Lecture 2: Hierarchy of pure states

Math Notes **Key Concepts** **Advanced Topics and Extra Details**

Contents

Last lecture I started by discussing two points: first, that we are interested in understanding how we can bring the tools and concepts of quantum information science into chemistry. The example I have started was the development of the non-Markovian quantum state diffusion equation that started in quantum optics. My second, possibly more important point, was that if you are interested in method development then you need to be thinking on a time-horizon of decades, not years. So, in the first lecture we demonstrated how the derivation of the NMQSD equation related back to the tools of quantum information science discussed in previous lectures. I claimed that in this lecture we would discuss what the modern developments on this method looks like.

In 2013, the foundational challenge facing the use of NMQSD

$$\hbar\frac{d}{dt}|\psi_{z^*}(t)\rangle = -i\hat{H}_{\mathrm{sys}}|\psi_{z^*}(t)\rangle + Z_z(t)\hat{L}|\psi_{z^*}(t)\rangle - \hat{L}^\dagger\int_0^t \alpha(t-s)\frac{\delta}{\delta Z_s^*}|\psi_{z^*}(t)\rangle ds \tag{1}$$

in practical calculations was the presence of the functional derivative which has no convenient analytic or numerical solution. As a result, NMQSD was solved approximately (e.g. the zeroth order functional expansion - ZOFE), but was not used directly for anything but toy models.

The solution to this was presented in Suess, Eisfeld, and Strunz, Phys. Rev. Lett. 113, 150403 (2014). The core insight of this manuscript is that you can replace the functional derivative with a hierarchy of auxiliary wave functions that looks exactly like the hierarchy we already know from HEOM. I will (briefly) demonstrate how that is derived and then we can move on to a combination of computational exercises and a discussion of modern developments on this method.

3 Deriving HOPS from NMQSD

As we discussed previously for the HEOM equation, it will be important for this equation that we can write the bath correlation function as a sum over exponentials

$$\alpha(t) = \sum_i g_i e^{-\gamma_i t} \tag{2}$$

where both g_i and γ_i are complex valued. I'm not going to dwell on this point, but the exponential decomposition of the thermal bath correlation function has several well established methods.

3.1 Define the $\hat{D}_t$ Operator

The basic problem we have arises from the presence of the functional derivative in our equation of motion. One of the most common tricks in theoretical chemistry when we have something that looks complicated is to give it a name: Alica, Bob, it doesn't matter. In this case, we are going to define a memory operator

$$\hat{D}_t = \int_{-\infty}^{\infty} ds\, \alpha(t-s)\frac{\delta}{\delta z_s^*} \tag{3}$$

which represents the problematic term. When the memory term acts on the wave function

$$\hat{D}_t|\psi_{\mathbf{z}}(t)\rangle = \int_{-\infty}^{\infty} ds\, \alpha(t-s)\frac{\delta|\psi_{\mathbf{z}}(t)\rangle}{\delta z_s^*} \tag{4}$$

we can use the same argument we did in the NMQSD derivation (recognizing that T=0 and causality limit the integral bounds) to limit this to

$$\hat{D}_t|\psi_{\mathbf{z}}(t)\rangle = \int_{0}^{t} ds\, \alpha(t-s)\frac{\delta|\psi_{\mathbf{z}}(t)\rangle}{\delta z_s^*}. \tag{5}$$

This allows us to rewrite the NMQSD equation in terms of the memory operator as

$$\hbar\frac{d}{dt}|\psi_{z^*}(t)\rangle = -i\hat{H}_{\text{sys}}|\psi_{z^*}(t)\rangle + Z_z(t)\hat{L}|\psi_{z^*}(t)\rangle - \hat{L}^\dagger\hat{D}_t|\psi_{\mathbf{z}}(t)\rangle. \tag{6}$$

Now, so far we have done a simple renaming and we already know that we can't solve the memory term. But what if we set our sites a little lower. Can we describe how the memory term evolves in time? let us take the time derivative of $\hat{D}_t$:

$$\dot{\hat{D}}_t = \frac{d}{dt}\left(\int_{-\infty}^{\infty} ds\, \alpha(t-s)\frac{\delta}{\delta z_s^*}\right)$$

Since the functional derivative $\frac{\delta}{\delta z_s^*}$ does not depend on t, we can bring the time derivative inside the integral:

$$\dot{\hat{D}}_t = \int_{-\infty}^{\infty} ds\, \frac{\partial}{\partial t}\alpha(t-s)\frac{\delta}{\delta z_s^*}$$

