Q&A Lecture 1

If all observables are defined via eigenproblems (measurement operator does not change the state), how is the collapse of the wave function promoted?

The measurement operation does change the state every time that the state is NOT an eigenvector of the specific operator that we are measuring. E.g. suppose that we want to measure momentum of an eigenvector of the coordinate operator. After the measurement, the system will no longer be in the eigenvector of the coordinates but in one of the eigenvectors of the momentum (collapse). In general, the collapse of the state (not the wave function, which is the representation of the state in the coordinate not the general definition of the state) is a postulate of quantum mechanics. It expresses the fact that after a measurement, if nothing "disturbs" the state (e.g. the measurement of another observable), we know with certainty that the system is in a certain eigenstate of the operator just measured.

In the description of our system, we have to make assumptions or approximations to make a system even 'computable' using a computer. Is it possible or even realistic to formally quantify the uncertainty that these approximations introduce into a model and how these propagate through a calculation? As simple example of this would be the selection of a basis set to describe our quantum systems, can we gauge its influence on a calculation in a formal manner so without empirically comparing different approximations?

There are different types of approximations - many of which will be discussed in future lectures - most of which can be tested numerically, other for which analytical bounds can be obtained. The selection of a basis per se is not an approximation, the approximation comes when we don't (we cannot) consider an infinite number of elements of the basis in our calculations. Then we introduce an "incompleteness" error whose effect needs to be tested by gradually increasing the basis size until differences in the results are below a preassigned threshold. (Cauchy convergence test) There are also procedures to dynamically adapt basis sizes for specific dynamical calculations to make sure that the error bound is preserved, following on the fly numerical tests.

I wonder how much work will be asked to do on a computer ?

As mentioned in class: notebooks and codes will be used to clarify concepts and provide examples. Some of the projects for the exam include a coding component - if this is something you are interested in. This is not a class where coding or running software is central: understanding the methods and and algorithms that enable the calculations is.

I know that the quantum state is basis independent. But it is just wierd to me that the state can represent the whole system, while it can be expressed either in the position basis or in the momentum basis. which does not make sense to me.

I am not sure I understand your question. Maybe you can help me by making more explicit what does not make sense to you. The fact that different representations can be used to provide the same (full) information content of a system actually exists - in a different way - also in classical. Think about using Cartesian of Spherical coordinates to represent a system of classical particles.

When studying a system, how to know if quantum approach is worth it, despite its complexity comparing to classical vision? Can both approaches be complementary?

I would rephrase slightly and ask "if a quantum approach is NECESSARY" (if we can get away with classical…we should). The need to go quantum depends on the energy and length scales at play - I'll say more in upcoming lectures - and on the thermodynamic conditions. There is therefore analytical and experimental information that can guide the choice. For example, it is known that systems containing light atoms (in particular H) can exhibit quantum properties at ambient conditions, while for other systems (e.g Ne) quantum features emerge only at low temperatures and high pressures.

In the sense that we can try to adapt classical approaches, in particular in simulation, to obtain useful approximations of quantum mechanics that facilitate both interpretation and calculations.

In quantum mechanical simulations, the timestep is a critical parameter. Are there methods that allow different timesteps for different regions of the system? For example, using longer timesteps where motion is slow - conceptually similar to QM/MM approaches that apply different levels of precision depending on the part of the system being studied?

There are approaches, known as multiple time steps algorithms, that enable what you describe. We may comment on them later in class, let me know if you want a reference. These are typically used in classical mechanics, but can be extended to quantum.

Is there a more intuitive way of thinking about the Lagrangian and Hamiltonian, and can we also find a deeper intuition connecting the quantum Hamiltonian with the classical one?

See above for their identical role in the evolution. Other than that, I might recall the correspondence principle by Dirac that basically says "if you have a classical observable, you can obtain the quantum analogue by turning phase space variables and their functions into operators"

As we have defined the time evolution of the system using Newtonian, Lagrangian, and Hamiltonian mechanics, which is applicable to each molecule, can we not use the laws of statistical mechanics to analyse the evolution of the system? I am confused about how we are going to evaluate so many molecules using the equations for each molecule.

