MIT Department of Chemistry
5.74, Spring 2004: Introductory Quantum Mechanics II
Instructor: Prof. Robert Field

Motion of Center of Wavepacket

Last time: Discussed experiments to monitor the central quantity

$$\langle \Psi(t) | \Psi(0) \rangle$$

in Heller's picture: the absorption spectrum, $I(\omega)$, is the FT of the autocorrelation function. $\Psi(0)$ in the autocorrelation function is the ground state, $V_g''(R)$, vibrational wavefunction $\left| g, v_g'' \right\rangle$ transferred vertically onto the excited state potential, $V_e'(R)$.

Is there a way to monitor $\langle \Psi(t) | \Psi(0) \rangle$ directly in the time domain? Many suggested schemes.

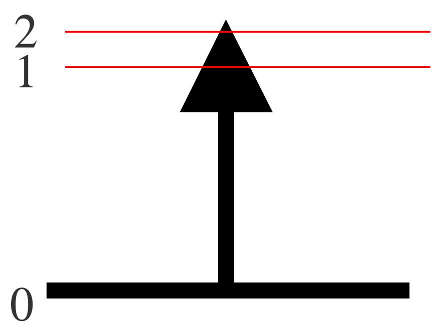
We need tools to examine various excitation/detection experimental schemes.

Excitation at $t = 0$, $\mathbf{E}(0)$
Evolution, $\mathbf{U}(t,0) = e^{-i\mathbf{H}t/\hbar}$
Detection, $\mathbf{D}$

$$\boldsymbol{\rho}(t) = \mathbf{U}(t,0)\mathbf{E}(0)\boldsymbol{\rho}(0)\mathbf{E}^{\dagger}(0)\mathbf{U}^{\dagger}(t,0)$$

Observation: Trace $(\mathbf{D}\, \boldsymbol{\rho}(t))$

Consider the simplest 3 level system first



Short excitation pulse

$$\Psi(t) = \beta|0\rangle e^{-iE_0 t/\hbar} + \alpha_1|1\rangle e^{-iE_1 t/\hbar} + \alpha_2|2\rangle e^{-iE_2 t/\hbar}$$

both eigenstates $|1\rangle$ and $|2\rangle$ are bright

$\beta = [1 - |\alpha_1|^2 + |\alpha_2|^2]^{1/2}$

$\alpha_i = c_i\mu_{i0}$ — c_i describes the intensity, spectral distribution, phase, and duration of the excitation pulse.

μ_{i0} is the electric dipole transition moment

$$\boldsymbol{\rho}(t) = |\Psi\rangle\langle\Psi| = \begin{pmatrix} |\beta|^2 & \beta\alpha_1^* e^{-i\omega_{01}t} & \beta\alpha_2^* e^{-i\omega_{02}t} \\ \beta^*\alpha_1 e^{+i\omega_{01}t} & |\alpha_1|^2 & \alpha_2^*\alpha_1 e^{-i\omega_{12}t} \\ \beta^*\alpha_2 e^{+i\omega_{02}t} & \alpha_2\alpha_1^* e^{+i\omega_{12}t} & |\alpha_2|^2 \end{pmatrix}$$

This $\boldsymbol{\rho}(t)$ is obtained by two transformations of $\rho(0)$

$$\boldsymbol{\rho}(t) = \mathbf{U}(t,0)\mathbf{E}(0)\boldsymbol{\rho}(0)\mathbf{E}^\dagger(0)\mathbf{U}^\dagger(t,0)$$

$\mathbf{E}(0)$ is the excitation matrix, operating at $t = 0$, on $\boldsymbol{\rho}(0)$.

$$\mathbf{E}(0) = \begin{pmatrix} \beta & \alpha_1^* & \alpha_2^* \\ \alpha_1 & 0 & 0 \\ \alpha_2 & 0 & 0 \end{pmatrix}$$

$$\mathbf{E}(0)\boldsymbol{\rho}(0)\mathbf{E}^{\dagger}(0)=\begin{pmatrix}\beta & \alpha_1^* & \alpha_2^* \\ \alpha_1 & 0 & 0 \\ \alpha_2 & 0 & 0\end{pmatrix}\begin{pmatrix}1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\beta^* & \alpha_1^* & \alpha_2^* \\ \alpha_1 & 0 & 0 \\ \alpha_2 & 0 & 0\end{pmatrix}$$

$$=\begin{pmatrix}\beta & \alpha_1^* & \alpha_2^* \\ \alpha_1 & 0 & 0 \\ \alpha_2 & 0 & 0\end{pmatrix}\begin{pmatrix}\beta^* & \alpha_1^* & \alpha_2^* \\ 0 & 0 & 0 \\ 0 & 0 & 0\end{pmatrix}$$

$$=\begin{pmatrix}|\beta|^2 & \beta\alpha_1^* & \beta\alpha_2^* \\ \alpha_1\beta^* & |\alpha_1|^2 & \alpha_1\alpha_2^* \\ \alpha_2\beta^* & \alpha_2\alpha_1^* & |\alpha_2|^2\end{pmatrix}$$

