

The Multiconfigurational Approach in Quantum Chemistry

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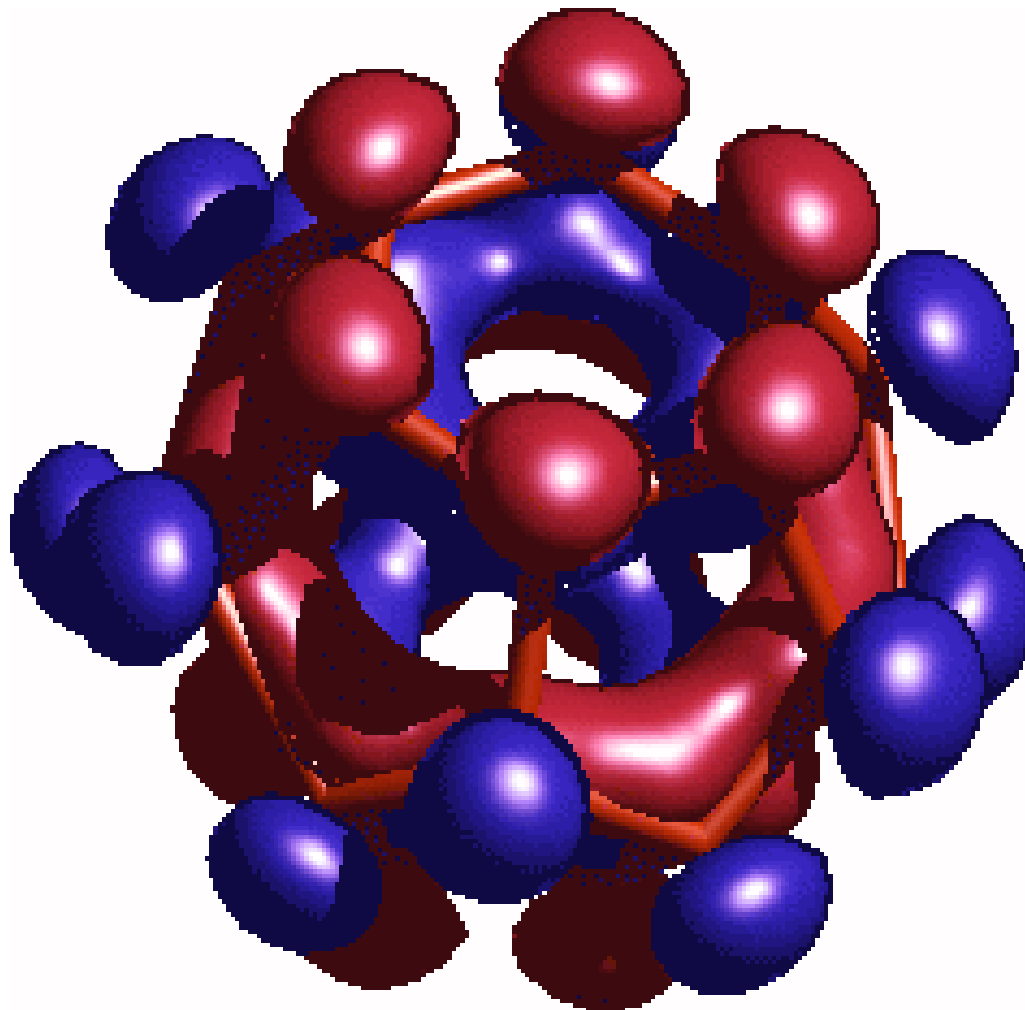
The Molecular Orbital

The basic concept for the construction of many-electron wave functions is the **Molecular Spin Orbital** $\phi_i(\mathbf{r}, s)$:

$$\phi_i(\mathbf{r}, s) = \varphi_i(\mathbf{r})\theta_i(s)$$

where $\varphi_i(\mathbf{r})$ is the **Molecular Orbital — MO** and $\theta_i(s)$ is a spin function.

A Molecular Orbital in the C_{24} Molecule



The Basis Set Expansion

The MO is usually expanded in a **Basis Set** $\chi_p, p = 1, m$:

$$\varphi_i = \sum_p C_{ip} \chi_p$$

The basis set is normally obtained atomic centered and the expansion is called **Linear Combination of Atomic Orbitals, LCAO**.

From a basis set of dimension m we can construct m MO's and $2m$ spin orbitals.

The Slater determinant

Using the spin-orbitals, we can construct anti-symmetric N -electron functions as **Slater determinants**:

$$\Phi_K = \hat{A}\{\phi_{K1}(x_1), \phi_{K2}(x_2) \cdots, \phi_{KN}(x_N)\}$$

where $x = \mathbf{r}, s$ and \hat{A} is an anti-symmetrizer. The number of such determinants is

$$K = \binom{2m}{N}$$

Weyl's Formula

Number of molecular orbitals:	n
Number of spin-orbitals:	$2n$
Number of electrons:	N
Spin quantum number	S

The Number of configuration state functions (*CSF's*) is:

$$K(n, N, S) = \frac{2S + 1}{n + 1} \binom{n + 1}{\frac{1}{2}N - S} \binom{n + 1}{\frac{1}{2}N + S + 1}$$

The Full CI Method

We can expand the wave function in the determinants:

$$\Psi = \sum_K C_K \Phi_K$$

Inserting into the Schrödinger equation and integrating gives the Secular Equation:

$$\sum_L (H_{KL} - E\delta_{KL})C_L = 0$$

This is called **Full CI** and becomes an exact solution in the limit of a complete basis set.

The First Order Reduced Density Matrix

$$\rho_1(x, x') = N \int \Psi^*(x', x_2, \dots, x_N) \Psi(x, x_2, \dots, x_N) dx_2 \dots dx_N$$

In spin-orbital representation:

$$\rho_1(x, x') = \sum_{i,j} \rho_{ij} \phi_i(x) \phi_j^*(x')$$

Matrix Elements of a One-Electron Operator

$$\hat{F} = \sum_{k=1}^N \hat{f}(k)$$

$$\langle \Psi | \hat{F} | \Psi \rangle = \sum_{k=1}^N \int \Psi^*(x_1, x_2, \dots, x_N) \hat{f}(x_k) \Psi(x_1, x_2, \dots, x_N) dx_1 \dots dx_N$$

$$\langle \Psi | \hat{F} | \Psi \rangle = N \int \Psi^*(x_1, x_2, \dots, x_N) \hat{f}(x_1) \Psi(x_1, x_2, \dots, x_N) dx_1 \dots dx_N$$

$$\langle \Psi | \hat{F} | \Psi \rangle = \int \hat{f}(x) \rho(x, x')_{x'=x} dx$$

$$\langle \Psi | \hat{F} | \Psi \rangle = \sum_{i,j} F_{ij} \rho_{ij}$$

Natural Spin-Orbitals

Transform the spin-orbitals such that ρ becomes diagonal:

$$\rho_1(x, x') = \sum_i \eta_i \phi_i(x) \phi_i^*(x')$$

η_i are the **Occupation Numbers**. They fulfill the condition:

$$0 \leq \eta_i \leq 1$$

The corresponding orbitals are called: **Natural Spin-Orbitals**

Separation of Spin

We can write the density matrix as:

$$\rho_1(x, x') = \rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}')\alpha\alpha'^* + \rho_{\beta\beta}(\mathbf{r}, \mathbf{r}')\beta\beta'^*$$

From this we can define the charge density matrix:

$$\rho_q(\mathbf{r}, \mathbf{r}') = \rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') + \rho_{\beta\beta}(\mathbf{r}, \mathbf{r}')$$

and the spin density matrix:

$$\rho_s(\mathbf{r}, \mathbf{r}') = \rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') - \rho_{\beta\beta}(\mathbf{r}, \mathbf{r}')$$

The Natural Orbitals

The charge density matrix can be expanded in the molecular orbitals

$$\rho_q(\mathbf{r}, \mathbf{r}') = \sum_{i,j} q_{ij} \varphi_i(\mathbf{r}) \varphi_j^*(\mathbf{r}')$$

Diagonalizing this matrix gives the **Natural Orbitals**

$$\rho_q(\mathbf{r}, \mathbf{r}') = \sum_i \eta_i \lambda_i(\mathbf{r}) \lambda_i^*(\mathbf{r}')$$

The occupation numbers η_i now fulfill: $0 \leq \eta_i \leq 2$

The charge density is the diagonal of the charge density matrix:

$$Q(\mathbf{r}) = \rho_q(\mathbf{r}, \mathbf{r})$$

Unrestricted Hartree-Fock Theory — UHF

Make the ansatz: $\Psi = \hat{A}\{\phi_1(x_1) \cdots \phi_N(x_N)\}$

The occupied orbitals are optimized using the variation principle.

The spin-orbitals are obtained as solutions to the UHF equations:

$$\hat{F}\phi_i = \epsilon_i\phi_i$$

where

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

The spin orbital occupation is 1 or 0 but the natural orbital occupation is non-integer: $0 \leq \eta \leq 2$

Restricted Hartree-Fock Theory — the Closed Shell

For most molecules close to equilibrium, UHF yields the solution:

$$\begin{aligned}\phi_{2i-1} &= \varphi_i\alpha \\ \phi_{2i} &= \varphi_i\beta\end{aligned}$$

which is a solution to the **Restricted Hartree-Fock** equations for closed shells:

$$\hat{F}\varphi_i = \epsilon_i\varphi_i$$

where

$$\hat{F} = \hat{h} + \sum_{j=1}^{N/2} (2\hat{J}_j - \hat{K}_j)$$

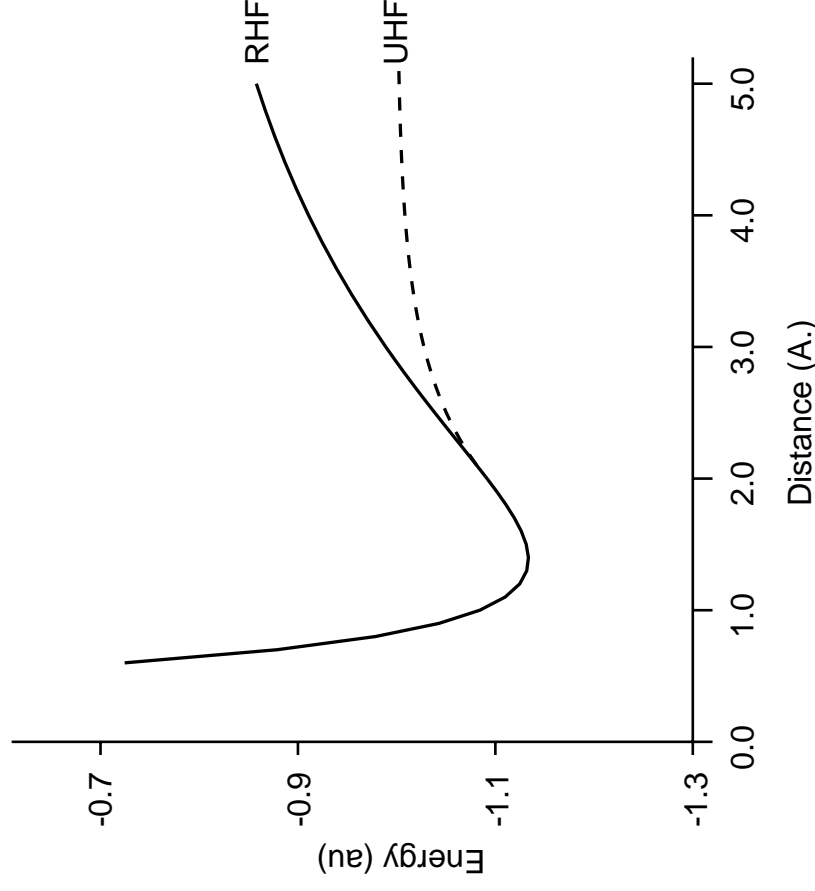
The natural orbital occupation numbers are now 2 or 0.

Stability of Restricted Hartree-Fock Theory for Closed Shells

Condition for a stable solution (a minimum):

All eigenvalues of the Hessian matrix are positive:

$$H_{ij} = \delta^2 E / \delta p_i \delta p_j$$



Molecular Orbitals for the H₂ Molecule



Use a minimal basis set: $(1s_A, 1s_B)$

The MO's are given by symmetry:

$$\sigma_g = N_g(1s_A + 1s_B), \quad \sigma_u = N_u(1s_A - 1s_B)$$

The closed shell HF configuration is: $\Phi_1 = (\sigma_g)^2 = \frac{1}{\sqrt{2}}|\sigma_g\alpha, \sigma_g\beta|$

With the spin-orbitals: $\phi_1 = \sigma_g\alpha$ and $\phi_2 = \sigma_g\beta$

UHF for H₂ (Coulson and Fischer, 1947)

$$\phi_1 = N(1s_A + \lambda 1s_B)\alpha$$

$$\phi_2 = N(\lambda 1s_A + 1s_B)\beta$$

which gives the UHF determinant, $\Phi_{UHF} = \frac{1}{\sqrt{2}}|\phi_1, \phi_2|$:

$$\Phi_{UHF} = c_1^2(\sigma_g)^2 - c_1c_2\sqrt{2}(\sigma_g\sigma_u)_T - c_2^2(\sigma_u)^2$$

where: $c_1 = N(1 + \lambda)/2N_g$ and $c_2 = N(1 - \lambda)/2N_u$

Note: Φ_{UHF} has not the correct symmetry and is a mixture of a singlet and a triplet.

The UHF Energy for H_2 as a function of λ

Introduce: $a_1 = c_1^2$, $a_2 = c_2^2$, $a_1 + a_2 = 1$. Then:

$$E(\lambda) = a_1^2 E_1 + 2a_1 a_2 (E_T - K_{gu}) + a_2^2 E_2$$

Where $E_1 = E(\sigma_g^2)$, $E_2 = E(\sigma_u^2)$, $E_T = E((\sigma_g \sigma_u)_T)$;

And: $K_{gu} = (\sigma_g \sigma_u | \sigma_g \sigma_u) = (J_{AA} - J_{AB})/2(1 - S^2)$

The stationary points (the UHF orbitals) are obtained by solving the equation:

$$dE/d\lambda = 0$$

The stability of the solution is obtained from the second derivative.

Stationary Solutions for the UHF Energy for H₂

Solution 1, if $(E_T - E_1) > K_{gu}$:

$\lambda = 1 (a_1 = 1)$	$d^2 E / d\lambda^2 > 0$	$\Phi_{UHF} = (\sigma_g)^2$
$\lambda = -1 (a_1 = 0)$	$d^2 E / d\lambda^2 < 0$	$\Phi_{UHF} = (\sigma_u)^2$

Solution 2, if $(E_T - E_1) \leq K_{gu}$:

$\lambda = 1 (a_1 = 1)$	$d^2 E / d\lambda^2 < 0$	Unstable
$\lambda = -1 (a_1 = 0)$	$d^2 E / d\lambda^2 < 0$	Unstable
$-1 < \lambda < 1 (a_1 < 1)$	$d^2 E / d\lambda^2 \geq 0$	Stable

Solution for the UHF Energy for H₂ for Large H-H Distance

λ becomes equal to zero for large values of R, corresponding to the wave function:

$$\Phi_{UHF} = \frac{1}{\sqrt{2}} |1s_A\alpha, 1s_B\beta|$$

The UHF wave function dissociates correctly but is unsymmetric and no eigenfunction of the spin operators.

Natural Orbitals for the UHF Wave Function for H_2

Express the spin orbitals in terms of the symmetry-adapted orbitals σ_g and σ_u :

$$\phi_1 = N(1s_A + \lambda 1s_B)\alpha = \varphi_1\alpha \text{ and } \phi_2 = N(\lambda 1s_A + 1s_B)\beta = \varphi_2\beta \text{ We get:}$$
$$\varphi_1 = c_1\sigma_g + c_2\sigma_u \text{ and } \varphi_2 = c_1\sigma_g - c_2\sigma_u.$$

The charge density is:

$$Q = \varphi_1^2 + \varphi_2^2 = 2c_1^2\sigma_g^2 + 2c_2^2\sigma_u^2 \text{ with } 2(c_1^2 + c_2^2) = 2.$$

Thus σ_g and σ_u are the natural orbitals, but their occupation numbers differ from 2 and 0.

Dissociation of H₂ in closed shell HF Theory

The HF function is: $\Phi_1 = \frac{1}{\sqrt{2}}|\sigma_g\alpha\sigma_g\beta| = \sigma_g(1)\sigma_g(2)\Theta_{2,0}$,

where $\sigma_g(1) = N_g(1s_A + 1s_B)$.

$$\begin{aligned}\Phi_1 &= N_g^2\{1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) \\ &\quad + s_A(1)1s_B(2) + s_B(1)1s_A(2)\}\Theta_{2,0}.\end{aligned}$$

Thus we have for large R: $\Phi \propto \Phi(H + H) + \Phi(H^+ + H^-)$.

