HARTREE-FOCK EQUATIONS

$|\tilde{\Phi}\rangle \rightarrow$ Slater determinant

$$E[\tilde{\Phi}] = \frac{\langle \tilde{\Phi}|H|\tilde{\Phi}\rangle}{\langle \tilde{\Phi}|\tilde{\Phi}\rangle}$$

$$\min_{\tilde{\Phi}} E[\tilde{\Phi}] = E[\Phi] \quad \checkmark$$

Φ: optimum determinant

We will rely on Thouless' theorem.

$$|\tilde{\Phi}\rangle = e^{C_1}|\Phi\rangle$$

$$C_1 = \sum_{a,i} \langle a|\hat{c}_1|i\rangle X_a^+ X_i$$

$$E[\tilde{\Phi}] = \frac{\langle \Phi | e^{C_1^\dagger} H e^{C_1} | \Phi \rangle}{\langle \Phi | e^{C_1^\dagger} e^{C_1} | \Phi \rangle}$$

(variational calculus)

$E[\tilde{\Phi}]$ ← functional

In standard calculus,

$$f = f(x_1, \ldots, x_n) \; ; \quad \left.\frac{\partial f}{\partial x_i}\right|_{x = x^{(0)}} = 0$$

← stationary point

$$df = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} dx_i = 0$$

$$f(x_1, \ldots, x_n) - f(x_1^{(0)}, \ldots, x_n^{(0)})$$

$$= \sum_{i=1}^{n} \left.\frac{\partial f}{\partial x_i}\right|_{x = x^{(0)}} (x_i - x_i^{(0)}) + \ldots$$

$\left.\frac{\partial f}{\partial x_i}\right|_{x = x^{(0)}}$ ← 0

$(x_i - x_i^{(0)})$ ← linear in $x - x^{(0)}$

$$\delta E[\Phi] = \text{terms in } E[\tilde{\Phi}] - E[\Phi] \text{ linear in } |\delta\Phi\rangle$$

1st variation of E

What is $|\delta\Phi\rangle$?

$$|\tilde{\Phi}\rangle - |\Phi\rangle = e^{C_1}|\Phi\rangle$$

$$-|\Phi\rangle = \left(1 + C_1 + \frac{1}{2}C_1^2 + \ldots\right)|\Phi\rangle$$

$$-|\Phi\rangle = C_1|\Phi\rangle + \ldots$$

$$|\delta\Phi\rangle = C_1|\Phi\rangle$$

We will now try to identify terms linear in C_1 in the difference $E[\tilde{\Phi}] - E[\Phi]$. Then, we will set $\delta E[\Phi]$ at 0.

$$E[\tilde{\Phi}] - E[\Phi] = \frac{\langle \Phi | e^{C_1^\dagger} H e^{C_1} | \Phi \rangle}{\langle \Phi | e^{C_1^\dagger} e^{C_1} | \Phi \rangle}$$

$$- E[\Phi] =$$

$$= \frac{\langle \Phi | (1 + C_1^\dagger + \frac{1}{2}(C_1^\dagger)^2 + \dots) H (1 + C_1 + \frac{1}{2} C_1^2 + \dots) | \Phi \rangle}{\langle \Phi | (1 + C_1^\dagger + \frac{1}{2}(C_1^\dagger)^2 + \dots)(1 + C_1 + \frac{1}{2} C_1^2 + \dots) | \Phi \rangle}$$

$$- E[\Phi] =$$

$$= \frac{\langle \Phi | H | \Phi \rangle + \langle \Phi | C_1^\dagger H | \Phi \rangle + \langle \Phi | H C_1 | \Phi \rangle + O(C_1^2)}{\langle \Phi | \Phi \rangle + \langle \Phi | C_1^\dagger | \Phi \rangle^{0} + \langle \Phi | C_1 | \Phi \rangle^{0} + O(C_1^2)}$$

$$- E[\Phi] =$$

$$= \frac{\langle \Phi | H | \Phi \rangle + \langle \Phi | C_1^\dagger H | \Phi \rangle + \langle \Phi | H C_1 | \Phi \rangle + O(C_1^2)}{1 + O(C_1^2)}$$

$$- E[\Phi] =$$

$\times$

$$\frac{1}{1+x} = 1 - x + \dots$$

$$E[\tilde{\Phi}] - E[\Phi] = \Big[\langle \Phi | H | \Phi \rangle + \langle \Phi | C_1^\dagger H | \Phi \rangle + \langle \Phi | H C_1 | \Phi \rangle + O(C_1^2) \Big] \Big[1 - O(C_1^2) \Big] - E[\Phi]$$

$$= \cancel{\langle \Phi | H | \Phi \rangle} + \underline{\langle \Phi | C_1^\dagger H | \Phi \rangle} + \underline{\langle \Phi | H C_1 | \Phi \rangle} + O(C_1^2) \cancel{- E[\Phi]}$$

$$E[\Phi] = \frac{\langle \Phi | H | \Phi \rangle}{\underbrace{\langle \Phi | \Phi \rangle}_{1}} = \langle \Phi | H | \Phi \rangle$$

$$\delta E[\Phi] = \langle \Phi | C_1^\dagger H | \Phi \rangle + \langle \Phi | H C_1 | \Phi \rangle$$

$$= \langle \Phi | C_1^\dagger H | \Phi \rangle + \text{c.c.}$$

At the stationary point $|\Phi\rangle$,

$$\delta E[\Phi] = 0.$$

$$\langle \Phi | C_1^\dagger H | \Phi \rangle = 0 \quad \forall C_1$$

$$(\langle \Phi | H C_1 | \Phi \rangle = 0)$$

We will assume that $|\Phi\rangle$ is also a Fermi vacuum.

