Fall 10-14-2003

# Density Matrix view of the Double Well Problem

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# A DENSITY MATRIX view of the DOUBLE WELL PROBLEM

## A State-to-State View

We have a system that consists of *matter* and a *radiaiton field*. Because these are coupled, one sees photon emission into the radiation field while the matter "decays" to lower lying states. We will describe the dynamics of this system, treating the coupling between the field and matter perturbatively.

### The unperturbed states

Suppose the matter has energy eigenstates

$$\psi_n \quad \longleftrightarrow \quad E_n$$

and that the field has a vacuum state

$$\Phi_0 \quad \longleftrightarrow \quad 0$$

and single photon states

$$\Phi_q \quad \longleftrightarrow \quad \hbar\omega_q$$

The matter and field will, to simplify the notation, both be considered *one-dimesional.* The label $q$ on the 1-photon states is the momentum of the photon. $\omega_q = cq$. Let $\hat{H}$ denote the Hamiltonian of the matter *and* the field.

Picture the system as phaving two kinds of states. The states

$$\Phi_0 \, \psi_n$$

correspond to matter in the $n^{th}$ energy eigenstate and no excitation in the field. These states have energies $E_n$. The states

$$\Phi_q \, \psi_m$$

have energies $E_m + \hbar\omega_q$. The collection of these states will be taken as a basis set.

### The perturbation

The states listed are not actually energy eigenstates because of a coupling between the matter and field. There will be an additional term in the Hamiltonian,

$$\hat{V} = -\hat{d} \cdot \hat{\mathcal{E}}$$

because of this coupling. $\hat{d}$ is the dipole moment of the matter and $\hat{\mathcal{E}}$ is the electric field associated with the $EM$ field.

Time-dependent perturbative analysis

The actual state of the system at time $t$ can be represented

$$\Psi(t) = \sum_n a_n(t) e^{-iE_n t/\hbar} \Phi_0 \phi_n + \sum_{m,q} c_{mq}(t) e^{-i(E_m + \hbar\omega_q)t/\hbar} \Phi_q \phi_m$$

The $a_n(t)$ and $c_{mq}(t)$ are the amplitudes of $\Psi$ in the basis set (in an interaction representation). The equation of motion

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = (\hat{H} + \hat{V})\Psi(t)$$

can be resolved in the basis set into the equations

$$i\hbar\, \dot{a}_n(t) e^{-iE_n t/\hbar} = -\sum_{m,q} c_{mq}(t) e^{-i(E_m+\hbar\omega_q)t/\hbar} \mathcal{E}_q^* d_{nm} \tag{1}$$

$$i\hbar\, \dot{c}_{mq}(t) e^{-i(E_m+\hbar\omega_q)t/\hbar} = -\sum_n a_n(t) e^{-iE_n t/\hbar} \mathcal{E}_q d_{mn} \tag{2}$$

with

$$\begin{aligned} d_{mn} &= \langle \psi_m | \hat{d} \psi_n \rangle \\ \mathcal{E}_q &= \langle \Phi_q | \hat{\mathcal{E}} \Phi_0 \rangle = \langle \Phi_0 | \hat{\mathcal{E}} \Phi_q \rangle^* \end{aligned}$$

These equations will now be solved with the initial conditions

$$c_{mq}(0) = 0, \qquad \text{all } m, q.$$

In the real system, the number of single photon states grows with the size of the "vacuum". In the infinite vacuum limit, only one photon states will be produced. We have simplified the description of the dynamics by implicitly ignoring multi-photon states, but this will be carried one step further: This no-photon initial condition will be applied ~ continuously in time. This is a little tricky, but the experiment we're trying to model has no photon-photon memory.

