Final report

on the NKFIH supported project no. 124018 entitled

"Development of a fragment-based ab initio method for the description of excited state and transport properties of polynucleotides"

1 Introduction

The last decades brought about a huge development of quantum chemical methodology: larger and larger molecules can be treated with increasing accuracy, and, at the same time, the quest for calculations to support experimental observations became more and more relevant. For the molecular ground state well established methods are available and quantum chemistry, mostly by Density Functional Theory (DFT) methods, is able to study structures and even reactions of large molecules, as big as polypeptides. Recent experiments, however, discovered the importance of new processes in these large molecules: electron transfer between distant regions, or excitations affecting not just a local domain are responsible for many interesting phenomena in biology and material science. Since ground state methods cannot describe such processes, there is a challenge to develop new tools which can treat excited states as well.

There are two possible routes towards this goal. One option is to develop new approximate methods, but maintaining the accuracy and reliability is not a trivial task. Alternatively, one can aim at defining multiscale approaches where only the important part of the system is handled at the high level, while the rest is approximated at lower level. Different types of embedding methods, like quantum mechanics/molecular mechanics (QM/MM) [1], "our own N-layered integrated molecular orbital and molecular mechanics" (ONIOM) [2], projector based embedding (PbE) [3], frozen density embedding (FDE) [4, 5] or local correlation methods [6, 7, 8] are available for describing local events in large systems. However, non-local phenomena often require too large active partitions in these calculations, rendering the realization impossible.

For such situations fragment methods [9] could be the preferred approach, where several "active" centers can be handled at a high level of theory and the property of the entire system is calculated from that of the individual fragments, considering proper coupling terms between them. The fragment methods are especially suited for non-covalently bound systems, since the fragmentation is natural.

2 Theoretical background for non-covalent interactions

The general Hamiltonian of two interacting fragments is given as

$$\hat{H}(\mathbf{r}_1,\mathbf{r}_2) = \hat{H}_1(\mathbf{r}_1) + \hat{H}_2(\mathbf{r}_2) + \hat{V}_{1,2}(\mathbf{r}_1,\mathbf{r}_2), \tag{1}$$

with $\hat{H}_i$ being the Hamiltonian of the non-interacting fragments and $\hat{V}_{1,2}(\mathbf{r}_1,\mathbf{r}_2)$ their interaction. With this Hamiltonian a perturbative treatment is possible, taking the product of the fragments' wave functions as the zeroth order. Let us introduce the proposed methodology on the simplest example of a supersystem consisting of two fragments, with just one excited state considered on both:

$$\begin{aligned}
\Psi_0(\mathbf{r}_1,\mathbf{r}_2) &= \Phi_{1,0}(\mathbf{r}_1)\Phi_{2,0}(\mathbf{r}_2) \\
\Psi_1(\mathbf{r}_1,\mathbf{r}_2) &= \Phi_{1,1}(\mathbf{r}_1)\Phi_{2,0}(\mathbf{r}_2) \\
\Psi_2(\mathbf{r}_1,\mathbf{r}_2) &= \Phi_{1,0}(\mathbf{r}_1)\Phi_{2,1}(\mathbf{r}_2),
\end{aligned} \tag{2}$$

where the indices 1 and 2 refer to the two subsystems with coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ and $\Phi_{i,k}$ is the k-th ($k = 0, 1$) eigenfunction of the Hamiltonian of fragment i:

$$\hat{H}_i(\mathbf{r}_i)\Phi_{i,k}(\mathbf{r}_i) = E_{i,k}\Phi_{i,k}(\mathbf{r}_i). \tag{3}$$

