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

# Quantum Mechanics course

*Two-hour exam*, January 2021

***Neither documents nor calculators are allowed.***

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## 1. Questions on the lecture material [9 points]

a) **[3 pts]** Discuss the various strategies that can be implemented for constructing approximate solutions to the Schrödinger equation. Illustrate your answer with an example.

b) **[2 pts]** Is the two-electron repulsion neglected in the Hartree–Fock method? If not, how is it described?

c) **[2 pts]** Does the Hückel method provide exact solutions to the many-electron Schrödinger equation? Justify your answer. What is the advantage of Hartree–Fock over Hückel?

d) **[2 pts]** How would you define the concept of electron correlation? How can we evaluate its impact on the energy?

## 2. Problem: Why is the ground-state energy of the harmonic oscillator nonzero? [12 points]

In order to answer the above question, we consider the following (more general) Schrödinger equation (in *one dimension*) for a particle of mass $m$,

$$\hat{H}_\lambda \left|\Psi_{\lambda,n}\right\rangle = E_{\lambda,n} \left|\Psi_{\lambda,n}\right\rangle, \quad \text{where} \quad \hat{H}_\lambda = \hat{T} + \lambda\hat{\mathcal{V}}, \quad \hat{T} = \frac{\hat{p}_x^2}{2m}, \quad \hat{\mathcal{V}} = \frac{1}{2}k\hat{x}^{2\ell}, \quad \hat{x}^{2\ell} \equiv x^{2\ell}\times, \tag{1}$$

and $\hat{p}_x \equiv -\mathrm{i}\hbar\dfrac{\mathrm{d}}{\mathrm{d}x}$ is the momentum operator. The real number $\lambda$ modulates the *strength* of the potential energy while $k > 0$ and the real exponent $\ell \neq 0$ are *constants*. The subscript $n$ in Eq. (1) refers to an energy level ($n = 0$ for the ground state).

a) **[2 pts]** Let $\Psi_{\lambda,n}(x)$ be the wave function that represents $\left|\Psi_{\lambda,n}\right\rangle$. We want to show that $E_{\lambda,n}$ can be determined from $E_{\lambda=1,n} = E_n$. For that purpose, we consider the following change of variable $x \rightarrow \tilde{x} = \alpha \times x$ and denote $\Psi_{\lambda,n}(x) = \tilde{\Psi}_{\lambda,n}(\alpha \times x)$. Show that

$$-\alpha^2\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\tilde{\Psi}_{\lambda,n}(\tilde{x})}{\mathrm{d}\tilde{x}^2} + \alpha^{-2\ell}\lambda \times \frac{1}{2}k\tilde{x}^{2\ell}\tilde{\Psi}_{\lambda,n}(\tilde{x}) = E_{\lambda,n}\tilde{\Psi}_{\lambda,n}(\tilde{x}). \tag{2}$$

*The Schrödinger reads*

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi_{\lambda,n}(x)}{\mathrm{d}x^2}+\frac{1}{2}k\lambda x^{2\ell}\Psi_{\lambda,n}(x)=E_{\lambda,n}\Psi_{\lambda,n}(x). \tag{3}$$

*Since* $\dfrac{\mathrm{d}\Psi_{\lambda,n}(x)}{\mathrm{d}x}=\dfrac{\mathrm{d}}{\mathrm{d}x}\left[\tilde{\Psi}_{\lambda,n}(\alpha x)\right]=\alpha\left.\dfrac{\mathrm{d}\tilde{\Psi}_{\lambda,n}(\tilde{x})}{\mathrm{d}\tilde{x}}\right|_{\tilde{x}=\alpha x}$, *it comes* $\dfrac{\mathrm{d}^2\Psi_{\lambda,n}(x)}{\mathrm{d}x^2}=\alpha^2\left.\dfrac{\mathrm{d}^2\tilde{\Psi}_{\lambda,n}(\tilde{x})}{\mathrm{d}\tilde{x}^2}\right|_{\tilde{x}=\alpha x}$, *thus leading, once* $x^{2\ell}$ *has been replaced by* $(\tilde{x}/\alpha)^{2\ell}$, *to Eq. (2).*

