Posted: 27.05.2020
Tutorial: 28.05.2020
Due: 04.06.2020

Problem Set 4

1. **LCAO as a variational problem** (5+3 points)

The LCAO method can be naturally formulated as a variational problem. Consider the Hamiltonian H and a set of *non-orthogonal* wave functions $|\phi_a\rangle$ ($a = 1, \dots, n$). The variational wave function is constructed as

$$|\psi\rangle = \sum_{a=1}^{n} c_a |\phi_a\rangle,$$

where c_a are variational parameters which should be determined by minimizing the variational energy

$$E[c^*, c] = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$

with respect to c_a and c_a^*.

Alternatively, you may formulate this variational problem by using a Lagrange multiplier λ to ensure that the variational ansatz $|\psi\rangle$ is normalized and considering the energy functional

$$E[c^*, c, \lambda] = \langle\psi|H|\psi\rangle - \lambda(\langle\psi|\psi\rangle - 1).$$

(a) Show that the optimal choice of variational parameters is determined by the secular equation

$$\sum_{b=1}^{n} (\langle\phi_a|H|\phi_b\rangle - E\langle\phi_a|\phi_b\rangle) c_b = 0,$$

whose nontrivial solution is obtained from

$$\det(\mathcal{H} - E\mathcal{S}) = 0.$$

Here $\mathcal{H}$ and $\mathcal{S}$ are $n \times n$ matrices with matrix elements $\mathcal{H}_{ab} = \langle\phi_a|H|\phi_b\rangle$ and $\mathcal{S}_{ab} = \langle\phi_a|\phi_b\rangle$, respectively.

(b) Show that one can turn the above secular equation (for the non-orthogonal basis) into an ordinary secular equation

$$\det(\mathcal{H}' - EI) = 0,$$

where I is the $n \times n$ identity matrix. What is $\mathcal{H}'$?

Hint: You may diagonalize the overlap matrix $\mathcal{S}$, which effectively orthogonalizes $|\phi_a\rangle$.