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

Exam in quantum mechanics

january 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: Hohenberg–Kohn theorem for a model Hamiltonian (13 points)

We consider a space of quantum states with dimension N and denote $\Big\{|u_i\rangle\Big\}_{i=1,\ldots,N}$ an orthonormal basis for that space. The Hamiltonian operator is defined as $\hat{H} = \hat{T} + \hat{V}$, where

$$\hat{T} = -t\sum_{i=1}^{N}\left(\sum_{j\neq i}^{N}|u_i\rangle\langle u_j|\right), \quad \hat{V} = \sum_{i=1}^{N} v_i|u_i\rangle\langle u_i|.$$

Real algebra will be used in the following. Note that $t > 0$. The problem aims at showing that the Hohenberg–Kohn theorem can be adapted to such a Hamiltonian.

a) **[2 pts]** Let $|\Psi_0\rangle = \sum_{i=1}^{N} C_i|u_i\rangle$ denote the exact normalized ground state of $\hat{H}$ associated with the exact ground-state energy E_0. Show that $E_0 = \langle\Psi_0|\hat{H}|\Psi_0\rangle$, $\langle u_j|\Psi_0\rangle = C_j$ and then conclude that $E_0 = \sum_{i=1}^{N} v_i C_i^2 - t\sum_{i=1}^{N}\left(\sum_{j\neq i}^{N} C_i C_j\right)$. Explain why, according to the variational principle, all the coefficients $\{C_i\}_{i=1,\ldots,N}$ are expected to have the same sign. **We will assume that they are all positive in the following**.

b) **[2 pts]** Show that none of the C_i coefficients are equal to zero. **Hint:** Explain why, for $1 \leq k \leq N$, $\langle u_k|\hat{H} - E_0|\Psi_0\rangle = 0$. Show that, if $C_k = 0$, then $\langle u_k|\hat{H} - E_0|\Psi_0\rangle = \langle u_k|\hat{H}|\Psi_0\rangle = -t\sum_{j\neq k}^{N} C_j$. Finally, use question 2. a) to prove that the latter sum must be strictly positive and conclude.

c) **[2 pts]** We consider another set $\{v_i'\}_{i=1,\ldots,N}$ that differ from $\{v_i\}_{i=1,\ldots,N}$ by more than a constant ($\forall i, v_i \neq v_i' + C$ where C does not depend on i) and denote $|\Psi_0'\rangle$ the exact normalized ground state of $\hat{H}' = \hat{T} + \hat{V}'$ that is associated with the exact ground-state energy E_0'. Show that $|\Psi_0\rangle \neq |\Psi_0'\rangle$.

Hint: first show that, for $1 \leq k \leq N$, $\langle u_k|\hat{V} - \hat{V}'|\Psi_0\rangle = (v_k - v_k')C_k$. Then show that the latter should also be equal to $(E_0 - E_0')C_k$ if $|\Psi_0\rangle = |\Psi_0'\rangle$. Deduce from question 2. b) that $v_k - v_k'$ should therefore be equal to $E_0 - E_0'$ for any k, and conclude.

d) **[2 pts]** We define the ground-state density as the set of values $\{n_i\}_{i=1,\ldots,N}$ that is defined as follows: $n_i = \langle\Psi_0|\hat{n}_i|\Psi_0\rangle$ with $\hat{n}_i = |u_i\rangle\langle u_i|$. Show that $n_i > 0$ and $\sum_{i=1}^{N} n_i = 1$. What is the physical meaning of n_i ?

e) **[1 pt]** We assume in the following that E_0 and E_0' are non-degenerate. Explain why, according to question 2. c), $\langle\Psi_0'|\hat{H}|\Psi_0'\rangle > E_0$ and $\langle\Psi_0|\hat{H}'|\Psi_0\rangle > E_0'$.