The energy at dissociation is:

$$E(r = \infty) = \frac{1}{2}(E(2H) + E(H^+) + E(H^-)) \approx E(2H) + 6.66 \text{ eV}.$$

Correct Wave Function for $R = \infty$

$$\Phi_{\infty} = \{s_A(1)1s_B(2) + s_B(1)1s_A(2)\}\Theta_{2,0}$$

with no ionic terms. They are important at $R = R_e$ but should disappear at $R = \infty$. Now introduce a new configuration:

$$\Phi_2 = \frac{1}{\sqrt{2}}|\sigma_u\alpha, \sigma_u\beta| = \sigma_u(1)\sigma_u(2)\Theta_{2,0}$$

$$\sigma_u(1) = N_u(1s_A - 1s_B)$$

$$\Phi_2 = N_u^2\{1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) - s_A(1)1s_B(2) - s_B(1)1s_A(2)\}\Theta_{2,0}.$$

The Two Configurational Solution

We find immediately that:

$$\Phi_{\infty} = \frac{1}{\sqrt{2}} \{ \Phi_1 - \Phi_2 \}$$

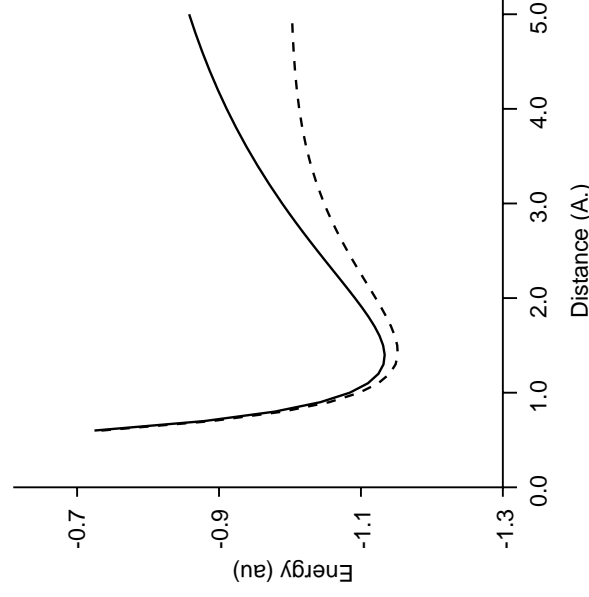
Assume now for all R :

$$\Phi = C_1 \Phi_1 + C_2 \Phi_2$$

The coefficients depend on R :

$$\begin{array}{lll} R \approx R_e & C_1 \approx 1 & C_2 \approx 0 \\ R = \infty & C_1 \approx \frac{1}{\sqrt{2}} & C_2 \approx -\frac{1}{\sqrt{2}} \end{array}$$

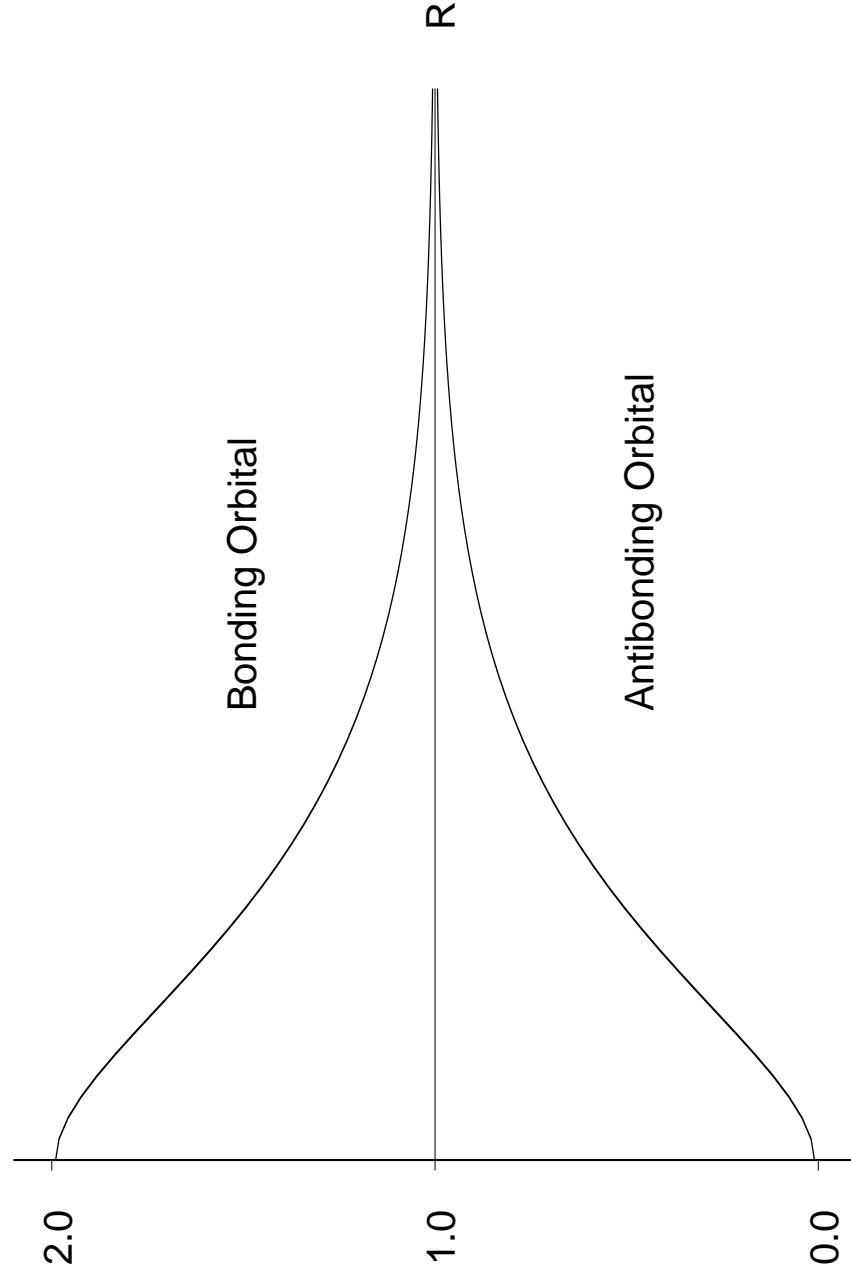
The Energy of H_2 as a Function of the Distance R



	$R_e(\text{Å})$	$D_e(\text{eV})$	$\omega_e(\text{cm}^{-1})$
SCF	0.736	3.63	4424 (Φ_1)
MCSCF	0.757	4.13	4355 (Φ_1, Φ_2)
Expt.	0.741	4.75	4401

The Quantum Chemical Description of a Chemical Bond Involves both the Bonding and the Antibonding Orbital!

Natural Occupation Numbers for the Orbital Pair:



A More Complicated Example: Cr_2

The chromium atom has six unpaired electrons, $(3d)^5(4s)$, 6S

These atomic orbitals can be used to construct the following molecular orbitals:

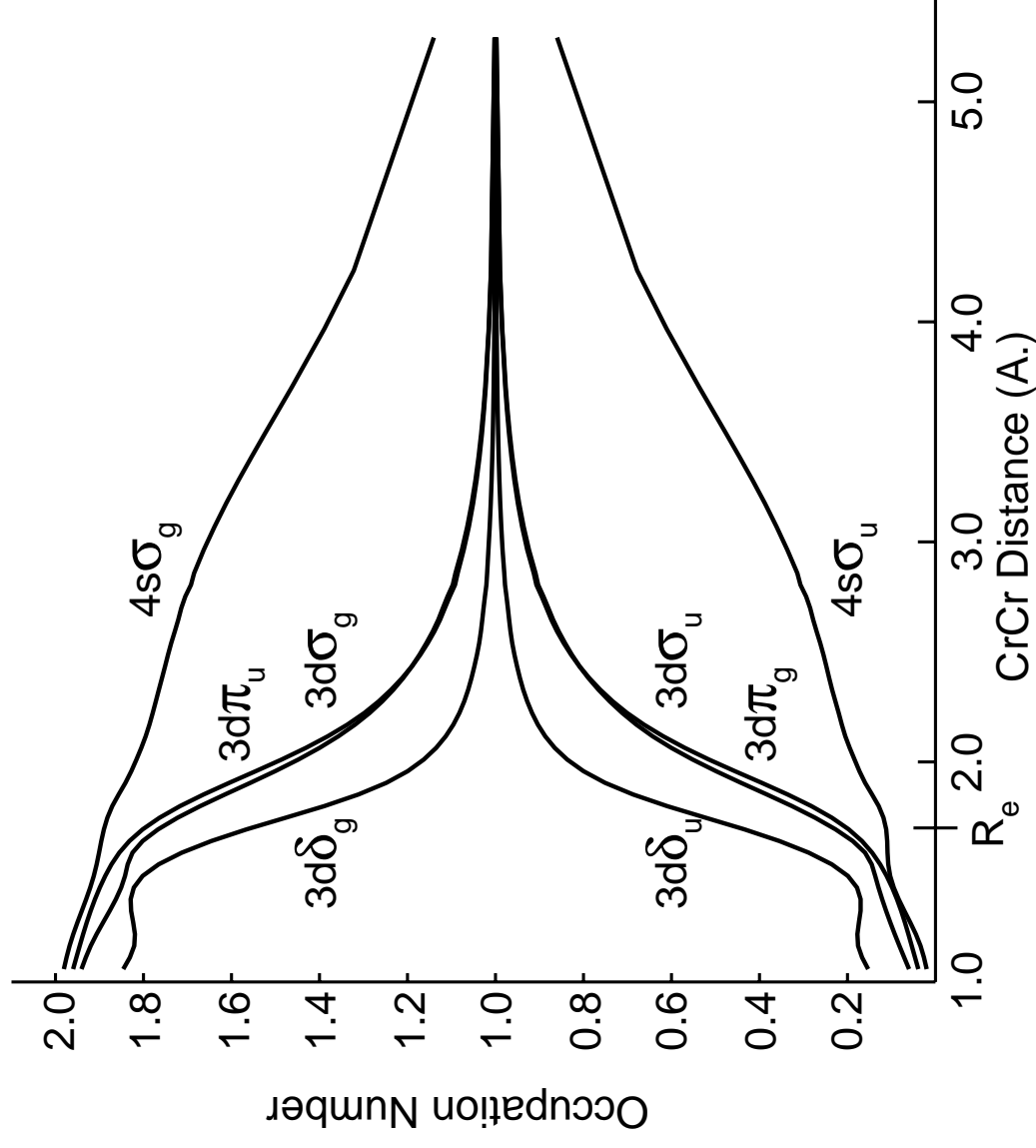
bonding: $4s\sigma_g$, $3d\sigma_g$, $3d\pi_u$, $3d\delta_g$

antibonding: $4s\sigma_u$, $3d\sigma_u$, $3d\pi_g$, $3d\delta_u$

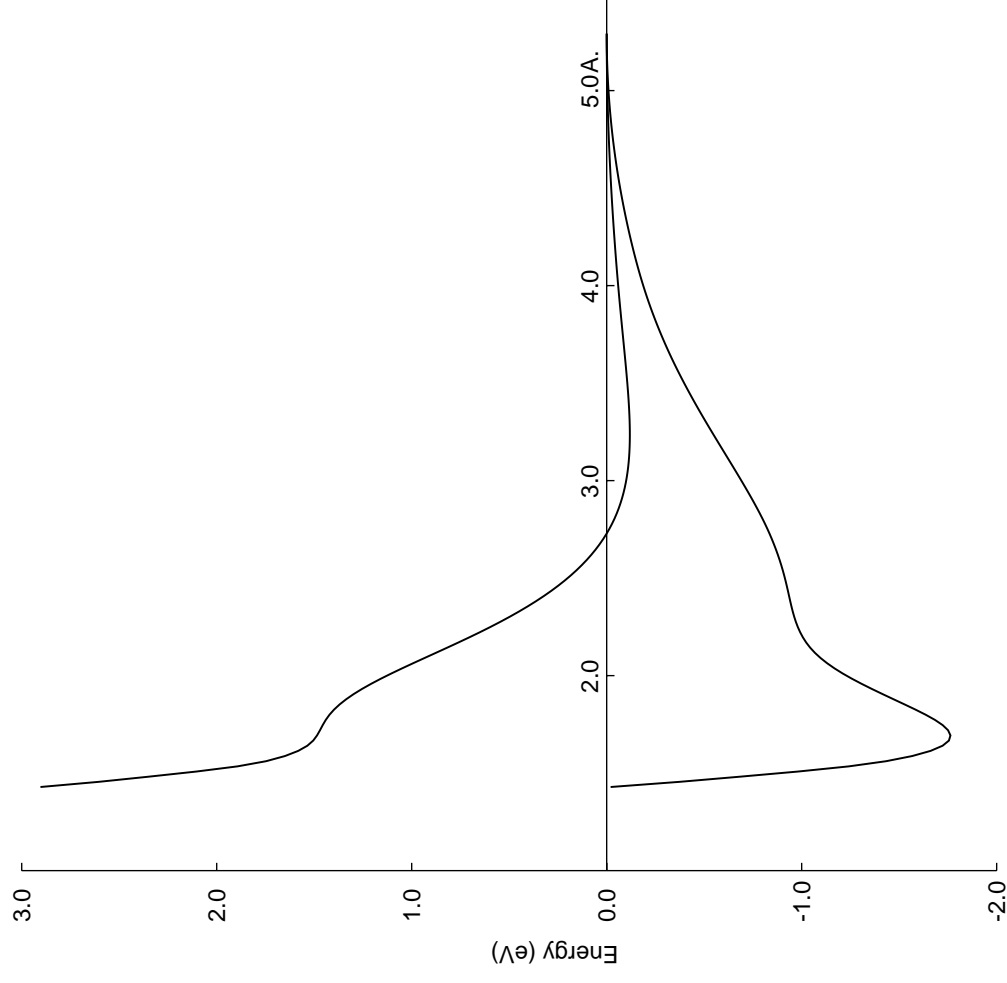
A sextuple bond can be formed!

Around 3000 configurations are needed for a correct description of the dissociation process.

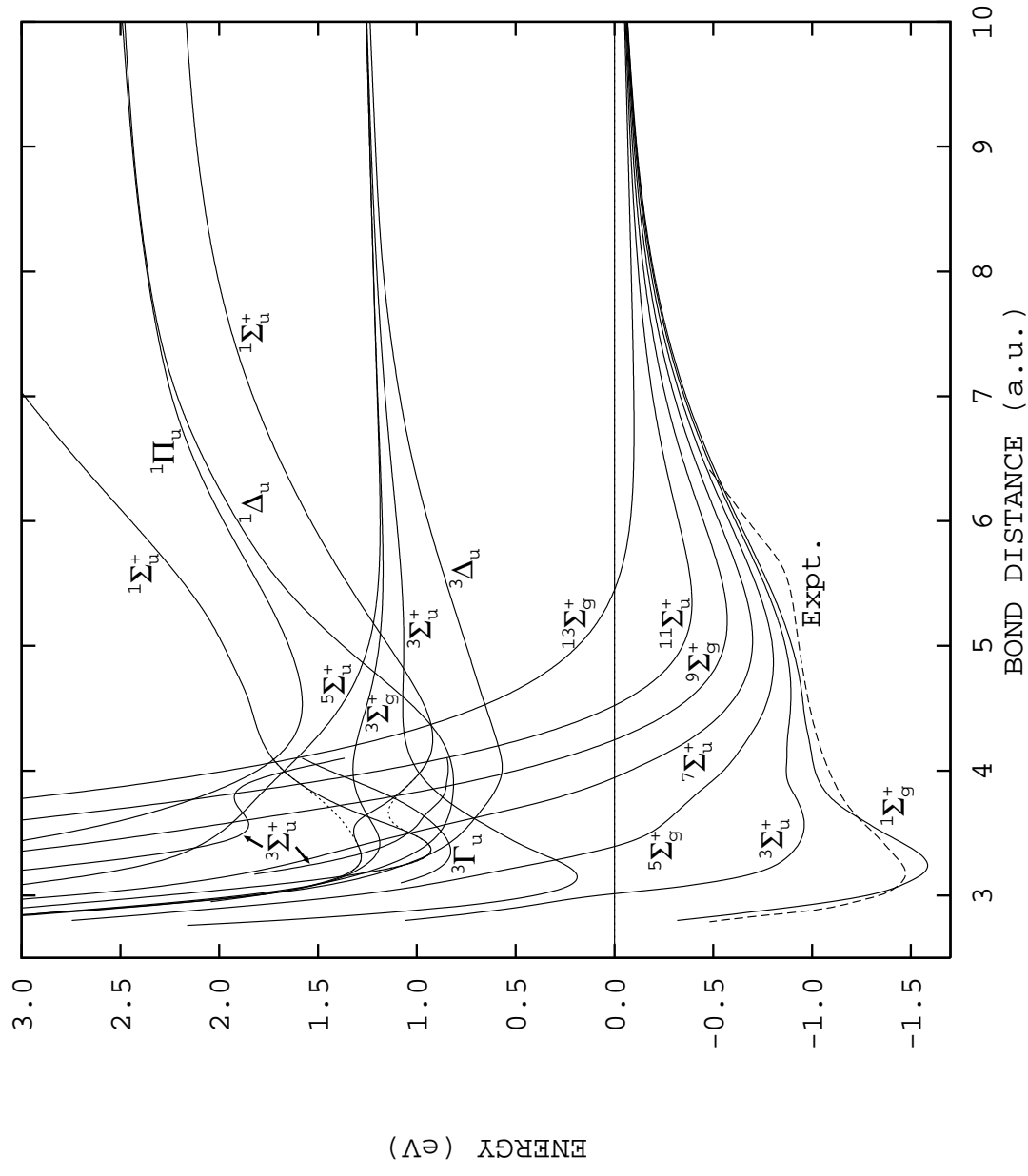
The Natural Orbital Occupation Numbers for Cr_2



CASSCF and CASPT2 Ground State Potentials for Cr₂



CASPT2 Potential Curves for Cr₂



Static Correlation

Consider two electrons, two MO's and the wave function:

$$\Phi = C_1(\varphi_1)^2 - C_2(\varphi_2)^2$$

The second order density is obtained as:

$$\rho_2(1, 2) = \frac{1}{2}\eta_1\varphi_1(1)^2\varphi_1(2)^2 + \frac{1}{2}\eta_2\varphi_2(1)^2\varphi_2(2)^2 - \sqrt{\eta_1\eta_2}\varphi_1(1)\varphi_2(1)\varphi_1(2)\varphi_2(2)$$

where $\eta_1 = 2C_1^2$ and $\eta_2 = 2C_2^2$ are the natural orbital occupation numbers. The last term separates the electrons in the pair.

Separation of the Electron Pair — Static Correlation



$$\varphi_1 = \sigma_g$$

$$\varphi_1 = 2s$$

$$\varphi_2 = \sigma_u$$

$$\varphi_2 = 2p$$

Static and Dynamic Correlation

Static Correlation

Large Separation of the electrons in a pair

Dynamic Correlation

Separation in the cusp region ($r_{12} \approx 0$)

Multiconfigurational quantum chemistry has been devised to include static correlation effects into the wave function.

Dynamic correlation is normally treated using other methods, as MRCI, MBPT, CASPT2, or Coupled Cluster methods.

