

Hartree-Fock methods of Quantum Chemistry

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1 Introduction

Explicit use of the wave function

- strict definition of any electronic state with any multiplicity
- density matrices (1st and 2nd order) calculated from wave function

Hierarchy of “infinitely improvable” approximations

- one-electron basis set
- correlation energy

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R. McWeeny *Methods of Molecular Quantum Mechanics*, Academic Press, London (1989)

P.R. Surján *Second Quantized Approach to Quantum Chemistry*, Springer Verlag, Heidelberg, (1989)

Mayer István *Fejezetek a kvantumkémiaiából*, BME, Budapest (1987)

B. Silvi *Cours de DEA*, Université P.& M. Curie, Paris (1992)

2 Historical Overview

Schrödinger 1926

Hartree 1928

Thomas Fermi 1927

Fock 1930

Dirac 1930

Moller-Plesset 1934

Weizsäcker 1935

Slater 1951

Cizek 1968

Kohn Sham 1965

Sham 1971

GGA

Becke 1993

HF,CC,MBPT,CI

Hybrid

KS DFT

True DFT

3 Variation theorem

The expectation value of the energy is equal to the eigenvalue of the Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (1)$$

Multiply by Ψ^* and integrate:

$$\langle \Psi | \hat{H} | \Psi \rangle = E \langle \Psi | \Psi \rangle \quad E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2)$$

The lowest energy belongs to the exact ground state wave function, i.e. for any approximate $\tilde{\Psi}$

$$E = \frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \geq E_0 \quad (3)$$

Eigenfunctions Ψ_k of the Hamiltonian form a complete, orthonormal basis

$$\tilde{\Psi} = \sum_k c_k \Psi_k \quad (4)$$

$$\langle \tilde{\Psi} | \tilde{\Psi} \rangle = \sum_i \sum_j c_i^* c_j \langle \Psi_i | \Psi_j \rangle = \sum_i |c_i|^2 \quad (5)$$

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \sum_i \sum_j c_i^* c_j E_j \langle \Psi_i | \Psi_j \rangle = \sum_i |c_i|^2 E_i \quad (6)$$

Energy

$$E = \frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} = \frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} \quad (7)$$

Since $E_i \geq E_0$

$$E = \frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \geq \frac{\sum_i |c_i|^2 E_0}{\sum_i |c_i|^2} = E_0 \quad (8)$$

The energy of an approximate wave function is upper bound of the exact energy.

3.1 Variation theorem II

The Schrödinger equation can be considered as a result of the variation theorem: we are looking for the wave function that makes stationary the energy functional

$$\delta E = \delta \left[\frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \right] = 0 \quad (9)$$

First variation

$$\delta E = \frac{\langle \delta \Psi | \hat{H} | \Psi \rangle \langle \Psi | \Psi \rangle - \langle \Psi | \hat{H} | \Psi \rangle \langle \delta \Psi | \Psi \rangle}{\langle \Psi | \Psi \rangle^2} + \text{c.c.} = 0 \quad (10)$$

This expression and its complex conjugate should be separately zero

$$\frac{\langle \delta \Psi | \hat{H} | \Psi \rangle \langle \Psi | \Psi \rangle}{\langle \Psi | \Psi \rangle} - \langle \delta \Psi | \Psi \rangle \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = 0 \quad (11)$$

we obtain another form of the variation theorem

$$\langle \delta \Psi | \hat{H} - E | \Psi \rangle = 0 \quad (12)$$

and since $\delta \Psi$ is arbitrary

$$(\hat{H} - E) \Psi = 0 \quad (13)$$

3.2 Stationary-value conditions

The variation theorem provides a necessary but not sufficient condition to have a minimum of the energy. Let us examine the general Taylor expansion of the energy functional.

Denote the wave function, containing the independent parameters p_1, p_2, \dots , by

$$\Psi(p_1, p_2, \dots | \mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N) \quad (14)$$

and the energy functional

$$E = H(p_1, p_2, \dots) = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (15)$$

The differential dH is:

$$dH = \sum_j \left\{ \frac{\langle \Psi | \hat{H} | \frac{\partial \Psi}{\partial p_j} \rangle}{\langle \Psi | \Psi \rangle} - \frac{\langle \Psi | \hat{H} | \Psi \rangle \langle \Psi | \frac{\partial \Psi}{\partial p_j} \rangle}{\langle \Psi | \Psi \rangle^2} \right\} dp_j + \text{c.c.} + \dots \quad (16)$$

The term in curly brackets is just the j -th component of the general "gradient vector" of the energy surface $E = H(p_1, p_2, \dots)$. With the notations

$$(H\nabla)_j = \frac{\langle \Psi | (\hat{H} - H) | \frac{\partial \Psi}{\partial p_j} \rangle}{\langle \Psi | \Psi \rangle} \quad (\nabla H)_j = \frac{\langle \frac{\partial \Psi}{\partial p_j} | (\hat{H} - H) | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (17)$$

the stationary-value conditions can be formulated as

$$(H\nabla)_j = (\nabla H)_j = 0 \quad \text{for all } j \quad (18)$$

Using the shorthand notation $\frac{\partial \Psi}{\partial p_j} = \Psi^j$ etc. the second derivatives are

$$(\nabla\nabla H)_{jk} = \frac{\langle \Psi^j | (\hat{H} - H) | \Psi^k \rangle - \langle \Psi^j | \Psi \rangle (\nabla H)_k - (\nabla H)_j \langle \Psi^k | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (19)$$

$$(\nabla H\nabla)_{jk} = \frac{\langle \Psi^j | (\hat{H} - H) | \Psi^k \rangle - \langle \Psi^j | \Psi \rangle (H\nabla)_k - (\nabla H)_j \langle \Psi | \Psi^k \rangle}{\langle \Psi | \Psi \rangle} \quad (20)$$

The variation around a point $\mathbf{p}_0 = (p_1^{(0)}, p_2^{(0)}, \dots)$ with $E = H(\mathbf{p}_0) = H_0$ can be written in terms of the above-defined tensors. Let $p_j = p_j^{(0)} + d_j$ then

$$\begin{aligned} \delta E &= \sum_j \left[d_j^* (\nabla H)_j + (H\nabla)_j d_j \right] \\ &+ \frac{1}{2} \sum_{jk} \left[d_j^* d_k^* (\nabla\nabla H)_{jk} + 2d_j^* (\nabla H\nabla)_{jk} d_k + (H\nabla\nabla)_{jk} d_j d_k \right] + \dots \end{aligned} \quad (21)$$

The generalized "forces" will be denoted by \mathbf{a} and \mathbf{a}^* and the blocks of the generalized Hessian matrix by

$$Q_{jk} = (\nabla H\nabla)_{jk} \quad \text{and} \quad M_{jk} = (\nabla\nabla H)_{jk}$$

The Taylor expansion of the energy around the point \mathbf{p}_0 is

$$E = H_0 + \begin{pmatrix} \mathbf{d} \\ \mathbf{d}^* \end{pmatrix}^\dagger \begin{pmatrix} \mathbf{a} \\ \mathbf{a}^* \end{pmatrix} + \frac{1}{2} \begin{pmatrix} \mathbf{d} \\ \mathbf{d}^* \end{pmatrix}^\dagger \begin{pmatrix} \mathbf{M} & \mathbf{Q} \\ \mathbf{Q}^* & \mathbf{M}^* \end{pmatrix} \begin{pmatrix} \mathbf{d} \\ \mathbf{d}^* \end{pmatrix} \quad (22)$$

In obvious notations:

$$E = H_0 + \mathbf{D}^\dagger \mathbf{A} + \frac{1}{2} \mathbf{D}^\dagger \mathbf{B} \mathbf{D} \quad (23)$$

This relationship can serve to minimize the wave function using the Newton-method

$$\begin{pmatrix} \mathbf{a} \\ \mathbf{a}^* \end{pmatrix} + \begin{pmatrix} \mathbf{M} & \mathbf{Q} \\ \mathbf{Q}^* & \mathbf{M}^* \end{pmatrix} \begin{pmatrix} \mathbf{d} \\ \mathbf{d}^* \end{pmatrix} = 0 \quad (24)$$

4 Separation of electronic and nuclear motions

Total Hamiltonian

$$\mathcal{H}(\mathbf{R}, \mathbf{r}) = - \underbrace{\sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \Delta_{\alpha}}_{\mathcal{J}_N} - \underbrace{\frac{\hbar^2}{2m_e} \sum_i \Delta_i}_{\mathcal{J}_e} + \underbrace{\sum_{i < j} \frac{1}{r_{ij}} - \sum_i \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{\alpha < \beta} \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}}}_{\mathcal{V}} \quad (25)$$

Let us introduce M an ‘‘average nuclear mass’’, the dimensionless number $\mu_{\alpha} = M/M_{\alpha}$ characterizing the nuclear mass of atom α , and the electron/nuclear mass ratio parameter

$$\kappa = \left(\frac{m}{M} \right)^{1/4} \quad (26)$$

Total Hamiltonian in atomic units

$$\begin{aligned} \mathcal{H}(\mathbf{R}, \mathbf{r}) &= -\frac{1}{2} \sum_i \Delta_i + \mathcal{V}(\mathbf{r}, \mathbf{R}) - \frac{\kappa^4}{2} \sum_{\alpha} \mu_{\alpha} \Delta_{\alpha} \\ &= \mathcal{H}_e(\mathbf{R}; \mathbf{r}) + \kappa^4 \mathcal{J}_N(\mathbf{R}) \end{aligned}$$

Consider $\kappa^4 \mathcal{J}_N$ as perturbation. At zero order we obtain the electronic Schrödinger equation

$$\mathcal{H}_e(\mathbf{r}; \mathbf{R}) \Psi_n(\mathbf{r}; \mathbf{R}) = U_n(\mathbf{R}) \Psi_n(\mathbf{r}; \mathbf{R}) \quad (27)$$

with the electronic Hamiltonian

$$\mathcal{H}_e = \mathcal{J}_e + \mathcal{V} \quad (28)$$

The solutions of the electronic Schrödinger equation form a complete basis of the eigenfunctions $\Psi_n(\mathbf{r}; \mathbf{R})$ on which the total wave function can be expanded

$$\Upsilon(\mathbf{r}, \mathbf{R}) = \sum_n \Xi_n(\mathbf{R}) \Psi_n(\mathbf{r}; \mathbf{R}) \quad (29)$$

with the nuclear coordinate dependent expansion coefficients, $\Xi_n(\mathbf{R})$.

Substitute the expansion into the Schrödinger equation

$$\sum_n \{ \mathcal{J}_N + \mathcal{H}_e \} \Xi_n(\mathbf{R}) \Psi_n(\mathbf{r}; \mathbf{R}) = \mathcal{E} \sum_n \Xi_n(\mathbf{R}) \Psi_n(\mathbf{r}; \mathbf{R}) \quad (30)$$

and use that Ψ_n are eigenfunctions of \mathcal{H}_e

$$\sum_n \{ \mathcal{J}_N + U_n(\mathbf{R}) \} \Xi_n(\mathbf{R}) \Psi_n(\mathbf{r}; \mathbf{R}) = \mathcal{E} \sum_n \Xi_n(\mathbf{R}) \Psi_n(\mathbf{r}; \mathbf{R}) \quad (31)$$

The nuclear kinetic energy operator leads to electron-nuclear coupling terms related to the variation of the electronic wave function with respect to the nuclear coordinates

$$\begin{aligned} & -\frac{1}{2} \sum_{\alpha} \mu_{\alpha} \Delta_{\alpha} [\Psi_n(\mathbf{r}; \mathbf{R}) \Xi_n(\mathbf{R})] = \\ & -\frac{1}{2} \sum_{\alpha} \mu_{\alpha} [\Psi_n \Delta_{\alpha} \Xi_n + 2(\nabla_{\alpha} \Psi_n \nabla_{\alpha} \Xi_n) + \Xi_n \Delta_{\alpha} \Psi_n] \end{aligned} \quad (32)$$

Multiply from left by $\Psi_k^*(\mathbf{r}; \mathbf{R})$, integrate over the electronic variables and denote the off-diagonal coupling matrix elements by

$$B_{kn} = \langle \Psi_k | \mathcal{J}_N | \Psi_n \rangle - \sum_{\alpha} \mu_{\alpha} \langle \Psi_k | \nabla_{\alpha} | \Psi_n \rangle \nabla_{\alpha} \quad (33)$$

The exact solution of the nuclear problem

$$\{\mathcal{T}_N + U_k(\mathbf{R}) + \langle \Psi_k | \mathcal{T}_N | \Psi_k \rangle - \mathcal{E}\} \Xi_k(\mathbf{R}) = \sum_{n \neq k} B_{kn} \Xi_n(\mathbf{R}) \quad (34)$$

requires the complete set of electronic eigenfunctions Ψ_n .

4.1 Born-Oppenheimer approximation

Provided the energy gap of electronic states is large, the matrix elements of \mathcal{T} and ∇_α are small. In this case the nuclei move on a single potential energy surface, $U_n(\mathbf{R})$, and the total wave function can be written in a simple product form

$$\Upsilon(\mathbf{R}, \mathbf{r}) = \Xi(\mathbf{R}) \Psi(\mathbf{r}; \mathbf{R})$$

Born-Oppenheimer approximation \Rightarrow all electron-nuclear coupling terms are neglected

$$\{\mathcal{T}_N + E_k(\mathbf{R})\} \Xi_k(\mathbf{R}) = \mathcal{E} \Xi_k(\mathbf{R}) \quad (35)$$

Adiabatic approximation \Rightarrow diagonal coupling term is retained

$$\{\mathcal{T}_N + E_k(\mathbf{R}) + \langle \Psi_k | \mathcal{T}_N | \Psi_k \rangle\} \Xi_k(\mathbf{R}) = \mathcal{E} \Xi_k(\mathbf{R}) \quad (36)$$

4.2 Breakdown of the Born-Oppenheimer approximation

The $\langle \Psi_i | \nabla_\alpha | \Psi_j \rangle$ coupling terms can be neglected only if the electronic states are well-separated.

Differentiate the electronic Schrödinger equation, multiply from left by Ψ_i , $i \neq j$ and integrate

$$\langle \Psi_i | \frac{\partial H_e}{\partial R_\alpha} | \Psi_j \rangle + \langle \Psi_i | H_e | \frac{\partial \Psi_j}{\partial R_\alpha} \rangle = \frac{\partial U_i}{\partial R_\alpha} \langle \Psi_i | \Psi_j \rangle + U_j \langle \Psi_i | \frac{\partial \Psi_j}{\partial R_\alpha} \rangle \quad (37)$$

after rearranging

$$\langle \Psi_i | \frac{\partial H_e}{\partial R_\alpha} | \Psi_j \rangle + U_i \langle \Psi_i | \nabla_\alpha | \Psi_j \rangle = \frac{\partial U_i}{\partial R_\alpha} \delta_{ij} + U_j \langle \Psi_i | \nabla_\alpha | \Psi_j \rangle \quad (38)$$

leading to the condition

$$\langle \Psi_i | \nabla_\alpha | \Psi_j \rangle = \langle \Psi_i | \frac{\partial H_e}{\partial R_\alpha} | \Psi_j \rangle / (U_j - U_i) \quad (39)$$

which indicates that a smaller energy gap leads to an enhanced coupling term (e.g. avoided crossings).

5 Electron Hamiltonian and wave function

Electronic Schrödinger equation

$$\{\mathcal{T}_e + \mathcal{V}_{eN} + \mathcal{V}_{ee} + \mathcal{V}_{NN}\} \Psi = E \Psi \quad (40)$$

or

$$\left\{ \sum_i \hat{h}(i) + \sum_{i,j} ' \hat{g}(i,j) + \mathcal{V}_{NN} \right\} \Psi = E \Psi \quad (41)$$

The many-electron wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$

1. describes a definite spin state

$$\hat{H}\hat{S}^2 - \hat{S}^2\hat{H} = 0 \quad \text{therefore} \quad \hat{S}^2\Psi = S(S+1)\Psi \quad (42)$$

2. is normalized

$$\int \Psi^*\Psi d\mathbf{x} = \int |\Psi|^2 d\mathbf{x} = 1 \quad (43)$$

3. satisfies the antisymmetry requirement

$$\hat{P}\Psi = \varepsilon_P\Psi \quad (44)$$

where $\varepsilon_P = \pm 1$ for a permutation of the arguments $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N$ comprising an even/odd number of interchanges.

In the following we discuss briefly some implications of these properties on the construction of the many-electron wave function.

5.1 Electron spin

Although the molecular Hamiltonian is usually spin-independent, we know from experiment (Zeeman effect) that electrons have an *intrinsic* magnetic moment. Therefore we introduce

spin angular momentum operators \hat{s}_α acting on the spin variable, σ

$$\hat{s}_z\eta(\sigma) = \lambda\eta(\sigma)$$

with two permitted solutions:

$$\begin{aligned} \hat{s}_z\alpha(\sigma) &= \frac{1}{2}\alpha(\sigma) \\ \hat{s}_z\beta(\sigma) &= -\frac{1}{2}\beta(\sigma) \end{aligned} \quad (45)$$

5.2 Spin operators and spin functions

Spin variable σ with possible values

$$\sigma = \pm 1 \quad (46)$$

Two spin functions

$$\begin{aligned} \alpha\left(\frac{1}{2}\right) &= 1 & \alpha\left(-\frac{1}{2}\right) &= 0 \\ \beta\left(\frac{1}{2}\right) &= 0 & \beta\left(-\frac{1}{2}\right) &= 1 \end{aligned} \quad (47)$$

orthonormalized

$$\begin{aligned} \int \alpha(\sigma)\alpha(\sigma)d\sigma &= \sum_{\sigma} \alpha^2(\sigma) = \alpha^2\left(\frac{1}{2}\right) + \alpha^2\left(-\frac{1}{2}\right) = 0^2 + 1^2 = 1 \\ \int \beta(\sigma)\beta(\sigma)d\sigma &= \sum_{\sigma} \beta^2(\sigma) = 1^2 + 0^2 = 1 \\ \int \alpha(\sigma)\beta(\sigma)d\sigma &= \sum_{\sigma} \alpha(\sigma)\beta(\sigma) = 0 \times 1 + 1 \times 0 = 0 \end{aligned} \quad (48)$$

eigenfunctions of \hat{s}_z and \hat{s}^2 operators ($\hbar = 1$)

$$\begin{aligned} \hat{s}^2\alpha(\sigma) &= \frac{3}{4}\alpha(\sigma) & \hat{s}_z\alpha(\sigma) &= \frac{1}{2}\alpha(\sigma) \\ \hat{s}^2\beta(\sigma) &= \frac{3}{4}\beta(\sigma) & \hat{s}_z\beta(\sigma) &= -\frac{1}{2}\beta(\sigma) \end{aligned} \quad (49)$$

behave as follows with the \hat{s}_\pm operators

$$\begin{aligned}\hat{s}_+\alpha(\sigma) &= 0 & \hat{s}_-\alpha(\sigma) &= \beta(\sigma) \\ \hat{s}_+\beta(\sigma) &= \alpha(\sigma) & \hat{s}_-\beta(\sigma) &= 0\end{aligned}\tag{50}$$

5.3 Total spin operators

Cartesian components of the total spin of an N-particle system

$$\hat{S} = \sum_i \hat{s}^{(i)} = \sum_i \begin{pmatrix} \hat{s}_x^{(i)} \\ \hat{s}_y^{(i)} \\ \hat{s}_z^{(i)} \end{pmatrix} = \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix}\tag{51}$$

Satisfy the commutation rules

$$[\hat{S}_\alpha, \hat{S}_\beta] = i\hat{S}_\gamma \quad (\alpha\beta\gamma = xyz, yzx, zxy)\tag{52}$$

Step-up and step-down operators

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y \quad \hat{S}_- = \hat{S}_x - i\hat{S}_y\tag{53}$$

in terms of which the $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$ operator is

$$\hat{S}^2 = \hat{S}_- \hat{S}_+ + \hat{S}_z + \hat{S}_z^2 = \hat{S}_+ \hat{S}_- - \hat{S}_z + \hat{S}_z^2\tag{54}$$

The simultaneous eigenfunctions $\Theta(S, M_S)$ of \hat{S}^2 and \hat{S}_z satisfy

$$\hat{S}^2\Theta(S, M_S) = S(S+1)\Theta(S, M_S) \quad \hat{S}_z\Theta(S, M_S) = M_S\Theta(S, M_S)\tag{55}$$

where \S is a positive half-integer and $M_S = S, S-1, \dots, -S$.

Step-down and step-up operators act as

$$\hat{S}_\pm\Theta(S, M_S) = \sqrt{S(S+1) - M_S(M_S \pm 1)}\Theta(S, M_S \pm 1)\tag{56}$$

5.4 Spin functions of a two-electron system

Form four possible spin-functions

$$\alpha(\sigma_1)\alpha(\sigma_2); \quad \alpha(\sigma_1)\beta(\sigma_2); \quad \beta(\sigma_1)\alpha(\sigma_2); \quad \beta(\sigma_1)\beta(\sigma_2)\tag{57}$$

One antisymmetric function

$$\Theta(0, 0) = \frac{1}{\sqrt{2}} (\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2))\tag{58}$$

Three symmetric functions

$$\begin{aligned}\Theta(1, 1) &= \alpha(\sigma_1)\alpha(\sigma_2) \\ \Theta(1, 0) &= \frac{1}{\sqrt{2}} (\alpha(\sigma_1)\beta(\sigma_2) + \beta(\sigma_1)\alpha(\sigma_2)) \\ \Theta(1, -1) &= \beta(\sigma_1)\beta(\sigma_2)\end{aligned}\tag{59}$$

For instance

$$\hat{S}_z\alpha(\sigma_1)\alpha(\sigma_2) = (s_z^{(1)} + s_z^{(2)})\alpha(\sigma_1)\alpha(\sigma_2) = \left(\frac{1}{2} + \frac{1}{2}\right)\alpha(\sigma_1)\alpha(\sigma_2)\tag{60}$$

In the case of two electrons, an antisymmetric total wave function can always be constructed as antisymmetric/symmetric combination of the space- and spin functions.

5.5 Space and spin orbitals

spatial orbitals $\phi_i(\mathbf{r})$

- wave functions of a single particle

$$\hat{h}(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

- describe the spatial distribution of an electron $\varrho_i(\mathbf{r}) = |\phi_i(\mathbf{r})|^2$
- form an orthonormal set

$$\int d\mathbf{r}\phi_i^*(\mathbf{r})\phi_j(\mathbf{r}) = \langle\phi_i|\phi_j\rangle = \delta_{ij}$$

spin orbitals $\psi_i(\mathbf{x})$

- simultaneous eigenfunctions of $\hat{h}(\mathbf{r})$ and \hat{s}_z
- products of spatial and spin functions

$$\psi_i(\mathbf{x}) = \phi_i(\mathbf{r})\eta_i(\sigma)$$

- orthonormality

$$\int d\mathbf{x}\psi_i^*(\mathbf{x})\psi_j(\mathbf{x}) = \int d\mathbf{r}\phi_i^*(\mathbf{r})\phi_j(\mathbf{r}) \int d\sigma\alpha(\sigma)^*\beta(\sigma) = \delta_{ij}\delta_{\alpha\beta}$$

6 Density matrices

We do not necessarily need N -electron all information contained in the $4N$ -variable wave function to obtain the energy and properties of the system. We introduce a hierarchy of functions that depend explicitly on one, two, three, etc. particle coordinates.

The probability of finding electron 1 in $d\mathbf{x}_1 = d\mathbf{r}_1 d\sigma_1$, while other electrons are anywhere, is

$$d\mathbf{x}_1 \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (61)$$

and the probability of finding *any* of the N electrons in $d\mathbf{x}_1$ is N times this, which can be written as $P(\mathbf{x}_1)d\mathbf{x}_1$, where

$$P(\mathbf{x}_1) = N \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (62)$$

The probability of finding an electron in \mathbf{r}_1 , without making reference to the spin coordinate is

$$\rho(\mathbf{r}_1) = \int P(\mathbf{x}_1)d\sigma_1 \quad (63)$$

This is the *electron density function* measured by X-ray crystallography.

The probability of finding any two electrons simultaneously in \mathbf{x}_1 and \mathbf{x}_2 is

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2) = N(N-1) \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)d\mathbf{x}_3 \dots d\mathbf{x}_N \quad (64)$$

and in the spinless version

$$\gamma(\mathbf{r}_1, \mathbf{r}_2) = \int \int \Gamma(\mathbf{x}_1)d\sigma_1 d\sigma_2 \quad (65)$$

6.1 Reduced density matrices

For the purposes of evaluating one- and two-electron operator expectation values, we need to generalize the density functions as follows

$$P(\mathbf{x}_1; \mathbf{x}'_1) = N \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (66)$$

and

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = N(N-1) \int \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_3 \dots d\mathbf{x}_N \quad (67)$$

The expectation value of a one-electron operator $\hat{H}_1 = \sum_i \hat{h}(i)$ is

$$\begin{aligned} \langle \Psi | \hat{H}_1 | \Psi \rangle &= \sum_{i=1}^N \int \dots \int d\mathbf{x}_1 d\mathbf{x}_{i-1} d\mathbf{x}_{i+1} \dots d\mathbf{x}_N \\ &\quad \times \int d\mathbf{x}_i \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \hat{h}(i) \Psi(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \end{aligned} \quad (68)$$

which can be written with the 1RDM as

$$\langle \Psi | \hat{H}_1 | \Psi \rangle = \int_{\mathbf{x}'_1 = \mathbf{x}_1} \hat{h}(1) P(\mathbf{x}_1; \mathbf{x}'_1) d\mathbf{x}_1 \quad (69)$$

where we put $\mathbf{x}'_1 = \mathbf{x}_1$ after the action of the operator on $P(\mathbf{x}_1; \mathbf{x}'_1)$, before performing the integral.

Similarly, for a two-electron operator

$$\langle \Psi | \hat{H}_2 | \Psi \rangle = \iint_{\substack{\mathbf{x}'_1 = \mathbf{x}_1 \\ \mathbf{x}'_2 = \mathbf{x}_2}} \hat{g}(1, 2) \Gamma(\mathbf{x}_1; \mathbf{x}'_1) d\mathbf{x}_1 d\mathbf{x}_2 \quad (70)$$

Higher than 2RDMs are not needed to describe the interaction in a molecular system.

7 Construction of the wave function

Consider a simplified problem, by neglecting the electron-electron interaction, leading to a sum of one-electron Hamiltonians

$$\hat{H} = \sum_i^N \hat{h}(i) \quad (71)$$

which has as eigenfunctions

$$\Psi^{\text{HP}} = \psi_i(\mathbf{x}_1) \psi_j(\mathbf{x}_2) \dots \psi_n(\mathbf{x}_N) \quad (72)$$

i.e. the product of one-electron functions, satisfying the following eigenequations

$$\hat{h}(i) \psi_j(\mathbf{x}_i) = \varepsilon_j \psi_j(\mathbf{x}_i) \quad (73)$$

where the electron i occupies the spin orbital $\psi_j(\mathbf{x}_i)$ with energy ε_j . The energy of this *Hartree product* is

$$\langle \Psi | \hat{H} | \Psi \rangle = \varepsilon_i + \varepsilon_j + \varepsilon_k + \dots + \varepsilon_n = E^{\text{HP}} \quad (74)$$

This wave function is obviously not a physically appropriate one (violates the Pauli principle) and the complete neglect of electron repulsion is a very crude approximation. Nevertheless, we can examine whether the idea of writing the N-electron wave function as a linear combination of product formed by one-electron functions, can lead to the exact solution.

7.1 Expansion theorem

Assume we have a complete set of functions $\{\chi_i(x_1)\}$ of a single variable x_1 . Then any arbitrary function of that variable can be expanded exactly as

$$\Phi(x_1) = \sum_i a_i \chi_i(x_1) \quad (75)$$

We can expand also a two-variable function of x_1 and x_2 on the same domain by holding x_2 fixed

$$\Phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1) \quad (76)$$

The ensemble of expansion coefficients $a_i(x_2)$ for each fixed x_2 coordinates, can be considered now as a new function of a single variable, that can be expanded as

$$a_i(x_2) = \sum_j b_{ij} \chi_j(x_2) \quad (77)$$

and substituting this expansion into that of $\Phi(x_1, x_2)$, we have

$$\Phi(x_1, x_2) = \sum_{ij} b_{ij} \chi_i(x_1) \chi_j(x_2) \quad (78)$$

This process can be extended to functions $\Phi(x_1, x_2, \dots, x_N)$ of any number of variables.

Let us collect the space and spin coordinates of an electron to \mathbf{x} . The one-electron functions, the spin orbitals, $\chi(\mathbf{x})$ enter into the general expansion

$$\Phi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) = \sum_{ijk\dots N} b_{ijk\dots N} \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \chi_k(\mathbf{x}_3) \dots \chi_N(\mathbf{x}_N) \quad (79)$$

However, the wave function should be antisymmetric with respect to the exchange of coordinates of two electrons. For two electrons

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = -\Phi(\mathbf{x}_2, \mathbf{x}_1) \quad (80)$$

which implies for the expansion coefficients that $b_{ij} = -b_{ji}$ and $b_{ii} = 0$, or

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_{i>j} b_{ij} \{\chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2)\} = \sum_{i>j} \sqrt{2} b_{ij} \det [\chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2)] \quad (81)$$

More generally, an arbitrary N -electron function can be expanded as linear combination of all possible N -electron determinants, formed from a complete set of one-electron spin orbitals, $\{\chi_i(\mathbf{x})\}$. Note that any complete set of one-electron spin orbitals can be used, in principle. Other possibilities ...

7.2 Configuration Interaction

Let us denote the N -electron determinants as Φ_I , which will be supposed to be real and orthonormal. The exact wave function, Ψ expanded on the fixed basis of these determinants

$$\Psi = \sum_I c_I \Phi_I \quad (82)$$

can be obtained by minimizing the expectation value of the Hamiltonian

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_{IJ} c_I c_J \langle \Phi_I | \hat{H} | \Phi_J \rangle = \sum_{IJ} c_I c_J H_{IJ} \quad (83)$$

We suppose that Ψ is normalized, i.e.

$$\langle \Psi | \Psi \rangle = \sum_{IJ} c_I c_J \langle \Phi_I | \Phi_J \rangle = \sum_I c_I^2 = 1 \quad (84)$$

Since we would like to preserve the normalization of the wave function, the constrained minimization method with Langrange multipliers is used, i.e. we minimize the function

$$\begin{aligned} \mathcal{L}(c_1, c_2, \dots, c_K, E) &= \langle \Psi | \hat{H} | \Psi \rangle - E \left(\langle \Psi | \Psi \rangle - 1 \right) \\ &= \sum_{IJ} c_I c_J H_{IJ} - E \left(\sum_I c_I^2 - 1 \right) \end{aligned} \quad (85)$$

The minimum of this function can be found from the condition

$$\frac{\partial \mathcal{L}}{\partial c_I} = 2 \sum_J c_J H_{IJ} - 2E c_I = 0 \quad (86)$$

which is just the standard eigenvalue problem of the Hamiltonian matrix

$$\mathbf{H} \mathbf{c} = E \mathbf{c} \quad (87)$$

Consider all the possible eigenvalues E_α of the Hamiltonian matrix

$$\mathbf{H} \mathbf{c}^\alpha = E_\alpha \mathbf{c}^\alpha \quad (88)$$

Let us introduce the \mathbf{C} and the diagonal matrix of the eigenvalues, \mathbf{E} , then we have

$$\mathbf{H} \mathbf{C} = \mathbf{C} \mathbf{E} \quad (89)$$

The α -th eigenvalue is the expectation value of the Hamiltonian with respect to Φ_α

$$\langle \Phi_\beta | \hat{H} | \Phi_\alpha \rangle = \sum_{IJ} c_I^\beta \langle \Psi_I | \hat{H} | \Psi_J \rangle c_J^\alpha = \sum_{IJ} (\mathbf{c}^\beta)^\dagger \mathbf{H} \mathbf{c}^\alpha = E_\alpha (\mathbf{c}^\beta)^\dagger \mathbf{c}^\alpha = E_\alpha \delta_{\alpha\beta} \quad (90)$$

The lowest eigenvalue is upper bound to the ground state energy. Higher eigenvalues are upper bounds to the energies of the excited states.

8 Method of determinants

We have seen that the *exact* N -electron wave function, satisfying the Pauli principle, can be expanded in terms of antisymmetrized products of one-electron functions.

Such wave functions correspond to well-known mathematical objects, the determinants, which we shall study in more details.

8.1 Permutation (symmetric) group

Consider N ordered indices

$$\{1, 2, 3, \dots, N\}$$

Define a permutation as

$$P\{1, 2, 3, \dots, N\} = \{p_1, p_2, p_3, \dots, p_N\}$$

which means that 1 is replaced by p_1 , etc.

Notation

$$P = \begin{pmatrix} 1 & 2 & \dots & N \\ p_1 & p_2 & \dots & p_N \end{pmatrix}$$

Product of two permutations is also permutation

$$\begin{aligned} PQ &= \begin{pmatrix} 1 & 2 & \dots & N \\ p_1 & p_2 & \dots & p_N \end{pmatrix} \begin{pmatrix} 1 & 2 & \dots & N \\ q_1 & q_2 & \dots & q_N \end{pmatrix} = \\ &= \begin{pmatrix} q_1 & q_2 & \dots & q_N \\ r_1 & r_2 & \dots & r_N \end{pmatrix} \begin{pmatrix} 1 & 2 & \dots & N \\ q_1 & q_2 & \dots & q_N \end{pmatrix} = \\ &= \begin{pmatrix} 1 & 2 & \dots & N \\ r_1 & r_2 & \dots & r_N \end{pmatrix} = R \end{aligned} \quad (91)$$

Inverse permutation:

$$\text{if } P = \begin{pmatrix} 1 & 2 & \dots & N \\ p_1 & p_2 & \dots & p_N \end{pmatrix} \quad \text{then } P^{-1} = \begin{pmatrix} p_1 & p_2 & \dots & p_N \\ 1 & 2 & \dots & N \end{pmatrix} \quad (92)$$

Unity:

$$I = \begin{pmatrix} 1 & 2 & \dots & N \\ 1 & 2 & \dots & N \end{pmatrix} \quad (93)$$

Associativity:

$$(PQ)R = R(RQ) \quad (94)$$

The ensemble of the possible permutations of N objects forms S_N , a symmetric group of rank N and of order $N!$.

