

University of Strasbourg, second year Master's level

Exam in advanced quantum chemistry

January 2017

duration of the exam session: 2h

Neither documents nor calculators are allowed.

The grading scale might be changed.

1. Questions about the lectures (10 points)

- a) [2 pts] What is the key idea underlying the Hartree–Fock (HF) approximation ? What is the definition of the correlation energy? Is the *full configuration interaction* (FCI) method exact ?
- b) [1 pt] What are the main differences between the first and second quantization formalisms ? How is the Pauli principle formulated in second quantization ?
- c) [2 pts] What are the various strategies used in wavefunction theory for modelling dynamical electron correlation ? What are the advantages and drawbacks of these strategies ?
- d) [1 pt] In *second-order Møller–Plesset perturbation theory* (MP2), which excitations contribute to the energy through second order ?
- e) [2 pts] What are the differences and similarities between HF and Kohn–Sham (KS) density-functional approaches ?
- f) [2 pts] The local density approximation (LDA) fails in describing both bond dissociations and dispersion forces. What is the reason ? Does it mean that KS density functional theory can only be applied to some electronic systems but not all ?

2. Natural orbital functional theory applied to the symmetric Hubbard dimer (15 points)

A simple but nontrivial description of the H_2 molecule is provided by the symmetric Hubbard dimer model for which the Hamiltonian reads $\hat{H}(t, U) = \hat{T} + \hat{U}$. The hopping operator \hat{T} (which is a simplified version of the kinetic energy operator) and the two-electron repulsion operator \hat{U} are written in second

quantization as follows,

$$\hat{\mathcal{T}} = -t \sum_{\sigma=\alpha,\beta} \left(\hat{a}_{1s_A,\sigma}^\dagger \hat{a}_{1s_B,\sigma} + \hat{a}_{1s_B,\sigma}^\dagger \hat{a}_{1s_A,\sigma} \right), \quad (1)$$

$$\hat{U} = U \left(\hat{a}_{1s_A,\alpha}^\dagger \hat{a}_{1s_A,\alpha} \hat{a}_{1s_A,\beta}^\dagger \hat{a}_{1s_A,\beta} + \hat{a}_{1s_B,\alpha}^\dagger \hat{a}_{1s_B,\alpha} \hat{a}_{1s_B,\beta}^\dagger \hat{a}_{1s_B,\beta} \right), \quad (2)$$

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 (H_A or H_B). The operators $\hat{a}_{1s_A,\sigma}^\dagger$ and $\hat{a}_{1s_B,\sigma}^\dagger$ create one electron with spin σ on the $1s$ orbital localized on H_A and H_B , respectively. The orthonormal basis to be considered for a ground-state FCI calculation in this context is

$$|\uparrow_A \downarrow_A\rangle = \hat{a}_{1s_A,\alpha}^\dagger \hat{a}_{1s_A,\beta}^\dagger |\text{vac}\rangle, \quad |\uparrow_B \downarrow_B\rangle = \hat{a}_{1s_B,\alpha}^\dagger \hat{a}_{1s_B,\beta}^\dagger |\text{vac}\rangle, \quad (3)$$

$$|\uparrow_A \downarrow_B\rangle = \hat{a}_{1s_A,\alpha}^\dagger \hat{a}_{1s_B,\beta}^\dagger |\text{vac}\rangle, \quad |\uparrow_B \downarrow_A\rangle = \hat{a}_{1s_B,\alpha}^\dagger \hat{a}_{1s_A,\beta}^\dagger |\text{vac}\rangle. \quad (4)$$

It can be shown that the ground-state energy of $\hat{H}(t, U)$ equals $E(t, U) = \frac{1}{2} \left(U - \sqrt{U^2 + 16t^2} \right)$ and that the associated normalized ground state reads

$$|\Psi(t, U)\rangle = C_1 \left(|\uparrow_A \downarrow_A\rangle + |\uparrow_B \downarrow_B\rangle \right) + C_3 \left(|\uparrow_A \downarrow_B\rangle + |\uparrow_B \downarrow_A\rangle \right), \quad (5)$$

with $C_1^2 + C_3^2 = \frac{1}{2}$ and

$$\frac{C_1}{C_3} = -\frac{E(t, U)}{2t}. \quad (6)$$

a) [1 pt] Let $\hat{a}_{g,\sigma}^\dagger = \frac{1}{\sqrt{2}} \left(\hat{a}_{1s_A,\sigma}^\dagger + \hat{a}_{1s_B,\sigma}^\dagger \right)$ and $\hat{a}_{u,\sigma}^\dagger = \frac{1}{\sqrt{2}} \left(\hat{a}_{1s_A,\sigma}^\dagger - \hat{a}_{1s_B,\sigma}^\dagger \right)$. Show from Eq. (1) that

