CB2070 Ex. session 13

① H_2 molecule with

$$|\Psi_{HF}\rangle = |\sigma_g \bar{\sigma}_g\rangle = \langle 1\bar{1}| \quad , \quad |\Psi_{g\bar{g}}^{u\bar{u}}\rangle = |\sigma_u \bar{\sigma}_u\rangle = |2\bar{2}\rangle$$

The CID wavefunction is

$$|\Psi_{CID}\rangle = c_0 |\Psi_{HF}\rangle + c_1 |\Psi_{g\bar{g}}^{u\bar{u}}\rangle$$

Determine $n(\bar{r})$ for the CID wave function in terms of spatial orbitals

From ex 1 of session 2 we have

$$\hat{n}(\bar{r}) = \sum_{i=1}^{N} \delta(\bar{r}-\bar{r}_i) = 2\,\delta(\bar{r}-\bar{r}_1)$$

indistinguishable particles   specifically for our case

We write

$$n(\bar{r}) = \langle \Psi_{CID} | \hat{n}(\bar{r}) | \Psi_{CID}\rangle = \left(c_0^* \langle \Psi_{HF}| + c_1^* \langle \Psi_{g\bar{g}}^{u\bar{u}}|\right) \hat{n}(\bar{r}) \left(c_0 |\Psi_{HF}\rangle + c_1 |\Psi_{g\bar{g}}^{u\bar{u}}\rangle\right)$$

$$= c_0^* c_0 \langle \Psi_{HF} | \hat{n}(\bar{r}) | \Psi_{HF}\rangle + c_1^* c_1 \langle \Psi_{g\bar{g}}^{u\bar{u}} | \hat{n}(\bar{r}) | \Psi_{g\bar{g}}^{u\bar{u}}\rangle + c_0^* c_1 \langle \Psi_{HF} | \hat{n}(\bar{r}) | \Psi_{g\bar{g}}^{u\bar{u}}\rangle$$
$$+ c_1^* c_0 \langle \Psi_{g\bar{g}}^{u\bar{u}} | \hat{n}(\bar{r}) | \Psi_{HF}\rangle$$

we use the rule for the matrix element of a one-electron operator between determinants that differ by two orbitals

$$\langle \Psi_{HF} | \hat{n}(\bar{r}) | \Psi_{g\bar{g}}^{u\bar{u}}\rangle = \langle \Psi_{g\bar{g}}^{u\bar{u}} | \hat{n}(\bar{r}) | \Psi_{HF}\rangle = 0$$

and since the coefficients are real, we can write $c_i^* c_i = c_i^2$

$$n(\bar{r}) = c_0^2 \langle \Psi_{HF} | \hat{n}(\bar{r}) | \Psi_{HF}\rangle + c_1^2 \langle \Psi_{g\bar{g}}^{u\bar{u}} | \hat{n}(\bar{r}) | \Psi_{g\bar{g}}^{u\bar{u}}\rangle$$

The determinants have the form

$$|\Psi_{HF}\rangle = |\sigma_g \bar{\sigma}_g\rangle = \frac{1}{\sqrt{2}}\left(\sigma_g(\bar{r}_1)\alpha(\omega_1)\sigma_g(\bar{r}_2)\beta(\omega_2) - \sigma_g(\bar{r}_1)\beta(\omega_1)\sigma_g(\bar{r}_2)\alpha(\omega_2)\right)$$

$$|\Psi_{g\bar{g}}^{u\bar{u}}\rangle = |\sigma_u \bar{\sigma}_u\rangle = \frac{1}{\sqrt{2}}\left(\sigma_u(\bar{r}_1)\alpha(\omega_1)\sigma_u(\bar{r}_2)\beta(\omega_2) - \sigma_u(\bar{r}_1)\beta(\omega_1)\sigma_u(\bar{r}_2)\alpha(\omega_2)\right)$$

