Harmonic oscillator - Vibration energy of molecules

The energy of a molecule is approximately the sum of the energies of translation of the electrons (kinetic energy), of inter-atomic vibration, of rotation of the molecule and that of the electronic states. The optical spectroscopy, i.e. the interaction of electromagnetic radiation with atoms or molecules, is one of the most important experimental techniques for investigating the structure of atoms and molecules. Indeed, essential informations are given by the absorption properties of molecules in different range of the electromagnetic spectrum, i.e. in different energy ranges related to each component of the energy of the molecules.

For instance, the electronic absorption spectra (UV-vis) are characteristic of the electronic states that will be studied during the second semester. The microwave absorption spectroscopy gives insight into the rotation of the molecules and, using a simple model, where the molecule is a rigid rotator, it is possible to evaluate the rotation energy, inertia moments or inter-atomic bond lengths. The energy levels of the vibration of a molecule and the rigidity of the inter-atomic bonds are investigated by using infrared spectroscopy. In that case, a simple model is the harmonic oscillator, whose potential energy is a good approximation of the inter-atomic potential around its minimum, in the vicinity of the equilibrium inter-atomic distance. For real case, it is necessary to consider the 3 dimensions of the space and the coupling between these motions.
In this tutorial, we will treat the vibrations of a molecule by considering only 1 dimension.

1. Definitions

One calls harmonic oscillator a particle moving in a potential $V(x) = \frac{1}{2}kx^2$ with $k > 0$. Such a particle is subject to a withdrawing force $F = -\frac{dV}{dx} = -kx$. The classical movement of such a particle of mass m is sinusoidal with pulsation $\omega = \sqrt{\frac{k}{m}}$. These movements arise anytime a particle vibrates around its equilibrium position since, at this position, the potential minimum may be approximated by a harmonic-like potential as given above.

a) Write the classical expression of the total energy of a 1D harmonic oscillator as a function of the position x and the impulsion p_x. Deduce the expression of the related Hamiltonian $\hat{H}$ related to the particle in quantum mechanics.

b) The following operators are used :
$\hat{X} = \sqrt{\frac{m\omega}{\hbar}}\hat{x}; \quad \hat{P}_x = \frac{1}{\sqrt{m\hbar\omega}}\hat{p}_x.$
Express the Hamiltonian $\hat{H}$ in terms of $\hat{X}$, $\hat{P}_x$ and ω. Verify that $[\hat{X}, \hat{P}_x] = i$.

c) In order to solve the problem, operators $\hat{a}$ and $\hat{a}^\dagger$ are introduced:
$\hat{a} = \frac{1}{\sqrt{2}}(\hat{X} + i\hat{P}_x); \quad \hat{a}^\dagger = \frac{1}{\sqrt{2}}(\hat{X} - i\hat{P}_x)$ (annihilation and creation operators).
Prove that $\hat{a}^\dagger$ is the adjoint of $\hat{a}$ (**hint:** use the fact that $\hat{p}_x$ and $\hat{x}$ are hermitians).
Show that $[\hat{a}, \hat{a}^\dagger] = 1$. Are $\hat{a}$ and $\hat{a}^\dagger$ associated to observables ?

d) Let $\hat{N} = \hat{a}^\dagger\hat{a}$ denote the so-called "counting operator". Show that $\hat{N}$ is hermitian and give its expression in terms of $\hat{X}$ and $\hat{P}_x$. Deduce the expression of the Hamiltonian in terms of $\hat{N}$ and ω. Conclude that the eigenvectors of $\hat{N}$ are eigenvectors of $\hat{H}$.

2. Solutions of the Schrödinger equation

a) Using questions 1.c) and 1.d), prove that $[\hat{N}, \hat{a}] = -\hat{a}$ and $[\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger$.

b) Let $|\Psi_\lambda\rangle$ be an eigenvector of $\hat{N}$ associated to the eigenvalue λ. Show that $\lambda \in \mathbb{R}^+$.

c) Show that for $\lambda \neq 0$, $\hat{a}|\Psi_\lambda\rangle$ is eigenvector of $\hat{N}$ with associated eigenvalue $\lambda - 1$. Show that $\hat{a}^\dagger|\Psi_\lambda\rangle$ is eigenvector of $\hat{N}$ with associated eigenvalue $\lambda + 1$. Justify the names "creation operator" and "annihilation operator" given to $\hat{a}^\dagger$ and $\hat{a}$ respectively.

