University of Strasbourg, second year Master's level

# Exam in advanced quantum chemistry

January 2016

duration of the exam session: 2h

***Neither documents nor calculators are allowed.***

***The grading scale might be changed.***

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## 1. Questions about the lectures (10 points)

Give detailed answers to the following questions:

a) **[2 pts]** What is the main difference between variational and non-variational quantum chemical methods ?

b) **[2 pts]** Explain why the Hartree–Fock (HF) method can be formulated as an orbitals rotation problem. How can the HF orbitals be optimized ? How can we verify in a configuration interaction (CI) calculation that the determinants are contructed from HF orbitals ? Does the full CI (FCI) energy depend on the choice of orbitals ?

c) **[1 pt]** What is the motivation for using a Coupled-Cluster (CC) ansatz for the wavefunction ?

d) **[2 pts]** Define the concept of static correlation. What is the appropriate method for its description ? How is the wavefunction parameterized within this method ? Is it possible to describe excited states with this method ? Does it provide accurate results ?

e) **[1 pt]** Does the energy depend explicitly on the electron density ?

f) **[2 pts]** Is it possible to describe ground-state electronic structures exactly with one single electron configuration ?

## 2. Problem: uniform Hubbard dimer (12 points)

Let us consider the Hubbard model Hamiltonian for the $H_2$ molecule which is written in second quantization as follows,

$$\hat{H}(t,U) = -t\left[\sum_{\sigma=\alpha,\beta}\left(\hat{a}^{\dagger}_{1s_A,\sigma}\hat{a}_{1s_B,\sigma}+\hat{a}^{\dagger}_{1s_B,\sigma}\hat{a}_{1s_A,\sigma}\right)\right] + U\hat{a}^{\dagger}_{1s_A,\alpha}\hat{a}_{1s_A,\alpha}\hat{a}^{\dagger}_{1s_A,\beta}\hat{a}_{1s_A,\beta} + U\hat{a}^{\dagger}_{1s_B,\alpha}\hat{a}_{1s_B,\alpha}\hat{a}^{\dagger}_{1s_B,\beta}\hat{a}_{1s_B,\beta}, \tag{1}$$

where $t > 0$ describes the delocalization of the electrons over the two hydrogen atoms while $U > 0$ models the repulsion between two electrons localized on the same hydrogen atom ($\mathrm{H}_A$ or $\mathrm{H}_B$). The operators $\hat{a}^\dagger_{1s_A,\sigma}$ and $\hat{a}^\dagger_{1s_B,\sigma}$ create one electron with spin $\sigma$ on the $1s$ orbital localized on $\mathrm{H}_A$ and $\mathrm{H}_B$, respectively.

a) **[2 pts]** The orthonormal basis to be considered for a ground-state FCI calculation in this context is

$$|\uparrow_A\downarrow_A\rangle = \hat{a}^\dagger_{1s_A,\alpha}\hat{a}^\dagger_{1s_A,\beta}|\mathrm{vac}\rangle, \tag{2}$$

$$|\uparrow_B\downarrow_B\rangle = \hat{a}^\dagger_{1s_B,\alpha}\hat{a}^\dagger_{1s_B,\beta}|\mathrm{vac}\rangle, \tag{3}$$

$$|\uparrow_A\downarrow_B\rangle = \hat{a}^\dagger_{1s_A,\alpha}\hat{a}^\dagger_{1s_B,\beta}|\mathrm{vac}\rangle, \tag{4}$$

$$|\downarrow_A\uparrow_B\rangle = \hat{a}^\dagger_{1s_A,\beta}\hat{a}^\dagger_{1s_B,\alpha}|\mathrm{vac}\rangle. \tag{5}$$

Show that, in this basis, the FCI Hamiltonian matrix equals $H^{\mathrm{FCI}}(t,U) = \begin{bmatrix} U & 0 & -t & t \\ 0 & U & -t & t \\ -t & -t & 0 & 0 \\ t & t & 0 & 0 \end{bmatrix}$.

