0.74 Å	0.74 Å
CO:	1.15 Å	1.19 Å	1.13 Å

  - 6-311G**: exponents and coefficients optimized at MP2 level
    (→HF with 6-311G** sometimes worse results than with 3-21G)

- **larger split valence polarization basis sets (e.g. 6-31G*) ⇒ systematic improvements with MP2, MP4 ..**

Basis Set limits:

- HF:
  - bond lengths too short ~ 0.015Å, ~ 2°
  - vibrational frequencies too high **(empirical scaling factor of ~ 0.9) (STO-3G: + 30 %, 3-21G 10-15 %)**
  - bond dissociation energies: ~ 20-40 kcal mo
- MP2. MP4..CI MP2 ~ 0.010Å, ~ 1°
  - improved bonds. somewhat too long
  - too high frequencies ~ 5-8 %
  - bond dissociation energies:
    ⇒ need large basis
    e.g. MP4

	6-31G*	**6-311++ G(3df, 3pd)**
H_2	**3.9**	**1.3**
N_2	**23.7**	**4.8**
$N_2 + 3H_2 \rightarrow 2\ NH_3$	**15.1**	**1.2**

"HF unfriendly problems":

- F_2 , F-O-O-F
- Cr_2 , ferrocene

- Be_2
- homolytic dissociation

Case Studies

HCN

method	ΔR_{CN}	ΔR_{CH}
HF/STO-3G	0.000	-0.005
HF/3-21G	0.016	0.015
HF/6-31G*	0.020	0.006
MP2/6-31G*	-0.024	0.005
HF/6-311G**	0.026	0.007
MP4/6-311G**	-0.031	0.001
MP3/6-311G**	0.007	0.001
DA(DZ/P)	0.012	0.023

F_2

bond dissociation enthalpy in kcal/mol

HF

STO-3G	-4.9
3-21G	-30.5
6-31G(d)	-39.5
6-311G(2df)	-41.8
6-311+G(3df)	-43.7

Comparison between different methods

6-311G(2df)

HF	**-41.8**
CASSCF(10,6)	**15.9**
MP2	**37.3**
MP4SDTQ	**34.9**
CCSD(T)	**33.9**

6-311+G(3df)

HF	**-43.7**
MP2	**36.5**
MP4SDTQ	**34.5**

3 (numerical)	[illegible]
BP86 (T=2F)	[illegible]
B3P86 '	36.7
[illegible] numerical	[illegible]
[illegible]	55.[illegible]
BLYP	41.[illegible]

exp **36.9**

ClO

bond dissociation enthalpies in kcal/mol

	$ClO_2 \rightarrow ClO + O$	$ClO \rightarrow Cl + O$
6-311+G(2df)		
UHF	**-29.1**	**2.6**
MP2	**68.2**	**55.2**
MP4SDTQ	**56.4**	**54.5**
CCSD(T)		**55.8**

CC - Methods

(R. Bartlett, J. Phys. Chem. 93, 1697 (1989))