f) **[2 pts]** Let us assume that $|\Psi_0'\rangle$ has the same density as $|\Psi_0\rangle$, which means that $\langle\Psi_0'|\hat{n}_i|\Psi_0'\rangle = n_i$ for $1 \leq i \leq N$. Show that, in this particular case, $\langle\Psi_0|\hat{V}|\Psi_0\rangle = \langle\Psi_0'|\hat{V}|\Psi_0'\rangle$ and $\langle\Psi_0|\hat{V}'|\Psi_0\rangle = \langle\Psi_0'|\hat{V}'|\Psi_0'\rangle$. Deduce from question 2. e) the following inequalities:

$$\langle\Psi_0|\hat{T}|\Psi_0\rangle > \langle\Psi_0'|\hat{T}|\Psi_0'\rangle \quad \text{and} \quad \langle\Psi_0|\hat{T}|\Psi_0\rangle < \langle\Psi_0'|\hat{T}|\Psi_0'\rangle.$$

Conclude.

g) **[1 pt]** Explain why not only the ground state but also the excited states of $\hat{H}$ can in principle be determined from the ground-state density.

h) **[1 pt]** Show that, according to question 2. a), the ground-state energy can here be expressed explicitly in terms of the ground-state density as follows: $E_0 = \sum_{i=1}^{N} v_i n_i - t\sum_{i=1}^{N}\left(\sum_{j\neq i}^{N}\sqrt{n_i n_j}\right)$.

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2 - a - • $\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle \longrightarrow \langle\Psi_0|\hat{H}|\Psi_0\rangle = E_0\underbrace{\langle\Psi_0|\Psi_0\rangle}_{1}$

therefore $\boxed{E_0 = \langle\Psi_0|\hat{H}|\Psi_0\rangle}$

• $|\Psi_0\rangle = \sum_{i=1}^{N} C_i|u_i\rangle \longrightarrow \langle u_j|\Psi_0\rangle = \sum_{i=1}^{N} C_i \underbrace{\langle u_j|u_i\rangle}_{\delta_{ji}}$

thus leading to $\boxed{\langle u_j|\Psi_0\rangle = C_j}$

• $E_0 = \langle\Psi_0|\hat{T}|\Psi_0\rangle + \langle\Psi_0|\hat{V}|\Psi_0\rangle$

$$= -t\sum_{i=1}^{N}\sum_{j\neq i}^{N} \underbrace{\langle\Psi_0|u_i\rangle}_{C_i^*}\underbrace{\langle u_j|\Psi_0\rangle}_{C_j}$$

$$+ \sum_{i=1}^{N} v_i \underbrace{\langle\Psi_0|u_i\rangle}_{C_i^*}\underbrace{\langle u_i|\Psi_0\rangle}_{C_i}$$

Since we are using real algebra, it comes

$$\boxed{E_0 = \sum_{i=1}^{N} v_i C_i^2 - t\sum_{i=1}^{N}\sum_{j\neq i}^{N} C_iC_j}$$

• According to the variational principle

$$E_0 = \min_{\Psi} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \min_{\substack{\Psi \text{ with} \\ \langle\Psi|\Psi\rangle=1}} \langle\Psi|\hat{H}|\Psi\rangle$$

The equality is fulfilled when $\Psi = \Psi_0$.
Therefore the coefficients $\{C_i\}_{i=1,\dots,N}$ are such that

$\sum_{i=1}^{N} v_iC_i^2 - t\underbrace{\sum_{i\neq j}^{N} C_iC_j}$ is equal to its lowest possible value

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this term reaches its lowest value when all products C_iC_j are positive $\Rightarrow$ all C_i values should have the same sign.

A stronger argument is obtained as follows:

Let $|\Psi\rangle = \sum_i D_i|u_i\rangle$ be a normalized state.

We consider the other state $|\bar{\Psi}\rangle = \sum_i |D_i||u_i\rangle$ for which all coefficients are positive (and therefore have the same sign).

$\forall\, i,j \qquad |D_i||D_j| \geqslant D_iD_j \longrightarrow -t|D_i||D_j| \leqslant -tD_iD_j$

thus leading to $-t\sum_{i\neq j}|D_i||D_j| \leqslant -t\sum_{i\neq j} D_iD_j$

that is equivalent to

$$\underbrace{\sum_i v_i|D_i|^2 - t\sum_{i\neq j}|D_i||D_j|}_{\langle\bar{\Psi}|\hat{H}|\bar{\Psi}\rangle} \leqslant \underbrace{\sum_i v_iD_i^2 - t\sum_{i\neq j}D_iD_j}_{\langle\Psi|\hat{H}|\Psi\rangle}$$

Conclusion: the lowest energy expectation value is obtained for a state $|\Psi\rangle$ with coefficients $\{D_i\}_{i=1,\dots,N}$ that all have the same sign.