Explain why, if we choose $\alpha^2=\alpha^{-2\ell}\lambda$ or, equivalently, $\alpha=\lambda^{\frac{1}{2(\ell+1)}}$, then $\tilde{\Psi}_{\lambda,n}$ becomes solution to the Schrödinger equation that is obtained from Eq. (1) when $\lambda$ is set to $\lambda=1$. Conclude that $E_{\lambda,n}=\lambda^{\frac{1}{\ell+1}}E_n$.

*If* $\alpha^2=\alpha^{-2\ell}\lambda$ *then Eq. (2) reads*

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\tilde{\Psi}_{\lambda,n}(\tilde{x})}{\mathrm{d}\tilde{x}^2}+\frac{1}{2}k\tilde{x}^{2\ell}\times\tilde{\Psi}_{\lambda,n}(\tilde{x})=\frac{E_{\lambda,n}}{\alpha^2}\tilde{\Psi}_{\lambda,n}(\tilde{x}), \tag{4}$$

*which is formally identical to the Schrödinger Eq. (3) in the particular case* $\lambda=1$. *As a result,*

$$\frac{E_{\lambda,n}}{\alpha^2}=E_n, \tag{5}$$

*or, equivalently,*

$$E_{\lambda,n}=\alpha^2E_n=\lambda^{\frac{1}{\ell+1}}E_n. \tag{6}$$

*We also note that* $\tilde{\Psi}_{\lambda,n}(\tilde{x})\sim\Psi_{\lambda=1,n}(\tilde{x})$ *or, equivalently,* $\Psi_{\lambda,n}(x)=\tilde{\Psi}_{\lambda,n}(\alpha x)\sim\Psi_{\lambda=1,n}\left(\lambda^{\frac{1}{2(\ell+1)}}\times x\right)$.

b) **[2 pts]** We assume that $|\Psi_{\lambda,n}\rangle$ in Eq. (1) is *normalized* for any $\lambda$. Prove the Hellmann–Feynman theorem $\dfrac{\mathrm{d}E_{\lambda,n}}{\mathrm{d}\lambda}=\left\langle\Psi_{\lambda,n}\middle|\dfrac{\partial\hat{H}_\lambda}{\partial\lambda}\middle|\Psi_{\lambda,n}\right\rangle$ and conclude from the previous question that $E_{\lambda,n}=(\ell+1)\lambda\left\langle\hat{\mathcal{V}}\right\rangle_{\Psi_{\lambda,n}}$, where $\left\langle\hat{A}\right\rangle_\Psi\overset{notation}{=}\langle\Psi|\,\hat{A}\,|\Psi\rangle$.

*We have shown previously that*

$$E_{\lambda,n}=\lambda^{\frac{1}{\ell+1}}E_n. \tag{7}$$

*Therefore*

$$\frac{\mathrm{d}E_{\lambda,n}}{\mathrm{d}\lambda}=\left\langle\hat{\mathcal{V}}\right\rangle_{\Psi_{\lambda,n}}\overset{Eq.(7)}{=}\frac{1}{\ell+1}\frac{\lambda^{\frac{1}{\ell+1}}}{\lambda}E_n, \tag{8}$$