$$-t \sum_{\sigma=\alpha,\beta} \left(\hat{a}_{g,\sigma}^\dagger \hat{a}_{g,\sigma} - \hat{a}_{u,\sigma}^\dagger \hat{a}_{u,\sigma} \right) = \hat{\mathcal{T}}.$$

b) [1 pt] Show from Eq. (5) that $C_g |\uparrow_g \downarrow_g\rangle + C_u |\uparrow_u \downarrow_u\rangle = |\Psi(t, U)\rangle$ where $|\uparrow_p \downarrow_p\rangle = \hat{a}_{p,\alpha}^\dagger \hat{a}_{p,\beta}^\dagger |\text{vac}\rangle$ for $p = g, u$ with $C_g = C_1 + C_3$ and $C_u = C_1 - C_3$.

c) [2 pts] The spin-summed one-electron reduced density matrix elements are defined in a given orthonormal orbital basis $\{\phi_p(\mathbf{r})\}_p$ as $D_{pq} = \sum_{\sigma=\alpha,\beta} \langle \Psi(t, U) | \hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} | \Psi(t, U) \rangle$. The orbitals that diagonalize this matrix are referred to as *natural orbitals*. Explain why $\hat{a}_{g,\sigma}^\dagger$ and $\hat{a}_{u,\sigma}^\dagger$ define a bonding (g) and an antibonding (u) orbital, respectively. Show that these orbitals are the natural orbitals of the symmetric Hubbard dimer. **Hint:** Explain from question 2.b) why $D_{ug} = 0$ by comparing the occupied orbitals in $|\Psi(t, U)\rangle$ and $\hat{a}_{u,\sigma}^\dagger \hat{a}_{g,\sigma} | \Psi(t, U) \rangle$.

d) [1 pt] Show from question 2.a) that the kinetic energy equals $\langle \Psi(t, U) | \hat{T} | \Psi(t, U) \rangle = -t(n_g - n_u)$ where $n_g = D_{gg}$ and $n_u = D_{uu}$.

e) [3 pts] Show from question 2.b) that $n_g = 2C_g^2$ and $n_u = 2C_u^2$. Conclude that $n_u = 2 - n_g$ and $n_g \geq 1$.

Hint: Explain why $\left(\sum_{\sigma=\alpha,\beta} \hat{a}_{p,\sigma}^\dagger \hat{a}_{p,\sigma} | \Psi(t, U) \rangle \right) = 2C_p | \uparrow_p \downarrow_p \rangle$ for $p = g, u$. Show that $C_g^2 + C_u^2 = 1$ and $C_g^2 = \frac{1}{2} + 2C_1C_3$. Explain why, according to Eq. (6), $C_1C_3 \geq 0$ and conclude.

f) [3 pts] Show from Eqs. (2) and (5) that the electronic repulsion energy equals

$$\langle \Psi(t, U) | \hat{U} | \Psi(t, U) \rangle = 2UC_1^2 = \frac{U}{2} (C_g^2 + C_u^2 + 2C_gC_u), \quad (7)$$

where, according to question 2.b), $C_gC_u = C_3^2 \left((C_1/C_3)^2 - 1 \right) \leq 0$. **Hint:** in order to prove that C_gC_u is negative, use Eq. (6) and the relation $E^2(t, U) - UE(t, U) - 4t^2 = 0$.

g) [2 pts] Conclude from questions 2.d), 2.e) and 2.f) that $E(t, U) = -2t(n_g - 1) + \frac{U}{2} (1 - \sqrt{n_g(2 - n_g)})$.

h) [2 pts] It can be shown that $n_g = 1 + \frac{1}{\sqrt{1 + \frac{U^2}{16t^2}}}$. Show that the latter natural orbital occupation

minimizes the energy functional $\mathcal{E}(n) = -2t(n - 1) + \frac{U}{2} (1 - \sqrt{n(2 - n)})$ with respect to n where

$1 \leq n \leq 2$ and that the minimum is the exact ground-state energy $E(t, U) = \mathcal{E}(n_g)$. **Hint:** Show that

$$\frac{\partial \mathcal{E}(n)}{\partial n} = -\frac{4t^2 (1 - (\nu/\nu_g)^2)}{\sqrt{1 - \nu^2} \left(2t\sqrt{1 - \nu^2} + \frac{U}{2}\nu \right)}$$

where $\nu = n - 1$ and $\nu_g = n_g - 1$.

