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Useful Tools for Quantum Chemistry

Paul Fleurat-Lessard
Mikael Kepenekian
mikael.kepenekian@ens-lyon.fr

1 Hartree Products and Slater Determinants

Let's consider a system of N electrons in N spinorbitals χ_i ($i \in 1, ..., N$). ϕ_i and s_i are defined as the spatial part and the spin part of the spinorbital χ_i respectively *i.e.* $\chi_i(x) = \phi_i(\mathbf{r})s_i(\omega)$.

We aim at the probability $P_{12}(\mathbf{r_1}, \mathbf{r_2})$ of finding the electron 1 in the volume $d\mathbf{r_1}$ centred on $\mathbf{r_1}$ and the electron 2 in the volume $d\mathbf{r_2}$ centred on $\mathbf{r_2}$.

1. Give an expression of $P_{12}(\mathbf{r_1}, \mathbf{r_2})$ depending on Ψ the electronic wave-function of the system.

2. On a first approach, let's consider that the electronic wave-function can be written as a Hartree product:

$$\Psi^H = \chi_1(x_1)...\chi_N(x_N)$$

   Conclude on $P_{12}(\mathbf{r_1}, \mathbf{r_2})$.

3. Ψ is now written as a Slater determinant constructed on the χ_i:

$$\begin{aligned}\Psi^S &= |\chi_1(x_1)...\chi_N(x_N)\rangle \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_1(x_2) & \cdots & \chi_1(x_N) \\ \chi_2(x_1) & \chi_2(x_2) & \cdots & \chi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_N(x_1) & \chi_N(x_2) & \cdots & \chi_N(x_N) \end{vmatrix}\end{aligned}$$

   What becomes $P_{12}(\mathbf{r_1}, \mathbf{r_2})$ when both electrons 1 and 2 have different spin ? same spin ? As a first step, one could consider a 2-electron system.

2 Properties of Slater Determinants

Let's consider the 2-electron Slater determinants:

$$\Psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(1) & \chi_i(2) \\ \chi_j(1) & \chi_j(2) \end{vmatrix} \qquad \Psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_k(1) & \chi_k(2) \\ \chi_l(1) & \chi_l(2) \end{vmatrix}$$

1. Norm and overlap

   (a) Let's suppose that the orbitals $\phi_i, \phi_j, \ldots$ form an orthonormalized basis set.

      i. Show that Ψ_1 is normalized.

      ii. Show that $\langle \Psi_1 | \Psi_2 \rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$.

   (b) We now consider that the orbitals are no longer orthonormalized. The overlap matrix is noted $\mathcal{S}$.

      i. Show that

$$\left\langle \begin{vmatrix} \chi_i(1) & \chi_i(2) \\ \chi_j(1) & \chi_j(2) \end{vmatrix} \middle| \begin{vmatrix} \chi_k(1) & \chi_k(2) \\ \chi_l(1) & \chi_l(2) \end{vmatrix} \right\rangle = 2\det(\mathcal{S})$$

      ii. How does $\langle \Psi_1 | \Psi_2 \rangle$ change ?

2. Slater's rules

   The goal is to derive Slater's rules in the case of systems with 2 then 3 electrons. For both systems, mono and bielectronic operators are written $\mathcal{O}_1$ and $\mathcal{O}_2$, respectively.

   (a) Let's consider a 2-electron system. The following notations are assumed:

$$0 = |\chi_i\chi_j\rangle \qquad S = |\chi_p\chi_j\rangle \qquad D = |\chi_p\chi_q\rangle$$

   Evaluate $\langle 0|\mathcal{O}_1|0\rangle$, $\langle 0|\mathcal{O}_1|S\rangle$, $\langle 0|\mathcal{O}_1|D\rangle$, $\langle 0|\mathcal{O}_2|0\rangle$, $\langle 0|\mathcal{O}_2|S\rangle$, $\langle 0|\mathcal{O}_2|D\rangle$.

   (b) Let's consider a 3-electron system. The following notations are assumed:

$$0 = |\chi_i\chi_j\chi_k\rangle \qquad S = |\chi_p\chi_j\chi_k\rangle$$
$$D = |\chi_p\chi_q\chi_k\rangle \qquad T = |\chi_p\chi_q\chi_r\rangle$$

   Same question. Evaluate also $\langle 0|\mathcal{O}_1|T\rangle$ et $\langle 0|\mathcal{O}_2|T\rangle$.

3. Applications

   (a) In this question, the system is ruled by a monoelectronic Hamiltonian written as a sum of $\hat{h}_i$ whose ϕ_i are eigenvectors corresponding to the eigenvalues ϵ_i:

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \hat{h}_i$$

$$\hat{h}_i \phi_j = \epsilon_j \phi_j$$

   What are the energies calculated with Ψ^H ? Ψ^S ? Conclude.

   (b) The system is now ruled by a Hartree-Fock Hamiltonian.

      i. Give an expression of this Hamiltonian.
      ii. How are changed the previous energies ?