Linear response of a Quantum system to oscilating external force 11.1.2019

In order to derive the general linear response of a quantum system we start by looking at the full time dependent solution of a two level system (H atom with a 1s and 2p orbital) in a driving field (electrical field)

We then use a small time (weak field) expansion to get the time dependent perturbation theory or linear response

In the end we generalize the results of a two level system to arbitrary quantum systems.

Example of H atom in oscilatory electric field

We include the 1s and $2p_z$ orbital in our basis. The unperturbed Hamiltonian is

$$H_0 = \varepsilon_{1s}\, a^\dagger_{1s} a_{1s} + \varepsilon_{2p}\, a^\dagger_{2p} a_{2p}$$

or in matrix form $\begin{pmatrix} \varepsilon_{1s} & 0 \\ 0 & \varepsilon_{2p} \end{pmatrix}$

$\varepsilon_{1s} = -1$ Ryd $\qquad \varepsilon_{2p} = -\frac{1}{4}$ Ryd

The electric field is given as

$\sin \omega t\, \vec{E}$ $\qquad$ with $\vec{E} = E_0 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

in the z direction

The Hamiltonian is

$$H_1 = e E_0 \sin \omega t\, \hat{z}$$

with $\hat{z}$ the position operator

in Matrix form we have:

$$\hat{z} = \begin{pmatrix} \langle \psi_{1s} | z | \psi_{1s} \rangle & \langle \psi_{1s} | z | \psi_{2s} \rangle \\ \langle \psi_{2s} | z | \psi_{1s} \rangle & \langle \psi_{2s} | z | \psi_{1s} \rangle \end{pmatrix}$$

with $\psi_{nlm} = Y_{lm}(\theta, \phi)\, R_{nl}(r)$

$$Y_{1s}(\theta,\phi) = \frac{1}{2\sqrt{\pi}}$$

$$Y_{2p_z}(\theta,\phi) = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta$$

$$R_{1s}(r) = 2 e^{-r/a_\mu} \left(\frac{1}{a_\mu}\right)^{3/2}$$

$$R_{2p}(r) = \frac{1}{2\sqrt{6}} e^{-r/2a_\mu}\, r \left(\frac{1}{a_\mu}\right)^{5/2}$$

yields

$$\hat{z} = \frac{128}{243}\sqrt{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{in units of } a_\mu$$

$$\sim 0.744 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

The eigen states of the position operator are $\sqrt{\frac{1}{2}}\left(\psi_{1s} + \psi_{2p_z}\right)$ with it's charge center at $+0.744$ a_μ

and $\sqrt{\frac{1}{2}}\left(\psi_{1s} - \psi_{2p_z}\right)$ with it's charge center at -0.744 a_μ

The electric field thus results in a driving force that drives the electron away from $z=0$ $\Rightarrow$ see ppt.

In order to have a driven Harmonic oscilator we also need a force that restorce the electron back to $z=0$.

This is contained in $H_0 = \begin{pmatrix} \varepsilon_{1s} & 0 \\ 0 & \varepsilon_{2p} \end{pmatrix}$

with $\varepsilon_{1s} = -1$ Ryd

$\varepsilon_{2p} = -\frac{1}{4}$ Ryd $\quad \left(E_n = -\frac{1}{n^2}\right)$

let's first shift the zero of energy such that

$$H_0 = \begin{pmatrix} 0 & 0 \\ 0 & w_0 \end{pmatrix} \quad \text{with } w_0 = \varepsilon_{2p} - \varepsilon_{1s} = \frac{3}{4}\,\text{Ryd}$$

In order to show that H_0 contains a restoring force we can plot $\langle H_0 \rangle$ as a function of $\langle z \rangle$

For $\phi = \cos\alpha\, \psi_{1s} + \sin\alpha\, \psi_{2pz}$

we have

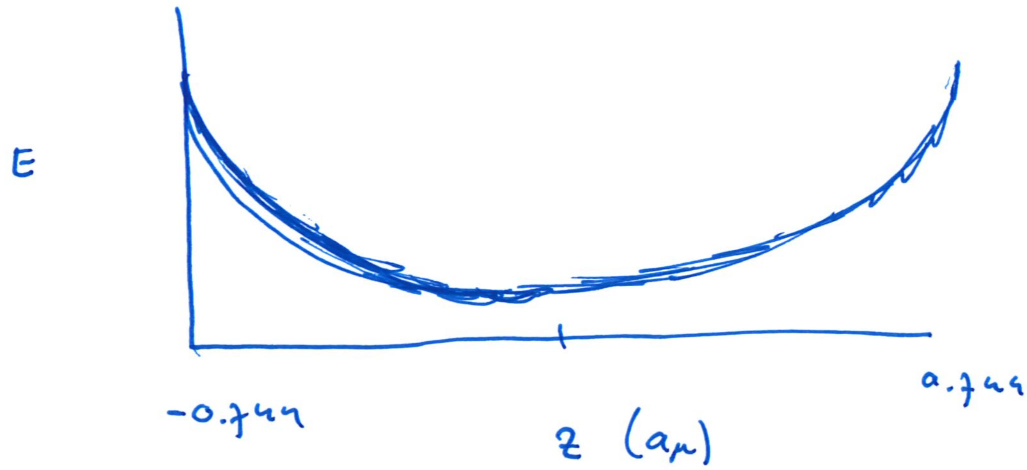
$$\langle \phi | z | \phi \rangle = 2 \cos\alpha \sin\alpha \quad \left(\text{in units of } \frac{128}{243}\sqrt{2}\, a_\mu\right)$$