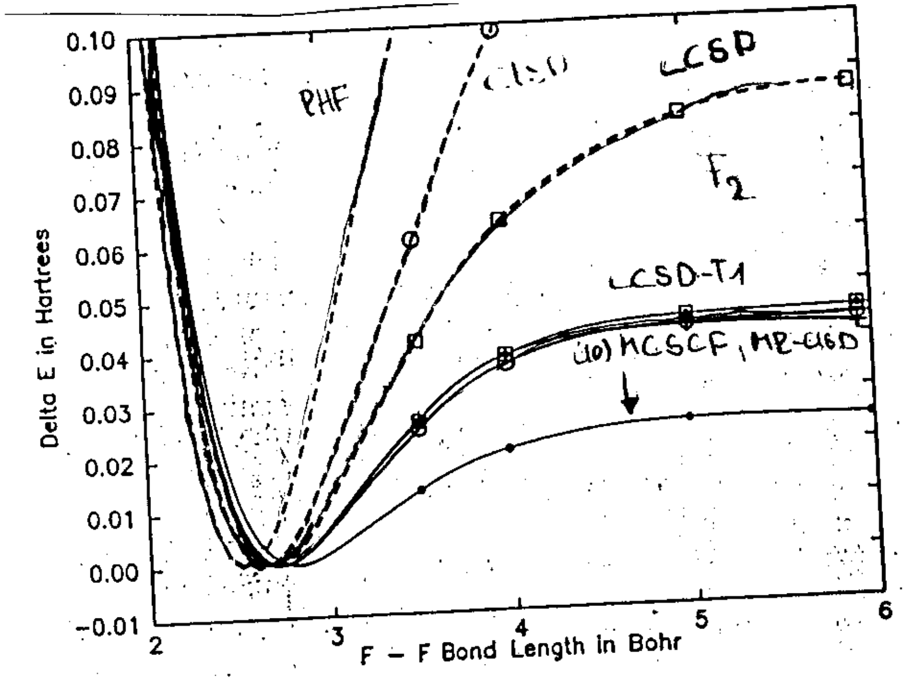
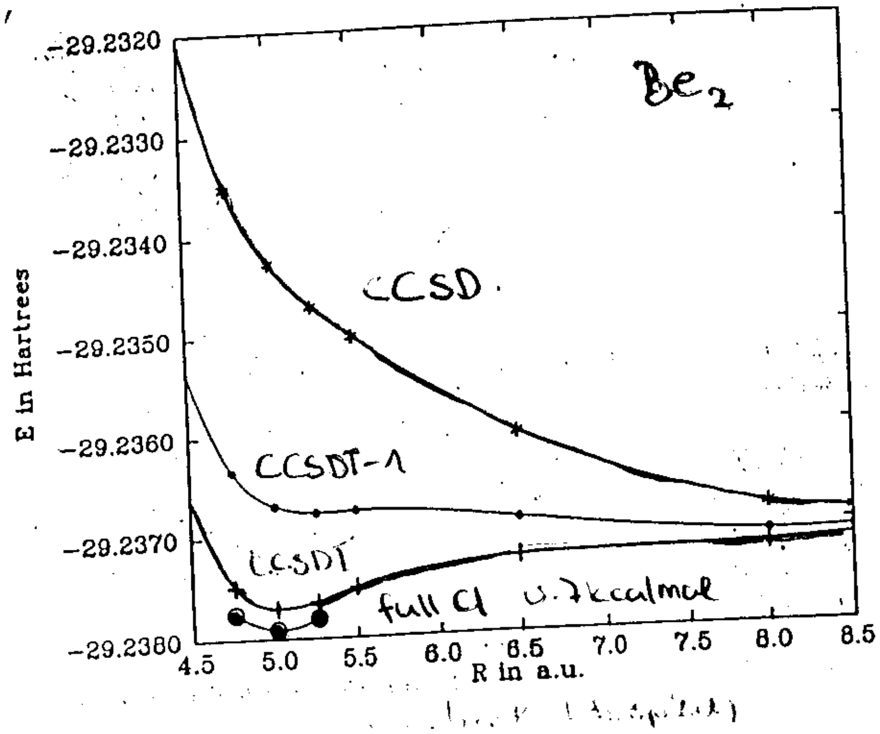
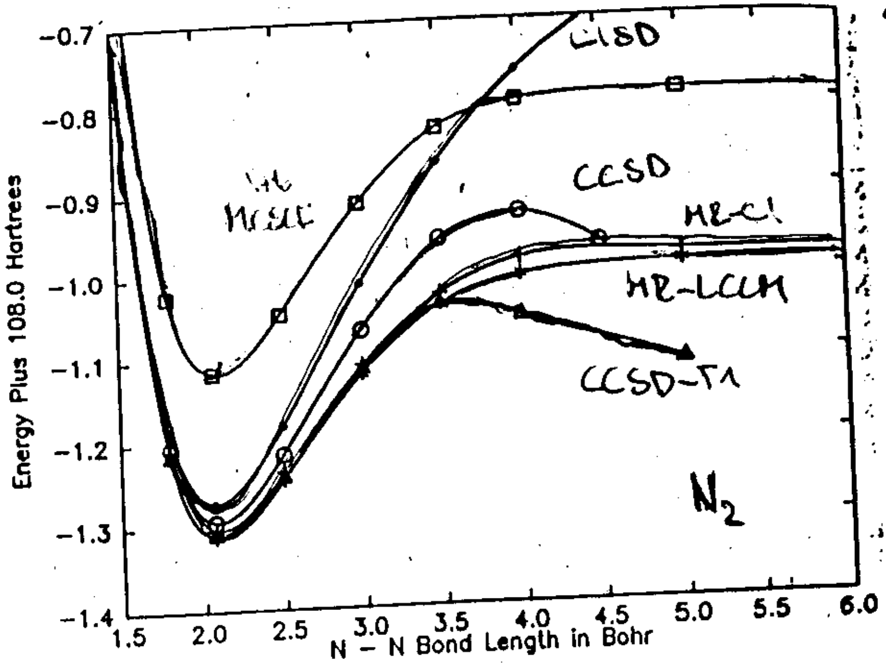