The quality of such a perturbational approach depends on the magnitude of the coupling terms. A fraction of their effects can be captured by repartitioning the Hamiltonian in Eqn. (1):

$$\begin{aligned}
\hat{H}(\mathbf{r}_1,\mathbf{r}_2) &= \hat{H}_1^{eff}(\mathbf{r}_1;\mathbf{r}_2) + \hat{H}_2(\mathbf{r}_2) + \Delta V_1(\mathbf{r}_1,\mathbf{r}_2) \\
\hat{H}(\mathbf{r}_1,\mathbf{r}_2) &= \hat{H}_2^{eff}(\mathbf{r}_1;\mathbf{r}_2) + \hat{H}_1(\mathbf{r}_2) + \Delta V_2(\mathbf{r}_1,\mathbf{r}_2),
\end{aligned} \tag{4}$$

where $\hat{H}_i^{eff} = \hat{H}_i + \hat{V}_i^{eff}$ includes the effect of the environment through an "embedding potential" $\hat{V}_i^{eff}$. The inclusion of the approximate "remainder potential" $\Delta V_i(\mathbf{r}_1,\mathbf{r}_2) \approx \hat{V}_{1,2}(\mathbf{r}_1,\mathbf{r}_2) - \hat{V}_i^{eff}$ is necessary to correct for the interactions which are not/cannot be accounted for when the eigenproblem of $\hat{H}_i^{eff}$ is solved (see later).

The fragment wave functions with tilde ($\tilde{\Phi}_{i,k}(\mathbf{r}_i)$) are eigenfunctions of $\hat{H}_i^{eff}$:

$$\hat{H}_i^{eff}\tilde{\Phi}_{i,1} = \tilde{E}_{i,1}\tilde{\Phi}_{i,1}, \tag{5}$$

thus include the effect of the other fragment's ground state through $\hat{V}_i^{eff}$. These perturbed fragment wave functions together with the eigenfunctions of the unperturbed ground states of the other fragment ($\Phi_{i,0}(\mathbf{r}_i)$)

can be used to construct improved wave functions of the entire system:

$$\begin{aligned}\tilde{\Psi}_0(\mathbf{r}_1,\mathbf{r}_2) &= \tilde{\Phi}_{1,0}(\mathbf{r}_1)\Phi_{2,0}(\mathbf{r}_2)\\ \tilde{\Psi}_1(\mathbf{r}_1,\mathbf{r}_2) &= \tilde{\Phi}_{1,1}(\mathbf{r}_1)\Phi_{2,0}(\mathbf{r}_2)\\ \tilde{\Psi}_2(\mathbf{r}_1,\mathbf{r}_2) &= \Phi_{1,0}(\mathbf{r}_1)\tilde{\Phi}_{2,1}(\mathbf{r}_2).\end{aligned} \tag{6}$$

The first function describes the ground state, while the second and third the excited states localized on the first fragment and on the second fragment, respectively. The corresponding energies are:

$$\begin{aligned}E_0 &= \tilde{E}_{1,0} + E_{2,0} + \Delta V_1\\ E_1 &= \tilde{E}_{1,1} + E_{2,0} + \Delta V_1\\ E_2 &= \tilde{E}_{2,1} + E_{1,0} + \Delta V_2\end{aligned} \tag{7}$$

To consider also Frenkel [10] or exciton coupling of the two chromophores on the fragments, the matrix of the Hamiltonian on the basis of the excited state functions in Eqn. (6) should be diagonalized:

$$\mathbf{H} = \begin{bmatrix}\tilde{E}_{1,1} + E_{2,0} + \Delta V_1 & \tilde{V}(1,2)\\ \tilde{V}(2,1) & E_{1,0} + \tilde{E}_{2,1} + \Delta V_2\end{bmatrix} \tag{8}$$

as first suggested by Frenkel [10]. To that end the so called excitonic or Frenkel coupling needs to be calculated:

$$\begin{aligned}\tilde{V}(1,2) &= \langle\tilde{\Psi}_1(\mathbf{r}_1,\mathbf{r}_2)|\hat{H}(\mathbf{r}_1,\mathbf{r}_2)|\tilde{\Psi}_2(\mathbf{r}_1,\mathbf{r}_2)\rangle\\ &= \langle\tilde{\Phi}_{1,1}(\mathbf{r}_1)\Phi_{2,0}(\mathbf{r}_2)|\hat{H}(\mathbf{r}_1,\mathbf{r}_2)|\Phi_{1,0}(\mathbf{r}_1)\tilde{\Phi}_{2,1}(\mathbf{r}_2)\rangle.\end{aligned} \tag{9}$$

The scheme suggested here has thus two main ingredients. First, a proper definition of the effective Hamiltonian $\hat{H}_i^{eff}$ is needed, which includes the intermolecular interactions compatible with the electronic structure method in use. Eventually, a corresponding ΔV_i is necessary to include the missing interaction terms. Second, an appropriate approximation for the Frenkel coupling between the excited states needs also to be established. The main goal of the project was to establish approximations for these terms which are compatible with high level electronic structure calculations and provide accuracy comparable to that of a direct calculation on the complex.

