M1 franco-allemand "Ingénierie des polymères" & M1 "Matériaux et nanosciences"

Exam in quantum mechanics

December 2017

duration of the exam session: 2h

Neither documents nor calculators are allowed.

The grading scale might be changed.

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1. Questions about the lectures (6 points)

a) **[3 pts]** Let $\hat{H}$ denote the Hamiltonian operator of the hydrogen atom and $\Phi_\alpha(x,y,z) = e^{-\alpha r^2}$ a trial wavefunction where $r = \sqrt{x^2+y^2+z^2}$ and $\alpha > 0$. Give the explicit expression for $\hat{H}$. Let $E(\alpha) = \dfrac{\langle\Phi_\alpha|\hat{H}|\Phi_\alpha\rangle}{\langle\Phi_\alpha|\Phi_\alpha\rangle}$. Is there any value of α such that $E(\alpha)$ equals the exact ground-state energy E_0 of the hydrogen atom ? Justify your answer. If not, how can we find the value of α such that $E(\alpha)$ is as close as possible to E_0 ?

b) **[3 pts]** What is the purpose of both Hartree–Fock and Hückel methods ? What is the main advantage of the former over the latter ? Is the Hartree–Fock approach in principle exact ? Justify your answers.

2. Problem I: the Heisenberg inequality and the harmonic oscillator (12 points)

According to the Heisenberg inequality, the standard deviations $\Delta x = \sqrt{\langle\Psi|\hat{x}^2|\Psi\rangle - \langle\Psi|\hat{x}|\Psi\rangle^2}$ and $\Delta p_x = \sqrt{\langle\Psi|\hat{p}_x^2|\Psi\rangle - \langle\Psi|\hat{p}_x|\Psi\rangle^2}$ for the position x and momentum p_x of a particle described by a quantum state $|\Psi\rangle$ are such that

$$\Delta x\, \Delta p_x \geq \hbar/2. \tag{1}$$

In this exercise, we consider a particle with mass m attached to a spring of constant k moving along the x axis. The corresponding (so-called one-dimensional harmonic oscillator) Hamiltonian reads

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2, \tag{2}$$

where $\omega = \sqrt{\dfrac{k}{m}}$. It can be shown that, by introducing the so-called annihilation operator $\hat{a}$ defined as follows,

$$\hat{a} = \frac{1}{\sqrt{2}}\left(\sqrt{\frac{m\omega}{\hbar}}\hat{x} + \frac{\mathrm{i}}{\sqrt{m\hbar\omega}}\hat{p}_x\right), \quad \text{where} \quad \mathrm{i}^2 = -1, \tag{3}$$

and its adjoint $\hat{a}^\dagger$ (referred to as creation operator), the Hamiltonian in Eq. (2) can be rewritten as

$$\hat{H} = \hbar\omega\left(\hat{N} + \frac{1}{2}\right), \tag{4}$$

where $\hat{N} = \hat{a}^\dagger\hat{a}$ is the so-called counting operator. By using the commutation rule

$$\left[\hat{a}, \hat{a}^\dagger\right] = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1, \tag{5}$$

it can finally be shown that the eigenvalues n of the counting operator are integers ($n = 0, 1, 2, \ldots$) and that the associated orthonormalized eigenvectors $\left\{|\Psi_n\rangle\right\}_{n=0,1,2,\ldots}$ are connected by the relation

$$\hat{a}^\dagger|\Psi_n\rangle = \sqrt{n+1}|\Psi_{n+1}\rangle. \tag{6}$$

a) **[2 pts]** Show that

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}^\dagger + \hat{a}\right) \quad \text{and} \quad \hat{p}_x = \mathrm{i}\sqrt{\frac{m\hbar\omega}{2}}\left(\hat{a}^\dagger - \hat{a}\right). \tag{7}$$

Conclude from Eq. (6) that $\langle\Psi_n|\hat{x}|\Psi_n\rangle = 0 = \langle\Psi_n|\hat{p}_x|\Psi_n\rangle$.