From (2),

$$c_{mq}(t) = \frac{i}{\hbar} \mathcal{E}_q \sum_n d_{mn} \int_0^t d\tau\, a_n(\tau) e^{i(E_m + \hbar\omega_q - E_n)\tau/\hbar}$$

which we insert into (1) to get

$$\dot{a}_n(t) = -\frac{1}{\hbar^2} \sum_{\ell,m} e^{i(E_n - E_m)t/\hbar} d_{nm} d_{m\ell} \sum_q \left|\mathcal{E}_q\right|^2 e^{-i\omega_q t/\hbar} \int_0^t d\tau\, a_\ell(\tau) e^{i(E_m + \hbar\omega_q - E_\ell)\tau/\hbar} \tag{3}$$

The 1D Field Model

The one-dimensional (scalar) field model gives a collection of modes for which, in the large vacuum limit,

$$\sum_q \left|\mathcal{E}_q\right|^2 f(\omega_q) = \sum_q \left|\langle\Phi_q|\hat{\mathcal{E}}\Phi_0\rangle\right|^2 f(\omega_q) \to \frac{\hbar}{2\pi\epsilon_0 c} \int d\omega_q\, \omega_q\, f(\omega_q)$$

The resonance condition, the condition that makes

$$\int_0^t d\tau\, a_\ell(\tau) e^{i(E_m + \hbar\omega_q - E_\ell)\tau/\hbar}$$

large, is

$$\omega_q = \frac{E_\ell - E_m}{\hbar}$$

So we can replace the $\omega_q$ in (3) with

$$\omega_q \to \frac{1}{\hbar}\mathcal{D}(E_\ell - E_m),$$

$\mathcal{D}(E)$ representing the density of states with photon energy $E$ in the radiation field. Since $\mathcal{D}(E) = 0$ for $E < 0$, only photon emission is possible, only matter de-excitation is possible.

With this representation for the field,

$$\dot{a}_n(t) = -\frac{1}{2\pi\epsilon_0\hbar^2 c} \sum_{\ell,m} e^{i(E_n - E_m)t/\hbar} d_{nm} d_{m\ell} \mathcal{D}(E_\ell - E_m) \int_0^t d\tau\, a_\ell(\tau) e^{i(E_m - E_\ell)\tau/\hbar} \int d\omega e^{-i\omega(t-\tau)} \tag{4}$$

The integral over $\omega$ in (4) gives $2\pi\delta(t-\tau)$ so the integration over $\tau$ can be trivially evaluated. (Almost trivially. Only half the $\delta$- function is picked up!) The upshot is that

$$\dot{a}_n(t) = -\frac{1}{2\epsilon_0\hbar^2 c}\sum_{\ell,m} e^{i(E_n-E_\ell)t/\hbar}\, d_{nm}d_{m\ell}\mathcal{D}(E_\ell - E_m)\, a_\ell(t)$$

Now we only apply this for very short times: times for which

$$e^{i(E_n-E_\ell)t/\hbar} \approx 1$$

We then reinitialize the system (sweep out any photon components) and run again. The conclusion is that

$$\dot{a}_n(t) = -\frac{1}{2\epsilon_0\hbar^2 c}\sum_{\ell,m} d_{nm}\mathcal{D}(E_\ell - E_m)\, d_{m\ell}\, a_\ell(t)$$

holds for *all* times. If

$$W_{n\ell} = \frac{1}{2\epsilon_0\hbar^2 c}\sum_{m} d_{nm}\mathcal{D}(E_\ell - E_m)\, d_{m\ell},$$

then

$$\dot{a}_n(t) = -\sum_{\ell} W_{n\ell}\, a_\ell(t) \tag{5}$$

(5) just represents a set of linear first order differential equations for the quantities $\{a_n(t)\}$. The actual time evolution will be a linear superposition of various modes, each of which has a single first order decay constant. Similar pictures describe single chain polymerization kinetics or stochastic nuclear decay schemes.

## Observe Something

Let $\hat{Q}$ correspond to some mechanical property of the system. Since the state changes with time, the expected value for $\hat{Q}$ will change in time.

$$\begin{aligned} Q(t) &= \langle \Psi(t)|\hat{Q}\Psi(t)\rangle \\ &= \sum_{n,m} a_n(t)^* e^{iE_n t/\hbar}\, Q_{nm}\, a_m(t) e^{-iE_m t/\hbar} \\ &\quad + \sum_{n,m,q} c_{nq}(t)^* e^{i(E_n+\hbar\omega_q)t/\hbar}\, Q_{nm}\, c_{mq}(t) e^{-i(E_m+\hbar\omega_q)t/\hbar} \\ &= \sum_{n,m} Q_{nm}\, e^{i(E_n-E_m)t/\hbar}\left\{ a_n(t)^*\, a_m(t) + \sum_q c_{nq}(t)^*\, c_{mq}(t)\right\} \end{aligned} \tag{6}$$

If the expression in braces in (6) were of the form $b_n(t)^* \, b_m(t)$, then (6) would have the *conventional* form

$$Q(t) = \langle \psi(t) | \hat{Q} \psi(t) \rangle$$

with

$$\psi(t) = e^{-i\hat{H}_M t/\hbar} \sum_n b_n(t) \, \psi_n,$$

$$\hat{H}_M = \text{the Hamiltonian of the matter.}$$

But the expression in the braces does not have this form because the expectation involves a mixture of states with different photon numbers. The *universe* of field + matter has a state function, but the subsystem of matter alone can not be characterized with a state function.