$$H = H_N + \langle \Phi | H | \Phi \rangle$$

$$= F_N + V_N + \langle \Phi | H | \Phi \rangle$$

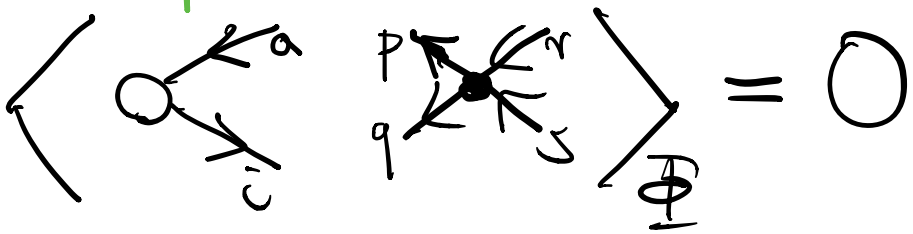
$$F_N = \sum_{p,q} \langle p|f|q\rangle N[X_p^\dagger X_q]$$

$$V_N = \frac{1}{2} \sum_{p,q,r,s} \langle pq|v|rs\rangle \times N[X_p^\dagger X_r X_q^\dagger X_s]$$

We obtain,

$$\langle \Phi|C_i^\dagger H|\Phi\rangle = \langle \Phi|C_i^\dagger F_N|\Phi\rangle + \cancel{\langle \Phi|C_i^\dagger V_N|\Phi\rangle}^{\,0} + \langle \Phi|H|\Phi\rangle \cancel{\langle \Phi|C_i^\dagger|\Phi\rangle}^{\,0} = 0$$

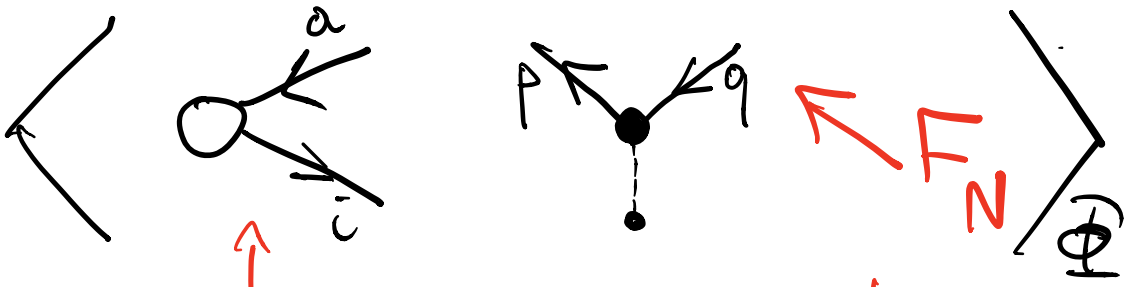
$\langle \Phi|C_i^\dagger V_N|\Phi\rangle$:



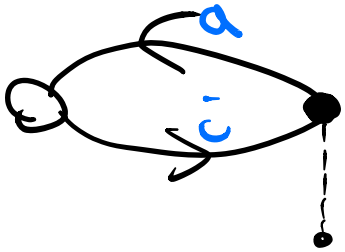
$= 0$

$$\langle \Phi | C_1^\dagger F_N | \Phi \rangle = 0$$

p,q - free



$$C_1^\dagger = \sum_{a,i} \langle a | \hat{c}_1 | i \rangle^* X_i^\dagger X_a$$



$= 0$

$w=1,\ s=(-1)^{1+1}=+1$

$$\sum_{a,i} \langle a | \hat{c}_1 | i \rangle^* \langle a | \hat{f} | i \rangle = 0$$

$$\langle a | \hat{f} | i \rangle = 0 \quad \forall$$

i,a

i - unocc. in $|\Phi\rangle$

a - occ. in $|\Phi\rangle$

$$\hat{f}|i\rangle \perp |a\rangle$$

$$\hat{f}|i\rangle = \sum_{j=1}^{N} \lambda_{ji}|j\rangle \quad \forall\, i=1,\dots,N$$

$$\lambda_{ji} = \langle j|\hat{f}|i\rangle$$

HARTREE-FOCK EQS.

