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

Quantum Mechanics course

Two-hour exam, January 2021

Neither documents nor calculators are allowed.

---

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 λ 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

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

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 λ is set to $\lambda = 1$. Conclude that $E_{\lambda,n} = \lambda^{\frac{1}{\ell+1}} E_n$.

b) **[2 pts]** We assume that $|\Psi_{\lambda,n}\rangle$ in Eq. (1) is *normalized* for any λ. 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 $\left\langle \hat{A} \right\rangle_\Psi \overset{notation}{=} \langle\Psi| \hat{A} |\Psi\rangle$.

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

$$\left\langle \hat{p}_x^2 \right\rangle_{\Psi_{\lambda,n}} = \frac{2m\ell}{\ell+1} E_{\lambda,n} \quad \text{and} \quad \left\langle \hat{x}^{2\ell} \right\rangle_{\Psi_{\lambda,n}} = \frac{2}{k\lambda(\ell+1)} E_{\lambda,n}. \tag{3}$$

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. (3), 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 $\ell \neq 0$].

e) **[2 pts]** We now want to describe the harmonic oscillator with spring constant k. For that purpose, which values of ℓ and λ 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. (3) and question 2. d),

$$(\Delta p_x)_{\Psi_n} (\Delta x)_{\Psi_n} = \frac{E_n}{\omega}, \tag{4}$$

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?

f) **[1 pt]** We return to the general problem where λ and ℓ 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)