# Q&A - Lecture 4

*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 classes. 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.

*What is the usefulness of the diabatic basis, if the electronic Hamiltonian is not diagonalizable in it? It seems to me like it doesn't have an upside compared to the electronic adiabatic basis.*

The electronic Hamiltonian is diagonalizable irrespective of the choice of the basis. I think that you mean that in the diabatic basis, its representation as a matrix is non-diagonal. Note that to diagonalize, you'd have to solve the eigenvalue and eigenvector problem for the matrix corresponding to the representation of the Hamiltonian in the diabatic basis. The resulting eigenvalues would be the adiabatic energies and the eigenvectors would be the adiabatic states. While it is true that the diabatic representation is often less useful for exact propagation, the advantage of the basis is that it is an "easier" starting point for approximations. These fall into two categories: empirical approximations of the interactions as represented by the electronic Hamiltonian. Given a molecular system, it is simpler to come up with good models for the diagonal and off diagonal elements of the electronic Hamiltonian (that only depend on the coordinates of the nuclei) than to model directly the adiabatic energies AND the non-adiabatic couplings in the adiabatic basis (the latter, in particular, depend both on the nuclear momentum and on the derivatives of the adiabatic states). One then takes the path of creating a diabatic model (this is done, for example, in the MSOFT notebook) and then obtains the adiabatic representation via diagonalisation as described above.

Furthermore, there are some approximate methods for the time-evolution (e.g. something called the mapping Hamiltonian method) that are constructed in the diabatic representation.

*Electronic states being close in energy doesn't necessarily mean they are also close to each other in space. Does this mean that two energetically close electronic states that are far apart in space can still transfer population states between one another? If so what are the limits to this if there are any?*

Yes, states that are far in space can still transfer population. However, this is limited by the structure of the non-adiabatic couplings that involve matrix elements of the nuclear momentum operator between two adiabatic states. This matrix element will be (in standard situations) smaller for states that are farther apart which, in turn, means that the transfer will be smaller. Exact limits are difficult to give in general, but they are related to the magnitude of these matrix elements.

*In the adiabatic basis, we have alpha and alpha’ term that I understood as x and y in the cartesian basis (x, y, z), another element of the same basis, but what is beta in the coupling term ?*

The indexes in the adiabatic basis (as in the diabatic) DO NOT represent Cartesian coordinates: they are collective symbols for all the compatible labels that can simultaneously be used to identify a state (so they could be coordinates and spin, or momenta and spin…). So the different labels, including beta are simply a notation to indicate states that may be the same or different (each one of them spans on all labels of the basis).

*In which situation would we use a diabatic basis?*

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More characteristics of the diabatic basis can be found in the attached paper — I have extracted the more relevant parts for us.

*We explained the transition from the first excited to the ground state by the presence of non-adiabatic coupling D_21. But we can also have the transition from the ground state to the first excited stated due to the coupling D_12. How are D_12 and D_21 connected?*

Correct: D_12 and D_21 are complex conjugate of each other. The matrix D is infact hermitian.

*Can you provide an example in which the effect of the coupling between electronic states is relevant, and one where it is not ? And do we often need to consider highly excited states ?*

As discussed in class, relevant: cis-trans isomerisation of rodophsine in vision. Not relevant: proton transfer in water via the Grotthus mechanism.

Not often, but it depends on how much energy we give the system, for example via the laser excitation that initiates a given non-adiabatic process. What happens more often is that there are subsequent transfers of population between different pairs of states.

*I did not fully understand the difference between adiabatic/diabatic vs. adiabatic/non-adiabatic.*

Adiabatic/diabatic refers to the choice of the electronic basis set (nuclei are always described in the coordinate representation). The adiabatic basis diagonalises the electronic Hamiltonian but is non-diagonal in the nuclear momentum. The diabatic basis is diagonal for the nuclear momentum but not for the electronic Hamiltonian.

Adiabatic/non-adiabatic refers to types of processes that take place during time-evolution. In adiabatic processes, everything happens on a single electronic state (typically the ground state). In non-adiabatic processes, there are transitions between electronic states.

*What causes a molecule to have two stable equilibrium positions?*

This is a rather common occurrence that arises when atoms in a molecule can organize themselves in different stable geometries. The example used in class of an isolated diatomic was not ideal because it is not easy to imagine this situation for this system. However, imagine a molecule like rodophsine that can have a cis and a trans conformation in its ground state.

*Can you explain again the difference between adiabatic, non-adiabatic and diabatic ?*

Adiabatic can refer to a basis set and to a type of process. Adiabatic basis is the one in which we use nuclear coordinates and eigenstates of the electronic Hamiltonian. Adiabatic process is one in which the system does not change electronic state. We have used diabatic to identify a different basis: coordinates for the nuclei and electronic eigenfunctions that DO NOT depend on the nuclear position (so the electronic Hamiltonian is non-diagonal in this representation). Non-adiabatic refers to a process in which the relative population of the electronic states changes in time.

*In class, you talked about the transitions from one state to another happening through coupling between these states, but I'm not sure that I understood well what it meant physically. In order for a transition to happen, is the coupling between states a condition for such a transition to happen ? Is there a physical/intuitive way to see that coupling ?*

I am not sure I understand the questions. The coupling between the states is indeed a condition for transitions. In the absence of these couplings the coupled channels equations for the different coefficients would be independent and each one of them would behave as an "isolated" system under the potential corresponding to one of the electronic states. The fact that the states are coupled represents the different ways in which energy can transfer in the molecule(/system) between the different degrees of freedom. Typically, couplings are larger in regions in which the electronic energy eigenvalues are similar so it does not take too much work to access one from the other. The work derives from variations in the energy of the nuclei.