Let's compare these equations to the conventional form of the H-F equations,

$$\hat{f}(x)\,\varphi_i(x) = \sum_{j=1}^{N} \lambda_{ji}\,\varphi_j(x), \quad i=1,\dots,N$$

$\hat{f}$: Fock operator

λ_{ji}: Lagrange multipliers

$$\hat{f}(x) = \hat{z}(x) + \hat{J}(x) - \hat{K}(x)$$

Coulomb exchange

$$\hat{J}(x)\chi(x) = \sum_{j=1}^{N}\left[\int dx' \varphi_j^*(x') v(x,x') \varphi_j(x')\right] \times \chi(x)$$

$$\hat{K}(x)\chi(x) = \sum_{j=1}^{N}\left[\int dx' \varphi_j^*(x') v(x,x') \chi(x')\right] \times \varphi_j(x)$$

This $\hat{f}(x)$ is the same as our f:

$$\langle p|\hat{f}|q\rangle = \langle p|\hat{z}|q\rangle + \langle p|\hat{J}|q\rangle - \langle p|\hat{K}|q\rangle$$

$$\langle p|\hat{J}|q\rangle = \int \varphi_p^*(x)\,\hat{J}(x)\,\varphi_q(x)\,dx$$

$$= \sum_{j=1}^{N} \int dx \int dx'\, \varphi_p^*(x)\,\varphi_j^*(x')\, v(x,x')\,\varphi_q(x)\,\varphi_j(x')$$

$$= \sum_{j=1}^{N} \langle pj|\hat{v}|qj\rangle$$

$x \quad x' \quad x \quad x'$

$$\langle p|\hat{K}|q\rangle = \int \varphi_p^*(x)\,\hat{K}(x)\,\varphi_q^*(x)\,dx$$

$$= \sum_{j=1}^{N} \int dx \int dx'\, \varphi_p^*(x)\,\varphi_j^*(x')$$

$$\times v(x,x')\,\varphi_j(x)\,\varphi_q(x')$$

$$= \sum_{j=1}^{N} \langle pj|\hat{v}|jq\rangle$$

$x \quad x' \quad x \quad x'$

$$\langle p|\hat{f}|q\rangle = \langle p|\hat{z}|q\rangle$$

$$+ \sum_{j=1}^{N} \left(\langle pj|\hat{v}|qj\rangle - \langle pj|\hat{v}|jq\rangle \right)$$

$$= \langle p|\hat{z}|q\rangle + \sum_{j=1}^{N} \langle pj|\hat{v}|q\underline{j}\rangle_A$$

$$\langle p|\hat{f}|q\rangle = \langle p|\hat{z}|q\rangle + \langle p|\hat{g}|q\rangle$$

$$\langle p|\hat{g}|q\rangle = \sum_{j}^{N} \langle pj|\hat{v}|qj\rangle_A$$

In practice, one solves

$$\hat{f}(x)\varphi_i(x) = \varepsilon_i \varphi_i(x) \quad \checkmark$$

CANONICAL H-F EQS.

In our case,

$$\hat{f}|i\rangle = \varepsilon_i|i\rangle, \quad i=1,\ldots,N \quad \checkmark$$

To obtain canonical HF equations, we take advantage of the invariance of the HF equations with respect of unitary transformations of single-particle states in $|\Phi\rangle$.

Let us look at the matrix

$$\underset{\sim}{\Lambda} = \begin{vmatrix} \lambda_{11} & \lambda_{12} \cdots & \lambda_{1N} \\ \lambda_{21} & \lambda_{22} \cdots & \lambda_{2N} \\ & \cdots & \\ \lambda_{N1} & \lambda_{N2} \cdots & \lambda_{NN} \end{vmatrix}$$

$$\lambda_{ij} = \langle i | \hat{f} | j \rangle$$

$\underset{\sim}{\Lambda}$ is hermitian.

We can always diagonalize a hermitian matrix with a unitary transformation:

$$\underset{\sim}{U}^{\dagger} \cdot \underset{\sim}{\Lambda} \cdot \underset{\sim}{U} = \begin{vmatrix} \varepsilon_1 & & 0 \\ & \varepsilon_2 & \\ & & \ddots \\ 0 & & & \varepsilon_n \end{vmatrix}$$

After applying this transformation to the H-F equations, we obtain

$$\hat{f}|\tilde{i}\rangle = \varepsilon_i |\tilde{i}\rangle$$

↑ transformed i's.

From now on, we will drop the tildes,

$$\hat{f}|i\rangle = \varepsilon_i |i\rangle \quad i = 1, \ldots, N$$

H-F equations represent a pseudo-eigenvalue problem:

$$\hat{f}[\varphi_1, \ldots, \varphi_N]\,\varphi_i(x) = \varepsilon_i\,\varphi_i(x), \quad i = 1, \ldots, N$$

We solve them using SCF:

1. We start with defining the initial guess, $\varphi_1^{(0)}, \ldots, \varphi_N^{(0)}$ (e.g., diagonalize $\hat{s}$, or use CNDO, Hückel, etc.)

