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

Exam in quantum mechanics

January 2017

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)

a) **[2 pts]** Show that the solution to the time-dependent Schrödinger equation with Hamiltonian $\hat{H}$ and initial quantum state $|\Psi(0)\rangle$ can be written as $|\Psi(t)\rangle = e^{-\mathrm{i}\hat{H}t/\hbar}|\Psi(0)\rangle$. **Hint:** use the formula $\dfrac{\mathrm{d}e^{-\mathrm{i}\hat{H}t/\hbar}}{\mathrm{d}t} = -\dfrac{\mathrm{i}\hat{H}}{\hbar}e^{-\mathrm{i}\hat{H}t/\hbar}$.

b) **[2 pts]** Show, in the particular case of a particle moving along the x axis with an interaction potential energy $V(x)$, how the time-independent Schrödinger equation is obtained from the time-dependent one.

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

d) **[2 pts]** What is the main difference between the variational principle and the stationarity condition ?

e) **[2 pts]** Explain briefly what are the Hartree–Fock and electron correlation energies.

2. Problem: Green's function for the one-dimensional harmonic oscillator (13 points)

Let us consider the Hamiltonian of the one-dimensional harmonic oscillator with frequency ω,

$$\hat{H} = \hbar\omega\left(\hat{N} + \frac{1}{2}\right), \tag{1}$$

where $\hat{N} = \hat{a}^\dagger\hat{a}$. The creation $\hat{a}^\dagger$ and annihilation $\hat{a}$ operators fulfill the commutation rule

$$\left[\hat{a}, \hat{a}^\dagger\right] = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1. \tag{2}$$

In the following, we denote $|\Psi_n\rangle$ a normalized eigenvector of $\hat{N}$ with eigenvalue n. It can be shown that n is a positive integer. The purpose of the problem is to show that some interesting properties of the quantum oscillator can be obtained without knowing $|\Psi_n\rangle$ explicitly. For that purpose, we will introduce the so-called one-particle time-ordered Green's function, which is simply referred to as Green's function in the following.

a) **[2 pts]** Show from Eq. (1) that $|\Psi_n\rangle$ is eigenvector of $\hat{H}$ with the associated energy $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$. Explain why $\hbar\omega/2$ is sometimes referred to as "energy of the vacuum" and why n can be interpreted as a number of (bosonic) particles with energy $\hbar\omega$.

b) **[1 pt]** The Green's function associated to $|\Psi_n\rangle$ is a function of time t (here we only consider positive times for simplicity) which is defined as follows,

$$G_n(t) = -\mathrm{i}\left\langle \Psi_n \middle| \hat{a}(t)\hat{a}^\dagger \middle| \Psi_n \right\rangle, \quad t \geq 0, \tag{3}$$

where $\mathrm{i}^2 = -1$ and $\hat{a}(t) = e^{\mathrm{i}\hat{H}t/\hbar}\,\hat{a}\,e^{-\mathrm{i}\hat{H}t/\hbar}$. Show that the Green's function can be rewritten as

$$G_n(t) = -\mathrm{i}\langle \Psi_n(t)|\tilde{\Psi}_n(t)\rangle, \tag{4}$$

where

$$|\Psi_n(t)\rangle \quad = \quad e^{-\mathrm{i}\hat{H}t/\hbar}|\Psi_n\rangle, \tag{5}$$

$$|\tilde{\Psi}_n(t)\rangle \quad = \quad \hat{a}\,e^{-\mathrm{i}\hat{H}t/\hbar}\,\hat{a}^\dagger|\Psi_n\rangle. \tag{6}$$

Hint: use the formula $\left(e^{\mathrm{i}\hat{H}t/\hbar}\right)^\dagger = e^{-\mathrm{i}\hat{H}t/\hbar}$.