d) Let us assume that λ is not an integer: it can therefore be written as $\lambda = m + q$ where $m \in \mathbb{N}$ and $0 < q < 1$. Let $|\Psi_\lambda^{m+1}\rangle = \hat{a}^{m+1}|\Psi_\lambda\rangle$. Show that $|\Psi_\lambda^{m+1}\rangle$ is eigenvector of $\hat{N}$ associated to $q - 1$. Conclude.

e) Show that all eigenvectors $|\Psi_n\rangle$ $(n \in \mathbb{N})$ of $\hat{N}$ can be obtained from the state $|\Psi_0\rangle$, usually referred to as "vacuum state", where $\hat{a}|\Psi_0\rangle = 0$.

f) Write the equation fulfilled by the wave function $\Psi_0(x)$ using questions 1.b), 1.c), and 2.e). Show that the solution is unique and give the expression of $\Psi_0(x)$ [**hint:** $\int_{-\infty}^{+\infty} dx\, e^{-\alpha x^2} = \sqrt{\dfrac{\pi}{\alpha}}$].

g) Give the eigenvalues (that are the energies of the 1D harmonic oscillator) and the corresponding eigenvectors of the Hamiltonian $\hat{H}$. Are the energies degenerate ? Calculate the energy difference between two successive levels and comment the result.

h) Is the energy of the vacuum state equal to zero ?

3. Application to diatomic molecules

The oscillation of the molecule HI around the equilibrium positions of the atoms may be modeled by an harmonic oscillator with mass $m = M_H$ (the iodine atom is quasi motionless) and force constant $k = 313.8$ N.m^{-1}. Calculate the frequency ν_0 of the oscillator. Evaluate the difference between two adjacent energy levels. Calculate the wavelength of light necessary to induce a transition between two contiguous levels. In which range of the spectrum of light is this wavelength ? It can be shown that the only allowed transitions are between contiguous levels (selection rules). Thus a given wavelength is characteristic of a given inter-atomic bond. It is the principle of spectroscopy. $M_H = 1.674\ 10^{-27}$ kg ; $h = 6.626\ 10^{-34}$ J.s ; $\hbar = h/2\pi = 1.054\ 10^{-34}$ J.s ; $c = 2.997\ 10^8$ m.s^{-1}. Avogadro's number : $N = 6.022\ 10^{23}$ mol^{-1}.

4. Model of the point charge elastically bound, in an electric field

One considers a particle (of charge q and mass m) which is bound to a nucleus, in the presence of a static electric field $\overrightarrow{\mathcal{E}} = \mathcal{E}\overrightarrow{e_x}$. This charge interacts with the nucleus through a potential energy $V(x) = m\omega^2 x^2/2$ where x denotes its position with respect to the nucleus and ω is a characteristic pulsation. This model is that of the elastically bound particle. The interaction energy between the bound system (particle+nucleus) and the electric field equals in classical mechanics $W = -q\mathcal{E}x$ (the nucleus is assumed to be at the fixed position $x = 0$). Write the Hamiltonian $\hat{H}(\mathcal{E})$ of the system in the presence of the electric field.

Using a variable change $u = x - x_0$, show that the Schrödinger equation is equivalent to that of a 1D harmonic oscillator (give the value of x_0). Give the possible values $E_n(\mathcal{E})$ of the energy as well as the corresponding eigenfunctions $\Psi_n(\mathcal{E})$. Let $\hat{D} = q\hat{x}$ denote the dipole moment operator and $\langle\hat{D}\rangle_{\Psi_n(\mathcal{E})} = \langle\Psi_n(\mathcal{E})|\hat{D}|\Psi_n(\mathcal{E})\rangle$ the expectation value for $\hat{D}$ in the state $|\Psi_n(\mathcal{E})\rangle$ with $\langle\Psi_n(\mathcal{E})|\Psi_n(\mathcal{E})\rangle = 1$. Prove the Hellmann-Feynman theorem:

$$\frac{dE_n(\mathcal{E})}{d\mathcal{E}} = -\langle\hat{D}\rangle_{\Psi_n(\mathcal{E})}.$$

Deduce the value of $\langle \hat{D} \rangle_{\Psi_n(\mathcal{E})}$ and show that the so-called "static polarisability" of the bound system $\alpha(0) = \frac{d \langle \hat{D} \rangle_{\Psi_n(\mathcal{E})}}{d\mathcal{E}} \bigg|_{\mathcal{E}=0}$ equals $\frac{q^2}{m\omega^2}$. What is the expectation value of the position $\hat{x}$ in the presence of the electric field ?

