PHY208 – atoms and lasers
Lecture 6

It’s a quantum world !

Daniel Suchet & Erik Johnson

Daniel.suchet@polytechnique.org
Erik.johnson@polytechnique.edu

Disclaimer

So far, we have used models with ad-hoc quantum mechanics ingredients

The point of this lecture is to show you where these ingredients really come from

The content of this lecture is for your culture interest, and for the connexion with other courses.

It will not be evaluated, neither in quizz nor in the final exam.

Hydrogen atom – Battleplan

What do we know ?

« Size » of an H atom $$\Delta x \Delta p_x \geq \frac{\hbar}{2} \rightarrow \simeq \frac{\hbar^2}{m_e e^2}$$

Quantum numbers $n,\, l,\, m$

Energy spectrum $E_n = -E_0/n^2$

What do we want to find ?

Recover these results (and more !) from basic principles
Identify consequences of these results

How are we going to get there ?

Quantum problem →operators, eigen states

Content

I. Reminder on the angular momentum

II. Hamiltonian for the hydrogen atom

III. Eigen states and eigen values

Ground state

Excited states

IV. Using results

Zeeman effect (again)

Selection rules

Rabi oscillations

Angular momentum - definition

Classical expression

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \begin{pmatrix} yp_z - zp_y \\ zp_x - xp_z \\ xp_y - yp_x \end{pmatrix}$$

Quantum operator

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = -i\hbar \begin{pmatrix} y\partial_z - z\partial_y \\ z\partial_x - x\partial_z \\ x\partial_y - y\partial_x \end{pmatrix}$$

In spherical coordinates (pure algebra)

$$L^2(f) = L_x^2(f) + L_y^2(f) + L_z^2(f) = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}(f)\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}f$$

$$\hat{L}_z = -\, i\hbar\partial_\varphi$$

Angular momentum - properties

Commutation (pure algebra again)

$$\mathbf{L} \times \mathbf{L} = i\hbar \mathbf{L}$$

$$\left[L^2,\, L_z\right] = 0$$

(actually, could be used to *define* angular momentum !)

Any observable provides a set of eigen functions which form a basis for all wavefunctions

$$\hat{O}\phi_n = O_n \phi_n \qquad \psi = \sum c_n \phi_n$$

If two observables commute, it is possible to find a basis of eigenfunctions share by both operators

$$[\hat{A}, \hat{B}] = 0 \Rightarrow \exists \{\phi_n\}, \begin{cases} \hat{A}\phi_n = A_n \phi_n \\ \hat{B}\phi_n = B_n \phi_n \end{cases} \quad \text{and}\, \psi = \sum c_n \phi_n$$

Eigen elements (pure algebra again)

Eigenstates of L^2 and Lz
= spherical harmonics

$$L^2 Y_{l,m}(\theta,\, \varphi) = l(l+1)\hbar^2$$

$$L_z Y_{l,m}(\theta,\, \varphi) = m\hbar,\; m \in \{-l,\, -l+1, ..., l-1,\, l\}$$

Content

I. Reminder on the angular momentum

II. Hamiltonian for the hydrogen atom

III. Eigen states and eigen values
- Ground state
- Excited states

IV. Using results
- Zeeman effect (again)
- Selection rules
- Rabi oscillations

Hydrogen atom - hamiltonian

Write down the Hamiltonian

$$H = \frac{p^2}{2m} + V(\mathbf{r}) = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{r}$$

Central symmetry → spherical coordinates

$$\begin{aligned}\Delta\psi &= \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}(\psi)\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\psi\right)\\ &= \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) - \frac{\hat{L}^2}{\hbar^2 r^2}\psi\end{aligned}$$

$$\hat{H}\psi = -\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{\hat{L}^2}{2m_e r^2}\psi - \frac{e^2}{r}\psi$$

Content

I. Reminder on the angular momentum

II. Hamiltonian for the hydrogen atom

III. Eigen states and eigen values

Ground state

Excited states

IV. Using results

Zeeman effect (again)

Selection rules

Rabi oscillations

Hydrogen atom – eigen equation

$$\hat{H}\psi = -\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{\hat{L}^2}{2m_e r^2}\psi - \frac{e^2}{r}\psi$$

What are the eigen functions / eigen values ?