c) **[2 pts]** Explain why $\left[\hat{H}, e^{-\mathrm{i}\hat{H}t/\hbar}\right] = 0$. Deduce from Eq. (1) that $\left[\hat{N}, e^{-\mathrm{i}\hat{H}t/\hbar}\right] = 0$ and conclude that $|\Psi_n(t)\rangle$ is eigenvector of $\hat{N}$ with eigenvalue n. **Hint:** use the relation $e^{-\mathrm{i}\hat{H}t/\hbar} = \sum_{p=0}^{+\infty} \frac{1}{p!}\left(\frac{-\mathrm{i}t}{\hbar}\right)^p \hat{H}^p$ for proving that the first commutator equals zero. Simplify $\hat{N}|\Psi_n(t)\rangle$ in order to conclude.

d) **[2 pts]** Show that $\left[\hat{N}, \hat{a}\right] = -\hat{a}$ and $\left[\hat{N}, \hat{a}^\dagger\right] = \hat{a}^\dagger$. Conclude by using question 2. c) that $|\tilde{\Psi}_n(t)\rangle$ is also eigenvector of $\hat{N}$ with eigenvalue n. Explain with words why this was somehow expected from Eq. (6). **Hint:** simplify $\hat{N}|\tilde{\Psi}_n(t)\rangle$ by using the commutators.

e) **[2 pts]** Explain with words how the time-dependent quantum states $|\Psi_n(t)\rangle$ and $|\tilde{\Psi}_n(t)\rangle$ differ. Deduce the physical meaning of the Green's function. **Hint:** focus on the number of particles while reading Eq. (6) from right to left. The evolution in time can be discussed by using question 1. a).

f) **[2 pts]** Show that $G_n(t) = -\mathrm{i}e^{-\mathrm{i}(E_{n+1}-E_n)t/\hbar}\langle\Psi_n(0)|\tilde{\Psi}_n(0)\rangle$. One of the reason why the Green's function formalism is popular in condensed matter physics is that the time dependence of the Green's function gives access to the energy that is necessary to add one particle to a given quantum system. Is this in agreement with the expression obtained for $G_n(t)$? **Hint:** use the first **hint** of question 2. c) and the fact that $\hat{a}^\dagger|\Psi_n\rangle$ is eigenvector of $\hat{H}$ with eigenvalue E_{n+1}.

g) **[2 pts]** We will finally show that it is possible to calculate the Green's function without knowing explicitly the eigenvectors of $\hat{H}$ and the corresponding energies, which is of high interest for studying more complicated quantum systems where, for example, the number of particles is large or infinite (like in solids). For that purpose, show from the **hint** of question 1. a) that $\dfrac{\mathrm{d}\hat{a}(t)}{\mathrm{d}t} = \dfrac{\mathrm{i}}{\hbar} e^{\mathrm{i}\hat{H}t/\hbar}\left[\hat{H}, \hat{a}\right] e^{-\mathrm{i}\hat{H}t/\hbar}$. Deduce from Eqs. (1) and (3), and question 2. d), the so-called equation of motion,

$$\frac{\mathrm{d}G_n(t)}{\mathrm{d}t} = -\mathrm{i}\omega G_n(t). \tag{7}$$

Explain why $G_n(0) = -\mathrm{i}(n+1)$ and conclude that $G_n(t) = -\mathrm{i}(n+1)e^{-\mathrm{i}\omega t}$. Comment on this result in the light of question 2. f). **Hint:** use the formula $\dfrac{\mathrm{d}e^{\mathrm{i}\hat{H}t/\hbar}}{\mathrm{d}t} = \dfrac{\mathrm{i}}{\hbar} e^{\mathrm{i}\hat{H}t/\hbar}\hat{H}$.

