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

Exam in Quantum Mechanics

January 2020

two-hour exam

Neither documents nor calculators are allowed.

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1. Questions on the lecture material (5 points)

a) **[2 pts]** Let us consider the two-electron Hartree product $\Phi(\mathbf{r}_1, \mathbf{r}_2) = \varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$, where φ is an orbital, $\mathbf{r}_1$ and $\mathbf{r}_2$ are the space coordinates of the first and second electron, respectively. Does $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ describe the ground state of two non-interacting electrons exactly ? Explain briefly how the orbital φ is determined in this case.

b) **[3 pts]** The Hartree–Fock method relies on a Hartree product (when applied to two interacting electrons). Does it mean that it neglects the two-electron repulsion ? Does it provide an exact description of the electronic structure ? Define the concept of electron correlation and explain (briefly) how the correlation energy can be calculated in practice.

2. Problem: imaginary-time-dependent Schrödinger equation (16 points)

We consider in this exercise any quantum system with time-independent and *hermitian* Hamiltonian $\hat{H}$.

a) **[2 pts]** Verify that the solution to the conventional time-dependent Schrödinger equation can be written as $|\Psi(t)\rangle = e^{-\mathrm{i}\hat{H}t/\hbar}\,|\Psi(0)\rangle$ where $|\Psi(0)\rangle \equiv |\Psi(t=0)\rangle$ is the quantum state of the system at time $t = 0$. **Hint**: the operator $e^{-\mathrm{i}\hat{H}t/\hbar}$ can be differentiated with respect to t as if $\hat{H}$ was just a number.

b) **[1 pt]** We will now proceed with a transformation, which is *a priori* unphysical, where (real) time t is replaced by a *pure imaginary time*: $|\Psi(t \rightarrow -\mathrm{i}\tau)\rangle = |\tilde{\chi}(\tau)\rangle = e^{-\hat{H}\tau/\hbar}\,|\Psi(0)\rangle$, where $\tau > 0$ and $\mathrm{i}^2 = -1$. Show that $\dfrac{d\,|\tilde{\chi}(\tau)\rangle}{d\tau} = -\dfrac{1}{\hbar}\hat{H}\,|\tilde{\chi}(\tau)\rangle$.

c) **[2 pts]** We consider the initial *normalized* state decomposition $|\Psi(0)\rangle = \sum_{I\geq 0} C_I\,|\Psi_I\rangle$ in the orthonormal basis $\{\Psi_I\}_{I\geq 0}$ of eigenvectors of $\hat{H}$, i.e. $\hat{H}\,|\Psi_I\rangle = E_I\,|\Psi_I\rangle$. Show that $|\tilde{\chi}(\tau)\rangle = \sum_{I\geq 0} C_I\; e^{-E_I\tau/\hbar}\,|\Psi_I\rangle$ and $\langle\tilde{\chi}(\tau)|\tilde{\chi}(\tau)\rangle = \sum_{I\geq 0} |C_I|^2\; e^{-2E_I\tau/\hbar}$. **Hint**: use the Taylor-expanded expressions $e^{-\hat{H}\tau/\hbar} = \displaystyle\sum_{n=0}^{+\infty} \frac{(-\tau)^n}{\hbar^n n!}\hat{H}^n$ and $e^{\xi} = \displaystyle\sum_{n=0}^{+\infty} \frac{\xi^n}{n!}$ where ξ is any number.

d) **[1 pt]** Conclude from question 2. c) that, unlike $|\Psi(t)\rangle$, the quantum state $|\tilde{\chi}(\tau)\rangle$ does not remain normalized as the so-called *imaginary time* τ evolves.

e) **[2 pts]** Let $E(\tau) = \langle\chi(\tau)|\,\hat{H}\,|\chi(\tau)\rangle$ be the imaginary-time-dependent *energy* where

$$|\chi(\tau)\rangle = \frac{|\tilde{\chi}(\tau)\rangle}{\sqrt{\langle\tilde{\chi}(\tau)|\tilde{\chi}(\tau)\rangle}}. \tag{1}$$