3 Results

3.1 Fragment methods for the ground state [11]

Systematic studies on the ground state of the complexes allowed us to select a proper effective Hamiltonian ($\hat{H}_i^{eff}$) compatible with Coupled Cluster type electronic structure calculations and the corresponding ΔV_i

potential. Two different models have been investigated to describe the electronic structure, see the recent paper [11].

One model is based on the QM/MM concept with point charges representing the environment which taken from different sources. Here the CHELPG (CHarges from ELectrostatic Potentials using a Grid-based) algorithm [12] was found to work well with CC methods. It has the important benefit of not being dependent on precalculated parameters like in convectional force fields (e.g. CHARM or AMBER), rather the charges are obtained for the specific system directly from the wave function of the method chosen. This scheme includes only electrostatic interaction between the fragments.

The second method is based on Projector-based Embedding (PbE) [3] using the Huzinaga-equation[13] to the embedding problem as suggested by Hégely et al. [14]. Here the entire system is calculated by DFT, followed by the localization of the occupied molecular orbitals (MOs) of the fragments, which results in the splitting of the density matrix into two parts corresponding to the fragments. The localization can be extended to the virtual orbital space, reducing the computational cost of the CC calculations. This scheme, besides the electrostatic interactions, also includes the Pauli-repulsion contribution of the interaction energy, although at the DFT level only.

The missing interactions terms (ΔV_i), i.e. the entire van-der-Waals potential for QM/MM and the dispersion for PbE, have also been included in several different forms. It was found that the extended Effective Fragment Potential (EFP2) developed by Gordon and coworkers [15] is an excellent choice.

These conclusions have been reached by careful analysis of potential energy curves obtained in test calculations on pyrrole-pyrrole and cytosine-uracil complexes. For more details see the original paper [11].

3.2 Fragment method for the excited state [16, 17]

The study on excited states [16, 17] relies heavily on the conclusion obtained for ground states above. Two conceptually different methods were included in this study. One is a QM/MM approach based on CHELPG point charges, augmented with the (ground state) dispersion and Pauli repulsion from EFP2, while the other is a Huzinaga projection based embedding model (PbE) augmented with an EFP2 (ground state) dispersion contribution.

As of the excitonic (Frenkel) coupling, two different approaches have been tested. One calculates this quantity using the transition dipoles (TrM) of the fragments, while the other one includes the entire Coulomb coupling. This latter has been calculated using the Transition Density Cube (TDC) method by Krueger et al. [18]. TDC calculations require a grid representation of the transition densities that we have programmed in the CFOUR [19] package. This implementation allows the calculation of the excitonic coupling at any level of theory where the transition density is available. Comparing the TrM and TDC schemes, the latter was found much better, the error becoming significant only at very short intermolecular distance, where the term from exchange repulsion cannot be neglected. This term is, however, not yet available for CC-type methods. We have not planned its implementation within this project, since, according to earlier literature, this term was not considered sizeable. However, we have disproved this concept in this study and plan to extend the procedure by the new term in a future project.

Obtaining proper reference data for validating the fragment models turned out to be a non-trivial task and in fact delayed the project heavily. Problems arise from, among others, a) converging the calculations to the proper states (in particular when diffuse basis sets are used), b) the presence of Charge Transfer (CT) type electronic states in the low-energy spectrum at small intermolecular distances, as well as c) the choice of counterpoise correction (CP) in excited states which is not well discussed in the literature. These issues were also discussed in paper [16].