Commutations ? $\left[H, L^2\right] = [H, L_z] = \left[L^2, L_z\right] = 0$ ⇒ Shared eigen basis !

$$H\psi = E\psi$$

Only r (no θ, φ)

$$L^2\psi = l(l+1)\hbar^2\,\psi$$

$$L_z\psi = m\hbar\,\psi$$

Only θ, φ (no r) ⇒ $\psi(\mathbf{r}) = R(r)Y_{l,m}(\theta, \varphi)$

⇓

Eigen equation : $-\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}(rR(r)) + \frac{l(l+1)}{2m_e r^2}\hbar^2 R(r) - \frac{e^2}{r}R(r) = E\,R$

Hydrogen atom – ground state

$$-\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}\left(rR(r)\right)+\frac{l(l+1)}{2m_e r^2}\hbar^2 R(r)-\frac{e^2}{r}R(r)=E\,R$$

Focus on the **ground** state → lowest possible energy → no angular momentum → l=0

$$-\frac{\hbar^2}{2m_e}\left(\frac{2}{r}R'+R''\right)-\frac{e^2}{r}R=E_0\,R$$

Ansatz : consider

$$R \underset{r\to\infty}{\simeq} R_0 e^{-r/a}$$

→

$$-\frac{\hbar^2}{2m_e}\left(-\frac{1}{a}\frac{2}{r}+\frac{1}{a^2}\right)-\frac{e^2}{r}=E_0$$

→

$$\frac{\hbar^2}{am_e}=e^2 \Rightarrow a_0=\frac{\hbar^2}{m_e e^2}$$

→

$$-\frac{\hbar^2}{2a^2 m_e}=E_0 \Rightarrow E_0=-\frac{m_e e^4}{2\hbar^2}$$

Hydrogen atom – excited states

$$-\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}(rR(r)) + \frac{l(l+1)}{2m_e r^2}\hbar^2 R(r) - \frac{e^2}{r}R(r) = E\,R$$

Now the more generic case :

Dimensionless units $\epsilon = \frac{E}{E_0}, \qquad \rho = \frac{r}{a_0}$ ⇒ $$\frac{1}{\rho}\frac{d^2}{d\rho^2}\rho R(\rho) - \frac{l(l+1)}{\rho^2}R(\rho) + \frac{2}{\rho}R(\rho) - \epsilon R(\rho) = 0$$

Ugly ? Yes ! But famous !

Textbook properties (pure algebra)

1. Has solutions iif $\epsilon = \frac{1}{(l+k+1)^2}, \; k \in \mathbb{N}$

2. In this case, $R(\rho) = e^{-\rho\sqrt{\epsilon}}\rho^l Q_{k,\,l}(\rho)$

Laguerre polynoms

Edmond Laguerre (X1853)

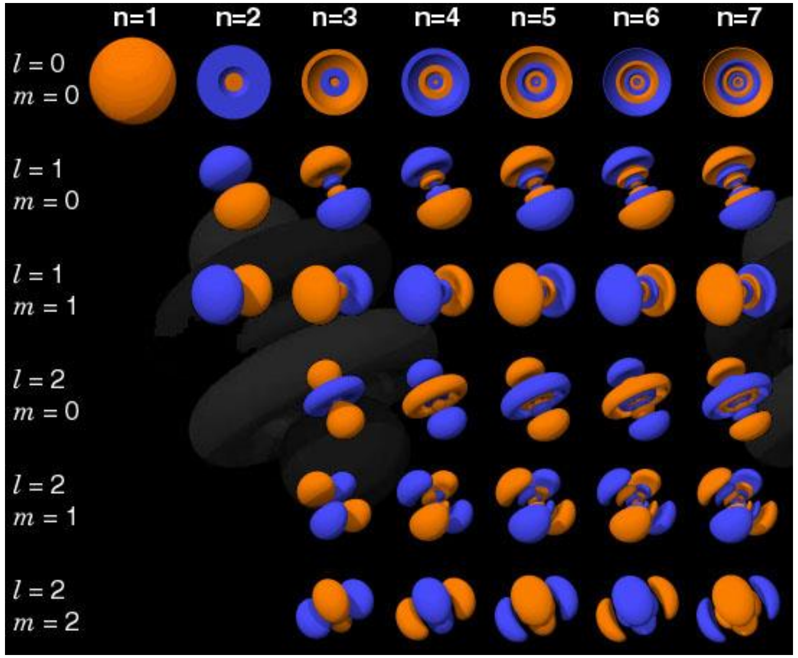
Hydrogen atom – final results

$$H = \frac{p^2}{2m} + V(\mathbf{r}) = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{r}$$

