# Q&A Lecture 11

*How do we obtain the mutual interaction potential w(r)? Does it take a known functional form, for example the standard Coulomb potential? Is it determined experimentally,  or analytically?*

The interaction potential is computed either ab initio (e.g. via DFT) or defined by the physical system we are interested in (so, for charged nuclei it would indeed be the standard Coulomb potential, but it could also be a Morse potential modelling bonding in a O_2 or H_2 molecule). When the potential is modelled via an assumed analytical form, the parameters in the model can be determined via comparisons with experiments (e.g. to ensure the correct bond distance of the molecule) or from comparison with highly accurate electronic structure calculations.

*My first question is related to the part where we artificially introduced the momenta into the quantum thermal average expression. We have stated that the kinetic energy of the quantum system is described by the terms corresponding to harmonic oscillators. Therefore, now that the momenta are introduced, do they describe the kinetic energy of the system, do they still have a physical meaning, or they represent just a mathematical trick to prove that a quantum NVT ensemble can be sampled through dynamics already seen for the classical NVT ensemble?*

In general, the introduced momenta do not have a physical meaning. We shall see in future classes that there are methods that attempt (with some, limited in my opinion success) to give them meaning.

*My second question is related to the part of the lecture when we talked about bosons and fermions. Why did we not consider from the beginning the type of particle that is present in the quantum system for which we computed the thermal average? Was it because since there is only one particle, there are no any other particles to exchange it with, and therefore it did not matter if it was a boson or fermion? Also, when analyzing quantum systems that have more than two particles, if I understand correctly, we are obliged to take into account their nature as bosons or fermions in order to perform a meaningful simulation.*

The fact that there was only one particle is one way to justify what we did. In fact, even for systems with more than one particles, it becomes necessary to specify the “nature" of the atoms with respect to exchange only when exchange can play a role. This can be quantified, for example by comparing the typical delocalisation of the particles (as measured, for example via the De Broglie wavelength or, equivalently, by the average radius of a closed path integral for the particle) and the typical distances among particles. When the latter is larger than the former, exchange does not really come into play. This is indeed the case for most molecular systems. So, there are plenty of meaningful simulations in which we can use directly the expression for the average that we derived.

*Does the spring stiffness in the ring polymer representation correspond to any physical quantity in the real quantum system, or is it just a mathematical artifact of the path integral formalism?*

The full spring term in the path integral corresponds to the kinetic energy of the quantum system and it would be the whole Hamiltonian for a free particle. The average of the square of the distances between the beads (equivalent to the end-to-end distance of the path configurations) is proportional to the spring distances and the stiffness plays the role of an inverse variance for the Gaussian distribution of these distances. As such, it can be connected with the mean radius of gyration (for closed paths) and it provides a measure of the quantum delocalisation of the particle.

*Does the stationary phase approximation relate to the central limit theorem in statistics?*

In what sense? I would say no: the stationary phase approximation relates to integrals of complex exponentials with a parameter governing the “fast oscillations” induced by the phase and providing information on the points in the domain of integration that provide the most important contributions to the integral. The central limit theorem deals with he asymptotic distribution of sums large numbers of identically distributed independent random variables and saying that it can be approximated via a Gaussian distribution.

*We get a term $\Sigma_j V(x_j)/N$ in the exponential of the path integral. Does this mean that the external potential essentially disappears for large $N$ leaving on the springs (for a fixed $\beta$)? How do we interpret this?*

Each term becomes smaller, but we have a larger number of terms to be summed so the external potential does not disappear…

*I know the chain can start from r0, then rN back to r0. But I can not see how this relates to periodic boundary condition. for example what this implies?  I thought rN back to r0 just mean that there is also a "spring term " connecting rN and r0.*

That was a very specific question relating to a “problem” with connecting (either via a spring or because - due to the delta(r_0-r_N) - the positions coincide, so no spring) two extremes of a chain in one dimension were it is not possible to wrap or bend directly. The convention is then to simply impose that the one dimensional space, a segment between - say - 0 and L, things are periodically repeated.