$$a) -t \sum_{\sigma} (\hat{a}_{g\sigma}^{\dagger} \hat{a}_{g\sigma} - \hat{a}_{u\sigma}^{\dagger} \hat{a}_{u\sigma}) = -t \sum_{\sigma} \left[\frac{1}{2} (\hat{a}_{A\sigma}^{\dagger} + \hat{a}_{B\sigma}^{\dagger}) (\hat{a}_{A\sigma} + \hat{a}_{B\sigma}) - \frac{1}{2} (\hat{a}_{A\sigma}^{\dagger} - \hat{a}_{B\sigma}^{\dagger}) (\hat{a}_{A\sigma} - \hat{a}_{B\sigma}) \right]$$

$$= -t \sum_{\sigma} (\hat{a}_{A\sigma}^{\dagger} \hat{a}_{B\sigma} + \hat{a}_{B\sigma}^{\dagger} \hat{a}_{A\sigma}) = \hat{T}$$

$$b) C_g |T_g b_g\rangle + C_u |T_u b_u\rangle = (C_1 + C_3) \underbrace{\hat{a}_{g\alpha}^{\dagger} \hat{a}_{g\beta}^{\dagger} |vac\rangle}_{\downarrow} + (C_1 - C_3) \underbrace{\hat{a}_{u\alpha}^{\dagger} \hat{a}_{u\beta}^{\dagger} |vac\rangle}_{\downarrow}$$

$$\frac{1}{2} (|\uparrow_A \downarrow_A\rangle + |\uparrow_A \downarrow_B\rangle + |\uparrow_B \downarrow_A\rangle + |\uparrow_B \downarrow_B\rangle) \quad \frac{1}{2} (|\uparrow_A \downarrow_B\rangle - |\uparrow_B \downarrow_A\rangle - |\uparrow_B \downarrow_B\rangle + |\uparrow_A \downarrow_A\rangle)$$

$$= C_1 (|\uparrow_A \downarrow_A\rangle + |\uparrow_B \downarrow_B\rangle) + C_3 (|\uparrow_A \downarrow_B\rangle + |\uparrow_B \downarrow_A\rangle) = |\Psi(t, \mathbf{r})\rangle$$

$$c) \hat{a}_{g\sigma}^{\dagger} |vac\rangle = |\phi_{g\sigma}\rangle = \frac{1}{\sqrt{2}} \left(\underbrace{\hat{a}_{A\sigma}^{\dagger} |vac\rangle}_{|1s_{A\sigma}\rangle} + \underbrace{\hat{a}_{B\sigma}^{\dagger} |vac\rangle}_{|1s_{B\sigma}\rangle} \right) \quad \text{and} \quad \hat{a}_{u\sigma}^{\dagger} |vac\rangle = |\phi_{u\sigma}\rangle = \frac{1}{\sqrt{2}} \left(\underbrace{\hat{a}_{A\sigma}^{\dagger} |vac\rangle}_{|1s_{A\sigma}\rangle} - \underbrace{\hat{a}_{B\sigma}^{\dagger} |vac\rangle}_{|1s_{B\sigma}\rangle} \right)$$

one-electron state (\leftrightarrow spin-orbital)

$$\phi_{g\sigma}(\vec{r}, \tau) = \delta_{\sigma\tau} \times \frac{1}{\sqrt{2}} (\phi_{1s_A}(\vec{r}) + \phi_{1s_B}(\vec{r}))$$

bonding orbital $\phi_g(\vec{r})$

is represented by the spin-orbital

$$\phi_{u\sigma}(\vec{r}, \tau) = \delta_{\sigma\tau} \times \frac{1}{\sqrt{2}} (\phi_{1s_A}(\vec{r}) - \phi_{1s_B}(\vec{r}))$$

anti-bonding orbital $\phi_u(\vec{r})$

$$\bullet D_{ug} = \sum_{\sigma} \langle \Psi(t, \mathbf{r}) | \hat{a}_{u\sigma}^{\dagger} \hat{a}_{g\sigma} | \Psi(t, \mathbf{r}) \rangle. \text{ Note that the density matrix is symmetric since, by using real algebra,}$$

$$\text{we have } D_{pq} = \sum_{\sigma} \langle \Psi(t, \mathbf{r}) | \hat{a}_{p\sigma}^{\dagger} \hat{a}_{q\sigma} | \Psi(t, \mathbf{r}) \rangle = \sum_{\sigma} \frac{\langle \Psi(t, \mathbf{r}) | \hat{a}_{p\sigma}^{\dagger} \hat{a}_{q\sigma} | \Psi(t, \mathbf{r}) \rangle^*}{\langle \hat{a}_{p\sigma}^{\dagger} \hat{a}_{q\sigma} | \Psi(t, \mathbf{r}) \rangle \langle \Psi(t, \mathbf{r}) |}$$

$$= \sum_{\sigma} \langle \Psi(t, \mathbf{r}) | \hat{a}_{q\sigma}^{\dagger} \hat{a}_{p\sigma} | \Psi(t, \mathbf{r}) \rangle = D_{qp}$$

