

Modelling of Molecular Systems Part I: Electronic Structure Theory

(VO PHT.105UF)

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Graz, WS 2017/18

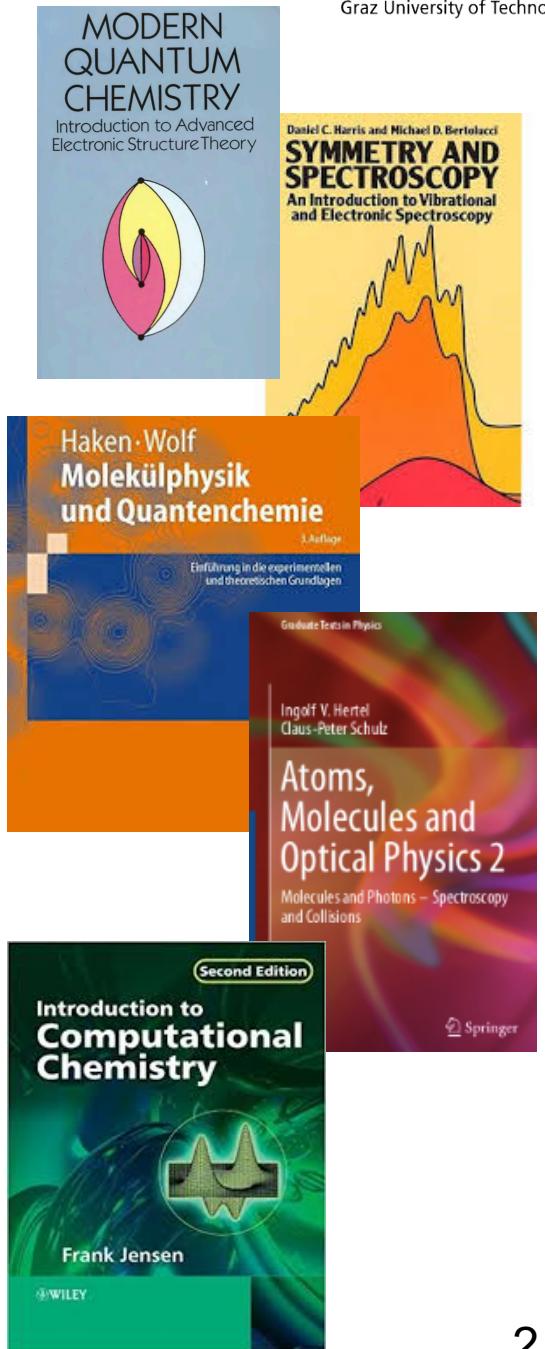
The electronic structure part of this lecture (Part I) is mostly based on the book “*Modern Quantum Chemistry*” by A. Szabo and N. Ostlund, Dover 1996.

In Part II of this lecture, dedicated to nuclear motion, several extensions towards molecular spectroscopy will be based on the book “*Symmetry and Spectroscopy*” by D.C. Harris and M.D. Bertolucci, Dover 1989.

Additionally, the book “*Atoms, Molecules and Optical Physics 2*” by I.V. Hertel and C.-P. Schulz, Springer 2015, will be used for the discussion of molecular vibration and symmetry.

The introductory chapter on group theory in the context of molecular physics follows the book “*Molecular Physics and Quantum Chemistry*” by H. Haken and H. C. Wolf, Springer 2006.

The planned introductions to solvent models and QM/MM approaches as well as the chapter on optimization techniques are taken from the book “*Introduction to Computational Chemistry*” by F. Jensen, Wiley 2007.



A) Introduction

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Introduction

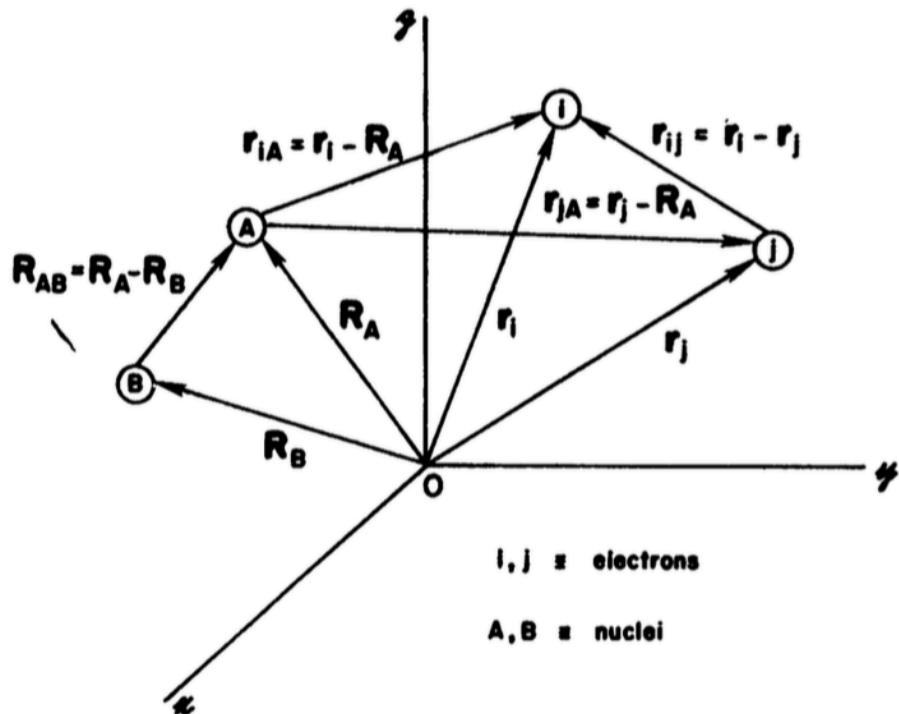


Figure 2.1 A molecular coordinate system: $i, j = \text{electrons}$; $A, B = \text{nuclei}$.

The corresponding Hamiltonian reads:

$$\begin{aligned} \mathcal{H} = & - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \\ & + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \end{aligned}$$

We introduced atomic units: $\left[-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right] \phi = \mathcal{E}\phi$

$\longrightarrow \left(-\frac{1}{2} \nabla'^2 - \frac{1}{r'} \right) \phi' = \mathcal{E}'\phi'$

$\lambda = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = a_0$

Table 2.1 Conversion of atomic units to SI units

Physical quantity	Conversion factor X	Value of X (SI)
Length	a_0	$5.2918 \times 10^{-11} \text{ m}$
Mass	m_e	$9.1095 \times 10^{-31} \text{ kg}$
Charge	e	$1.6022 \times 10^{-19} \text{ C}$
Energy	\mathcal{E}_a	$4.3598 \times 10^{-18} \text{ J}$
Angular momentum	\hbar	$1.0546 \times 10^{-34} \text{ Js}$
Electric dipole moment	ea_0	$8.4784 \times 10^{-30} \text{ Cm}$
Electric polarizability	$e^2 a_0^2 \mathcal{E}_a^{-1}$	$1.6488 \times 10^{-41} \text{ C}^2 \text{m}^2 \text{J}^{-1}$
Electric field	$\mathcal{E}_a e^{-1} a_0^{-1}$	$5.1423 \times 10^{11} \text{ V m}^{-1}$
Wave function	$a_0^{-3/2}$	$2.5978 \times 10^{15} \text{ m}^{-3/2}$

1 Hartree $\approx 27.2 \text{ eV} \approx 630 \text{ kcal/mol} \approx 219000 \text{ cm}^{-1}$

1 mHartree $\approx 219 \text{ cm}^{-1}$

1 cm $^{-1}$ $\approx 3/2 \text{ K}$

The Born-Oppenheimer Approach:

Wave function depending on electronic and nuclear coordinates:

$$\Psi(\vec{r}_1, \vec{r}_1, \dots, \vec{r}_n, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N),$$

To each wf corresponds an eigenvalue E according to

$$(\mathcal{H} - E)\Psi = 0$$

The Hamiltonian consists of three parts:

$$T_E = -\frac{\hbar^2}{2m} \sum_{i=1}^{3n} \frac{\partial^2}{\partial r_i^2},$$

$$T_K = -\frac{\hbar^2}{2} \sum_{j=1}^{3N} \frac{1}{M_j} \frac{\partial^2}{\partial R_j^2},$$

$$V = V(\vec{r}_1, \dots, \vec{r}_n, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) = V(\mathbf{r}, \mathbf{R}).$$

The Born-Oppenheimer Approach:

Last term couples electrons and nuclei! Our Approximation: Solving the electronic part at fixed nuclear geometry,

$$[T_E + V(\mathbf{r}, \mathbf{R}) - W_m(\mathbf{R})] \Phi_m(\mathbf{r}, \mathbf{R}) = 0.$$



Expanding the total solution of the Schrödinger Eq. in electronic coordinates,

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{m=0}^{\infty} \chi_m(\mathbf{R}) \Phi_m(\mathbf{r}, \mathbf{R})$$

We can write it as

$$[T_E + T_K + V(\mathbf{r}, \mathbf{R}) - E] \sum_{m=0}^{\infty} \chi_m(\mathbf{R}) \Phi_m(\mathbf{r}, \mathbf{R}) = 0$$

Multiplication with Φ_n^* an integration over electron coordinates gives

$$\sum_{m=0}^{\infty} \int d\mathbf{r} \Phi_n^*(\mathbf{r}, \mathbf{R}) [T_E + T_K + V(\mathbf{r}, \mathbf{R}) - E] \chi_m(\mathbf{R}) \Phi_m(\mathbf{r}, \mathbf{R}) = 0$$

Using ♦ we can write this equation as

$$\sum_{m=0}^{\infty} \int d\mathbf{r} \Phi_n^*(\mathbf{r}, \mathbf{R}) [T_K + W_m(\mathbf{R}) - E] \chi_m(\mathbf{R}) \Phi_m(\mathbf{r}, \mathbf{R}) = 0 \quad \spadesuit$$

From orthogonality $\int d\mathbf{r} \Phi_n^* \Phi_m = \delta_{nm}$ follows:

$$\sum_{m=0}^{\infty} \left[\int d\mathbf{r} \Phi_n^*(\mathbf{r}, \mathbf{R}) T_K \Phi_m(\mathbf{r}, \mathbf{R}) + (W_m(\mathbf{R}) - E) \delta_{nm} \right] \chi_m(\mathbf{R}) = 0$$

What is the effect of the differential operator?

$$\frac{\partial}{\partial R_j} \Phi_m \chi_m = \frac{\partial \Phi_m}{\partial R_j} \chi_m + \Phi_m \frac{\partial \chi_m}{\partial R_j}$$

$$\frac{\partial^2}{\partial R_j^2} \Phi_m \chi_m = \frac{\partial^2 \Phi_m}{\partial R_j^2} \chi_m + 2 \frac{\partial \Phi_m}{\partial R_j} \frac{\partial \chi_m}{\partial R_j} + \Phi_m \frac{\partial^2 \chi_m}{\partial R_j^2}$$

We can write the first term of  as:

$$\begin{aligned} \int d\mathbf{r} \Phi_n^* T_K \Phi_m \chi_m &= - \sum_j \frac{\hbar^2}{2M_j} \int d\mathbf{r} \Phi_n^* \frac{\partial^2 \Phi_m}{\partial R_j^2} \chi_m - 2 \sum_j \frac{\hbar^2}{2M_j} \int d\mathbf{r} \Phi_n^* \frac{\partial \Phi_m}{\partial R_j} \frac{\partial \chi_m}{\partial R_j} \\ &\quad - \underbrace{\sum_j \frac{\hbar^2}{2M_j} \frac{\partial^2 \chi_m}{\partial R_j^2} \delta_{nm}}_{T_K \chi_m \delta_{nm}}. \end{aligned}$$

Finally we obtain:

$$\left[- \sum_j \frac{\hbar^2}{2M_j} \frac{\partial^2}{\partial R_j^2} + W_n(\mathbf{R}) - E \right] \chi_n(\mathbf{R}) = \sum_m \sum_j \frac{\hbar^2}{M_j} \int d\mathbf{r} \Phi_n^* \frac{\partial \Phi_m}{\partial R_j} \frac{\partial \chi_m}{\partial R_j} + \sum_m \sum_j \frac{\hbar^2}{2M_j} \int d\mathbf{r} \Phi_n^* \frac{\partial^2 \Phi_m}{\partial R_j^2} \chi_m$$

This corresponds to a system of coupled diff. equations. We define:

$$\Lambda_{nm} = \sum_j \frac{\hbar^2}{M_j} \int d\mathbf{r} \Phi_n^* \left[\frac{\partial}{\partial R_j} \Phi_m \right] \frac{\partial}{\partial R_j} + \sum_j \frac{\hbar^2}{2M_j} \int d\mathbf{r} \Phi_n^* \left[\frac{\partial^2}{\partial R_j^2} \Phi_m \right]$$

And obtain: $[T_K + W_n(\mathbf{R}) - E] \chi_n(\mathbf{R}) = \sum_m \Lambda_{nm} \cdot \chi_m(\mathbf{R})$

What is now the **BORN-OPPENHEIMER APPROACH?**

We assume $\Lambda_{nm} = 0$.

The motions of electrons and nuclei are decoupled, and we describe the nuclear part via

$$[T_K + W_n(\mathbf{R}) - E] \chi_n(\mathbf{R}) = 0$$

The total wavefunction is now a product of nuclear and electronic function,

$$\Psi_{nv}(\mathbf{r}, \mathbf{R}) = \Phi_n(\mathbf{r}, \mathbf{R}) \chi_v(\mathbf{R})$$

What has to be fulfilled for this to be valid?

$$\frac{|\langle \chi_{ns} | \Lambda_{nm} | \chi_{ms'} \rangle|}{|E_{ns} - E_{ms'}|} \ll 1$$

The concept of orbitals

We define a set of orthonormal spatial functions

$$\int d\mathbf{r} \psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) = \delta_{ij}$$

Any function could be expanded in this basis if complete: $f(\mathbf{r}) = \sum_{i=1}^{\infty} a_i \psi_i(\mathbf{r})$

We introduce the spin as inner degree of freedom,

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases}$$

If the spatial functions are orthonormal, so is the product:

$$\int d\mathbf{x} \chi_i^*(\mathbf{x})\chi_j(\mathbf{x}) = \langle \chi_i | \chi_j \rangle = \delta_{ij}$$

The Hartree product function

Let us assume a simplified Hamiltonian $\mathcal{H} = \sum_{i=1}^N h(i)$

This operator has a set of eigenfunctions which we take as spin orbitals $\{\chi_j\}$,

$$h(i)\chi_j(\mathbf{x}_i) = \varepsilon_j \chi_j(\mathbf{x}_i)$$

And we can write

$$\Psi^{\text{HP}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \cdots \chi_k(\mathbf{x}_N)$$

with

$$\mathcal{H}\Psi^{\text{HP}} = E\Psi^{\text{HP}} \quad \text{and} \quad E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k$$

What is the problem here?

Its an uncorrelated WF!

$$|\Psi^{\text{HP}}(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 \cdots d\mathbf{x}_N = |\chi_i(\mathbf{x}_1)|^2 d\mathbf{x}_1 |\chi_j(\mathbf{x}_2)|^2 d\mathbf{x}_2 \cdots |\chi_k(\mathbf{x}_N)|^2 d\mathbf{x}_N$$

Solution to this problem: The introduction of Slater Determinants

Example: 2 electrons

$$\Psi_{12}^{\text{HP}}(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \quad \Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-1/2}(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2))$$

or

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-1/2} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) \end{vmatrix}$$

More general:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \cdots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \cdots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \cdots & \chi_k(\mathbf{x}_N) \end{vmatrix}$$

Short-hand notation: $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = |\chi_i\chi_j \cdots \chi_k\rangle$

Watch out: The Slater determinant incorporates correlation!

The exchange correlation between two electrons of same spin.

Compare two situations

Different spatial and spin orbitals:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\rangle \quad \begin{aligned} \chi_1(\mathbf{x}_1) &= \psi_1(\mathbf{r}_1)\alpha(\omega_1) \\ \chi_2(\mathbf{x}_2) &= \psi_2(\mathbf{r}_2)\beta(\omega_2) \end{aligned}$$

$$|\Psi|^2 d\mathbf{x}_1 d\mathbf{x}_2 = \frac{1}{2} |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_2(\mathbf{r}_2)\beta(\omega_2) - \psi_1(\mathbf{r}_2)\alpha(\omega_2)\psi_2(\mathbf{r}_1)\beta(\omega_1)|^2 d\mathbf{x}_1 d\mathbf{x}_2$$

For the probability we find

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 &= \int d\omega_1 d\omega_2 |\Psi|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{2} [|\psi_1(\mathbf{r}_1)|^2|\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2|\psi_2(\mathbf{r}_1)|^2] d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned}$$

Therefore the electron motion is uncorrelated. Consider the case of identical spatial orbitals

$$\psi_1 = \psi_2 \quad P(\mathbf{r}_1, \mathbf{r}_2) = |\psi_1(\mathbf{r}_1)|^2 |\psi_1(\mathbf{r}_2)|^2$$

Note also that $P(\mathbf{r}_1, \mathbf{r}_1) \neq 0$!

Now, lets assume two electrons of same spin (in different orbitals of course)

$$\chi_1(\mathbf{x}_1) = \psi_1(\mathbf{r}_1)\beta(\omega_1)$$

$$\chi_2(\mathbf{x}_2) = \psi_2(\mathbf{r}_2)\beta(\omega_2)$$

One finds

$$P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \{ |\psi_1(\mathbf{r}_1)|^2 |\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2 |\psi_2(\mathbf{r}_1)|^2$$

$$- [\psi_1^*(\mathbf{r}_1)\psi_2(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)\psi_1(\mathbf{r}_2) + \psi_1(\mathbf{r}_1)\psi_2^*(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_1^*(\mathbf{r}_2)] \}$$

Extra cross term

Note that $P(\mathbf{r}_1, \mathbf{r}_1) = 0$, so there exists a so-called Fermi hole!

A quick overview: The Hartree-Fock wave function and excited determinants

We start from a single Slater determinant $|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_N\rangle$,

obtained via application of the **Variational Method** (details given later).

The corresponding energy, $E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle$
is called the Hartree-Fock energy.

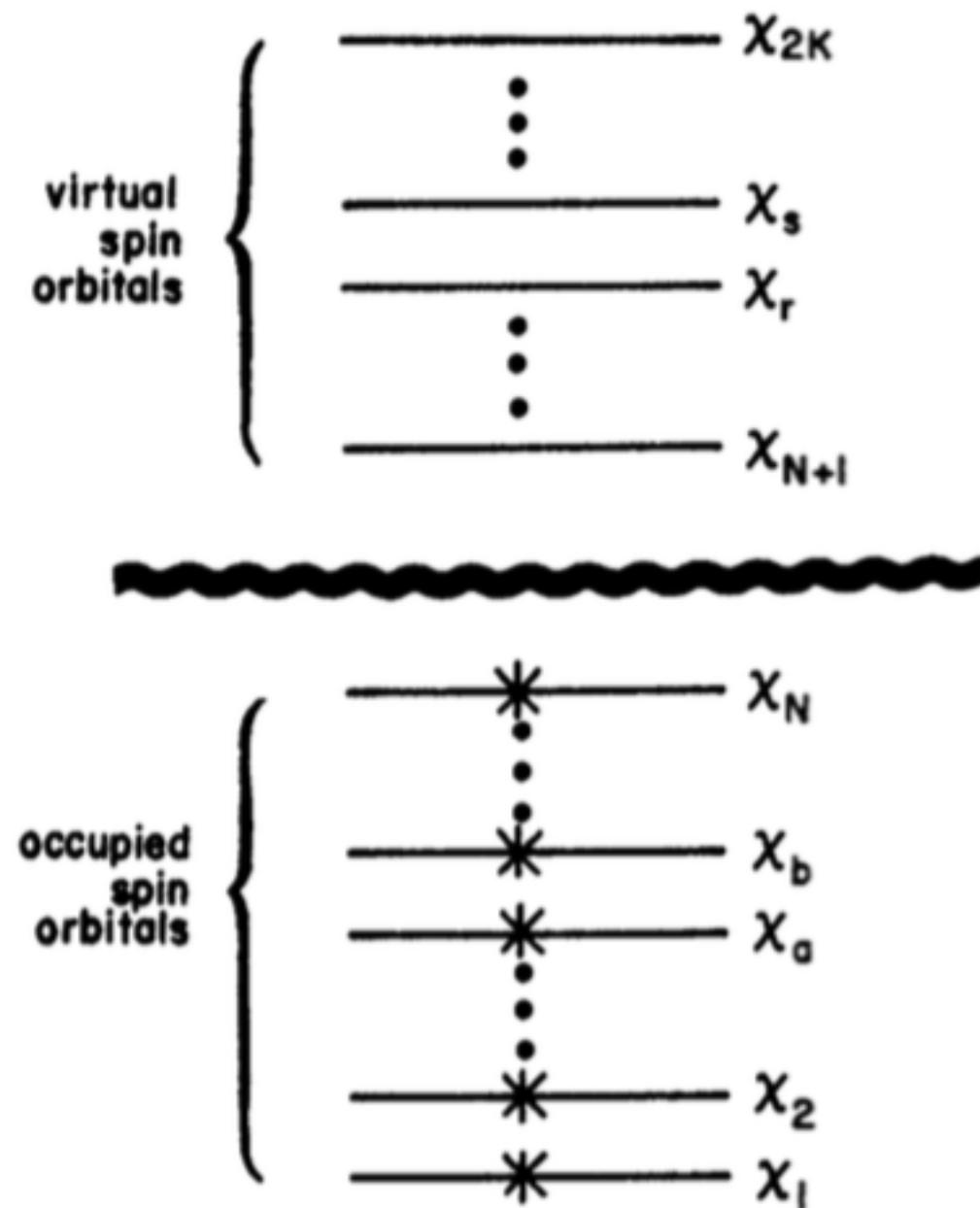
By minimizing the energy with respect to the choice of orbitals one derives a set of equations

$$f(i)\chi(\mathbf{x}_i) = \varepsilon\chi(\mathbf{x}_i)$$

With the Fock operator defined as $f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{\text{HF}}(i)$

Introduction

Definitions and nomenclature:



The HF ground state wf $|\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$

A simple example – the H₂ molecule

LCAO method: $\psi_i(\mathbf{r}) = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu}(\mathbf{r})$

$$\psi_1 = [2(1 + S_{12})]^{-1/2}(\phi_1 + \phi_2)$$

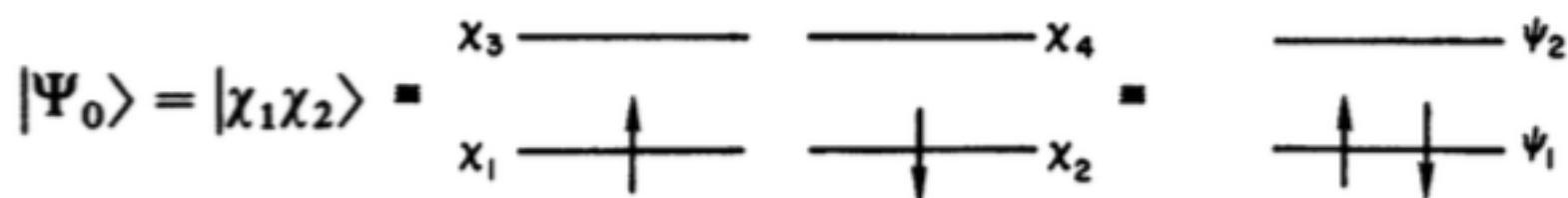
$$\psi_2 = [2(1 - S_{12})]^{-1/2}(\phi_1 - \phi_2)$$

$$\chi_1(\mathbf{x}) = \psi_1(\mathbf{r})\alpha(\omega)$$

$$\chi_2(\mathbf{x}) = \psi_1(\mathbf{r})\beta(\omega)$$

$$\chi_3(\mathbf{x}) = \psi_2(\mathbf{r})\alpha(\omega)$$

$$\chi_4(\mathbf{x}) = \psi_2(\mathbf{r})\beta(\omega)$$



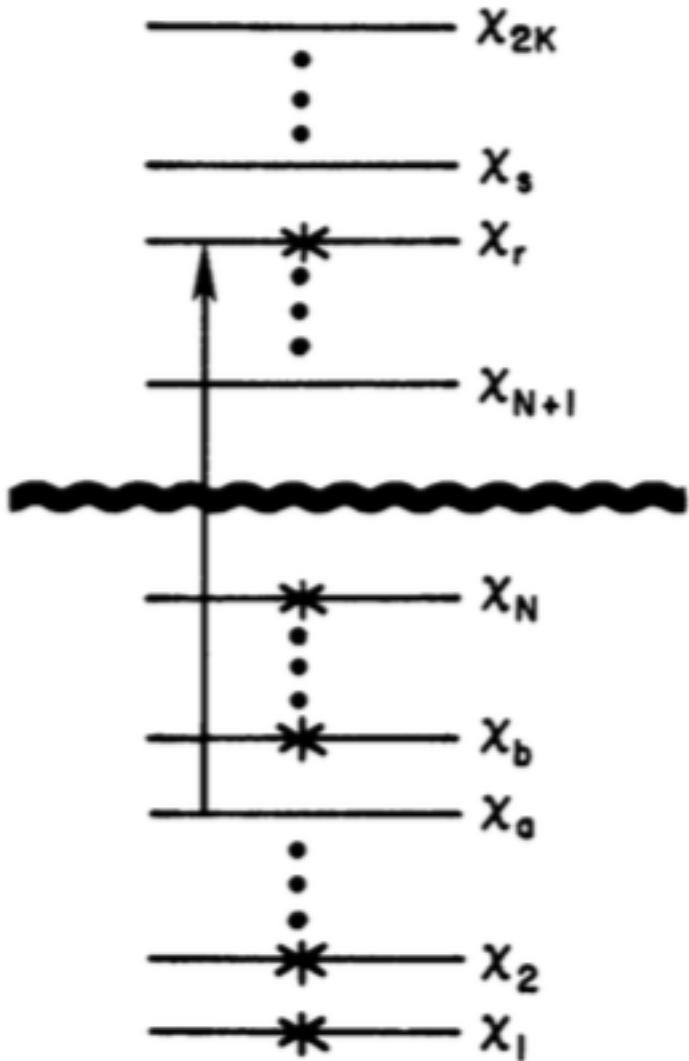
Alternative notation: $|\Psi_0\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle$

$$\begin{array}{ll} \chi_1 \equiv \psi_1 & \chi_2 \equiv \bar{\psi}_1 \\ \chi_3 \equiv \psi_2 & \chi_4 \equiv \bar{\psi}_2 \end{array}$$

The definition of excited states

Single excited determinant:

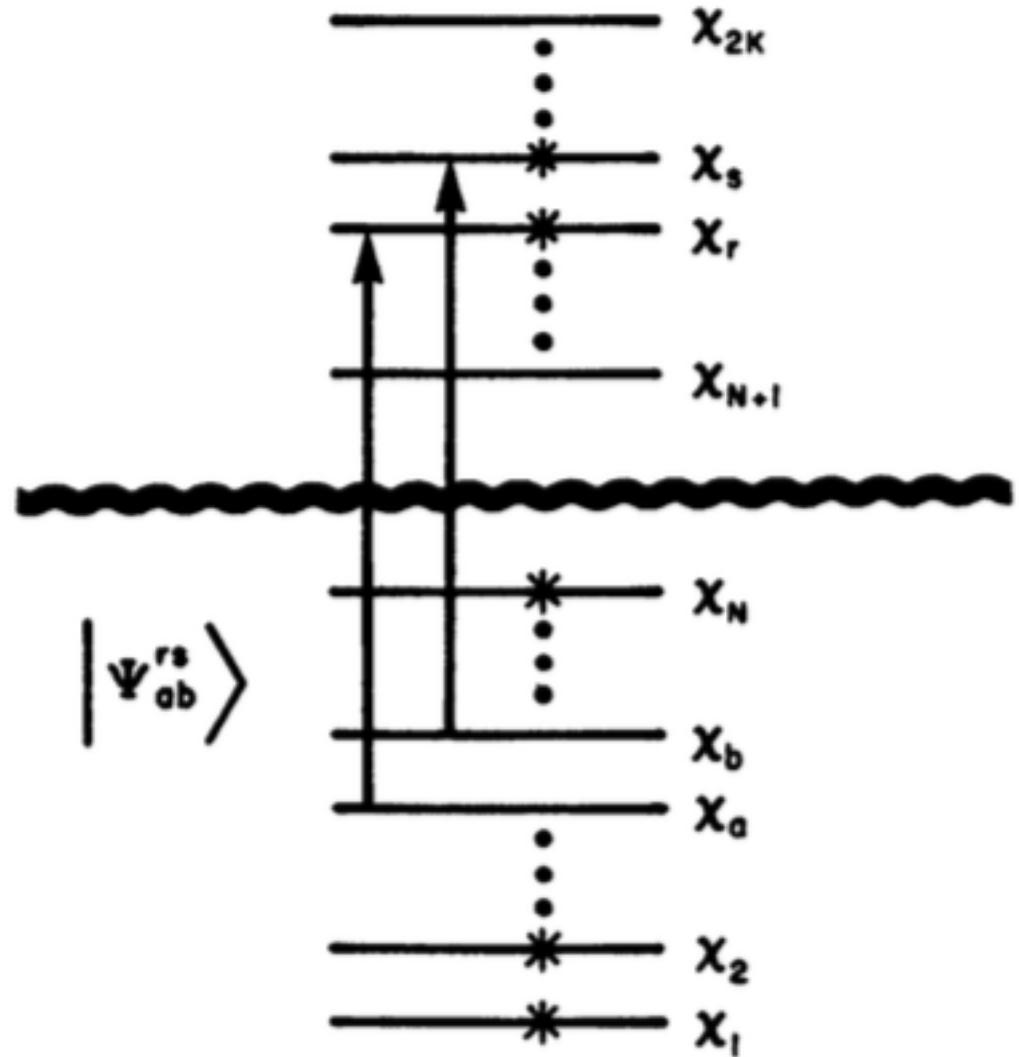
$$|\Psi_a^r\rangle = |\chi_1 \chi_2 \cdots \chi_r \chi_b \cdots \chi_N\rangle$$

$$|\Psi_a^r\rangle$$


The definition of excited states

Doubly excited determinant:

$$|\Psi_{ab}^{rs}\rangle = |\chi_1\chi_2 \cdots \chi_r\chi_s \cdots \chi_N\rangle$$



Assuming a complete set of basis functions $\{\chi_i(x)\}$, we can expand any function of two variables via

$$\Phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1)$$

The first coefficient can be expanded as well:

$$a_i(x_2) = \sum_j b_{ij} \chi_j(x_2)$$

This leads to

$$\Phi(x_1, x_2) = \sum_{ij} b_{ij} \chi_i(x_1) \chi_j(x_2)$$

For antisymmetric wf, we have to insist that $b_{ij} = -b_{ji}$ and $b_{ii} = 0$,

$$\begin{aligned} \Phi(x_1, x_2) &= \sum_i \sum_{j>i} b_{ij} [\chi_i(x_1) \chi_j(x_2) - \chi_j(x_1) \chi_i(x_2)] \\ &= \sum_{i<j} 2^{1/2} b_{ij} |\chi_i \chi_j\rangle \end{aligned}$$

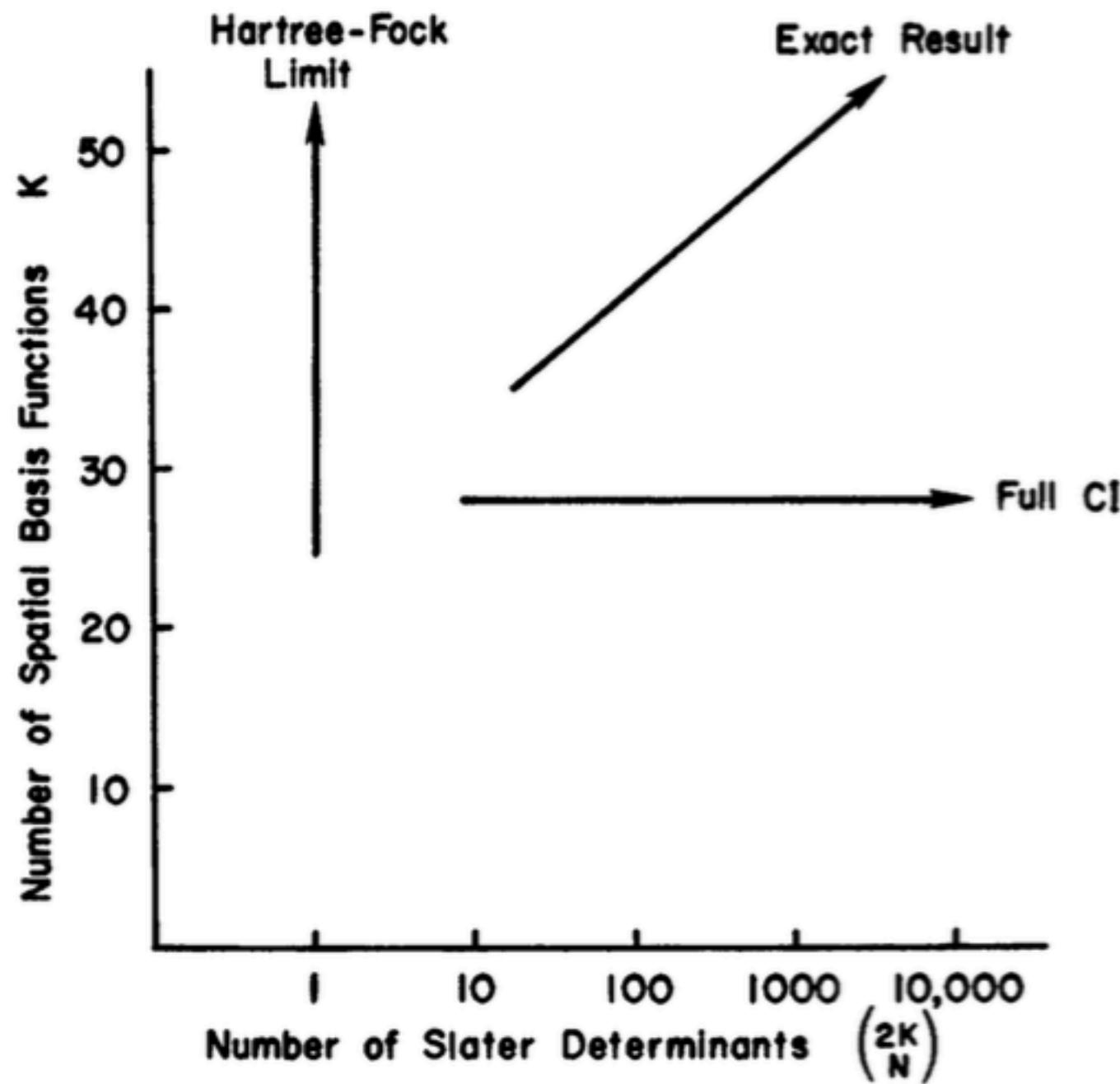
Generalization to more variables, i.e. the N electron problem:

$$|\Phi\rangle = c_0 |\Psi_0\rangle + \sum_{ra} c_a^r |\Psi_a^r\rangle + \sum_{\substack{a < b \\ r < s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a < b < c \\ r < s < t}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \dots$$

Definition of the HF energy: $E_{\text{corr}} = E_0 - E_0$

Only approached in case of infinite basis set. However, even relatively small finite basis is already tricky...

