SCF methods, basis sets, and integrals

Lecture II: Spin and Roothaan–Hall

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Preface

- So far, we have considered the molecular orbitals φ_k to depend on the coordinates of the electron.

- One may have assumed that they are the three Cartesian coordinates of the electron's position in space, $\mathbf{r}_i = \{x_i, y_i, z_i\}$.

- At the same time, we have introduced the antisymmetry of the wavefunction in an *ad hoc* manner, since the electrons are fermions.

- The electron is known to have a spin with a quantum number $s = \frac{1}{2}$, the z-component of which is quantised to take one of the possible values, $m_s = \pm\frac{1}{2}$.

- In order for electron spin to have meaning in Hartree–Fock theory, we must let the orbitals depend on it.

Spin functions α and β

- Let the functions α and β be orthonormal eigenfunctions of the spin operators $\hat{s}^2$ and $\hat{s}_z$,

$$\hat{s}^2\alpha = \tfrac{3}{4}\alpha, \quad \hat{s}_z\alpha = +\tfrac{1}{2}\alpha$$

$$\hat{s}^2\beta = \tfrac{3}{4}\beta, \quad \hat{s}_z\beta = -\tfrac{1}{2}\beta$$

- We let the orbitals depend on the spin by attaching an extra label (superscript) to it,

$$\varphi_{k\alpha} = \varphi_k^\alpha(\mathbf{r})\alpha, \qquad \varphi_{k\beta} = \varphi_k^\beta(\mathbf{r})\beta$$

- The functions $\varphi_k^\alpha(\mathbf{r})$ and $\varphi_k^\beta(\mathbf{r})$ are spatial orbitals, that is, functions that depend only on $\mathbf{r} = (x, y, z)$.

- The functions $\varphi_{k\alpha}$ and $\varphi_{k\beta}$ are spin orbitals that depend on spatial *and* spin coordinates.

Sums over spin orbitals

- Having attached a spin label to the orbitals, we must write sums of the orbitals in the following manner:

$$\text{without spin}: \sum_{k=1}^{n} \Rightarrow \text{ with spin}: \sum_{\sigma=\alpha,\beta} \sum_{k=1}^{n_\sigma} \quad (n_\alpha + n_\beta = n)$$

- There is a sum over σ over the two spin cases and then (dependent on the first sum) a second sum over the number of orbitals with that spin.

- Note that sums over electrons just remain unchanged, for example

$$\hat{H} = \hat{V}_{nn} + \sum_{\mu=1}^{n} \hat{h}_\mu + \sum_{\nu=2}^{n} \sum_{\mu=1}^{\nu-1} \frac{1}{r_{\mu\nu}}$$

Integration over spin coordinates

- To take spin into account, we must rewrite sums over orbitals in the following manner:

$$\sum_{i,j} h_{ij} = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \varphi_i | \hat{h} | \varphi_j \rangle \;\; \Rightarrow \;\; \sum_{\sigma=\alpha,\beta} \sum_{k=1}^{n_\sigma} \sum_{\rho=\alpha,\beta} \sum_{l=1}^{n_\rho} \langle \varphi_{k\sigma} | \hat{h} | \varphi_{l\rho} \rangle$$

- The expressions seem to become more lengthy, but fortunately, the rules for spin integration are very simple,

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1, \qquad \langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$

- Hence, in terms of the Kronecker delta function,

$$\langle \varphi_{k\sigma} | \hat{h} | \varphi_{l\rho} \rangle = \langle \sigma | \rho \rangle \times \langle \varphi_k^\sigma | \hat{h} | \varphi_l^\rho \rangle = \delta_{\sigma\rho} \int [\varphi_k^\sigma(\mathbf{r})]^* \, \hat{h} \, \varphi_l^\rho(\mathbf{r}) d\mathbf{r}$$

- Spin integration thus yields

$$\sum_{i,j}^{n} h_{ij} = \sum_{k,l}^{n_\alpha} \langle \varphi_k^\alpha | \hat{h} | \varphi_l^\alpha \rangle + \sum_{k,l}^{n_\beta} \langle \varphi_k^\beta | \hat{h} | \varphi_l^\beta \rangle$$

- Note that the integration would be more complicated for an operator that depends on spin, such as $\hat{\boldsymbol{\ell}} \cdot \hat{\mathbf{s}}$,

$$\langle \varphi_{k\sigma} | \hat{\boldsymbol{\ell}} \cdot \hat{\mathbf{s}} | \varphi_{l\rho} \rangle = \langle \varphi_k^\sigma | \hat{\boldsymbol{\ell}} | \varphi_l^\rho \rangle \cdot \langle \sigma | \hat{\mathbf{s}} | \rho \rangle$$

- We shall not be concerned with spin-dependent operators in this course!

Two-electron integration over spin coordinates

- We are now ready to integrate over the spin coordinates in antisymmetrised two-electron integrals,

$$
\begin{aligned}
\langle \varphi_{i\sigma}\varphi_{j\rho}||\varphi_{k\tau}\varphi_{l\omega}\rangle &= \langle \varphi_{i\sigma}\varphi_{j\rho}|\varphi_{k\tau}\varphi_{l\omega}\rangle - \langle \varphi_{i\sigma}\varphi_{j\rho}|\varphi_{l\omega}\varphi_{k\tau}\rangle \\
&= \delta_{\sigma\tau}\delta_{\rho\omega}\langle \varphi_i^{\sigma}\varphi_j^{\rho}|\varphi_k^{\tau}\varphi_l^{\omega}\rangle - \delta_{\sigma\omega}\delta_{\rho\tau}\langle \varphi_i^{\sigma}\varphi_j^{\rho}|\varphi_l^{\omega}\varphi_k^{\tau}\rangle
\end{aligned}
$$

- Hence, we obtain for four different cases:

$$
\begin{aligned}
\langle \varphi_{i\alpha}\varphi_{j\alpha}||\varphi_{k\alpha}\varphi_{l\alpha}\rangle &= \langle \varphi_i^{\alpha}\varphi_j^{\alpha}|\varphi_k^{\alpha}\varphi_l^{\alpha}\rangle - \langle \varphi_i^{\alpha}\varphi_j^{\alpha}|\varphi_l^{\alpha}\varphi_k^{\alpha}\rangle \\
\langle \varphi_{i\alpha}\varphi_{j\alpha}||\varphi_{k\beta}\varphi_{l\beta}\rangle &= 0 \\
\langle \varphi_{i\alpha}\varphi_{j\beta}||\varphi_{k\alpha}\varphi_{l\beta}\rangle &= \langle \varphi_i^{\alpha}\varphi_j^{\beta}|\varphi_k^{\alpha}\varphi_l^{\beta}\rangle \\
\langle \varphi_{i\alpha}\varphi_{j\alpha}||\varphi_{k\alpha}\varphi_{l\beta}\rangle &= 0
\end{aligned}
$$

- Note that in case of $\langle \alpha\beta||\alpha\beta\rangle = \langle \alpha\beta|\alpha\beta\rangle - \langle \alpha\beta|\beta\alpha\rangle$, the last term vanishes.

