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Nonorthogonal configuration interaction to study electron and excitation energy transfer

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Nonorthogonal configuration interaction to study electron and excitation energy transfer

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Nonorthogonal configuration interaction to study electron and excitation energy transfer

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*Dedicated to Amma and Appa, who have taught me more than I could ever learn,
supported me throughout my life, in every decision I made.*

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INTRODUCTION

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1.1. MOTIVATION AND BACKGROUND

THEORETICAL modeling is a powerful tool to gain understanding of the properties of materials [1]. It provides us with key insights necessary to understand how molecules interact with each other, how they interact with light, and the environment, or how we can combine them to make new ones [2]. On a larger scale, it enables us to understand chemical reactions, their kinetics, etc. which is essential when looking for viable renewable sources of energy, and to understand biological phenomena like enzyme catalysis, protein folding, encoding in DNA, to name a few. The knowledge obtained in turn is used to develop better technology for renewable energy, healthcare, among others.

Research in this field formally came to being early in the twentieth century with the development of quantum mechanics (QM) [3–5]. As one of the most important advancements in the study of material properties, quantum mechanics was able to explain the mismatch between theoretical predictions based on classical physics and experimental observations on sub-microscopic particles (e.g., black body radiation) made in the late nineteenth and early twentieth century. QM tells us that at this small length-scale matter and wave nature are interchangeable. In QM, all information of an entity in space is contained in its *wavefunction*. The wavefunction provides probabilistic information about a system consisting of one or more particles (electrons and/or nuclei), and physically *observable* quantities (like energy, position, momentum, spin and orbital angular moments, dipole moments, etc.) can be obtained by calculating the expectation value of an *operator* acting on the wavefunction [6, 7]. When we describe much larger systems (like ones visible to the naked eye), quantum effects become in many cases less important and they end up following the more familiar (and easier to solve) equations of classical mechanics.

QM is very successful in describing the behavior of electrons in molecules, giving rise to the study of electronic structure which is extensively used in the theoretical modeling of materials [8]. One important motivation behind studies on electronic structure is to obtain a computationally tractable solution to the electronic Schrödinger equation for a given set of coordinates of atomic nuclei and the total number of electrons in the system. Interactions of electrons with other electrons, with nuclei (through Coulombic forces or through vibronic coupling), and light are responsible for almost all observable phenomena. One such class of interesting phenomena involves the transfer of charges or energy brought about by a change in the electron density in the molecule(s). Excitation energy transfer (EET) or electron transfer (ET) reactions are part of many vital processes in nature and technology like cellular respiration, protein folding, and functioning of optoelectronic devices [9–12]. It is therefore desirable to have a simple yet rigorous and qualitatively correct theoretical description of these processes to get a better understanding, look for underlying trends, and to aid in future experiments.

Most intuitively, a theoretical description is based on a model that best resembles the real system and its properties, while using the least number of parameters. Although they do not provide a wholesome description of the system, these *phenomenological models* have aided our understanding of materials to a great extent. Some of the most successful models that have been used concerning ET and EET processes are discussed later in the chapter. On the other end of the spectrum of theoretical models lies the full

quantum mechanical description of a system obtained from solving the Schrödinger equation. Unfortunately, the Schrödinger equation cannot be solved analytically for anything more than two interacting particles (hence exact solutions only exist for systems like the hydrogen atom). Numerous schemes have been developed to approximate the exact solutions of the Schrödinger equation and have been applied to study larger and physically relevant systems and is an active field of research.

Within the choice of a non-relativistic Hamiltonian, a preliminary step in reducing the complexity is to decouple the electron from the nuclear movement. This is called the Born-Oppenheimer approximation [13] and is valid in most cases since nuclei move around three orders of magnitude slower than electrons. The starting point for electronic structure calculations based on a many-electron wavefunction is the Hartree-Fock (HF) theory [14], which treats the electron-electron interactions in a mean-field manner as a consequence of approximating the exact wavefunction as a single Slater determinant, which is an antisymmetrized product of one-electron functions, also known as spinorbitals. A spinorbital is a product of a spatial one-particle function or 'orbital' and a 'spin function' that describes the spin angular momentum of the particle. It is common practice to expand the one-electron functions in the Slater determinant in a set of basis functions, which converts solving the Hartree-Fock equations in a matrix problem, which can be efficiently solved on modern computer architectures [15, 16]. Although the Hartree-Fock wavefunction is a very good approximation for many properties of relatively simple systems, it is insufficient to describe many processes like bond breaking, electronic excitations, reaction paths (transition states) or more complex system, for example those containing transition metals.

The exact solution for a given one-electron basis set is obtained by expanding the many-electron wavefunction as a linear combination of all Slater determinants that can be formed by distributing the electrons in all possible ways over the orbitals and variationally optimizing the coefficients of expansion, a so-called full configuration interaction (FCI), though this calculation is impossible to perform for systems larger than a few atoms. Truncated CI wavefunctions can be used to study larger systems. These wavefunctions are generated by extending the Hartree-Fock (single determinant) wavefunction with Slater determinants that differ by one, two or more orbital occupations. Increasing the number of determinants in the wavefunction leads us to different multiconfigurational methods like singles and doubles CI(CISD), multireference CI (MRCI) [17], complete active space self-consistent field (CASSCF) [18, 19], etc. These wavefunctions cover a much broader application range than the HF wavefunction, and are, for example, better suited to describe excited states.

Other ways to improve on the HF solution and obtain a 'correlated' wavefunction are through perturbation theory (PT) and the coupled cluster (CC) formalism. The most commonly used type of perturbation theory is the (second-order) Møller-Plesset perturbation theory (MP2). These theories can also be used with multiconfigurational reference wavefunctions (MRPT, MRCC). These post Hartree-Fock methods typically improve the results substantially compared to those based on the mean-field treatment provided by Hartree-Fock, but of course come with the burden that the time-to-solution increases rapidly.

One major change in perceiving the electronic problem came with the development of

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density functional theory (DFT) [20–22]. DFT aims at the electron density rather than the wavefunction and is based on the Hohenberg-Kohn theorem that states that the energy is a unique functional of the density. Though formally exact, the analytical expression for this functional is only known for a homogeneous electron gas, and numerous approximate expressions have been developed, often using experimental data [23, 24], but also based on pure formal considerations [25–27]. DFT and its extension for excited states, time-dependent DFT (TDDFT) [28, 29], are very useful tools and are now routinely used to accurately predict properties of large molecules with the computational costs comparable to a HF calculation. The problem though is that the results are often strongly functional and material dependent, which makes it difficult to systematically improve the quality of the calculation.

Both the above described wavefunction based methods and the Kohn-Sham implementation of DFT rely on mutually orthogonal molecular orbitals, but this restriction on the one-electron functions is not a requirement for describing the electronic structure. In fact, the very first quantum mechanical description of a chemical bond by Heitler and London made use of a nonorthogonal set of orbitals. The theory that emerged from this study is known as Valence Bond (VB) theory [30], and offers a chemically intuitive description of bonding in terms of so-called Lewis structures, hence making it easy to translate the computational results to chemically relevant concepts like electron transfer/sharing etc. This comes at a price because the nonorthogonality between the VB structures complicates significantly the calculation of the elements of the overlap and Hamiltonian matrices spanned by the different VB structures.

The work presented in this thesis is an alternative multiconfigurational wavefunction based method called nonorthogonal configuration interaction (NOCI). NOCI combines the accuracy of standard multiconfigurational methods with the intuitive interpretation of the wave function inherent to VB. It includes full orbital relaxation, a rigorous treatment of static electron correlation and, as will be shown later in this thesis, can be extended with dynamic correlation effects and the influence of accounting, in an approximate way, for the immediate surrounding of the quantum region. In contrast to traditional CI approaches that use a single set of orthogonal orbitals to expand the wavefunction in terms of many-electron functions (determinants or configuration state functions), the NOCI wavefunction consists of a small number of configurations, each expressed in its own optimal set of orbitals that do not necessarily have any constraints for orthogonality among them. This ability to account for orbital relaxation offers NOCI a conceptual advantage in comparison to methods that use one set of orbitals to express all electronic states of interest. Take a state-average CASSCF for contrast, where the orbitals are optimized for a fifty-fifty average of a local excited state and a charge-transfer excited state. Using the same set of orbitals for both states could easily lead to a description that is not suited for either ground or the excited states [31].

The possibility to expand the NOCI wavefunction in terms of physically motivated diabatic states makes the method a good candidate for studies on electron and energy transfer processes, as is described in this thesis. As in valence bond methods, the use of nonorthogonal orbitals makes the evaluation of matrix elements between different nonorthogonal states computationally complex. We have nevertheless developed a method to overcome this difficulty to a considerable extent [32]. There have been many

(essentially similar) implementations over the years that have been used to evaluate matrix elements over nonorthogonal determinant pairs [33–47]. Our implementation is based on the code GNOME written in Groningen in the 1980s [41]. In our new implementation of NOCI, called NOCI-Fragments [48], we expand the NOCI wavefunction for an ensemble of molecules using many-electron basis functions (MEBFs); which are antisymmetrized and spin-adapted products of fragment wavefunctions [49]. A fragment corresponds usually to one of the molecules in the ensemble under study, but can also consist of two or more molecules, or even only a specific part of one molecule, for example in donor-acceptor molecules. The fragment wavefunctions used in this research are typically CASSCF wavefunctions, but can be any type of (multiconfigurational) wavefunction. The collection of fragment wavefunctions used for the construction of the MEBFs must be chosen carefully to ensure that all relevant physical mechanisms of the ensemble are covered: local excitations on the fragments, charge transfer processes, exciton delocalization to name a few that are relevant for singlet fission.

In this thesis, we present developmental work on NOCI-Fragments to make the method computationally tractable while treating large molecular systems. This approach is used to study electron and energy transfer processes in molecular clusters. We focus on the singlet fission process which has been widely studied in the quantum chemistry community for its capability to increase the photoconversion efficiency of organic photovoltaics [50–52]. Further, we present methods to include dynamic electron correlation and investigate effects caused by the environment. The remainder of this chapter is designed to provide an overview of electron and energy transfer processes and the theoretical approaches used to study them, with a special focus on singlet fission.

1.2. MODELING ELECTRON AND ENERGY TRANSFER

THE photoexcitation of a molecule (chromophore) can result in charge (electron) or exciton (electron-hole pair) transport to a neighbor. These processes called electron transfer (ET) and excitation energy transfer (EET), result in changes in the electronic configuration of the molecules. Such processes constitute many fundamental phenomena in biology and optoelectronics, hence they have been widely studied [53–57]. A theoretical understanding of the processes is valuable in fields like medicine and energy production, where similar processes have been found to occur. Although fundamentally different, the electron and energy transfer processes can be theoretically described using similar schemes [58, 59].

The schemes are centered around the calculation of the electronic coupling factor (V_{if}), which is important for the transition rate between the initial (i) and final (f) states. The electronic coupling is in turn determined by the Hamiltonian matrix element between the initial and final diabatic states. In the most basic description of ET and EET, the coupling is dominated by the interaction between the MOs where there has been a change in occupancy. Transition rates between electronic states in optoelectronic processes are generally well approximated by the Fermi golden rule,

$$k_{if} = \frac{2\pi}{\hbar} |V_{if}|^2 \rho(E_i \simeq E_f) \quad (1.1)$$

1

where (k_{if}) is the rate, and $\rho(E_i \simeq E_f)$ is the (weighted) Franck-Condon density of states factor, which arises from conservation of energy. Therefore, for an efficient transfer, we need a large coupling factor V_{if} . Worth mentioning is that Eq. 1.1 is valid in the weak-coupling limit and is the starting point for theories on electron and excitation transfers like the well-known Marcus [60] and Förster [61] theories. In essence, these are electronic structure problems so we can use one of the numerous quantum chemical methods (ab-initio and semi-empirical) we have at our disposal to study the processes. Some of the most straightforward methods to calculate (V_{if}) are based on simple phenomenological models.