The basis $\{\chi_i | i = 1, 2, \dots, 2K\}$ yields $\binom{2K}{N}$ determinants!

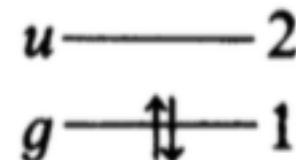


Let's visit H₂ again:

$$N = 2 \quad \binom{4}{2} = \frac{4!}{2!2!} = 6$$

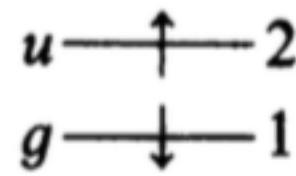
Ground state

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle$$

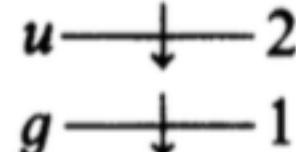


Single excitations

$$|\Psi_1^2\rangle = |2\bar{1}\rangle$$



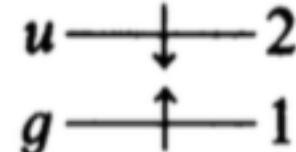
$$|\Psi_1^1\rangle = |\bar{2}1\rangle$$



$$|\Psi_1^2\rangle = |12\rangle$$

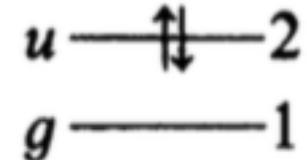


$$|\Psi_1^1\rangle = |1\bar{2}\rangle$$



Double excitations

$$|\Psi_{11}^{22}\rangle = |2\bar{2}\rangle$$



For symmetry reasons we obtain

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + c_{1\bar{1}}^{2\bar{2}}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle$$

How are coefficients evaluated?

Minimum energy wf

$$\mathbf{H} = \begin{pmatrix} \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle & \langle \Psi_0 | \mathcal{H} | \Psi_{1\bar{1}}^{2\bar{2}} \rangle \\ \langle \Psi_{1\bar{1}}^{2\bar{2}} | \mathcal{H} | \Psi_0 \rangle & \langle \Psi_{1\bar{1}}^{2\bar{2}} | \mathcal{H} | \Psi_{1\bar{1}}^{2\bar{2}} \rangle \end{pmatrix}$$

By diagonalization of the CI matrix!

Let's have a closer look at these matrix elements...

Operators and matrix elements

Continuing our thoughts on H₂, lets have a look at the Hamiltonian first again:

$$\mathcal{H} = \left(-\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \left(-\frac{1}{2} \nabla_2^2 - \sum_A \frac{Z_A}{r_{2A}} \right) + \frac{1}{r_{12}}$$

$$= h(1) + h(2) + \frac{1}{r_{12}}$$

two electron term

'Core Hamiltonian', a one-electron term

How do matrix elements look like for Slater determinants?

Operators and matrix elements

$$\begin{aligned} \langle \Psi_0 | h(1) | \Psi_0 \rangle &= \int d\mathbf{x}_1 d\mathbf{x}_2 [2^{-1/2}(\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2))]^* \\ &\quad \times h(\mathbf{r}_1)[2^{-1/2}(\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2))] \\ &= \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 \{ \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)h(\mathbf{r}_1)\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) + \chi_2^*(\mathbf{x}_1)\chi_1^*(\mathbf{x}_2)h(\mathbf{r}_1)\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) \\ &\quad - \cancel{\chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)h(\mathbf{r}_1)\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)} - \cancel{\chi_2^*(\mathbf{x}_1)\chi_1^*(\mathbf{x}_2)h(\mathbf{r}_1)\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)} \} \end{aligned}$$

Zero after integration over \mathbf{x}_2

$$\langle \Psi_0 | h(1) | \Psi_0 \rangle = \frac{1}{2} \int d\mathbf{x}_1 \chi_1^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_1(\mathbf{x}_1) + \frac{1}{2} \int d\mathbf{x}_1 \chi_2^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_2(\mathbf{x}_1)$$

Finally, since $\langle \Psi_0 | h(2) | \Psi_0 \rangle = \langle \Psi_0 | h(1) | \Psi_0 \rangle$:

$$\langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle = \int d\mathbf{x}_1 \chi_1^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_1(\mathbf{x}_1) + \int d\mathbf{x}_1 \chi_2^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_2(\mathbf{x}_1)$$

Or, in short hand notation: $\boxed{\langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle = \langle 1|h|1 \rangle + \langle 2|h|2 \rangle}$

Operators and matrix elements

$$\begin{aligned}
 \langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle &= \int d\mathbf{x}_1 d\mathbf{x}_2 [2^{-1/2}(\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2))]^* \\
 &\quad \times r_{12}^{-1}[2^{-1/2}(\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2))] \\
 &= \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 \{ \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) + \chi_2^*(\mathbf{x}_1)\chi_1^*(\mathbf{x}_2)r_{12}^{-1}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) \\
 &\quad - \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) - \chi_2^*(\mathbf{x}_1)\chi_1^*(\mathbf{x}_2)r_{12}^{-1}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \}
 \end{aligned}$$

First and second term are equal, so are third and forth, since $r_{12} = r_{21}$

$$\begin{aligned}
 \langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle &= \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \\
 &\quad - \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)
 \end{aligned}$$

Which we write as

$$\boxed{\langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle = \langle 12 | 12 \rangle - \langle 12 | 21 \rangle}$$

Operators and matrix elements

where we introduce a short notation for two-electron integrals:

$$\langle ij | kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2)$$

It's still too much to write for busy computational chemists, so we further introduce the notation

$$\begin{aligned} \langle ij || kl \rangle &= \langle ij | kl \rangle - \langle ij | lk \rangle \\ &= \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} (1 - \mathcal{P}_{12}) \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) \end{aligned}$$

Note the following relations:

$$\langle ij | kl \rangle = \langle ji | lk \rangle \quad \langle ij | kl \rangle = \langle kl | ij \rangle^* \quad \langle ij || kk \rangle = 0$$

Operators and matrix elements

Watch out, sometimes an alternative notation is used (Chemists' notation) :

$$[i|h|j] = \langle i|h|j \rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1)$$

$$[ij|kl] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) r_{12}^{-1} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2)$$

And yet another one for pure spatial orbitals...

$$(i|h|j) = h_{ij} = (\psi_i|h|\psi_j) = \int d\mathbf{r}_1 \psi_i^*(\mathbf{r}_1) h(\mathbf{r}_1) \psi_j(\mathbf{r}_1)$$

$$(ij|kl) = (\psi_i\psi_j|\psi_k\psi_l) = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1) r_{12}^{-1} \psi_k^*(\mathbf{r}_2) \psi_l(\mathbf{r}_2)$$

$J_{ij} = (ii|jj)$ Coulomb integrals

$K_{ij} = (ij|ji)$ Exchange integrals

Generalizations

The one-electron operator $\mathcal{O}_1 = \sum_{i=1}^N h(i)$

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

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

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

$|L\rangle = |\cdots pn \cdots\rangle$

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

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

$|L\rangle = |\cdots pq \cdots\rangle$

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

Generalizations

The two-electron operator

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

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

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

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

$$|L\rangle = |\cdots pn \cdots\rangle$$

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

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

$$|L\rangle = |\cdots pq \cdots\rangle$$

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

Generalizations

With that, the HF energy can be rewritten as

$$E_0 = \sum_a^N \langle a | h | a \rangle + \frac{1}{2} \sum_a^N \sum_b^N \langle ab | | ab \rangle \quad \text{or}$$

$$E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \sum_a^N [a | h | a] + \frac{1}{2} \sum_a^N \sum_b^N [aa | bb] - [ab | ba]$$



What happens if $a == b$?

From spin to spatial orbitals

Again, back to H₂ first:

$$E_0 = \langle \chi_1 | h | \chi_1 \rangle + \langle \chi_2 | h | \chi_2 \rangle + \langle \chi_1 \chi_2 | \chi_1 \chi_2 \rangle - \langle \chi_1 \chi_2 | \chi_2 \chi_1 \rangle$$

$$E_0 = [\chi_1 | h | \chi_1] + [\chi_2 | h | \chi_2] + [\chi_1 \chi_2 | \chi_2 \chi_2] - [\chi_1 \chi_2 | \chi_2 \chi_1]$$

Spin orbitals are products of spatial functions times spin:

$$\chi_1(\mathbf{x}) \equiv \psi_1(\mathbf{x}) = \psi_1(\mathbf{r})\alpha(\omega)$$

$$\chi_2(\mathbf{x}) \equiv \bar{\psi}_1(\mathbf{x}) = \psi_1(\mathbf{r})\beta(\omega)$$

$$E_0 = [\psi_1 | h | \psi_1] + [\bar{\psi}_1 | h | \bar{\psi}_1] + [\psi_1 \psi_1 | \bar{\psi}_1 \bar{\psi}_1] - [\psi_1 \bar{\psi}_1 | \bar{\psi}_1 \psi_1]$$

From spin to spatial orbitals

Using $\langle \beta | \beta \rangle = 1$, we have

$$[\bar{\psi}_1 | h | \bar{\psi}_1] = \int d\mathbf{r}_1 \psi_1^*(\mathbf{r}_1) h(\mathbf{r}_1) \psi_1(\mathbf{r}_1) \equiv (\psi_1 | h | \psi_1)$$

In general:

$$[\psi_i | h | \psi_j] = [\bar{\psi}_i | h | \bar{\psi}_j] = (\psi_i | h | \psi_j)$$

$$[\psi_i | h | \bar{\psi}_j] = [\bar{\psi}_i | h | \psi_j] = 0$$

For two-electron integrals:

$$\begin{aligned} [\psi_1 \psi_1 | \bar{\psi}_1 \bar{\psi}_1] &= \int d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 \psi_1^*(\mathbf{r}_1) \alpha^*(\omega_1) \psi_1(\mathbf{r}_1) \alpha(\omega_1) r_{12}^{-1} \\ &\quad \times \psi_1^*(\mathbf{r}_2) \beta^*(\omega_2) \psi_1(\mathbf{r}_2) \beta(\omega_2) \end{aligned}$$

$$\begin{aligned} [\psi_1 \psi_1 | \bar{\psi}_1 \bar{\psi}_1] &= \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_1^*(\mathbf{r}_1) \psi_1(\mathbf{r}_1) r_{12}^{-1} \psi_1^*(\mathbf{r}_2) \psi_1(\mathbf{r}_2) \\ &\equiv (\psi_1 \psi_1 | \psi_1 \psi_1) \end{aligned}$$

From spin to spatial orbitals

But:

$$[\psi_1 \bar{\psi}_1 | \bar{\psi}_1 \psi_1] = \int d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 \psi_1^*(\mathbf{r}_1) \alpha^*(\omega_1) \psi_1(\mathbf{r}_1) \beta(\omega_1) r_{12}^{-1}$$
$$\times \psi_1^*(\mathbf{r}_2) \beta(\omega_2) \psi_1(\mathbf{r}_2) \alpha(\omega_2) = 0$$



Check the bars on each side!

In general:

$$[\psi_i \psi_j | \psi_k \psi_l] = [\psi_i \psi_j | \bar{\psi}_k \bar{\psi}_l] = [\bar{\psi}_i \bar{\psi}_j | \psi_k \psi_l] = [\bar{\psi}_i \bar{\psi}_j | \bar{\psi}_k \bar{\psi}_l] = (\psi_i \psi_j | \psi_k \psi_l)$$

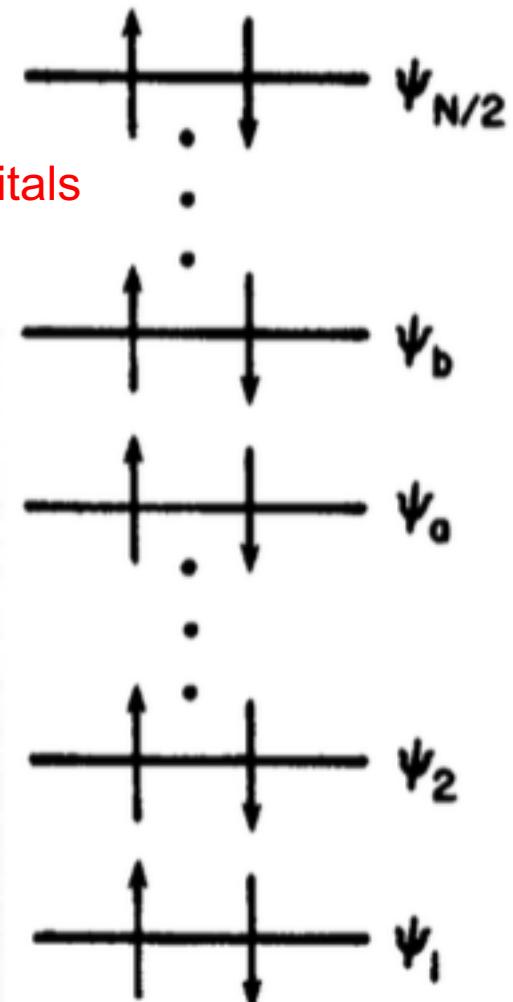
From spin to spatial orbitals

What about **closed-shell** wave functions?

$$\begin{aligned} |\Psi_0\rangle &= |\chi_1\chi_2\chi_3\chi_4 \cdots \chi_{N-1}\chi_N\rangle \\ &= |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2 \cdots \psi_{N/2}\bar{\psi}_{N/2}\rangle \end{aligned}$$

$$E_0 = \sum_a^N [a|h|a] + \frac{1}{2} \sum_a^N \sum_b^N [aa|bb] - [ab|ba]$$

of spin orbitals



From spin to spatial orbitals

Let's split the sums in alpha and beta parts...

$$\sum_a^N \chi_a = \sum_a^{N/2} \psi_a + \sum_a^{N/2} \bar{\psi}_a$$

Same for the double sums:

$$\begin{aligned}\sum_a^N \sum_b^N \chi_a \chi_b &= \sum_a^N \chi_a \sum_b^N \chi_b \\ &= \sum_a^{N/2} (\psi_a + \bar{\psi}_a) \sum_b^{N/2} (\psi_b + \bar{\psi}_b) \\ &= \sum_a^{N/2} \sum_b^{N/2} \psi_a \psi_b + \psi_a \bar{\psi}_b + \bar{\psi}_a \psi_b + \bar{\psi}_a \bar{\psi}_b\end{aligned}$$

From spin to spatial orbitals

Now reduce the equation:

$$E_0 = \sum_a^N [a|h|a] + \frac{1}{2} \sum_a^N \sum_b^N [aa|bb] - [ab|ba]$$

The one-electron terms first:

$$\sum_a^N [a|h|a] = \sum_a^{N/2} [a|h|a] + \sum_a^{N/2} [\bar{a}|h|\bar{a}] = 2 \sum_a^{N/2} (\psi_a|h|\psi_a)$$

From spin to spatial orbitals

Then, the two-electron terms:

$$\frac{1}{2} \sum_a^N \sum_b^N [aa|bb] - [ab|ba]$$

$$= \frac{1}{2} \left\{ \sum_a^{N/2} \sum_b^{N/2} [aa|bb] - [ab|ba] + \sum_a^{N/2} \sum_b^{N/2} [aa|\bar{bb}] - [\bar{ab}|\bar{ba}] \right. \\ \left. + \sum_a^{N/2} \sum_b^{N/2} [\bar{aa}|bb] - [\bar{ab}|b\bar{a}] + \sum_a^{N/2} \sum_b^{N/2} [\bar{aa}|\bar{bb}] - [\bar{ab}|\bar{ba}] \right\}$$

$$= \sum_a^{N/2} \sum_b^{N/2} 2(\psi_a \psi_a | \psi_b \psi_b) - (\psi_a \psi_b | \psi_b \psi_a)$$

We obtain:

$$E_0 = 2 \sum_a^{N/2} (\psi_a | h | \psi_a) + \sum_a^{N/2} \sum_b^{N/2} 2(\psi_a \psi_a | \psi_b \psi_b) - (\psi_a \psi_b | \psi_b \psi_a)$$

From spin to spatial orbitals

Rewritten in chemists' notation for spatial orbitals:

$$E_0 = 2 \sum_a (a|h|a) + \sum_{ab} 2(aa|bb) - (ab|ba)$$

And in physicists' notation (not unambiguous without limits, see convention below)

$$E_0 = 2 \sum_a^{N/2} \langle a|h|a \rangle + \sum_{ab}^{N/2} 2\langle ab|ab \rangle - \langle ab|ba \rangle$$

(e.g. here the limits are $n/2$, therefore it must be spatial orbitals)

Coulomb and Exchange Integrals

First, the one-electron part:

$$(a|h|a) \equiv h_{aa} = \int d\mathbf{r}_1 \psi_a^*(\mathbf{r}_1) \left(-\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \right) \psi_a(\mathbf{r}_1)$$

Now let's have a closer look at the two-electron integrals and indices:

$$(aa|bb) = \int d\mathbf{r}_1 d\mathbf{r}_2 |\psi_a(\mathbf{r}_1)|^2 r_{12}^{-1} |\psi_b(\mathbf{r}_2)|^2 \quad J_{ij} = (ii|jj) = \langle ij | ij \rangle$$

Coulomb integral

$$(ab|ba) = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_a^*(\mathbf{r}_1) \psi_b(\mathbf{r}_1) r_{12}^{-1} \psi_b^*(\mathbf{r}_2) \psi_a(\mathbf{r}_2) \quad K_{ij} = (ij|ji) = \langle ij | ji \rangle$$

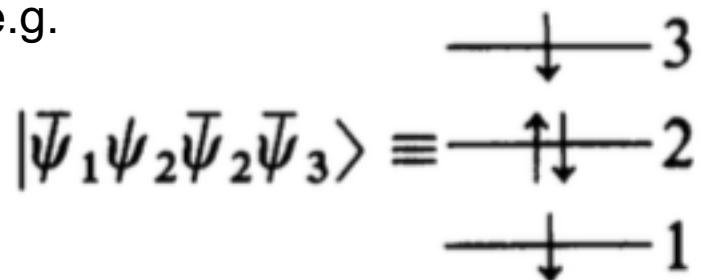
Exchange integral

We obtain:

$$E_0 = 2 \sum_a h_{aa} + \sum_{ab} 2J_{ab} - K_{ab}$$

Coulomb and Exchange Integrals

The contributions to the total energy can be easily derived for any given wf, also for an open shell wf such as e.g.



by applying the following rules:

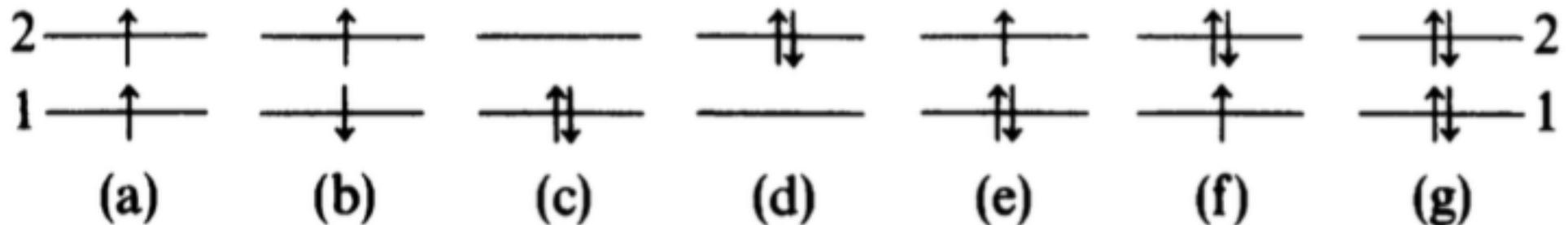
1. Each electron in orbital i , irrespective of spin, contributes the term h_{ii} to the energy.
2. Each unique pair of electrons in spatial orbitals i and j , irrespective of their spin, contributes a term J_{ij} to the energy.
3. Each unique pair of electrons in spatial orbitals i and j with parallel spin contributes a term K_{ij} to the energy.

Here:

$$h_{11} + 2h_{22} + h_{33} + J_{22} + J_{13} + 2J_{12} + 2J_{23} - K_{23} - K_{12} - K_{13}$$

Coulomb and Exchange Integrals

Other examples:



- a. $h_{11} + h_{22} + J_{12} - K_{12}$.
- b. $h_{11} + h_{22} + J_{12}$.
- c. $2h_{11} + J_{11}$.
- d. $2h_{22} + J_{22}$.
- e. $2h_{11} + h_{22} + J_{11} + 2J_{12} - K_{12}$.
- f. $2h_{22} + h_{11} + J_{22} + 2J_{12} - K_{12}$.
- g. $2h_{11} + 2h_{22} + J_{11} + J_{22} + 4J_{12} - 2K_{12}$.

Spin-adapted configurations

We start with single electron wfs:

$$s^2|s, m_s\rangle = s(s+1)|s, m_s\rangle$$

$$s_z|s, m_s\rangle = m_s|s, m_s\rangle$$

Its spin state is fully described by these two quantum numbers. With this choice, we have

$$s^2|\alpha\rangle = \frac{3}{4}|\alpha\rangle,$$

$$s^2|\beta\rangle = \frac{3}{4}|\beta\rangle$$

$$s_x|\alpha\rangle = \frac{1}{2}|\beta\rangle,$$

$$s_x|\beta\rangle = \frac{1}{2}|\alpha\rangle$$

$$s_z|\alpha\rangle = \frac{1}{2}|\alpha\rangle,$$

$$s_z|\beta\rangle = -\frac{1}{2}|\beta\rangle$$

$$s_y|\alpha\rangle = \frac{i}{2}|\beta\rangle,$$

$$s_y|\beta\rangle = -\frac{i}{2}|\alpha\rangle$$

We further define ladder operators: $s_+ = s_x + is_y$

$$s_- = s_x - is_y$$

with the effect

$$s_+|\alpha\rangle = 0,$$

$$s_+|\beta\rangle = |\alpha\rangle$$

$$s_-|\alpha\rangle = |\beta\rangle,$$

$$s_-|\beta\rangle = 0$$

Spin-adapted configurations

Using the commutator relations for angular momenta,

$$[s_x, s_y] = i s_z, \quad [s_y, s_z] = i s_x, \quad [s_z, s_x] = i s_y$$

The total spin operator can also be expressed by the ladder operators plus one component:

$$\mathbf{s}^2 = s_+ s_- - s_z + s_z^2$$

$$\mathbf{s}^2 = s_- s_+ + s_z + s_z^2$$

NOW: Adaptation to many electron systems!

We define the total spin angular momentum as

$$\vec{\mathcal{S}} = \sum_{i=1}^N \vec{s}(i)$$

Projections:

$$\mathcal{S}_I = \sum_{i=1}^N s_I(i) \quad I = x, y, z$$

Ladder:

$$\mathcal{S}_\pm = \sum_{i=1}^N s_\pm(i)$$

(def. works for Slater determinants)

Spin-adapted configurations

$$\begin{aligned}\mathcal{S}^2 &= \vec{\mathcal{S}} \cdot \vec{\mathcal{S}} = \sum_{i=1}^N \sum_{j=1}^N \vec{s}(i) \cdot \vec{s}(j) \\ &= \mathcal{S}_+ \mathcal{S}_- - \mathcal{S}_z + \mathcal{S}_z^2 \\ &= \mathcal{S}_- \mathcal{S}_+ + \mathcal{S}_z + \mathcal{S}_z^2\end{aligned}$$

Since our Hamiltonian is independent of spin we know

$$[\mathcal{H}, \mathcal{S}^2] = 0 = [\mathcal{H}, \mathcal{S}_z]$$

Which tells us, that they share a set of eigenfunctions:

$$\mathcal{S}^2 |\Phi\rangle = S(S+1) |\Phi\rangle$$

$$\mathcal{S}_z |\Phi\rangle = M_S |\Phi\rangle$$

Spin-adapted configurations

How can we make sure that our total electron wf is an eigenfunction of \mathcal{S}^2 and \mathcal{S}_z ?

Easy case: Restricted closed-shell determinant

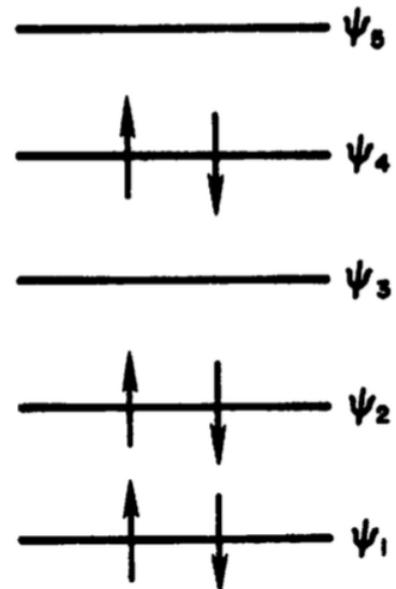
Easy case: Restricted open-shell determinant with parallel spins in singly occ. orbitals

Medium case: Restricted open-shell determinant without further restrictions

Impossible case: Unrestricted open-shell determinants

Spin-adapted configurations

Restricted closed shell wf:

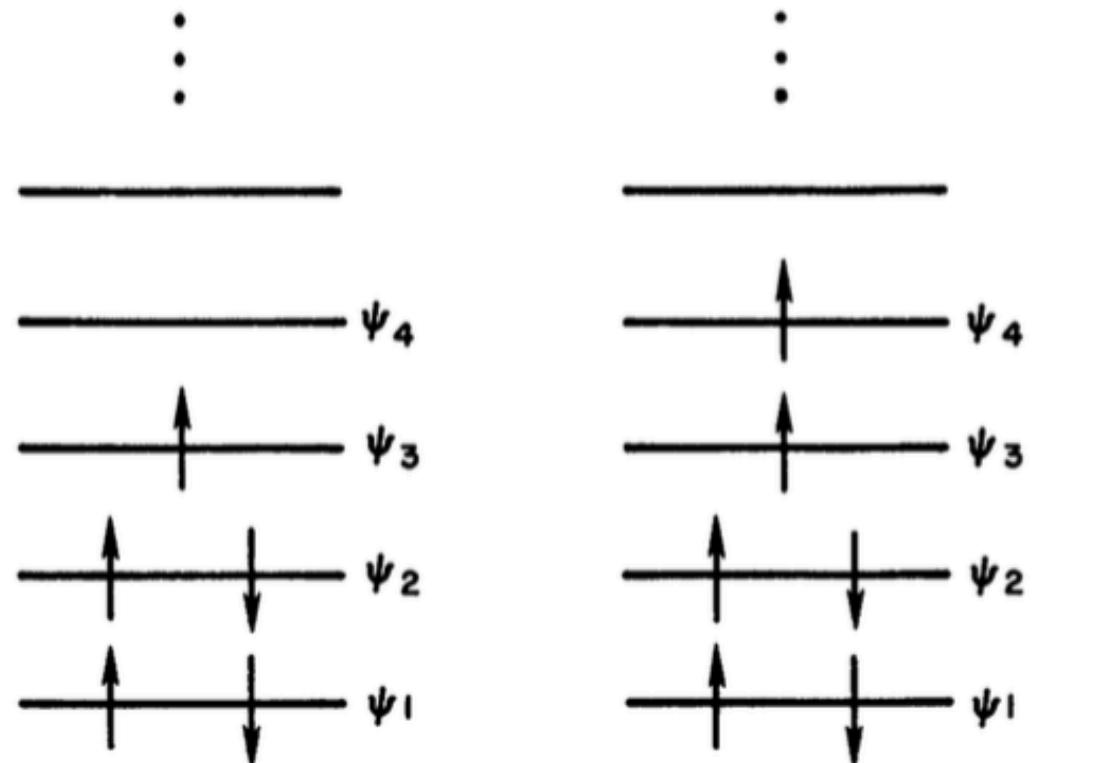


$$|\Psi\rangle = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_4 \bar{\psi}_4\rangle$$

$S = 0, M_S = 0$

Spin-adapted configurations

Restricted open shell, special case:



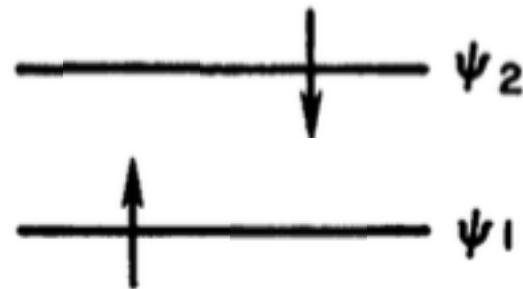
$$|{}^2\Psi\rangle = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3\rangle \quad |{}^3\Psi\rangle = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \psi_4\rangle$$

$$S = 1/2, M_S = 1/2$$

$$S = 1, M_S = 1$$

Spin-adapted configurations

Restricted open shell, problematic case:



$$M_S = 0, \text{ but } S = ?$$

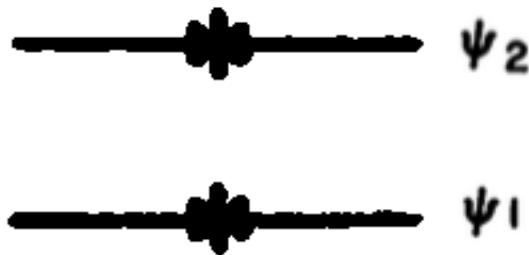
The solution:

$$\begin{aligned} |^1\Psi_1^2\rangle &= 2^{-1/2}(|\Psi_1^{\frac{1}{2}}\rangle + |\Psi_1^{\frac{3}{2}}\rangle) \\ &= 2^{-1/2}(|1\bar{2}\rangle + |2\bar{1}\rangle) \\ &= 2^{-1/2}[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)]2^{-1/2}(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \end{aligned}$$

Spin-adapted configurations

Restricted open shell, problematic case:

Arrow notation does no longer apply!



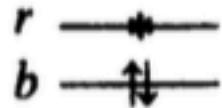
M_S = 0, but S = ?

The solution:

$$\begin{aligned} |^1\Psi_1^2\rangle &= 2^{-1/2}(|\Psi_1^{\bar{2}}\rangle + |\Psi_1^2\rangle) \\ &= 2^{-1/2}(|1 \bar{2}\rangle + |2 \bar{1}\rangle) \\ &= 2^{-1/2}[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)]2^{-1/2}(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \end{aligned}$$

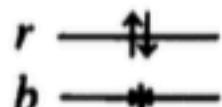
Spin-adapted configurations

Restricted open shell, general case, double excitation examples:



$$|{}^1\Psi_{aa}^{rs}\rangle = 2^{-1/2}(|\Psi_{aa}^{r\bar{r}}\rangle + |\Psi_{aa}^{s\bar{r}}\rangle)$$

$$S = 0, M_S = 0$$



$$|{}^1\Psi_{ab}^{rr}\rangle = 2^{-1/2}(|\Psi_{ab}^{\bar{r}r}\rangle + |\Psi_{ab}^{r\bar{r}}\rangle)$$

$$S = 0, M_S = 0$$



$$|{}^4\Psi_{ab}^{rs}\rangle = (12)^{-1/2}(2|\Psi_{ab}^{rs}\rangle + 2|\Psi_{ab}^{\bar{r}\bar{s}}\rangle - |\Psi_{ab}^{\bar{s}r}\rangle + |\Psi_{ab}^{\bar{r}s}\rangle + |\Psi_{ab}^{r\bar{s}}\rangle - |\Psi_{ab}^{s\bar{r}}\rangle)$$



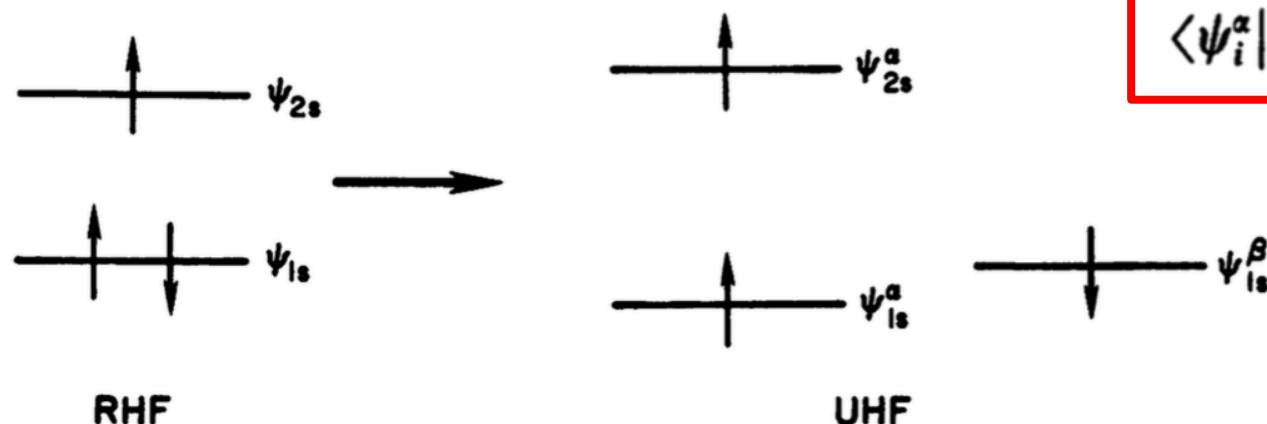
$$|{}^B\Psi_{ab}^{rs}\rangle = \frac{1}{2}(|\Psi_{ab}^{\bar{r}r}\rangle + |\Psi_{ab}^{\bar{s}s}\rangle + |\Psi_{ab}^{r\bar{s}}\rangle + |\Psi_{ab}^{s\bar{r}}\rangle)$$

$$S = 0, M_S = 0$$

Spin-adapted configurations

Unrestricted open shell, very problematic case

Example: the Li atom



$$|{}^2\Psi_{\text{RHF}}\rangle = |\psi_{1s}\bar{\psi}_{1s}\psi_{2s}\rangle$$

$$M_S = 1/2, S = 1/2$$

$$|\Psi_{\text{UHF}}\rangle = |\psi_{1s}^a\bar{\psi}_{1s}^b\psi_{2s}^a\rangle$$

$$M_S = 1/2, \text{ but } S = ?$$

Unrestricted determinants are not eigenfunctions of S^2 and can not be spin-adapted!
 However, their energy is lower, and they are often good approximations to higher spin states.