Using the derivative property of the exponential BCF

$$\frac{\partial}{\partial t}\alpha(t) = -\gamma\, g\, e^{-\gamma t} = -\gamma\, \alpha(t) \tag{7}$$

we can rewrite the derivative of the memory term as

$$\dot{\hat{D}}_t = \int_{-\infty}^{\infty} ds\, \left(-w\, \alpha(t-s)\right)\frac{\delta}{\delta z_s^*} = -w\int_{-\infty}^{\infty} ds\, \alpha(t-s)\frac{\delta}{\delta z_s^*} = -w\hat{D}_t.$$

Note this the close analogy to the closure condition that we discussed with HEOM and also arises due to the exponential form of the bath correlation function.

3.2 NMQSD in tersm of the memory operator

This allows us to say something rather remarkable about the memory term in the NMQSD equation. Starting from the expression

$$\hat{D}_t|\psi_{\mathbf{z}}(t)\rangle \tag{8}$$

we could consider the time-evolution of the memory term and use the chain rule to write

$$\frac{d}{dt}\left(\hat{D}_t|\psi_{\mathbf{z}}(t)\rangle\right) = \frac{d}{dt}\left(\hat{D}_t\right)|\psi_{\mathbf{z}}(t)\rangle + \hat{D}_t\frac{d}{dt}\left(|\psi_{\mathbf{z}}(t)\rangle\right). \tag{9}$$

The first term we just solved, while the second term gives us

$$\hat{D}_t\left(-i\hat{H}_{\rm sys}|\psi_{z^*}(t)\rangle + Z_z(t)\hat{L}|\psi_{z^*}(t)\rangle - \hat{L}^\dagger\hat{D}_t|\psi_{\mathbf{z}}(t)\rangle\right)/\hbar \tag{10}$$

$$= \frac{1}{\hbar}\left(-i\hat{H}_{\rm sys}\hat{D}_t|\psi_{z^*}(t)\rangle + \hat{D}_t Z_z(t)\hat{L}|\psi_{z^*}(t)\rangle - \hat{L}^\dagger\hat{D}_t^2|\psi_{\mathbf{z}}(t)\rangle\right) \tag{11}$$

$$= \frac{1}{\hbar}\left(-i\hat{H}_{\rm sys}\hat{D}_t|\psi_{z^*}(t)\rangle + \left(Z_z(t)\hat{D}_t + \alpha(0)\right)\hat{L}|\psi_{z^*}(t)\rangle - \hat{L}^\dagger\hat{D}_t^2|\psi_{\mathbf{z}}(t)\rangle\right) \tag{12}$$

$$= \frac{1}{\hbar}\left(-i\hat{H}_{\rm sys}\hat{D}_t|\psi_{z^*}(t)\rangle + Z_z(t)\hat{L}\hat{D}_t|\psi_{z^*}(t)\rangle + \alpha(0)|\psi_{z^*}(t)\rangle - \hat{L}^\dagger\hat{D}_t^2|\psi_{\mathbf{z}}(t)\rangle\right) \tag{13}$$

where we have made use of the following identity

$$[\hat{D}_t, Z_z(s)] = \alpha(t-s) \tag{14}$$

and the fact that the memory operator does not act on operators in the system Hilbert space (they do not depend on the stochastic process).

Commutator of the memory operator and stochstic process
The functional derivative satisfies $\left[\frac{\delta}{\delta z_s^*}, z_{s'}^*\right] = \delta(s-s')$ (delta function). If that is not immediately clear, add a 'trial function' $f(z_s^*)$ and remember to use the chain rule on the derivative term if it is not already the right-most object.

Using this commutator property we have

$$\left[\hat{D}_t, z_s^*\right] = \int du\, \alpha(t-u)\left[\frac{\delta}{\delta z_u^*}, z_s^*\right] = \int du\, \alpha(t-u)\delta(u-s) = \alpha(t-s).$$

Applying this to our term (setting $s=t$):

$$\hat{D}_t\left(z_t^*|\psi_t\rangle\right) = z_t^*\hat{D}_t|\psi_t\rangle + \left[\hat{D}_t, z_t^*\right]|\psi_t\rangle.$$

