MCSCF Gradient

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Abstract

This note is largely follow the materials in "Quantum Chemistry and Dynamics of Excited States" Chapter 1 and Chapter 9,10

1 Basic Concepts

1.1 Hamiltonian

The hamiltonian for K nuclei and N elctrons is given by

$$\hat{H} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{|r_i - r_j|} - \sum_{i=1}^{N}\sum_{A=1}^{K}\frac{Z_A}{|r_i - r_A|} \tag{1}$$

The one-electron operator in the Hamiltonian is the kinetic energy and teh nuclei-electron atration ,and is expressed by

$$\begin{aligned} h_{pq} &= \langle \phi_p | \hat{h} | \phi_q \rangle & (2)\\ &= \int \phi_p^*(r) \left(-\frac{1}{2}\nabla^2 - \sum_{A=1}^{N} \frac{Z_A}{|r_i - r_A|} \right) \phi_q(r) dr & (3)\\ & & (4) \end{aligned}$$

The two-electron repulsion integral (in chemist's notation) is

$$\begin{aligned} (pq|rs) = g_{pqrs} &= \langle \phi_p \phi_r | \hat{g} | \phi_q \phi_s \rangle & (5)\\ &= \int \phi_p^*(r_1)\phi_r^*(r_2)\frac{1}{|r_1 - r_2|}\phi_q(r_1)\phi_s(r_2) dr_1 dr_2 & (6) \end{aligned}$$

Some alternative notations for two-electron integrals are

$$\langle pq|rs \rangle = (pr|qs) \tag{7}$$

$$\langle pq||rs \rangle = \langle pq|rs \rangle - \langle pq|sr \rangle \tag{8}$$

Permutation symmetry

$$g_{pqrs} = g_{rspq} \tag{9}$$

real function symmetry

$$g_{pqrs} = g_{qprs} = g_{pqsr} = g_{qpsr} \tag{10}$$

with totally eight-fold symmetry

1.2 Index conventions

- $a, b, c, d, \cdots$ denote empty (virtual) orbitals
- $i, j, k, l, \cdots$ denote doubly occupied (inactive) orbitals
- $t, u, v, x, \cdots$ denote active orbitals
- $p, q, r, s, \cdots$ denote general orbitals

1.3 Second Quantization

In second quantization the hamiltonian becomes

$$\hat{H} = \sum_{pq} h_{pq}\hat{E}_{pq} + \frac{1}{2}\sum_{pqrs}(pq|rs)\hat{e}_{pqrs} \tag{11}$$

where the summation are now in terms of elctronic orbitals.

the operator

$$\hat{E}_{pq} \equiv \sum_{\sigma=\{\alpha,\beta\}} \hat{a}^{\dagger}_{p_\sigma}\hat{a}_{q_\sigma} \tag{12}$$

is the spin-averaged electron replacement operator,which moves one electron from spatial orbital q to p.

the operator

$$\begin{aligned}
\hat{e}_{pqrs} &\equiv \sum_{\sigma,\tau=\{\alpha,\beta\}} \hat{a}^{\dagger}_{p_\sigma}\hat{a}^{\dagger}_{r_\tau}\hat{a}_{s_\tau}\hat{a}_{q_\sigma} &(13)\\
&= -\sum_{\sigma,\tau=\{\alpha,\beta\}} \hat{a}^{\dagger}_{r_\tau}\hat{a}^{\dagger}_{p_\sigma}\hat{a}_{s_\tau}\hat{a}_{q_\sigma} &(14)\\
&= -\sum_{\sigma,\tau=\{\alpha,\beta\}} \hat{a}^{\dagger}_{r_\tau}(-\hat{a}_{s_\tau}\hat{a}^{\dagger}_{p_\sigma} + \delta_{ps,\sigma\tau})\hat{a}_{q_\sigma} &(15)\\
&= \hat{E}_{rs}\hat{E}_{pq} - \delta_{ps}\hat{E}_{rq} &(16)
\end{aligned}$$

1.3.1 Some Commutator and anti-commutator realationship

Operator Identities

$$\begin{aligned}
[\hat{A}, \hat{B}\hat{C}] &= [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] &(17)\\
[\hat{A}, \hat{B}\hat{C}] &= [\hat{A}, \hat{B}]_{+}\hat{C} - \hat{B}[\hat{A}, \hat{C}]_{+} &(18)\\
& &(19)
\end{aligned}$$

$$
\begin{aligned}
[\hat{a}_p^\dagger \hat{a}_q, \hat{a}_r^\dagger] &= \hat{a}_p^\dagger [\hat{a}_q, \hat{a}_r^\dagger]_+ - [\hat{a}_p^\dagger, \hat{a}_r^\dagger]_+ \hat{a}_q && (20)\\
&= \hat{a}_p^\dagger \delta_{qr} && (21)
\end{aligned}
$$