**Hint**: apply $\hat{H}(t,U)$ in Equation (1) to each ket of the basis first and simplify the expressions.

b) **[1 pt]** How would you show that the ground-state energy equals $E(t,U) = \frac{1}{2}\Big(U - \sqrt{U^2 + 16t^2}\Big)$ ?

c) **[1 pt]** The normalized ground state associated with $E(t,U)$ can be expressed as follows,

$$|\Psi(t,U)\rangle = C_1|\uparrow_A\downarrow_A\rangle + C_2|\uparrow_B\downarrow_B\rangle + C_3|\uparrow_A\downarrow_B\rangle + C_4|\downarrow_A\uparrow_B\rangle. \tag{6}$$

Show that $C_1 = C_2$, $C_3 = -C_4$, $C_1^2 + C_3^2 = \frac{1}{2}$ and $C_1/C_3 = -\frac{E(t,U)}{2t}$.

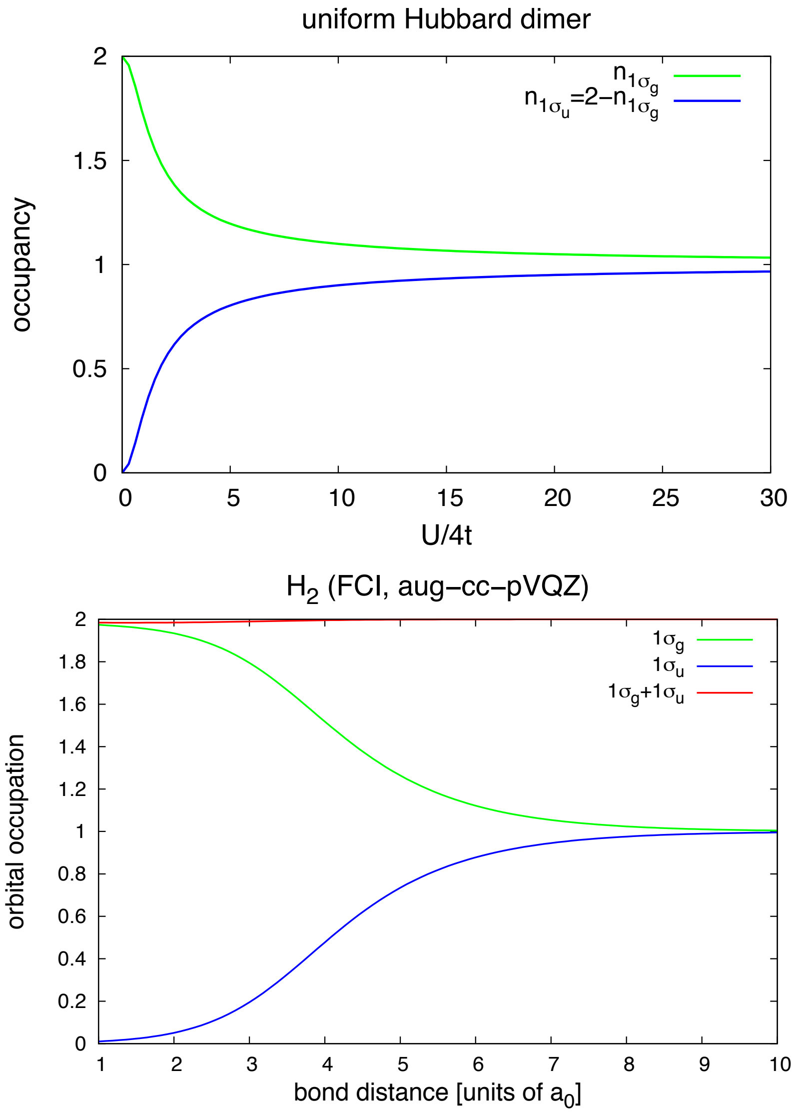
d) **[2 pts]** Show from questions b) and c) that, when $U/t \to 0$, the exact normalized ground state becomes $|\Psi(U/t \to 0)\rangle = \frac{1}{2}\Big(|\uparrow_A\downarrow_A\rangle + |\uparrow_B\downarrow_B\rangle + |\uparrow_A\downarrow_B\rangle - |\downarrow_A\uparrow_B\rangle\Big)$. Is there any electron correlation in the state $|\Psi(U/t \to 0)\rangle$ ? **Hint**: introduce $\hat{a}^\dagger_{1\sigma_g,\sigma} = \frac{1}{\sqrt{2}}\Big(\hat{a}^\dagger_{1s_A,\sigma} + \hat{a}^\dagger_{1s_B,\sigma}\Big)$, show that $|\Psi(U/t \to 0)\rangle = \hat{a}^\dagger_{1\sigma_g,\alpha}\hat{a}^\dagger_{1\sigma_g,\beta}|\mathrm{vac}\rangle$, and conclude.