Phenomenological models are a useful way to rationalize empirical observations in those cases for which a first principles approach becomes too involved. In our case of ET and EET, evaluation of the coupling follows a general recipe: We employ a two-state model where the Hamiltonian can be represented using mutually orthogonal initial and final diabatic states (E_i, E_f) , and the eigenstates,

$$\begin{pmatrix} E_i & H_{if} \\ H_{if} & E_f \end{pmatrix} \Leftrightarrow \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \quad (1.2)$$

with eigenvalues E_1 and E_2 ,

$$E_{1,2} = \frac{E_i + E_f}{2} \pm \sqrt{\left(\frac{E_i - E_f}{2}\right)^2 + H_{if}^2} \quad (1.3)$$

The value of the coupling can now be evaluated in the following ways; first, we have the energy based schemes. When $E_i = E_f$, it follows that the coupling is half the ΔE_{12} value and for non-degenerate initial and final states the coupling becomes $H_{if} = \frac{1}{2}(\Delta E_{12} - \Delta E_{if})$.

$$|E_1 - E_2| = 2|H_{if}| \quad (1.4)$$

A basic estimate can be obtained by assuming that electron transfer can be modeled as a one-electron process where the energies between initial and final states are evaluated using Koopmans' theorem in Hartree-Fock theory.

$$|\epsilon_1 - \epsilon_2| = 2|H_{if}| \quad (1.5)$$

with $\epsilon_{1,2}$ the HOMO and LUMO energies of the two molecules involved in the transfer. A more general expression also takes into account the overlap between final and initial state,

$$V_{if} = \frac{H_{if} - (E_i + E_f)S_{if}/2}{1 - S_{if}^2} \quad (1.6)$$

A simple example would be to use two Hartree-Fock wavefunctions to describe the two states. The second group of procedures to estimate the coupling is based on the use of external operators such as dipole or charge difference operators to define charge-localized states and then transform the two state Hamiltonian accordingly to determine the coupling. The Generalized Mulliken-Hush (GMH) scheme [62, 63] is based on the

dipole operator and the coupling is given by,

$$V_{if} = \frac{\mu_{12}\Delta E_{12}}{\sqrt{(\mu_1 - \mu_2)^2 + 4\mu_{12}^2}} \quad (1.7)$$

where μ_{12} is the transition dipole moment, ΔE_{12} is the energy difference and μ_1, μ_2 are the permanent dipoles. In a similar scheme called the fragment charge difference (FCD) scheme, the charge difference operator Δq_{mn} is used to calculate the coupling,

$$V_{if} = \frac{\Delta q_{12}\Delta E_{12}}{\sqrt{(q_1 - q_2)^2 + 4q_{12}^2}} \quad (1.8)$$

where q_1, q_2 are the values of the localized charges. The multistate variant of FCD has been implemented in the evaluation of couplings [64]. The fragment spin difference (FSD) and fragment excitation difference (FED) models are variants of the aforementioned schemes, implemented by Hsu and coworkers [65, 66]. The authors evaluate electronic couplings for singlet fission using FSD and diabatic couplings of few energy transfer systems through the FED model.

Although phenomenological models provide a convenient way to gain understanding of many interesting phenomena and can be used as a tool to modify materials in a non-empirical manner, their applicability is limited to, in most cases, a particular type of systems only. Additionally, the accuracy of each prediction from these models is dependent on the number of parameters and semi-empirical factors used. The use of quantum mechanical first principles based methods is hence highly desirable for such studies [66–81]. We mention here some studies that are relevant within the context of this thesis.

Recently Bai and coworkers evaluated electronic couplings for donor-acceptor interfaces using molecular orbital overlaps designed to study energy transfer from the principles of Dexter's theory [82]. Parker and coworkers use products of multiconfigurational restricted active space self-consistent field (RASSCF) wavefunctions to describe the molecular wavefunctions and a subsequent 'active space decomposition' strategy specifically developed to be able to study excitation energy transfer processes while still maintaining the diabatic picture [75]. Mayhall showed the possibility of describing multi-excitonic properties using a wavefunction made from single excitations through the restricted active space spin-flip (RAS-SF) method [76]. In the work, RAS-SF wavefunctions have been used to solve the model Hamiltonian describing the exciton generation process. Constrained DFT (CDFT) is effective in studying the kinetics of electron transfer [83, 84]. The electron transfer process in a condensed system has been effectively studied through the Marcus rate theory by Holmberg and coworkers, who used CDFT for the work [77]. CDFT in combination with the generalized Mulliken-Hush method has been used in the calculation of electronic coupling between diabatic states in the work of Yang and coworkers [78]. The possibility to use DFT in combination with a suitable diabaticization scheme that yields diabatic states has been studied by Mao and coworkers [81]. They use absolutely localized molecular orbitals (ALMO) generated from DFT results and evaluate diabatic couplings between these diabatic states. A comprehensive study on the use of a diabatic basis formed using CI-singles wavefunctions and applied to study singlet

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fission was performed by Berkelbach and coworkers [85, 86]. The work extends further to include the dynamics of singlet fission triplet excitons based on Redfield theory [87]. The HOMO/LUMO model from Michl and coworkers has been used to study excitation energy transfer in singlet fission [50, 51, 88]. Here the interaction is described only in terms of the frontier orbitals with all lower orbitals treated as frozen. This has been applied to study many cases, among which is a study on different configurations of an ethylene dimer [89]. Morrison and Herbert used a *Ab-Initio* Frenkel Davydov Exciton Model (AIFDEM) to study singlet fission process [90, 91]. The nonorthogonal electronic states in AIFDEM are described using Hartree-Fock or configuration interaction-single excitations (CIS) wavefunctions. By transforming the orbitals to natural transition orbitals the length of the expansion of CIS wavefunctions can be strongly reduced, which largely speeds up the calculation. Alam and coworkers used AIFDEM to study the role of charge transfer states and charge separation on the rate of singlet fission [92].

1.3. SINGLET FISSION

DISCOVERED half a century ago, singlet fission (SF) is a photo-physical process where one exciton splits into two electron-hole pairs [93]. It has come to prominence in the last two decades due to the promise it holds for the organic photovoltaic industry [94]. Singlet fission is found to be capable of increasing the photo-conversion efficiency of organic solar cells by converting high-energy photons (whose energy is otherwise partly lost due to thermalization) to multiple charge carriers [50, 51, 88]. A spin-allowed radiationless energy transfer process generates two triplet excitons from one singlet exciton. Hence, the organic photovoltaic community found SF as an effective way to go beyond the ‘Shockley-Queisser limit’ [95] of photovoltaic power conversion efficiency of a standard single-junction diode. The Shockley-Queisser limit is at around 31% because of losses due to unabsorbed photons, and thermalization of the excess energy of the absorbed photons. So far, experiments have shown that this can be increased to as far as 43% by using high-energy photons to produce charge carriers through singlet fission.

Figure 1.1 | Schematic representation of the singlet fission process showing the S_0S_0 , S_1S_0 , and 1TT states.

The most widely accepted (and studied) model of SF can be summarized as follows; upon photo-excitation one of the two chromophores is excited directly or indirectly from the ground state S_0S_0 to the lowest excited singlet state S_1S_0 , this process is followed by the formation of two triplet states, one on the excited chromophore and the other on one of its nearest neighbours, coupled to a total spin singlet, so that the transition is spin allowed. This state is commonly denoted as the 1TT state.

The 1TT state is a linear combination of products of triplet spin functions on each molecule coupled to singlet,

$$|^1TT\rangle = \frac{1}{\sqrt{3}}(|T_+T_- \rangle + |T_-T_+ \rangle - |T_0T_0 \rangle) \quad (1.10)$$

where T_+ , T_- , and T_0 are the $m_s = 1, -1$, and 0 spin-triplet states of the two chromophores. The process of energy transfer in singlet fission is shown schematically in Fig. 1.1. Studies have also shown that there is a high probability that the singlet exciton S_1 is delocalized over neighboring chromophores in a crystal-packed structure [96, 97]. Yet, in all cases the coupling matrix element between a local S_1S_0 state and a 1TT state on the same two molecules plays a dominant role in the transition probability. Therefore we pay much attention to the computation of this coupling matrix element. The effect of delocalization on the SF rate and other possible scenarios that thereby arise are discussed in Chapter 5. We also focus on SF occurring from the lowest excited singlet exciton. The justification for this comes from Kasha's rule, which says that excitations to higher excited states would result in the subsequent fast decay to the S_1 state [98]. It is noteworthy that there have also been studies into the possibility of SF occurring from higher vibrational levels and higher excited singlets [99, 100]. Studies on the mechanism of singlet fission also show the existence of different pathways for the fission based on the presence and effect of charge-transfer states. Shown schematically in Fig. 1.2, the direct pathway (green) where the excited singlet forms the triplet states through a direct energy transfer. The two-step mechanism (shown in blue and red) consists in the formation of the triplets after relaxation from an 'intermediate' CT state (either $D_1^+D_1^-$ or $D_1^-D_1^+$). This can happen in cases where the CT states show similar energies to the S_1S_0 state (or equivalently S_0S_1 for symmetrical dimers). The third, charge-transfer mediated pathway can also arise when the CT state is considerably higher in energy compared to the S_1S_0 . The CT-mediated pathway is observed to be the favored channel when a significant increase in electronic coupling between the diabatic S_1S_0 and 1TT is observed due to the mixing in of the CT states.

Figure 1.2 | Direct (green arrow) and two step mechanism (red and blue arrows) of singlet fission. The CT mediated mechanism follows the same route as the direct mechanism but for the fact that the CT states are mixed with the S_0S_1 and 1TT states. We shall see in Chapter 4 that this mixing affects the electronic coupling.

The 1TT state is difficult to observe in experiment as it is spectroscopically dark. However, singlet fission rates have been determined by observing the population of triplets formed. This is usually done with transient absorption, delayed fluorescence, or Raman spectroscopy, and results have been reported on materials like crystalline pentacene, rubrene, diphenylisobenzofuran, and in carotenoids [101–105]. We are still far from commercially implementing singlet fission layers on thin-film organics solar cells even though promising results are available. For example, an SF layer was successfully incorporated into a heterojunction solar cell using phthalocyanine, tetracene, and C_{60} [106]. To exploit the full potential of this process, we need a clear theoretical understanding of the mechanism behind this reaction. We start with a first principles based description of the SF states.

In processes like SF where a significant amount of static electronic correlation needs to be described, Hartree-Fock theory is not the most adequate computational method. The description of multi-excitonic 1TT state is not straightforward with DFT-based approaches. Standard DFT is essentially only capable of describing the ground state and its extension to TDDFT widens the applicability to excited states, but charge transfer states and bi-excitonic states are not trivial to treat. While in the case of SF we need to describe a state with two electron-hole pairs. A broken-symmetry description is not easily obtained as it is in general not the lowest solution and the orbital optimization will typically lead to the lower-lying closed shell solution. A description of the bi-excitonic state based on spin-flip DFT was recently published [107] and could become an alternative for the high-level correlated electronic structure methods for the study of singlet fission.

As an aside, a few lines are dedicated to the classification of methodologies used to

study electron and energy transfer processes. Based on the method we use, the study of electronic states in singlet fission can be approached through an adiabatic or diabatic picture. Both these methodologies are essentially correct, but each comes with advantages and flaws which can be relevant to the quantity studied [108, 109]. Adiabatic states are eigenfunctions of the Hamiltonian under the Born-Oppenheimer approximation. These eigenstates which form a complete basis in the given Hilbert space can also be expressed as a linear combination of chemically interpretable states, giving us the diabatic states. Interpreting the electronic states (for example, a singlet excited, triplet excited, or a charge-transfer state) in this diabatic basis is favorable while evaluating entities like relative energies and electronic couplings between diabatic states involved in singlet fission. This makes the use of diabatic basis states describing the molecules by forming many-electron basis functions (MEBFs) using these states a favorable procedure to study singlet fission.

Many theoretical studies are based on computation of adiabatic electronic states. Zimmerman and coworkers used a spin-flip variant of the restricted active space method called RAS-2SF to study singlet fission [110–112]. The approach makes use of a wavefunction that accounts for static correlation and the spin-flip methodology [113, 114] is employed to reach the different diabatic states. Krylov and coworkers studied the SF procedure using the same methodology [115, 116]. Similar implementations could also be seen in the work of Casanova and coworkers [52]. The HOMO-LUMO model from Michl and coworkers has been routinely used in the studies of SF [89, 101, 117, 118]. Berkelbach and coworkers used a CI-based approach containing single excitations (CIS) to build the diabatic basis [85, 86]. Coto and coworkers studied the effect of relative energies of the low lying excited states and its implication on the mechanism of singlet fission in a system of pentacene molecules [119]. The effect of vibronic coupling on the rate of singlet fission has been studied by Tempelaar and coworkers [120].

The calculation of electronic coupling between the states is dependent on the method used. In the adiabatic picture, the entity evaluated is called the derivative coupling [121, 122]. Derivative couplings show how the wavefunction changes as a function of the nuclear coordinates along the energy landscape. They are traditionally calculated as analytical gradients which are available in most quantum chemistry packages. In the diabatic picture, the coupling between diabatic states A and B is simply the matrix element $\langle A|\hat{H}|B\rangle$ [123].

As discussed before, in the weak-coupling limit between the initial and final states, the rate constant for a singlet fission process can be calculated using the Fermi golden rule shown in Eqn. 1.1. In addition to being effective, SF needs also to fulfil some thermodynamic conditions on the energies of the chromophores,

$$E_{S_1} \geq 2E_{T_1} \quad (1.11)$$

$$E_{T_2} > 2E_{T_1} \quad (1.12)$$

$$E_{Q_1} > 2E_{T_1} \quad (1.13)$$

where the energies with S_n , T_n , and Q_n correspond to the n th singlet, triplet, and quintet states, respectively. The first condition turns out to be the most important in the process and ensures that SF is energetically favorable. The other two conditions ensure that the two triplets remain as separate electron-hole pairs and do not fuse into an excited triplet

1

or quintet state on one chromophore. Searching for efficient SF chromophores means that in addition to a large coupling, we also have to satisfy these conditions. Although most molecules that exhibit these properties have been found to show significant singlet fission rates, exceptions do exist [80].

The studies on singlet fission carried out in this thesis is done with the use of nonorthogonal configuration interaction (NOCI). The diabatic electronic states are formed as antisymmetrized products of molecular wavefunctions [49]. These so called many-electron basis functions (MEBFs) are then used as the basis over which the NOCI wavefunction is expanded. This has formed the basis for subsequent work [89, 118, 124, 125].

This approach provides us with the necessary description of the diabatic states involved. The SF process is also turning into a heavily researched topic by the quantum dynamics community. Numerous groups have reported using quantum [126, 127], mixed quantum-classical dynamics [128, 129], or quasi-classical molecular dynamics methods to study singlet fission [130, 131]. We restrict ourselves here to the methods used to describe the diabatic electronic states involved and ways to obtain the electronic coupling between them.