8.2 Antisymmetrizer

Projection operator, selects the antisymmetric component of a many-electron function.

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_{P \in S_N} \epsilon_P P \quad (95)$$

with

$$\epsilon_P = (-1)^P$$

Idempotent: $\hat{A}\hat{A} = \text{const} \times \hat{A}$

$$\hat{A}\hat{A} = \left(\frac{1}{\sqrt{N!}} \right)^2 \sum_{P \in S_N} \epsilon_P P \sum_{Q \in S_N} \epsilon_Q Q = \frac{1}{N!} \sum_{P \in S_N} \sum_{Q \in S_N} (-1)^{p+q} PQ \quad (96)$$

for a given P , if Q runs over S_N , the product $R = PQ$ runs over all the $N!$ elements of S_N :

$$\frac{1}{N!} \sum_{P \in S_N} \underbrace{\left[\sum_{R \in S_N} (-1)^r R \right]}_{\sqrt{N!}\hat{A}} = \sqrt{N!}\hat{A} \quad (97)$$

Hermitian: $\hat{A}^\dagger = \hat{A}$, i.e. $\langle \hat{A}\Psi | \Psi \rangle = \langle \Psi | \hat{A}\Psi \rangle$

$$\begin{aligned} &\langle \hat{A}\Psi(1, 2, \dots, N) | \Psi(1, 2, \dots, N) \rangle = \\ &\sum_{P \in S_N} \epsilon_P \langle P^{-1}P\Psi(1, 2, \dots, N) | P^{-1}\Psi(1, 2, \dots, N) \rangle \end{aligned} \quad (98)$$

Insertion of P^{-1} changes only the order of variables of integration. If P runs over all permutations, then so does $P^{-1} = Q$ too:

$$\begin{aligned} \sum_{P \in S_N} \epsilon_P \langle \Psi(1, 2, \dots, N) | P^{-1} \Psi(1, 2, \dots, N) \rangle &= \\ \sum_{Q \in S_N} \epsilon_Q \langle \Psi(1, 2, \dots, N) | Q \Psi(1, 2, \dots, N) \rangle &= \\ \langle \Psi(1, 2, \dots, N) | \hat{A} \Psi(1, 2, \dots, N) \rangle & \end{aligned} \quad (99)$$

8.3 Why antisymmetrizer?

Consider a $Q \in S_N$ then

$$Q\hat{A} = \frac{1}{\sqrt{N!}} \sum_{P \in S_N} (-1)^q (-1)^q (-1)^p QP = (-1)^q \frac{1}{\sqrt{N!}} \sum_{R \in S_N} (-1)^r R = (-1)^q \hat{A} \quad (100)$$

Apply Q , a permutation of the N variables in $\Phi(1, 2, \dots, N)$ to

$$\Psi(1, 2, \dots, N) = \hat{A}\Phi(1, 2, \dots, N)$$

, where $\Phi(1, 2, \dots, N)$ is an arbitrary function.

$$\begin{aligned} Q\Psi(1, 2, \dots, N) &= Q\hat{A}\Phi(1, 2, \dots, N) \\ &= (-1)^q \hat{A}\Phi(1, 2, \dots, N) \\ &= (-1)^q \Psi(1, 2, \dots, N) \end{aligned} \quad (101)$$

After the action of \hat{A} , the function $\Phi(1, 2, \dots, N)$ becomes antisymmetric.

9 Determinant wave function

The wave function obtained after the action of the antisymmetrizer on a Hartree-product can be written as a determinant:

$$\begin{aligned} D_K &= \hat{A}[\phi_{k_1}(1)\phi_{k_2}(2)\dots\phi_{k_N}(N)] \\ &= \frac{1}{\sqrt{N!}} \det[\phi_{k_1}(1)\phi_{k_2}(2)\dots\phi_{k_N}(N)] \end{aligned} \quad (102)$$

$$D_K = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{k_1}(1) & \phi_{k_2}(1) & \dots & \phi_{k_N}(1) \\ \phi_{k_1}(2) & \phi_{k_2}(2) & \dots & \phi_{k_N}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{k_1}(N) & \phi_{k_2}(N) & \dots & \phi_{k_N}(N) \end{vmatrix} \quad (103)$$

9.1 Invariance properties of the determinant wave function

Mixing of the orbitals constituting the determinant leaves it invariant (up to a constant factor).

Let us consider the wave function

$$\Phi = \hat{A}[\phi_1(2)\phi_2(2)\dots\phi_N(N)] = \frac{1}{\sqrt{N!}} \det\{\mathbf{A}\} \quad (104)$$

where $A_{ij} = \phi_j(i)$. Apply a linear transformation on the set of orbitals $\{\phi_k\}$

$$\psi_j = \sum_k T_{kj} \phi_k \quad (105)$$

The determinant wave function built from the new set of orbitals is

$$\Psi = \hat{A} [\psi_1(2)\psi_2(2) \dots \psi_N(N)] = \frac{1}{\sqrt{N!}} \det \{\mathbf{B}\} \quad (106)$$

where $B_{ij} = \psi_j(i)$.

Using the transformation equation

$$\psi_j(i) = B_{ij} = \sum_k T_{kj} \phi_k(i) = \sum_k A_{ik} T_{kj} = (\mathbf{AT})_{ij} \quad (107)$$

Determinant of the product of two matrices is equal to the product of the determinants

$$\Psi = \frac{1}{\sqrt{N!}} \det \mathbf{B} = \frac{1}{\sqrt{N!}} \det \mathbf{AT} = \frac{1}{\sqrt{N!}} \det \mathbf{A} \det \mathbf{T} = \det \mathbf{T} \cdot \Phi \quad (108)$$

If the transformation is unitary $\mathbf{U}^{-1} = \mathbf{U}^\dagger$, then $|\det \mathbf{U}| = 1$ and the wave function is invariant with respect to the unitary transformation of the spin orbitals.

Corollary: any determinant wave function can be written in terms of orthonormal spin orbitals.

Let the overlap matrix

$$S_{ij} = \langle \psi_i | \psi_j \rangle \neq \delta_{ij}$$

and choose \mathbf{T} a the following orthogonalization transformation (Löwdin orthogonalization)

$$\mathbf{T} = \mathbf{S}^{-1/2} \mathbf{V} \quad (109)$$

where \mathbf{V} is an arbitrary unitary matrix. In fact,

$$\begin{aligned} \langle \phi_i | \phi_j \rangle &= \left\langle \sum_\ell T_{\ell i} \psi_\ell \middle| \sum_k T_{k j} \psi_k \right\rangle = \sum_{\ell k} T_{\ell i}^* \langle \psi_\ell | \psi_k \rangle T_{k j} \\ &= \sum_{\ell k} T_{i \ell}^\dagger S_{\ell k} T_{k j} = (\mathbf{T}^\dagger \mathbf{S} \mathbf{T})_{ij} \\ &= \left(\mathbf{V}^\dagger \mathbf{S}^{-1/2} \mathbf{S} \mathbf{S}^{-1/2} \mathbf{V} \right)_{ij} \\ &= (\mathbf{V}^\dagger \mathbf{V})_{ij} = \delta_{ij} \end{aligned} \quad (110)$$

9.2 Physical meaning of the determinant wave function

Consider a two-electron system with spin orbitals $\psi_1(\mathbf{x}_1)$ and $\psi_2(\mathbf{x}_2)$

◦ **Hartree product**

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2)$$

Two particle density matrix

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2) = 2\Psi^*(\mathbf{x}_1, \mathbf{x}_2)\Psi(\mathbf{x}_1, \mathbf{x}_2) = |\psi_1(\mathbf{x}_1)|^2 |\psi_2(\mathbf{x}_2)|^2 \quad (111)$$

the simultaneous probability of finding electron-one in $d\mathbf{x}_1$ at \mathbf{x}_1 and in \mathbf{x}_2 at \mathbf{x}_2 is a simple product of the densities associated with the two electrons and the indistinguishability of the electrons is not respected.

- **Determinant with electrons having opposite spins**

$$|\Psi(1, 2)\rangle = \hat{A}|\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\rangle = \hat{A}|\phi_1(\mathbf{r}_1)\alpha(\sigma_1)\phi_2(\mathbf{r}_2)\beta(\sigma_2)\rangle$$

Spin-dependent two-particle reduced density matrix

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2} \{ \phi_1(\mathbf{r}_1)\alpha(\sigma_1)\phi_2(\mathbf{r}_2)\beta(\sigma_2) - \phi_1(\mathbf{r}_2)\alpha(\sigma_2)\phi_2(\mathbf{r}_1)\beta(\sigma_1) \}^2 \quad (112)$$

The spinless 2RDM is obtained by integration of the spin variables

$$\gamma(\mathbf{r}_1, \mathbf{r}_2) = \int d\sigma_1 \int d\sigma_2 \Gamma(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2} \{ |\phi_1(\mathbf{r}_1)|^2 |\phi_2(\mathbf{r}_2)|^2 + |\phi_1(\mathbf{r}_2)|^2 |\phi_2(\mathbf{r}_1)|^2 \} \quad (113)$$

The indistinguishability of the electrons is reflected by the average of two terms, but the two electrons are uncorrelated. In particular, if the space part of the orbitals is the same,

$$\gamma(\mathbf{r}_1, \mathbf{r}_1) \neq 0 \quad (114)$$

i.e. there is a finite probability of finding two electrons of opposite spins at the same point in space.

- **Determinant with electrons having parallel spins**

$$|\Psi(1, 2)\rangle = \hat{A}|\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\rangle = \hat{A}|\phi_1(\mathbf{r}_1)\beta(\sigma_1)\phi_2(\mathbf{r}_2)\beta(\sigma_2)\rangle$$

After integration the spin dependent 2RDM, we obtain

$$\begin{aligned} \gamma(\mathbf{r}_1, \mathbf{r}_2) &= \int \int d\sigma_1 d\sigma_2 \Gamma(\mathbf{x}_1, \mathbf{x}_2) \\ &= \frac{1}{2} \left\{ |\phi_1(\mathbf{r}_1)|^2 |\phi_2(\mathbf{r}_2)|^2 + |\phi_1(\mathbf{r}_2)|^2 |\phi_2(\mathbf{r}_1)|^2 \right. \\ &\quad \left. - [\phi_1^*(\mathbf{r}_1)\phi_2(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2)\phi_1(\mathbf{r}_2) + \phi_1(\mathbf{r}_1)\phi_2^*(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_1^*(\mathbf{r}_2)] \right\} \end{aligned} \quad (115)$$

Electrons of the same spin are correlated (*Fermi hole*) as it can be seen by calculating the probability of finding two electrons at the same point \mathbf{r}_1

$$\gamma(\mathbf{r}_1, \mathbf{r}_1) = 0 \quad (116)$$

In a Slater-determinant the motion of electrons with parallel spin is correlated but the motion of electrons with opposite spin is not.

10 Matrix elements between determinant wave functions

Two determinants constructed from two sets of spin orbitals $\{u_i\}$ and $\{v_j\}$:

$$U^* = \hat{A} [u_1^*(1)u_2^*(2) \dots u_N^*(N)] \quad \text{and} \quad V = \hat{A} [v_1(1)v_2(2) \dots v_N(N)]$$

Consider the product U^*V

$$U^*V = \hat{A} [u_1^*(1)u_2^*(2) \dots u_N^*(N)] \cdot \hat{A} [v_1(1)v_2(2) \dots v_N(N)] \quad (117)$$

It can be written using that $\hat{A}^\dagger = \hat{A}$ and $\hat{A}^2 = \sqrt{N!}\hat{A}$ as

$$\begin{aligned} U^*V &= [u_1^*(1)u_2^*(2) \dots u_N^*(N)] \cdot \hat{A}^\dagger \hat{A} [v_1(1)v_2(2) \dots v_N(N)] \\ &= \sqrt{N!} [u_1^*(1)u_2^*(2) \dots u_N^*(N)] \hat{A} [v_1(1)v_2(2) \dots v_N(N)] \\ &= [u_1^*(1)u_2^*(2) \dots u_N^*(N)] \det [v_1(1)v_2(2) \dots v_N(N)] \end{aligned}$$

The determinant $\det \{\mathbf{V}\}$ is multiplied N times by factors of type $u_i^*(i)$.

Since the multiplication of a determinant by a number is equivalent to multiplying one of its rows by the same number, we can arrange this expression by attributing each multiplicative factor to one of the rows in the following way

$$\begin{aligned} U^*V &= \det [u_1^*(1)v_1(1) \cdot \dots \cdot u_i^*(i)v_i(i) \cdot \dots \cdot u_N^*(N)v_N(N)] \\ &= \det \{u_i^*(i)v_k(i)\} \end{aligned} \quad (118)$$

The product of two Slater determinants is also a determinant, formed from products of the one-electron functions.

Matrix element of an operator \hat{O}

$$\begin{aligned} \langle U|\hat{O}|V\rangle &= \int \dots \int d\mathbf{x}_1 \dots d\mathbf{x}_N \hat{O}(1, 2, \dots, N) \\ &\quad \times \det [u_1^*(1)v_1(1) \cdot \dots \cdot u_i^*(i)v_i(i) \cdot \dots \cdot u_N^*(N)v_N(N)] \end{aligned} \quad (119)$$

10.1 Laplace expansion formulae

An arbitrary determinant can be expanded according to the Laplace expansion formulae.

1. First order expansion formula

$$\det\{\mathbf{A}\} = \sum_k a_k(i) \mathcal{D}(i|k) \quad (120)$$

where $a_k(i) = A_{ik}$, the minor, formed by the i -th row and k -th column, and $\mathcal{D}(i|k)$ is the corresponding cofactor, i.e. the signed determinant of the matrix obtained by deleting from the original one the k -th row and i -th column:

$$(-1)^{k+i} \begin{vmatrix} A_{11} & A_{12} & \dots & A_{1,k-1} & A_{1,k+1} & \dots & A_{1N} \\ A_{21} & A_{22} & \dots & A_{2,k-1} & A_{2,k+1} & \dots & A_{2N} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ A_{i-1,1} & A_{i-1,2} & \dots & A_{i-1,k-1} & A_{i-1,k+1} & \dots & A_{i-1,N} \\ A_{i+1,1} & A_{i+1,2} & \dots & A_{i+1,k-1} & A_{i+1,k+1} & \dots & A_{i+1,N} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ A_{N1} & A_{N2} & \dots & A_{N,k-1} & A_{N,k+1} & \dots & A_{NN}(N) \end{vmatrix}$$

Applied to the product of two determinants:

$$U^* \cdot V = \sum_k u_i^*(i)v_k(i) \mathcal{D}(k|i) \quad (121)$$

2. Second-order Laplace expansion formula

$$\det\{\mathbf{A}\} = \frac{1}{2} \sum_{k\ell} \begin{vmatrix} A_{ik} & A_{i\ell} \\ A_{jk} & A_{j\ell} \end{vmatrix} \mathcal{D}(ij|k\ell) \quad (122)$$

where the minor is a 2×2 determinant formed by the k and ℓ -th rows and i and j -th columns, and $\mathcal{D}(ij|k\ell)$ is the corresponding cofactor, i.e. the signed determinant of the matrix obtained by deleting from the original one the k and ℓ -th row and i and j -th column.

Applied to the product of two determinants:

$$U^* \cdot V = \sum_{k<\ell} \begin{vmatrix} u_i^*(i)v_k(i) & u_i^*(i)v_\ell(i) \\ u_j^*(j)v_k(j) & u_j^*(j)v_\ell(j) \end{vmatrix} \mathcal{D}(ij|k\ell) \quad (123)$$

10.2 Overlap of two determinants

Applying the general result for $\hat{O} = 1$

$$\begin{aligned} \langle U|V \rangle &= \int \cdots \int d\mathbf{x}_1 \dots d\mathbf{x}_N \det [u_1^*(1)v_1(1) \cdots u_i^*(i)v_i^*(i) \cdots u_N^*(N)v_N(N)] \\ &= \det \left[\int d\mathbf{x}_1 u_1^*(1)v_1(1) \cdots \int d\mathbf{x}_i u_i^*(i)v_i(i) \cdots \int d\mathbf{x}_N u_N^*(N)v_N(N) \right] \end{aligned} \quad (124)$$

which is an antisymmetrized product of N one-particle overlap integrals.

$$\langle U|V \rangle = \det [\langle u_1|v_1 \rangle \langle u_2|v_2 \rangle \cdots \langle u_N|v_N \rangle] = \det \{ \langle u_i|v_j \rangle \} \quad (125)$$

determinant of the overlap matrix $S_{u_i v_j}$ formed from the two sets of spin orbitals

$$\langle U|V \rangle = \det \{ \mathbf{S} \} \quad (126)$$

10.3 Matrix elements of one-electron operators

Let H_1 a the symmetric sum of $h(i)$ one-electron operators:

$$\hat{H}_1 = \sum_i \hat{h}(i) \quad (127)$$

First-order Laplace expansion formula of the product of determinants and put into the general result

$$\begin{aligned} \langle U|\hat{H}_1|V \rangle &= \sum_i \sum_k \left\{ \int d\mathbf{x}_i u_i^*(i) \hat{h}(i) v_k(i) \right\} \times \\ &\quad \times \left\{ \int \cdots \int d\mathbf{x}_i \dots d\mathbf{x}_{i-1} d\mathbf{x}_{i+1} \dots d\mathbf{x}_N \mathcal{D}(k|i) \right\} \end{aligned} \quad (128)$$

The first part is just a one-electron integral. The second part, analogous to the overlap integral discussed above, is the $a_k(i) = A_{ik}$ cofactor of the determinant of the overlap matrix $\langle u_i|v_k \rangle$. $\mathcal{D}(k|i)$ is the determinant of the overlap matrix obtained by deleting the i -th row and k -th column.

The standard expression of an inverse matrix

$$(\mathbf{S}^{-1})_{ik} = \frac{\mathcal{D}(k|i)}{\det\{\mathbf{S}\}} \quad (129)$$

the matrix elements of a one-electron operator can be written in terms of the one-electron integrals, the determinant of the overlap matrix and its inverse

$$\langle U|H_1|V \rangle = \sum_{i,k} \langle u_i|h|v_k \rangle (\mathbf{S}^{-1})_{ik} \det\{\mathbf{S}\} \quad (130)$$

10.4 Matrix elements of two-electron operators

Let us consider the two-electron symmetric operator

$$\hat{H}_2 = \frac{1}{2} \sum'_{i,j} \hat{g}(i,j) \quad (131)$$

Taking the second-order Laplace expansion of the determinant product in the matrix element expression and using the expression for the integral of the second-order cofactor, $\mathcal{D}(ij|k\ell)$

$$\mathcal{D}(ij|k\ell) = [(\mathbf{S}^{-1})_{ki} (\mathbf{S}^{-1})_{\ell j} - (\mathbf{S}^{-1})_{kj} (\mathbf{S}^{-1})_{\ell i}] \det\{\mathbf{S}\} \quad (132)$$

we have the following expression

$$\begin{aligned} \langle U|\hat{H}_2|V\rangle = \sum_{i<j} \sum_{k<\ell} \left\{ \int \int d\mathbf{x}_i d\mathbf{x}_j [u_i^*(i)v_k(i)\hat{g}(i,j)u_j^*(j)v_\ell(j) - \right. \\ \left. - u_i^*(i)v_\ell(i)\hat{g}(i,j)u_j^*(j)v_k(j)] \right\} \\ \times \left\{ (\mathbf{S}^{-1})_{ki}(\mathbf{S}^{-1})_{\ell j} - (\mathbf{S}^{-1})_{kj}(\mathbf{S}^{-1})_{\ell i} \right\} \det\{\mathbf{S}\} \quad (133) \end{aligned}$$

10.5 Notations for two-electron integrals

Two-electron integral of spin orbitals $\psi(\mathbf{x}) = \phi(\mathbf{x})\eta(\sigma)$ in the bra-ket notation

$$\begin{aligned} \int \int d\mathbf{x}_1 d\mathbf{x}_2 \psi_i^*(1)\psi_k(1)\hat{g}(1,2)\psi_j^*(2)\psi_\ell(2) = \langle \psi_i^*(1)\psi_j^*(2) | \psi_k(1)\psi_\ell(2) \rangle \\ = \langle ij | k\ell \rangle \quad (134) \end{aligned}$$

This is the *physicist's notation*, respecting the conventions for the bra and ket vectors

$$\begin{aligned} \langle ij | &= \psi_i^*(1)\psi_j^*(2) \\ |k\ell\rangle &= \psi_k(1)\psi_\ell(2) \end{aligned}$$

The *antisymmetrized two-electron integral*, appearing in the matrix elements of the the two-electron operators, is usually denoted as

$$\langle ij | k\ell \rangle - \langle ij | \ell k \rangle = \langle ij || k\ell \rangle \quad (135)$$

The *chemist's notation* emphasizes that a two-electron integral is the electrostatic interaction of two charge distributions

$$\int \int d\mathbf{x}_1 d\mathbf{x}_2 \underbrace{\psi_i^*(1)\psi_k(1)}_{\rho_{ik}(1)} \hat{g}(1,2) \underbrace{\psi_j^*(2)\psi_\ell(2)}_{\rho_{j\ell}(2)} = [ik|j\ell] \quad (136)$$

In numerical calculations is more advantageous to express integrals directly in spatial orbitals. The transformation is obvious using the orthogonality of the spin functions

$$[ik|j\ell] = (\phi_i\phi_k|\phi_j\phi_\ell)\delta_{\eta_i\eta_k}\delta_{\eta_j\eta_\ell} \quad (137)$$

In particular,

$$\langle ij || ij \rangle = \begin{cases} \text{parallel spin} & [ii|jj] - [ij|ij] = (ii|jj) - (ij|ij) \\ \text{antiparallel spin} & [ii|\bar{j}\bar{j}] - [\bar{i}\bar{j}|\bar{i}\bar{j}] = (ii|jj) \end{cases} \quad (138)$$

10.6 Summary of matrix element rules

- o overlap

$$\langle U|V\rangle = \det\{\mathbf{S}\} \quad (139)$$

- o one-electron operator

$$\langle U|\hat{H}_1|V\rangle = \sum_{i,k} \langle u_i|\hat{h}|v_k\rangle (\mathbf{S}^{-1})_{ik} \det\{\mathbf{S}\} \quad (140)$$

- o two-electron operator

$$\langle U|\hat{H}_2|V\rangle = \sum_{i<j} \sum_{k<\ell} \langle ij || k\ell \rangle \left\{ (\mathbf{S}^{-1})_{ki}(\mathbf{S}^{-1})_{\ell j} - (\mathbf{S}^{-1})_{kj}(\mathbf{S}^{-1})_{\ell i} \right\} \det\{\mathbf{S}\} \quad (141)$$

10.7 Slater rules

We need these results applied to the special case of determinants built from a unique set of orthonormal spin orbitals, $\{\psi_i\}$. Let D such a determinant, any other determinant can be generated by replacing one, two, or more spin orbitals $\{a, b, c, d, \dots\}$ occupied in D by other spin orbitals, $\{r, s, t, u, \dots\}$ not occupied in D

$$D(a \rightarrow r) = D_a^r \quad D(a \rightarrow r, b \rightarrow s) = D_{ab}^{rs} \quad D(a \rightarrow r, b \rightarrow s, c \rightarrow t) = D_{abc}^{rst}$$

Overlap

$$\langle D|D \rangle = \det \{\mathbf{S}\} \quad (142)$$

since $S_{ab} = \delta_{ab}$

$$\langle D|D \rangle = 1 \quad (143)$$

If the two determinants differ in at least one orbital

$$\langle D|D_a^r \rangle = 0 \quad (144)$$

since due to the orthogonality of the orbitals $S_{ar} = 0 \quad \forall \quad a$, i.e. one row in the determinant $\det \{\mathbf{S}\}$ is zero.

One-electron matrix elements

$$\langle U|H_1|V \rangle = \sum_{i,k} \langle u_i|h|v_k \rangle (\mathbf{S}^{-1})_{ik} \det\{\mathbf{S}\}$$

- $U = V = D$, since $S_{ik} = \delta_{ik}$ and $\det \{\mathbf{S}\} = 1$

$$\langle D|\hat{H}_1|D \rangle = \sum_i \langle \psi_i|\hat{h}|\psi_i \rangle \quad (145)$$

- $V = D$ and $U = D_a^r$ only one cofactor is nonzero

$$\langle D_a^r|\hat{H}_1|D \rangle = \langle \psi_r|\hat{h}|\psi_a \rangle \quad (146)$$

- $V = D$ and $U = D_{ab}^{rs}$ all cofactors are zero

$$\langle D_{ab}^{rs}|\hat{H}_1|D \rangle = 0 \quad (147)$$

Two-electron matrix elements

$$\langle U|\hat{H}_2|V \rangle = \sum_{i<j} \sum_{k<\ell} \langle ij||k\ell \rangle \left\{ (\mathbf{S}^{-1})_{ki} (\mathbf{S}^{-1})_{\ell j} - (\mathbf{S}^{-1})_{kj} (\mathbf{S}^{-1})_{\ell i} \right\} \det\{\mathbf{S}\}$$

- $U = V = D$ then $\mathcal{D}(ij||k\ell) = \delta_{ik}\delta_{\ell j}$ since $i = \ell$ and $k = j$ cases cannot occur

$$\begin{aligned} \langle D|\hat{H}_2|D \rangle &= \sum_{i<j} \sum_{k<\ell} \langle ik||j\ell \rangle \left(\delta_{ik}\delta_{j\ell} - \delta_{jk}\delta_{i\ell} \right) \\ &= \sum_{i<j} \sum_{k<\ell} \langle ij||k\ell \rangle \delta_{ik}\delta_{j\ell} = \sum_{i<j} \langle ij||ij \rangle \end{aligned} \quad (148)$$

- $U = D_a^r$ apply the general formula

$$\langle U | \hat{H}_2 | V \rangle = \sum_{i < j} \sum_{k < \ell} \langle u_i u_j | | v_k v_\ell \rangle \mathcal{D}(ij|k\ell) \quad (149)$$

the \mathbf{S} matrix is diagonal, excepted the S_{aa} element.

- $i = k = a$ case: $\mathcal{D}(aj|a\ell) = \delta_{j\ell}$ and sum over $\ell = j > a$

$$\sum_{\ell > a} \langle r\ell | | a\ell \rangle$$

- $j = \ell = a$ case: $\mathcal{D}(ia|ka) = \delta_{ik}$ and sum over $k = i < a$

$$\sum_{k < a} \langle kr | | ka \rangle = \sum_{\ell < a} \langle r\ell | | a\ell \rangle$$

Summarizing these two cases

$$\langle D_a^r | \hat{H}_2 | D \rangle = \sum_{\substack{j=1 \\ j \neq a}}^N \langle rj | | aj \rangle \quad (150)$$

- $U = D_{ab}^{rs}$ only one non-zero cofactor, $\mathcal{D}(ab|ab) = 1$

$$\langle D_{ab}^{rs} | \hat{H}_2 | D \rangle = \langle rs | | ab \rangle \quad (151)$$

10.8 Variation of a determinant wave function

The determinant

$$|\Psi\rangle = \mathcal{A}[\psi_1(1)\psi_2(2)\dots\psi_N(N)] \quad (152)$$

can be varied through the variation of the one-electron orbitals:

$$\psi_a \rightarrow \psi_a + \delta\psi_a = \psi_a + p_a \psi_a' \quad (153)$$

where ψ_a' is an *arbitrary* spin orbital and p_a is a complex variation parameter.

$$|\Psi + \delta\Psi\rangle = \mathcal{A}[\{\psi_1(1) + p_1\psi_1'\}\{\psi_2(2) + p_2\psi_2'\}\dots\{\psi_N(N) + p_N\psi_N'\}] \quad (154)$$

This is a sum of 2^N determinant. To first order in the p_a parameters the variation is a sum of singly excited determinants:

$$|\delta\Psi\rangle = \sum_a p_a |\Psi(\psi_a \rightarrow \psi_a')\rangle \quad (155)$$

Let the \hat{Q} the projection operator on the subspace of the orbitals that are occupied in the determinant and \hat{P} the projector to its orthogonal complement

$$\hat{Q} = \sum_i^N |\psi_i\rangle\langle\psi_i| \quad \hat{P} = 1 - \hat{Q} = \sum_{r \notin \{a\}} |\psi_r\rangle\langle\psi_r| \quad (156)$$

The *arbitrary* spin orbital ψ_a' can be decomposed as:

$$p_a |\psi_a'\rangle = \sum_b^N q_{ba} |\psi_b\rangle + \sum_r p_{ra} |\psi_r\rangle \quad (157)$$

where the set of orbitals $\{\psi_r\}$ are taken from the orthogonal complement of the occupied set $\{\psi_a\}$. $\sum_b^N q_{ba}\psi_b$ does not change the determinant, up to a factor of normalization. An arbitrary variation of a determinant can be written as a sum of singly excited determinants

$$|\delta\Psi\rangle = \sum_a^N \sum_r \rho_{ra} |\Psi_a^r\rangle \quad (158)$$

11 Method of Second Quantization

Up to now, we satisfied the antisymmetry requirement by using determinant wave function. The same goal can be achieved by transferring this antisymmetry property on the algebraic properties of electron creation and annihilation operators.

No essentially new physics, just a convenient way to handle wave functions, operators and matrix elements.

11.1 Representations of determinant wave functions

The determinant wave function can be considered as an ordered product of occupied spin orbitals

$$D(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Leftrightarrow |\psi_1\psi_2\dots\psi_a\dots\psi_b\dots\psi_N| \quad (159)$$

The set of occupied spin orbitals is the *electron configuration*.

Particle number representation:

the number of electrons filling each of the orbitals *occupation number* is given explicitly ($n_i = 0$ or 1)

$$D(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Leftrightarrow |n_1n_2\dots n_k\dots n_\ell\dots n_M\rangle \quad (160)$$

For instance:

$$\begin{aligned} |D\rangle &= |11111\dots 1100\dots 000\dots 000\rangle \\ |D_a^r\rangle &= |11101\dots 1100\dots 100\dots 000\rangle \end{aligned}$$

11.2 Fock space

The *Fock space* is the vector space constituted of all the possible “kets”, corresponding to the total number of electrons between 0 and M .

The *vacuum state* is an abstract state with 0 electron:

$$|\text{vac}\rangle = |0_10_20_3\dots 0_M\rangle \quad (161)$$

Properties of the vacuum:

- normalization $\langle \text{vac} | \text{vac} \rangle = 1$ (162)
- orthogonal to all other states

Second quantized operators manipulate the occupation numbers of the vectors in the Fock-space.

11.3 Creation of electrons

A one-electron state, $\psi_k(1)$ can be represented by the creation of an electron on the spin orbital ψ_k

$$|k\rangle = a_k^+ |\text{vac}\rangle \quad (163)$$

A two-electron state, $\Psi(1, 2)$ is represented in the wave function language as a Slater determinant

$$D(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_i(1) & \psi_k(1) \\ \psi_i(2) & \psi_k(2) \end{vmatrix} \quad (164)$$

The same state is written in a second quantization language as

$$D(1, 2) \Leftrightarrow |ik\rangle = a_i^+ a_k^+ |\text{vac}\rangle \quad (165)$$

As a consequence of the antisymmetry property of $D(1, 2)$

$$D(1, 2) = -D(2, 1) \quad (166)$$

we have

$$a_i^+ a_k^+ |\text{vac}\rangle = -a_k^+ a_i^+ |\text{vac}\rangle \quad (167)$$

The antisymmetry of the wave function is translated as an algebraic property of the creation operators:

$$a_i^+ a_k^+ + a_k^+ a_i^+ = 0 \quad (168)$$

The creation operators of electrons (fermions) anticommute:

$$[a_k^+, a_i^+]_+ = 0 \quad (169)$$

If $k = i$

$$a_i^+ a_i^+ = -a_i^+ a_i^+ = 0 \quad (170)$$

We are not allowed to create electrons twice on the same spin orbital:

Pauli principle.

11.4 Annihilation of electrons

The operator that removes an electron from a spin orbital is called the *annihilation operator*

$$a_i |i\rangle = |\text{vac}\rangle \quad (171)$$

We are not allowed to remove an electron from the vacuum

$$a_i |\text{vac}\rangle = 0 \quad (172)$$

In order to annihilate an electron on the orbital ψ_i , this orbital should be immediately to the right of the annihilator, e.g.

$$a_i |ik\rangle = a_i a_i^+ a_k^+ |\text{vac}\rangle = a_k^+ |\text{vac}\rangle = |k\rangle \quad (173)$$

If the position of the spin orbital ψ_i was not appropriate, we must do transpositions until it is placed to the right of a_i

$$a_i |ki\rangle = a_i a_k^+ a_i^+ |\text{vac}\rangle = -a_i a_i^+ a_k^+ |\text{vac}\rangle = -a_k^+ |\text{vac}\rangle = -|k\rangle \quad (174)$$

The sign depends on the number of transpositions:

- even number of transpositions: + sign

$$a_3 a_2^+ a_1^+ a_3^+ |\text{vac}\rangle = -a_3 a_2^+ a_3^+ a_1^+ |\text{vac}\rangle = +a_3 a_3^+ a_2^+ a_1^+ |\text{vac}\rangle = a_2^+ a_1^+ |\text{vac}\rangle \quad (175)$$

- odd number of transpositions: - sign

$$a_3 a_2^+ a_3^+ a_1^+ |\text{vac}\rangle = -a_3 a_3^+ a_2^+ a_1^+ |\text{vac}\rangle = -a_2^+ a_1^+ |\text{vac}\rangle \quad (176)$$

The ψ_k function can be written as

$$|k\rangle = a_k^+ |\text{vac}\rangle \quad (188)$$

and the adjoint of the analogous definition for $\psi_i = |i\rangle$

$$\langle i| = \langle \text{vac}| (a_i^+)^{\dagger} \quad (189)$$

The scalar product, i.e. the overlap integral is

$$S_{ik} = \langle \text{vac}| (a_i^+)^{\dagger} a_k^+ |\text{vac}\rangle \quad (190)$$

Since $S_{ik} = \delta_{ik}$ is diagonal

$$(a_i^+)^{\dagger} a_k^+ |\text{vac}\rangle = \delta_{ik} |\text{vac}\rangle \quad (191)$$

After comparison with Eq.(186) we conclude that

$$a_i = (a_i^+)^{\dagger} \quad (192)$$

i.e. in the case of orthonormal basis functions, the annihilation operator is the adjoint of the creation operator.