Two-electron integration over spin coordinates

- We are now ready to integrate over the spin coordinates in the two-electron expectation value over the Slater determinant,

$$\sum_{i,j} \langle ij||ij \rangle = \sum_{i,j} \langle i\,j||i\,j \rangle + \sum_{i,\overline{j}} \langle i\,\overline{j}||i\,\overline{j} \rangle + \sum_{\overline{i},j} \langle \overline{i}\,j||\overline{i}\,j \rangle + \sum_{\overline{i},\overline{j}} \langle \overline{i}\,\overline{j}||\overline{i}\,\overline{j} \rangle$$

- For simplicity, α orbitals are denoted by the index "k" and β orbitals by "$\overline{k}$".

- We obtain:

$$\sum_{i,j} \langle ij||ij \rangle = \sum_{i,j} \langle i\,j||i\,j \rangle + \sum_{\overline{i},\overline{j}} \langle \overline{i}\,\overline{j}||\overline{i}\,\overline{j} \rangle + 2\sum_{i,\overline{j}} \langle i\,\overline{j}|\,i\,\overline{j} \rangle$$

- The sum over "k" runs from 1 to n_α and the sum over "$\overline{k}$" runs from 1 to n_β.

$\langle \Phi | \hat{H} | \Phi \rangle$ with spin orbitals

- Putting it all together, we obtain the following expression for the expectation value of the Hamiltonian over the SD:

$$E[\Phi] = V_{nn} + \sum_i h_{ii} + \sum_{\bar{i}} h_{\bar{i}\bar{i}} + \tfrac{1}{2} \sum_{i,j} \langle i\,j || i\,j \rangle + \tfrac{1}{2} \sum_{\bar{i},\bar{j}} \langle \bar{i}\,\bar{j} || \bar{i}\,\bar{j} \rangle + \sum_{i,\bar{j}} \langle i\,\bar{j} | i\,\bar{j} \rangle$$

- We can split the last term into two sums

$$\sum_{i,\bar{j}} \langle i\,\bar{j} | i\,\bar{j} \rangle = \tfrac{1}{2} \sum_i \langle i | \hat{J}^{(\beta)} | i \rangle + \tfrac{1}{2} \sum_{\bar{j}} \langle \bar{j} | \hat{J}^{(\alpha)} | \bar{j} \rangle$$

and obtain

$$
\begin{aligned}
E[\Phi] &=& V_{nn} + \sum_i h_{ii} + \tfrac{1}{2} \sum_i \langle i | \hat{J}^{(\alpha)} + \hat{J}^{(\beta)} - \hat{K}^{(\alpha)} | i \rangle \\
&& + \sum_{\bar{j}} h_{\bar{j}\bar{j}} + \tfrac{1}{2} \sum_{\bar{j}} \langle \bar{j} | \hat{J}^{(\alpha)} + \hat{J}^{(\beta)} - \hat{K}^{(\beta)} | \bar{j} \rangle
\end{aligned}
$$

Exchange operators $\hat{K}^{(\alpha)}$ and $\hat{K}^{(\beta)}$

- Since exchange only occurs between electrons with like spins, we can define exchange operators $\hat{K}^{(\alpha)}$ and $\hat{K}^{(\beta)}$ that give the same result as $\hat{K}$ when acting on a spin orbital with spin function α respectively β,

$$\hat{K}^{(\alpha)} f(\mathbf{r})\alpha = \sum_{m=1}^{n_\alpha} \left(\int \frac{\left[\varphi_m^\alpha(\mathbf{r}')\right]^* f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) \varphi_m^\alpha(\mathbf{r})\alpha, \quad \hat{K}^{(\alpha)} g(\mathbf{r})\beta = 0$$

$$\hat{K}^{(\beta)} f(\mathbf{r})\alpha = 0, \quad \hat{K}^{(\beta)} g(\mathbf{r})\beta = \sum_{m=1}^{n_\beta} \left(\int \frac{\left[\varphi_m^\beta(\mathbf{r}')\right]^* g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) \varphi_m^\beta(\mathbf{r})\beta$$

- Accordingly, we define

$$\hat{F}^{(\alpha)} = \hat{h} + \hat{J} - \hat{K}^{(\alpha)} \text{ and } \hat{F}^{(\beta)} = \hat{h} + \hat{J} - \hat{K}^{(\beta)}$$

Spin-unrestricted Hartree–Fock theory

- The straightforward implementation of the equations obtained thus far is known as *unrestricted Hartree–Fock* (UHF) theory.

- In UHF theory, there are two sets of MOs, which are the α and β spin orbitals, eigenfunctions of the operators $\hat{F}^{(\alpha)}$ and $\hat{F}^{(\beta)}$,

$$\hat{F}^{(\alpha)}\varphi_k^\alpha(\mathbf{r})\alpha = \varepsilon_k^\alpha \varphi_k^\alpha(\mathbf{r})\alpha, \quad \hat{F}^{(\beta)}\varphi_k^\beta(\mathbf{r})\beta = \varepsilon_k^\beta \varphi_k^\beta(\mathbf{r})\beta$$

- The two equations are *coupled* through the Coulomb operator $\hat{J}$, which depends on *all* MOs.

- Note that the two sets of spatial orbitals $\{\varphi_k^\alpha(\mathbf{r})\}$ and $\{\varphi_k^\beta(\mathbf{r})\}$ are completely independent. Spatial orbitals of the α set need not be orthogonal on the β set.

- The equations may be solved iteratively. The α orbitals define $\hat{K}^{(\alpha)}$, the β orbitals define $\hat{K}^{(\beta)}$, and all orbitals define $\hat{J}$.

Spatial and spin symmetries

- Molecules may possess symmetry. Some may perhaps display no symmetry at all (C_1 point group), but many are symmetric with respect to a plane of reflection, etc.

- We define symmetry operations R_i of a given point group G that map the nuclear coordinates x_A onto themselves, $R_i\, x_A = y_A$. They induce operators in function space as

$$\hat{\mathcal{R}}_i \Phi(x_\mu; x_A) = \Phi(x_\mu; R_i^{-1} x_A) = \psi(x_\mu; x_A)$$

- These operators commute with the clamped-nuclei Hamiltonian,

$$[\hat{\mathcal{R}}_i, \hat{H}] = 0 \quad \forall\ R_i \in G$$

and hence, the exact electronic wavefunctions are (or can be chosen as) eigenfunctions of both $\hat{\mathcal{R}}_i$ and $\hat{H}$,

$$\hat{\mathcal{R}}_i \Psi_k(x_\mu; x_A) = \rho_{ik} \Psi_k(x_\mu; x_A)$$

Spatial and spin symmetries

- As long as the Hamiltonian does not refer to spin, it commutes with spin operators, and the spin quantum numbers (*e.g.*, S, M_S are constants of motion. Any electronic wavefunction should also be eigenfunction of the spin operators,

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

  Hence, we are looking for eigenfunctions of $\hat{H}$, $\hat{S}^2$, $\hat{S}_z$ and all $\hat{R}_i$ of the point group!

- The UHF approach as we know it so far yields approximate wavefunctions that may or may not be eigenfunctions of the spatial symmetry and spin operators.