TABLE I: Mean Absolute Error of Correlation Energies (kcal/mol) for CC Methods and Other Single-Reference (RHF) Correlated Methods Compared to Full CI[a,b]

	F^-	Ne	FH(DZP), BH(DZP), H_2O(DZ), H_2O(DZP)		
			R_e	$1.5R_e$	$2.0R_e$
CISD[c]	8.4	4.8	5.5	14.1	34.2
CISDT[c]	6.5	3.2	4.3	9.4	21.6
CISDTQ[c,d]	0.4	0.1	0.2	0.5	1.7
LCCD	6.1	0.7	0.8	1.1	11.2
CCD	7.1	1.6	1.7	5.9	16.5
CCSD	3.8	1.8	1.9	4.4	8.6
MBPT(4)	3.2	0.4	1.1	3.1	7.8
MBPT(5)[e]	–	–	0.8	2.6	9.2
MBPT(5) + [2,1]Padé[e]	–	–	0.3	1.1	8.3
CCSD + T(CCSD)	0.7	0.1	0.2	0.4	3.2
CCSDT-1	0.7	0.1	0.3	0.7	1.3
CCSDT	0.4	0.1	0.2	0.6	0.9





Cr_2

	re[Å]	De (eV ~~kcal/mol~~)
HF	1.465	-19.4
CCSD	1.560	-2.9
CCSD(T)	1.621	0.5
DFT	1.59	1.5
exp.	1.679	1.4

(Scuseria 1992)

what I didn't talk about:

- Gaussian-2 Theory G2 (Pople)

  ↳ highly accurate ($\Delta E \sim 1-2$ kcal/mol)

  D_e, E_A, IP, EA's

  - start with QCISD(T) 6-311G(d,p)

    ↳ series of additivity approximations

basis set corrections $\left\{ \begin{array}{ll} \text{MP4:} & \text{diffuse sp, pol. (2df)} \\ \text{MP2:} & \text{3df/2p} \end{array} \right.$

- 'higher level correction'

G2 set of molecules: 1st & 2nd row

- Semiempirical methods

  CNDO, MINDO, MNDO, AM1, PM3

Outlook:

- $\mathcal{O}(N)$ HF .... MP2? ..... ??

- "new Hylleras methods": "r_{12}-methods"

  $\text{MP2-}r_{12}$, $\overset{\text{MP4-}r_{12}}{\text{MP3-}r_{12}}$, $\text{CID-}r_{12}$, $\text{CEPA-}r_{12}$

  $\text{CCSD-}r_{12}$ $\text{CCSD(T)-}r_{12}$

  gaussian geminals

- QMC-Methods: VQMC, DQMC, GFQMC, PIQMC

  H_3^+, He_n, H_2O, $H + H_2 \rightarrow H_2 + H$ (PES), LiH, $C_2 - C_{20}$

  Si_n

  + solids (C: diamond & graphite), Si

  $\Delta E \sim 1\mu H$

- extension of QC methods to extended systems:

  MBPT-n, CC for solids?

- DFT

Gaussian 94

What is Gaussian 94?

Gaussian 94 is a quantum chemistry program package to perform ab initio and semiempirical calculations.