2-b- . $\hat{H}|\psi_0\rangle = E_0|\psi_0\rangle \longrightarrow (\hat{H}-E_0)|\psi_0\rangle = 0$ therefore

$$\boxed{\langle u_k|\hat{H}-E_0|\psi_0\rangle = 0}$$

• $\langle u_k|\hat{H}-E_0|\psi_0\rangle = \langle u_k|\hat{H}|\psi_0\rangle - E_0 \underbrace{\langle u_k|\psi_0\rangle}_{C_k}$

if $C_k = 0$ then

$$\langle u_k|\hat{H}-E_0|\psi_0\rangle = \underbrace{\langle u_k|\hat{T}|\psi_0\rangle}_{-t\sum_{j\neq k}^{N}\langle u_j|\psi_0\rangle} + \underbrace{\langle u_k|\hat{V}|\psi_0\rangle}_{v_k \underbrace{\langle u_k|\psi_0\rangle}_{0}}$$

therefore
$$\boxed{\langle u_k|\hat{H}-E_0|\psi_0\rangle = -t\sum_{j\neq k}^{N} C_j = 0} \quad (1)$$

$\forall j\neq k \quad C_j \geqslant 0$. We already assumed that $C_k = 0$. One of the coefficients $C_1, C_2, \dots, C_{k-1}, C_{k+1}, \dots C_N$ must be non-zero otherwise $C_j = 0 \ \forall j \Rightarrow |\psi_0\rangle = 0$ (!)

We can conclude that $\left(\sum_{j\neq k}^{N} C_j\right) > 0$ and, since $t>0$,

$$-t\sum_{j\neq k}^{N} C_j < 0$$

↘ cannot be equal to zero, which is not possible according to equation (1).

Conclusion: $C_i > 0 \quad \forall\, 1\leq i\leq N$.

2-c- . $\langle u_k|\hat{V}-\hat{V}'|\psi_0\rangle = \langle u_k|\hat{V}|\psi_0\rangle - \langle u_k|\hat{V}'|\psi_0\rangle$

$$= v_k\langle u_k|\psi_0\rangle - v_k'\langle u_k|\psi_0\rangle$$

$$= (v_k - v_k')C_k$$

• $(\hat{T}+\hat{V})|\psi_0\rangle = E_0|\psi_0\rangle$ and $(\hat{T}+\hat{V}')|\psi_0'\rangle = E_0'|\psi_0'\rangle$

if $|\psi_0\rangle = |\psi_0'\rangle$ then, by subtracting the two equations, we obtain

$$(\hat{V}-\hat{V}')|\psi_0\rangle = (E_0 - E_0')|\psi_0\rangle \longrightarrow \langle u_k|\hat{V}-\hat{V}'|\psi_0\rangle = (E_0-E_0')C_k$$

Therefore $(v_k - v_k')C_k = (E_0-E_0')C_k \quad \forall k$

Since $C_k > 0$ (non-zero) $\longrightarrow \underbrace{(v_k - v_k') = E_0 - E_0' \ \forall k}_{\text{absurd!}}$

2-d- . $n_i = \langle\psi_0|u_i\rangle\langle u_i|\psi_0\rangle = C_i^2 > 0$

• $\sum_{i=1}^{N} n_i = \sum_{i=1}^{N}\langle\psi_0|\hat{n}_i|\psi_0\rangle = \langle\psi_0|\underbrace{\sum_{i=1}^{N}\hat{n}_i}_{\hat{\mathbb{1}} \text{ (resolution of the identity)}}|\psi_0\rangle$

$$= \langle\psi_0|\psi_0\rangle$$
$$= 1$$

• n_i is the probability of being in the state $|u_i\rangle$.

