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Tutorial II

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Reminder

On considère un hamiltonien $H = H_0 + W$ indépendant du temps et on suppose que l'on connaît les état stationnaires de H_0. On suppose aussi que le spectre de H_0 est purement discret et connu.

On note

$$H_0 \left|\psi_{0n}^i\right\rangle = E_{0n} \left|\psi_{0n}^i\right\rangle, \tag{1}$$

où le i est l'indice de dégénérescence, $i \in \{1, ..., g_n\}$, 0 est l'indice qui rappelle que ce sont les kets propre de H_0 et n est l'indice de la valeur propre.

On a la relation de fermeture

$$\sum_{n\geq 0} \sum_{i=1}^{g_n} \left|\psi_{0n}^i\right\rangle \left\langle\psi_{0n}^i\right| = 1 \tag{2}$$

On suppose que les énergies associées à W sont "petites" par rapport à celles associées à H_0. W correspond à la perturbation et est un opérateur hermitique. On ne connaît pas le spectre de $H = H_0 + W$ et on cherche à l'approximer. Pour cela, on pose : $W = \lambda H_1$, où λ est un paramètre réel. λ est supposé "petit" et H_1 possède des énergies du même ordre de grandeur que H_0.

Au final, le résultat ne doit pas dépendre de λ. On cherche les solutions approchées de l'équation de Schrödinger Stationnaire :

$$(H_0 + \lambda H_1) |\psi\rangle = E |\psi\rangle \tag{3}$$

Avec les conditions,

$$\begin{cases} \lim\limits_{\lambda\to 0} E = E_0, \text{ où } E_0 \text{ est l'une des valeurs propre de } H_0 \\ \lim\limits_{\lambda\to 0} |\psi\rangle = |\psi_0\rangle, \text{ où } |\psi_0\rangle \text{ correspond à } E_0 \end{cases} \tag{4}$$

Désormais on développe le ket propre $|\psi\rangle$ sur la forme d'une série perturbative,

$$|\psi\rangle = |0\rangle + \lambda |1\rangle + \lambda^2 |2\rangle + \cdots = \sum_{n\geq 0} \lambda^n |n\rangle \tag{5}$$

où les kets $|n\rangle$ sont à déterminer. On applique la même démarche pour l'énergie E,

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots = \sum_{n\geq 0} \lambda^n E_n \tag{6}$$

où les E_n doivent être calculées.

> **Attention :** $|n\rangle$ et E_n sont les corrections perturbatives à calculer. A priori,
>
> $$|n\rangle \neq \left|\psi_{0n}^i\right\rangle \qquad\qquad E_n \neq E_{0n}$$

De l'équation (3), on peut écrire

$$(H_0 + \lambda H_1)(|0\rangle + \lambda |1\rangle + \lambda^2 |2\rangle + \cdots) = (E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots)(|0\rangle + \lambda |1\rangle + \lambda^2 |2\rangle + \cdots) \tag{7}$$

Et ainsi, en développant et en regroupant les termes en puissance de λ, on obtient

$$\text{à l'ordre 0,} \qquad H_0 |0\rangle = E_0 |0\rangle \tag{8}$$

$$\text{à l'ordre 1,} \qquad H_0 |1\rangle + H_1 |0\rangle = E_0 |1\rangle + E_1 |0\rangle \tag{9}$$

$$\text{à l'ordre 2,} \qquad H_0 |2\rangle + H_1 |1\rangle = E_0 |2\rangle + E_1 |1\rangle + E_2 |0\rangle \tag{10}$$

Par ailleurs, $|\psi\rangle$ doit être normé pour obéir aux postulats de la Mécanique Quantique. On obtient donc la relation

$$\langle \psi | \psi \rangle = 1 = \left(\sum_n \lambda^n \langle n| \right) \left(\sum_{n'} \lambda^{n'} |n'\rangle \right) \tag{11}$$

En regroupant les puissance de λ, on obtient

$$\left\{ \begin{aligned} \langle 0|0\rangle &= 1 \\ \langle 0|1\rangle + \langle 1|0\rangle &= 0 \\ \langle 0|2\rangle + \langle 1|1\rangle + \langle 2|0\rangle &= 0 \end{aligned} \right. \tag{12}$$

Comme ces conditions ne suffisent par à préciser la solution, on rajoute

$$\langle 0|i\rangle \in \mathbb{R}, \ \forall i \tag{13}$$

C'est une condition de phase très pratique. On peut alors en déduire,

$$\left\{ \begin{aligned} &\langle 0|1\rangle = 0 \\ &\langle 0|2\rangle = -\frac{1}{2} \langle 1|1\rangle \end{aligned} \right. \tag{14}$$

En effet, d'après (12),

$$\langle 0|1\rangle = -\langle 1|0\rangle = -\langle 0|1\rangle^* \overset{(13)}{=} -\langle 0|1\rangle \tag{15}$$

Donc, $\langle 0|1\rangle = 0$.

Il est maintenant nécessaire de préciser si l'état perturbé est généré ou pas.