We write

$$\langle \Psi_{HF} | \hat{n}(\bar{r}) | \Psi_{HF}\rangle = \frac{1}{2} 2 \iint d\bar{r}_1 d\bar{r}_2 \left[\sigma_g^\dagger(\bar{r}_1)\alpha^\dagger(\omega_1)\sigma_g^\dagger(\bar{r}_2)\beta^\dagger(\omega_2) - \sigma_g^\dagger(\bar{r}_1)\beta^\dagger(\omega_1)\sigma_g^\dagger(\bar{r}_2)\alpha^\dagger(\omega_2)\right]$$

$$\times\, \delta(\bar{r}-\bar{r}_1)\left[\sigma_g(\bar{r}_1)\alpha(\omega_1)\sigma_g(\bar{r}_2)\beta(\omega_2) - \sigma_g(\bar{r}_1)\beta(\omega_1)\sigma_g(\bar{r}_2)\alpha(\omega_2)\right]$$

where ω_1, ω_2 are just "spin variables" which we will soon integrate over

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① cont'd

We get four terms. Considering each separately:

A: $$\iint d\bar{r}_1 d\bar{r}_2\ \sigma_g^+(\bar{r}_1)\alpha^+(\omega_1)\sigma_g^+(\bar{r}_2)\beta^+(\omega_2)\ \delta(\bar{r}-\bar{r}_1)\ \sigma_g(\bar{r}_1)\alpha(\omega_1)\sigma_g(\bar{r}_2)\beta(\omega_2)$$

by integrating over spin variables and recalling that
$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1\ ,\ \ \langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$

integration over $d\bar{r}_2 = 1$

we get

$$A = \iint d\bar{r}_1 d\bar{r}_2\ \sigma_g^+(r_1)\sigma_g^+(r_2)\ \delta(\bar{r}-\bar{r}_1)\ \sigma_g(\bar{r}_1)\sigma_g(\bar{r}_2) = \int d\bar{r}_1\ \sigma_g^+(\bar{r}_1)\delta(\bar{r}-\bar{r}_1)\ \sigma_g(\bar{r}_1)$$

$$= \sigma_g^*(\bar{r})\sigma_g(\bar{r}) = |\sigma_g|^2$$

spatial orbitals are real

$\delta(\bar{r}-\bar{r}_1)$ "picks out" the value of the orbital that is a function of $\bar{r}_1$ at position $\bar{r}$

Continuing:

B: $$\iint d\bar{r}_1 d\bar{r}_2\ \sigma_g^+(\bar{r}_1)\alpha^+(\omega_1)\sigma_g^+(\bar{r}_2)\beta^+(\omega_2)\ \delta(\bar{r}-\bar{r}_1)\ \sigma_g(\bar{r}_1)\beta(\omega_1)\sigma_g(\bar{r}_2)\alpha(\omega_2)$$

$$= 0 \quad \text{since} \quad \int d\omega_1\, \alpha(\omega_1)\beta(\omega_1) = 0$$

C: $$\iint d\bar{r}_1 d\bar{r}_2\ \sigma_g^+(\bar{r}_1)\beta^+(\omega_1)\sigma_g^+(\bar{r}_2)\alpha^+(\omega_2)\ \delta(\bar{r}-\bar{r}_1)\ \sigma_g(\bar{r}_1)\alpha(\omega_1)\sigma_g(\bar{r}_2)\beta(\omega_2)$$

$= 0$ same argument as for C

D: $$\iint d\bar{r}_1 d\bar{r}_2\ \sigma_g^+(\bar{r}_1)\beta^+(\omega_1)\sigma_g^+(\bar{r}_2)\alpha^+(\omega_2)\ \delta(\bar{r}-\bar{r}_1)\ \sigma_g(\bar{r}_1)\beta(\omega_1)\sigma_g(\bar{r}_2)\alpha(\omega_2)$$

integrating over spin and $d\bar{r}_2$

$$= \int d\bar{r}_1\ \sigma_g^+(\bar{r}_1)\ \delta(\bar{r}-\bar{r}_1)\ \sigma_g(\bar{r}_1) = |\sigma_g(\bar{r})|^2$$