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1/GF

a) $\hat H|\psi_n\rangle = \hbar\omega \underbrace{\hat N|\psi_n\rangle}_{n|\psi_n\rangle} + \frac{\hbar\omega}{2}|\psi_n\rangle = \underbrace{\left(n\hbar\omega + \frac{\hbar\omega}{2}\right)}_{E_n}|\psi_n\rangle$

n is the number of quanta of energy $\hbar\omega$. These quanta of energy could be "carried" by particles like photons, for example. When $n=0$, there are no particles, hence the name "energy of the vacuum" given to $E_0 = \frac{\hbar\omega}{2}$. Note that we can have an arbitrary number of particles in the same quantum state with individual energy $\hbar\omega$. That's why the particles are bosonic.

b) $G_n(t) = -i\langle\psi_n| e^{i\hat H t/\hbar}\,\hat a\, e^{-i\hat H t/\hbar}\hat a^\dagger|\psi_n\rangle$

$= -i \langle \underbrace{(e^{i\hat Ht/\hbar})^\dagger}_{*\ e^{-i\hat Ht/\hbar}}\psi_n | \underbrace{\hat a\, e^{-i\hat Ht/\hbar}\hat a^\dagger|\psi_n\rangle}_{|\tilde\psi_n(t)\rangle}$

thus leading to $G_n(t) = -i\langle\psi_n(t)|\tilde\psi_n(t)\rangle$

* $(e^{\hat A})^\dagger = \left(\sum_{p=0}^{+\infty} \frac{\hat A^p}{p!}\right)^\dagger = \sum_{p=0}^{+\infty}\frac{(\hat A^p)^\dagger}{p!} = \sum_{p=0}^{+\infty} \frac{(\hat A^\dagger)^p}{p!} = e^{\hat A^\dagger}$

for $\hat A = i\frac{\hat H t}{\hbar}$, $\hat A^\dagger = -i\frac{\hat H^\dagger t}{\hbar} = -i\hat H t/\hbar$.

c) • $\hat H e^{-i\hat Ht/\hbar} = \hat H\sum_{p=0}^{+\infty}\left(-\frac{it}{\hbar}\right)^p\frac{\hat H^p}{p!} = \underbrace{\left(\sum_{p=0}^{+\infty}\left(-\frac{it}{\hbar}\right)^p\frac{\hat H^p}{p!}\right)}_{e^{-i\hat Ht/\hbar}}\hat H$

Therefore $[\hat H, e^{-i\hat Ht/\hbar}]=0$

• $\underbrace{[\hat H, e^{-i\hat Ht/\hbar}]}_{\overset{\|}{0}} = \underbrace{[\hbar\omega\hat N, e^{-i\hat Ht/\hbar}]}_{\hbar\omega[\hat N,\, e^{-i\hat Ht/\hbar}]} + \underbrace{\left[\frac{\hbar\omega}{2}\hat{\mathbb{1}}, e^{-i\hat Ht/\hbar}\right]}_{0}$

thus leading to $[\hat N, e^{-i\hat Ht/\hbar}] = 0$ (1)

• $\hat N|\psi_n(t)\rangle = \hat N e^{-i\hat Ht/\hbar}|\psi_n\rangle = e^{-i\hat Ht/\hbar}\underbrace{\hat N|\psi_n\rangle}_{n|\psi_n\rangle}$

Consequence of (1)

$\Rightarrow \boxed{\hat N|\psi_n(t)\rangle = n|\psi_n(t)\rangle}$.

d) $[\hat N,\hat a] = \hat a^\dagger\hat a\hat a - \hat a\hat a^\dagger\hat a = -\underbrace{[\hat a,\hat a^\dagger]}_{1}\hat a$

$\Rightarrow [\hat N,\hat a] = -\hat a$

Similarly $[\hat N,\hat a^\dagger] = \hat a^\dagger\hat a\hat a^\dagger - \hat a^\dagger\hat a^\dagger\hat a = \hat a^\dagger\underbrace{[\hat a,\hat a^\dagger]}_{1} = \hat a^\dagger$

$\hat N|\tilde\psi_n(t)\rangle = \hat N\hat a\, e^{-i\hat Ht/\hbar}\hat a^\dagger|\psi_n\rangle$

$= (-\hat a + \hat a\hat N)\,e^{-i\hat Ht/\hbar}\hat a^\dagger|\psi_n\rangle$

$= -\hat a\, e^{-i\hat Ht/\hbar}\hat a^\dagger|\psi_n\rangle$

Consequence of (1)