Perturbation d'un état de H_0 non dégénéré

Énergie au premier ordre de perturbation

On étudie la perturbation de l'état $|\psi_{0n}^{g_n}\rangle$, vérifiant $H_0 |\psi_{0n}^{g_n}\rangle = E_{0n} |\psi_{0n}^{g_n}\rangle$. Comme l'état est non dégénéré, $g_n = 1$ te on supprime l'indice :

$$|\psi_{0n}^{g_n}\rangle \longrightarrow |\psi_{0n}\rangle$$

On cherche $|\psi_n\rangle$ et E_n, vérifiant $H|\psi_n\rangle = E_n|\psi_n\rangle$ en utilisant la méthode vue précédemment. On note les série perturbatives

$$\begin{cases} |\psi_n\rangle = |0n\rangle + \lambda|1n\rangle + \lambda^2|2n\rangle + \cdots \\ E_n = E_{0n} + \lambda E_{1n} + \lambda^2 E_{2n} + \cdots \end{cases}$$

> **A noter** : on garde l'indice n pour se souvenir que $|\psi_n\rangle$ et E_n viennent de $|\psi_{0n}\rangle$ et E_{0n} où n peut-être associé à un nombre quantique.

Tout ce qui a été dit précédemment reste vrai et on a

$$\begin{cases} \lim\limits_{\lambda\to 0}|\psi_n\rangle = |0n\rangle = |\psi_{0n}\rangle \text{ il n'y a pas d'ambiguité ici car la valeur propre n'est pas dégénéré} \\ \lim\limits_{\lambda\to 0} E_n = E_{0n} \end{cases}$$

Avec ces notations, la relation (9) devient

$$H_0|1n\rangle + H_1|\psi_{0n}\rangle = E_{0n}|1n\rangle + E_{1n}|\psi_{0n}\rangle$$

En prenant le produit scalaire avec $\langle\psi_{0n}|$, on obtient

$$\langle\psi_{0n}|H_0|1n\rangle + \langle\psi_{0n}|H_1|\psi_{0n}\rangle = E_{0n}\langle\psi_{0n}|1n\rangle + E_{1n}\langle\psi_{0n}|\psi_{0n}\rangle$$

> **Simplification** :
>
> $$\langle\psi_{0n}|H_0|1n\rangle = E_{0n}\langle\psi_{0n}|1n\rangle$$
>
> Car,
>
> $$H_0|\psi_{0n}\rangle = E_{0n}|\psi_{0n}\rangle$$

On obtient au final,

$$E_{1n} = \langle\psi_{0n}|H_1|\psi_{0n}\rangle + \mathcal{O}(\lambda^2)$$

$$\begin{aligned} E_n &= E_{0n} + \lambda\langle\psi_{0n}|H_1|\psi_{0n}\rangle + \mathcal{O}(\lambda^2) \\ &= E_{0n} + \langle\psi_{0n}|\lambda H_1|\psi_{0n}\rangle + \mathcal{O}(\lambda^2) \\ &= E_{0n} + \langle\psi_{0n}|W|\psi_{0n}\rangle + \mathcal{O}(\lambda^2) \end{aligned}$$

On trouve ainsi la correction de l'énergie au premier ordre.

Etat propre au premier ordre pour un état non dégénéré

On cherche $|1n\rangle$ tel que

$$|\psi_n\rangle = |\psi_{0n}\rangle + \lambda\,|1n\rangle + \mathcal{O}(\lambda^2)$$

On se sert de la relation de fermeture de la base de H_0, $\{|\psi_{0p}^i\rangle\}$,

$$\sum_p \sum_{i=1}^{g_p} |\psi_{0p}^i\rangle\,\langle\psi_{0p}^i| = 1,$$

pour écrire

$$|1n\rangle = \sum_p \sum_{i=1}^{g_p} |\psi_{0p}^i\rangle\,\langle\psi_{0p}^i|1n\rangle\,,$$

où les inconnues sont $\langle\psi_{0p}^i|1n\rangle$. On se sert de l'équation (9) que l'on projette sur $\langle\psi_{0p}^i|$ pour $n \neq p$,

$$\langle\psi_{0p}^i|\,H_0\,|1n\rangle + \langle\psi_{0p}^i|\,H_1\,|\psi_{0p}^i\rangle = E_{0n}\,\langle\psi_{0p}^i|1n\rangle + E_1\,\langle\psi_{0p}^i|\psi_{0n}\rangle$$

Ce qu'on peut réécrire,

$$E_{0p}\,\langle\psi_{0p}^i|1n\rangle + \langle\psi_{0p}^i|\,H_1\,|\psi_{0p}^i\rangle = E_{0n}\,\langle\psi_{0p}^i|1n\rangle + \cancel{E_1\,\langle\psi_{0p}^i|\psi_{0n}\rangle}$$

> **Simplification** :
>
> $$\begin{cases} H_0\,|\psi_{0p}^i\rangle = E_{0p}\,|\psi_{0p}^i\rangle \\ H_0\,|\psi_{0n}\rangle = E_{0n}\,|\psi_{0n}\rangle \end{cases} \Longrightarrow \langle\psi_{0p}^i|\psi_{0n}\rangle = 0$$
>
> Car $p \neq n$.