e) **[1 pt]** Explain why, when $U/t \to +\infty$, the ground state becomes $|\Psi(U/t \to +\infty)\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow_A\downarrow_B\rangle - |\downarrow_A\uparrow_B\rangle\Big)$. Why is this solution referred to as "strongly correlated" ?

f) **[2 pts]** Let $n_A = \sum_{\sigma=\alpha,\beta}\langle\Psi(t,U)|\hat{a}^\dagger_{1s_A,\sigma}\hat{a}_{1s_A,\sigma}|\Psi(t,U)\rangle$ and $n_B = \sum_{\sigma=\alpha,\beta}\langle\Psi(t,U)|\hat{a}^\dagger_{1s_B,\sigma}\hat{a}_{1s_B,\sigma}|\Psi(t,U)\rangle$. What is the physical meaning of $n_A$ and $n_B$ ? Show that $n_A = 2C_1^2 + C_3^2 + C_4^2$ and $n_B = 2C_2^2 + C_3^2 + C_4^2$. Conclude from question c) that $n_A = n_B = 1$.

g) **[2 pts]** Let $n_{1\sigma_g} = \sum_{\sigma=\alpha,\beta}\langle\Psi(t,U)|\hat{a}^\dagger_{1\sigma_g,\sigma}\hat{a}_{1\sigma_g,\sigma}|\Psi(t,U)\rangle$ (see question d)). Show that $n_{1\sigma_g} = \frac{1}{2}(n_A + n_B + n_{AB})$ where $n_{AB} = \sum_{\sigma=\alpha,\beta}\Big\langle\Psi(t,U)\Big|\Big(\hat{a}^\dagger_{1s_A,\sigma}\hat{a}_{1s_B,\sigma} + \hat{a}^\dagger_{1s_B,\sigma}\hat{a}_{1s_A,\sigma}\Big)\Big|\Psi(t,U)\Big\rangle$. Show that, according to

Figure 1: Occupation of the $1\sigma_g$ orbital obtained at the FCI level in the Hubbard dimer (top panel) and in the hydrogen molecule (bottom panel).



the Hellmann–Feynman theorem $\dfrac{\partial E(t,U)}{\partial t} = \left\langle \Psi(t,U) \middle| \dfrac{\partial \hat{H}(t,U)}{\partial t} \middle| \Psi(t,U) \right\rangle$, we have $n_{AB} = -\dfrac{\partial E(t,U)}{\partial t}$. Conclude from question f) that

$$n_{1\sigma_g} = 1 + \frac{1}{\sqrt{1 + \dfrac{U^2}{16t^2}}}. \tag{7}$$

h) **[1 pt]** The expression in Equation (7) as well as accurate quantum chemical FCI values for $n_{1\sigma_g}$ in $H_2$ are plotted in Figure 1. Comment on the results in the light of questions d) and e).

# Exam_M2_2015-2016

a) • $$\hat{H}(t,U)|\uparrow_A\downarrow_A\rangle = -t\sum_{\sigma}\hat{a}^{+}_{1s_B,\sigma}\,\hat{a}_{1s_A,\sigma}|\uparrow_A\downarrow_A\rangle + \underbrace{U\hat{n}_{A\uparrow}\,\hat{n}_{A\downarrow}|\uparrow_A\downarrow_A\rangle}_{U|\uparrow_A\downarrow_A\rangle} + \underbrace{U\hat{n}_{B\uparrow}\,\hat{n}_{B\downarrow}|\uparrow_A\downarrow_A\rangle}_{0}$$

where $\hat{n}_{I\uparrow}$ and $\hat{n}_{I\downarrow}$ operators count the number of electrons (0 or 1) with spin $\alpha$ and $\beta$, respectively, on the atom I.

