Q&A Lecture 3

The interaction term seen today in class could be understood as the interaction term of the interaction picture of a 2-state quantum optic system?

It plays the same role, in that it represents an off-diagonal term in the Hamiltonian of a 2-state (but more generally n-state) system.

What do the non-adiabatic couplings mean here exactly and what is meant by adiabaticity?

The non-adiabatic couplings are the terms in the equation responsible for coupling the evolution of the expansion coefficients associated with the different electronic states. They determine the flux among the probabilities to find the system in the different states. Adiabaticity (we'll see more about this in the next class) is the lack of energy flux between two systems. In our case it will indicate a situation in which the ions move in only one of the electronic states.

For the continuous coordinate basis, when the Dirac delta is obtained the function is non-zero only when x=x'. For it to be continuous does this imply that there is an infinite set of values for x'? And how does this differ from when a delta function is obtained using a discrete basis?

There is indeed an infinite set of values for x'. In fact, they are the same set as for x. The symbols simply indicate labels for these values that can be the same or different — like in the case of a discrete labels. The delta function is not "obtained" using the basis but it is a mathematical object that can be defined also in situations where there is no basis. It is used in our case to represent a critical property of standard basis (i.e. orthonormality). Conceptually the "continuous" (i.e. Dirac) delta and the discrete (i.e. Kronecker) delta are essentially identical. Their mathematical definition is not immediately the same due, in particular, to the fact that the continuous case requires dealing with some mathematical subtleties.

During the lecture, we derived some differential equations to solve the 1D time dependent Schrodinger equation, however, the SOFT algorithm uses a different approach to solve the problem. Does it mean that the differential equations that we found during the lecture are hard to solve numerically? Why do we suddenly use a different approach, or how are the two methods related?

A recurring theme in the class will be that exploiting different forms of quantum mechanics and/or different methods of solutions to the quantum dynamical problem leads to different results in terms of accuracy and numerical cost. Exploring these different situations is part of what we want to do. The partial differential equation form of the Sch. equation could be solved via an algorithm but numerical integration of this type of equations is typically unstable. Solving in the exponential form has some immediate advantages (e.g. the numerical solver preserves the norm of the state). The two forms of the equation are equivalent and one can go from the exponential to the differential by, for example, representing the short time step in the exponential form as done in SOFT in the coordinate representation, a Trotter split of the exponential of the Hamiltonian, and then doing a first order Taylor expansion of the exponents in the short time step. Rearranging the terms gives the time-dependent Schr. in the coordinate representation. Happy to show you in class if need be.

We could find important properties of a quantum system (continuous positions of a particle, discrete energies, position of electrons and nuclei of a more complex system) by projecting the wave function on a well-chosen basis, however would there be other important eigenvector bases to be able to describe a quantum system and thus obtain other informations on the system?

The wavefunction is the coefficient of the expression of the abstract state. We DO NOT project coefficients, but the state itself. The choice of the best basis depends on the observation we are interested in making. In general, for a given operator, the best basis is the basis of its eigenvectors. For the time-evolution (dictated by the Hamiltonian operator), the best basis would be the basis of the eigenfunctions of this operator. These are, however, usually impossible to determine, hence the use of (e.g. coordinates). Other relevant eigenbasis in the context of molecular systems include spin - when the electrons are explicitely taken into account - momenta - when looking at the kinetic energy - and, for example, angular momenta. These (except momenta) are typically used to describe, together with coordinates, what you may have encountered in previous courses: the orbitals.

When calculating the c(t) coefficients for the adiabatic electronic hamiltonian, do the D coefficients only depend on other electronic states but not on the nuclei?

The D in the equation is not a coefficient, but an operator - I will say more about this in class and you can find its exact nature in the notes uploaded on the Moodle on the coupled channel equation. The operator D depends both on the electronic state and on the nuclear momentum.

