M1 Matériaux et nanosciences

Examen de Mécanique Quantique (english version)

december 2013

Tous les documents ainsi que les calculatrices sont interdits.

Le barème proposé est uniquement indicatif (l'examen est noté sur 22 points).

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1. Questions about the lectures (12 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) **[3 pts]** In quantum mechanics, an observable is connected with an operator. Give an example for a particle. What mathematical property does this operator have ? Does quantum theory enable you to know exactly what will be measured for that observable ?

c) **[2 pts]** What is the spin of the electron ? In which theory is it described ? How is the quantum state of the electron written in such a theory ?

d) **[2 pts]** Compare Hückel and Hartree–Fock methods.

e) **[3 pts]** What is the electron correlation energy ?

2. Problem (10 points): variational principle for the excited states

Let $\hat{H}$ be the Hamiltonian of a quantum system whose orthonormal basis of eigenstates is denoted $\{|\Psi_i\rangle\}_{i=0,1,2,...}$ with the associated eigenvalues $\{E_i\}_{i=0,1,2,...}$. We assume in the following that the latter are all non-degenerate and ordered as follows:

$$E_0 < E_1 < E_2 < ...$$

Let $|\Psi\rangle = \sum_i C_i|\Psi_i\rangle$ be any normalized quantum state written in the basis of the eigenvectors of $\hat{H}$. **Real algebra will be used in the following**.

a) **[1 pt]** Show that $\sum_i C_i^2 = 1$ and $E_0 \leq \langle\Psi|\hat{H}|\Psi\rangle$.

b) **[2 pts]** Let us consider the quantum state $|\Psi(\xi)\rangle = \xi|\Psi_0\rangle + \sqrt{(1-\xi^2)}|\Psi_1\rangle$, where ξ is a real number and $0 \leq \xi \leq 1$. Show, by considering the particular case $\xi = 0$, that the stationarity condition is fulfilled for the first excited state. Show then, when investigating the sign of $\langle\Psi(\xi)|\hat{H}|\Psi(\xi)\rangle - E_1$ for $\xi > 0$, that the energy of the first excited state E_1 is not locally (that is for small ξ values) a minimum for the energy expectation value.

c) **[1 pt]** Let $|\Psi'\rangle = \sum_i C'_i|\Psi_i\rangle$ be another normalized quantum state. Show that

$$\langle\Psi|\hat{H}|\Psi\rangle - E_0 + \langle\Psi'|\hat{H}|\Psi'\rangle - E_1 = \sum_{i=0}^{1}(p_i - 1)E_i + \sum_{i>1} p_i E_i,$$

where $p_i = C_i^2 + (C'_i)^2$.

d) **[1 pt]** Deduce from the normalization of $|\Psi\rangle$ and $|\Psi'\rangle$ that $\sum_{i=0}^{1}(1-p_i) - \sum_{i>1} p_i = 0.$

e) **[1 pt]** Conclude that

$$\langle\Psi|\hat{H}|\Psi\rangle - E_0 + \langle\Psi'|\hat{H}|\Psi'\rangle - E_1 = \sum_{i=0}^{1}(1-p_i)(E_1 - E_i) + \sum_{i>1} p_i(E_i - E_1).$$

Hint : start from the expression $\langle\Psi|\hat{H}|\Psi\rangle - E_0 + \langle\Psi'|\hat{H}|\Psi'\rangle - E_1 + E_1 \times \left(\sum_{i=0}^{1}(1-p_i) - \sum_{i>1} p_i\right)$.

f) **[2 pts]** We now assume that $|\Psi\rangle$ and $|\Psi'\rangle$ are orthonormal and we denote $\{|\Psi^{(k)}\rangle\}_{k=2,3,\ldots}$ the complementary orthonormal states such that $|\Psi\rangle, |\Psi'\rangle, \{|\Psi^{(k)}\rangle\}_{k=2,3,\ldots}$ is an orthonormal basis for the all space of quantum states. The eigenstate $|\Psi_i\rangle$ is decomposed in that new basis as follows:

$$|\Psi_i\rangle = C|\Psi\rangle + C'|\Psi'\rangle + \sum_{k=2,3,\ldots} C^{(k)}|\Psi^{(k)}\rangle.$$

Show that $\langle\Psi_i|\Psi_i\rangle \geq C^2 + (C')^2$, $C = C_i$ and $C' = C'_i$. Conclude that $p_i \leq 1$.

g) **[2 pts]** Deduce from questions 2. e) and 2. f) that

$$E_0 + E_1 \leq \langle\Psi|\hat{H}|\Psi\rangle + \langle\Psi'|\hat{H}|\Psi'\rangle.$$

Explain then how the ground $|\Psi_0\rangle$ and the first excited $|\Psi_1\rangle$ states can be obtained simultaneously and variationally.