$+ \hat a\, e^{-i\hat Ht/\hbar}\underbrace{\hat N\hat a^\dagger}_{(\hat a^\dagger + \hat a^\dagger\hat N)}|\psi_n\rangle$

thus leading to

$\hat N|\tilde\psi_n(t)\rangle = \hat a\, e^{-i\hat Ht/\hbar}\hat a^\dagger\underbrace{N|\psi_n\rangle}_{n|\psi_n\rangle}$

$\Rightarrow \boxed{\hat N|\tilde\psi_n(t)\rangle = n|\tilde\psi_n(t)}$

$$|\tilde{\psi}_n(t)\rangle = \underbrace{\hat{a}\,\underbrace{e^{-i\hat{H}t/\hbar}\,\underbrace{\hat{a}^{\dagger}\underbrace{|\psi_n\rangle}_{n\text{-particle quantum state}}}_{(n+1)\text{-particle quantum state}}}_{(n+1)\text{-particle quantum state (according to question 2.c))}}}_{n\text{-particle quantum state}}$$

Note that $\hat{a}^{\dagger}|\psi_n\rangle$ is eigenvector of $\hat{N}$ with eigenvalue $(n+1)$

n-particle quantum state (the annihilation operator reduces by 1 the number of particles)

(*) adding and removing (later) a particle to the system has a significant impact on that system.

e) $|\psi_n(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi_n\rangle$

$|\psi_n\rangle$: initial n-particle state

$e^{-i\hat{H}t/\hbar}$: gives the evolution in time of the n-particle state

$$|\tilde{\psi}_n(t)\rangle = \hat{a}\,\underbrace{e^{-i\hat{H}t/\hbar}\,\underbrace{\hat{a}^{\dagger}|\psi_n\rangle}_{\text{new initial state where 1 particle has been added to the system}}}_{\text{state at time } t \text{ with the new } (n+1)\text{-particle initial state}}$$

and then a particle is removed at time t.

Difference between $|\psi_n(t)\rangle$ and $|\tilde{\psi}_n(t)\rangle$: While, in $|\psi_n(t)\rangle$, we just let the system evolve in time with an initial n-particle state, $|\tilde{\psi}_n(t)\rangle$ describes a situation where, at the initial time $t=0$, we add a particle, then let the system evolve in time and, at time t, we remove the added particle. The inner product $\langle\psi_n(t)|\tilde{\psi}_n(t)\rangle$ quantifies the difference between the two scenarios. If it is close to zero, it means that the 2 states are very different or, in other words, (*)

f) $\bullet$ $|\psi_n(t)\rangle = \sum_{p=0}^{+\infty}\left(\frac{-it}{\hbar}\right)^p \frac{\hat{H}^p|\psi_n\rangle}{p!}$

$$= \sum_{p=0}^{+\infty}\frac{(-it)^p (E_n)^p}{p!\,\hbar^p}|\psi_n\rangle$$

Since $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

$$\Rightarrow |\psi_n(t)\rangle = e^{-iE_nt/\hbar}\underbrace{|\psi_n\rangle}_{|\psi_n(0)\rangle} \quad (2)$$

$\bullet$ $$|\tilde{\psi}_n(t)\rangle = \hat{a}\,\underbrace{e^{-i\hat{H}t/\hbar}\,\underbrace{\hat{a}^{\dagger}|\psi_n\rangle}_{\text{eigenvector of } \hat{H} \text{ with energy } E_{n+1}}}_{e^{-iE_{n+1}t/\hbar}\,\hat{a}^{\dagger}|\psi_n\rangle}$$

according to (2) (use $n \longrightarrow n+1$)

$$\Rightarrow |\tilde{\psi}_n(t)\rangle = e^{-iE_{n+1}t/\hbar}\underbrace{\hat{a}\,\hat{a}^{\dagger}|\psi_n\rangle}_{|\tilde{\psi}_n(0)\rangle}$$

Conclusion:
$$G_n(t) = -i\,\langle\psi_n(t)|\tilde{\psi}_n(t)\rangle$$
$$= -i\,e^{iE_nt/\hbar}\,e^{-iE_{n+1}t/\hbar}\langle\psi_n(0)|\tilde{\psi}_n(0)\rangle$$
$$= -i\,e^{-i(E_{n+1}-E_n)t/\hbar}\langle\psi_n(0)|\tilde{\psi}_n(0)\rangle$$

This is the only part that varies with time.

