M1 franco-allemand "Ingénierie des polymères" & M1 "Matériaux et nanosciences"

Exam in quantum mechanics

December 2015

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 (9 points)

Give detailed answers to the following questions:

a) [**2 pts**] How is the time-independent Schrödinger equation related to the time-dependent one ?

b) [**2 pts**] Can we talk about determinism in quantum mechanics ?

c) [**2 pts**] Explain briefly what time-independent perturbation theory is and what it is useful for ?

d) [**1 pt**] What do Hückel and Hartree–Fock methods have in common ?

e) [**2 pts**] What is the electron correlation energy ?

2. Problem: density matrices and mean-field approximation for two particles (13 points)

Let us consider two **identical but distinguishable** particles that can occupy one-particle states $\{|\varphi_i\rangle\}_{i=1,2,\ldots,N}$. The latter states will simply be referred to as orbitals in the following. The space of quantum states for the two particles consists of the N^2 two-particle states $\{|\varphi_i, \varphi_j\rangle\}_{i=1,2,\ldots,N;j=1,2,\ldots,N}$ in which the first particle occupies the orbital φ_i while the second particle occupies the orbital φ_j. Note that, in our model, the two particles can occupy the same orbital. For simplicity, **we will use real algebra** as well as the notation $|i, j\rangle = |\varphi_i, \varphi_j\rangle$. Moreover, the basis of two-particle states is considered to be orthonormal:

$$\langle p, l|i, j\rangle = \delta_{pi}\delta_{lj}. \tag{1}$$

a) **[1 pt]** Let $|\Psi\rangle = \sum_{i,j=1}^{N} C_{ij}|i,j\rangle$ be an arbitrary two-particle state. Show that, according to Eq. (1), $C_{pl} = \langle p,l|\Psi\rangle$. Deduce the resolution of the identity: $\sum_{i,j=1}^{N} |i,j\rangle\langle i,j| = \hat{\mathbb{1}}$.

b) **[3 pts]** Let us first consider that the two particles do not interact. The total Hamiltonian can be written as $\hat{h} = \hat{h}_1 + \hat{h}_2$ where $\hat{h}_1$ and $\hat{h}_2$ are the Hamiltonians of the first and second particles, respectively. Explain briefly why they act as follows on the two-particle states: $\hat{h}_1|i,j\rangle = \sum_{k=1}^{N} h_{ki}|k,j\rangle$ and $\hat{h}_2|i,j\rangle = \sum_{k=1}^{N} h_{kj}|i,k\rangle$. Show that $\langle p,l|\hat{h}_1|i,j\rangle = h_{pi}\delta_{lj}$ and $\langle p,l|\hat{h}_2|i,j\rangle = h_{lj}\delta_{ip}$. Conclude from question 2. a) that

$$\hat{h} = \hat{\mathbb{1}}\hat{h}\hat{\mathbb{1}} = \sum_{p,i=1}^{N} h_{pi}\hat{n}_{pi}, \tag{2}$$

where the one-particle density matrix operator equals $\hat{n}_{pi} = \sum_{j=1}^{N}\Big(|p,j\rangle\langle i,j| + |j,p\rangle\langle j,i|\Big)$.

c) **[2 pts]** Let us assume that the two particles are in the normalized quantum state $|\Psi\rangle$. Explain without calculations why $0 \leq \langle\Psi|\hat{n}_{ii}|\Psi\rangle \leq 2$. What is the physical meaning of $\langle\Psi|\hat{n}_{ii}|\Psi\rangle$?

d) **[2 pts]** Let us consider the more realistic situation where the two particles interact. The total Hamiltonian equals $\hat{H} = \hat{h} + \hat{U}_{12}$ where $\hat{U}_{12} = \sum_{i,j,k,l=1}^{N} U_{ijkl}\,\hat{n}_{ijkl}$ is the operator that describes the interaction between the particles. The two-particle density matrix operator is defined as $\hat{n}_{ijkl} = |i,j\rangle\langle k,l|$. We denote $|\Psi_0\rangle$ the exact normalized ground state of $\hat{H}$ associated with the ground-state energy E_0. Show that $E_0 = \langle\Psi_0|\hat{H}|\Psi_0\rangle$ and conclude that, in order to calculate E_0, both one-particle $n_{pi} = \langle\Psi_0|\hat{n}_{pi}|\Psi_0\rangle$ and two-particle $n_{ijkl} = \langle\Psi_0|\hat{n}_{ijkl}|\Psi_0\rangle$ density matrices are needed.