The “bra” corresponding to the “ket”

$$|D\rangle = a_N^+ \dots a_2^+ a_1^+ |\text{vac}\rangle$$

is

$$\langle D| = \langle \text{vac}| a_1 a_2 \dots a_N$$

11.7 Non-orthogonal functions

Overlap matrix is non-diagonal

$$S_{\mu\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle = \langle \text{vac}| (\chi_{\mu}^+)^{\dagger} \chi_{\nu}^+ |\text{vac}\rangle \quad (193)$$

Introduce the notation

$$(\chi_{\mu}^+)^{\dagger} = \chi_{\mu}^- \quad (194)$$

Following anticommutation relation can be derived

$$[\chi_{\nu}^+, \chi_{\mu}^-]_+ = S_{\mu\nu} \quad (195)$$

Take an auxiliary Löwdin-orthogonalized basis $\psi_{\lambda} = \sum_{\mu} S_{\lambda\mu}^{-1/2} \chi_{\mu}$. The creation and annihilation operators can be transformed to this basis as

$$\psi_{\lambda}^+ = \sum_{\mu} S_{\lambda\mu}^{-1/2} \chi_{\mu}^+ \quad \chi_{\mu}^+ = \sum_{\lambda} S_{\mu\lambda}^{1/2} \psi_{\lambda}^+ \quad (196)$$

$$\psi_{\tau}^- = \sum_{\nu} S_{\nu\tau}^{-1/2} \chi_{\nu}^- \quad \chi_{\nu}^- = \sum_{\tau} S_{\tau\nu}^{1/2} \psi_{\tau}^- \quad (197)$$

Applying these transformations

$$[\chi_{\nu}^+, \chi_{\mu}^-]_+ = \sum_{\lambda\tau} S_{\mu\lambda}^{1/2} S_{\tau\nu}^{1/2} [\psi_{\lambda}^+, \psi_{\tau}^-]_+ = \sum_{\lambda\tau} S_{\mu\lambda}^{1/2} S_{\tau\nu}^{1/2} \delta_{\lambda\tau} = S_{\mu\nu} \quad (198)$$

The operator χ_{μ}^- is not a true annihilation operator, for instance

$$\chi_{\mu}^- |\chi_{\mu} \chi_{\lambda}\rangle = S_{\mu\mu} |\chi_{\lambda}\rangle - S_{\mu\lambda} |\chi_{\mu}\rangle \quad (199)$$

11.8 Properties of creation and annihilation operators: Summary

Properties of the vacuum

$$\begin{aligned}\langle \text{vac} | \text{vac} \rangle &= 1 \\ a_k | \text{vac} \rangle &= 0 \\ \langle \text{vac} | a_k^+ &= 0\end{aligned}$$

Anticommutation relations (Pauli principle)

$$\begin{aligned}[a_i^+, a_k^+]_+ &= 0 \\ [a_i, a_k]_+ &= 0 \\ [a_i^+, a_k]_+ &= \delta_{ik}\end{aligned}$$

Adjoint relation

$$a_k = (a_k^+)^\dagger$$

Correspondences

$$\begin{aligned}|\psi_i\rangle &\Leftrightarrow a_i^+ |\text{vac}\rangle \\ |D\rangle &\Leftrightarrow a_N^+ \dots a_2^+ a_1^+ |\text{vac}\rangle \\ \langle \psi_i | &\Leftrightarrow \langle \text{vac} | a_i \\ |D\rangle &\Leftrightarrow \langle \text{vac} | a_1 a_2 \dots a_N\end{aligned}$$

11.9 Particle number operator

A sequence of annihilation and creation operators acting on the same orbital

$$\hat{n}_i = a_i^+ a_i$$

“measures” the occupation number of this orbital, i.e. tells if it is occupied ($n_i = 1$) or if it is empty ($n_i = 0$)

$$\hat{n}_i |D\rangle = a_i^+ a_i |n_1 \dots n_i \dots n_M\rangle = n_i |n_1 \dots n_i \dots n_M\rangle = n_i |D\rangle \quad (200)$$

Determinant wave function is eigenfunction of \hat{n}_i with eigenvalue n_i .

Operator of the *total number of particles*

$$\hat{N} = \sum_{i=1}^M \hat{n}_i = \sum_{i=1}^M a_i^+ a_i \quad (201)$$

Single determinants are eigenfunctions of \hat{N}

$$\hat{N} |D\rangle = \sum_{i=1}^M n_i |D\rangle = N |D\rangle \quad (202)$$

as well as multi-determinant wave functions

$$\hat{N} |\Psi\rangle = \sum_K c_K \hat{N} |D_K\rangle = \sum_K c_K \sum_{i=1}^M n_{iK} |D_K\rangle = \sum_K c_K N |D_K\rangle = N |\Psi\rangle \quad (203)$$

11.10 Representation of operators

In the first quantization representation an operator \hat{A}^S transforms the function Ψ to another one Φ

$$\hat{A}^S|\Psi\rangle = |\Phi\rangle$$

We are looking for the second quantized operator that performs the analogous transformation between wave functions in particle number representation.

$$\begin{array}{ccc} |\Phi\rangle & \xrightarrow{\hat{A}^S} & |\Psi\rangle \\ \Downarrow & \text{?} & \Downarrow \\ |\Phi^\pm\rangle & \xrightarrow{\hat{A}^F} & |\Psi^\pm\rangle \end{array}$$

The operator \hat{A}^S acts on one of the functions $\phi_i \in \{\phi_k\}_{k=1}^M$ of the orthonormal set. The transformed function ψ_i can be developed in the same basis $\{\phi_k\}_{k=1}^M$.

Let us follow step-by-step the correspondences between the first- and second-quantized picture:

FIRST QUANTIZATION		SECOND QUANTIZATION
$\hat{A}^S \phi_i\rangle = \psi_i\rangle$		$\hat{A}^F\phi_i^+ \text{vac}\rangle = \psi_i^+ \text{vac}\rangle$
$ \psi_i\rangle = \sum_k c_{ik} \phi_k\rangle$		$\psi_i^+ = \sum_k c_{ik}\phi_k^+$
$\hat{A}^S \phi_i\rangle = \sum_k c_{ik} \phi_k\rangle$		$\hat{A}^F\phi_i^+ \text{vac}\rangle = \sum_k c_{ik}\phi_k^+ \text{vac}\rangle$
$\langle\phi_\ell \hat{A}^S \phi_i\rangle = \sum_k c_{ik}\langle\phi_\ell \phi_k\rangle$		\Downarrow
$A_{\ell i} = c_{i\ell}$	\Rightarrow	$\hat{A}^F\phi_i^+ = \sum_k A_{ki}\phi_k^+$

Complete this expression formally by ϕ_i^-

$$\hat{A}^F\phi_i^+\phi_i^- = \sum_k A_{ki}\phi_k^+\phi_i^-$$

Sum on all basis functions ϕ_i

$$\hat{A}^F \underbrace{\sum_i \phi_i^+\phi_i^-}_{\hat{N}} = \sum_{ki} A_{ki}\phi_k^+\phi_i^-$$

The particle number operator acts as a unit operator on one-electron functions, therefore we can write

$$\hat{A}^F = \sum_{ki} A_{ki}\phi_k^+\phi_i^- \quad (204)$$

11.11 One-electron operators

In the Schrödinger representation

$$\hat{A}^S = \sum_{i=1}^N \hat{A}(i) \quad (205)$$

The action of this operator on a Slater determinant leads to a linear combination of Slater determinants

$$\hat{A}^S|\Phi\rangle = |\Psi\rangle = \sum_i^N \sum_k^M c_{ik} |\phi_1 \dots \phi_k \dots \phi_N| \quad (206)$$

The second-quantized counterpart of this expression is

$$\hat{A}^F \phi_N^+ \dots \phi_i^+ \dots \phi_1^+ |\text{vac}\rangle = \sum_i^N \sum_k^M A_{ki} \phi_N^+ \dots \phi_k^+ \dots \phi_1^+ |\text{vac}\rangle \quad (207)$$

We shall prove that the above result is obtained, if we apply the previously “derived” form of the second-quantized operator, i.e.

$$\hat{A}^F = \sum_i^M \sum_k^M A_{ki} \phi_k^+ \phi_i^- \quad (208)$$

Let us study the expression

$$\sum_i^M \sum_k^M A_{ki} \phi_k^+ \phi_i^- \phi_N^+ \dots \phi_i^+ \dots \phi_1^+ |\text{vac}\rangle \quad (209)$$

the orbital i should be occupied, otherwise ϕ_i^- would give zero \Rightarrow summation over i is limited to N instead of M

migrate ϕ_i^+ to the first position:

$$\pm \phi_i^+ \phi_N^+ \dots \phi_{i-1}^+ \phi_{i+1}^+ \dots \phi_1^+ |\text{vac}\rangle$$

using the anticommutation relation and that the spin orbital i has already been moved out of the string

$$\phi_k^+ \phi_i^- \phi_i^+ = \phi_k^+ (1 - \underbrace{\phi_i^+ \phi_i^-}_{\hat{n}_i}) = \phi_k^+$$

migrate ϕ_k^+ back to the place of ϕ_i^+ . We need the same number of permutations, therefore we recover the possible sign change

In effect, we retrieve the expression

$$\hat{A}^F \phi_N^+ \dots \phi_i^+ \dots \phi_1^+ |\text{vac}\rangle = \sum_i^N \sum_k^M A_{ki} \phi_N^+ \dots \phi_k^+ \dots \phi_1^+ |\text{vac}\rangle \quad (210)$$

The second-quantized operator does not depend on the number of electrons.

11.12 Two-electron operators

Two-electron operator in the Schrödinger picture

$$\hat{A}^S = \sum_{i < j}^N \hat{A}(ij)$$

e.g. electron repulsion operator

$$\hat{V}_{ee} = \sum_{i < j}^N \frac{1}{r_{ij}}$$

transforms a pair of orbitals simultaneously

$$\sum_{i > j} \hat{A}(ij) |\phi_1 \dots \phi_i \dots \phi_j \dots \phi_N| \sum_{i < j}^N \sum_{k\ell} c_{ij,k\ell} |\phi_1 \dots \phi_k \dots \phi_\ell \dots \phi_N| \quad (211)$$

with

$$c_{ij,k\ell} = \int \int d\mathbf{x}_1 d\mathbf{x}_2 \phi_k^*(1) \phi_i(1) \frac{1}{r_{12}} \phi_\ell^*(2) \phi_j(2) = \langle k\ell | ij \rangle$$

Following an analogous reasoning, we obtain the following expression for the second-quantized form of the electron repulsion operator

$$\hat{V}_{ee}^F = \frac{1}{2} \sum_{ijkl} \langle ij | k\ell \rangle \phi_i^+ \phi_j^+ \phi_\ell^- \phi_k^- \quad (212)$$

Note the reversed order of indices k and ℓ !

11.13 Reduced density matrices

The expectation value of a one-electron operator

$$\hat{A} = \sum_{\mu\nu} A_{\mu\nu} a_\mu^+ a_\nu$$

is

$$\langle \hat{A} \rangle = \sum_{\mu\nu} A_{\mu\nu} \langle a_\mu^+ a_\nu \rangle \quad (213)$$

where the quantity in brackets is the one-particle reduced density matrix (1RDM)

$$P_{\nu\mu} = \langle a_\mu^+ a_\nu \rangle \quad (214)$$

The expectation value of a one-electron operator can be written as a trace

$$\langle \hat{A} \rangle = \sum_{\mu\nu} A_{\mu\nu} P_{\nu\mu} = \sum_{\mu} (AP)_{\mu\mu} = \text{Tr}(AP) \quad (215)$$

Analogously, the expectation value of a two-electron operator

$$\langle \hat{A} \rangle = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} A_{\mu\nu\lambda\sigma} \langle a_\mu^+ a_\nu^+ a_\sigma a_\lambda \rangle \quad (216)$$

can be written as a trace

$$\langle \hat{A} \rangle = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} A_{\mu\nu\lambda\sigma} \Gamma_{\lambda\sigma\mu\nu} \quad (217)$$

with the two-particle reduced density matrix, $\Gamma_{\lambda\sigma\mu\nu}$

$$\Gamma_{\lambda\sigma\mu\nu} = \langle a_\mu^+ a_\nu^+ a_\sigma a_\lambda \rangle \quad (218)$$

The symmetry properties of Γ are determined by Hermitian symmetry and anticommutation relations

$$\begin{aligned}
\Gamma_{\lambda\sigma\mu\nu} &= \langle a_\mu^+ a_\nu^+ a_\sigma a_\lambda \rangle = \langle a_\lambda^+ a_\sigma^+ a_\nu a_\mu \rangle = \Gamma_{\mu\nu\lambda\sigma} \\
&= -\langle a_\mu^+ a_\nu^+ a_\lambda a_\sigma \rangle = -\Gamma_{\sigma\lambda\mu\nu} \\
&= -\langle a_\nu^+ a_\mu^+ a_\sigma a_\lambda \rangle = -\Gamma_{\lambda\sigma\nu\mu} \\
&= \langle a_\nu^+ a_\mu^+ a_\lambda a_\sigma \rangle = \Gamma_{\sigma\lambda\nu\mu}
\end{aligned} \tag{219}$$

The diagonal elements are zero (Pauli principle)

$$\Gamma_{\mu\mu\lambda\sigma} = \Gamma_{\mu\mu\lambda\lambda} = 0 \tag{220}$$

Normalization of the 2RDM

$$\begin{aligned}
\text{Tr}\Gamma &= \sum_{\mu\nu} \Gamma_{\mu\nu\mu\nu} = \sum_{\mu\nu} \langle \nu^+ \mu^+ \mu^- \nu^- \rangle = - \sum_{\mu\nu} \langle \mu^+ \nu^+ \mu^- \nu^- \rangle \\
&= - \sum_{\mu\nu} \langle \mu^+ \{ \delta_{\mu\nu} - \nu^- \mu^+ \} \nu^- \rangle \\
&= - \sum_{\mu\nu} \{ \delta_{\mu\nu} \langle \mu^+ \nu^- \rangle - \langle \mu^+ \mu^- \nu^+ \nu^- \rangle \} \\
&= - \sum_{\mu} \langle \hat{n}_\mu \rangle + \sum_{\mu\nu} \langle \hat{n}_\mu \hat{n}_\nu \rangle \\
&= N^2 - N
\end{aligned} \tag{221}$$

The 1RDM is derivable from the 2RDM by contraction

$$\sum_{\lambda} \Gamma_{\nu\lambda\mu\lambda} = \sum_{\lambda} \langle \mu^+ \lambda^+ \lambda^- \nu^- \rangle = (1 - N) \langle \mu^+ \nu^- \rangle = (1 - N) P_{\nu\mu} \tag{222}$$

11.14 Hamiltonian and energy expressions

In an orthonormal basis $\{\phi_\mu\}_{\mu=1}^M$ the electronic Hamiltonian is

$$\hat{H} = \sum_{\mu\nu} h_{\mu\nu} a_\mu^+ a_\nu + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle \mu\nu | \lambda\sigma \rangle a_\mu^+ a_\nu^+ a_\sigma a_\lambda \tag{223}$$

The SQ Hamiltonian

- is not equal to the usual one: it is a projection on a finite (M -dimensional) space of one-electron basis functions
- is independent of the number of electrons - this dependence is shifted to the wave function

The electronic energy – expectation value of the Hamiltonian – can be calculated using the one- and two-particle RDMs

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{\mu\nu} h_{\mu\nu} P_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle \mu\nu | \lambda\sigma \rangle \Gamma_{\lambda\sigma\mu\nu} \tag{224}$$

This form of the energy expression is used in current quantum chemical calculations.

An alternative energy expression is based on the *reduced two-particle Hamiltonian*, defined as

$$\hat{H} = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} K_{\lambda\sigma}^{\mu\nu} a_{\mu}^+ a_{\nu}^+ a_{\sigma}^- a_{\lambda}^- \quad (225)$$

where the matrix elements are

$$K_{\lambda\sigma}^{\mu\nu} = \frac{1}{1-N} (\delta_{\nu\sigma} h_{\mu\lambda} + \delta_{\mu\lambda} h_{\nu\sigma}) + \langle \mu\nu | \lambda\sigma \rangle \quad (226)$$

and the energy can be written in terms of the 2RDM

$$E = \sum_{\mu\nu\lambda\sigma} K_{\lambda\sigma}^{\mu\nu} \Gamma_{\lambda\sigma\mu\nu} \quad (227)$$

(cf. DFT, where the energy is a functional on the one-particle density). Unconstrained variation of $\Gamma_{\lambda\sigma\mu\nu}$ leads to much too low energies, since Γ should satisfy additional N-representability conditions.

Rosina's theorem: The ground state 2RDM completely determines the exact N-particle ground state wave function (and p -RDMs) without any specific information about the Hamiltonian.

Contracted Schrödinger equations are of the following structure

$$K \cdot {}^2D + K \cdot {}^3D + K \cdot {}^4D = E \cdot {}^2D$$

11.15 Calculation of matrix elements

Let us consider first operator strings with vacuum:

1. we cannot annihilate on the vacuum

$$\langle \text{vac} | a_i^+ a_k | \text{vac} \rangle = 0 \quad (228)$$

2. use the anticommutation rule and the previous result

$$\langle \text{vac} | a_i a_k^+ | \text{vac} \rangle = \langle \text{vac} | (\delta_{ik} - a_k^+ a_i) | \text{vac} \rangle = \delta_{ik} \quad (229)$$

3. $\langle \text{vac} | a_i a_j a_k^+ a_{\ell}^+ | \text{vac} \rangle = ?$

$$\begin{aligned} a_i a_j a_k^+ a_{\ell}^+ &= a_i (\delta_{kj} - a_k^+ a_j) a_{\ell}^+ = a_i a_{\ell}^+ \delta_{kj} - a_i a_k^+ a_j a_{\ell}^+ = \\ &= (\delta_{i\ell} - a_{\ell}^+ a_i) \delta_{kj} - (\delta_{ik} - a_k^+ a_i) (\delta_{j\ell} - a_{\ell}^+ a_j) = \delta_{i\ell} \delta_{kj} - \delta_{ik} \delta_{j\ell} + \text{zeros} \end{aligned} \quad (230)$$

A graphical evaluation rule can also be deduced

$$\langle \text{vac} | a_i a_j a_k^+ a_{\ell}^+ | \text{vac} \rangle = \delta_{i\ell} \delta_{kj} - \delta_{ik} \delta_{j\ell} \quad (231)$$

11.16 Matrix elements between single determinants

Let us calculate

$$\langle \text{HF} | \phi_i^+ \phi_k^- | \text{HF} \rangle = \langle \text{vac} | \phi_1^- \dots \phi_N^- \phi_i^+ \phi_k^- \phi_N^+ \dots \phi_1^+ | \text{vac} \rangle$$

We proceed by steps

1. if $i, k \in \{1, \dots, N\}$, the matrix element is zero
2. if $i, k \in \{1, \dots, N\}$, we order the pairs $a_a a_a^\dagger$ ($a \neq i, k; i \neq k$) by an even number of transpositions

$$\langle \text{vac} | \phi_i^- \phi_k^- \phi_i^+ \phi_k^+ \phi_i^- \phi_k^+ \phi_i^+ \phi_k^- \phi_N^- \phi_N^+ \dots \phi_1^- \phi_1^+ | \text{vac} \rangle = \langle \text{vac} | \phi_i^- \phi_k^- \phi_i^+ \phi_k^+ \phi_i^- \phi_k^+ \phi_i^+ \phi_k^- | \text{vac} \rangle = 0$$

3. if $i, k \in \{1, \dots, N\}$ and $i = k$, we order all pairs $a \neq i$

$$\langle \text{vac} | \phi_i^- \phi_i^+ \phi_i^- \phi_i^+ \phi_N^- \phi_N^+ \dots \phi_1^- \phi_1^+ | \text{vac} \rangle = \langle \text{vac} | \phi_i^- \phi_i^+ \phi_i^- \phi_i^+ | \text{vac} \rangle = 1$$

Taking the sum of the three cases

$$\langle \text{HF} | \phi_i^+ \phi_k^- | \text{HF} \rangle = n_i \delta_{ik} \quad (232)$$

11.17 Fermi vacuum

Evaluation of matrix elements involving single determinant (Hartree-Fock, HF) wave functions can be simplified, since the creation and annihilation operators that generate the $\langle \text{HF} |$ and $| \text{HF} \rangle$ states, respectively, have only a passive role.

$$\langle \phi_i^+ \dots \phi_k^- \rangle_{\text{HF}} = \underbrace{\langle \text{vac} | \phi_1^- \phi_2^- \dots \phi_N^- | \phi_i^+ \dots \phi_k^- \rangle}_{\langle \text{HF} |} \underbrace{\phi_N^+ \dots \phi_2^+ \phi_1^+ | \text{vac} \rangle}_{| \text{HF} \rangle}$$

Therefore we define a *Fermi-vacuum*, which has analogous properties to the true vacuum.

VACUUM	FERMI VACUUM
$a_i \text{vac} \rangle = 0$	$\phi_i^- \text{HF} \rangle = 0 \quad \text{if} \quad n_i = 0$
$\langle \text{vac} a_i^+ = 0$	$\langle \text{HF} \phi_i^+ = 0 \quad \text{if} \quad n_i = 0$
$\langle \text{vac} a_i^+ a_k \text{vac} \rangle = 0$	$\langle \text{HF} \phi_i^+ \phi_k^- \text{HF} \rangle = n_k \delta_{ik}$
$\langle \text{vac} a_k a_i^+ \text{vac} \rangle = \delta_{ik}$	$\langle \text{HF} \phi_k^- \phi_i^+ \text{HF} \rangle = (n_k - 1) \delta_{ik}$

The evaluation of matrix elements consists in simply to find all the combinations of the type

$$\underline{a_k a_i^+} \quad \underline{\phi_i^+ \phi_k^-}$$

and associate to them the factor

$$\delta_{ik} \quad n_k \delta_{ik}$$

with a sign depending on the number of permutations.

11.18 Slater rules – an example

One-electron matrix element $\langle D_a^r | \hat{H}_1 | D \rangle$

Using

$$\langle D_a^r | = \langle \text{HF} | a_a^+ a_r \quad \text{and} \quad \hat{H}_1 = \sum_{ij} h_{ij} a_i^+ a_j$$

the matrix element is

$$\langle D_a^r | \hat{H}_1 | D \rangle = \sum_{ij} h_{ij} \langle \text{HF} | a_a^+ a_r a_i^+ a_j | \text{HF} \rangle \quad (233)$$

Taking the possible pairings and associating them the factors

$$a_i^+ a_k \Rightarrow n_k \delta_{ik} \quad \text{and} \quad a_i a_k^+ \Rightarrow (1 - n_k) \delta_{ik}$$

we have

$$\begin{aligned} \langle D_a^r | \hat{H}_1 | D \rangle &= \sum_{ij} h_{ij} \{ n_a \delta_{aj} (1 - n_r) \delta_{ri} + n_r \delta_{ar} n_j \delta_{ij} \} \\ &= \sum_{ij} h_{ij} \delta_{aj} \delta_{ri} = h_{ra} \end{aligned} \quad (234)$$

11.19 Energy of a single determinant

Expectation value of the electronic Hamiltonian with the single-determinant wave function

$$\begin{aligned} E_{\text{HF}} &= \sum_{\mu\nu} h_{\mu\nu} \langle \text{HF} | \chi_\mu^+ \chi_\nu^- | \text{HF} \rangle + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} (\mu\lambda | \nu\sigma) \langle \text{HF} | \chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^- | \text{HF} \rangle \\ &= \sum_{\mu\nu} h_{\mu\nu} P_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} (\mu\lambda | \nu\sigma) (P_{\sigma\nu} P_{\lambda\mu} - P_{\sigma\mu} P_{\lambda\nu}) \end{aligned} \quad (235)$$

After permutation of the dummy indices

$$E_{\text{HF}} = \sum_{\mu\nu} h_{\mu\nu} P_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\nu\mu} P_{\sigma\lambda} \{ (\mu\nu | \lambda\sigma) - (\mu\lambda | \nu\sigma) \} \quad (236)$$

Remembering the definition of the Fock matrix

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\mu\nu\lambda\sigma} P_{\sigma\lambda} \{ (\mu\nu | \lambda\sigma) - (\mu\lambda | \nu\sigma) \} \quad (237)$$

the Hartree-Fock energy can be written as a trace

$$E_{\text{HF}} = \frac{1}{2} \text{Tr}(\mathbf{h} + \mathbf{F})\mathbf{P} \quad (238)$$

12 Hartree-Fock theory

Explicit variation of the energy of a determinant constructed up from a set of orthogonal orbitals

- orthogonality of orbitals should be preserved during the variation process
- modify energy functional by the method of Lagrange multipliers
- mathematically problematic: the orthogonality of orbitals is anticipated in the energy expression to be varied

Apply the variation principle for an arbitrary variation of the determinant

- take the most general variation of a one-determinant wave function
- a condition is given for stationary character of the energy of a one-determinant wave function (Brillouin theorem)
- obtain the Hartree-Fock equations from the Brillouin theorem

12.1 Brillouin theorem

Take the expression of the variation principle

$$\langle \delta\Psi | \hat{H} - E | \Psi \rangle = 0 \quad (239)$$

and substitute the general variation of a one-determinant wave function

$$\sum_i^N \sum_r p_{ri}^* \langle \Psi(\psi_i \rightarrow \psi_r) | \hat{H} - E | \Psi \rangle = 0 \quad (240)$$

Since the p_{ri} variation parameters are independent, each term should vanish individually, and since $p_{ri} \rightarrow 0$ but $p_{ri} \neq 0$, we can simplify as

$$\langle \Psi(\psi_i \rightarrow \psi_r) | \hat{H} | \Psi \rangle - E \langle \Psi(\psi_i \rightarrow \psi_r) | \Psi \rangle = 0 \quad (241)$$

The overlap of two determinants differing in one orthogonal spin orbital vanishes

$$\langle \Psi(\psi_i \rightarrow \psi_r) | \hat{H} | \Psi \rangle = 0 \quad (242)$$

Since this condition is trivially satisfied if the spin of ψ_i and ψ_r is different, we can constrain the variation to spin orbitals $\psi_r = \phi_r(\mathbf{r})\eta_r(\sigma)$ having the same spin component as ψ_i

$$\langle \Psi(\phi_i\eta_i \rightarrow \phi_r\eta_i) | \hat{H} | \Psi \rangle = 0 \quad (243)$$

Brillouin theorem: Stationary one-determinant wave function does not interact with the singly excited configurations.

Equivalent to the variation principle applied to a one-determinant wave function.

12.2 Unrestricted Hartree-Fock equations

Consider the determinant wave function

$$\Psi = \det[\psi_1(1)\psi_2(2)\dots\psi_N(N)] \quad (244)$$

If the $\{\psi_i\}$ spin orbitals were not orthogonal, they can always be orthogonalized (c.f. invariance property of determinants).

Apply the Brillouin theorem

$$\langle \Psi(\phi_i\eta_i \rightarrow \phi_r\eta_i) | \hat{H} | \Psi \rangle = 0 \quad (245)$$

Use the **Slater rules**

$$\langle \Psi_i^r | \hat{H} | \Psi \rangle = \langle \psi_r | \hat{h} | \psi_i \rangle + \sum_{\substack{j=1 \\ j \neq i}}^N \langle \psi_r \psi_j | | \psi_i \psi_j \rangle \quad (246)$$

and write the expression in spatial orbitals for the case of $\eta_i = \eta_r$ we obtain

$$(\phi_r | \hat{h} | \phi_i) + \sum_{\substack{j=1 \\ j \neq i}}^N \left\{ (\phi_r \phi_i | \phi_j \phi_j) - (\phi_r \phi_j | \phi_j \phi_i) \delta_{\eta_i \eta_j} \right\} = 0 \quad (247)$$

Introduce (local) the Coulomb-

$$\hat{J}_j \phi(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{\phi_j(\mathbf{r}_2)^* \phi_j(\mathbf{r}_2)}{r_{12}} \phi(\mathbf{r}_1) \quad (248)$$

and (nonlocal) exchange operators

$$\hat{K}_j \phi(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{\phi_j^*(\mathbf{r}_2) \phi(\mathbf{r}_2)}{r_{12}} \phi_j(\mathbf{r}_1) \quad (249)$$

The orbital form of the Brillouin-conditions

$$(\phi_r | \hat{h} + \sum_{\substack{j=1 \\ j \neq i}}^N \{ \hat{J}_j - \hat{K}_j \delta_{\eta_i \eta_j} \} | \phi_i) = 0 \quad (250)$$

Since ϕ_r lies in the orthogonal complement of the occupied orbitals, it is sufficient to require that

$$\left\{ \hat{h} + \sum_{\substack{j=1 \\ j \neq i}}^N (\hat{J}_j - \hat{K}_j \delta_{\eta_i \eta_j}) \right\} \phi_i = \sum_{j=1}^N \lambda_{ji} \phi_j \delta_{\eta_i \eta_j} \quad (251)$$

i.e. the function obtained after the action of the operator in curly brackets **Fockian** lies entirely in the space of the occupied orbitals of the same spin.

Let us apply this result to an unrestricted determinant made of n_a α and n_b β orbitals, $\{\phi_i^\alpha\}_{i=1}^{n_a}$ and $\{\phi_i^\beta\}_{i=1}^{n_b}$. Use the Coulomb- and exchange operators defined separately for orbitals with α and β spin, to obtain the following two sets of equations

$$\left\{ \hat{h} + \sum_{\substack{j=1 \\ j \neq i}}^{n_a} (\hat{J}_j^a - \hat{K}_j^a) + \sum_{j=1}^{n_b} \hat{J}_j^b \right\} \phi_i^\alpha = \sum_{j=1}^{n_a} \epsilon_{ji}^a \phi_j^\alpha \quad (252)$$

$$\left\{ \hat{h} + \sum_{j=1}^{n_a} \hat{J}_j^a + \sum_{\substack{j=1 \\ j \neq i}}^{n_b} (\hat{J}_j^b - \hat{K}_j^b) \right\} \phi_i^\beta = \sum_{j=1}^{n_b} \epsilon_{ji}^b \phi_j^\beta \quad (253)$$

which are coupled by the Coulomb-interaction with electrons of antiparallel spin. Since $\hat{J}_j^a \phi_j^\alpha = \hat{K}_j^a \phi_j^\alpha$, we can remove the summation restriction by adding the

$$\hat{J}_j^a \phi_j^\alpha - \hat{K}_j^a \phi_j^\alpha = 0 \quad (254)$$

self-repulsion term and define the Fock-operators, which are now identical for all orbitals in a given set (α or β)

$$\hat{F}^a = \hat{h} + \sum_{j=1}^{n_a} (\hat{J}_j^a - \hat{K}_j^a) + \sum_{j=1}^{n_b} \hat{J}_j^b \quad \hat{F}^b = \hat{h} + \sum_{j=1}^{n_a} \hat{J}_j^a + \sum_{j=1}^{n_b} (\hat{J}_j^b - \hat{K}_j^b) \quad (255)$$

The UHF equations are obtained in the following form

$$\hat{F}^a | \phi_i^\alpha \rangle = \sum_{j=1}^{n_a} \epsilon_{ji}^a | \phi_j^\alpha \rangle \quad \hat{F}^b | \phi_i^\beta \rangle = \sum_{j=1}^{n_b} \epsilon_{ji}^b | \phi_j^\beta \rangle \quad (256)$$

It is quite impractical to solve directly these coupled integro-differential equations. Before bringing them to a more convenient form, check some properties of the Fockian.

The Fock operator does not change if constructed from a set of orbitals obtained by a unitary transformation of the orbitals of the *same* spin

Unitary transformation

$$\phi_i = \sum_j^{n_a} U_{ji} \phi'_j \quad \phi'_i = \sum_j^{n_a} (\mathbf{U}^\dagger)_{ji} \phi_j \quad (257)$$

Consider, for instance, the Coulomb operator

$$\sum_i^{n_a} \hat{J}_i^a = \sum_i^{n_a} \int d\mathbf{r}_2 \frac{\phi_i^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2)}{r_{12}} = \sum_i^{n_a} \sum_{j,k}^{n_a} \int d\mathbf{r}_2 \frac{U_{ji}^* \phi'_j{}^*(\mathbf{r}_2) U_{ki} \phi'_k(\mathbf{r}_2)}{r_{12}} \quad (258)$$

Using the unitary character of the transformation, $U_{ji}^* = (\mathbf{U}^\dagger)_{ij} = (\mathbf{U}^{-1})_{ij}$ we obtain

$$\sum_i^{n_a} \sum_{j,k}^{n_a} U_{ki} (\mathbf{U}^\dagger)_{ij} \int d\mathbf{r}_2 \frac{\phi'_j{}^*(\mathbf{r}_2) \phi'_k(\mathbf{r}_2)}{r_{12}} = \sum_j^{n_a} \int d\mathbf{r}_2 \frac{\phi'_j{}^*(\mathbf{r}_2) \phi'_j(\mathbf{r}_2)}{r_{12}} = \sum_j^{n_a} \hat{J}_j^a \quad (259)$$

The Fock operator is hermitian

Exchange operator

$$\begin{aligned} \langle \phi | \hat{K}_i \psi \rangle &= \int d\mathbf{r}_1 \phi^*(\mathbf{r}_1) \left[\int d\mathbf{r}_2 \frac{\phi_i^*(\mathbf{r}_2) \psi(\mathbf{r}_2)}{r_{12}} \phi_i(\mathbf{r}_1) \right] \\ &= \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\phi^*(\mathbf{r}_1) \phi_i^*(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \psi(\mathbf{r}_2)}{r_{12}} = \langle \phi \phi_i | \phi_i \psi \rangle \end{aligned} \quad (260)$$

$$\begin{aligned} \langle \hat{K}_i \phi | \psi \rangle &= \int d\mathbf{r}_1 \left[\int d\mathbf{r}_2 \frac{\phi_i^*(\mathbf{r}_2) \phi(\mathbf{r}_2)}{r_{12}} \phi_i(\mathbf{r}_1) \right]^* \psi(\mathbf{r}_1) \\ &= \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\phi_i^*(\mathbf{r}_1) \phi^*(\mathbf{r}_2) \psi(\mathbf{r}_1) \phi_i(\mathbf{r}_2)}{r_{12}} = \langle \phi_i \phi | \psi \phi_i \rangle \end{aligned} \quad (261)$$

After an interchange of the integration variables

$$\langle \phi | \hat{K}_i \psi \rangle = \langle \phi \phi_i | \phi_i \psi \rangle = \langle \phi_i \phi | \psi \phi_i \rangle = \langle \hat{K}_i \phi | \psi \rangle \quad \text{Q.E.D.} \quad (262)$$

We can show analogously that the same holds for the Coulomb operator. The Fock operator, being itself the sum of hermitian operators, is hermitian too.

