Q&A Lecture 11

If the observable operator A corresponds to a quantity with eigenvectors in the momentum basis, like momentum itself, does the path integral derivation still work, since classical-like average expression only appears, because the potential term has a nice form in the coordinate basis?

Momentum dependent average can also be computed in the path integral formalism, expressing the matrix element of the momentum related operator via a change of basis to go in the momentum representation "around" the operator and then back to the coordinate representation. This requires one extra step before applying the Trotter factorisation to write

\int dx_0 <x_0 | e^{-\beta \hat H} f(\hat p) | x_0> = \int dx_0 \int dp <x_0 | e^{-\beta \hat H} |p><p| f(\hat p) | x_0> = \int dx_0 \int dp <x_0 | e^{-\beta \hat H} |p><p| | x_0> f(\hat p) = \int dx_0 \int dp \int dx_1 <x_0 | e^{-\beta \hat H}|x_1><x_1 |p><p| | x_0> f(\hat p) = \int dx_0 \int dx_1 <x_0 | e^{-\beta \hat H}|x_1> F(x_0,x_1)

In the last term, F(x_0,x_1) is the result of the integral over p. (a) If this function contains a delta in (x_0-x_1), we can do also the integral over x_1 and go back to the standard case. (b) If not, we have the estimator F and we can still use Trotter to compute the matrix element of the exponential of the Hamiltonian. However, the chain that results from this is now "open", i.e. it starts in x_1 and ends in x_0 and these two coordinates are not, in general, the same. This changes the form of W, but classical canonical sampling can still be used. For example, a very important p-dependent observable, the kinetic energy, has an estimator in (a)…can't think of one in (b) right now…but I'll keep thinking!

In my understanding, the Feynman path integral seems the method to calculate the physical value of a whole system. Are different methods used to calculate the time average of a physical value?

Not sure I understand the question. The path integral provides an explicity expression for the canonical probability density of the (whole) system. When multiplied by the expression of the observable (x in the case considered in class) and summed over all the possible states of the system this gives the static (time-independent) average of the observable. In early classes we saw that this static average can also be obtained as an average over the states visited in time along a trajectory compatible with the probability density. This we call a time average, but because we sum over all possible times, also this average is static (in the sense of time-independent). There are other averages where there is an explicit dependence on time, these are called time-correlation functions and are used, for example, to measure diffusion or vibrational spectra. We did not discuss those, at least for now.

When we talk about the interaction between to particle in the quantum average, we said that only the coordinate x_k with the same index interact (x1_x with x2_k), why is it the case?

Let's focus on one of the "slices" of the path integral for two particles. The matrix element looks like: <x1_{k+1},x2__{k+1}|e^{\beta/N (\hat p1^2+\hat p2^2)/2m}e^{\beta/N V(\hat x1,\hat x2)}|x1_k,x2_k> (where with }|x1_k,x2_k> we indicate a tensor product of the basis elements for particles 1 and 2). Since the basis is a basis of eigenvectors for the two particle system, we have <x1_{k+1},x2__{k+1}|e^{\beta/N V(\hat x1,\hat x2)}|x1_k,x2_k> (where with }|x1_k,x2_k>= <x1_{k+1},x2__{k+1}||x1_k,x2_k> (where with }|x1_k,x2_k>e^{\beta/N V(x1_k,x2_k)}. Here you see that each potental term only "touches" same k coordinates.

Does the path integral represent the propagation of a system?

The expression that we have obtained in the equation for the quantum average represents the quantum thermal probability density (some people interpret this as a propagation in imaginary time — or inverse temperature). At the end of class, I discussed how the same steps can take us to a path integral expression for the time-evolution (i.e. the time propagator) for the system.

How do we deal with the case when T is extremely small, where we require a extremely large time step n?

n is not a time-step (unless you mean time step in imaginary time?). It is rather the number of additional “particles” that we have to use to enforce the Trotter approximation. You are correct that, the larger this control parameter, the more expensive the calculation. There are methods - known as ring contraction schemes that try to mitigate this effort, but they are beyond the scope of this class. Alternatives imply using approximate sampling dynamics - e.g. something called the quantum thermal bath (I might say something about this in the next class).