Spin-adapted configurations

Unrestricted open shell, very problematic case

Example: the Li atom

Unrestricted wfs are always contaminated by higher spin components. They can be expanded as

$$|{}^1\Psi\rangle = c_1^1|1\rangle + c_3^1|3\rangle + c_5^1|5\rangle + \dots$$

And their expectation value for S^2 is given by

$$\langle S^2 \rangle_{\text{UHF}} = \langle S^2 \rangle_{\text{Exact}} + N^\beta - \sum_i^N \sum_j^N |S_{ij}^{\alpha\beta}|^2$$

with

$$\langle S^2 \rangle_{\text{Exact}} = \left(\frac{N^\alpha - N^\beta}{2} \right) \left(\frac{N^\alpha - N^\beta}{2} + 1 \right)$$

and

$$\langle \psi_i^\alpha | \psi_j^\beta \rangle = S_{ij}^{\alpha\beta}$$

The Hartree Fock Approximation

The Hartree-Fock Approximation

Quick overview

The ground state wf: $|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$

Its corresponding energy: $E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_{ab} \langle ab | | ab \rangle$

$$= \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_{ab} [aa | bb] - [ab | ba]$$

How do we determine the MOs?

By solving a set of integro-differential equations, stemming from a minimization with respect to energy under the constraint

$$\langle \chi_a | \chi_b \rangle = \delta_{ab}$$

The Hartree-Fock Approximation

Quick overview

These equations, the Hartree-Fock equations, have the form:

$$h(1)\chi_a(1) + \sum_{b \neq a} \left[\int d\mathbf{x}_2 |\chi_b(2)|^2 r_{12}^{-1} \right] \chi_a(1) - \sum_{b \neq a} \left[\int d\mathbf{x}_2 \chi_b^*(2) \chi_a(2) r_{12}^{-1} \right] \chi_b(1) = \varepsilon_a \chi_a(1)$$

with $h(1) = -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}}$

We define two operators,

Coulomb: $\mathcal{J}_b(1)\chi_a(1) = \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) \right] \chi_a(1)$

Exchange: $\mathcal{K}_b(1)\chi_a(1) = \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_a(2) \right] \chi_b(1)$

nonlocal!

The Hartree-Fock Approximation

Quick overview

How are these operators related to the Coulomb and exchange integrals J and K ?

$$\langle \chi_a(1) | \mathcal{J}_b(1) | \chi_a(1) \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_a^*(1) \chi_a(1) r_{12}^{-1} \chi_b^*(2) \chi_b(2) = [aa|bb]$$

$$\langle \chi_a(1) | \mathcal{K}_b(1) | \chi_a(1) \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_a^*(1) \chi_b(1) r_{12}^{-1} \chi_b^*(2) \chi_a(2) = [ab|ba]$$

(Chemist's notation ☺)

We can now rewrite the HF equations as

$$\left[h(1) + \sum_{b \neq a} \mathcal{J}_b(1) - \sum_{b \neq a} \mathcal{K}_b(1) \right] \chi_a(1) = \varepsilon_a \chi_a(1)$$

or shorter as

$$f|\chi_a\rangle = \varepsilon_a |\chi_a\rangle$$

Fock operator

The Hartree-Fock Approximation

Quick overview

The Fock operator is defined as $f(\mathbf{l}) = h(\mathbf{l}) + \sum_b \mathcal{J}_b(\mathbf{l}) - \mathcal{K}_b(\mathbf{l}),$

where we have used that $[\mathcal{J}_a(\mathbf{l}) - \mathcal{K}_a(\mathbf{l})]\chi_a(\mathbf{l}) = 0$

We can interpret the Fock operator as an effective one-electron operator with two terms:

$$f(\mathbf{l}) = h(\mathbf{l}) + v^{\text{HF}}(\mathbf{l})$$

The second term corresponds to the HF potential $v^{\text{HF}}(\mathbf{l}) = \sum_b \mathcal{J}_b(\mathbf{l}) - \mathcal{K}_b(\mathbf{l})$

The Hartree-Fock Approximation

Quick overview

Again, note the effect of K on orbital a :

$$\begin{aligned}\mathcal{K}_b(1)\chi_a(1) &= \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_a(2) \right] \chi_b(1) \\ &= \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \mathcal{P}_{12} \chi_b(2) \right] \chi_a(1)\end{aligned}$$

Here we introduced the particle exchange operator. With it, the Fock operator takes the form

$$\begin{aligned}f(1) &= h(1) + v^{\text{HF}}(1) \\ &= h(1) + \sum_b \int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} (1 - \mathcal{P}_{12}) \chi_b(2)\end{aligned}$$

The Hartree-Fock Approximation

Now the derivation: Minimizing the energy of a Slater determinant
with respect to its spin orbitals...

We minimize under the constraint of orthonormal spin orbitals:

$$\int d\mathbf{x}_1 \chi_a^*(1)\chi_b(1) = [a|b] = \delta_{ab}$$

Therefore, we apply the technique of Lagrange multipliers:

$$\mathcal{L}[\{\chi_a\}] = E_0[\{\chi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba}([a|b] - \delta_{ab})$$

with the energy given by

Kronecker delta

$$E_0[\{\chi_a\}] = \sum_{a=1}^N [a|h|a] + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [aa|bb] - [ab|ba]$$

The Hartree-Fock Approximation

Now the derivation: Minimizing the energy of a Slater determinant
with respect to its spin orbitals...

We introduce an infinitesimal variation to the spin orbitals $\chi_a \rightarrow \chi_a + \delta\chi_a$

$$\delta\mathcal{L} = \delta E_0 - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} \delta[a|b] = 0$$

With $\delta[a|b] = [\delta\chi_a|\chi_b] + [\chi_a|\delta\chi_b]$ we obtain

$$\begin{aligned} \delta E_0 &= \sum_{a=1}^N [\delta\chi_a|h|\chi_a] + [\chi_a|h|\delta\chi_a] \\ &\quad + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a\chi_a|\chi_b\chi_b] + [\chi_a\delta\chi_a|\chi_b\chi_b] + [\chi_a\chi_a|\delta\chi_b\chi_b] + [\chi_a\chi_a|\chi_b\delta\chi_b] \\ &\quad - \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a\chi_b|\chi_b\chi_a] + [\chi_a\delta\chi_b|\chi_b\chi_a] + [\chi_a\chi_b|\delta\chi_b\chi_a] + [\chi_a\chi_b|\chi_b\delta\chi_a] \end{aligned}$$

The Hartree-Fock Approximation

Now the derivation: Minimizing the energy of a Slater determinant
with respect to its spin orbitals...

We introduce an infinitesimal variation to the spin orbitals $\chi_a \rightarrow \chi_a + \delta\chi_a$

$$\delta\mathcal{L} = \delta E_0 - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} \delta[a|b] = 0$$

With $\delta[a|b] = [\delta\chi_a|\chi_b] + [\chi_a|\delta\chi_b]$ we obtain

$$\begin{aligned} \delta E_0 &= \sum_{a=1}^N [\delta\chi_a|h|\chi_a] + [\chi_a|h|\delta\chi_a] \\ &\quad + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a\chi_a|\chi_b\chi_b] + [\chi_a\delta\chi_a|\chi_b\chi_b] + [\chi_a\chi_a|\delta\chi_b\chi_b] + [\chi_a\chi_b|\chi_b\delta\chi_b] \\ &\quad - \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a\chi_b|\chi_b\chi_a] + [\chi_a\delta\chi_b|\chi_b\chi_a] + [\chi_a\chi_b|\delta\chi_b\chi_a] + [\chi_a\chi_b|\chi_b\delta\chi_a] \end{aligned}$$

same terms after renaming indices

The Hartree-Fock Approximation

Now the derivation: Minimizing the energy of a Slater determinant
with respect to its spin orbitals...

With $\langle ij | kl \rangle = \langle kl | ij \rangle^*$ or $[ij | kl] = [ji | lk]^*$ this can be written as

$$\delta E_0 = \sum_{a=1}^N [\delta\chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a \chi_a | \chi_b \chi_b] - [\delta\chi_a \chi_b | \chi_b \chi_a]$$

+ complex conjugate

The same goes for the Lagrange multiplier term:

again, indices renamed

$$\begin{aligned} \sum_{ab} \varepsilon_{ba} ([\delta\chi_a | \chi_b] + [\chi_a | \delta\chi_b]) &= \sum_{ab} \varepsilon_{ba} [\delta\chi_a | \chi_b] + \sum_{ab} \varepsilon_{ab} [\chi_b | \delta\chi_a] \\ &= \sum_{ab} \varepsilon_{ba} [\delta\chi_a | \chi_b] + \sum_{ab} \varepsilon_{ba}^* [\delta\chi_a | \chi_b]^* \\ &= \sum_{ab} \varepsilon_{ba} [\delta\chi_a | \chi_b] + \text{complex conjugate} \end{aligned}$$



The Hartree-Fock Approximation

Now the derivation: Minimizing the energy of a Slater determinant

$$\delta \mathcal{L} = \sum_{a=1}^N [\delta \chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta \chi_a \chi_a | \chi_b \chi_b] - [\delta \chi_a \chi_b | \chi_b \chi_a]$$

$$- \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} [\delta \chi_a | \chi_b] + \text{complex conjugate}$$

$$\delta \mathcal{L} = \sum_{a=1}^N \int d\mathbf{x}_1 \delta \chi_a^*(1) \left[h(1) \chi_a(1) + \sum_{b=1}^N (\mathcal{J}_b(1) - \mathcal{K}_b(1)) \chi_a(1) - \sum_{b=1}^N \varepsilon_{ba} \chi_b(1) \right]$$

$$+ \text{complex conjugate} = 0$$

Since $\delta \chi_a^*(1)$ is arbitrary, we find that the expression in brackets must be zero:

$$\left[h(1) + \sum_{b=1}^N \mathcal{J}_b(1) - \mathcal{K}_b(1) \right] \chi_a(1) = \sum_{b=1}^N \varepsilon_{ba} \chi_b(1) \quad a = 1, 2, \dots, N$$

We identify this bracketed term as the Fock operator:

$$f|\chi_a\rangle = \sum_{b=1}^N \varepsilon_{ba} |\chi_b\rangle$$



One last issue....

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The Hartree-Fock Approximation

Now the derivation: Minimizing the energy of a Slater determinant
with respect to its spin orbitals...

$$f|\chi_a\rangle = \sum_{b=1}^N \epsilon_{ba} |\chi_b\rangle$$

This is a generalized eigenvalue problem. To obtain the ‘canonical’ orbitals, we have to apply a rotation.

$$\chi'_a = \sum_b \chi_b U_{ba}$$

The unitary matrix U preserves their orthonormality!

$$|\Psi_0\rangle = (N!)^{-1/2} \det(\mathbf{A})$$

$$\det(\mathbf{AB}) = \det(\mathbf{A}) \det(\mathbf{B})$$

$$|\Psi'_0\rangle = \det(\mathbf{U}) |\Psi_0\rangle$$

$$\begin{aligned} \mathbf{A}' = \mathbf{AU} &= \begin{pmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{pmatrix} \begin{pmatrix} U_{11} & U_{12} & \cdots & U_{1N} \\ U_{21} & U_{22} & \cdots & U_{2N} \\ \vdots & \vdots & & \vdots \\ U_{N1} & U_{N2} & \cdots & U_{NN} \end{pmatrix} \\ &= \begin{pmatrix} \chi'_1(1) & \chi'_2(1) & \cdots & \chi'_N(1) \\ \chi'_1(2) & \chi'_2(2) & \cdots & \chi'_N(2) \\ \vdots & \vdots & & \vdots \\ \chi'_1(N) & \chi'_2(N) & \cdots & \chi'_N(N) \end{pmatrix} \end{aligned}$$

A single Slater determinant wave function stays untouched upon rotation -> orbitals not unique!

The Hartree-Fock Approximation

Now the derivation: Minimizing the energy of a Slater determinant
with respect to its spin orbitals...

We take advantage of this finding to perform a special rotation.

First: What happens to operators upon rotation?

$$\begin{aligned} \text{Coulomb: } \sum_a \mathcal{J}'_a(1) &= \sum_a \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} \chi_a'(2) \\ &= \sum_{bc} \left[\sum_a U_{ba}^* U_{ca} \right] \int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_c(2) \end{aligned}$$

Using $\sum_a U_{ba}^* U_{ca} = (\mathbf{U}\mathbf{U}^\dagger)_{cb} = \delta_{cb}$ we find:

$$\sum_a \mathcal{J}'_a(1) = \sum_b \int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) = \sum_b \mathcal{J}_b(1)$$

Invariant. Nothing happens. Same for exchange.

The Hartree-Fock Approximation

Now the derivation: Minimizing the energy of a Slater determinant
with respect to its spin orbitals...

We take advantage of this finding to perform a special rotation.

First: What happens to operators upon rotation?

Second: What happens to Lagrange multipliers?

We multiply  from left with $\langle \chi_c |$ to obtain $\langle \chi_c | f | \chi_a \rangle = \sum_{b=1}^N \varepsilon_{ba} \langle \chi_c | \chi_b \rangle = \varepsilon_{ca}$

The Lagrange multipliers are matrix elements of the Fock matrix!

$$\begin{aligned}\varepsilon'_{ab} &= \int d\mathbf{x}_1 \chi_a^*(1) f(1) \chi_b'(1) \\ &= \sum_{cd} U_{ca}^* U_{db} \int d\mathbf{x}_1 \chi_c^*(1) f(1) \chi_d(1) \\ &= \sum_{cd} U_{ca}^* \varepsilon_{cd} U_{db} \quad \text{or, in matrix form: } \boldsymbol{\varepsilon}' = \mathbf{U}^\dagger \boldsymbol{\varepsilon} \mathbf{U}\end{aligned}$$

The Hartree-Fock Approximation

Now the derivation: Minimizing the energy of a Slater determinant
with respect to its spin orbitals...

We take advantage of this finding to perform a special rotation.

First: What happens to operators upon rotation?

Second: What happens to Lagrange multipliers?

We multiply  from left with $\langle \chi_c |$ to obtain $\langle \chi_c | f | \chi_a \rangle = \sum_{b=1}^N \varepsilon_{ba} \langle \chi_c | \chi_b \rangle = \varepsilon_{ca}$

The Lagrange multipliers are matrix elements of the Fock matrix!

$$\begin{aligned}\varepsilon'_{ab} &= \int d\mathbf{x}_1 \chi_a^*(1) f(1) \chi_b'(1) \\ &= \sum_{cd} U_{ca}^* U_{db} \int d\mathbf{x}_1 \chi_c^*(1) f(1) \chi_d(1) \\ &= \sum_{cd} U_{ca}^* \varepsilon_{cd} U_{db} \quad \text{or, in matrix form: } \boldsymbol{\varepsilon}' = \mathbf{U}^\dagger \boldsymbol{\varepsilon} \mathbf{U}\end{aligned}$$

Canonical orbitals!

Idea: Let's chose a rotation so that F is diagonal! $f|\chi_a\rangle = \varepsilon_a|\chi_a\rangle$

Koopmans' Theorem

First, let's have a look at the Fock operator in the MO basis:

$$\langle \chi_i | f | \chi_j \rangle = \varepsilon_j \langle \chi_i | \chi_j \rangle = \varepsilon_j \delta_{ij}$$

Obviously, it's a diagonal matrix. Its entries can be written as

$$\begin{aligned}\varepsilon_i &= \langle \chi_i | f | \chi_i \rangle = \langle \chi_i | h + \sum_b (\mathcal{J}_b - \mathcal{K}_b) | \chi_i \rangle \\ &= \langle \chi_i | h | \chi_i \rangle + \sum_b \langle \chi_i | \mathcal{J}_b | \chi_i \rangle - \langle \chi_i | \mathcal{K}_b | \chi_i \rangle \\ &= \langle i | h | i \rangle + \sum_b \langle ib | ib \rangle - \langle ib | bi \rangle \\ &= \langle i | h | i \rangle + \sum_b \langle ib | ib \rangle\end{aligned}$$

The Hartree-Fock Approximation

Koopmans' Theorem

We can distinguish between energies of occupied and virtual orbitals:

$$\varepsilon_a = \langle a | h | a \rangle + \sum_{b=1}^N \langle ab | ab \rangle$$

$$\varepsilon_r = \langle r | h | r \rangle + \sum_{b=1}^N \langle rb | rb \rangle$$

Using $\langle aa | aa \rangle = 0$, we obtain

This sum has one term less than the one below

$$\varepsilon_a = \langle a | h | a \rangle + \sum_{b \neq a} \cancel{\langle ab | ab \rangle} - \langle ab | ba \rangle$$

$$\varepsilon_r = \langle r | h | r \rangle + \sum_b \langle rb | rb \rangle - \langle rb | br \rangle$$

What does that mean?

The Hartree-Fock Approximation

Koopmans' Theorem

First, we discover something interesting when we add up all orbital energies:

$$\sum_a^N \varepsilon_a = \sum_a^N \langle a | h | a \rangle + \sum_a^N \sum_b^N \langle ab | | ab \rangle$$

By comparing this to the energy of a HF Slater determinant

$$E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \sum_a^N \langle a | h | a \rangle + \frac{1}{2} \sum_a^N \sum_b^N \langle ab | | ab \rangle$$

we realize that the HF energy **IS NOT** just the sum of the orbital energies!

$$E_0 \neq \sum_a^N \varepsilon_a$$

The Hartree-Fock Approximation

Koopmans' Theorem

Now we compare the HF energies of an N and an N-1 electron wave function:

$$^N E_0 = \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_a \sum_b \langle ab | | ab \rangle$$

We remove an electron from MO c:

$$^{N-1} E_c = \sum_{a \neq c} \langle a | h | a \rangle + \frac{1}{2} \sum_{a \neq c} \sum_{b \neq c} \langle ab | | ab \rangle$$

Assuming unaffected orbitals, the ionisation energy can then be estimated as:

$$\begin{aligned} \text{IP} &= {}^{N-1} E_c - {}^N E_0 \\ &= -\langle c | h | c \rangle - \frac{1}{2} \sum_{a[b=c]} \langle ab | | ab \rangle - \frac{1}{2} \sum_{b[a=c]} \langle ab | | ab \rangle \\ &= -\langle c | h | c \rangle - \frac{1}{2} \sum_a \langle ac | | ac \rangle - \frac{1}{2} \sum_b \langle cb | | cb \rangle \\ &= -\langle c | h | c \rangle - \sum_b \langle cb | | cb \rangle = -\varepsilon_c \end{aligned}$$

The Hartree-Fock Approximation

Koopmans' Theorem

In a second step, we add an electron to the neutral wave function:

$$|^{N+1}\Psi^r\rangle = a_r^\dagger |^N\Psi_0\rangle$$

We define the electron affinity via $\text{EA} = {}^N E_0 - {}^{N+1} E^r$ with

$${}^{N+1} E^r = \langle {}^{N+1}\Psi^r | \mathcal{H} | {}^{N+1}\Psi^r \rangle$$

Similar to the result for the IP, we obtain

$${}^N E_0 - {}^{N+1} E^r = -\langle r | h | r \rangle - \sum_b \langle rb | | rb \rangle = -\varepsilon_r$$

Koopmans' Theorem:

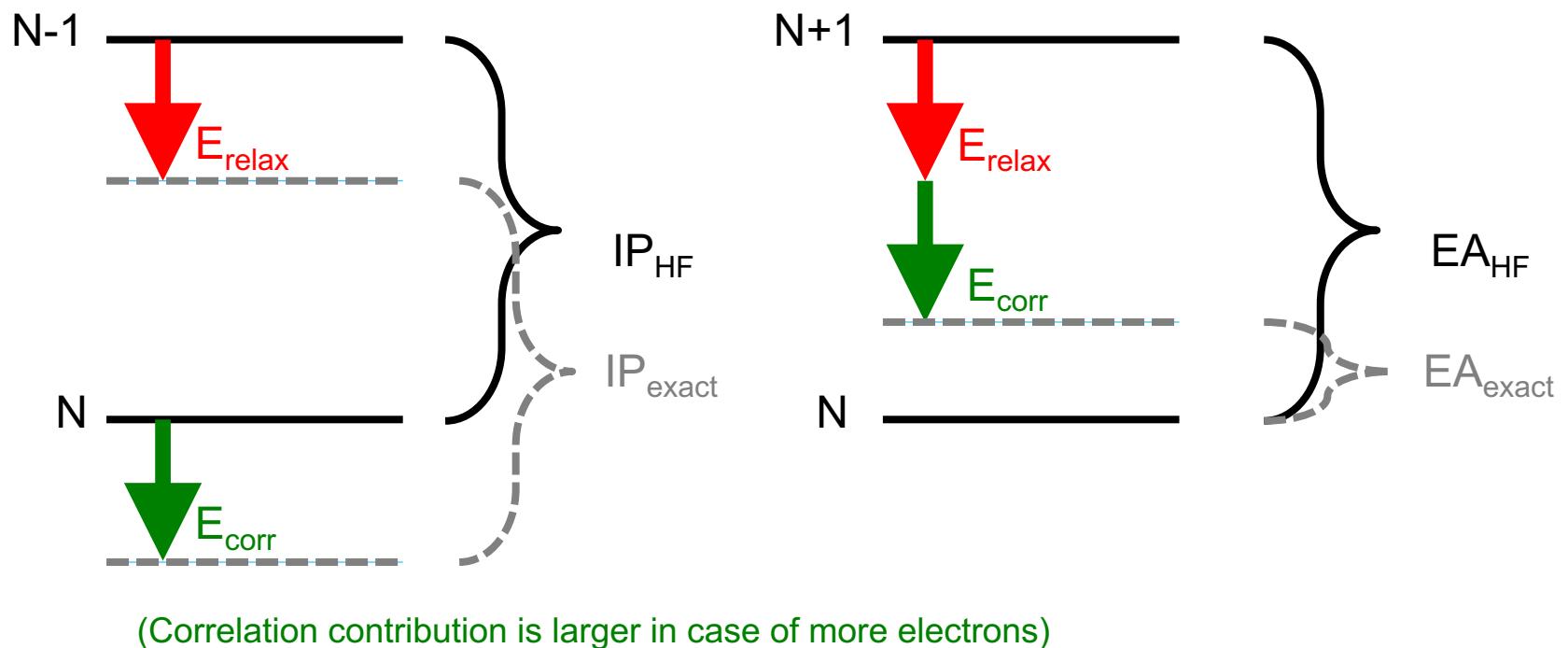
The negative MO energy of the occupied orbital c corresponds to the energy needed to create an ionized state ($N-1$) by removing an electron from c .

The negative MO energy of the virtual orbital r corresponds to the energy needed to add an electron ($N+1$) by occupying orbital r .

Note that this is an approximation! It only holds if we assume unrelaxed orbitals!

The Hartree-Fock Approximation

Koopmans' Theorem is just an approximation...



It's good for IPs due to error cancelling, but bad for EAs!

The Hartree-Fock Approximation

Brillouin's Theorem

We talked briefly about CI expansions:

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{ra} c_a^r |\Psi_a^r\rangle + \dots$$

Considering only singly excited determinants, we have the following CI matrix:

$$\begin{pmatrix} \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle & \langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle \\ \langle \Psi_a^r | \mathcal{H} | \Psi_0 \rangle & \langle \Psi_a^r | \mathcal{H} | \Psi_a^r \rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_a^r \end{pmatrix} = \epsilon_0 \begin{pmatrix} c_0 \\ c_a^r \end{pmatrix}$$

What about the off-diagonal elements?

$$\langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle = \langle a | h | r \rangle + \sum_b \langle ab | | rb \rangle$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle = \langle \chi_a | f | \chi_r \rangle$$

$$\langle \chi_i | f | \chi_j \rangle = 0, (i \neq j) \quad \longrightarrow \quad \begin{pmatrix} E_0 & 0 \\ 0 & \langle \Psi_a^r | \mathcal{H} | \Psi_a^r \rangle \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = E_0 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

The Hartree-Fock Approximation

Brillouin's Theorem

We talked briefly about CI expansions:

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{ra} c'_a |\Psi_a^r\rangle + \dots$$

Considering only singly excited determinants, we have the following CI matrix:

$$\begin{pmatrix} \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle & \langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle \\ \langle \Psi_a^r | \mathcal{H} | \Psi_0 \rangle & \langle \Psi_a^r | \mathcal{H} | \Psi_a^r \rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c'_a \end{pmatrix} = \epsilon_0 \begin{pmatrix} c_0 \\ c'_a \end{pmatrix}$$

What about the off-diagonal elements?

$$\langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle = \langle a | h | r \rangle + \sum_b \langle ab | | rb \rangle$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle = \langle \chi_a | f | \chi_r \rangle$$

$$\langle \chi_i | f | \chi_j \rangle = 0, (i \neq j) \quad \longrightarrow \quad \begin{pmatrix} E_0 & 0 \\ 0 & \langle \Psi_a^r | \mathcal{H} | \Psi_a^r \rangle \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = E_0 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

Brillouin's Theorem: Singly excited determinants do not directly improve the ground state!

The Hartree-Fock Approximation

The Hartree-Fock Hamiltonian

What did we actually solve? Which operator corresponds to the HF wave function?

It is not this one yet...

$$\mathcal{H}|\Phi_0\rangle = \mathcal{E}_0|\Phi_0\rangle$$

exact nonrelativistic ground state

We used the variational principle to get the best single-determinant solution!
The corresponding operator has the form

$$\mathcal{H}_0 = \sum_{i=1}^N f(i),$$

and its eigenvalue is $\sum_{\alpha} \varepsilon_{\alpha}$.

The Hartree-Fock Approximation

The Hartree-Fock Hamiltonian

We can do a perturbation extension of the exact energy:

$$\mathcal{E}_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \dots$$

$$E_0^{(0)} = \sum_a \varepsilon_a \quad \text{with} \quad \mathcal{H}_0 |\Psi_0\rangle = E_0^{(0)} |\Psi_0\rangle$$

We now define the perturbation as

$$\mathcal{V} = \mathcal{H} - \mathcal{H}_0$$

$$= \sum_{i=1}^N h(i) + \sum_{i=1}^N \sum_{j>i}^N r_{ij}^{-1} - \sum_{i=1}^N f(i)$$

$$= \sum_{i=1}^N \sum_{j>i}^N r_{ij}^{-1} - \sum_{i=1}^N v^{\text{HF}}(i)$$

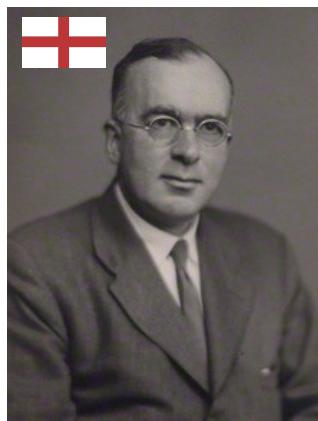
The Hartree-Fock Approximation

The Hartree-Fock Hamiltonian

With this, we find:

$$\begin{aligned} E_0 &= \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \langle \Psi_0 | \mathcal{H}_0 | \Psi_0 \rangle + \langle \Psi_0 | \mathcal{V} | \Psi_0 \rangle \\ &= \sum_a \varepsilon_a + \langle \Psi_0 | \mathcal{V} | \Psi_0 \rangle = E_0^{(0)} + E_0^{(1)} \end{aligned}$$

The Hartree-Fock energy corresponds to first order perturbation theory!