b) **[1 pt]** Explain why, according to Eq. (4), the energies of the one-dimensional harmonic oscillator are $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$ and the corresponding eigenstates are $|\Psi_n\rangle$ with $n = 0, 1, 2, \ldots$

c) **[1 pt]** Deduce from question 2. b) and Eq. (2) that, for a given eigenstate $|\Psi_n\rangle$, the expectation value of $\hat{p}_x^2$ is obtained from the one of $\hat{x}^2$ as follows,

$$\langle\Psi_n|\hat{p}_x^2|\Psi_n\rangle = m\hbar\omega(2n+1) - m^2\omega^2\langle\Psi_n|\hat{x}^2|\Psi_n\rangle. \tag{8}$$

d) **[0.5 pt]** In order to determine the expectation value of $\hat{x}^2$ for $|\Psi_n\rangle$, we propose to introduce a real variable λ and the λ-dependent Hamiltonian

$$\hat{H}(\lambda) = \frac{\hat{p}_x^2}{2m} + \frac{\lambda}{2}m\omega^2\hat{x}^2. \tag{9}$$

Its normalized eigenvectors and associated eigenvalues are denoted $|\Psi_n(\lambda)\rangle$ and $E_n(\lambda)$, respectively. What is the connection between $\hat{H}(\lambda)$ and the problem we are interested in ?

e) **[2.5 pts]** Explain why $E_n(\lambda) = \left\langle \Psi_n(\lambda) \middle| \hat{H}(\lambda) \middle| \Psi_n(\lambda) \right\rangle$. Prove the Hellmann–Feynman theorem,

$$\frac{\mathrm{d}E_n(\lambda)}{\mathrm{d}\lambda} = \left\langle \Psi_n(\lambda) \middle| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \middle| \Psi_n(\lambda) \right\rangle, \tag{10}$$

and conclude that $\langle \Psi_n(\lambda) | \hat{x}^2 | \Psi_n(\lambda) \rangle = \dfrac{2}{m\omega^2} \dfrac{\mathrm{d}E_n(\lambda)}{\mathrm{d}\lambda}$.

f) **[1 pt]** Explain why, according to Eqs. (2) and (9), $E_n(\lambda) = \sqrt{\lambda}\hbar\omega \left(n + \dfrac{1}{2}\right)$. **Hint**: introduce the λ-dependent frequency $\omega(\lambda) = \omega\sqrt{\lambda}$, rewrite $\hat{H}(\lambda)$ in terms of $\omega(\lambda)$ and compare the expression with the one in Eq. (2). Conclude from question 2. b).

g) **[1 pt]** Conclude from questions 2. d), e), and f) that $\langle \Psi_n | \hat{x}^2 | \Psi_n \rangle = \dfrac{\hbar}{m\omega} \left(n + \dfrac{1}{2}\right)$.

h) **[1 pt]** Deduce from questions 2. c) and g) that $\langle \Psi_n | \hat{p}_x^2 | \Psi_n \rangle = m\hbar\omega \left(n + \dfrac{1}{2}\right)$.

i) **[2 pts]** Verify from questions 2. a), g) and h) that the solutions to the Schrödinger equation for the one-dimensional harmonic oscillator fulfill the Heisenberg inequality in Eq. (1). What is remarkable about the ground state $|\Psi_0\rangle$?

3. Problem II: one-dimensional harmonic oscillator in the presence of a uniform and static electric field (4 points)

Let us consider a particle with charge q and mass m that is attached to a spring of constant k and that moves along the x axis. In the presence of a uniform and static electric field of intensity $\mathcal{E}$, the total Hamiltonian operator varies with $\mathcal{E}$ as follows, $\hat{H}(\mathcal{E}) = \hat{H} - q\mathcal{E}\hat{x}$, where the operators $\hat{H}$ and $\hat{x}$ are defined in Eqs. (4) and (7), respectively.

a) **[2 pts]** Let us introduce the $\mathcal{E}$-dependent creation and annihilation operators, $\hat{a}^\dagger(\mathcal{E}) = \hat{a}^\dagger - \dfrac{q\mathcal{E}}{\omega\sqrt{2m\hbar\omega}}$, and $\hat{a}(\mathcal{E}) = \hat{a} - \dfrac{q\mathcal{E}}{\omega\sqrt{2m\hbar\omega}}$. Show that $\left[\hat{a}(\mathcal{E}), \hat{a}^\dagger(\mathcal{E})\right] = 1$ and that the $\mathcal{E}$-dependent Hamiltonian can be rewritten as $\hat{H}(\mathcal{E}) = \hbar\omega \left(\hat{a}^\dagger(\mathcal{E})\hat{a}(\mathcal{E}) + \dfrac{1}{2}\right) - \dfrac{q^2\mathcal{E}^2}{2m\omega^2}$.