On a donc,

$$\langle\psi_{0p}^i|1n\rangle = \frac{\langle\psi_{0p}^i|\,H_1\,|\psi_{0n}\rangle}{(E_{0n} - E_{0p})} \qquad (p \neq n)$$

Pour $p = n$, on calcul $\langle\psi_{0n}|1n\rangle$ à partir de la relation (14) : $\langle 0|1\rangle = 0$. On a donc

$$\langle\psi_{0n}|1n\rangle = 0$$

On en déduit au premier ordre le ket $|\psi_n\rangle$,

$$|1n\rangle = \sum_{p\neq n} \sum_{i=1}^{g_p} |\psi_{0p}^i\rangle\,\frac{\langle\psi_{0p}^i|\,H_1\,|\psi_{0n}\rangle}{(E_{0n} - E_{0p})}$$

D'où pour l'état résultat au premier ordre,

$$\begin{aligned} |\psi_n\rangle &= |\psi_{0n}\rangle + \lambda\,|1n\rangle + \mathcal{O}(\lambda^2) \\ &= |\psi_{0n}\rangle + \sum_{p\neq n}\sum_{i=1}^{g_p} |\psi_{0p}^i\rangle \frac{\langle\psi_{0p}^i|\,H_1\,|\psi_{0n}\rangle}{(E_{0n}-E_{0p})} + \mathcal{O}(\lambda^2) \end{aligned}$$

Pour la "petitesse", un critère à vérifier peut-être $|\,\langle\psi_{0p}^i|\,W\,|\psi_{0n}\rangle\,| \ll |E_{0n}-E_{0p}|$

Perturbation d'un état de H_0 dégénéré

Énergie au premier ordre de perturbation

Si E_{0n} st dégénérée, il existe plusieurs état $|\psi_{0n}^i\rangle$ qui lui correspondent puisque $i = \{1, ..., g_n\}$. Cependant les valeurs propre de $H = H_0 + W$ peuvent être ou ne pas être dégénérée. Maintenant, il faut traiter la $\lim_{\lambda\to 0}|\psi_n\rangle$ car à priori on retourne dans l'espace de dégénérescence de E_{0n} de dimension g_n.

On peut écrire $\lim_{\lambda\to 0}|\psi_n\rangle = |\varphi_{0n}\rangle$ avec $|\varphi_{0n}\rangle$ égale à une combinaison linéaire des $|\psi_{0n}^i\rangle$. C'est-à-dire,

$$|\varphi_{0n}\rangle = \sum_{j=1}^{g_n} |\psi_{0n}^j\rangle \langle\psi_{0n}^j|\varphi_{0n}\rangle$$

> **Remarque** : Nous avons
>
> $$\left\langle\psi_{0n}^j\middle|\varphi_{0n}\right\rangle = 0$$
>
> si $p \neq n$ puisque $E_{0p} \neq E_{0n}$, les deux vecteurs sont orthogonaux lorsque les valeurs propres son différentes.

Le point de départ est toujours

$$\begin{cases} E_n = E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots \\ |\psi_n\rangle = |0_n\rangle + \lambda\,|1_n\rangle + \cdots \end{cases}, \qquad \begin{cases} \lim\limits_{\lambda\to 0} E_n = E_{0n} \\ \lim\limits_{\lambda\to 0}|\psi_n\rangle = |\varphi_{0n}\rangle \end{cases}$$

On se sert maintenant de la relation (9) avec les notations adaptées. On rajoute l'indice n pour bien marquer que c'est un état d'énergie E_{0n} qui est perturbé. On a

$$H_0\,|1n\rangle + H_1\,|0n\rangle = E_{0n}\,|1n\rangle + E_{1n}\,|0n\rangle$$

d'après (9) comme $|0n\rangle = |\varphi_{0n}\rangle$, on obtient

$$H_0\,|1n\rangle + H_1\,|\varphi_{0n}\rangle = E_{0n}\,|1n\rangle + E_{1n}\,|\varphi_{0n}\rangle$$

En prenant le produit scalaire avec $\langle\varphi_{0n}^i|$, on obtient

$$\cancel{\left\langle\varphi_{0n}^i\right| H_0 \left|1n\right\rangle} + \left\langle\varphi_{0n}^i\right| H_1 \left|\varphi_{0n}\right\rangle = \cancel{E_{0n}\left\langle\varphi_{0n}^i\middle|1n\right\rangle} + E_{1n}\left\langle\varphi_{0n}^i\middle|\varphi_{0n}\right\rangle$$

On en déduit,

$$\left\langle\psi_{0n}^i\right| H_1 \left|\varphi_{0n}\right\rangle = E_{1n}\left\langle\psi_{0n}^i\middle|\varphi_{0n}\right\rangle, \qquad \forall i \in \{1, ..., g_n\} \tag{16}$$

Comme

$$\left|\varphi_{0n}\right\rangle = \sum_{j=1}^{g_n} \left|\psi_{0n}^j\right\rangle \left\langle\psi_{0n}^j\middle|\varphi_{0n}\right\rangle$$

on a la relation,

$$H_1\left|\varphi_{0n}\right\rangle = \sum_{j=1}^{g_n} H_1\left|\psi_{0n}^j\right\rangle \left\langle\psi_{0n}^j\middle|\varphi_{0n}\right\rangle$$