$$\Rightarrow \hat{H}(t,U)|\uparrow_A\downarrow_A\rangle = -t\underbrace{\hat{a}^{+}_{1s_B,\alpha}\,\hat{a}^{+}_{1s_A,\beta}|vac\rangle}_{-|\downarrow_A\uparrow_B\rangle} + t\underbrace{\hat{a}^{+}_{1s_B,\beta}\,\hat{a}^{+}_{1s_A,\alpha}|vac\rangle}_{-|\uparrow_A\downarrow_B\rangle} + U|\uparrow_A\downarrow_A\rangle$$

• Similarly

$$\hat{H}(t,U)|\uparrow_B\downarrow_B\rangle = -t\sum_{\sigma}\hat{a}^{+}_{1s_A,\sigma}\,\hat{a}_{1s_B,\sigma}|\uparrow_B\downarrow_B\rangle + U|\uparrow_B\downarrow_B\rangle = -t\underbrace{\hat{a}^{+}_{1s_A,\alpha}\,\hat{a}^{+}_{1s_B,\beta}|vac\rangle}_{|\uparrow_A\downarrow_B\rangle} + t\underbrace{\hat{a}^{+}_{1s_A,\beta}\,\hat{a}^{+}_{1s_B,\alpha}|vac\rangle}_{|\downarrow_A\uparrow_B\rangle} + U|\uparrow_B\downarrow_B\rangle$$

• $$\hat{H}(t,U)|\uparrow_A\downarrow_B\rangle = -t\,\hat{a}^{+}_{1s_A,\beta}\,\hat{a}_{1s_B,\beta}|\uparrow_A\downarrow_B\rangle - t\,\hat{a}^{+}_{1s_B,\alpha}\,\hat{a}_{1s_A,\alpha}|\uparrow_A\downarrow_B\rangle$$

$$= +t\underbrace{\hat{a}^{+}_{1s_A,\beta}\,\hat{a}^{+}_{1s_A,\alpha}|vac\rangle}_{-|\uparrow_A\downarrow_A\rangle} - t\underbrace{\hat{a}^{+}_{1s_B,\alpha}\,\hat{a}^{+}_{1s_B,\beta}|vac\rangle}_{|\uparrow_B\downarrow_B\rangle}$$

since $\hat{n}_{A\downarrow}|\uparrow_A\downarrow_B\rangle = 0$

$\hat{n}_{B\uparrow}|\uparrow_A\downarrow_B\rangle = 0$

$\hat{n}_{B\downarrow}|\uparrow_A\downarrow_B\rangle = |\uparrow_A\downarrow_B\rangle$

• Similarly $$\hat{H}(t,U)|\downarrow_A\uparrow_B\rangle = -t\,\hat{a}^{+}_{1s_A,\alpha}\,\hat{a}_{1s_B,\alpha}|\downarrow_A\uparrow_B\rangle - t\,\hat{a}^{+}_{1s_B,\beta}\,\hat{a}_{1s_A,\beta}|\downarrow_A\uparrow_B\rangle$$

$$= +t\underbrace{\hat{a}^{+}_{1s_A,\alpha}\,\hat{a}^{+}_{1s_A,\beta}|vac\rangle}_{|\uparrow_A\downarrow_A\rangle} - t\underbrace{\hat{a}^{+}_{1s_B,\beta}\,\hat{a}^{+}_{1s_B,\alpha}|vac\rangle}_{-|\uparrow_B\downarrow_B\rangle}$$

2/Ex

Conclusion:

$$[\hat{H}(t,U)] = \begin{bmatrix} U & 0 & -t & t \\ 0 & U & -t & t \\ -t & -t & 0 & 0 \\ +t & +t & 0 & 0 \end{bmatrix} = H^{FCI}(t,U)$$

b) $$\begin{vmatrix} U-E & 0 & -t & t \\ 0 & U-E & -t & t \\ -t & -t & -E & 0 \\ t & t & 0 & -E \end{vmatrix} = 0 \Leftrightarrow (U-E)\begin{vmatrix} (U-E) & -t & t \\ -t & -E & 0 \\ t & 0 & -E \end{vmatrix} - t\begin{vmatrix} 0 & -t & t \\ U-E & -t & t \\ t & 0 & -E \end{vmatrix} - t\begin{vmatrix} 0 & -t & t \\ U-E & -t & t \\ -t & -E & 0 \end{vmatrix} = 0$$