The test calculations were performed on stacked homodimers of pyrrole, cytosine and uracil, as well as on the cytosine-uracil complex. In addition, the homodimer of formaldehyde was investigated as a smaller complex. The details of these test calculations can be found in the paper [16], here we summarize only the most important conclusions. As of the electronic structure calculations, QM/MM with CHELPG point charges of the environment is proved to be good choice. However, PbE, due to the use of localized and truncated virtual space, fails with diffuse basis sets, giving, incorrectly, repulsive potential energy curves. It was found that correction for van-der-Waals-type interactions (dispersion and Pauli repulsion) is inevitable, and EFP2 provides a convenient and accurate way to include them. Excitonic interaction calculated with TDC scheme can provide a qualitative description of the Frenkel splitting. Potential energy curves calculated this way are reasonably accurate above 4 Å intermolecular distance, i.e. from the minimum towards dissociation.

3.3 Benchmarking on Charge Transfer (CT) states [20, 21, 22]

As mentioned in the Introduction, one way of obtaining accurate results for large system is the development of accurate approximate methods. Such methods of the Coupled Cluster (CC) hierarchy are available in the literature, like CC2 [23] or ADC(2) [24]. In a series of papers we have investigated their performance compared to high level CC methods for CT states.

In the first one [20] we proposed a new benchmark set consisting of dimers having low-energy CT states. On this set, the vertical excitation energy has been calculated with Coupled Cluster methods including triple excitations (CC3, CCSDT-3, CCSD(T)(a)*), as well as with methods including full or approximate doubles (CCSD, STEOM-CCSD, CC2, ADC(2), EOM-CCSD(2)). The results show that the popular CC2 and ADC(2) methods are much less accurate for CT states than for valence states. On the other hand, EOM-CCSD seems to have similar systematic overestimation of the excitation energies for both types of states. Among the triples methods the novel EOM-CCSD(T)(a)* method including noniterative triple excitations is found to stand out with its consistently good performance for all types of states, delivering essentially EOM-CCSDT quality results.

In the second paper [21] we have extended the previous study to the potential energy curves. Besides the global view of these curves, special attention has been paid to the region of the crossing which will be essential when testing fragment methods. It was found that triple excitations are needed to accurately describe potential energy surfaces of CT states. The somewhat larger error of CCSD for CT states can be explained by its size extensivity error and the overestimation of the asymptotic excitation energy. Second order approximations are not advantageous for the error cancellation, in fact CC2 is much worse for CT states than any other method investigated here. The results also show that the location of the (avoided) crossings of local and CT states depend very much on the accurate description of the CT states. Failure to describe this topology might affect dynamics, and a warning, in particular in case of CC2, should be issued if CT states play a role in the physics of the problem.

In the third paper [22] we have investigated spin-scaled versions of the CC2 and ADC(2) methods, since earlier we have found these are superior for e.g Rydberg states [25, 26]. The so called SOS-CC2 and SCS-CC2 [27, 28] calculations showed slight improvement of the results with respect to the original CC2 version. In addition to statistics on the accuracy of vertical excitation energies at equilibrium and infinite separation of bimolecular complexes, potential energy surfaces of the ammonia-fluorine complex are also reported. The results show the capability of spin-component-scaled approaches to reduce the large errors of their regular counterparts to a significant extent, outperforming even the coupled-cluster single and double method in many cases. The cost-effective scaled-opposite-spin variants are found to provide a remarkably good agreement with the CCSDT-3 reference data, thereby being the recommended method of choice in the study of charge-transfer states.

In summary, we have obtained that approximate versions of the CC methods are not capable to describe CT states accurately, which underlines the importance of the fragment method to be developed. Unfortunately, CT states could not be included in the fragment methodology yet, because, contrary to previous assumptions, dipole-dipole coupling cannot be used here.

3.4 Tests on electron affinities and ionization potentials [29]

In the paper [29], the CC2 and ADC(2) wave function models and their spin-component scaled modifications are adopted for predicting vertical ionization potentials (VIPs) and electron affinities (VEAs). The ionic solutions are obtained as electronic excitations in the continuum orbital formalism, making the use of existing, widespread quantum chemistry codes with minimal modifications possible, in full consistency with the treatment of charge transfer excitations. The performance of different variants is evaluated via benchmark calculations on various sets from previous works, containing small- and medium-sized systems, including the nucleobases. It is shown that with the spin-scaled approximate methods, in particular the scaled opposite-spin variant of the ADC(2) method, the accuracy of EOM-CCSD is achievable at a fraction of the computational cost, also outperforming many common electron propagator approaches.