1.4. OUTLINE OF THESIS

THE remainder of the thesis is organized as follows. Chapter 2 describes the fundamentals of nonorthogonal configuration interaction, which we develop further in the rest of the thesis. Chapter 3 describes the formation of a reduced common molecular orbital basis which is used to re-express the one- and two-electron integrals and describe the different mutually nonorthogonal electronic states. It will be shown how it massively reduces computation time without almost no loss in accuracy in the calculation of relevant quantities. A simple but effective mechanism is introduced to reduce the number of determinant pairs needed for the evaluation of NOCI matrix elements. Chapter 4 discusses how to include dynamic correlation through a correction term in our NOCI Hamiltonian matrix. We also investigate the effect of dynamic correlation included directly in the wavefunction through the application of effective Hamiltonian theory. Chapter 5 describes the effect of using an embedding scheme to imitate a realistic distribution of molecules around the central unit(s). The results of a model study on how the electronic coupling is affected by the delocalization of excitations over multiple chromophores is also discussed. Finally the main conclusions and outlook of the chapter are given.

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2

THEORETICAL FRAMEWORK

2

ABSTRACT

This chapter shortly discusses the different theoretical approaches that are used to describe the electronic structure of systems relevant to singlet fission or other electron and exciton transfer processes. Focus is on the Non Orthogonal Configuration Interaction for Fragments (NOCI-Fragments) method. NOCI-Fragments is a nonorthogonal configuration interaction approach especially designed for ensembles of molecules or fragments, and has been found to be a suitable theoretical method to study electron and excitation transfer processes. The other implementations of NOCI are also compared with NOCI-Fragments for their suitability to study singlet fission.

2.1. INTRODUCTION TO ELECTRONIC STRUCTURE THEORY

THE previous chapter outlined the motivation to develop theoretical methods to study electronic processes in charge and energy transfer reactions. This chapter focuses on the methods used in our investigations. The reader is provided with some theoretical background necessary to understand the basics of electronic structure theory with the emphasis on nonorthogonal configuration interaction which is the focus of this thesis. This chapter gives only a concise summary of the concepts and for a complete picture, the books referred to herein provide an in-depth review of this subject [1–3].

The aim of quantum chemical studies is to obtain an accurate description of particles (nuclei and electrons) and to explain observable physical phenomena through a first-principles (based) approach. The quantum mechanical solution to the many-body problem is provided by the Schrödinger equation and the form taken depends on the situation. The time-dependent equation describes the state of a system evolving with time and the time-independent equation describes stationary states of an isolated system. For the electronic structure problem in the non-relativistic domain, we restrict ourselves to solving the time-independent Schrödinger equation,

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (2.1)$$

where the operator $\hat{H}$ is the electronic Hamiltonian and E is the eigenvalue and the wavefunction Ψ is the corresponding eigenfunction. The $\hat{H}$ operator consists of a set of operations that when carried out over a Hilbert space spanned over which the wavefunction is defined, gives us a description of all the interactions in the system. In molecular quantum mechanics, $\hat{H}$ contains all interactions involving nuclei and electrons in a system. According to the Born-Oppenheimer (BO) approximation [4], owing to a large difference in the timescales between the motion of nuclei and the motion of electrons, the two can be decoupled. This suggests that the nuclear and electronic wavefunctions are separable. Using the BO approximation, we can then write the electronic Hamiltonian (in atomic units) of a system of N electrons moving in the field of M nuclei with fixed coordinates as,

$$\hat{H} = -\sum_i^N \frac{1}{2} \nabla_i^2 - \sum_i^N \sum_A^M \frac{Z_A}{R_{iA}} + \sum_{i<j}^N \frac{1}{r_{ij}} + V \quad (2.2)$$

where V is the nuclear repulsion energy, R_{iA} the distance between nucleus A and electron i , r_{ij} the distance between electrons i and j . The electronic wavefunction Ψ contains information on the spatial coordinates and the spin of electrons in the system. Analytical solutions to the Schrödinger equation exist only for single-electron systems like the hydrogen atom. In the case of many-electron systems, we must account for the correlation due to instantaneous electronic movements. To exactly account for this effect is not possible with the computational power available today. Hence, over the years ingenious ways have been devised to find suitable approximations to exact theories. The type of physical phenomena that needs to be described plays a major role in our selection of an appropriate method to use for its description. The variational principle is a central tenet in quantum chemistry for the evaluation of approximate energies and wavefunctions of a physical system. The variational principle states that the energy of a trial wavefunction is

always an upper bound to the exact ground state energy. A good ‘trial’ wavefunction is one that gives us the lowest energy from the variationally optimized parameters.

The simplest approximation to the exact many-electron wave function consists of a single antisymmetrized product of one-electron functions, the so-called Slater determinant. The one-electron functions, better known as orbitals are optimized to minimize the total energy through the variational principle. The resulting wave function gives an optimal description of the electronic structure within the mean-field approximation, that is, each electron interacts with the average field generated by all the other electrons. The wavefunction so obtained is the Hartree-Fock wavefunction.

2

2.2. CORRELATED ELECTRONIC STRUCTURE METHODS

THE difference between the true energy and the Hartree-Fock energy of a system is known as the correlation energy. Over the years, multiple approaches have been used to recover the correlation energy by going beyond the Hartree-Fock single determinantal description. We discuss a few of the methods most relevant to this thesis below.

Configuration Interaction The inclusion of more than a single Slater determinant in the wavefunction is one way to recover electron correlation. Configuration Interaction (CI) based methods do just this. In CI, we treat electron correlation by building wavefunctions comprised of linear combinations of Slater determinants. These are excited from a Hartree-Fock reference and the occupations of orbitals are varied to include all molecular orbitals (MOs). The CI wavefunction can be written as,

$$|\Psi_{CI}\rangle = C_0|\Psi_{HF}\rangle + \sum_{ia} C_i^a |\Psi_i^a\rangle + \sum_{\substack{i<j \\ a<b}} C_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \sum_{\substack{i<j<k \\ a<b<c}} C_{ijk}^{abc} |\Psi_{ijk}^{abc}\rangle + \dots \quad (2.3)$$

where $|\Psi_{HF}\rangle$ is the HF reference wavefunction, $|\Psi_i^a\rangle, |\Psi_{ij}^{ab}\rangle, |\Psi_{ijk}^{abc}\rangle$ are the singly, doubly, triply excited Slater determinants, and C s the corresponding variationally optimized coefficients. In CI-based methods we solve the Schrödinger equation for the electronic Hamiltonian in a chosen CI-space, which is essentially a matrix eigenvalue problem from which we can (variationally) obtain the energy eigenvalues and CI coefficients.

In the limit of the chosen spatial parts of the orbital basis set, the CI expansion can be chosen to include all possible occupations. This is called full-CI and is formally exact in the chosen basis set expansion, meaning that we can obtain the true energy of the system using this method when a complete basis set is used. The computational effort required is determined by the number of determinants present in a full-CI calculation. This increases combinatorially with the number of basis functions and electrons in the system hence a full-CI calculation (using a finite basis set) can be performed only for small molecules. Based on the number of excitations from the reference determinant, CI methods can be classified into CI-singles (CIS), CI-singles doubles (CISD) etc. The CIS

and CISD wavefunctions are written as,

$$|\Psi_{CIS}\rangle = C_0|\Psi_{HF}\rangle + \sum_{ia} C_i^a |\Psi_i^a\rangle \quad (2.4)$$

$$|\Psi_{CISD}\rangle = C_0|\Psi_{HF}\rangle + \sum_{ia} C_i^a |\Psi_i^a\rangle + \sum_{\substack{i < j \\ a < b}} C_{ij}^{ab} |\Psi_{ij}^{ab}\rangle \quad (2.5)$$

Based on an ‘active space’ of molecular orbitals, the CI can also be expanded using only a few selected determinants, giving rise to the complete active space-CI (CASCI) method. Another method belonging to the CI family that is worth mentioning is the selected-CI (sCI) method [5–7]. Instead of truncation by excitation level, one can also intend to select only those determinants which would make the largest contribution to the full CI wave functions. Selection can either be done by estimating the importance of a determinant with perturbation theory or through a stochastic procedure.

Although truncated-CI offers a possibility to describe larger systems, the method fails to be size extensive, meaning that the calculated energy does not scale with the system size. This is an important property to determine the quality and usability of a computational method [8].

Multiconfigurational self-consistent field In cases where there are multiple dominant (that is, having large expansion coefficients) configurations in the wavefunction we resort to a multi-configurational self-consistent field (MCSCF) based approach. An MCSCF wavefunction is a variationally optimized linear combination of configurations with variationally optimized orbitals. The MCSCF wavefunction can be written as,

$$|\Psi_{MCSCF}\rangle = \sum_K C_K |\Psi_K\rangle \quad (2.6)$$

where the $|\Psi_K\rangle$ represents a (linear combination of) Slater determinant(s). In the MCSCF process, the orbital optimization and the variational evaluation of the expansion coefficients are performed simultaneously. This results in a set of determinants that optimally describe that molecular system. Due to this, MCSCF is ideal for recovering static electron correlation.

Two famous types of MCSCF wavefunctions are complete active space self consistent field (CASSCF) [9, 10] and restricted active space self consistent field (RASSCF) [11]. CASSCF divides the space spanned by the MOs into three orbital subspaces. These are the inactive, active, and virtual orbitals. The inactive space contains MOs that have an unaltered occupation number of two in all determinants, the active space contains orbitals with variable occupation and the virtuals have occupation zero in all of the wavefunction expansion. In CASSCF, a FCI is performed in the active space. The RASSCF method is similar, but the active space is further divided into three viz., the RAS1, RAS2, and RAS3 spaces. Configurations are generated with constraints on the number of allowed holes and electrons in the RAS1 and RAS3 spaces, respectively, and no restrictions on the RAS2 space.

Figure 2.1 | Division of MO space in the CASSCF method into the inactive, active and virtual orbitals. In the RASSCF formulation the active space is divided into three subspaces; RAS1, RAS2, and RAS3.

The choice of the active space, represented as: (number of electrons, number of orbitals), plays a crucial role in the CASSCF procedure and is molecule and problem dependent. The selection of active space is hence not a black-box procedure and requires careful scrutiny to obtain a satisfactory description of the electronic structure. In our NOCI calculations, details of which are discussed in the upcoming sections, we use CASSCF wavefunctions to describe each molecular electronic state, thereby capturing the necessary static correlation in a molecular fragment. For the inclusion of dynamic correlation in the wavefunction, methods like perturbation theory are necessary.

While studying excited states using CASSCF, we can use either the ‘state-averaged’ or ‘state-specific’ implementations. In a state-averaged CASSCF calculation, we obtain a solution in which the orbitals are optimized to describe a chosen set of states in an averaged way, hence, none of the particular states is described with an optimal set of orbitals. This may become a problem in cases where neutral and charge-transfer states are described using the same canonical reference orbitals. In a state-specific CASSCF, we can converge to a higher energy solution that may belong to an excited state, expressed in its ‘own’ set of orbitals. We are however risking the possibility to run into technical problems like variational collapse to the ground state, and root flipping.

The wallclock time needed for CASSCF has exponential scaling with respect to the size of the active space. The most effective solution to the exponential scaling problem to date has been the use of density matrix renormalization group (DMRG) [12, 13]. Density matrix renormalisation group theory was introduced by White and Noack [14, 15] in the early 1990s as an extension of the standard renormalisation group theory of Wilson [16]. The method was first illustrated for the $S = 1/2$ and $S = 1$ Heisenberg chains, but soon extended to electronic structure calculations for molecular systems as alternative for full CI or CASSCF calculations [17]. Over the last decade the method has been further developed and can now easily treat systems with 30 or more active orbitals [18].

Perturbation theory The Rayleigh-Schrödinger perturbation theory (RSPT) tells us how the many-body energy can be written as a perturbative expansion of corrections to the reference Hamiltonian. The Hamiltonian is split as,

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{V} \quad (2.7)$$

where $\hat{H}^{(0)}$ is the zeroth-order Hamiltonian, $\hat{V}$ the perturbation, and λ is a parameter that can take any value between zero and one. The respective energy and the wavefunction are expanded in a series in powers of the parameter λ as,

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \dots \quad (2.8)$$

$$\Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \lambda^3 \Psi^{(3)} + \dots \quad (2.9)$$

where $E^{(0)}$ is an eigenvalue of zeroth-order Hamiltonian $\hat{H}^{(0)}$. Møller-Plesset perturbation theory (MPPT) is a formulation of RSPT wherein the Fock operator functions as the unperturbed Hamiltonian and the HF-wavefunction as the zeroth-order wavefunction. Usually expanded to the second-order (MP2), this formulation is frequently used in quantum chemistry as a way to go beyond HF theory to evaluate the correlation energy. Higher orders increase steeply in computational effort and do not always perform better than MP2. A drawback of MPPT is that the method is not variational and a systematic improvement to the wavefunction cannot be made due to the divergent nature of the perturbation expansion in certain cases like when the zero-order energies of excited determinants are close to the ground state energy. The effectiveness of the perturbative treatment is also highly dependent on the quality of the reference wavefunction. In cases where a strong multireference character is seen, an MCSCF wavefunction can also be used as the reference. For example, a multireference formulation like CASPT2 uses the CASSCF wavefunction as the zeroth-order wavefunction [19–22]. CASPT2 is an adequate way to account for the dynamic correlation in systems where static correlation is already accounted for and is therefore frequently used in electronic structure calculations. An improvement of CASPT2 is the *n*-electron valence state perturbation theory (NEVPT2) method [23–25]. Instead of using a Fock-like effective one-electron operator as in CASPT2, NEVPT2 applies the Dyall Hamiltonian as zeroth-order Hamiltonian which contains explicit two-electron terms and is therefore much less prone to the appearance of near-degenerate zeroth-order energies. We use CASPT2 and NEVPT2 in this thesis in an upcoming chapter as a possible way to include dynamic correlation in NOCI.