$$
\begin{aligned}
[\hat{a}_p^\dagger \hat{a}_q, \hat{a}_s] &= \hat{a}_p^\dagger [\hat{a}_q, \hat{a}_s]_+ - [\hat{a}_p^\dagger, \hat{a}_s]_+ \hat{a}_q && (22)\\
&= -\delta_{ps} \hat{a}_q && (23)
\end{aligned}
$$

$$
\begin{aligned}
[\hat{a}_p^\dagger \hat{a}_q, \hat{a}_r^\dagger \hat{a}_s] &= \hat{a}_r^\dagger [\hat{a}_p^\dagger \hat{a}_q, \hat{a}_s] + [\hat{a}_p^\dagger \hat{a}_q, \hat{a}_r^\dagger] \hat{a}_s && (24)\\
&= \delta_{qr} \hat{a}_p^\dagger \hat{a}_s - \delta_{ps} \hat{a}_r^\dagger \hat{a}_q && (25)
\end{aligned}
$$

$$
\begin{aligned}
[\hat{a}_p^\dagger \hat{a}_q, \hat{a}_r^\dagger \hat{a}_s \hat{a}_m^\dagger \hat{a}_n] &= \hat{a}_r^\dagger \hat{a}_s [\hat{a}_p^\dagger \hat{a}_q, \hat{a}_m^\dagger \hat{a}_n] + [\hat{a}_p^\dagger \hat{a}_q, \hat{a}_r^\dagger \hat{a}_s] \hat{a}_m^\dagger \hat{a}_n && (26)\\
&= \hat{a}_r^\dagger \hat{a}_s (\delta_{qm} \hat{a}_p^\dagger \hat{a}_n - \delta_{pn} \hat{a}_m^\dagger \hat{a}_q) + (\delta_{qr} \hat{a}_p^\dagger \hat{a}_s - \delta_{ps} \hat{a}_r^\dagger \hat{a}_q) \hat{a}_m^\dagger \hat{a}_n && (27)\\
&= \delta_{qm} \hat{a}_r^\dagger \hat{a}_s \hat{a}_p^\dagger \hat{a}_n - \delta_{pn} \hat{a}_r^\dagger \hat{a}_s \hat{a}_m^\dagger \hat{a}_q + \delta_{qr} \hat{a}_p^\dagger \hat{a}_s \hat{a}_m^\dagger \hat{a}_n - \delta_{ps} \hat{a}_r^\dagger \hat{a}_q \hat{a}_m^\dagger \hat{a}_n && (28)
\end{aligned}
$$

The following commutation relations apply to the one and two-electron replacement operator

$$
\begin{aligned}
[\hat{E}_{pq}, \hat{a}_{r_\sigma}^\dagger] &= \sum_{\tau=\alpha,\beta} [\hat{a}_{p_\tau}^\dagger \hat{a}_{q_\tau}, \hat{a}_{r_\sigma}^\dagger] && (29)\\
&= \sum_{\tau=\alpha,\beta} \delta_{\sigma,\tau} \delta_{qr} \hat{a}_{p_\tau}^\dagger && (30)\\
&= \delta_{qr} \hat{a}_{p_\sigma}^\dagger && (31)
\end{aligned}
$$

$$
\begin{aligned}
[\hat{E}_{pq}, \hat{a}_{s_\sigma}] &= \sum_{\tau=\alpha,\beta} [\hat{a}_{p_\tau}^\dagger \hat{a}_{q_\tau}, \hat{a}_{s_\sigma}] && (32)\\
&= \sum_{\tau=\alpha,\beta} -\delta_{ps} \delta_{\sigma\tau} \hat{a}_{q_\tau} && (33)\\
&= -\delta_{ps} \hat{a}_{q_\sigma} && (34)
\end{aligned}
$$

$$
\begin{aligned}
[\hat{E}_{pq}, \hat{a}_{r_\sigma}^\dagger \hat{a}_{s_\sigma}] &= \hat{a}_{r_\sigma}^\dagger [\hat{E}_{pq}, \hat{a}_{s_\sigma}] + [\hat{E}_{pq}, \hat{a}_{r_\sigma}^\dagger] \hat{a}_{s_\sigma} && (35)\\
&= \hat{a}_{r_\sigma}^\dagger (-\delta_{ps} \hat{a}_{q_\sigma}) + \delta_{qr} \hat{a}_{p_\sigma}^\dagger \hat{a}_{s_\sigma} && (36)\\
&= \delta_{qr} \hat{a}_{p_\sigma}^\dagger \hat{a}_{s_\sigma} - \delta_{ps} \hat{a}_{r_\sigma}^\dagger \hat{a}_{q_\sigma} && (37)
\end{aligned}
$$

$$
\begin{aligned}
[\hat{E}_{pq}, \hat{E}_{rs}] &= \sum_{\sigma=\alpha,\beta} [\hat{E}_{pq}, \hat{a}^\dagger_{r_\sigma} \hat{a}_{s_\sigma}] && (38)\\
&= \sum_{\sigma=\alpha,\beta} \delta_{qr} \hat{a}^\dagger_{p_\sigma} \hat{a}_{s_\sigma} - \delta_{ps} \hat{a}^\dagger_{r_\sigma} \hat{a}_{q_\sigma} && (39)\\
&= \delta_{qr} \hat{E}_{ps} - \delta_{ps} \hat{E}_{rq} && (40)
\end{aligned}
$$