Construct

$$\hat{f}^{(0)} = \hat{f}[\varphi_1^{(0)}, \ldots \varphi_N^{(0)}],$$

Solve

$$\hat{f}^{(0)} \varphi_i^{(1)} = \varepsilon_i^{(1)} \varphi_i^{(1)}$$

↖ eigenvalue problem for $\hat{f}^{(0)}$

2. Construct

$$\hat{f}^{(1)} = \hat{f}[\varphi_1^{(1)}, \ldots, \varphi_N^{(1)}].$$

Solve

$$\hat{f}^{(1)} \varphi_i^{(2)} = \varepsilon_i^{(2)} \varphi_i^{(2)}$$

3. Construct

$$\hat{f}^{(2)} = \hat{f}[\varphi_1^{(2)}, \ldots, \varphi_N^{(2)}].$$

Solve $\hat{f}^{(2)} \varphi_i^{(3)} = \varepsilon_i^{(3)} \varphi_i^{(3)}$.

And so on, until convergence.

$$|\varepsilon_i^{(n+1)} - \varepsilon_i^{(n)}| < \delta \quad \forall i$$

$$\|\varphi_i^{(n+1)} - \varphi_i^{(n)}\| < \delta' \quad \forall i$$

Usually combined with accelerators.

DIIS, SOSCF, ...

Once we solve the H-F eqs. for single-particle states occupied in $|\Phi\rangle$, we can solve

$$\hat{f}|a\rangle = \varepsilon_a |a\rangle$$

$\hat{f} = \hat{f}[\varphi_1, \ldots, \varphi_N]$

$|a\rangle$: unoccupied in $|\Phi\rangle$

$|a\rangle \perp |i\rangle$

We do this by introducing one-particle basis sets and representing single-particle states as

basis functions

$$\varphi_i(x) = \sum_{\mu=1}^{M} d_{\mu i}\, \chi_\mu(x)$$

$$\varphi_a(x) = \sum_{\mu=1}^{M} d_{\mu a}\, \chi_\mu(x)$$

Typically, $M > N$.

Let's talk about multiple solutions of H-Fegs.

Consider a closed-shell molecule:

spin-orbital

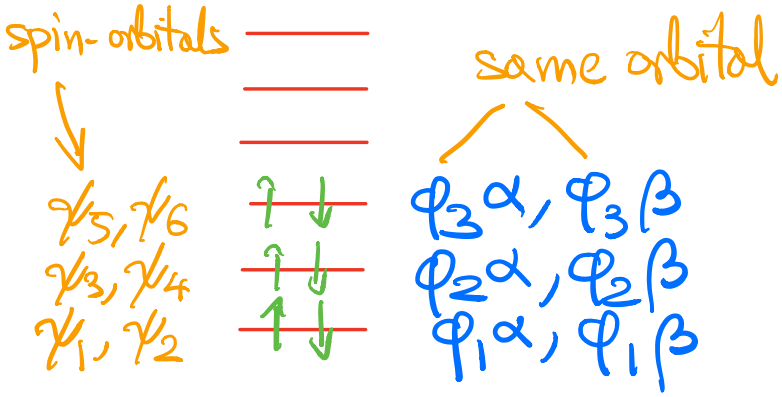
orbital

$$\psi_{2p-1}(x) = \phi_p(\vec{r})\,\alpha$$

$$\psi_{2p}(x) = \phi_p(\vec{r})\,\beta$$

spin-orbitals

same orbital



RHF

$(S=0, S_z=0)$

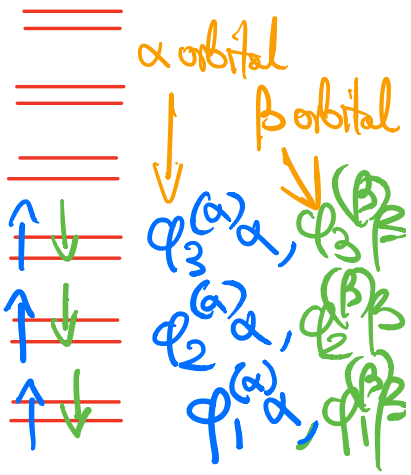
DODS: different orbitals for different spins

$$\psi_{2p-1}(x) = \phi_p^{(\alpha)}(\vec{r})\,\alpha$$

$$\psi_{2p}(x) = \phi_p^{(\beta)}(\vec{r})\,\beta$$

α orbital

β orbital



UHF

$(S\neq 0, S_z=0)$

$$E_{RHF} \geq E_{UHF}$$

When RHF becomes UHF, we say that RHF is triplet stable.

RHF determinant is an eigenfunction of S^2, S_z ($S=0$ for a closed shell).

UHF determinant is spin-contaminated (UHF determinant is NOT an eigenfunction of S^2).

SYMMETRY DILEMMA

Per-Olov Löwdin (Fukutome)

UHF does not break the S_z symmetry.