Density functional theory A revolutionary way to the study electronic structure of molecules came about in the 1960s with the development of density functional theory (DFT) through the works of Walter Kohn and coworkers [26–28]. The central idea of DFT is based on the two Hohenberg-Kohn theorems which tell us about the existence of a true ground state energy for a system. The first Hohenberg-Kohn theorem says that the ground state properties of an *N*-electron system are only dependent on the ‘electronic density’ which is a quantity that can be represented using three spatial coordinates (instead of the customary 3*N* coordinates required by wavefunction based methods). The second theorem tells that the correct ground state electron density for a system is one that minimizes the total energy functional of the electron density. Limited to

ground state energies, DFT allows for a correlated treatment of the electrons. Though formally exact, the expression for the DFT energy potential is dependent on an ‘exchange-correlation energy functional (xc)’. This has to be estimated and is done through an ab-initio approximation of the system or semi-empirically. Research on the development of functionals tailored to study the physical problem at hand has been an active area of research for decades [29–31]. The local density approximation (LDA) is the simplest approximation of the xc and is based on the homogeneous electron gas model. An improvement to LDA is the generalized gradient approximation (GGA), which includes local densities and the first derivative of those densities in the approximation. Today, some of the most used functionals belong to the category called hybrid functionals. Few of the most used functionals go by names like B3LYP, PBE0, HSE, etc., and are based on the extent of a Hartree-Fock exchange that is included to improve the performance.

The dependence of the accuracy of a calculation on the functional makes DFT a black-box method where a systematic improvement of the quality of answers is no longer feasible, unlike the wavefunction based methods. Of late, there have been innumerable improvements in DFT that have been able to treat few problems like dispersive interactions, self-interaction error among others [32–34]. The work of Gross and coworkers resulted in the development of time-dependent density functional theory (TDDFT) which contrary to conventional DFT allows us to also describe excited states using DFT [35–38]. Linear response TDDFT is one of the most popular methods used to study excited states and has been routinely used in the studies of energy and excitation transfer.

Coupled-cluster theory Developed initially to solve problems in nuclear physics [39], the coupled-cluster (CC) method was also adopted by the quantum chemistry community as an alternative to calculate the correlation energy [40–43]. The coupled-cluster wavefunction is written using an exponential ansatz,

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Psi_0\rangle \quad (2.10)$$

where $|\Psi_0\rangle$ is the reference wavefunction (usually a Hartree-Fock wavefunction), and $\hat{T}$ is the cluster-operator which is written using the N-particle excitation operators as,

$$\hat{T} = \hat{T}^1 + \hat{T}^2 + \dots + \hat{T}^N \quad (2.11)$$

where each of the $\hat{T}^k$ can be expanded using second quantization to functions of the creation and annihilation operators. The T operator is normally truncated after the second term to cater to limited computational resources, but a perturbative correction for the triples is usually included, known as CCSD(T). Coupled cluster theory performs very well for most systems and additionally, the exponential ansatz ensures that the method is size consistent and size extensive. One drawback of CC however is that the method is not variational.

Spin-flip methods Relatively different approaches to recover electron correlation are the spin-flip (SF) based methods. The spin-flip strategy has been extensively used in conjunction with DFT, coupled cluster (CC), and CI giving rise to variants like SF-DFT (and SF-TDDFT), SF-CC, SF-CI [44–47]. The idea behind the spin-flip method is to start

with a high-spin reference and apply spin-flipping excitations to obtain a wavefunction with the desired spin-eigenvalue. The wavefunction is then a linear combination of determinants obtained from the initial high-spin reference. The technique has been shown to work for studying excited states, explaining bond breaking, the description of diradicals and triradicals, [48, 49]. The quality of the wavefunction obtained through the spin-flip method is highly dependent on the choice of high-spin reference. The method also scales unfavorably (exponential) with the size of the active space and does not directly account for dynamic correlation. A frequently used variant is the restricted active space spin-flip (RAS-SF) variant and it has been used for studying avoided crossings, conical intersections, and charge and energy transfer properties [50, 51]. Another interesting variant is the spin-flip NOCI (SF-NOCI) by Mayhall and coworkers [52]. This is discussed separately later on in the chapter.

Valence bond theory The use of one set of orthogonal orbitals to construct all Slater determinants in which the many-electron wave functions are expanded simplifies tremendously the computational procedure and is nowadays the dominant choice for wavefunction-based calculations. Alternatively, electronic structure calculations can also be performed within the valence bond (VB) approach [53, 54], a computationally more complex, but chemically more intuitive method that is based on nonorthogonal orbitals. The VB description of chemical bonding remains very close to the concepts derived from the Lewis structures of molecules and is therefore very attractive to translate computational results into simple, chemically relevant concepts.

The orbitals in VB theory are designed to be localized on the constituent atoms or bonding regions, which is in contrast to the delocalized orbitals of MO theory that span the space of the whole molecule. In the VB ansatz, atom centered, overlapping orbitals are used to describe bonding. This was later extended to also include description of ionic configurations and radicals. In the earliest instance of its validity, VB theory could correctly describe the dissociation of H_2 through the localization of the electrons to their parent hydrogens [55]. Through the years many variations of the VB method have been developed such as the VBSCF [56, 57], breathing orbital VB (BOVB) [58], spin-coupled VB [59–61], among others [62–66].

Nonorthogonal configuration interaction An approach to treat excited states that has gained a lot of attention in recent days is nonorthogonal configuration interaction (NOCI). In a standard CI-based approach, we generate the excited determinants through excitations from a ground state reference wavefunction using one common set of orthogonal orbitals. The resulting determinants or configuration state functions (CSFs) are thus orthogonal as well. To avoid lengthy CI expansions, we can describe each electronic state in its own set of optimized orbitals and account therewith for orbital relaxation effects. The resulting orbitals and hence the configurations (or determinants) describing each state may be nonorthogonal to one other. A CI calculation with this nonorthogonal basis is a nonorthogonal CI (NOCI). The NOCI wavefunction can be written as,

$$\Psi_{NOCI} = \sum_k C_k \Phi_k \quad (2.12)$$

where the wavefunctions Φ_k s are of any type, like a Hartree-Fock or a multiconfigurational wavefunction like CASSCF. These wavefunctions form the basis for the NOCI. The energies and expansion coefficients C_k are obtained by solving the generalized eigenvalue problem,

$$\mathbf{H}\mathbf{C} = \epsilon\mathbf{S}\mathbf{C} \quad (2.13)$$

where $\mathbf{S}$ is the overlap matrix of the many-electron basis functions Φ_k . In addition to describing orbital relaxation, NOCI possesses distinct advantages over other approaches for handling excited states. The NOCI wavefunction is considerably more compact than a CI wavefunction used to describe an excited state. Similar to valence bond theory, the NOCI wavefunction can also be expanded in terms of a limited number of Lewis structures or configurations thereby making it possible to relate the electronic structure to chemically intuitive concepts. Advancements in computer hardware coupled with the possibility to use highly parallelized algorithms have resulted in the resurgence of methods like NOCI, where the evaluation of matrix elements can be conveniently parallelized. Our implementation of NOCI is called NOCI-Fragments [67, 68] and is the focus of this thesis, we also cite here a few recent works on NOCI [52, 69–87].

2.3. NOCI-FRAGMENTS

CONSIDER the case of electronic processes that may take place in a molecular ensemble, for example charge and energy transfer processes (like singlet fission) we discussed in the previous chapter. To obtain an unbiased description, we need electronic wavefunctions that are capable of describing the molecular ensemble. NOCI-Fragments is a method which allows us to do this. NOCI-Fragments is based around the GNOME code [88, 89] written in Groningen in the 1980s to evaluate matrix elements between nonorthogonal pairs of determinants. The NOCI-Fragments code is designed to get as input the integrals and wavefunctions generated from quantum chemistry softwares. The molecular wavefunctions used are usually multiconfigurational (CASSCF) wavefunctions expanded as linear combinations of determinants. The wavefunction of a molecular cluster is formed by taking antisymmetrized products of the individual molecular wavefunctions [90]. These cluster wavefunctions are called the many electron basis functions (MEBFs). The NOCI wavefunction for the cluster is expanded in these MEBFs. For example, consider molecular (CASSCF) wavefunctions describing the different electronic states in a singlet fission process, on two molecular fragments A and B . These wavefunctions are written as: $\Psi_{S_0}^A, \Psi_{S_1}^A, \Psi_{T_1}^A, \Psi_{D_1^+}^A, \Psi_{D_1^-}^A$ on fragment A , and $\Psi_{S_0}^B, \Psi_{S_1}^B, \Psi_{T_1}^B, \Psi_{D_1^+}^B, \Psi_{D_1^-}^B$ on fragment B . A few examples of the MEBFs that can be formed are,

$$\Psi_{S_0S_0}^{AB} = \hat{A}(\Psi_{S_0}^A \times \Psi_{S_0}^B) \quad (2.14)$$

$$\Psi_{S_0S_1}^{AB} = \hat{A}(\Psi_{S_0}^A \times \Psi_{S_1}^B) \quad (2.15)$$

$$\Psi_{T_1T_1}^{AB} = \hat{A}(\Psi_{T_1}^A \times \Psi_{T_1}^B) \quad (2.16)$$

$$\Psi_{D_1^+D_1^-}^{AB} = \hat{A}(\Psi_{D_1^+}^A \times \Psi_{D_1^-}^B) \quad (2.17)$$

where $\hat{A}$ is the antisymmetrization operator. In NOCI-Fragments, the MEBFs that make the NOCI wavefunction can comprise any number of molecular wavefunctions in the

cluster, giving the likeness to a ‘cluster approximation’ for evaluation of properties of solids. NOCI based methods have an advantage over others because we can express the wavefunction in terms of chemically interpretable configurations. In NOCI-Fragments, each cluster electronic state is expressed in terms of the component diabatic MEBFs.

Once the integrals are obtained, the next task in the NOCI-Fragments process is the evaluation of the Hamiltonian and overlap matrix elements; $\langle \Phi_k | \hat{H} | \Phi_l \rangle$ and $\langle \Phi_k | \Phi_l \rangle$ between the nonorthogonal MEBFs. The evaluation of matrix elements between different determinant pairs can be done independent of each other, making this a trivially parallelizable procedure. NOCI-Fragments has been implemented in GronOR [67, 68], an open-source software package started as a collaboration between the University of Groningen and Oak Ridge National Laboratory, USA. The following subsections are devoted to explaining the evaluation of matrix elements in NOCI-Fragments and the implementation of the code in GronOR.

2.3.1. EVALUATION OF MATRIX ELEMENTS

An efficient computational scheme for the evaluation of Hamiltonian matrix elements between Slater determinants, that are built from different and mutually nonorthogonal orbital sets was introduced by Van Montfort, Broer, and Nieuwpoort [88, 89, 91]. Here we follow closely the derivation given by Broer [88]. Consider two determinantal wavefunctions Φ_a and Φ_b

$$\Phi_a = \mathcal{A} \begin{vmatrix} \chi_1(1) & \chi_1(2) & \dots & \chi_1(N) \\ \chi_2(1) & \chi_2(2) & \dots & \chi_2(N) \\ \vdots & & \ddots & \vdots \\ \chi_N(1) & \chi_N(2) & \dots & \chi_N(N) \end{vmatrix}, \Phi_b = \mathcal{B} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \dots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \dots & \phi_2(N) \\ \vdots & & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \dots & \phi_N(N) \end{vmatrix} \quad (2.18)$$

where $\mathcal{A}$ and $\mathcal{B}$ are normalization constants. The spin-orbital sets $\{\chi_i\}$ and $\{\phi_i\}$ are not constrained to be orthogonal. We may have non-zero values for all the overlap integrals, $\langle \chi_i | \chi_j \rangle$, $\langle \phi_i | \phi_j \rangle$, $\langle \chi_i | \phi_j \rangle$. The electronic Hamiltonian $\hat{H}$ of a N electron system can be written in terms of sums over one and two-electron operators. The operators written explicitly are,

$$\hat{o}_1(i) = -\frac{1}{2} \nabla_i^2 - \sum_A^M \frac{Z_A}{R_{iA}} \quad (2.19)$$

$$\hat{o}_2(i, j) = \frac{1}{r_{ij}} \quad (2.20)$$

where ∇ is the differential operator with regard to the position. The matrix elements of one and two-electron operators between two determinantal wavefunctions are,

$$I_1 = \langle \Phi_a | O_1 | \Phi_b \rangle, \quad (2.21)$$

$$I_2 = \langle \Phi_a | O_2 | \Phi_b \rangle \quad (2.22)$$

where $\hat{O}_1 = \sum_i^N \hat{o}_1(i)$ and $\hat{O}_2 = \sum_{i < j}^N \hat{o}_2(i, j)$. Using the formalism of Löwdin [92, 93], this can be written in terms of integrals over the molecular orbitals as,