$$
\begin{aligned}
[\hat{e}_{pqrs}, \hat{E}_{xy}] &= [\hat{E}_{rs}\hat{E}_{pq} - \delta_{ps}\hat{E}_{rq}, \hat{E}_{xy}] && (41)\\
&= [\hat{E}_{rs}\hat{E}_{pq}, \hat{E}_{xy}] - \delta_{ps}[\hat{E}_{rq}, \hat{E}_{xy}] && (42)\\
&= \hat{E}_{rs}[\hat{E}_{pq}, \hat{E}_{xy}] + [\hat{E}_{rs}, \hat{E}_{xy}]\hat{E}_{pq} - \delta_{ps}[\hat{E}_{rq}, \hat{E}_{xy}] && (43)\\
&= \hat{E}_{rs}(\delta_{qx}\hat{E}_{py} - \delta_{py}\hat{E}_{xq}) + (\delta_{sx}\hat{E}_{ry} - \delta_{ry}\hat{E}_{xs})\hat{E}_{pq} - \delta_{ps}(\delta_{qx}\hat{E}_{ry} - \delta_{ry}\hat{E}_{xq}) && (44)\\
&= \delta_{qx}(\hat{E}_{rs}\hat{E}_{py} - \delta_{ps}\hat{E}_{ry}) - \delta_{py}\hat{E}_{rs}\hat{E}_{xq} && (45)\\
&\quad \delta_{sx}\hat{E}_{ry}\hat{E}_{pq} - \delta_{ry}(\hat{E}_{xs}\hat{E}_{pq} - \delta_{ps}\hat{E}_{xq}) && (46)\\
&= \delta_{qx}\hat{e}_{pyrs} - \delta_{py}\hat{E}_{rs}\hat{E}_{xq} + \delta_{py}\delta_{sx}\hat{E}_{rq} + \delta_{sx}\hat{E}_{ry}\hat{E}_{pq} - \delta_{sx}\delta_{py}\hat{E}_{rq} - \delta_{ry}\hat{e}_{pqxs} && (47)\\
&= \delta_{qx}\hat{e}_{pyrs} - \delta_{py}\hat{e}_{xqrs} + \delta_{sx}\hat{e}_{pqry} - \delta_{ry}\hat{e}_{pqxs} && (48)
\end{aligned}
$$

Another way is to summation over equation 26

1.4 Density Matrix

Given a general wavefunction $|\Psi\rangle$, we define the one-particle and two-particle density matrices as

$$D_{pq} \equiv \langle\Psi|\hat{E}_{pq}|\Psi\rangle \tag{49}$$

and

$$\Gamma_{pqrs} \equiv \langle\Psi|\hat{e}_{pqrs}|\Psi\rangle \tag{50}$$

It is important to note the four-fold permutational symmetry of the two-electron density matrix:

1.4.1 Calculation of Density Matrix

In Case of Closed Shell Hartree Fock

$$|\Psi_{HF}\rangle = \prod_{i=1}^{N/2} (\hat{a}^\dagger_{i_\alpha} \hat{a}^\dagger_{i,\beta})|0\rangle \tag{51}$$

Using fermi vacuum we get

$$
\begin{aligned}
D_{pq} &= \langle \Psi_{HF} | \hat{E}_{pq} | \Psi_{HF} \rangle && (52)\\
&= \langle \Psi_{HF} | \sum_{\sigma=\alpha,\beta} \hat{a}^{\dagger}_{p_\sigma} \hat{a}_{q_\sigma} | \Psi_{HF} \rangle && (53)\\
&= D^{\alpha}_{pq} + D^{\beta}_{pq} && (54)\\
&= \langle 0 || 0 \rangle && (55)\\
&= 2\delta_{pq} && (56)
\end{aligned}
$$

$$
\begin{aligned}
\Gamma_{pqrs} &= \langle 0 || 0 \rangle && (57)\\
&= && (58)
\end{aligned}
$$

For MCSCF

$$
|\Psi_{MCSCF}\rangle = \sum_I C_I |I\rangle \tag{59}
$$

$$
\begin{aligned}
D_{pq} &= \langle \Psi_{MCSCF} | \hat{E}_{pq} | \Psi_{MCSCF} \rangle && (60)\\
&= \sum_I \sum_J C_I C_J \langle I | \hat{E}_{pq} | J \rangle && (61)\\
&= \sum_I |C_I|^2 \langle I | \hat{E}_{pq} | I \rangle + \sum_I \sum_{J \neq I} C_I C_J \langle I | \hat{E}_{pq} | J \rangle && (62)
\end{aligned}
$$

