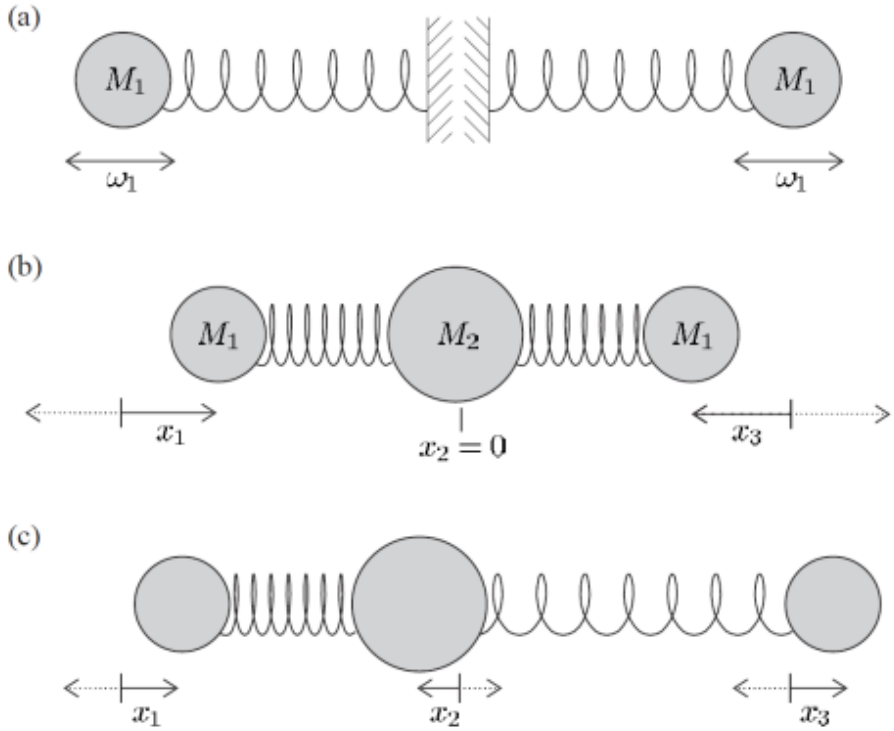
Note: 2x2 matrices occur also in classical mechanics. Example:



From: C. Foot, Atomic Physics, Appendix A

$$M_1\ddot{x}_1 = \kappa(x_2 - x_1)\,,$$
$$M_2\ddot{x}_2 = -\kappa(x_2 - x_1) + \kappa(x_3 - x_2)\,,$$
$$M_1\ddot{x}_3 = -\kappa(x_3 - x_2)\,,$$

$$\begin{pmatrix}\ddot{u}\\ \ddot{v}\end{pmatrix} = \begin{pmatrix} -\left(\omega_1^2+\omega_2^2\right) & \omega_2^2 \\ \omega_2^2 & -\left(\omega_1^2+\omega_2^2\right)\end{pmatrix}\begin{pmatrix}u\\ v\end{pmatrix}$$

with

$$u = x_2 - x_1 \text{ and } v = x_3 - x_2$$

$$\kappa/M_1 = \omega_1^2 \text{ and } \kappa/M_2 = \omega_2^2$$

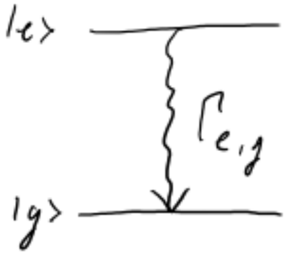
Determinant:
$$\left(\omega_1^2 - \omega^2\right)\left(\omega_1^2 + 2\omega_2^2 - \omega^2\right) = 0$$

Eigenfrequencies:
$$\omega = \omega_1 \text{ and } \omega' = \sqrt{\omega_1^2 + 2\omega_2^2}$$

Density Matrix Approach

Problem: The Schrödinger equation describes unitary time evolution, so it leaves the system in a pure state. It cannot describe decoherence or uncontrolled loss of atoms, phase, ...

Could use hamiltonian with complex eigenenergies $E_g \to E_g + i\,\Gamma_{g,f}/2$.



However, many other processes (even spontaneous emission) cannot be described in this way

$\Rightarrow$ Need density matrix formalism

Pure State:

Wave function $|\Psi(t)\rangle = \sum_n c_n(t)\,|\Psi_n\rangle$

Some complete set of eigenstates

Operator A in this basis:

$$A_{nm} = \langle \Psi_n | A | \Psi_m \rangle$$

Time-dependent expectation value

$$\langle A \rangle_t = \langle \Psi(t) | A | \Psi(t) \rangle$$

$$= \sum_{m,n} c_m^*(t)\, c_n(t)\, A_{mn}$$

$$= \sum_{m,n} \rho_{nm}(t) A_{mn} = \underline{\mathrm{Tr}\left(\rho(t) A\right)}$$

with $\rho(t) = |\Psi\rangle\langle\Psi|$

$\rho_{mn} = c_m^*(t)\, c_n(t)$

ρ_{nn} populations

$\rho_{mn},\ m \neq n$ coherences.