- Restrictions must be imposed to ensure that eigenfunctions of all of the relevant operators are obtained.

A broken-symmetry UHF wavefunction

- A UHF calculation on two Na atoms at a distance of 10 a_0 can be performed in such a manner that the determinant becomes

$$\Phi = |\ldots 3s_A^\alpha \alpha \ldots 3s_B^\beta \beta \ldots| \equiv |A\alpha\, B\beta|$$

- The $1s$, $2s$ and $2p$ shells are fully occupied and can be ignored. The notation $|A\alpha\, B\beta|$ means that we consider a two-electron determinant that consists of two spin orbitals: a $3s$ atomic orbital on atom A with α spin and a $3s$ atomic orbital on B with β spin.


Spin-down

Spin-up
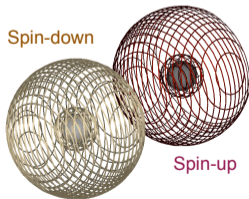
- The figure shows the spin density $3s_A^2 - 3s_B^2$ obtained from $|A\alpha\, B\beta|$.

- Φ is not eigenfunction of an operator that interchanges the nuclei,

$$\hat{\mathcal{R}}_i |A\alpha\, B\beta| = |B\alpha\, A\beta|$$

Broken-symmetry UHF wavefunctions

- Although UHF determinants such as the one for Na···Na seem unphysical, they may be useful in various applications of MO theory (*e.g.*, *unrestricted Kohn–Sham (UKS) theory*).

- Heisenberg exchange couplings J may be estimated.
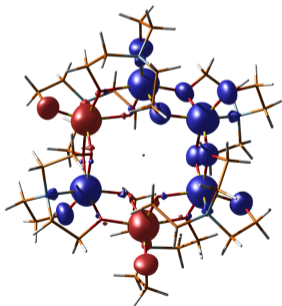
- The figure shows the spin density of a selected UKS solution for the "ferric wheel" $Na^+@Fe_6(tea)_6$ (H_3tea = triethanolamine).

- $\langle\Phi|\hat{S}_z|\Phi\rangle = 5\,\hbar$, but $\langle\Phi|\hat{S}^2|\Phi\rangle \approx 40\,\hbar^2$.

- The underlying UKS determinant is clearly not an eigenfunction of rotations about the S_6 axis.

Spin-restricted Hartree–Fock theory

- In Hartree–Fock theory, the orbitals are optimised by the variation method. We assume that those orbitals leading to the lowest energy $\langle \Phi | \hat{H} | \Phi \rangle$ are the "best" in a general sense.

- The orbitals can be optimised without worrying much about spin and spatial symmetries (as in UHF theory), but one can also apply constraints.

- The following table shows Hartree–Fock energies of the NO· radical ($R_{\mathrm{NO}} = 115.1$ pm, def2-QVZPP basis).

Spin symmetry constraints?	Spatial symmetry constraints?	State	E/E_{h}
No	No	?	−129.308 11
Yes	No	Doublet	−129.300 26
Yes	Yes	$^2\Pi$	−129.298 06

- What is the "best" calculation?

Closed-shell Hartree–Fock theory

- An important and frequent situation occurs when the electronic situation under consideration is a spin singlet ($S = 0, M_S = 0$).

- The number of electrons is *even*.

- We require that the spin orbitals occur in pairs having the same spatial function (perfect spin pairing),

$$\varphi_k^\alpha(\mathbf{r}) = \varphi_k^\beta(\mathbf{r})$$

- The determinant is then an eigenfunction of the operators $\hat{S}^2$, $\hat{S}_z$, $\hat{S}_+$ and $\hat{S}_-$, with eigenvalue 0 in all cases.

- We find that

$$
\begin{aligned}
E[\Phi] &= V_{nn} + 2 \sum_i h_{ii} + \sum_{i,j} \langle i\,j || i\,j \rangle + \sum_{i,j} \langle i\,j | i\,j \rangle \\
&= V_{nn} + 2 \sum_i h_{ii} + \sum_{i,j} \left(2\langle i\,j | i\,j \rangle - \langle i\,j | j\,i \rangle \right)
\end{aligned}
$$

Closed-shell Hartree–Fock theory

- The two Fock operators $\hat{F}^{(\alpha)}$ and $\hat{F}^{(\beta)}$ are identical in closed–shell restricted Hartree–Fock (RHF) theory.

- Thus, the work and memory requirements are reduced by ca. 50% compared to UHF.

- The Fock operator can be written as

$$\hat{F}^{(\alpha)} = \hat{h} + 2\hat{J}^{(\alpha)} - \hat{K}^{(\alpha)}$$

- RHF is commonly used, since many stable main-group molecules have an even number of electrons and a singlet ground state.

- Often, when the UHF approach is applied to a stable closed-shell molecule, the same solution is obtained as with the RHF method (but with more work).

- Do we know when UHF gives a lower energy than RHF?

Singlet and triplet instabilities in RHF theory

- We consider nondegenerate electronic states with an even number of electrons.

- Nondegenerate RHF states are stationary with respect to symmetry-breaking rotations, but they may not be stable, that is, they may be saddle points.

- To find out, one has to compute the second derivative with respect to the wavefunction parameters (electronic Hessian), including the parameters that change the RHF solution into a UHF state or a symmetric solution into a nonsymmetric wavefunction.

- Triplet instabilities: There is a UHF state lower than RHF.

- Singlet instabilities: A SD with symmetry lower than the molecule's point group has a lower energy than a SD that transforms as an irreducible representation of that point group.

Triplet instability in H_2

- The figure shows potential energy curves of H_2 obtained from RHF and UHF calculations (cc-pVTZ).

- Beyond about $R = 2.3\ a_0$, the UHF treatment yields a lower energy than RHF.

- Note that the UHF guess must have

$$\varphi_k^\alpha \neq \varphi_k^\beta$$

- At $R = 3\ a_0$, the spin-contaminated UHF state has $\langle \hat{S}^2 \rangle \approx 0.67\ \hbar^2$.
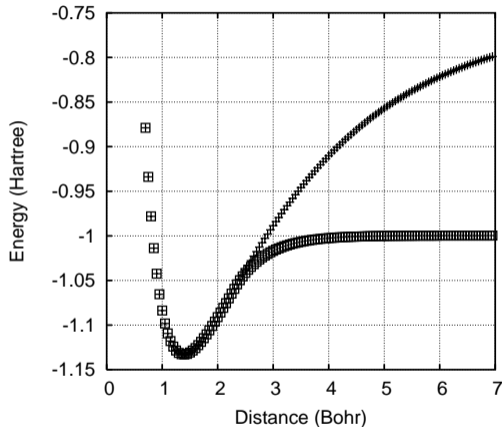

$+$ = RHF, $\square$ = UHF

Singlet instability in the $C_3H_5\cdot$ radical

- We optimise the geometry at the restricted HF level (ROHF/cc-pVDZ) in C_{2v} symmetry $\Rightarrow$ $R_{CC} = 2.5980\ a_0$, $\angle_{CCC} = 124.49°$.

- Things look fine until we compute the harmonic vibrational frequencies from numerical differences of analytic gradients (as done with `NumForce` of `Turbomole`).