Et donc

$$\left\langle\psi_{0n}^i\right| H_1 \left|\varphi_{0n}\right\rangle = \sum_{j=1}^{g_n} \left\langle\psi_{0n}^i\right| H_1 \left|\psi_{0n}^j\right\rangle \left\langle\psi_{0n}^j\middle|\varphi_{0n}\right\rangle$$

Avec (16) on a,

$$E_{1n}\left\langle\psi_{0n}^i\middle|\varphi_{0n}\right\rangle = \sum_{j=1}^{g_n} \left\langle\psi_{0n}^i\right| H_1 \left|\psi_{0n}^j\right\rangle \left\langle\psi_{0n}^j\middle|\varphi_{0n}\right\rangle$$

Que l'on peut aussi écrire

$$\sum_{j=1}^{g_n} \left(\left\langle\psi_{0n}^i\right| H_1 \left|\psi_{0n}^j\right\rangle - E_{1n}\delta_{ij}\right) \left\langle\psi_{0n}^j\middle|\varphi_{0n}\right\rangle = 0 \qquad \forall i \in \{1, ..., g_n\}$$

C'est une équation aux valeurs propres et vecteurs propres matricielles.

En calculant le polynôme caractéristique

$$\det\left(\left\langle\psi_{0n}^i\right| H_1 \left|\psi_{0n}^j\right\rangle - E_{1n}\delta_{ij}\right) = 0$$

On obtient les corrections à l'ordre 1 notées $E_{1n}^{(k)}$. Elles peuvent être dégénérées également.

Si les valeurs propres sont toutes non dégénérées, on dit que la dégénérescence est levée. Sinon on dit qu'elle est partiellement levée ou pas levée.

$$E^{(k)} = E_{0n} + \lambda E_{1n}^{(k)} = E_{0n} + \tilde{E}_{1n}^{(k)}$$

où $E_{1n}^{(k)}$ est issu de la diagonalisation de H_0 et $\tilde{E}_{1n}^{(k)}$ de la diagonalisation de $W = \lambda H_1$

Aux valeurs propre $E_{1n}^{(k)}$ correspondent des état spropres $\left\{\left|\varphi_{0n}^{(k)}\right\rangle\right\}$. Ils sont d'ordre zéro car ce sont des superpositions des état $|\psi_{0n}^i\rangle$, $i \in \{1, ..., g_n\}$.

EXERCISE I : Stark effect in atomic Hydrogen

The Stark effect is the removal of degeneracy between energy levels in the presence of a constant electric field $\vec{\mathcal{E}}$. This field must be strong enough that we can neglect the fine structure effects, but not intense enough to ionize the atom, *i.e.*, 10^5 V/m $< \mathcal{E} <$ 10^7 V/m.

In the absence of an electric field, the Hamiltonian of the hydrogen atom is denoted as H_0. In the presence of a field $\vec{\mathcal{E}}$ it is given by $H = H_0 + H_1$. We'll choose the z axis parallel to $\vec{\mathcal{E}}$. The interaction of the atom with the electric field is written by H_1, which will be treated as a perturbation.

We remind you that the unperturbed energy levels of hydrogen are :

$$E_n^{(0)} = -\frac{E_I}{n^2}, \qquad (n = 1, 2, ...)$$

where E_I is the ionisation energy : $E_I = \frac{e^2}{2a_0} = 1\mathcal{R} = 13.6$ eV (1 Rydberg). Here $e^2 = \frac{q^2}{4\pi\epsilon_0}$ and $a_0 = \frac{\hbar^2}{m_e e^2} \simeq 0.53$ Åis the Bohr radius.

We also recall the expressions for the corresponding wavefunctions $\varphi_{n,l,m}(0 \leq l \leq n-1, -l \leq m \leq +l)$:

- **1s state :**

$$\varphi_{1,0,0} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

- **2s state :**

$$\varphi_{2,0,0} = \frac{1}{\sqrt{8\pi a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

- **2p state :**

$$\varphi_{2,1,+1} = -\frac{1}{8\sqrt{\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta e^{+i\varphi} \quad \varphi_{2,1,0} = \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta \quad \varphi_{2,1,-1} = +\frac{1}{8\sqrt{\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta e^{-i\varphi}$$

1. Give the expression for H_1 (*hint : think of an atom as a pair of charges separated by distance r*).

   For a classical eletrical dipole its energy is given by $-\vec{\mu} \cdot \vec{\mathcal{E}}$. In quantum mechanics, we will replace μ with its operator $\hat{\mu}$,

   $$H_1 = -\hat{\mu} \cdot \vec{\mathcal{E}} = q\mathcal{E}\hat{z}$$

   we can see it as a linear potential.

2. We are initially interested in the $n = 1$ level of hydrogen. Show that, within first order corrections, that the energy of the $|1s\rangle$ state is not modified.