we see that A and D are identical. Thus

$$\langle\Psi_{HF}|\hat{n}(\bar{r})|\Psi_{HF}\rangle = 2|\sigma_g(\bar{r})|^2$$

By following the same procedure, we obtain

$$\langle\Psi_{g\bar{g}}^{u\bar{u}}|\hat{n}(\bar{r})|\Psi_{g\bar{g}}^{u\bar{u}}\rangle = 2|\sigma_u(\bar{r})|^2$$

and finally

$$n^{CID}(\bar{r}) = 2c_0^2|\sigma_g(\bar{r})|^2 + 2c_1^2|\sigma_g(\bar{r})|^2$$

Q.E.D

① Alternative:

We can also approach the problem via derived expressions for matrix elements between determinants and one-electron operators and using the notation

$$|\Psi_{HF}\rangle = |1\bar{1}\rangle \quad , \quad |\Psi_{g\bar{g}}^{u\bar{u}}\rangle = |2\bar{2}\rangle$$

instead.

For the HF,HF we write

$$\langle\Psi_{HF}|\hat{n}(\bar{r})|\Psi_{HF}\rangle = \sum_{i}^{N} \langle i|\hat{n}(\bar{r})|i\rangle = \langle 1|\hat{n}(\bar{r})|1\rangle + \langle\bar{1}|\hat{n}(\bar{r})|\bar{1}\rangle$$

$i = 1, \bar{1}$

$$= 2\langle 1|\hat{n}(\bar{r})|1\rangle = 2\int \sigma_g^+(1)\,\delta(\bar{r}-\bar{r}_1)\,\sigma_g(1)\,d\bar{r}_1 = 2|\sigma_g(\bar{r})|^2$$

spin integration

This "1" refers to electron 1!

Also:

$$\langle\Psi_{g\bar{g}}^{u\bar{u}}|\hat{n}(\bar{r})|\Psi_{g\bar{g}}^{u\bar{u}}\rangle = \sum_{i=2,\bar{2}} \langle i|\hat{n}(\bar{r})|i\rangle = \langle 2|\hat{n}(\bar{r})|2\rangle + \langle\bar{2}|\hat{n}(\bar{r})|\bar{2}\rangle$$

$$= 2\langle 2|\hat{n}(\bar{r})|2\rangle = 2\int \sigma_u^+(\bar{r}_1)\,\delta(\bar{r}-\bar{r}_1)\,\sigma_u(\bar{r}_1)\,d\bar{r}_1 = 2|\sigma_u(\bar{r})|^2$$

We get

$$n^{CI}(\bar{r}) = 2c_0^2|\sigma_g(\bar{r})|^2 + 2c_1^2|\sigma_u(\bar{r})|^2$$

as with the first approach/notation.

(2) The probabilistic interpretation of the wave function is

$$n(\bar{r},\bar{r}') = N(N-1)\int \Psi^\dagger(\bar{r},\bar{r}',\bar{r}_3,\ldots,\bar{r}_N)\,\Psi(\bar{r},\bar{r}',\bar{r}_3,\ldots,\bar{r}_N)\,d\bar{r}_3\ldots d\bar{r}_N$$

Lecture notes 1

We have

$$\hat{n}(\bar{r},\bar{r}') = \sum_{j>i}^{N}\left[\delta(\bar{r}-\bar{r}_i)\delta(\bar{r}'-\bar{r}_j)+\delta(\bar{r}-\bar{r}_j)\delta(\bar{r}'-\bar{r}_i)\right]$$

$$= \frac{N(N-1)}{2}\left[\delta(\bar{r}-\bar{r}_1)\delta(\bar{r}'-\bar{r}_2)+\delta(\bar{r}-\bar{r}_2)\delta(\bar{r}'-\bar{r}_1)\right]$$