How to get started:

The first thing you have to do if you want to run Gaussian 94 on the machines in NO F34 is to create a job-file (named e.g. rung94) and an input file (e.g. h2o2.inp). These files look like this:

Job-File:

```
#!/bin/csh

limit coredumpsize 0
limit descriptors 2000
setenv g94root /usr/local
source $g94root/g94/bsd/g94.login

# This is where the temporary files go:
setenv GAUSS_SCRDIR /tmp/name_of_your_scratch_directory
if (! (-e /tmp/name_of_your_scratch_directory) ) then
      mkdir /tmp/name_of_your_scratch_directory
endif

# This is the directory to work in:
cd /dirname

# This invokes Gaussian94 with the input file h2o2.inp
# (the output file will be h2o2.log)
g94 h2o2.inp
```

Input-File:

```
# method (e.g. SCF=direct) basis (e.g. STO-3G) option (e.g. opt)
[blank line]
Title
[blank line]
0 1                     charge: 0, multiplicity 1 (usually)
h                       the first atom of your molecule is hydrogen
o 1 roh                 2nd atom: oxygen, distance to atom1: roh
o 2 roo 1 angle         3rd atom: oxygen, distance to atom2: roo, angle 3-2-1
h 3 roh 2 angle 1 d     4th atom: hydrogen, " to atom3: roh, angle 4-3-2, torsional angle (4321):
[blank line]
roh 0.9
roo 1.4
angle 105.0
d 120.0
[blank line]
```

Input Description:

This is only a short summary of the most frequently used commands, have a look to the Gaussian manual for more. (In the following valid Gaussian keywords are printed in *italics*).

Method

HF: This requests a Hartree-Fock type calculation. Restricted HF (*RHF*) is used for singlets and unrestricted HF (*UHF*) is used for higher multiplets. Default is RHF.

MP2: This requests a Hartree-Fock calculation followed by a second-order Møller-Plesset correlation correction.

MP3: This will add the third order Møller-Plesset correction to MP2

MP4: This will add the forth order Møller-Plesset correction to MP3

VWN: This will perform a density functional calculation with the local (spin) density approximation (LDA, LSDA) using the correlation functional of Vosko, Wilk and Nusair and the Slater exchange

BLYP: This requests a density functional calculation including the gradient correction of Becke (1988) to the exchange and the form of Lee, Yang and Parr for the correlation functional

B3LYP: This results in a density functional calculation with Becke's 3 parameter formula.

MNDO, AM1, PM3: These request a semiempirical calculation using the specified Hamiltonian. If you take one of these semiempirical methods you don't have to specify a basis because this is part of the model

If you specify *SCF=direct*, a direct SCF calculation will be performed in which the two-electron integrals are recomputed as needed. This is possible for nearly all available methods.
Note that for single-point SCF calculations a loose convergence criterion is used in the interest of speed.

Basis
This keyword specifies the basis set to be used. The following basis sets are stored in the program:

STO-3G	H-Xe
3-21G	H-Xe
6-21G	H-Cl
4-31G	H-Ne
6-31G	H-Cl
6-311G	H-Br

For most of these basis sets you can also use polarization functions (*,**) or add diffuse functions (+,++).

Option

SP: Single point energy calculation. At the place of variables for the geometry, you set the constants and leave away the part with the initial guesses

Opt: With the input file as described above, Gaussian will optimize the geometry of your molecule. You can set some distances or angles to a constant value by using this value instead of the variables in your molecule specification

pop: With this keyword you can control the printing of the molecular orbitals and perform several types of population analysis.

pop=none No orbitals are printed, no population analysis is done

pop=regular (default) The five highest and the five lowest orbitals are printed, along with the density matrices and a Mulliken population analysis

pop=MK Produces charges fit to the electrostatic potential at points selected according to the Merz-Singh-Kollman scheme

pop=CHELP Produces charges fit to the electrostatic potential at points selected according to the CHELP scheme

pop=CHELPG Produces charges fit to the electrostatic potential at points selected according to the CHELPG scheme

Freq: Requests determination of force constants and the resulting vibrational frequencies. Intensities are also computed. The force constants are computed analytically if possible, by single numerical differentiation for methods for which only first derivatives are available, and by double numerical differentiation for those methods for which only energies are available. When frequencies are done analytically, polarizabilities are also computed.