Near Degeneracy

Back to H_2 :

$$E(\sigma_g)^2 = E(\sigma_g)^2 \text{ at } R = \infty$$

In general when two configurations Φ_1 and Φ_2 have the same energy and their interaction is not zero:

$$\Psi = \frac{1}{\sqrt{2}}\{\Phi_1 - \Phi_2\}$$

If Φ_1 and Φ_2 are close in energy we obtain:

$$\Psi = C_1\Phi_1 + C_2\Phi_2$$

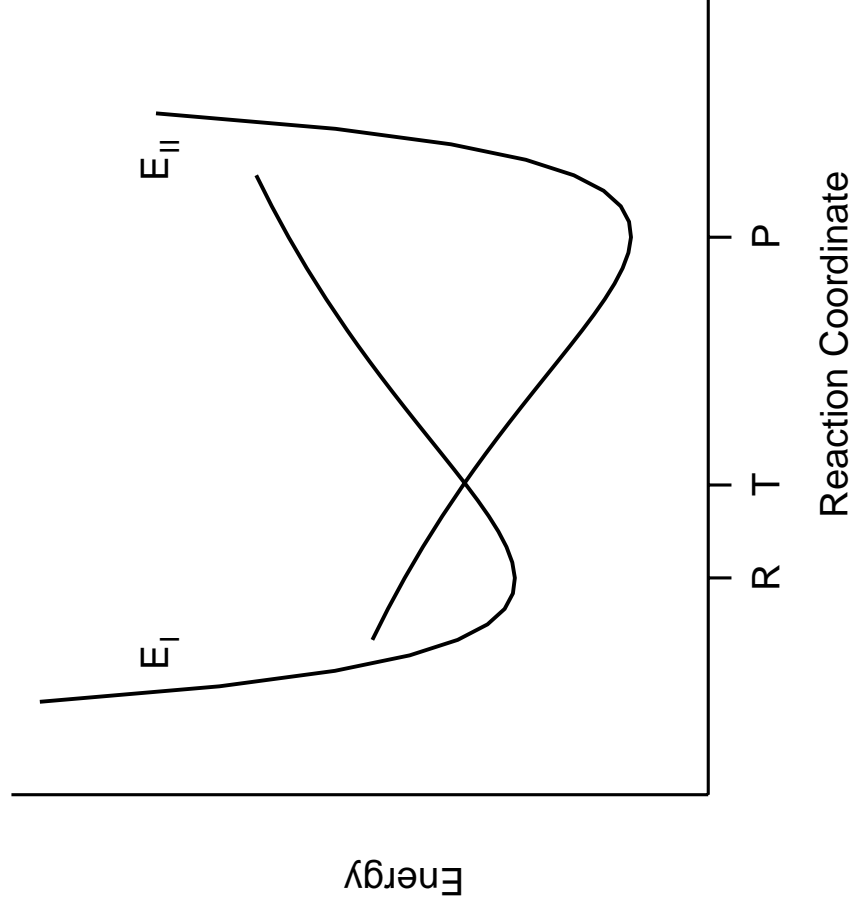
with both C_1 and C_2 appreciably different from zero.

We have **Near Degeneracy** and a multiconfigurational treatment is necessary.

Transition States on Energy Surfaces

Consider a Chemical reaction: *Reactants* \Rightarrow *Transition State* \Rightarrow *Products*

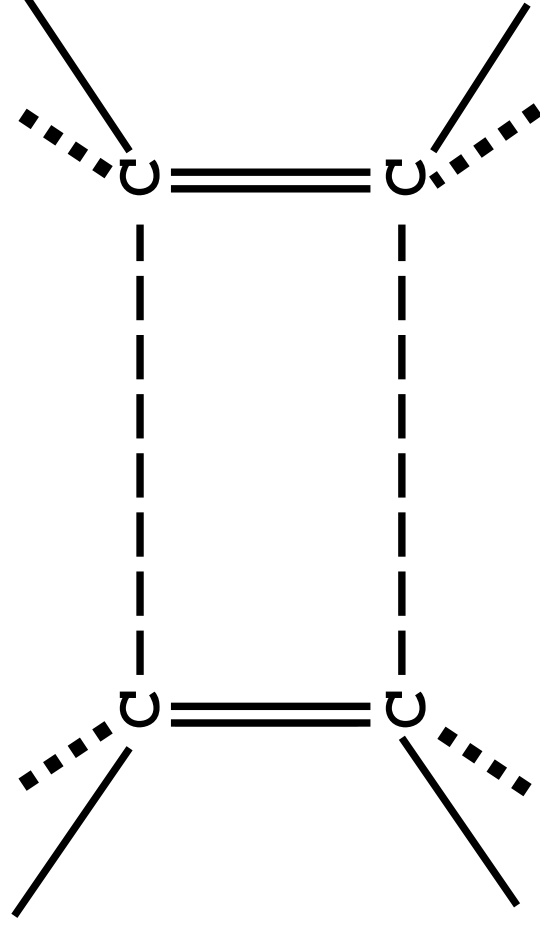
The electronic configurations Φ_R and Φ_P are in general different:



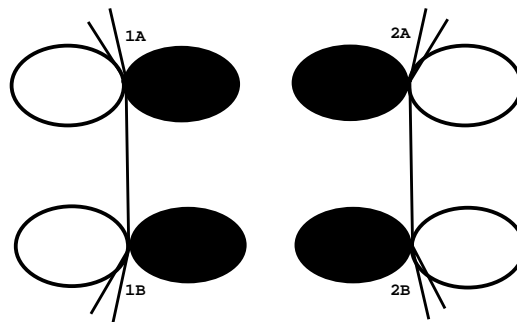
Dimerization of Ethene to Cyclobutane

Consider the chemical reaction: $C_2H_4 + C_2H_4 \rightarrow C_4H_8$

Assume a D_{2h} reaction path:



Dimerization of Ethene to Cyclobutane — Reactants



Active orbitals: π_1 , π_1^* , π_2 , and π_2^* .

The wave function is: $\Psi_{R=\infty} = \dots(\pi_1)^2(\pi_2)^2$ or $\Psi_{R=\infty} = \dots(\pi_+)^2(\pi_-)^2$

where in the D_{2h} symmetry:

$$\pi_+ = \frac{1}{\sqrt{2}}(\pi_1 + \pi_2) = \frac{1}{2}(\pi_{1A} + \pi_{1B} + \pi_{2A} + \pi_{2B})$$

$$\pi_- = \frac{1}{\sqrt{2}}(\pi_1 - \pi_2) = \frac{1}{2}(\pi_{1A} + \pi_{1B} - \pi_{2A} - \pi_{2B})$$

Dimerization of Ethene to Cyclobutane — Products

$$\begin{aligned}\sigma_A &\propto (\pi_{1A} + \pi_{2A}) \\ \sigma_B &\propto (\pi_{1B} + \pi_{2B}).\end{aligned}$$

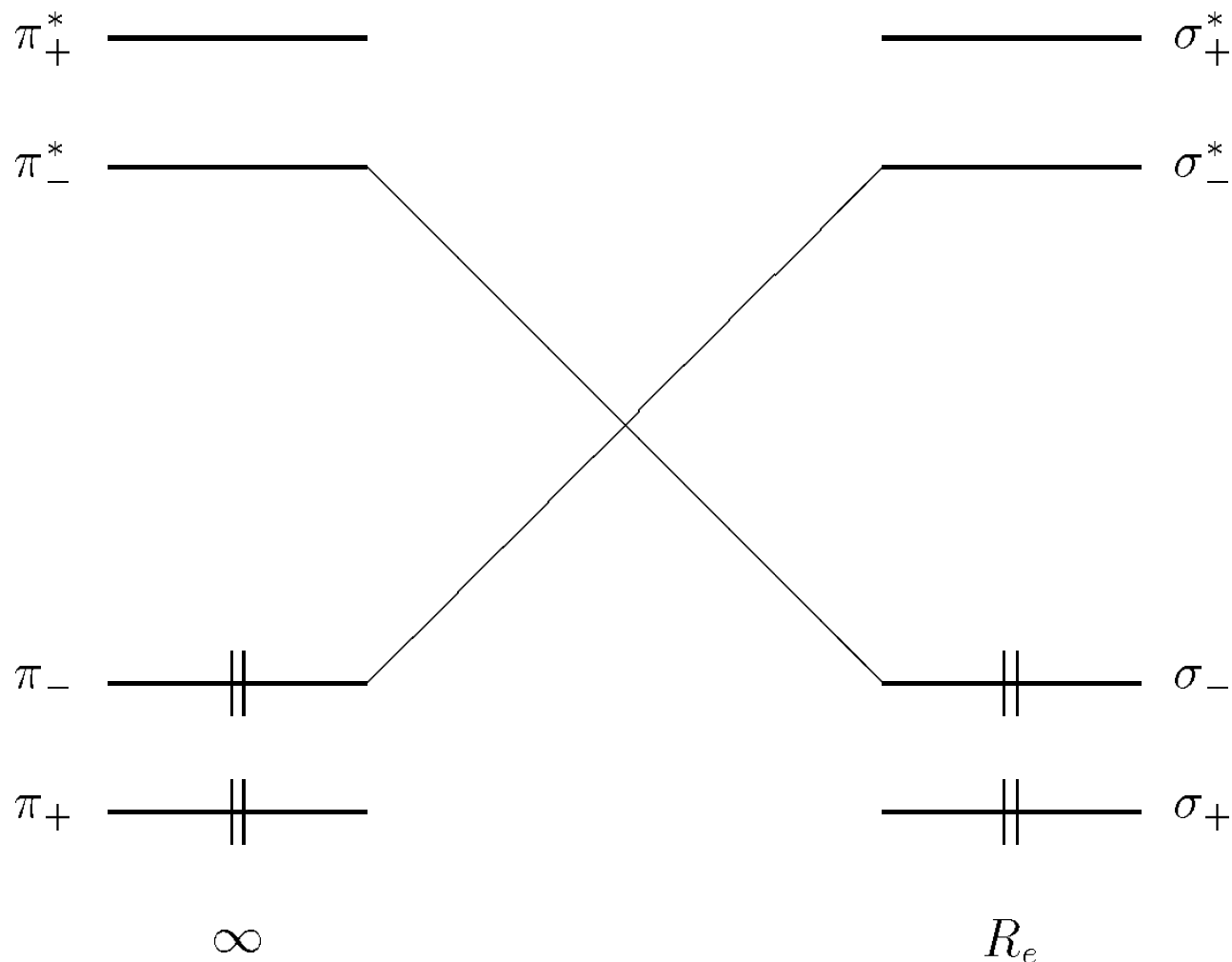
The electronic configuration is now:

$$\Psi_{R=R_e} = \dots(\sigma_A)^2(\sigma_B)^2 \text{ or } \Psi_{R=R_e} = \dots(\sigma_+)^2(\sigma_-)^2, \text{ where}$$

$$\begin{aligned}\sigma_+ &= \frac{1}{\sqrt{2}}(\sigma_A + \sigma_B) = \frac{1}{2}(\pi_{1A} + \pi_{1B} + \pi_{2A} + \pi_{2B}) = \pi_+ \\ \sigma_- &= \frac{1}{\sqrt{2}}(\sigma_A - \sigma_B) = \frac{1}{2}(\pi_{1A} - \pi_{1B} + \pi_{2A} - \pi_{2B}) = \pi_-^*\end{aligned}$$

The electronic configurations are thus different.

Orbital Energy Correlation Diagram — for a Forbidden Chemical Reaction

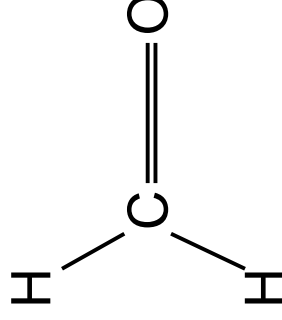
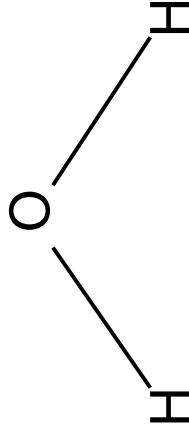


Most molecules have a well defined electronic configuration in the ground state at the equilibrium geometry.

Or, using a more chemical language:

Most molecules have all their valencies saturated in chemical bonds.

Example: some oxygen containing systems:



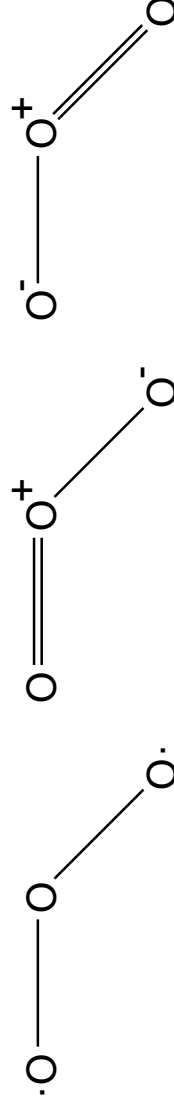
with two valencies saturated.

Hartree-Fock theory gives in these cases a valid description of the electronic structure.

Unsaturated Valencies

Example: the Ozone molecule (O_3)

There is no way to saturate all valencies. Several structures are possible:



A single electronic configuration does not describe the electronic structure.



Let us take a closer look

The Electronic Structure of Ozone

Different structures correspond to different occupations of the localized orbitals π_A , π_B , and π_C . Symmetry orbitals are:

$$\pi_1 = c_{11}\pi_A + c_{12}(\pi_B + \pi_C)$$

$$\pi_2 = c_{21}(\pi_B - \pi_C)$$

$$\pi_3 = c_{31}\pi_A + c_{32}(\pi_B + \pi_C)$$

Hartree-Fock configuration: $(\pi_1)^2(\pi_2)^2$

The MCSCF Wave Function of Ozone

Full CI in the π -orbital base includes the configurations:

$$\Phi_1 = (\pi_1)^2(\pi_2)^2, \Phi_2 = (\pi_1)^2(\pi_3)^2, \Phi_3 = (\pi_2)^2(\pi_3)^2, \Phi_4 = (\pi_2)^2(\pi_1\pi_3)_S$$

$$\Psi = \sum_{m=1}^4 C_m \Phi_m$$

Result of such a calculation: $C_1 = 0.89$, $C_2 = -0.45$, C_3 and $C_4 \approx 0$.

Examples of Near-Degeneracies

- At dissociation limits for chemical bonds.
- Molecules with unfilled valencies in their ground electronic state.
- Molecules containing atoms with low lying excited states (Li, Be, Transition metals, etc).
- Frequently in excited states.
- Along reactions paths in many chemical and photochemical reactions.

A multiconfigurational wave function is needed for the description of the electronic structure in these systems, even at the lowest level of theory.

The Multiconfigurational Approach in Quantum Chemistry

Two schools of quantum chemistry:

The "English" School

The "Scandinavian" School

Reference Function:

One configuration (HF, UHF)

An MCSCF (CASSCF) wave function

Correlation:

MPX, CC, DFT

Dynamic Correlation

MRCI, MRCC (not yet), CASPT2

Software:

GAUSSIAN, ACES, ...

MOLCAS, MOLPRO, ...

"Black Box"

No "Black Box"

Active Orbitals and the Complete Active Space

Construction of the MCSCF wave function:

Divide the occupied MO's into two groups:

Inactive Orbitals Occ.No. 2

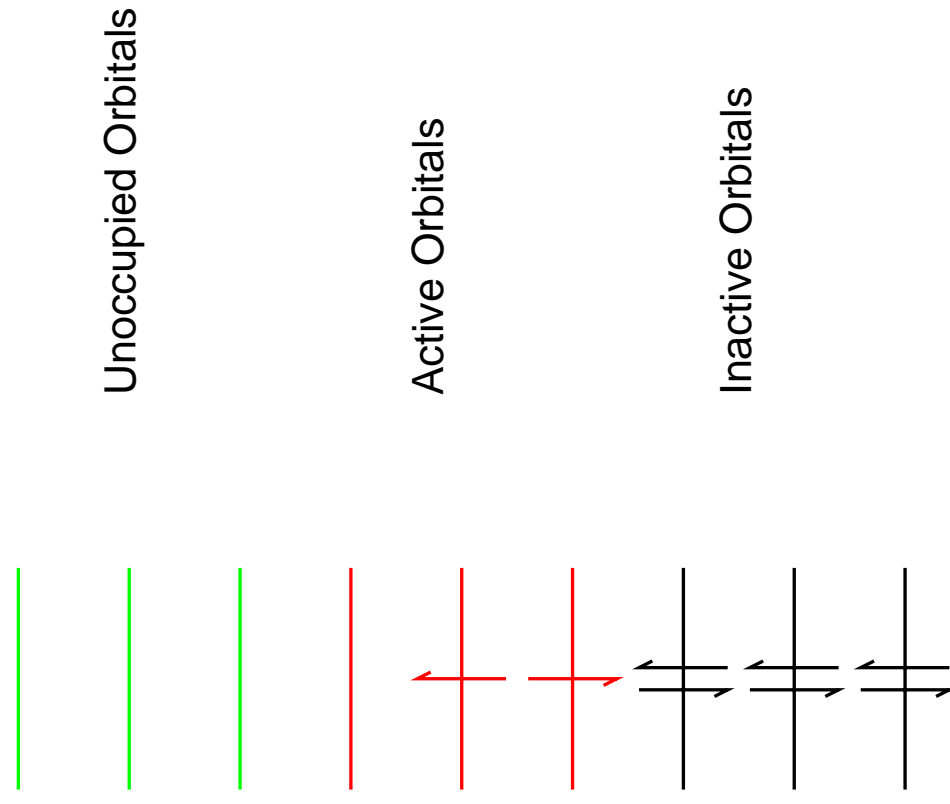
Active Orbitals Occ.No. Varies

Include all electronic configurations that can be obtained by distributing the active electrons among the active orbitals in all possible ways consistent with a given overall spin and space symmetry.

This is the Complete Active Space (CAS) wave function

The CASSCF method: Optimize the CI coefficients and the MO's for a CAS wave function.

Orbital Spaces for CAS Wave Functions



Size of the CAS Wave Functions for $S=0$

N:	2	4	6	8	10	12	14
n: 1	1	-	-	-	-	-	-
2	3	1	-	-	-	-	-
3	6	6	1	-	-	-	-
4	10	20	10	1	-	-	-
5	15	50	50	15	1	-	-
6	21	105	175	105	21	1	-
7	28	196	490	490	196	28	1
8	36	336	1176	1764	1176	336	36
9	45	540	2520	5292	5292	2520	540
10	55	825	4950	13860	19404	13860	4950
11	66	1210	9075	32670	60984	60984	32670
12	78	1716	15730	70785	169884	226512	169884
13	91	2366	26026	143143	429429	736164	736164

Examples CAS Wave Functions

Molecule	active orbitals	Electrons	No. of CSF's
H_2	σ_g, σ_u	2	2
O_3	π_1, π_2, π_3	4	4
$2C_2H_4$	4 π orbitals	4	8
$C_{10}H_{10}$	10 π orbitals	10	4396(1A_g) 7360(3A_g)
UO_2	12	14	70880(C_{2v})
UO_2^+	13	13	322388(C_{2v})

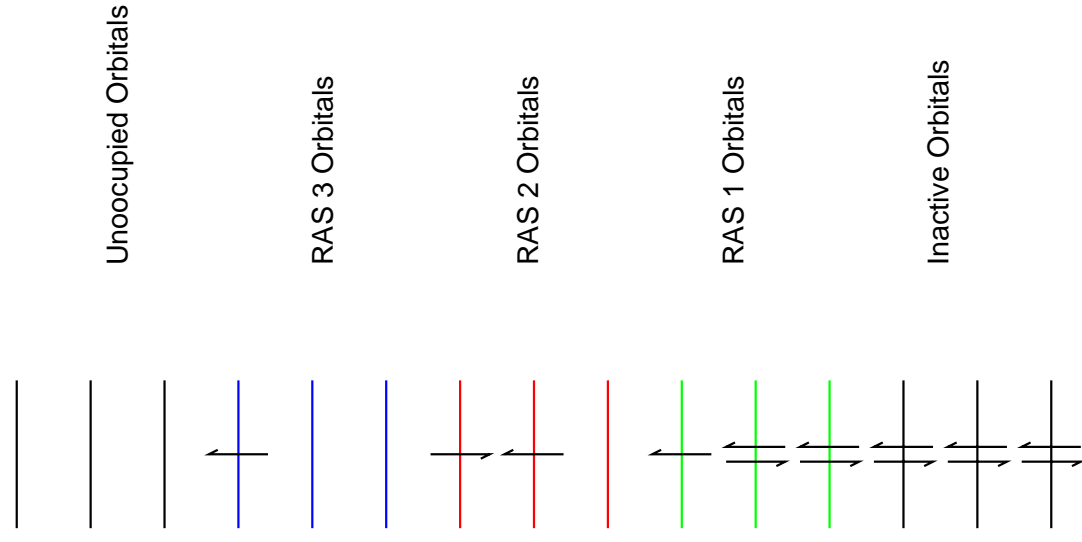
The Restricted Active Space (RAS) SCF Method

Divide the occupied MO's into four groups:

Inactive Orbitals	Occ.No. 2
RAS1 Orbitals	Max number of holes
RAS2 (Active) Orbitals	Occ.No. Varies
RAS3 Orbitals	Max number of electrons

This is thus a CAS with the additional possibility to excite out of some doubly occupied orbitals and into some virtual orbitals.