Problème : principe variationnel pour les états excités

a. • $\langle\psi|\hat{H}|\psi\rangle = \sum_i c_i \langle\psi|\underbrace{\hat{H}|\psi_i\rangle}_{E_i|\psi_i\rangle} = \sum_i E_i c_i \langle\psi|\psi_i\rangle$

or $\langle\psi_i|\psi\rangle = c_i$ donc $\langle\psi|\hat{H}|\psi\rangle = \sum_i E_i c_i \underbrace{c_i^*}_{c_i \text{ (algèbre réel)}}$

soit $\langle\psi|\hat{H}|\psi\rangle = \sum_i E_i c_i^2$

• Comme $(E_i - E_0) c_i^2 \geq 0 \quad \forall i$

$\langle\psi|\hat{H}|\psi\rangle \geq \sum_i E_0 c_i^2 = E_0 \sum_i c_i^2$

or $\langle\psi|\psi\rangle = \sum_i c_i \langle\psi|\psi_i\rangle = \sum_i c_i^2 = 1$

d'où $\boxed{\langle\psi|\hat{H}|\psi\rangle \geq E_0}$

b. • $|\psi(\xi)\rangle = \xi|\psi_0\rangle + (1-\xi^2)^{1/2}|\psi_1\rangle$

$\langle\psi(\xi)|\psi(\xi)\rangle = \xi\langle\psi(\xi)|\psi_0\rangle + (1-\xi^2)^{1/2}\langle\psi(\xi)|\psi_1\rangle$

$= \xi^2 + (1-\xi^2) = 1$

La valeur moyenne de l'énergie s'écrit donc

$E(\xi) = \langle\psi(\xi)|\hat{H}|\psi(\xi)\rangle$

$= \xi\langle\psi(\xi)|\underbrace{\hat{H}|\psi_0\rangle}_{E_0|\psi_0\rangle} + (1-\xi^2)^{1/2}\langle\psi(\xi)|\underbrace{\hat{H}|\psi_1\rangle}_{E_1|\psi_1\rangle}$

d'où $E(\xi) = \xi^2 E_0 + (1-\xi^2)E_1 = \xi^2(E_0 - E_1) + E_1$

$\frac{\partial E(\xi)}{\partial \xi} = 2\xi(E_0 - E_1)$

donc $\boxed{\left.\frac{\partial E(\xi)}{\partial \xi}\right|_{\xi=0} = 0}$ ← condition de stationnarité vérifiée en $\xi = 0$ qui correspond à $|\psi(\xi=0)\rangle = |\psi_1\rangle$.

• $E(\xi) - E_1 = \langle\psi(\xi)|\hat{H}|\psi(\xi)\rangle - E_1$

$= \underbrace{\xi^2}_{>0}\underbrace{(E_0 - E_1)}_{<0} < 0$

d'où $\boxed{\langle\psi(\xi)|\hat{H}|\psi(\xi)\rangle < E_1}$

→ ce n'est donc pas localement un minimum de la valeur moyenne de l'énergie c- $\langle\psi|\hat{H}|\psi\rangle - E_0 + \langle\psi'|\hat{H}|\psi'\rangle - E_1$

$$= \sum_i c_i^2 E_i + \sum_i (c_i')^2 E_i - E_0 - E_1$$

avec $p_i = c_i^2 + (c_i')^2$ on obtient

$$\langle\psi|\hat{H}|\psi\rangle - E_0 + \langle\psi'|\hat{H}|\psi'\rangle - E_1$$

$$= \underbrace{\sum_i p_i E_i}_{p_0 E_0 + p_1 E_1 + \sum_{i>1} p_i E_i} - E_0 - E_1 = \sum_{i=0}^{1} (p_i - 1) E_i + \sum_{i>1} p_i E_i$$