• According to question b)

$$\hat{a}_{u\sigma}^+ \hat{a}_{g\sigma} | \Psi(t, \sigma) \rangle = C_g \hat{a}_{u\sigma}^+ \hat{a}_{g\sigma} | \uparrow_g \downarrow_g \rangle + C_u \hat{a}_{u\sigma}^+ \hat{a}_{g\sigma} | \uparrow_u \downarrow_u \rangle$$

↓
Corresponds to a Slater determinant where ϕ_u and ϕ_g are singly occupied

||
0 since ϕ_g is NOT occupied in $|\uparrow_u \downarrow_u\rangle$

↓
it is therefore orthogonal to both $|\uparrow_g \downarrow_g\rangle$ AND $|\uparrow_u \downarrow_u\rangle$ and therefore to $|\Psi(t, \sigma)\rangle$.

Conclusion: $\langle \Psi(t, \sigma) | \hat{a}_{u\sigma}^+ \hat{a}_{g\sigma} | \Psi(t, \sigma) \rangle = 0 \quad \forall \sigma \rightarrow D_{ug} = 0$.

Therefore ϕ_u and ϕ_g are the natural orbitals of the symmetric dimer.

d) $\langle \Psi(t, \sigma) | \hat{T} | \Psi(t, \sigma) \rangle = -t \sum_{\sigma} \left[\langle \Psi(t, \sigma) | \hat{a}_{g\sigma}^+ \hat{a}_{g\sigma} | \Psi(t, \sigma) \rangle - \langle \Psi(t, \sigma) | \hat{a}_{u\sigma}^+ \hat{a}_{u\sigma} | \Psi(t, \sigma) \rangle \right] = -t (D_{gg} - D_{uu}) = -t (n_g - n_u)$

question a)

e) • According to question b), $(\sum_{\sigma} \hat{a}_{g\sigma}^+ \hat{a}_{g\sigma}) | \Psi(t, \sigma) \rangle = (\sum_{\sigma} \hat{a}_{g\sigma}^+ \hat{a}_{g\sigma} | \uparrow_g \downarrow_g \rangle) \times C_g = \sum_{\sigma} C_g | \uparrow_g \downarrow_g \rangle = 2 C_g | \uparrow_g \downarrow_g \rangle$

Therefore $n_g = 2 C_g \langle \Psi(t, \sigma) | \uparrow_g \downarrow_g \rangle$

Counts the number of electrons occupying $\phi_{g\sigma}$ (one here!)

⇒ $n_g = 2 C_g^2$

Similarly we have $\sum_{\sigma} \hat{a}_{u\sigma}^+ \hat{a}_{u\sigma} | \Psi(t, \sigma) \rangle = C_u \sum_{\sigma} \hat{a}_{u\sigma}^+ \hat{a}_{u\sigma} | \uparrow_u \downarrow_u \rangle = 2 C_u | \uparrow_u \downarrow_u \rangle$ and $n_u = 2 C_u \langle \Psi(t, \sigma) | \uparrow_u \downarrow_u \rangle$

⇒ $n_u = 2 C_u^2$

• $n_u + n_g = 2 (C_g^2 + C_u^2) = 2 ((C_1 + C_3)^2 + (C_1 - C_3)^2) = 4 (C_1^2 + C_3^2) = 2 \Rightarrow n_u = 2 - n_g$

question b)

• $C_g^2 = C_1^2 + C_3^2 + 2C_1C_3 = \frac{1}{2} + 2C_1C_3$

$\rightarrow n_g = 1 + 4C_1C_3$ where $C_1C_3 = C_3^2 \cdot \frac{C_1}{C_3} = -C_3^2 \frac{E(t, \omega)}{2t}$

and $E(t, \omega) = \frac{1}{2} (\omega - \sqrt{\omega^2 + 16t^2}) \leq 0 \Rightarrow C_1C_3 \geq 0 \Rightarrow \boxed{n_g \geq 1}$

f) According to Eq. (5), $\hat{U}|\psi(t, \omega)\rangle = C_1 \left(\underbrace{\hat{U}|\uparrow_A \downarrow_A\rangle}_{\omega|\uparrow_A \downarrow_A\rangle} + \underbrace{\hat{U}|\uparrow_B \downarrow_B\rangle}_{\omega|\uparrow_B \downarrow_B\rangle} \right)$ since $\hat{U}|\uparrow_A \downarrow_B\rangle = \hat{U}|\uparrow_B \downarrow_A\rangle = 0$