How to run Gaussian94 jobs:

The best way to run your Gaussian job is in the background with the command:

'csh rung94 &'

(Don't forget to make your script executable with the Unix command: **chmod +x rung94** before trying to run it!) Gaussian 94 will calculate the optimized geometry or whatever you requested and will put all results and possibly errors in a file called h2o2.log.
In case of an error abortion you can look up the error and the latest results or guesses about geometry in the file h2o2.log.

Problems that can occur:

- If Gaussian 94 aborts with an error no temporary files will be deleted. You have to do that manually in the directory you specified in your job file.
- Your guesses or constant values for the geometry have to be floating point numbers (i.e. you need a decimal point even if redundant).
- Angles (except torsional angles) must be in the interval 0 - 180 °. You have to define your geometry in such a way that there is no possibility for the values for angles to leave this interval.
- Broken Symmetry: if e.g. a planar molecule gets because of numeric instabilities non planar, the program will abort. Try the last guess for geometry as a new input or define your molecule non-symmetric by using different variables.
- Taking the last guess as a new input is normally a good way to get further on in your calculations.
- Expensive jobs take more time as you expect them (large temporary files, disk access may take a lot more of the time than the calculations do), don't worry.

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Exercise 3

A) Geometry Optimization of Lithium Hydride (LiH)

Task:
Calculate the equilibrium bond length and the dipole moment of the molecule LiH using the HF, MP2, MP4, LSDA, BLYP and B3LYP methods.
Try to find 'an optimal' basis set (i.e. the smallest basis set that results in essentially converged results) by starting with a minimal basis set (STO-3G) and successively increasing the size of the basis.
(a) Which basis sets would you suggest to use for the different methods? Are polarization functions important? On the heavy atoms only? On the hydrogen, too? What is the effect of diffuse functions on the heavy atom or on the hydrogen? (b) How do the results of the different methods compare to the experimental values?

Optional I:
Try to calculate the binding energy of LiH with the HF method and a 6-31G** basis set (aid: The binding energy of the molecule is the difference of its total energy and the total energy of the constituent atoms).

Optional II:
From intermediate points encountered during the geometry optimization you can 'by hand' obtain the harmonic frequency (in cm^{-1}) of the LiH stretching vibration: Calculate numerically the curvature of the potential energy curve from a few points around the minimum. Convert this to a force constant and use the reduced mass of LiH to obtain the frequency (be careful with unit conversions). Compare the performance of various approximations in reproducing the experimental value (1405.65 cm^{-1}). NB: You could have used the *freq* option in Gaussian to calculate frequencies. However, this involves additional computations: Just imagine you were doing the AuSn molecule for which every point would take several days of cpu time.

Practical Aid:
A Gaussian94 input with a reasonable starting geometry would look like this:

```
>>> start
# MP4 6-311g** opt=z-matrix scf=direct

LiH (MBT4)

0 1
Li
H 1 r

r 1.6

>>> end
```

Exercise 3

B) Internal Rotation in Hydrogen Peroxide (H_2O_2)

Task:

Perform geometry optimizations for H_2O_2 using the following approximations:

	method	basis set		method	basis set
(a)	HF	STO-3G	(f)	LSDA	6-31g**
(b)	HF	3-21g	(g)	BLYP	6-31g**
(c)	HF	6-31g	(h)	B3LYP	6-31g**
(d)	HF	6-31g**	(i)	MNDO	
(e)	MP2	6-31g**	(j)	PM3	

Report the following characteristic structural properties for every approximation (experimental results are given in parentheses):

bond lengths
O-O (1.475 Å)
O-H (0.965 Å)

bond angles
O-O-H (94.8.0°)

dihedral angles
H-O-O-H (119.8°)

For those approximations which gave an optimized H-O-O-H dihedral angle different form 180° (trans) perform an additional optimization with the central dihedral angle fixed at 180° (but optimizing all other degrees of freedom) and calculate the trans barrier to internal rotation (in kJ/mol). The experimental value is 4.6 kJ/mol.