   Let $E^{(1)}$ be the energy correction of the first order perturbated state,

$$H_0 \left|\psi^{(1)}\right\rangle + H_1 \left|\psi^{(0)}\right\rangle = E^{(1)} \left|\psi^{(0)}\right\rangle + E^{(0)} \left|\psi^{(1)}\right\rangle$$

   To find $E^{(1)}$, we can premultiply by $\left\langle\psi^{(0)}\right|$, and using

$$\left\langle\psi^{(0)}\middle|\psi^{(0)}\right\rangle = 1 \qquad\qquad \left\langle\psi_j^{0}\middle|\psi_k^{(0)}\right\rangle = \delta_{j,k}$$

   but, be careful, since in general $\left|\psi^{(1)}\right\rangle \cdots \left|\psi^{(n)}\right\rangle$ are not necessarily normal and orthogonal. But, we know that

$$\left\langle\psi^{(0)}\middle|\psi^{(k)}\right\rangle = 0 \quad \text{for } k > 0$$

   So we get,

$$\begin{aligned} E^{(1)} &= \left\langle\psi^{(0)}\right| H_1 \left|\psi^{(0)}\right\rangle \\ &= \int_{-\infty}^{+\infty} \mathrm{d}^3 r \psi^{(0)*}(r) H_1 \psi^{(0)} \end{aligned}$$

   But $\psi^{(0)} \equiv \varphi_{1,0,0}$ which is an even function. The integral of an odd function over all space is 0. So we get,

$$E^{(1)} = 0$$

3. Let $\vec{\mu} = q\vec{r}$ be the operator associated with the electric dipole moment, where $\vec{r}$ is the operator associated with the position of the electron and q is its charge. Express the Hamiltonian H as a function of $\vec{\mu}$ and show that $\langle\psi_1|\, \mu_z \,|\psi_1\rangle = -\frac{\mathrm{d}E_1(\mathcal{E})}{\mathrm{d}\mathcal{E}}$. We denote $|\psi_1\rangle$ with energy $E_1(\mathcal{E})$ as the state obtained from the state $|1s\rangle$ following the application of the electric field, within first order perturbation theory.

$$\begin{cases} H(\mathcal{E}) = H_0 - \mu_z \mathcal{E} \\ H(\mathcal{E} + \mathrm{d}\mathcal{E}) = H(\mathcal{E}) - \mu_z \mathrm{d}\mathcal{E} \end{cases}$$

$$\begin{aligned} E_1(\mathcal{E} + \mathrm{d}\mathcal{E}) &= \langle\psi_1|\, H(\mathcal{E} + \mathrm{d}\mathcal{E}) \,|\psi_1\rangle \\ &= \langle\psi_1|\, H(\mathcal{E}) \,|\psi_1\rangle - \langle\psi_1|\, \mu_z \mathrm{d}\mathcal{E} \,|\psi_1\rangle \\ &= E_1(\mathcal{E}) - \langle\psi_1|\, \mu_z \,|\psi_1\rangle \,\mathrm{d}\mathcal{E} \end{aligned}$$

   hence,

$$\langle\psi_1|\, \mu_z \,|\psi_1\rangle = -\frac{\mathrm{d}}{\mathrm{d}\mathcal{E}} E_1(\mathcal{E})$$

4. Show that $E_1(\mathcal{E}) = E_1^{(0)} - \frac{1}{2}\alpha\mathcal{E}^2$, where α represents the polarisability of the hydrogen atom.

   We remind ourselves,

$$H_0 \left|\psi^{(1)}\right\rangle + H_1 \left|\psi^{(0)}\right\rangle = E^{(0)} \left|\psi^{(1)}\right\rangle + E^{(1)} \left|\psi^{(0)}\right\rangle \tag{17}$$

   with,

$$\left\langle\psi^{(0)}\middle|\psi^{(k)}\right\rangle = 0 \text{ for } k > 0$$

   We premultiply (17) by $\left\langle\psi^{(0)}\right|$

$$\cancel{\left\langle\psi^{(0)}\right| H_0 \left|\psi^{(1)}\right\rangle} + \left\langle\psi^{(0)}\right| H_1 \left|\psi^{(0)}\right\rangle = \cancel{E^{(0)} \left\langle\psi^{(0)}\middle|\psi^{(1)}\right\rangle} + E^{(1)} \cancel{\left\langle\psi^{(0)}\middle|\psi^{(0)}\right\rangle}$$

   And so we get,

$$E^{(1)} = \left\langle\psi^{(0)}\right| H_1 \left|\psi^{(0)}\right\rangle$$

   But, $H_1 = -\hat{\mu}\mathcal{E}$, and so we get $E^{(1)} = 0$ as shown in question 2.
   We would like to use the identity operator (so-called the completeness relation)

$$\hat{1} = \sum_{\phi} |\phi\rangle \langle\phi|$$

$$\hat{1} H_2 \left|\psi^{(0)}\right\rangle = \sum_{\phi \neq \psi} \left|\phi^{(0)}\right\rangle \left\langle\phi^{(0)}\right| H_1 |\psi_0\rangle$$

$$E^{(1)} = \left\langle\psi^{(0)}\right| H_1 \left|\psi^{(0)}\right\rangle$$

$$\begin{aligned} \left|\psi^{(1)}\right\rangle &= \sum_{\phi \neq \psi} \frac{\left\langle\phi^{(0)}\right| H_1 \left|\psi^{(0)}\right\rangle}{E_\psi^{(0)} - E_\phi^{(0)}} \left|\phi^{(0)}\right\rangle \\ &= -\mathcal{E} \sum_{nlm, n>1} \frac{\langle nlm| \mu_z |1s\rangle}{E_1^{(0)} - E_{nlm}^{(0)}} |nlm\rangle + \mathcal{O}(\mathcal{E}^2) \end{aligned}$$