$\mathbf{U}(t,0)$ is the time evolution matrix. If $\rho(0)$ is expressed in the eigen-basis

$$\mathbf{U}(t,0)=e^{-i\mathbf{H}t/\hbar}=\begin{pmatrix}e^{-i\mathbf{E}_0t/\hbar} & 0 & 0 \\ 0 & e^{-i\mathbf{E}_1t/\hbar} & 0 \\ 0 & 0 & e^{-i\mathbf{E}_2t/\hbar}\end{pmatrix}$$

$$\boldsymbol{\rho}(t)=\mathbf{U}(t,0)\mathbf{E}(0)\boldsymbol{\rho}(0)\mathbf{E}^{\dagger}(0)\mathbf{U}^{\dagger}(t,0)=\begin{pmatrix}|\beta|^2 & \beta\alpha_1^*e^{-i\omega_{01}t} & \beta\alpha_2^*e^{-i\omega_{02}t} \\ \beta^*\alpha_1e^{+i\omega_{01}t} & |\alpha_1|^2 & \alpha_2^*\alpha_1e^{-i\omega_{12}t} \\ \beta^*\alpha_2e^{+i\omega_{02}t} & \alpha_2\alpha_1^*e^{+i\omega_{12}t} & |\alpha_2|^2\end{pmatrix}$$

as required from $|\Psi(t)\rangle\langle\Psi(t)|$

If the bright state is not an eigenstate, it is often convenient to set up $\boldsymbol{\rho}(0)$, $\mathbf{E}(0)$, and $\mathbf{H}$ in the zero-order basis set. Then find the transformation that diagonalizes $\mathbf{H}$ and apply it to $\rho_{(0)}^{(0)}$.

$$\mathbf{T}^{\dagger}\mathbf{H}\mathbf{T} = \begin{pmatrix} E_0 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_2 \end{pmatrix}$$

$$\mathbf{T}^{\dagger}\boldsymbol{\rho}_{(0)}^{(0)}\mathbf{T} = \boldsymbol{\rho}(0)$$

Now, we have a choice of several detection schemes.

Detection could involve:

(i) modification of a beam of probe radiation;

(ii) detection of emitted radiation through a filter or monochromator.

Let us consider the latter possibility.

Now there are several more possibilities:

(a) the detector is blind to radiation at ω_{10} (and ω_{12});

(b) the detector is sensitive to radiation at both ω_{10} and ω_{20} (but not ω_{12}), and both ω_{10} and ω_{20} radiation are detected with the same phase;

(c) same as (b) but ω_{10} is detected with phase opposite that at ω_{20}.

This could be based on a polarization trick. The $1 \leftarrow 0$ transition is $\Delta M = 0$ (z-polarized) and $2 \leftarrow 0$ is $\Delta M = \pm 1$ (x or y-polarized). Detection with polarizer at $+\pi/4$ and $-\pi/4$ would correspond to cases (b) and (c).

Detection: $I(t) = \text{Trace}\,(\mathbf{D}\,\boldsymbol{\rho}(t))$

For detection of radiation in transition back to $|0\rangle$

$$\mathbf{D} = \sum_{i,j} |i\rangle \mu_{i0} \mu_{0j} \langle j|$$

$$\text{Trace}\big(\mathbf{D}\boldsymbol{\rho}(t)\big) = D_{22}\rho_{22} + D_{11}\rho_{11} + D_{12}\rho_{21} + D_{21}\rho_{12}$$

(a) If we set $\mu_{10} = 0$, $\mu_{20} \neq 0$ (blind to ω_{10})

$$I(\mathrm{t}) = D_{22}\rho_{22} = |\mu_{20}|^2 \, |\alpha_2|^2$$

If we set $\mu_{20} = 0$, $\mu_{10} \neq 0$ (blind to ω_{20})

$$I(t) = |\mu_{10}|^2 \, |\alpha_1|^2$$

(b) If we set $\mu_{10} = \mu_{20} = \mu$, $\alpha_1 = \alpha_2 = \alpha$

$$\begin{aligned} I(t) &= |\mu_{20}|^2 |\alpha_2|^2 + |\mu_{10}|^2 |\alpha_1|^2 + \mu_{10}\mu_{02}\alpha_1^* \alpha_2 e^{i\omega_{12}t} + \mu_{20}\mu_{01}\alpha_1 \alpha_2^* e^{-i\omega_{12}t} \\ &= 2|\mu|^2|\alpha|^2 + 2|\mu|^2|\alpha|^2 \cos\omega_{12}t \\ &= 2|\mu|^2|\alpha|^2[1+\cos\omega_{12}t] \qquad \text{“phased up” at } t = 0 \end{aligned}$$

Quantum Beats. 100% amplitude, modulation.