1.5 Symmetry of two-electron orbital density-matrix element

permutation sysmmetry :

$$
\begin{aligned}
\Gamma_{pqrs} &= \langle \Psi | \hat{e}_{pqrs} | \Psi \rangle && (63)\\
&= \langle \Psi | \sum_{\sigma,\tau=\alpha,\beta} \hat{a}^{\dagger}_{p_\sigma} \hat{a}^{\dagger}_{r_\tau} \hat{a}_{s_\tau} \hat{a}_{q_\sigma} | \Psi \rangle && (64)\\
&= \langle \Psi | \sum_{\sigma,\tau=\alpha,\beta} \hat{a}^{\dagger}_{r_\tau} \hat{a}^{\dagger}_{p_\sigma} \hat{a}_{q_\sigma} \hat{a}_{s_\tau} | \Psi \rangle \equiv \Gamma_{rspq} && (65)
\end{aligned}
$$

Hermitian symmetry :

$$
\begin{aligned}
\Gamma_{pqrs} &= \langle \Psi | \hat{e}_{pqrs} | \Psi \rangle && (66)\\
&= \langle \Psi | \sum_{\sigma,\tau=\alpha,\beta} \hat{a}^{\dagger}_{p_\sigma} \hat{a}^{\dagger}_{r_\tau} \hat{a}_{s_\tau} \hat{a}_{q_\sigma} | \Psi \rangle && (67)\\
&= \langle \Psi | \sum_{\sigma,\tau=\alpha,\beta} (\hat{a}^{\dagger}_{q_\sigma} \hat{a}^{\dagger}_{s_\tau} \hat{a}_{r_\tau} \hat{a}_{p_\sigma})^{\dagger} | \Psi \rangle && (68)\\
&= \Gamma^{*}_{qpsr} && (69)
\end{aligned}
$$

For real wavefunction

$$
\Gamma_{pqrs} = \Gamma_{rspq} = \Gamma_{qpsr} = \Gamma_{srpq} \tag{70}
$$

2 Orbital Rotation

Given a set of orthonormal orbtial $\{\phi_p\}$ we get an unitary transformed orbital

$$\tilde{\phi}_p = \sum_q \phi_q U_{qp} \tag{71}$$

The unitary matrix can be written in terms anti-hermitial matrxi κ

$$U = \exp -\kappa \quad \kappa^\dagger = -\kappa \tag{72}$$

Let us begin by considering the relationship between spin-orbital transofrmations in first quantization and the transformations of creation operator in second quantization.

In first quantization

$$\Phi = |\phi_{p_1}\phi_{p_2}\cdots\phi_{p_N}| \tag{73}$$

$$\tilde{\Phi} = |\tilde{\phi}_{p_1}\tilde{\phi}_{p_2}\cdots\tilde{\phi}_{p_N}| \tag{74}$$

$$\tilde{\Phi} = \sum_{q_1,q_2,\cdots,q_n} U_{q_1p_1}U_{q_2p_2}\cdots U_{q_Np_N}|\phi_{q_1}\phi_{q_1}\cdots\phi_{q_N}| \tag{75}$$

In second quantization

$$|k\rangle = \hat{a}^\dagger_{p_1}\hat{a}^\dagger_{p_2}\cdots\hat{a}^\dagger_{p_N}|0\rangle \tag{76}$$

$$|\tilde{k}\rangle = \hat{\tilde{a}}^\dagger_{p_1}\hat{\tilde{a}}^\dagger_{p_2}\cdots\hat{\tilde{a}}^\dagger_{p_N}|0\rangle \tag{77}$$

Then

$$\hat{\tilde{a}}^\dagger_{p_1}\hat{\tilde{a}}^\dagger_{p_2}\cdots\hat{\tilde{a}}^\dagger_{p_N}|0\rangle = \sum_{q_1,q_2\cdots q_N} U_{q_1,p_1}\cdots U_{q_N,p_N}\hat{a}^\dagger_{p_1}\hat{a}^\dagger_{p_2}\cdots\hat{a}^\dagger_{p_N}|0\rangle \tag{78}$$

$$\hat{\tilde{a}}_p{}^\dagger = \sum_q \hat{a}^\dagger_q U_{qp} = \sum_q \hat{a}^\dagger_q[\exp(-\kappa)]_{qp} \tag{79}$$

Next consider the operator

$$\bar{a}^\dagger_p = \exp(-\kappa)\hat{a}^\dagger_p\exp(\kappa) \tag{80}$$

Let the operator κ

$$\kappa = \sum_{p,q}\kappa_{pq}\hat{a}^\dagger_p a_q \tag{81}$$

$$[\hat{a}^\dagger_p, \kappa] = \sum_{m,n}\kappa_{mn}[\hat{a}^\dagger_p, \hat{a}^\dagger_m\hat{a}_n] \tag{82}$$