1-a) $E_{tot} = \frac{1}{2m} P_x^2 + \frac{1}{2} k x^2$ $\hat{H} = \frac{\hat{P}_x^2}{2m} + \frac{1}{2} k \hat{x}^2 = \frac{\hat{P}_x^2}{2m} + \frac{1}{2} \omega^2 m \hat{x}^2$

b) $\hat{X} = \sqrt{\frac{m\omega}{\hbar}} \hat{x}$, $\hat{P}_x = \frac{1}{\sqrt{m\hbar\omega}} \hat{P}_x$; $\hat{H} = \hbar\omega \left(\frac{1}{2} \hat{P}_x^2 + \frac{1}{2} \hat{X}^2 \right)$

$[\hat{x}, \hat{P}_x] \Psi = \sqrt{\frac{m\omega}{\hbar}} \hat{x} \cdot \frac{1}{\sqrt{m\hbar\omega}} \frac{\hbar}{i} \frac{\partial \Psi(x)}{\partial x} - \sqrt{\frac{m\omega}{\hbar}} \frac{1}{\sqrt{m\hbar\omega}} \frac{\hbar}{i} \frac{\partial}{\partial x}(x \Psi(x))$

$= -\frac{1}{i} \Psi(x) = i \Psi(x) \Rightarrow [\hat{x}, \hat{P}_x] = i$

c) Rappel: $(\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$, $(\hat{A} + i\hat{B})^\dagger = \hat{A}^\dagger - i\hat{B}^\dagger$; $(AB)^\dagger = B^\dagger A^\dagger$

$\hat{x}$ et $\hat{P}_x$ hermitiques donc $\hat{x}^\dagger = \hat{x}$ et $\hat{P}_x^\dagger = \hat{P}_x$

$(\hat{a})^\dagger = \frac{1}{\sqrt{2}} (\hat{x}^\dagger - i\hat{P}_x^\dagger) = \frac{1}{\sqrt{2}} (\hat{x} - i\hat{P}_x) = \hat{a}^\dagger$ $\hat{a}$ et $\hat{a}^\dagger$ sont adjoints

$[\hat{a}, \hat{a}^\dagger] \Psi(x) = \left[\frac{1}{\sqrt{2}} (\hat{x} + i\hat{P}_x) \frac{1}{\sqrt{2}} (\hat{x} - i\hat{P}_x) - \frac{1}{2} (\hat{x} - i\hat{P}_x)(\hat{x} + i\hat{P}_x) \right] \Psi(x)$

$= \frac{1}{2} \left(\hat{x}^2 \Psi(x) + i \hat{P}_x \hat{x} \Psi(x) - i \hat{x} \hat{P}_x \Psi(x) + \hat{P}_x^2 \Psi(x) \right)$

$- \frac{1}{2} \left(\hat{x}^2 \Psi(x) - i \hat{P}_x \hat{x} \Psi(x) + i \hat{x} \hat{P}_x \Psi(x) + \hat{P}_x^2 \Psi(x) \right)$

$= i [\hat{P}_x, \hat{x}] \Psi(x) = i (-i) \Psi(x) = \Psi(x) \Rightarrow [\hat{a}, \hat{a}^\dagger] = 1$

$\hat{a}$ et $\hat{a}^\dagger$ ne sont pas hermitiques $\Rightarrow$ pas associés à des observables

d) $\hat{N} = \hat{a}^\dagger \hat{a}$, $\hat{N}^\dagger = (\hat{a}^\dagger \hat{a})^\dagger = \hat{a}^\dagger (\hat{a}^\dagger)^\dagger = \hat{a}^\dagger \hat{a} = \hat{N}$

$\Rightarrow \hat{N}$ est hermitique

$\hat{N} = \frac{1}{2} (\hat{x} - i\hat{P}_x)(\hat{x} + i\hat{P}_x) = \frac{1}{2} (\hat{x}^2 + i[\hat{x}, \hat{P}_x] + \hat{P}_x^2) = \frac{1}{2} (\hat{x}^2 + \hat{P}_x^2 - 1)$

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

$|\Psi\rangle$ vecteur propre de $\hat{N}$ $\Rightarrow$ $\hat{N}|\Psi\rangle = \lambda|\Psi\rangle \Leftrightarrow \hbar\omega \hat{N}|\Psi\rangle = \hbar\omega \lambda|\Psi\rangle$

$\Leftrightarrow \hbar\omega (\hat{N} + \frac{1}{2})|\Psi\rangle = \hbar\omega (\lambda + \frac{1}{2})|\Psi\rangle \Leftrightarrow \hat{H}|\Psi\rangle = E|\Psi\rangle$

$|\Psi\rangle$ est vecteur propre de $\hat{N}$, de valeur propre λ et vecteur propre de $\hat{H}$, de valeur propre $E = \hbar\omega(\lambda + \frac{1}{2})$

$\Rightarrow$ si l'on calcule λ, on pourra calculer l'énergie du système .