- We find one imaginary frequency with wavenumber $\approx 3777i$ cm^{-1}.

- The allyl radical ($C_3H_5\cdot$) provides an example of a singlet instability.
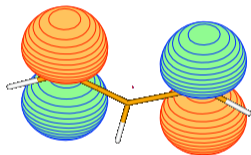
- The unpaired electron occupies the nonbonding π orbital ($1a_2$) and the SD transforms as $^2A_2$.

Restricted open-shell Hartree–Fock theory

- Consider a case where n_c spatial orbitals are doubly occupied with perfect spin pairing —the closed shells— and n_o are singly occupied, all with α spins, the open shells:

$$\Phi = |\varphi_{1\alpha}\varphi_{1\beta}\varphi_{2\alpha}\varphi_{2\beta}\cdots\varphi_{n_c\alpha}\varphi_{n_c\beta}\varphi_{(n_c+1)\alpha}\varphi_{(n_c+2)\alpha}\cdots\varphi_{(n_c+n_o)\alpha}|$$

- This SD is eigenfunction of $\hat{S}_z$ with eigenvalue $M_S = \frac{n_o}{2}$.

- Furthermore, $\hat{S}_+\Phi = 0$, because raising the spin is either not possible (when the orbital has already $m_s = 1/2$) or creates an orbital that is already contained in the SD.

- Hence, $\hat{S}^2\Phi = \left(\hat{S}_-\hat{S}_+ + \hat{S}_z^2 + \hat{S}_z\right)\Phi = \frac{n_o}{2}(\frac{n_o}{2}+1)\Phi \Rightarrow S = \frac{n_o}{2}$

- The ROHF determinant is an eigenfunction of $\hat{S}^2$ with quantum number $S = \frac{n_o}{2}$.

- An high-spin open shell.

Restricted open-shell Hartree–Fock theory

- We shall use indices $i, j, k, \ldots$ for doubly occupied orbitals and $s, t, u, \ldots$ for singly occupied orbitals.

- The energy can then be written as

$$
\begin{aligned}
E[\Phi] \;=\;& V_{nn} + 2\sum_i h_{ii} + \sum_s h_{ss} + \sum_{i,j} \left[2\langle ij|ij \rangle - \langle ij|ji \rangle \right] \\
+\;& \sum_{i,t} \left[2\langle it|it \rangle - \langle it|ti \rangle \right] + \tfrac{1}{2} \sum_{s,t} \left[\langle st|st \rangle - \langle st|ts \rangle \right]
\end{aligned}
$$

- It may also be written as ($J_{pq} = \langle pq|pq \rangle$, $K_{pq} = \langle pq|qp \rangle$):

$$
\begin{aligned}
E[\Phi] \;=\;& f \left[2\sum_s h_{ss} + f \sum_{s,t} \left(2aJ_{st} - bK_{st} \right) + 2\sum_{i,t} \left(2J_{it} - K_{it} \right) \right] \\
+\;& V_{nn} + 2\sum_i h_{ii} + \sum_{i,j} \left(2J_{ij} - K_{ij} \right)
\end{aligned}
$$

Roothaan parameters a and b

$$E[\Phi] = f \left[2 \sum_s h_{ss} + f \sum_{s,t} \left(2a J_{st} - b K_{st} \right) + 2 \sum_{i,t} \left(2J_{it} - K_{it} \right) \right] + \dots$$

- f is the occupancy of the open shell ($f = 1$ means complete occupany and $f = \frac{1}{2}$ refers to a half-filled shell (or MO).

- For the closed-shell case, $f = 1$ and $a = b = 1$.

- For all *single-electron* cases, $a = b = 0$. The fractional occupation f depends on the degeneracy of the shell (*e.g.*, $f = 1/10$ in a d^1 configuration).

- For high-spin half-filled shells (*e.g.*, the N atom's $^4S(p^3)$ state), $f = \frac{1}{2}$ and $a = 1$, $b = 2$.

- Roothaan has shown that the above energy expression can be used for atoms with p^n shells and linear molecules with π^n shells. The method fails for most d^n configurations.

Closed- and open-shell Fock operators

- The variation method leads to the closed- and open-shell Fock operators

$$
\begin{aligned}
\hat{F}^c &= \hat{h} + \sum_i (2\hat{J}_i - \hat{K}_i) + f \sum_s (2\hat{J}_s - \hat{K}_s) \\
\hat{F}^o &= \hat{h} + \sum_i (2\hat{J}_i - \hat{K}_i) + f \sum_s (2a\hat{J}_s - b\hat{K}_s)
\end{aligned}
$$

- The Hartree–Fock equations can be written as

$$
\langle \varphi_a | \hat{F}^c | \varphi_i \rangle = 0, \quad \langle \varphi_a | \hat{F}^o | \varphi_s \rangle = 0, \quad \langle \varphi_i | \hat{F}^c - f\hat{F}^o | \varphi_s \rangle = 0
$$

- ROHF theory is a complex field, which requires a careful reading of the literature and program manuals (*e.g.*, `Turbomole`).

- For example, would you have known that $a = b = 8/9$ for the $O_2^- \cdot$ radical?

Example: the ^3P ground state of the O atom

- Calculations performed in the aug-cc-pVQZ basis set.

- Calculation with `Turbomole` in T_d symmetry:

```
$ closed shells

a1  1-2  ( 2 )

$ open shells type=1

t2  1  ( 4/3 )

$ roothaan 1

 a = 15/16    b = 9/8
```

- ROHF ground-state energy: $E = -74.808\,078\,382\ E_{\text{h}}$

Example: the ^3P ground state of the O atom

- Next, switch to C_1 symmetry and copy the ROHF orbitals to the file containing the α spin orbitals as well as to the file containing the β spin orbitals.

- Evaluation of the UHF expectation value using these spin orbitals gives:

$$\langle \Phi | \hat{H} | \Phi \rangle = -74.808\,078\,382 \; E_\mathrm{h}$$

- This results could also be obtained by running a state-averaged CASSCF calculation in D_{2h} symmetry.

- `Molpro` input:

  ```
  {casscf;closed,2;wf,8,4,2;wf,8,6,2;wf,8,7,2}
  ```

- (State average of the $^3B_{1g}$, $^3B_{2g}$, and $^3B_{3g}$ states.)

Self-consistent field theory: The LCAO expansion

- *Brute-force* numerical methods can be used to solve the Hartree–Fock equations for (di)atoms (by finite differences and finite elements methods, multi-grid techniques).

- The Hartree–Fock equations are one-electron equations and one may think that the problem is three-dimensional.

- However, the nonlocal exchange contribution makes the problem of solving the Hartree–Fock equations for a general molecule six-dimensional.

- This is why certain DFT programs have no "hybrid" functionals implemented, which include Hartree–Fock exchange. Computationally, $\hat{K}$ is much more complicated than $\hat{J}$.