RAS Orbital Spaces



Some Typical Ras Wave Functions

- Closed Shell SCF (RAS1, RAS2, RAS3 empty).
- SDTQ...CI with a closed shell reference function (RAS2 empty).
- CASSCF (RAS1 and RAS3 empty).
- SDCl with a CASSCF reference (max two holes in RAS1 and max two electrons in RAS3).
- Polarization CI (max one hole in RAS1).

Optimization of MCSCF Wave Functions

Wave Function: $\Psi = \sum_m c_m \Phi_m$
or: $|0\rangle = \sum_m c_m |m\rangle$

Objective: to optimize the molecular orbitals and the MC coefficients using the variational principle:

$$E = \frac{\langle 0 | \hat{H} | 0 \rangle}{\langle 0 | 0 \rangle}$$

The Non-Relativistic Hamiltonian in Second Quantization Formalism

$$\hat{H} = \sum_{i,j} h_{ij} \hat{E}_{ij} + \frac{1}{2} \sum_{i,j,k,l} g_{ijkl} (\hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il}).$$

where

$$h_{ij} = \int \phi_i^*(\mathbf{x}) \hat{h}(\mathbf{x}) \phi_j(\mathbf{x}) d\mathbf{x}$$

$$g_{ijkl} = \int \phi_i^*(\mathbf{x}_1) \phi_k^*(\mathbf{x}_2) \hat{G}(\mathbf{x}_1, \mathbf{x}_2) \phi_j(\mathbf{x}_1) \phi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

Are the one- and two-electron integrals.

The "Excitation Operator" $\hat{E}_{ij} = \hat{a}_{i\alpha}^\dagger \hat{a}_{j\alpha} + \hat{a}_{i\beta}^\dagger \hat{a}_{i\beta}$

Matrix Elements of the One-Electron Operator

$$\hat{H}_1 = \sum_{i,j} h_{ij} \hat{E}_{ij}$$
$$\langle m | \hat{H}_1 | n \rangle = \sum_{i,j} h_{ij} \langle m | \hat{E}_{ij} | n \rangle = \sum_{i,j} h_{ij} D_{ij}^{mn},$$

D_{ij}^{mn} are the *one-electron coupling coefficients*

The energy contribution is:

$$\langle 0 | \hat{H}_1 | 0 \rangle = \sum_{i,j} h_{ij} D_{ij},$$

where $D_{ij} = \langle \Psi | \hat{E}_{ij} | \Psi \rangle = \sum_{m,n} c_m^* c_n D_{ij}^{mn}$ are the elements of the *first order reduced density matrix (1-matrix)*.

Matrix Elements of the Two-Electron Operator

$$\hat{H}_2 = \frac{1}{2} \sum_{i,j,k,l} g_{ijkl} (\hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il})$$
$$\langle m | \hat{H}_2 | n \rangle = \sum_{i,j,k,l} g_{ijkl} P_{ijkl}^{mn}$$

where P_{ijkl}^{mn} are the *two-electron coupling coefficients*

The energy contribution is:

$$\langle 0 | \hat{H}_2 | 0 \rangle = \sum_{i,j,k,l} g_{ijkl} P_{ijkl},$$

where $P_{ijkl} = \sum_{m,n} c_m^* c_n P_{ijkl}^{mn}$ are the elements of the *second order reduced density matrix (2-matrix)*.

The Energy Expression

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i,j} h_{ij} D_{ij} + \sum_{i,j,k,l} g_{ijkl} P_{ijkl}.$$

The molecular orbital coefficients appear in the one- and two-electron integrals, h_{ij} and g_{ijkl} .

The CI coefficients are included in **D** and **P**.

$$E = E\{\varphi, \mathbf{c}\}$$

Unitary Transformations of the Spin Orbitals

Consider a unitary transformation of the orbitals: $\phi' = \phi U$, where $U^\dagger U = \mathbf{1}$

How does the corresponding Slater determinants transform?

Look first at the transformation of the annihilation and creation operators:

$$\hat{a}'_i = \sum_j \hat{a}_j U_{ji}^*$$

$$\hat{a}'_i^\dagger = \sum_j \hat{a}_j^\dagger U_{ji}$$

Introducing $\hat{T} = \sum_{i,j} T_{ij} \hat{a}_i^\dagger \hat{a}_j$ ($T_{ij} = -T_{ji}^*$), we can write:

$$\hat{a}'_i = e^{-\hat{T}} \hat{a}_i e^{\hat{T}}$$

$$\hat{a}'_i^\dagger = e^{-\hat{T}} \hat{a}_i^\dagger e^{\hat{T}}$$

The Exponential Form of a Unitary Operator

The matrix \mathbf{T} is anti-Hermitian: $\mathbf{T}^\dagger = -\mathbf{T}$

We can prove the formula by expanding the exponential operator using the anti-commutator rule for the annihilation and creation operators:

$$\hat{a}'_i^\dagger = \hat{a}_i^\dagger + [\hat{a}_i^\dagger, \hat{T}] + \frac{1}{2} [[\hat{a}_i^\dagger, \hat{T}], \hat{T}] + \dots$$

Collecting the terms we obtain:

$$e^{-\hat{T}} \hat{a}_i^\dagger e^{\hat{T}} = \sum_k \hat{a}_k^\dagger (\mathbf{1} - \mathbf{T} + \frac{1}{2} \mathbf{T}^2 + \dots)_{ki} = \sum_k \hat{a}_k^\dagger (e^{-\mathbf{T}})_{ki}$$

Thus $\mathbf{U} = e^{-\mathbf{T}}$ with $\mathbf{T}^\dagger = -\mathbf{T}$

A unitary matrix can always be written in this form!

Transformation of the Slater Determinant

For a Slater determinant we obtain:

$$\begin{aligned} |m'\rangle &= \hat{a}'_i{}^\dagger \hat{a}'_j{}^\dagger \hat{a}'_k{}^\dagger \cdots |vac\rangle = e^{-\hat{T}} \hat{a}_i{}^\dagger e^{\hat{T}} e^{-\hat{T}} \hat{a}_j{}^\dagger e^{\hat{T}} \cdots |vac\rangle = \\ &e^{-\hat{T}} \hat{a}_i{}^\dagger \hat{a}_j{}^\dagger \hat{a}_k{}^\dagger \cdots |vac\rangle = e^{-\hat{T}} |m\rangle \end{aligned}$$

It follows that:

$$|0'\rangle = e^{-\hat{T}} |0\rangle$$

This gives the transformation of the total wave function when a unitary transformation is performed on the orbitals.

We note that the wave function remains normalized after the transformation!

From Spin-Orbitals to Orbitals

If we order the spin-orbitals as:

$$\phi = (\varphi\alpha, \varphi\beta)$$

The matrix \mathbf{T} is blocked:

$$\mathbf{T} = \begin{pmatrix} \mathbf{T}_{\alpha\alpha} & \mathbf{T}_{\alpha\beta} \\ \mathbf{T}_{\beta\alpha} & \mathbf{T}_{\beta\beta} \end{pmatrix}$$

Since we are only transforming the MO's, the off-diagonal block are zero and we have $\mathbf{T}_{\alpha\alpha} = \mathbf{T}_{\beta\beta} = \mathbf{T}$ and

$$\hat{T} = \sum_{i,j} T_{ij} (\hat{a}_{i\alpha}^\dagger \hat{a}_{j\alpha} + \hat{a}_{i\beta}^\dagger \hat{a}_{j\beta}) = \sum_{i,j} T_{ij} \hat{E}_{ij}$$

or for real operators :

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

Unitary Transformations of the Configuration Space

The wave function: $|0\rangle = \sum_m C_m |m\rangle$ with $\sum_m |C_m|^2 = 1$

The complementary space: $|K\rangle = \sum_m C_m^K |m\rangle$ with $\sum_m C_m^K C_m^L = \delta_{kl}$.

Define a *Replacement operator* for state $|0\rangle$ as:

$$\hat{S} = \sum_{K \neq 0} S_{K0} (|K\rangle \langle 0| - |0\rangle \langle K|),$$

where S_{K0} are variational parameters and $\hat{S}^\dagger = -\hat{S}$.

A unitary transformation of the state function $|0\rangle$ is obtained as:

$$|0'\rangle = e^{\hat{S}} |0\rangle$$

Note that the transformed function remains normalized.

The Overall Transformation of the Wave Function

$$|0'\rangle = e^{\hat{T}} e^{\hat{S}} |0\rangle$$

Note \hat{T} and \hat{S} do not commute.

The energy expression:

$$E(\mathbf{T}, \mathbf{S}) = \langle 0 | e^{-\hat{S}} e^{-\hat{T}} \hat{H} e^{\hat{T}} e^{\hat{S}} | 0 \rangle,$$

where the parameters \mathbf{T} and \mathbf{S} can now be varied freely.

The goal is to find \mathbf{T} and \mathbf{S} such that the energy becomes stationary:

$$\frac{\delta E}{\delta T_{ij}} = 0$$
$$\frac{\delta E}{\delta S_{K0}} = 0$$

The Newton-Raphson Optimization Method - 1

Suppose we want to find a stationary point for the function $E(\mathbf{p})$, where \mathbf{p} is a set of parameters, which can be freely varied.

Start with a guessed value, which for simplicity is set to zero $\mathbf{p}_0 = \mathbf{0}$.

Expand the function E around this point:

$$E(\mathbf{p}) = E(0) + \sum_i \left(\frac{\partial E}{\partial p_i} \right)_0 p_i + \frac{1}{2} \sum_{i,j} p_i \left(\frac{\partial^2 E}{\partial p_i \partial p_j} \right)_0 p_j + \dots$$

or in vector notation:

$$E(\mathbf{p}) = E(0) + \mathbf{g}^\dagger \mathbf{p} + \frac{1}{2} \mathbf{p}^\dagger \mathbf{H} \mathbf{p} + \dots$$

The Newton-Raphson Optimization Method - 2

Here we have defined the gradient vector \mathbf{g} and the Hessian matrix \mathbf{H} :

$$g_i = \left(\frac{\partial E}{\partial p_i} \right)_0 \quad \text{and} \quad H_{ij} = \left(\frac{\partial^2 E}{\partial p_i \partial p_j} \right)_0$$

The stationary point is obtained as solutions to the equation: $\partial E / \partial p_i = 0$, which gives the set of linear equations:

$$\mathbf{g} + \mathbf{H}\mathbf{p} = 0 \quad \text{or} \quad \mathbf{p} = -\mathbf{H}^{-1}\mathbf{g}$$

These equations are solved iteratively until convergence: ($\mathbf{p}_N = \mathbf{0}$).

Taylor Expansion of the Energy around $T = 0$ and $S = 0$

The energy expression:

$$E(\mathbf{T}, \mathbf{S}) = \langle 0 | e^{-\hat{S}} e^{-\hat{T}} \hat{H} e^{\hat{T}} e^{\hat{S}} | 0 \rangle$$

Expanding this to second order in \mathbf{T} and \mathbf{S} gives:

$$\begin{aligned} E(\mathbf{T}, \mathbf{S}) &= \langle 0 | \hat{H} \\ &+ [\hat{H}, \hat{T}] + [\hat{H}, \hat{S}] \\ &+ \frac{1}{2} [[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{2} [[\hat{H}, \hat{S}], \hat{S}] + [[\hat{H}, \hat{T}], \hat{S}] + \dots | 0 \rangle \end{aligned}$$

The Orbital Gradient

$$\langle 0 | [\hat{H}, \hat{T}] | 0 \rangle = \sum_{i>j} T_{ij} \langle 0 | [\hat{H}, \hat{E}_{ij}^-] | 0 \rangle$$

which gives the derivative as:

$$g_{ij}^o = \langle 0 | [\hat{H}, \hat{E}_{ij}^-] | 0 \rangle$$

The superscript o is used to denote derivatives with respect to the orbital parameters. This is the **Extended Brillouin's Theorem**.

Now we introduce the explicit form of \hat{H} and use

$$[\hat{E}_{ij}, \hat{E}_{kl}] = \hat{E}_{il} \delta_{jk} - \hat{E}_{kj} \delta_{il}$$

to obtain:

$$\frac{1}{2} g_{pq}^o = F_{pq} - F_{qp},$$

The MCSCF Fock Matrix

where

$$F_{pq} = \sum_{\alpha} h_{\alpha p} D_{\alpha q} + 2 \sum_{\alpha, \beta, \gamma} (\alpha\beta|\gamma p) P_{\alpha\beta\gamma q}.$$

D and P are the first- and second-order reduced density matrices:

$$\begin{aligned} D_{\alpha\beta} &= \langle 0 | \hat{E}_{\alpha\beta} | 0 \rangle \\ P_{\alpha\beta\gamma\delta} &= \frac{1}{2} \langle 0 | \hat{E}_{\alpha\beta} \hat{E}_{\gamma\delta} - \delta_{\beta\gamma} \hat{E}_{\alpha\delta} | 0 \rangle. \end{aligned} \quad (1)$$

For optimized orbitals we have

$$F^{\dagger} = F$$

The MCSCF Fock Matrix - Continued

The definition of F implies: $F_{pa} = 0$ if a is an external orbital. Also $F_{pq} = F_{qp}$ if p, q are inactive or external

Inactive	$F^T = F$	0	0
Active	$F^T = F$	0	0
External	$F^T = F$	0	0

The Closed Shell Fock Matrix

In the closed shell (no active orbitals we have):

$$\begin{aligned}D_{ij} &= 2\delta_{ij} \\ P_{ijkl} &= 2\delta_{ij}\delta_{kl} - \delta_{jk}\delta_{il}.\end{aligned}$$

The Fock matrix takes the well known form:

$$F_{pi} = 2(h_{pi} + \sum_j \{2(jj|pi) - (pj|ij)\}).$$

where the index i corresponds to an occupied orbital. The condition for optimized orbitals is then: $F_{pi} = F_{ip}$, which is trivially fulfilled for occupied orbitals. Thus the effective condition is:

$$F_{ai} = 0$$

where a is an external orbital. This condition can easily be transformed into the normal HF equations.

The CASSCF Fock Matrix

For CASSCF wave function we have (t, u both active orbitals)

$$g_{tu}^o = \langle 0 | \hat{H} (\hat{E}_{tu} - \hat{E}_{ut}) | 0 \rangle$$
$$(\hat{E}_{tu} - \hat{E}_{ut}) | 0 \rangle = \sum_K a_K | K \rangle$$

Assuming that \hat{H} is diagonal in the $|K\rangle$ basis we have:

$$\langle 0 | \hat{H} | K \rangle = E_0 \delta_{0K}$$

Thus: $g_{tu}^o = 2E_0 \langle 0 | (\hat{E}_{tu} - \hat{E}_{ut}) | 0 \rangle = 0$ and

$$F_{tu} = F_{ut}$$

Rotations between active orbitals are redundant for CASSCF wave functions!

The CI gradient

$$\langle 0 | [\hat{H}, \hat{S}] | 0 \rangle = \sum_{K \neq 0} S_{K0} (\langle 0 | \hat{H} | K \rangle + \langle K | \hat{H} | 0 \rangle)$$

we obtain for real wave functions the derivative:

$$g_{ij}^c = 2 \langle 0 | \hat{H} | K \rangle$$

The optimized wave function does not interact with the orthogonal complement.

It is a solution to the secular problem:

$$(\mathbf{H} - E\mathbf{1})\mathbf{C} = \mathbf{0}$$

The Hessian Matrix

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}^{cc} & \mathbf{H}^{co} \\ \mathbf{H}^{oc} & \mathbf{H}^{oo} \end{pmatrix}$$
$$\mathbf{H}^{co} = \mathbf{H}^{(oc)\dagger}$$

The CI part of the Hessian:

From $\frac{1}{2}\langle 0 | [[\hat{H}, \hat{S}], \hat{S}] | 0 \rangle$ we obtain:

$$H_{KL}^{cc} = 2(\langle K | \hat{H} | L \rangle - \delta_{KL} \langle 0 | \hat{H} | 0 \rangle) = 2(H_{KL} - E_0 \delta_{KL}).$$

The Orbital Part of the Hessian Matrix

From $\frac{1}{2}\langle 0 | [[\hat{H}, \hat{T}], \hat{T}] | 0 \rangle$ we obtain:

$$H_{ij,kl}^{oo} = \langle 0 | \hat{E}_{ij}^- \hat{E}_{kl}^- \hat{H} | 0 \rangle + \langle 0 | \hat{H} \hat{E}_{ij}^- \hat{E}_{kl}^- | 0 \rangle - 2\langle 0 | \hat{E}_{ij}^- \hat{H} \hat{E}_{kl}^- | 0 \rangle$$

The Coupling Part of the Hessian Matrix

From $\frac{1}{2}\langle 0 | [[\hat{H}, \hat{T}], \hat{S}] | 0 \rangle$ we obtain:

$$H_{K,ij}^{co} = H_{ij,K}^{oc} = 2\langle K | [\hat{H}, \hat{E}_{ij}^-] | 0 \rangle$$

The Newton-Raphson Equations

$$\begin{pmatrix} \mathbf{a} & \mathbf{b} \\ \mathbf{b}^\dagger & \mathbf{c} \end{pmatrix} \begin{pmatrix} \mathbf{S} \\ \mathbf{T} \end{pmatrix} = - \begin{pmatrix} \mathbf{v} \\ \mathbf{w} \end{pmatrix}$$

where we have introduced the simplified notations:

$$\mathbf{a} = \frac{1}{2}\mathbf{H}^{cc}, \quad \mathbf{b} = \frac{1}{2}\mathbf{H}^{co}, \quad \mathbf{c} = \frac{1}{2}\mathbf{H}^{oo}, \quad \mathbf{v} = \frac{1}{2}\mathbf{g}^c, \quad \mathbf{w} = \frac{1}{2}\mathbf{g}^o$$

The NR equations in their present form are complicated to solve due to the presence of the CI states $|K\rangle$.