   So we plug this expression in the expression of $E^{(2)}$:

$$\begin{aligned} E^{(2)} &= \left\langle\psi^{(0)}\right| H_1 \left|\psi^{(1)}\right\rangle \\ &= \mathcal{E}^2 \mathcal{E} \sum_{nlm, n>1} \frac{\langle nlm| \mu_z |1s\rangle}{E_1^{(0)} - E_{nlm}^{(0)}} |nlm\rangle \langle 1s| \mu_z |nlm\rangle \\ &= -\frac{\alpha}{2}\mathcal{E}^2 \end{aligned}$$

   with α the electric polarisability, an always positive quantity,

$$\alpha = -2 \sum nlm, n > 1 \frac{|\langle nlm| \mu_z |1s\rangle|^2}{E_1^{(0)} - E_{nlm}^{(0)}}$$

5. Assuming that $|E_1^{(0)} - E_n^{(0)}|$ is of the order of 1 atomic unit ($1\mathcal{R}$) for all n, show that $\alpha = \frac{2}{\mathcal{R}} \langle 1s| \mu_z^2 |1s\rangle$.

   We can explicitely write the $| \langle | \rangle |^2$ quantity,

$$\alpha \approx \frac{2}{\mathcal{R}} \sum_{nlm, n>1} \langle 1s| \mu_z |nlm\rangle \langle nlm| \mu_z |1s\rangle$$

   it does looks like a completeness relation, but we need the sum to start for $n > 0$, but we know that $\langle 1s| \mu_z |1s\rangle = 0$, so starting at $n > 0$ or $n > 1$ is the same, so

$$\alpha \approx \frac{2}{\mathcal{R}} \langle 1s| \mu_z^2 |1s\rangle$$

6. Give the expression for α as a function of a_0 and compare to the experimentally determined value : $\alpha_{\text{exp.}} = 6.6 \times 10^{-31}$ m^3.

$$\begin{aligned}
\alpha &\approx \frac{2}{\mathcal{R}} \langle 1s| \mu_z^2 |1s\rangle \\
&= \frac{2e^2}{\mathcal{R}} \langle 1s| z^2 |1s\rangle \\
&= \frac{2e^2}{\mathcal{R}} \int_{\mathbb{R}} \mathrm{d}^3 r |\varphi_{100}|^2 z^2 \\
&= \frac{2e^2}{\mathcal{R}} a_0^2 \\
&= 4a_0^3 \\
&= 6 \times 10^{-31} \text{ m}^3
\end{aligned}$$

7. We now focus on the $n = 2$ level. Show using first order degenerate state perturbation theory that the electric field lifts the degeneracy of the state.

$$|\psi\rangle = \sum_{i \in \mathbb{N}} \chi_i \left|\phi_i^{(0)}\right\rangle$$

   And so,

$$(H_0 + H_1) |\psi\rangle = (E^{(0)} + E^{(1)} + \cdots) |\psi\rangle$$

   we pre-multiply by $\langle \phi_j|$,

$$\sum_{i \in \mathbb{N}} \langle \phi_j| H_0 + H_1 |\phi_i\rangle \chi_i = (E^{(0)} + E^{(1)})\chi_j$$

$$\sum_{n'l'm'} \left[\langle nlm| H_0 |n'l'm'\rangle + \langle nlm| q\mathcal{E}z |n'l'm'\rangle\right] \chi_{n'l'm'} = (E^{(0)} + E^{(1)})\chi_{nlm}$$

$$\cancel{E^{(0)}\chi_{nlm}} + \sum_{n'l'm'} \langle nlm| q\mathcal{E}z |n'l'm'\rangle \chi_{n'l'm'} = \cancel{E^{(0)}\chi_{nlm}} + E^{(1)}\chi_{nlm}$$

We can express as a matrix,

$$H_1 = \begin{pmatrix} 0 & 0 & 3q\mathcal{E}a_0 & 0 \\ 0 & 0 & 0 & 0 \\ 3q\mathcal{E}a_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

The matrix column are $(|200\rangle, |211\rangle, |210\rangle, |21-1\rangle)$. There is lot's of zeros because of selection rules,

$$|211\rangle \propto e^{i\varphi} \Longrightarrow \int_0^\pi \mathrm{d}\varphi e^{\pm\varphi} = 0$$

8. Provide expressions for the eigenenergies and eigenvectors associated with each sublevel.

We want to diagonalize the matrix,

$$\det\left(H - \lambda\hat{1}\right) = 0$$

Thus,

$$\begin{vmatrix} -\lambda & 0 & 3q\mathcal{E}a_0 & 0 \\ 0 & -\lambda & 0 & 0 \\ 3q\mathcal{E}a_0 & 0 & -\lambda & 0 \\ 0 & 0 & 0 & -\lambda \end{vmatrix}$$