2)a) $[\hat{N}, \hat{a}] \Psi = \hat{N}\hat{a}\Psi - \hat{a}\hat{N}\Psi = (\hat{a}^\dagger\hat{a}\hat{a} - \hat{a}\hat{a}^\dagger\hat{a})\Psi$

$= ([\hat{a}, \hat{a}^\dagger]\hat{a})\Psi = -\hat{a}\Psi$, $[\hat{N}, \hat{a}] = -\hat{a}$

$[\hat{N}, \hat{a}^\dagger]\Psi = (\hat{N}\hat{a}^\dagger - \hat{a}^\dagger\hat{N})\Psi = (\hat{a}^\dagger\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}^\dagger\hat{a})\Psi = \hat{a}^\dagger[\hat{a}, \hat{a}^\dagger]\Psi = \hat{a}^\dagger\Psi$

$\Leftrightarrow [\hat{N}, \hat{a}^\dagger] = +\hat{a}^\dagger$

b) $\hat{N}$ est hermitique $\Leftrightarrow \lambda \in \mathbb{R}$

$\hat{N}|\Psi_\lambda\rangle = \lambda|\Psi_\lambda\rangle = \hat{a}^\dagger\hat{a}|\Psi_\lambda\rangle$ } $\times \langle\Psi_\lambda|$

$\Leftrightarrow \lambda \langle\Psi_\lambda|\Psi_\lambda\rangle = \langle\Psi_\lambda|\hat{a}^\dagger\hat{a}|\Psi_\lambda\rangle$

$\Leftrightarrow \lambda \underbrace{\langle\Psi_\lambda|\Psi_\lambda\rangle}_{>0} = \underbrace{\|\hat{a}|\Psi_\lambda\rangle\|^2}_{>0}$ $\Leftrightarrow \lambda \geq 0$

Rq: si $\lambda = 0$, $\|\hat{a}|\Psi_\lambda\rangle\|^2 = 0 \Leftrightarrow \hat{a}|\Psi_\lambda\rangle = 0$

c) de même si $\lambda \neq 0$, $\hat{a}|\Psi_\lambda\rangle \neq 0$ $([\hat{N}, \hat{a}] = -\hat{a})$

$\hat{a}|\Psi_\lambda\rangle$ est vecteur propre de $\hat{N}$: $\hat{N}\hat{a}|\Psi_\lambda\rangle = -\hat{a}|\Psi_\lambda\rangle + \hat{a}\hat{N}|\Psi_\lambda\rangle$

$= -\hat{a}|\Psi_\lambda\rangle + \hat{a}\lambda|\Psi_\lambda\rangle$

$\hat{N}\hat{a}|\Psi_\lambda\rangle = (\lambda - 1)\hat{a}|\Psi_\lambda\rangle$

$\Rightarrow$ valeur propre associée à $|\Psi_\lambda\rangle$:
$(\lambda - 1)$

si $\lambda \neq 0$ $\hat{a}^\dagger|\Psi_\lambda\rangle \neq 0$

et $\hat{N}\hat{a}^\dagger|\Psi_\lambda\rangle = \hat{a}^\dagger|\Psi_\lambda\rangle + \hat{a}^\dagger\hat{N}|\Psi_\lambda\rangle = (\lambda + 1)\hat{a}^\dagger|\Psi_\lambda\rangle$

$\hat{a}^\dagger$ opérateur création, si on l'applique à $|\Psi_\lambda\rangle$, on passe du niveau λ à $\lambda + 1$

$\hat{a}$ opérateur annihilation, ——— $|\Psi_\lambda\rangle$, ——— λ à $\lambda - 1$

d) Supposons λ non entier $\Leftrightarrow \lambda = m + q$ avec $m \in \mathbb{N}$ et $0 < q < 1$

$\hat{a}|\Psi_\lambda\rangle$ est vecteur propre de $\hat{N}$, de valeur propre $\lambda - 1$

$\hat{a}^2|\Psi_\lambda\rangle$ est vecteur propre de $\hat{N}$, de valeur propre $\lambda - 2$

$\hat{a}^{m+1}|\Psi_\lambda\rangle$ ——— $\hat{N}$, ——— $\lambda - m - 1$

or $\lambda = m + q$ avec $0 < q < 1$ donc $\lambda - m - 1 < 0$, ce qui n'est pas possible puisque les valeurs propres $\in \mathbb{R}^+$.