The Hartree-Fock Approximation

An algebraic solution of the HF equations for closed shell systems:
The Roothaan Equations

First, we eliminate the spin dependence:

For restricted MOs we have $\chi_i(\mathbf{x}) = \begin{cases} \psi_j(\mathbf{r})\alpha(\omega) \\ \psi_j(\mathbf{r})\beta(\omega) \end{cases}$

Our closed shell ground state is given by

$$|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_{N-1}\chi_N\rangle = |\psi_1\bar{\psi}_1 \cdots \psi_a\bar{\psi}_a \cdots \psi_{N/2}\bar{\psi}_{N/2}\rangle$$

We have to integrate out the spin functions as we did before for the HF energies.

$$\begin{aligned} f(\mathbf{x}_1)\chi_i(\mathbf{x}_1) &= \varepsilon_i\chi_i(\mathbf{x}_1) \\ f(\mathbf{x}_1)\psi_j(\mathbf{r}_1)\alpha(\omega_1) &= \varepsilon_j\psi_j(\mathbf{r}_1)\alpha(\omega_1) \end{aligned}$$

An algebraic solution of the HF equations for closed shell systems:
The Roothaan Equations

First, we **eliminate the spin dependence**:

We multiply from left with $\alpha^*(\omega_1)$ and obtain

$$\left[\int d\omega_1 \alpha^*(\omega_1) f(\mathbf{x}_1) \alpha(\omega_1) \right] \psi_j(\mathbf{r}_1) = \varepsilon_j \psi_j(\mathbf{r}_1)$$

The Fock operator has the form

$$f(\mathbf{x}_1) = h(\mathbf{r}_1) + \sum_c^N \int d\mathbf{x}_2 \chi_c^*(\mathbf{x}_2) r_{12}^{-1} (1 - \mathcal{P}_{12}) \chi_c(\mathbf{x}_2),$$

so that we obtain

$$\begin{aligned} \left[\int d\omega_1 \alpha^*(\omega_1) f(\mathbf{x}_1) \alpha(\omega_1) \right] \psi_j(\mathbf{r}_1) &= \left[\int d\omega_1 \alpha^*(\omega_1) h(\mathbf{r}_1) \alpha(\omega_1) \right] \psi_j(\mathbf{r}_1) \\ &\quad + \left[\sum_c \int d\omega_1 d\mathbf{x}_2 \alpha^*(\omega_1) \chi_c^*(\mathbf{x}_2) r_{12}^{-1} (1 - \mathcal{P}_{12}) \chi_c(\mathbf{x}_2) \alpha(\omega_1) \right] \psi_j(\mathbf{r}_1) \\ &= \varepsilon_j \psi_j(\mathbf{r}_1) \end{aligned}$$

The Hartree-Fock Approximation

An algebraic solution of the HF equations for closed shell systems:
The Roothaan Equations

First, we eliminate the spin dependence:

With the definition of the closed shell Fock operator

$$f(\mathbf{r}_1) = \int d\omega_1 \alpha^*(\omega_1) f(\mathbf{x}_1) \alpha(\omega_1)$$

We can rewrite the equation as

$$\begin{aligned} f(\mathbf{r}_1)\psi_j(\mathbf{r}_1) &= h(\mathbf{r}_1)\psi_j(\mathbf{r}_1) + \sum_c \int d\omega_1 d\mathbf{x}_2 \alpha^*(\omega_1) \chi_c^*(\mathbf{x}_2) r_{12}^{-1} \chi_c(\mathbf{x}_2) \alpha(\omega_1) \psi_j(\mathbf{r}_1) \\ &\quad - \sum_c \int d\omega_1 d\mathbf{x}_2 \alpha^*(\omega_1) \chi_c^*(\mathbf{x}_2) r_{12}^{-1} \chi_c(\mathbf{x}_1) \alpha(\omega_2) \psi_j(\mathbf{r}_2) \\ &= \varepsilon_j \psi_j(\mathbf{r}_1) \end{aligned}$$

Now, we apply the same trick as before and split the sum in two separate sums over α and β spin!

$$\sum_c \rightarrow \sum_c^{N/2} + \sum_{\bar{c}}^{N/2}$$

The Hartree-Fock Approximation

An algebraic solution of the HF equations for closed shell systems:
The Roothaan Equations

First, we eliminate the spin dependence:

$$f(\mathbf{r}_1)\psi_j(\mathbf{r}_1) = h(\mathbf{r}_1)\psi_j(\mathbf{r}_1)$$

same

$$\left. \begin{aligned} &+ \sum_c^{N/2} \int d\omega_1 d\omega_2 d\mathbf{r}_2 \alpha^*(\omega_1) \psi_c^*(\mathbf{r}_2) \alpha^*(\omega_2) r_{12}^{-1} \psi_c(\mathbf{r}_2) \alpha(\omega_2) \alpha(\omega_1) \psi_j(\mathbf{r}_1) \\ &+ \sum_c^{N/2} \int d\omega_1 d\omega_2 d\mathbf{r}_2 \alpha^*(\omega_1) \psi_c^*(\mathbf{r}_2) \beta^*(\omega_2) r_{12}^{-1} \psi_c(\mathbf{r}_2) \beta(\omega_2) \alpha(\omega_1) \psi_j(\mathbf{r}_1) \\ &- \sum_c^{N/2} \int d\omega_1 d\omega_2 d\mathbf{r}_2 \alpha^*(\omega_1) \psi_c^*(\mathbf{r}_2) \alpha^*(\omega_2) r_{12}^{-1} \psi_c(\mathbf{r}_1) \alpha(\omega_1) \alpha(\omega_2) \psi_j(\mathbf{r}_2) \\ &- \sum_c^{N/2} \int d\omega_1 d\omega_2 d\mathbf{r}_2 \alpha^*(\omega_1) \psi_c^*(\mathbf{r}_2) \beta^*(\omega_2) r_{12}^{-1} \psi_c(\mathbf{r}_1) \beta(\omega_1) \alpha(\omega_2) \psi_j(\mathbf{r}_2) \end{aligned} \right.$$
$$= \varepsilon_j \psi_j(\mathbf{r}_1)$$

The Hartree-Fock Approximation

An algebraic solution of the HF equations for closed shell systems:
The Roothaan Equations

First, we eliminate the spin dependence:

$$\begin{aligned} f(\mathbf{r}_1)\psi_j(\mathbf{r}_1) &= h(\mathbf{r}_1)\psi_j(\mathbf{r}_1) + \left[2 \sum_c^{N/2} \int d\mathbf{r}_2 \psi_c^*(\mathbf{r}_2) r_{12}^{-1} \psi_c(\mathbf{r}_2) \right] \psi_j(\mathbf{r}_1) \\ &\quad - \left[\sum_c^{N/2} \int d\mathbf{r}_2 \psi_c^*(\mathbf{r}_2) r_{12}^{-1} \psi_j(\mathbf{r}_2) \right] \psi_c(\mathbf{r}_1) \\ &= \varepsilon_j \psi_j(\mathbf{r}_1) \end{aligned}$$

The Hartree-Fock Approximation

An algebraic solution of the HF equations for closed shell systems:
The Roothaan Equations

First, we eliminate the spin dependence:

$$\begin{aligned} f(\mathbf{r}_1)\psi_j(\mathbf{r}_1) &= h(\mathbf{r}_1)\psi_j(\mathbf{r}_1) + \left[2 \sum_c^{N/2} \int d\mathbf{r}_2 \psi_c^*(\mathbf{r}_2) r_{12}^{-1} \psi_c(\mathbf{r}_2) \right] \psi_j(\mathbf{r}_1) \\ &\quad - \left[\sum_c^{N/2} \int d\mathbf{r}_2 \psi_c^*(\mathbf{r}_2) r_{12}^{-1} \psi_j(\mathbf{r}_2) \right] \psi_c(\mathbf{r}_1) \\ &= \varepsilon_j \psi_j(\mathbf{r}_1) \end{aligned}$$

This is equal to $f(\mathbf{r}_1) = h(\mathbf{r}_1) + \sum_a^{N/2} \int d\mathbf{r}_2 \psi_a^*(\mathbf{r}_2) (2 - \mathcal{P}_{12}) r_{12}^{-1} \psi_a(\mathbf{r}_2)$

Or to $f(1) = h(1) + \sum_a^{N/2} 2J_a(1) - K_a(1)$ with $J_a(1) = \int d\mathbf{r}_2 \psi_a^*(2) r_{12}^{-1} \psi_a(2)$

$$K_a(1)\psi_i(1) = \left[\int d\mathbf{r}_2 \psi_a^*(2) r_{12}^{-1} \psi_i(2) \right] \psi_a(1)$$

The Hartree-Fock Approximation

An algebraic solution of the HF equations for closed shell systems:
The Roothaan Equations

Second, we introduce a **set of K basis functions** for the spatial part:

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu} \quad i = 1, 2, \dots, K$$

The problem reduces to the optimization of these coefficients:

$$f(1) \sum_v C_{vi} \phi_v(1) = \varepsilon_i \sum_v C_{vi} \phi_v(1)$$

After multiplication from left with $\phi_{\mu}^{*}(1)$ we obtain:

$$\sum_v C_{vi} \int d\mathbf{r}_1 \phi_{\mu}^{*}(1) f(1) \phi_v(1) = \varepsilon_i \sum_v C_{vi} \int d\mathbf{r}_1 \phi_{\mu}^{*}(1) \phi_v(1)$$

The Hartree-Fock Approximation

An algebraic solution of the HF equations for closed shell systems:
The Roothaan Equations

$$\sum_v C_{vi} \underbrace{\int d\mathbf{r}_1 \phi_\mu^*(1)f(1)\phi_v(1)}_F = \varepsilon_i \sum_v C_{vi} \underbrace{\int d\mathbf{r}_1 \phi_\mu^*(1)\phi_v(1)}_S$$

Fock matrix: $F_{\mu\nu} = \int d\mathbf{r}_1 \phi_\mu^*(1)f(1)\phi_\nu(1)$ Overlap matrix: $S_{\mu\nu} = \int d\mathbf{r}_1 \phi_\mu^*(1)\phi_\nu(1)$

With these definitions we can write

$$\sum_v F_{\mu v} C_{vi} = \varepsilon_i \sum_v S_{\mu v} C_{vi} \quad i = 1, 2, \dots, K$$

$$\boxed{\mathbf{FC} = \mathbf{SC}\varepsilon}$$

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ \vdots & \vdots & & \vdots \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix}$$

$$\varepsilon = \begin{pmatrix} \varepsilon_1 & & & \\ & \varepsilon_2 & & \\ & & \ddots & \\ 0 & & & \varepsilon_K \end{pmatrix}$$

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}_\delta$?

Introduction of the charge density matrix:

What is the probability to find an electron at \mathbf{r} ? $\rho(\mathbf{r}) = 2 \sum_a^{N/2} |\psi_a(\mathbf{r})|^2$

Obviously, $\int d\mathbf{r} \rho(\mathbf{r}) = 2 \sum_a^{N/2} \int d\mathbf{r} |\psi_a(\mathbf{r})|^2 = 2 \sum_a^{N/2} 1 = N$

Again, using our basis set expansion $\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_\mu \quad i = 1, 2, \dots, K$

we obtain $\rho(\mathbf{r}) = 2 \sum_a^{N/2} \psi_a^*(\mathbf{r}) \psi_a(\mathbf{r})$

$$= 2 \sum_a^{N/2} \sum_v C_{va}^* \phi_v^*(\mathbf{r}) \sum_\mu C_{\mu a} \phi_\mu(\mathbf{r})$$

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}_\delta$?

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_{\mu\nu} \left[2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^* \right] \phi_\mu(\mathbf{r}) \phi_\nu^*(\mathbf{r}) \\ &= \sum_{\mu\nu} P_{\mu\nu} \phi_\mu(\mathbf{r}) \phi_\nu^*(\mathbf{r}),\end{aligned}$$

where we have introduced the charge density matrix

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^*$$

With it, we can rewrite the Fock operator as

$$\begin{aligned}f(\mathbf{r}_1) &= h(\mathbf{r}_1) + v^{\text{HF}}(\mathbf{r}_1) \\ &= h(\mathbf{r}_1) + \frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma} \left[\int d\mathbf{r}_2 \phi_\sigma^*(\mathbf{r}_2) (2 - \mathcal{P}_{12}) r_{12}^{-1} \phi_\lambda(\mathbf{r}_2) \right]\end{aligned}$$

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}_\delta$?

The Fock matrix is the matrix representation of the Fock operator

$$f(1) = h(1) + \sum_a^{N/2} 2J_a(1) - K_a(1)$$

in our basis:

$$\begin{aligned} F_{\mu\nu} &= \int d\mathbf{r}_1 \phi_\mu^*(1) f(1) \phi_\nu(1) \\ &= \int d\mathbf{r}_1 \phi_\mu^*(1) h(1) \phi_\nu(1) + \sum_a^{N/2} \int d\mathbf{r}_1 \phi_\mu^*(1) [2J_a(1) - K_a(1)] \phi_\nu(1) \\ &= H_{\mu\nu}^{\text{core}} + \sum_a^{N/2} 2(\mu\nu | aa) - (\mu a | av) \end{aligned}$$

with

$$H_{\mu\nu}^{\text{core}} = \int d\mathbf{r}_1 \phi_\mu^*(1) h(1) \phi_\nu(1) ; \quad h(1) = -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|}$$

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}_\delta$?

$$H_{\mu\nu}^{\text{core}} = T_{\mu\nu} + V_{\mu\nu}^{\text{nuc}}$$

We can distinguish between the kinetic and the Coulomb part:

$$T_{\mu\nu} = \int d\mathbf{r}_1 \phi_\mu^*(1) \left[-\frac{1}{2} \nabla_1^2 \right] \phi_\nu(1)$$
$$V_{\mu\nu}^{\text{nuc}} = \int d\mathbf{r}_1 \phi_\mu^*(1) \left[-\sum_A \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} \right] \phi_\nu(1)$$

This part of the Fock operator has to be evaluated **only once!**

The real problem is what remains:

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_a^{N/2} \sum_{\lambda\sigma} C_{\lambda a} C_{\sigma a}^* [2(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)]$$
$$= H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)]$$
$$= H_{\mu\nu}^{\text{core}} + G_{\mu\nu}$$

The two-electron part

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SCs}$?

Problem: The G matrix contains a large number of integrals of the form

$$(\mu\nu|\lambda\sigma) = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_\mu^*(1)\phi_\nu(1)r_{12}^{-1}\phi_\lambda^*(2)\phi_\sigma(2)$$

Bigger Problem: The Fock matrix depends on the density matrix, or equivalently, on the coefficients C:

$$\mathbf{F(C)C} = \mathbf{SCs}$$

The G part of the Fock operator makes an iterative approach necessary.

Before discussing the SCF procedure as a whole...

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}_\varepsilon$?

... we transform the generalized eigenvalue problem into a standard EVP:

The basis set is not orthonormal, hence we find $\int d\mathbf{r} \phi_\mu^*(\mathbf{r})\phi_\nu(\mathbf{r}) = S_{\mu\nu}$

Now, we search for a non unitary matrix X which transforms our orbitals via

$$\phi'_\mu = \sum_v X_{v\mu} \phi_v \quad \mu = 1, 2, \dots, K \quad \spadesuit$$

into an orthonormal set

$$\int d\mathbf{r} \phi'^*_\mu(\mathbf{r})\phi'_v(\mathbf{r}) = \delta_{\mu v} \quad \heartsuit$$

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}\varepsilon$?

To do this, we insert ♠ into ❤

$$\begin{aligned}\int d\mathbf{r} \phi_\mu^*(\mathbf{r}) \phi_\nu'(\mathbf{r}) &= \int d\mathbf{r} \left[\sum_\lambda X_{\lambda\mu}^* \phi_\lambda^*(\mathbf{r}) \right] \left[\sum_\sigma X_{\sigma\nu} \phi_\sigma(\mathbf{r}) \right] \\ &= \sum_\lambda \sum_\sigma X_{\lambda\mu}^* \int d\mathbf{r} \phi_\lambda^*(\mathbf{r}) \phi_\sigma(\mathbf{r}) X_{\sigma\nu} \\ &= \sum_\lambda \sum_\sigma X_{\lambda\mu}^* S_{\lambda\sigma} X_{\sigma\nu} \stackrel{!}{=} \delta_{\mu\nu}\end{aligned}$$

Or, in matrix form,

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} \stackrel{!}{=} \mathbf{1}$$

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}_g$?

Which \mathbf{X} can do the trick?

1) Symmetric orthogonalization: $\mathbf{X} \equiv \mathbf{S}^{-1/2} = \mathbf{Us}^{-1/2}\mathbf{U}^\dagger$
(Spectral theorem)

$$\mathbf{S}^{-1/2}\mathbf{SS}^{-1/2} = \mathbf{S}^{-1/2}\mathbf{S}^{1/2} = \mathbf{S}^0 = \mathbf{1}$$

2) Canonical orthogonalization: $\mathbf{X} = \mathbf{Us}^{-1/2}$

\mathbf{X} is obtained by dividing each column of \mathbf{U} by the square root of its corresponding eigenvalue,

$$X_{ij} = U_{ij}/s_j^{1/2}$$

$$\mathbf{X}^\dagger \mathbf{SX} = (\mathbf{Us}^{-1/2})^\dagger \mathbf{S} \mathbf{U} \mathbf{s}^{-1/2} = \mathbf{s}^{-1/2} \mathbf{U}^\dagger \mathbf{S} \mathbf{U} \mathbf{s}^{-1/2} = \mathbf{s}^{-1/2} \mathbf{ss}^{-1/2} = \mathbf{1}$$

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}_g$?

Which \mathbf{X} can do the trick?

1) Symmetric orthogonalization: $\mathbf{X} \equiv \mathbf{S}^{-1/2} = \mathbf{Us}^{-1/2}\mathbf{U}^\dagger$
(Spectral theorem)

$$\mathbf{S}^{-1/2}\mathbf{SS}^{-1/2} = \mathbf{S}^{-1/2}\mathbf{S}^{1/2} = \mathbf{S}^0 = \mathbf{1}$$

2) Canonical orthogonalization: $\mathbf{X} = \mathbf{Us}^{-1/2}$ Better choice!

\mathbf{X} is obtained by dividing each column of \mathbf{U} by the square root of its corresponding eigenvalue,

$$X_{ij} = U_{ij}/s_j^{1/2}$$

$$\mathbf{X}^\dagger \mathbf{SX} = (\mathbf{Us}^{-1/2})^\dagger \mathbf{S} \mathbf{U} \mathbf{s}^{-1/2} = \mathbf{s}^{-1/2} \mathbf{U}^\dagger \mathbf{S} \mathbf{U} \mathbf{s}^{-1/2} = \mathbf{s}^{-1/2} \mathbf{ss}^{-1/2} = \mathbf{1}$$

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}_\mathbf{s}$?

Canonical orthogonalization allows a reduction of the dimension if basis set shows linear dependence.

We sort the eigenvalues in \mathbf{s} according to their size from large to small

$$s_1 > s_2 > s_3 > \dots$$

and drop those m that are below a given threshold to obtain a truncated \mathbf{X}

$$\tilde{\mathbf{X}} = \begin{pmatrix} U_{1,1}/s_1^{1/2} & U_{1,2}/s_2^{1/2} & \dots & U_{1,K-m}/s_{K-m}^{1/2} \\ U_{2,1}/s_1^{1/2} & U_{2,2}/s_2^{1/2} & \dots & U_{2,K-m}/s_{K-m}^{1/2} \\ \vdots & \vdots & & \vdots \\ U_{K,1}/s_1^{1/2} & U_{K,2}/s_2^{1/2} & \dots & U_{K,K-m}/s_{K-m}^{1/2} \end{pmatrix}$$

of dimension $K \times (K - m)$, leading to a new basis $\phi'_\mu = \sum_{v=1}^K \tilde{X}_{v\mu} \phi_v \quad \mu = 1, 2, \dots, K - m$

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}\varepsilon$?

A very last (technical) note:

It is not convenient to work in the orthogonal basis throughout the whole SCF procedure.

The integrals $(\mu\nu|\lambda\sigma)$ would have to be **re-evaluated or transformed**.

Better: We transform the coefficient matrix \mathbf{C} : $\mathbf{C}' = \mathbf{X}^{-1}\mathbf{C}$ $\mathbf{C} = \mathbf{X}\mathbf{C}'$

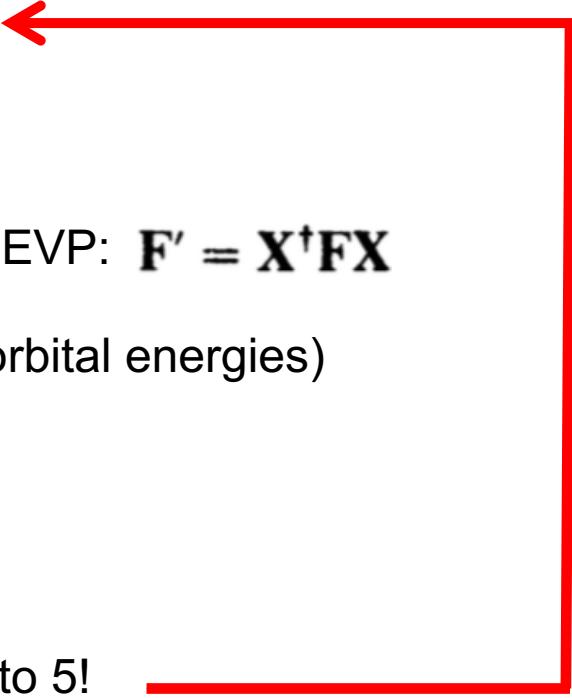
Our eigenvalue problem has the form: $\mathbf{FXC}' = \mathbf{SC}'\varepsilon$

With the definition $\mathbf{F}' = \mathbf{X}^\dagger \mathbf{FX}$ we obtain $\boxed{\mathbf{F}'\mathbf{C}' = \mathbf{C}'\varepsilon}$

Now we are ready to discuss the whole SCF routine...

The Hartree-Fock Approximation

How to solve $\mathbf{FC} = \mathbf{SC}_g$?

- 1) Specify the molecule (atoms and structure), the number of electrons and a basis set.
- 2) Calculate all integrals required: $S_{\mu\nu}$, $H_{\mu\nu}^{\text{core}}$, and $(\mu\nu|\lambda\sigma)$
- 3) Diagonalize S to get X
- 4) Make a guess for P
- 5) Calculate G from P and the integrals $(\mu\nu|\lambda\sigma)$ 
- 6) Build the whole Fock matrix $\mathbf{F} = \mathbf{H}^{\text{core}} + \mathbf{G}$
- 7) Transform the Fock matrix to obtain the standard EVP: $\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}$
- 8) Diagonalize \mathbf{F}' to obtain \mathbf{C}' and the eigenvalues (orbital energies)
- 9) Do the back-transformation $\mathbf{C} = \mathbf{X} \mathbf{C}'$
- 10) Form a new density matrix P from C
- 11) Converged? If yes, we are done, if no, go back to 5!

Problems which might occur during the SCF procedure

- 1) Specify the molecule (atoms and structure), the number of electrons and a basis set.
- 2) Calculate all integrals required: $S_{\mu\nu}$, $H_{\mu\nu}^{\text{core}}$, and $(\mu\nu|\lambda\sigma)$

Problem: Number of integrals is proportional to $K^4/8$

Solution:

- a) Use a smaller basis set...
- b) Use precontracted basis sets
- c) Take advantage of symmetries! Many elements are 0.
- d) Find optimum between writing to disc, writing to memory or performing direct evaluations whenever needed.

Problems which might occur during the SCF procedure

- 1) Specify the molecule (atoms and structure), the number of electrons and a basis set.
- 2) Calculate all integrals required: $S_{\mu\nu}$, $H_{\mu\nu}^{\text{core}}$, and $(\mu\nu|\lambda\sigma)$
- 3) Diagonalize S to get X

Problem: Basis set shows linear dependence

Solution: Projection into subspace.

Problems which might occur during the SCF procedure

- 1) Specify the molecule (atoms and structure), the number of electrons and a basis set.
- 2) Calculate all integrals required: $S_{\mu\nu}$, $H_{\mu\nu}^{\text{core}}$, and $(\mu\nu|\lambda\sigma)$
- 3) Diagonalize S to get X
- 4) Make a guess for P

Problem: Right, a guess. For K x K values?

Possible solutions:

- a) Make a zero guess ("Core Hamiltonian")
- b) Use an approximation (e.g. "Hueckel")

The Hartree-Fock Approximation

Problems which might occur during the SCF procedure

- 1) Specify the molecule (atoms and structure), the number of electrons and a basis set.
- 2) Calculate all integrals required: $S_{\mu\nu}$, $H_{\mu\nu}^{\text{core}}$, and $(\mu\nu|\lambda\sigma)$
- 3) Diagonalize S to get X
- 4) Make a guess for P
- 5) ...
.
.
.
- 11) Converged?

Problem: Not converged.

Possible solutions:

- a) Improve guess
- b) Oscillation? Try SCF Damping
- c) DIIS method

A few words about SCF convergence

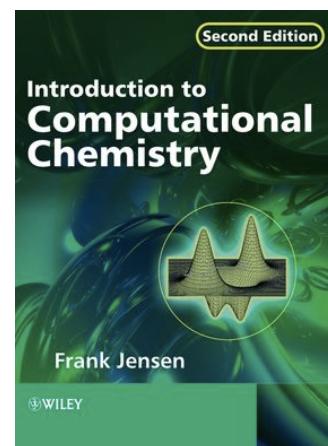
There is no guarantee of SCF convergence. Particularly problematic are calculations with large, diffuse basis sets and distorted geometries (e.g. transition states)

Possible solutions:

- 1) Extrapolation involving the last few steps
- 2) Damping: $\mathbf{P}'_{n+1} = \omega \mathbf{P}_n + (1 - \omega) \mathbf{P}_{n+1}$
- 3) Level shifting: Think back of our interpretation of the SCF procedure as diagonalization

of the Fock matrix. Shifting the virtual orbital energies reduces mixing artificially, which stabilizes (but also slows down) convergence.

(density matrix, Jensen's notation is 'D')



A few words about SCF convergence

Possible solutions:

- 4) Direct inversion in the iterative subspace (DIIS):

A series of SCF steps produces a series of densities P_1, P_2, P_3, \dots and a series of Fock matrices F_1, F_2, F_3, F_4 .

Pulay's ansatz: We define an error for each step via $E_i = F_i P_i S - S P_i F_i$, and use the trace of the product matrix of $E_i E_i^T$ as scalar indicator for the total error:

$$\text{ErrF}(\mathbf{c}) = \text{trace}(\mathbf{E}_{n+1} \cdot \mathbf{E}_{n+1}^T)$$

We then search for a linear combination of recent E matrices (e.g. the last 10) that minimizes the error.

$$\mathbf{E}_{n+1} = \sum_{i=0}^n c_i \mathbf{E}_i \quad , \quad \sum_{i=0}^n c_i = 1$$

A few words about SCF convergence

Possible solutions:

- 4) Direct inversion in the iterative subspace (DIIS):

Minimization with respect to the normalization constraint leaves us with a system of equations:

$$\begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} & -1 \\ a_{21} & a_{22} & \cdots & a_{2n} & -1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} & -1 \\ -1 & -1 & \cdots & -1 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \\ -\lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ -1 \end{pmatrix}$$

$$a_{ij} = \text{trace}(\mathbf{E}_i \cdot \mathbf{E}_j)$$

$$\mathbf{A}\mathbf{c} = \mathbf{b}$$

A few words about SCF convergence

Possible solutions:

- 4) Direct inversion in the iterative subspace (DIIS):

We calculate the vector $\mathbf{c} = \mathbf{A}^{-1}\mathbf{b}$

And build a new Fock matrix $\mathbf{F}_n^* = \sum_{i=0}^n c_i \mathbf{F}_i$

in the subspace of the last n iterations.

A few words about SCF convergence

Possible solutions:

- 5) Direct minimization:

Remember again that the SCF iteration steps can be interpreted as rotations in the MO space:

$$\phi' = \mathbf{U}\phi = e^{\mathbf{X}}\phi$$

The matrix X contains the parameters describing the unitary transformation. Requesting orthogonality leads to the constraint of X being antisymmetric.

$$\mathbf{U}^\dagger \mathbf{U} = (e^{\mathbf{X}})^\dagger (e^{\mathbf{X}}) = (e^{\mathbf{X}^\dagger})(e^{\mathbf{X}}) = (e^{-\mathbf{X}})(e^{\mathbf{X}}) = 1$$

If the orbitals are real, the transformation is just orthogonal. In the simplified case of just 2 orbitals we find

A few words about SCF convergence

Possible solutions:

5) Direct minimization:

angle of rotation for a particular MO pair

$$\mathbf{X} = \begin{pmatrix} 0 & \alpha \\ -\alpha & 0 \end{pmatrix}$$

$$\mathbf{U} = e^{\mathbf{X}} = \begin{pmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{pmatrix}$$

In each SCF iteration, we try to make the nondiagonal block entries corresponding to “occupied-virtual” combinations vanish. Alternatively, we can think of this problem as a standard minimization via the following approach...

The Hartree-Fock Approximation

After convergence: Properties of the electronic WF

Let us assume we have a set of converged MOs:

$$E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle$$

$$E_0 = 2 \sum_a^{N/2} h_{aa} + \sum_a^{N/2} \sum_b^{N/2} 2J_{ab} - K_{ab}$$

With the MO energies,

$$\varepsilon_a = f_{aa} = h_{aa} + \sum_b^{N/2} 2J_{ab} - K_{ab}$$

we can write the total energy as

$$E_0 = \sum_a^{N/2} (h_{aa} + f_{aa}) = \sum_a^{N/2} (h_{aa} + \varepsilon_a)$$

The Hartree-Fock Approximation

After convergence: Properties of the electronic WF

In a given basis set the energy can also be written as

$$E_0 = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\nu\mu} (H_{\mu\nu}^{\text{core}} + F_{\mu\nu})$$

at any stage of the SCF procedure.

Our first expectation value of interest is the **total energy** of a molecule:

$$E_{\text{tot}} = E_0 + \sum_A \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}$$

Another expectation value of interest could be the **dipole moment**:

$$\hat{\mu} = \sum_i q_i \mathbf{r}_i \quad \hat{\mu} = \left\langle \Psi_0 \left| - \sum_{i=1}^N \mathbf{r}_i \right| \Psi_0 \right\rangle + \sum_A Z_A \mathbf{R}_A$$

After convergence: Properties of the electronic WF

The dipole moment corresponds to a sum over one-electron operators, similar to the core Hamiltonian. In general, we can write this type of operator as

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

Each operator in the sum depends only on the coordinates of a single electron. Expectation values for this type of operators are of the form

$$\langle \mathcal{O}_1 \rangle = \langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle = \sum_a^{N/2} (\psi_a | h | \psi_a) = \sum_{\mu\nu} P_{\mu\nu} (\nu | h | \mu)$$

The Hartree-Fock Approximation

After convergence: Properties of the electronic WF

We obtain $\hat{\mu} = - \sum_{\mu} \sum_{\nu} P_{\mu\nu}(v|\mathbf{r}|\mu) + \sum_A Z_A \mathbf{R}_A$

We can calculate each component separately:

$$\mu_x = - \sum_{\mu} \sum_{\nu} P_{\mu\nu}(v|x|\mu) + \sum_A Z_A X_A ,$$

with

$$(v|x|\mu) = \int d\mathbf{r}_1 \phi_v^*(\mathbf{r}_1) x_1 \phi_{\mu}(\mathbf{r}_1)$$

Another expectation value of obvious interest is the **charge density itself**:

$$\rho(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \phi_{\mu}(\mathbf{r}) \phi_{\nu}^*(\mathbf{r})$$

The Hartree-Fock Approximation

After convergence: Properties of the electronic WF

It would be interesting to find a measure of how the electrons are distributed over atoms. There is no unique definition of e⁻ per atoms, but from

$$N = 2 \sum_a^{N/2} \int d\mathbf{r} |\psi_a(\mathbf{r})|^2$$

it follows that

$$N = \sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\nu\mu} = \sum_{\mu} (\mathbf{PS})_{\mu\mu} = \text{tr } \mathbf{PS}$$

Now (if we want) we can interpret $(\mathbf{PS})_{\mu\mu}$ as the number of electrons associated with ϕ_{μ} . This is called the a **Mulliken Population Analysis**: We sum over all contributions of AOs belonging to the same atom, and obtain a net charge of atom A by calculating

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu}$$

Basis sets

STOs and GTOs...

STOs, or **Slater Type Orbitals**, are inspired by the atomic orbitals, i.e. the solutions of an atomic Schrödinger equation. The normalized 1s STO centered at atom A has the form

$$\phi_{1s}^{\text{SF}}(\zeta, \mathbf{r} - \mathbf{R}_A) = (\zeta^3/\pi)^{1/2} e^{-\zeta|\mathbf{r} - \mathbf{R}_A|}$$

GTOs, or **Gaussian Type orbitals**, are of the form

$$\phi_{1s}^{\text{GF}}(\alpha, \mathbf{r} - \mathbf{R}_A) = (2\alpha/\pi)^{3/4} e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2}$$

STOs and GTOs...

What is so good about GTOs?

The integrals are much easier to evaluate in a GTO basis. The typical integrals

$$(\mu_A v_B | \lambda_C \sigma_D) = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_{\mu}^{A*}(\mathbf{r}_1) \phi_{v}^B(\mathbf{r}_1) r_{12}^{-1} \phi_{\lambda}^{C*}(\mathbf{r}_2) \phi_{\sigma}^D(\mathbf{r}_2)$$

can be evaluated fully analytically. Products of Gaussian functions are Gaussian functions themselves

$$\phi_{1s}^{\text{GF}}(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_{1s}^{\text{GF}}(\beta, \mathbf{r} - \mathbf{R}_B) = K_{AB} \phi_{1s}^{\text{GF}}(p, \mathbf{r} - \mathbf{R}_P)$$

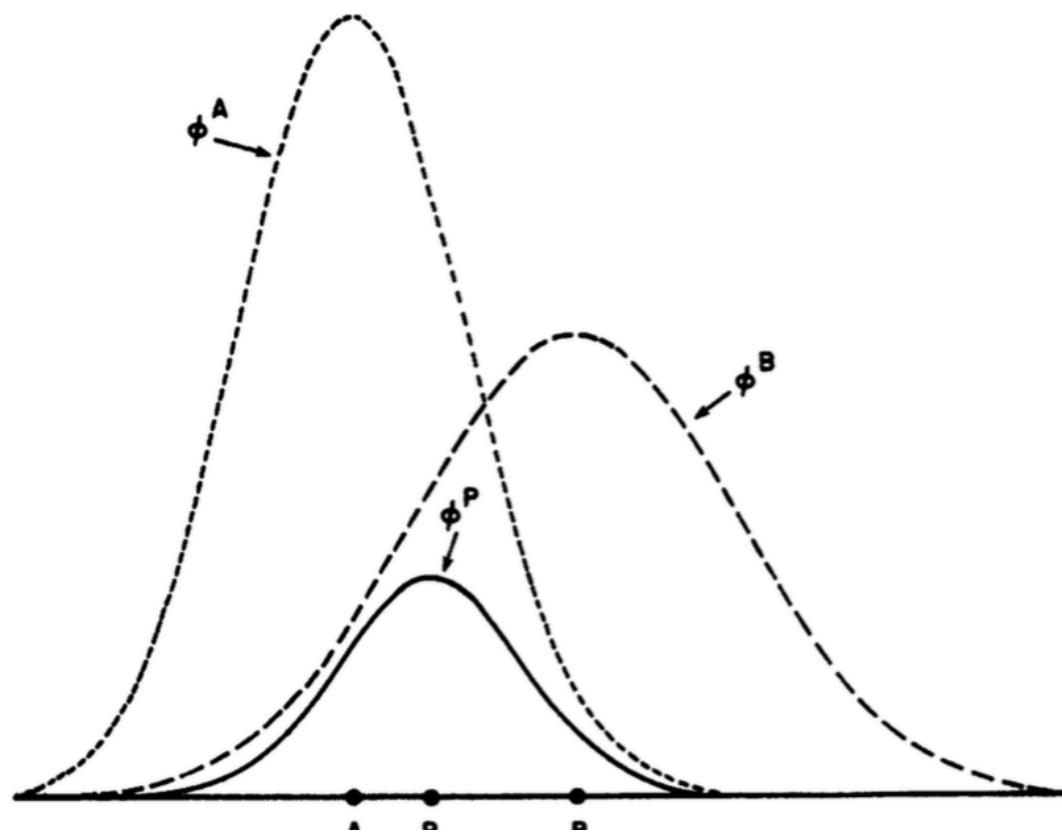
$$K_{AB} = \left(\frac{2}{\pi}\right)^{3/2} (\alpha\beta)^{3/4} \quad \begin{matrix} \text{with} \\ \exp[-\alpha\beta/(\alpha + \beta)|\mathbf{R}_A - \mathbf{R}_B|^2] \end{matrix}$$

The new exponent is given by $p = \alpha + \beta$ and the function is centered at

$$\mathbf{R}_P = (\alpha\mathbf{R}_A + \beta\mathbf{R}_B)/(\alpha + \beta)$$

STOs and GTOs...

What is so good about GTOs?



The product of two gaussian functions A and B.

STOs and GTOs...

What is so good about GTOs?