$$I_1 = \sum_i^N \sum_j^N \langle \chi_i | o_1 | \phi_j \rangle \cdot S(i, j) \quad (2.23)$$

$$I_2 = \sum_{k > i}^N \sum_{l > j}^N \langle \chi_i \chi_k | (1 - p_{12}) o_2 | \phi_j \phi_l \rangle \cdot S(ik, jl) \quad (2.24)$$

where $\hat{p}_{12}$ is the permutation operator. In general $\hat{p}_{ij}$ interchanges electron labels i and j . $S(i, j)$ is the (i, j) th first order cofactor of the matrix of overlap integrals. A cofactor of a matrix is defined as the determinant of the matrix $\mathbf{S}$ with the i^{th} row and j^{th} column removed (this entity is called a minor), multiplied by the factor $(-1)^{i+j}$. Correspondingly the second order cofactor $S(ik, jl)$ is the determinant of matrix $\mathbf{S}$ with rows i, k and columns j, l removed and multiplied by the factor $(-1)^{i+j+k+l}$. The second order cofactor $S(pr, qs)$ of a square matrix can be written in a factorized form [91],

$$S(pq, rs) = (1 - \hat{p}_{pq})(1 - \hat{p}_{rs})X_{pq}Y_{rs} \quad (2.25)$$

where the matrices X, Y are of dimension N^2 , and whereas the supermatrix of second order cofactors contains $\approx (1/8)N^4$ elements. We can apply a corresponding orbital transformation [94–97] to the set of spin-orbitals χ and ϕ ,

$$\chi'_i = \sum_j^N \chi_j T_{ji}^a \quad (2.26)$$

$$\phi'_i = \sum_j^N \phi_j T_{ji}^b \quad (2.27)$$

where $\mathbf{T}^a, \mathbf{T}^b$ are transformation matrices which fulfil the following conditions: The determinantal wavefunction is unchanged by this transformation,

$$\Phi_a = |\chi'_1 \chi'_2 \dots \chi'_N| \quad (2.28)$$

$$\Phi_b = |\phi'_1 \phi'_2 \dots \phi'_N| \quad (2.29)$$

and the overlap matrix S' between the new sets is constrained to be diagonal,

$$S'_{ij} = \langle \chi'_i | \phi'_j \rangle = \lambda_i \delta_{ij} \quad (2.30)$$

The matrix elements of the one and two electron operators now become,

$$I_1 = \sum_i^N \langle \chi'_i | o_1 | \phi'_i \rangle \cdot \prod_{\alpha \neq i}^N \lambda_\alpha \quad (2.31)$$

$$I_2 = \sum_{k > i}^N \langle \chi'_i \chi'_k | (1 - p_{12}) o_2 | \phi'_i \phi'_k \rangle \cdot \prod_{\alpha \neq i, k}^N \lambda_\alpha \quad (2.32)$$

This already simplifies the calculation of I_2 considerably but we still need a set of two-electron integrals expressed in terms of two different sets of molecular orbitals. In the

original GNOME implementation, the corresponding molecular orbitals $\{\chi'\}$ and $\{\phi'\}$ are expressed in the atomic basis functions $\{z\}$ and $\{z'\}$ of dimension m and n ($m, n \geq N$),

$$\chi'_i = \sum_p^m z_p C_{pi} \quad (2.33)$$

$$\phi'_i = \sum_p^n z'_p D_{pi} \quad (2.34)$$

We substitute this in the formulae for matrix elements giving,

$$I_1 = \sum_p^m \sum_q^n \langle z_p | o_1 | z'_q \rangle \cdot \sum_i C_{ip}^\dagger D_{qi} \cdot \prod_{\alpha \neq i}^N \lambda_\alpha \quad (2.35)$$

$$I_2 = \sum_{r>p}^m \sum_{s>q}^n \langle z_p z_r | (1 - p_{12}) o_2 | z'_q z'_s \rangle \cdot \sum_{k>i} C_{ip}^\dagger C_{kr}^\dagger D_{qi} D_{sk} \cdot \prod_{\alpha \neq i, k}^N \lambda_\alpha \quad (2.36)$$

rearranging the terms of I_2 we get,

$$I_2 = \sum_{r>p}^m \sum_{s>q}^n \langle z_p z_r | (1 - p_{12}) o_2 | z'_q z'_s \rangle \cdot B(pq, rs) \quad (2.37)$$

with

$$B(pr, qs) = \frac{1}{2} (1 - \hat{p}_{pr}) (1 - \hat{p}_{qs}) \cdot \sum_{k, i} C_{ip}^\dagger C_{kr}^\dagger D_{qi} D_{sk} \cdot \prod_{\alpha \neq i, k}^N \lambda_\alpha \quad (2.38)$$

Factorization of the ‘transformed second-order co-factor’ B is also possible and leads to the final expression of I_2 as

$$I_2 = \sum_{r>p}^m \sum_{s>q}^n \langle z_p z_r | (1 - p_{12}) o_2 | z'_q z'_s \rangle \cdot (1 - p_{pr}) (1 - p_{qs}) \cdot F(\omega)_{pq} G(\omega)_{rs} \quad (2.39)$$

where ω is the number of singularities in the overlap matrix S i.e., the number of zero diagonal elements in S' . There are three cases giving a non-zero matrix element I_2 ,

a) $\omega = 0$ (No singularities in S). In this case $\lambda_\alpha \neq 0; \alpha = 1, \dots, N$ so,

$$F(0)_{pq} = \frac{1}{2} \sum_i C_{ip}^\dagger D_{qi} \lambda_i^{-1} \quad (2.40)$$

$$G(0)_{pq} = 2F(0)_{pq} \prod_{\alpha}^N \lambda_\alpha = 2|S|F(0)_{pq} \quad (2.41)$$

yields the expression for I_2 . $|S|$ is the determinant of S .

b) $\omega = 1$ (One singularity in S). $\lambda_\mu = 0; \lambda_\alpha \neq 0 (\alpha \neq \mu)$ which reduces the expression of B to

$$B(pr, qs) = (1 - \hat{p}_{pr}) (1 - \hat{p}_{qs}) C_{p\mu}^\dagger D_{\mu q} \sum_{i \neq \mu}^N C_{ir}^\dagger D_{si} \sum_{\alpha \neq \mu, i}^N \lambda_\alpha \quad (2.42)$$

where,

$$F(1)_{pq} = \sum_{i \neq \mu}^N C_{ip}^\dagger D_{qi} \lambda_i^{-1} \quad (2.43)$$

$$G(1)_{pq} = C_{\mu p}^\dagger D_{q\mu} \prod_{\alpha \neq \mu}^N \lambda_\alpha \quad (2.44)$$

I_2 can be written in the form of equation 2.39.

c) Two singularities in S ,

$$\lambda_\mu = \lambda_\nu = 0 (\alpha \neq \mu, \nu)$$

$$B(pr, qs) = (1 - \hat{p}_{pr})(1 - \hat{p}_{qs})F_{pq}G_{rs} \quad (2.45)$$

with,

$$F(2)_{pq} = C_{vp}^\dagger D_{qv} \quad (2.46)$$

$$G(2)_{pq} = C_{\mu p}^\dagger D_{q\mu} \prod_{\alpha \neq \mu \neq \nu} \lambda_\alpha \quad (2.47)$$

and I_2 can be written as equation 2.39. More singularities make $I_2 = 0$. We can therefore evaluate I_2 from equations 2.39 to 2.47. The one-electron matrix element I_1 is only non-zero if there is at most one singularity in S .

$$I_1 = \sum_p^m \sum_q^n \langle z_q | O_1 | z'_q \rangle G(\omega), \omega = 0, 1 \quad (2.48)$$

Note that $\{z\}$ and $\{z'\}$ can be chosen to be identical to the original sets $\{\chi\}$ and $\{\phi\}$ by setting, $\mathbf{C} = \mathbf{T}^{\mathbf{a}}$ and $\mathbf{D} = \mathbf{T}^{\mathbf{b}}$. The resulting expressions for non-zero matrix elements are then in terms of original spin-orbitals, with factorized cofactors. If unitary matrices are chosen for $\mathbf{T}^{\mathbf{a}}$ and $\mathbf{T}^{\mathbf{b}}$, van Montfort's [91] expressions for I_1 and I_2 are obtained. A generalization to the case where different orbitals are used for different spins can be found in the work of Broer and Nieuwpoort [89].

2.3.2. IMPLEMENTATION IN GRONOR

The implementation of NOCI-Fragments begins with the generation of molecular wavefunctions for the fragments and integrals for the cluster from standard quantum chemistry packages. Presently, we obtain multiconfigurational wavefunctions (CASSCF type) and the one-, and two-electron integrals from GAMESS-UK [98] and OpenMolcas [99] through interfaces written to these two programs. Note that the wavefunctions are expanded in terms of determinants, which is currently a requirement for the evaluation of the matrix elements. The CASSCF molecular wavefunctions are used in forming spin-adapted antisymmetrized product wavefunctions which we call many-electron basis functions (MEBFs) in which the NOCI wavefunction is expanded. The electronic couplings that we wish to obtain between different diabatic states in electron, energy transfer processes are evaluated using the interaction matrix elements between the MEBFs. The GNOME code (discussed in the previous section) utilizes these wavefunctions and integrals in the

evaluation of the Hamiltonian and overlap matrix elements between these nonorthogonal determinant pairs which make up the MEBFs. The generation of the MEBFs and evaluation of matrix elements using the GNOME code is carried out by the GronOR software [67, 68]. The complete details on the procedure can be obtained from the work of Straatsma and coworkers [68], here we give a simplified view of the execution of GronOR and the parallelization strategy that is followed.

The number of determinant pairs between the MEBFs is in many cases enormous but the evaluation of matrix elements containing these determinant pairs turns out to be independent of each other. This makes the calculation trivially parallelizable. In GronOR, a hybrid OpenMP/MPI based parallelization strategy is used. Communication between OpenMP threads in a node is done using OpenMP and inter-node communication is performed using MPI. The code is also GPU-accelerated using OpenACC directives for hybrid GPU/CPU architectures. The evaluation of matrix elements require the two-electron integrals to be stored in memory. Each rank utilizes a set of integrals that are stored in memory. This means that ideally, we would want the size of the two-electron integral file to be as small as possible. Unfortunately, the integral file size scales steeply with the system size and chosen AO basis, and thus for chemically relevant systems with decent basis sets, it easily exceeds normally available amount of GPU memory on even the largest supercomputers. We solved this bottleneck with the construction of a reduced common molecular orbital basis [100] that made it possible to store many more copies of the integrals in memory and hence more ranks could be fit in the GPU memory which is usually much smaller than the CPU memory. We discuss in detail the reduced common basis in Chapter 3.

GronOR is based on a task-based master-worker model where the contribution from each determinant pair is processed in batches by groups of worker processes. One master process is responsible for communicating the tasks to be performed and collecting the results from worker groups. In turn, each group of worker processes is controlled by a head process that is responsible for the communication with the master. The number of processes within a group is determined by the amount of available memory per process to hold the two-electron integrals, and if the two-electron integrals are larger than the memory of one processing unit then they are spread over multiple units. GronOR has an efficient load balancing scheme and is also fault resilient software execution with respect to choice of hardware due to an ‘asynchronous’ task assignment to the worker groups by the master. This implies that a hardware failure in one of the nodes (or worker groups) does not result in a job failure. Recently a checkpoint restart to start jobs from the last successful point has been implemented by Straatsma and coworkers that ensures that walltime spent on large calculations is not wasted. These and further developments and updates on the ongoing work on the code can be found in <http://www.gitlab.com/gronor>.

2.4. OTHER IMPLEMENTATIONS OF NOCI

To complete the overview of the state of the art in NOCI, we include some lines on the other alternative implementations of the NOCI procedure. Though these methods may differ in flavor, implementation, or chemical application, a common aspect is that

the Hamiltonian matrix elements are evaluated between Slater-determinants expressed in terms of nonorthogonal sets of orbitals.

Olsen and coworkers developed an approach for performing CI and orbital optimizations for wavefunctions with mutually nonorthogonal orbitals [69]. The method was developed to be in line with the spin-coupled valence bond method [59, 60] which allows for the use of a compact hierarchy of the wavefunction expansions. Høyvik and co-workers extended this method to include a generalized localization scheme for orbital optimizations when nonorthogonal orbitals are employed [72]. Kähler and Olsen developed a method to include dynamic correlation as a perturbative correction in their NOCI implementation, which was intended to be used for systems where a large number of active electrons (more than what is generally treated using CASSCF) need to be described by the multiconfigurational wavefunction [70]. An internally contracted scheme was used to reduce the unfavorable scaling that arises, hence the name nonorthogonal internally contracted with second-order perturbative corrections (NICPT2). They further developed this formalism to include Dyllal's Hamiltonian to account for two-electron interactions within the active space and third-order corrections in the perturbative expansion [71]. This method has been shown to give an adequate description of some strongly correlated systems like the Chromium dimer. Yet, no studies have been reported in the direction of molecular clusters, which is the focus of NOCI-Fragments.

Chen and coworkers used a reduced density matrix approach for the description of nonorthogonal orbitals and applied the same for their studies on VB theory [79–82]. They worked on deriving a more generalized Wick's theorem, which gives a many-body wavefunction expansion using second-quantization. Intending to use this with the VB-SCF method [56], they also developed algorithms for analytical gradients and Hessians, included dynamic correlation using second-order perturbation theory, among other significant developments.