We can break more symmetries, e.g., S_z.

$$|\sigma\rangle = a|\alpha\rangle + b|\beta\rangle$$

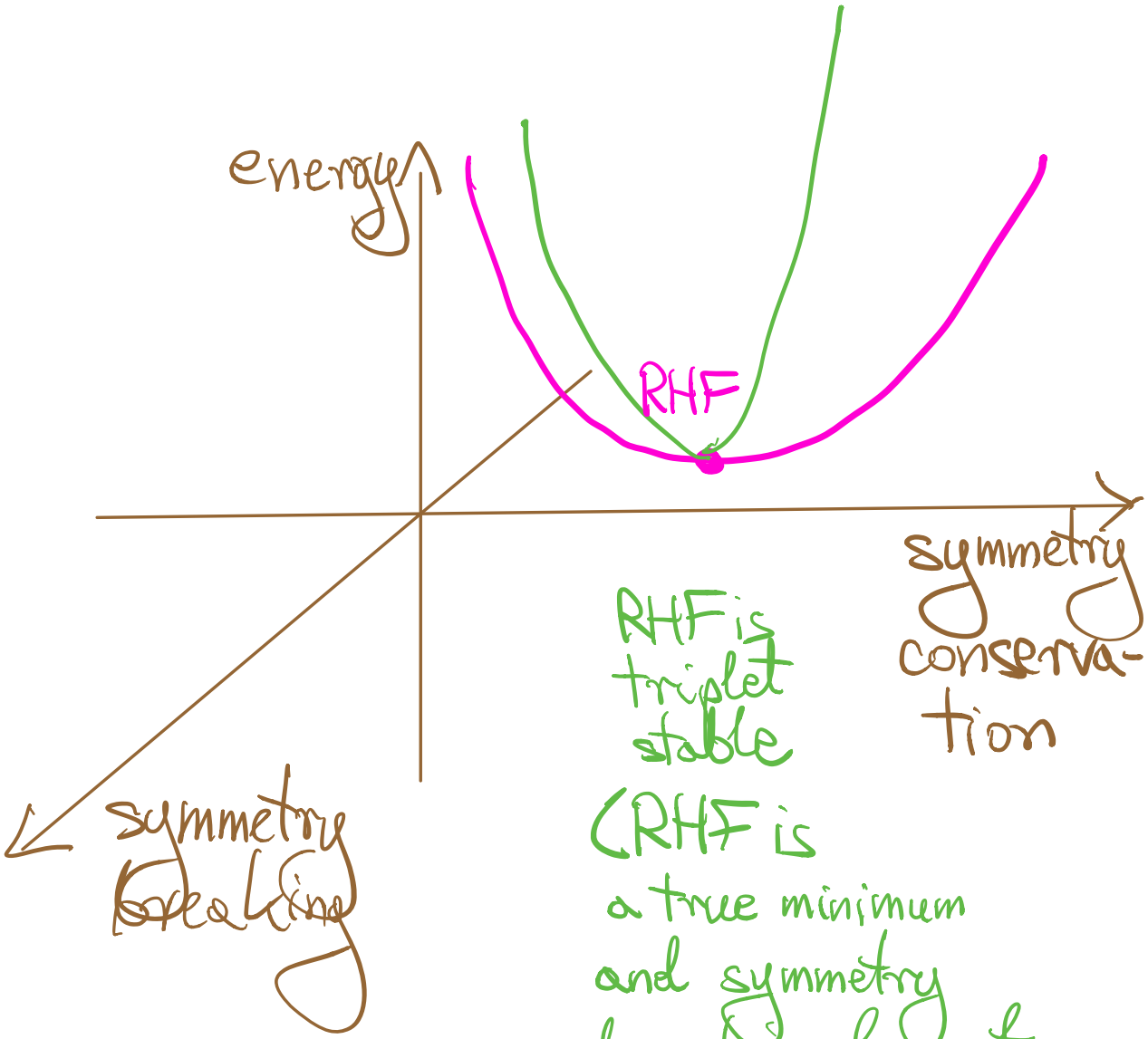
$$\psi_{p\sigma} = \phi_p \sigma$$

After breaking symmetries, and solving H-F (or other mean-field) equations, we can restore them using projection operators.

$$\underbrace{P_{S=0}|UHF\rangle}_{\text{multi-determinantal state}} = P_{S=0} e^{U_1}|RHF\rangle$$