12.3 Canonical UHF equations

ϵ_{ji} are the elements of a hermitian Fock-operator matrix

$$\hat{F}^a |\phi_i^\alpha\rangle = \sum_j^{n_a} \epsilon_{ji} |\phi_j^\alpha\rangle \quad (263)$$

$$\langle \phi_k^\alpha | \hat{F}^a | \phi_i^\alpha \rangle = \sum_j^{n_a} \epsilon_{ji} \underbrace{\langle \phi_k^\alpha | \phi_j^\alpha \rangle}_{\delta_{kj}} = \epsilon_{ki} \quad (264)$$

Since \hat{F}^a can be constructed from any set of orbitals that is obtained by a unitary transformation of the orbitals of the same spin, we can take \mathbf{U} that diagonalizes the hermitian ϵ matrix

$$(\mathbf{U}^\dagger \epsilon \mathbf{U})_{ik} = \epsilon'_{ik} = \epsilon_i^{\phi_i'} \delta_{ik} \quad (265)$$

In fact, this transformation applied to the orbitals leads to a diagonal ϵ matrix

$$\begin{aligned}\epsilon'_{ik} &= \left\langle \sum_j U_{ji} \phi_j^\alpha | \hat{F}^a | \sum_\ell U_{\ell k} \phi_\ell^\alpha \right\rangle = \sum_{j,\ell} U_{ji}^* \underbrace{\langle \phi_j^\alpha | \hat{F}^a | \phi_\ell^\alpha \rangle}_{\epsilon_{j\ell}^a} U_{\ell k} = \\ &= \sum_{j,\ell} U_{ji}^* \epsilon_{j\ell}^a U_{\ell k} = (\mathbf{U}^\dagger \boldsymbol{\epsilon} \mathbf{U})_{ik} = \epsilon_i^{a'} \delta_{ik}\end{aligned}\quad (266)$$

There exists a set of spin orbitals for which the Fockian is diagonal. Using this basis set the canonical unrestricted Hartree-Fock equations are obtained

$$\begin{aligned}\hat{F}^a \phi_i^\alpha &= \epsilon_i^a \phi_i^\alpha & i = 1, 2, \dots, \infty \\ \hat{F}^b \phi_i^\beta &= \epsilon_i^b \phi_i^\beta & i = 1, 2, \dots, \infty\end{aligned}\quad (267)$$

that are coupled pseudo-eigenvalue equations. The first n_a and n_b solutions are the **occupied orbitals** while the remaining solutions are the **virtual orbitals**.

- Although the eigenfunctions of the HF-equations have no physical meaning (the wave function is invariant to their unitary transformation) the eigenvalues (orbitals energies) can be approximately related to the ionization potentials (Koopmans theorem).
- An infinite number of equivalent orbital sets can be obtained by unitary transformations of the canonical orbitals. Chosen according to some well-defined criteria, these unitary transformations may lead to orbitals with specific properties, i.e. the localized orbitals, closer to our feeling about chemical bonding.

12.4 Unrestricted Hartree-Fock energy expression

Let us apply the general result for the expectation value of the Hamiltonian for a single determinant built from $N = n_a + n_b$ spin orbitals

$$E = \sum_i^{n_a+n_b} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_i^{n_a+n_b} \sum_j^{n_a+n_b} \langle ij | ij \rangle \quad (268)$$

Separate sums over orbitals of spin α and spin β and write integrals in terms of space orbitals

$$\begin{aligned}E &= \sum_i^{n_a} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_i^{n_a} \left\{ \sum_j^{n_a+n_b} \langle ii | jj \rangle - \sum_j^{n_a} \langle ij | ij \rangle \right\} + \\ &+ \sum_i^{n_b} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_i^{n_b} \left\{ \sum_j^{n_a+n_b} \langle ii | jj \rangle - \sum_j^{n_b} \langle ij | ij \rangle \right\}\end{aligned}\quad (269)$$

Use the notations

$$\begin{aligned}h_{ii}^{\alpha\alpha} &= \langle i^\alpha | \hat{h} | i^\alpha \rangle & J_{ij}^{\alpha\alpha} &= \langle i^\alpha i^\alpha | j^\alpha j^\alpha \rangle \\ J_{ij}^{\alpha\beta} &= \langle i^\alpha i^\alpha | j^\beta j^\beta \rangle & K_{ij}^{\alpha\alpha} &= \langle i^\alpha j^\alpha | i^\alpha j^\alpha \rangle\end{aligned}\quad (270)$$

and the energy expression can also be written as

$$\begin{aligned}
E &= \sum_i^{n_a} h_{ii}^{\alpha\alpha} + \frac{1}{2} \sum_i^{n_a} \sum_j^{n_a} \{J_{ij}^{\alpha\alpha} - K_{ij}^{\alpha\alpha}\} + \frac{1}{2} \sum_i^{n_a} \sum_j^{n_b} J_{ij}^{\alpha\beta} + \\
&+ \sum_i^{n_b} h_{ii}^{\beta\beta} + \frac{1}{2} \sum_i^{n_b} \sum_j^{n_b} \{J_{ij}^{\beta\beta} - K_{ij}^{\beta\beta}\} + \frac{1}{2} \sum_i^{n_b} \sum_j^{n_a} J_{ij}^{\beta\alpha}
\end{aligned} \tag{271}$$

Orbital energies are the diagonal matrix elements of the α - and β -spin Fock operators in a **canonical** molecular orbital basis, e.g.

$$\begin{aligned}
\epsilon_i^\alpha &= (\phi_i^\alpha | \hat{F}^\alpha | \phi_i^\alpha) = (i^\alpha | \hat{h} + \sum_j^{n_a} (\hat{J}_j^a - \hat{K}_j^a) + \sum_j^{n_b} \hat{J}_j^b | i^\alpha) \\
&= h_{ii}^{\alpha\alpha} + \sum_j^{n_a} \{J_{ij}^{\alpha\alpha} - K_{ij}^{\alpha\alpha}\} + \sum_j^{n_b} J_{ij}^{\alpha\beta}
\end{aligned} \tag{272}$$

The sum of orbital energies

$$\begin{aligned}
\sum_i^{n_a+n_b} \epsilon_i &= \sum_i^{n_a} h_{ii}^{\alpha\alpha} + \sum_i^{n_a} \sum_j^{n_a} \{J_{ij}^{\alpha\alpha} - K_{ij}^{\alpha\alpha}\} + \sum_i^{n_a} \sum_j^{n_b} J_{ij}^{\alpha\beta} \\
&+ \sum_i^{n_b} h_{ii}^{\beta\beta} + \sum_i^{n_b} \sum_j^{n_b} \{J_{ij}^{\beta\beta} - K_{ij}^{\beta\beta}\} + \sum_i^{n_b} \sum_j^{n_a} J_{ij}^{\beta\alpha} \neq E
\end{aligned} \tag{273}$$

is not equal to the total energy, due to the double counting of electron-electron interactions.

12.5 Spin properties of the UHF wave function

Eigenfunction of the \hat{S}_z operator

$$\hat{S}_z |D\rangle = \frac{1}{2} (n^\alpha - n^\beta) |D\rangle \tag{274}$$

but not eigenfunction of the $\hat{S}^2 = \hat{S}_- \hat{S}_+ + \hat{S}_z + \hat{S}_z^2$ operator!

For example, a two-electron DODS (different orbitals different spin) system $|D\rangle = |\hat{A}[\phi^\alpha \bar{\phi}^\beta]\rangle$

$$\hat{S}^2 |D\rangle = \hat{A}[\hat{S}_- \hat{S}_+ \phi^\alpha \bar{\phi}^\beta + \hat{S}_z \phi^\alpha \bar{\phi}^\beta + \hat{S}_z^2 \phi^\alpha \bar{\phi}^\beta]$$

where we use that $[\hat{S}^2, \hat{A}] = 0$.

Last two terms are zero, since $(n^\alpha - n^\beta) = 0$.

$$\hat{S}_- \hat{S}_+ \{\phi^\alpha \bar{\phi}^\beta\} = \hat{S}_- \{\phi^\alpha \phi^\beta\} = \bar{\phi}^\alpha \phi^\beta + \phi^\alpha \bar{\phi}^\beta \tag{275}$$

The two-electron UHF wave function is not eigenfunction of the \hat{S}^2 operator

$$\hat{S}^2 |D\rangle = |D\rangle + \hat{A}[\bar{\phi}^\alpha \phi^\beta] \neq (S(S+1)|D\rangle \tag{276}$$

Expectation value of \hat{S}^2 is

$$\begin{aligned}
\langle D | \hat{S}^2 | D \rangle &= \langle D | D \rangle + \langle \hat{A} \phi^\alpha \bar{\phi}^\beta | \hat{A} \bar{\phi}^\alpha \phi^\beta \rangle \\
&= 1 + \begin{vmatrix} \langle \phi^\alpha | \bar{\phi}^\alpha \rangle & \langle \bar{\phi}^\alpha | \bar{\phi}^\beta \rangle \\ \langle \phi^\alpha | \phi^\beta \rangle & \langle \bar{\phi}^\alpha | \phi^\alpha \rangle \end{vmatrix} = 1 - |S^{\alpha\beta}|^2
\end{aligned} \tag{277}$$

12.6 Symmetry dilemma

While the exact solutions of the molecular Schrödinger equation are eigenfunctions of all the operators that commute with the molecular Hamiltonian, this is not necessarily the case for an approximate (e.g. UHF) solution. This can be the case for the symmetry operation of the molecular point group and it is the case for the \hat{S}^2 operator, which has the expectation value for a UHF wave function:

$$\langle \hat{S}^2 \rangle_{\text{UHF}} = \underbrace{\left(\frac{n^\alpha - n^\beta}{2} \right) \left(\frac{n^\alpha - n^\beta}{2} + 1 \right)}_{\langle \hat{S}^2 \rangle_{\text{exact}}} + n^\beta - \sum_i \sum_j |S_{ij}^{\alpha\beta}|^2 \quad (278)$$

If we require that the solutions have the correct symmetry, it appears as a constraint (restriction) in the variation problem, and leads necessarily to a higher energy than the solution of the unconstrained (unrestricted) problem. We should decide whether we give up the symmetry requirements to get a better energy or we restrict the solutions on physical grounds and obtain a worse energy. This is the Löwdin symmetry dilemma.

12.7 Restricted Hartree-Fock equations

A determinant built up from pairs of spin orbitals composed of the same space orbital multiplied by either $\alpha(\sigma)$ or $\beta(\sigma)$ is a restricted determinant. The case of closed shells, i.e. $N = 2n$ is particularly important

$$\Psi = \mathcal{A} \{ \phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) \dots \phi_n(2n-1)\bar{\phi}_n(2n) \} \quad (279)$$

Instead of repeating the derivation from the Brillouin theorem, we can simply consider this problem as a special case of the UHF equations with $n_a = n_b = n$ and $\hat{J}_i^a = \hat{J}_i^b = \hat{J}_i$, etc. We obtain

$$\hat{F} = \hat{h} + \sum_{j=1}^n 2\hat{J}_j - \hat{K}_j \quad (280)$$

where the summation is over the n space orbitals. The *canonical* molecular orbitals are obtained as eigenfunctions of the canonical RHF equations

$$\hat{F}|\phi_i\rangle = \epsilon_i|\phi_i\rangle \quad i = 1, 2, \dots, \infty \quad (281)$$

with orbital energies as eigenvalues.

12.8 RHF energy expression

Closed shell RHF electronic energy in terms of n space orbitals

$$E = 2 \sum_i^n (i|\hat{h}|i) + \sum_i^n \sum_j^n 2(ii|jj) - (ij|ji) = 2 \sum_i^n h_{ii} + \sum_i^n \sum_j^n 2J_{ij} - K_{ij} \quad (282)$$

Orbital energies are the diagonal elements (and eigenvalues) of the RHF Fock operator and using integrals in space orbitals in the chemists' (charge density) convention

$$\epsilon_i = h_{ii} + \sum_j^n 2J_{ij} - K_{ij} = (i|\hat{h}|i) + \sum_j^n 2(ii|jj) - (ij|ji) \quad (283)$$

The sum of the energies of the n doubly occupied orbitals

$$\sum_i^{2n} \epsilon_i = 2 \sum_i^n h_{ii} + 2 \sum_j^n 2J_{ij} - K_{ij} \neq E \quad (284)$$

is not equal to the total energy.

12.9 Orbital energies

$$\langle \psi_i | \hat{F} | \psi_j \rangle = \varepsilon_j \langle \psi_i | \psi_j \rangle = \varepsilon_j \delta_{ij} \quad (285)$$

$$\varepsilon_i = \langle i | \hat{h} | i \rangle + \sum_b^N \langle ib | ib \rangle \quad (286)$$

- Occupied orbitals

$$\varepsilon_a = \langle a | \hat{h} | a \rangle + \sum_{\substack{b=1 \\ b \neq a}}^N \langle ab | ab \rangle \quad (287)$$

where $\langle aa | aa \rangle = 0$ is used. The energy of an occupied orbital corresponds to a particle moving in a $N - 1$ -electron potential.

- Virtual orbitals

$$\varepsilon_r = \langle r | \hat{h} | r \rangle + \sum_{b=1}^N \langle rb | rb \rangle \quad (288)$$

describe electrons in the potential of all the N electrons of the Hartree-Fock ground state.

12.10 Koopmans theorem

Let us group together those terms of the electronic energy, which depend on a given molecular orbital, e.g. k

$$E_N = \sum_{i \neq k}^N \langle i | \hat{h} | i \rangle + \langle k | \hat{h} | k \rangle + \frac{1}{2} \sum_{i \neq k}^N \sum_{j \neq k}^N \langle ij | ij \rangle + \sum_{i \neq k}^N \langle ik | ik \rangle + \frac{1}{2} \langle kk | kk \rangle \quad (289)$$

Since the self-interaction $\langle kk | kk \rangle = 0$, the last term is 0 and we can drop the summation restriction

$$E_N = \sum_{i \neq k}^N \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i \neq k}^N \sum_{j \neq k}^N \langle ij | ij \rangle + \langle k | \hat{h} | k \rangle + \sum_i^N \langle ik | ik \rangle = E_{N-1}(k) + \epsilon_k \quad (290)$$

The negative of the orbital energy is equal to the energy difference of $(N - 1)$ -electron and the N -electron determinants, the ionization potential,

$$IP = E_{N-1}(k) - E_N = -\epsilon_k \quad (291)$$

provided we neglect the orbital relaxation effects (spin orbitals are supposed to be frozen in the $(N - 1)$ -electron determinant).

Similarly, we can examine the energy of an $(N + 1)$ -electron determinant, obtained by adding a virtual spin orbital ψ_r to the N -electron determinant.

$$E_{N+1} = E_N + \langle r | \hat{h} | r \rangle + \sum_i^N \langle ri | ri \rangle = E_N + \epsilon_r \quad (292)$$

The electron affinity, EA, can be approximated as the negative of the virtual orbital energy:

$$EA = E_N - E_{N+1}(r) = -\epsilon_r \quad (293)$$

Koopmans theorem: Provided that the spin-orbitals satisfy the canonical HF equations, and the same set of orbitals are used to describe the neutral system and its ions, their energy difference is stationary against spin-orbital variations.

12.11 Excitation operators - Generalities

Define an *excitation operator* by

$$\hat{O}_n^\dagger|0\rangle = |n\rangle \quad (294)$$

In bra-ket representation

$$\hat{O}_n^\dagger = |n\rangle\langle 0| \quad (295)$$

The corresponding de-excitation operator

$$\hat{O}_n = |0\rangle\langle n| \quad (296)$$

Apply the commutator $[\hat{H}, \hat{O}_n^\dagger]$ to the exact ground state wave function

$$\begin{aligned} [\hat{H}, \hat{O}_n^\dagger]|0\rangle &= \hat{H}\hat{O}_n^\dagger|0\rangle - \hat{O}_n^\dagger\hat{H}|0\rangle = \hat{H}|n\rangle - E_0\hat{O}_n^\dagger|0\rangle \\ &= E_n\hat{O}_n^\dagger|0\rangle - E_0\hat{O}_n^\dagger|0\rangle = \Delta E_{0n}\hat{O}_n^\dagger|0\rangle \end{aligned} \quad (297)$$

This leads to the (super)operator equation

$$[\hat{H}, \hat{O}_n^\dagger] = \Delta E_{0n}\hat{O}_n^\dagger \quad (298)$$

Excitation energy as Rayleigh quotient

$$\Delta E_{0n} = \frac{\langle 0|\hat{O}_n[\hat{H}, \hat{O}_n^\dagger]|0\rangle}{\langle 0|\hat{O}_n\hat{O}_n^\dagger|0\rangle} \quad (299)$$

These are the basic relations of the EOM (equation of motion) approach.

12.12 Generalized Koopmans theorem

An ionization process can be described by the operator

$$\hat{O}_n^\dagger = \sum_r c_r^* a_r = \hat{O}^+ \quad (300)$$

which creates a positive ion by removing one electron. The ionization potential, ΔE^+ is

$$\Delta E^+ = \frac{\sum_{rs} c_r^* c_s \langle 0| a_s^+ [\hat{H}, a_r] |0\rangle}{\sum_{rs} c_r^* c_s \langle 0| a_s^+ a_r |0\rangle} = \frac{\mathbf{c}^\dagger \mathbf{K} \mathbf{c}}{\mathbf{c}^\dagger \mathbf{P} \mathbf{c}} \quad (301)$$

In the denominator we recognize the density matrix elements, and in the numerator we have the matrix elements of the Koopmans operator

$$K_{rs} = \langle 0| a_s^+ [\hat{H}, a_r] |0\rangle \quad (302)$$

After expansion of the SQ Hamiltonian operator

$$\begin{aligned} K_{rs} &= \left\langle \sum_{tu} h_{tu} (s^+ t^+ u^- r^- - s^+ r^- t^+ u^-) \right. \\ &\quad \left. + \frac{1}{2} \sum_{tuvw} \langle tu|vw\rangle (s^+ t^+ u^+ w^- v^- r^- - s^+ r^- t^+ u^+ w^- v^-) \right\rangle \end{aligned} \quad (303)$$

Applying the anticommutation relations we obtain the 1RDM operator

$$s^+ t^+ u^- r^- - s^+ r^- t^+ u^- = s^+ t^+ u^- r^- - s^+ (\delta_{rt} - t^+ r^-) u^- = -\delta_{rt} s^+ u^- \quad (304)$$

and the 2RDM operator

$$\begin{aligned}
& s^+ t^+ u^+ w^- v^- r^- - s^+ r^- t^+ u^+ w^- v^- = \\
& s^+ t^+ u^+ w^- v^- r^- - s^+ (\delta_{rt} - t^+ r^-) u^+ w^- v^- = \\
& s^+ t^+ u^+ w^- v^- r^- - \delta_{rt} s^+ u^+ w^- v^- + s^+ t^+ (\delta_{ru} - u^+ r^-) w^- v^- = \\
& -\delta_{rt} s^+ u^+ w^- v^- - \delta_{ru} s^+ t^+ w^- v^- = -\delta_{rt} s^+ u^+ w^- v^- + \delta_{ru} s^+ t^+ w^- v^-
\end{aligned} \tag{305}$$

$$\begin{aligned}
K_{rs} &= -\left\langle \sum_{tu} h_{tu} \delta_{rt} s^+ u^- + \frac{1}{2} \sum_{tuv} \langle tu|vw \rangle (\delta_{rt} s^+ u^+ w^- v^- - \delta_{ru} s^+ t^+ w^- v^-) \right\rangle \\
&= -\left\langle \sum_u h_{ru} s^+ u^- + \frac{1}{2} \left(\sum_{uvw} \langle ru|vw \rangle s^+ u^+ w^- v^- - \sum_{tvw} \langle tr|vw \rangle s^+ t^+ w^- v^- \right) \right\rangle \\
&= -\left[\sum_t h_{rt} P_{ts} + \sum_{tuv} \langle rt|uv \rangle \Gamma_{uv,st} \right]
\end{aligned} \tag{306}$$

The condition for a stationary value of ΔE^+ is

$$\delta \Delta E^+ = \frac{\delta \mathbf{c}^\dagger \mathbf{K} \mathbf{c}}{\mathbf{c}^\dagger \mathbf{P} \mathbf{c}} - \left(\frac{\mathbf{c}^\dagger \mathbf{K} \mathbf{c}}{\mathbf{c}^\dagger \mathbf{P} \mathbf{c}} \right) \frac{\delta \mathbf{c}^\dagger \mathbf{P} \mathbf{c}}{\mathbf{c}^\dagger \mathbf{P} \mathbf{c}} + \text{c.c.} = 0 \tag{307}$$

leading to the matrix equation

$$\mathbf{K} \mathbf{c} = \Delta E^+ \mathbf{P} \mathbf{c} \tag{308}$$

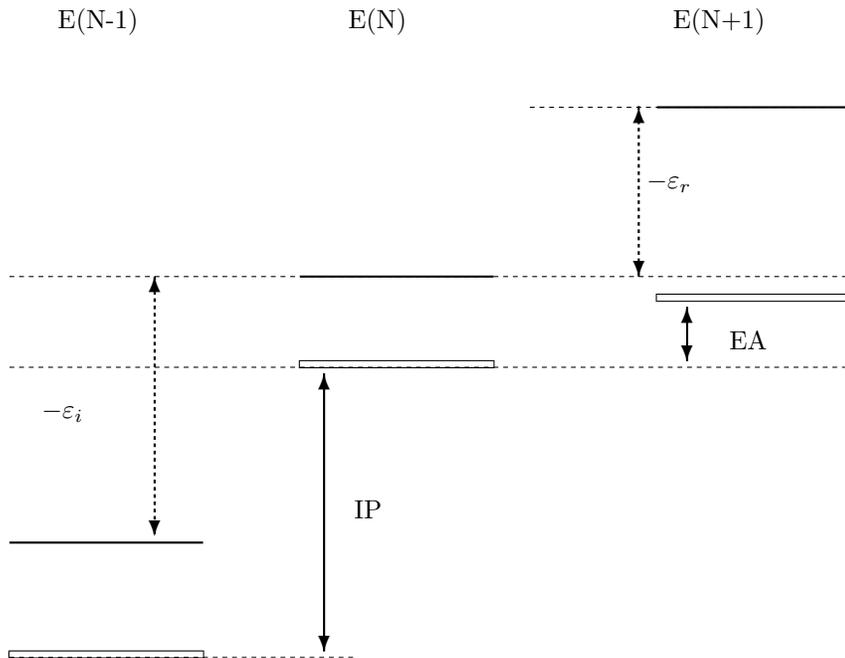
For a HF wave function $\mathbf{P} = \mathbf{I}$ and the Koopmans matrix is

$$K_{rs} = -\left[\sum_t h_{rt} \delta_{ts} + \sum_{tuv} \langle rt|uv \rangle n_u n_v (\delta_{tu} \delta_{rv} - \delta_{tv} \delta_{ru}) \right] = -F_{rs} \tag{309}$$

equal to the matrix of the Fock operator, which has as eigenvalues the orbital energies. It can be concluded that for a HF wave function the variational ionization potential is just the orbital energy $\Delta E^+ = -\varepsilon_i$ and the corresponding excitation operator is a_i , which removes an occupied spin orbital from the HF determinant.

12.13 How good is the Koopmans theorem?

- orbital relaxation correction - lowers the energy of the ions
- correlation energy correction - depends on the number of electrons



Two errors compensate each other for the ionization potential, enhance each other for the electron affinity.

12.14 Excited states

Excite an electron from the i -th occupied to the r -th virtual level of a RHF wave function. Two possible excited determinants

$$\Psi_i^r \quad \Psi_i^{\bar{r}} \quad (310)$$

Their linear combinations form pure singlet and triplet states

$${}^1\Psi = \frac{1}{2}(\Psi_i^r + \Psi_i^{\bar{r}}) \quad (311)$$

$${}^3\Psi = \frac{1}{2}(\Psi_i^r - \Psi_i^{\bar{r}}) \quad (312)$$

The excitation energies $\Delta E_{S,T}$ in this *single transition approximation*, (*STA*) depend on the orbital energies and the electron-electron interactions.

$$E_{S,T} = \frac{1}{2} \left(\langle \Psi_i^r | \hat{H} | \Psi_i^r \rangle + \langle \Psi_i^{\bar{r}} | \hat{H} | \Psi_i^{\bar{r}} \rangle \pm \langle \Psi_i^{\bar{r}} | \hat{H} | \Psi_i^r \rangle \pm \langle \Psi_i^r | \hat{H} | \Psi_i^{\bar{r}} \rangle \right) \quad (313)$$

The first two matrix elements are equal (just α and β are interchanged) and the last two are complex conjugates, which are also equal for real wave functions.

The energy of the excited determinant is obtained from the ground state energy by removing ε_i and replacing it by ε_r and correcting for the missing e^- -repulsion term between electrons of parallel spin

$$\langle \Psi_i^r | \hat{H} | \Psi_i^r \rangle = E_0 + \varepsilon_r - \varepsilon_i - \langle \phi_r | \hat{J}_i - \hat{K}_i | \phi_r \rangle \quad (314)$$

Transition matrix element between determinants that differ in two spin orbitals

$$\begin{aligned} \langle \Psi_i^r | \hat{H} | \Psi_i^{\bar{r}} \rangle &= \langle \phi_1 \bar{\phi}_1 \dots \phi_r \bar{\phi}_i \dots | \hat{H} | \phi_1 \bar{\phi}_1 \dots \phi_i \bar{\phi}_r \dots \rangle \\ &= \langle r\bar{i} | i\bar{r} \rangle = [r\bar{i} | i\bar{r}] - [r\bar{i} | \bar{r}i] = (ri | ir) - 0 = K_{ir} \end{aligned}$$

Summarizing these results

$$E_{S,T} = \frac{1}{2} \left\{ 2(E_0 + \varepsilon_r - \varepsilon_i - J_{ir} + K_{ir}) \pm 2K_{ir} \right\} \quad (315)$$

Excitation energies

$$\Delta E_S = \varepsilon_r - \varepsilon_i - J_{ir} + 2K_{ir} \quad (316)$$

$$\Delta E_T = \varepsilon_r - \varepsilon_i - J_{ir} \quad (317)$$

Relative magnitude of singlet/triplet splittings can sometimes be estimated from the shape of the occupied and virtual orbitals, as the self-energy of the transition density $\phi_i^*(\mathbf{r})\phi_r(\mathbf{r})$.

13 EOM for excited states

Let us use the equation of motion method for electronic excited states. Define the singlet excitation operator

$$\hat{O}_n^\dagger = \frac{1}{2} \sum_{ar} X_{ar}^* (a_{r\alpha}^+ a_{a\alpha}^- + a_{r\beta}^+ a_{a\beta}^-) = \sum_{ar} X_{ar}^* \hat{E}_{ar}^\dagger \quad (318)$$

and its adjoint

$$\hat{O}_n = \frac{1}{2} \sum_{ar} X_{ar} (a_{a\alpha}^+ a_{r\alpha}^- + a_{a\beta}^+ a_{r\beta}^-) = \sum_{ar} X_{ar} \hat{E}_{ar} \quad (319)$$

The excitation energy can be obtained from

$$\Delta E_n = \frac{\langle 0 | \hat{O}_n [\hat{H}, \hat{O}_n^\dagger] | 0 \rangle}{\langle 0 | \hat{O}_n \hat{O}_n^\dagger | 0 \rangle} \quad (320)$$

Substitution of the excitation operators

$$\Delta E_n = \frac{\sum_{ar} \sum_{bs} X_{ar}^* X_{bs} \langle 0 | \hat{E}_{bs} [\hat{H}, \hat{E}_{ar}^\dagger] | 0 \rangle}{\sum_{ar} \sum_{bs} X_{ar}^* X_{bs} \langle 0 | \hat{E}_{bs} \hat{E}_{ar}^\dagger | 0 \rangle} \quad (321)$$

The matrix elements in the denominator

$$\langle 0 | \hat{E}_{bs} \hat{E}_{ar}^\dagger | 0 \rangle = \frac{1}{4} (\langle 0 | a_{b\alpha}^+ a_{a\alpha} + a_{b\beta}^+ a_{a\beta} | 0 \rangle \delta_{rs}) = \frac{1}{2} \rho_{ab} \quad (322)$$

is the half of the spinless one-particle reduced density matrix. Define \mathbf{Q} as

$$Q_{bs,ar} = 2 \langle 0 | \hat{E}_{bs} [\hat{H}, \hat{E}_{ar}^\dagger] | 0 \rangle \quad (323)$$

and the excitation energy expression in matrix form

$$\Delta E_n = \frac{\mathbf{X}^\dagger \mathbf{Q} \mathbf{X}}{\mathbf{X}^\dagger \boldsymbol{\rho} \mathbf{X}} \quad (324)$$

The stationary condition leads to the matrix equation

$$\mathbf{Q} \mathbf{X} = \Delta E \boldsymbol{\rho} \mathbf{X} \quad (325)$$

In the special case of a one-determinant HF wave function as ground state $\boldsymbol{\rho} = \mathbf{I}$ and

$$Q_{bs,ar} = 2 (\langle 1 | D_b^s | \hat{H} | 1 | D_a^r \rangle - \delta_{ab} \delta_{sr} \langle D | \hat{H} | D \rangle) \quad (326)$$

The \mathbf{Q} matrix is the single-CI matrix (TDA – Tamm-Dancoff approximation). The diagonal elements are the STA excitation energies that we have already derived previously

$$Q_{ar,ar} = \varepsilon_a - \varepsilon_b - (aa|rr) + 2(ar|ar) \quad (327)$$

while the off-diagonal elements are

$$Q_{bs,ar} = -(ab|sr) + 2(ar|bs) \quad (328)$$

The use of TDA is mandatory when the STA gives *qualitatively wrong* results. For instance, the benzene excited states

- 4 possible single excitations between doubly degenerate HOMO to doubly degenerate LUMO
- four-fold degenerate i.r. with 4 identical STA excitation energies
- TDA leads to the correct symmetry-adapted combinations and splitting of the excitation energies

TDA is often used with semi-empirical model Hamiltonians (PPP, CNDO/S) and sometimes also with ab initio (e.g. Gaussian program).

13.1 Hartree-Fock density matrix

The operator of the one-particle reduced density matrix in SQ is

$$\hat{\rho}(\mathbf{x}_1; \mathbf{x}'_1) = \sum_{k\ell} \psi_\ell(\mathbf{x}_1) \psi_k^*(\mathbf{x}'_1) k^+ \ell^- \quad (329)$$

Since the 1RDM can be expanded as

$$\rho(\mathbf{x}_1; \mathbf{x}'_1) = \sum_{k\ell} \psi_\ell^*(\mathbf{x}_1) P_{\ell k} \psi_k(\mathbf{x}'_1) \quad (330)$$

the matrix elements $P_{\ell k} = \langle k^+ \ell^- \rangle$ form a discrete representation of the 1RDM.

In the case of a single determinant HF wave function the 1RDM on the basis the MOs

$$P_{ki} = \langle \text{HF} | \psi_i^+ \psi_k^- | \text{HF} \rangle = n_k \delta_{ik} \quad (331)$$

is diagonal. The trace of P_{ki} is equal to $N = \sum_i^M n_i$, the number of electrons.

The density matrix of a HF wave function is idempotent. This property follows simply from the fact that $n_i = 0$ or $n_i = 1$, therefore

$$(\mathbf{P}^2)_{k\ell} = \sum_i P_{ki} P_{i\ell} = \sum_i n_k \delta_{ik} \cdot n_i \delta_{\ell i} = n_k^2 \delta_{k\ell} = P_{k\ell} \quad (332)$$

The idempotency of the one-particle reduced density matrix is a necessary and sufficient condition for the one-determinant character of the wave function.

13.2 Natural orbitals

For multi-configurational (e.g. CI) wave functions the 1RDM is not necessarily diagonal. Nevertheless, since \mathbf{P} is hermitian, one can find a unitary matrix \mathbf{U} that $\mathbf{U}^\dagger \mathbf{P} \mathbf{U}$ be diagonal. Let \mathbf{U} such a matrix. Then the transformation from the original (MO) and the new basis is

$$\eta_i = \sum_k \psi_k U_{ki} \quad \psi_k = \sum_i \eta_i (\mathbf{U}^\dagger)_{ik} = \sum_i \eta_i U_{ki}^* \quad (333)$$

Substituting this transformation to the expansion of the 1RDM

$$\hat{\rho}(\mathbf{x}_1; \mathbf{x}'_1) = \sum_{k\ell} \sum_{ij} U_{\ell i}^* \eta_i(\mathbf{x}_1) P_{\ell k} U_{kj} \eta_j^*(\mathbf{x}'_1) \quad (334)$$

Since \mathbf{U} has been chosen such that $\mathbf{U}^\dagger \mathbf{P} \mathbf{U}_{ij} = \lambda_i \delta_{ij}$

$$\hat{\rho}(\mathbf{x}_1; \mathbf{x}'_1) = \sum_i \lambda_i \eta_i(\mathbf{x}_1) \eta_i^*(\mathbf{x}'_1) \quad (335)$$

The orbitals, that diagonalize the 1RDM are called **natural orbitals**. Let us write the wave function as a linear combination of determinants built from the natural orbitals. In this case the diagonal elements of the density matrix

$$\begin{aligned} P_{ii} = \lambda_i &= \sum_K \sum_L c_K^* c_L \langle D_K | \eta_i^+ \eta_i^- | D_L \rangle \\ &= \sum_K \sum_L c_K^* c_L n_i^L \langle D_K | D_L \rangle = \sum_K |c_K|^2 n_i^K \end{aligned} \quad (336)$$

are n_i^K is the occupation number of the i -th NO in determinant K . The diagonal elements, λ_i , can be any number between 0 and 1. The matrix representation of the 1RDM for a multi-configurational wave function is not idempotent.