*Why does Trotter pathintegral of the real time propagator becomes impossible to sample with classical dynamics ?*

The notion of sampling implies that there is an underlying probability (density) associated with the average. In the real time path integral, we do not end up with an expression that can be interpreted as a classical probability- as you mention in the summary - we have an oscillating function instead of a positive definite weight. Since there is nothing to sample, we cannot compute the integral exactly via classical dynamics. however, as we shall see in the next lecture, the stationary phase approximation tells us that the most important real time paths are still classical trajectories — although not Nose-Hoover ones.

*In the case of multi-particle system, why do beads only interact with the corresponding bead (same index) of other particles?*
You can find more details on the derivation in the book by Tuckerman, Chapter 12. To give you an argument: each bead index corresponds to a given time-slice in imaginary time. For each slice we have to evaluate all interactions, so both external and intramolecular. If you have more than one particle, each one of them is represented by a different “polymer” and the beads correspond to different time-slices. So, interactions are computed among polymers but at the same time-slice (i.e. among corresponding beads).

*For the quantum chains, I find it disturbing that the potential for inter-particle interactions is called internal potential. Is there any explanation ? If it is between particles, why is it not an external potential ?*

This is actually quite standard nomenclature (not just quantum or path integrals). Interactions between elements “inside” the system are called internal and depend on the two or more particles’ positions (e.g. electrostatic interactions between particles). Interactions due to an external field such as e.g. gravity originate from causes “outside” the system and typically act on all particles but via equations that involve one of them at the time.

*We discussed about Bosons and Fermions, is this related to the time evolution derivations that we did ? If yes, how is it related ?*

Good question. The propagator, i.e. the matrix element between to coordinate states of the exponential of the Hamiltonian times i over hbar times t, does not explicitly change with statistics. However, the state does so the wave functions at the initial and final times need to be antysimmetrical for fermions and symmetrical for bosons and the Hamiltonian might contain interactions (e.g. spin dependent) that are specific to the symmetry of the system.

*How do we combine the time evolution path integral and the quantum average path integral for different properties of the system to get the complete dynamics of the system parameters with time?*

If the question is how can we discuss states that are not just pure wave functions but that - for example - are in the quantum canonical ensemble, then we'll say something about this in future classes. As a spoiler: you need to write the trace of something the time average of an operator (something that you can express in the Heisenberg representation).

*Is the 1D bead-chain structure an artifact of using a 1D imaginary time, and would using a higherdimensional imaginary-time manifold invalidate the path-integral formulation for quantum statistics?*

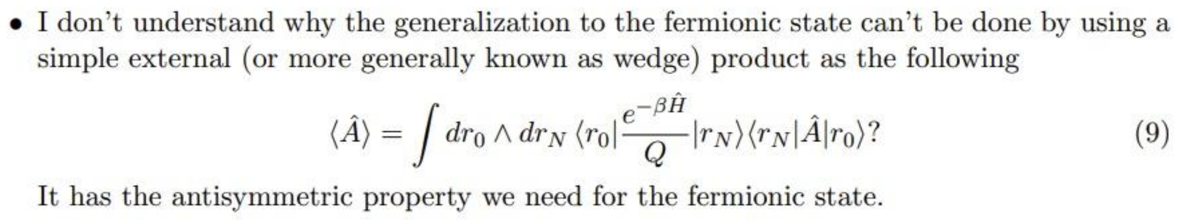
The imaginary time can ONLY be one dimensional since it is associated with the temperature parameter that is a scalar. The 1d-structure that we saw in class orginated from the fact that we choose to start from the simpler - notationally - case of one particle in one dimension. As discussed on Wednesday, going to more than one particle and dimensions does not hinder the formulation.