So:

$$\langle\Psi|\hat{n}(\bar{r},\bar{r}')|\Psi\rangle = \int \Psi^\dagger(\bar{r}_1,\bar{r}_2,\ldots,\bar{r}_N)\left[\delta(\bar{r}-\bar{r}_1)\delta(\bar{r}'-\bar{r}_2)+\delta(\bar{r}-\bar{r}_2)\delta(\bar{r}'-\bar{r}_1)\right]\Psi(\bar{r}_1,\bar{r}_2,\ldots,\bar{r}_N)\times d\bar{r}_1 d\bar{r}_2\ldots d\bar{r}_N$$

$$= \int\Big[\Psi^\dagger(\bar{r}_1,\bar{r}_2,\ldots,\bar{r}_N)\delta(\bar{r}-\bar{r}_1)\delta(\bar{r}'-\bar{r}_2)\Psi(\bar{r}_1,\bar{r}_2,\ldots,\bar{r}_N)$$
$$+\Psi^\dagger(\bar{r}_1,\bar{r}_2,\ldots,\bar{r}_N)\delta(\bar{r}-\bar{r}_2)\delta(\bar{r}'-\bar{r}_1)\Psi(\bar{r}_1,\bar{r}_2,\ldots,\bar{r}_N)\,d\bar{r}_1 d\bar{r}_2\ldots d\bar{r}_N\Big]$$

Integrating over $\bar{r}_1$ and $\bar{r}_2$ leads to the substitutions

$\bar{r}_1\to\bar{r},\ \bar{r}_2\to\bar{r}'$

in the first term, and

$\bar{r}_1\to\bar{r}',\ \bar{r}_2\to\bar{r}$

in the second term.

Thus, we get

$$n(\bar{r},\bar{r}') = \frac{N(N-1)}{2}\int\Big[\Psi^\dagger(\bar{r},\bar{r}',\bar{r}_3,\ldots,\bar{r}_N)\Psi(\bar{r},\bar{r}',\bar{r}_3,\ldots,\bar{r}_N)$$
$$+\Psi^\dagger(\bar{r}',\bar{r},\bar{r}_3,\ldots,\bar{r}_N)\Psi(\bar{r}',\bar{r},\bar{r}_3,\ldots,\bar{r}_N)\Big]d\bar{r}_3\ldots d\bar{r}_N$$

$\bar{r}$ and $\bar{r}'$ are just dummy variables, so the two terms in the integrals are equal (in two separate sums/integrals)

We obtain

$$n(\bar{r},\bar{r}') = N(N-1)\int\Psi^\dagger(\bar{r},\bar{r}',\bar{r}_3,\ldots,\bar{r}_N)\Psi(\bar{r},\bar{r}',\bar{r}_3,\ldots,\bar{r}_N)\,d\bar{r}_3\ldots d\bar{r}_N$$

which is exactly the probabilistic interpretation.

Q.E.D

③ We have

$$|\Psi_{CID}\rangle = c_0|\Psi_{HF}\rangle + c_1|\Psi_{g\bar{g}}^{u\bar{u}}\rangle = c_0|\sigma_g\bar{\sigma}_g\rangle + c_1|\sigma_u\bar{\sigma}_u\rangle = c_0|1\bar{1}\rangle + c_1|2\bar{2}\rangle$$

$$\hat{n}(\bar{r},\bar{r}') = \sum_{j>i}^{N}\left[\delta(\bar{r}-\bar{r}_i)\delta(\bar{r}'-\bar{r}_j) + \delta(\bar{r}-\bar{r}_j)\delta(\bar{r}'-\bar{r}_i)\right]$$

$$n(\bar{r},\bar{r}') = \langle\Psi_{CID}|\hat{n}(\bar{r},\bar{r}')|\Psi_{CID}\rangle$$

$$= c_0^*c_0\overset{A}{\langle\Psi_{HF}|\hat{n}(\bar{r},\bar{r}')|\Psi_{HF}\rangle} + c_1^*c_1\overset{B}{\langle\Psi_{g\bar{g}}^{u\bar{u}}|\hat{n}(\bar{r},\bar{r}')|\Psi_{g\bar{g}}^{u\bar{u}}\rangle}$$

