

# Quantum Computing for Quantum Chemistry - Exercises

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## 1 Lecture 2

1. Using the linear combination of atomic orbitals. Solve the secular equation on a computer to get the bonding and anti bonding energies and orbitals. I am in the process of making a python notebook.

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = E \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} \quad (1)$$

With the Hamiltonian elements given by:

$$\begin{aligned} H_{AB} &= \int d\mathbf{r} s_A^*(\mathbf{r}) H_{LCAO} s_A(\mathbf{r}) \\ &= \int d\mathbf{r} \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{|\mathbf{r}-R_A|}{a_0}} \left[ \nabla_A^2 + \frac{1}{|\mathbf{r}-R_A|} + \frac{1}{|\mathbf{r}-R_B|} \right] \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{|\mathbf{r}-R_B|}{a_0}}. \end{aligned} \quad (2)$$

and the overlap elements

$$\begin{aligned} S_{AB} &= \int d\mathbf{r} s_A^*(\mathbf{r}) s_A(\mathbf{r}) \\ &= \int d\mathbf{r} \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{|\mathbf{r}-R_A|}{a_0}} \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{|\mathbf{r}-R_B|}{a_0}}. \end{aligned} \quad (3)$$

Where the LCAOs to use are:

$$s_A = \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{|\mathbf{r}-R_A|}{a_0}} \quad s_B = \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{|\mathbf{r}-R_B|}{a_0}} \quad (4)$$

where  $a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e}$

Hint; Using a discretized grid in  $\mathbf{r} = \mathbf{x} + \mathbf{y} + \mathbf{z}$  and a numerical integrator in numpy. Or try a sympy analytical integral solver.

- (a) Solve the secular equation  $\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c}$  for the bonding of two  $1s$  orbitals in Hydrogen
  - (b) Plot the density  $|\sigma_g(\mathbf{r})|^2$  showing the electron cusps in the  $\mathbf{x}, \mathbf{y}$  plane.
2. The variational principle states that the expectation value of an approximate ground state (i.e. an ansatz state) with the Hamiltonian is always higher than the true ground-state energy, such that

$$\langle \psi_a | H | \psi_a \rangle \geq E_g \quad (5)$$

where  $|\psi_a\rangle$  is the ansatz state,  $H$  is the Hamiltonian and  $E_g$  is the ground state energy.

- (a) Can this principle be justified through physical intuition?
  - (b) How can this principle be used computationally?
  - (c) Can this principle be proved mathematically? (Hint: decompose  $|\psi_a\rangle$  in the eigenbasis of the Hamiltonian.)
  - (d) If the relation (5) is an exact equality, what does it imply about  $|\psi_a\rangle$ ?
3. For the wavefunction  $\psi(\mathbf{x}) = c_1\phi_1(\mathbf{x}) + c_2\phi_2(\mathbf{x})$ . Where the basis is  $\int \phi_1(\mathbf{x})\phi_2(\mathbf{x}) = 0$ .

- (a) What does  $\int \phi_1(\mathbf{x})\phi_2(\mathbf{x}) = 0$  signify?
- (b) Evaluate:

$$\frac{\partial}{\partial c_n} \int \psi^*(\mathbf{x}) \hat{H} \psi(\mathbf{x}) d\mathbf{x} = 0 \quad (6)$$

What satisfies the  $= 0$  condition?

- (c) Find the general form of equation 6 when  $\psi(\mathbf{x}) = \sum_n c_n \phi_n(\mathbf{x})$  when  $\psi$  is orthogonal.
- (d) Physically what does this condition being satisfied represent
- (e) From this expression derive the Secular equation for an orthogonal basis

$$\mathbf{H}\mathbf{c} - E\mathbf{c} = 0 \quad (7)$$

- (f) Find the general form of equation 6 when  $\psi(\mathbf{x}) = \sum_n c_n \phi_n(\mathbf{x})$  when  $\psi$  is not orthogonal.
- (g) From this expression derive the Secular equation for a non-orthogonal basis

$$\mathbf{H}\mathbf{c} - E\mathbf{S}\mathbf{c} = 0 \quad (8)$$

4. Derive the variational principle for excited states.