*Quantum averages re-introduce the notion of quantum nuclei that do not have definite trajectories. They lead us to define ring-polymers as a way to approximate the quantum average. Does this mean that on top of considering N beads per quantum particle, we also have to choose a way to calculate the potential at each step so that we could have ring-polymer + Car-Parinello, ring-polymer + MaZe and ring-polymer + exact minimization of electronic Hamiltonian?*

Yes indeed, if we compute the interactions among the nuclei ab initio (e.g. via DFT) we need to choose the way in which the forces are computed and all possibilities that you indicate are used.

*Additionally, what are systems of interest where the classical average and the quantum average largely differ?*

Any system at sufficiently large pressure and low temperature. At ambient conditions, mostly (but not only) systems in which H atoms are present, including water!



- I don't understand why the generalization to the fermionic state can't be done by using a simple external (or more generally known as wedge) product as the following

$$\langle \hat{A} \rangle = \int dr_0 \wedge dr_N \, \langle r_0 | \frac{e^{-\beta \hat{H}}}{Q} | r_N \rangle \langle r_N | \hat{A} | r_0 \rangle ? \tag{9}$$

  It has the antisymmetric property we need for the fermionic state.

The problem is not so much writing the average for the fermions (this can indeed be done in several ways) but in computing it. Since the antisymmetry comes with a minus sign for odd permutations of particles indexes and since these odds permutations are legitimate states, we no longer have a positive definite function that can be interpreted directly as a probability and sampled via trajectories.

*We discussed the issues related to the consideration of fermions/bosons for the expression as classical isomorphism, but is there also a link that can be made between a classical and quantum system in the high-temperature limit?*

The high-temperature limit is indeed one way to connect the quantum and classical expressions for the averages and it can be shown that the two canonical distributions coincide. A formal way to see this is to note that, for large T, the factor 1/k_bT multiplying the Hamiltonian operator is already small and we don't need Trotter to separate the exponential of the kinetic and potential energy. From this, it is quite straightforward to show that the classical and quantum probability densities are the same.

*In the Trotterization scheme, we want β/N to remain small, but this term is inversely proportional to the temperature, implying that the number of beads required would become extremely large at sufficiently low temperatures. Can this method be applied to near absolute zero simulation?*

The very high number of beads needed at very low temperatures is indeed the main limiting factor of direct path integral approaches for quantum averages. There are several methods (known as ring contraction techniques or path integral Langevin) that mitigate this issue that remains, however, significant. That said, path integrals are the golden standard in terms of rigour and accuracy and have been pushed to very high (order of several hundred) beads and low (order of a few kelvin) temperatures. We shall see an alternative that tries to eliminate the problem of the number of beads at the cost of a somewhat ad hoc approach in future classes.
*Please explain why we can equivalently treat one chain as two chains in the classical isomorphism. How can the external potential energy term V (rk+1) be reasonably split*

*into two terms? Or we can prove that two particles with V (r(1)) + V (r(2)) can effectively give the correct result?*

You can find more details on this in the book by Tuckerman, chapter 12. To give you an input: when we are dealing with more than one particle, the basis that we use is the tensor product of the coordinates of all the particles (so, for two particles, we would have |r^1, r^2>). The single particle operators in the Hamiltonian act ony on corresponding particles (so, the kinetic energy of particle 1 operates only on r^1, and the kinetic energy of particle 2 only on r^2 and the same for the external potentials), while the potential coupling the particles depends on all of their coordinates (so W is a function of all coordinates). At the exponent, we then end up with sums of single particles terms (that generate the different chains) and the coupling (that connects beads of equal index on different chains).

*If we were to consider the time evolution of a coherent system how would this look in the path integral formulation? In this case would the paths of the environment have to be added in if we were considering decoherence?*

Not sure what you mean by coherent system…if it's a system coupled with an environment then yes, the paths of the environment would have to be included in the description. This would happen by first defining the environmental part of the Hamiltonian, and then adding the coordinates of the environment to the basis. If the environment can - as it is often done - be modelled as a bath of harmonic oscillators coupled with the system, there are some simplifications that arise because - at least in part - the bath can be integrated out.