$$+ c_0^*c_1\overset{C}{\langle\Psi_{HF}|\hat{n}(\bar{r},\bar{r}')|\Psi_{g\bar{g}}^{u\bar{u}}\rangle} + c_1^*c_0\overset{D}{\langle\Psi_{g\bar{g}}^{u\bar{u}}|\hat{n}(\bar{r},\bar{r}')|\Psi_{HF}\rangle}$$

and recalling the two-electron operator matrix elements:

$$\langle\Psi|\hat{O}_2|\Psi\rangle = \frac{1}{2}\sum_{i,j}^{N}\langle ij|\hat{O}_2|ij\rangle - \langle ij|\hat{O}_2|ji\rangle$$

$$\langle\Psi|\hat{O}_2|\Psi_{ij}^{st}\rangle = \langle ij|\hat{O}_2|st\rangle - \langle ij|\hat{O}_2|ts\rangle$$

$$\langle\Psi_{ij}^{st}|\hat{O}_2|\Psi\rangle = \langle st|\hat{O}_2|ij\rangle - \langle st|\hat{O}_2|ji\rangle$$

For term "A" we get

$$A: \langle\Psi_{HF}|\hat{n}(\bar{r},\bar{r}')|\Psi_{HF}\rangle = \frac{1}{2}\sum_{i=1,\bar{1}}\sum_{j=1,\bar{1}}\langle ij|\hat{n}(\bar{r},\bar{r}')|ij\rangle - \langle ij|\hat{n}(\bar{r},\bar{r}')|ji\rangle$$

$$= \frac{1}{2}\Big[\cancel{\langle 11|\hat{n}(\bar{r},\bar{r}')|11\rangle - \langle 11|\hat{n}(\bar{r},\bar{r}')|11\rangle} + \langle 1\bar{1}|\hat{n}(\bar{r},\bar{r}')|1\bar{1}\rangle$$

$$- \langle 1\bar{1}|\hat{n}(\bar{r},\bar{r}')|\bar{1}1\rangle + \cancel{\langle\bar{1}\bar{1}|\hat{n}(\bar{r},\bar{r}')|\bar{1}\bar{1}\rangle - \langle\bar{1}\bar{1}|\hat{n}(\bar{r},\bar{r}')|\bar{1}\bar{1}\rangle}$$

$$+ \langle\bar{1}1|\hat{n}(\bar{r},\bar{r}')|\bar{1}1\rangle - \langle\bar{1}1|\hat{n}(\bar{r},\bar{r}')|1\bar{1}\rangle\Big]$$

$$= \frac{1}{2}\Big[\langle 1\bar{1}|\hat{n}(\bar{r},\bar{r}')|1\bar{1}\rangle - \underbrace{\langle 1\bar{1}|\hat{n}(\bar{r},\bar{r}')|\bar{1}1\rangle}_{0} + \langle\bar{1}1|\hat{n}(\bar{r},\bar{r}')|\bar{1}1\rangle - \underbrace{\langle\bar{1}1|\hat{n}(\bar{r},\bar{r}')|1\bar{1}\rangle}_{0}\Big]$$

integrating over spin, we get

$$= \frac{1}{2}\Big[\langle 11|\hat{n}(\bar{r},\bar{r}')|11\rangle + \langle 11|\hat{n}(\bar{r},\bar{r}')|11\rangle\Big] = \langle 11|\hat{n}(\bar{r},\bar{r}')|11\rangle$$

for a system of two electrons $\hat{n}(\bar{r},\bar{r}') = \frac{2(2-1)}{2}\left[\delta(\bar{r}-\bar{r}_1)\delta(\bar{r}'-\bar{r}_2) + \delta(\bar{r}-\bar{r}_2)\delta(\bar{r}'-\bar{r}_1)\right]$

$$\Rightarrow \iint d\bar{r}_1 d\bar{r}_2\, \sigma_g^\dagger(\bar{r}_1)\sigma_g^\dagger(\bar{r}_2)\left[\delta(\bar{r}-\bar{r}_1)\delta(\bar{r}'-\bar{r}_2) + \delta(\bar{r}-\bar{r}_2)\delta(\bar{r}'-\bar{r}_1)\right]\sigma_g(\bar{r}_1)\sigma_g(\bar{r}_2)$$