Transformation to the CI basis $|m\rangle$

Introduce a matrix C containing the $M-1$ CI vectors C^K in columns.

The matrices a , b , and c , can now be transformed to the corresponding matrices in the basis $|m\rangle$:

$$a = C^\dagger A C \quad b = C^\dagger B \quad v = C^\dagger G$$

where

$$A_{mn} = \langle m | \hat{H} - E_0 \delta_{mn} | n \rangle, \quad B_{m,ij} = \langle m | [\hat{H}, \hat{E}_{ij}^-] | 0 \rangle, \quad G_m = \langle 0 | \hat{H} | m \rangle$$

Removing the Matrix \mathbf{C}

The NR equations now have the form:

$$\begin{pmatrix} \mathbf{C}^\dagger \mathbf{A} \mathbf{C} & \mathbf{C}^\dagger \mathbf{B} \\ \mathbf{B}^\dagger \mathbf{C} & \mathbf{c} \end{pmatrix} \begin{pmatrix} \mathbf{S} \\ \mathbf{T} \end{pmatrix} = - \begin{pmatrix} \mathbf{C}^\dagger \mathbf{G} \\ \mathbf{w} \end{pmatrix}$$

Now, introduce variations of the CI coefficients:

$$\hat{S}|0\rangle = \sum_K S_{K0}|K\rangle = \sum_K \sum_m S_{K0} C_m^K |m\rangle = \sum_m \delta C_m^0 |m\rangle,$$

where we have introduced the vector $\delta \mathbf{C}_0 = \mathbf{C} \mathbf{S}$, which gives $\mathbf{S} = \mathbf{C}^\dagger \delta \mathbf{C}_0$ because $\mathbf{C}^\dagger \mathbf{C} = \mathbf{1}$

But $\delta \mathbf{C}_0$ contains M variational parameters and \mathbf{S} only $M - 1$. This redundancy must be removed.

The NR Equations in the Configuration Basis

Introduce $S_0 = \mathbf{C}_0^\dagger \delta \mathbf{C}_0$

Demand that $S_0 = 0$ by adding the equation $zS_0 = 0$ with $z \neq 0$.

Add this equation to the NR equation:

$$\begin{pmatrix} z & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{C}_0^\dagger \mathbf{A} \mathbf{C} & \mathbf{C}_0^\dagger \mathbf{B} \\ \mathbf{0} & \mathbf{B}^\dagger \mathbf{C} & c \end{pmatrix} \begin{pmatrix} \mathbf{C}_0^\dagger \delta \mathbf{C}_0 \\ \mathbf{C}_0^\dagger \delta \mathbf{C}_0 \\ \mathbf{T} \end{pmatrix} = - \begin{pmatrix} 0 \\ \mathbf{C}_0^\dagger \mathbf{G} \\ \mathbf{w} \end{pmatrix}$$

This equation is now multiplied with the unitary rotation:

$$\begin{pmatrix} \mathbf{U} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}$$

The NR Equations in the Configuration Basis - Continued

where U is the $M \times M$ matrix (C_0, C) with all CI vectors. Introduce the projection matrices:

$$P = C_0 C_0^\dagger \quad \text{and} \quad Q = \mathbf{1} - C_0 C_0^\dagger = C C^\dagger$$

We obtain the final NR equations in the form:

$$\begin{pmatrix} zP + QAQ & QB \\ B^\dagger Q & c \end{pmatrix} \begin{pmatrix} \delta C_0 \\ T \end{pmatrix} = - \begin{pmatrix} QG \\ w \end{pmatrix}$$

The variations δC_0 and T has to be transformed into the unitary operators $e^{\hat{S}}$ and $e^{\hat{T}}$.

The Unitary Transformations from the Solutions of the NR Equations.

$\mathbf{T} \Rightarrow e^{\mathbf{T}} \Rightarrow$ new MO's (see exercise 14 for details).

$\delta\mathbf{C}_0 \Rightarrow \mathbf{S} = \mathbf{C}^\dagger \delta\mathbf{C}_0 \Rightarrow e^{\hat{S}} \Rightarrow$ new CI vector

According to exercise 15 we have:

$$e^{\hat{S}}|0\rangle = \cos\Theta|0\rangle + \frac{1}{\Theta}\sin\Theta\hat{S}|0\rangle,$$

where $\Theta = \sqrt{\sum_{K \neq 0} S_{K0}^2} = \sqrt{\delta\mathbf{C}_0^\dagger \mathbf{Q} \delta\mathbf{C}_0}$

and $\hat{S}|0\rangle = \sum_K S_{K0}|K\rangle = \sum_m \delta C_m^0|m\rangle$

We can thus obtain the new CI vector directly from the variations $\delta\mathbf{C}_0$ and the projection matrix \mathbf{Q} .

Size of the NR Equations.

Number of orbitals $n \approx 10 - 500$

Number of CI basis states:

1. Determinants: $1 \leq M \leq 10^7$
2. CSF's: $1 \leq M \leq 10^6$

A typical case (UO_2^+ with ECP's, C_{2v} symmetry):

Number of inactive orbitals, n_i :	17
Number of active orbitals, n_a /electrons:	13/13
Total number of orbitals:	177
Number of orbital rotations $\approx n(n_i + n_a)$:	5310
Number of determinants:	736 288
Number of CSF's:	322 388

On an SGI/Octane R10000 each iteration takes 0.37 min.

An Iterative Method for Solving Large Systems of Linear Equations

Write a system of linear equations in the form:

$$(\mathbf{A}_0 - \mathbf{A})\mathbf{x} = \mathbf{b},$$

where \mathbf{A}_0 is a diagonal non-singular matrix (eq the diagonal part of the Hessian). Solve for \mathbf{x} :

$$\mathbf{x} = \mathbf{A}_0^{-1} \mathbf{A} \mathbf{x} + \mathbf{A}_0^{-1} \mathbf{b}$$

with the formal solution:

$$\mathbf{x} = \mathbf{A}_0^{-1} \sum_{n=0}^{\infty} (\mathbf{A}')^n \mathbf{b},$$

where $\mathbf{A}' = \mathbf{A} \mathbf{A}_0^{-1}$.

The series only slowly convergent, if at all.

An Iterative Method with Improved Convergence

Construct a set of orthogonal vectors:

$$\mathbf{x}_0 = \mathbf{A}_0^{-1}\mathbf{b}; \quad \mathbf{x}_1 = \mathbf{A}'\mathbf{x}_0 - \frac{\mathbf{x}_0^\dagger \mathbf{A}'\mathbf{x}_0}{\mathbf{x}_0^\dagger \mathbf{x}_0} \mathbf{x}_0 \quad \cdots \quad \mathbf{x}_{n+1} = \mathbf{A}'\mathbf{x}_n - \sum_{l=0}^n \frac{\mathbf{x}_l^\dagger \mathbf{A}'\mathbf{x}_n}{\mathbf{x}_l^\dagger \mathbf{x}_l} \mathbf{x}_l;$$

Form a linear combination of these vectors:

$$\mathbf{x} = \sum_{i=0}^n \alpha_i \mathbf{x}_i.$$

Determine α by minimizing the least square error:

$$f = ((\mathbf{A}_0 - \mathbf{A})\mathbf{x} - \mathbf{b})^\dagger ((\mathbf{A}_0 - \mathbf{A})\mathbf{x} - \mathbf{b})$$

Normally converges in less than 10 iterations even for large dimensions.

The σ -vector

A crucial operation is the formation of the matrix product:

$$\mathbf{d} = \mathbf{A}'\mathbf{x} = \mathbf{A}_0^{-1}\mathbf{A}\mathbf{x} = \mathbf{A}_0^{-1}\boldsymbol{\sigma},$$

where:

$$\boldsymbol{\sigma} = \mathbf{A}\mathbf{x}$$

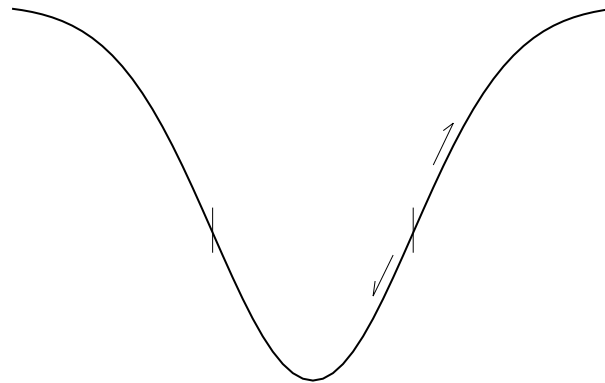
For example, choose \mathbf{A} as the CI part of the Hessian:

$$d_m = \sum_{n \neq m} \frac{H_{mn} \delta C_n}{H_{mm} - E_0}$$

This is exactly the same equation as is used to update the CI vector in the Davidson iterative method for large CI matrices.

Note: the explicit form of \mathbf{H} is not needed, only the product $\mathbf{H}\mathbf{C}$. This is the basis of, so called "**Direct Methods**" in CI and MCSCF.

Convergence of the Newton-Raphson Method



Local Region

Convergence in the local region is second order: $\varepsilon_{n+1} \propto \varepsilon_n^2$

Convergence outside the local region cannot be guaranteed. It may be slow, or the calculation may diverge.

Step size and sign control can force the solution towards the local region.

The Augmented Hessian (AM) Method

This method gives automatic mode damping and sign control.

Write the Newton-Raphson equations as

$$\mathbf{H}\mathbf{p} = -\mathbf{g}$$

Where \mathbf{p} contains all the parameters.

Replace this equation by the secular problem:

$$\begin{pmatrix} \mathbf{0} & \mathbf{g}^\dagger \\ \mathbf{g} & \mathbf{H} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{p} \end{pmatrix} = E \begin{pmatrix} 1 \\ \mathbf{p} \end{pmatrix}.$$

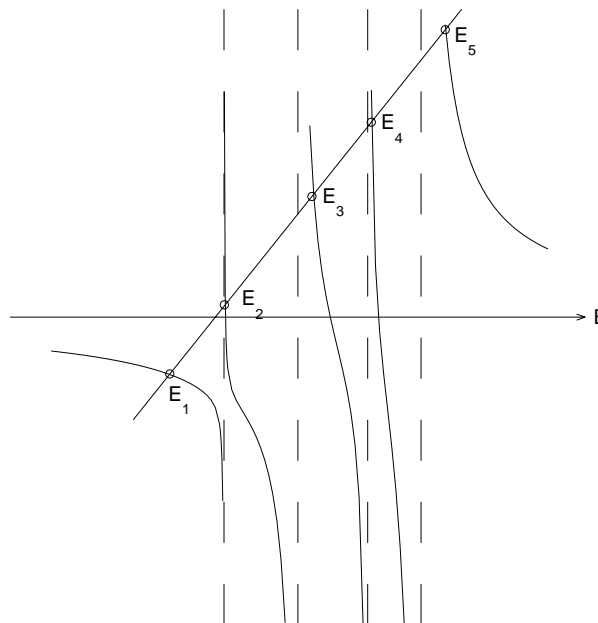
This is the Augmented Hessian equation.

Analysis of the Augmented Hessian (AM) Method

Transform to a basis where \mathbf{H} is diagonal: $H_{ii} = \varepsilon_i$

The NR Method: $p_i = -g_i/\varepsilon_i$; The AM method: $p_i = -g_i/(\varepsilon_i - E)$

$\varepsilon_{i-1} \leq E_i \leq \varepsilon_i$: thus automatic sign and mode damping.



Calculation of the Orbital Gradient

The orbital gradient:

$$\frac{1}{2}g_{pq}^o = F_{pq} - F_{qp},$$

where

$$F_{pq} = \sum_{\alpha} h_{\alpha p} D_{\alpha q} + 2 \sum_{\alpha, \beta, \gamma} (\alpha\beta|\gamma p) P_{\alpha\beta\gamma q}.$$

Divide α into inactive (i, j, k, l, \dots) and active (t, u, v, x, \dots) orbitals:

$$F_{ip} = 2(F_{ip}^I + F_{ip}^A)$$

$$F_{tp} = \sum_v D_{tv} F_{vp}^I + 2 \sum_{u, v, x} P_{tuvx} (pu|vx),$$

$$F_{pq}^I = h_{pq} + \sum_k [2(pq|kk) - (pk|qk)]$$

$$F_{pq}^A = \sum_{v, x} D_{vx} [(pq|vx) - \frac{1}{2}(pv|qx)].$$

Calculation of the Fock Matrices

1. Compute AO one- and two-electron integrals.
2. Compute the Fock matrices F^I and F^A .
3. Transform to MO two-electron integrals $(pu|vx)$, where p runs over *all* orbitals but u, v, x only over the *active orbitals* (First order transformation).
4. Compute $Q_{tp} = \sum_{u,v,x} P_{tuvx}(pu|vx)$ and add to F_{tp} .

The Orbital Hessian

The general expression of the orbital Hessian in terms of integrals and density matrices is:

$$\begin{aligned}
 H_{ij,kl}^{oo} &= \langle 0 | \hat{E}_{ij}^- \hat{E}_{kl}^- \hat{H} | 0 \rangle + \langle 0 | \hat{H} \hat{E}_{ij}^- \hat{E}_{kl}^- | 0 \rangle - 2 \langle 0 | \hat{E}_{ij}^- \hat{H} \hat{E}_{kl}^- | 0 \rangle \\
 &= 2(1 - \hat{P}_{pq})(1 - \hat{P}_{rs})((F_{rs} + F_{sp})\delta_{qr} - 2h_{ps}D_{qr} \\
 &\quad + 2 \sum_{\alpha,\beta} [4(p\alpha|r\beta)P_{q\alpha s\beta} + 2(pr|\alpha\beta)P_{qs\alpha\beta}]),
 \end{aligned}$$

where \hat{P}_{pq} is a permutation operator. As an example choose $pq = at$ and $rs = bu$, where a, b are external and t, u are active orbitals:

$$\begin{aligned}
 H_{at,ub}^{oo} &= 2(D_{tu}F_{ab}^I - \delta_{ab}F_{tu} \\
 &\quad + \sum_{v,x} [P_{tuvx}(ab|vx) + (P_{txvu} + P_{txuv})(ax|bv)]). \quad (2)
 \end{aligned}$$

Calculation of the Orbital Hessian

1. Compute the Fock matrices F^I and F .
2. Transform to MO two-electron integrals $(px|qv)$, where p, q runs over *all* orbitals but u, v, x only over all *occupied* orbitals (Second order transformation).
3. Generate H^{oo} or directly the product $H^{oo}T$

Calculation of the Coupling term in the Hessian

$$H_{K,ij}^{co} = H_{ij,K}^{oc} = 2\langle K | [\hat{H}, \hat{E}_{ij}^-] | 0 \rangle$$

The coupling term has the same structure as the orbital gradient, but involves transition densities. It is therefore difficult to compute. Some implementations try to proceed without the coupling term.

Partitioning of the Newton-Raphson Equations

$$\begin{pmatrix} \mathbf{a} & \mathbf{b} \\ \mathbf{b}^\dagger & \mathbf{c} \end{pmatrix} \begin{pmatrix} \mathbf{S} \\ \mathbf{T} \end{pmatrix} = - \begin{pmatrix} \mathbf{v} \\ \mathbf{w} \end{pmatrix}$$

Solve for \mathbf{S} from the first row:

$$\mathbf{S} = -\mathbf{a}^{-1}\mathbf{v} - \mathbf{a}^{-1}\mathbf{b}\mathbf{T},$$

Insert into second row to obtain an equation for \mathbf{T} :

$$(\mathbf{c} - \mathbf{b}^\dagger\mathbf{a}^{-1}\mathbf{b})\mathbf{T} = -\mathbf{w} + \mathbf{b}^\dagger\mathbf{a}^{-1}\mathbf{v}.$$

or,

$$\mathbf{H}'\mathbf{T} = -\mathbf{g}$$

where \mathbf{H}' is the **partitioned orbital Hessian**.

Problem: It is not easy to invert the CI matrix \mathbf{a} .

The Unfolded two-Step Newton-Raphson Approach

Neglect the difficult coupling term. This leads to the equations:

$$(\mathbf{H} - E_0 \mathbf{1})\mathbf{C} = \mathbf{0}$$

and

$$c\mathbf{T} = -w$$

Solve iteratively for the CI coefficients \mathbf{C}

and the orbital rotation parameters \mathbf{T} .

The Super-CI Approach

An MCSCF calculation is converged when:

$$g_K^c = 2\langle 0 | \hat{H} | K \rangle = 0$$

and

$$g_{pq}^o = 2\langle 0 | \hat{H} \hat{E}_{pq}^- | 0 \rangle = 0$$

The first equation is fulfilled when $(\mathbf{H} - E_0 \mathbf{1})\mathbf{C} = \mathbf{0}$ and the second when the interaction between $|0\rangle$ and

$$|pq\rangle = \hat{E}_{pq}^- |0\rangle = 0$$

The super-CI method: Diagonalize the Hamiltonian in the space $|K\rangle, |pq\rangle$.

The Super-CI Method in the Unfolded Two-Step Procedure

Neglect the coupling term and write the super-CI wave function as:

$$|SCI\rangle = |0\rangle + \sum_{p>q} t_{pq}|pq\rangle$$

The computational steps:

1. Solve the CI secular equation to obtain $|0\rangle$.
2. Solve the super-CI secular problem.
3. Use $e^{\hat{t}}$ to obtain new orbitals, or alternatively use the natural orbitals.
4. Iterate until all t_{pq} are zero, that is until: $\langle 0|\hat{H}\hat{E}_{pq}^-|0\rangle = 0$.