Why do we choose in our calcultions to firstly apply the exponential of the momentum and then apply the exponential of the potential? Why don't we do the reverse?

The end result of the calculation should not depend on the order: after you apply the Trotter approximation you are in an approximation in which the two exponentials commute. That said, I think that in class we applied first the exponential of the potential.

We introduced over the last week that the electrons are treated as density. Since we "split" the particle in N parts, what are the consequences on the density?

The particles that we have “split” are the ions. However, you are right that - when we obtain the potential V from a ground state variational density for the electrons - something happens. In fact, since this potential must be evaluated (independently) at the position of each bead (i.e. N times) we need to perform the self-consistent minimization of the density N times per time step.

In the expression for W the mass appears, but is this supposed to be the mass of a “bead” k, or of the original particle ? If it is the mass of the original particle then how do we choose the masses for the beads?

The mass that appears in W is the mass of the original particle. You are, however, correct in saying that - in order to sample via a trajectory, we have to associate a set of (fictitious) momenta to the beads. The mass associated with these momenta in the fictitious kinetic energy that we use to generate the trajectory (so not the original kinetic energy of the problem) is a parameter in our hands. Usually, this mass is chosen the same as the mass of the original particles, but sometimes it can be changed (e.g. made smaller to try to accellerate the sampling).

Can we use path-integral approach with non-interacting fermions (which intrinsically "interact" through Pauli exclusion principle)?

Yes, in fact path-integral approaches are used also for interacting fermions. The key difficulty - a consequence of the Pauli exclusion principle - is that one needs to account for the behaviour of the system under particle exchange. This can be done using different techniques all of which are at the basis of the so-called Quantum Monte Carlo methods.

If we start with a system with a few particles and the hamiltonian has a few interaction term, after the Trotter approximation, what does the interpretation of the new classical fictitious system read?

Not sure I understand the question…let's indicate with n the few particles in the system. Each one of them turns into a ring polymer of N beads, and beads of the same index k from the different ring polymers interact.

In the path integral formulation for thermal averages, harmonic potentials result in smooth Gaussian contributions that complement the kinetic energy terms. However, what happens if we choose to describe the potential experienced by each of the beads using a non-harmonic potential? How does it interact with or complement the kinetic energy terms? Do the steep changes in a non-harmonic potential introduce discontinuities or unphysical artifacts?

First I would like to make sure about something. The integral over the momentum representation of the kinetic energy part will ALWAYS result in the Gaussian terms we wrote in class. Then, I guess, your question refers to the explicit form of the V potential. This can be completely general and its non-harmonicity does not create particular problems. The sum of the Gaussians and V, what we called W in class, will act as an overall potential term that will be derived with respect to beads coordinates to determine the force in the Nose-Hoover dynamics. The nature of this force, in particular the terms coming from the derivative of V, is not particularly different than in standard classical systems and does not pose specific additional challenges.

In our original full molecular Hamiltonian, we also 2 electron interaction terms. Those terms would represent interactions between corresponding beads (with the same k value) in the different rings, right?

The theory as discussed in class referred to the ionic degrees of freedom in the Born-Oppenheimer approximations and subject to a potential V. In ab initio cases, this potential would correspond to the electronic ground state (estimate of). One can also do path integrals for electrons, but this is more delicate due to the Pauli principle. In any case, when pair interactions are present, like in the example with the two ring polimers discussed in class, they behave as you describe.

Quantum average approximated with the trotter approximation imposes a large N, but how can we calculate the average of an operator if the number of particles N in our canonical system is small (N is fixed, I can't vary it otherwise the system would no longer be canonical) ? Should we change our technique?

I think that there is a misunderstanding, probably induced by notation. I have used the symbol N to indicate the total number of particles (which as you say is fixed) in the NVT ensemble and then, in the context of the path integral to indicate the number of beads in

which each particle is “split” via the Trotter approximation (we called these the beads in the closed polymer that represents the trace of the quantum canonical density). Let’s correct this by indicating the number of beads as P. Then for a system of N particles, we have to examine NP coordinates. N correspond to the physical particles, P come from the path integral representation are introduced as a computational tool (a bit like in extended Lagrangians).

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