13.3 Two-particle density matrix for a HF wave function

The matrix representation of the two-particle reduced density matrix is obtained from the following expectation value

$$\Gamma_{lk,ij}^{\text{HF}} = \langle \text{HF} | \psi_i^+ \psi_j^+ \psi_k^- \psi_l^- | \text{HF} \rangle = n_i n_j (\delta_{jk} \delta_{il} - \delta_{jl} \delta_{ik}) \quad (337)$$

in the basis of molecular orbitals.

The two-particle density matrix of a one-determinant wave function can be expressed by the elements of the 1RDM matrix elements as

$$\Gamma_{lk,ij}^{\text{HF}} = P_i P_{jk} - P_{lj} P_{ki} \quad (338)$$

The first part corresponds to the Coulomb-component

$$\Gamma_{lk,ij}^{\text{HF,Coul}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = P(\mathbf{x}_1, \mathbf{x}'_1) P(\mathbf{x}_2, \mathbf{x}'_2) \quad (339)$$

and the second part first part is the exchange-component

$$\Gamma_{lk,ij}^{\text{HF,exch}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = -P(\mathbf{x}_1, \mathbf{x}'_2) P(\mathbf{x}_2, \mathbf{x}'_1) \quad (340)$$

14 Hartree-Fock-Hall-Roothan equations

The UHF and RHF equations can be brought to a more practical form, by writing the molecular orbitals as linear combination of some fixed functions. In quantum chemistry, these are usually some approximations to atomic orbitals (AO). In this LCAO approximation

$$\phi_i = \sum_{\mu=1}^m c_{\mu i} \chi_{\mu} \quad (341)$$

where $c_{\mu i} = (\mathbf{c}_i)_{\mu}$ is an element of the column vector of the expansion coefficients. We suppose that the m basis functions (AOs) are linearly independent and in general, form a non-orthogonal set. The $c_{\mu i}$ MO-coefficients are *not* true linear variation parameters, since the HF equations are only pseudo-eigenvalue equations.

We can proceed again from the Brillouin condition

$$\langle \Psi(\phi_i \rightarrow \phi'_i) | \hat{H} | \Psi \rangle = 0 \quad (342)$$

and we suppose that both ϕ_i and ϕ'_i can be expanded in the same AO basis

$$\phi_i = \sum_{\mu=1}^m c_{\mu i} \chi_{\mu} \quad \phi'_i = \sum_{\mu=1}^m q_{\mu} \chi_{\mu} \quad (343)$$

Introduce the projection operator to the subspace of occupied orbitals

$$\hat{P} = \sum_{j=1}^{occ} |\phi_j\rangle \langle \phi_j| \quad (344)$$

Any function $\hat{P}|\psi\rangle = \hat{P}|\sum_{\nu} p_{\nu} \chi_{\nu}\rangle$ lies in the occupied subspace and any function $(1 - \hat{P})|\psi\rangle = (1 - \hat{P})|\sum_{\nu} p_{\nu} \chi_{\nu}\rangle$ is orthogonal to this subspace. Since the p_{ν} coefficients are arbitrary, we should require the fulfillment of the Brillouin theorem for all functions of the form $|\phi'\rangle = (1 - \hat{P})|\chi_{\nu}\rangle$.

Using the Slater rules

$$\langle \phi' | \hat{F} | \phi_i \rangle = 0 \quad (345)$$

and substituting the definition $\langle \phi' |$

$$\langle \chi_{\nu} | (1 - \hat{P}) \hat{F} | \phi_i \rangle = \langle \chi_{\nu} | \hat{F} | \phi_i \rangle - \langle \chi_{\nu} | \sum_{j=1}^{occ} \phi_j \rangle \underbrace{\langle \phi_j | \hat{F} | \phi_i \rangle}_{\varepsilon_{ji}} = 0 \quad (346)$$

Putting the LCAO expansion of $|\phi_i\rangle$ and $|\phi_j\rangle$

$$\langle \chi_{\nu} | \hat{F} | \sum_{\mu=1}^m c_{\mu i} \chi_{\mu} \rangle = \sum_{j=1}^{occ} \langle \chi_{\nu} | \sum_{\mu=1}^m c_{\mu i} \chi_{\mu} \rangle \varepsilon_{ji} \quad (347)$$

Supposing that we have already performed the unitary transformation that diagonalizes the ε matrix, and using obvious matrix element notations

$$\sum_{\mu=1}^m F_{\nu\mu} c_{\mu i} = \varepsilon_i \sum_{\mu=1}^m S_{\nu\mu} c_{\mu i} \quad (348)$$

The result is a generalized pseudo-eigenvalue equation

$$\mathbf{F} \mathbf{c}_i = \varepsilon_i \mathbf{S} \mathbf{c}_i \quad i = 1, 2, \dots, m \quad (349)$$

which can be written in matrix form by constructing the $m \times m$ MO coefficient matrix, \mathbf{C} , from the column vectors of the expansion coefficients

$$\mathbf{FC} = \varepsilon \mathbf{SC} \quad (350)$$

Solutions

N (in closed shell RHF case $N/2$) occupied orbitals

$m - N$ virtual orbitals

The Hartree-Fock-Roothaan equations are not equivalent with the Hartree-Fock equations. By increasing the basis set we can only approach the ‘‘Hartree-Fock limit’’.

14.1 P-matrix

In the LCAO-theory we use frequently the projector to the subspace of occupied orbitals, expressed by the LCAO coefficients

$$\hat{P} = \sum_{i=1}^{occ} |\phi_i\rangle\langle\phi_i| = \sum_{\mu\nu} \sum_{j=1}^m c_{i\mu} c_{i\nu}^* |\chi_\mu\rangle\langle\chi_\nu| = \sum_{\mu\nu} P_{\mu\nu} |\chi_\mu\rangle\langle\chi_\nu| \quad (351)$$

In components, and also in matrix notation using the column vector of the LCAO coefficients, \mathbf{c}_i

$$P_{\mu\nu} = \sum_{i=1}^{occ} c_{i\mu} c_{i\nu}^* \quad \mathbf{P} = \sum_{i=1}^{occ} \mathbf{c}_i \mathbf{c}_i^\dagger \quad (352)$$

In the RHF case it is used multiplied with a factor of 2

$$\mathbf{D} = 2\mathbf{P}$$

The P-matrix is often called *density matrix*. The electronic density has the expression

$$\varrho(\mathbf{r}) = \sum_i^{occ} \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \chi_\nu^*(\mathbf{r}) \chi_\mu(\mathbf{r}) \quad (353)$$

The P-matrix appears in the expectation values of one-electron operators.

The operator \hat{P} is a projector, i.e. $\hat{P}^2 = \hat{P}$. The idempotency of its matrix representation in the MO basis and in any *orthonormal* basis is a criterion for the one-determinant character of the underlying wave function.

However, this property does not hold for its matrices in a non-orthogonal basis, like the AO basis

$$\langle\chi_\mu|\hat{P}|\chi_\nu\rangle = \sum_i^{occ} \langle\chi_\mu|\phi_i\rangle\langle\phi_i|\chi_\nu\rangle = \sum_i^{occ} (\mathbf{SPS})_{\mu\nu} \quad (354)$$

which is obviously not idempotent.

Let us calculate that component of an arbitrary orbital $\psi = \sum_\tau d_\tau \chi_\tau$ which lies in the occupied subspace. Using the \hat{P} projection operator

$$\hat{P}|\psi\rangle = \sum_{i=1}^{occ} |\phi_i\rangle\langle\phi_i|\psi\rangle = \sum_{\mu} p_\mu |\chi_\mu\rangle \quad (355)$$

Using the LCAO expansions of \hat{P} and ψ

$$\hat{P}|\psi\rangle = \sum_{\mu\nu} \sum_{\tau} P_{\mu\nu} d_{\tau} |\chi_{\mu}\rangle \langle \chi_{\nu} | \chi_{\tau}\rangle = \sum_{\mu\nu} \sum_{\tau} P_{\mu\nu} S_{\nu\tau} d_{\tau} |\chi_{\mu}\rangle = \sum_{\mu\nu} (\mathbf{PS})_{\mu\tau} d_{\tau} |\chi_{\mu}\rangle$$

The matrix of the projection, \mathbf{PS} can be deduced from

$$p_{\mu} = \sum_{\nu} (\mathbf{PS})_{\mu\nu} d_{\nu} \quad (356)$$

The \mathbf{PS} matrix is idempotent. To see that, consider the expression of the overlap of two molecular orbitals

$$\langle \phi_i | \phi_j \rangle = \sum_{\mu} \sum_{\nu} c_{\mu i}^* c_{\nu j} \langle \chi_{\mu} | \chi_{\nu} \rangle = \delta_{ij} \quad (357)$$

in matrix notation

$$\mathbf{c}_i^{\dagger} \mathbf{S} \mathbf{c}_j = \delta_{ij} \quad (358)$$

to calculate the square of the \mathbf{PS} matrix

$$\mathbf{PSPS} = \sum_i^{\text{occ}} \sum_j^{\text{occ}} \mathbf{c}_i \mathbf{c}_i^{\dagger} \mathbf{S} \mathbf{c}_j \mathbf{c}_j^{\dagger} \mathbf{S} = \sum_i^{\text{occ}} \sum_j^{\text{occ}} \mathbf{c}_i \delta_{ij} \mathbf{c}_j^{\dagger} \mathbf{S} = \sum_i^{\text{occ}} \mathbf{c}_i \mathbf{c}_i^{\dagger} \mathbf{S} = \mathbf{PS} \quad (359)$$

The trace of the \mathbf{PS} matrix is equal to the number of electrons.

$$N = \int d\mathbf{r} \varrho(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \int d\mathbf{r} \chi_{\nu}^*(\mathbf{r}) \chi_{\mu}(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\nu\mu} = \sum_{\mu} (\mathbf{PS})_{\mu\mu} \quad (360)$$

The \mathbf{PS} matrix can be considered as the correct representation of the one-particle reduced density matrix (1RDM).

14.2 Population analysis

Total number of electrons (AO basis)

$$N = \sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\nu\mu} = \sum_{\mu} (\mathbf{PS})_{\mu\mu} \quad (361)$$

Each term can be interpreted as the number of electrons associated to the orbital χ_{μ} . Since the AO-s are assigned to atoms, we can group together the net charge (electronic + nuclear) associated with an atom A

$$Q^A(\text{Mulliken}) = Z_A - \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu} \quad (362)$$

This is the *Mulliken population analysis*. It corresponds to the halving of the electron density associated with a pair of AOs.

This definition of the atomic charge is not unique. Since $\text{Tr} \mathbf{AB} = \text{Tr} \mathbf{BA}$

$$N = \sum_{\mu} (\mathbf{S}^{\alpha} \mathbf{P} \mathbf{S}^{1-\alpha})_{\mu\mu} \quad (363)$$

with a value of $\alpha \leq 1$. In particular

$$Q^A(\text{Löwdin}) = Z_A - \sum_{\mu \in A} (\mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2})_{\mu\mu} \quad (364)$$

This is the *Löwdin-population analysis*.

14.3 Potential-fitted charges

The electrostatic properties (multipole moments, electrostatic potential, etc.) cannot be described by Mulliken (or Löwdin) charges correctly. Take the molecular dipole moment.

$$\begin{aligned}
\boldsymbol{\mu} &= \sum_A Z_A \mathbf{R}^A - \sum_A \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu} \langle \chi_{\mu} | \hat{\mathbf{r}} | \chi_{\nu} \rangle \\
&= \sum_A Z_A \mathbf{R}^A - \sum_A \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu} \langle \chi_{\mu} | \mathbf{R}^A + \hat{\mathbf{r}}^A | \chi_{\nu} \rangle \\
&= \sum_A Z_A \mathbf{R}^A - \sum_A \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} \mathbf{R}^A - \sum_A \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu} \langle \chi_{\mu} | \hat{\mathbf{r}}^A | \chi_{\nu} \rangle \\
&= \sum_A Q^A \mathbf{R}^A - \sum_A \boldsymbol{\mu}^A = \boldsymbol{\mu}(\text{Mulliken}) + \sum_A \boldsymbol{\mu}_A
\end{aligned} \tag{365}$$

If the molecular multipoles (dipole, etc.) are wrong, asymptotic behaviour of the electrostatic potential calculated from them

$$V(\mathbf{r}_k) = \sum_A \frac{Q^A}{|\mathbf{r}_k - \mathbf{R}_A|} \tag{366}$$

is also incorrect.

Approximately correct electrostatics can be obtained from fitted charges. Take the expression of the potential on a grid of points

$$V(\mathbf{r}_k) = \sum_a \frac{q^a}{|\mathbf{r}_k - \mathbf{R}_a|} = \sum_a T^{ka} q^a \quad k = 1, \dots, N_{grid} \tag{367}$$

and look for the best set of charges that reproduce the quantum chemically calculated electrostatic potential in the same points,

$$\mathcal{V}_k = \sum_A \frac{Z^A}{|\mathbf{r}_k - \mathbf{R}_A|} - \sum_{\mu\nu} P_{\mu\nu} \langle \chi_{\mu} | \frac{1}{|\mathbf{r}_k - \mathbf{r}|} | \chi_{\nu} \rangle \tag{368}$$

This leads to an overdetermined system of equations ($N_{grid} \gg N_a$)

$$\mathcal{V}_k = \sum_a T^{ka} q^a \tag{369}$$

In matrix form, the formal solution (in the least squares sense)

$$\begin{aligned}
\mathbf{v} &= \mathbf{T} \mathbf{q} \\
\mathbf{q} &= (\mathbf{T}^\dagger \mathbf{T})^{-1} \mathbf{v}
\end{aligned} \tag{370}$$

Depend to some extent on the choice of sampling grid.

14.4 Covalent bond orders

Correlation of fluctuation of the number of electrons associated to two atoms

$$B_{AB} = -2(\langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle) \tag{371}$$

is considered as a measure of the covalent bond order between two atoms.

It can be shown that it is related to the change of correlation content during bond formation in the diatomic fragment. The deviation of the pair density from the simple product of one-particle densities is the correlation function, $f(\mathbf{r}_1, \mathbf{r}_2)$

$$\gamma(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \varrho(\mathbf{r}_1) \varrho(\mathbf{r}_2) [1 + f(\mathbf{r}_1, \mathbf{r}_2)] \quad (372)$$

Integrated on a given region (e.g. atomic region), it gives the total correlation content

$$F(\Omega_A, \Omega_A) = \int_{\Omega_A} d\mathbf{r}_1 \int_{\Omega_A} d\mathbf{r}_2 \varrho(\mathbf{r}_1) \varrho(\mathbf{r}_2) f(\mathbf{r}_1, \mathbf{r}_2) \quad (373)$$

The correlation content is dominated by the exchange correlation component, therefore the bond order is often related to directly with the exchange part of the above quantity

$$B_{AB} = 2 \int_{\Omega_A} d\mathbf{r}_1 \int_{\Omega_B} d\mathbf{r}_2 [\varrho_\alpha(\mathbf{r}_2; \mathbf{r}_1) \varrho_\alpha(\mathbf{r}_1; \mathbf{r}_2) + \varrho_\beta(\mathbf{r}_2; \mathbf{r}_1) \varrho_\beta(\mathbf{r}_1; \mathbf{r}_2)] \quad (374)$$

Using Mulliken's definition of the atomic population, we get the following bond order definition

$$B_{AB} = \sum_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} + (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} \quad (375)$$

Gives 1 for single, 2 for double and 3 for triple bonds.

14.5 Implementation of the HFR equations: SCF procedure

We suppose that a reasonable initial guess of the P-matrix, $\mathbf{P}^{(0)}$, is available. For a closed shell system

- Calculate the one-electron integrals to form the core-Hamiltonian matrix

$$H_{\mu\nu}^{core} = T_{\mu\nu} + V_{\mu\nu}^{nucl} \quad (376)$$

- Calculate the list of two-electron integrals

$$(\mu\nu|\lambda\sigma) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \chi_\mu^*(1) \chi_\nu(1) r_{12}^{-1} \chi_\lambda^*(2) \chi_\sigma(2) \quad (377)$$

There are $O(K^4/8)$ unique integrals, therefore this step constitutes the major part of the computational effort.

- Form the Fock matrix of the n -th iteration

$$F_{\mu\nu}^{(n)} = H_{\mu\nu}^{core} + \sum_{\lambda\sigma} P_{\lambda\sigma}^{(n-1)} [2(\mu\nu|\lambda\sigma) - (\mu\lambda|\sigma\nu)] = H_{\mu\nu}^{core} + G_{\mu\nu}(\mathbf{P}^{(n-1)}) \quad (378)$$

- Solve the matrix equation

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \quad (379)$$

- Introduce the *canonical orthogonalization* (avoiding problems with linearly dependent basis sets) by the following equations

$$\mathbf{U}^\dagger \mathbf{SU} = \mathbf{s} \quad \mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2} \quad (380)$$

- Transform the Roothaan equations directly by substituting $\mathbf{C} = \mathbf{XC}'$

$$\begin{aligned} \mathbf{FXC}' &= \mathbf{SXC}'\boldsymbol{\varepsilon} \\ (\mathbf{X}^\dagger \mathbf{FX})\mathbf{C}' &= (\mathbf{X}^\dagger \mathbf{SX})\mathbf{C}'\boldsymbol{\varepsilon} \end{aligned} \quad (381)$$

- Diagonalize $\mathbf{F}' = (\mathbf{X}^\dagger \mathbf{F} \mathbf{X})$ to get \mathbf{C}' and ϵ
- Transform back the coefficient matrix to the original basis

$$\mathbf{C} = \mathbf{X} \mathbf{C}' \quad (382)$$

- Form a new P-matrix

$$\mathbf{P}^{n+1} = \mathbf{C} \mathbf{C}^\dagger \quad (383)$$

- Check convergence by comparing $\mathbf{P}^{(n)}$ and $\mathbf{P}^{(n+1)}$; if necessary start a new cycle

14.6 Direct SCF procedure

After a few SCF cycles, most of the P-matrix elements do not change appreciably. Consider the Fockian update formula

$$\mathbf{F}^{(n)} = \mathbf{H} + \mathbf{G}(\mathbf{P}^{(n-1)}) \quad (384)$$

The density matrix of the $(n-1)$ th iteration is $\mathbf{P}^{(n-1)} = \mathbf{P}^{(n-2)} + \Delta\mathbf{P}^{(n-1)}$. Since

$$\mathbf{F}^{(n-1)} = \mathbf{H} + \mathbf{G}(\mathbf{P}^{(n-2)}) \quad (385)$$

the update formula can be written also as

$$\mathbf{F}^{(n)} = \mathbf{F}^{(n-1)} + \mathbf{G}(\Delta\mathbf{P}^{(n-1)}) \quad (386)$$

The matrix of two-electron update matrix

$$\mathbf{G}(\Delta\mathbf{P}^{(n-1)})_{\mu\nu} = \sum_{\lambda\sigma} \Delta P_{\lambda\sigma}^{(n-1)} [2(\mu\mu|\lambda\sigma) - (\mu\lambda|\sigma\nu)] \quad (387)$$

is sparse and we need only those two-electron integrals, which are multiplied by $|\Delta P_{\mu\nu}^{(n-1)}| > \epsilon$. These integrals can be calculated directly, at each iteration, thus reducing huge data storage and disk access overheads.

14.7 Basis sets

- Slater type orbitals (STO) or exponential orbitals (ETO)

$$\chi_{nlm}^{STO}(\mathbf{r}_a) = N r_a^{n-1} e^{-\zeta r_a} \cdot Y_\ell^m(\theta_a, \phi_a) \quad (388)$$

- correct $R \rightarrow 0$ and $R \rightarrow \infty$ behaviour
- atomic HF orbitals are linear combinations of a few STOs
- a molecular basis set may contain one, two (*double* ζ), three (*triple* ζ), four (*quadruple* ζ), etc. sets of STOs per atom
- Electron repulsion integrals (ERI) are difficult to calculate for more than two centers

- Gaussian type orbitals (GTO)

$$\begin{aligned} g_{uvw}(\mathbf{r}_a) &= N x^u y^v z^w \cdot e^{-\alpha r_a^2} && \text{(Cartesian)} \\ g_{nlm}(\mathbf{r}_a) &= N e^{-\alpha r_a^2} r_a^{n-1} \cdot Y_\ell^m(\theta_a, \phi_a) && \text{(spherical)} \end{aligned} \quad (389)$$

- incorrect behaviour at $R \rightarrow 0$ (no cusp) and at $R \rightarrow \infty$ (too fast decay)
- much more (5–10 times) GTOs are needed to describe an atomic HF orbital
- basis functions are fixed combination of primitive Gaussians: *contracted Gaussian functions*
- easy calculation of ERIs for three and four centers too (product theorem)

14.8 Product theorem for Gaussian functions

The ERIs involve the product of two primitive Gaussian functions

$$\exp(-\alpha r_a^2) \exp(-\beta r_b^2) = \prod_{i=x,y,z} \exp(-\alpha(r_i - A_i)^2 - \beta(r_i - B_i)^2) \quad (390)$$

We can transform the exponent, e.g. for the component x

$$\begin{aligned} -\alpha(x - A_x)^2 - \beta(x - B_x)^2 &= -\alpha(x^2 - 2A_x x + A_x^2) - \beta(x^2 - 2B_x x + B_x^2) \\ &= -(\alpha + \beta) \left(x^2 - 2x \frac{\alpha A_x + \beta B_x}{\alpha + \beta} + \frac{\alpha A_x^2 + \beta B_x^2}{\alpha + \beta} \right) \\ &= -(\alpha + \beta) \left[\left(x - \frac{\alpha A_x + \beta B_x}{\alpha + \beta} \right)^2 - \frac{\alpha \beta}{\alpha + \beta} (A_x - B_x)^2 \right] \end{aligned} \quad (391)$$

leading to a new Gaussian function

$$\exp\left(-\frac{\alpha\beta}{\alpha + \beta} (A_x - B_x)^2\right) \cdot \exp\left(-(\alpha + \beta)(x - X_{AB})^2\right) \quad (392)$$

with $(\alpha + \beta)$ exponent and

$$X_{AB} = \frac{\alpha A_x + \beta B_x}{\alpha + \beta} \quad (393)$$

center. It means that even four-center integrals can be handled as easily as two-center ones.

14.9 Contracted Gaussian functions

Reduce the number of variational parameters in the HFR equations by taking fixed linear combination of primitive functions

$$\chi_\mu^{CGF}(\mathbf{r} - \mathbf{R}_A) = \sum_{p=1}^L d_{p\mu} g_p(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_A) \quad (394)$$

- STO-nG basis sets
obtained as least square fits to STO basis function with $\zeta = 1.0$
- generalized contraction
MOs from atomic GTO calculations
- ANO basis
atomic natural orbitals from correlated atomic calculations
- split-valence basis sets
minimal contracted basis for core orbitals, more flexibility for valence shell: valence double zeta (VDZ), valence triple zeta (VTZ)
- polarization functions
have higher angular quantum number than the highest occupied atomic orbital
- diffuse functions
to describe excited states, negative ions

14.10 Second Quantized Hamiltonian in AO basis

In non-orthogonal basis, like the AO basis, creation and annihilation operators follow the anticommutation relation

$$[\chi_\nu^+, \chi_\mu^-]_+ = S_{\mu\nu} \quad (395)$$

and the operators χ_μ^- do not act as true annihilation operators. Try to find the “true” annihilation operators $\tilde{\chi}_\mu^-$ associated with χ_ν^+ , by requiring to satisfy the usual anticommutation rule

$$[\chi_\mu^+, \tilde{\chi}_\nu^-]_+ = \delta_{\mu\nu} \quad (396)$$

Expand $\tilde{\chi}_\nu^-$ as linear combination of χ_λ^-

$$\tilde{\chi}_\nu^- = \sum_\lambda L_{\nu\lambda} \chi_\lambda^- \quad (397)$$

Substitution into Eq.(396) gives

$$[\chi_\mu^+, \tilde{\chi}_\nu^-]_+ = \sum_\lambda L_{\nu\lambda} [\chi_\mu^+, \chi_\lambda^-]_+ = \sum_\lambda L_{\nu\lambda} S_{\lambda\mu} = \delta_{\mu\nu} \quad (398)$$

The above relationship is satisfied if $\mathbf{L} = \mathbf{S}^{-1}$

$$\tilde{\chi}_\nu^- = \sum_\lambda S_{\nu\lambda}^{-1} \chi_\lambda^- \quad (399)$$

In general, a set of functions $\{\tilde{\chi}_i\}$ form the bi-orthogonal set related to the non-orthogonal set $\{\chi_i\}$ if they satisfy the $\langle \tilde{\chi}_i | \chi_j \rangle = \delta_{ij}$ relation. The $\tilde{\chi}_\lambda^-$ operators form a bi-orthogonal set related to χ_μ^- .

Let us write the Hamiltonian with the symmetrically orthogonalized auxiliary AO basis set $\psi_i = \sum_\mu S_{i\mu}^{-1/2} \chi_\mu^-$. In this orthogonal basis the Hamiltonian has the usual form

$$\hat{H} = \sum_{ij} h_{ij} \psi_i^+ \psi_j^- + \frac{1}{2} \sum_{ijkl} \langle ij|kl \rangle \psi_i^+ \psi_j^+ \psi_l^- \psi_k^- \quad (400)$$

After transformation of the *operators* to the original overlapping AO basis

$$\begin{aligned} \hat{H} &= \sum_{ij} \sum_{\mu\nu} h_{ij} S_{\mu i}^{-1/2} S_{j\nu}^{-1/2} \chi_\mu^+ \chi_\nu^- \\ &+ \frac{1}{2} \sum_{ijkl} \sum_{\mu\nu\lambda\sigma} \langle ij|kl \rangle S_{\mu i}^{-1/2} S_{\nu j}^{-1/2} S_{l\sigma}^{-1/2} S_{k\lambda}^{-1/2} \chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^- \end{aligned} \quad (401)$$

Transform back the one-electron integrals too into the original basis

$$h_{ij} = \sum_{\alpha\beta} S_{i\alpha}^{-1/2} S_{\beta j}^{-1/2} h_{\alpha\beta} \quad (402)$$

and similarly for the two-electron integrals. Summation over i, k and j, l leads to the following relatively simple form

$$\hat{H} = \sum_{\mu\nu\alpha\beta} S_{\mu\alpha}^{-1} h_{\alpha\beta} S_{\beta\nu}^{-1} \chi_\mu^+ \chi_\nu^- + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \sum_{\alpha\beta\gamma\delta} S_{\mu\alpha}^{-1} S_{\nu\beta}^{-1} \langle \alpha\beta|\gamma\delta \rangle S_{\gamma\sigma}^{-1} S_{\delta\lambda}^{-1} \chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^- \quad (403)$$

We can take advantage of the simple anticommutation relations between χ_μ^+ and $\tilde{\chi}_\lambda^-$, if we use the above Hamiltonian in the following form

$$\hat{H} = \sum_{\mu\nu} h_{\mu\nu} \chi_\mu^+ \tilde{\chi}_\nu^- + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle \tilde{\mu}\tilde{\lambda}|\nu\sigma \rangle \chi_\mu^+ \chi_\nu^+ \tilde{\chi}_\sigma^- \tilde{\chi}_\lambda^- \quad (404)$$

where the half-transformed integrals are defined as

$$h_{\tilde{\mu}\nu} = \sum_{\lambda} S_{\mu\lambda}^{-1} h_{\lambda\nu} \quad (405)$$

and

$$(\tilde{\mu}\tilde{\lambda}|\nu\sigma) = \sum_{\tau\epsilon} S_{\mu\tau}^{-1} S_{\lambda\epsilon}^{-1} (\tau\epsilon|\nu\sigma) \quad (406)$$

In order to calculate the expectation values of the operator strings in this energy expression, let us consider the AO/MO transformations in both original and bi-orthogonal bases.

$$\phi = \mathbf{C}^\dagger \chi \quad \chi = (\mathbf{C}^\dagger)^{-1} \phi \quad (407)$$

using that the MOs are orthonormal

$$\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1} \quad (\mathbf{C}^\dagger)^{-1} = \mathbf{S} \mathbf{C} \quad (408)$$

and the definition of the bi-orthogonal orbitals

$$\tilde{\chi} = \chi^\dagger \mathbf{S}^{-1} = \phi^\dagger \mathbf{C}^\dagger \quad (409)$$

we get the relationships

$$\chi_\mu^+ = \sum_i (\mathbf{C}^\dagger \mathbf{S})_{i\mu} \phi_i^+ \quad \tilde{\chi}_\mu^- = \sum_i c_{\mu i} \phi_i^- \quad (410)$$

Substitution of these expressions and taking the expectation value

$$\begin{aligned} \langle \chi_\mu^+ \tilde{\chi}_\nu^- \rangle &= (\mathbf{P} \mathbf{S})_{\nu\mu} \\ \langle \chi_\mu^+ \chi_\nu^+ \tilde{\chi}_\sigma^- \tilde{\chi}_\lambda^- \rangle &= \sum_{\eta\tau} \Gamma_{\sigma\lambda\eta\tau} S_{\eta\mu} S_{\tau\nu} \end{aligned} \quad (411)$$

In the special case of HF wave functions we obtain for the two-particle string

$$\begin{aligned} \langle \text{HF} | \chi_\mu^+ \chi_\nu^+ \tilde{\chi}_\sigma^- \tilde{\chi}_\lambda^- | \text{HF} \rangle &= \sum_{\eta\tau} (P_{\sigma\tau} P_{\lambda\eta} - P_{\sigma\eta} P_{\lambda\tau}) S_{\eta\mu} S_{\tau\nu} \\ &= (\mathbf{P} \mathbf{S})_{\sigma\nu} (\mathbf{P} \mathbf{S})_{\lambda\mu} - (\mathbf{P} \mathbf{S})_{\sigma\mu} (\mathbf{P} \mathbf{S})_{\lambda\nu} \end{aligned} \quad (412)$$

14.11 Hellmann-Feynman theorem

Consider a Hamiltonian, which depends on one or more parameters, α_i

$$\hat{H}(\boldsymbol{\alpha}) = \hat{H}(0) + \sum_i \alpha_i \hat{A}_i \quad (413)$$

The first derivative of the total energy for a (normalized) Hartree-Fock determinant wave function, D is

$$\frac{\partial E}{\partial \alpha_i} = \frac{\partial}{\partial \alpha_i} \langle D | \hat{H} | D \rangle = \left\langle \frac{\partial D}{\partial \alpha_i} | \hat{H} | D \right\rangle + \langle D | \frac{\partial \hat{H}}{\partial \alpha_i} | D \rangle + \left\langle D | \hat{H} | \frac{\partial D}{\partial \alpha_i} \right\rangle \quad (414)$$

Since the Hartree-Fock wave function is stationary with respect to *any* variation in the class of one-determinant wave functions, we remain with

$$\frac{\partial E}{\partial \alpha} = \langle D | \frac{\partial \hat{H}}{\partial \alpha} | D \rangle = \langle D | \hat{A}_i | D \rangle \quad (415)$$

The *exact* Hartree-Fock wave function satisfies the Hellmann-Feynman theorem.

Let us apply this result to the calculation of the molecular dipole moment. The Hamiltonian in the presence of an electric field

$$\hat{H}(\mathbf{F}) = \hat{H}(0) + F_\alpha \hat{\mu}_\alpha$$

where $\hat{\mu}_\alpha$ is the $\alpha = x, y, z$ component of the multipole moment operator. Expanding the total energy in Taylor series

$$E(\mathbf{F}) = E(0) + \left(\frac{\partial E(\mathbf{F})}{\partial F_\alpha} \right)_{\mathbf{F}=0} F_\alpha + \frac{1}{2} \left(\frac{\partial^2 E(\mathbf{F})}{\partial F_\alpha \partial F_\beta} \right)_{\mathbf{F}=0} F_\alpha F_\beta + \dots \quad (416)$$

The dipole moment is defined as

$$\mu_\alpha = - \left(\frac{\partial E(\mathbf{F})}{\partial F_\alpha} \right)_{\mathbf{F}=0} \quad (417)$$

According the previous result, the dipole moment can be calculated from a HF wave function as the expectation value

$$\mu_\alpha = - \langle D | \hat{\mu}_\alpha | D \rangle \quad (418)$$

In the case of non-variational wave functions the molecular properties must be calculated from the energy derivatives.

14.12 Hartree-Fock gradients

Exact solutions of the molecular Hamiltonian require infinite basis sets. The advantage of the SQ formalism is that eigenfunctions of the SQ Hamiltonian *in a given finite basis set* are exact solutions of this model Hamiltonian. Therefore, the Hellmann-Feynman theorem applies to its exact eigenfunctions, as well as variational solutions, like the Hartree-Fock wave function, in the given finite basis.

The derivative of the energy can be calculated as

$$\delta E = \langle \Psi | \delta \hat{H} | \Psi \rangle \quad (419)$$

The derivative of the SQ Hamiltonian

$$\delta \hat{H} = \sum_{\mu\nu} \delta h_{\bar{\mu}\nu} \chi_\mu^+ \tilde{\chi}_\nu^+ + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta \langle \tilde{\mu}\tilde{\lambda} | \nu\sigma \rangle \chi_\mu^+ \chi_\nu^+ \tilde{\chi}_\sigma^- \tilde{\chi}_\lambda^- \quad (420)$$

Use the expectation values of the operator strings and the following relationships to calculate the derivative of the half-transformed AO-integrals, e.g.

$$\delta(\mathbf{S}^{-1}\mathbf{h}) = \delta\mathbf{S}^{-1} \cdot \mathbf{h} + \mathbf{S}^{-1} \cdot \delta\mathbf{h} \quad \delta\mathbf{S}^{-1} = \mathbf{S}^{-1} \delta\mathbf{S} \mathbf{S}^{-1} \quad (421)$$

We obtain for the special case HF wave function

$$\delta E^{\text{HF}} = \sum_{\mu\nu} \delta h_{\mu\nu} P_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta \langle \mu\nu | \lambda\sigma \rangle (P_{\lambda\mu} P_{\sigma\nu} - P_{\lambda\nu} P_{\sigma\mu}) - \sum_{\mu\nu\lambda\sigma} F_{\mu\nu} P_{\nu\lambda} \delta S_{\lambda\sigma} S_{\sigma\mu}^{-1} \quad (422)$$

Using the definition of the P-matrix and the SCF condition $\sum_\nu F_{\mu\nu} c_{\nu i} = \varepsilon_i \sum_\nu S_{\mu\nu} c_{\nu i}$ the last term can be rewritten as

$$- \sum_{\mu\nu} \underbrace{\sum_i^{\text{occ}} \varepsilon_i c_{\mu i} c_{\nu i}^*}_{W_{\mu\nu}} \delta S_{\nu\mu} \quad (423)$$

and we obtain the final result

$$\delta E^{\text{HF}} = \sum_{\mu\nu} \delta h_{\mu\nu} P_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta \langle \mu\nu | \lambda\sigma \rangle (P_{\lambda\mu} P_{\sigma\nu} - P_{\lambda\nu} P_{\sigma\mu}) - \sum_{\mu\nu} W_{\mu\nu} \delta S_{\nu\mu} \quad (424)$$

This expression is completely general. In the special case of forces the derivatives are taken with respect to the nuclear coordinates. Since the atomic orbitals follow the nuclei (*orbital following*) the geometrical derivatives of the integrals enter in the force expression (wave function forces).