Combining these expressions, we can now rewrite the time-derivative of the memory term in the NMQSD equation as

$$\hbar\frac{d}{dt}\left(\hat{D}_t|\psi_{\mathbf{z}}(t)\rangle\right) = \hbar\frac{d}{dt}\left(\hat{D}_t\right)|\psi_{\mathbf{z}}(t)\rangle + \hbar\hat{D}_t\frac{d}{dt}\left(|\psi_{\mathbf{z}}(t)\rangle\right) \tag{15}$$

$$= -\hbar\gamma\hat{D}_t|\psi_{\mathbf{z}}(t)\rangle + \left(-i\hat{H}_{\rm sys}\hat{D}_t|\psi_{z^*}(t)\rangle + Z_z(t)\hat{L}\hat{D}_t|\psi_{z^*}(t)\rangle + \alpha(0)|\psi_{z^*}(t)\rangle - \hat{L}^\dagger\hat{D}_t^2|\psi_{\mathbf{z}}(t)\rangle\right) \tag{16}$$

$$= \left(-i\hat{H}_{\rm sys} - \hbar\gamma + Z_z(t)\hat{L}\right)\hat{D}_t|\psi_{z^*}(t)\rangle + \alpha(0)|\psi_{z^*}(t)\rangle - \hat{L}^\dagger\hat{D}_t^2|\psi_{\mathbf{z}}(t)\rangle. \tag{17}$$

There is only one term in here that we do not already know, and that is the second operation of the memory operator. This suggests that we could iteratively construct equations that describe successively higher-order influences of the bath memory on the system dynamics.

3.3 Hierarchy of pure states

The key insight to managing the functional derivative in the original NMQSD equation is to realize that we can rewrite it into a hierarchy of auxiliary wave functions exactly like the structure of

HEOM. To do that, we start by a simple renaming of the memory operator acting on the physical wave function as an auxiliary wave function

$$|\psi_{\mathbf{z}}^{(k)}(t)\rangle = \hat{D}_t^k |\psi_{\mathbf{z}}(t)\rangle \tag{18}$$

where we call the function constructed by k-actions of the memory operator the k^{th} auxiliary wave function.

This allows us to rewrite the NMQSD equation as

$$\hbar \frac{d}{dt}|\psi_{z^*}(t)\rangle = -i\hat{H}_{\text{sys}}|\psi_{z^*}(t)\rangle + Z_z(t)\hat{L}|\psi_{z^*}(t)\rangle - \hat{L}^\dagger|\psi_{\mathbf{z}}^{(1)}(t)\rangle \tag{19}$$

where the time-evolution of the physical wave function now depends on the value of the first-order auxiliary wave function. We can also solve for the time-evolution of the first-order auxiliary wave function - in fact we already did that - and we can now write that expression as

$$\hbar \frac{d}{dt}|\psi_{\mathbf{z}}^{(1)}(t)\rangle = \left(-i\hat{H}_{\text{sys}} - \hbar\gamma + Z_z(t)\hat{L}\right)|\psi_{\mathbf{z}}^{(1)}(t)\rangle + \alpha(0)|\psi_{z^*}(t)\rangle - \hat{L}^\dagger|\psi_{\mathbf{z}}^{(2)}(t)\rangle. \tag{20}$$

If we were to write down the time-evolution of the second auxiliary wave function we would discover a similar equation that now depends on $|\psi_{\mathbf{z}}^{(1)}(t)\rangle, |\psi_{\mathbf{z}}^{(2)}(t)\rangle$, and a new term $|\psi_{\mathbf{z}}^{(3)}(t)\rangle$. The general solution to the k^{th} order auxiliary wave function can be written as

$$\hbar \frac{d}{dt}|\psi_{\mathbf{z}}^{(k)}(t)\rangle = \left(-i\hat{H}_{\text{sys}} - k\left(\hbar\gamma\right) + Z_z(t)\hat{L}\right)|\psi_{\mathbf{z}}^{(k)}(t)\rangle \tag{21}$$

$$+ \alpha(0)|\psi_{z^*}^{(k-1)}(t)\rangle \tag{22}$$

$$- \hat{L}^\dagger|\psi_{\mathbf{z}}^{(k+1)}(t)\rangle. \tag{23}$$

You can visualize this as a ladder of auxiliary wave functions which are coupled to their nearest neighbors. We have, in essence traded off the in getting rid of the functional derivative is that we are no longer solving one differential equation we are solving a system of differential equations. This system of differential equations has catastrophic scaling with the number of exponentials required to describe a single thermal environment and the number of thermal environments.