Head-Gordon and coworkers contributed to the field of NOCI through a few different implementations discussed herein. Mayhall and coworkers developed a spin-flip variant of NOCI [52]. This method utilized a spin-flipped wavefunction obtained from a high-spin reference for the NOCI. A restricted open-shell Hartree-Fock (ROHF) wavefunction is used as a reference and the spin-flipped excitations in a localized orbital active space are used as the many-electron functions over which the NOCI is expanded. This is obtained through a spin-flip complete active space (SF-CAS) procedure where the CI wavefunction for each configuration is an expansion of all the spin-flipped excitations from the ROHF wavefunction. Partial inclusion of orbital relaxation in each of the configurations involved is carried out with the SF-NOCI procedure. Sundstrom and Head-Gordon used different Hartree-Fock solutions as the basis for the NOCI [73]. They applied this idea to also study (multi-electron) excited states. This method has the advantage that the initial wavefunction is not multideterminantal like in NOCI-Fragments hence it is computationally more viable, but the proper description of static correlation effects in strongly correlated systems may be absent due to the selection of only a few HF solutions as the basis for the NOCI.

Yost and coworkers further worked on this formalism to study a multireference perturbation method for excited states [74], and a correction using MP2 to the NOCI [75]. A resolution of identity (RI) based simplification to this NOCI-MP2 was also developed by

the group in a later work [76]. Oosterbaan and coworkers developed a nonorthogonal configuration interaction singles (NOCIS) method as an extension of the configuration interaction singles (CIS) while also considering orbital relaxation effects [77, 78]. The method was applied to study core excitations. The NOCIS wavefunction is composed of single determinantal ROHF wavefunctions of each atom (or cation) of the molecule.

Thom and Head-Gordon [83, 101] developed a method to locate HF-states using a metadynamics based approach. Using a method developed by Laio and Parrinello [102] to study local minima in molecular dynamics calculations, they obtain multiple broken-symmetry solutions whose interaction with each other can be simulated using a NOCI based approach. Multiple mean-field like solutions to the HF equations had previously been used in studies of excited states in the Maximum Overlap Method (MOM) of Gill and coworkers [103] where they evaluate matrix elements between sets of orbitals that do not have any orthogonality constraints. The method of Thom and Head-Gordon uses restricted Hartree-Fock (RHF) or Unrestricted Hartree-Fock (UHF) solutions to describe the energy minimas and subsequently as the basis functions for the NOCI expansion. In many cases (for example, the dissociation of H_2) we need more than one UHF solution for a proper description of the wavefunction. This is because the spin symmetry of the state breaks beyond a certain ‘Coulson-Fischer point’ resulting in mixing of the lowest triplet with the ground state singlet. This spin polarization results in a general energy lowering. Since the existence of two UHF solutions is not always guaranteed, Burton and coworkers [84–86] also included solutions that fall in the complex plane in a ‘holomorphic Hartree-Fock’ approach. This extra dimension ensures that two solutions (two sets of orbitals) can be obtained. The work has further been extended recently to obtain nonorthogonal matrix elements based on a derivation of generalized Slater-Condon rules using Wick’s theorem [104].

Nite and Jiménez-Hoyos [87] developed a state averaged resonating Hartree-Fock (sa-ResHF) method which they used to study excited states. The authors include spin-projection and orbital relaxation effects in this approach. The results from sa-resHF are then compared with the description obtained from using low-lying HF solutions to excited states as the starting point for the NOCI.

Glebov [105] and coworkers developed a method similar to the NOCI-Fragments approach. They study exciton coupling in their system using two approaches. The first method, called the nonorthogonal product approach (NOPA) uses CASSCF molecular wavefunctions and the cluster is described using antisymmetrized products of these individual wavefunctions. This is similar to the formation of MEBFs in the NOCI-Fragments procedure except that charge-transfer states are only included in a variant called NOPA-CT. In the second variety called localized orbital configuration interaction (LOCI), the CI wavefunction is composed of all possible determinants of a chosen active space in the system. This approach is similar to a CASSCF procedure with localized basis functions (MOs) from each molecule. Since LOCI is based on a CASCI formalism, the CT configurations are also considered and the solutions dominated by these were identified as CT states. Both these methods are then used independently to calculate the matrix elements between localized orbitals or nonorthogonal states.

Malmqvist [106] has proposed a method to efficiently evaluate one and two-electron transition density matrices through a series of nonunitary transformations. This is done

by the biorthogonalization of orbital sets. The wavefunctions used were of type MCSCF. This method has been adopted in many later works (for example the state interaction approach in Molcas). Most relevant to this thesis is the work of Olsen and coworkers [107] who used this approach to obtain transition probabilities between states described using nonorthogonal orbitals. Knecht and coworkers [108] recently used this idea and expanded the state interaction approach for matrix product states (MPS) wavefunctions. These MPS wavefunctions are used in the density matrix renormalization group (DMRG) SCF procedure. DMRG is one of the most efficient methods to go beyond a certain active size for computationally prohibitive CASSCF calculations [12, 13, 17, 109]. Although it is not a method where NOCI is performed, the example of a transformation of MPS wavefunctions with mutually nonorthogonal orbitals is mentioned as an interesting way for NOCI calculations where large active spaces are required.

An ab-initio implementation of the Frenkel Davydov exciton model (AIFDEM) made of singly excited monomer basis states was proposed by Morrison and Herbert as a way to study excitations in crystals [110, 111]. The AIFDEM uses direct products of ground and excited configuration state functions (CSFs) of each fragment as the basis over which the Hamiltonian is diagonalized. In the case of excited states, CIS wavefunctions and for ground states HF wavefunctions are usually used. These ‘excitonic’ bases are not orthogonal hence they are solved using the generalized eigenvalue equation. To reduce complexity during the computation the authors shift to a natural transition orbital (NTO) basis and the matrix elements between nonorthogonal orbitals are then evaluated after a corresponding orbital transformation.

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3

REDUCED COMMON MOLECULAR ORBITAL BASIS

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ABSTRACT

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The NOCI-Fragments approach has been found to be a promising alternative to study electron and excitation energy processes. The advantages of NOCI-Fragments are interpretation of the wavefunction in terms of chemically interpretable states, and the direct accessibility of electronic coupling between diabatic states. Bottlenecks in this method are the large number of two-electron integrals that has to be handled for the calculation of an electronic coupling matrix element and the enormous number of matrix elements over determinant pairs that have to be evaluated for the calculation of one matrix element between the many-electron basis functions (MEBFs) over which the NOCI wavefunction is expanded. We show here how a reduced common molecular orbital basis significantly reduces the number of two-electron integrals that need to be handled. The results obtained with this basis do not show significant loss of accuracy in relevant quantities like electronic couplings and vertical excitation energies. We also show a significant reduction in computation time with almost no loss in accuracy when matrix elements over determinant pairs with small weights are neglected in the NOCI.

3.1. INTRODUCTION

As discussed before, the rate of energy and electron transfer processes from one molecule to another is to a large extent proportional to the electronic coupling of the initial and final diabatic electronic states. Since this coupling is determined by a nondiagonal Hamiltonian matrix element (see Eq. 1.1 from Chapter 1), an efficient and accurate evaluation of these matrix elements is of utmost importance. In the previous chapter, we saw how to evaluate Hamiltonian matrix elements between sets of mutually nonorthogonal determinant pairs. We saw that the one- and two-electron integrals are expressed in terms of atom centered orbitals (AOs) and so were the first- and second-order co-factors of the overlap matrix, respectively. Despite the factorization of the second-order co-factors, the evaluation of the matrix elements using integrals expressed in this AO basis is still extremely costly but for the smallest systems. The algorithmic scaling to the fourth-order in the number of basis functions makes it very hard to study molecules relevant for singlet fission and other electron and energy transfer processes with sufficiently large basis sets. If we first take a step back to see how the computational cost is reduced in standard orthogonal CI, we might come up with a solution to this bottleneck. In standard CI approaches based on orthogonal Slater determinants (that is, all determinants are expressed in the same set of orthonormal molecular orbitals), the integrals are transformed from the AO basis to this MO basis.

$$\langle ij|kl\rangle = \sum_{\mu} \sum_{\nu} \sum_{\rho} \sum_{\sigma} C_{\mu}^i C_{\nu}^j C_{\rho}^k C_{\sigma}^l \langle \mu\nu|\rho\sigma\rangle \quad (3.1)$$

where $\langle \mu\nu|\rho\sigma\rangle$ and $\langle ij|kl\rangle$ are the two-electron integrals in the AO and MO bases respectively. An improvement to this $O(N^8)$ scaling procedure of course exists, where the integral transformation is carried out for two indices at a time,

$$\langle ij|\rho\sigma\rangle = \sum_{\mu} \sum_{\nu} C_{\mu}^i C_{\nu}^j \langle \mu\nu|\rho\sigma\rangle \quad (3.2)$$

$$\langle ij|kl\rangle = \sum_{\rho} \sum_{\sigma} C_{\rho}^k C_{\sigma}^l \langle ij|\rho\sigma\rangle \quad (3.3)$$

which scales as $O(N^5)$. The transformation simplifies enormously the calculation of the matrix elements but does not immediately lead to a reduction of the number of integrals since the number of functions in the new basis used to express the integrals is of course the same as before; there are always as many MOs as there are AOs. However, in the integral transformation we can freeze the deep core orbitals and remove the highest lying virtual ones thereby drastically reducing the number of integrals. Going back to the nonorthogonal CI approach, the fact that each state is expressed in a different set of MOs complicates the transformation of the integrals to an MO basis. Nevertheless, there are still several options for transformation: (i) perform an integral transformation for each matrix element over MEBFs, expressing the integrals in the MOs of the Slater determinants occurring in the MEBFs under study; (ii) concatenate all the MOs of the different electronic states and use this as the MO basis leading to a single integral transformation; and (iii) generate one compact MO basis common to all electronic states. The first two options are straightforward but computationally not very advantageous. In the first case, one has

to perform costly four-index transformations multiple times, while in the second case the cure can be worse than the disease as the number of MOs that describe the different electronic states can become larger than the number of functions in the AO basis when two or more molecular electronic states are considered in the NOCI.

In this chapter, we explore the efficiency and accuracy of the third option and introduce a new way to first construct a basis set common to all considered electronic states and then express the integrals in this new basis. The construction of the new basis is based on the understanding that many of the molecular orbitals are actually rather similar in the different electronic states and that a small subset of the basis used in option (ii) is actually enough to represent all states with high precision. The rest can be considered redundant and can therefore be eliminated. This procedure leads to a compact, linear independent basis that strongly reduces the number of integrals without losing accuracy.

After describing the procedure to construct the common MO basis, we discuss in detail the trade-off between accuracy and computational resources (memory and wall-clock time) of transforming the integrals to this new common basis. Using the new set of integrals in the NOCI-Fragments approach seems to provide agreeable answers even after much reduction in the integral file size. To complete the picture, we also report the dependency on the thresholds that are used to decide whether a determinant pair is relevant for the matrix element between two nonorthogonal states. The introduction of a common MO basis and the selection of the determinant pairs based on the product of their CI coefficients has significantly pushed forward the limit of application.

3.2. GENERATION OF REDUCED COMMON MOLECULAR ORBITAL BASIS

CONSIDER K different electronic states of one of the molecules (or fragments) of the cluster under study. Typically, each molecular state Ψ_μ in NOCI-Fragments is described by a multiconfigurational self-consistent field (MCSCF) wavefunction expanded in terms of Slater determinants. The determinants themselves can be written in terms of antisymmetrized products of MOs. The MOs are linear combinations of all N atom centered orbital (AO) basis functions in the fragment

$$|\phi_i^\mu\rangle = \sum_{j=1}^N c_{ij}^\mu |\chi_j\rangle, \quad (3.4)$$

where μ is one of the electronic states from the set K , and c_{ij}^μ are the orbital coefficients optimized for state μ . The MOs of each state are orthogonal among each other, but not necessarily orthogonal to the MOs of other electronic states.

$$S_{ij}^{\mu\nu} = \langle \phi_i^\mu | \phi_j^\nu \rangle = \begin{cases} \delta_{ij} & \text{if } \mu = \nu, \\ \sum_{k,l}^N c_{ki}^\mu c_{lj}^\nu s_{kl} & \text{if } \mu \neq \nu. \end{cases} \quad (3.5)$$

where s_{kl} is the overlap between AOs, c_{ki}^μ are the MO coefficients (k, l run over the AOs and i, j are the MO indices). By grouping together the MOs with non-zero occupation of

all K states, a common basis for the given set of electronic states of the molecule can be formed.

$$\{\phi_1^1, \phi_2^1, \dots, \phi_{n_1}^1, \phi_1^2, \phi_2^2, \dots, \phi_{n_2}^2, \phi_1^3, \phi_2^3, \dots, \phi_{n_3}^3, \dots, \phi_1^K, \phi_2^K, \dots, \phi_{n_K}^K\} \quad (3.6)$$

where ϕ_i^μ is the i^{th} MO in the μ^{th} electronic state, and n_μ is the number of MOs with non-zero occupation for each state μ . The matrix of MO coefficients $\mathbf{C}$ has dimensions $(M \times N)$, with $M = \sum_{\mu=1}^K n_\mu$. Although the orbitals of different electronic states are different, they are still similar enough to make that such a common basis has linear dependencies that need to be removed before further processing. To do so we first diagonalize the overlap matrix $\mathbf{S}$, dimension $(M \times M)$, of the common MO basis defined in Eq. 3.6.