*First, what are typical smart choices for basis to create a closed loop? Im assuming its going to diagonalize something but cant imagine what it might be for any specific scenario for example.*

The basis choice in path integrals is fixed and it's the coordinate basis. The loop will be automatically closed if the OBSERVABLE is diagonal in this basis (so, any function of the operator of the positions of the particles). There are ways to construct estimators that give a closed loop also for other types of observables, including some that depend on momenta. One important trick here is that some observables, e.g. the energy, can be obtained via thermodynamic relationships as the derivatives of the logarithm of the partition function. You can find more material on this in the book by Tuckerman, chapter 12.

*Also, since we completely invented momenta variable to do nose-hoover, what would be the relation between these variables and the position. In classical observables the* *relation was obvious, but here am I allowed to change it as I wish or does it still need to obey the classical isomorphism?*

Nice question. You are allowed to change the relationship with respect to a classical analogy but I think that this would actually be counterproductive. We introduced the momenta in the way we did to make it possible to use classically based (Nose-Hoover) dynamics as a sampler. If we break the notion that the momenta are proportional to the time-derivatives of the positions things get more complicated.

*Could you clarify how the system is represented in the path integral formulation? Specifically, I'm trying to understand why a single particle is described by N beads along its trajectory, what those beads are, and how this relates to the idea of a path in the path integral approach.*

I would recommend that you look at Chapter 12 of the book by Tuckerman and then set up a meeting to go over remaining doubts. This question is a bit like "could you re-explain what we did in class in the last two lectures": this is not a problem per se but I would like you to start from a structured basis before I try to help.

*As for my question, I did not understand the remark wrt. bosonic and fermionic systems. Are these statistics not already accounted for in the |psi> that we use to compute the average of an operator?*

In the thermal average, the wave function is not directly implied. As you have seen in class, we start from an expression that involves the trace of the observable and the probability density operators. The symmetry is incorporated, in this you are correct, in the representation (e.g. by explicitly accounting for permutations and their signature in the way we define the "sum over all possible states": we integrate over a set of labeled coordinates but then we sum over all possible permutations and introduce a sign to the power of the permutation). These permutations must then be sampled and this cannot be done simply via a Nose-Hoover dynamics.

*Could you explain the physical intuition behind the equivalence of the kinetic energy of the quantum particle and the harmonic oscillator potentials among the chain of particles? How do we characterise the error due to the stationary phase approximation?It seems that it would only hold for small times, when the factor in front of the (rk+1 − rk)2 terms in the time evolved state is large and hence the oscillations in the higher-order terms would cancel out.*

I'll discuss this in the next class.

*We went over Gaussian integrals. These create a nice analogy with the classical system, but does it introduce an assumption that these values are normally distributed? Could we have non-normal distributions or is this not physical?*

I assume that you mean when we introduced the momenta to use Nose-Hoover sampling. In this case, we can only assume Gaussian distribution (as per the classical Maxwell-Boltzmann law) since our goal is to reconstruct a "Hamiltonian" for the extended system and the kinetic energy is quadratic in classical momenta (also in quantum, actually). The simple Gaussian form we have used is appropriate for all systems that have what is called a normal form of the Hamiltonian in which kinetic energy depends only on momenta and potential energy depends only on positions (an exception would be charged systems in external magnetic field)

*If I may follow up, how would we then, in conceptual terms, go about more complicated systems? I can imagine that in research we are often interested in charged systems or systems in an external field.*

Actually, systems in external magnetic fields are not so commonly treated (at least not at the level of the atoms, there is a lot of research, e.g. in spintronics, about electron's spins and magnetic fields). There are generalisations of the path integral formalism — described to some extend in this reference

*Is there a way to evaluate quantum thermal averages linked to time-dependent properties of the systems (e.g. correlation functions) ?*

This will be discussed in future classes.