$$= \sum_{m,n}\kappa_{mn}(-\delta_{p,n}\hat{a}^\dagger_m) \tag{83}$$

$$= -\sum_m \kappa_{mp}\hat{a}^\dagger_m \tag{84}$$

$$
\begin{aligned}
[[\hat{a}_p^\dagger, \kappa], \kappa] &= -\sum_m \kappa_{mp} [\hat{a}_m^\dagger, \kappa] && (85) \\
&= -\sum_m \kappa_{mp} (-\sum_n \kappa_{nm} \hat{a}_n^\dagger) && (86) \\
&= \sum_m \sum_n \kappa_{mp} \kappa_{nm} \hat{a}_n^\dagger && (87) \\
&= \sum_n (\kappa^2)_{np} \hat{a}_n^\dagger && (88)
\end{aligned}
$$

$$
[[\hat{a}_p^\dagger, \kappa], \cdots], \kappa]_k = (-1)^k \sum_n (\kappa^k)_{np} \hat{a}_n^\dagger \tag{89}
$$

$$
\begin{aligned}
\bar{a}_p^\dagger &= \exp(-\kappa) \hat{a}_p^\dagger \exp(\kappa) && (90) \\
&= \hat{a}_p^\dagger + [\hat{a}_p^\dagger, \kappa] + \frac{1}{2!} [[\hat{a}_p^\dagger, \kappa], \kappa] + \cdots && (91) \\
&= \sum_m \delta_{mp} \hat{a}_m^\dagger + \sum_m (-1) \kappa_{mp} \hat{a}_m^\dagger + \sum_m \frac{1}{2!} (-1)^2 (\kappa^2)_{mp} \hat{a}_m^\dagger + \cdots + \sum_m \frac{1}{n!} (-\kappa)_{mp}^n \hat{a}_m^\dagger && (92) \\
&= \sum_m \left(\delta_{mp} + (-\kappa_{mp}) + \frac{1}{2} (-\kappa)_{mp} + \cdots + \frac{1}{n!} (-\kappa)_{mp}^n \right) a_m^\dagger && (93) \\
&= \sum_m (I + (-\kappa) + \frac{1}{2!} \kappa^2 + \cdots + \frac{1}{n!} \kappa^n)_{mp} \hat{a}_p^\dagger && (94) \\
&= \sum_m \left(\exp(-\kappa) \right)_{mp} \hat{a}_m && (95) \\
&= \hat{\bar{a}}_p && (96)
\end{aligned}
$$

$$
\kappa |0\rangle = \sum_{pq} \hat{a}_p^\dagger \hat{a}_q |0\rangle = 0 \tag{97}
$$

$$
\exp(\kappa) |0\rangle = 1 + \kappa + \frac{1}{2!} \kappa^2 + \cdots |0\rangle = |0\rangle \tag{98}
$$

$$
\begin{aligned}
|\tilde{k}\rangle &= \hat{\bar{a}}_{p_1} \cdots \hat{\bar{a}}_{p_N} |0\rangle && (99) \\
&= \exp(-\kappa) \hat{a}_{p_1}^\dagger \exp(k) \cdots \exp(-\kappa) \hat{a}_{p_N}^\dagger \exp(\kappa) |0\rangle && (100) \\
&= \exp(-\kappa) \hat{a}_{p_1} \cdots \hat{a}_{p_N} \exp(\kappa) |0\rangle && (101) \\
&= \exp(-\kappa) \hat{a}_{p_1} \cdots \hat{a}_{p_N} |0\rangle && (102) \\
&= \exp(-\kappa) |k\rangle && (103)
\end{aligned}
$$

That is the relationship of two wavefunction in second quantization. The problem is the justification of

$$
\kappa = \sum_{pq} \kappa_{pq} \hat{a}_p^\dagger \hat{a}_q \tag{104}
$$

2.1 Spin-Adapted Rotation

3 Gradient

$$|\Psi_{MCSCF}\rangle = e^{-\hat{\kappa}} \left(\sum_I c_I |I\rangle \right) \tag{105}$$

with $\hat{\kappa}$ the ortibal rotation operator

$$\hat{\kappa} = \sum_{p<q} \kappa_{pq} (\hat{E}_{pq} - \hat{E}_{qp}) \tag{106}$$

$$E = \langle \Psi_{MCSCF} | \hat{H} | \Psi_{MCSCF} \rangle \tag{107}$$

$$= (\langle I | e^{\kappa} \hat{H} e^{-\kappa} | I \rangle) \tag{108}$$

$$= \langle I | \hat{H} + [\hat{H}, \kappa] + \frac{1}{2!} [[\hat{H}, \kappa], \kappa] + \cdots | I \rangle \tag{109}$$

$$= \langle I | \hat{H} + \sum_{pq} \kappa_{pq} [\hat{H}, \hat{E}_{pq} - \hat{E}_{qp}] + \frac{1}{2!} \sum_{pq} \sum_{rs} \kappa_{pq} \kappa_{rs} [[\hat{H}, \hat{E}_{pq} - \hat{E}_{qp}], \hat{E}_{rs} - \hat{E}_{sr}] + \cdots | I \rangle \tag{110}$$