$$\mathbf{S}' = \mathbf{U}^\dagger \mathbf{S} \mathbf{U} \quad (3.7)$$

The matrix of eigenvectors ($\mathbf{U}$) defines a new set of MOs to describe the electronic states and linear dependencies are removed by only considering the L vectors whose eigenvalues ($\mathbf{S}'$) are larger than a given threshold (τ_{MO}).

$$\mathbf{U} \xrightarrow{\tau_{MO}} \mathbf{V} \quad (3.8)$$

We now have a reduced common basis $\mathbf{V}$, of dimension $(L \times M)$, from $\mathbf{U}$ of dimension $(M \times M)$, where $L < M$. Next, we express $\mathbf{V}$ in the AO basis by

$$\mathbf{B} = \mathbf{C}(\mathbf{S}'')^{-\frac{1}{2}} \mathbf{V} \quad (3.9)$$

where $\mathbf{S}''$ contains the L largest eigenvalues of $\mathbf{S}'$ and $\mathbf{B}$ constitutes a set of orthogonal vectors of dimension $L \times N$ for the fragment under consideration. Finally, matrices $\mathbf{D}^\mu$ with dimension $(n_\mu \times L)$ are constructed to express the MOs of each electronic state μ in the common compact basis $\mathbf{B}$.

$$\mathbf{D}^\mu = \mathbf{B}^\dagger \mathbf{s} \mathbf{C}^\mu \quad (3.10)$$

where $\mathbf{C}^\mu$ is the matrix of MO coefficients in terms of AOs for each electronic state μ . In a strictly orthogonal approach with one set of MOs to express all the electronic states, the $\mathbf{D}^\mu$ matrices are unit matrices, but this is not the case here. The MOs are written in terms of the new compact basis for the molecule under consideration as

$$|\phi_i^\mu\rangle = \sum_{j=1}^L d_{ij}^\mu |b_j\rangle \quad (3.11)$$

In the standard NOCI approach where only one molecule is considered this is the end of the transformation procedure. In the case of NOCI-Fragments the procedure is repeated for all other molecules (fragments) in the system and after collecting the resulting basis sets of all molecules, the one- and two-electron integrals are transformed to the common MO basis of the whole cluster. Increasing the value of the threshold τ_{MO} leads to a loss of information about the nonorthogonality between the states in the common MO basis. To what extent this affects the elements of the NOCI matrix is the subject of the first part of the Results and Discussion section.

The number of determinant pairs that need to be considered in the calculation of an element of the NOCI matrix scales roughly with the fourth power of the number of determinants in the CAS used to generate one molecular/fragment wavefunctions. This makes the application of any but the smallest CAS prohibitive. There is, however, a simple solution to this bottleneck realizing that the contribution of each determinant pair in the NOCI matrix element is weighted by the product of the CI coefficients of the two determinants. Hence the contribution of two determinants each having a coefficient of the order of 10^{-6} is multiplied by 10^{-12} making it negligible in most cases except where the matrix element turns out to be exceptionally large. The large valued Hamiltonian matrix elements are the ones with a big overlap matrix element and these can be selectively left unchanged in the list of determinant pairs while the many determinant pairs with small contributions are removed. To explore the possibilities of neglecting a large portion of the determinant pairs, we have introduced a second threshold in the NOCI procedure, τ_{det} , which eliminates all determinant pairs whose product of CI coefficients is smaller than the threshold.

3.3. SCOPE OF THE METHOD

BEFORE putting the influence of the new thresholds to the test, we first stress that the NOCI-Fragments implementation is not meant to be a general electronic structure method. In fact, from the very beginning, that method is known to perform rather poorly in the description of covalent bonds [1–3]. When building the MEBFs of the NOCI from atomic wavefunctions for F, F^- , and F^+ , i.e., using the individual atoms as fragments, the energy rises too steep at short internuclear distances, the equilibrium distance of ~ 1.7 Å is too long and the dissociation energy is too small. These inaccuracies are a direct consequence of how the orbitals of the 'fragments' are optimized (in the isolated atoms), leading to a large Pauli repulsion between the fragments. A slightly better description is obtained with a standard NOCI calculation where the $|\dots\sigma_g^2|$ and $|\dots\sigma_u^2|$ determinants (both expressed in their own optimal set of MOs) are used, but with this choice of MEBFs expressed in delocalized MOs, it is better to follow a standard MCSCF approach with these two configurations.

Instead, the NOCI-Fragments method compares very well to other approaches for the calculation of electronic couplings between weakly coupled states [4]. Furthermore, the direct comparison of the excitation energies in a benzene dimer as a function of the intermolecular distance compares well with a standard CASSCF approach for the dimer, although deviations are getting larger when the two molecules approach each other.

3.4. COMPUTATIONAL DETAILS

THE first test case considered was the slip-stacked pyridine dimer as depicted in Figure 3.1. This dimer is small enough to perform a large set of test calculations within a reasonable time, yet showing the most relevant many-electron states that play a role in intermolecular electron and energy transfer processes. The geometry of the molecule was optimized using DFT with B3LYP/6-311G** and the dimer was formed by placing

the second unit (with identical internal coordinates) on the z -axis at a perpendicular distance of $4a_0$ to the first, and sliding it by $7a_0$ along the x -axis and then by $5a_0$ along the y -axis. In addition to the ground state (S_0), we also considered the following molecular states: first excited singlet (S_1), the lowest triplet excited state (T_1), and the cationic (D_1^+) and anionic (D_1^-) states. The optimal MOs of these states ($|\phi_i^\mu\rangle$ of Eq. 3.4) are generated in CASSCF calculations with an active space formed by either 4 electrons in 4 active orbitals (CAS(4,4)) or 6 electrons in 6 orbitals (CAS(6,6)). The common MO basis (Eq. 3.9) was generated with a program written in f95, which also expresses the molecular wavefunctions in the new basis (Eq. 3.10). All the single molecule calculations and the transformation of integrals to the common MO basis for the dimer were performed with the GAMESS-UK package [5].

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Figure 3.1 | Ball and stick representation of the slip-stack arranged pyridine dimer. Dark spheres show carbon, blue represent nitrogen and the lighter spheres show hydrogens.

The construction of the MEBFs and the subsequent calculation of the matrix elements was done with the GronOR code [6, 7] on the Summit supercomputer at Oak Ridge National Laboratory (Tennessee, USA). The 4608 nodes of this machine are composed of two CPUs (totaling 44 cores) that share 512 GB of memory and 6 GPUs with 16 GB each. All runs, unless otherwise specified, were run on 32 nodes, each with 6 ranks per node. GronOR scales linearly with the number of cores up to the machine limit.

Test calculations were done on the following systems following the same procedure as outlined for the pyridine case: **1** - pyridine dimer cc-pVTZ, **2** - pyridine dimer 6-311G**, **3** - naphthalene dimer cc-pVDZ, **4** - pyridine tetramer 6-311G**, **5** - pyridine tetramer cc-pVTZ, **6** - tetracene dimer cc-pVDZ. The pyridine tetramer test cases were constructed by placing one pyridine molecule $7a_0$ vertically above and one $7a_0$ below the dimer geometry. The results for systems **2** to **6** show the same trend as test system **1** so have not been included in the text of this thesis. The results for systems **2** to **6** can be found in the supporting information (SI) of Ref. [8]. The coordinates of all test systems are also listed there.

The test cases have been chosen with the latest applications of our group in mind [4, 9–12]. These focus mainly on inter- and intramolecular electron and energy transfer processes that occur in singlet fission [13–16], donor-acceptor charge transfer, [17–19] and exciton delocalization and dispersion [20–22]. In all these cases, several diabatic molecular states with different number of electrons and different electronic configurations play a fundamental role, and hence, orbital relaxation is an important factor for

obtaining an accurate theoretical description. This mostly organic playground is of course not the only area of chemistry where NOCI can be applied; systems with transition metals have also been studied, but have usually been restricted to rather small (model) complexes [2, 23–26]. The approach presented here will certainly also make the study of more realistic transition metal systems within reach. Roughly speaking, the transformation of integrals to the common MO basis means that our NOCI implementation no longer scales with the size of the atomic orbital basis but rather with the number of electrons in the system, as the dimension of the common MO basis is only slightly larger than half the number of electrons in the system. Different from orthogonal CI approaches, we only need to consider the MOs with non-zero occupation in the integral transformation.

3.5. RESULTS AND DISCUSSION

FIGURE 3.2 shows the eigenvalues of the molecular orbital overlap matrix of the pyridine molecule for the five states S_0 , S_1 , T_1 , D_1^+ and D_1^- . The first 23 basis functions of the common MO basis with eigenvalues close to five describe the common part of the occupied (19 inactive and 4 active) orbitals of the five electronic states. The next functions with smaller eigenvalues (the first 15 are depicted in Fig. 3.3) are responsible for the description of the nonorthogonality, or the difference, in the orbitals of the different electronic states. Although not easily interpreted, basis functions 1-4 and 6 seem to describe differences in the π -orbitals of the different electronic states, and functions 5, 7-10 can be considered to take into account possible changes in the C-H bonds. It becomes more difficult to assign a role for functions 11-15.

Figure 3.2 | Eigenvalues of the MO overlap matrix of the five electronic states considered for the pyridine molecule.

In fact, the functions with the smallest eigenvalues are just linear dependent coun-

terparts of the basis functions with larger eigenvalues, and hence, going to the right in Fig. 3.2, the functions with eigenvalues smaller than 1 gradually change their role from describing the nonorthogonality between the states to being simple linear dependent vectors not carrying any significant information. In the next section, we determine the optimal value for truncating the common MO basis to remove the linear dependencies but still maintaining the basis flexible enough to express the differences between the electronic states.

The functions shown in Fig. 3.3 describe the largest part of the nonorthogonality between the S_0 , S_1 , T_1 , D_1^+ and D_1^- states of the pyridine molecule described with a CAS(4,4) wavefunction. Functions 1-4 and 6 describe the polarization of the π orbitals, which cause the largest differences between the states. For example, the cationic and anionic states have 5 and 7 electrons in the π -orbitals, which makes the optimal shape quite different in the neutral and the charged electronic states. Therefore, a description of all the states in a common MO basis requires this flexibility. Eliminating these orbitals from the basis would effectively remove the nonorthogonality between the states and return to a state-average description. The functions 5, 7-10 are used to take into account the polarization of the C-H bonds. The shape of the functions with smaller eigenvalues (11-15 and from thereon) becomes increasingly more complicated, and their importance steadily decreases to become more and more the linear dependent counterparts of the functions with larger eigenvalues.

Figure 3.3 | Graphical representation of the 15 functions from the common MO basis with the largest eigenvalues (excepting the first 23 with eigenvalues close to 5 (see Fig. 3.2)).

3.5.1. DETERMINATION OF THE OPTIMAL τ_{MO}

As expected, increasing the value of the threshold for eliminating vectors from the common MO basis increases the difference in the total energies of the MEBFs of the pyridine dimer with respect to the reference values obtained with the AO basis. A roughly linear increase is observed on a double log plot for all the systems that we looked at. Thresholds of 10^{-8} lead to energy differences of the order of $10^{-8} E_h$, while the much bigger threshold of 10^{-3} eliminates so many functions from the basis that the calculated total energy deviates by approximately $10^{-3} E_h$. Such large deviations are of course unacceptable if accurate total energies are required, but the total energy is not exactly the property that defines the physics of the system under study. For a better insight into what can be considered as a safe threshold for eliminating functions from the common MO basis we have to look into other quantities. The first one that we have analyzed is the electronic coupling V_{ij} between the S_0S_1 and 1TT MEBFs. These two electronic configurations play a fundamental role in the rationalization of singlet fission [9, 13, 14] and the matrix element $\langle S_0S_1 | \hat{H} | ^1TT \rangle$ is a key element in the calculation of the electronic coupling V_{ij} between the two normalized MEBFs Ψ_i and Ψ_j :

$$V_{ij} = \frac{\langle \Psi_i | \hat{H} | \Psi_j \rangle - \frac{(\langle \Psi_i | \hat{H} | \Psi_i \rangle + \langle \Psi_j | \hat{H} | \Psi_j \rangle)}{2} \cdot \langle \Psi_i | \Psi_j \rangle}{1 - \langle \Psi_i | \Psi_j \rangle^2} \quad (3.12)$$

Figure 3.4 compares V_{ij} obtained with the AO basis to those calculated with the common MO basis, varying the threshold for linear dependencies. Pyridine CAS(4,4) molecular wavefunctions with the cc-pVTZ basis set were used to construct the MEBFs. Moving to the right along the τ_{MO} axis, more basis functions are eliminated from the common MO basis with increasing threshold.

Although the coupling is much smaller than in systems with singlet fission properties – for example the calculated NOCI-Fragments coupling for a tetracene dimer is around 50 meV [4], it allows us to draw conclusions about the dependence of the coupling on the threshold. It is seen that for τ_{MO} smaller or equal to 10^{-4} the coupling is exactly the same as the one calculated with the AO basis. A small deviation of less than 0.1 meV is found when $\tau_{MO} = 10^{-3}$ and even with the 10^{-2} threshold a reasonable coupling is obtained. From Figure 3.5 it can be derived that this behavior is general to all 15 off-diagonal elements of the NOCI matrix. The mean absolute error (α) and the maximum absolute deviation (δ) in the electronic coupling plotted in the figure are calculated with corresponding values in the AO basis as reference. Negligible differences are observed up to $\tau_{MO} = 10^{-3}$, and increasing the threshold by a factor of ten introduces small deviations.