Discuss the relative importance of basis set size, polarization functions and electron correlation for the calculated equilibrium geometry and the rotational barrier. How do you judge the performance of (a) the DFT methods and (b) the semiempirical methods? Around which temperature do you expect that the trans form of H_2O_2 is significantly populated?

Practical Aid:
An example for a Gaussian94 input performing a geometry optimization of H_2O_2 with the H-O-O-H dihedral fixed at 180° is given below:

```
>>> start
# HF 6-31G opt=z-matrix scf=direct

H2O2, HF 6-31G optimization with H-O-O-H fixed at 180 degrees

0 1
H
O 1 ho
O 2 oo 1 hoo
H 3 ho 2 hoo 1 hooh

ho 0.965
oo 1.452
hoo 100.0
hooh 180.0

>>> end
```

Exercise 4

A) Inversion of Ammonia (NH_3)

Task:
Perform geometry optimizations for NH_3 using the following approximations:

	method	basis set		method	basis set
(a)	HF	STO-3G	(f)	LSDA	6-31g**
(b)	HF	3-21g	(g)	BLYP	6-31g**
(c)	HF	6-31g	(h)	B3LYP	6-31g**
(d)	HF	6-31g**	(i)	MNDO	
(e)	MP2	6-31g**	(j)	PM3	

Perform also a partial geometry optimization for the planar transition state (D_{3h} symmetry). Report the N-H bond length, the H-N-H bond angle and the dipole moment for the equilibrium configuration and for the planar transition state and compare them to the experimental values. From the total energies of the optimized structures calculate the inversion barrier (experimental value: 24.4 kJ/mol). Discuss the relative importance of basis set size, polarization functions and electron correlation for the calculated properties. How well do the different approximations perform?
The inversion barrier calculated is that for NH_3 in the gas phase. In which direction will it change in an aprotic polar solvent?

Practical Aid:
Here is an input for the planar transition state conformation of NH_3. Note the use of a dummy atom X.

```
>>> start
# HF 6-31G** opt=z-matrix scf=direct

NH3, barrier

0 1
N
X 1 1.0
H 1 nh 2 nhx
H 1 nh 2 nhx 3 120.0
H 1 nh 2 nhx 3 -120.0

nh 1.0
nhx 90.0

>>> end
```

Exercise 4

B) Semiempirical Methods

Task:

(1) Perform geometry optimizations for benzene, nitro benzene, aniline, and p-nitro aniline using the following semiempirical methods: MNDO, AM1, PM3. Are the resulting geometries reasonable? Compare with expected bond lengths, bond angles, planarity etc..

(2) Calculate the dipole moments of all compounds at their optimized geometries using all semiempirical methods. Discuss (dis)agreement with experiment (experimental values: benzene: 0, nitro benzene: 4.22 debyes, aniline: 1.13 debyes).

(3) For all compounds and all semiempirical methods calculate atomic charges by (i) Mulliken population analysis and (ii) one of the electrostatic potential fitting methods: MK, CHELP or CHELPG. Your discussion should answer the questions:

- Do the atomic charges reproduce the molecular dipole moments?
- How different are the charges on two atoms which are related by symmetry (i.e. whose charges should be identical)?
- How do the charges of the phenyl (or phenylene) carbon atoms (dis)agree with known rules for the direction of an electrophilic attack?
- Would an electrophilic substitution reaction be accelerated compared to benzene?

- All HF methods give the orbital energies as a by-product. From the energy difference of the highest occupied (HOMO) and the lowest unoccupied (LUMO) orbital estimate the wave length of the transition from the ground state to the first electronically excited state. Does the wave length agree with known observations (experimental values, color of the four compounds)?

- Based on your experience which of the three semiempirical schemes would you recommend for: (i) molecular geometries? (ii) charge distribution (dipole moment, quadrupole moment)? (iii) electronic spectra?

Practical Aid:
In Gaussian94 Mulliken population analysis are performed by default. Electrostatic potential fits are invoked by the '*pop=*' keyword.
The line

```
# MNDO opt=z-matrix pop=chelpg
```

will cause a geometry optimization using the MNDO method. For both the initial and the final conformation, a Mulliken population analysis and an electrostatic potential fit using the CHELPG scheme will be performed.

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