$$= \sigma_g^\dagger(\bar{r})\sigma_g^\dagger(\bar{r}')\sigma_g(\bar{r})\sigma_g(\bar{r}') + \sigma_g^\dagger(\bar{r}')\sigma_g^\dagger(\bar{r})\sigma_g(\bar{r}')\sigma_g(\bar{r})$$

$$= 2|\sigma_g(\bar{r})|^2|\sigma_g(\bar{r}')|^2$$

3 cont'd

For the "B" term we obtain our result in exactly the same manner

B: $\langle \Psi_{g\bar{g}}^{u\bar{u}} | \hat{n}(\bar{r},\bar{r}') | \Psi_{g\bar{g}}^{u\bar{u}} \rangle = 2|\sigma_u(\bar{r})|^2 |\sigma_u(\bar{r}')|^2$

"C" has different determinants in its "bra" and "ket" states and we write in accordance with the matrix element expression:

$$\langle \Psi_{HF} | \hat{n}(\bar{r},\bar{r}') | \Psi_{g\bar{g}}^{u\bar{u}} \rangle = \langle 1\bar{1} | \hat{n}(\bar{r},\bar{r}') | 2\bar{2} \rangle - \underbrace{\langle 1\bar{1} | \hat{n}(\bar{r},\bar{r}') | \bar{2}2 \rangle}_{0 \text{ by spin-integration}} = \langle 11 | \hat{n}(\bar{r},\bar{r}') | 22 \rangle$$

$$= \iint d\bar{r}_1 d\bar{r}_2\, \sigma_g^*(\bar{r}_1)\sigma_g^*(\bar{r}_2)\left[\delta(\bar{r}-\bar{r}_1)\delta(\bar{r}'-\bar{r}_2) + \delta(\bar{r}-\bar{r}_2)\delta(\bar{r}'-\bar{r}_1)\right]\sigma_u(\bar{r}_1)\sigma_u(\bar{r}_2)$$

$$= \sigma_g^*(\bar{r})\sigma_u(\bar{r})\sigma_g^*(\bar{r}')\sigma_u(\bar{r}') + \sigma_g^*(\bar{r}')\sigma_u(\bar{r}')\sigma_g^*(\bar{r})\sigma_u(\bar{r}) = 2\sigma_g^*(\bar{r})\sigma_u(\bar{r})\sigma_g^*(\bar{r}')\sigma_u(\bar{r}')$$

For "D" we have (skipping some steps since it follows "C" procedure

$$\langle \Psi_{g\bar{g}}^{u\bar{u}} | \hat{n}(\bar{r},\bar{r}') | \Psi_{HF} \rangle = \langle 22 | \hat{n}(\bar{r},\bar{r}') | 11 \rangle$$

$$= \iint d\bar{r}_1 d\bar{r}_2\, \sigma_u^*(\bar{r}_1)\sigma_u^*(\bar{r}_2)\left[\delta(\bar{r}-\bar{r}_1)\delta(\bar{r}'-\bar{r}_2) + \delta(\bar{r}-\bar{r}_2)\delta(\bar{r}'-\bar{r}_1)\right]\sigma_g(\bar{r}_1)\sigma_g(\bar{r}_2)$$

$$= 2\sigma_u^*(\bar{r})\sigma_g(\bar{r})\sigma_u^*(\bar{r}')\sigma_g(\bar{r}')$$

Since the spatial orbitals are real, $C = D$ and we get

$$n(\bar{r},\bar{r}') = 2c_0^2|\sigma_g(\bar{r})|^2|\sigma_g(\bar{r}')|^2 + 2c_1^2|\sigma_u(\bar{r})|^2|\sigma_u(\bar{r}')|^2$$
$$+ 4c_0c_1\,\sigma_g(\bar{r})\sigma_u(\bar{r})\sigma_g(\bar{r}')\sigma_u(\bar{r}')$$

QED.