2-e- According to the variational principle applied to $\hat{H}$ and then for $\hat{H}'$, and since $|\Psi_0\rangle \neq |\Psi_0'\rangle$, (*)

$$\langle \Psi_0' | \hat{H} | \Psi_0' \rangle > E_0 \quad \text{and} \quad \langle \Psi_0 | \hat{H}' | \Psi_0 \rangle > \underbrace{E_0'}$$

E_0: ground-state energy for $\hat{H}$ — E_0': ground-state energy for $\hat{H}'$

(*) <u>Complement:</u> Let $\{|\Psi_i\rangle\}_{i=0,\dots,N-1}$ denote the eigenvectors of $\hat{H}$ associated with $\{E_i\}_{i=0,\dots,N-1}$. For any <u>normalized</u> state $|\Psi\rangle = \sum_{i=0}^{N-1} \alpha_i |\Psi_i\rangle$,

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=0}^{N-1} \alpha_i \langle \Psi | \hat{H} | \Psi_i \rangle = \sum_{i=0}^{N-1} \alpha_i^2 E_i$$

$$\rightarrow \langle \Psi | \hat{H} | \Psi \rangle - E_0 = \sum_{i=0}^{N-1} \alpha_i^2 (E_i - E_0) \quad \text{since } \langle \Psi | \Psi \rangle = \sum_{i=0}^{N-1} \alpha_i^2 = 1$$

$$= \sum_{i=1}^{N-1} \alpha_i^2 (E_i - E_0)$$

if E_0 is non-degenerate then $(E_i - E_0) > 0 \quad \forall i \geq 1$

if $|\Psi\rangle \neq |\Psi_0\rangle$ then one of the coefficients $\{\alpha_i\}_{i=1,\dots,N-1}$ must be non-zero $\Rightarrow$ $\boxed{\langle \Psi | \hat{H} | \Psi \rangle - E_0 > 0}$

2-f- if $n_i = \langle \Psi_0' | \hat{n}_i | \Psi_0' \rangle \;\forall i$ then

$$\langle \Psi_0' | \hat{V} | \Psi_0' \rangle = \sum_{i=1}^{N} v_i \underbrace{\langle \Psi_0' | \hat{n}_i | \Psi_0' \rangle}_{n_i} = \sum_{i=1}^{N} v_i \langle \Psi_0 | \hat{n}_i | \Psi_0 \rangle$$

$$= \langle \Psi_0 | \hat{V} | \Psi_0 \rangle$$

and similarly $\langle \Psi_0' | \hat{V}' | \Psi_0' \rangle = \sum_{i=1}^{N} v_i' n_i = \langle \Psi_0 | \hat{V}' | \Psi_0 \rangle$

According to question 2-e)

$$\langle \Psi_0' | \hat{T} | \Psi_0' \rangle + \cancel{\langle \Psi_0' | \hat{V} | \Psi_0' \rangle} > \langle \Psi_0 | \hat{T} | \Psi_0 \rangle + \cancel{\langle \Psi_0 | \hat{V} | \Psi_0 \rangle}$$

and

$$\langle \Psi_0 | \hat{T} | \Psi_0 \rangle + \cancel{\langle \Psi_0 | \hat{V}' | \Psi_0 \rangle} > \langle \Psi_0' | \hat{T} | \Psi_0' \rangle + \cancel{\langle \Psi_0' | \hat{V}' | \Psi_0' \rangle}$$

thus leading to

$$0 < \langle \Psi_0' | \hat{T} | \Psi_0' \rangle - \langle \Psi_0 | \hat{T} | \Psi_0 \rangle < 0 \quad (!)$$

absurd!

<u>Conclusion:</u> There is a one-to-one correspondence between $\{n_i\}_{i=1,\dots,N}$ and $\{v_i\}_{i=1,\dots,N}$.

2-g- The ground-state density determines $\{v_i\}_{i=1,\dots,N}$ and therefore the Hamiltonian $\hat{H}$, since $\hat{V}$ is fully determined by $\{v_i\}_{i=1,\dots,N}$.

Consequently, not only the ground-state energy, but also the excited-state energies are functional of the ground-state density.

2-h- $n_i = C_i^2$ and $C_i > 0 \rightarrow C_i = \sqrt{n_i}$

thus leading to, according to question 2-a,

$$\boxed{E_0 = \sum_{i=1}^{N} v_i n_i - t \sum_{i=1}^{N} \sum_{j \neq i}^{N} \sqrt{n_i n_j}}$$