Now for a mixed state

Wave function $|\Psi_i(t)\rangle = \sum_n c_n^i(t)\,|\Psi_n\rangle$
with probability p_i

Some complete set of eigenstates

Operator A in this basis:

$$A_{nm} = \langle \Psi_n | A | \Psi_m \rangle$$

Time-dependent expectation value

$$\langle A \rangle_t = \sum_i \langle \Psi_i(t) | A | \Psi_i(t) \rangle \, p_i$$

$$= \sum_i \sum_{m,n} c_m^{i*}(t)\, c_n^i(t)\, A_{mn}\, p_i$$

$$= \sum_{m,n} \rho_{nm}(t) A_{mn} = \underline{\mathrm{Tr}\left(\rho(t) A\right)}$$

with $\rho(t) = \sum_i |\Psi_i\rangle\langle\Psi_i|\, p_i \;\hat{=}\; \overline{|\Psi\rangle\langle\Psi|}$

$$\rho_{mn} = \sum_i c_m^{i*}(t)\, c_n^i(t)\, p_i$$

ρ_{nn} populations

$\rho_{mn},\ m \neq n$ coherences.

Integrated in one equation

- quantum mechanical average
- ensemble average

Time evolution of the density operator:

$$i\hbar \dot{\rho} = [H, \rho]$$

Trace: $\mathrm{Tr}\,\rho = \sum_i p_i = 1$

$$\mathrm{Tr}\,\rho^2 = \sum_i p_i^2 \leq 1$$

$= 1$ for pure state

Density matrix formalism for arbitrary two-level systems

Isomorphism with classical magnetic moments

General 2×2 Hamiltonian

$$H = \frac{\hbar}{2}\left(\cancel{\bar{\omega}\mathbb{1}} + \omega_1 \sigma_x + \omega_2 \sigma_y + \omega_0 \sigma_z\right)$$

$$= \frac{\hbar}{2}\,\vec{\omega}\cdot\vec{\sigma} \qquad \vec{\omega} = (\omega_1, \omega_2, \omega_0)$$

General ρ:

$$\rho = \frac{1}{2}\left(r_0 \mathbb{1} + r_1 \sigma_x + r_2 \sigma_y + r_3 \sigma_z\right)$$

$$\mathrm{Tr}\,\rho = r_0 \overset{!}{=} 1 \qquad \vec{r} = (r_1, r_2, r_3) \text{ Bloch vector}$$

Pset 1: Show that $i\hbar\dot{\rho} = [H, \rho]$ implies the equation of motion

$$\frac{d\vec{r}}{dt} = \vec{\omega}\times\vec{r}$$

$\Rightarrow$ Precession of $\vec{r}$ about $\vec{\omega}$.

Generalizes our previous result for a spin $\frac{1}{2}$ system. Using Heisenberg equations of motion, we have shown

$$\frac{d}{dt}\vec{S} = \vec{\omega} \times \vec{S}.$$

The above now generalizes this result for mixed states with $|r_1|^2 + |r_2|^2 < 1$, i.e. for ensemble averages that have less than the maximum possible magnetic moment.

Note that hamiltonian time evolution does not alter the purity of a state:

$$\operatorname{tr} \rho^2 = \text{const.}$$

Check: $\operatorname{tr} \rho^2 = \frac{1}{2}\left(r_0^2 + r_1^2 + r_2^2 + r_3^2\right)$

$$= \frac{1}{2}\left(1 + \vec{r}^{\,2}\right)$$

Since $\dot{\vec{r}} \perp \vec{r}$, the length of $\vec{r}$ does not change $\Rightarrow \operatorname{tr} \rho^2 = \text{constant}.$

Bloch equations, relaxation $\Rightarrow$ 8.422

Thermal equilibrium $\rho^T = \frac{1}{Z} e^{-H_0/k_B T}$

$$\rho \xrightarrow[\text{relaxation}]{} \rho^T$$

Phenomenological treatment of damping

$$\dot{\rho} = \frac{1}{i\hbar}[H, \rho] - (\rho - \rho^T)/T_e$$

with T_e - equilibration time

In many cases:

		relaxes:
T_1 -	population / energy decay time	r_z
T_2 -	coherences / dephasing	r_x, r_y

$T_2 < T_1$ **typically**

$$\dot{r}_z = (\vec{\omega} \times \vec{r})_z - (r_z - r_z^T)/T_1$$

$$\dot{r}_{x,y} = (\vec{\omega} \times \vec{r})_{x,y} - (r_{x,y} - \underbrace{r_{x,y}^T}_{\overset{!}{0} \text{ in thermal equilibrium}})/T_2$$

Bloch equations (Bloch 1946)

Sequence - in order of energy scales:

- Electronic Structure $1e^-$ H
  $2e^-$ He
- Fine structure
- Lamb shift
- Hyperfine structure
- External fields: $\vec{B}$, $\vec{E}$, $\vec{E}(t)$