For s-type orbitals one obtains

$$\begin{aligned} (\mu_A \nu_B | \lambda_C \sigma_D) &= K_{AB} K_{CD} \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_{1s}^{\text{GF}}(p, \mathbf{r}_1 - \mathbf{R}_P) r_{12}^{-1} \phi_{1s}^{\text{GF}}(q, \mathbf{r}_2 - \mathbf{R}_Q) \\ &= 2\pi^{5/2} / [(\alpha + \beta)(\gamma + \delta)(\alpha + \beta + \gamma + \delta)^{1/2}] \\ &\quad \times \exp[-\alpha\beta/(\alpha + \beta)|\mathbf{R}_A - \mathbf{R}_B|^2 - \gamma\delta/(\gamma + \delta)|\mathbf{R}_C - \mathbf{R}_D|^2] \\ &\quad \times F_0[(\alpha + \beta)(\gamma + \delta)/(\alpha + \beta + \gamma + \delta)|\mathbf{R}_P - \mathbf{R}_Q|^2] \end{aligned}$$

with

$$F_0(t) = t^{-1/2} \int_0^{t^{1/2}} dy e^{-y^2} = \frac{1}{2}(\pi/t)^{1/2} \operatorname{erf}(t^{1/2})$$

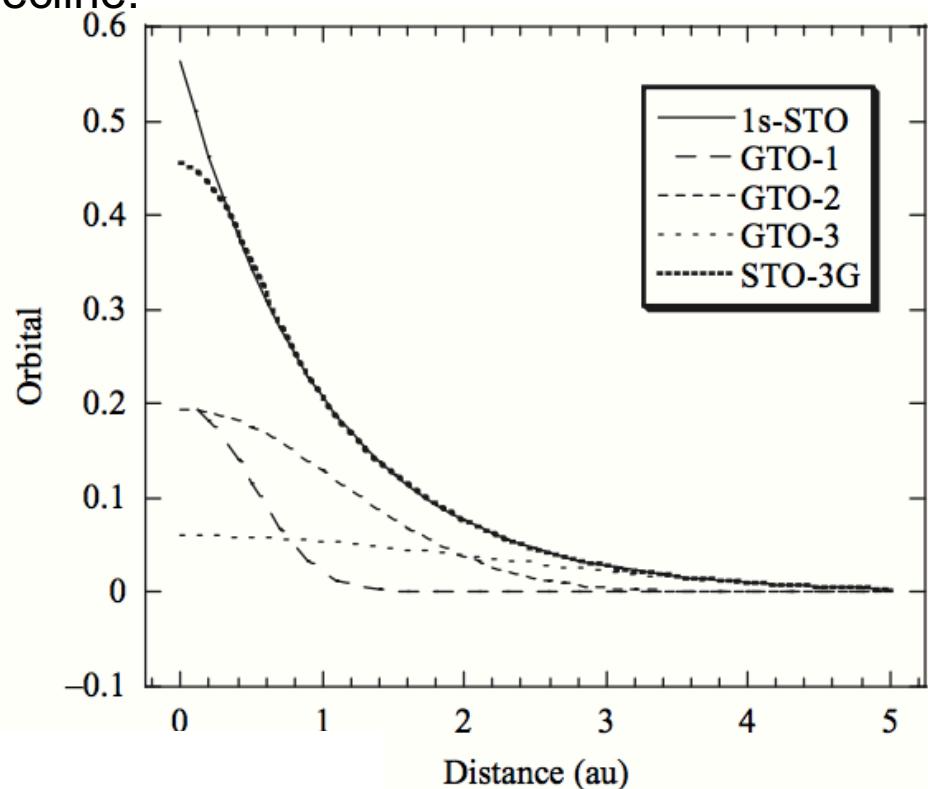
STOs and GTOs...

What is bad about GTOs?

They are not the optimum basis functions due to the wrong first derivative at the nucleus and their faster asymptotic decline.

A possible solution: **Contraction**

We approximate a STO by a linear combination of GTOs.



Contracted Gaussian Function

↗

$$\phi_{\mu}^{\text{CGF}}(\mathbf{r} - \mathbf{R}_A) = \sum_{p=1}^L d_{p\mu} \phi_p^{\text{GF}}(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_A)$$

How to handle higher angular momentum basis functions

Choosing Gaussian basis functions, we may write higher angular momentum basis functions as

$$\phi_{\zeta,n,l,m}(r, \theta, \varphi) = N Y_{l,m}(\theta, \varphi) r^{2n-2-l} e^{-\zeta r^2}$$

in polar coordinates, or as

$$\phi_{\zeta,l_x,l_y,l_z}(x, y, z) = N x^{l_x} y^{l_y} z^{l_z} e^{-\zeta r^2}$$

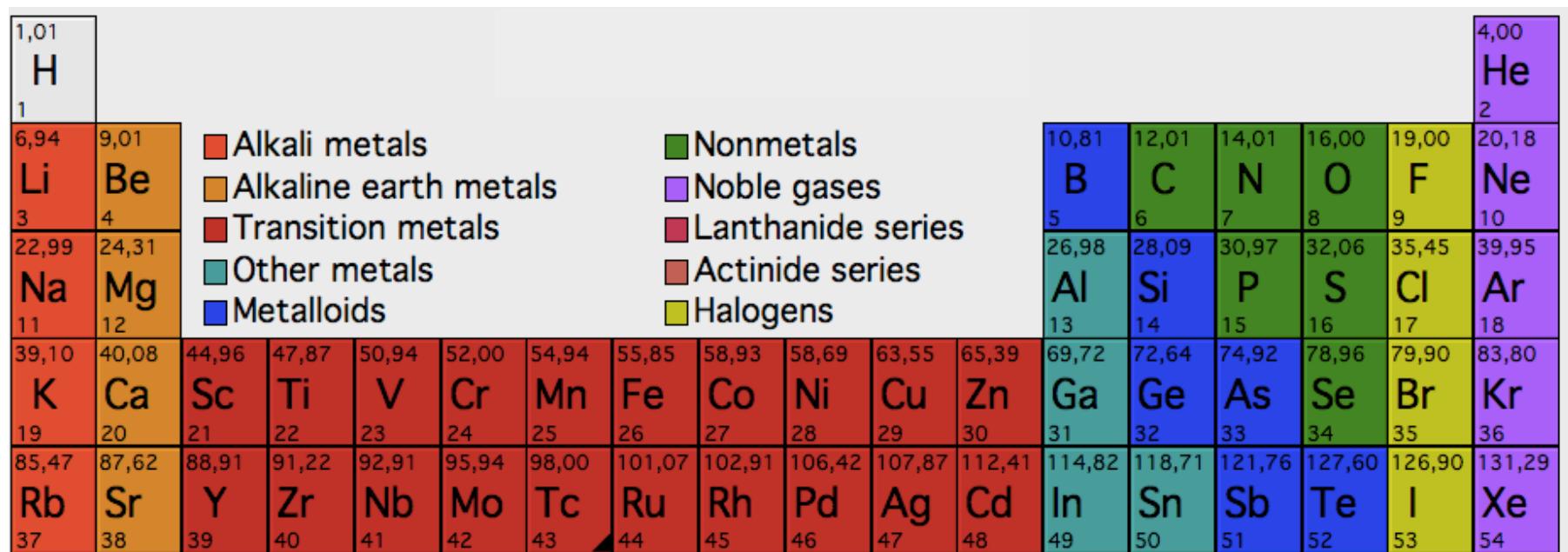
in Cartesian coordinates.

Here, the sum of l_i determines the angular momentum, e.g. $0+0+1 = 1$ for a p_z orbital.

Note the different number of basis functions in the spherical and Cartesian definitions for $l > 1$, e.g. for d functions (6 Cartesian, but 5 spherical functions)

On the classification of basis sets

- 1) Type: STO or GTO
- 2) Size: Minimum, DZ, TZ,...



Periodic table of elements showing atomic number, symbol, and mass number. The elements are grouped into categories:

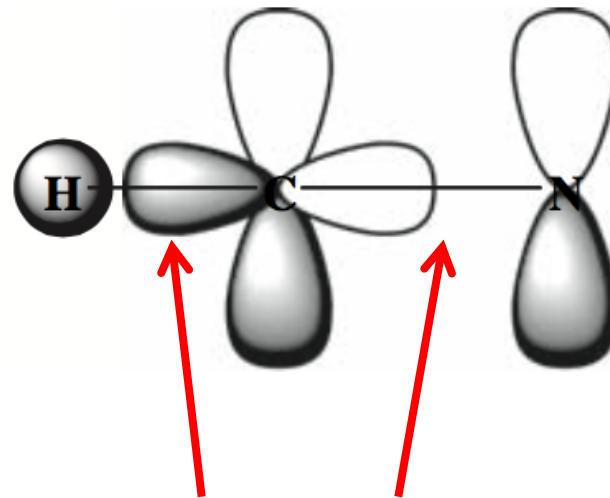
- Alkali metals:** Li, Na, K, Rb
- Alkaline earth metals:** Be, Mg, Ca, Sr
- Transition metals:** Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Cd
- Other metals:** Y, Zr, Nb, Mo, Tc
- Metalloids:** Ge, As, Se, Br, I
- Nonmetals:** B, C, N, O, F, S, Cl, Ar, Ga, Ge, As, Se, Br, I
- Noble gases:** He, Ne, Kr, Xe
- Lanthanide series:** (Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)
- Actinide series:** (Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md)
- Halogens:** F, Cl, Br, I

$$\phi_{\zeta, l_x, l_y, l_z}(x, y, z) = N x^{l_x} y^{l_y} z^{l_z} e^{-\zeta r^2}$$

“Zeta”

What is the advantage of a DZ basis set?

Look at HCN:

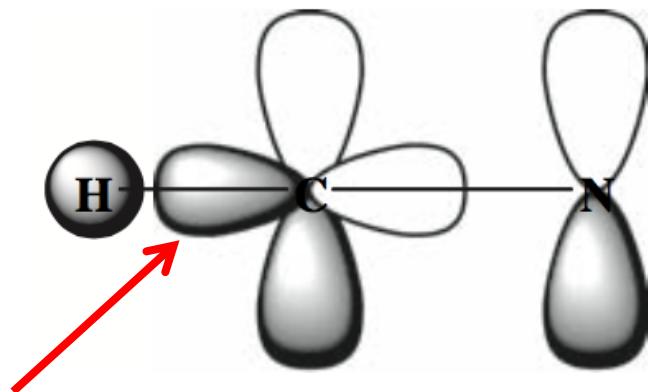


p orbitals would like to have different character for C-H and C-N

More economic: “Valence split” basis sets; DZ, TZ etc. are mostly referring to basis sets where only valence orbitals are multiplied

1) Modifications: polarization and diffuse functions

Polarization: Look at HCN again. How could the C-H bond description be improved?



By adding a p-type function to H!

In general: Adding higher angular momenta functions improves the flexibility of the electron density.

Note: This is especially important for correlation (think of avoidance options for each electron: “in-out” and “angular” correlation. Angular momentum convergence is slower for higher correlated methods).

Notation: DZP or pVDZ or by adding a '*' to Pople's notation.

Diffuse functions: Functions with small exponents are added to the basis set. They occupy a larger region of space, important for molecules with 'soft' electron densities. More important for DFT (See Lynch et al., JPC A, 107, 1384 (2003)).

Notation: A '+' added to Pople's notation, or an "aug" to Dunning sets.

A few examples:

- 3-21G
- 6-311+G*
- 6-31G(3df,3pd)
- cc-pVDZ
- aug-cc-pVTZ

How can I obtain a basis set? **In theory...**

By solving a highly non-linear optimization problem (atomic energies, orbital energies, wf properties such as the polarizability).

An interesting finding: The ratio between two successive exponents is approximately constant. Assuming a constant ratio reduces the optimization effort.

Even tempered basis sets: $\zeta_i = \alpha\beta^i; i = 1, 2, \dots, M$

$$\ln(\ln \beta) = b \ln M + b'$$

$$\ln \alpha = a \ln(\beta - 1) + a'$$

a, b, a', and b' depend only on the atom and function type.

Well tempered basis sets:

$$\zeta_i = \alpha\beta^{i-1} \left(1 + \gamma \left(\frac{i}{M} \right)^\delta \right); i = 1, 2, \dots, M$$

Put more emphasis on valence region!

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Basis sets

How can I obtain a basis set? In practice...

Basis Set Exchange: v1.2.2

Feedback About Release Notes Help

Total: 545 published basis sets

All
3-21++G
3-21++G*
3-21G
3-21G*
3-21G* Polarization
3-21GSP
4-22GSP
4-31G
5ZP
5ZP-DKH
6-31++G
6-31++G*
6-31++G**
6-31+G
6-31+G*

Search Basis Set Name

Format: NWChem Optimized General Contractions

"3-21++G" Basis Set Information

VDZD Valence Double Zeta + Diffuse Functions on All Atoms
Primary Developer: N/A
Last Modified: Mon, 15 Jan 2007 23:47:08 GMT

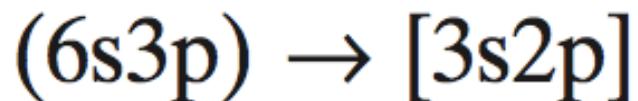
Contributor: Dr. David Feller
Curation Status: published

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[User annotations...](#)

<https://bse.pnl.gov/bse/portal>

Example 1: 3-21G for C

```
*****
C      0
S      3   1.00
      172.2560000      0.0617669
      25.9109000      0.3587940
      5.5333500      0.7007130
SP     2   1.00
      3.6649800      -0.3958970      0.2364600
      0.7705450      1.2158400      0.8606190
SP     1   1.00
      0.1958570      1.0000000      1.0000000
*****
```



Example 2: 6-311+G* for C

```
*****
C      0
S      6   1.00
        4563.2400000      0.00196665
        682.0240000      0.0152306
        154.9730000      0.0761269
        44.4553000      0.2608010
        13.0290000      0.6164620
        1.8277300      0.2210060
SP     3   1.00
        20.9642000      0.1146600      0.0402487
        4.8033100      0.9199990      0.2375940
        1.4593300      -0.00303068      0.8158540
SP     1   1.00
        0.4834560      1.0000000      1.0000000
SP     1   1.00
        0.1455850      1.0000000      1.0000000
SP     1   1.00
        0.0438000      1.0000000      1.0000000
D     1   1.00
        0.6260000      1.0000000
*****
*****
```

Example 3: 6-31G(3df,3pd) for C

```
*****
C     0
S     6   1.00
      3047.5249000      0.0018347
      457.3695100      0.0140373
      103.9486900      0.0688426
      29.2101550      0.2321844
      9.2866630      0.4679413
      3.1639270      0.3623120
SP    3   1.00
      7.8682724      -0.1193324      0.0689991
      1.8812885      -0.1608542      0.3164240
      0.5442493      1.1434564      0.7443083
SP    1   1.00
      0.1687144      1.0000000      1.0000000
D     1   1.00
      2.5040000      1.0000000
D     1   1.00
      0.6260000      1.0000000
D     1   1.00
      0.1565000      1.0000000
F     1   1.00
      0.8000000      1.0000000
*****

```

Example 4: cc-pVDZ for C

```
*****
C      0
S     8   1.00
       6665.0000000          0.0006920
       1000.0000000          0.0053290
       228.0000000          0.0270770
       64.7100000          0.1017180
       21.0600000          0.2747400
       7.4950000          0.4485640
       2.7970000          0.2850740
       0.5215000          0.0152040
S     8   1.00
       6665.0000000         -0.0001460
       1000.0000000         -0.0011540
       228.0000000         -0.0057250
       64.7100000         -0.0233120
       21.0600000         -0.0639550
       7.4950000         -0.1499810
       2.7970000         -0.1272620
       0.5215000          0.5445290
S     1   1.00
       0.1596000          1.0000000
P     3   1.00
       9.4390000          0.0381090
       2.0020000          0.2094800
       0.5456000          0.5085570
P     1   1.00
       0.1517000          1.0000000
D     1   1.00
       0.5500000          1.0000000
*****
```

Example 5: aug-cc-pVTZ for C

```
*****
C      0
S     8   1.00
    8236.0000000      0.0005310      P     3   1.00
    1235.0000000      0.0041080      18.7100000      0.0140310
    280.8000000      0.0210870      4.1330000      0.0868660
    79.2700000      0.0818530      1.2000000      0.2902160
    25.5900000      0.2348170      P     1   1.00
    8.9970000      0.4344010      0.3827000      1.0000000
    3.3190000      0.3461290      P     1   1.00
    0.3643000      -0.0089830      0.1209000      1.0000000
S     8   1.00
    8236.0000000      -0.0001130      P     1   1.00
    1235.0000000      -0.0008780      0.0356900      1.0000000
    280.8000000      -0.0045400      D     1   1.00
    79.2700000      -0.0181330      1.0970000      1.0000000
    25.5900000      -0.0557600      D     1   1.00
    8.9970000      -0.1268950      0.3180000      1.0000000
    3.3190000      -0.1703520      D     1   1.00
    0.3643000      0.5986840      0.1000000      1.0000000
S     1   1.00
    0.9059000      1.0000000      F     1   1.00
S     1   1.00
    0.1285000      1.0000000      0.7610000      1.0000000
S     1   1.00
    0.0440200      1.0000000      F     1   1.00
                                         0.2680000      1.0000000
*****
```

Basis set extrapolation

Basis set families such as the cc sets allow to give an estimate of the basis set limit via extrapolation (e.g., as a function of the highest angular momentum)

either for total energies,

$$E(L_{\max}) = E(\infty) + A e^{-BL_{\max}}$$

$$E(L_{\max}) = E(\infty) + A(L_{\max} + 1) e^{-B\sqrt{L_{\max}}}$$

or for the correlation part of the energy

$$\Delta E_{\text{corr},\infty} = \frac{N^3 \Delta E_{\text{corr},N} - M^3 \Delta E_{\text{corr},M}}{N^3 - M^3}$$

In the latter case, only two calculations with $L_{\max} = N$ and M are needed.

Basis set superposition error (BSSE)

One problem of finite basis sets is **balance**, another is the energy dependence on nuclear coordinates, i.e. on the actual atom positions.

There are three ways out of this:

- 1) Make the basis huge.



Frustrating for diploma students.

Basis set superposition error (BSSE)

One problem of finite basis sets is **balance**, another is the energy dependence on nuclear coordinates, i.e. on the actual atom positions.

There are three ways out of this:

- 1) Make the basis huge.



Or their equipment.

Basis set superposition error (BSSE)

One problem of finite basis sets is **balance**, another is the energy dependence on nuclear coordinates, i.e. on the actual atom positions.

There are three ways out of this:

- 1) Make the basis huge.
- 2) Basis set extrapolation.
- 3) BSSE corrections.

The counterpoise correction (see David Sherrill, July 2010, <http://vergil.chemistry.gatech.edu/notes/cp.pdf>)

First, the typical uncorrected interaction energy between monomers A and B:

$$\Delta E_{int}(AB) = \underbrace{E_{AB}^{AB}(AB)}_{\text{(geometry)}} - E_A^A(A) - E_B^B(B)$$

Now, the isolated monomer energies will change with distance between A and B. One way of correcting is to determine the energies

$$\begin{aligned} E_{BSSE}(A) &= E_A^{AB}(A) - E_A^A(A), \\ E_{BSSE}(B) &= E_B^{AB}(B) - E_B^B(B), \end{aligned}$$

Using these corrections, we can calculate the interaction energy via

$$\Delta E_{int}^{CP}(AB) = E_{AB}^{AB} - E_A^{AB} - E_B^{AB}$$

Problems: Overcorrection, balance issues

The counterpoise correction (see David Sherrill, July 2010, <http://vergil.chemistry.gatech.edu/notes/cp.pdf>)

For the binding energy it gets a little bit more complicated...

$$\begin{aligned} E_{BSSE}(A) &= E_{AB}^{AB}(A) - E_{AB}^A(A) \\ E_{BSSE}(B) &= E_{AB}^{AB}(B) - E_{AB}^B(B) \end{aligned}$$

Now, we obtain a slightly longer expression,

$$\Delta E_{bind}^{CP}(AB) = E_{AB}^{AB}(AB) - E_A^A(A) - E_B^B(B) - E_{AB}^{AB}(A) + E_{AB}^A(A) - E_{AB}^{AB}(B) + E_{AB}^B(B)$$

since $E_{AB}^A(A) \neq E_A^A(A)$ and $E_{AB}^B(B) \neq E_B^B(B)$,

And reorder to

$$\Delta E_{bind}^{CP}(AB) = [E_{AB}^{AB}(AB) - E_{AB}^{AB}(A) - E_{AB}^{AB}(B)] + [E_{AB}^A(A) - E_A^A(A)] + [E_{AB}^B(B) - E_B^B(B)]$$

Interaction energy

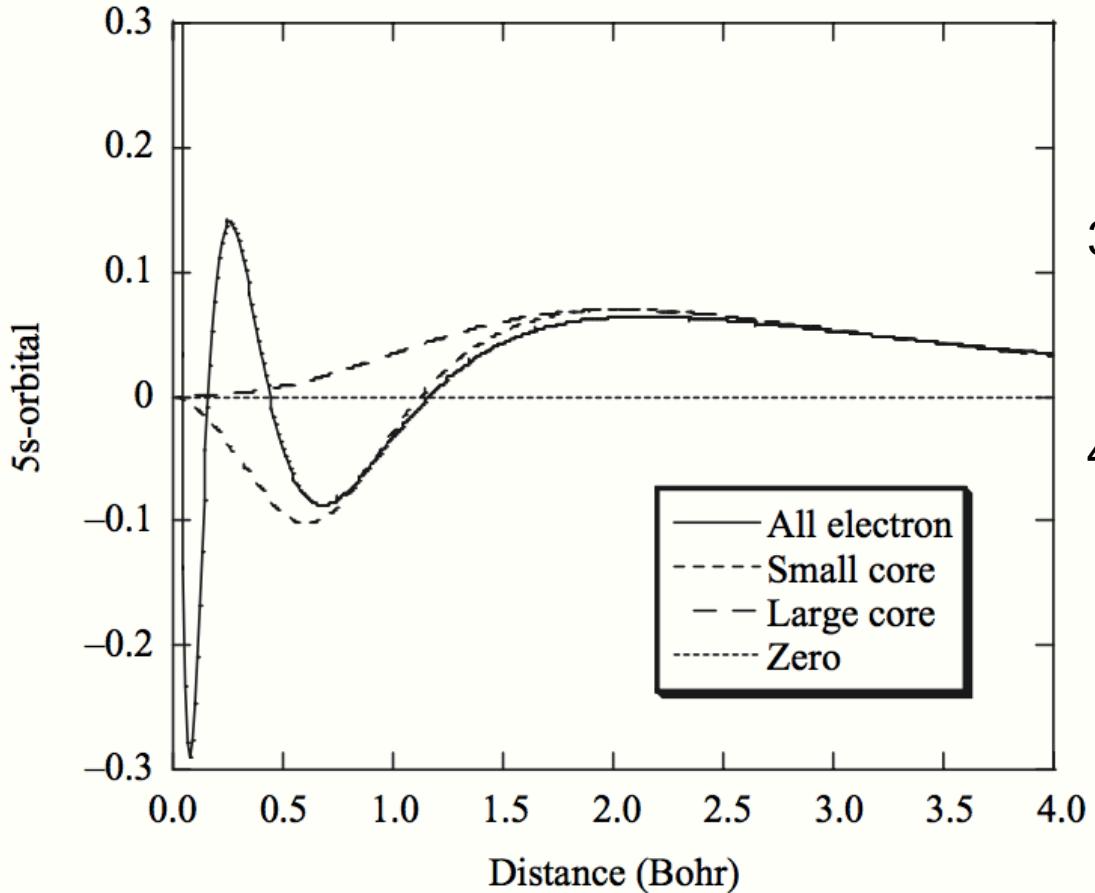
Deformation energies

Effective core or ‘pseudo’ potentials

Idea: Reduce computational effort by partial replacement of inner electrons.

Four major steps for the generation:

- 1) All electron calculation.
- 2) Replace valence orbitals by nodeless pseudo-orbitals, which behave correctly in valence region but do not have a nodal structure in the core region.
- 3) Replace the core e- by an effective potential consisting of a set of analytical functions (typically gaussians for GTOs)
- 4) Fit the potential parameters until agreement with all-electron wf or some of its properties.



Effective core or ‘pseudo’ potentials

Mathematical ansatz (taken from Molpro manual):

$$V_{ps} = -\frac{Z - n_{core}}{r} + V_{l_{max}} + \sum_{l=0}^{l_{max}-1} (V_l - V_{l_{max}}) \mathcal{P}_l + \sum_{l=1}^{l'_{max}} \Delta V_l \mathcal{P}_l \vec{l} \cdot \vec{s} \mathcal{P}_l;$$

with $V_{l_{max}} = \sum_{j=1}^{n_{l_{max}}} c_j r^{m_j-2} e^{-\gamma_j r^2}$

and $V_l - V_{l_{max}} = \sum_{j=1}^{n_l} c_j^l r^{m_j^l-2} e^{-\gamma_j^l r^2}$

Example 6: LANL2DZ for Cs (55 e⁻)

Basis:				ECP:			
****				CS 0			
Cs	0			CS-ECP	3	46	
S	3	1.00		f-ul potential			
				6			
		0.8709000	-1.1604798	0	636.7840130		-0.0805109
		0.5393000	1.4198515	1	147.8912446		-33.4311448
		0.1724000	0.5872905	2	42.5724911		-193.9270887
S	4	1.00		2	11.2427883		-56.8301433
		0.8709000	0.8237727	2	3.5689707		-18.6504975
		0.5393000	-1.0709181	2	1.3107462		-2.5411399
		0.1724000	-0.9085122	s-ul potential			
		0.0393000	1.0774049	3			
S	1	1.00		0	40.8648070		3.0499934
		0.0151000	1.0000000	1	10.9329329		37.9677514
P	3	1.00		2	2.2294903		45.2340673
		1.4680000	-0.1321033	p-ul potential			
		0.4134000	0.6572410	4			
		0.1536000	0.4756456	0	118.8598171		4.6406951
P	2	1.00		1	30.6847958		62.0313533
		0.1458000	-0.1680556	2	10.1762999		129.5909481
		0.0279000	1.0665746	2	1.8272850		31.5186825
P	1	1.00		d-ul potential			
		0.0113000	1.0000000	4			
****				0	16.0081704		7.3054473
				1	2.6488291		33.2785760
				2	14.5555672		53.1296948
				2	0.6703604		16.2118878

Example calculations

Table 3.11 SCF total energies (a.u.) of H₂ with the standard basis sets

Basis set	Energy
STO-3G	-1.117
4-31G	-1.127
6-31G**	-1.131
HF-limit ^a	-1.134

^a J. M. Schulman and D. N. Kaufman, *J. Chem. Phys.* **53**: 477 (1970).

Table 3.12 SCF total energies (a.u.) of N₂ and CO with the standard basis sets

Basis set	N ₂	CO
STO-3G	-107.496	-111.225
4-31G	-108.754	-112.552
6-31G*	-108.942	-112.737
HF-limit ^a	-108.997	-112.791

^a P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta* **28**: 213 (1973).

Table 3.13 SCF total energies (a.u.) for the ten-electron series with the standard basis sets

Basis set	CH ₄	NH ₃	H ₂ O	FH
STO-3G	-39.727	-55.454	-74.963	-98.571
4-31G	-40.140	-56.102	-75.907	-99.887
6-31G*	-40.195	-56.184	-76.011	-100.003
6-31G**	-40.202	-56.195	-76.023	-100.011
HF-limit ^a	-40.225	-56.225	-76.065	-100.071

^a P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta* **28**: 213 (1973).

Table 3.14 Ionization potential (a.u.) of H₂ obtained via Koopmans' theorem

Basic set	Ionization potential
STO-3G	0.578
4-31G	0.596
6-31G**	0.595
Near-HF-limit ^a	0.595
Experiment	0.584

^a J. M. Schulman and D. M. Kaufman, *J. Chem. Phys.* **53**: 477 (1970).

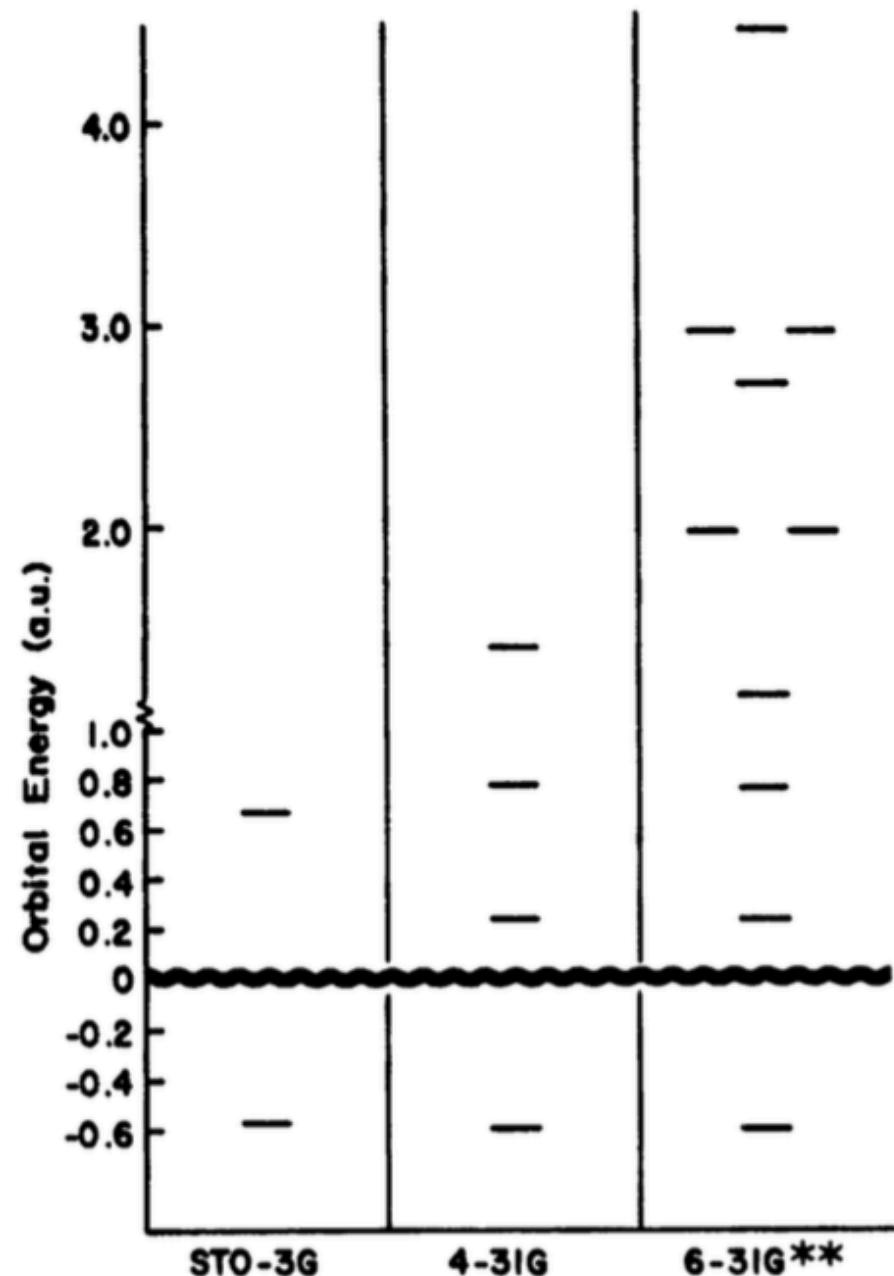
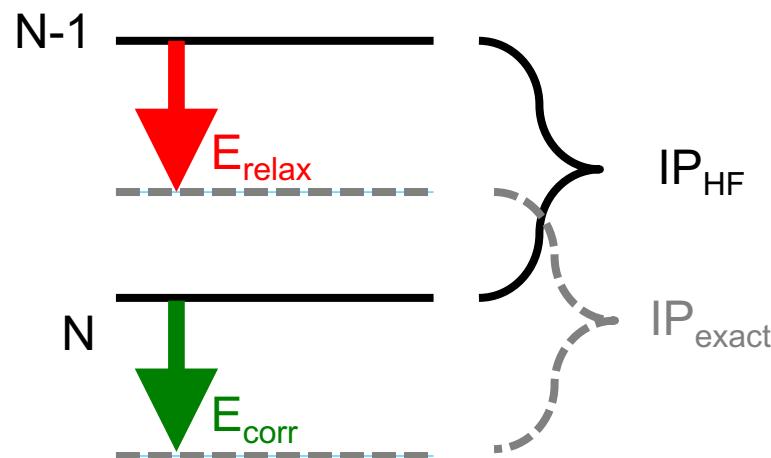


Table 3.15 The first two ionization potentials (a.u.) of CO obtained via Koopmans' theorem

Basis set	Ion symmetry	
	$^2\Sigma$	$^2\Pi$
STO-3G	0.446	0.551
4-31G	0.549	0.640
6-31G*	0.548	0.633
Near-HF-limit ^a	0.550	0.640
Experiment	0.510	0.620

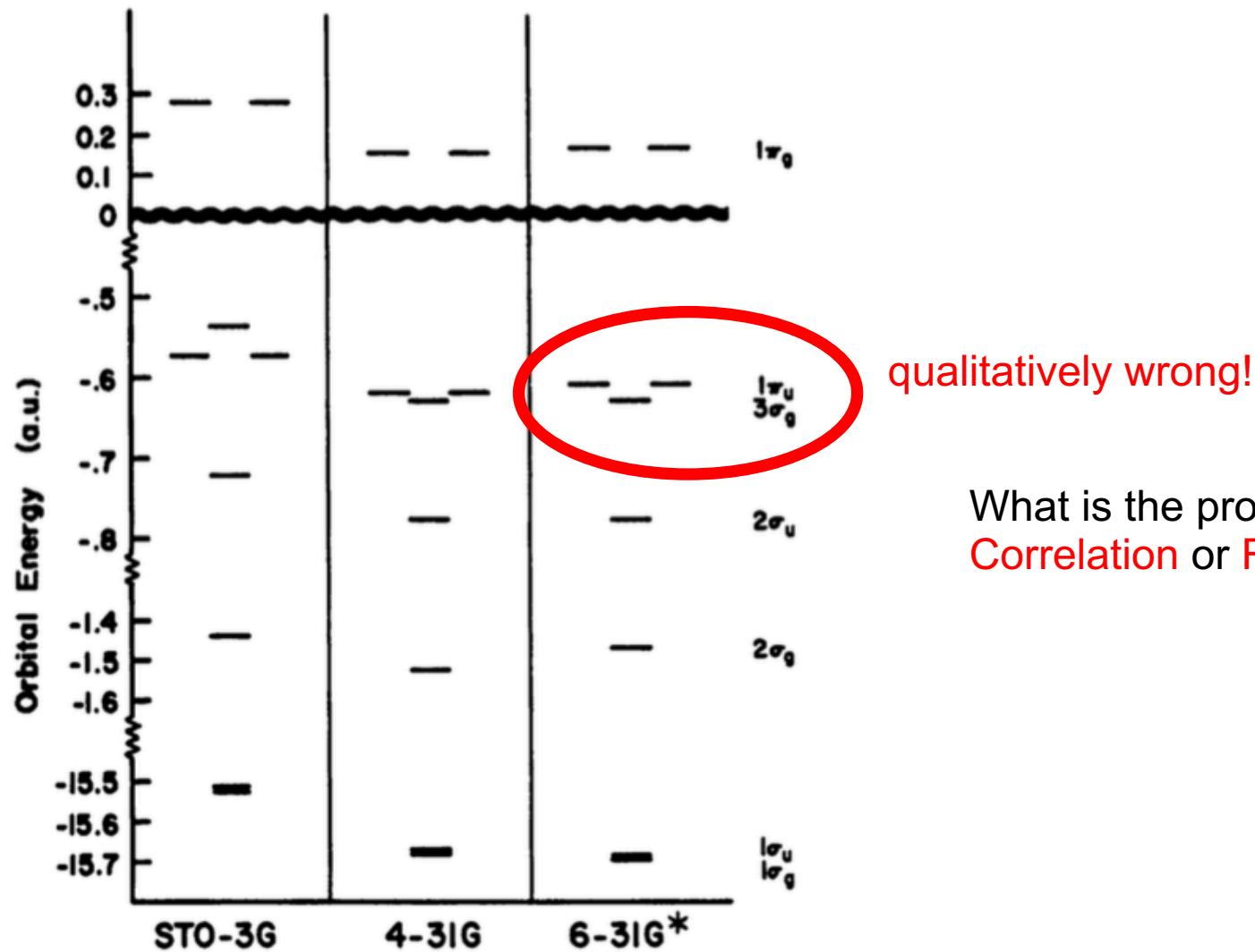
^a W. M. Huo, *J. Chem. Phys.* **43**: 624 (1965).