- In the following, we shall expand the MOs in a basis of atomic orbitals (AOs),

$$\varphi_k^\sigma(\mathbf{r}) = \sum_{\mu=1}^{N_{\mathrm{bas}}} \chi_\mu(\mathbf{r})\, C_{\mu i}^\sigma$$

The Roothaan–Hall equations

- To simplify the derivation of the Roothaan–Hall equations as much as possible, we
    1. ... assume that the MOs are real (and hence, also the MO coefficients $C^\sigma_{\mu i}$),
    2. ... ignore spin (but shall return to it later), and
    3. ... use the Mulliken notation for two-electron integrals:

$$\langle \mu\rho|\nu\tau \rangle = \int \int \chi_\mu(\mathbf{r})\chi_\rho(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\chi_\nu(\mathbf{r})\chi_\tau(\mathbf{r}')d\mathbf{r}d\mathbf{r}' = (\mu\nu|\rho\tau)$$

Obviously:

$$
\begin{aligned}
\sum_{i=1}^{n}\langle\varphi_i|\hat{h}|\varphi_i\rangle &= \sum_{i=1}^{n}\sum_{\mu=1}^{N_{\text{bas}}}C_{\mu i}\langle\chi_\mu|\hat{h}|\varphi_i\rangle = \sum_{i=1}^{n}\sum_{\mu=1}^{N_{\text{bas}}}\sum_{\nu=1}^{N_{\text{bas}}}C_{\mu i}\langle\chi_\mu|\hat{h}|\chi_\nu\rangle C_{\nu i} \\
&= \sum_{\mu=1}^{N_{\text{bas}}}\sum_{\nu=1}^{N_{\text{bas}}}D_{\mu\nu}\langle\chi_\mu|\hat{h}|\chi_\nu\rangle = \sum_{\mu=1}^{N_{\text{bas}}}\sum_{\nu=1}^{N_{\text{bas}}}D_{\mu\nu}h_{\mu\nu}
\end{aligned}
$$

The Roothaan–Hall equations

- We have introduced the density matrix $\mathbf{D}$, where the summation is over all (spin) orbitals,

$$D_{\mu\nu} = \sum_{i=1}^{n} C_{\mu i} C_{\nu i}, \quad \text{or } \mathbf{D} = \mathbf{CC}^{\mathrm{T}}$$

- By inserting the LCAO expansion also into the two-electron energy contribution, we obtain (here and in the following, we omit the summation limits):

$$E[\mathbf{C}] = V_{nn} + \sum_{\mu,\nu} D_{\mu\nu} h_{\mu\nu} + \tfrac{1}{2} \sum_{\mu,\nu} \sum_{\rho,\tau} \left[D_{\mu\nu} D_{\rho\tau} - D_{\mu\rho} D_{\nu\tau} \right] (\mu\nu|\rho\tau)$$

- The orbitals are orthonormal,

$$\mathbf{C}^{\mathrm{T}} \mathbf{S} \mathbf{C} = \mathbf{1}, \quad \text{with } S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$$

The Lagrangian

- We are interested in finding the MO coefficients $\mathbf{C}$ that minimise the SCF energy $E(\mathbf{C})$ in the sense of the variation method, but we cannot simply require the first derivatives of $E(\mathbf{C})$ to be zero for all $C_{\mu i}$.

- Rather, we must minimise $E(\mathbf{C})$ under the constraint that the MOs remain orthonormal. This can be done using Lagrange's method of undetermined multipliers,

$$F[\mathbf{C}, \boldsymbol{\lambda}] = E[\mathbf{C}] + \mathrm{Tr}\left[(\mathbf{1} - \mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C})\boldsymbol{\lambda}\right]$$

- Note that the unit matrix $\mathbf{1}$ and the matrix of Lagrange multipliers $\boldsymbol{\lambda}$ are $n \times n$ matrices while $\mathbf{S}$ is a $N_{\mathrm{bas}} \times N_{\mathrm{bas}}$ matrix. The MO-coefficients matrix $\mathbf{C}$ has N_{bas} rows and n columns.
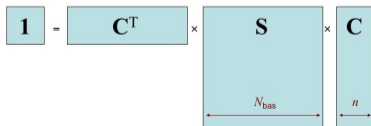
Minimising the Lagrangian

- We require the Lagrange functional $F[\mathbf{C}, \boldsymbol{\lambda}]$ to be stationary with respect to the coefficients $\mathbf{C}$ and multipliers $\boldsymbol{\lambda}$,

$$\frac{\partial F[\mathbf{C}, \boldsymbol{\lambda}]}{\partial C_{\omega i}} = 0 \quad \forall\, C_{\omega i}, \qquad \frac{\partial F[\mathbf{C}, \boldsymbol{\lambda}]}{\partial \lambda_{kl}} = 0 \quad \forall\, \lambda_{kl} \;\Leftrightarrow\; \mathbf{1} - \mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} = \mathbf{0}$$

- While the equation to the right is just the normalisation condition, the equations to the left are the Roothaan–Hall equations.

- The gradient is easily computed by taking partial derivatives with respect to $D_{\kappa\lambda}$,

$$
\begin{aligned}
\frac{\partial E[\mathbf{C}]}{\partial C_{\omega i}} &= \sum_{\kappa, \lambda} \frac{\partial E[\mathbf{C}]}{\partial D_{\kappa\lambda}} \frac{\partial D_{\kappa\lambda}}{\partial C_{\omega i}} = 2 \sum_{\lambda} \frac{\partial E[\mathbf{C}]}{\partial D_{\omega\lambda}} C_{\lambda i} \\
&= 2 \sum_{\lambda} h_{\omega\lambda} C_{\lambda i} \;+\; \text{two-electron terms} = 2(\mathbf{h}\mathbf{C})_{\omega i} \;+\; \text{two-electron terms}
\end{aligned}
$$

Minimising the Lagrangian

- Similarly, we obtain for the orthonormality constraint,

$$\frac{\partial \mathrm{Tr}\left[(\mathbf{1} - \mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C})\boldsymbol{\lambda}\right]}{\partial C_{\omega i}} = -2\left(\mathbf{S}\mathbf{C}\boldsymbol{\lambda}\right)_{\omega i}$$

- Hence,

$$\begin{aligned}
\frac{\partial F[\mathbf{C}, \boldsymbol{\lambda}]}{\partial C_{\omega i}} &= 2(\mathbf{h}\mathbf{C})_{\omega i} - 2\left(\mathbf{S}\mathbf{C}\boldsymbol{\lambda}\right)_{\omega i} + \text{ two-electron terms} \\
&= 2(\mathbf{F}\mathbf{C})_{\omega i} - 2\left(\mathbf{S}\mathbf{C}\boldsymbol{\lambda}\right)_{\omega i} = 0 \quad \forall\ C_{\omega i}
\end{aligned}$$

$$\boxed{\mathbf{F}} \times \boxed{\mathbf{C}} - \boxed{\mathbf{S}} \times \boxed{\mathbf{C}} \times \boxed{\boldsymbol{\lambda}}$$

The two-electron terms add to the one-electron Hamiltonian to yield the Fock operator. The Roothaan–Hall equations thus read:

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\lambda}$$

Canonical Roothaan–Hall equations

- The Roothaan–Hall equations in the LCAO Ansatz are nothing but the translation of the coupled integro-differential Hartree–Fock equations into the language of standard linear algebra,

$$\hat{F}\varphi_i = \sum_m \varphi_m \lambda_{mi} \iff \mathbf{FC} = \mathbf{SC}\boldsymbol{\lambda}$$

- As for Hartree–Fock, orthogonal transformations of the MOs (*i.e.*, columns of $\mathbf{C}$) do neither change the energy $E[\mathbf{C}]$ nor the Lagrangian $F[\mathbf{C}, \boldsymbol{\lambda}]$.