We shall indeed use statistical mechanics to connect the microscopic to the macroscopic observations. The strength of classical simulations, however, is that they enable access to the (approximate) solution of the evolution equations for each molecule. More on both points is coming up in future lectures.

How do we describe the dynamics in the case of a timedependent Hamiltonian? What is the equivalent description of quantum
dynamics for states represented by density matrices?

In the quantum case, I assume: if the Hamiltonian commutes at the different times, you substitute \hat{H}t with the integral over time (say from zero to t) of the Hamiltonian operator at the exponent. If commutation does not hold, then one has to introduce something more complicated called the time-ordering of the evolution operator. If we adopt a density matrix representation, the basic evolution equation says that the time derivative of the density matrix is equal to the commutator of H and the density matrix (barring factors of i and hbar).

Are there other bases we can choose for the quantum state that is not the position basis (ie, not the wavefunction) when solving the Schrödinger equation, and in what ways are they useful?

Yes, in fact the choice of the “best” basis depends on the specific problem most often depending on the nature of the interaction potential. If this is zero, for example, then the Hamiltonian only has a kinetic energy and the best basis is the momentum. For other systems, like the harmonic oscillator, a basis describing the occupation number of states might be more appropriate. We’ll discuss some examples in class in future lectures.

The time-dependent Schrödinger equation is non-relativistic, and is hence inappropriate for systems containing particles with velocities approaching c. Are there examples of chemical systems where the non-relativistic approximation is not appropriate ?

Relativistic effects might affect some spectroscopic properties of heavy atoms, but the overwhelming majority of chemical problems does not require them.

Why is the SchrÅNodinger picture so widely used when it has all the uncertainties and the probabilistic point of view when we have Bohemian mechanics which conveys the deterministic and non-local picture of quantum mechanics and also makes sense physically? And, will the course touch upon this aspect of QM?

While it is true that Bohmian reintroduces the notion of trajectories, I am not sure that it makes more sense physically. Note that the uncertainty principle holds also in this framework. Also, from a numerical point of view, the solution of the equations is not easier than with other formulations. The quantum potential is highly non trivial to compute (and can be singular). At the moment, I don't think that we'll discuss Bohmian in the course.

The Schrödinger equation describes how the state of a system evolves, but what about observables? Can we write a time-evolution for a given operator? I heard about the Heisenberg equation but how does it link to the Schrödinger equation?

The time evolution for an operator is determined - as you say - by the Heisenberg equation, stating that the time derivative of the operator is proportional (barring i and hbar) to the commutator of the operator and the Hamiltonian. This is analogous to the fact that in classical mechanics the time evolution of an observable is equal to the Poisson parenthesis of the observable with the Hamiltonian. The Schrödinger (focusing on the states and their evolution) and Heisenberg (focusing on observables and their evolution) "points of view" are perfectly equivalent and can - in fact - be "transformed" into each other staring by the time derivative of the time average of an operator. The equations are, of course, different because they act on different objects.

During the lecture, it was discussed that the wavefunction is the projection of the state in a certain basis set. In applications that I have seen so far (for example: harmonic oscillator, rigid-rotor, H atom) the basis chosen was the one corresponding to the position space. However, I know that another possibility would be to choose the projection on the momentum space. My question would be, why would one choose to project on the momentum space, what would be the advantages of doing so and for which applications would one choose the momentum space projection?

The momentum basis is not particularly advantageous, except in the case of free particles. The reason why you have seen the coordinate as a privileged choice is that (most) interactions, i.e. the potential energy operators in the Hamiltonian, are functions of the coordinates and therefore simple to represent in that basis. The kinetic energy operator also has a relatively simple expression in the coordinate basis as it amounts to a Laplacian (or

second derivative with respect to coordinates). On the other hand, representing the potential energy operator in the momentum is not - in general - as simple. A curious exception would be a quadratic potential, so the harmonic oscillator, in which the potential can be represented as second derivatives with respect to the momenta.