$$\Leftrightarrow (U-E)\left[Et^2 - E\left(-E(U-E) - t^2\right)\right] - t\left[+t\left(-E(U-E)\cancel{-t^2}\right)\cancel{+t\left(t^2\right)}\right] - t\left[\cancel{+t\left(t^2\right)} + t\left(-E(U-E)\cancel{-t^2}\right)\right] = 0$$

$$\Leftrightarrow (U-E)\left[2Et^2 + E^2(U-E)\right] + Et^2(U-E) + Et^2(U-E) = 0$$

$$\Leftrightarrow (U-E)\left[4Et^2 + E^2(U-E)\right] = 0 \Rightarrow (U-E)E\underbrace{\left[4t^2 + E(U-E)\right]}_{=0} = 0$$

$E = 0$ or $E = U$ → Excited-state solutions.

$$\boxed{E^2 - EU - 4t^2 = 0} \Rightarrow E = \frac{U - \sqrt{U^2 + 16t^2}}{2}$$ (ground-state energy)

c) • $\hat{H}^{FCI}(t,U)\begin{bmatrix} C_1\\ C_2\\ C_3\\ C_4\end{bmatrix} = E(t,U)\begin{bmatrix} C_1\\ C_2\\ C_3\\ C_4\end{bmatrix} \Rightarrow \begin{cases} UC_1 - tC_3 + tC_4 = EC_1 & (1)\\ UC_2 - tC_3 + tC_4 = EC_2 & (2)\\ -tC_1 - tC_2 = EC_3 & (3)\\ tC_1 + tC_2 = EC_4 & (4)\end{cases}$

(1) − (2) ⇒ $U(C_1-C_2) = E(C_1-C_2) \Leftrightarrow (C_1-C_2)\underbrace{(U-E)}_{\neq 0} = 0 \rightarrow \boxed{C_1 = C_2}$ (5)

(3) and (4) ⇒ $\underset{\neq 0}{E}C_3 = -EC_4 \rightarrow \boxed{C_3 = -C_4}$

- $\langle\Psi(t,U)|\Psi(t,U)\rangle = 1 \rightarrow C_1^2 + C_2^2 + C_3^2 + C_4^2 = 1 \Rightarrow \boxed{C_1^2 + C_3^2 = \frac{1}{2}}$

- (3) and (5) ⇒ $-2tC_1 = EC_3 \rightarrow \boxed{\frac{C_1}{C_3} = -\frac{E(t,U)}{2t}}$

d) • $\frac{C_1}{C_3} = -\frac{1}{4t}\left(U - \sqrt{U^2 + 16t^2}\right) = -\frac{1}{4}\left[\frac{U}{t} - \sqrt{\left(\frac{U}{t}\right)^2 + 16}\right] \xrightarrow[U/t\to 0]{} 1$

Therefore $C_1 \rightarrow C_3$ and $|\Psi(t,U)\rangle \longrightarrow |\Psi(U/t\to 0)\rangle = \frac{1}{2}\left(|\uparrow_A\downarrow_A\rangle + |\uparrow_B\downarrow_B\rangle + |\uparrow_A\downarrow_B\rangle - |\downarrow_A\uparrow_B\rangle\right)$

$2C_1^2 = \frac{1}{2} \rightarrow C_1 = \frac{1}{2}$

- With $\hat{a}^\dagger_{1\sigma_g,\sigma} = \frac{1}{\sqrt{2}}\left(\hat{a}^\dagger_{1s_A,\sigma} + \hat{a}^\dagger_{1s_B,\sigma}\right) \rightarrow \underbrace{\hat{a}^\dagger_{1\sigma_g,\alpha}\,\hat{a}^\dagger_{1\sigma_g,\beta}\,|vac\rangle}_{\text{Slater determinant } |1\sigma_g^\alpha 1\sigma_g^\beta|} = \frac{1}{2}\left(|\uparrow_A\downarrow_B\rangle + |\uparrow_A\downarrow_B\rangle - |\downarrow_A\uparrow_B\rangle + |\uparrow_B\downarrow_B\rangle\right)$

$= |\Psi(U/t\to 0)\rangle$

→ no correlation!