- Hence, we can choose the orbitals such that $\boldsymbol{\lambda}$ becomes the diagonal matrix $\boldsymbol{\varepsilon}$. These orbitals are the canonical MOs,

$$\hat{F}\varphi_i = \varphi_i \varepsilon_i \iff \mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \implies \mathbf{FC}_i = \mathbf{SC}_i \varepsilon_i$$

($\mathbf{C}_i$ is the i-th column of the matrix $\mathbf{C}$).

An orthonormal basis

- The Roothaan–Hall equation is a generalized matrix eigenvalue equation. To solve it, it is convenient to bring it on a conventional matrix eigenvalue form without $\mathbf{S}$.

- Let $\mathbf{U}$ be a real, nonsingular matrix: $\mathbf{U}\mathbf{U}^{-1} = \mathbf{U}^{-1}\mathbf{U} = \mathbf{1}$. We can insert $\mathbf{U}\mathbf{U}^{-1}$ into the Roothaan–Hall equation and obtain:

$$
\begin{aligned}
\mathbf{FC} = \mathbf{SC}\varepsilon &\quad\Leftrightarrow\quad (\mathbf{FU})(\mathbf{U}^{-1}\mathbf{C}) = (\mathbf{SU})(\mathbf{U}^{-1}\mathbf{C})\varepsilon \\
&\quad\Leftrightarrow\quad (\mathbf{U}^{\mathrm{T}}\mathbf{FU})(\mathbf{U}^{-1}\mathbf{C}) = (\mathbf{U}^{\mathrm{T}}\mathbf{SU})(\mathbf{U}^{-1}\mathbf{C})\varepsilon
\end{aligned}
$$

- The matrix $\mathbf{U}$ can be chosen such that $\mathbf{U}^{\mathrm{T}}\mathbf{SU} = \mathbf{1}$. We then obtain

$$
\tilde{\mathbf{F}}\tilde{\mathbf{C}}_i = \tilde{\mathbf{C}}_i\varepsilon_i, \qquad \text{with } \tilde{\mathbf{F}} = \mathbf{U}^{\mathrm{T}}\mathbf{FU} \text{ and } \tilde{\mathbf{C}} = \mathbf{U}^{-1}\mathbf{C}
$$

- The matrix $\mathbf{U}$ defines an orthonormal basis $\{\phi_\tau\}$, expanded in our original basis,

$$
\phi_\tau(\mathbf{r}) = \sum_{\mu=1}^{N_{\mathrm{bas}}} \chi_\mu(\mathbf{r})\, U_{\mu\tau}
$$

An orthonormal basis

- Of course, the final MOs are still expanded in the original basis,

$$\varphi_i(\mathbf{r}) = \sum_{\tau=1}^{N_{\mathrm{bas}}} \phi_\tau(\mathbf{r})\, \tilde{C}_{\tau i} = \sum_{\tau=1}^{N_{\mathrm{bas}}} \sum_{\mu=1}^{N_{\mathrm{bas}}} \chi_\mu(\mathbf{r})\, U_{\mu\tau}\, \tilde{C}_{\tau i} = \sum_{\mu=1}^{N_{\mathrm{bas}}} \chi_\mu(\mathbf{r})\, C_{\mu i}$$

- Hence, we see that $\mathbf{C} = \mathbf{U}\tilde{\mathbf{C}}$.

- During the SCF iterations (*vide infra*), we can simply use the MO coefficients from the previous iteration, $\mathbf{C}^{(k-1)}$ as an orthonormal basis and compute

$$\tilde{\mathbf{F}} = \left[\mathbf{C}^{(k-1)}\right]^{\mathrm{T}} \mathbf{F} \mathbf{C}^{(k-1)}$$

  The new coefficients are then obtained as $\mathbf{C}^{(k)} = \mathbf{C}^{(k-1)}\tilde{\mathbf{C}}$.

- In actual calculations, an orthonormal basis is constructed before starting the SCF iterations. How should we start?

An orthonormal basis

- In the first SCF iteration, we can orthogonalise the AOs using the Gram–Schmidt approach: The first AO is taken as is. The second AO is orthogonalised against the first, the third against the first two, the fourth against the first three, and so on.

- Alternatively, we start by diagonalising the overlap matrix $\mathbf{S}$,

$$\mathbf{V}^{\mathrm{T}}\mathbf{S}\mathbf{V} = \boldsymbol{\sigma}$$

with $\boldsymbol{\sigma}$ diagonal and $\mathbf{V}$ an orthogonal matrix. We then form the matrix

$$\mathbf{U} = \mathbf{V}\boldsymbol{\sigma}^{-\frac{1}{2}}, \qquad \mathbf{U}^{\mathrm{T}}\mathbf{S}\mathbf{U} = \boldsymbol{\sigma}^{-\frac{1}{2}}\mathbf{V}^{\mathrm{T}}\mathbf{S}\mathbf{V}\boldsymbol{\sigma}^{-\frac{1}{2}} = \boldsymbol{\sigma}^{-\frac{1}{2}}\boldsymbol{\sigma}\boldsymbol{\sigma}^{-\frac{1}{2}} = \mathbf{1}$$

- This canonical orthogonalisation has the advantage that we can identify a near (or exact) linear dependency in the basis set (an eigenvalue $\sigma_{\mu\mu} \approx 0$) and remove the corresponding column $\mathbf{V}_\mu$ simply by setting $\sigma_{\mu\mu}^{-1/2} = 0$.

An orthonormal basis

- It is also possible to define $\mathbf{U}$ as

$$\mathbf{U} = \mathbf{S}^{-\frac{1}{2}} = \mathbf{V}\boldsymbol{\sigma}^{-\frac{1}{2}}\mathbf{V}^{\mathrm{T}}, \qquad \mathbf{U}^{\mathrm{T}}\mathbf{S}\mathbf{U} = \mathbf{S}^{-\frac{1}{2}}\mathbf{S}\mathbf{S}^{-\frac{1}{2}} = \mathbf{1}$$
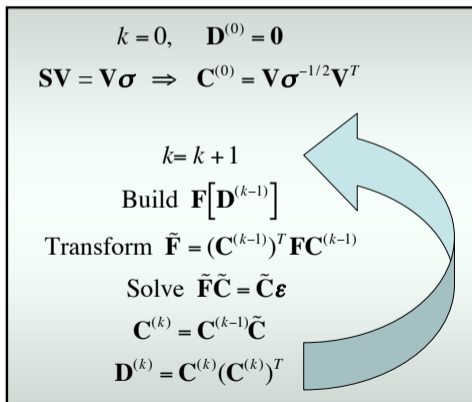
  The advantage of this symmetric orthogonalisation is that the new basis is as close to the original set as possible.

