CB2070 Ex. session 2

① We have
$$\hat{n}(\bar{r}) = \sum_{i=1}^{N} \delta(\bar{r}-\bar{r}_i)$$
Show that
$$n(\bar{r}) = \langle \Psi | \hat{n}(\bar{r}) | \Psi \rangle$$
Agrees with
$$n(\bar{r}) = N \int \Psi^{\dagger}(\bar{r}, \ldots, \bar{r}_N) \Psi(\bar{r}, \ldots, \bar{r}_N)\, d\bar{r}_2 \ldots d\bar{r}_N$$
$$n(\bar{r}_1) = \sum_{i=1}^{N} |\psi_i(\bar{r}_1)|^2$$

$$n(\bar{r}) = \sum_{i}^{N} \int \Psi^{\dagger}(\bar{r}_1, \ldots, \bar{r}_N)\, \delta(\bar{r}-\bar{r}_i)\, \Psi(\bar{r}_1, \ldots, \bar{r}_N)\, d\bar{r}_1 \ldots d\bar{r}_N$$

say $\bar{r}_i = \bar{r}_1$, $\delta(\bar{r}-\bar{r}_1)$ picks out the wfs at point "$\bar{r}$" when integrated

$$\Rightarrow n(\bar{r}) = \overset{\text{indist. particles}}{N} \int \Psi^{\dagger}(\bar{r}, \bar{r}_2, \ldots, \bar{r}_N) \Psi(\bar{r}, \bar{r}_2, \ldots, \bar{r}_N)\, d\bar{r}_2 \ldots d\bar{r}_N$$

which is exactly equal to the probabilistic interpretation

② N-electron system described by Slater determinant

p. 76 in Szabo & Ostlund

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \sum_{i}^{N!} (-1)^{p_i} P_i \{\psi_1(\bar{r}_1), \ldots, \psi_N(\bar{r}_N)\}$$

$$n(\bar{r}) = N \frac{1}{\sqrt{N!}} \frac{1}{\sqrt{N!}} \sum_{i,j}^{N!} \int (-1)^{p_i} (-1)^{p_j} \underbrace{P_i\{\ \}^{\dagger} P_j\{\ \}}\, d\bar{r}_2 \ldots d\bar{r}_N$$

in order to be nonzero, the electron at position $\bar{r}$ must be in the same orbital. This happens $(N-1)!$ times

Integrating over all space for the remaining electrons give 1 due to orthogonal basis functions which reduces the sum to one elec since the permutations must be identical to be nonzero

$N(N-1)! = N!$

$$n(\bar{r}) = \frac{N}{N!}(N-1)! \sum_{k}^{N} \psi_k^*(\bar{r}) \psi_k(\bar{r})$$
$$= \sum_{k}^{N} \psi_k^*(\bar{r}) \psi_k(\bar{r}) = \sum_{k}^{N} |\psi_k|^2$$

One-particle summation: one-particle density computed without interaction with the other $N-1$ electrons

CB2070 Ex sess 2 cont'd

p 72 in Szabo & Ostlund

(3) N-electron system described by an SD, show

$$n(\bar{r}_1, \bar{r}_2) = \sum_{i,j}^{N} \left[|\psi_i(\bar{r}_1)|^2 |\psi_j(\bar{r}_2)|^2 - \psi_i^\dagger(\bar{r}_1)\psi_j^\dagger(\bar{r}_2)\psi_j(\bar{r}_1)\psi_i(\bar{r}_2) \right]$$

The two-particle probability density

$$n(\bar{r}_1, \bar{r}_2) = N(N-1) \int \Psi^\dagger(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N)\Psi(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N)\, d\bar{r}_3, \ldots, d\bar{r}_N$$

# of electron pairs: $\frac{N(N-1)}{2}$

Inserting SD

$$n(\bar{r}_1, \bar{r}_2) = N(N-1)\frac{1}{\sqrt{N!}}\frac{1}{\sqrt{N!}}\sum_{i,j}^{N!}\int (-1)^{p_i}(-1)^{p_j} P_i^\dagger\{\ \} P_j\{\ \}\, d\bar{r}_3, \ldots, d\bar{r}_N$$

In order to get non-zero result, P_i and P_j may only differ in the orbitals that are occupied by electron 1 and 2 (or be identical)

$P_j = P_i$ or $P_j = P_{12}P_i$ where P_{12} permutes electron 1 and 2

We can then write only one sum over i

$$n(\bar{r}_1, \bar{r}_2) = \frac{N(N-1)}{N!}\sum_{i}^{N!}\int P_i^\dagger\{\ \}\left(P_i\{\ \} - P_{12}P_i\{\ \}\right) d\bar{r}_3 \ldots d\bar{r}_N$$

due to antisymmetry: $P_{12}P_i$ differs from P_i by the interchange of electron 1 and 2 $\Rightarrow$ factor of -1

There are $(N-2)!$ ways to arrange electrons 3 - N when 1 and 2 are fixed, so we can write

$$n(\bar{r}_1, \bar{r}_2) = \frac{N(N-1)}{N!}(N-2)!\sum_{k,l}^{N}\psi_k^*(\bar{r}_1)\psi_l^*(\bar{r}_2)\left(\psi_k(\bar{r}_1)\psi_l(\bar{r}_2) - \psi_k(\bar{r}_2)\psi_l(\bar{r}_1)\right)$$

$N! = N(N-1)! \Rightarrow \frac{N(N-1)}{N(N-1)!} = \frac{(N-1)}{(N-1)!} = \frac{1}{(N-2)!}$ since $(N-1)! = 1\cdot 2 \cdot \ldots \cdot (N-2)(N-1)$ this disappears

$\Rightarrow$ prefactor to sum becomes 1 and we get (renaming the indices k, l):

$$n(\bar{r}_1, \bar{r}_2) = \sum_{i}^{N}\sum_{j}^{N} |\psi_i(\bar{r}_1)|^2 |\psi_j(\bar{r}_2)|^2 - \psi_i^*(\bar{r}_1)\psi_j^*(\bar{r}_2)\psi_j(\bar{r}_1)\psi_i(\bar{r}_2)$$

Self-interaction is avoided since the two terms are equal when $i=j$. The remaining N-2 electrons do not appear in the expression at all. QED

Wrt spin: since $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$ and $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$, the second term will be zero in the case where orbitals i and j have opposite spin. This shows that there is no correlation between electrons of opposite spin. Meanwhile, this term remains nonzero for same-spin electrons, showing that there is correlation.