The Super-CI Secular Problem

The super-CI states $|pq\rangle$ are not orthonormal:

$$S_{pq,rs} = \langle 0 | \hat{E}_{pq}^- \hat{E}_{rs}^- | 0 \rangle \neq \delta_{pq,rs}.$$

but they are orthogonal to the reference MC state:

$$\langle 0 | pq \rangle = \langle 0 | \hat{E}_{pq}^- | 0 \rangle = 0$$

The matrix elements of the Hamiltonian:

$$\begin{aligned} H_{0,pq} &= \langle 0 | \hat{H} | pq \rangle = \langle 0 | \hat{H} \hat{E}_{pq}^- | 0 \rangle = w_{pq}, \\ H_{pq,rs} &= \langle pq | \hat{H} | rs \rangle = \langle 0 | \hat{E}_{pq}^- \hat{H} \hat{E}_{rs}^- | 0 \rangle = d_{pq,rs}. \end{aligned}$$

The secular problem:

$$\begin{pmatrix} 0 & \mathbf{w}^\dagger \\ \mathbf{w} & \mathbf{d} - E_0 \mathbf{S} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{t} \end{pmatrix} = -\epsilon_{SCI} \begin{pmatrix} 1 & \mathbf{0} \\ \mathbf{0} & \mathbf{S} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{t} \end{pmatrix}.$$

Comparing Super-CI and Newton-Raphson

The Newton-Raphson equations in the augmented Hessian form:

$$\begin{pmatrix} 0 & \mathbf{w}^\dagger \\ \mathbf{w} & \mathbf{c} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{T} \end{pmatrix} = -\epsilon_{AM} \begin{pmatrix} 1 \\ \mathbf{T} \end{pmatrix},$$

where the orbital Hessian matrix elements are defined as:

$$c_{pq,rs} = \frac{1}{2} \langle 0 | \hat{E}_{pq}^- \hat{E}_{rs}^- \hat{H} | 0 \rangle + \frac{1}{2} \langle 0 | \hat{H} \hat{E}_{pq}^- \hat{E}_{rs}^- | 0 \rangle - \langle 0 | \hat{E}_{pq}^- \hat{H} \hat{E}_{rs}^- | 0 \rangle.$$

The corresponding Super-CI matrix elements are:

$$d_{pq,rs} - E_0 S_{pq,rs} = -\langle 0 | \hat{E}_{pq}^- \hat{H} \hat{E}_{rs}^- | 0 \rangle + E_0 \langle 0 | \hat{E}_{pq}^- \hat{E}_{rs}^- | 0 \rangle.$$

The super-CI matrix elements contain third-order density matrices!
Super-CI is an approximation to Newton-Raphson.

An Effective One-Electron Approximation in Super-CI

Approximate the matrix d by replacing the Hamiltonian by an effective one-electron operator:

$$\hat{H}' = \sum_{p,q} f_{pq} \hat{E}_{pq}.$$

where the matrix f has the elements:

$$f_{pq} = F_{pq}^I + F_{pq}^A + \sum_{r,s} D_{rs} [(pq|rs) - \frac{1}{2}(pr|qs)].$$

This matrix has the property that:

$$f_{pp} = -IP_p \text{ when } \eta_{pp} = 2 \text{ and } \quad f_{pp} = -EA_p \text{ when } \eta_{pp} = 0.$$

IP = ionization energy, EA = electron affinity!

Redundant variables in MCSCF wave functions

If the energy is independent of a specific parameter p_i selected from $\{\mathbf{T}, \mathbf{S}\}$ we have

$$\frac{\delta E}{\delta p_i} = 0$$

and

$$\frac{\delta^2 E}{\delta p_i \delta p_k} = 0 \quad (\text{all } p_k).$$

The Hessian is singular and the NR equations become indeterminate.

A simple example: T_{ij} where i, j are both inactive orbitals.

Redundant parameters should be removed from the parameter list.

Redundant Variables in CASSCF Wave Functions

T_{ij} where i, j are both **inactive** orbitals.

T_{uv} where u, v are both **active** orbitals.

$$\begin{aligned}
 g_{tu}^o &= 2\langle 0 | \hat{H} (\hat{E}_{tu} - \hat{E}_{ut}) | 0 \rangle \\
 (\hat{E}_{tu} - \hat{E}_{ut}) | 0 \rangle &= \sum_{K \neq 0} C_K | K \rangle \\
 g_{tu}^o &= 2 \sum_{K \neq 0} C_K \langle 0 | K \rangle = 0
 \end{aligned}$$

Non-redundant orbital variables in CASSCF:

T_{pi} i inactive, p active or external.

T_{ap} p active, a external.

MCSCF Calculations on Excited States

More Difficult than ground state calculations:

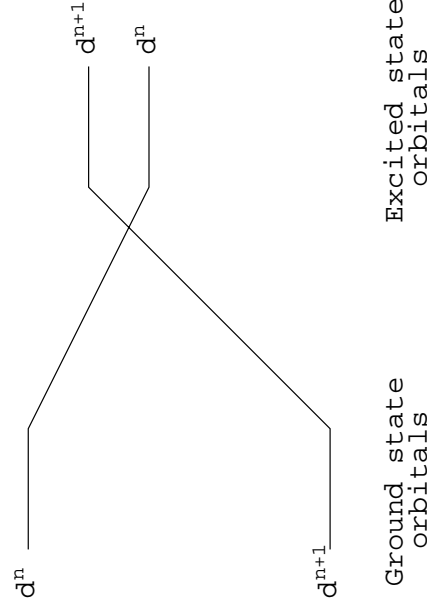
1. Convergence to a saddle point (normally the Hessian has $n-1$ negative eigenvalues in the n :th state).
2. Root flipping may occur.
3. Converged MCSCF wave functions for two roots of the same symmetry are in general non-orthogonal.

An Example of Root Flipping

A transition metal atom (Ni for example):

Ground state: $3d^{n+1}4s$ dominates; Excited state: $3d^n4s^2$ dominates

The two sets of 3d orbitals are different



Another example was found in a calculation of the first excited state of A' symmetry in the radical CCCN.

Root Flipping in the First Excited State of A' Symmetry in the CCCN Radical

The energy of the ground state is: -168.077552 au

Correct energy of the excited state: -168.040109 au

Optimizing orbitals for the second root gives the "convergence" pattern:

Iteration	Energy (au)
41	-168.038556
42	.031756
43	.033249
44	.038482
45	.033077
46	.033476
47	.038438
48	.034226
49	.033672
50	.038224

Calculations Using Average Orbitals

$$E_{aver} = \sum_{I=1}^M \omega_I E_I$$

is the average energy for M states formed from a common set of orbitals and configuration state functions. ω_I are the weighting factors.

The average energy can be written in the form:

$$E_{aver} = \sum_{i,j} h_{ij} \tilde{D}_{ij} + \sum_{i,j,k,l} g_{ijkl} \tilde{P}_{ijkl}.$$

where $\tilde{D}_{ij} = \sum_{I=1}^M \omega_I D_{ij}^I$ and $\tilde{P}_{ijkl} = \sum_{I=1}^M \omega_I P_{ijkl}^I$

The same program can be used for average orbital calculations!

Advantages with Average Orbitals

1. Orthogonality: $\langle I | J \rangle = 0$.
2. Normally much less convergence problems.
3. Easy to compute transition properties.
4. One calculation for all states

Disadvantages with Average Orbitals

Orbitals may be very different in different electronic states!

An Example: C_2H_4

Consider the active space π_u, π_g with two active electrons.

For the ground (N) state: $\langle \pi_g | z^2 | \pi_g \rangle = 1.69$

For the excited (V) state: $\langle \pi_g | z^2 | \pi_g \rangle = 9.13$

N state: $C_1(\pi_u)^2 + C_2(\pi_g)^2$

V state: $(\pi_u \pi_g)_S$

You need at least two π_g orbitals active. Even this is not enough for the difficult V-state

Separate CASSCF Calculations for Each State

1. Can be performed sometimes, but not always due to root flipping and convergence problems.
2. Check eigenvalues of Hessian if available.
3. Be careful with local minima and general characterization of the solution.
4. Beware of the non-orthogonality problem!
5. How do we compute transition properties?

The RASSCF (CASSCF) State Interaction Method — RASSI(CASSI)

Suppose we have RASSCF wave function for two electronic states, $|X\rangle$ and $|Y\rangle$.

We want to compute the transition moment $\langle X | \hat{\mu} | Y \rangle$ where the dipole operator is: $\hat{\mu} = \sum_{pq} \boldsymbol{\mu}_{pq} \hat{E}_{pq}$.

We obtain

$$\langle X | \hat{\mu} | Y \rangle = \sum_{pq}^{XY} D_{pq}^{XY} \boldsymbol{\mu}_{pq},$$

where

$$D_{pq}^{XY} = \langle X | \hat{E}_{pq} | Y \rangle = \sum_{m,n} C_m^X C_n^Y D_{pq}^{mn}$$

are the **transition density matrices** .

The Non-Orthogonality Problem

Calculation of the coupling coefficients is easy if the two states use the same MO basis: D_{pq}^{mn} are the normal coupling coefficients.

The same is true if the MO's are not the same but they are mutually orthonormal (bi-orthonormal).

Can we transform the two sets of MO's to such a form without destroying the character of the wave function?

Yes, this is possible for RASSCF wave functions

The Bi-Orthonormal Transformation

Assume you have one set of MO's for state X and one for state Y : φ_X and φ_Y .

$$\langle \varphi_X | \varphi_Y \rangle = \mathbf{S}_{XY} \neq \mathbf{1}$$

The bi-orthonormal MO's are φ_A and φ_B .

They are obtained through a linear transformation of the original orbitals:

$$\begin{aligned}\varphi_A &= \varphi_X \mathbf{C}_{AX} \\ \varphi_B &= \varphi_Y \mathbf{C}_{BY},\end{aligned}$$

where we require:

$$\langle \varphi_A | \varphi_B \rangle = \mathbf{C}_{AX}^\dagger \mathbf{S}_{XY} \mathbf{C}_{BY}$$

The condition on the transformation is then: $\mathbf{S}_{XY}^{-1} = \mathbf{C}_{BY} \mathbf{C}_{AX}^\dagger$

The Bi-Orthonormal Transformation — Continued

The transformation may not destroy the character of the wave function.

For CASSCF wave functions inactive orbitals may not transform into active orbitals. Thus the matrix has the form:

$$\mathbf{C}_{AX} = \begin{pmatrix} \mathbf{C}_{AX}^{ii} & \mathbf{0} \\ \mathbf{C}_{AX}^{ai} & \mathbf{C}_{AX}^{aa} \end{pmatrix}$$

This transformation is non-unitary, but the only demand is *bi-orthonormality*.

The CI coefficients are transformed to the new basis through a sequence of one-index transformations.

This is a necessary condition for the usefulness of the approach.

RASSI Method

Transformation to a bi-orthonormal basis makes it possible to compute the transition densities \mathbf{D}^{AB} and \mathbf{P}^{AB} .

This can be used to compute transition properties, but also:

The overlap integrals: $\langle X | Y \rangle$ and the Hamiltonian matrix elements $\langle X | \hat{H} | Y \rangle$.

We can then solve the secular problem:

$$\begin{pmatrix} \mathbf{H}_{XX} - E\mathbf{1} & \mathbf{H}_{XY} - E\mathbf{S}_{XY} \\ \mathbf{H}_{YX} - E\mathbf{S}_{YX} & \mathbf{H}_{YY} - E\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{c}_X \\ \mathbf{c}_Y \end{pmatrix} = 0$$

The resulting states are **orthogonal** and **non-interacting**.

The method can handle several hundred CASSCF (RASSCF) states.

An Example: the Molecule OUO

A CASSCF/CASPT2 study was undertaken to study the geometry, vibrational frequencies, and the lower electronic states.

The active space is the $5f$ and $7s$ orbitals on uranium (8 active orbitals) with two active electrons.

Calculations were performed on a grid in C_i (C_1) symmetry .

Relativistic ANO basis sets were used. Scalar relativity according to the Douglas-Kroll schem. Spin-orbit effects with RASSI.

CASSCF Input in MOLCAS for the Triplet $(5f)^2$ States in OUO

```
Title                Inactive
OUO Triplet gerade states 26 27
Symmetry            Ras2
1                   1 7
Spin                CiRoot
3                   21 21 1
nActEl
2 0 0
End of input
```

CASSCF/CASPT2 Energies for the Triplet $(5f)^2$ States in OOU

State	CASSCF(au)	Rel. E(eV)	CASPT2(au)	Rel. E(eV)
3H_g	-28097.896231	0.00	-28098.657966	0.00
${}^3\Sigma_g^-$	-28097.886152	0.27	-28098.650259	0.21
${}^3\Pi_g$	-28097.874967	0.58	-28098.648731	0.25
${}^3\Phi_g$	-28097.841403	1.49	-28098.614119	1.19
${}^3\Pi_g$	-28097.833583	1.70	-28098.624029	0.92
${}^3\Gamma_g$	-28097.833544	1.71	-28098.606665	1.40
${}^3\Sigma_g^-$	-28097.820054	2.07	-28098.623903	0.93
${}^3\Delta_g$	-28097.807974	2.40	-28098.587820	1.91
${}^3\Sigma_g^-$	-28097.762949	3.63	-28098.550800	2.92
${}^3\Delta_g$	-28097.722200	4.74	-28098.484518	4.72
${}^3\Phi_g$	-28097.702693	5.27	-28098.468040	5.17
${}^3\Pi_g$	-28097.613035	7.71	-28098.398870	7.05

Dynamic Electron Correlation

The classical definition:

$$E_{corr} = E_{exact} - E_{HF}$$

Where E_{exact} is the exact eigenvalue of for the corresponding Schrödinger equation and E_{HF} is the Hartree-Fock energy (maybe unrestricted).

The statistical definition:

Two electrons move independently if:

$$\rho_2(x_1; x_2) = \rho_1(x_1, x_1)\rho_1(x_2, x_2),$$

where $\rho_2(x_1; x_2)$ is the probability density for finding electron 1 around x_1 electron 2 around x_2 . $\rho_1(x_1, x_1)$ is the one-electron density matrix.

Hartree-Fock Theory

The Hartree-Fock wave function:

$$\Psi_{HF} = \hat{A}\{\psi_1(x_1)\psi_2(x_2)\cdots\psi_N(x_N)\}$$

The second order density:

$$\rho_2(x_1; x_2) = \rho_1(x_1, x_1)\rho_1(x_2, x_2) - \rho_1(x_1, x_2)\rho_1(x_2, x_1)$$

Two electrons with parallel spins:

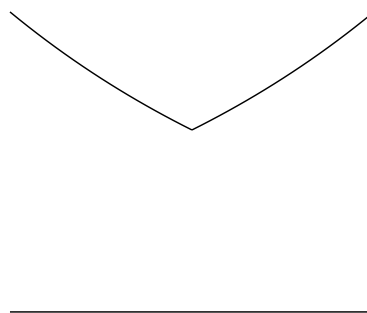
$$P_2^{\alpha\alpha}(\mathbf{r}_1; \mathbf{r}_2) = D_1^{\alpha}(\mathbf{r}_1, \mathbf{r}_1)D_1^{\alpha}(\mathbf{r}_2, \mathbf{r}_2) - D_1^{\alpha}(\mathbf{r}_1, \mathbf{r}_2)D_1^{\alpha}(\mathbf{r}_2, \mathbf{r}_1)$$

Two electrons with anti-parallel spins:

$$P_2^{\alpha\beta}(\mathbf{r}_1; \mathbf{r}_2) = D_1^{\alpha}(\mathbf{r}_1, \mathbf{r}_1)D_1^{\beta}(\mathbf{r}_2, \mathbf{r}_2)$$

The Coulomb Hole

Behavior of the wave function when $r_{12} \rightarrow 0$ for electrons with anti-parallel spins (**the Coulomb hole**).



$$\Psi(r_{12}) \propto \exp(r_{12}/2)$$

Behavior of the wave function when $r_{12} \rightarrow 0$ for electrons with parallel spins (**the Fermi hole**).

$$\Psi(r_{12}) \propto r_{12} \exp(r_{12}/2) \cos\Theta$$

Quantum Chemistry and Dynamic Correlation

Some different ways to treat dynamic correlation in quantum chemistry:

- Include r_{12} explicitly into the wave function (Hylleraas, Kutzelnigg).
- Configuration interaction methods (CI).
- Coupled Cluster expansions.
- Perturbation theory (MP2, MPX, CASPT2).
- Density Functional Theory.

The Multi-Reference CI Method

1. Select a number of reference configurations $\Phi(I)$ based on a MCSCF calculation.
2. Generate all singly, $\Phi(I)_i^x$ and doubly, $\Phi(I)_{ij}^{xy}$ excited configurations. i, j are occupied orbitals and x, y occupied or external orbitals.
3. Construct the wave function as a linear combination of these configurations:

$$\Psi_{MRCI} = \sum_I \left[C(I)\Phi(I) + \sum_{i,x} C_i^x(I)\Phi(I)_i^x + \sum_{i,j,x,y} C_{ij}^{xy}(I)\Phi(I)_{ij}^{xy} \right]$$

4. Solve the corresponding secular problem: $(\mathbf{H} - E\mathbf{S})\mathbf{C} = 0$

The Davidson Diagonalization Method

An iterative solution to the CI secular equation may be obtained by a simple iterative method (one root only):

$$C_{\mu}^{k+1} = C_{\mu}^k + \frac{1}{E^k - H_{\mu\mu}} \left(\sum_{\nu} H_{\mu\nu} C_{\nu}^k - E^k C_{\mu}^k \right)$$

where E^k is the energy obtained at iteration k . Slowly convergent, but set:

$$C = \sum_i \alpha_i C^i$$

and solve for the α_i variationally. This converges rapidly.

The Direct CI Method

The crucial step in a CI calculation is the formation of the σ vector:

$$\sigma = HC$$

where C is a trial CI vector and H are the matrix elements of the Hamiltonian matrix:

$$\hat{H} = \sum_{p,q} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{p,q,r,s} (pq|rs) (\hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps})$$

The σ vector is then:

$$\sigma_{\mu} = \sum_{\nu} \left[\sum_{p,q} h_{pq} A_{pq}^{\mu\nu} + \frac{1}{2} \sum_{p,q,r,s} (pq|rs) A_{pqrs}^{\mu\nu} \right] C_{\nu}$$

where $A_{pq}^{\mu\nu}$ and $A_{pqrs}^{\mu\nu}$ are the so-called *direct CI coupling coefficients*.

Advantages and Disadvantages with the MRCI approach

- Probably the most accurate method for small molecules.
- Balanced calculations for several electronic states.
- Can be made more and more exact by including more reference configurations. In practise very accurate results may be obtained by including reference configurations with a weight larger than 0.001-0.002.
- MRCI is not size-extensive. Approximate corrections (Davidson, ACPF) may help to some extent.
- The size of the CI expansion grows quickly with the number of reference configurations.
- It is an impossible method for large molecules (more than 10 atoms).

