

Assignment-2: Many-Electron Systems (22/05/2024)

- Using the general rules for matrix elements, for the one- and the two-electron operators, \mathcal{O}_1 and \mathcal{O}_2 , respectively, write down the values of the matrix elements, $\langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle$ and $\langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle$, where $|\Psi_0\rangle = |\chi_1 \cdots \chi_a \chi_b \cdots \chi_N\rangle$ is the Hartree-Fock ground state for the N electron system.
- Derive the matrix elements for
 - $|K\rangle = |\chi_m(1)\chi_n(2)\cdots\rangle, |L\rangle = |\chi_p(1)\chi_n(2)\cdots\rangle$
 - $|K\rangle = |\chi_m(1)\chi_n(2)\cdots\rangle, |L\rangle = |\chi_p(1)\chi_q(2)\cdots\rangle$
- A different procedure for deriving the above matrix element uses the theorem that $\langle K | H | L \rangle = \sqrt{N!} \langle K^{HP} | H | L \rangle$, where $|K^{HP}\rangle$ is the Hartree product corresponding to the determinant $|K\rangle$, that is, $|K\rangle = |\chi_m(x_1)\chi_n(x_2)\cdots\rangle$ and $|K^{HP}\rangle = \chi_m(x_1)\chi_n(x_2)\cdots$. Prove this theorem. Use this theorem to derive the matrix elements of a sum of one-electron operators.
- By integrating out the spin, show that the full CI matrix for minimal basis H_2 model is

$$\mathbf{H} = \begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (12|21) & 2(2|h|2) + (22|22) \end{pmatrix}$$
- Show, using the properties of determinants, that, $(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger) |K\rangle = 0$ for every $|K\rangle$ in the set $\{|\chi_1\chi_2\rangle, |\chi_1\chi_3\rangle, |\chi_1\chi_4\rangle, |\chi_2\chi_3\rangle, |\chi_2\chi_4\rangle, |\chi_3\chi_4\rangle\}$.
- Show, using the properties of determinants, that, $(a_1 a_2^\dagger + a_2^\dagger a_1) |K\rangle = 0$ and $(a_1 a_1^\dagger + a_1^\dagger a_1) |K\rangle = |K\rangle$ for every $|K\rangle$ in the set $\{|\chi_1\chi_2\rangle, |\chi_1\chi_3\rangle, |\chi_1\chi_4\rangle, |\chi_2\chi_3\rangle, |\chi_2\chi_4\rangle, |\chi_3\chi_4\rangle\}$.
- Given a state $|K\rangle = |\chi_1\chi_2 \cdots \chi_N\rangle$, show that, $\langle K | a_i^\dagger a_j | K \rangle = 1$, if $i = j$ and $i \in \{1, 2, \dots, N\}$, but is zero otherwise.