In our case, the Green's function is periodic with frequency $\frac{(E_{n+1}-E_n)}{\hbar}$. So, indeed, knowing the time-evolution of the Green's function gives access to the "particle affinity" $E_n - E_{n+1}$.

g) • $$\frac{d\hat{a}(t)}{dt} = \left(\frac{d e^{i\hat{H}t/\hbar}}{dt}\right)\hat{a}\, e^{-i\hat{H}t/\hbar} + e^{i\hat{H}t/\hbar}\,\hat{a}\,\frac{d}{dt}e^{-i\hat{H}t/\hbar}$$

where, in the general case,

$$\frac{d}{dt}e^{\hat{A}t} = \frac{d}{dt}\sum_{p=0}^{+\infty}\frac{\hat{A}^p t^p}{p!} = \sum_{p=1}^{+\infty}\frac{\hat{A}^p}{p!}\,p\,t^{p-1}$$

$$= \underbrace{\sum_{p=1}^{+\infty}\hat{A}\,\frac{\hat{A}^{p-1}t^{p-1}}{(p-1)!}}_{\hat{A}\,e^{\hat{A}t}} = \underbrace{\sum_{p=1}^{+\infty}\frac{\hat{A}^{p-1}t^{p-1}\hat{A}}{(p-1)!}}_{e^{\hat{A}t}\,\hat{A}}$$

Therefore $$\frac{d\hat{a}(t)}{dt} = e^{\frac{i\hat{H}t}{\hbar}}\left(\frac{i\hat{H}}{\hbar}\right)\hat{a}\,e^{-i\hat{H}t/\hbar} + e^{i\hat{H}t/\hbar}\,\hat{a}\left(-\frac{i\hat{H}}{\hbar}\right)e^{-i\hat{H}t/\hbar}$$

$$= \frac{i}{\hbar}\,e^{\frac{i\hat{H}t}{\hbar}}\,[\hat{H},\hat{a}]\,e^{-i\hat{H}t/\hbar}$$

• Since $[\hat{H},\hat{a}] = [\hbar\omega\hat{N} + \frac{\hbar\omega}{2}, \hat{a}] = \hbar\omega\,[\hat{N},\hat{a}] = -\hbar\omega\hat{a}$

it comes $$\boxed{\frac{d\hat{a}(t)}{dt} = -i\omega\,\hat{a}(t)}$$

and $$\frac{dG_n(t)}{dt} = -i\,\langle\Psi_n|\frac{d\hat{a}(t)}{dt}\hat{a}^\dagger|\Psi_n\rangle$$

$$= -i\omega \times \underbrace{(-i)\langle\Psi_n|\hat{a}(t)\,\hat{a}^\dagger|\Psi_n\rangle}_{G_n(t)}$$

$$\Rightarrow \boxed{\frac{dG_n(t)}{dt} = -i\omega\,G_n(t)} \quad (3)$$

$$G_n(0) = -i\,\langle\Psi_n|\underbrace{\hat{a}\hat{a}^\dagger}_{1+\hat{a}^\dagger\hat{a}}|\Psi_n\rangle = -i\,\langle\Psi_n|\hat{N}+1|\Psi_n\rangle = -i\,(\underbrace{\langle\Psi_n|\hat{N}|\Psi_n\rangle}_{n|\Psi_n\rangle} + 1)$$

$$\Rightarrow G_n(0) = -i\,(n+1)$$

From (3) it comes

$$G_n(t) = G_n(0)\,e^{-i\omega t} = \boxed{-i(n+1)\,e^{-i\omega t} = G_n(t)}$$

where $\omega = (E_{n+1}-E_n)/\hbar$

in agreement with the expression given in question 2. f).