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### Physical Meaning of Orbitals in Adiabatic Linear Response Time-Dependent Orbital Functional Theories

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# Summary

An important part of the field of theoretical chemistry is the determination of potential energy curves. These curves can be obtained by solving the electronic Schrödinger equation for several sets of nuclear coordinates. In case of small molecules one can obtain very accurate approximations to the exact wavefunctions and their associated energies for both the ground state and excited states. However, one cannot obtain accurate quantities for larger molecules due to the fact that the computational effort scales unfavorably when the system size is increased. One can avoid calculating the wavefunction by using the fact that there is a one to one mapping between the ground state energy and the electronic density of the system. An exact expression for this mapping is unknown, so one has to use approximations. These approximate density functionals are known to generate accurate and computationally inexpensive results for many systems. One can also often obtain accurate results for excited states by using the time dependent version of density functional theory. In **Chapter 2** it is accentuated that these methods do not only yield good results, but that the Kohn-Sham orbitals that are generated by accurate approximate functionals give an easily understandable physical picture of ionizations and excitations within molecules. One can, however, not use these methods for all states and systems due to some of the approximations that are made in both the ground and excited state methods. For instance, it is not possible to describe chemical bond breaking with these methods. One can also not describe excited states in which multiple “electrons” are excited at the same time. A large amount of approximations have been researched in order to fix these issues. However, up until this point no practical and universal solution has come up. Instead of trying new approximations within density functional theory one can instead move to a more expanded theory which has more options. The density matrix functional theory goes beyond density functional theory and uses the density matrix instead of just the density of the electronic system. The exact mapping between the density matrix and the ground state energy is known for systems that contain 2 electrons. One has also been able to generate ap-

## SUMMARY

proximate functionals that are able to accurately describe the bond breaking process for many-electron systems like  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$ . It is also possible to generate excited state curves by using the time dependent version. However, it has been shown that the time dependent density matrix functional theory is not able to generate accurate results. In order to still obtain accurate curves an extension was added to the density matrix functional theory. It has been shown that the resulting time dependent phase including natural orbital theory is able to get exact excitation energies for systems that contain 2 electrons. The excitation energy is not the only quantity of importance in case one is looking at the excitation processes in a molecule, it is also important to know if a molecule is going to absorb incoming photons. The relative absorption ability of each of the excitations can be related to the oscillator strength of the excitation. In **Chapter 3** the PINO oscillator strength formula is derived, and applied to the  $\text{H}_2$  and  $\text{HeH}^+$  molecules. Up until this point the PINO theory has only been applied to systems that contain 2 electrons. It is important to see whether this theory can also be used to generate accurate excited state potential energy curves for many-electron molecules. A new functional that yields very accurate potential energy curves for quasi 2 electron systems ( $\text{LiH}$ ,  $\text{Li}_2$ ) is derived in **Chapter 4**. In addition to the new functional it is also shown that most of the functionals that were used to generate ground state curves cannot be used for excited state calculations. Furthermore, it is shown that it is likely that future functionals should use a linear dependence on the natural occupation number ( $n_i$ ) for the diagonal elements of the two-body density matrix ( $\Gamma_{iii}$ ). The excitation energies are described very accurately for the systems described above. However, the excitations cannot be easily interpreted due to the fact that many orbital to orbital transitions are involved. In **Chapter 5** it is proposed to bypass the problem by performing a transformation of the “virtual” orbitals to so called natural excitation orbitals (NEOs). It is shown that the NEOs are almost equivalent to the “exact” Kohn-Sham orbitals for the  $\text{H}_2$  molecule. Since we have used an exact functional for this molecule the equivalence of the orbitals can be viewed as a confirmation of the findings in **Chapter 2**.