Raleyigh-Schrödinger Perturbation Theory

The Hamiltonian:

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}_1.$$

The wave function:

$$\Psi = \Psi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \dots$$

The energy:

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \dots.$$

Insert the above into the Schrödinger equation and collect terms order by order:

$$\begin{aligned}\hat{H}_0|\Psi_0\rangle &= E_0|\Psi_0\rangle, \\ (\hat{H}_0 - E_0)|\Psi_1\rangle &= (E_1 - \hat{H}_1)|\Psi_0\rangle, \\ (\hat{H}_0 - E_0)|\Psi_2\rangle &= (E_1 - \hat{H}_1)|\Psi_1\rangle + E_2|\Psi_0\rangle.\end{aligned}$$

Second Order Perturbation Theory

Solve the first order equation by expanding Ψ_1 in a basis:

$$\Psi_1 = \sum_{\mu} C_{\mu} \Phi_{\mu},$$

with $\Psi_0 = \Phi_0$ and $\langle \Phi_{\mu} | \Phi_{\nu} \rangle = \delta_{\mu\nu}$. Obtain C_{μ} from the first order equation:

$$\sum_{\nu} \left(E_0 \delta_{\mu\nu} - \langle \Phi_{\mu} | \hat{H}_0 | \Phi_{\nu} \rangle \right) C_{\nu} = \langle \Phi_{\mu} | \hat{H}_1 | \Phi_0 \rangle$$

If the Φ_{μ} are eigenfunctions of \hat{H}_0 with eigenvalues E_{μ} we obtain trivially:

$$C_{\mu} = - \frac{\langle \Phi_{\mu} | \hat{H}_1 | \Psi_0 \rangle}{E_{\mu} - E_0}$$

with the second order energy:

$$E_2 = - \sum_{\mu} \frac{|\langle \Phi_{\mu} | \hat{H}_1 | \Psi_0 \rangle|^2}{E_{\mu} - E_0}.$$

Second Order Møller-Plesset Theory (MP2)

The zeroth order wave function is a closed shell HF determinant. We define the zeroth order Hamiltonian as:

$$\hat{H}_0 = \hat{P}_0 \hat{F} \hat{P}_0 + \sum_{\mu} \hat{P}_{\mu} \hat{F} \hat{P}_{\mu},$$

Where $\hat{P}_0 = |0\rangle\langle 0|$ is a projection operator onto the reference function and $\hat{P}_{\mu} = |\mu\rangle\langle\mu|$. \hat{F} is the Hartree-Fock operator:

$$\hat{F} = \sum_p \epsilon_p \hat{E}_{pp},$$

The functions Φ_{μ} are doubly excited with respect to the HF state, ($\mu = ij \rightarrow ab$):

$$|ij \rightarrow ab\pm\rangle = N_{aibj} (\hat{E}_{ai} \hat{E}_{bj} \pm \hat{E}_{aj} \hat{E}_{bi}) |\Psi_0\rangle.$$

Multiconfigurational Second Order Perturbation Theory (CASPT2)

Assume now the the reference function is a CASSCF wave function instead of Hartree-Fock. The configuration space will now be divided up as:

The reference function: $\Psi_0 = |CASSCF\rangle = |0\rangle;$
 The complimentary CAS space: $|K\rangle;$
 SD substitutions from this space: $|pqrs\rangle = \hat{E}_{pq}\hat{E}_{rs}|\Psi_0\rangle;$
 The remaining configuration space: $|X\rangle.$

Only the SD space will interact with $|0\rangle!$

The zeroth order Hamiltonian:

$$\hat{H}_0 = \hat{P}_0\hat{F}\hat{P}_0 + \hat{P}_K\hat{F}\hat{P}_K + \hat{P}_{SD}\hat{F}\hat{P}_{SD} + \hat{P}_X\hat{F}\hat{P}_X,$$

The Fock Operator in CASPT2

The one-electron operator appearing in \hat{H}_0 is defined as:

$$\hat{F} = \sum_{p,q} f_{pq} \hat{E}_{pq},$$

with

$$f_{pq} = h_{pq} + \sum_{r,s} D_{rs} [(pq|rs) - \frac{1}{2}(pr|qs)].$$

This matrix has the property that:

For inactive orbitals: $f_{pp} = -IP_p$

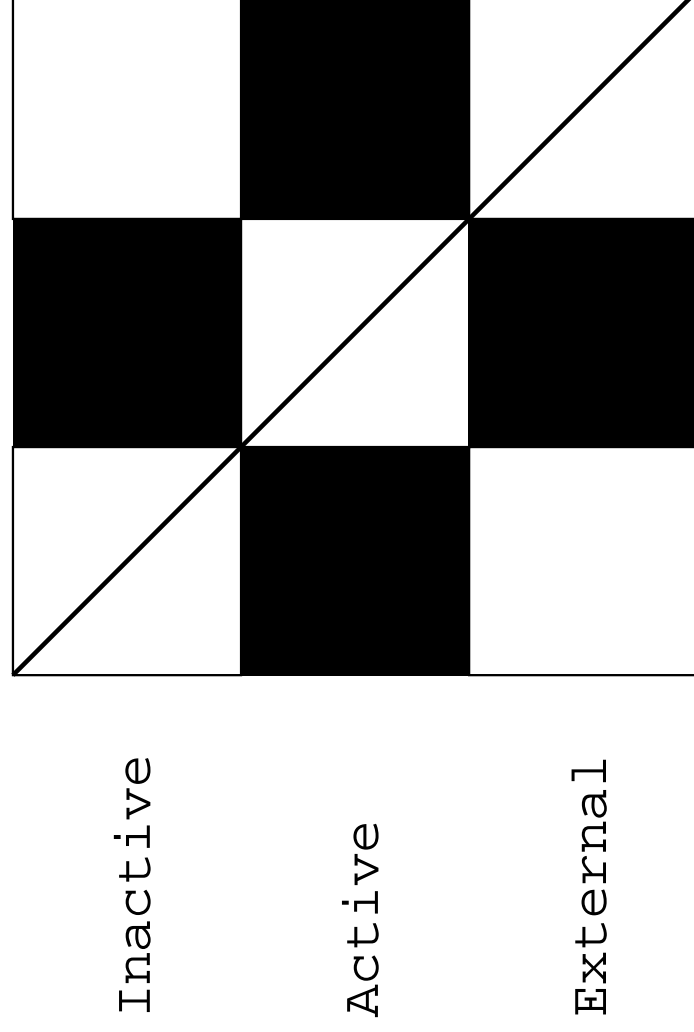
For external orbitals: $f_{pp} = -EA_p$

If $\eta_p = 1$: $f_{pp} = -\frac{1}{2}(IP_p + EA_p)$

This formulation is somewhat unbalanced and will favor systems with open shells, leading for example to too low binding energies.

The Structure of the Fock Matrix

The Fock matrix is made diagonal within each subspace:



However, non-diagonal elements remain!

The Fock Matrix Elements and the First Order Equation

The matrix elements of \hat{F} will contain up to fourth order density matrices:

$$\langle pqr s | \hat{F} | p' q' r' s' \rangle = \sum_{\alpha, \beta} f_{\alpha\beta} \langle \Psi_0 | \hat{E}_{sr} \hat{E}_{qp} \hat{E}_{\alpha\beta} \hat{E}_{p'q'} \hat{E}_{r's'} | \Psi_0 \rangle.$$

The first order equation:

$$(\mathbf{H}_0 - E_0 \mathbf{S}) \mathbf{C} = -\mathbf{V},$$

May be split into a large number of equations, one for each of 8 excitation types, which are un-coupled in the case of a diagonal \mathbf{F} .

The coupling via non-diagonal elements may then be re-introduced in a second iterative step.

The $|axyz\rangle$ case

An example: The $|axyz\rangle$ states (3 active, one eternal index). The first order equation is:

$$(\epsilon_a \mathbf{S} + \mathbf{B}) \mathbf{C}_a = -\mathbf{V}_a$$

Step 1: Diagonalize \mathbf{S} and remove linear dependencies (once for all a).

$$(\epsilon_a \mathbf{1} + \mathbf{B}') \mathbf{C}'_a = -\mathbf{V}'_a$$

Step 2: Diagonalize \mathbf{B} (also independent of a).

$$(\epsilon_a \mathbf{1} - \epsilon'' \mathbf{1}) \mathbf{C}''_a = -\mathbf{V}''_a$$

or for one component κ :

$$C''_{a\kappa} = -V''_{a\kappa} / (\epsilon_a - \epsilon''_{\kappa})$$

with the contribution to the second order energy:

$$E_2 = - \sum_{a,\kappa} (V''_{a\kappa})^2 / (\epsilon_a - \epsilon''_{\kappa})$$

Computational steps in CASPT2

- Perform a CASSCF calculation, single state or state average.
- Transform the Fock matrix to pseudo-diagonal form
- Transform two-electron integrals with at least two indices corresponding to occupied orbitals (second order transformation).
- Compute the matrices S and B and diagonalize them.
- Compute the second order energy in the "diagonal" approximation.
- Solve the large system of linear equations introducing the coupling arising from the non-diagonal blocks of the Fock matrix F .

Intruder States in CASPT2

- CASPT2 will only be an adequate method when the perturbation is small.
- All large CI coefficients should be included in the CAS space.
- When large coefficients appear in the second order wave function (the weight of the reference function is small), the active space should in general be increased.
- However, when the interaction of that specific state with the reference function is small, the state may be removed using a level shift technique.
- This is the intruder state problem in CASPT2.

The Reference Weight

Write the first order wave function as:

$$|\Psi'\rangle = |\Psi_0\rangle + |\Psi_1\rangle$$

The norm is $\langle\Psi'|\Psi'\rangle = 1 + S_1$. Introducing $\omega = 1/(1 + S)$ we can write the normalized function as:

$$|\Psi\rangle = \sqrt{\omega}|\Psi_0\rangle + \sqrt{1 - \omega}|\Psi_1\rangle$$

Since CASPT2 is an (almost) size-extensive method, ω will decrease when the number of electrons increases. An order of magnitude measure can be obtained from the formula:

$$\omega = (1 + \alpha)^{-N/2},$$

where N is the number of electrons and α is a constant of the order 0.015. For $N = 10$ this gives $\omega = 0.93$, while for $N = 100$ we obtain $\omega = 0.48$. Much smaller numbers is an indication of an intruder state.

The level Shifted CASPT2

Introduce a level shift ε in the first order equation:

$$(\hat{H}_0 - E_0 + \varepsilon)\tilde{\Psi}_1 = (E_1 - \hat{H}_1)\Psi_0,$$

The tilde indicates a level shifted first order wave function. For a diagonal zeroth order Hamiltonian we can write the second order energy as:

$$\tilde{E}_2 = E_2 + \varepsilon \sum_{\mu} |\tilde{C}_{\mu}|^2 \left(1 + \frac{\varepsilon}{\epsilon_{\mu} - E_0} \right),$$

Assuming that $\epsilon_{\mu} - E_0 \gg \varepsilon$ and neglecting quadratic terms, we obtain:

$$E_2 \approx \tilde{E}_2 - \varepsilon \left(\frac{1}{\tilde{\omega}} - 1 \right).$$

This technique removes the effect of the intruder state without largely effect the contributions from the other states!

Multi-State (MS) CASPT2

Assume a number of CASSCF wave functions, Ψ_i , $i = 1, N$, obtained in a state average calculation.

The corresponding (single state) CASPT2 functions are: χ_i , $i = 1, N$.

The functions $\Psi_i + \chi_i$ are used as basis functions in a variational calculation where all terms higher than second order are neglected.

The corresponding effective Hamiltonian has the elements :

$$(H_{eff})_{ij} = \delta_{ij}E_i + \langle \Psi_i | \hat{H} | \chi_j \rangle,$$

where E_i is the CASSCF energy for state i .

Always recommended when several states of the same symmetry are considered.

Advantages with the CASPT2 Approach

- A CAS wave function is the reference (orbitals must not be optimized). Very general type of electronic structures may be treated.
- The formalism is independent of the size of the CAS CI space. Thus large expansions of Ψ_0 may be used.
- The size of the contracted SD space is never large and is independent of the CAS CI space.
- The formalism is (almost) size-extensive. Therefore a large number of electrons may be correlated (more than 100 in practical applications).
- The method has the same orbital invariance as the CASSCF method.

Applications of the CASPT2 Approach

- Energy surface for ground and excited states.
- Electronic spectroscopy, including all types of excited states (singly, doubly, etc. excited, valence and Rydberg states, charge transfer, etc.).
- The whole periodic system from H to Pu (scalar relativity in CASSCF, spin-orbit with RASSI).
- Radicals and bi-radicals, positive and negative ions.
- Large molecules where MRCI is not applicable (calculations on systems with up to 50 atoms have been performed).

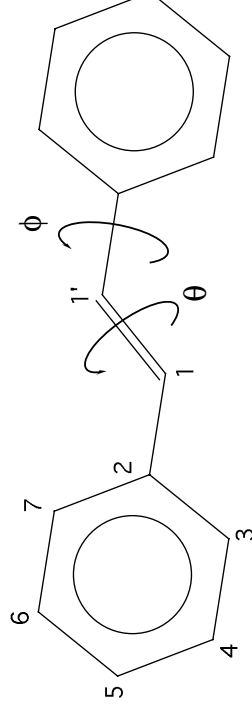
Problems with the CASPT2 Approach

- The active space may become prohibitively large (today's limit 12-15 active orbitals).
- The intruder state problem.
- The zeroth order Hamiltonian has a (small) systematic error.
- Transition properties are obtained at the CASSCF level.
- It is not a **Black Box** method.

How to Choose Active Orbitals?

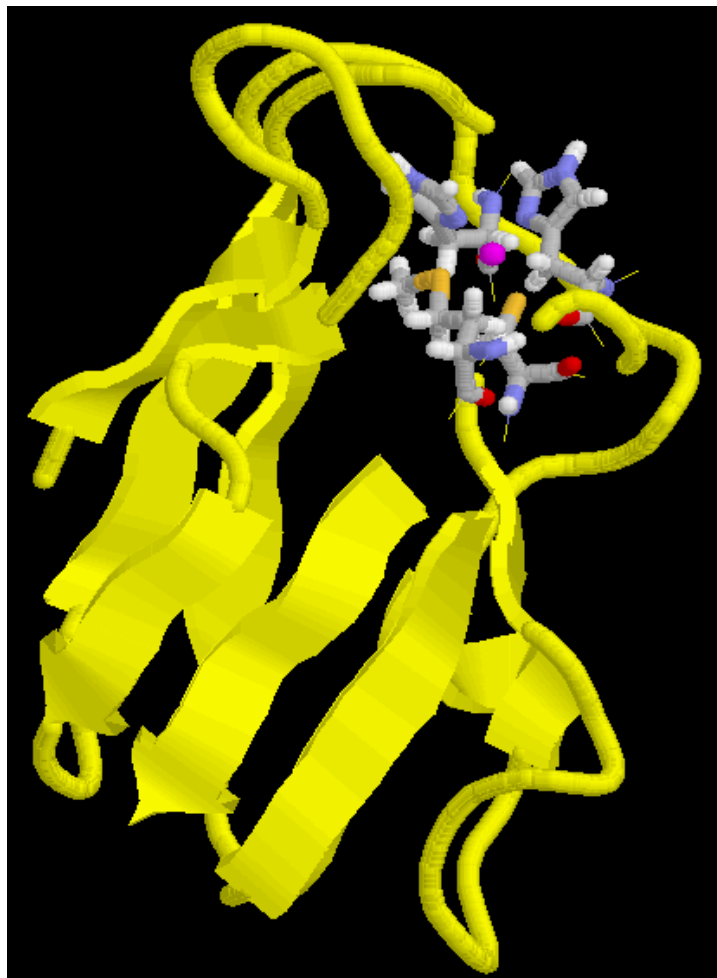
- There is no general answer to this question. Attempts have been made but with rather limited success.
- If you have no idea, choose a large active space and run RASSCF(SDTQ...) with only a small number of orbitals in RAS2.
- This has to be done on several points on an energy surface.
- Choose as active the orbitals with occupation numbers > 0.02 or < 1.98 . If this is not possible, choose another method.
- Use the same active space for the whole surface.

Excited States of Conjugated Organic Molecules



- Use preferably all π -orbitals.
- Add appropriate lone-pair orbitals.
- Add 3s,3p,3d Rydberg orbitals if the spectrum extends into this region.
Note that this requires special basis sets.
- Sometimes it is necessary to add extra valence orbitals in order to avoid intruder states. Alternatively level shift can be used.

Excited States in Transition metal Compounds



Active Spaces in TM compounds

- For Mn-Cu use preferably 2 orbitals per doubly occupied 3d orbital (the double shell effect). These may include ligand orbitals for bond forming 3d orbitals. This is enough for d-d transitions in ionic compounds (10 orbitals).
- If CT transitions, corresponding ligand orbital must be included.
- Sometimes it is not possible to find an appropriate active space that is small enough!
- Core correlation and relativistic effects are important already for the first row of TM.

Small Molecules

- Use full valence space or even one orbital per electron.
- H(1s), Li-N(2s,2p), O-Ne(2p), etc
- TM(nd,(n+1)s,(n+1)p), only nd for ions.
- Lanthanides and actinides: nf,(n+1)d,(n+2)s, less for highly valent ions.

A Case Study: Potential Curves for the X- and A-States of CrH

- CASSCF/CASPT2 calculations of the two lowest potential curves for the CrH molecule, both of ${}^6\Sigma^+$ symmetry.
- Basis set: ANO-L Cr/7s6p4d2f1g and H/3s2p1d and later ANO-CC: Cr/8s7p5d3f2g
- Active space: Cr: 3d,4s,4p and H: 1s (7 electrons in 10 orbitals)
- Scalar relativistic effects from the Douglas-Kroll Hamiltonian.
- C_{2v} Symmetry used first, then C_2 .
- 3s,3p and valence electrons correlated at the CASPT2 level of theory.
- About 20 points on the potential computed, smallest spacing 0.1 au.
- Calculations performed on a 600MHz laptop with 128 Mb memory.