- Although the number of small eigenvalues of $\mathbf{S}$ may change along a potential curve and thus lead to unpleasant discontinuities in the energy, it often is a prerequisite to post-Hartree–Fock calculations (CI, CC) to remove eigenvalues smaller than, say, 10^{-7} (relative to normalised AOs).

- A near linear dependence leads to MOs with large coefficients alternating in sign, and hence, significant round-off errors may occur in integral-transformation steps,

$$(pq|rs) = \sum_{\kappa}\sum_{\lambda}\sum_{\mu}\sum_{\nu} C_{\kappa p}C_{\lambda q}C_{\mu r}C_{\nu s}(\kappa\lambda|\mu\nu)$$

Solving the Roothaan–Hall equations

The box below shows a simple algorithm for solving the Roothaan–Hall equations by the self-consistent-field procedure.

$$k = 0, \quad \mathbf{D}^{(0)} = \mathbf{0}$$

$$\mathbf{SV} = \mathbf{V}\boldsymbol{\sigma} \;\Rightarrow\; \mathbf{C}^{(0)} = \mathbf{V}\boldsymbol{\sigma}^{-1/2}\mathbf{V}^T$$

$$k = k + 1$$

$$\text{Build } \mathbf{F}\left[\mathbf{D}^{(k-1)}\right]$$

$$\text{Transform } \tilde{\mathbf{F}} = (\mathbf{C}^{(k-1)})^T \mathbf{F} \mathbf{C}^{(k-1)}$$

$$\text{Solve } \tilde{\mathbf{F}}\tilde{\mathbf{C}} = \tilde{\mathbf{C}}\boldsymbol{\varepsilon}$$

$$\mathbf{C}^{(k)} = \mathbf{C}^{(k-1)}\tilde{\mathbf{C}}$$

$$\mathbf{D}^{(k)} = \mathbf{C}^{(k)}(\mathbf{C}^{(k)})^T$$

Roothaan–Hall equations for UHF

- In UHF theory, the α and β spin orbitals are expanded in the same AO basis,

$$\varphi_k^\alpha(\mathbf{r}) = \sum_{\mu=1}^{N_{\text{bas}}} \chi_\mu(\mathbf{r}) C_{\mu k}^\alpha, \quad \varphi_k^\beta(\mathbf{r}) = \sum_{\mu=1}^{N_{\text{bas}}} \chi_\mu(\mathbf{r}) C_{\mu k}^\beta$$

With these orbitals, a density matrix can be defined for each of the spins (assuming real MOs),

$$D_{\mu\nu}^\alpha = \sum_{i=1}^{n_\alpha} C_{\mu i}^\alpha C_{\nu i}^\alpha, \quad D_{\mu\nu}^\beta = \sum_{i=1}^{n_\beta} C_{\mu i}^\beta C_{\nu i}^\beta,$$

- We can now write the energy

$$E[\Phi] = V_{nn} + \sum_i h_{ii} + \sum_{\bar{i}} h_{\bar{i}\bar{i}} + \tfrac{1}{2} \sum_{i,j} \langle i\,j || i\,j \rangle + \tfrac{1}{2} \sum_{\bar{i},\bar{j}} \langle \bar{i}\,\bar{j} || \bar{i}\,\bar{j} \rangle + \sum_{i,\bar{j}} \langle i\,\bar{j} | i\,\bar{j} \rangle$$

as a function of the density matrices $\mathbf{D}^\alpha$ and $\mathbf{D}^\beta$.

Roothaan–Hall equations for UHF

We obtain

$$
\begin{aligned}
E[\Phi] &= V_{nn} + \sum_{\mu\nu}[D^{\alpha}_{\mu\nu} + D^{\beta}_{\mu\nu}]h_{\mu\nu} \\
&+ \tfrac{1}{2}\sum_{\kappa\lambda\mu\nu} D^{\alpha}_{\mu\nu}D^{\alpha}_{\kappa\lambda}[(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] \\
&+ \tfrac{1}{2}\sum_{\kappa\lambda\mu\nu} D^{\beta}_{\mu\nu}D^{\beta}_{\kappa\lambda}[(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] + \sum_{\kappa\lambda\mu\nu} D^{\alpha}_{\mu\nu}D^{\beta}_{\kappa\lambda}(\mu\nu|\kappa\lambda)
\end{aligned}
$$

which can be rewritten using $\mathbf{D} = \mathbf{D}^{\alpha} + \mathbf{D}^{\beta}$ and $\mathbf{D}^{\mathrm{spin}} = \mathbf{D}^{\alpha} - \mathbf{D}^{\beta}$,

$$
\begin{aligned}
E[\Phi] &= V_{nn} + \sum_{\mu\nu} D_{\mu\nu}h_{\mu\nu} + \frac{1}{4}\sum_{\kappa\lambda\mu\nu} D_{\mu\nu}D_{\kappa\lambda}[2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] \\
&- \frac{1}{4}\sum_{\kappa\lambda\mu\nu} D^{\mathrm{spin}}_{\mu\nu}D^{\mathrm{spin}}_{\kappa\lambda}(\mu\kappa|\nu\lambda)
\end{aligned}
$$

Roothaan–Hall equations for UHF

- We also obtain two Fock matrices (in the AO basis),

$$F_{\mu\nu}^{\alpha} \quad = \quad h_{\mu\nu} \; + \tfrac{1}{2} \sum_{\kappa\lambda} \left\{ D_{\kappa\lambda}[2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] - D_{\kappa\lambda}^{\mathrm{spin}}(\mu\kappa|\nu\lambda) \right\}$$

$$F_{\mu\nu}^{\beta} \quad = \quad h_{\mu\nu} \; + \tfrac{1}{2} \sum_{\kappa\lambda} \left\{ D_{\kappa\lambda}[2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] + D_{\kappa\lambda}^{\mathrm{spin}}(\mu\kappa|\nu\lambda) \right\}$$

- We now obtain the following UHF Roothaan–Hall equations (including the closed-shell case):

$$\mathbf{F}^{\alpha}\mathbf{C}^{\alpha} = \mathbf{S}\mathbf{C}^{\alpha}\boldsymbol{\varepsilon}^{\alpha}$$

$$\mathbf{F}^{\beta}\mathbf{C}^{\beta} = \mathbf{S}\mathbf{C}^{\beta}\boldsymbol{\varepsilon}^{\beta}$$

$$\Leftrightarrow \begin{pmatrix} \mathbf{F}^{\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{F}^{\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{C}^{\beta} \end{pmatrix} = \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{S} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{C}^{\beta} \end{pmatrix} \begin{pmatrix} \boldsymbol{\varepsilon}^{\alpha} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\varepsilon}^{\beta} \end{pmatrix}$$

Guess of initial orbitals

- In order to converge the SCF procedure quickly, it is important to have an accurate guess of the orbitals for the first iteration or an accurate guess of the trial density. There are several possibilities:

  1. We start with $\mathbf{D}^{(0)} = (\mathbf{D}^{\text{spin}})^{(0)} = \mathbf{0}$. Electron repulsion is neglected in the first iteration (bare nuclear Hamiltonian).