Hydrogen:

Bohr postulates

- Coulomb interaction, stationary orbits
- $L = n\hbar$

$\Rightarrow$ Rydberg formula

$$E_n = -\underbrace{\left(\underbrace{\frac{m e^4}{2\hbar^2}}_{R_\infty} \underbrace{\frac{M}{M+m}}_{\text{reduced mass factor}}\right)}_{R_H} \cdot \frac{1}{n^2}$$

Further "early QM" improvements:

elliptical orbits (Wilson - Sommerfeld quantization)

Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

In spherical coordinates

$$\nabla^2 f = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r f) - \frac{\vec{\ell}^2}{r^2} f$$

$\hbar^2 \vec{\ell}^2$ = operator for angular momentum squared

Eigenvectors of $\vec{\ell}^2$ and ℓ_z:

spherical harmonics $Y_{\ell m}(\vartheta, \varphi)$

$$\vec{\ell}^2 Y_{\ell m}(\vartheta,\varphi) = \ell(\ell+1) Y_{\ell m}$$

$$\ell_z Y_{\ell m}(\vartheta,\varphi) = m Y_{\ell m}$$

$$Y_{00}(\vartheta,\varphi) = \frac{1}{\sqrt{4\pi}} = \text{const.}$$

$$Y_{10}(\vartheta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\vartheta$$

$$Y_{1\pm1}(\vartheta,\varphi) = \mp\sqrt{\frac{3}{8\pi}}\sin\vartheta\, e^{\pm i\varphi} \propto \frac{x \pm iy}{r}$$

$$d\vartheta \sin\vartheta\, |Y_{\ell m}|^2 = 1$$

$Y_{\ell m}$ orthonormal

$$\int_0^{\pi} d\vartheta \sin\vartheta\, Y_{\ell m}(\vartheta,\varphi) Y_{\ell' m'}(\vartheta,\varphi) = \delta_{\ell\ell'}\delta_{mm'}$$

Radial Schrödinger Equation $\psi = \frac{u(r)}{r} Y_{\ell m}(\vartheta,\varphi)$

$$-\frac{\hbar^2}{2m} u''(r) + \left\{\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} - \frac{e^2}{r} - E\right\} u = 0$$

Let's look for bound state solutions $E = -|E|$

Substitute $\rho^2 = \frac{2m|E|}{\hbar^2} r^2$; $\lambda^2 = \frac{2m e^4}{\hbar^2 |E|}$

$$\Rightarrow \quad \frac{d^2 u}{d\rho^2} + \left\{-\frac{\ell(\ell+1)}{\rho^2} + \frac{\lambda}{\rho} - 1\right\} u = 0$$

Quantization from requiring $u(\infty) \to 0$

$$\lambda = 2n$$

$$\Rightarrow \boxed{E = -\frac{m e^4}{2\hbar^2}\frac{1}{n^2}}$$

Hydrogen

Relevant distance scales:

$$a_0 = \frac{\hbar^2}{me^2} = \frac{\hbar c}{e^2}\,\frac{\hbar}{mc} = \frac{1}{\alpha}\lambda_c$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{n^2 a_0}$$

$$\langle r \rangle = \frac{n^2 a_0}{Z}\left\{1 + \frac{1}{2}\left(1 - \frac{\ell(\ell+1)}{n^2}\right)\right\}$$

$$|\psi_{n00}(0)|^2 = \frac{1}{\pi}\left(\frac{Z}{n a_0}\right)^3$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)}\left(\frac{Z}{n a_0}\right)^3$$

$$\xrightarrow[\ell = n-1]{} \approx \left(\frac{Z}{n^2 a_0}\right)^3 \quad \text{for large } n$$

$$1s: \quad \psi_{100}(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$\psi_{n\ell m}(r) = \#\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^{\ell} e^{-\frac{Zr}{na_0}} \cdot f\left(\frac{Zr}{na_0}\right)$$

Important fact: Energies $E_{nlm} = -13.6\,eV \frac{1}{n^2}$ <u>independent</u> of l! Special property of the Coulomb-potential!

In fact $n = n_r + l$

radial quantum # gives degree of polynomial (# of zeroes)

angular momentum

How many l's do I have for given n? Only n different ones: $l = 0, \ldots, n-1$.

Simple way to see this:

centrifugal p. is $\frac{\hbar^2 l(l+1)}{m r_0^2}$ where

$$\frac{l(l+1)}{m r_0^2} \simeq \frac{e^2}{r_0}$$

$$\Rightarrow r_0 \simeq \frac{l^2 \hbar^2}{m e^2} = l^2 a_0$$

$\Rightarrow$ bottom of potential is at $\approx -\frac{\hbar^2}{m a_0^2 l^2}$

Need $E > -\frac{\hbar^2}{m a_0^2 l^2}$

or $|E| < \frac{\hbar^2}{m a_0^2 l^2} \Rightarrow l < n$!