Table 3.16 The first two ionization potentials (a.u.) of N₂ obtained via Koopmans' theorem

Basis set	Ion symmetry	
	$^2\Sigma$	$^2\Pi$
STO-3G	0.540	0.573
4-31G	0.629	0.621
6-31G*	0.630	0.612
Near-HF-limit ^a	0.635	0.616
Experiment	0.573	0.624

^a P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.* **44**: 1973 (1966).

Koopman's theorem is not truly quantitative, but a good estimate in most cases!

N₂ orbital energies

qualitatively wrong!

What is the problem?
Correlation or Relaxation?

N₂ orbital energies – is relaxation the problem?

Let's do the test:

Table 3.27 SCF calculations on the ground state of N₂ (restricted) and two states of N₂⁺ (unrestricted) with a 6-31G* basis set. Vertical ($R_e = 2.074$ a.u.) ionization potentials are shown, and experimental values are in parenthesis

State	Total Energy (a.u.)	Ionization Potential (a.u.)
N ₂ (¹ Σ _g)	- 108.94235	
N ₂ ⁺ (² Π _u)	- 108.37855	0.564 (0.624)
N ₂ ⁺ (² Σ _g)	- 108.36597	0.576 (0.573)

Still wrong, error must be lack of correlation!

Table 3.18 SCF equilibrium bond lengths (a.u.) of H₂

Basis set	Bond length
STO-3G	1.346
4-31G	1.380
6-31G**	1.385
Experiment	1.401

Table 3.19 SCF equilibrium bond lengths (a.u.) of N₂ and CO

Basis set	N ₂	CO
STO-3G	2.143	2.166
4-31G	2.050	2.132
6-31G*	2.039	2.105
Near-HF-limit	2.013 ^a	2.081 ^b
Experiment	2.074	2.132

^a P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.* **44**: 1973 (1966).

^b W. M. Huo, *J. Chem. Phys.* **43**: 624 (1965).

No quantitative agreement, but correct trends in series of related molecules

Examples

Wave function properties: charges and dipole moment

Table 3.22 A Mulliken SCF population analysis for the ten-electron series. The entries are the net charges on the hydrogens

Basis set	CH ₄	NH ₃	H ₂ O	FH
STO-3G	0.06	0.16	0.18	0.21
4-31G	0.15	0.30	0.39	0.48
6-31G*	0.16	0.33	0.43	0.52
6-31G**	0.12	0.26	0.34	0.40

Table 3.25 SCF dipole moments (a.u.) for the ten-electron series and the standard basis sets

Basis set	NH ₃	H ₂ O	FH
STO-3G	0.703	0.679	0.507
4-31G	0.905	1.026	0.897
6-31G*	0.768	0.876	0.780
6-31G**	0.744	0.860	0.776
Near-HF-limit	0.653 ^a	0.785 ^b	0.764 ^c
Experiment	0.579	0.728	0.716

Table 3.23 A Löwdin SCF population analysis for the ten-electron series. The entries are the net charges on the hydrogens

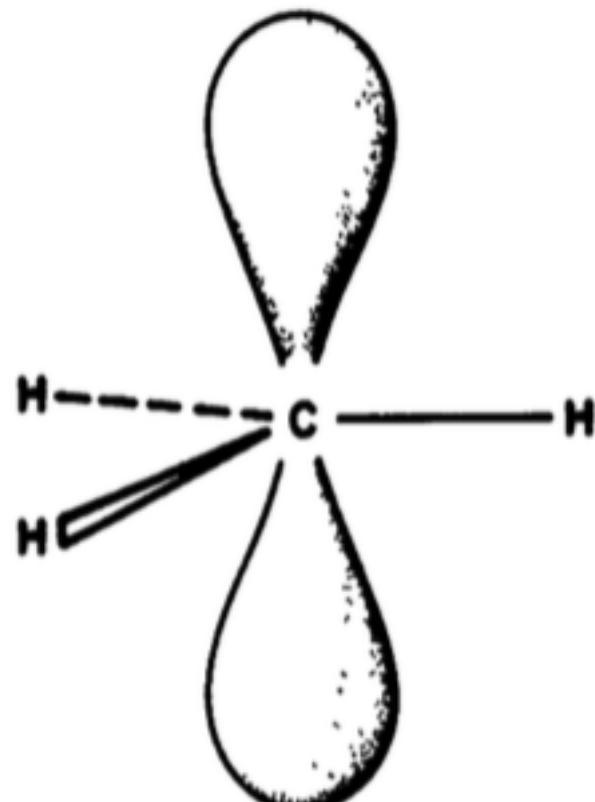
Basis set	CH ₄	NH ₃	H ₂ O	FH
STO-3G	0.03	0.10	0.13	0.15
4-31G	0.10	0.20	0.28	0.36
6-31G*	0.16	0.27	0.36	0.45
6-31G**	0.11	0.18	0.23	0.27

Table 3.24 SCF dipole moment (a.u.) of CO for the standard basis sets. A positive dipole moment corresponds to C⁻O⁺

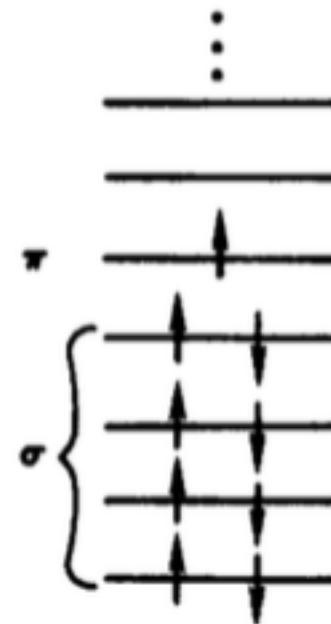
Basis set	Dipole moment
STO-3G	0.066
4-31G	-0.237
6-31G*	-0.131
Near-HF-limit ^a	-0.110
Experiment	0.044

^a A. D. McLean and M. Yoshimine, *Intern. J. Quantum Chem.* **15**: 313 (1967).

The methyl radical:



$$\rho^S(\mathbf{r}) = |\psi_\pi(\mathbf{r})|^2$$

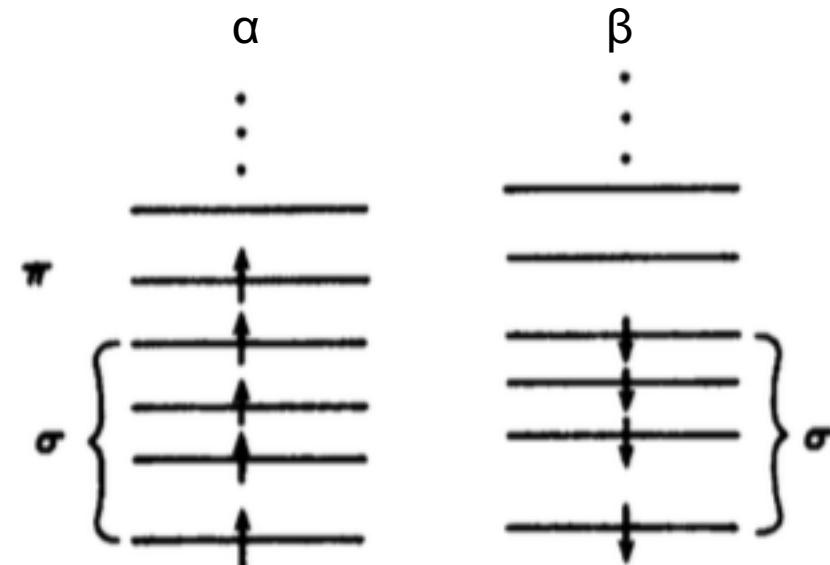
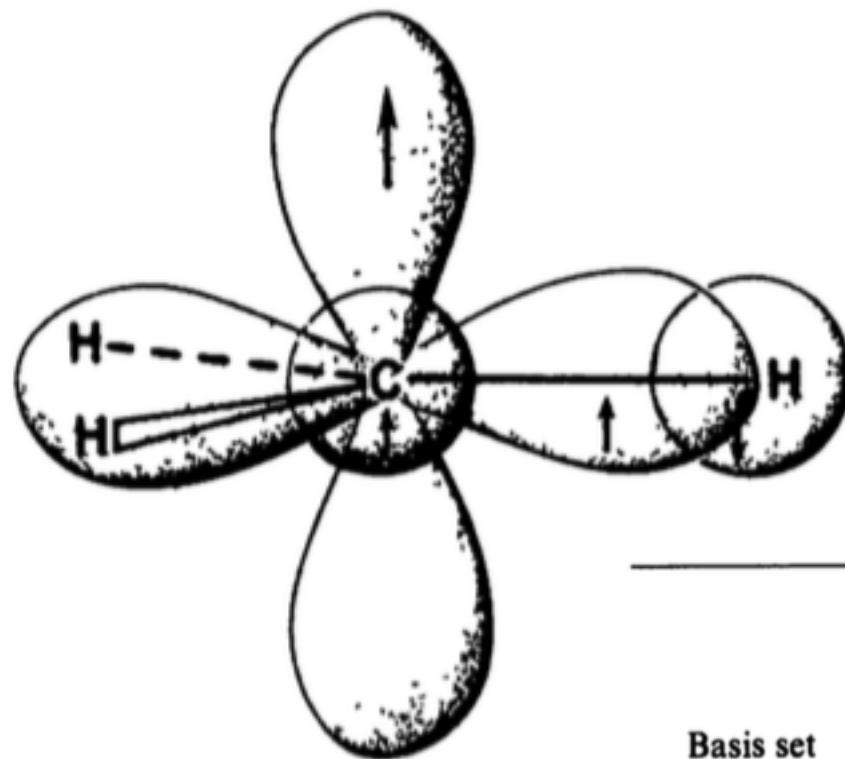


Spin density at nuclei **is zero in RHF calculations**,
but experiment shows:

$$a^H(\text{Gauss}) = 1592\rho^S(\mathbf{R}_H)$$

$$a^C(\text{Gauss}) = 400.3\rho^S(\mathbf{R}_C)$$

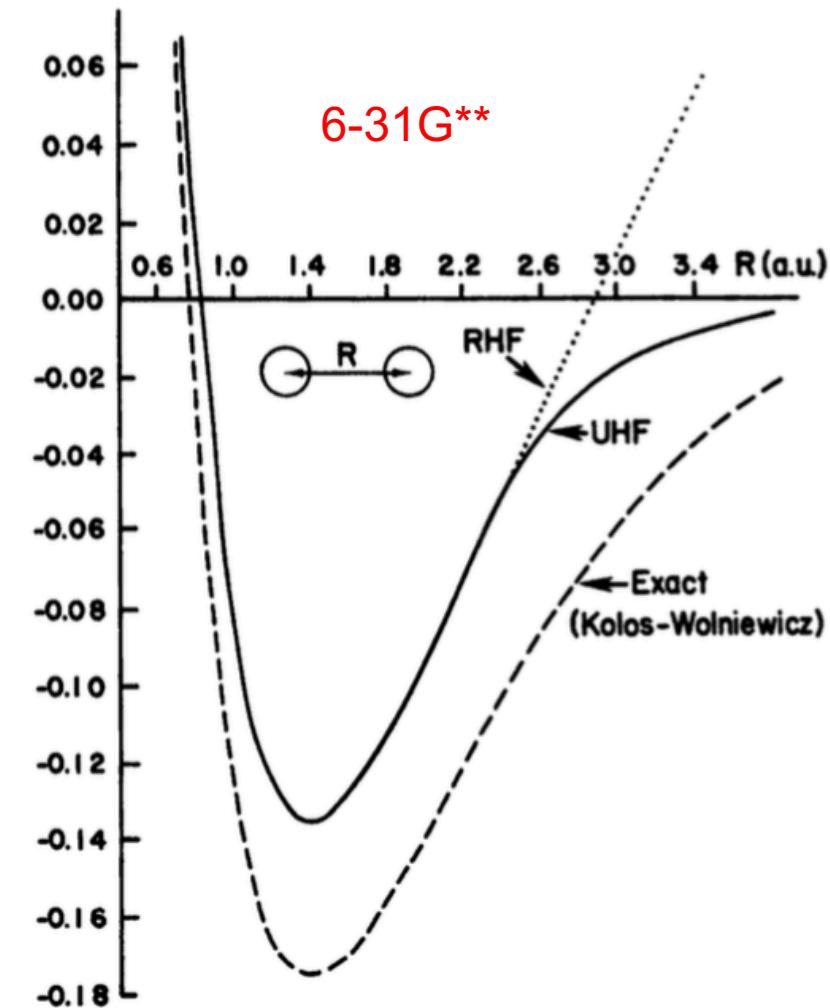
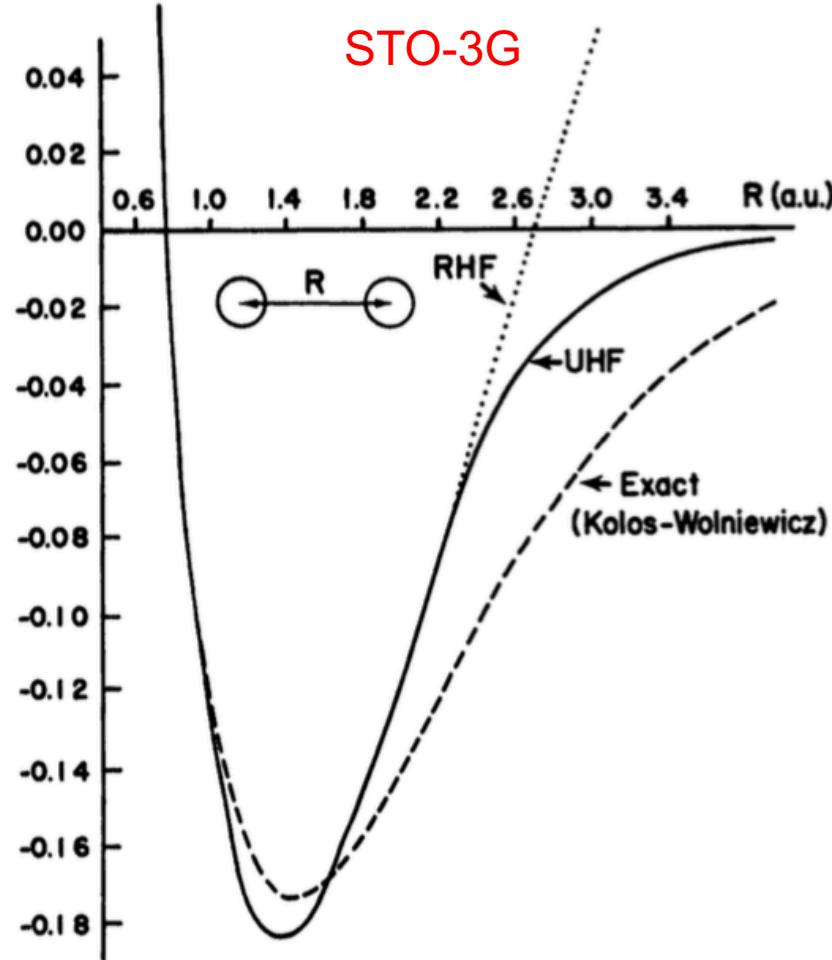
The methyl radical:



UHF solves the problem:
 One half of the electrons also feels exchange correction!

Basis set	Spin density (a.u.)		Coupling constant (Gause)		
	C	H	a^c	a^h	$\langle S^2 \rangle$
STO-3G	+0.2480	-0.0340	+99.3	-54.2	0.7652
4-31G	+0.2343	-0.0339	+93.8	-54.0	0.7622
6-31G*	+0.1989	-0.0303	+79.6	-48.3	0.7618
6-31G**	+0.1960	-0.0296	+78.5	-47.1	0.7614
Experiment			+38.3	-23.0	0.75

We find a deviation of the RHF PES from the correct curve:



The UHF solution is qualitatively correct, but still shows big deviations...

CI and CC methods

We remember the definition of the correlation energy:

$$E_{\text{corr}} = E_0 - E_0$$

We obtain this energy by diagonalizing the N-electron Hamiltonian in a basis of N-electron slater determinants (or, to be more accurate, of spin adapted functions)

How big is this basis?
 In total we can build $\binom{2K}{N}$ different determinants.

Let's sort them with respect to the number of excitations:

$$\begin{aligned}
 |\Phi_0\rangle &= c_0|\Psi_0\rangle + \sum_{ar} c_a^r |\Psi_a^r\rangle + \sum_{\substack{a < b \\ r < s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle \\
 &\quad + \sum_{\substack{a < b < c \\ r < s < t}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \sum_{\substack{a < b < c < d \\ r < s < t < u}} c_{abcd}^{rstu} |\Psi_{abcd}^{rstu}\rangle + \dots
 \end{aligned}$$

We can simplify the summations by removing the index constraints:

$$\begin{aligned}
 |\Phi_0\rangle = & c_0|\Psi_0\rangle + \left(\frac{1}{1!}\right)^2 \sum_{ar} c_a^r |\Psi_a^r\rangle + \left(\frac{1}{2!}\right)^2 \sum_{abrs} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle \\
 & + \left(\frac{1}{3!}\right)^2 \sum_{\substack{abc \\ rst}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \left(\frac{1}{4!}\right)^2 \sum_{\substack{abcd \\ rstu}} c_{abcd}^{rstu} |\Psi_{abcd}^{rstu}\rangle + \dots
 \end{aligned}$$

We introduced prefactors $(1/n!)^2$ to insure correct counting, e.g. for 2e⁻ excitations

$$c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle, \quad c_{ba}^{rs} |\Psi_{ba}^{rs}\rangle, \quad c_{ab}^{sr} |\Psi_{ab}^{sr}\rangle, \quad \text{and} \quad c_{ba}^{sr} |\Psi_{ba}^{sr}\rangle$$

are equal, giving rise to a factor 1/4.

How many n-tuple excitations are possible (singles, doubles, etc.)?

$$\binom{N}{n} \binom{2K - N}{n}$$

The last equation can be rewritten in symbolic form as

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + c_S|S\rangle + c_D|D\rangle + c_T|T\rangle + c_Q|Q\rangle + \dots$$

Now we build the CI matrix, taking advantage of the following simplifications:

- There is no coupling between the HF determinants and the singly excited determinants. (Brilloin's theorem)
- Only matrix elements between determinants differing by not more than 2 orbitals can give a nonzero value.

	$ \Psi_a^r\rangle$	$ \Psi_{ab}^{rs}\rangle$	$ \Psi_{abc}^{rst}\rangle$	$ \Psi_{abcd}^{rstu}\rangle$	\dots
$ \Psi_0\rangle$	$ S\rangle$	$ D\rangle$	$ T\rangle$	$ Q\rangle$	\dots
$\langle \Psi_0 $	$\langle \Psi_0 \mathcal{H} \Psi_0 \rangle$	0	$\langle \Psi_0 \mathcal{H} D \rangle$	0	\dots
$\langle S $		$\langle S \mathcal{H} S \rangle$	$\langle S \mathcal{H} D \rangle$	$\langle S \mathcal{H} T \rangle$	\dots
$\langle D $			$\langle D \mathcal{H} D \rangle$	$\langle D \mathcal{H} T \rangle$	$\langle D \mathcal{H} Q \rangle$
$\langle T $				$\langle T \mathcal{H} T \rangle$	$\langle T \mathcal{H} Q \rangle$
$\langle Q $					$\langle Q \mathcal{H} Q \rangle$
\vdots					\vdots

$\langle S | \mathcal{H} | T \rangle \leftrightarrow \langle \Psi_a^r | \mathcal{H} | \Psi_{cde}^{tuv} \rangle$
 $\langle D | \mathcal{H} | D \rangle \leftrightarrow \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{cd}^{tu} \rangle$

The formulas to calculate these matrix elements are known to us...

SINGLE EXCITATIONS

$$\langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle = 0$$

$$\langle {}^1\Psi_a^r | \mathcal{H} - E_0 | {}^1\Psi_b^s \rangle = (\varepsilon_r - \varepsilon_a) \delta_{rs} \delta_{ab} - (rs | ba) + 2(ra | bs)$$

DOUBLE EXCITATIONS

$$\langle \Psi_0 | \mathcal{H} | {}^1\Psi_{aa}^{rr} \rangle = K_{ra}$$

$$\langle \Psi_0 | \mathcal{H} | {}^1\Psi_{aa}^{rs} \rangle = 2^{1/2} (sa | ra)$$

$$\langle \Psi_0 | \mathcal{H} | {}^1\Psi_{ab}^{rr} \rangle = 2^{1/2} (rb | ra)$$

$$\langle \Psi_0 | \mathcal{H} | {}^A\Psi_{ab}^{rs} \rangle = 3^{1/2} ((ra | sb) - (rb | sa))$$

$$\langle \Psi_0 | \mathcal{H} | {}^B\Psi_{ab}^{rs} \rangle = (ra | sb) + (rb | sa)$$

The formulas to calculate these matrix elements are known to us...

DOUBLE EXCITATIONS

$$\langle {}^1\Psi_{aa}^{rr} | \mathcal{H} - E_0 | {}^1\Psi_{aa}^{rr} \rangle = 2(\varepsilon_r - \varepsilon_a) + J_{aa} + J_{rr} - 4J_{ra} + 2K_{ra}$$

$$\langle {}^1\Psi_{aa}^{rs} | \mathcal{H} - E_0 | {}^1\Psi_{aa}^{rs} \rangle = \varepsilon_r + \varepsilon_s - 2\varepsilon_a + J_{aa} + J_{rs} + K_{rs} - 2J_{sa} - 2J_{ra} + K_{sa} + K_{ra}$$

$$\langle {}^1\Psi_{ab}^{rr} | \mathcal{H} - E_0 | {}^1\Psi_{ab}^{rr} \rangle = 2\varepsilon_r - \varepsilon_a - \varepsilon_b + J_{rr} + J_{ab} + K_{ab} - 2J_{rb} - 2J_{ra} + K_{rb} + K_{ra}$$

$$\begin{aligned} \langle {}^A\Psi_{ab}^{rs} | \mathcal{H} - E_0 | {}^A\Psi_{ab}^{rs} \rangle = & \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b + J_{ab} + J_{rs} - K_{ab} \\ & - K_{rs} - J_{sb} - J_{sa} - J_{rb} - J_{ra} + \frac{3}{2}(K_{sb} + K_{sa} + K_{rb} + K_{ra}) \end{aligned}$$

$$\begin{aligned} \langle {}^B\Psi_{ab}^{rs} | \mathcal{H} - E_0 | {}^B\Psi_{ab}^{rs} \rangle = & \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b + J_{ab} + J_{rs} + K_{ab} \\ & + K_{rs} - J_{sb} - J_{sa} - J_{rb} - J_{ra} + \frac{1}{2}(K_{sb} + K_{sa} + K_{rb} + K_{ra}) \end{aligned}$$

$$\langle {}^A\Psi_{ab}^{rs} | \mathcal{H} | {}^B\Psi_{ab}^{rs} \rangle = (3/4)^{1/2}(K_{sb} - K_{sa} - K_{rb} + K_{ra})$$

Expressing the correlation energy

We start by writing the exact ground state wave function in an **intermediate normalized form**:

$$\begin{aligned}
 |\Phi_0\rangle = & |\Psi_0\rangle + \sum_{ct} c_c^t |\Psi_c^t\rangle + \sum_{\substack{c < d \\ t < u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle \\
 & + \sum_{\substack{c < d < e \\ t < u < v}} c_{cde}^{tuv} |\Psi_{cde}^{tuv}\rangle + \sum_{\substack{c < d < e < f \\ t < u < v < w}} c_{cdef}^{tuvw} |\Psi_{cdef}^{tuvw}\rangle + \dots
 \end{aligned}$$

The wave function is not normalized, but it has the property

$$\langle \Psi_0 | \Phi_0 \rangle = 1$$

Now, we solve the Schrödinger Equation

$$\mathcal{H} |\Phi_0\rangle = \mathcal{E}_0 |\Phi_0\rangle$$

The latter can be reformulated to an evaluation of the correlation energy:

$$(\mathcal{H} - E_0)|\Phi_0\rangle = (\mathcal{E}_0 - E_0)|\Phi_0\rangle = E_{\text{corr}}|\Phi_0\rangle$$

Multiplication from the left with the HF wf we obtain:

$$\langle \Psi_0 | \mathcal{H} - E_0 | \Phi_0 \rangle = E_{\text{corr}} \langle \Psi_0 | \Phi_0 \rangle = E_{\text{corr}}$$

An expansion in excited determinants yields

$$\begin{aligned} \langle \Psi_0 | \mathcal{H} - E_0 | \Phi_0 \rangle &= \langle \Psi_0 | \mathcal{H} - E_0 \left(|\Psi_0\rangle + \sum_{ct} c_c^t |\Psi_c^t\rangle + \sum_{\substack{c < d \\ t < u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle + \dots \right) \rangle \\ &= \sum_{\substack{c < d \\ t < u}} c_{cd}^{tu} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle \end{aligned}$$

The double excitation coefficients alone determine the exact energy!

However, that does not mean that only double excitations need to be evaluated.

The double coeffs are affected by the presence of other excitations. This can be seen by multiplication with e.g. a singly excited determinant from the left:

$$\langle \Psi_a^r | \mathcal{H} - E_0 | \Phi_0 \rangle = E_{\text{corr}} \langle \Psi_a^r | \Phi_0 \rangle$$

Expanding the exact wf, we obtain

$$\sum_{ct} c_c^t \langle \Psi_a^r | \mathcal{H} - E_0 | \Psi_c^t \rangle + \sum_{\substack{c < d \\ t < u}} c_{cd}^{tu} \langle \Psi_a^r | \mathcal{H} | \Psi_{cd}^{tu} \rangle + \sum_{\substack{c < d < e \\ t < u < v}} c_{cde}^{tuv} \langle \Psi_a^r | \mathcal{H} | \Psi_{cde}^{tuv} \rangle \\ = E_{\text{corr}} c_a^r$$

Repeating this with doubles, triples, and so on gives a large set of coupled equations.

We have a score to settle: The application of Full CI to H₂

The HF wf is of the form $|\Psi_0\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle$

The exact wf can be expanded as

$$|\Phi_0\rangle = |\Psi_0\rangle + c_1^2 |2\bar{1}\rangle + c_{\bar{1}}^2 |1\bar{2}\rangle + c_{\bar{1}}^2 |12\rangle + c_1^2 |\bar{2}1\rangle + c_{1\bar{1}}^2 |2\bar{2}\rangle$$

Now, we have to consider **spin**. The spin adapted singlet excited determinant is given by

$$|{}^1\Psi_1^2\rangle = 2^{-1/2}(|1\bar{2}\rangle + |2\bar{1}\rangle)$$

With this, we obtain

$$|\Phi_0\rangle = |\Psi_0\rangle + c_1^2 |{}^1\Psi_1^2\rangle + c_{1\bar{1}}^2 |2\bar{2}\rangle$$

Finally, we realize the the second term of the rhs is of ungerade **symmetry** and does not contribute.

$$|\Phi_0\rangle = |\Psi_0\rangle + c_{1\bar{1}}^2 |2\bar{2}\rangle = |\Psi_0\rangle + c_{1\bar{1}}^2 |\Psi_{1\bar{1}}^{2\bar{2}}\rangle$$

We have a score to settle: The application of Full CI to H₂

Therefore, the CI matrix has the form

$$\mathbf{H} = \begin{pmatrix} \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle & \langle \Psi_0 | \mathcal{H} | \Psi_{1\bar{1}}^{2\frac{1}{2}} \rangle \\ \langle \Psi_{1\bar{1}}^{2\frac{1}{2}} | \mathcal{H} | \Psi_0 \rangle & \langle \Psi_{1\bar{1}}^{2\frac{1}{2}} | \mathcal{H} | \Psi_{1\bar{1}}^{2\frac{1}{2}} \rangle \end{pmatrix}$$

with

$$\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = E_0 = 2h_{11} + J_{11}$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_{1\bar{1}}^{2\frac{1}{2}} \rangle = \langle 1\bar{1} | 2\bar{2} \rangle = (12 | 12) = K_{12} = \langle \Psi_{1\bar{1}}^{2\frac{1}{2}} | \mathcal{H} | \Psi_0 \rangle$$

$$\langle \Psi_{1\bar{1}}^{2\frac{1}{2}} | \mathcal{H} | \Psi_{1\bar{1}}^{2\frac{1}{2}} \rangle = 2h_{22} + J_{22}$$

We have a score to settle: The application of Full CI to H₂

We solve the CI eigenvalue problem

$$\begin{pmatrix} E_0 & K_{12} \\ K_{12} & \langle \Psi_{1\bar{1}}^{2\frac{1}{2}} | \mathcal{H} | \Psi_{1\bar{1}}^{2\frac{1}{2}} \rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix} = \varepsilon \begin{pmatrix} c_0 \\ c_1 \end{pmatrix}$$

and obtain

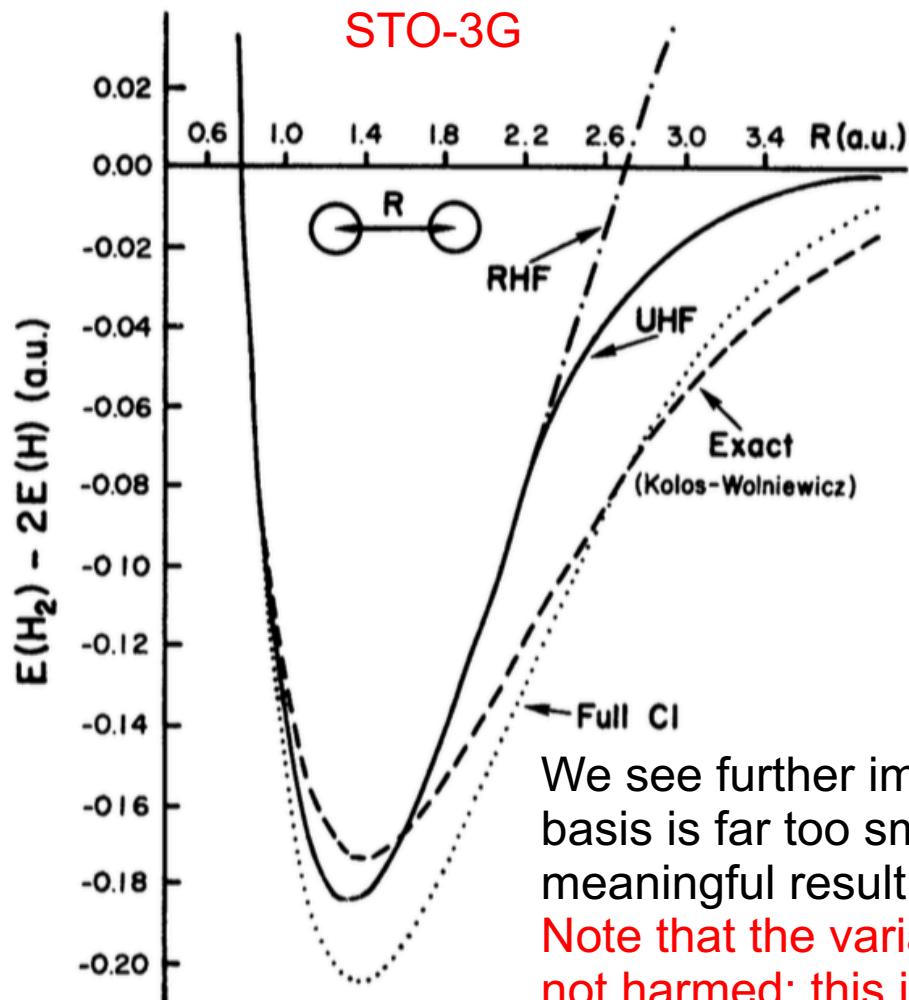
$$\varepsilon_0 = E_0 + E_{\text{corr}} = \underbrace{2h_{11} + J_{11}}_{\text{RHF energy}} + \Delta - (\Delta^2 + K_{12}^2)^{1/2},$$

using the definition

$$2\Delta = \langle \Psi_{1\bar{1}}^{2\frac{1}{2}} | \mathcal{H} - E_0 | \Psi_{1\bar{1}}^{2\frac{1}{2}} \rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}$$

We have a score to settle: The application of Full CI to H₂

In the minimum basis set, our PES has now the form



We see further improvement, but the basis is far too small to give a meaningful result.
 Note that the variational principle is not harmed: this is a relative, not an absolute energy.