The general expression of the orbital derivative is

$$\frac{\partial E}{\partial \kappa_{pq}} |_{\kappa_{pq}=0} = \langle I | [\hat{H}, \hat{E}_{pq} - \hat{E}_{qp}] | I \rangle \tag{111}$$

$$= \langle I | [\hat{H}, \hat{E}_{pq}] | I \rangle - \langle I | [\hat{H}, \hat{E}_{qp}] | I \rangle \tag{112}$$

$$[\hat{H}, \hat{E}_{xy}] = [\sum_{pq} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{e}_{pqrs}, \hat{E}_{xy}] \tag{113}$$

$$= \sum_{pq} h_{pq} [\hat{E}_{pq}, \hat{E}_{xy}] + \sum_{pqrs} \frac{1}{2} g_{pqrs} [\hat{e}_{pqrs}, \hat{E}_{xy}] \tag{114}$$

$$= \sum_{pq} h_{pq} (\delta_{qx} \hat{E}_{py} - \delta_{py} \hat{E}_{xq}) + \frac{1}{2} \sum_{pqrs} g_{pqrs} \left(\delta_{qx} \hat{e}_{pyrs} - \delta_{py} \hat{e}_{xqrs} + \delta_{sx} \hat{e}_{pqry} - \delta_{ry} \hat{e}_{pqxs} \right) \tag{115}$$

We need the symmetry of density matrix and molecule integral to simplify the terms.

3.1 conventional symmetry

$$\langle\Psi|[\hat{H},\hat{E}_{xy}]|\Psi\rangle = \sum_{pq} h_{pq}\delta_{qx}D_{py} - \sum_{pq} h_{pq}\delta_{py}D_{xq} \tag{116}$$

$$+\frac{1}{2}\sum_{pqrs} g_{pqrs}\left(\delta_{qx}\Gamma_{pyrs} - \delta_{py}\Gamma_{xqrs} + \delta_{sx}\Gamma_{pqry} - \delta_{ry}\Gamma_{pqxs}\right) \tag{117}$$

$$= \sum_{p} h_{px}D_{py} - \sum_{q} h_{yq}D_{xq} \tag{118}$$

$$+\frac{1}{2}\left(\sum_{prs} g_{pxrs}\Gamma_{pyrs} - \sum_{qrs} g_{yqrs}\Gamma_{xqrs} + \sum_{pqr} g_{pqrx}\Gamma_{pqry} - \sum_{qps} g_{pqys}\Gamma_{pqxs}\right) \tag{119}$$

$$= \sum_{p} h_{xp}D_{py} - \sum_{p} h_{yp}D_{px} + \frac{1}{2}\left(\sum_{prs} g_{pxrs}\Gamma_{pyrs} + \sum_{pqr} g_{rxpq}\Gamma_{rypq}\right) \tag{120}$$

$$-\frac{1}{2}\left(\sum_{qrs} g_{yqrs}\Gamma_{xqrs} + \sum_{qps} g_{yspq}\Gamma_{xspq}\right) \tag{121}$$

$$= \sum_{p} h_{xp}D_{py} - \sum_{p} h_{yp}D_{py} + \sum_{prs} g_{pxrs}\Gamma_{pyrs} - \sum_{qrs} g_{yqrs}\Gamma_{xqrs} \tag{122}$$

Introducint the generalized Fock matrices as

$$F_{xy} = \sum_{p} h_{xp}D_{py} + \sum_{prs} g_{pxrs}\Gamma_{pyrs} \tag{123}$$

we get

$$\langle\Psi|[\hat{H},\hat{E}_{xy}]|\Psi\rangle = F_{xy} - F_{yx} \tag{124}$$

$$\frac{\partial E}{\partial \kappa_{pq}} = 2(F_{pq} - F_{qp}) \tag{125}$$

with with D and Γ being the one and two-particle density matrices,respectively.

3.2 Evaluation of Generalized Fock Matrix

The consider is that the contraction range is in the whole range,and we want to seperate the contraction range into inactive and active to take advantage of the structure of RDMs of inactive parts

When the second index of the generalized Fock matrix is inactive and the first is general

$$F_{pi} = \sum_r h_{pr} D_{ri} + \sum_{rst} g_{rpst} \Gamma_{rist} \tag{126}$$

$$= \sum_r h_{pr} 2\delta_{ri} + \sum_{rs} \left(\sum_t g_{rpst} \Gamma_{rist} \right) \tag{127}$$

$$= \sum_r h_{pr} 2\delta_{ri} + \sum_{rs} \left(\sum_j g_{rpsj} \Gamma_{risj} + \sum_u g_{rpsu} \Gamma_{risu} \right) \tag{128}$$

$$= 2h_{pi} + \sum_{rs} \left(\sum_j g_{rpsj} (4\delta_{ri}\delta_{sj} - 2\delta_{is}\delta_{rj}) + \sum_u g_{rpsu} \Gamma_{risu} \right) \tag{129}$$