Donc λ ne peut pas ne pas être entier $\Rightarrow \lambda \in \mathbb{N}$

2) d) Que se passe-t-il si $\lambda = m \in \mathbb{N}$? (3 /)

$\hat{a}^m |\Psi_\lambda\rangle$ est vecteur propre de $\hat{N}$, de valeur propre $\lambda - m = 0$

d'après 2)b) on sait que $\hat{a}^{m+1}|\Psi_\lambda\rangle = 0$

$\Rightarrow$ dans ce cas on n'obtient pas de $|\Psi\rangle$ non nul vecteur propre de $\hat{N}$ de valeur propre < 0 $\Rightarrow$ c'est possible $\Rightarrow m \in \mathbb{N}$.

e) $\hat{a}^m |\Psi_\lambda\rangle$ est le vecteur propre $|\Psi_0\rangle$ de valeur propre $\lambda = 0$

si j'applique $\hat{a}^+$ à $|\Psi_0\rangle$ j'ai $\hat{a}^+|\Psi_0\rangle$ ———— $\lambda = 1$

$\hat{a}^{+2}|\Psi_0\rangle$ ———— $\lambda = 2$

$\vdots$

et $\forall k \in \mathbb{N}$, $\hat{a}^{+k}|\Psi_0\rangle$ ———— $\lambda = k$

donc tous les vecteurs propres $|\Psi_m\rangle$ peuvent être obtenus en appliquant $\hat{a}^+$, à partir de $|\Psi_0\rangle$

f) Pour $\lambda = 0$, $\hat{a}|\Psi_0\rangle = 0 \iff \frac{1}{\sqrt{2}}(\hat{X} + i\hat{P}_x)|\Psi_0\rangle = 0$

$\iff \sqrt{\frac{m\omega}{\hbar}}\, x\, \Psi_0(x) + \frac{i}{\sqrt{m\hbar\omega}}\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi_0(x) = 0$

$\iff \frac{m\omega}{\hbar} x\, dx = -\frac{d\Psi_0(x)}{\Psi_0(x)}$

$\iff \Psi_0(x) = K\, e^{-\frac{1}{2}\frac{m\omega}{\hbar}x^2}$

$\Rightarrow$ La solution est unique car toutes les fonctions solutions de l'équation sont proportionnelles entre elles.

$\Rightarrow$ normalisation $\displaystyle\int_{-\infty}^{+\infty}\Psi_0^*\Psi_0\, dx = \int_{-\infty}^{+\infty}K^2 e^{-\frac{m\omega}{\hbar}x^2} = K^2\sqrt{\frac{\pi\hbar}{m\omega}} = 1$

$\iff K = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$

$\Rightarrow \boxed{\Psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}}$

g) Les valeurs propres de $\hat{H}$ sont $\hbar\omega\left(m+\frac{1}{2}\right)$ avec $m \in \mathbb{N}$ (cf question 1.d)

$\Rightarrow$ pour $m = 0$: $E_0 = \frac{\hbar\omega}{2}$ et $\Psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}$

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2) g) (suite) On construit les autres fonctions d'onde à partir de Ψ_0, en (4 /)
utilisant $\hat{a}^+$

$$|\Psi_1\rangle = \frac{\hat{a}^+|\Psi_0\rangle}{\sqrt{\langle\hat{a}^+\Psi_0|\hat{a}^+\Psi_0\rangle}} = \underbrace{\frac{\hat{a}^+|\Psi_0\rangle}{\sqrt{\langle\Psi_0|\hat{a}\hat{a}^+|\Psi_0\rangle}}}_{\text{normalisation}}$$

or $\hat{a}\hat{a}^+ = 1 + \hat{a}^+\hat{a} = 1 + \hat{N} \iff \langle\Psi_0|1+\hat{N}|\Psi_0\rangle = (1+0)\underbrace{\langle\Psi_0|\Psi_0\rangle}_{1}$

$\iff |\Psi_1\rangle = \frac{\hat{a}^+|\Psi_0\rangle}{\sqrt{1}}$ avec $E_1 = \hbar\omega\left(1+\frac{1}{2}\right) = \frac{3}{2}\hbar\omega$

de même $|\Psi_2\rangle = \frac{\hat{a}^+|\Psi_1\rangle}{\sqrt{\langle a^+\Psi_1|a^+\Psi_1\rangle}} = \frac{\hat{a}^{+2}|\Psi_0\rangle}{\sqrt{1\times 2}}$ avec $E_2 = \hbar\omega\left(2+\frac{1}{2}\right) = \frac{5}{2}\hbar\omega$

$$|\Psi_m\rangle = \frac{(\hat{a}^+)^m|\Psi_0\rangle}{\sqrt{m!}}$$ avec $E_m = \hbar\omega\left(m+\frac{1}{2}\right)$

$\hookrightarrow$ ce sont les polynômes d'Hermite.