Thus it is just the diagonalization of two 2×2 matrices,

$$\begin{vmatrix} -\lambda & 0 & 3q\mathcal{E}a_0 & 0 \\ 0 & -\lambda & 0 & 0 \\ 3q\mathcal{E}a_0 & 0 & -\lambda & 0 \\ 0 & 0 & 0 & -\lambda \end{vmatrix} = \lambda^2\left(\lambda^2 - (3q\mathcal{E}a_0)^2\right) = 0$$

and we get,

$$\lambda_1 = +3q\mathcal{E}a_0 \qquad \lambda_2 = -3q\mathcal{E}a_0 \qquad \lambda_3 = 0 \qquad \lambda_4 = 0$$

And so the eigenvectors,

$$(H - \lambda\hat{1})X = 0$$

We get,

$$X_1 = \frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right) \quad X_X = \frac{1}{\sqrt{2}}\left(-|200\rangle + |210\rangle\right) \quad X_3 = |211\rangle \quad X_4 = |21-1\rangle$$

EXERCISE II : Two-dimensional harmonic oscillator

A particle with mass m, subject to displacement in the x-y plane, is described the Hamiltonian :

$$H_0 = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{1}{2}k(x^2 + y^2) \qquad k > 0$$

We wish to study the effect of a perturbation $W = \alpha xy$ with $\alpha \ll k$.

1. Recalling the results from the one-dimensional harmonic oscillator, express without calculation, the eigenvalues of H_0 and their possible degree of degeneracy, as well as the corresponding eigenvectors.

$$|n_x, n_y\rangle = |n_x\rangle \otimes |n_y\rangle$$

$$H_0 = H_x + H_y$$

$$\begin{cases} H_x |n_x\rangle = \hbar\omega \left(n_x + \frac{1}{2}\right) |n_x\rangle \\ H_y |n_y\rangle = \hbar\omega \left(n_y + \frac{1}{2}\right) |n_y\rangle \end{cases}$$

Meaning,

$$H_0 |n_x, n_y\rangle = (n_x + n_y + 1) |n_x, n_y\rangle$$

Thus,

$$E_{n_x,n_y} = \hbar\omega(n_x + n_y + 1)$$

The eigenenergies are $n + 1$ fold degenerate.

2. Using time-independent perturbation theory, determine the effect of W on the first excited level of H_0. It is sufficient to limit ourselves to the first order for the energies and zeroth order for the state vectors.

For the forst excited level, there is two degenerate level : $|10\rangle$ and $|01\rangle$, meaning we can write the matrix (W),

$$(W) = \begin{pmatrix} \langle 10| \hat{W} |10\rangle & \langle 10| \hat{W} |01\rangle \\ \langle 01| \hat{W} |10\rangle & \langle 01| \hat{W} |01\rangle \end{pmatrix}$$

where the off-diagonal terms stands for coupling.

> **Reminder** : for the harmonic oscillator,
>
> $$|0_\rho\rangle = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta\rho^2/2} \qquad\qquad |1_\rho\rangle = \left(\frac{\beta}{\pi}\right)^{1/4} \sqrt{2\beta}e^{-\beta\rho^2/2}$$
>
> were $\rho = x, y$ here, and
>
> $$\frac{1}{\sqrt{\beta}} = a_{\text{HO}} \qquad\qquad \beta = \frac{m\omega}{\hbar}$$

So, we can see that

$$|10\rangle \propto xe^{-x^2}e^{-y^2} \qquad\qquad |01\rangle \propto ye^{-x^2}e^{-y^2}$$

So, straight away we know that the diagonal terms vanish, *i.e.*,

$$\langle 10|\,\hat{W}\,|10\rangle = \langle 01|\,\hat{W}\,|01\rangle = 0$$

with the same argument made before, the integration of an odd function over all space is 0.
So now we can perform the calculation for the off-diagonal terms,

$$\begin{aligned}
\langle 10|\,\hat{W}\,|01\rangle &= \iint_{-\infty}^{+\infty} \mathrm{d}x\mathrm{d}y \left[\left(\frac{\beta}{\pi}\right)^{1/4} \sqrt{2\beta}xe^{-\beta(x^2+y^2)/2}\right] \alpha xy \left[\left(\frac{\beta}{\pi}\right)^{1/4} \sqrt{2\beta}ye^{-\beta(x^2+y^2)/2}\right] \\
&= \frac{2\beta^2}{\pi}\alpha \left(\int_{-\infty}^{+\infty} \mathrm{d}x x^2 e^{-\beta x^2}\right)^2 \\
&= \frac{2\beta^2}{\pi}\alpha \cdot \left(\frac{\sqrt{\pi}}{2\beta^{3/2}}\right)^2 \\
&= \frac{\alpha}{2\beta}
\end{aligned}$$

Meaning, the perturbation matrix is

$$(W) = \begin{pmatrix} 0 & \alpha/2\beta \\ \alpha/2\beta & 0 \end{pmatrix}$$

The eigenvalues are

$$\lambda_\pm = \pm\frac{\alpha}{2\beta} = \pm\frac{\alpha\hbar}{2m\omega}$$

And the associated eigenenergies,

$$E_\pm = 2\hbar\omega \pm \frac{\alpha\hbar}{2m\omega}$$

And the eigenstates,

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2}}\left(|10\rangle \pm |01\rangle\right)$$