$$= 2h_{pi} + \sum_{rj} 4g_{rpjj}\delta_{ri} - \sum_{sj} 2g_{jpsj}\delta_{is} + \sum_{rsu} g_{rpsu}(2\delta_{ir} D_{su} - \delta_{is} D_{ru}) \tag{130}$$

$$= 2h_{pi} + \sum_j 4g_{ipjj} - \sum_j 2g_{jpij} + \sum_{su} 2g_{ipsu} D_{su} - \sum_{ru} g_{rpiu} D_{ru} \tag{131}$$

$$= 2h_{pi} + 2\sum_j (2g_{ipjj} - g_{jpij}) + 2(\sum_{su} (g_{ipsu} - \frac{1}{2} g_{spiu}) D_{su})) \tag{132}$$

$$= 2(F^I_{pi} + F^A_{pi}) \tag{133}$$

$$D_{ip} = \langle \Psi | \sum_\sigma \hat{a}^\dagger_{i_\sigma} \hat{a}_{p_\sigma} | \Psi \rangle = 2\delta_{ip} \tag{134}$$

$$\Gamma_{risj} = \langle \Psi | \sum_{\sigma,\tau=\alpha,\beta} \hat{a}^\dagger_{r_\sigma} \hat{a}^\dagger_{s_\tau} \hat{a}_{j_\tau} \hat{a}_{i_\sigma} | \Psi \rangle \tag{135}$$

$$= \sum_{\sigma,\tau=\alpha,\beta} \delta_{ir}\delta_{\sigma\sigma}\delta_{sj}\delta_{\tau\tau} - \delta_{is}\delta_{\sigma\tau}\delta_{jr}\delta_{\sigma\tau} \tag{136}$$

$$= 4\delta_{ir}\delta_{sj} - 2\delta_{is}\delta_{jr} \tag{137}$$

$$\Gamma_{risu} = \langle \Psi | \sum_{\sigma,\tau=\alpha,\beta} \hat{a}^\dagger_{r_\sigma} \hat{a}^\dagger_{s_\tau} \hat{a}_{u_\tau} \hat{a}_{i_\sigma} | \Psi \rangle \tag{138}$$

$$= 2\delta_{ir} D_{su} - \delta_{is} D_{ru} \tag{139}$$

$$F^I_{pi} = h_{pi} + \sum_j (2g_{ipjj} - g_{jpij}) \tag{140}$$

$$F^A_{pi} = \sum_{su} (g_{ipsu} - \frac{1}{2} g_{spiu}) D_{su}) = \sum_{uv} (g_{ipuv} - \frac{1}{2} g_{upiv}) D_{uv} \tag{141}$$

The equation 141 use only active orbital density matrix.

When the second index is active, and the first index is general, we have

$$F_{pu} = \sum_r h_{pr} D_{ru} + \sum_{rst} g_{rpst} \Gamma_{rust} \tag{142}$$

$$= \sum_v h_{pv} D_{vu} + \sum_{rs} \left(\sum_i g_{rpsi} \Gamma_{rusi} + \sum_v g_{rpsv} \Gamma_{rusv} \right) \tag{143}$$

$$= \sum_v h_{pv} D_{vu} + \sum_{rs} \sum_i g_{rpsi} (2\delta_{si} D_{ru} - \delta_{ri} D_{su}) + \sum_{rsv} g_{rpsv} \Gamma_{rusv} \tag{144}$$

$$= \sum_v h_{pv} D_{vu} + \sum_{ri} (2g_{rpii}) D_{ru} - \sum_{is} g_{ipsi} D_{su} + \sum_{rsv} g_{rpsv} \Gamma_{rusv} \tag{145}$$

$$= \sum_v h_{pv} D_{vu} + \sum_r (\sum_i (2g_{rpii}) - \sum_i g_{ipri}) D_{ru} + \sum_{wxv} g_{wpxv} \Gamma_{wuxv} \tag{146}$$

$$= \sum_v h_{pv} D_{vu} + \sum_v (\sum_i (2g_{vpii} - g_{ipvi}) D_{vu} + \sum_{wxv} g_{wpxv} \Gamma_{wuxv} \tag{147}$$

$$= \sum_v \left(h_{pv} + \sum_i (2g_{vpii} - g_{ipvi}) \right) D_{vu} + \sum_{wxv} g_{wpxv} \Gamma_{wuxv} \tag{148}$$

$$= F^I_{pv} D_{uv} + Q_{pu} \tag{149}$$

This equation also need D_{uv} active density matrix and Γ_{wuxv} active 2-RDM.