First Attempt: The X-state with the ANO-L basis set

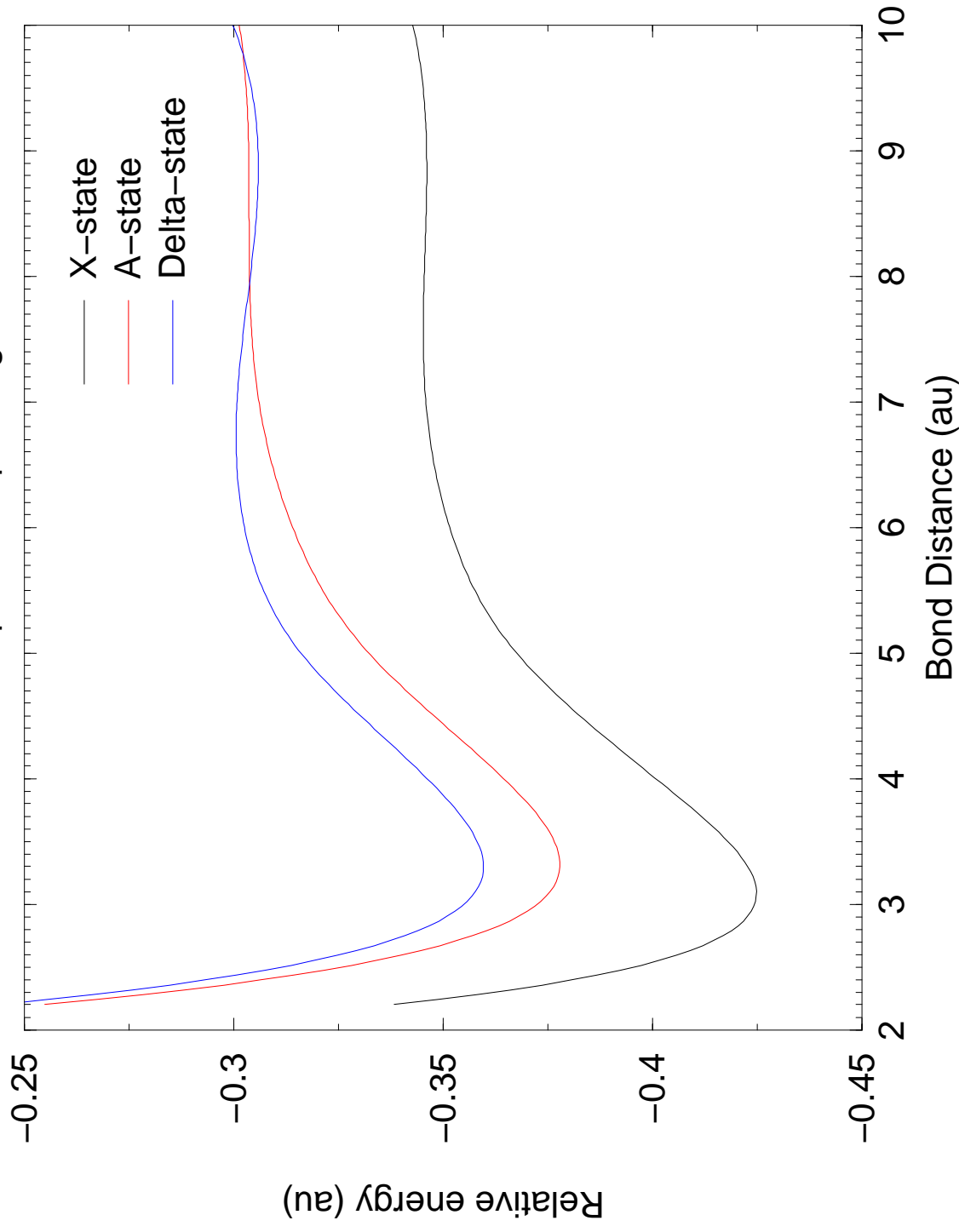
	Calc	ICMRCI	Expt
$R_e(\text{\AA})$	1.650	1.670	1.655
$D_0(\text{eV})$	2.16	2.16	1.93 ± 0.07
$\omega_e(\text{cm}^{-1})$	1586	1601	1656
$\omega_e x_e(\text{cm}^{-1})$	25.4	30.1	30.5

The X- and A-State

The first attempt failed, the reason being the appearance of the ${}^6\Delta$ state close to the A-state. Thus this state had to be included in the calculations and a state average calculation over three states was performed. Active space reduced to 5111 (no $4p\pi$). The results are:

Potential curves for CrH

5111 Active space, 7s6p4d2f1g ANO-L



Spectroscopic Constants for the X- and A-State

	$X^6\Sigma^+$			$A^6\Sigma^+$		
	Calc	ICMRCI	Expt	Calc	ICMRCI	Expt
$R_e(\text{\AA})$	1.634	1.670	1.655	1.755	1.764	1.786
$D_0(\text{eV})$	2.14	2.16	1.93 ± 0.07	2.00	-	?
$T_0(\text{cm}^{-1})$	-	-	-	10217	-	-
$\omega_e(\text{cm}^{-1})$	1680	1601	1656	1534	1545	1525
$\omega_e x_e(\text{cm}^{-1})$	30.7	30.1	30.5	25.8	22.1	27.1

Computed separation between $\text{Cr}(^7\text{S})$ and $\text{Cr}(^5\text{D})$ is 9088 or 9431 cm^{-1} (exp 8090).

These results are unsatisfactory for two reasons: wrong basis set and symmetry breaking, since only one component of the $^6\Delta$ is included. So, change to ANO-CC and reduce symmetry to C_2

The ANO-CC Basis Set and C_2 Symmetry

Average over four states, only C_2 symmetry. First calculation fails, since GS converges to excited limit.

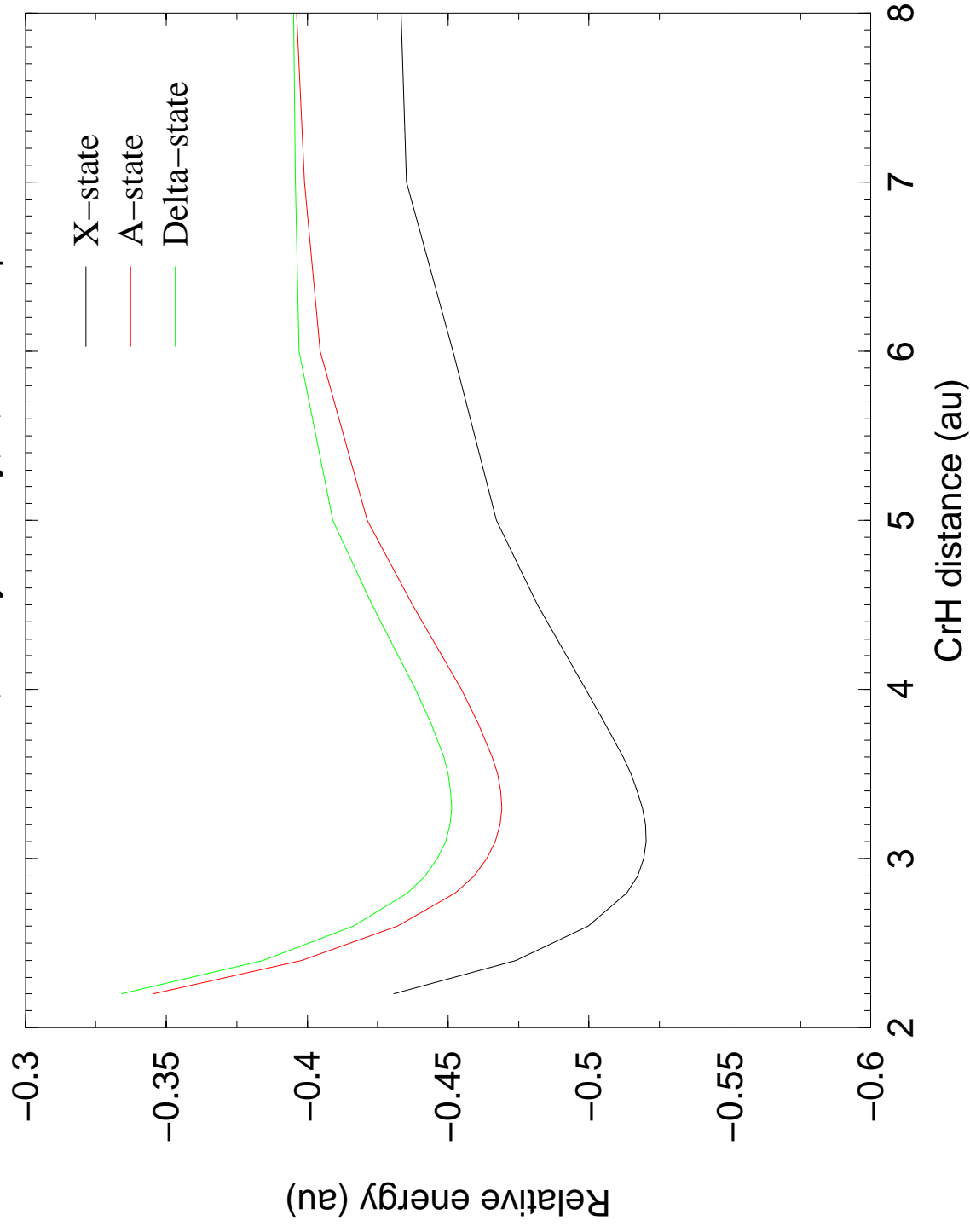
	$X^6\Sigma^+$		$A^6\Sigma^+$	
	Calc	Expt	Calc	Expt
$R_e(\text{\AA})$	1.655	1.655	1.749	1.774
$D_0(\text{eV})$	2.19	1.93 ± 0.07	1.95	?
$T_0(\text{cm}^{-1})$	-	-	11212	-
$\omega_e(\text{cm}^{-1})$	1643	1656	1560	1515
$\omega_e x_e(\text{cm}^{-1})$	29.6	30.5	22.7	21.5
$\Delta G_{1/2}(\text{cm}^{-1})$	1583	-	1513^b	-

^aComputed separation between $\text{Cr}(^7\text{S})$ and $\text{Cr}(^5\text{D})$ is 8210 or 8418 cm^{-1} (exp 8090).

^bThe value for CrD is 1090 cm^{-1} (expt 1066).

CrH Potentials

ANO-CC, C2 Symmetry, 6,2 active space



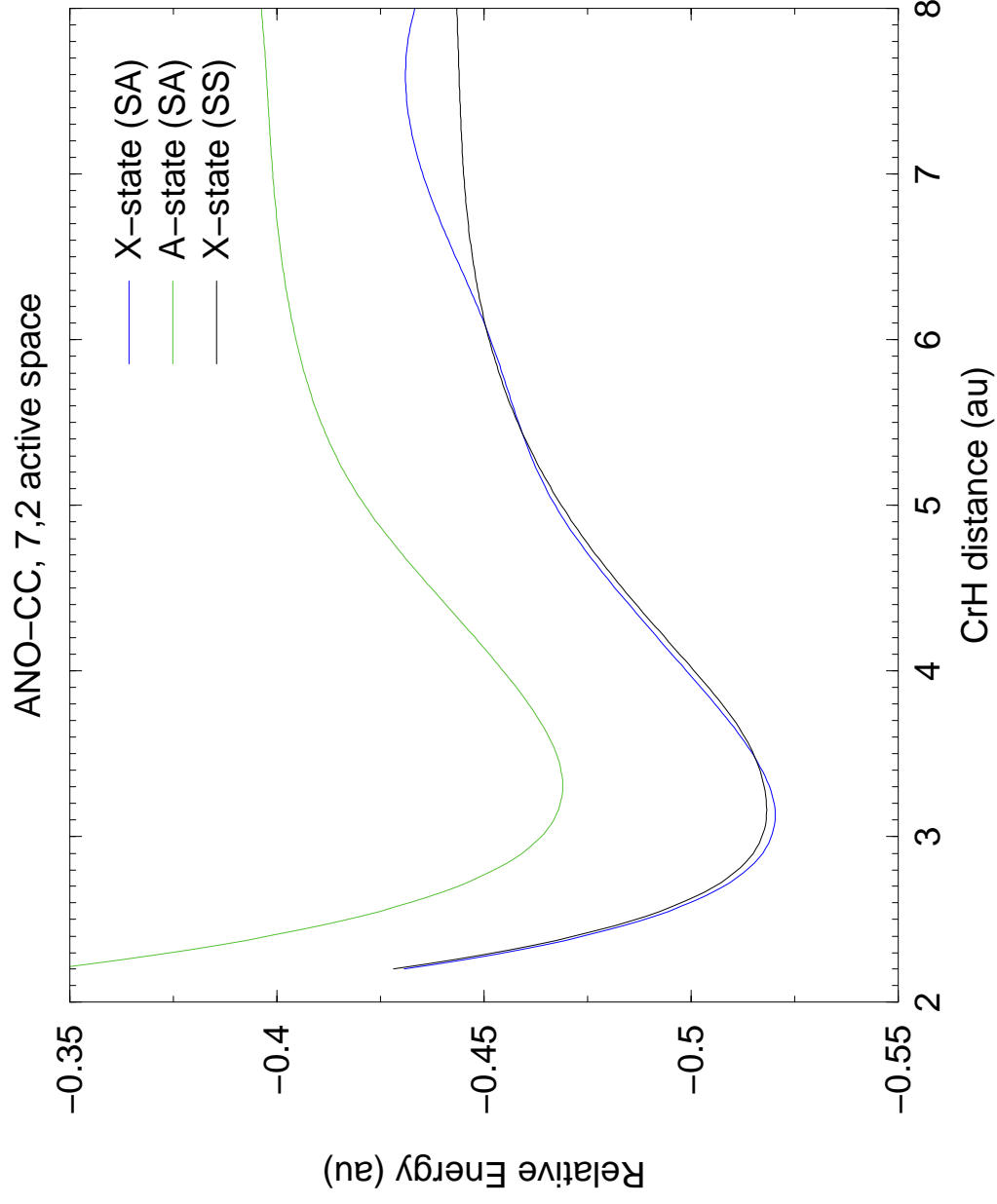
The Ground State Only

Single state calculation for the ground state. Difficulties to converge to the right state. Thresholds decreased. Finally:

	Calc. (SS)	Calc. (SA)	Expt.
$R_e(\text{\AA})$	1.672	1.655	1.655
$D_0(\text{eV})$	2.05	2.19	1.93 ± 0.07
$\omega_e(\text{cm}^{-1})$	1390	1643	1656
$\omega_e x_e(\text{cm}^{-1})$	17.5	29.6	30.5
$\Delta G_{1/2}(\text{cm}^{-1})$	1403	1583	-

No improvement. State average and MS-CASPT2 takes better account of the interaction between the two close lying states of ${}^6\Sigma^+$ symmetry.

CrH potential X- and A-state

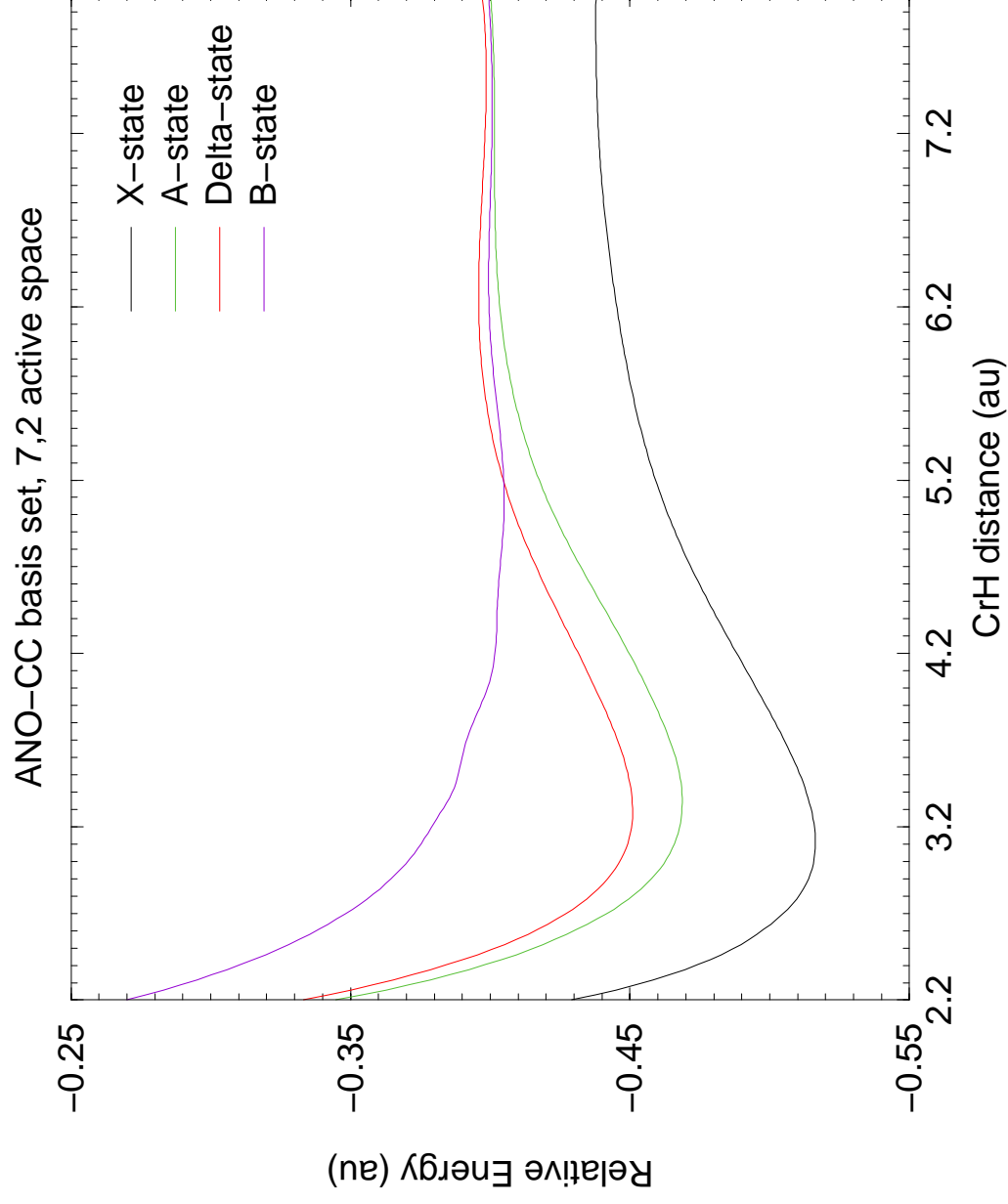


The dissociation limits

Calculations at $R=100.0$ au for the atomic states (5 states average).
Relative energies for Cr in cm^{-1} .

State	CASSCF	CASPT2	MS-CASPT2	Expt.
${}^7\text{S}({}^7\Sigma^+)$	-	-	-	-
${}^5\text{S}({}^5\Sigma^+)$	7151	8271	8235	7593
${}^5\text{D}({}^5\Sigma^+)$	1706	8305	8339	8090
${}^5\text{D}({}^5\Delta)$	2460	8840	8840	8090

CrH Potentials with Five States



CrH potential with a five state average CASSCF/MS-CASPT2

	$X^6\Sigma^+$			$A^6\Sigma^+$		
	Calc	ICMRCI	Expt	Calc	ICMRCI	Expt
$R_e(\text{\AA})$	1.644	1.670	1.655	1.773	1.764	1.774
$D_0(\text{eV})$	2.07	2.16	1.93 ± 0.07	1.80	-	?
$T_0(\text{cm}^{-1})$	-	-	-	10409	-	-
$\omega_e(\text{cm}^{-1})$	1609	1601	1656	1505	1545	1515
$\omega_e x_e(\text{cm}^{-1})$	28.6	30.1	30.5	16.5	22.1	21.5
$\Delta G_{1/2}(\text{cm}^{-1})$	1549	-	-	1472^b	-	-

^bThe value for CrD is 1060 cm^{-1} (expt 1066).