b) **[1 pt]** Conclude from the introduction of Problem I that the *exact* energies of the one-dimensional harmonic oscillator in the presence of the electric field are $E_n(\mathcal{E}) = \hbar\omega \left(n + \dfrac{1}{2}\right) - \dfrac{q^2\mathcal{E}^2}{2m\omega^2}$. **Hint:** let $|\Psi_n(\mathcal{E})\rangle$ be an eigenvector of $\hat{N}(\mathcal{E}) = \hat{a}^\dagger(\mathcal{E})\hat{a}(\mathcal{E})$. Explain why, according to question 3. a), the associated eigenvalue is an integer n and conclude.

c) **[1 pt]** Explain briefly why, for this particular system, perturbation theory through second order is *exact* for the energy.

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Problem I

a) $$\hat{a} = \frac{1}{\sqrt{2}}\left[\sqrt{\frac{m\omega}{\hbar}}\,\hat{x} + \frac{i}{\sqrt{m\hbar\omega}}\,\hat{p}_x\right] \longrightarrow \hat{a}^\dagger = \underbrace{\frac{1}{\sqrt{2}}}_{\in\mathbb{R}}\left[\underbrace{\sqrt{\frac{m\omega}{\hbar}}}_{\in\mathbb{R}}\,\hat{x}^\dagger + \left(\frac{i}{\sqrt{m\hbar\omega}}\right)^*\hat{p}_x^\dagger\right]$$

$$\Rightarrow \hat{a}^\dagger = \frac{1}{\sqrt{2}}\left[\sqrt{\frac{m\omega}{\hbar}}\,\hat{x} - \frac{i}{\sqrt{m\hbar\omega}}\,\hat{p}_x\right] \Rightarrow \begin{cases} \hat{a}^\dagger + \hat{a} = \frac{2}{\sqrt{2}}\sqrt{\frac{m\omega}{\hbar}}\,\hat{x} \\ \hat{a}^\dagger - \hat{a} = -\frac{2i}{\sqrt{2}}\frac{1}{\sqrt{m\hbar\omega}}\,\hat{p}_x \end{cases}$$

thus leading to $\boxed{\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}^\dagger + \hat{a}\right)}$ and $\boxed{\hat{p}_x = i\sqrt{\frac{m\hbar\omega}{2}}\left(\hat{a}^\dagger - \hat{a}\right)}$

Consequently $\langle\psi_n|\hat{x}|\psi_n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\langle\psi_n|\hat{a}^\dagger|\psi_n\rangle + \langle\psi_n|\hat{a}|\psi_n\rangle\right)$ and $\langle\psi_n|\hat{p}_x|\psi_n\rangle = i\sqrt{\frac{m\hbar\omega}{2}}\left(\langle\psi_n|\hat{a}^\dagger|\psi_n\rangle - \langle\psi_n|\hat{a}|\psi_n\rangle\right)$

where $\underset{=0}{\langle\psi_n|\hat{a}^\dagger|\psi_n\rangle} = \sqrt{n+1}\,\underbrace{\langle\psi_n|\psi_{n+1}\rangle}_{0 \text{ (orthonormal basis of eigenvectors)}}$ and $\langle\psi_n|\hat{a}|\psi_n\rangle = \langle\hat{a}\psi_n|\psi_n\rangle^* = \langle\psi_n|\hat{a}^\dagger|\psi_n\rangle^* = 0$

and therefore $\boxed{\langle\psi_n|\hat{x}|\psi_n\rangle = \langle\psi_n|\hat{p}_x|\psi_n\rangle = 0}$

b) $$\hat{H}|\psi_n\rangle = \hbar\omega\underbrace{\hat{N}|\psi_n\rangle}_{n|\psi_n\rangle} + \frac{\hbar\omega}{2}|\psi_n\rangle = \underbrace{\hbar\omega\left(n+\tfrac{1}{2}\right)}_{\text{eigenvalue } E_n \text{ (energy)}}\underbrace{|\psi_n\rangle}_{\text{eigenvector (or eigenstate)}}$$

c) Since $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \Rightarrow \langle\psi_n|\hat{H}|\psi_n\rangle = E_n\underbrace{\langle\psi_n|\psi_n\rangle}_{1}$

