M1 "Sciences et Génies des Matériaux" & M1 franco-allemand "Polymères"

Quantum Mechanics course

Two-hour exam, January 2023

Lecturer: *E. Fromager*

1. Questions on the lectures [10 points]

a) **[4 pts]** Which mathematical functions are used for describing the state of a particle moving along the x axis in classical Newton and quantum mechanics, respectively? Write the fundamental time-dependent equations that these functions are supposed to fulfill.

b) **[4 pts]** How does the wave function $\Psi(\vec{r})$, where $\vec{r} \equiv (x, y, z)$ denotes a position that the particle under study could have in the three-dimensional real space, relate to the quantum state $|\Psi\rangle$ of that particle? Explain the notation $\Psi(\vec{r}\,') = \langle \vec{r}\,'|\Psi\rangle$, where $\vec{r}\,' \equiv (x', y', z')$ is some given fixed position. Let $\hat{x}$ denote the x coordinate position operator. Why, according to the postulates of quantum mechanics, should we expect the following equality to be fulfilled: $\hat{x}\,|\vec{r}\,'\rangle = x'\,|\vec{r}\,'\rangle$? Deduce that $(\hat{x}\Psi)(\vec{r}\,') = \langle \vec{r}\,'|\hat{x}|\Psi\rangle = x' \times \Psi(\vec{r}\,')$.

c) **[2 pts]** What is the general idea behind perturbation theory? How do we technically derive the perturbation expansion of the energies for a given Hamiltonian $\hat{H}$?

2. Exercise I: Generalization of the Heisenberg inequality [5 points]

Let A and B be two observables to which we associate the Hermitian quantum operators $\hat{A}$ and $\hat{B}$, respectively. The purpose of the exercise is to show that, for any normalized quantum state $|\Psi\rangle$, the following inequality holds,

$$(\Delta A)_\Psi (\Delta B)_\Psi \geq \frac{1}{2}\left|\langle\Psi|[\hat{A},\hat{B}]|\Psi\rangle\right|, \tag{1}$$

where $(\Delta A)_\Psi = \sqrt{\left\langle\Psi\middle|\left(\hat{A} - \langle\Psi|\hat{A}|\Psi\rangle \times \hat{\mathbb{1}}\right)^2\middle|\Psi\right\rangle}$ and $(\Delta B)_\Psi = \sqrt{\left\langle\Psi\middle|\left(\hat{B} - \langle\Psi|\hat{B}|\Psi\rangle \times \hat{\mathbb{1}}\right)^2\middle|\Psi\right\rangle}$ are the standard deviations for the measurement of A and B, respectively. The operator $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is the commutator of $\hat{A}$ and $\hat{B}$, and $\hat{\mathbb{1}}$ is the identity operator.

a) **[1.5 pts]** Let α be a ***real*** number that we use to construct the α-dependent quantum state $|\Psi(\alpha)\rangle = \left[\left(\hat{A} - \langle\Psi|\hat{A}|\Psi\rangle \times \hat{\mathbb{1}}\right) + \mathrm{i}\alpha\left(\hat{B} - \langle\Psi|\hat{B}|\Psi\rangle \times \hat{\mathbb{1}}\right)\right]|\Psi\rangle$, where $\mathrm{i}^2 = -1$. Show that the square norm $N(\alpha) = \langle\Psi(\alpha)|\Psi(\alpha)\rangle$ can be written as $N(\alpha) = (\Delta A)_\Psi^2 + (\Delta B)_\Psi^2\,\alpha^2 + \alpha\, C_\Psi$, where $C_\Psi = \langle\Psi|\hat{C}|\Psi\rangle$ and $\hat{C} = \mathrm{i}[\hat{A},\hat{B}]$.

b) **[1 pt]** Why do we expect C_Ψ to be a real number? Prove it by showing that $\hat{C}$ is Hermitian.

c) **[0.5 pts]** Show that $N(\alpha) = (\Delta B)^2_\Psi \left[\left(\alpha + \dfrac{C_\Psi}{2(\Delta B)^2_\Psi}\right)^2 + \dfrac{1}{(\Delta B)^2_\Psi}\left((\Delta A)^2_\Psi - \dfrac{C^2_\Psi}{4(\Delta B)^2_\Psi}\right)\right]$.

d) **[1 pt]** Explain why $N(\alpha)$ is positive for any value of α [**Hint:** See its definition in question 2. a)]. Show that the generalized Heisenberg inequality of Eq. (1) is recovered when $\alpha = -\dfrac{C_\Psi}{2(\Delta B)^2_\Psi}$.

e) **[1 pt]** Conclude that the commutator of two operators determines if the corresponding observables can be measured simultaneously or not. Show that the famous inequality of Heisenberg is recovered from Eq. (1) when $\hat{A}$ and $\hat{B}$ are the position $\hat{x} \equiv x\times$ and momentum $\hat{p}_x \equiv -\mathrm{i}\hbar\partial/\partial x$ operators, respectively.