3.5 Role of environment

An algorithm to consider environmental effects has been worked out in our laboratory, the corresponding manual can be accessed here. It is based on a molecular dynamics simulation to consider the changing distribution of solvent molecules. During the simulation snapshots are taken and the excitation energies are calculated by the given electronic structure method including the solvent molecules in a QM/MM framework. One important, and far from being trivial, step of the algorithm is the assignment of the corresponding states from the different snapshots, which then allows the calculation of the mean values and the standard deviation of the excitation energies. An important technical question was how long a simulation had to be in order to reach convergence of the procedure to an accuracy of 0.01 eV. It turned out that this can be achieved with a 200 ps long simulation, however, qualitative results can be obtained already with 5 ps. The algorithm is thus ready to be used also with the fragment method.

The algorithm has been tested to predict the effect of the solvents on the excitation energies of small molecules. The difference of the excitation energies of formaldehyde in aqueous solution and in vacuum was calculated with the CC2, SOS-ADC(2), CCSD and CCSDT methods. The results of the various calculations agree well, but in some cases the CC2 results showed a significant difference to the other results. It was observed that the difference between the excitation energies in aqueous solutions and in vacuum may vary from a few hundredths to several tenths of eV, while the standard deviation is at most 0.2 eV. The solvent effect on Rydberg states was larger than on valence states. It was also concluded that the method is unable to predict the effect of apolar solvents, which was not surprising, since only electrostatic interactions are modeled in QM/MM.

The results were not published yet, but a BSc thesis [30] was completed on the topic.

3.6 Electron transfer in non-covalently bound systems [31]

One important application of the fragment method will be the description of electron transfer in large (biological) systems. We made the first steps in this direction by developing a method for simulating electron transport, which uses quantities close to chemical intuition and obtainable from quantum chemical calculations. The role of molecular vibrations that facilitate the transport by being responsible for the periodic behaviour of these quantities was shown by normal mode analysis. The results support a mechanism involving the electron's direct hopping between the electrodes, without its presence on the molecule, with the prime importance of the bending vibrations that periodically alter the molecule–electrode interactions. Our approach [31] provides an alternative insight into the role of nuclear motions in the electron transport process, one which is more expressive from the chemical perspective. This concept was demonstrated by describing the electron transport through the single-molecule junction of benzene-1,4-diamine, the latter considered as a "good conductor". By continuing the project, calculations on a "good insulator" (1,4-diazabicyclo[2.2.2]octane) showed that indeed in this case the transport is facilitated much less by the vibrations.

3.7 Improvement of electronic structure program packages [32, 33]

Although not in the original plans, I have participated in writing two research papers about popular quantum chemistry codes Columbus [32] and CFOUR [33], being a principal developer of these codes. These papers summarize the new features of these popular codes, including the development produced in my group in Budapest. Therefore, these papers are, in my opinion, important tools to advertise our efforts on electronic structure methods and help make them acknowledged.

4 Impact

Besides the ten papers [20, 21, 22, 29, 11, 16, 17, 31, 32, 33] we published on the results of this NKFIH project, the principal investigator has been invited to several big conferences to present invited talks. These meetings include the WATOC conference (Vancouver, Canada), the ACS Spring Meeting (San Diego, USA), the 60th and 61st Sanibel Symposium (St. Simon Island, USA) and the EuCo-CC (Perugia, Italy). The effort by my students contributed to this work considerably, resulting in five BSc and four MSc theses, as well as several poster presentations (and poster prizes) at international conferences.

New questions arose during this study, which were not foreseen when designing the project. These include the BSSE correction for excited states, van-der-Waals interactions in excited states, inclusion of exchange coupling in excitonic interactions. We are in particular excited about the project which aims at correcting the PbE scheme when used with diffuse basis sets and the application of the fragment scheme for electron transfer. Fortunately, a new NKFIH grant has been awarded to us which will enable us to attack these problems.

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