What's the definition of V_di in the MSOFT notebook? It looks like the combination of the ground state and the first excited state. If I understand well, the potential in interaction of nuclears and electrons are coulomb potential. Why can we select the potential as double harmonic potential in the MSOFT notebook?

The MSOFT notebook is designed to mimic the solution of the non-adiabatic problem for MODEL systems for which we prescribe the form of the “electronic” states and of their couplings. There is no direct connection with the molecular systems discussed in class for the interactions. The structure of the equation is however the same, and so these are useful models to understand the meaning of the different terms in the equation and typical behaviours of the coefficients.

I read that a adiabatic tranfer of electron between two molecules happens in the same potential energy surface. Would that mean that the coulomb interaction potential for the two electron will be zero?

No, it simply means that the system remains on the same electronic eigenstate. This eigenstate is determined by the coulomb interactions…Think about the H atom as an example, you have Coulomb interactions but the shape of the energy levels is not Coulomb...

My first question is : when we define the eigenstates of the electrons, does it imply that we describe a single state simultaneously for all the electrons ? Can we consider for example the state α as being the ground state of the electrons while β, γ etc. are different excited states ?

Yes, this is correct. By the way, electrons being indistiguishable quantum particles, we could not do otherwise.

I would also like to confirm the following: does the non-adiabatic coupling only occur between electronic states that are degenerate in energy (both the kinetic and potential energy are the same at the point where the particle can go in either state)? I am talking about the case where we had the double harmonic potential (MSOFT notebook).

Not necessarily, though it is true that non-adiabatic couplings are usually larger when the states get close.

What are some real-world applications of studying systems of interacting ions and electrons with this formalism?

Examples of non-adiabatic phenomena include: the trans-cis reaction of rodophsine responsible for human vision, some non-radiative damage in DNA basis related to skin cancers, modelling of materials for solar cells, understanding of solar energy storage in chlorophil…in general, photochemistry goes via non-adiabatic reactions described by the coupled channel equation.

How does the separation of electronic and nuclear motion affect the accuracy of the simulations?

If separation means choice of the basis as the product of coordinates for the nuclei and adiabatic states for the electrons, then this does not affect the accuracy of the simulation (e.g. in MSOFT) at all. It is an exact representation of the interacting system. If separation means separation of typical time-scales in the nuclear and electronic motion, then there are many consequences that we shall discuss in class starting with the next lecture.

Given the computational complexity of including non-adiabatic coupling terms throughout a simulation, is it feasible to dynamically switch from using the Born-Oppenheimer approximation to incorporating non-adiabatic effects only in regions where potential energy surfaces interact? How can we manage this transition smoothly while ensuring accurate energy conservation and nuclear dynamics?

We'll discuss these aspects of the practical solution of the equation in upcoming classese. As a "spoiler": the non-adiabatic couplings are in fact often zero over extended regions of space. In the exact solution (e.g. MSOFT) this manifests in the fact that the off-diagonal elements of the representation of the electronic hamiltonian are zero or very small. One can therefore monitor them and only enforce diagonalization of the matrix (as explained in the notebook) when they are above a given threshold. The monitoring is needed and not necessarily cheap, but the diagonalization is avoided. If the chosen threshold for "zero" off-diagonal matrix elements is well chosen, all properties will be respected within numerical accuracy. In approximate methods, to be discussed (e.g. Surface Hopping) the same strategy is adopted - i.e. a controlled switching on of the non-adiabaticity - and additional measures are taken to make sure that the nuclei behave properly. This is achieved, for example, via rescaling of appropriate quantities in the nuclear dynamics. We'll see more about this later in class.

We introduce electronic adiabatic basis as the eigenstates of h_ee. Is it always true that this basis can be represented as a tensor product |R> and |α>? Or is it an approximation? If it is an approximation, how accurate is it?

The representation is exact and it is always possible to construct the basis as the tensor product. The problem - and the approximations - arise because it is in general impossible to obtain the adiabatic basis exaclty. More on this in future classes.