We have a score to settle: The application of Full CI to H_2

With a larger basis set we are almost there.

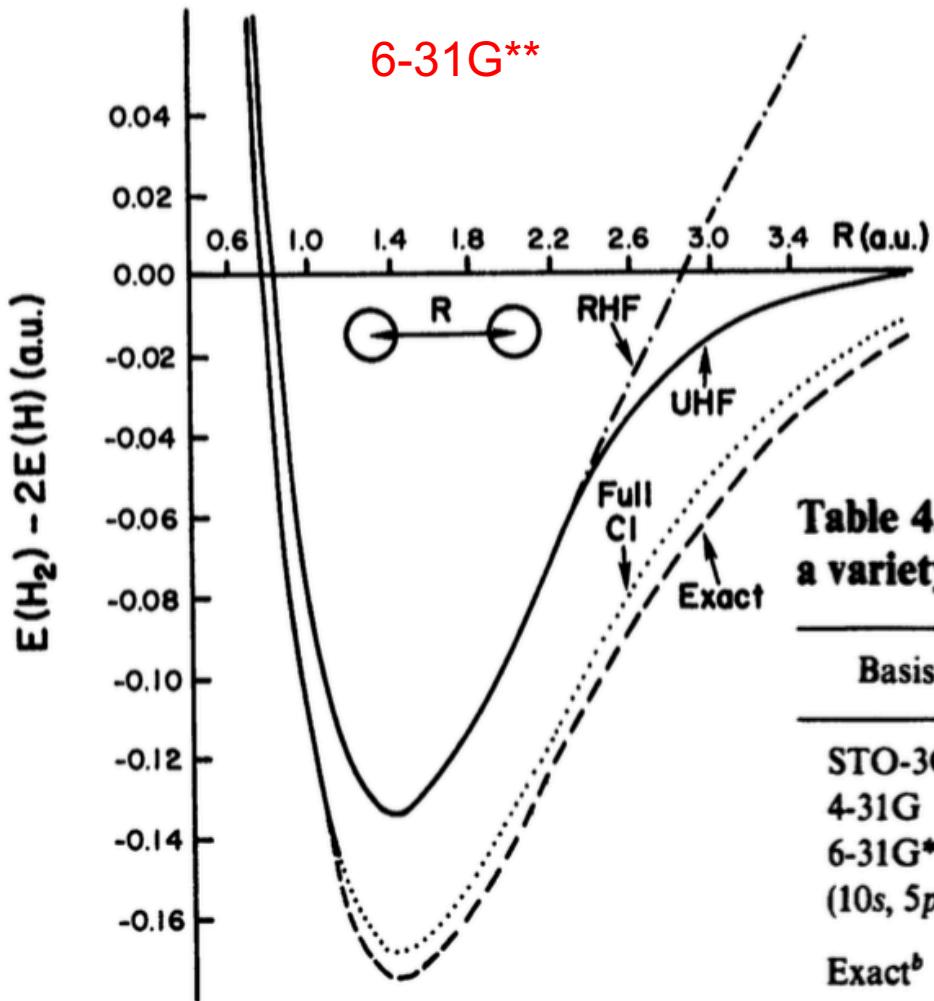


Table 4.2 The correlation energy (a.u.) of H_2 at $R = 1.4$ a.u. in a variety of basis sets

Basis set	DCI	SDCI	Contribution of singles
STO-3G	-0.02056	-0.02056	0
4-31G	-0.02487	-0.02494	-0.00007
6-31G**	-0.03373	-0.03387	-0.00014
(10s, 5p, 1d) ^a	-0.03954	-0.03969	-0.00015
Exact ^b		-0.0409	

Generalization: CI with single and double excitations - CISD

The intermediate normalized wf is of the form $|\Phi_{\text{DCI}}\rangle = |\Psi_0\rangle + \sum_{\substack{c < d \\ t < u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle$

Substitution in

$$(\mathcal{H} - E_0)|\Phi_0\rangle = (\mathcal{E}_0 - E_0)|\Phi_0\rangle = E_{\text{corr}}|\Phi_0\rangle$$

gives

$$(\mathcal{H} - E_0) \left(|\Psi_0\rangle + \sum_{\substack{c < d \\ t < u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle \right) = E_{\text{corr}} \left(|\Psi_0\rangle + \sum_{\substack{c < d \\ t < u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle \right)$$

We multiply by $\langle \Psi_0 |$ and $\langle \Psi_{ab}^{rs} |$

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

$$\langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{\substack{c < d \\ t < u}} c_{cd}^{tu} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle = c_{ab}^{rs} E_{\text{corr}}$$

Generalization: CI with single and double excitations - CISD

Defining

$$(\mathbf{B})_{rasb} = \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle$$

$$(\mathbf{D})_{rasb, tcud} = \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle$$

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

leaves us with the following system of equations

$$\mathbf{B}^\dagger \mathbf{c} = E_{\text{corr}}$$

$$\mathbf{B} + \mathbf{D}\mathbf{c} = \mathbf{c}E_{\text{corr}}$$

or, in matrix notation,

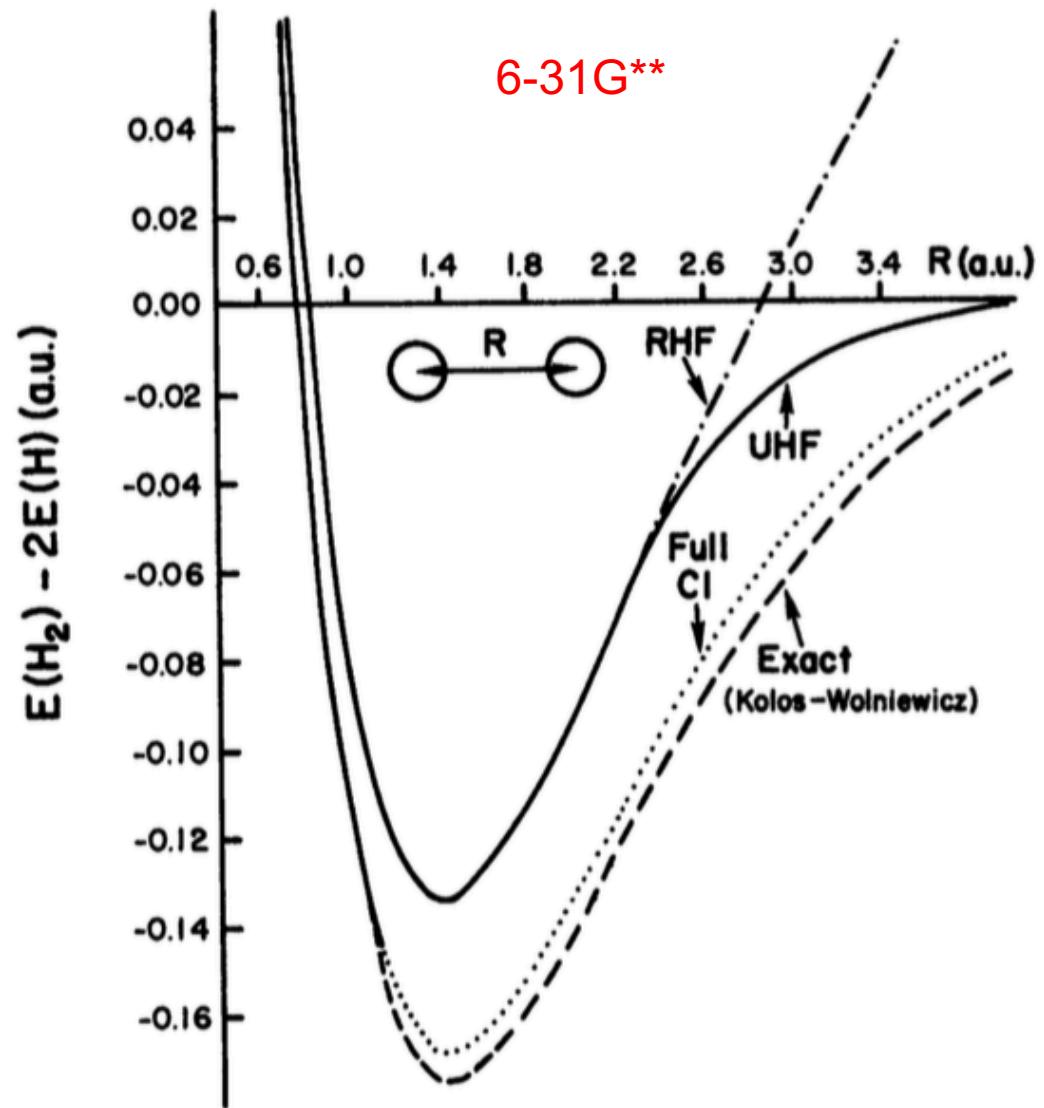
$$\begin{pmatrix} 0 & \mathbf{B}^\dagger \\ \mathbf{B} & \mathbf{D} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{c} \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} 1 \\ \mathbf{c} \end{pmatrix}$$

This is just the matrix representation of H in the basis of suitable excited determinants!

Big improvements to HF: Some results

Table 4.3 Equilibrium bond length (a.u.) of H₂

Basis set	SCF	Full CI
STO-3G	1.346	1.389
4-31G	1.380	1.410
6-31G**	1.385	1.396
Exact ^a		1.401



Big improvements to HF: Some results

Table 4.9 Ionization potentials (a.u.) of N₂ obtained using Koopmans' theorem and by performing a SDCI calculation on both N₂ and N₂⁺ (A large basis consisting of 6s, 4p, 3d, 2f Slater-type orbitals was used)^a

Orbital	Koopmans'	SDCI	Experiment
3σ _g	0.635	0.580	0.573
1π _u	0.615	0.610	0.624

Table 4.10 The effect of single excitations on the dipole moment (a.u.) of CO within an extended STO basis^a (A positive dipole moment corresponds to C⁻O⁺)

Wave function	Energy	Dipole moment
SCF	-112.788	-0.108
SCF + 138 doubles	-113.016	-0.068
SCF + 200 doubles	-113.034	-0.072
SCF + 138 doubles + 62 singles	-113.018	+0.030
Experiment		+0.044

Truncated CI and the problem of size consistency

An approximative scheme for the energy is said to be **size consistent** if the total energy of a system equals the sum of the energies of its noninteracting subsystems.

What is so good about this property? It's essential for chemistry, think of the accuracy of a reaction



where each system might have a different number of electrons.

Which theories are size consistent? Hartree Fock, Full CI, Coupled Cluster

Truncated CI is not size consistent. Think of CISD for noninteracting 2H_2

Truncated CI and the problem of size consistency

Details for two H_2 molecules at large distance:

We write the HF ground state as $|\Psi_0\rangle = |1_1\bar{1}_11_2\bar{1}_2\rangle$

Because of the distance we assume that $(1_11_1|1_21_2)$ is zero,

so that

$$^2E_0 = 2(2\varepsilon_1 - J_{11})$$

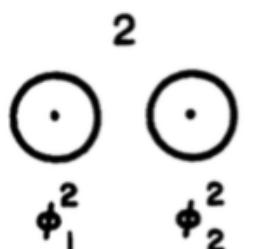
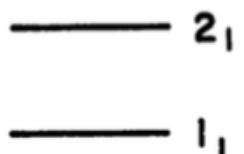
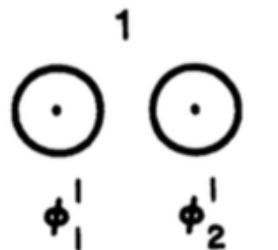
with

$$J_{11} = (1_11_1|1_11_1) = (1_21_2|1_21_2)$$

$$|1_1\rangle = (2(1+S_{12}))^{-1/2} (\phi_1^1 + \phi_2^1) \quad |1_2\rangle = (2(1+S_{12}))^{-1/2} (\phi_1^2 + \phi_2^2)$$

$$|2_1\rangle = (2(1-S_{12}))^{-1/2} (\phi_1^1 - \phi_2^1) \quad |2_2\rangle = (2(1-S_{12}))^{-1/2} (\phi_1^2 - \phi_2^2)$$

This is the molecule index



Truncated CI and the problem of size consistency

Now lets do CISD for 2H_2 , which is equivalent to CID due to symmetry. We find

$$\begin{aligned} |\Phi_0\rangle &= |\Psi_0\rangle + c_1|2_1\bar{2}_11_2\bar{1}_2\rangle + c_2|1_1\bar{1}_12_2\bar{2}_2\rangle \\ &= |\Psi_0\rangle + \sum_{i=1}^2 c_i|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle \end{aligned}$$

The doubly excited configuration



can not mix with any of the above.

Truncated CI and the problem of size consistency

For the matrix elements between the HF ground state and the symmetry allowed doubly excited wf we find

$$\begin{aligned}
 \langle \Psi_0 | \mathcal{H} | 2_1\bar{2}_1 1_2\bar{1}_2 \rangle &= \langle \Psi_0 | \mathcal{H} | \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \rangle \\
 &= \langle 1_1\bar{1}_1 | | 2_1\bar{2}_1 \rangle = [1_1 2_1 | \bar{1}_1 \bar{2}_1] - [1_1 \bar{2}_1 | \bar{1}_1 2_1] \\
 &= (1_1 2_1 | 1_1 2_1) = (1_1 2_1 | 2_1 1_1) \\
 &= K_{12}
 \end{aligned}$$

The two doubly excited wfs do not mix (four MOs different), so we have

$$\begin{pmatrix} 0 & K_{12} & K_{12} \\ K_{12} & 2\Delta & 0 \\ K_{12} & 0 & 2\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \end{pmatrix} = {}^2E_{\text{corr}}(\text{DCI}) \begin{pmatrix} 1 \\ c_1 \\ c_2 \end{pmatrix}$$

$$2\Delta = \langle \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} | \mathcal{H} - E_0 | \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}$$

Truncated CI and the problem of size consistency

This gives the system of equations

$$K_{12}(c_1 + c_2) = {}^2E_{\text{corr}}(\text{DCI})$$

$$K_{12} + 2\Delta c_1 = {}^2E_{\text{corr}}(\text{DCI})c_1$$

$$K_{12} + 2\Delta c_2 = {}^2E_{\text{corr}}(\text{DCI})c_2$$

From the last two we get

$$c_1 = c_2 = \frac{K_{12}}{}^2E_{\text{corr}}(\text{DCI}) - 2\Delta$$

Inserting in the first equation we obtain

$${}^2E_{\text{corr}}(\text{DCI}) = \frac{2K_{12}^2}{}^2E_{\text{corr}}(\text{DCI}) - 2\Delta$$

Truncated CI and the problem of size consistency

Solving this quadratic equation we find

$$^2E_{\text{corr}}(\text{DCI}) = \Delta - (\Delta^2 + 2K_{12}^2)^{1/2}$$

Note that this is not twice the CISD monomer result (which is exact, remember, just $2e^-$):

$$^1E_{\text{corr}}(\text{DCI}) = ^1E_{\text{corr}}(\text{exact}) = \Delta - (\Delta^2 + K_{12}^2)^{1/2}$$

Even worse, this error gets bigger for larger systems. Let us look at N H_2 molecules for example:

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{i=1}^N c_i |\Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i}\rangle$$

A straightforward generalization of the CI matrix is given by:

$$\begin{pmatrix} 0 & K_{12} & K_{12} & \cdots & K_{12} \\ K_{12} & 2\Delta & 0 & \cdots & 0 \\ K_{12} & 0 & 2\Delta & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & 0 \\ K_{12} & 0 & 0 & 0 & 2\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix} = {}^N E_{\text{corr}}(\text{DCI}) \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix}$$

Truncated CI and the problem of size consistency

Again the double excitations on individual molecules are identical,

$$c_i = c_1 = \frac{K_{12}}{^N E_{\text{corr}}(\text{DCI}) - 2\Delta}$$

so that we obtain from the first row of the CI matrix

$$^N E_{\text{corr}}(\text{DCI}) = K_{12} \sum_{i=1}^N c_i = N K_{12} c_1$$

Combining both we end up with

$$^N E_{\text{corr}}(\text{DCI}) = \frac{N K_{12}^2}{^N E_{\text{corr}}(\text{DCI}) - 2\Delta}$$

Solving the quadratic equation again we find

$$^N E_{\text{corr}}(\text{DCI}) = \Delta - (\Delta^2 + N K_{12}^2)^{1/2}$$

Truncated CI and the problem of size consistency

So, finally we have

$$^N E_{\text{corr}}(\text{DCI}) = \Delta - (\Delta^2 + N K_{12}^2)^{1/2},$$

but the correct energy for N non-interacting H_2 molecules is

$$^N E_{\text{corr}}(\text{exact}) = N^1 E_{\text{corr}}(\text{exact}) = N(\Delta - (\Delta^2 + K_{12}^2)^{1/2})$$

We realize that this error grows with the system size. For small systems it's almost negligible, but for large N it shows a very unpleasant behavior:

For $N \rightarrow \infty$ we find $^N E_{\text{corr}}(\text{DCI}) \sim -N^{1/2} K_{12}$

$$\lim_{N \rightarrow \infty} \frac{^N E_{\text{corr}}(\text{DCI})}{N} = 0$$

CI and CC methods

Truncated CI and the problem of size consistency

An interesting detail: For full CI on 2 H₂ (i.e., CIDQ) we would find

$$|\Phi_0\rangle = |\Psi_0\rangle + c_1|2_1\bar{2}_11_2\bar{1}_2\rangle + c_2|1_1\bar{1}_12_2\bar{2}_2\rangle + c_3|2_1\bar{2}_12_2\bar{2}_2\rangle$$

$$\begin{pmatrix} 0 & K_{12} & K_{12} & 0 \\ K_{12} & 2\Delta & 0 & K_{12} \\ K_{12} & 0 & 2\Delta & K_{12} \\ 0 & K_{12} & K_{12} & 4\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} = {}^2E_{\text{corr}} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} \quad \xrightarrow{\hspace{1cm}} \quad \begin{aligned} c_1 &= \frac{2K_{12}}{}^2E_{\text{corr}} - 4\Delta \\ c_1 &= c_2 \\ c_3 &= \frac{{}^2E_{\text{corr}}}{{}^2E_{\text{corr}} - 4\Delta} \end{aligned}$$

From line 1 in the CI matrix and $c_1=c_2$ we see that ${}^2E_{\text{corr}} = 2K_{12}c_1$,

and from this follows that $c_3 = \frac{{}^2E_{\text{corr}}}{{}^2E_{\text{corr}} - 4\Delta} = \frac{2K_{12}c_1}{{}^2E_{\text{corr}} - 4\Delta} = (c_1)^2$

This shows that it might be reasonable to express higher coeffs by products of lower coeffs, which is a basic concept of the Coupled Cluster approach.

Coupled Cluster Theory

The energy of a macroscopic system is an extensive thermodynamic property. Therefore, it has to be proportional to the number of particles. For post-HF wfs this means:
The correlation energy per particle should be constant.

A first step: The independent electron pair approximation – an alternative way to full CI

We remember that the exact energy can be expressed just by doubly excited coefficients:

$$E_{\text{corr}} = \sum_{a < b} \sum_{r < s} c_{ab}^{rs} \langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle = \frac{1}{4} \sum_{ab} \sum_{rs} c_{ab}^{rs} \langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle$$

This suggests that we can write the total energy as a sum of contributions from each occupied pair:

$$E_{\text{corr}} = \sum_{a < b} e_{ab} \quad e_{ab} = \sum_{r < s} c_{ab}^{rs} \langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle$$

We don't want to do Full CI now. Can we approximate the pair energies somehow?
This would reduce the N^2 interaction problem to $N(N-1)/2$ 2e⁻ problems...

Coupled Cluster Theory

The simplest approach: Let us forget all remaining $N-2$ electrons for a while, and let only two electrons correlate by exciting them into virtual orbitals.

We construct ‘pair wfs’ for them (neglecting single excitations here for brevity):

$$|\Psi_{ab}\rangle = |\Psi_0\rangle + \sum_{r < s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle$$

The corresponding energy is given by

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

Now, we minimize this energy to get the best possible pair function by our standard procedure: construct a matrix representation in the basis of the available wfs, diagonalize it and find the lowest eigenvalue:

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

Coupled Cluster Theory

Using our definition of the pair wf we have

$$\mathcal{H} \left(|\Psi_0\rangle + \sum_{t < u} c_{ab}^{tu} |\Psi_{ab}^{tu}\rangle \right) = E_{ab} \left(|\Psi_0\rangle + \sum_{t < u} c_{ab}^{tu} |\Psi_{ab}^{tu}\rangle \right)$$

We multiply by the HF wf and the doubly excited wfs to obtain

$$E_0 + \sum_{t < u} c_{ab}^{tu} \langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{tu} \rangle = E_{ab}$$

$$\langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{t < u} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{ab}^{tu} \rangle c_{ab}^{tu} = E_{ab} c_{ab}^{rs}$$

Using the definition of the pair energy, we rewrite this as

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

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

Coupled Cluster Theory

In matrix form, we obtain

$$\begin{pmatrix} 0 & \mathbf{B}_{ab}^\dagger \\ \mathbf{B}_{ab} & \mathbf{D}_{ab} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{c}_{ab} \end{pmatrix} = e_{ab} \begin{pmatrix} 1 \\ \mathbf{c}_{ab} \end{pmatrix}$$

with $(\mathbf{D}_{ab})_{rs,tu} = \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{tu} \rangle$

$$(\mathbf{B}_{ab})_{rs} = \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle$$

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

This system of equations is solved **for every pair**. The total correlation energy is then given by

$$E_{\text{corr}}(\text{IEPA}) = \sum_{a < b} e_{ab}$$

We summarize: IEPA is like CID for each pair separately. It is size consistent, but **not variational** (only in the pair energies, not in the sum).

Coupled Cluster Theory

Some approximations to the pair equations allow to make comparisons to other post-HF methods:

Let us assume no coupling between excited determinants, so

$$\langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{t < u} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{ab}^{tu} \rangle c_{ab}^{tu} = E_{ab} c_{ab}^{rs}$$

reduces to

The sum is gone!

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

Solving this equation for c_{ab} and inserting it in the relation

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

we obtain

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

The pair energy is small compared to the denominator

Coupled Cluster Theory

The result is called the Epstein-Nesbet pair correlation energy (typically an overestimation):

$$e_{ab}^{\text{EN}} = - \sum_{r < s} \frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle|^2}{\langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{rs} \rangle} \quad E_{\text{corr}}(\text{EN}) = \sum_{a < b} e_{ab}^{\text{EN}}$$

One last approximation is to express the denominator by MO energy differences:

$$\langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{rs} \rangle \cong \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b$$

$$e_{ab}^{\text{FO}} = \sum_{r < s} \frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

With this, we obtain a total energy

‘First order’

$$E_{\text{corr}}(\text{FO}) = \sum_{a < b} \sum_{r < s} \frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \sum_{a < b} \sum_{r < s} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

This is equivalent to **Moller-Plesset Perturbational Theory of second order (MP2)**!

Coupled Cluster Theory

The next step: An extension to the independent electron pair approximation – the CC method

As usual, we start from the exact wf in a series expansion with respect to electronic excitations:

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

For simplicity, singles, triples and higher odd numbers of excitations are neglected.

To determine the variational energy of this wf, we substitute it into

$$(\mathcal{H} - E_0) |\Phi_0\rangle = E_{\text{corr}} |\Phi_0\rangle$$

and multiply from left with $\langle \Psi_0 |$, $\langle \Psi_{ab}^{rs} |$, $\langle \Psi_{abcd}^{rstu} |$, etc

Coupled Cluster Theory

This yields a system of equations

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

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

and so on...

We notice a hierarchy of couplings between coeffs of higher excitations. How can we obtain a decoupling?

Setting the quadruple coeffs zero? Decouples, but gives just CID. Alternatives?

The Coupled Cluster Approach. Let's find a way to express the quadruples through doubles!

Coupled Cluster Theory

We remember our non-interacting 2 H_2 example:

$$|\Phi_0\rangle = |1_1 \bar{1}_1 1_2 \bar{1}_2\rangle + c_{1_1 \bar{1}_1}^2 |2_1 \bar{2}_1 1_2 \bar{1}_2\rangle + c_{1_2 \bar{1}_2}^2 |1_1 \bar{1}_1 2_2 \bar{2}_2\rangle \\ + c_{1_1 \bar{1}_1 1_2 \bar{1}_2}^{2_1 \bar{2}_1 2_2 \bar{2}_2} |2_1 \bar{2}_1 2_2 \bar{2}_2\rangle$$

We found that the last coeff fulfills the relation $c_{1_1 \bar{1}_1 1_2 \bar{1}_2}^{2_1 \bar{2}_1 2_2 \bar{2}_2} = (c_{1_1 \bar{1}_1}^2)(c_{1_2 \bar{1}_2}^2)$

Why is this valid?
 For two molecules separated by an infinite distance **the antisymmetry condition can be dropped.**

$$|\Phi_0\rangle = [|1_1 \bar{1}_1\rangle + c_{1_1 \bar{1}_1}^2 |2_1 \bar{2}_1\rangle] [|1_2 \bar{1}_2\rangle + c_{1_2 \bar{1}_2}^2 |2_2 \bar{2}_2\rangle] \\ = |1_1 \bar{1}_1\rangle |1_2 \bar{1}_2\rangle + c_{1_1 \bar{1}_1}^2 |2_1 \bar{2}_1\rangle |1_2 \bar{1}_2\rangle + c_{1_2 \bar{1}_2}^2 |1_1 \bar{1}_1\rangle |2_2 \bar{2}_2\rangle \\ + c_{1_1 \bar{1}_1 1_2 \bar{1}_2}^{2_1 \bar{2}_1 2_2 \bar{2}_2} |2_1 \bar{2}_1\rangle |2_2 \bar{2}_2\rangle$$

Just a product function!

Coupled Cluster Theory

Obviously, in real systems we can not assume independent pairs of electrons, but we can make **an approximation**

$$C_{abcd}^{rstu} \cong C_{ab}^{rs} * C_{cd}^{tu}$$

↗ symbolic product

Unfortunately, it is a little more laborious due to the interchangeable electrons...

$$\begin{aligned}
 C_{abcd}^{rstu} &\cong C_{ab}^{rs} * C_{cd}^{tu} = C_{ab}^{rs} C_{cd}^{tu} - \langle C_{ab}^{rs} * C_{cd}^{tu} \rangle \\
 &= C_{ab}^{rs} C_{cd}^{tu} - C_{ac}^{rs} C_{bd}^{tu} + C_{ad}^{rs} C_{bc}^{tu} - C_{ab}^{rt} C_{cd}^{su} + C_{ac}^{rt} C_{bd}^{su} - C_{ad}^{rt} C_{bc}^{su} \\
 &\quad + C_{ab}^{ru} C_{cd}^{st} - C_{ac}^{ru} C_{bd}^{st} + C_{ad}^{ru} C_{bc}^{st} + C_{ab}^{tu} C_{cd}^{rs} - C_{ac}^{tu} C_{bd}^{rs} + C_{ad}^{tu} C_{bc}^{rs} \\
 &\quad - C_{ab}^{su} C_{cd}^{rt} + C_{ac}^{su} C_{bd}^{rt} - C_{ad}^{su} C_{bc}^{rt} + C_{ab}^{st} C_{cd}^{ru} - C_{ac}^{st} C_{bd}^{ru} + C_{ad}^{st} C_{bc}^{ru}
 \end{aligned}$$

There are 18 distinct ways to get a quadruple excitation from a double excitation!

Coupled Cluster Theory

After substitution in our set of equations we obtain

$$\begin{aligned} & \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{\substack{c < d \\ t < u}} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \\ & + \sum_{\substack{c < d \\ t < u}} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{abcd}^{rstu} \rangle (c_{ab}^{rs} * c_{cd}^{tu}) = \left(\sum_{\substack{c < d \\ t < u}} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \right) c_{ab}^{rs} \end{aligned}$$

Using the fact that $\langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{abcd}^{rstu} \rangle = \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle$ for ab not cd and rs not tu ,
 (remember rules for exp. values of 2e-op.)

And that $c_{ab}^{rs} * c_{cd}^{tu}$ vanishes for $ab=cd$ or $rs=tu$,

(not more than two electrons per MO)

Coupled Cluster Theory

we obtain

$$\begin{aligned}
 & \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{\substack{c < d \\ t < u}} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} - \sum_{\substack{c < d \\ t < u}} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle \\
 & + \sum_{\substack{c < d \\ t < u}} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle c_{ab}^{rs} c_{cd}^{tu} = \left(\sum_{\substack{c < d \\ t < u}} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} \right) c_{ab}^{rs}
 \end{aligned}$$

where we have used the definition $c_{ab}^{rs} * c_{cd}^{tu} = c_{ab}^{rs} c_{cd}^{tu} - \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle$

This simplifies to

$$\langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{\substack{c < d \\ t < u}} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} - \sum_{\substack{c < d \\ t < u}} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle = 0$$

Together with

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

this forms the CC approach.

A brief characteristics of the CC equations: This system of equations is **nonlinear**. It can not be solved via a matrix diagonalization. The solution, a CC wf, is size consistent.

Coupled Cluster Theory

The Cluster Expansion of the wave function

An elegant way to obtain the CC formalism uses second quantization. We write doubly excited determinants as

$$|\Psi_{ab}^{rs}\rangle = a_r^\dagger a_s^\dagger a_b a_a |\Psi_0\rangle$$

A CID wf can then be written as

$$|\Psi_{\text{DCI}}\rangle = \left(1 + \frac{1}{4} \sum_{abrs} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a \right) |\Psi_0\rangle$$

We now introduce a wf, which by construction has its higher excitations coeffs approximated by doubles coeffs. It can be written as

$$|\Phi_{\text{CC_A}}\rangle = \exp(\mathcal{T}_2) |\Psi_0\rangle \quad \text{with} \quad \mathcal{T}_2 = \frac{1}{4} \sum_{abrs} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a$$

Coupled Cluster Theory

This is better understood when the exponential function is expanded as

$$\exp(x) = 1 + x + \frac{1}{2}x^2 + \dots$$

$$\begin{aligned} |\Phi_{\text{CCA}}\rangle &= \left(1 + \frac{1}{4} \sum_{abrs} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a + \frac{1}{32} \sum_{abcd} \sum_{rstu} c_{ab}^{rs} c_{cd}^{tu} a_r^\dagger a_s^\dagger a_b a_a a_t^\dagger a_u^\dagger a_d a_c + \dots \right) |\Psi_0\rangle \\ &= |\Psi_0\rangle + \frac{1}{4} \sum_{abrs} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \frac{1}{32} \sum_{abcd} \sum_{rstu} c_{ab}^{rs} c_{cd}^{tu} |\Psi_{abcd}^{rstu}\rangle + \dots \end{aligned}$$

After some lengthy algebra one obtains

$$|\Phi_{\text{CCA}}\rangle = |\Psi_0\rangle + \sum_{\substack{a < b \\ r < s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a < b < c < d \\ r < s < t < u}} c_{ab}^{rs} * c_{cd}^{tu} |\Psi_{abcd}^{rstu}\rangle + \dots$$

Putting this wf into the Schrödinger equation leads to $(\mathcal{H} - E_0) |\Phi_{\text{CCA}}\rangle = E_{\text{corr}} |\Phi_{\text{CCA}}\rangle$

Multiplication by $\langle \Psi_0 |$ and $\langle \Psi_{ab}^{rs} |$ again leads to the CC equations.

CI and CC methods

Coupled Cluster Theory

Some results...

Energies for H₂O

E_{corr}

SDCI ^a	-0.2756
IEPA ^a	-0.3274
L-CCA ^b	-0.2908
CCA ^b	-0.2862
Estimated full CI	-0.296 ± 0.001
Exact	-0.37

^a B. J. Rosenberg and I. Shavitt, *J. Chem. Phys.* **63**: 2162 (1975).

^b R. J. Bartlett, I. Shavitt, and G. D. Purvis, *J. Chem. Phys.* **71**: 281 (1979).

Geometries for H₂O

	SCF ^a	SDCI ^a	L-CCA ^b	CCA ^b	Experiment
R_e (a.u.)	1.776	1.800	1.810	1.806	1.809
θ_e	106.1°	104.9°	104.6°	104.7°	104.5°
f_{RR}	9.79	8.88	8.51	8.67	8.45
$f_{\theta\theta}$	0.88	0.81	0.80	0.80	0.76

^a B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.* **65**: 4072 (1976).

^b R. J. Bartlett, I. Shavitt, and G. D. Purvis, *J. Chem. Phys.* **71**: 281 (1979).