Eigen functions = atomic orbitals

$$\psi(\mathbf{r}) = R(r)Y_{l,m}(\theta,\,\varphi)$$

$$R(\rho) = e^{-\rho\sqrt{\epsilon}}\rho^l Q_{k,\,l}(\rho)$$



wwnorton.com/

Eigen values = quantum numbers

$$L^2 = l(l+1)\hbar^2$$

$$L_z = m\hbar$$

$$E = -\frac{m_e e^4}{2\hbar^2}\frac{1}{\underbrace{(l+k+1)}_{n}^2},\ k \in \mathbb{N}$$

Content

I. Reminder on the angular momentum

II. Hamiltonian for the hydrogen atom

III. Eigen states and eigen values
- Ground state
- Excited states

IV. Using results
- Zeeman effect (again)
- Selection rules
- Rabi oscillations

Application 1: Zeeman shift

Add an B field: $$H = \frac{p^2}{2m} + V(\mathbf{r}) + g_e \left(\frac{q}{2m_e}\right) \hat{\mathbf{L}}.\mathbf{B}$$ Energy shift ?

Reminder : Perturbation theory $$\Delta E_n = \langle \psi_n | \hat{V}_{\text{perturbation}} | \psi_n \rangle$$

Injecting

$$\psi(\mathbf{r}) = R(r) Y_{l,m}(\theta, \varphi)$$

$$\begin{aligned}
\Delta E &= \int d^3\mathbf{r}\, \psi^*(\mathbf{r}) \times \left(\frac{g_e q B}{2m_e} \hat{L}_z \psi(\mathbf{r}) \right) \\
&= \frac{g_e q B}{2m_e} \int d^3\mathbf{r}\, \psi^*(\mathbf{r}) \times (-i\hbar \partial_\varphi \psi(\mathbf{r})) \\
&= \frac{g_e q B}{2m_e} \left(\int dr\, |R(r)|^2 \right) \left(\int \sin\theta d\theta d\varphi\, Y^*_{l,m}(\theta, \varphi) \times (-i\hbar \partial_\varphi Y_{l,m}(\theta, \varphi)) \right) \\
&= \frac{g_e q B}{2m_e} \times 1 \times \int \sin\theta d\theta d\varphi\, Y^*_{l,m}(\theta, \varphi) \times (m\hbar Y_{l,m}(\theta, \varphi)) \\
&= \frac{g_e q B}{2m_e} m\hbar \times 1 \times 1
\end{aligned}$$

(could be derived directly from)

$$L_z |\psi_{n,l,m}\rangle = m\hbar |\psi_{n,l,m}\rangle$$

Application 2: Selection rules

Add an EM wave

$$H = \frac{p^2}{2m} + V(\mathbf{r}) - (q\hat{\mathbf{r}})\,.\mathbf{E_0}\cos\omega t$$

Time evolution ?

Decompose on atomic orbitals

$$|\psi\rangle = \sum c_k(t)\,|\psi_k\rangle$$

(k accounts for n, l and m here)

Inject in Schrodinger equation

$$\begin{aligned} i\hbar\partial_t c_k &= E_k c_k - \sum_m \frac{\langle\psi_m|\, q\hat{\mathbf{r}}\,|\psi_k\rangle\,.\mathbf{E_0}}{2} c_m\left(e^{i\omega t} + e^{-i\omega t}\right) \\ &= E_k c_k - \sum_m \hbar\Omega_{mk} c_m\left(e^{i\omega t} + e^{-i\omega t}\right) \end{aligned}$$

$$\hbar\Omega_{mk} = -\langle\psi_m|\, q\hat{\mathbf{r}}\,|\psi_k\rangle\,.\mathbf{E_0}$$

Non trivial evolution depends on Rabi frequency

Isidor Isaac Rabi

Application 2: Selection rules

Non zero Rabi frequency ?

$$\hbar\Omega_{mk} = -\langle\psi_m|\, q\hat{\mathbf{r}}\, |\psi_k\rangle\, .\mathbf{E_0}$$

$$\langle\psi_i|\,\hat{\mathbf{r}}\,|\psi_j\rangle = \int r^2 \sin\theta dr d\theta d\varphi \begin{pmatrix} r\sin\theta\cos\varphi \\ r\sin\theta\sin\varphi \\ r\cos\theta \end{pmatrix} R^*_{n_i}(\mathbf{r}) R_{n_j}(\mathbf{r}) Y^*_{l_i,m_i}(\theta,\varphi) Y_{l_j,m_j}(\theta,\varphi)$$

$$= \propto \frac{\mathbf{u_x} + i\mathbf{u_y}}{2} \int d\varphi\, e^{i(1+m_j-m_i)} + \frac{\mathbf{u_x} - i\mathbf{u_y}}{2} \int d\varphi\, e^{i(-1+m_j-m_i)} + \mathbf{u_z} \int d\varphi\, e^{i(m_j-m_i)}$$