Are these tools ever going to be enough to simulate systems of interest (at a reasonable cost) such as protein folding dynamics and interactions with other complexes or are AI tools more promising? (As it worked for protein folding and I've seen it used in determining the ground state for some quantum systems with Pr. Carleo).

It depends on how you define system of interest. Protein folding is indeed a challenge where AI has proven more effective than standard simulations for standard proteins, but whether this will hold true, for example, for predicting more likely states of disordered proteins is still an open question. I would be curious to understand better what you mean with ground state prediction of some quantum systems. AI needs high quality data to perform in this kind of problems (for the proteins, it benefitted from simulation and experimental info available in the protein data banks, for the quantum ground states it typically starts from high quality quantum monte carlo points): to produce these physics based simulations are still needed. Furthermore, the tool to adopt depends on the kind of question you need to answer. AI is great at correlating and is certainly an important tool. The techniques that we will discuss are better at “causal” explanations.

How easily can you combine computational chemistry with other fields like organic chemistry ?

Computational chemistry is a very general tool that can be applied to different specific topics. Organic chemistry is one of these and there are several very successful examples, for example in describing at the microscopic level relevant reactions. The difficulty increases with the size of the system and how precise a characterisation of the interactions is needed. We’ll say more about these points in future lectures.

By the end of the course, what level of theoretical and computational mastery should we aim for? For example, should we expect to be able to set up and run a quantum simulation of a simple molecule (like water) or at least compare quantum results with a classical model to benchmark our understanding?

You can find the main objectives (that, as said we'll fine tune during the semester based on the interactions with all of you) in the description of the course.

In some cases, an observable does not admit an orthonormal eigenbasis, such as the position operator for a free particle. I understand physically how such an eigenbasis would be problematic, as it would break the symmetry of free space, but doesn't this violate the property that self-adjoint operators have orthonormal eigenbases?

An observable - being an Hermitian operator - ALWAYS admits an orthogonal (and then orthonormal) basis. We certainly can use the position operator basis for a free particle, but this would not be the most convenient choice since we know what are the eigenvectors of the free particle Hamiltonian (momentum eigenfunctions). Both coordinate and momenta are complete basis sets so they can be transformed into one another and used to describe any state (well, not spin, but that's a different story).

We discussed that simulating short time scales is necessary to fully understand the dynamics in e.g. a water molecule at increased temperature. How short do the time steps have to be to fully understand vibrations in molecules? For example, let's say that a vibration has an oscillatory period of 15 fs. How short do the time steps between each calculation have to be to get a full understanding of this vibration? Is a simple Nyquist sampling frequency enough?

The time-step needs to be small enough to (a) resolve to a sufficient degree the time-scale of the studied motion (so say a tenth of the oscillation period or smaller) and (b) keep the simulation stable. There are numerical tests that enable us to set the time-step according to these criteria that we shall see in future lectures.

The Hamiltonian drives unitary evolution without changing norms, yet classical Hamiltonians scale O(N). Therefore, how do we justify approximating quantum exponentials for molecules without losing that precious unitarity?

I think that there is a bit of confusion here between dimensional (and computational) scaling and unitarity. The dimensions of classical and quantum Hamiltonian (and more in general of the phase space and of the number of components in the quantum state vector) scales linearly with the number of degrees of freedom. Unitarity is a property of the time evolution operator that is satisfied (when external driving is absent) in both cases. For quantum mechanics, it

is evident - as you say - via the form of the evolution operator. An exponential (unitary) evolution operator can be defined also in classical and it's called the Liouvillian - we may see this in class. Also, in classical dynamics there is a theorem (the Liouville theorem) that ensures that the "volume of phase space" is preserved under conservative dynamics, which is another way to look at the same thing.