*thus leading to*

$$\lambda^{\frac{1}{\ell+1}} E_n = E_{\lambda,n} = (\ell+1)\lambda \left\langle \hat{\mathcal{V}} \right\rangle_{\Psi_{\lambda,n}}. \tag{9}$$

c) **[2 pts]** Explain why $\left\langle \hat{T} \right\rangle_{\Psi_{\lambda,n}} = E_{\lambda,n} - \lambda \left\langle \hat{\mathcal{V}} \right\rangle_{\Psi_{\lambda,n}}$. Deduce from question 2. b) the virial theorem $\left\langle \hat{T} \right\rangle_{\Psi_{\lambda,n}} = \ell \left\langle \lambda\hat{\mathcal{V}} \right\rangle_{\Psi_{\lambda,n}}$, and conclude that

$$\left\langle \hat{p}_x^2 \right\rangle_{\Psi_{\lambda,n}} = \frac{2m\ell}{\ell+1} E_{\lambda,n} \quad \text{and} \quad \left\langle \hat{x}^{2\ell} \right\rangle_{\Psi_{\lambda,n}} = \frac{2}{k\lambda(\ell+1)} E_{\lambda,n}. \tag{10}$$

*Since*

$$\left\langle \hat{H}(\lambda) \right\rangle_{\Psi_{\lambda,n}} = \langle \Psi_{\lambda,n} | \hat{H}(\lambda) | \Psi_{\lambda,n} \rangle \overset{Eq.~(1)}{=} E_{\lambda,n} \langle \Psi_{\lambda,n} | \Psi_{\lambda,n} \rangle = E_{\lambda,n}, \tag{11}$$

*it comes* $E_{\lambda,n} = \left\langle \hat{T} \right\rangle_{\Psi_{\lambda,n}} + \lambda \left\langle \hat{\mathcal{V}} \right\rangle_{\Psi_{\lambda,n}}$, *thus leading to*

$$\left\langle \hat{T} \right\rangle_{\Psi_{\lambda,n}} = E_{\lambda,n} - \lambda \left\langle \hat{\mathcal{V}} \right\rangle_{\Psi_{\lambda,n}} \overset{Eq.~(9)}{=} \ell\lambda \left\langle \hat{\mathcal{V}} \right\rangle_{\Psi_{\lambda,n}}. \tag{12}$$

*Therefore,*

$$\left\langle \hat{T} \right\rangle_{\Psi_{\lambda,n}} = E_{\lambda,n} - \frac{1}{\ell} \left\langle \hat{T} \right\rangle_{\Psi_{\lambda,n}} \Leftrightarrow \left\langle \hat{T} \right\rangle_{\Psi_{\lambda,n}} = \frac{\ell}{\ell+1} E_{\lambda,n} \tag{13}$$

*and*

$$\left\langle \hat{\mathcal{V}} \right\rangle_{\Psi_{\lambda,n}} = \frac{1}{\ell\lambda} \left\langle \hat{T} \right\rangle_{\Psi_{\lambda,n}} = \frac{E_{\lambda,n}}{\lambda(\ell+1)}. \tag{14}$$

*We obtain Eq. (10) from Eqs. (13) and (14) by noticing that* $\langle \hat{p}_x^2 \rangle_{\Psi_{\lambda,n}} = 2m \left\langle \hat{T} \right\rangle_{\Psi_{\lambda,n}}$ *and* $\left\langle \hat{x}^{2\ell} \right\rangle_{\Psi_{\lambda,n}} = \frac{2}{k} \left\langle \hat{\mathcal{V}} \right\rangle_{\Psi_{\lambda,n}}$.

d) **[2 pts]** We assume that $\Psi_{\lambda,n}(x)$ is a *real* wave function and that $|\Psi_{\lambda,n}(-x)|^2 = |\Psi_{\lambda,n}(x)|^2$. These assumptions are justified in questions 2. f) and g). Explain briefly why, in this case, $\langle \hat{p}_x \rangle_{\Psi_{\lambda,n}} = \langle \hat{x} \rangle_{\Psi_{\lambda,n}} = 0$. Let $(\Delta A)_\Psi \overset{notation}{=} \sqrt{\left\langle \hat{A}^2 \right\rangle_\Psi - \left\langle \hat{A} \right\rangle_\Psi^2}$. Conclude, by evaluating $(\Delta p_x)_{\Psi_{\lambda,n}}$ from Eq. (10), that fluctuations in the momentum can occur only if the energy $E_{\lambda,n}$ associated to $|\Psi_{\lambda,n}\rangle$ is nonzero [we recall that $\ell \neq 0$].