*In the case of an adiabatic basis, the coupling terms correspond to how the motion of the nuclei brings about the interaction between different states, while the diagonal terms in the coupling matrix relate to how the mass of the nuclei changes within the landscape of the different potential energy surfaces as the curvature changes. How should I interpret the diagonal and off-diagonal terms in the coupling matrix in the case of a diabatic basis? Also, in the case of diabatic PESs, where different surfaces can cross, how does this crossing affect the effective nuclear mass?*

The diagonal terms play the role of the potential for the evolution (similar to the electronic hamiltonian eigenvalue in the adibatic basis), while the off-diagonal bring about the interaction between different states.

I can’t see an effect of the crossing on the nuclear mass. What do you have in mind here?

*Consider the nuclei and electrons system, as prof mentioned in class, the computation of classical dynamics is much cheaper than solving the quantum dynamics. Thus we can solve the classical dynamics for nuclei and then solve the quantum dynamics for electrons. But I didn’t fully understand how to choose the potential for the classical dynamics for nuclei. Why we choose the ground state energy of the electrons as the potential? How can we testify this approximation method's validity?*

The ground state for the electrons is chosen because we assume that the process is adiabatic (there are many interesting adiabatic processes) and that the system is in equilibrium, in the sense that the electrons have had time to relax to their most probable state, which is indeed the state of lowest energy. We’ll say more about this in the next class.

*What does population represent in the MSOFT notebook, and how can I relate it to the coupled channel equation? Likewise, I didn't quite understand what the norm of the graph at the bottom right represents and why it is constant.*

The population is the marginal probability to find the electrons in a given state, without information on where the nuclei are. As such, it is the integral over the nuclear positions of the modulus square of the coefficients that are the unknown in the coupled channel equation.

It is the sum of the populations on all electronic states. This sum - together with the integral over the nuclear coordinates performed to define the populations - gives the norm of the state of the system. This norm is constant and equal to one.

*When staying on one PES and setting coupling coeff. to 0, resolution of SE becomes way easier as we can use variational principle. In this case, we talk about ab initio methods. In practice, when and why is the use of diabatic basis more relevant ? What are the occurrences that are better described by this basis?*

We talk about ab initio when the electronic energy is obtained quantum mechanically and the ions move classically. More on this in the next class.

Federica and Edrick have uploaded the first few pages of a paper that addresses this question on the Moodle. Have a look and let me know if you wish to discuss further.

*When you present the notebook, you said that one could "break" the simulation, what do you mean by that? Does it means that at some point the simulation becomes incorrect ? If yes I'm not too sure on how to identify when it is incorrect, could you give me some examples of parameters that lead to failure (for SOFT for example) ?*

Any simulation algorithm is based on approximations that lead to computable solutions. In the case of SOFT, the key approximation is the Trotter break up of the exponential of the Hamiltonian. The validity of this approximation depends on the size of the time step dt. So, a way to "break" the simulation is by choosing a time step that is too large. The simulation with a time step that is too large is indeed incorrect. This would manifest itself - for example - in the fact that the energy of the system - computed as the average value of the Hamiltonian at each time step - would not be conserved. You can see this in the notebook by choosing the potential with the barrier and running the simulation with different time steps.

*What are the differences between Hamiltonians of the adiabatic system and the diabatic system? They looked very similar.*

The Hamiltonian is the same for both cases…the way in which the system evolves on the states is different. However, if what you mean is that the curves in the MSOFT notebook associated to the REPRESENTATION of the Hamiltonian in the two different basis look similar…this is not really true. We can look at the differences together if you wish.

*In diabatic conditions, the excited wave packet can be (partially/fully) transferred back down to the ground state but is dependent upon the degree of coupling. What does this "coupling" mean from a physical standpoint? Is it as in photochemistry where transitions are dependent on the degree of overlap between the wavefunctions of the excited and ground state?*

The coupling represents the projection of one of the states onto another state after it has been transformed by the action of the Hamiltonian. The explicit form of this projection depends on the representation chosen (e.g. adiabatic or diabatic). In some cases, the overlap is key but not always. For example, in the adiabatic basis, it is the overlap of the DERIVATIVE of a coefficient with another coefficient and not directly the overlap that determines the strength of the coupling.

*Is the choice of the method we use motivated by some physical or chemical specifications of the molecule we are trying to solve? Is it the case that some methods would perform* *better than others on some molecules while performing worse on other molecules? Or is there a strict hierarchy between the methods? If a method is very detailed and considers finer details, it might perform the best on small systems, but will it incur very non-tractable computational costs for even fairly large molecules? What do we do in such cases for fairly large molecules? To re-iterate, do we just try different methods till we find the best, or is the choice-of-algorithm decision guided by some physical or chemical factors?*

The choice of the method is determined by physical and chemical considerations and by the experimental conditions we are mimicking. For example, a photochemical reaction will require non-adiabatic methods, while proton trasfer in water via the Grotthus mechanism is adiabatic. That said, there is a hierarchy in that the coupled channel equation (with no approximations) is the most general way to describe a system of nuclei and electrons interacting via Coulomb. The set of approximations described in class comes, as you indicate, with different numerical costs that can indeed become too large to include any quantum effects for large molecules. In these cases, there is not much we can do…except work on new approximations. Importantly, however, there are many interesting cases that we can afford to compute. I'll say more on the validity of different schemes as we encounter them in more detail in the class.