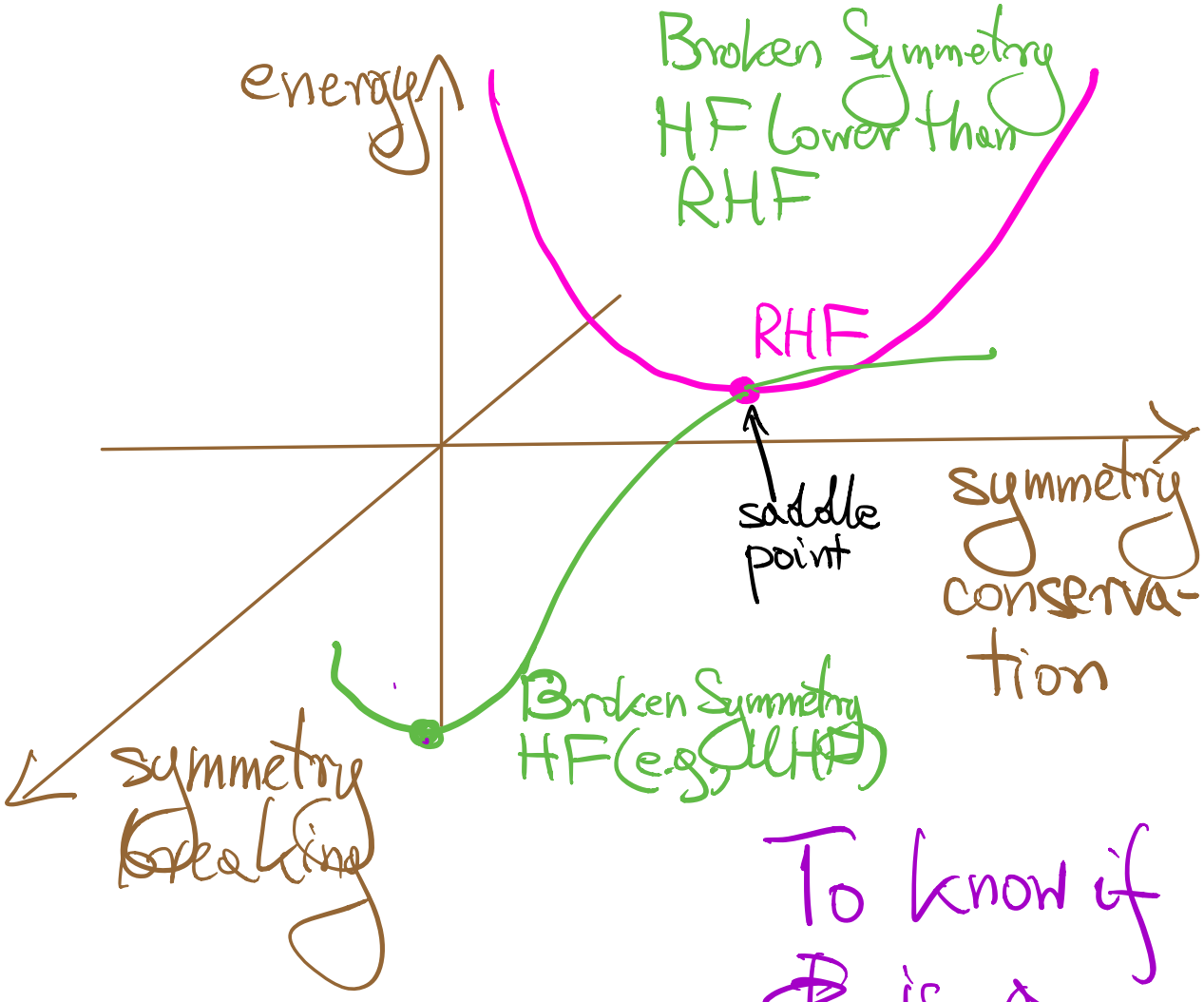
U_1: Thouless operator

$$= e^{K_1+K_2+K_4+\ldots}|RHF\rangle$$



RHF is triplet stable

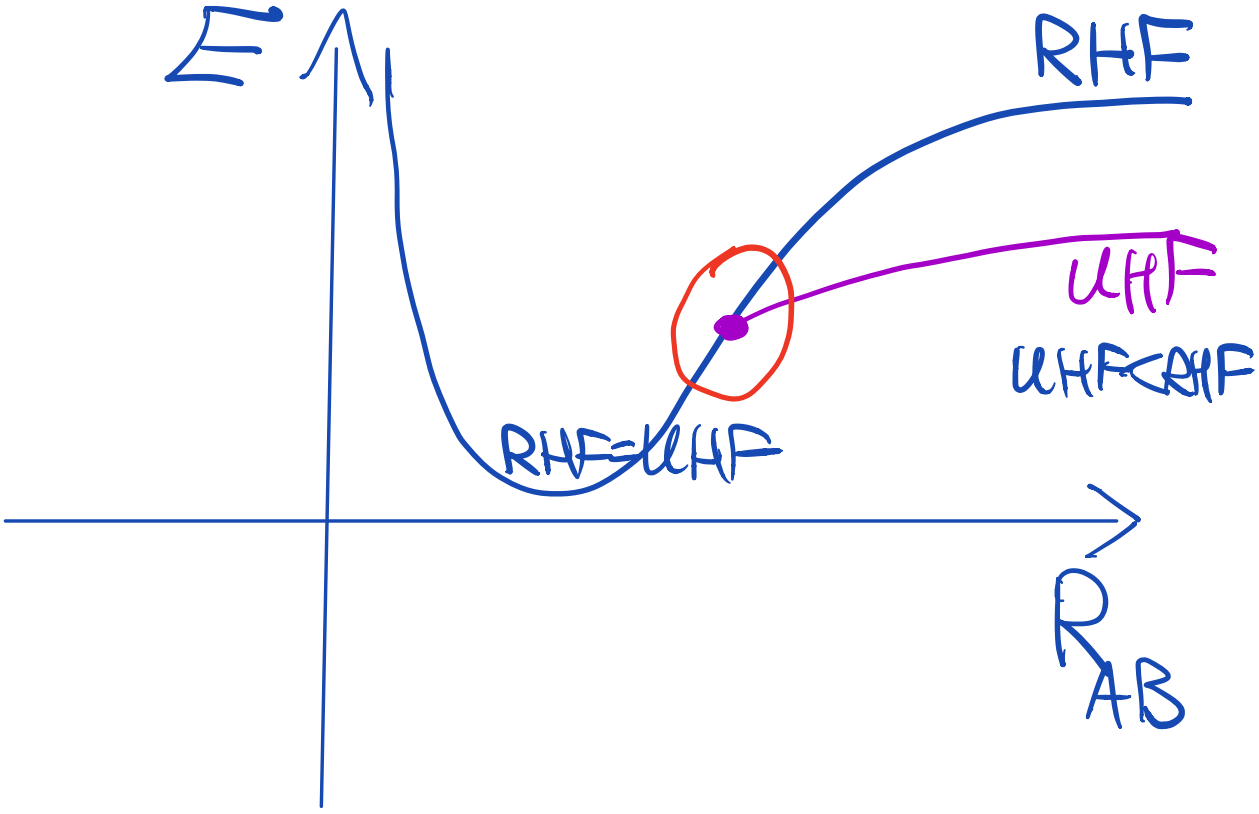
CRHF is a true minimum and symmetry breaking does not lower it)