or, equivalently, $\frac{1}{2m}\langle\psi_n|\hat{p}_x^2|\psi_n\rangle + \frac{1}{2}m\omega^2\langle\psi_n|\hat{x}^2|\psi_n\rangle = E_n$

thus leading to $\langle\psi_n|\hat{p}_x^2|\psi_n\rangle = 2m\left[\hbar\omega\left(n+\frac{1}{2}\right) - \frac{1}{2}m\omega^2\langle\psi_n|\hat{x}^2|\psi_n\rangle\right]$

$$\Rightarrow \boxed{\langle\psi_n|\hat{p}_x^2|\psi_n\rangle = m\hbar\omega(2n+1) - m^2\omega^2\langle\psi_n|\hat{x}^2|\psi_n\rangle}$$

d) $\hat{H}(\lambda=1) = \hat{H} \longleftarrow$ Hamiltonian we are interested in.

e) $\hat{H}(\lambda)|\psi_n(\lambda)\rangle = E_n(\lambda)|\psi_n(\lambda)\rangle \Rightarrow E_n(\lambda) = \langle\psi_n(\lambda)|\hat{H}(\lambda)|\psi_n(\lambda)\rangle$ since $\boxed{\langle\psi_n(\lambda)|\psi_n(\lambda)\rangle = 1 \quad \forall\lambda}$. Therefore

$$\frac{dE_n(\lambda)}{d\lambda} = \left\langle\frac{d\psi_n(\lambda)}{d\lambda}\right|\underbrace{\hat{H}(\lambda)|\psi_n(\lambda)\rangle}_{E_n(\lambda)|\psi_n(\lambda)\rangle} + \langle\psi_n(\lambda)|\hat{H}(\lambda)\left|\frac{d\psi_n(\lambda)}{d\lambda}\right\rangle + \langle\psi_n(\lambda)|\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\psi_n(\lambda)\rangle$$

$$\left\langle\underbrace{\hat{H}(\lambda)\psi_n(\lambda)}_{E_n(\lambda)\psi_n(\lambda)}\right|\left.\frac{d\psi_n(\lambda)}{d\lambda}\right\rangle \rightarrow \underbrace{E_n^*(\lambda)}_{E_n(\lambda)}\left\langle\psi_n(\lambda)\left|\frac{d\psi_n(\lambda)}{d\lambda}\right.\right\rangle$$

Thus leading to $$\frac{dE_n(\lambda)}{d\lambda} = E_n(\lambda)\times\underbrace{\left[\left\langle\frac{d\psi_n(\lambda)}{d\lambda}\right|\psi_n(\lambda)\rangle + \langle\psi_n(\lambda)\left|\frac{d\psi_n(\lambda)}{d\lambda}\right\rangle\right]}_{\frac{d}{d\lambda}\left[\langle\psi_n(\lambda)|\psi_n(\lambda)\rangle\right] = \frac{d}{d\lambda}[1] = 0} + \langle\psi_n(\lambda)|\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\psi_n(\lambda)\rangle$$

Thus we obtain the Hellmann-Feynman theorem

$\boxed{\frac{dE_n(\lambda)}{d\lambda} = \langle\psi_n(\lambda)|\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\psi_n(\lambda)\rangle}$. Since $\frac{\partial\hat{H}(\lambda)}{\partial\lambda} = \frac{1}{2}m\omega^2\hat{x}^2$, it comes $\frac{dE_n(\lambda)}{d\lambda} = \langle\psi_n(\lambda)|\frac{1}{2}m\omega^2\hat{x}^2|\psi_n(\lambda)\rangle$

or, equivalently, $\boxed{\langle\psi_n(\lambda)|\hat{x}^2|\psi_n(\lambda)\rangle = \frac{2}{m\omega^2}\frac{dE_n(\lambda)}{d\lambda}}$

f) $\hat{H}(\lambda) = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m[\omega(\lambda)]^2\hat{x}^2$ where $\omega(\lambda) = \sqrt{\lambda}\,\omega$ i.e. $\omega^2(\lambda) = \lambda\omega^2$. It means that $\hat{H}(\lambda)$ is nothing but the Hamiltonian of the harmonic oscillator with frequency $\omega(\lambda)$. As a result, its energies are quantized as follows, $E_n(\lambda) = \hbar\omega(\lambda)\left(n+\frac{1}{2}\right)$ where $n\in\mathbb{N}$ or, equivalently, $\boxed{E_n(\lambda) = \sqrt{\lambda}\,\hbar\omega\left(n+\frac{1}{2}\right)}$.