Dégénérescence ? supposons $|\Psi_m\rangle$ vecteur propre de $\hat{N}$ de valeur propre m et non dégénéré

$$\hat{N}|\Psi_m\rangle = m|\Psi_m\rangle$$

est-ce que $|\Psi_{m+1}\rangle$ est également non dégénéré ?

on sait que $\hat{a}|\Psi_{m+1}\rangle$ est vecteur propre de $\hat{N}$, de valeur propre m

or, on suppose $|\Psi_m\rangle$ non dégénéré donc $|\Psi_m\rangle$ et $\hat{a}|\Psi_{m+1}\rangle$ sont proportionnels

$\hat{a}|\Psi_{m+1}\rangle = C\,|\Psi_m\rangle$

$\iff \hat{a}^+\hat{a}|\Psi_{m+1}\rangle = C\,\hat{a}^+|\Psi_m\rangle$

$\iff \hat{N}|\Psi_{m+1}\rangle = C\,\hat{a}^+|\Psi_m\rangle$

$\iff (m+1)|\Psi_{m+1}\rangle = C\,\hat{a}^+|\Psi_m\rangle$

$\iff |\Psi_{m+1}\rangle = \frac{C}{m+1}\hat{a}^+|\Psi_m\rangle$

$\iff \hat{a}^+|\Psi_m\rangle$ et $|\Psi_{m+1}\rangle$ sont proportionnels et associés à la même valeur propre
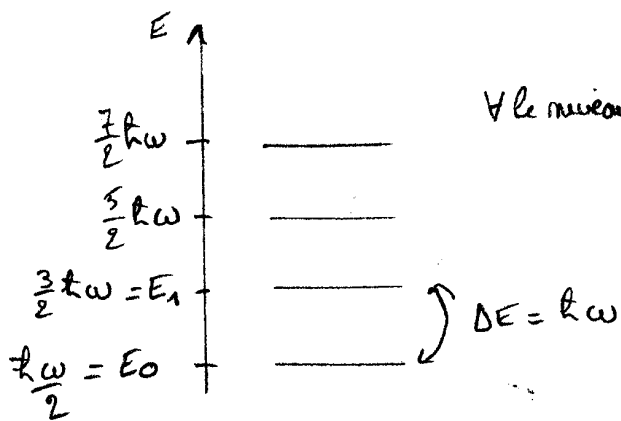
$\Rightarrow |\Psi_{m+1}\rangle$ non dégénéré.

or $|\Psi_0\rangle$ est non dégénéré $\Rightarrow |\Psi_1\rangle$ est non dégénéré
$\Rightarrow |\Psi_2\rangle$ ————
$\Rightarrow |\Psi_m\rangle$ est non dégénéré

Énergie entre deux niveaux successifs = $\Delta E = E_{m+1} - E_m = \hbar\omega$
ne dépend pas de m

E

$\frac{7}{2}\hbar\omega$ ——

$\frac{5}{2}\hbar\omega$ ——

$\frac{3}{2}\hbar\omega = E_1$ ——

$\frac{\hbar\omega}{2} = E_0$ —— $\Big\}\ \Delta E = \hbar\omega$

$\forall$ le niveau, pour passer au niveau supérieur, on absorbe toujours le même énergie $\hbar\omega$, donc le spectre d'absorption de vibration ne contient qu'une bande d'absorption correspondant à cette énergie.

(seule transition permise)

2)h) L'énergie de l'état fondamental (appelé aussi l'énergie du vide), n'est pas nulle !

3) Molécule H-I , $k = 313,8\ N\ m^{-1} = \omega^2 m \implies \omega = \sqrt{\dfrac{k}{m}}$

fréquence de l'oscillateur : $\nu_0 = \dfrac{\omega}{2\pi} = 6,89 \cdot 10^{13}\ Hz$ et $\Delta E = \hbar\omega = \nu_0 h = 4,56 \cdot 10^{-20} J$

$E = \dfrac{hc}{\lambda} \implies \lambda = 4,35 \cdot 10^{-6}\ m \ \hat{=}\ \dfrac{1}{\lambda} = \dfrac{\nu_0}{c} = 2299\ cm^{-1}$

on observe une bande d'absorption caractéristique de la vibration de la liaison H-I dans l'infra-rouge.