To know if Φ is a minimum, one has to compute the second variation (Hessian)

Thouless stability conditions (Paldus, Čížek)

Typically, in QC,



BRUECKNER MAXIMUM OVERLAP ORBITALS

exact (FCI) state

$$S[\tilde{\Phi}] = \mathrm{Re}\,\langle \Psi | \tilde{\Phi} \rangle / \|\tilde{\Phi}\|$$

$$\|\tilde{\Phi}\| = \sqrt{\langle \tilde{\Phi} | \tilde{\Phi} \rangle}$$

Brueckner determinant

$$S[\Phi_B] = \max_{\tilde{\Phi}} S[\tilde{\Phi}]$$

Finding the maximum of $S[\tilde{\Phi}]$ is equivalent to minimizing the distance

between the normalized $|\tilde{\Phi}\rangle$ and $|\Psi\rangle$:

$\|\tilde{\Phi}'\|=1$

$$|\tilde{\Phi}'\rangle = |\tilde{\Phi}\rangle / \|\tilde{\Phi}\|$$

$\|\Psi'\|=1$

$$|\Psi'\rangle = |\Psi\rangle / \|\Psi\|$$

Square of the distance between $\tilde{\Phi}'$ and Ψ'

$$d^2_{\tilde{\Phi}',\Psi'} = \|\Psi' - \tilde{\Phi}'\|^2$$

$$= \langle \Psi' - \tilde{\Phi}' | \Psi' - \tilde{\Phi}' \rangle$$

$$= 2 - 2\,\mathrm{Re}\langle \Psi' | \tilde{\Phi}' \rangle$$

$$= 2\left(1 - S[\tilde{\Phi}]/\|\Psi\|\right)$$

Calculate $\delta S[\tilde{\Phi}]$ and require that

$$\delta S[\Phi_B] = 0 .$$

Using $|\tilde{\Phi}\rangle = e^{C_1}|\Phi_B\rangle$,

$$S[\tilde{\Phi}] - S[\Phi_B]$$

$$= \mathrm{Re}\,\frac{\langle\Psi|e^{C_1}|\Phi_B\rangle}{\sqrt{\langle\Phi_B|e^{C_1^\dagger}e^{C_1}|\Phi_B\rangle}}$$

$$- \mathrm{Re}\,\frac{\langle\Psi|\Phi_B\rangle}{\langle\Phi_B|\Phi_B\rangle = 1}$$

$$= \mathrm{Re}\,\frac{\langle\Psi|(1+C_1+\frac{1}{2}C_1^2+\dots)|\Phi_B\rangle}{\sqrt{1+\langle\Phi_B|C_1^\dagger C_1|\Phi_B\rangle+\dots}}$$

$$- \mathrm{Re}\langle\Psi|\Phi_B\rangle$$

$$(1+x)^{-\frac{1}{2}} = 1-\frac{1}{2}x+\dots$$

$$= \mathrm{Re}\Big[\langle\Psi|\Phi_B\rangle+\langle\Psi|C_1|\Phi_B\rangle + O(C_1^2)\Big]\Big[1-O(C_1^2)\Big]$$

$$- \mathrm{Re}\langle\Psi|\Phi_B\rangle$$

$$= \mathrm{Re}\langle \Psi | C_1 | \Phi_B \rangle + O(C_1^2)$$

linear in C_1

Thus,

$$\delta S[\Phi_B] = \mathrm{Re}\langle \Psi | C_1 | \Phi_B \rangle$$

Let us rewrite $|\Psi\rangle$ in terms of Brueckner spin-orbitals $|i\rangle$ and $|a\rangle$ (i – occ. in $|\Phi_B\rangle$, a – unocc. in $|\Phi_B\rangle$). We obtain,

