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

Quantum Mechanics course

Two-hour exam, January 2022

Neither documents nor calculators are allowed.

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1. Questions on the lecture material [6 points]

a) **[3 pts]** Discuss the various strategies that can be implemented for constructing approximate solutions to the time-independent Schrödinger equation. Illustrate your answer with two examples.

b) **[1 pt]** Does the Hückel method provide exact solutions to the many-electron Schrödinger equation? Justify your answer.

c) **[2 pts]** How similar and different are the Rayleigh–Ritz variational principle and the stationarity condition for the energy?

2. Exercise: Perturbation theory through infinite order [16 points]

We explore in the following a formally exact construction of the solutions to the time-independent Schrödinger equation,

$$\hat{H}\left|\Psi\right\rangle = E\left|\Psi\right\rangle, \tag{1}$$

where the Hamiltonian operator $\hat{H} = \hat{H}_0 + \hat{W}$ is decomposed into a so-called unperturbed one $\hat{H}_0$, for which the Schrödinger equation is easy to solve, and the complementary (so-called perturbation) operator $\hat{W}$. Let $\{|u_j\rangle\}$ be the complete *orthonormal* basis of solutions to the unperturbed Schrödinger equation,

$$\hat{H}_0\left|u_j\right\rangle = \mathcal{E}_j\left|u_j\right\rangle, \ \ \forall j, \tag{2}$$

where $\{\mathcal{E}_j\}$ are the unperturbed energies.

a) **[2 pts]** Let us introduce the quantum operators $\hat{P} = |u_i\rangle\langle u_i|$ and $\hat{Q} = \sum_{k\neq i}|u_k\rangle\langle u_k|$, where $|u_i\rangle$ is one of the unperturbed solutions and $\{|u_k\rangle\}_{k\neq i}$ are all the remaining ones. Explain why $\hat{P}$ is referred to as the projector operator onto the unperturbed solution $|u_i\rangle$. Show that $\hat{P}^2 = \hat{P}$. Explain why $\hat{P} + \hat{Q} = \hat{\mathbb{1}}$, where $\hat{\mathbb{1}}$ is the identity operator. You may answer the latter question by considering the expansion of any quantum state $|\chi\rangle$ in the basis of the unperturbed solutions, *i.e.*, $|\chi\rangle = C_i |u_i\rangle + \sum_{l\neq i} C_l |u_l\rangle$, so that you can evaluate $\left(\hat{P}+\hat{Q}\right)|\chi\rangle$. Finally, conclude that $\hat{Q}^2 = \left(\hat{\mathbb{1}}-\hat{P}\right)^2 = \hat{Q}$.

b) **[2 pts]** Explain why, if $\left|\tilde{\Psi}\right\rangle$ is a solution to the true Schrödinger Eq. (1) for the energy E, then $|\Psi\rangle = \xi\left|\tilde{\Psi}\right\rangle$, where $\xi \neq 0$, is also a solution. We will assume in the following that

$$\hat{P}\,|\Psi\rangle = |u_i\rangle\,. \tag{3}$$

Which value of ξ should we use to ensure that the above (so-called intermediate normalization) condition is fulfilled? One can read in textbooks that perturbation theory, which relies on Eq. (3), breaks down when the solution to the true Schrödinger equation does not overlap with the unperturbed one. Comment on this statement by calculating the value of ξ in the latter special case.

c) **[2 pts]** Explain why, in the light of question 2. a) and Eq. (3), $|\Psi\rangle = \hat{P}\,|u_i\rangle + \hat{Q}\,|\Psi\rangle$, where, according to Eq. (1), $\hat{Q}\hat{H}\left(\hat{P}\,|u_i\rangle + \hat{Q}\,|\Psi\rangle\right) = E\hat{Q}\,|\Psi\rangle$, or, equivalently,

$$\hat{Q}\,|\Psi\rangle = \left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}\hat{Q}\hat{H}\hat{P}\,|u_i\rangle\,, \tag{4}$$

where $\left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}$ denotes the *inverse* of the operator $E\hat{Q} - \hat{Q}\hat{H}\hat{Q}$.

d) **[2 pts]** Explain why, according to Eqs. (1) and (3), $\hat{P}\hat{H}\left(\hat{P}\,|u_i\rangle + \hat{Q}\,|\Psi\rangle\right) = E\,|u_i\rangle$, and deduce from question 2. c) that the unperturbed solution $|u_i\rangle$ is solution to a so-called *effective* Schrödinger equation

$$\hat{H}_{\text{eff}}(E)\,|u_i\rangle = E\,|u_i\rangle\,, \tag{5}$$

where

$$\hat{H}_{\text{eff}}(E) = \hat{P}\hat{H}\hat{P} + \hat{P}\hat{H}\left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}\hat{Q}\hat{H}\hat{P}. \tag{6}$$