*As readily seen from the following equation,*

$$(\Delta p_x)_{\Psi_{\lambda,n}} = \sqrt{\langle \hat{p}_x^2 \rangle_{\Psi_{\lambda,n}}} \overset{Eq.~(10)}{=} \sqrt{\frac{2m\ell}{\ell+1}} \times \sqrt{E_{\lambda,n}}, \tag{15}$$

*the standard deviation from zero of the momentum vanishes (which means that there are no fluctuations) if and only if the energy $E_{\lambda,n}$ equals zero. The amplitude of the fluctuations is therefore directly connected to the value of the energy.*

e) **[2 pts]** We now want to describe the harmonic oscillator with spring constant $k$. For that purpose, which values of $\ell$ and $\lambda$ should we use in Eq. (1)? We denote $\Psi_n := \Psi_{\lambda=1,n}$ and $E_n := E_{\lambda=1,n}$. Show that, according to Eq. (10) and question 2. d),

$$(\Delta p_x)_{\Psi_n} (\Delta x)_{\Psi_n} = \frac{E_n}{\omega}, \tag{16}$$

where $\omega = \sqrt{\dfrac{k}{m}}$. Explain why, according to the Heisenberg uncertainty principle, the lowest (so-called ground-state) energy $E_0$ of the harmonic oscillator cannot be equal to zero. It can be shown that $E_0 = \hbar\omega/2$. What is remarkable in this case?

*We have $\lambda = 1$ and $\ell = 1$ for a spring with constant $k$. Note that, according to question 2. d), $(\Delta x)_{\Psi_n} = \sqrt{\langle \hat{x}^2 \rangle_{\Psi_n}}$. Therefore, in this case,*

$$(\Delta p_x)_{\Psi_n} (\Delta x)_{\Psi_n} \overset{Eq.~(15)}{=} \sqrt{m}\sqrt{E_{\lambda=1,n}}\sqrt{\langle \hat{x}^2 \rangle_{\Psi_n}} \overset{Eq.~(10)}{=} \sqrt{\frac{m}{k}} E_{\lambda=1,n} = \frac{E_n}{\omega}. \tag{17}$$

*According to the Heisenberg uncertainty principle, we can conclude that*

$$E_n = \omega\, (\Delta p_x)_{\Psi_n} (\Delta x)_{\Psi_n} \geq \hbar\omega/2. \tag{18}$$

*Note that the lower bound $\hbar\omega/2$ is actually reached when the harmonic oscillator is in its ground state. In other words, in this very special case, the Heisenberg inequality becomes an equality, which is remarkable.*

f) **[1 pt]** We return to the general problem where $\lambda$ and $\ell$ values are not specified. Show that the complex conjugate $\Psi^*_{\lambda,n}(x)$ of the wave function $\Psi_{\lambda,n}(x)$ is solution to the Schrödinger equation with the same energy $E_{\lambda,n}$. By considering the linear combinations $\Psi^*_{\lambda,n}(x) \pm \Psi_{\lambda,n}(x)$, conclude that it is relevant to consider *real* wave functions only, as we did in question 2. d).

g) **[1 pt]** Show, by considering the particular case $\alpha = -1$ in Eq. (2), that $\Psi_{\lambda,n}(-x)$ is solution to the Schrödinger equation with the same energy $E_{\lambda,n}$ as $\Psi_{\lambda,n}(x)$. Deduce that the combinations

$\Psi_{\lambda,n}(-x) \pm \Psi_{\lambda,n}(x)$ are also solutions. Explain finally why this allows us to consider only wave functions that are either *even* [*i.e.* $\Psi(-x) = \Psi(x)$] or *odd* [*i.e.* $\Psi(-x) = -\Psi(x)$], as we did in question 2. d)