Excercise 6, Summer 2017

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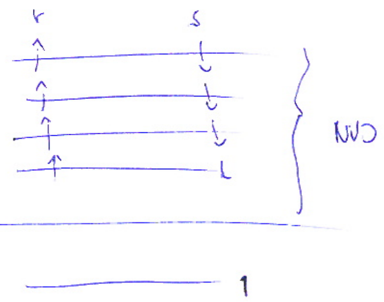
Method CID

CID Hamiltonian =

$\langle 0\|H\|0\rangle$	$\langle 0\|H\|D\rangle$
$\langle D\|H\|0\rangle$	$\langle D\|H\|D\rangle$

Effect of single excitations is very weak due to the second order coupling to the ground state.



- How many doble excitations do I have?

(singlet state)

$\uparrow\downarrow$ vs. $\downarrow\uparrow$ configurations with exchanged spins give antisymmetric total wave function

It is enough to assume that the first electron has spin up and the second has spin down. NCSF = NVO * NVO

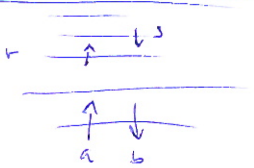
- We split the Hamiltonian to

A	B
	C

(A) $\langle 0 | H | 0 \rangle = E^{HF}$

$$H = \sum_{i=1}^{2} h(i) + \frac{1}{r_{12}}$$

(B.) $\langle 0 | H | \Psi_{ab}^{rs} \rangle \overset{\substack{SCR \\ 1c,2c}}{=} [ar||bs] = [ar|bs] - \underbrace{[as|br]}_{\text{spin-orthogonality}} = [ar|bs]$



C. $\langle \Psi_{ab}^{rs} | H | \Psi_{ab}^{tu} \rangle$

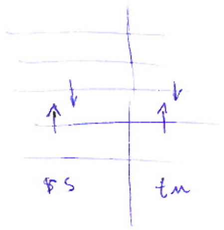
We do not have Slater-Condon rules for $\langle \Psi_{ab}^{rs} | H | \Psi_{ab}^{tu} \rangle$.

We need to derive them for the case of He here.

We distinguish 4 cases

1. $r = t$ & $s = u$

$\langle \Psi_{ab}^{rs} | H | \Psi_{ab}^{rs} \rangle =$ Mean HF energy in two orbitals r, s

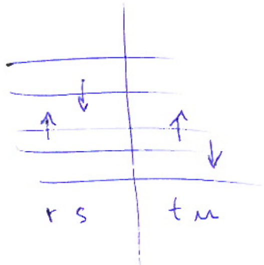


$$= \langle r|h|r\rangle + \langle s|h|s\rangle + \frac{1}{2}\sum_{ij}^{2} [ii||jj]$$

$$+ \frac{1}{2}\left\{ \cancel{[rr||rr]} + [rr||ss] + [ss||rr] + \cancel{[ss||ss]} \right\}$$

$$= \underline{\langle r|h|r\rangle + \langle s|h|s\rangle + [rr||ss]}$$

2. $r = t$ & $s \neq u$



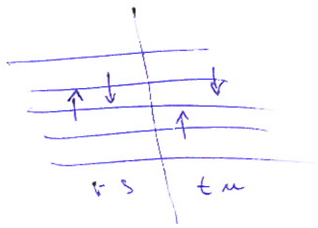
$$\langle \Psi_{ab}^{rs} | H | \Psi_{ab}^{ru} \rangle = \frac{1}{2!} \left\langle |\varphi_r(1)\varphi_s(2)| \sum_i^2 h(i) + \frac{1}{r_{12}} |\varphi_r(1)\varphi_u(2)| \right\rangle$$

$$= \langle s|h|u\rangle + \frac{1}{2}\left\{ [rr|su] + [su|rr] - [sr|ru] - [ru|sr] \right\}$$

spin-orthogonality

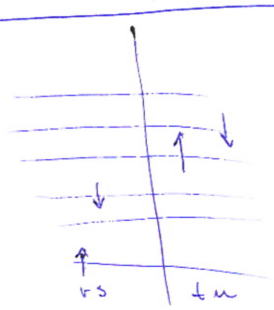
$$= \langle s|h|u\rangle + [rr|su]$$

3. $r \neq t$ & $s = u$



$$\langle \Psi_{ab}^{rs} | H | \Psi_{ab}^{ts} \rangle = \underline{\langle r|h|t\rangle + [ss|rt]}$$

4. $r \neq t$ & $s \neq u$



$$\langle \Psi_{ab}^{rs} | H | \Psi_{ab}^{tu} \rangle \overset{SCR\ 1c}{=} \frac{1}{2!} \left\langle |\varphi_r(1)\varphi_s(2)| \frac{1}{r_{12}} |\varphi_t(1)\varphi_u(2)| \right\rangle =$$

$$= [rt|su] - \cancel{[ru|st]}$$

spin-orthogonality