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.

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

With the Hamiltonian elements given by:

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

and the overlap elements

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

Where the LCAOs to use are:

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

where $a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{e^2 m_e}$

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 $\mathbf{Hc} = E\mathbf{Sc}$ 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

$$\langle \psi_a | H | \psi_a \rangle \geq E_g \tag{5}$$

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

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 ψ is orthogonal.

(d) Physically what does this condition being satified represent

(e) From this expression derive the Secular equation for an orthogonal basis

$$\mathbf{Hc} - E\mathbf{c} = 0 \tag{7}$$

(f) Find the general form of equation 6 when $\psi(\mathbf{x}) = \sum_n c_n\phi_n(\mathbf{x})$ when ψ is not orthogonal.

(g) From this expression derive the Secular equation for a non-orthogonal basis

$$\mathbf{Hc} - E\mathbf{Sc} = 0 \tag{8}$$

4. Derive the variational principle for excited states.

Lecture 2 – Solutions

(a)

(b)   i. Yes. Nature will find the optimal solution. If your ansatz state was within the relevant Hilbert space and had *lower* energy than the ground state, then this itself would have to be the ground state. Hence, the ground state energy must be the lowest energy state in the full Hilbert space, so our ansatz can only ever be higher.

   ii. We can use it to guide optimisation to find a good approximation to the true ground state – the lower our energy goes, the "better" our ansatz state.

   iii. We decompose our ansatz state in the eigenbasis of the Hamiltonian:
$$|\psi\rangle_a = \sum_i c_i |\phi\rangle_i \tag{9}$$

   then
$$\langle\psi|_a H |\psi\rangle_a = \sum_i \sum_j c_i^* c_j \langle\phi|_i H |\phi\rangle_j \tag{10}$$

   $|\phi\rangle$ are eigenvectors of the Hamiltonian, so:
$$\langle\psi|_a H |\psi\rangle_a = \sum_i \sum_j c_i^* c_j E_j \langle\phi|_i |\phi\rangle_j \tag{11}$$

   $|\phi\rangle_i$ and $|\phi\rangle_j$ are orthonormal:
$$\langle\psi|_a H |\psi\rangle_a = \sum_i |c_i|^2 E_i \tag{12}$$

   E_0 is the ground state energy and $|c_i|^2$ is always positive, so the minimum this can be is E_0 (when $c_0 = 1$ and other $c_i = 0$). Thus:
$$\langle\psi|_a H |\psi\rangle_a \geq E_0 \tag{13}$$

   iv. $|\psi\rangle_a$ is the exact ground state (or in the ground subspace).

(c)   i. For two fermions occupying two fermionic modes, we have the state $|11\rangle$. Exchanging the fermions between the orbitals is described by $a_0^\dagger a_1^\dagger a_0 a_1$. Operating on the state with the exchange operator:
$$a_0^\dagger a_1^\dagger a_0 a_1 |11\rangle \tag{14}$$

   By eqns (??):
$$a_0^\dagger a_1^\dagger a_0 a_1 |11\rangle = -a_0^\dagger a_0^\dagger_1 a_1 |11\rangle \tag{15}$$

   By eqns (??):
$$-a_0^\dagger a_0^\dagger_1 a_1 |11\rangle = -|11\rangle \tag{16}$$

   So exchanging the "location" of the two fermions has yielded a minus sign - i.e. the state is antisymmetric with respect to particle exchange.

ii. We note that the annihilation operator

iii.

iv. $a^\dagger \rightarrow X - iY$, $a \rightarrow X + iY$ (this might be a "just have to spot it" type of question, but one could go via generating a matrix representation). We can't make a circuit for this - it's not unitary. To show it doesn't work as a way to simulate fermions, plug $a^\dagger \rightarrow X - iY$, $a \rightarrow X + iY$ into $a_i^\dagger, a_j$. After some algebra we get $2X_iX_j + 2Y_iY_j$, which is not $\delta_{i,j}$. So this substitution does not replicate the fermionic anticommutation relations.

v. https://en.wikipedia.org/wiki/Jordan-Wigner_transformation