14.13 BSSE

Take a complex A∪B and trace the energy as a function of their separation, $E_{\text{A} \cup \text{B}}(\mathbf{R}, \mathbf{\Omega})$. As a consequence of the *orbital-following principle*, we have a different basis set at each distance and relative orientation. In particular, for the interaction energy

$$\Delta E = E_{\text{A} \cup \text{B}}(\mathbf{R}, \mathbf{\Omega}) - E_{\text{A} \cup \text{B}}(\mathbf{R} = \infty, \mathbf{\Omega}) = E_{\text{A} \cup \text{B}}(\mathbf{R}, \mathbf{\Omega}) - E_{\text{A}} - E_{\text{B}} \quad (425)$$

At small separations the partner basis functions improve the monomer description (nothing to do with the physical interaction) and lead to an extra stabilization of the complex.

Remedy: Boys-Bernardi counterpoise correction

Calculate monomer energies in the dimer basis at each geometry

$$\Delta E = E_{\text{A} \cup \text{B}}(\mathbf{R}, \mathbf{\Omega}) - E_{\text{A}}(\text{A} \cup \text{B} | \mathbf{R}, \mathbf{\Omega}) - E_{\text{B}}(\text{A} \cup \text{B} | \mathbf{R}, \mathbf{\Omega}) \quad (426)$$

As an example, the dissociation curve of the Ar dimer. An artificial minimum appears in the RHF calculations; after counterpoise correction the potential curve has no minimum (electron correlation would be needed to describe the van der Waals minimum in this system).

14.14 Response properties

In the Taylor-expansion of the total energy of a system in the presence of an external perturbation

$$E(\mathbf{F}) = E(0) + \left(\frac{\partial E(\mathbf{F})}{\partial F_{\alpha}} \right)_{\mathbf{F}=0} F_{\alpha} + \frac{1}{2} \left(\frac{\partial^2 E(\mathbf{F})}{\partial F_{\alpha} \partial F_{\beta}} \right)_{\mathbf{F}=0} F_{\alpha} F_{\beta} + \dots \quad (427)$$

the second-order terms are related to the polarizability, i.e. linear *response* of the system to the perturbation

$$\alpha_{\alpha\beta} = \left(\frac{\partial^2 E(\mathbf{F})}{\partial F_{\alpha} \partial F_{\beta}} \right)_{\mathbf{F}=0} \quad (428)$$

We can apply the general Taylor-expansion of the energy by remarking that in the presence of an external perturbation

$$\begin{aligned} \hat{H} &= \hat{H}_0 + \hat{H}' \\ \mathbf{a} &= \nabla H = \nabla H_0 + \nabla H' \end{aligned} \quad (429)$$

If the unperturbed energy is variational, $\nabla H_0 = 0$, we obtain the following equation for the parameter variations, \mathbf{d} that make the perturbed system energy stationary

$$\begin{pmatrix} \nabla H' \\ H' \nabla \end{pmatrix} + \begin{pmatrix} \mathbf{M} & \mathbf{Q} \\ \mathbf{Q}^* & \mathbf{M}^* \end{pmatrix} \begin{pmatrix} \mathbf{d} \\ \mathbf{d}^* \end{pmatrix} = 0 \quad (430)$$

which simplifies in case of real wave function and perturbation as

$$\nabla H' + (\mathbf{M} + \mathbf{Q})\mathbf{d} = \mathbf{0} \quad (431)$$

The first order parameter change, \mathbf{d} is proportional to the derivative of the Hamiltonian $\mathbf{a} = \nabla H'$

$$\mathbf{d} = (\mathbf{M} + \mathbf{Q})^{-1} \mathbf{a} \quad (432)$$

In the case of an external field perturbation $\hat{H}' = \sum_{\alpha} F_{\alpha} \hat{\mu}_{\alpha}$ the energy can be expressed as

$$E = E_0 - 2 \sum_{\alpha} \sum_{\beta} F_{\alpha} (\nabla \mu_{\alpha})^{\dagger} (\mathbf{M} + \mathbf{Q})^{-1} (\mu_{\beta} \nabla) F_{\beta} \quad (433)$$

Comparison with the definition of the electric dipole polarizability yields immediately

$$\alpha_{\alpha\beta} = (\nabla \mu_{\alpha})^{\dagger} (\mathbf{M} + \mathbf{Q})^{-1} (\mu_{\beta} \nabla) \quad (434)$$

14.15 General wave function variation

We have seen that the first order variation of a single determinant wave function can be parameterized as

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{ar} p_{ar} |\Psi_a^r\rangle \quad (435)$$

A more general approach, valid to any kind of wave function and also to higher order variations, can be developed by SQ.

Let us describe the variation of orbitals as resulting from a unitary transformation, $\psi'_i = \sum_k \psi_k U_{ki}$, which means that the corresponding creation and annihilation operators transform according to

$$\begin{aligned} a_i^{\dagger} &= \sum_k a_k^{\dagger} U_{ki} \\ a_i' &= \sum_k a_k U_{ki}^* \end{aligned} \quad (436)$$

- The unitary transformation can be written as

$$a_i^{\dagger} = \exp(-i\hat{\Lambda}) a_i^{\dagger} \exp(i\hat{\Lambda}) \quad (437)$$

where $\hat{\Lambda}$ is a hermitian operator

$$\hat{\Lambda} = \sum_i \sum_j \Lambda_{ij} a_i^{\dagger} a_j \quad (438)$$

Using the expansion of the exponential operator

$$\exp(-i\hat{\Lambda}) a_i^{\dagger} \exp(i\hat{\Lambda}) = a_i^{\dagger} + [a_i^{\dagger}, i\hat{\Lambda}] + \frac{1}{2} [[a_i^{\dagger}, i\hat{\Lambda}], i\hat{\Lambda}] + \dots \quad (439)$$

The commutator expressions can be simplified using the anticommutator relationships, e.g.

$$\begin{aligned} [a_i^{\dagger}, a_k^{\dagger} a_l] &= a_i^{\dagger} a_k^{\dagger} a_l - a_k^{\dagger} a_l a_i^{\dagger} \\ &= -a_k^{\dagger} a_i^{\dagger} a_l - a_k^{\dagger} a_l a_i^{\dagger} \\ &= -a_k^{\dagger} (\delta_{il} - a_l a_i^{\dagger}) - a_k^{\dagger} a_l a_i^{\dagger} = -a_k^{\dagger} \delta_{il} \end{aligned} \quad (440)$$

Applied to the first commutator

$$[a_i^{\dagger}, i\hat{\Lambda}] = \sum_{kl} i\Lambda_{kl} [a_i^{\dagger}, a_k^{\dagger} a_l] = \sum_{kl} i\Lambda_{kl} (-a_k^{\dagger} \delta_{il}) = -\sum_k a_k^{\dagger} i\Lambda_{ki} \quad (441)$$

The second-order commutator yields

$$[[a_i^+, i\hat{\Lambda}], i\hat{\Lambda}] = \sum_k a_k^+ (i\hat{\Lambda}i\hat{\Lambda})_{ki} \quad (442)$$

and finally one can show that

$$\exp(-i\hat{\Lambda})a_i^+ \exp(i\hat{\Lambda}) = \sum_k a_k^+ (1 - i\hat{\Lambda} + \frac{1}{2}(i\hat{\Lambda}i\hat{\Lambda}) + \dots)_{ki} = \sum_k a_k^+ \exp(-i\hat{\Lambda})_{ki} \quad (443)$$

This is a unitary transformation, provided that $\mathbf{\Lambda}$ is hermitian, i.e. we can parameterize the transformation as

$$\mathbf{U} = \exp(-i\mathbf{\Lambda}) \quad (444)$$

- The effect of orbital transformations is identical to a unitary (norm conserving!) transformation of the wave function. Consider a transformed determinant Ψ

$$\begin{aligned} |\Psi'\rangle &= a_1'^+ a_2'^+ \dots a_N'^+ |\text{vac}\rangle \\ &= e^{(-i\hat{\Lambda})} a_1^+ e^{(i\hat{\Lambda})} e^{(-i\hat{\Lambda})} a_2^+ e^{(i\hat{\Lambda})} \dots e^{(-i\hat{\Lambda})} a_N^+ e^{(i\hat{\Lambda})} |\text{vac}\rangle \\ &= \exp(-i\hat{\Lambda}) a_1^+ a_2^+ \dots a_N^+ |\text{vac}\rangle = \exp(-i\hat{\Lambda}) |\Psi\rangle \end{aligned} \quad (445)$$

and the result holds for any linear combination of determinants too.

- Since the hermitian matrix $\mathbf{\Lambda}$ can be expressed with the real symmetric and antisymmetric matrices $\boldsymbol{\lambda}$ and \mathbf{K} as $\mathbf{\Lambda} = \boldsymbol{\lambda} + i\mathbf{K}$ and the purely imaginary part of the transformation concerns only an uninteresting phase factor $\exp(i\boldsymbol{\lambda})$, we can write

$$\hat{U} = \exp(-i\hat{\Lambda}) = \exp(\hat{K}) \quad (446)$$

- For small values of the transformation parameters, Λ_{kl} , we can expand the exponential operator as

$$|\Psi'\rangle = \exp(\hat{K})|\Psi\rangle = |\Psi\rangle + \sum_{kl} K_{kl} a_k^+ a_l |\Psi\rangle - \frac{1}{2} \sum_{kl} \sum_{mn} K_{kl} K_{mn} a_k^+ a_l a_m^+ a_n |\Psi\rangle + \dots \quad (447)$$

Bring the operator product of last term in the normal order

$$a_k^+ a_l a_m^+ a_n = a_k^+ (\delta_{lm} - a_m^+ a_l) a_n = \delta_{lm} a_k^+ a_n + a^k a_m^+ a_n a_l \quad (448)$$

and the transformed wave function is written as a linear combination of singly-, doubly-, etc. excited configurations

$$|\Psi'\rangle = |\Psi\rangle + \sum_{kl} K_{kl} |\Psi_l^k\rangle - \frac{1}{2} \sum_{kl} \sum_{mn} K_{kl} K_{mn} (\delta_{lm} |\Psi_l^k\rangle + |\Psi_{ln}^{km}\rangle) + \dots \quad (449)$$

14.16 Coupled Hartree-Fock equations

Having a general expression of the parameterization of the wave function, we can write the energy as

$$\begin{aligned} E &= \langle \Psi | e^{-\hat{K}} \hat{H} e^{\hat{K}} | \Psi \rangle \\ &= \langle \Psi | (1 - \hat{K} + \frac{1}{2!} \hat{K}^2 - \dots) \hat{H} (1 + \hat{K} + \frac{1}{2!} \hat{K}^2 + \dots) | \Psi \rangle \\ &= \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | [\hat{H}, \hat{K}] | \Psi \rangle + \frac{1}{2!} \langle \Psi | [[\hat{H}, \hat{K}], \hat{K}] | \Psi \rangle + \dots \end{aligned} \quad (450)$$

The operator \hat{K} can be written in term of the one-particle excitation operators \hat{E}_{ij} as

$$\hat{K} = \sum_{ij} p_{ij} a_i^\dagger a_j = \sum_{ij} p_{ij} \hat{E}_{ij} \quad (451)$$

and the Taylor expansion of the energy (for real wave function and variations)

$$E = \langle \Psi | \hat{H} | \Psi \rangle + \sum_{ij} p_{ij} \langle \Psi | [\hat{H}, \hat{E}_{ij}] | \Psi \rangle + \frac{1}{2!} \sum_{ij} \sum_{kl} p_{ij} p_{kl} \langle \Psi | [[\hat{H}, \hat{E}_{ij}], \hat{E}_{kl}] | \Psi \rangle + \dots \quad (452)$$

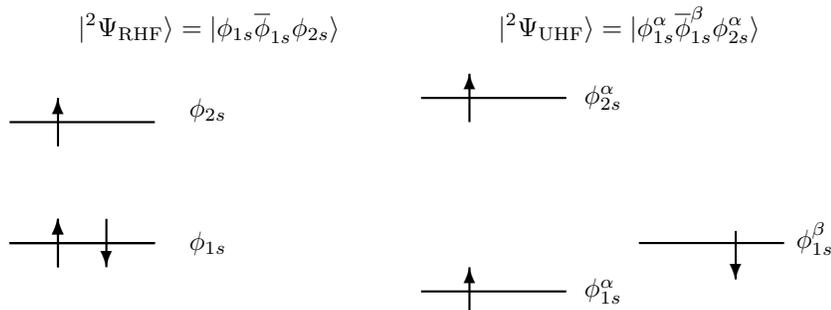
The M and Q matrices can be identified as

$$\begin{aligned} Q_{ij,kl} &= \langle \Psi | \hat{E}_{ij} \hat{H} \hat{E}_{kl} + \hat{E}_{kl} \hat{H} \hat{E}_{ij} | \Psi \rangle \\ M_{ij,kl} &= -\langle \Psi | \hat{H} \hat{E}_{ij} \hat{E}_{kl} + \hat{E}_{kl} \hat{E}_{ij} \hat{H} | \Psi \rangle \end{aligned} \quad (453)$$

The matrix elements in the second derivative of the energy for the special case of a Hartree-Fock wave function are obtained after expansion of the SQ operators.

15 Comparison of RHF and UHF solutions

Example of the Li atom



$1s\alpha$ and $1s\beta$ electrons experience different effective potentials (with and without exchange interaction with $2s\alpha$). The $2s\alpha$ electron “polarizes” the $1s$ shell, and the corresponding spatial functions tend to be different.

The unrestricted doublet state can be expanded on the basis of exact doublet, quadruplet, etc. states:

$$|^2\Psi_{\text{UHF}}\rangle = c_2|2\rangle + c_4|4\rangle + c_6|6\rangle + \dots \quad (454)$$

Since the contamination comes always from higher multiplicity components, $\langle S^2 \rangle_{\text{UHF}}$ is always too large, as can be seen from its [expression](#).

15.1 RHF solution of minimal basis H_2

The molecular orbitals are fully determined by symmetry

$$\begin{aligned} \phi_1 &= \frac{1}{\sqrt{2(1+S_{AB})}} (\chi_a + \chi_b) \\ \phi_2 &= \frac{1}{\sqrt{2(1-S_{AB})}} (\chi_b - \chi_a) \end{aligned} \quad (455)$$

where χ_a and χ_b are $1s$ atomic orbitals on the two H atoms.

As the form of orbitals does not depend on the intermolecular separation, we can analyze the case $R_{ab} \rightarrow \infty$, when $S_{ab} = \langle \chi_a | \chi_b \rangle \rightarrow 0$. The one-determinant RHF wave function

$$\begin{aligned}
\Psi_{R \rightarrow \infty}^{\text{RHF}} &= \hat{\mathcal{A}}[\phi_1(1)\alpha(1) \phi_1(2)\beta(2)] \\
&= \frac{1}{2} \hat{\mathcal{A}}[\{\chi_a(1) + \chi_b(1)\}\alpha(1) \{\chi_a(2) + \chi_b(2)\}\beta(2)] \\
&= \frac{1}{2} \{\hat{\mathcal{A}}[\chi_a \bar{\chi}_a] + \hat{\mathcal{A}}[\chi_b \bar{\chi}_b] \quad \text{ionic terms} \\
&\quad + \hat{\mathcal{A}}[\chi_a \bar{\chi}_b] + \hat{\mathcal{A}}[\chi_b \bar{\chi}_a] \} \quad \text{covalent terms}
\end{aligned} \tag{456}$$

The RHF wave function has an equal weight of “ionic” and “covalent” terms, instead of the correct dissociation limit

$$\Psi_{R \rightarrow \infty} = \frac{1}{\sqrt{2}} \{\hat{\mathcal{A}}[\chi_a \bar{\chi}_b] + \hat{\mathcal{A}}[\chi_b \bar{\chi}_a]\} \tag{457}$$

i.e. the symmetrized combination of two H-atom wave functions.

15.2 UHF orbitals of minimal basis H_2

The unrestricted orbitals are not symmetry-constrained. The one degree of freedom can be incorporated easily if we write the unrestricted orbitals as linear combination of the restricted ones

$$\phi_1^{\alpha,\beta} = \cos \theta \phi_1 \pm \sin \theta \phi_2 \quad \phi_2^{\alpha,\beta} = \mp \sin \theta \phi_1 + \cos \theta \phi_2 \tag{458}$$

These are the unitary transformations which bring the orbitals from the original RHF set $\{\phi_1, \phi_2\}$ to the UHF ones.

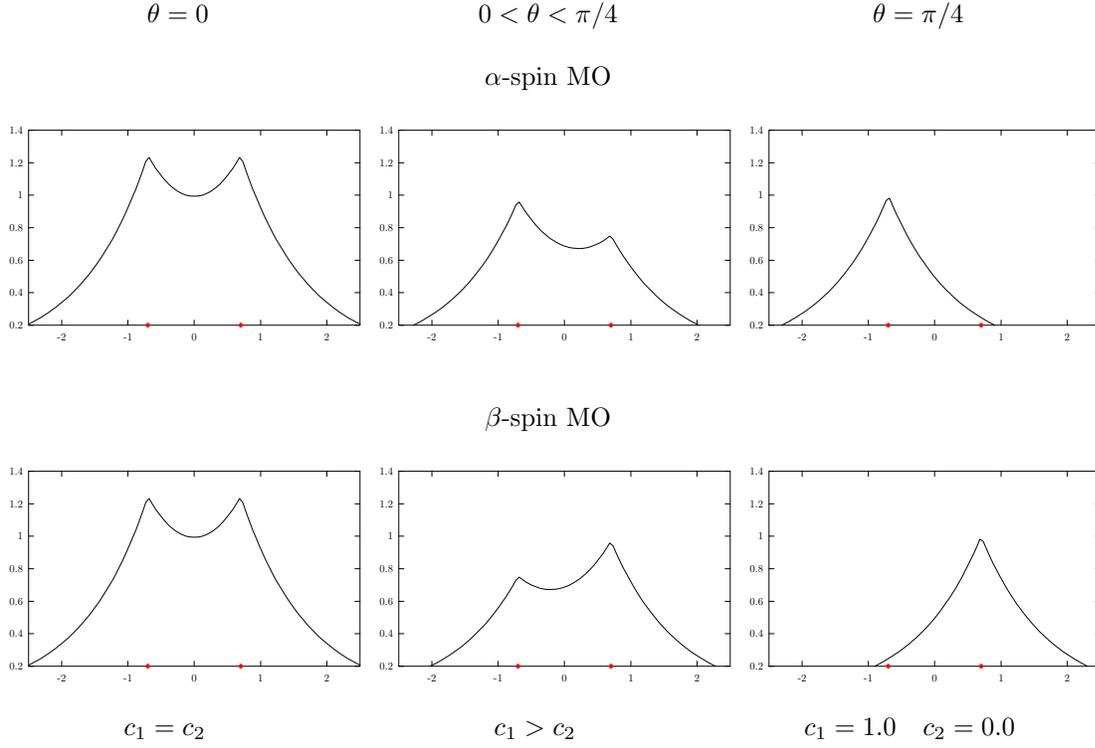
$$\mathbf{U}^{\alpha,\beta} = \begin{pmatrix} \cos \theta & \pm \sin \theta \\ \mp \sin \theta & \cos \theta \end{pmatrix} = \exp \begin{pmatrix} 0 & \pm \theta \\ \mp \theta & 0 \end{pmatrix} \tag{459}$$

The two occupied orbitals of interest can be written in terms of the AOs as

$$\phi_1^\alpha = c_1 \chi_a + c_2 \chi_b \quad \phi_1^\beta = c_2 \chi_a + c_1 \chi_b \tag{460}$$

with the coefficients

$$c_{1,2} = \frac{1}{\sqrt{2(1+S_{ab})}} \cos \theta \pm \frac{1}{\sqrt{2(1-S_{ab})}} \sin \theta \tag{461}$$



15.3 UHF solutions for minimal basis H_2

UHF energy

$$E_0 = (\phi_1^\alpha | \hat{h} | \phi_1^\alpha) + (\phi_1^\beta | \hat{h} | \phi_1^\beta) + (\phi_1^\alpha \phi_1^\alpha | \phi_1^\beta \phi_1^\beta) \quad (462)$$

can be written after expanding the UHF orbitals in terms of the integrals over RHF MOs as

$$E_0(\theta) = 2 \cos^2 \theta h_{11} + 2 \sin^2 \theta h_{22} + \cos^4 \theta J_{11} + \sin^4 \theta J_{22} + 2 \cos^2 \theta \sin^2 \theta (J_{12} - 2K_{12}) \quad (463)$$

The energy is extremum if

$$\begin{aligned} dE_0(\theta)/d\theta &= 4 \cos \theta \sin \theta \\ &\times [h_{22} - h_{11} + \sin^2 \theta J_{22} - \cos^2 \theta J_{11} \\ &+ (\cos^2 \theta - \sin^2 \theta)(J_{12} - 2K_{12})] = 0 \end{aligned} \quad (464)$$

- RHF solution exists at any interatomic distance with $\theta = 0$, i.e.

$$4 \cos \theta \sin \theta = 0 \quad (465)$$

with energy

$$E_0(0) = 2h_{11} + J_{11} = 2\varepsilon_1 - J_{11} \quad (466)$$

- UHF solution exists, if at a given R the values of integrals are such that

$$[h_{22} - h_{11} + \sin^2 \theta J_{22} - \cos^2 \theta J_{11} + (\cos^2 \theta - \sin^2 \theta)(J_{12} - 2K_{12})] = 0 \quad (467)$$

i.e. the equation

$$\cos^2 \theta = \frac{h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} \quad (468)$$

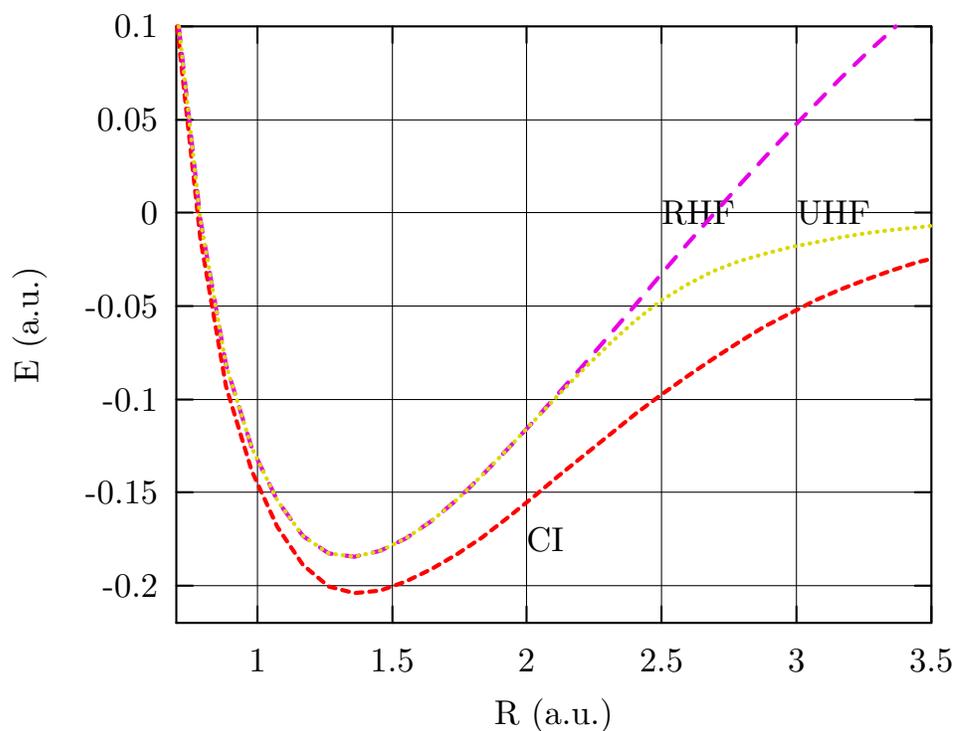
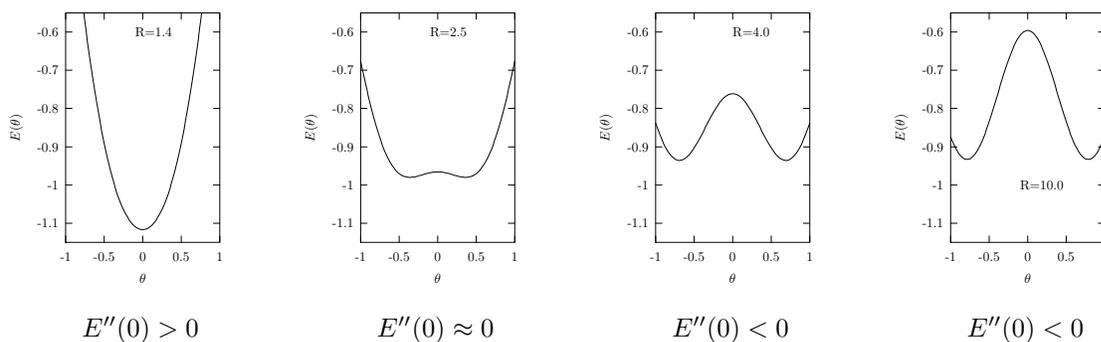
can be satisfied.

15.4 Stability of the RHF/UHF solutions

The nature of the restricted solution can be studied through the second derivative of the energy

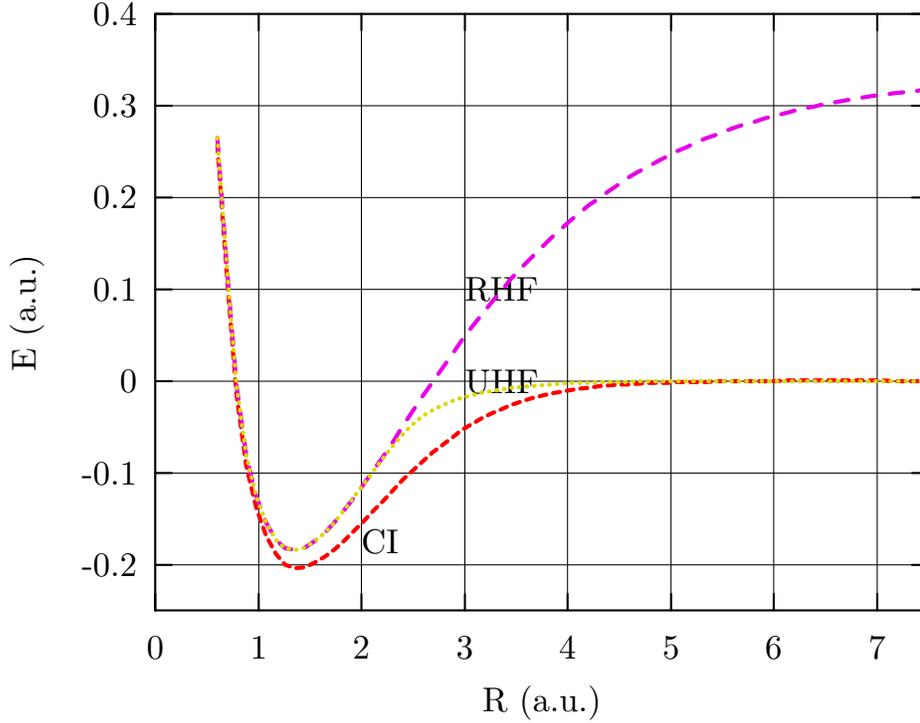
$$\begin{aligned} d^2 E(\theta)/d\theta^2|_{\theta=0} = E''(0) &= 4(h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}) \\ &= 4(\varepsilon_2 - \varepsilon_1 - J_{12} - K_{12}) \end{aligned} \quad (469)$$

At the “saddle point” ($E''(0) = 0$) the UHF and RHF solutions become separated.



15.5 Behaviour at dissociation

The UHF wave function tends to the correct dissociation limit, while the RHF leads to a “dissociation catastrophe”.



The UHF wave function in the $R \rightarrow \infty$ limit is

$$\Psi_{R \rightarrow \infty}^{\text{UHF}} = \hat{A}[\chi_a(1)\bar{\chi}_b(2)] \quad (470)$$

Instead of the correct (symmetrical) form

$$\Psi_{R \rightarrow \infty} = \frac{1}{\sqrt{2}} \{ \hat{A}[\chi_a(1)\bar{\chi}_b(2)] + \hat{A}[\chi_b(1)\bar{\chi}_a(2)] \} \quad (471)$$

Although the orbitals are correct, the wave function is not!

Expand the UHF wave function using the unitary transformation of the orbitals

$$\begin{aligned} |\Psi^{\text{UHF}}\rangle &= |\phi_1^\alpha \bar{\phi}_1^\beta\rangle = |(\cos \theta \phi_1 + \sin \theta \phi_2)(\cos \theta \bar{\phi}_1 - \sin \theta \bar{\phi}_2)\rangle \\ &= \cos^2 \theta |\phi_1 \bar{\phi}_1\rangle - \sin^2 \theta |\phi_2 \bar{\phi}_2\rangle - \cos \theta \sin \theta \underbrace{[|\phi_1 \bar{\phi}_2\rangle - |\phi_2 \bar{\phi}_1\rangle]}_{\sqrt{2}|^3\Psi_1^2\rangle} \end{aligned} \quad (472)$$

There is a triplet contaminant, with growing weight as R increases. At the dissociation limit ($\theta = \pi/4$)

$$|\Psi_{R \rightarrow \infty}^{\text{UHF}}\rangle = \frac{1}{2} [|\phi_1 \bar{\phi}_1\rangle - |\phi_2 \bar{\phi}_2\rangle] - \frac{1}{2} |^3\Psi_1^2\rangle \quad (473)$$

The triplet contaminant is the price to pay for having a one-determinant wave function.

16 Configuration interaction method

The multi-configurational wave function

$$\begin{aligned} |\Phi\rangle &= c_0 |\Psi\rangle + \left(\frac{1}{1!}\right)^2 \sum_{ar} c_a^r |\Psi_a^r\rangle + \left(\frac{1}{2!}\right)^2 \sum_{abrs} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle \\ &+ \left(\frac{1}{3!}\right)^2 \sum_{\substack{abc \\ rst}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \left(\frac{1}{4!}\right)^2 \sum_{\substack{abcd \\ rstu}} c_{abcd}^{rstu} |\Psi_{abcd}^{rstu}\rangle + \dots \end{aligned} \quad (474)$$

where the coefficients are the eigenvectors of the CI-matrix.
The CI wave function is not normalized in the sense that

$$\langle \Phi | \Phi \rangle = 1 + \sum_{ab} (c_a^b)^2 + \left(\frac{1}{2!}\right)^4 \sum_{abrs} (c_{ab}^{rs})^2 + \dots \quad (475)$$

However, it satisfies the **intermediate normalization condition**

$$\langle \Psi | \Phi \rangle = 1 \quad (476)$$

Schrödinger equation

$$\hat{H}|\Phi\rangle = \varepsilon_0|\Phi\rangle \quad (477)$$

By subtracting $E_0|\Phi\rangle$

$$(\hat{H} - E_0)|\Phi\rangle = (\varepsilon_0 - E_0)|\Phi\rangle = E_{\text{corr}}|\Phi\rangle \quad (478)$$

multiplication and integration by $\langle \Psi |$

$$\langle \Psi | \hat{H} - E_0 | \Phi \rangle = E_{\text{corr}} \langle \Psi | \Phi \rangle = E_{\text{corr}} \quad (479)$$

lets appear explicitly the **correlation energy**, E_{corr} .

Substitute the CI-expansion of the wave function

$$\begin{aligned} \langle \Psi | \hat{H} - E_0 | \Phi \rangle &= \langle \Psi | \hat{H} - E_0 \left(|\Psi\rangle + \sum_{ct} c_c^t |\Psi_c^t\rangle + \sum_{\substack{c<d \\ t<u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle + \dots \right) \\ &= \sum_{\substack{c<d \\ t<u}} c_{cd}^{tu} \langle \Psi | \hat{H} | \Psi_{cd}^{tu} \rangle \end{aligned} \quad (480)$$

The (unnormalized) coefficients of the double excited configurations determine the correlation energy

$$E_{\text{corr}} = \sum_{\substack{c<d \\ t<u}} c_{cd}^{tu} \langle \Psi | \hat{H} | \Psi_{cd}^{tu} \rangle \quad (481)$$

In order to know these coefficients exactly, we must solve the full CI problem!