g) $$\frac{dE_n(\lambda)}{d\lambda} = \frac{1}{2}\frac{1}{\sqrt{\lambda}}\hbar\omega\left(n+\frac{1}{2}\right) \xrightarrow[\lambda=1]{} \left.\frac{dE_n(\lambda)}{d\lambda}\right|_{\lambda=1} = \frac{\hbar\omega}{2}\left(n+\frac{1}{2}\right) \rightarrow \langle\underbrace{\psi_n(\lambda=1)}_{\psi_n!}|\hat{x}^2|\underbrace{\psi_n(\lambda=1)}_{\psi_n!}\rangle = \frac{\cancel{2}}{m\omega^2}\cdot\frac{\hbar\omega}{\cancel{2}}\left(n+\frac{1}{2}\right)$$ thus leading to $\boxed{\langle\psi_n|\hat{x}^2|\psi_n\rangle = \frac{\hbar}{m\omega}\left(n+\frac{1}{2}\right)}$.

h) $$\langle\psi_n|\hat{p}_x^2|\psi_n\rangle = m\hbar\omega(2n+1) - m^2\omega^2\cdot\frac{\hbar}{m\omega}\left(n+\frac{1}{2}\right) = m\hbar\omega(2n+1) - \frac{m\hbar\omega}{2}(2n+1) = \boxed{m\hbar\omega\left(n+\frac{1}{2}\right) = \langle\psi_n|\hat{p}_x^2|\psi_n\rangle}.$$

i) For $|\psi\rangle = |\psi_n\rangle$, $\Delta_x^2 = \langle\psi_n|\hat{x}^2|\psi_n\rangle - \underbrace{\langle\psi_n|\hat{x}|\psi_n\rangle}_{0}^2$ and $\Delta_{p_x}^2 = \langle\psi_n|\hat{p}_x^2|\psi_n\rangle - \underbrace{\langle\psi_n|\hat{p}_x|\psi_n\rangle}_{0}^2 \Rightarrow \Delta x = \sqrt{\frac{\hbar}{m\omega}\left(n+\frac{1}{2}\right)}$ and $\Delta p_x = \sqrt{m\hbar\omega\left(n+\frac{1}{2}\right)}$

Thus leading to $\Delta x.\Delta p_x = \sqrt{\frac{\hbar}{m\omega}}\cdot\sqrt{m\hbar\omega}\left(n+\frac{1}{2}\right) = \boxed{\hbar\left(n+\frac{1}{2}\right) = \Delta x\Delta p_x} \Rightarrow \Delta x\Delta p_x = \frac{\hbar}{2} + n\hbar \geqslant \frac{\hbar}{2}$.

Conclusion: indeed, $|\psi_n\rangle$ fulfills the Heisenberg inequality. Interestingly, the lower bound $\frac{\hbar}{2}$ is reached exactly when $n=0$ i.e. when the particle is in the ground state of the harmonic oscillator.

Problem II

a) $$[\hat a(\mathcal{E}), \hat a^\dagger(\mathcal{E})] = \hat a(\mathcal{E})\,\hat a^\dagger(\mathcal{E}) - \hat a^\dagger(\mathcal{E})\,\hat a(\mathcal{E}) = \left(\hat a - \frac{q\mathcal{E}}{\omega\sqrt{2m\hbar\omega}}\hat{\mathbb{1}}\right)\left(\hat a^\dagger - \frac{q\mathcal{E}}{\omega\sqrt{2m\hbar\omega}}\hat{\mathbb{1}}\right)$$

$$- \left(\hat a^\dagger - \frac{q\mathcal{E}}{\omega\sqrt{2m\hbar\omega}}\hat{\mathbb{1}}\right)\left(\hat a - \frac{q\mathcal{E}}{\omega\sqrt{2m\hbar\omega}}\hat{\mathbb{1}}\right)$$