4 - Model of the point charge elastically bound, in an electric field

$$\hat{H}(\mathcal{E}) = \frac{\hat{p_x}^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2 - q\mathcal{E}\hat{x}$$

- Schrödinger equation $\quad \hat{H}(\mathcal{E})\chi = E(\mathcal{E})\chi$

  energy in the presence of the electric field

  wave function in the presence of the electric field

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \chi - q\mathcal{E}x\chi = E(\mathcal{E})\chi$$

Since $\quad \frac{1}{2}m\omega^2 x^2 - q\mathcal{E}x = \frac{1}{2}m\omega^2\left(x^2 - \frac{2q\mathcal{E}}{m\omega^2}x\right)$

$$= \frac{1}{2}m\omega^2\left[\left(x - \frac{q\mathcal{E}}{m\omega^2}\right)^2 - \frac{q^2\mathcal{E}^2}{m^2\omega^4}\right]$$

$$(1) \Leftrightarrow \boxed{-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + \frac{1}{2}m\omega^2(x-x_0)^2\chi = \left(E(\mathcal{E}) + \frac{1}{2}\frac{q^2\mathcal{E}^2}{m\omega^2}\right)\chi}$$

Let $x_0 = \frac{q\mathcal{E}}{m\omega^2}$, $E' = E(\mathcal{E}) + \frac{1}{2}\frac{q^2\mathcal{E}^2}{m\omega^2}$ (2)

Change of variable $\quad u = x - x_0$

$$\chi(x) = \chi(u+x_0) = \Phi(u)$$

$$\left.\frac{d\Phi}{du}\right|_u = \left.\frac{d\chi}{dx}\right|_{u+x_0} \quad \text{and} \quad \left.\frac{d^2\Phi}{du^2}\right|_u = \left.\frac{d^2\chi}{dx^2}\right|_{u+x_0}$$

Therefore (1) can be rewritten as

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\Phi}{du^2} + \frac{1}{2}m\omega^2 u^2 \Phi = E'\Phi} \quad (3)$$

(3) is formally identical to the Schrödinger equation of a 1D harmonic oscillator of energy E' and corresponding eigenfunction Φ.

- We know from section 2 that E' is quantized and can be written as $\quad E'_n = (n+\frac{1}{2})\hbar\omega \quad n\in\mathbb{N}$

According to (2), the energy of a 1D harmonic oscillator in the presence of a static electric field is quantized and equals

$$E_n(\mathcal{E}) = E'_n - \frac{1}{2}\frac{q^2\mathcal{E}^2}{m\omega^2}$$

$$\boxed{E_n(\mathcal{E}) = (n+\frac{1}{2})\hbar\omega - \frac{1}{2}\frac{q^2\mathcal{E}^2}{m\omega^2} \quad, \quad n\in\mathbb{N}}$$

. From section 2 we know that the eigenfunction Φ_m associated to E_m'

is equal to ψ_m ($\leftarrow$ we explained previously how it can be

obtained from the creation operator $\hat{a}^+$ and the vacuum wave function ψ_0)

$$\Phi_m(u) = \psi_m(u) = \chi_m(u + x_0)$$

Therefore the eigenfunction χ_m of the bound system in the presence

of the electric field, associated to $E_n(\mathcal{E})$, is equal to:

$$\boxed{\chi_m(x) = \psi_m(x - x_0)} \qquad (4)$$

In the following we denote $\psi_n(\mathcal{E}) = \chi_m$ $\leftarrow$ depends on $\mathcal{E}$ since $x_0 = \dfrac{q\mathcal{E}}{m\omega^2}$

We thus rewrite the Schrödinger equation as

$$\hat{H}(\mathcal{E})\,\psi_m(\mathcal{E}) = E_n(\mathcal{E})\,\psi_m(\mathcal{E}) \qquad \forall \mathcal{E}.$$

$$\Rightarrow \quad \dot{E}_n(\mathcal{E})\,\langle \psi_m(\mathcal{E})|\psi_m(\mathcal{E})\rangle = \langle \psi_m(\mathcal{E})|\hat{H}(\mathcal{E})|\psi_m(\mathcal{E})\rangle$$

Comment: Note that χ_m is normalized since, according to Eq.(4)

$$\langle \chi_m | \chi_m \rangle = \langle \psi_m(\mathcal{E})|\psi_m(\mathcal{E})\rangle = \int_{-\infty}^{+\infty} dx\, |\chi_m(x)|^2 = \int_{-\infty}^{+\infty} dx\, |\psi_m(x - x_0)|^2$$

$$= \int_{-\infty}^{+\infty} du\, |\psi_m(u)|^2 = 1$$

$\qquad$ $\hookleftarrow$ the solution ψ_m of the 1D harmonic oscillator is normalized.