$$\Gamma_{rusi} = \langle \Psi | \sum_{\sigma,\tau=\alpha,\beta} \hat{a}^\dagger_{r_\sigma} \hat{a}^\dagger_{s_\tau} \hat{a}_{i_\tau} \hat{a}_u | \Psi \rangle \tag{150}$$

$$= 2\delta_{si} D_{ru} - \delta_{ri} D_{su} \tag{151}$$

Finally, if the first index is virtual then

$$F_{ap} = 0 \tag{152}$$

3.3 CT symmetry

$$g_{pqrs} = (p_0 q_1 | r_0 s_1) \neq (q_0 p_1 | r_0 s_1) \tag{153}$$

3.4 Hessian

3.5 CI calculation

Slater Condon Rule

$$|\Psi_{MCSCF}\rangle = \sum_I C_I |I\rangle \tag{154}$$

$$E = \langle \Psi_{MCSCF} | \hat{H} | \Psi_{MCSCF} \rangle \tag{155}$$

$$= \sum_{IJ} C_I C_J \langle I | \hat{H} | J \rangle \tag{156}$$

$$\tag{157}$$

$$\langle \Psi_{MCSCF} | \Psi_{MCSCF} \rangle = \sum_{IJ} C_I C_J \langle I | J \rangle = \sum_I C_I^2 = 1 \tag{158}$$

$$\frac{\partial L}{\partial C_K} = \frac{\partial \left(E - \epsilon (\sum_I C_I^2 - 1) \right)}{\partial C_K} = \sum_J C_J \langle K | H | J \rangle - \epsilon C_K = 0 \tag{159}$$

$$\mathbf{HC} = \epsilon \mathbf{C} \tag{160}$$

Using Slater Condon Rule to Calculate $\mathbf{H}$:

$$\langle I | \hat{H} | J \rangle = \langle I | \sum_{pq} h_{pq} \hat{E}_{pq} + \sum_{pqrs} g_{pqrs} \hat{e}_{pqrs} | J \rangle \tag{161}$$

- $|J\rangle = \hat{E}_{xy} \hat{E}_{uv} |I\rangle$
- $|J\rangle = \hat{E}_{uv} |I\rangle$

$$\mathbf{H}_{IJ} = \langle I | \hat{E}_{uv} | J \rangle \tag{162}$$

- $|J\rangle = |I\rangle$

$$\mathbf{H}_{II} = \langle I | \sum_{pq} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{e}_{pqrs} | I \rangle \tag{163}$$

$$= \sum_{pq} h_{pq} \langle I | \hat{E}_{pq} | I \rangle + \frac{1}{2} \sum_{pqrs} g_{pqrs} \langle I | \hat{E}_{rs} \hat{E}_{pq} - \delta_{ps} \hat{E}_{rq} | I \rangle \tag{164}$$

$$= \sum_p h_{pp} n_p + \sum_{pr} g_{pprr} \langle I | \hat{E}_{rr} \hat{E}_{pp} | I \rangle + \sum_{pr} g_{prrp} \langle I | \hat{E}_{rp} \hat{E}_{pr} - \hat{E}_{rr} | I \rangle \tag{165}$$

3.6 CT symmetry

4 Implementation

4.1 integral transformation

$$V_{ip} = \sum_s (2 g_{ipss} - g_{spis}) \tag{166}$$

$$= \sum_s \sum_{\mu\nu\lambda\sigma} (2 g_{\mu\nu\lambda\sigma} C_{\mu i} C_{\nu p} C_{\lambda s} C_{\sigma s} - g_{\mu\nu\lambda\sigma} C_{\mu s} C_{\nu p} C_{\lambda i} C_{\sigma s}) \tag{167}$$

$$= \sum_{\nu\nu\lambda\sigma} 2 g_{\mu\nu\lambda\sigma} C_{\mu i} C_{\nu p} \sum_s C_{\lambda s} C_{\sigma s} - g_{\mu\nu\lambda\sigma} C_{\nu p} C_{\lambda i} \sum_s C_{\mu s} C_{\sigma s} \tag{168}$$

$$= \sum_{\nu\nu\lambda\sigma} 2 g_{\mu\nu\lambda\sigma} C_{\mu i} C_{\nu p} D_{\lambda\sigma} - g_{\mu\nu\lambda\sigma} C_{\nu p} C_{\lambda i} D_{\mu\sigma} \tag{169}$$

$$J_{ip} = \sum_{uv} g_{ipuv} D_{uv} \tag{170}$$

$$= \sum_{uv} \sum_{\mu\nu\lambda\sigma} g_{\mu\nu\lambda\sigma} C_{\mu i} C_{\nu p} C_{\lambda u} C_{\nu v} D_{uv} \tag{171}$$

$$= \sum_{\mu\nu\lambda\sigma} g_{\mu\nu\lambda\sigma} C_{\mu i} C_{\nu p} \sum_{uv} C_{\lambda u} C_{\nu v} D_{uv} \tag{172}$$

$$= \sum_{\mu\nu\lambda\sigma} g_{\mu\nu\lambda\sigma} C_{\mu i} C_{\nu p} D_{\lambda\sigma} \tag{173}$$

$$D_{\lambda\sigma} = \sum_{uv} C_{\lambda\mu} C_{\sigma\nu} D_{\mu\nu} \tag{174}$$

$$F_{tp1} = \sum_{u} F^{I}_{pu} D_{tu} = \sum_{u} \sum_{\mu\nu} F^{I}_{\mu\nu} C_{\mu p} C_{\nu u} D_{tu} \tag{175}$$