$$\langle \phi | H | \phi \rangle = w_0 (\sin\alpha)^2$$

$$= w_0 (1 - \cos^2\alpha)$$

$$\langle \phi | z | \phi \rangle = 2 \sqrt{-\frac{\langle \phi | H | \phi \rangle}{w_0} + 1} \sqrt{\frac{\langle \phi | H | \phi \rangle}{w_0}}$$

$$\langle \phi | H | \phi \rangle = w_0 \frac{1}{2} \left(1 - \sqrt{1 - \langle z \rangle^2} \right)$$



$$E = \frac{1}{2}\left(1 - \sqrt{1-z^2}\right)$$

$$= \underbrace{\frac{z^2}{4}}_{\text{Harmonic oscilator}} + \underbrace{\frac{z^4}{16} + \dots}_{\text{corrections}}$$

Our total time dependent Hamiltonian is

$$H(t) = \begin{pmatrix} 0 & V \sin \omega t \\ V \sin \omega t & \omega_0 \end{pmatrix}$$

with $V = e E_0 \mu$

and μ the dipole moment

$$\mu = \langle \varphi_{1s} | z | \varphi_{2p_z} \rangle = 0.744 \text{ au}$$

We need to solve the time dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \psi(t) = H \psi(t)$$

for $V = 0$ the solution would be

$$\psi(t) = \{ \cos \alpha \ , \ e^{-i\omega_0 t} \sin \alpha \}$$

so take as a solution for arbitrary V

$$\psi(t) = \{ a(t) , \quad e^{-i\omega_0 t} b(t) \}$$

we can now insert this into the schrödinger equation and solve

$$\frac{i\partial}{\partial t} \psi(t) = \left\{ i \frac{da(t)}{dt} , \quad i e^{-i\omega_0 t} \left(\frac{db(t)}{dt} - i\omega_0 b(t) \right) \right\}$$

$$H \psi(t) = \left\{ e^{-it\omega_0} V \sin(\omega t) b(t), \quad e^{-it\omega_0} \omega_0 b(t) + V \sin \omega t \, a(t) \right\}$$

This yields a coupled set of two differential equations. we can solve this numerically (money labor) or aproximately analitical

We Have

$$i \frac{da(t)}{dt} = \cancel{\tfrac{1}{\hbar}}\, e^{-i\omega_0 t} \, V \sin(\omega t) \, b(t)$$

$$= \frac{1}{2} i V \left(e^{-i(\omega_0 + \omega)t} - e^{-i(\omega_0 - \omega)t} \right) b(t)$$

or

$$a(t) = \int \frac{1}{2} V b(t) \left(e^{-i(\omega_0+\omega)t} - e^{-i(\omega_0-\omega)t} \right) dt$$

For $\omega \sim \omega_0$ $\quad e^{-i(\omega_0+\omega)t}$ oscilates much faster then $e^{-i(\omega_0-\omega)t}$

the integral over an oscilating function is small $\Rightarrow$

$$a(t) = -\int \frac{1}{2} V b(t) \, e^{-i(\omega_0-\omega)t} \, dt$$

$\Rightarrow$ rotating wave aproximation

Solving the resulting equations yields

$$a(t) = e^{\frac{1}{2} i t(\omega - \omega_0)} \left[\cos t\Omega - \frac{i(\omega-\omega_0)\sin t\Omega}{2\Omega} \right]$$

$$b(t) = e^{-\frac{1}{2} i t(\omega+\omega_0)} \, V \, \frac{\sin t\Omega}{2\Omega}$$

with $\Omega = \frac{1}{2}\sqrt{V^2 + (\omega-\omega_0)^2}$

and $a(t=0) = 1 \qquad b(t=0) = 0$

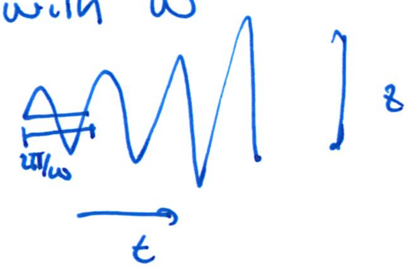
- We find that the occupation of the $2p_z$ orbital oscilates with the frequency Ω

  $\Rightarrow$ Rabi frequency.

- We find that the phase between the 1s and $2p_z$ orbital oscilate with the frequency ω

  $\Rightarrow$ $\langle z \rangle$ oscilates with ω

  $\Rightarrow$ driven oscilator



- Besides the term proportional to $\cos \Omega t$ in $a(t)$ there is a term proportional to $\sin \Omega t \quad e^{\frac{1}{2} it(\omega - \omega_0)}$

this term is there to fullfill $a(t=0) = 1$
$b(t=0) = 0$

a drivn harmonic oscilator can oscilate at it's eign frequency, besides the forced part.