$$\Rightarrow \frac{dE_m(\mathcal{E})}{d\mathcal{E}} = \frac{d}{d\mathcal{E}}\langle \psi_m(\mathcal{E})|\hat{H}(\mathcal{E})|\psi_m(\mathcal{E})\rangle$$

$$= \langle \frac{d\psi_m(\mathcal{E})}{d\mathcal{E}}|\hat{H}(\mathcal{E})|\psi_m(\mathcal{E})\rangle$$

$$+ \langle \psi_m(\mathcal{E})|\frac{\partial \hat{H}(\mathcal{E})}{\partial \mathcal{E}}|\psi_m(\mathcal{E})\rangle$$

$$+ \langle \psi_m(\mathcal{E})|\hat{H}(\mathcal{E})|\frac{d\psi_m(\mathcal{E})}{d\mathcal{E}}\rangle$$

$$= E_n(\mathcal{E})\langle \frac{d\psi_m(\mathcal{E})}{d\mathcal{E}}|\psi_m(\mathcal{E})\rangle + \underbrace{\langle \hat{H}(\mathcal{E})\psi_m(\mathcal{E})|\frac{d\psi_m(\mathcal{E})}{d\mathcal{E}}\rangle}$$

$$+ \langle \psi_m(\mathcal{E})|\frac{\partial \hat{H}(\mathcal{E})}{\partial \mathcal{E}}|\psi_m(\mathcal{E})\rangle$$

$$\underset{\shortparallel}{E_n^*(\mathcal{E})}\langle \psi_m(\mathcal{E})|\frac{d\psi_m(\mathcal{E})}{d\mathcal{E}}\rangle$$

$$E_n(\mathcal{E})$$

$$\frac{dE_n(\varepsilon)}{d\varepsilon} = E_n(\varepsilon)\,\underbrace{\frac{d\langle \psi_n(\varepsilon)|\psi_n(\varepsilon)\rangle}{d\varepsilon}}_{0} + \langle \psi_n(\varepsilon)|\frac{\partial \hat{H}(\varepsilon)}{\partial \varepsilon}|\psi_n(\varepsilon)\rangle$$

since $\langle \psi_n(\varepsilon)|\psi_n(\varepsilon)\rangle = 1 \quad \forall \varepsilon$

we then obtain the Hellmann–Feynman theorem:

$$\boxed{\frac{dE_n(\varepsilon)}{d\varepsilon} = \langle \psi_n(\varepsilon)|\frac{\partial \hat{H}(\varepsilon)}{\partial \varepsilon}|\psi_n(\varepsilon)\rangle}$$

$$\frac{\partial \hat{H}(\varepsilon)}{\partial \varepsilon} = -q\hat{x} = -\hat{D}$$

$$\Rightarrow \boxed{\frac{dE_n(\varepsilon)}{d\varepsilon} = -\langle \hat{D}\rangle_{\psi_n(\varepsilon)}}$$

$$E_n(\varepsilon) = (n+\tfrac{1}{2})\hbar\omega - \tfrac{1}{2}\frac{q^2\varepsilon^2}{m\omega^2} \Rightarrow \frac{dE_n(\varepsilon)}{d\varepsilon} = -\frac{q^2\varepsilon}{m\omega^2}$$

$$\Rightarrow \boxed{\langle \hat{D}\rangle_{\psi_n(\varepsilon)} = \frac{q^2\varepsilon}{m\omega^2}}$$

Static polarizability $\alpha(0) = \dfrac{d\langle \hat{D}\rangle_{\psi_n(\varepsilon)}}{d\varepsilon}\Big|_0 = \dfrac{q^2}{m\omega^2}$

$\downarrow$

note that the static polarizability is a property of the system (nucleus + particle). It does not depend on the electric field!

$$\langle \hat{D}\rangle_{\psi_n(\varepsilon)} = \frac{q^2\varepsilon}{m\omega^2} = q\underbrace{\langle \psi_n(\varepsilon)|\hat{x}|\psi_n(\varepsilon)\rangle}_{\langle \hat{x}\rangle_{\psi_n(\varepsilon)}}$$

$$\Rightarrow \boxed{\langle \hat{x}\rangle_{\psi_n(\varepsilon)} = \frac{q\varepsilon}{m\omega^2} = x_0}$$

Comment: In the ground state ($n=0$) the wave function equals

$$\psi_0(\varepsilon)_{(x)} = \chi_0(x) = \psi_0(x-x_0) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}(x-x_0)^2}$$

if $q>0$ and $\varepsilon>0$: $x_0>0$ which is consistent with classical mechanics