$$\left.\begin{array}{l} = \hat a\hat a^\dagger \cancel{- \frac{q\mathcal{E}}{\omega\sqrt{2m\hbar\omega}}\hat a} \cancel{- \frac{q\mathcal{E}}{\omega\sqrt{2m\hbar\omega}}\hat a^\dagger} \cancel{+ \frac{q^2\mathcal{E}^2}{2\omega^3 m\hbar}\hat{\mathbb{1}}} \\ - \hat a^\dagger\hat a \cancel{+ \frac{q\mathcal{E}}{\omega\sqrt{2m\hbar\omega}}\hat a^\dagger} \cancel{+ \frac{q\mathcal{E}}{\omega\sqrt{2m\hbar\omega}}\hat a} \cancel{- \frac{q^2\mathcal{E}^2}{2m\hbar\omega^3}\hat{\mathbb{1}}} \end{array}\right\} \begin{array}{l}\hat a\hat a^\dagger \\ -\hat a^\dagger\hat a\end{array}$$

$$= [\hat a, \hat a^\dagger]$$

Therefore $\boxed{[\hat a(\mathcal{E}), \hat a^\dagger(\mathcal{E})] = 1}$ Ⓐ

Moreover,

$$\hbar\omega\left(\hat a^\dagger(\mathcal{E})\hat a(\mathcal{E}) + \frac{1}{2}\right) = \hbar\omega\left(\hat a^\dagger\hat a + \frac{1}{2}\right) - \underbrace{\underbrace{\hbar\cancel{\omega}\cdot\frac{q\mathcal{E}}{\cancel{\omega}\sqrt{2m\hbar\omega}}}_{q\mathcal{E}\cdot\sqrt{\frac{\hbar}{2m\omega}}}(\hat a^\dagger + \hat a)}_{q\mathcal{E}\hat x} + \hbar\omega\cdot\frac{q^2\mathcal{E}^2}{2m\hbar\omega^3} = \underbrace{\hat H - q\mathcal{E}\hat x}_{\hat H(\mathcal{E})} + \frac{q^2\mathcal{E}^2}{2m\omega^2},$$

Thus leading to $\boxed{\hat H(\mathcal{E}) = \hbar\omega\left(\hat a^\dagger(\mathcal{E})\hat a(\mathcal{E}) + \frac{1}{2}\right) - \frac{q^2\mathcal{E}^2}{2m\omega^2}}$.

b) According to Eq. Ⓐ, the eigenvalues of $\hat a^\dagger(\mathcal{E})\,\hat a(\mathcal{E}) = \hat N(\mathcal{E})$ are integers n $(n = 0, 1, 2, \ldots)$. If we denote $|\psi_n(\mathcal{E})\rangle$ the associated eigenvectors then

$$\hat H(\mathcal{E})|\psi_n(\mathcal{E})\rangle = \hbar\omega\,\hat N(\mathcal{E})\,|\psi_n(\mathcal{E})\rangle + \frac{\hbar\omega}{2}|\psi_n(\mathcal{E})\rangle - \frac{q^2\mathcal{E}^2}{2m\omega^2}|\psi_n(\mathcal{E})\rangle$$

$$= \underbrace{\left(\hbar\omega\left(n + \frac{1}{2}\right) - \frac{q^2\mathcal{E}^2}{2m\omega^2}\right)}_{E_n(\mathcal{E})}|\psi_n(\mathcal{E})\rangle$$

c) A perturbation expansion of the energy (where the electric field is treated as a perturbation i.e. $\mathcal{E}$ is "small") would read as follows,

$$E_n(\mathcal{E}) = \underbrace{E_n(\mathcal{E}=0)}_{E_n = (n+\frac{1}{2})\hbar\omega} + \tilde E_n^{(1)}\mathcal{E} + \tilde E_n^{(2)}\mathcal{E}^2 + \tilde E_n^{(3)}\mathcal{E}^3 + \ldots\ldots \quad \text{where} \quad \boxed{\tilde E_n^{(k)} = \frac{1}{k!}\frac{d^k E_n(\mathcal{E})}{d\mathcal{E}^k}\bigg|_{\mathcal{E}=0}}$$

$\boxed{k \geqslant 1}$

The latter expression should be compared with the exact expression (which is valid even when the electric field is strong!)

$$E_n(\mathcal{E}) = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{q^2\mathcal{E}^2}{2m\omega^2} \Rightarrow \tilde E_n^{(1)} = 0, \quad \tilde E_n^{(2)} = -\frac{q^2}{2m\omega^2} \quad \text{and} \quad \tilde E_n^{(k)} = 0 \ \text{for } k \geqslant 3!$$

Conclusion: in this particular case, the energy obtained through second order is exact.