17 Structure of the CI matrix

The CI matrix

$$\begin{pmatrix} \langle \Psi | \hat{H} | \Psi \rangle & 0 & \langle \Psi | \hat{H} | D \rangle & 0 & 0 & \dots \\ & \langle S | \hat{H} | S \rangle & \langle S | \hat{H} | D \rangle & \langle S | \hat{H} | T \rangle & 0 & \dots \\ & & \langle D | \hat{H} | D \rangle & \langle D | \hat{H} | T \rangle & \langle D | \hat{H} | Q \rangle & \dots \\ & & & \langle T | \hat{H} | T \rangle & \langle T | \hat{H} | Q \rangle & \dots \\ & & & & \langle Q | \hat{H} | Q \rangle & \dots \end{pmatrix} \quad (482)$$

- Brillouin theorem $\langle \Psi | \hat{H} | S \rangle = 0$
- Slater rules $\langle \Psi | \hat{H} | T \rangle = \langle \Psi | \hat{H} | Q \rangle = \langle S | \hat{H} | Q \rangle = 0$
- nonzero blocks are sparse
- double excitations play a predominant role
- by indirect coupling all types of excitations contribute to the correlation energy

17.1 Doubly excited CI

Neglect all configurations except the doubly excited ones

$$|\Phi_{\text{DCI}}\rangle = |\Psi\rangle + \sum_{\substack{c<d \\ t<u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle \quad (483)$$

After substitution into

$$(\hat{H} - E_0)|\Phi_{\text{DCI}}\rangle = E_{\text{corr}}|\Phi_{\text{DCI}}\rangle \quad (484)$$

and successive multiplication by $\langle\Psi|$ and by $\langle\Psi_{ab}^{rs}|$ we obtain the system of equations

$$\begin{aligned} \sum_{\substack{c<d \\ t<u}} c_{cd}^{tu} \langle\Psi|\hat{H}|\Psi_{cd}^{tu}\rangle &= E_{\text{corr}} \\ \langle\Psi_{ab}^{rs}|\hat{H}|\Psi\rangle + \sum_{\substack{c<d \\ t<u}} c_{cd}^{tu} \langle\Psi_{ab}^{rs}|\hat{H} - E_0|\Psi_{cd}^{tu}\rangle &= c_{ab}^{rs} E_{\text{corr}} \end{aligned} \quad (485)$$

Introduce the matrix notations

$$\begin{aligned} (\mathbf{B})_{rasb} &= \langle\Psi_{ab}^{rs}|\hat{H}|\Psi\rangle \\ (\mathbf{D})_{rasb,tcud} &= \langle\Psi_{ab}^{rs}|\hat{H} - E_0|\Psi_{cd}^{tu}\rangle \\ (\mathbf{c})_{rasb} &= c_{ab}^{rs} \end{aligned} \quad (486)$$

and the DCI matrix equations are

$$\begin{pmatrix} 0 & \mathbf{B}^\dagger \\ \mathbf{B} & \mathbf{D} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{c} \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} 1 \\ \mathbf{c} \end{pmatrix} \quad (487)$$

17.2 Approximate solutions of the DCI equations

The exact solution of the DCI problem is the lowest eigenvalue of the CI matrix

$$\begin{pmatrix} 0 & \mathbf{B}^\dagger \\ \mathbf{B} & \mathbf{D} \end{pmatrix} \quad (488)$$

We can solve this problem by the matrix partitioning technique by considering the corresponding partitioned system of equations

$$\mathbf{B}^\dagger \mathbf{c} = E_{\text{corr}} \quad (489)$$

$$\mathbf{B} + \mathbf{D} \mathbf{c} = \mathbf{c} E_{\text{corr}} \quad (490)$$

Solve the second equation for \mathbf{c}

$$\mathbf{c} = -(\mathbf{D} - \mathbf{1} E_{\text{corr}})^{-1} \mathbf{B} \quad (491)$$

and

$$E_{\text{corr}} = -\mathbf{B}^\dagger (\mathbf{D} - \mathbf{1} E_{\text{corr}})^{-1} \mathbf{B} \quad (492)$$

As a first approximation we can set $E_{\text{corr}} = 0$ in the denominator and get

$$E_{\text{corr}} \approx -\mathbf{B}^\dagger \mathbf{D}^{-1} \mathbf{B} \quad (493)$$

This expression is not variational (not upper bound to the energy) but size-extensive (unlike truncated CI).

As a further simplification, we neglect off-diagonal elements of \mathbf{D} , i.e.

$$(\mathbf{D}^{-1})_{rasb,tucd} = \frac{\delta_{ac}\delta_{bd}\delta_{rt}\delta_{su}}{\langle \Psi_{ab}^{rs} | \hat{H} - E_0 | \Psi_{ab}^{rs} \rangle} \quad (494)$$

and the correlation energy becomes approximately

$$E_{\text{corr}} \approx - \sum_{\substack{a < b \\ r < s}} \frac{\langle \Psi | \hat{H} | \Psi_{ab}^{rs} \rangle \langle \Psi_{ab}^{rs} | \hat{H} | \Psi \rangle}{\langle \Psi_{ab}^{rs} | \hat{H} - E_0 | \Psi_{ab}^{rs} \rangle} = \sum_{\substack{a < b \\ r < s}} E_{\text{corr}} \binom{rs}{ab} \quad (495)$$

sum of double-excitation contributions.

17.3 Natural orbitals

Natural orbitals diagonalize the 1RDM for any (including multi-configurational) wave function. Take a two-electron singlet system with the following CI expansion

$$|{}^1\Phi\rangle = c_0 |1\bar{1}\rangle + \sum_{r=2}^K c_1^r |{}^1\Psi_1^r\rangle + \frac{1}{2} \sum_{r=2}^K \sum_{s=2}^K c_{11}^{rs} |{}^1\Psi_{11}^{rs}\rangle \quad (496)$$

where the spin-adapted singlet configuration functions (CF) are

$$|{}^1\Psi_1^r\rangle = \frac{1}{\sqrt{2}} (|1\bar{r}\rangle + |r\bar{1}\rangle) \quad |{}^1\Psi_{11}^{rs}\rangle = \frac{1}{\sqrt{2}} (|r\bar{s}\rangle + |s\bar{r}\rangle) \quad (497)$$

Substitute these CFs

$$\begin{aligned} |{}^1\Phi\rangle &= c_0 |1\bar{1}\rangle + \frac{1}{\sqrt{2}} \sum_{r=2}^K c_1^r \{ |1\bar{r}\rangle + |r\bar{1}\rangle \} + \frac{1}{\sqrt{2}} \sum_{r=2}^K \sum_{s=2}^K c_{11}^{rs} \{ |r\bar{s}\rangle + |s\bar{r}\rangle \} \\ &= \sum_{i=1}^K \sum_{j=1}^K C_{ij} |i\bar{j}\rangle \end{aligned} \quad (498)$$

where the C_{ij} coefficients form a symmetric matrix. The CI expansion contains K^2 terms. The 1RDM can be calculated as

$$\begin{aligned} P(\mathbf{x}_1, \mathbf{x}'_1) &= \sum_{ij} \sum_{kl} C_{ij}^* C_{kl} \int [i^*(1)\bar{j}^*(2) - i^*(2)\bar{j}^*(1)] [k^*(1')\bar{l}^*(2) - k^*(2)\bar{l}^*(1')] d2 \\ &= \sum_{ij} (\mathbf{C}\mathbf{C}^\dagger)_{ij} [i(1)j^*(1') + \bar{i}(1)\bar{j}^*(1')] \end{aligned} \quad (499)$$

Let us choose a transformation \mathbf{U} such that

$$\mathbf{U}^\dagger \mathbf{C} \mathbf{U} = \mathbf{d} \quad (500)$$

where \mathbf{d} is a diagonal matrix. The orbitals η_k obtained from the transformation

$$\eta_k = \sum_i \psi_i U_{ik} \quad \text{and} \quad \psi_i = \sum_m \eta_m U_{im} \quad (501)$$

diagonalize the 1RDM

$$P(\mathbf{x}_1, \mathbf{x}'_1) = \sum_i d_i^2 [\eta_i(1)\eta_i^*(1') + \bar{\eta}_i(1)\bar{\eta}_i^*(1')] \quad (502)$$

Substitution in the CI expansion leads to

$$\begin{aligned} \sum_{ij} C_{ij} |i\bar{j}\rangle &= \sum_{ij} \sum_{mn}^K U_{im} C_{ij} U_{jn} |\eta_m \bar{\eta}_n\rangle \\ &= \sum_{mn}^K (U^\dagger C U)_{mn} |\eta_m \bar{\eta}_n\rangle = \sum_m^K d_m |\eta_m \bar{\eta}_m\rangle \end{aligned} \quad (503)$$

which contains only K terms instead of K^2 !

17.4 Minimal basis H_2 molecule

Out of the six possible determinants four symmetry adapted configuration functions (CFs) can be formed

$$\begin{aligned} X^1 \Sigma_g^+ & \quad |\Psi\rangle & = |1\bar{1}\rangle \\ B^1 \Sigma_u^+ & \quad |^1\Psi_1^2\rangle & = |1\bar{2}\rangle + |2\bar{1}\rangle \\ E^1 \Sigma_g^+ & \quad |^1\Psi_{11}^{22}\rangle & = |2\bar{2}\rangle \\ b^3 \Sigma_u^+ & \quad |^3\Psi_1^2\rangle & = \begin{cases} |12\rangle \\ |1\bar{2}\rangle - |2\bar{1}\rangle \\ |\bar{1}\bar{2}\rangle \end{cases} \end{aligned}$$

Taking into account the spin multiplicity (singlet and triplet) and space symmetry (g or u), the CI matrix has the following structure

$$\begin{pmatrix} \langle ^1\Psi | \hat{H} | ^1\Psi \rangle & \langle ^1\Psi | \hat{H} | ^1\Psi_{11}^{22} \rangle & 0 & 0 \\ \langle ^1\Psi_{11}^{22} | \hat{H} | ^1\Psi_{11}^{22} \rangle & \langle ^1\Psi_{11}^{22} | \hat{H} | ^1\Psi_{11}^{22} \rangle & 0 & 0 \\ & & \langle ^1\Psi_1^2 | \hat{H} | ^1\Psi_1^2 \rangle & 0 \\ & & & \langle ^3\Psi_1^2 | \hat{H} | ^3\Psi_1^2 \rangle \end{pmatrix} \quad (504)$$

The energies of the $B^1 \Sigma_u^+$ state is given by

$$\begin{aligned} \langle ^1\Psi_1^2 | \hat{H} | ^1\Psi_1^2 \rangle &= \frac{1}{2} (\langle 1\bar{2} | \hat{H} | 1\bar{2} \rangle - \langle 2\bar{1} | \hat{H} | 1\bar{2} \rangle - \langle 1\bar{2} | \hat{H} | 2\bar{1} \rangle + \langle 2\bar{1} | \hat{H} | 2\bar{1} \rangle) \\ &= h_{11} + h_{22} + J_{12} + K_{12} \end{aligned} \quad (505)$$

and of the $b^3 \Sigma_u^+$ state

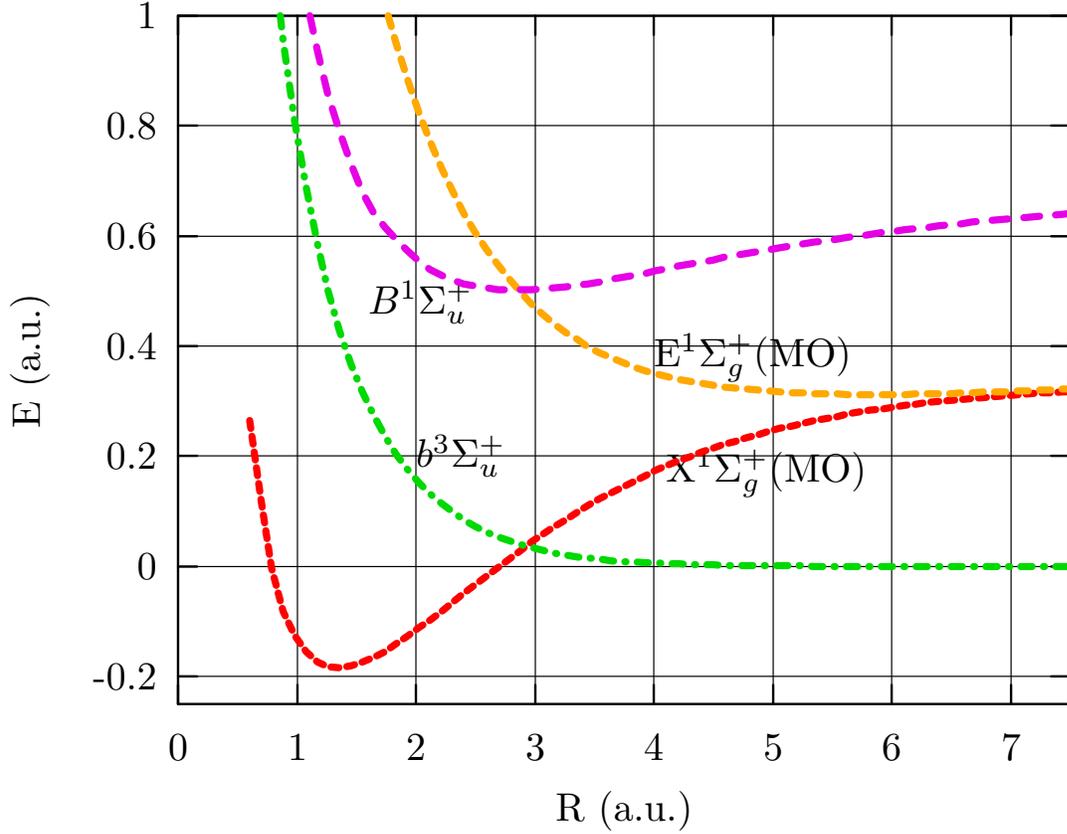
$$\langle ^3\Psi_1^2 | \hat{H} | ^3\Psi_1^2 \rangle = \langle 12 | \hat{H} | 12 \rangle = h_{11} + h_{22} + J_{12} - K_{12} \quad (506)$$

which lies below the corresponding singlet state (Hund's rule) and tends to the limit of $E(H)$ at $R \rightarrow \infty$.

The MO energies of the two $^1 \Sigma_g^+$ states are

$$E^{\text{MO}}(X^1 \Sigma_g^+) = 2h_{11} + J_{11} \quad E^{\text{MO}}(E^1 \Sigma_g^+) = 2h_{22} + J_{22} \quad (507)$$

which dissociate to the same limit (in the MO approximation!).



17.5 DCI of the minimal basis H_2

To solve the 2×2 CI problem we need the matrix elements

$$(\mathbf{B})_{21\bar{2}\bar{1}} = \langle \Psi_{1\bar{1}}^{2\bar{2}} | \hat{H} | \Psi \rangle = \langle \bar{1} | | 2\bar{2} \rangle = [1\bar{2} | \bar{1}\bar{2}] - [1\bar{2} | \bar{1}\bar{2}] = (12 | 12) - 0 = K_{12} \quad (508)$$

and

$$(\mathbf{D})_{21\bar{2}\bar{1}, 21\bar{2}\bar{1}} = \langle \Psi_{1\bar{1}}^{2\bar{2}} | \hat{H} - E_0 | \Psi_{1\bar{1}}^{2\bar{2}} \rangle = 2h_{22} + J_{22} - 2h_{11} - J_{11} \quad (509)$$

Using the orbital energies

$$\varepsilon_1 = h_{11} + J_{11} \quad \varepsilon_2 = h_{22} + 2J_{12} - K_{12} \quad (510)$$

we can write

$$(\mathbf{D})_{21\bar{2}\bar{1}, 21\bar{2}\bar{1}} = 2\Delta = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12} \quad (511)$$

The DCI matrix takes the simple form

$$\begin{pmatrix} 0 & K_{12} \\ K_{12} & 2\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} 1 \\ c \end{pmatrix} \quad (512)$$

The solution can be found from

$$K_{12} + 2\Delta c = E_{\text{corr}} c \quad c = \frac{K_{12}}{E_{\text{corr}} - 2\Delta} \quad (513)$$

$$K_{12}c = E_{\text{corr}} \quad E_{\text{corr}} = \frac{K_{12}^2}{E_{\text{corr}} - 2\Delta} \quad (514)$$

The exact (in minimal basis) correlation energy is

$$E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + K_{12}^2} \quad (515)$$

At dissociation $\varepsilon_1 = \varepsilon_2$, $h_{11} = h_{22} = E(H)$. Since all two-electron integrals $J_{11} = J_{22} = J_{12} = K_{12} = (\chi_a \chi_a | \chi_a \chi_a)$ tend to the same value, $\Delta = 0$ and the total energy

$$E^{\text{CI}}(X^1\Sigma_g^+) = 2h_{11} + J_{11} + \Delta - \sqrt{\Delta^2 + K_{12}^2} \quad (516)$$

tends to $2E(H)$.

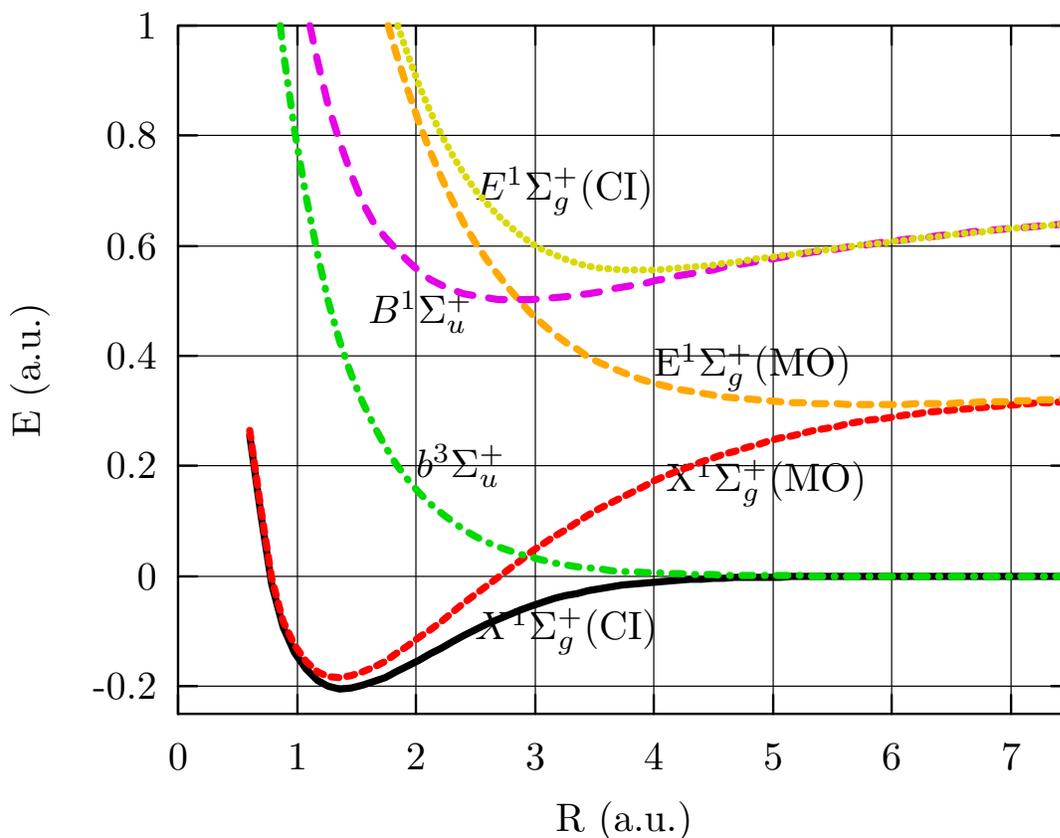
In this limit the CI coefficient

$$c = \frac{-K_{12}}{\Delta + (\Delta^2 + K_{12}^2)^{1/2}} \rightarrow -1 \quad (517)$$

which means that the CI wave function in the dissociation limit

$$|\Psi_{R \rightarrow \infty}^{\text{CI}}\rangle = |\Psi\rangle + |\Psi_{11}^{22}\rangle = |\chi_a \bar{\chi}_b\rangle + |\chi_b \bar{\chi}_a\rangle \quad (518)$$

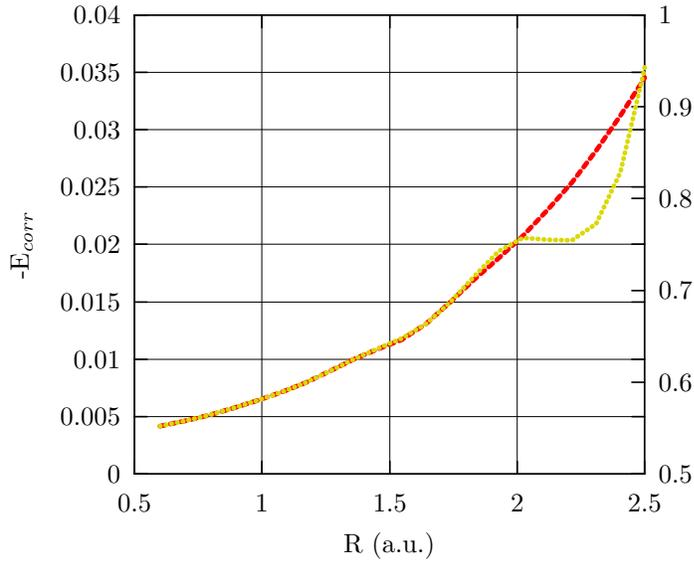
is the linear combination of two ground state H atoms.



17.6 Approximate CI solution of minimal basis H_2

Use the approximate correlation energy expression

$$E_{\text{corr}} \approx -B^\dagger D^{-1} B \quad (519)$$



Since $\mathbf{B} = K_{12}$ and $\mathbf{D}^\dagger = 2\Delta$ we get immediately the estimation

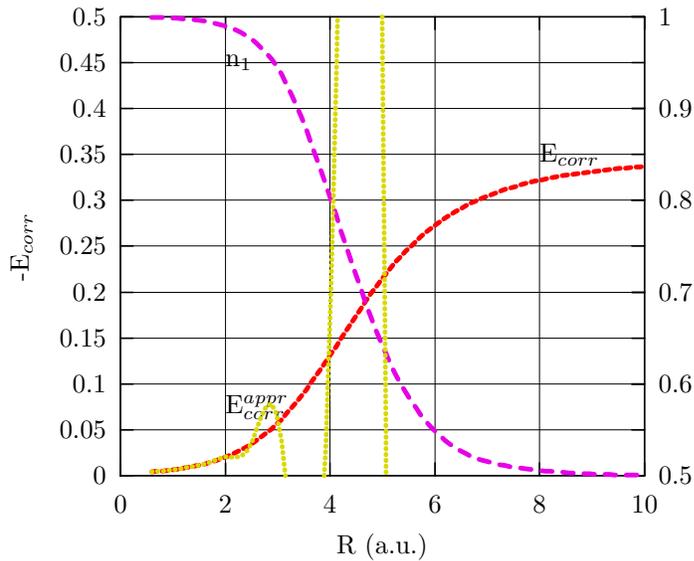
$$E_{\text{corr}} \approx -\frac{K_{12}}{2\Delta}$$

In this special case, the one-particle density matrix is diagonal in the original MO basis (NO=MO). Using the normalized CI expansion coefficients

$$C_{11} = \frac{1}{\sqrt{1+c^2}} \quad C_{22} = \frac{c}{\sqrt{1+c^2}} \quad (520)$$

the P-matrix

$$\begin{pmatrix} C_{11}^2 & 0 \\ 0 & C_{22}^2 \end{pmatrix} \quad (521)$$



The “perturbational” correlation energy is a good approximation as far as $n_1 \approx 1$ and it deteriorates when the wave function becomes multi-configurational ($n_1 < 1$).

17.7 Size-consistency problem

The energy of a non-interacting dimer (N-mer) should be the sum of monomer energies. The Hartee-Fock wave function of an infinitely separated dimer of H_2 molecules is

$$|\Psi_0\rangle = |1_1 \bar{1}_1 1_2 \bar{1}_2\rangle \quad (522)$$

with the energy

$$E_0 = 4h_{11} + \langle 1_1 \bar{1}_1 || 1_1 \bar{1}_1 \rangle + \langle 1_2 \bar{1}_2 || 1_2 \bar{1}_2 \rangle + 2\langle 1_1 \bar{1}_1 || 1_2 \bar{1}_2 \rangle = 2(2h_{11} + J_{11}) \quad (523)$$

sum of the monomer energies.

The DCI wave function involves only “local” excitations

$$|\Phi\rangle = |\Psi_0\rangle + \sum_{i=1}^2 c_i |\Phi_{1_i \bar{1}_i}^{2_i \bar{2}_i}\rangle \quad (524)$$

Matrix elements

$$\langle \Psi | \hat{H} | \Phi_{1_1 \bar{1}_1}^{2_1 \bar{2}_1} \rangle = \langle 1_1 \bar{1}_1 || 2_1 \bar{2}_1 \rangle = (1_1 2_1 | 1_1 2_1) = K_{12} \quad (525)$$

and the DCI matrix is

$$\begin{pmatrix} 0 & K & K \\ K & 2\Delta & 0 \\ K & 0 & 2\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c \\ c \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} 1 \\ c \\ c \end{pmatrix} \quad (526)$$

leading to the equations

$$K_{12} + 2\Delta c = E_{\text{corr}} c \quad c = \frac{K_{12}}{E_{\text{corr}} - 2\Delta} \quad (527)$$

$$2Kc = E_{\text{corr}} \quad E_{\text{corr}} = \frac{2K_{12}^2}{E_{\text{corr}} - 2\Delta} \quad (528)$$

DCI correlation energy of the dimer

$$^{(2)}E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + 2K_{12}^2} \quad (529)$$

is not equal to the sum of monomer correlation energies

$$^{(2)}E_{\text{corr}} \neq 2^{(1)}E_{\text{corr}} = 2\Delta - 2\sqrt{\Delta^2 + K_{12}^2} \quad (530)$$

Similar result holds for an N-mer:

$$^{(N)}E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + NK_{12}^2} \quad (531)$$

which means that the DCI (truncated CI) correlation energy per monomer tends to 0 with increasing system size.

If we take the approximate correlation energy expression, applied to an N-mer

$$^{(N)}E_{\text{corr}} \approx -\sum_i^N \frac{\mathbf{B}_i^\dagger \mathbf{B}_i}{\mathbf{D}_i} = -\frac{NK}{2\Delta} \quad (532)$$

i.e. N times the approximate monomer correlation energy.

17.8 Full CI of a non-interacting H₂ dimer

The wave function includes a quadruple excitation too

$$|\Phi\rangle = |\Psi_0\rangle + c_1 |2_1 \bar{2}_1 1_2 \bar{1}_2\rangle + c_2 |1_1 \bar{1}_1 2_2 \bar{2}_2\rangle + c_3 |2_1 \bar{2}_1 2_2 \bar{2}_2\rangle \quad (533)$$

The FCI matrix is augmented with respect to the DCI one

$$\begin{pmatrix} 0 & K & K & 0 \\ K & 2\Delta & 0 & K \\ K & 0 & 2\Delta & K \\ 0 & K & K & 4\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c \\ c \\ c_3 \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} 1 \\ c \\ c \\ c_3 \end{pmatrix} \quad (534)$$

Solve the equations by taking first the fourth and first rows

$$2Kc + 4\Delta c_3 = E_{\text{corr}} c_3 \qquad c_3 = \frac{2Kc}{E_{\text{corr}} - 4\Delta} \quad (535)$$

$$2Kc = E_{\text{corr}} c \qquad E_{\text{corr}} = \frac{E_{\text{corr}}}{E_{\text{corr}} - 4\Delta} \quad (536)$$

Using the second row

$$K + 2\Delta c + Kc_3 = E_{\text{corr}} c \quad (537)$$

and substitution of c_3

$$c = \frac{2K}{E_{\text{corr}} - 4\Delta} \quad (538)$$

which leads to the equation for the correlation energy

$$E_{\text{corr}} = \frac{2K^2}{E_{\text{corr}} - 4\Delta} \quad (539)$$

and the solution is twice the monomer correlation energy

$$E_{\text{corr}} = 2(\Delta - \sqrt{\Delta^2 + K^2}) \quad (540)$$

Remark that the coefficient of the quadruple excitation

$$c_3 = \frac{2Kc}{E_{\text{corr}} - 4\Delta} = c \times c \quad (541)$$

18 Rayleigh-Schroedinger perturbation theory

18.1 Schroedinger equation with perturbation

We are looking for the ground state solution of the problem

$$\hat{H}\psi = (\hat{H}_0 + \hat{V})\psi = E\psi \quad (542)$$

and we already know the (exact) solution of the zero-order problem

$$\hat{H}_0\varphi_0 = E_0\varphi_0 \quad (543)$$

Let us write $\Delta E = E - E_0$, the energy correction

$$(\hat{H}_0 - E_0)\psi = (\Delta E - \hat{V})\psi \quad (544)$$

and in order to fix the phase of ψ , impose the intermediate normalization

$$\langle \varphi_0 | \psi \rangle = 1 \quad (545)$$

Introduce the reduced resolvent operator as

$$\hat{R}_0 = (1 - |\varphi_0\rangle\langle\varphi_0|)(\hat{H}_0 - E_0)^{-1} \quad (546)$$

which can be regarded as the inverse of the operator $\hat{H}_0 - E_0$ in the space of functions orthogonal to φ_0

$$\hat{R}_0(\hat{H}_0 - E_0) = 1 - |\varphi_0\rangle\langle\varphi_0| \quad (547)$$

Multiplying the Schrödinger equation by \hat{R}_0

$$\hat{R}_0(\hat{H}_0 - E_0)\psi = \hat{R}_0(\Delta E - \hat{V})\psi \quad (548)$$

using the definition of the resolvent and the intermediate normalization an equation is obtained for the wave function

$$\psi = \varphi_0 + \hat{R}_0(\Delta E - \hat{V})\psi \quad (549)$$

After multiplication of the Schrödinger equation by $\langle \varphi_0 |$

$$\langle \varphi_0 | (\hat{H}_0 - E_0) | \psi \rangle = \langle \varphi_0 | (\Delta E - \hat{V}) | \psi \rangle \quad (550)$$

we get the energy correction

$$\Delta E = \langle \varphi_0 | \hat{V} | \psi \rangle \quad (551)$$

18.2 Iterative solution of the perturbed Schroedinger equation

These equations can be solved iteratively

$$\begin{aligned} \Delta E_n &= \langle \varphi_0 | \hat{V} | \psi_{n-1} \rangle \\ \psi_n &= \varphi_0 + \hat{R}_0(\Delta E_n - \hat{V})\psi_n \end{aligned} \quad (552)$$

To the lowest orders of iteration we find by using $\psi_0 = \varphi_0$ and $\hat{R}_0\varphi_0 = 0$

$$\begin{aligned} \Delta E_1 &= \langle \varphi_0 | \hat{V} | \psi_0 \rangle \\ \psi_1 &= \varphi_0 - \hat{R}_0\hat{V}\psi_0 \\ \Delta E_2 &= \langle \varphi_0 | \hat{V} | \psi_1 \rangle = \langle \varphi_0 | \hat{V} | \psi_0 \rangle - \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \psi_0 \rangle = \Delta E_1 - \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \psi_0 \rangle \\ \psi_2 &= \varphi_0 - \hat{R}_0(\Delta E_2 - \hat{V})\psi_1 \\ &= \varphi_0 - \hat{R}_0(\langle \varphi_0 | \hat{V} | \psi_0 \rangle - \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \psi_0 \rangle - \hat{V})(\varphi_0 - \hat{R}_0\hat{V}\psi_0) \\ &= \varphi^{(1)} - \hat{R}_0(\hat{V} - \Delta E_2)\hat{R}_0\hat{V}\varphi_0 \end{aligned} \quad (553)$$

18.3 H-atom in electric field

Hamiltonian of the H-atom in an electric field, F_z

$$\hat{H} = \hat{H}_0 + \hat{z}F_z \quad \text{where} \quad \hat{H}_0 = -\frac{1}{2}\Delta - \frac{1}{r} \quad (554)$$

The Hamiltonian of the isolated H-atom has

the lowest eigenvalue $E_0 = -\frac{1}{2}$ and eigenfunction $\varphi_0 = \frac{1}{\sqrt{\pi}}e^{-r}$.