$\rightarrow \langle \psi(t, \omega) | \hat{U} | \psi(t, \omega) \rangle = C_1^2 \omega + C_1^2 \omega = 2C_1^2 \omega = 2\omega \times \left(\frac{C_g + C_u}{2} \right)^2 = \frac{\omega}{2} (C_g^2 + C_u^2 + 2C_g C_u)$

where $C_g C_u = (C_1 + C_3)(C_1 - C_3) = C_1^2 - C_3^2 = C_3^2 \left(\frac{C_1^2}{C_3^2} - 1 \right)$ question b)

Therefore $\boxed{C_g C_u \leq 0}$

$\frac{E^2(t, \omega)}{4t^2} - 1 = \frac{E^2(t, \omega) - 4t^2}{4t^2} = \frac{\omega E(t, \omega)}{4t^2} \leq 0$ Eq. (6)

g) $E(t, \omega) = \langle \psi(t, \omega) | \hat{T} | \psi(t, \omega) \rangle + \langle \psi(t, \omega) | \hat{U} | \psi(t, \omega) \rangle = -t(n_g - (2 - n_g)) + \frac{\omega}{2} (1 + 2C_g C_u)$ question e)

Since $C_g C_u \leq 0$, it comes $C_g C_u = -|C_g C_u| = -\sqrt{C_g^2 C_u^2} = -\sqrt{n_g/2 \times n_u/2} = -\frac{\sqrt{n_g n_u}}{2}$ question e)

Conclusion: $\boxed{E(t, \omega) = -2t(n_g - 1) + \frac{\omega}{2} (1 - \sqrt{n_g(2 - n_g)})}$

h) $E(n) = -2t(n-1) + \frac{\omega}{2} (1 - \sqrt{n(2-n)}) \rightarrow \frac{\partial E(n)}{\partial n} = -2t + \frac{\omega}{2} \times \frac{1}{2} (2-2n) \frac{1}{\sqrt{n(2-n)}} = -2t + \frac{\omega}{2} \frac{1}{\sqrt{(1+v)(1-v)}}$

where $v = n-1$, thus leading to $\frac{\partial E(n)}{\partial n} = -2t + \frac{\omega v/2}{\sqrt{1-v^2}} = \frac{-2t\sqrt{1-v^2} + \omega v/2}{\sqrt{1-v^2}} = \frac{\frac{\omega^2 v^2}{4} - 4t^2(1-v^2)}{\sqrt{1-v^2}(\frac{\omega v}{2} + 2t\sqrt{1-v^2})}$

$\Rightarrow \frac{\partial E(n)}{\partial n} = \frac{-4t^2}{\sqrt{1-v^2}(\frac{\omega v}{2} + 2t\sqrt{1-v^2})} \times \left[1 - v^2 \left(1 + \frac{\omega^2}{16t^2} \right) \right] \Rightarrow \boxed{\frac{\partial E(n)}{\partial n} = \frac{-4t^2(1 - (v/v_g)^2)}{\sqrt{1-v^2}(\frac{\omega v}{2} + 2t\sqrt{1-v^2})}}$

Since $1 \leq n \leq 2$, $0 \leq \nu \leq 1$. As readily seen,

4/NOFT.

Note that $1 < n_g < 2 \Rightarrow 0 < \nu_g < 1$

$$\left\{ \begin{array}{l} \frac{\partial \Sigma(n)}{\partial n} < 0 \quad \text{when } \nu < \nu_g \\ \frac{\partial \Sigma(n)}{\partial n} = 0 \quad \text{when } \nu = \nu_g \rightarrow n = n_g \\ \frac{\partial \Sigma(n)}{\partial n} > 0 \quad \text{when } \nu > \nu_g \end{array} \right.$$

Conclusion: $\Sigma(n)$ reaches a minimum at

$n = n_g$ when n varies in the range $1 \leq n \leq 2$ and the minimum is equal to the exact ground-state energy $\Sigma(n_g) = E(t, \omega)$ (according to question g)).