  2. We use the orbitals from another calculation, for example, a calculation carried out in a smaller AO basis,

  $$\mathbf{D}^{(0)}_{\text{large basis}} = \tilde{\mathbf{S}}^{\text{T}} \mathbf{D}_{\text{small basis}} \tilde{\mathbf{S}}, \quad \tilde{S}_{\mu\nu} = \langle \chi_{\mu,\text{small}} | \chi_{\nu,\text{large}} \rangle$$

  3. We use the density obtained from extended Hückel theory (EHT), projected onto the actual basis set.

  4. We construct the trial density as superposition of atomic densities. This density can be diagonalised and the eigenvectors with near integer occupation numbers can be used as trial orbitals.

Level shifting

- In order to converge the SCF procedure quickly (or to converge it at all), it may be needed to monitor the convergence process and to manipulate the Fock matrix,

$$\tilde{\mathbf{F}}\tilde{\mathbf{C}} = \tilde{\mathbf{C}}\varepsilon, \quad \text{with } \tilde{\mathbf{F}} = \left[\mathbf{C}^{(k-1)}\right]^{\mathrm{T}}\mathbf{F}\mathbf{C}^{(k-1)} \quad \text{and } \mathbf{C}^{(k)} = \mathbf{C}^{(k-1)}\tilde{\mathbf{C}}$$

- Near convergence, $\tilde{\mathbf{C}}$ will be close to unity, $\tilde{\mathbf{C}} = \mathbf{1} + \boldsymbol{\omega}$. The values of $\boldsymbol{\omega}$ can be estimated from first-order perturbation theory,

$$\omega_{ia} = \frac{\tilde{F}_{ia}}{\tilde{F}_{aa} - \tilde{F}_{ii}} = \frac{\tilde{F}_{ia}}{\varepsilon_a^{(k-1)} - \varepsilon_i^{(k-1)}}$$

- If there is a small HOMO–LUMO gap (in the previous iteration), then the corresponding ω_{ia} is large and can cause oscillations.

- We can stabilise the iterations by adding a level shift $\Delta > 0$ to the diagonal elements of the virtuals, $\tilde{F}_{aa} \to \tilde{F}_{aa} + \Delta$.

Damping

- Another way to reduce ω_{ia} (also when $\Delta = 0$) is by reducing the off-diagonal elements $\tilde{F}_{ia}$,

$$\omega_{ia} = \frac{\tilde{F}_{ia}}{\tilde{F}_{aa} - \tilde{F}_{ii} + \Delta}, \qquad \tilde{F}_{ia} \to \alpha \tilde{F}_{ia}, \qquad 0 < \alpha < 1$$

- This can for example be achieved by adding the Fock matrix of the previous iteration (which is diagonal) with a certain weight (e.g., $\beta = 0.5$) to the present Fock matrix,

$$\tilde{F}_{ii} \to \tilde{F}_{ii} + \beta \varepsilon_i^{(k-1)}, \qquad \tilde{F}_{aa} \to \tilde{F}_{aa} + \beta \varepsilon_a^{(k-1)}$$

- Level shifting and damping can be combined. Level shifting reduces the mixing of high-lying occupied MOs with low-lying virtual MOs. Damping reduces *all mixing*.

- Neither of the techniques help to accelerate creepingly slow SCF procedures.

Fermi smearing (in DFT)

- The idea of Fermi smearing is to compute density matrices $\mathbf{D}$ and $\mathbf{D}^{\mathrm{spin}}$ from partially occupied orbitals. These density matrices are then used to build Fock matrices, to obtain new orbitals, and so on.

- Fractional occupation numbers $n_p \in [0, 1]$ are computed as a function of a temperature T when the HOMO–LUMO gap drops below a given threshold (μ is the Fermi level),

$$n_p = \tfrac{1}{2}\mathsf{erfc}\left(\frac{\epsilon_p - \mu}{fT}\right), \qquad f = 4k_B/\sqrt{\pi}$$

- When the energy has converged to within a given threshold, the Fermi smearing is switched off ($T = 0$).

- Calculation of fractional occupation numbers often requires much higher damping and level shifting.

Pulay's DIIS procedure

- Let us be concerned with a general iterative procedure in which we try to solve

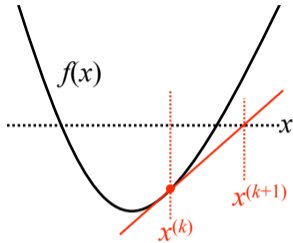$$\mathbf{f}[\mathbf{x}] = \mathbf{0}$$

- Examples include:

  1. **Geometry optimizations**, where $\mathbf{x}$ is the geometry and $\mathbf{f}[\mathbf{x}]$ the gradient. If not yet converged in iteration step number k, we have

  $$\mathbf{f}[\mathbf{x}^{(k)}] = \mathbf{g}^{(k)} \neq \mathbf{0}, \qquad \mathbf{g}^{(k)} \Rightarrow \mathbf{x}^{(k+1)}$$

  2. **Coupled-cluster calculations**, where $\mathbf{x}$ contains the amplitudes, $\mathbf{f}[\mathbf{x}]$ are the amplitudes equations and $\mathbf{g}^{(k)}$ the vector functions.

  3. **SCF calculations**, where $\mathbf{F}[\mathbf{D}^{(k)}]\mathbf{D}^{(k)}\mathbf{S} - \mathbf{S}\mathbf{D}^{(k)}\mathbf{F}[\mathbf{D}^{(k)}] = \mathbf{g}^{(k)}$

Pulay's DIIS procedure

- As an example of Pulay's DIIS method, we apply it to a simple Newton–Raphson procedure to solve $f(x) = 0$. From a given $x^{(k)}$, we obtain a new $x^{(k+1)}$ via

$$x^{(k+1)} = x^{(k)} - \frac{f(x^{(k)})}{f'(x^{(k)})}$$

- After having obtained a series of n approximations $x^{(1)}, x^{(2)}, \ldots, x^{(n)}$, we construct the linear combination

$$\tilde{x} = \sum_{k=1}^{n} d_k \, x^{(k)}, \quad \text{with the constraint} \quad \sum_{k=1}^{n} d_k = 1$$

- The d_k's are obtained from requiring that $||f(\tilde{x})||^2 = \min$.

Pulay's DIIS procedure

- To compute $f(\tilde{x})$, we approximate the function as

$$f(\tilde{x}) \approx \sum_{k=1}^{n} d_k \, f(x^{(k)}),$$

- Minimising the appropriate Lagrangian leads to

$$\begin{pmatrix} f(x^{(1)})f(x^{(1)}) & \ldots & f(x^{(1)})f(x^{(n)}) & -1 \\ f(x^{(2)})f(x^{(1)}) & \ldots & f(x^{(2)})f(x^{(n)}) & -1 \\ \vdots & & \vdots & \vdots \\ f(x^{(n)})f(x^{(1)}) & \ldots & f(x^{(n)})f(x^{(n)}) & -1 \\ 1 & \ldots & 1 & 0 \end{pmatrix} \begin{pmatrix} d_1 \\ d_2 \\ \vdots \\ d_n \\ \lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{pmatrix}$$

- In SCF theory, the d_k's are used to extrapolate directly the Fock matrix.