Many Particle Perturbation Theory

Rayleigh-Schrödinger Perturbation Theory – a quick overview

- Non-variational technique, but size consistent at each order (Brueckner, Goldstone)
- Divides the Hamiltonian into a zeroth order part H_0 (eigenproblem solved) and a perturbation V
- Exact energy would be an infinite sum over contributions of all orders
- The n -th order contains terms which are products of n matrix elements $\langle\phi|V|\phi\rangle$

More concrete:

- We will start from the Hartree-Fock Hamiltonian as H_0 (also called Møller-Plesset PT)

The general form of the problem: $\mathcal{H}|\Phi_i\rangle = (\mathcal{H}_0 + V)|\Phi_i\rangle = \epsilon_i|\Phi_i\rangle$

We know the eigenvalues and eigenvectors for H_0 :

$$\mathcal{H}_0|\Psi_i^{(0)}\rangle = E_i^{(0)}|\Psi_i^{(0)}\rangle \quad \text{or} \quad \mathcal{H}_0|i\rangle = E_i^{(0)}|i\rangle$$

Many Particle Perturbation Theory

Perturbative Expansion of the Correlation Energy: The Møller Plesset Series (MP2, MP4,...)

We partition the Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{V}$ with

$$\mathcal{H}_0 = \sum_i f(i) = \sum_i [h(i) + v^{\text{HF}}(i)] \quad \mathcal{V} = \sum_{i < j} r_{ij}^{-1} - \mathcal{V}^{\text{HF}} = \sum_{i < j} r_{ij}^{-1} - \sum_i v^{\text{HF}}(i)$$

Using the Physicists' notation $\int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) = \langle ij | kl \rangle$

we can write $\left\langle \Psi_0 \left| \sum_{i < j} r_{ij}^{-1} \right| \Psi_{ab}^{rs} \right\rangle = \langle ab | rs \rangle$

$$v^{\text{HF}}(1) \chi_j(\mathbf{x}_1) = \sum_b \langle b | r_{12}^{-1} | b \rangle \chi_j(\mathbf{x}_1) - \sum_b \langle b | r_{12}^{-1} | j \rangle \chi_b(\mathbf{x}_1)$$

$$\langle i | v^{\text{HF}} | j \rangle = v_{ij}^{\text{HF}} = \sum_b \langle ib | jb \rangle - \langle ib | bj \rangle = \sum_b \langle ib | jb \rangle$$

Many Particle Perturbation Theory

Perturbative Expansion of the Correlation Energy

The HF function is an eigenfunction of H_0 :

$$\mathcal{H}_0 |\Psi_0\rangle = E_0^{(0)} |\Psi_0\rangle \quad E_0^{(0)} = \sum_a \varepsilon_a$$

The first order energy correction is given by

$$\begin{aligned} E_0^{(1)} &= \langle \Psi_0 | \gamma | \Psi_0 \rangle \\ &= \langle \Psi_0 | \sum_{i < j} r_{ij}^{-1} | \Psi_0 \rangle - \langle \Psi_0 | \sum_i v^{\text{HF}}(i) | \Psi_0 \rangle \\ &= \frac{1}{2} \sum_{ab} \langle ab | | ab \rangle - \sum_a \langle a | v^{\text{HF}} | a \rangle \\ &= -\frac{1}{2} \sum_{ab} \langle ab | | ab \rangle \end{aligned}$$

The HF energy is the sum of zero and first order correction, i.e.

$$E_0 = E_0^{(0)} + E_0^{(1)} = \sum_a \varepsilon_a - \frac{1}{2} \sum_{ab} \langle ab | | ab \rangle$$

Perturbative Expansion of the Correlation Energy

How does the second order correction look like?

In general, we have $E_0^{(2)} = \sum' \frac{|\langle 0 | \gamma | n \rangle|^2}{E_0^{(0)} - E_n^{(0)}}$

Obviously, $|0\rangle = |\Psi_0\rangle$, but what are the excited states to sum over?

It can't be singles ... $\langle \Psi_0 | \gamma | \Psi_a^r \rangle = \langle \Psi_0 | \mathcal{H} - \mathcal{H}_0 | \Psi_a^r \rangle$
 $= \langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle - f_{ar} = 0$

It can't be triples since they do not mix with the ground state.

Therefore, it must be....

Perturbative Expansion of the Correlation Energy

Doubles! Knowing that $\mathcal{H}_0 |\Psi_{ab}^{rs}\rangle = (E_0^{(0)} - (\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)) |\Psi_{ab}^{rs}\rangle$

we obtain

$$E_0^{(2)} = \sum_{\substack{a < b \\ r < s}} \frac{|\langle \Psi_0 | \sum_{i < j} r_{ij}^{-1} | \Psi_{ab}^{rs} \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \sum_{\substack{a < b \\ r < s}} \frac{|\langle ab | |rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

The second order energy can also be expressed as sum of contributions of pairs of electrons in occupied orbitals:

$$E_0^{(2)} = \sum_{a < b} e_{ab}^{\text{FO}}$$

with

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

First order pair theory is identical with MP2 (compare slide 188)

Perturbative Expansion of the Correlation Energy

The third order correction is already a bit more elaborate:

$$\begin{aligned} E_0^{(3)} = & \frac{1}{8} \sum_{abcdrs} \frac{\langle ab || rs \rangle \langle cd || ab \rangle \langle rs || cd \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_c + \varepsilon_d - \varepsilon_r - \varepsilon_s)} \\ & + \frac{1}{8} \sum_{abrstu} \frac{\langle ab || rs \rangle \langle rs || tu \rangle \langle tu || ab \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_a + \varepsilon_b - \varepsilon_t - \varepsilon_u)} \\ & + \sum_{abcrst} \frac{\langle ab || rs \rangle \langle cs || tb \rangle \langle rt || ac \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_t)} \end{aligned}$$

Many Particle Perturbation Theory

Are HF and MP2 really size-extensive?

Again, we consider a system of N noninteracting H_2 molecules.

$$\begin{array}{ccccccc} \underline{2_1} & \underline{2_2} & \underline{2_3} & \dots & \underline{2_N} & \varepsilon_2 \\ \hline \underline{1_1} & \underline{1_2} & \underline{1_3} & & \underline{1_N} & \varepsilon_1 \end{array}$$

Testing HF:

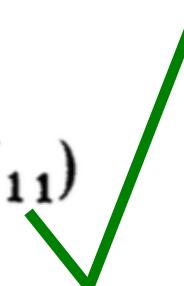
$$|\Psi_0\rangle = |1_1\bar{1}_1 1_2\bar{1}_2 \cdots 1_N\bar{1}_N\rangle$$

$$E_0^{(0)} = \langle \Psi_0 | \mathcal{H}_0 | \Psi_0 \rangle = 2 \sum_{i=1}^N \langle 1_i | f | 1_i \rangle = 2N\varepsilon_1$$

$$E_0^{(1)} = \langle \Psi_0 | \mathcal{V} | \Psi_0 \rangle = - \sum_{i=1}^N \langle 1_i 1_i | 1_i 1_i \rangle = - NJ_{11}$$

Therefore, we obtain

$$E_0 = \langle \Psi_0 | \mathcal{H}_0 + \mathcal{V} | \Psi_0 \rangle = E_0^{(0)} + E_0^{(1)} = N(2\varepsilon_1 - J_{11})$$



Many Particle Perturbation Theory

Are HF and MP2 really size-extensive?

Testing MP2:

$$E_0^{(2)} = \sum_n \frac{|\langle 0 | \gamma | n \rangle|^2}{E_0^{(0)} - E_n^{(0)}}$$

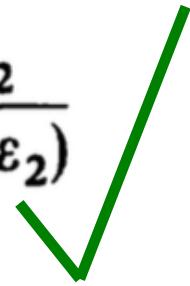
Again $|0\rangle = |\Psi_0\rangle$, and the states to sum over are double excitations of the form $|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle$:

$$E_0^{(0)} - E_n^{(0)} = 2(\varepsilon_1 - \varepsilon_2)$$

$$\langle \Psi_0 | \gamma | \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \rangle = \langle 1_i \bar{1}_i | 2_i \bar{2}_i \rangle - \cancel{\langle 1_i \bar{1}_i | \bar{2}_i 2_i \rangle} = \langle 11 | 22 \rangle = K_{12}$$

The summation over n can be replaced by a summation over i , and we obtain

$$E_0^{(2)} = \sum_{i=1}^N \frac{|\langle \Psi_0 | \gamma | \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \rangle|^2}{2(\varepsilon_1 - \varepsilon_2)} = \frac{NK_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}$$



Many Particle Perturbation Theory

Geometries of the 10-electron series:

		STO-3G	4-31G	6-31G*	6-31G**	Experiment
	CH_4	SCF $E_0^{(2)}$	2.047 2.077	2.043 2.065	2.048 2.060	2.048 2.048
	NH_3	SCF $E_0^{(2)}$	1.952 1.997	1.873 1.907	1.897 1.922	1.897 1.912
	H_2O	SCF $E_0^{(2)}$	1.871 1.916	1.797 1.842	1.791 1.831	1.782 1.816
	FH	SCF $E_0^{(2)}$	1.812 1.842	1.742 1.790	1.722 1.765	1.703 1.740

A Significant improvement!

Interesting behavior for binding energy in cases of multiple bonding:

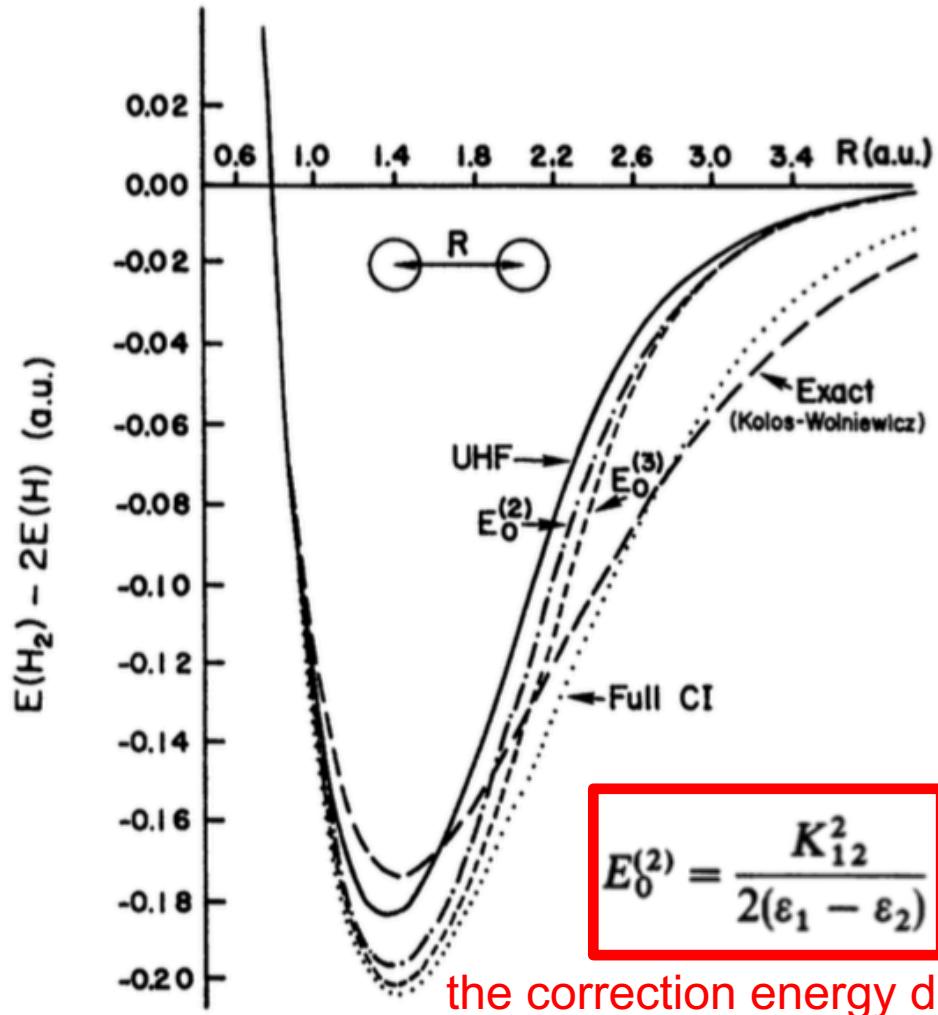
	N_2			CO		
Basis set	SCF	$E_0^{(2)}$	$E_0^{(2)} + E_0^{(3)}$	SCF	$E_0^{(2)}$	$E_0^{(2)} + E_0^{(3)}$
STO-3G	2.143	2.322	2.222	2.166	2.264	2.216
4-31G	2.050	2.171	2.098	2.132	2.216	2.169
6-31G*	2.039	2.133	2.109	2.105	2.175	2.145
Experiment		2.074			2.132	

SCF underestimates, MP2 overcompensates, and MP3 repairs MP2 flaw (somewhat).

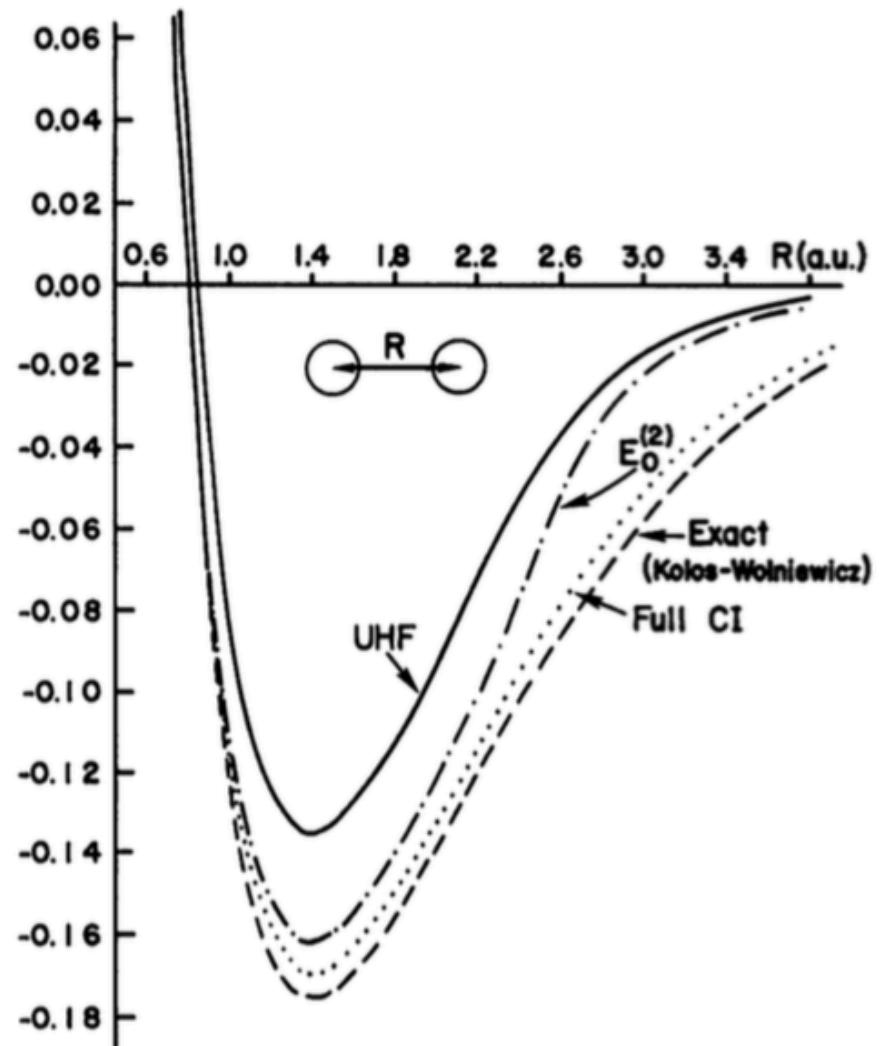
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Many Particle Perturbation Theory

MPx far from equilibrium distance: A problem...



STO-3G basis set



6-31G** basis set

Density Functional Theory

The Hohenberg-Kohn Theorems I and II

Theorem I: For any system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$, the density is uniquely determined. In other words:
The external potential is a unique functional of the density.

Proof: By reductio ad absurdum. Our Hamiltonian has the form

$$\mathbf{H}_e = - \sum_{i=1}^{N_{\text{elec}}} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N_{\text{elec}}} \sum_{A=1}^{N_{\text{nuclei}}} \frac{\mathbf{Z}_A}{|\mathbf{R}_A - \mathbf{r}_i|} + \sum_{i=1}^{N_{\text{elec}}} \sum_{j>i}^{N_{\text{elec}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{A=1}^{N_{\text{nuclei}}} \sum_{B=1}^{N_{\text{nuclei}}} \frac{\mathbf{Z}_A \mathbf{Z}_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

We assume now that two different external potentials would give the same density:

$$\langle \Psi' | \mathbf{H} | \Psi' \rangle > E_0$$

$$\langle \Psi' | \mathbf{H}' | \Psi' \rangle + \langle \Psi' | \mathbf{H} - \mathbf{H}' | \Psi' \rangle > E_0$$

$$E'_0 + \langle \Psi' | \mathbf{V}_{\text{ext}} - \mathbf{V}'_{\text{ext}} | \Psi' \rangle > E_0$$

$$E'_0 + \int \rho(\mathbf{r})(\mathbf{V}_{\text{ext}} - \mathbf{V}'_{\text{ext}}) d\mathbf{r} > E_0$$

Repeating the same with $\langle \Psi | \mathbf{H}' | \Psi \rangle > E'_0$ gives $E_0 + \int \rho(\mathbf{r})(\mathbf{V}'_{\text{ext}} - \mathbf{V}_{\text{ext}}) d\mathbf{r} > E'_0$

From this follows $E'_0 + E_0 > E'_0 + E_0$, which can't be right.

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Theorem II: A **universal functional** for the energy can be defined in terms of the density. The exact ground state is the global minimum value of this functional $E[\rho(\mathbf{r})]$.

Proof: The external potential is uniquely determined by the density.

From our studies on HF-theory we know that the potential uniquely determines the gs wf (except in degenerate situations). With that, all the other observables of the system such as kinetic energy are also uniquely determined. It follows that minimizing the total energy with respect to $\rho(\mathbf{r})$ (i.e. as a functional of $\rho(\mathbf{r})$), one finds the total energy of the ground state. The correct density that minimizes the energy is then the ground state density.

We sum up our insights from both theorems: The energy of the electronic ground state is completely determined by the electron density.

The big advantage of DFT compared to wf-based approaches: The wf depends on $3N$ spatial and N spin coordinates, the density only on 3 spatial coordinates, independent of the system size.

Okay. How to proceed?

Density Functional Theory

Option 1: Orbital-free approaches

Let us try to find ρ -dependent expressions for the terms in the Hamiltonian.

Easy part:

$$E_{\text{ne}}[\rho] = - \sum_a^{N_{\text{nuclei}}} \int \frac{Z_a(\mathbf{R}_a) \rho(\mathbf{r})}{|\mathbf{R}_a - \mathbf{r}|} d\mathbf{r}$$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Not so easy part: T and K ?

Early attempts of Thomas, Fermi, Bloch and Dirac:

$$T_{\text{TF}}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}$$

$$K_{\text{D}}[\rho] = -C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}$$

$$C_F = \frac{3}{10} (3\pi^2)^{2/3}$$

$$C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3}$$

The expressions are based on the **uniform electron gas**. This is good for metals, but poor for molecules. Largest problem: Molecules do not exist.

Density Functional Theory

Strategy: Improving the approach by addition of terms

Kinetic part:

Weizsäcker energy with $\lambda=1/9$

$$T[\rho] = T_{\text{TF}}[\rho] + T_2[\rho] + T_4[\rho] + T_6[\rho] + \dots$$

$$T_2[\rho] = \lambda \tau_w[\rho]; \quad \tau_w[\rho] = \int \frac{|\nabla \rho(\mathbf{r})|^2}{8\rho(\mathbf{r})} d\mathbf{r}$$

Accuracy: T_{TF} about -10%, T_2 about -1%

$$T_4[\rho] = \left(540(3\pi)^{\frac{2}{3}}\right)^{-1} \int \rho^{\frac{1}{3}}(\mathbf{r}) \left\{ \left(\frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})} \right)^2 - \frac{9}{8} \left(\frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})} \right) \left(\frac{\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} \right)^2 + \frac{1}{3} \left(\frac{\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} \right)^4 \right\} d\mathbf{r}$$

Exchange part:

$$K[\rho] = K_D[\rho] + K_2[\rho] + K_4[\rho] + \dots$$

$$K_2[\rho] = -\frac{5}{216}(3\pi^5)^{-1/3} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho^{4/3}(\mathbf{r})} d\mathbf{r}$$

Accuracy: Bonding can be described, but far inferior to WF based approaches.

The **orbital-free** approach is not yet applicable to real systems, but under development and a current research topic of DFT.

Option 2: Kohn-Sham DFT

The main problem is the representation of the kinetic energy T . The KS-idea: **Split T into a large part to be calculated exactly, and a second, smaller part to be guessed...**

For the exact calculation orbitals are reintroduced, which increases complexity to $3N$ again, and the numerical method becomes **similar to HF** for the evaluation of

$$T, V_{\text{en}} \text{ and } V_{\text{ee}}.$$

Justification:

We assume the following Hamiltonian with λ between 0 and 1:

$$\mathbf{H}_\lambda = \mathbf{T} + \mathbf{V}_{\text{ext}}(\lambda) + \lambda \mathbf{V}_{\text{ee}}$$

Here comes a thought experiment: If $\lambda = 1$, then $V_{\text{ext}} = V_{\text{ne}}$. Now we reduce λ , but **change V_{ext} accordingly so that the density stays the same.**

In the case of $\lambda = 0$, the kinetic energy can be expressed as $T_s = \sum_{i=1}^{N_{\text{elec}}} \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle$.

's' for Slater Determinant

Our dirty little secret: We use this expression also for $\lambda > 0$.

Okay, here comes the final Kohn-Sham DFT expression:

$$E_{\text{DFT}}[\rho] = T_s[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

By equating the DFT energy with the exact energy we define E_{xc} :

$$E_{\text{xc}}[\rho] = (T[\rho] - T_s[\rho]) + (E_{\text{ee}}[\rho] - J[\rho])$$

↑
kinetic correlation part

↑
exchange-correlation part

The ‘reduced’ task of KS-DFT development is the approximation of the E_{xc} functional only, while orbital-free DFT needs to find expressions for kinetic, exchange and correlation contributions.

Exchange and correlation holes – a comparison to WF approaches

Why can't we use more from an MO-based HF-like approach to also improve E_{xc} ?

The exchange energy is the larger contribution, so it would make sense to take it from HF. In HF theory, we can split exchange and correlation energy in a short- and a long-range part. Long-range corresponds to ‘static’ correlation, short range to ‘dynamic’ correlation. The long-range correlation in the wf formalism effectively cancels the long-range exchange part.

The problem: In DFT exchange and correlation are more ‘local’, since they are expressed as functionals of the density at a given point (and maybe some derivatives, i.e. a local expansion). Cancellation at long range should be granted by the E_{xc} functional, which is not the case if we mix HF exchange with DFT correlation.

Let's look at it in a more formal way:

$$\rho_2^{\text{indep}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N_{\text{elec}} - 1}{N_{\text{elec}}} \rho_1(\mathbf{r}_1) \rho_1(\mathbf{r}_2) = \left(1 - \frac{1}{N_{\text{elec}}}\right) \rho_1(\mathbf{r}_1) \rho_1(\mathbf{r}_2)$$

This is the probability of finding e_1 at \mathbf{r}_1 if e_2 is at \mathbf{r}_2 in the case of non-interacting electrons.

Density Functional Theory

However, electrons have charge and spin, so a correction needs to be introduced:

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho_1(\mathbf{r}_1)\rho_1(\mathbf{r}_2) + \rho_1(\mathbf{r}_1)h_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2)$$

This defines the so-called exchange-correlation hole:

$$h_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho_1(\mathbf{r}_1)} - \rho_1(\mathbf{r}_2)$$

We can split it into parts: $h_{\text{xc}} = h_{\text{x}} + h_{\text{c}}$

$$h_{\text{x}} = h_{\text{x}}^{\alpha\alpha} + h_{\text{x}}^{\beta\beta}$$

$$h_{\text{c}} = h_{\text{c}}^{\alpha\alpha} + h_{\text{c}}^{\beta\beta} + h_{\text{c}}^{\alpha\beta}$$

Integration over the whole volume gives

$$\int h_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho_1(\mathbf{r}_1)} d\mathbf{r}_1 d\mathbf{r}_2 - \int \rho_1(\mathbf{r}_2) d\mathbf{r}_2 = \frac{N_{\text{elec}}(N_{\text{elec}} - 1)}{N_{\text{elec}}} - N_{\text{elec}} = -1$$

It can be shown that the Fermi or exchange hole integrates to -1, and the Coulomb hole to 0.

Density Functional Theory

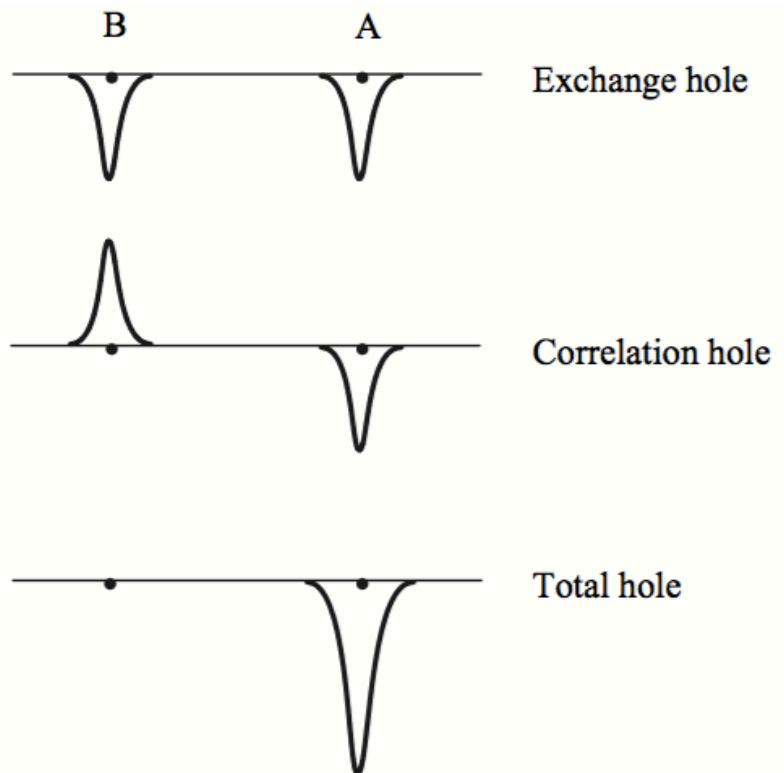
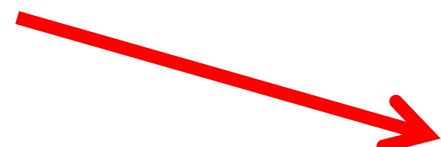
Now, remember, in the DFT formalism we have a general expression for J and K as functionals of the density, e.g.

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Note that this is not zero for a single electron!
(the problem of self interaction in DFT)

For H_2 at infinite distance we would find:

The delocalization due to exchange gets cancelled by the growing 'static' correlation!



How can we find a suitable exchange-correlation functional E_{xc} ?

Typically, a combination of two main concepts is applied:

A) The are **several constraints** that should be fulfilled:

- The functional should be self-interaction free
- For a constant density one should obtain the uniform electron gas result
- The exchange energy should scale linear with distance upon separation
- The Lieb-Oxford condition should be fulfilled: $E_x[\rho] \geq E_{xc}[\rho] \geq 2.273E_x^{\text{LDA}}[\rho]$
- ...

B) **Parameter fitting** to experimental data (or, more common, to CC results)

Density Functional Theory

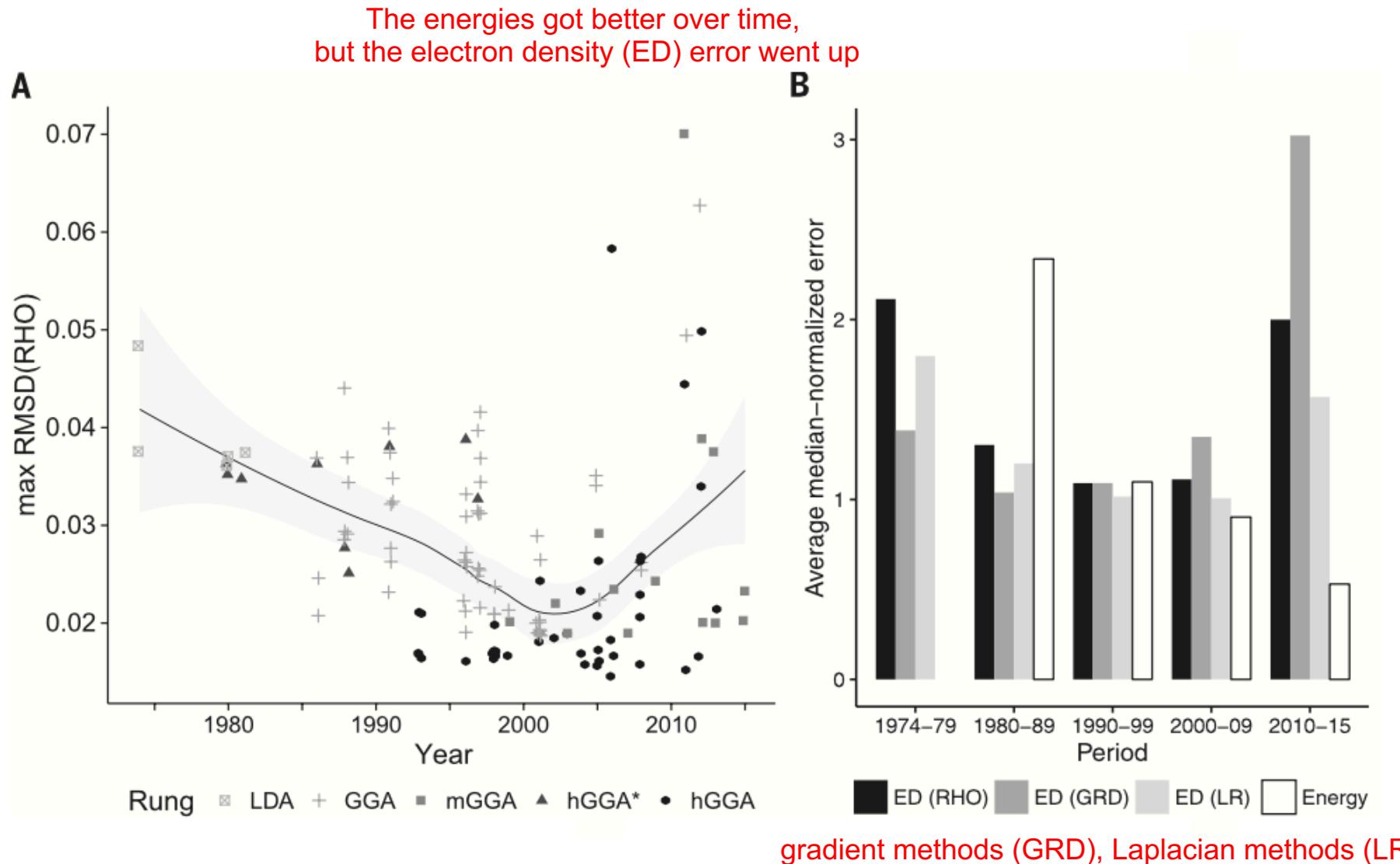
J. P. Perdew's Jakob's ladder of DFT improvement

Table 6.1 Perdew classification of exchange-correlation functionals

Level	Name	Variables	Examples
1	Local density	ρ	LDA, LSDA, X_α
2	GGA	$\rho, \nabla\rho$	BLYP, OPTX, OLYP, PW86, PW91, PBE, HCTH
3	Meta-GGA	$\rho, \nabla\rho, \nabla^2\rho$ or τ	BR, B95, VSXC, PKZB, TPSS, τ -HCTH
4	Hyper-GGA	$\rho, \nabla\rho, \nabla^2\rho$ or τ <i>HF exchange</i>	H+H, ACM, B3LYP, B3PW91, O3LYP, PBE0, TPSSh, τ -HCTH-hybrid
5	Generalized RPA	$\rho, \nabla\rho, \nabla^2\rho$ or τ <i>HF exchange</i> <i>Virtual orbitals</i>	OEP2

Density Functional Theory

The problem of overfitting occurs for highly parametrized functionals:
(Medvedev et al., Science 2017 355, aah5975)



Density Functional Theory

The problem of overfitting occurs for highly parametrized functionals:
(Medvedev et al., Science 2017 355, aah5975)

Table 1. The L1 methods (yielding the best densities), their rungs, years, and normalized errors (NE).

Method	Rung	Year	Max NE
CCSD	Ab initio		0.000
MP4sdq	Ab initio		0.246
MP3	Ab initio		0.967
MP2	Ab initio		1.514
mPW3PBE	hGGA	1998	1.778
APFD	hGGA	2012	1.813
B3PW91	hGGA	1993	1.816
PBEO	hGGA	1999	1.818
B98	hGGA	1998	1.826
BHLYP	hGGA	1993	1.851
B97-3	hGGA	2005	1.883
mPW1PBE	hGGA	1998	1.910
B3P86	hGGA	1993	1.937
B3LYP	hGGA	1993	2.123

Table 2. The L2 methods (yielding the worst densities), their rungs, years, and normalized errors (NE).

Method	Rung	Year	Max NE
Xα*	LDA	1974	3.777
SP86	GGA	1986	3.821
M06-L	mGGA	2006	3.974
SVWN1RPA	LDA	1980	3.977
SPBE	GGA	1997	3.978
SVWN	LDA	1980	3.984
SPZ81	LDA	1981	3.985
SPW91	GGA	1991	3.989
M06-2X	hGGA	2006	4.027
SOP	GGA	1997	4.182
SLYP	GGA	1988	4.429
M08-SO	hGGA	2008	4.676
SLATER*	LDA	1974	4.864

strong
parametrizations!

M05	hGGA	2005	7.652
MN12-L	mGGA	2012	8.995
M11	hGGA	2011	10.191
MN12-SX	hGGA	2012	13.005
M11-L	mGGA	2011	15.316