- The position of the electron is given by

$$\langle \psi(t) | z | \psi(t) \rangle = a^*(t)\, b(t) + a(t)\, b^*(t)$$

$$= 2V(\omega - \omega_0) \sin \omega t \, \frac{\sin^2 \Omega t}{4\Omega^2}$$

$$+ V \cos \omega t \, \frac{\sin 2\Omega t}{2\Omega}$$

the amplitude of the oscilation in modified by $\sin 2\Omega t$. i.e. each time when the 1s or $2p_z$ orbital is maximal occupied there is no oscilation.

In order to calculate the linear response we take V small and make a series expansion of $z(t)$

$$z(t) = V \frac{\sin \omega t - \sin \omega_0 t}{\omega - \omega_0} + O(V^2)$$

the $\sin \omega_0 t$ part comes from the

$$2V(\omega-\omega_0) \sin \omega t \quad \frac{\sin 2 \Omega t}{4\Omega^2} \quad \text{term}$$

and is related to the eigen-oscilation $(a(t=0)=1)$ and not a response

the response is

$$z(t) = \frac{V \sin(\omega t)}{\omega - \omega_0}$$

and $\chi = \frac{1}{\omega - \omega_0}$

clasically we found

$$\frac{1}{2m} \frac{2}{\omega^2 - \omega_0^2} = \frac{1}{2m} \frac{1}{\omega_0} \left(\frac{1}{\omega - \omega_0} - \frac{1}{\omega + \omega_0} \right)$$

the $\frac{1}{2m}$ and $\frac{1}{\omega_0}$ are related to the classical response where we divided by a force and the q.m. response when we divide by V

the missing term $\frac{1}{\omega + \omega_0}$ is a real problem.

we have

$$\chi = \frac{1}{\omega - \omega_0}$$

$$\sigma = -i\omega \frac{1}{\omega - \omega_0}$$

$$f = -\omega^2 \frac{1}{\omega - \omega_0}$$

For large ω $\sigma \to -i$ i.e. absorption at infinite frequencies

and $f \to \infty$ i.e. divergent diffraction at infinite frequencies

both are not ok.

The problem is in the rotating wave aproximation. we neglected $e^{-i(\omega+\omega_0)t}$ and only kept $e^{-i(\omega-\omega_0)t}$

If we look at $\psi(t)$ upto linear order in V we find

$$\psi(t) = \left\{ 1, \; \frac{e^{-it(\omega+\omega_0)/2} \, V \, \sin\left(\frac{1}{2}t(\omega-\omega_0)\right)}{\omega-\omega_0} \right\}$$

which does not satisfy the Schrödinger equation upto linear order in V

(It only does after making the rotating wave aproximation)

Based on the clusical result we can guess a valid solutin upto linear order in V

$$\Psi = \left\{ 1,\ \frac{e^{-it(\omega+\omega_0)/2}\, V \sin\left(\tfrac{1}{2}t(\omega-\omega_0)\right)}{\omega-\omega_0} + \frac{e^{-it(-\omega+\omega_0)/2}\, V \sin\left(\tfrac{1}{2}t(-\omega-\omega_0)\right)}{-\omega-\omega_0} \right\}$$

and indeed now

$$i\frac{\partial}{\partial t}\Psi = H\Psi$$ upto linear order in V

In order to calculate the linear response we have

$$\langle \psi | x | \psi \rangle = \frac{2V\left(\omega_0 \sin(t\omega) - \omega \sin(t\omega_0)\right)}{\omega^2 - \omega_0^2}$$

where we again neglect the $\sin t\omega_0$ -term and find

$$\chi = \frac{2\omega_0}{\omega^2 - \omega_0^2}$$

$$= \left(\frac{1}{\omega - \omega_0} - \frac{1}{\omega + \omega_0}\right)$$

If we want to express this as an operator such that the ground-state expectation value yields the response function we need to find an operator whose expectation value is $\frac{1}{\omega_0} = \frac{1}{\varepsilon_p - \varepsilon_s}$

for the ground-state.

note that $z\,\phi_{1s} \rightarrow \phi_{2p_z}$

such that $\frac{1}{H} z\,\phi_{1s} = \frac{1}{\varepsilon_p} \phi_{2p}$

and $$\chi = \langle \phi_{1s} | z \frac{1}{\omega - H + \varepsilon_{1s}} z | \phi_{1s} \rangle$$

$$- \langle \phi_{1s} | z \frac{1}{\omega + H - \varepsilon_{1s}} z | \phi_{1s} \rangle$$

In general for any operator O we have

$$\chi_O = \langle \phi | O \frac{1}{\omega - H + E_0 + i0^+} O | \phi \rangle$$

$$- \langle \phi | O \frac{1}{\omega + H - E_0 + i0^+} O | \phi \rangle$$

with $E_0 = \langle \phi | H | \phi \rangle$

and the small imaginary part to make sure we pick the right branch.