Show that $|\chi(\tau)\rangle$ is normalized and that

$$E(\tau) = \frac{\sum\limits_{I\geq 0}|C_I|^2 E_I e^{-2E_I\tau/\hbar}}{\sum\limits_{I\geq 0}|C_I|^2 e^{-2E_I\tau/\hbar}} = \frac{|C_0|^2 E_0 + \sum\limits_{I>0}|C_I|^2 E_I e^{-2(E_I-E_0)\tau/\hbar}}{|C_0|^2 + \sum\limits_{I>0}|C_I|^2 e^{-2(E_I-E_0)\tau/\hbar}}. \tag{2}$$

f) **[1 pt]** We assume in the following that $C_0 \neq 0$ and that the ground-state energy E_0 is not degenerate. Show that the latter is recovered at infinite imaginary time, whatever the values of the excited-state coefficients $\{C_I\}_{I>0}$ are, i.e. $E_0 = \lim\limits_{\tau\to+\infty} E(\tau)$.

g) **[1 pt]** We now assume that, at the initial time $\tau = 0$, the coefficients are all equal, i.e. $C_I = C$ for $I \geq 0$. Show that, in this case, the energy at finite imaginary time τ is formally identical to the average energy $\sum_{I\geq 0} E_I e^{-\beta E_I}/\sum_{I\geq 0} e^{-\beta E_I}$ of a canonical ensemble at temperature $T = \frac{1}{k_B\beta}$ where k_B is Boltzmann's constant. How is the (fictitious) temperature T connected to the imaginary time τ ?

h) **[3 pts]** Show that, according to question 2. b) and Eq. (1), the normalized quantum state $|\chi(\tau)\rangle$ fulfills the following imaginary-time-dependent Schrödinger equation:

$$-\hbar\frac{d\,|\chi(\tau)\rangle}{d\tau} = \left(\hat{H} - E(\tau)\right)|\chi(\tau)\rangle\,. \tag{3}$$

Hint: prove that $\dfrac{d}{d\tau}\left(\dfrac{1}{\sqrt{\langle\tilde{\chi}(\tau)|\tilde{\chi}(\tau)\rangle}}\right) = \dfrac{\langle\tilde{\chi}(\tau)|\,\hat{H}\,|\tilde{\chi}(\tau)\rangle}{\hbar\,\langle\tilde{\chi}(\tau)|\tilde{\chi}(\tau)\rangle^{3/2}} = \dfrac{E(\tau)}{\hbar\sqrt{\langle\tilde{\chi}(\tau)|\tilde{\chi}(\tau)\rangle}}$. Then, show that $\dfrac{d\,|\chi(\tau)\rangle}{d\tau} = -\dfrac{1}{\hbar}\hat{H}\,|\chi(\tau)\rangle + \dfrac{E(\tau)}{\hbar}\,|\chi(\tau)\rangle$ and conclude.

i) **[3 pts]** Let $\hat{A}$ be any time-independent operator. Deduce from Eq. (3) the Ehrenfest theorem in imaginary times:

$$\frac{d\,\langle\chi(\tau)|\,\hat{A}\,|\chi(\tau)\rangle}{d\tau} = -\frac{1}{\hbar}\,\langle\chi(\tau)|\left(\hat{H}\hat{A} + \hat{A}\hat{H}\right)|\chi(\tau)\rangle + \frac{2E(\tau)}{\hbar}\,\langle\chi(\tau)|\,\hat{A}\,|\chi(\tau)\rangle\,. \tag{4}$$

Show, by considering the particular case $\hat{A} = \hat{H}$, that $\dfrac{dE(\tau)}{d\tau} = -\dfrac{2}{\hbar}\,(\Delta H)^2_{\chi(\tau)}$, where the standard deviation for the energy and any quantum state $|\Psi\rangle$ reads $(\Delta H)_\Psi = \sqrt{\langle\Psi|\,\hat{H}^2\,|\Psi\rangle - \langle\Psi|\,\hat{H}\,|\Psi\rangle^2}$. Comment on this result.