If E // (ux + i uy) = σ+ polarized, then non zero if mi = mj +1

➡ If E // (ux - i uy) = σ- polarized, then non zero if mi = mj -1

If E // (uz) = π polarized, then non zero if mi = mj

Application 3: Rabi oscillation

Isidor Isaac Rabi

Back to time evolution

$$i\hbar\partial_t c_k = E_k c_k - \sum_m \hbar\Omega_{mk} c_m \left(e^{i\omega t} + e^{-i\omega t}\right)$$

For simplicity :

Start in state « n_0 » at t=0

Only coupled to state « n_1 »

(calculation detailled in the textbook)

$$|c_{n_0}(t)|^2 = 1 - \frac{\Omega^2}{\Omega^2+\delta^2}\sin^2\left(\frac{\sqrt{\Omega^2+\delta^2}}{2}t\right)$$

$$|c_{n_1}(t)|^2 = \frac{\Omega^2}{\Omega^2+\delta^2}\sin^2\left(\frac{\sqrt{\Omega^2+\delta^2}}{2}t\right)$$

Two typical frequencies

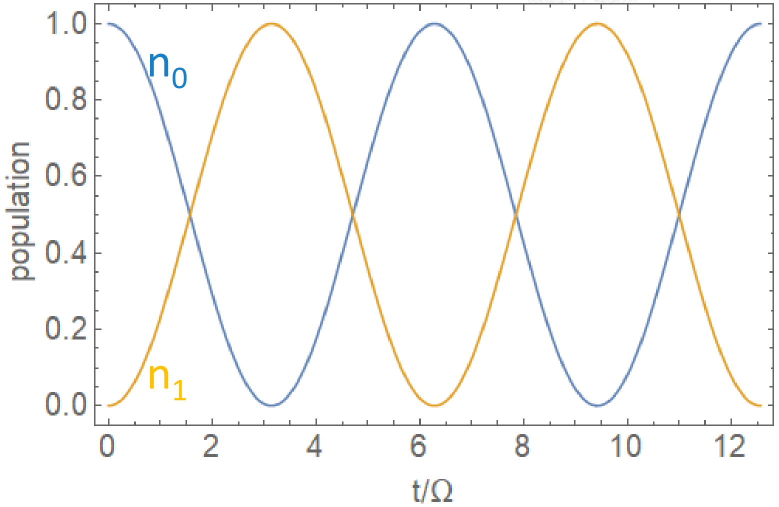
Rabi frequency

$$\hbar\Omega = -\langle\psi_{n_1}|\, q\hat{\mathbf{r}}\, |\psi_{n_0}\rangle\,.\mathbf{E_0}$$

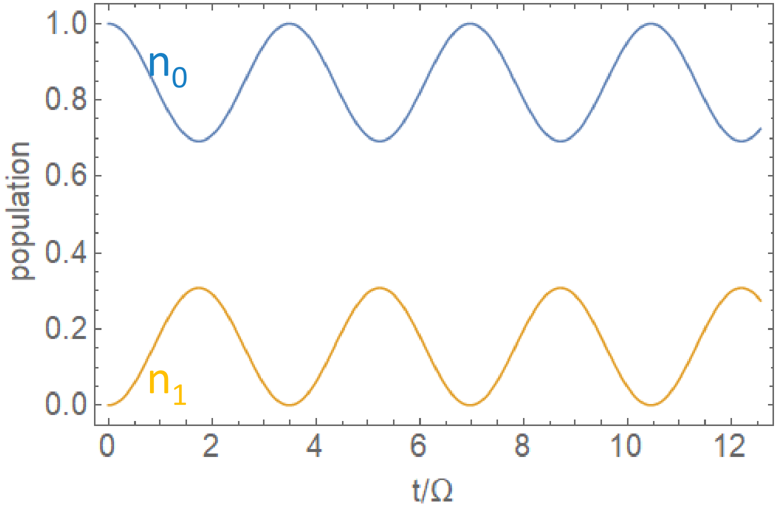
Detuning

$$\delta = \omega_{\text{light}} - \frac{E_{n_1} - E_{n_0}}{\hbar}$$

At resonance (δ = 0)



Out of resonance (δ = 1,5 Ω)



Take home message