3. Exercise II: Second-order perturbation theory and energy fluctuations [6 points]

From the decomposition $\hat{H} = \hat{H}_0 + \hat{W}$ of the Hamiltonian of interest into a simpler (so-called unperturbed) Hamiltonian $\hat{H}_0$ and the perturbation operator $\hat{W} = \hat{H} - \hat{H}_0$, it can be shown that the difference in expectation value for $\hat{H}$ between the true normalized ground state $|\Psi_0\rangle$ of $\hat{H}$ and the unperturbed normalized ground state $|\Phi_0\rangle$, which is eigenvector of $\hat{H}_0$ associated to the unperturbed energy $\mathcal{E}_0$, reads through second order $\langle\Psi_0|\hat{H}|\Psi_0\rangle - \langle\Phi_0|\hat{H}|\Phi_0\rangle = \sum_{j>0} \dfrac{|\langle\Phi_0|\hat{W}|\Phi_j\rangle|^2}{\mathcal{E}_0 - \mathcal{E}_j} + \ldots$, where $\{|\Phi_j\rangle\}_{j>0}$ are the orthonormalized excited states of $\hat{H}_0$ associated to the unperturbed excited-state energies $\{\mathcal{E}_j\}_{j>0}$.

a) **[1 pt]** Show that $\langle\Phi_0|\hat{W}|\Phi_j\rangle \underset{j>0}{=} \langle\Phi_0|\hat{H}|\Phi_j\rangle$ and conclude that $|\langle\Phi_0|\hat{W}|\Phi_j\rangle|^2 \underset{j>0}{=} \langle\Phi_0|\hat{H}|\Phi_j\rangle\langle\Phi_j|\hat{H}|\Phi_0\rangle$.

b) **[0.5 pts]** We assume that the unperturbed "$0 \rightarrow j$" excitation energy does not vary significantly with j, *i.e.*, $\mathcal{E}_j - \mathcal{E}_0 \overset{j>0}{\approx} \Omega_0$. Deduce from the previous question that

$$\langle\Psi_0|\hat{H}|\Psi_0\rangle - \langle\Phi_0|\hat{H}|\Phi_0\rangle \approx -\frac{1}{\Omega_0}\left\langle \Phi_0 \middle| \hat{H}\left(\sum_{j>0} |\Phi_j\rangle\langle\Phi_j|\right)\hat{H} \middle| \Phi_0 \right\rangle + \ldots \tag{2}$$

c) **[1 pt]** Deduce from the resolution of the identity that
$\langle\Psi_0|\hat{H}|\Psi_0\rangle - \langle\Phi_0|\hat{H}|\Phi_0\rangle \approx -\dfrac{1}{\Omega_0}\left[\langle\Phi_0|\hat{H}^2|\Phi_0\rangle - \left(\langle\Phi_0|\hat{H}|\Phi_0\rangle\right)^2\right] + \ldots$

d) **[2 pts]** We consider the standard deviation in energy for the true system when it is in the unperturbed ground state, *i.e.*, $(\Delta H)_{\Phi_0} = \sqrt{\left\langle \Phi_0 \middle| \left(\hat{H} - \langle\Phi_0|\hat{H}|\Phi_0\rangle \times \hat{\mathbb{1}}\right)^2 \middle| \Phi_0 \right\rangle}$. Show that $(\Delta H)^2_{\Phi_0} = \langle\Phi_0|\hat{H}^2|\Phi_0\rangle - \left(\langle\Phi_0|\hat{H}|\Phi_0\rangle\right)^2$. What is the fundamental reason why $(\Delta H)_{\Phi_0}$ differs from zero? How does this observation connect to the concept of energy fluctuation? **Hint:** You may begin your answer with a comparison of $(\Delta H)^2_{\Psi_0}$ with $(\Delta H)^2_{\Phi_0}$.

e) **[1.5 pts]** Conclude from question 3. c) that applying second-order perturbation theory to the ground state essentially consists in describing ground-state energy fluctuations around the energy obtained through first order.