Remark : there is an other approach to compute the matrix elements without doing any integrals, we define the ladder operators,

$$\hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle\,, \qquad \hat{a}^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle$$

Where the operator $\hat{a}$ is so-called the "annihilation" operator and $\hat{a}^\dagger$ the "creation" operator.
So we can express x and y with them,

$$x = \frac{1}{\sqrt{2\beta}}(a_x + a_x^\dagger) \qquad y = \frac{1}{\sqrt{2\beta}}(a_y + a_y^\dagger)$$

So,

$$\hat{W} = \frac{\alpha}{2\beta}(a_x + a_x^\dagger)(a_y + a_y^\dagger)$$

And so,

$$\begin{aligned}\hat{W}\,|10\rangle &= \frac{\alpha}{2\beta}(a_x + a_x^\dagger)\,|1_x\rangle \otimes (a_y + a_y^\dagger)\,|0_y\rangle \\ &= \frac{\alpha}{2\beta}(|0_x\rangle + \sqrt{2}\,|2_x\rangle) \otimes |1_y\rangle \\ &= \frac{\alpha}{2\beta}(|01\rangle + \sqrt{2}\,|21\rangle)\end{aligned}$$

Meaning that,

$$\langle 01|\,\hat{W}\,|10\rangle = \frac{\alpha}{2\beta}(\langle 01|01\rangle + \cancel{\sqrt{2}\,\langle 01|21\rangle}) = \frac{\alpha}{2\beta}$$

Doing that for the 4 matrix elements allows us to compute the perturbation matrix.

3. Compare the eigenenergies to the exact solution obtained by transforming $H_0 + W$ according to the substitution $x \to \frac{X+Y}{\sqrt{2}}$, $y \to \frac{X-Y}{\sqrt{2}}$. Note that the potential energy $U(x,y) = \frac{1}{2}k(x^2+y^2) + \alpha xy$ can be put in the form : $U(X,Y) = \frac{1}{2}k_1X^2 + \frac{1}{2}k_yY^2$, where k_1, k_2 are constants to be specified.

$$\begin{aligned}\frac{1}{2}k(x^2+y^2) + \alpha xy &\longrightarrow \frac{k}{4}\left(X^2 + 2XY + Y^2 + X^2 - 2XY + Y^2\right) + \frac{\alpha}{2}(X^2 - Y^2) \\ &\longrightarrow \frac{1}{2}k_1X^2 + \frac{1}{2}k_2Y^2\end{aligned}$$

with

$$k_1 = \left(1 + \frac{\alpha}{k}\right) \qquad k_2 = \left(1 - \frac{\alpha}{k}\right)$$

We know

$$\hat{p}_x = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$$

So,

$$\frac{\mathrm{d}}{\mathrm{d}x} = \left[\frac{\partial}{\partial X}\frac{\partial X}{\partial x} + \frac{\partial}{\partial Y}\frac{\partial Y}{\partial x}\right] = \frac{1}{\sqrt{2}}\left[\frac{\partial}{\partial X} + \frac{\partial}{\partial Y}\right]$$

Meaning,

$$\hat{p}_x = \frac{1}{\sqrt{2}}[\hat{p}_X + \hat{p}_Y] \qquad \hat{p}_y = \frac{1}{\sqrt{2}}[\hat{p}_X - \hat{p}_Y]$$

So our hamiltonian is now,

$$\hat{H} = \frac{p_X^2}{2m} + \frac{p_Y^2}{2m} + \frac{1}{2}k_1X^2 + \frac{1}{2}k_2Y^2$$

And our eigenenergies,

$$E_{n_x,n_y} = \hbar\Omega_X\left(n_x + \frac{1}{2}\right) + \hbar\Omega_Y\left(n_y + \frac{1}{2}\right)$$

With

$$\Omega_X = \sqrt{\frac{k+\alpha}{m}} \qquad \Omega_Y = \sqrt{\frac{k-\alpha}{m}}$$

We can see that now there is a broken symmetry ; indeed $\Omega_X \neq \Omega_Y$ when $\alpha \neq 0$.

$$\begin{aligned}
E_{00} &= \frac{\hbar}{2}\left(\Omega_X + \Omega_Y\right) \\
&= \frac{\hbar\omega}{2}\left(\sqrt{1+\frac{\alpha}{m\omega^2}} + \sqrt{1-\frac{\alpha}{m\omega^2}}\right) \\
&\approx \frac{\hbar\omega}{2}\left(1 + \cancel{\frac{\alpha}{m\omega^2}} + 1 \cancel{- \frac{\alpha}{m\omega^2}}\right) \\
&= \frac{\hbar\omega}{2}
\end{aligned}$$

The first order ground-state is unperturbed.

$$\begin{aligned}
E_{01} &= \frac{\hbar}{2}\left(\Omega_X + 3\Omega_Y\right) \\
&\approx \frac{\hbar\omega}{2}\left(1 + \frac{\alpha}{2m\omega^2} + 3 - \frac{3\alpha}{2m\omega^2}\right) \\
&= 2\hbar\omega - \frac{\alpha\hbar}{2m\omega}
\end{aligned}$$

$$E_{10} = 2\hbar\omega + \frac{\alpha\hbar}{2m\omega}$$