e) $\frac{C_1}{C_3} \xrightarrow[U/t \to +\infty]{} -\frac{1}{4}\left[\frac{U}{t} - \sqrt{\left(\frac{U}{t}\right)^2}\right] \longrightarrow 0 \rightarrow C_3 \gg C_1 \longrightarrow C_1^2 + C_3^2 \simeq C_3^2 = \frac{1}{2}$

Therefore $|\Psi(t,U)\rangle \xrightarrow[U/t \to +\infty]{} \frac{1}{\sqrt{2}}\left(|\uparrow_A \downarrow_B\rangle - |\downarrow_A \uparrow_B\rangle\right)$

$\downarrow \quad \swarrow$

if one electron is on $H_A$, the other one is on $H_B$, hence the name "strongly correlated solution".

f) - $n_A$ and $n_B$ are the occupation of the $1s_A$ and $1s_B$ orbitals, respectively.

- $n_A = \langle \Psi(t,U) | \hat{n}_{A\uparrow} + \hat{n}_{A\downarrow} | \Psi(t,U)\rangle$ with $\hat{n}_{A\uparrow} |\Psi(t,U)\rangle = C_1 |\uparrow_A \downarrow_A\rangle + C_3 |\uparrow_A \downarrow_B\rangle$
  $\hat{n}_{A\downarrow} |\Psi(t,U)\rangle = C_1 |\uparrow_A \downarrow_A\rangle + C_4 |\downarrow_A \uparrow_B\rangle$

$\rightarrow n_A = C_1^2 + C_3^2 + C_1^2 + C_4^2 = 2C_1^2 + C_3^2 + C_4^2 = 2C_1^2 + 2C_3^2$

Similarly $n_B = C_2^2 + C_4^2 + C_2^2 + C_3^2 = 2C_2^2 + C_3^2 + C_4^2 = 2\underset{\overset{\downarrow}{C_1^2}}{\boxed{C_2^2}} + 2C_3^2$

Therefore $\boxed{n_A = n_B = 1}$

g) - $\hat{n}_{1\sigma_g} = \sum_\sigma \hat{a}^+_{1\sigma_g,\sigma} \hat{a}_{1\sigma_g,\sigma} = \frac{1}{2}\left( \underbrace{\sum_\sigma \hat{a}^+_{1s_A,\sigma} \hat{a}_{1s_A,\sigma}}_{\hat{n}_A} + \underbrace{\sum_\sigma \hat{a}^+_{1s_B,\sigma} \hat{a}_{1s_B,\sigma}}_{\hat{n}_B} + \underbrace{\sum_\sigma \left( \hat{a}^+_{1s_A,\sigma} \hat{a}_{1s_B,\sigma} + \hat{a}^+_{1s_B,\sigma} \hat{a}_{1s_A,\sigma} \right)}_{\hat{n}_{AB}} \right)$

$\rightarrow n_{1\sigma_g} = \langle \Psi(t,U) | \hat{n}_{1\sigma_g} | \Psi(t,U)\rangle = \frac{1}{2}\left(n_A + n_B + n_{AB}\right)$

- $\frac{\partial E(t,U)}{\partial t} = \langle \Psi(t,U) | \boxed{\frac{\partial \hat{H}(t,U)}{\partial t}} | \Psi(t,U)\rangle = -n_{AB} \Rightarrow n_{1\sigma_g} = \frac{1}{2}\left(2 - \frac{\partial E(t,U)}{\partial t}\right) = 1 - \frac{\frac{1}{2} \times \frac{1}{2}\left(-\frac{1}{2}\right) 32t}{\sqrt{U^2 + 16t^2}}$

$\rightarrow -\hat{n}_{AB}$

Thus leading to $n_{\log} = 1 + \frac{4t}{\sqrt{U^2+16t^2}}$

or $\boxed{n_{\log} = 1 + \frac{1}{\sqrt{1+\frac{U^2}{16t^2}}}}$

h) The Hubbard model is able to describe qualitatively weakly correlated (at equilibrium) and strongly correlated (in the dissociation limit) regimes.

The strength of electron correlation is controlled by the bond distance in $H_2$ and the parameter $U/t$ in the Hubbard dimer.