$$|\Psi\rangle = c_0^{(B)} |\Phi_B\rangle$$

$$+ C_1^{(B)} |\Phi_B\rangle + \cdots$$

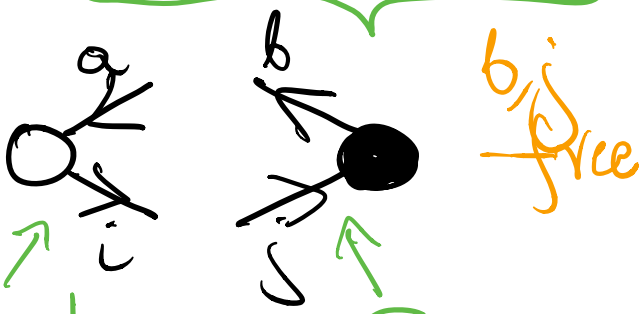
$$C_1^{(B)} = \sum_{a,i} {}^{(B)}C_a^i \, X_a^\dagger X_i$$

$$\delta S[\Phi_B] = \mathrm{Re}\langle \Psi | C_1 | \Phi_B \rangle$$

$$= \mathrm{Re}\langle \Phi_B | C_1^{(B)\dagger} C_1 | \Phi_B \rangle$$

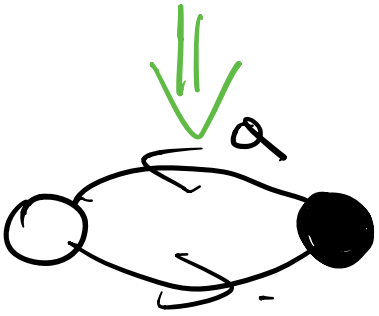
$$= 0$$

$$\mathrm{Re}\sum_{a,i}\left({}^{(B)}C_a^i\right)^* \langle \Phi_B | X_i^\dagger X_a C_1 | \Phi_B \rangle = 0$$



$$\left(\Sigma_i^a\right)^\dagger = X_i^\dagger X_a \qquad C_1$$

$$C_1 = \sum_{b_j} \langle b | \hat{c}_1 | j \rangle \times X_b^\dagger X_j$$



$$= \langle a | \hat{c}_1 | i \rangle$$

$$\mathrm{Re}\sum_{a,i}\left({}^{(B)}C_a^i\right)^* \langle a | \hat{c}_1 | i \rangle = 0$$

$$\left({}^{(B)}C_a^i\right)^* = 0 \quad \forall \; i, a$$

$$\boxed{C_1^{(B)} = 0}$$

$$|\Psi\rangle = C_0^{(B)} |\Phi_B\rangle + \sum_{n=2}^{N} C_n^{(B)} |\Phi_B\rangle$$

There are no singles in $|\Psi\rangle$ if we express it using Brueckner

spin-orbitals.

In practice, instead of the exact $|\Psi\rangle$ we can use highly correlated states, such as those obtained with the coupled-cluster (CC) theory,

$$|\Psi\rangle = e^{T_1 + T_2 + \cdots} |\Phi_0\rangle$$

to generate $|\Phi_B\rangle$.

When $|\Phi\rangle = |\Phi_0\rangle$,

$T_1 = 0$, so in every iteration of CC, in addition to solving for T_n, we rotate orbitals to zero T_1 (BCC)

Brueckner CC theory

Comparison of Brueckner and HF determinants (orbitals):

In MBPT,

$$|\Psi\rangle = |\Phi\rangle + |\Psi^{(1)}\rangle + |\Psi^{(2)}\rangle + \cdots$$

$$= |\Phi\rangle + \sum_{n=1}^{\infty} |\Psi^{(n)}\rangle .$$

When $|\Phi\rangle = |\Phi_{HF}\rangle$,

$|\Psi_S^{(1)}\rangle = 0$, so that

singles (contributions from $|\Phi_i^a\rangle$)

$$|\Psi\rangle = |\Phi_{HF}\rangle + |\Psi_D^{(1)}\rangle$$

(doubles only)

$+ \ldots$ (singles in higher orders)

When $|\Phi\rangle = |\Phi_B\rangle$,

$$|\Psi\rangle = |\Phi_B\rangle + \sum_{n=1}^{\infty} |\Psi^{(n)}\rangle$$

and

$$\sum_{n=1}^{\infty} |\Psi_S^{(n)}\rangle = 0$$

(singles in all orders vanish)

This means that if we can approximate $|\Psi\rangle$ by $|\Phi_{HF}\rangle + |\Psi^{(1)}\rangle$,

where we know that there are no singles in $|\Psi^{(1)}\rangle$, $|\Phi_{HF}\rangle \approx |\Phi_0\rangle$. However, if $|\Psi^{(n)}\rangle$ with $n > 1$ become important, $|\Phi_0\rangle$ can be very different than $|\Phi_{HF}\rangle$, since $|\Psi^{(n)}\rangle$ with $n > 1$ have singles in the H-F case, but

they do not have them in the Brueckner case. Brueckner orbitals may be better than H-F orbitals when $|\Phi_{HF}\rangle$ is a poor approximation to $|\Psi\rangle$ (as in more multi-reference situations).