By comparing Eqs. (1), (2) and (5), explain why the *energy-dependent* Hamiltonian $\hat{H}_{\text{eff}}(E)$ is referred to as effective Hamiltonian. Show finally that the true energy can be expressed exactly as follows:

$$E = \langle u_i|\hat{H}_{\text{eff}}(E)|u_i\rangle = \mathcal{E}_i + \langle u_i|\hat{W}|u_i\rangle + \langle u_i|\hat{H}\left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}\hat{Q}\hat{H}|u_i\rangle\,. \tag{7}$$

e) **[2 pts]** We want to express the exact (so-called resolvent) operator $\hat{R}(E) = \left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}$ in terms of the unperturbed one $\hat{R}_0(E) = \left[E\hat{Q} - \hat{Q}\hat{H}_0\hat{Q}\right]^{-1}$. Show that $\hat{R}^{-1}(E) = \hat{R}_0^{-1}(E) - \hat{\Sigma}$, where $\hat{\Sigma} = \hat{Q}\hat{W}\hat{Q}$, and deduce that $\hat{R}_0(E)\hat{\Sigma}\hat{R}(E) = \hat{R}(E) - \hat{R}_0(E)$. Conclude that

$$\begin{aligned}\hat{R}(E) &= \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}_0(E)\hat{\Sigma}\hat{R}(E)\\ &= \sum_{p=0}^{+\infty}\left(\hat{R}_0(E)\hat{\Sigma}\right)^p \hat{R}_0(E).\end{aligned} \tag{8}$$

f) **[1 pt]** Deduce from Eqs. (7) and (8) that

$$E = \mathcal{E}_i + \langle u_i|\hat{W}|u_i\rangle + \sum_{p=0}^{+\infty} \langle u_i|\hat{H}\left(\hat{R}_0(E)\hat{Q}\hat{W}\hat{Q}\right)^p \hat{R}_0(E)\hat{Q}\hat{H}|u_i\rangle\,. \tag{9}$$

g) **[1 pt]** Explain why $\hat{R}_0(E) = \sum_{l\neq i} \dfrac{|u_l\rangle\langle u_l|}{E-\mathcal{E}_l}$.

Hint: Show that $\hat{Q}\,|u_l\rangle \overset{l\neq i}{=} |u_l\rangle$ [see question 2. a)] and then verify, according to the definition in question 2. e) and Eq. (2), that $\hat{R}_0^{-1}(E)\sum_{l\neq i}\dfrac{|u_l\rangle\langle u_l|}{E-\mathcal{E}_l} = \left(E\hat{Q} - \hat{Q}\hat{H}_0\hat{Q}\right)\sum_{l\neq i}\dfrac{|u_l\rangle\langle u_l|}{E-\mathcal{E}_l} = \sum_{l\neq i}|u_l\rangle\langle u_l|$. Conclude.

h) **[2 pts]** Show that, according to question 2. g), $\hat{R}_0(E)\hat{H}\,|u_i\rangle = \hat{R}_0(E)\left(\mathcal{E}_i\hat{\mathbb{1}} + \hat{W}\right)|u_i\rangle = \hat{R}_0(E)\hat{W}\,|u_i\rangle$, $\hat{Q}\hat{H}\,|u_i\rangle = \hat{Q}\left(\mathcal{E}_i\hat{\mathbb{1}} + \hat{W}\right)|u_i\rangle = \hat{Q}\hat{W}\,|u_i\rangle$, and $\hat{R}_0(E)\hat{Q} = \hat{R}_0(E)$. Deduce from Eq. (9) the formally exact expansion of the energy through infinite order in $\hat{W}$:

$$E = \mathcal{E}_i + \langle u_i|\hat{W}|u_i\rangle + \sum_{p=0}^{+\infty} \langle u_i|\hat{W}\left(\hat{R}_0(E)\hat{W}\hat{Q}\right)^p \hat{R}_0(E)\hat{W}|u_i\rangle\,. \tag{10}$$

Implementing the above expression for practical calculations is not trivial, even through a given *finite* order p. Why?

i) **[2 pts]** In order to establish a clearer connection with regular perturbation theory, we proceed with the following substitution, $\hat{W} \to \alpha\hat{W}$, where $0 \leq \alpha \leq 1$. Explain why the expansion through second order in α of the energy can be written as

$$\begin{aligned} E \to E(\alpha) &= \mathcal{E}_i + \alpha\,\langle u_i|\hat{W}|u_i\rangle + \alpha^2\,\langle u_i|\hat{W}\hat{R}_0(E(\alpha))\hat{W}|u_i\rangle + \ldots && (11)\\ &\approx \mathcal{E}_i + \alpha\,\langle u_i|\hat{W}|u_i\rangle + \alpha^2\,\langle u_i|\hat{W}\hat{R}_0\left(\mathcal{E}_i\right)\hat{W}|u_i\rangle\,. && (12)\end{aligned}$$

Conclude from question 2. g) that, within the present formalism, the regular perturbation expansion of the energy is recovered through second order:

$$E(\alpha) \approx \mathcal{E}_i + \alpha\,\langle u_i|\hat{W}|u_i\rangle + \alpha^2 \sum_{l\neq i}\frac{\langle u_i|\hat{W}|u_l\rangle\,\langle u_l|\hat{W}|u_i\rangle}{\mathcal{E}_i - \mathcal{E}_l}. \tag{13}$$