e) **[1 pt]** Show that the one-particle density matrix can be deduced from the two-particle one. **Hint:** use question 2. b) to simplify the sum $\sum_{j=1}^{N}\Big(n_{pjij} + n_{jpji}\Big)$ and conclude.

f) **[2 pts]** Within the so-called mean-field (MF) approximation, it is assumed that the ground state can be written as $|\Phi^{\mathrm{MF}}\rangle = \sum_{i,j=1}^{N} C_iC_j|i,j\rangle$ where $\sum_{j=1}^{N} C_j^2 = 1$. Show that the mean-field two-particle density matrix $n_{ijkl}^{\mathrm{MF}} = \langle\Phi^{\mathrm{MF}}|\hat{n}_{ijkl}|\Phi^{\mathrm{MF}}\rangle$ can be deduced from the one-particle one $n_{pi}^{\mathrm{MF}} = \langle\Phi^{\mathrm{MF}}|\hat{n}_{pi}|\Phi^{\mathrm{MF}}\rangle$.
Hint: Show that $\langle k,l|\Phi^{\mathrm{MF}}\rangle = C_kC_l$, $\langle\Phi^{\mathrm{MF}}|i,j\rangle = C_iC_j$, $n_{pi}^{\mathrm{MF}} = 2C_pC_i$ and conclude.

g) **[2 pts]** Express the mean-field energy $\langle\Phi^{\mathrm{MF}}|\hat{H}|\Phi^{\mathrm{MF}}\rangle$ in terms of the one-particle density matrix elements n_{pi}^{MF}, the one- and two-particle Hamiltonian matrix elements h_{pi} and U_{ijkl}. How can we obtain the coefficients $\{C_i\}_{i=1,2,\ldots,N}$ that give the "best" mean-field approximation to the exact ground state $|\Psi_0\rangle$?

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a) $$\langle p,\ell|\psi\rangle = \sum_{i,j} C_{ij} \underbrace{\langle p,\ell|i,j\rangle}_{\delta_{pi}\delta_{\ell j}} = C_{p\ell}$$

$$|\psi\rangle = \sum_{i,j} C_{ij}|i,j\rangle = \sum_{ij}\langle ij|\psi\rangle|ij\rangle = \underbrace{\left(\sum_{ij}|ij\rangle\langle ij|\right)}_{\hat{\mathbb{1}}}|\psi\rangle$$

b) • $$\hat h_1|i,j\rangle = \sum_k h_{ki}|k,j\rangle \quad \text{and} \quad \hat h_2|i,j\rangle = \sum_k h_{kj}|i,k\rangle$$

unchanged

unchanged

only acts on the state of the first particle

only acts on the state of the second particle

Same matrix element since the two particles are identical.

• $$\langle p,\ell|\hat h_1|i,j\rangle = \sum_k h_{ki}\underbrace{\langle p,\ell|k,j\rangle}_{\delta_{pk}\delta_{\ell j}} = h_{pi}\delta_{\ell j}$$

$$\langle p,\ell|\hat h_2|i,j\rangle = \sum_k h_{kj}\underbrace{\langle p,\ell|i,k\rangle}_{\delta_{pi}\delta_{\ell k}} = h_{\ell j}\delta_{pi}$$

• $$\hat h = \sum_{p,\ell,i,j}|p,\ell\rangle\underbrace{\langle p,\ell|\hat h|i,j\rangle}_{\langle p,\ell|\hat h_1|i,j\rangle + \langle p,\ell|\hat h_2|i,j\rangle}\langle i,j|$$

$$\hat h = \sum_{p,\ell,i,j}\left(h_{pi}\delta_{\ell j} + h_{\ell j}\delta_{pi}\right)|p,\ell\rangle\langle i,j| = \sum_{p,i,j} h_{pi}|p,j\rangle\langle i,j| + \sum_{\ell,i,j} h_{\ell j}|i,\ell\rangle\langle i,j|$$

$$\sum_{p,i,j} h_{pi}|j,p\rangle\langle j,i| \;\; = \;\; \sum_{\ell,i,j} h_{\ell j}|i,\ell\rangle\langle i,j|$$

