Exercise Sheet 3

Due: 14.05.24 14h00

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General Regulations.

- Please hand in your solutions in groups of up to two people.
- Your solutions to theoretical exercises can be either handwritten notes (scanned), or typeset using LaTeX. In case you hand in handwritten notes, please make sure that they are legible and not too blurred or low resolution.
- For the practical exercises, always provide the (commented) code as well as the output, and don't forget to explain/interpret the latter. Please hand in both the notebook (`.ipynb`), as well as an exported pdf.
- Submit all your files in the Übungsgruppenverwaltung, only once for your group.

1 Antisymmetrization

In general, the normalized, two electron wave function Φ may be written using a Slater determinant

$$\Phi(1,2) = \frac{1}{\sqrt{n!}}|\phi_1\overline{\phi}_1|,$$

or by using the anti-symmetrizer $\hat{\mathcal{A}}$

$$\Phi'(1,2) = \hat{\mathcal{A}}\psi_1(1)\psi_2(2),$$

where the spin-orbitals are given by the multiplication of spatial orbital ϕ_1 and spin functions α and β:

$$\psi_1(j) = \phi_1(j)\alpha(j) \quad \text{and} \quad \psi_2(j) = \phi_1(j)\beta(j)$$

The anti-symmetrizer is given by a sum over all $n!$ permutations $\hat{P}$, with parities $(-1)^p$,

$$\hat{\mathcal{A}} = \frac{1}{\sqrt{n!}}\sum_P (-1)^p \hat{P}$$

(a) Show that, $\Phi(1,2)$ and $\Phi'(1,2)$ are equal. (2 pts)

The anti-symmetrizer satisfies, for each permutation $\hat{P}$

$$\hat{P}\hat{\mathcal{A}} = (-1)^p\hat{\mathcal{A}}$$

(b) Verify this expression for $n = 2$. (3 pts)

(c) Prove $\hat{\mathcal{A}}^2 = \sqrt{n!}\hat{\mathcal{A}}$ (3 pts)

2 Undetermined multiplier method of Lagrange

The column vector $\mathbf{x} \in \mathbb{R}^n$ has components x_i. The real functions $f(\mathbf{x})$ and $g(\mathbf{x})$ are given by

$$f(\mathbf{x}) = \mathbf{x}^\top \mathbf{H}\mathbf{x}$$
$$g(\mathbf{x}) = \mathbf{x}^\top \mathbf{x} - 1$$

where $\mathbf{H}$ is a real, symmetric, $n \times n$ matrix, i.e. $H_{ij} = H_{ji}$ for $i, j = 1, \ldots, n$.

Show that the minimization of $f(\mathbf{x})$ with the constraint that $g(\mathbf{x}) = 0$ leads to an eigenvalue problem. (6 pts)

3 Energy contributions at third order

(a) Show that

$$\langle \pi | \sum_i \hat{h}_i | \hat{P}_{123} \pi \rangle = 0.$$

(3 pts)

(b) Show that

$$\langle \pi | \hat{g}_{12} | \hat{P}_{123} \pi \rangle = 0.$$

(3 pts)