## The Density Matrix

But the expected value of $\hat{Q}$ will always be a linear combination of the matrix elements $Q_{mn}$. The mechanical system can always be characterized by giving the coefficients $\rho_{nm}(t)$ in the expression

$$Q(t) = \sum_{m,n} Q_{mn} \, \rho_{nm}(t)$$

Since $\hat{Q}$ could be anything, the $\rho_{nm}(t)$ are the generic answer to "What is the state of the mechanical system?"

If we imagine that the coefficients $\rho_{nm}(t)$ are the matrix elements of some operator $\hat{\rho}(t)$, then

$$Q(t) = \sum_{m,n} Q_{mn} \, \rho_{nm}(t) = \sum_m \left[ \hat{Q} \, \hat{\rho}(t) \right]_{mm} = \mathrm{Tr}[\hat{Q} \hat{\rho}(t)] \tag{7}$$

$\hat{\rho}(t)$ is the matter's density matrix and (6) identifies it's explicit representation,

$$\rho_{mn}(t) = e^{i(E_n - E_m)t/\hbar} \left\{ a_n(t)^* \, a_m(t) + \sum_q c_{nq}(t)^* \, c_{mq}(t) \right\} \tag{8}$$

Since $\rho_{mn}(t)^* = \rho_{nm}(t)$, $\hat{\rho}(t)$ is Hermitian. We want to continuously invoke the "no-photon" conditions, however, so we replace (8) with

$$\rho_{mn}(t) = e^{i(E_n - E_m)t/\hbar} \, a_n(t)^* \, a_m(t) \tag{9}$$

## The Equation of Motion

We started with a system that consisted with two parts, but shifted to questions about just one part. The equations of motion (1-2) describe the dynamics of the entire system. Can we describe the dynamics of the mechanical subsystem alone?

Since we know the equations of motion for the $a_n(t)$, we can calculate how rapidly the $\rho_{nm}(t)$ evolve in time:

$$
\begin{aligned}
\dot{\rho}_{mn}(t) =& \frac{i}{\hbar}(E_n - E_m)\, e^{i(E_n-E_m)t/\hbar}\, a_n(t)^*\, a_m(t) \\
&+ e^{i(E_n-E_m)t/\hbar}\, \{a_n(t)^*\, \dot{a}_m(t) + \dot{a}_n(t)^*\, a_m(t)\} \\
=& \frac{i}{\hbar}(E_n - E_m)\, e^{i(E_n-E_m)t/\hbar}\, a_n(t)^*\, a_m(t) \\
&- e^{i(E_n-E_m)t/\hbar}\left[\sum_\ell W_{m\ell}\, a_n(t)^*\, \dot{a}_\ell(t) + \sum_\ell W_{n\ell}^*\, a_\ell(t)^*\, a_m(t)\right] \\
=& \frac{i}{\hbar}(E_n - E_m)\, \rho_{mn}(t) \\
&- \sum_\ell \left[W_{m\ell}\, \rho_{\ell n}(t)\, e^{i(E_m-E_\ell)t/\hbar} + \rho_{m\ell}(t)^*\, W_{n\ell}^*\, e^{i(E_\ell-E_n)t/\hbar}\right]
\end{aligned}
$$

As an operator equation, this is

$$
\frac{d\hat{\rho}(t)}{dt} = -\frac{i}{\hbar}[\hat{H}_M, \hat{\rho}(t)] - \left[\hat{\Gamma}(t)\, \hat{\rho}(t) + \hat{\rho}(t)\, \hat{\Gamma}(t)\right]
$$

with

$$
\hat{\Gamma}(t) = e^{i\hat{H}_M t/\hbar}\, \hat{W}\, e^{-i\hat{H}_M t/\hbar}
$$