$i \to j$

$j \to i$

$\ell \to p$

thus leading to

$$\hat h = \sum_{p,i} h_{pi}\underbrace{\left(\sum_j\left[|p,j\rangle\langle i,j| + |j,p\rangle\langle j,i|\right]\right)}_{\hat n_{pi}}$$

c) $$\langle\psi|\hat n_{ii}|\psi\rangle = \sum_j \langle\psi|i,j\rangle\langle i,j|\psi\rangle + \sum_j\langle\psi|j,i\rangle\langle j,i|\psi\rangle$$

$$= \overbrace{\underbrace{\sum_j|\langle i,j|\psi\rangle|^2}_{\text{probability that the first particle occupies the orbital } \varphi_i}}^{0\le\cdots\le 1\ (*)} + \overbrace{\underbrace{\sum_j|\langle j,i|\psi\rangle|^2}_{\text{probability that the second particle occupies the orbital } \varphi_i}}^{0\le\cdots\le 1\ (*)}$$

Therefore $$0 \le \underbrace{\langle\psi|\hat n_{ii}|\psi\rangle}_{\text{can be interpreted as the occupation number of the orbital } \varphi_i.} \le 2$$

(*) Note that $0 \le \sum_j |\langle i,j|\psi\rangle|^2 \le \underbrace{\sum_i \sum_j |\langle i,j|\psi\rangle|^2}_{\sum_{i,j} \langle\psi|i,j\rangle\langle i,j|\psi\rangle = \langle\psi|\psi\rangle = 1}$

and $0 \le \sum_j |\langle j,i|\psi\rangle|^2 \le \underbrace{\sum_i \sum_j |\langle j,i|\psi\rangle|^2}_{\sum_{i,j} \langle\psi|j,i\rangle\langle j,i|\psi\rangle = \langle\psi|\psi\rangle = 1}$.

d) $\hat{H}|\psi_0\rangle = E_0|\psi_0\rangle \rightarrow \langle\psi_0|\hat{H}|\psi_0\rangle = E_0 \underbrace{\langle\psi_0|\psi_0\rangle}_{1} = E_0$.

$$E_0 = \sum_{pi} h_{pi} \langle\psi_0|\hat{n}_{pi}|\psi_0\rangle + \sum_{ijkl} U_{ijkl} \langle\psi_0|\hat{n}_{ijkl}|\psi_0\rangle$$

$$\boxed{E_0 = \sum_{pi} h_{pi} n_{pi} + \sum_{ijkl} U_{ijkl} n_{ijkl}}$$

e) $\sum_j (n_{pjij} + n_{jpji}) = \langle\psi_0|\sum_j (|p,j\rangle\langle i,j| + |j,p\rangle\langle j,i|)|\psi_0\rangle = \langle\psi_0|\hat{n}_{pi}|\psi_0\rangle$

thus leading to $\boxed{n_{pi} = \sum_j (n_{pjij} + n_{jpji})}$

f) $\langle k,l|\Phi^{MF}\rangle = \sum_{ij} C_i C_j \underbrace{\langle k,l|i,j\rangle}_{\delta_{ki}\delta_{lj}} = C_k C_l$

$\Rightarrow \langle i,j|\Phi^{MF}\rangle = C_i C_j \rightarrow \langle\Phi^{MF}|i,j\rangle = (C_i C_j)^* = C_i C_j$

real algebra

$$h^{MF}_{pi} = \langle\Phi^{MF}|\hat{n}_{pi}|\Phi^{MF}\rangle$$

$$= \sum_j \langle\Phi^{MF}|p,j\rangle\langle i,j|\Phi^{MF}\rangle + \sum_j \langle\Phi^{MF}|j,p\rangle\langle j,i|\Phi^{MF}\rangle$$

$$h^{MF}_{pi} = \sum_j \left(C_p C_j C_i C_j + C_j C_p C_i C_j\right)$$

$$= 2 C_p C_i \underbrace{\sum_j C_j^2}_{1}.$$

Therefore $\boxed{h^{MF}_{pi} = 2 C_p C_i}$.

As a result,

$$h^{MF}_{ijkl} = \underbrace{\langle\Phi^{MF}|i,j\rangle}_{C_i C_j} \underbrace{\langle k,l|\Phi^{MF}\rangle}_{C_k C_l}$$

$$\boxed{h^{MF}_{ijkl} = \frac{h^{MF}_{ij} h^{MF}_{kl}}{4}}$$

g) $\langle\Phi^{MF}|\hat{H}|\Phi^{MF}\rangle = \sum_{pi} h_{pi} h^{MF}_{pi} + \sum_{ijkl} U_{ijkl} \frac{h^{MF}_{ij} h^{MF}_{kl}}{4} \longrightarrow$ should be minimized with respect to all the coefficients C_i (variational principle)