First iteration in the energy yields zero

$$\Delta E_1 = F_z \langle \varphi_0 | \hat{z} | \psi_0 \rangle = \mu_z \cdot F_z = 0 \quad (555)$$

First iteration in the wave function leads to the equation

$$\begin{aligned} \psi_1 &= \varphi_0 - \hat{R}_0\hat{V}\varphi_0 \\ (\hat{H}_0 - E_0)\psi_1 &= -(\hat{V} - \Delta E_1)\varphi_0 \\ \left(-\frac{1}{2}\Delta - \frac{1}{r} + \frac{1}{2}\right)\psi_1 &= -\frac{1}{\sqrt{\pi}}F_z z e^{-r} \end{aligned} \quad (556)$$

which has the solution

$$\psi_1 = -\frac{F_z}{\sqrt{\pi}} z \left(\frac{r}{2} - 1\right) e^{-r} \quad (557)$$

Second energy iteration

$$\Delta E_2 = F_z \langle \varphi_0 | \hat{z} | \psi_1 \rangle = -\frac{9}{4} \cdot F_z^2 \quad (558)$$

This leads to a development of the energy in the powers of F_z

$$E = E_0 + \Delta E_2 = E_0 - \frac{9}{4} \cdot F_z^2 \quad (559)$$

the dipole polarizability is

$$\alpha = - \left(\frac{\partial^2 E}{\partial F_z^2} \right)_{F_z=0} = \frac{9}{2} \text{ a.u.} \quad (560)$$

18.4 Rayleigh-Schrodinger perturbation expansion

Assuming that the iteration process converges, the exact wave function and energy can be expanded in power series of a perturbation parameter λ

$$(\hat{H}_0 + \lambda \hat{V})\psi = \Delta E \psi \quad (561)$$

as

$$\Delta E = \sum_{n=1}^{\infty} \lambda^n \Delta E^{(n)} \quad \text{and} \quad \psi = \sum_{n=0}^{\infty} \lambda^n \psi^{(n)} \quad (562)$$

Substitute the series expansions in

$$\Delta E = \langle \varphi_0 | \hat{V} | \psi \rangle \quad \text{and} \quad \psi = \varphi_0 + \hat{R}_0(\Delta E - \hat{V})\psi$$

leading to

$$\begin{aligned} \sum_{n=1}^{\infty} \lambda^n \Delta E^{(n)} &= \sum_{m=0}^{\infty} \lambda^{m+1} \langle \varphi_0 | \hat{V} | \psi^{(m)} \rangle \\ \sum_{n=1}^{\infty} \lambda^n \psi^{(n)} &= \varphi_0 + \hat{R}_0 \left(\sum_{m=1}^{\infty} \lambda^m \Delta E^{(m)} - \lambda \hat{V} \right) \sum_{k=1}^{\infty} \lambda^k \psi^{(k)} \end{aligned} \quad (563)$$

and collect terms of the same power to obtain the general recursion formulae

$$\begin{aligned} \Delta E^{(n)} &= \langle \varphi_0 | \hat{V} | \psi^{(n-1)} \rangle \\ \psi^{(n)} &= -\hat{R}_0 \hat{V} \psi^{(n-1)} - \sum_{k=1}^{n-1} \Delta E^{(k)} \hat{R}_0 \psi^{(n-k)} \end{aligned} \quad (564)$$

18.5 Explicit formulae at low orders

The reduced resolvent has the spectral resolution

$$\hat{R}_0 = \sum_{k \neq 0} \frac{|\varphi_k\rangle \langle \varphi_0|}{E_k - E_0} \quad (565)$$

◦ **First order**

$$\Delta E^{(1)} = \langle \varphi_0 | \hat{V} | \varphi_0 \rangle \quad (566)$$

$$\psi^{(1)} = -\hat{R}_0 \hat{V} \varphi_0 = - \sum_{k \neq 0} \frac{\langle \varphi_k | \hat{V} | \varphi_0 \rangle}{E_k - E_0} \varphi_k \quad (567)$$

The wave function corrections are often expressed in terms of the expansion coefficients $c_k^{(n)} = \langle \varphi_k | \psi^{(n)} \rangle$ on the basis of the eigenfunctions of the zero order Hamiltonian

$$c_k^{(1)} = - \sum_{k \neq 0} \frac{\langle \varphi_k | \hat{V} | \varphi_0 \rangle}{E_k - E_0} \quad (568)$$

◦ **Second order**

Energy

$$\begin{aligned} E^{(2)} &= \langle \varphi_0 | \hat{V} | \psi^{(1)} \rangle = - \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \varphi_0 \rangle \\ &= - \sum_{k \neq 0} \frac{\langle \varphi_0 | \hat{V} | \varphi_k \rangle \langle \varphi_k | \hat{V} | \varphi_0 \rangle}{E_k - E_0} \end{aligned} \quad (569)$$

Wave function

$$\begin{aligned} \psi^{(2)} &= \hat{R}_0 \hat{V} \hat{R}_0 \hat{V} \psi^{(1)} + \hat{R}_0 E^{(1)} \hat{R}_0 \hat{V} \psi^{(0)} = \\ &= \hat{R}_0 \hat{V} \hat{R}_0 \hat{V} \varphi_0 - \hat{R}_0 \langle \hat{V} \rangle \hat{R}_0 \hat{V} \varphi_0 = \hat{R}_0 \bar{V} \hat{R}_0 \hat{V} \varphi_0 \end{aligned} \quad (570)$$

where we used the definitions

$$\langle \hat{V} \rangle = \langle \varphi_0 | \hat{V} | \varphi_0 \rangle \quad \text{and} \quad \bar{V} = \hat{V} - \langle \hat{V} \rangle \quad (571)$$

◦ **Third order**

$$\begin{aligned} \Delta E^{(3)} &= \langle \varphi_0 | \hat{V} | \psi^{(2)} \rangle = - \langle \varphi_0 | \hat{V} \hat{R}_0 \bar{V} \hat{R}_0 \hat{V} | \varphi_0 \rangle \\ &= \sum_{k \neq 0} \sum_{l \neq 0} \frac{\langle \varphi_0 | \hat{V} | \varphi_k \rangle \langle \varphi_k | \bar{V} | \varphi_l \rangle \langle \varphi_l | \hat{V} | \varphi_0 \rangle}{(E_k - E_0)(E_l - E_0)} \end{aligned} \quad (572)$$

Summary of energy corrections

$$\Delta E^{(1)} = \langle \hat{V} \rangle \quad (573)$$

$$\Delta E^{(2)} = \langle \hat{V} \hat{R}_0 \hat{V} \rangle \quad (574)$$

$$\Delta E^{(3)} = \langle \hat{V} \hat{R}_0 \bar{V} \hat{R}_0 \hat{V} \rangle \quad (575)$$

$$\Delta E^{(4)} = \langle \hat{V} \hat{R}_0 (\bar{V} \hat{R}_0 \bar{V} - \langle \bar{V} \hat{R}_0 \bar{V} \rangle) \hat{R}_0 \hat{V} \rangle \quad (576)$$

$$\begin{aligned} \Delta E^{(5)} &= \langle \hat{V} \hat{R}_0 (\bar{V} \hat{R}_0 \bar{V} \hat{R}_0 \bar{V} - \langle \bar{V} \hat{R}_0 \bar{V} \hat{R}_0 \bar{V} \rangle \\ &\quad - \bar{V} \hat{R}_0 \langle \bar{V} \hat{R}_0 \bar{V} \rangle - \langle \bar{V} \hat{R}_0 \bar{V} \rangle \hat{R}_0 \bar{V}) \hat{R}_0 \hat{V} \rangle \end{aligned} \quad (577)$$

18.6 Energy with the first-order wave function

The energy (Rayleigh quotient)

$$E = \frac{\langle \psi | \hat{H} + \lambda \hat{V} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (578)$$

with the first order wave function, $\psi = \varphi_0 + \lambda \psi^{(1)} = \varphi_0 - \lambda \hat{V} \hat{R}_0 \varphi_0$

$$E = \frac{\langle \varphi_0 - \lambda \varphi_0 \hat{V} \hat{R}_0 | \hat{H} + \lambda \hat{V} | \varphi_0 - \lambda \hat{V} \hat{R}_0 \varphi_0 \rangle}{1 + \lambda^2 \langle \varphi_0 \hat{V} \hat{R}_0 | \hat{R}_0 \hat{V} \varphi_0 \rangle} \quad (579)$$

After expanding the denominator and using that $\hat{R}_0\hat{H}_0\varphi_0 = 0$

$$\begin{aligned}
E = & (E_0 + \lambda E^{(1)} - 2\lambda^2 \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \varphi_0 \rangle + \\
& + \lambda^2 \langle \varphi_0 | \hat{V} \hat{R}_0 (\hat{H} + \lambda \hat{V}) \hat{R}_0 \hat{V} | \varphi_0 \rangle) \times \\
& \times (1 - \lambda^2 \langle \varphi_0 | \hat{V} \hat{R}_0 | \hat{R}_0 \hat{V} \varphi_0 \rangle)
\end{aligned} \tag{580}$$

and collecting terms of the same order

$$\begin{aligned}
E = & E_0 + \lambda E^{(1)} - \\
& - \lambda^2 2 \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \varphi_0 \rangle - \\
& - \lambda^2 \langle \varphi_0 | \hat{V} \hat{R}_0 (\hat{H} - E_0) \hat{R}_0 \hat{V} | \varphi_0 \rangle \\
& + \lambda^3 \langle \varphi_0 | \hat{V} \hat{R}_0 (\hat{V} - E^{(1)}) \hat{R}_0 \hat{V} | \varphi_0 \rangle
\end{aligned} \tag{581}$$

Use that $E^{(1)} = \langle \hat{V} \rangle$ and $\hat{R}_0(\hat{H} - E_0) = 1 - |\varphi_0\rangle\langle\varphi_0|$ and obtain the previously derived 3rd order energy expression

$$E = E_0 + \langle \varphi_0 | \hat{V} | \varphi_0 \rangle - \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \varphi_0 \rangle + \langle \varphi_0 | \hat{V} \hat{R}_0 (\hat{V} - \langle \hat{V} \rangle) \hat{R}_0 \hat{V} | \varphi_0 \rangle \tag{582}$$

This result can be generalized: the n th order wave function determines the $(2n-1)$ th order energy expression, provided the normalization is taken into account.

The perturbational energy is not a upper bound to the exact energy, but the Rayleigh-quotient is an upper bound.

18.7 Deformation energy and perturbation energy

Up to second order the Rayleigh quotient can be written as a sum of two terms, the expectation value of the zero order Hamiltonian

$$\frac{\langle \varphi - \lambda \varphi \hat{V} \hat{R}_0 | \hat{H} | \varphi - \lambda \hat{V} \hat{R}_0 \varphi \rangle}{1 + \lambda^2 \langle \varphi \hat{V} \hat{R}_0 | \hat{R}_0 \hat{V} \varphi \rangle} = E_0 + \lambda^2 \langle \varphi | \hat{V} \hat{R}_0 \hat{V} | \varphi \rangle = E_0 + \Delta E_{\text{def}}^{(2)} \tag{583}$$

and the expectation value of the perturbation operator

$$\frac{\langle \varphi - \lambda \varphi \hat{V} \hat{R}_0 | \lambda \hat{V} | \varphi - \lambda \hat{V} \hat{R}_0 \varphi \rangle}{1 + \lambda^2 \langle \varphi \hat{V} \hat{R}_0 | \hat{R}_0 \hat{V} \varphi \rangle} = \lambda \langle \varphi | \hat{V} | \varphi \rangle - \lambda^2 2 \langle \varphi | \hat{V} \hat{R}_0 \hat{V} | \varphi \rangle = E^{(1)} + \Delta E_{\text{stab}}^{(2)} \tag{584}$$

The second order correction to the expectation value of the perturbation is twice the second order energy correction and it is twice the *energy raise* of the wave function due to the deformation of the wave function.

$$\Delta E_{\text{stab}}^{(2)} = -2\Delta E_{\text{def}}^{(2)} \tag{585}$$

18.8 Dalgarno's (2n+1) theorem

Although the recursion formulae would suggest that we need the $(n-1)$ order wave function correction to calculate the n -th order energy correction, as the previous example showed, there is a much stronger statement:

In order to obtain the $(2n+1)$ order energy correction, it is sufficient to know the n -th order wave function correction.

Wave function

$$\psi = \sum_k^n \psi^{(k)} + \mathcal{O}(\lambda^{n+1}) \tag{586}$$

Energy

$$E = \sum_k^n \sum_l^n \langle \psi^{(k)} | \hat{H} | \psi^{(l)} \rangle + \mathcal{O}(\lambda^{2n+2}) \quad (587)$$

Transformation formulae (Löwdin)

$$\begin{aligned} \Delta E^{(2n)} &= \langle \varphi_0 | \hat{V} | \psi^{(2n-1)} \rangle \\ &= \langle \psi^{(n)} | \hat{V} | \psi^{(n-1)} \rangle - \sum_{k=1}^n \sum_{l=1}^n \Delta E^{(2n-k-l)} \langle \psi^{(k)} | \psi^{(l)} \rangle \end{aligned} \quad (588)$$

$$\begin{aligned} \Delta E^{(2n+1)} &= \langle \varphi_0 | \hat{V} | \psi^{(2n)} \rangle \\ &= \langle \psi^{(n)} | \hat{V} | \psi^{(n)} \rangle - \sum_{k=1}^n \sum_{l=1}^n \Delta E^{(2n+1-k-l)} \langle \psi^{(k)} | \psi^{(l)} \rangle \end{aligned} \quad (589)$$

Computational difficulties increase significantly at $2n$ orders.

18.9 Perturbational correction of expectation values

Expectation value of an arbitrary Hermitian operator, \hat{B} with a first order wave function $\psi \approx (1 + \hat{R}_0 \hat{V})\varphi$

$$\bar{B} = \frac{\langle \varphi - \lambda \varphi \hat{V} \hat{R}_0 | \hat{B} + \lambda \hat{V} | \varphi - \lambda \hat{V} \hat{R}_0 \varphi \rangle}{1 + \lambda^2 \langle \varphi \hat{V} \hat{R}_0 | \hat{R}_0 \hat{V} \varphi \rangle} \quad (590)$$

Expanding up to first order in the perturbation

$$\langle \varphi | \hat{B} + \hat{B} \hat{R}_0 \hat{V} + \hat{V} \hat{R}_0 \hat{B} + \hat{V} \hat{R}_0 (\hat{B} - B_0) \hat{R}_0 \hat{V} | \varphi \rangle = B_0 + \Delta B^{(1)} \quad (591)$$

Suppose that the perturbation is of the form $\hat{V} = \mathbf{a} \hat{A} = \hat{A} \mathbf{a}^\dagger$, then

$$\Delta B^{(1)} = \mathbf{a}^\dagger \langle \hat{A} \hat{R}_0 \hat{B} + \hat{B} \hat{R}_0 \hat{A} \rangle \mathbf{a} = \mathbf{a}^\dagger K(\hat{A} \hat{B}) \mathbf{a} \quad (592)$$

where $K(\hat{A} \hat{B}) = \langle \hat{A} \hat{R}_0 \hat{B} + \hat{B} \hat{R}_0 \hat{A} \rangle$ is the linear response function.

18.10 Partitioning method

Let us consider an orthonormal basis $\{\varphi_k\}$ divided into two subsets, A and B, containing n_A and n_B functions, respectively. The result, obtained by using only n_A functions can be improved by adding the n_B extra functions, i.e. the secular equations are partitioned as

$$\begin{pmatrix} \mathbf{H}^{AA} & \mathbf{H}^{AB} \\ \mathbf{H}^{BA} & \mathbf{H}^{BB} \end{pmatrix} \begin{pmatrix} \mathbf{c}^A \\ \mathbf{c}^B \end{pmatrix} = E \begin{pmatrix} \mathbf{c}^A \\ \mathbf{c}^B \end{pmatrix} \quad (593)$$

which is equivalent to the system of equations

$$\begin{aligned} \mathbf{H}^{AA} \mathbf{c}^A + \mathbf{H}^{AB} \mathbf{c}^B &= E \mathbf{c}^A \\ \mathbf{H}^{BA} \mathbf{c}^A + \mathbf{H}^{BB} \mathbf{c}^B &= E \mathbf{c}^B \end{aligned} \quad (594)$$

A formal solution can be obtained by expressing \mathbf{c}^B from the second equation

$$\mathbf{c}^B = (E \mathbf{1}_{BB} - \mathbf{H}^{BB})^{-1} \mathbf{H}^{BA} \mathbf{c}^A \quad (595)$$

and inserting it into the first one leading to

$$\mathbf{H}_{\text{eff}}\mathbf{c}^A = E\mathbf{c}^A \quad (596)$$

The effective Hamiltonian is an $n_A \times n_A$ matrix

$$\mathbf{H}_{\text{eff}} = \mathbf{H}^{AA} + \mathbf{H}^{AB}(\mathbf{E}\mathbf{1}_{BB} - \mathbf{H}^{BB})^{-1}\mathbf{H}^{BA} \quad (597)$$

including implicitly the effect of the n_B other functions. The effective Hamiltonian depends on the yet unknown energy, E , therefore the solution should be obtained by iteration.

Take the case $n_A = 1$, $\mathbf{c}_A = \mathbf{c}_1 = 1$, then \mathbf{H}_{eff} is just a single element

$$E = \mathbf{H}_{\text{eff}} = f(E) \quad (598)$$

Insert as a first approximation $E = H_{11}$ and expand the inverse matrix, using $(\mathbf{I} + \mathbf{\Delta})^{-1} = \mathbf{I} - \mathbf{\Delta} + \mathbf{\Delta}^2$ leading to second order in the off-diagonal elements

$$E = H_{11} + \sum_{\kappa > 1} \frac{H_{1\kappa}H_{\kappa 1}}{H_{11} - H_{\kappa\kappa}} \quad (\kappa > 1) \quad (599)$$

The expansion coefficients in the \mathbf{c}^B vector (c.f. above)

$$\mathbf{c}^B = (\mathbf{E}\mathbf{1}_{BB} - \mathbf{H}^{BB})^{-1}\mathbf{H}^{BA}\mathbf{c}^A \quad (600)$$

can be approximated similarly as

$$c_\kappa = \frac{H_{\kappa 1}}{H_{11} - H_{\kappa\kappa}} \quad (601)$$

Analogous to RSPT, but

- basis is finite
- no *a priori* separation of the Hamiltonian is necessary
- complete set of eigenfunctions not needed
- analogies with RSPT to handled with caution

To make the connection with RSPT clear, choose the eigenfunctions of \hat{H}_0 as basis

$$\hat{H}_0\varphi_k = E_k^{(0)}\varphi_k \quad (602)$$

and the relevant matrix elements are

$$H_{11} = \langle \varphi_1 | \hat{H}_0 + \hat{V} | \varphi_1 \rangle = E_1^{(0)} + \langle \varphi_1 | \hat{V} | \varphi_1 \rangle \quad (603)$$

$$H_{1k} = \langle \varphi_1 | \hat{H}_0 + \hat{V} | \varphi_k \rangle = \langle \varphi_1 | \hat{V} | \varphi_k \rangle \quad (604)$$

By application of the previously derived results we obtain for the perturbational corrections to the i -th state

$$E_i = E_i^{(0)} + \langle \varphi_i | \hat{V} | \varphi_i \rangle + \sum_{k(\neq i)} \frac{\langle \varphi_i | \hat{V} | \varphi_k \rangle \langle \varphi_k | \hat{V} | \varphi_i \rangle}{E_i^{(0)} - E_k^{(0)}} \quad (605)$$

$$\psi_i = \varphi_i + \sum_{k(\neq i)} c_{ik}\varphi_k = \varphi_i - \sum_{k(\neq i)} \frac{\langle \varphi_k | \hat{V} | \varphi_i \rangle}{E_i^{(0)} - E_k^{(0)}}\varphi_k \quad (606)$$

(Quasi)-degenerate cases can be handled by taking ($n_A > 1$).

In non-orthogonal basis sets the matrix equations are

$$\begin{pmatrix} \mathbf{H}^{AA} & \mathbf{H}^{AB} \\ \mathbf{H}^{BA} & \mathbf{H}^{BB} \end{pmatrix} \begin{pmatrix} \mathbf{c}^A \\ \mathbf{c}^B \end{pmatrix} = E \begin{pmatrix} \mathbf{M}^{AA} & \mathbf{M}^{AB} \\ \mathbf{M}^{BA} & \mathbf{M}^{BB} \end{pmatrix} \begin{pmatrix} \mathbf{c}^A \\ \mathbf{c}^B \end{pmatrix} \quad (607)$$

where \mathbf{M} is the overlap (metric) matrix of the basis. The effective equation is

$$\mathbf{H}_{\text{eff}} \mathbf{c}^A = E \mathbf{M}^{AA} \mathbf{c}^A \quad (608)$$

with the effective Hamiltonian

$$\mathbf{H}^{AA} + (\mathbf{H}^{AB} - E \mathbf{M}^{AB})(E \mathbf{1}_{BB} - \mathbf{H}^{BB})^{-1}(\mathbf{H}^{BA} - E \mathbf{M}^{BA}) \quad (609)$$

and the energy to second order is

$$E = \frac{H_{00}}{M_{00}} + \sum_k \frac{[H_{k0} - M_{k0}(H_{00}/M_{00})]^2}{[H_{00}/M_{00} - (H_{kk}/M_{kk})]} \quad (610)$$

19 RSPT treatment of intramolecular correlation

Let us separate the N-electron Hamiltonian into two parts

$$\hat{H} = \hat{H}_0 + \hat{W} \quad (611)$$

where \hat{H}_0 is the Hartree-Fock Hamiltonian

$$\hat{H}_0 = \sum_i \hat{F}(i) \quad (612)$$

and the perturbation is the difference between the HF and total Hamiltonians

$$\hat{W} = \hat{H} - \sum_i \hat{F}(i) = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i \hat{J}(i) - \hat{K}(i) \quad (613)$$

which often called the fluctuation potential.

The zero order wave function is the Hartree-Fock determinant.

The zero order energy is the sum of occupied orbital energies

$$E^{(0)} = \langle \Psi | \sum_i \hat{F}(i) | \Psi \rangle = \sum_a^N \varepsilon_a \quad (614)$$

The first order energy correction is just the “double counting correction” we discussed in the Hartree-Fock theory

$$E^{(1)} = \langle \Psi | \hat{W} | \Psi \rangle = \sum_{a<b} \langle ab || ab \rangle - \sum_a \sum_b (J_{ab} - K_{ab}) = - \sum_{a<b} \langle ab || ab \rangle \quad (615)$$

The Hartree-Fock energy is

$$E_0 = E^{(0)} + E^{(1)} = \sum_a^N \varepsilon_a - \frac{1}{2} \sum_a^N \sum_b^N \langle ab || ab \rangle \quad (616)$$

In order to apply the second order energy and first order wave function correction formulae, the “intermediate states”, φ_k should be identified \Rightarrow excited determinants formed from the complete set of eigenfunctions of \hat{F} .

- singly excited determinants

$$\langle \Psi | \hat{W} | \Psi_a^r \rangle = \langle \Psi | \hat{H} - \hat{H}_0 | \Psi_a^r \rangle = \langle \Psi | \hat{H} | \Psi_a^r \rangle - F_{ar} = 0 \quad (617)$$

they cannot contribute by the virtue of the Brillouin theorem and HF equations.

- triply (and higher) excited determinants do not contribute – Slater rules
- double excitations, $|\Psi_{ab}^{rs}\rangle$ – yes

Application of the general formula leads to

$$E^{(2)} = - \sum_{\substack{a < b \\ r < s}} \frac{\langle \Psi | \hat{W} | \Psi_{ab}^{rs} \rangle \langle \Psi_{ab}^{rs} | \hat{W} | \Psi \rangle}{\langle \Psi_{ab}^{rs} | \hat{H}_0 - E^{(0)} | \Psi_{ab}^{rs} \rangle} \quad (618)$$

Let us use that

$$\langle \Psi_{ab}^{rs} | \hat{H}_0 - E^{(0)} | \Psi_{ab}^{rs} \rangle = -(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s) \quad (619)$$

and the Slater rules

$$\langle \Psi | \hat{W} | \Psi_{ab}^{rs} \rangle = \langle \Psi | \sum_{i < j} \frac{1}{r_{ij}} | \Psi_{ab}^{rs} \rangle = \langle ab || rs \rangle \quad (620)$$

we end up the second order Møller-Plesset (or MBPT) correction

$$E^{(2)} = \sum_{\substack{a < b \\ r < s}} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \frac{1}{4} \sum_{abrs} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (621)$$

In terms of the regular integrals the second order energy

$$E^{(2)} = \frac{1}{2} \sum_{abrs} \frac{\langle ab || rs \rangle \langle rs || ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{2} \sum_{abrs} \frac{\langle ab || rs \rangle \langle rs || ba \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (622)$$

and for closed shells in terms of spatial orbitals

$$E^{(2)} = 2 \sum_{abrs}^{N/2} \frac{\langle ab || rs \rangle \langle rs || ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{abrs}^{N/2} \frac{\langle ab || rs \rangle \langle rs || ba \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (623)$$

19.1 Third order MBPT energy

The third order energy expression is more laborious

$$\begin{aligned} E^{(3)} = & \frac{1}{8} \sum_{abcdrs} \frac{\langle ab || rs \rangle \langle cd || ab \rangle \langle rs || cd \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_c + \varepsilon_d - \varepsilon_r - \varepsilon_s)} \\ & + \frac{1}{8} \sum_{abrstu} \frac{\langle ab || rs \rangle \langle rs || tu \rangle \langle tu || ab \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_a + \varepsilon_b - \varepsilon_t - \varepsilon_u)} \\ & + \sum_{abcrst} \frac{\langle ab || rs \rangle \langle cs || tb \rangle \langle rt || ac \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_t)} \end{aligned} \quad (624)$$

19.2 Comparison with the partitioning method

We have already seen (c.f. discussion of the CI method) that the DCI correlation energy can be obtained from the following matrix

$$\begin{pmatrix} \langle \Psi | \hat{H}_0 + \hat{W} | \Psi \rangle & \langle \Psi | \hat{W} | \Psi_{ab}^{rs} \rangle & \dots & \langle \Psi | \hat{W} | \Psi_{cd}^{tu} \rangle \\ \langle \Psi_{ab}^{rs} | \hat{W} | \Psi \rangle & \langle \Psi_{ab}^{rs} | \hat{H}_0 + \hat{W} | \Psi_{ab}^{rs} \rangle & \dots & \langle \Psi_{ab}^{rs} | \hat{W} | \Psi_{cd}^{tu} \rangle \\ \dots & \dots & \dots & \dots \\ \langle \Psi_{cd}^{tu} | \hat{W} | \Psi \rangle & \langle \Psi_{cd}^{tu} | \hat{W} | \Psi_{ab}^{rs} \rangle & \dots & \langle \Psi_{cd}^{tu} | \hat{H}_0 + \hat{W} | \Psi_{cd}^{tu} \rangle \end{pmatrix} \quad (625)$$

where we used the notations

$$\begin{pmatrix} \langle \Psi | \hat{H}_0 + \hat{W} | \Psi \rangle & \mathbf{B}_{abrs} \\ \mathbf{B}_{abrs}^\dagger & \mathbf{D}_{abrs,cdtu} \end{pmatrix} \quad (626)$$

and the correlation energy is

$$\Delta E = \sum_{abrs} \sum_{cdtu} \mathbf{B}_{abrs}^\dagger (\mathbf{D}_{abrs,cdtu})^{-1} \mathbf{B}_{abrs} \quad (627)$$

Decompose the $\mathbf{D}_{abrs,cdtu}$ matrix $\mathbf{D} = \mathbf{K} + \mathbf{W}$, i.e. as a sum of a diagonal (\mathbf{K}) and non-diagonal (\mathbf{W}) contribution and expand the inverse matrix

$$\begin{aligned} \mathbf{D}^{-1} &= (\mathbf{K} + \mathbf{W})^{-1} = [\mathbf{K}(1 + \mathbf{K}^{-1}\mathbf{W})]^{-1} \\ &= (1 + \mathbf{K}^{-1}\mathbf{W})^{-1} \mathbf{K}^{-1} = \mathbf{K}^{-1} - \mathbf{K}^{-1}\mathbf{W}\mathbf{K}^{-1} + \mathbf{K}^{-1}\mathbf{W}\mathbf{K}^{-1}\mathbf{W}\mathbf{K}^{-1} \dots \end{aligned} \quad (628)$$

Since the inverse of the diagonal matrix \mathbf{K}_{ab}^{rs} is trivial, the approximate correlation energy has the form

$$\Delta E = \sum_{abrs} \mathbf{B}_{abrs}^\dagger (\mathbf{K}_{ab}^{rs})^{-1} \mathbf{B}_{abrs} \quad (629)$$

Two possible choices for the partition

- Møller-Plesset partition

$$\mathbf{K}_{ab}^{rs}(\text{MP}) = \langle \Psi_{ab}^{rs} | \hat{H}_0 | \Psi_{ab}^{rs} \rangle = E^{(0)} - (\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s) \quad (630)$$

leading to the MP2 result

$$\Delta E(\text{MP2}) = \frac{1}{4} \sum_{abrs} \frac{\mathbf{B}_{abrs}^\dagger \mathbf{B}_{abrs}}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (631)$$

- Epstein-Nesbet partitioning

$$\mathbf{K}_{ab}^{rs}(\text{EN}) = \langle \Psi_{ab}^{rs} | \hat{H}_0 + \hat{W} | \Psi_{ab}^{rs} \rangle = \mathbf{K}_{ab}^{rs}(\text{MP}) - d_{ab}^{rs} \quad (632)$$

leading to

$$\Delta E(\text{EN}) = \frac{1}{4} \sum_{abrs} \sum_{cdtu} \frac{\mathbf{B}_{abrs}^\dagger \mathbf{B}_{abrs}}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s) - d_{ab}^{rs}} \quad (633)$$

which is the result obtained previously as an approximate correlation energy expression.

19.3 Partial summation of MBPT series

Second order correction

$$E(2) = \frac{1}{4} \sum_{abrs} \langle ab||rs \rangle \langle rs||ab \rangle (K_{ab}^{rs})^{-1} \quad (634)$$

A component of the third order correction

$$E(3) = \frac{1}{4} \sum_{abrs} \langle ab||rs \rangle d_{ab}^{rs} \langle rs||ab \rangle (K_{ab}^{rs})^{-1} \quad (635)$$

where

$$d_{ab}^{rs} = \langle ab||ab \rangle + \langle rs||rs \rangle - \langle ar||ar \rangle - \langle br||br \rangle - \langle as||as \rangle - \langle bs||bs \rangle \quad (636)$$

Similar terms come in fourth-, fifth-, etc. order

$$\begin{aligned} E(2) + E(3) + \dots &= \frac{1}{4} \sum_{abrs} K^{-1} \langle ab||rs \rangle \langle rs||ab \rangle \left[1 + \left(\frac{d}{K} \right) + \left(\frac{d}{K} \right)^2 + \dots \right] \\ &= \frac{1}{4} \sum_{abrs} \frac{\langle ab||rs \rangle \langle rs||ab \rangle}{K(1 - d/K)} \end{aligned} \quad (637)$$

We obtain by partial summation the Epstein-Nesbet result.

19.4 MBPT correlation energy of minimal basis H₂

The exact correlation energy was found for this system as

$$E_{\text{corr}} = \Delta - (\Delta^2 + K_{12}^2)^{1/2} \quad (638)$$

with

$$\Delta = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12} \quad (639)$$

We can apply directly the formulae by considering that $a = b = 1$ and $r = s = 2$. Second order

$$E^{(2)} = 2 \frac{\langle 11|22 \rangle \langle 22|11 \rangle}{2(\varepsilon_1 - \varepsilon_2)} - \frac{\langle 11|22 \rangle \langle 22|11 \rangle}{2(\varepsilon_1 - \varepsilon_2)} = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \quad (640)$$

The third order result can be obtained from the general formula by taking into account that the first order energy correction

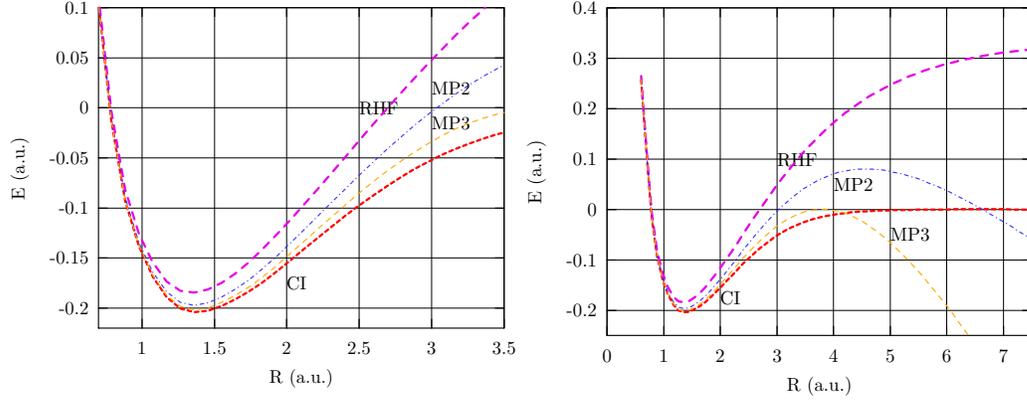
$$E^{(1)} = \langle \Psi | \hat{W} | \Psi \rangle = -J_{11} \quad (641)$$

and the perturbation matrix element

$$\langle \Psi | \hat{W} | \Psi_{11}^{2\bar{2}} \rangle = \langle 1\bar{1} | 2\bar{2} \rangle = \langle 11 | 22 \rangle = K_{12} \quad (642)$$

Third order energy

$$E^{(3)} = \frac{K_{12}^2 (J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)} \quad (643)$$



19.5 Size-consistency

N-mer of non-interacting H_2 molecules
 Second order energy

$$E^{(2)} = \sum_{i=1}^N \frac{|\langle \Psi | \hat{W} | \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \rangle|^2}{2(\varepsilon_1 - \varepsilon_2)} = \frac{NK_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \quad (644)$$

is N times the monomer MP2 energy.

Third order energy correction

$$E^{(3)} = \frac{NK_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2} \quad (645)$$

The general result is true: the MPn energy correction is size-consistent.

19.6 Size-consistent methods

The size consistency can be qualitatively discussed by invoking the one- and two-particle excitation operators

$$\hat{T}_1 = \sum_{ar} T_a^r a_r^+ a_a \quad \hat{T}_2 = \sum_{abrs} T_{ab}^{rs} a_r^+ a_s^+ a_b a_a \quad (646)$$

- o SDCI wave function of a complex

$$(1 + \hat{T}_1^A + \hat{T}_2^A)|\Psi^A\rangle(1 + \hat{T}_1^B + \hat{T}_2^B)|\Psi^B\rangle = |\Psi^{AB}(SDCI)\rangle + (\hat{T}_1^A \hat{T}_2^B + \dots)|\Psi^A \Psi^B\rangle$$

which is not of SDCI form

- o coupled cluster wave functions (CCSD) of a complex

$$\exp(\hat{T}_1^A + \hat{T}_2^A)|\Psi^A\rangle \exp(\hat{T}_1^B + \hat{T}_2^B)|\Psi^B\rangle = \exp(\hat{T}_1^A + \hat{T}_1^B + \hat{T}_2^A + \hat{T}_2^B)|\Psi^A \Psi^B\rangle$$

is still of the CCSD form.

19.7 Local MP2

One can use localized (Wannier-) orbitals instead of canonical ones in the MPn theory. Problem: Fock operator is not diagonal.

First order wave function correction satisfies $\psi^{(1)} = \varphi_0 - \hat{R}_0 \hat{W} \varphi_0$, i.e.

$$(\hat{H}_0 - E^{(0)})\psi^{(1)} = -\hat{W}\varphi_0 \quad (647)$$

Let $\varphi_0 = \Psi_0$, the Hartree-Fock wave function written in localized orbitals and the first order wave function correction is

$$\psi^{(1)} = \sum_{ab} \sum_{rs} T_{rs}^{ab} \Psi_{ab}^{rs} \quad (648)$$

with r, s localized virtual orbitals.

$$\sum_{abrs} (\hat{H}_0 - E^{(0)}) |\Psi_{ab}^{rs}\rangle T_{rs}^{ab} = -\hat{W} |\Psi_0\rangle \quad (649)$$

Multiplication from left by $\langle \Psi_{cd}^{tu} |$ leads to the linear equations

$$\sum_{abrs} \langle \Psi_{cd}^{tu} | \hat{H}_0 - E^{(0)} | \Psi_{ab}^{rs}\rangle T_{rs}^{ab} = -\langle \Psi_{cd}^{tu} | \hat{W} | \Psi_0\rangle \quad (650)$$

which can be solved directly for the unknown amplitudes, T_{rs}^{ab} , and the MP2 energy is

$$E^{(\text{LMP2})} = \sum_{abrs} T_{rs}^{ab} \langle \Psi_0 | \hat{W} | \Psi_{ab}^{rs}\rangle \quad (651)$$

Advantage: linear scaling correlation method!

Of course, this is a generalization of the canonical MP2 result, where the linear equations can be solved analytically, since

$$\langle \Psi_{cd}^{tu} | \hat{H}_0 - E^{(0)} | \Psi_{ab}^{rs}\rangle = \delta_{ac} \delta_{bd} \delta_{rt} \delta_{su} (\varepsilon_t + \varepsilon_u - \varepsilon_b - \varepsilon_c) \quad (652)$$

is a diagonal matrix.