(c) if we set $\mu_{10} = -\mu_{20} = \mu$, $\alpha_1 = \alpha_2 = \alpha$

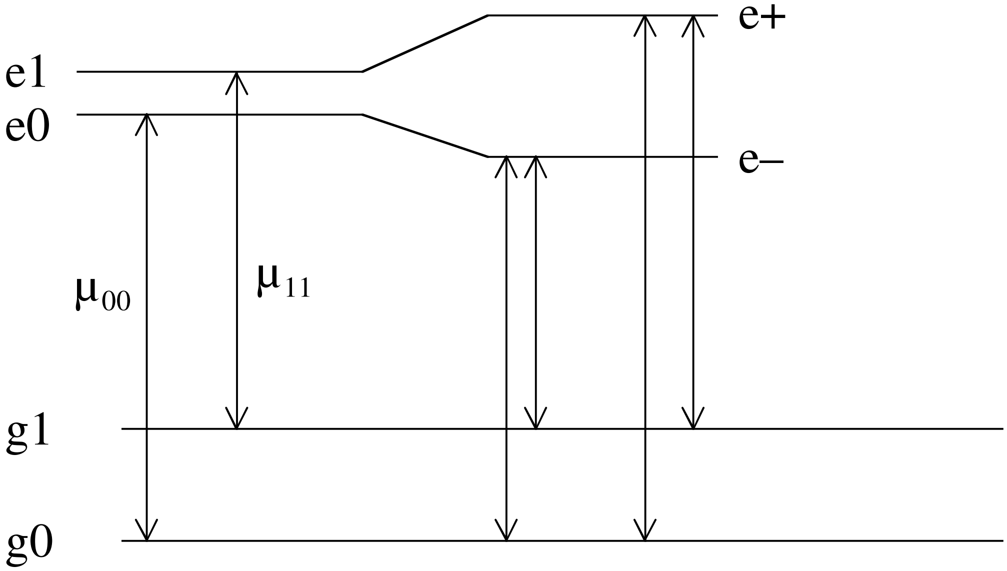
$$I(t) = 2|\mu|^2 \, |\alpha|^2[1-\cos\omega_{12}t] \quad \text{“phased out” at } t = 0$$

If, instead of both eigenstates being bright, we excite a system with one bright state and one dark state, at $t = 0$ we form $\Psi(0) = \psi_{\text{bright}} = \cos\theta\psi_1 + \sin\theta\psi_2$

$$\underbrace{\psi_1 + \sin\theta\psi_2}_{\text{eigenstates}}$$

Then **E** and **D** could be expressed in terms of bright states rather than eigenstates. In that case, α_1 and α_2 include $\cos\theta$ and $\sin\theta$ factors, and the phase of the Quantum Beats could depend on θ through α_1, α_2.

Zewail experiment



$$\mathbf{H}_e = \begin{pmatrix} e_{e1} & H_{e1e0} \\ H_{e1e0} & E_{e0} \end{pmatrix}$$

μ_{00} and $\mu_{11} \neq 0$ in zero-order basis
$\mu_{10} = \mu_{01} = 0$ in zero-order basis

because of $H_{e1e0} \neq 0$, both e+ and e– are bright from both g0 and g1.

But e1 is bright from g1 and dark wrt g0
e0 is bright from g0 and dark wrt g1

as a result, detecting at $\omega_{e+,g1}$ is phased up at $t = 0$ but at $\omega_{e+,g0}$ is phased out at $t = 0$. Vice versa for $\omega_{e-,g1}$ and $\omega_{e-,g0}$.

Figure removed due to copyright reasons.

We can use this **ρ**, **E, U, D** formalism to describe much more complicated experiments.

* Another sudden perturbation between $t = 0$ and time of detection.

* Detection could be using a beam of coherent radiation. Then one would integrate over t. Off resonance? Spectrally not a simple δ-function.

* Include elements of **D** that correspond to detection via $\left|\varepsilon_{\text{molecule}}(t) + \varepsilon_{\text{local oscillator}}(t)\right|^2$ cross term.