d- $\displaystyle\sum_{i=0}^{1} (1-p_i) - \sum_{i>1} p_i = 2 - \sum_{i=0}^{1} p_i - \sum_{i>1} p_i$

$$= 2 - \sum_i p_i = 2 - \sum_i \left[c_i^2 + (c_i')^2\right] = 0$$

or $\langle\psi|\psi\rangle = 1 = \sum_i c_i^2$

et $\langle\psi'|\psi'\rangle = 1 = \sum_i (c_i')^2$

D'où $\boxed{\displaystyle\sum_{i=0}^{1} (1-p_i) - \sum_{i>1} p_i = 0}$

e-

$$\langle\psi|\hat{H}|\psi\rangle - E_0 + \langle\psi'|\hat{H}|\psi'\rangle - E_1$$

$$= \langle\psi|\hat{H}|\psi\rangle - E_0 + \langle\psi'|\hat{H}|\psi'\rangle - E_1 + E_1 \times \underbrace{\left(\sum_{i=0}^{1} (1-p_i) - \sum_{i>1} p_i\right)}_{=0}$$

$$= \sum_{i=0}^{1} (p_i - 1) E_i + E_1 \sum_{i=0}^{1} (1-p_i) + \sum_{i>1} p_i E_i - E_1 \sum_{i>1} p_i$$

d'après la question c-

Donc

$$\boxed{\begin{aligned}&\langle\psi|\hat{H}|\psi\rangle - E_0 + \langle\psi'|\hat{H}|\psi'\rangle - E_1 \\ &= \sum_{i=0}^{1} \underbrace{(1-p_i)}_{\text{signe à déterminer !}} \underbrace{(E_1 - E_i)}_{\geqslant 0} + \sum_{i>1} \underbrace{p_i}_{\geqslant 0} \underbrace{(E_i - E_1)}_{>0}\end{aligned}}$$

Eq. 1

f- $|\psi_i\rangle = c|\psi\rangle + c'|\psi'\rangle + \displaystyle\sum_{k=2,3,\dots} c^{(k)} |\psi^{(k)}\rangle$

$$\langle\psi_i|\psi_i\rangle = c\,\underbrace{\langle\psi_i|\psi\rangle}_{c} + c'\,\underbrace{\langle\psi_i|\psi'\rangle}_{c'} + \sum_{k=2,3,\dots} c^{(k)}\,\underbrace{\langle\psi_i|\psi^{(k)}\rangle}_{c^{(k)}}$$

$$= c^2 + (c')^2 + \sum_{k=2,3,\dots} (c^{(k)})^2 \geqslant c^2 + (c')^2$$

or $c = \langle\psi|\psi_i\rangle = \langle\psi_i|\psi\rangle = c_i$ et $c' = \langle\psi'|\psi_i\rangle = \langle\psi_i|\psi'\rangle = c_i'$

D'où $\langle \psi_i | \psi_i \rangle = 1 \geq c_i^2 + (c_i')^2 = p_i$

soit $\boxed{p_i \leq 1}$

g- $1 - p_i \geq 0$ donc d'après l'Eq. 1

$$\boxed{\langle \psi | \hat{H} | \psi \rangle + \langle \psi' | \hat{H} | \psi' \rangle \geq E_0 + E_1}$$

Ainsi

$$\boxed{E_0 + E_1 = \min_{\substack{\psi, \psi' \\ \langle \psi | \psi' \rangle = 0}} \left\{ \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} + \frac{\langle \psi' | \hat{H} | \psi' \rangle}{\langle \psi' | \psi' \rangle} \right\}}$$

principe variationnel pour l'ensemble {état fondamental, 1er état excité}

on constate que le minimum est atteint, par exemple, lorsque $|\psi\rangle = |\psi_0\rangle$ et $|\psi'\rangle = |\psi_1\rangle$.

Il est donc possible de déterminer le 1er état excité (et l'état fondamental en même temps) en <u>minimisant</u> la somme des valeurs moyennes de l'énergie

$$\frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} + \frac{\langle \psi' | \hat{H} | \psi' \rangle}{\langle \psi' | \psi' \rangle}$$

avec la condition d'orthogonalité $\langle \psi | \psi' \rangle = 0$.