Figure 3.4 | Electronic coupling V_{ij} (in meV) between S_0S_1 and 1TT for the pyridine dimer test system as function of the threshold τ_{MO} for removing basis functions from the common MO basis. AO refers to the value obtained with the AO basis.

Figure 3.5 | Mean absolute error (α) and maximum absolute deviation (δ) (both in meV) of the electronic couplings among the 5 MEBFs of the NOCI with respect to the values obtained with the AO basis.

Having established that the results of the AO basis can be reproduced with the common MO basis, we now focus on the computational savings. Keeping the number of nodes and other computational parameters constant, we have compared the wall-clock time and the size of the integral file for the calculation of the 21 unique elements in the

6×6 NOCI matrix for different values of τ_{MO} .

Figure 3.6 | Integral file size in MB (left), and computer time in seconds (right) as function of the threshold τ_{MO} .

Figure 3.6 shows a dramatic drop in the computer time when the AO basis is replaced by the common MO basis with $\tau_{MO} = 10^{-7}$. The use of larger thresholds only slightly reduces the time. On smaller machines, the decrease in the computer time continues to larger thresholds as can be seen in Figure 3.7.

The size of the integral file, and hence, the memory requirements, decreases more steadily as a function of the threshold and is about three orders of magnitude smaller for $\tau_{MO} = 10^{-3}$ than the integral file using the AO basis. In comparison to the original AO basis of 570 basis functions, the maximum size of the common MO basis set is 230: 10 electronic states (S_0, S_1, T_1, D_1^+ and D_1^- on both molecules), each with 19 inactive + 4 active = 23 occupied orbitals. This is already reduced to 148 basis functions by applying a threshold of 10^{-7} , and less than one-third of the basis functions is retained when τ_{MO} increases to 10^{-3} .

Figure 3.7 | Computer wall-clock time (in seconds) as function of τ_{MO} when performed using two GPUs on the computer cluster.

Figure 3.8 | Excitation energies ΔE (in eV) for three states calculated using different τ_{MO} . AO refers to the value obtained with the AO basis.

The last element that we checked was the performance of the common MO basis to reproduce the relative energies of the MEBFs taking the S_0S_0 configuration as reference energy. The first feature that strikes the eye in Figure 3.8 is the fact that pyridine dimer is definitely not a candidate to show singlet fission. The 1TT configuration lies way too high in energy with respect to the S_0S_1 state, while they should be close in energy for

singlet fission. More important for the present study is that the relative energies are not affected by the change from AO basis to common MO basis unless the threshold for linear dependencies is very high, although the differences with the AO basis are marginal even for $\tau_{MO} = 10^{-3}$.

We performed the same set of tests for other molecules mentioned in the computational details and obtained the same trend in the results. The mean errors α and maximum deviations δ in electronic coupling given in Figure 3.9 are small in all cases, except for tetracene dimer (**6**), for which we observe a deviation of around 10 meV in a coupling which is as large as 77 meV in the reference calculation (see SI of Ref. [8]). From the ratios of integral file sizes depicted in Figure 3.10, we can see that the integral file size is reduced by approximately two orders of magnitude in all systems, which is especially important for calculations on larger systems. Finally, the speed-up (reduction of the wall-clock time) is also close to two orders of magnitude in the systems **1**, **3** and **4**. For system **2**, we find a slightly smaller reduction because this system is rather small anyway and the impact of expressing the integrals in the common MO basis is not so well seen in the large-scale computer used in this study. For systems **5** and **6**, we have not been able to perform the NOCI calculation in the AO basis due to the excessive size of the integral file (reference calculation for α and δ are the ones with $\tau_{MO} = 10^{-9}$). The reduced number of basis functions implies shorter summations in the evaluation of nonorthogonal matrix elements compared to the AO basis. The reduced common MO basis also makes it now possible to have multiple ranks processing the integrals in GPUs for large systems, hence accelerating the calculation even more.

Figure 3.9 | Mean absolute error (α) and maximum absolute deviation (δ) (both in meV) of the electronic couplings among the 5 MEBFs of the NOCI with respect to the values obtained with the AO basis, with $\tau_{MO} = 10^{-4}$ for the six different test systems.

Figure 3.10 | Ratio of the integral file size (in %) in the MO basis (ω_{MO}) and the AO basis (ω_{AO}) for the test systems at $\tau_{MO} = 10^{-4}$.

To close the discussion of the influence of the truncation of the common MO basis, we would like to stress that the analysis of the underlying physics of the system under study is not done at the one-electron level in our implementation of NOCI, but rather at the many-electron level by looking at the relative importance of the different MEBFs in the final N-electron wavefunctions obtained by diagonalizing the NOCI matrix. Since the initial diabatic character of the functions is strictly maintained during the calculation, the coefficients in the NOCI wavefunction give a direct indication of the importance of the MEBFs, which can univocally be assigned to physical concepts such as charge transfer, local excitation, relaxed hole states, etc. The threshold for reducing the common MO basis must be chosen such that only the linear dependencies are removed from the basis. Making the threshold too large will lead to a removal of functions that are needed to account for the nonorthogonality between the different electronic states and therefore too large a value of τ_{MO} will lead to a basis that is not flexible enough for a proper description of the fragment wavefunctions.

3.5.2. SELECTION OF DETERMINANT PAIRS: CASE STUDY ON PYRIDINE DIMER

Starting again with the matrix element between the 1TT and S_0S_1 states of the pyridine dimer (CAS(6,6) / 6-311G**) with the integrals already expressed using a common MO basis with $\tau_{MO} = 10^{-4}$, Fig. 3.11 shows how the size of the coupling varies with increasing determinant pair threshold τ_{det} .

3

Figure 3.11 | Electronic coupling V_{ij} (in meV) between $S_0 S_1$ and $^1 T T$ as function of the determinant threshold τ_{det} .

The calculated values are virtually the same for τ_{det} smaller or equal to 10^{-5} . For larger thresholds, we see very small deviations, and filtering out all determinant pairs with a CI coefficient product smaller than 10^{-3} affects the NOCI matrix element by not more than 0.3 meV. Figure 3.12 compares the number of determinants pairs that were considered in the calculation of these matrix elements to the time it took to process all the pairs and calculate the matrix elements for the NOCI matrix.

Figure 3.12 | Number of determinant pairs that were used to construct the NOCI matrix and the time for the NOCI calculation (in seconds) as functions of τ_{det} .

These calculations were performed on 256 Summit nodes with 6 ranks per node and show how the number of determinant pairs decreases steadily with increasing τ_{det} . Taking a threshold of 10^{-4} the reduction in the number of determinant pairs is almost four orders of magnitude compared to the smallest threshold that we have used. From Figure 3.11 it is seen that using a threshold of 10^{-4} does not significantly affect the calculated coupling, but reduces the computer time by more than two orders of magnitude as seen in Figure 3.12.

3

Figure 3.13 | Mean absolute error (α) and maximum absolute deviation (δ) (both in meV) of the electronic couplings among the 5 MEBFs of the NOCI with respect to $\tau_{det} = 10^{-9}$, which was the smallest value we chose to examine.

The same behavior is observed for the other matrix elements. Figure 3.13 represents the mean absolute error and the maximum absolute deviation (both in meV) as function of τ_{det} . The results remain stable up to $\tau_{det} = 10^{-5}$, for higher thresholds, we start to observe small deviations. The excited state energies in Figure 3.14 are hardly sensitive to the value of the threshold, even with a value of 10^{-3} , the changes are minimal.

Figure 3.14 | Excitation energies ΔE (in eV) for three states calculated using different τ_{det} .

The figures show that up to $\tau_{det} = 10^{-5}$, there is nearly no loss in accuracy, while the computational time is drastically reduced. The introduction of the threshold for determinant pairs τ_{det} makes the NOCI much less dependent on the size of the active space employed for the calculation of the molecular wavefunctions. These are effectively filtered out by the threshold on the determinant pairs and although the calculation time of the NOCI matrix becomes longer when a larger CAS is applied in the fragment, the increase is much less prominent than the quartic dependence (N^4 , with N the number of determinants in the fragment CAS wavefunction) that can be expected without filtering.

This one case study is likely not enough to establish $\tau_{det} = 10^{-5}$ as a universally applicable threshold for all systems, but this very straightforward method to reduce the number of determinant pairs that need to be evaluated in the calculation of the matrix elements pushes forward the border of applicability of the NOCI method. For a more general approach, it is most probably unavoidable to leave behind the complete active space expansion of the fragment functions. We are currently investigating the use of the ICE-CI approach developed by Neese and co-workers based on the CIPSI approach of Huron, Malrieu, and Rancurel.[27] In this approach, the multiconfigurational wavefunction is constructed iteratively to only include the most important configurations. Hence, the final wavefunction does, by definition, not contain any 'configurational deadwood'.

3.6. CONCLUSIONS

IN a NOCI each state is expressed in its own optimal molecular orbital set and this complicates the transformation of the integrals to an MO basis, commonly applied in configuration interaction calculations with one set of orthogonal MOs. Instead, we have introduced a common MO basis constructed by grouping together all the MOs of the different electronic states, followed by an orthogonalization and the removal of the

linear dependencies through a threshold that can be varied to find the optimal trade-off between accuracy and computational cost.

The introduction of a common MO basis set to express the wavefunctions of the different electronic states effectively reduces the computational cost of NOCI calculations. The transformation of the one- and two-electron integrals to this common MO basis drastically reduces the size of the integral files and allows to keep the integrals in memory, either using the shared memory of a group of CPUs (GPUs), or multiple copies, each on a single CPU (GPU), depending on the amount of memory available. Furthermore, the reduced number of basis functions in the common MO basis makes the summations in the calculation of the nonorthogonal matrix elements much shorter than for the AO basis that has been applied so far in NOCI.

Test calculations on the pyridine dimer (and on the larger systems presented in the supporting information of reference [8]) show that the threshold for removing the linear dependencies in the common MO basis (τ_{MO}) can be safely taken to be 10^{-4} and if needed even ten times larger to generate some additional savings (for example, on smaller computers). A consequence of rewriting the integrals in the common MO basis is that it has become much more efficient to apply AO basis sets of good quality in the calculations of the fragments, as the NOCI cost does no longer directly scale with the size of the AO basis but rather with the number of electrons.

The second important bottleneck in the NOCI is the huge number of matrix elements over determinant pairs that need to be evaluated for the calculation of a single matrix element over MEBFs. The introduction of a second parameter in the method, τ_{det} , allows the consideration of much larger active spaces in the fragment calculations. The τ_{det} parameter removes all the determinant pairs whose product of CI coefficients in the MEBFs is smaller than the threshold and effectively removes what is sometimes called the configurational ‘deadwood’. While the values of the matrix elements of MEBFs do not critically depend on the threshold for the linear dependency in the common basis (unless very large thresholds are used), the screening of the determinant pairs has a larger impact on the results. A threshold of 10^{-5} turns out to be the largest one for reliable matrix elements, but checking with smaller (or larger) thresholds is advised.

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3.8. AUTHOR CONTRIBUTIONS

R.K.K. performed the research based on the theory devised by R.W.A.H. and CdG. R.K.K. drafted the manuscript under the supervision of R.W.A.H., CdG, and R.B.

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4

INCLUSION OF DYNAMIC CORRELATION IN NOCI-FRAGMENTS

... and the effect on direct and charge transfer mediated couplings in singlet fission.

ABSTRACT

4

In this chapter it is discussed how the effect of dynamic electron correlation has been incorporated into the nonorthogonal configuration interaction (NOCI) energies and the NOCI wavefunction. The NOCI-Fragments approach uses complete active space self-consistent field (CASSCF) molecular wavefunctions to form the many-electron basis functions (MEBFs) for the NOCI. In a first approach to include dynamical correlation the diagonal Hamiltonian matrix elements of the NOCI matrix, corresponding to the MEBF energies, are shifted using the molecular energies from CASPT2 and NEVPT2. In a second approach, a dynamic correlation dressed complete active space (DCD-CAS(2)) wavefunction is used instead of a CASSCF wavefunction in the NOCI procedure. The results on test molecules benzene, pyridine, and naphthalene are reported, showing that dynamic correlation does not affect the direct coupling between the MEBFs, but has a significant effect on the relative MEBF energies. This changes the charge-transfer mediated electronic couplings between the excited singlet and the 1T state.

4.1. INTRODUCTION

QUANTUM chemical methods have become an ubiquitous tool in chemical research [1–3]. The methods can reach sufficient accuracy for reliable predictions of chemical and physical properties, and analysis methods exist for interpreting the results [4–11]. A vast toolbox of approaches nowadays exist, ranging from fast and simple to computationally expensive, but highly accurate methods. Accurate methods, such as configuration interaction (CI) are difficult to interpret, due to the large number of configuration state functions included in the wavefunction, whereas the Hartree-Fock wavefunction though easier to interpret in terms of chemical concepts, lacks accuracy. For calculating ground state properties, density functional theory (DFT) is in principle a valuable alternative. It is easy to interpret, efficient and able to include dynamical electron correlation. However, it does not account for static correlation, so the treatment of biradicaloid molecules, which form an important class of molecules that are considered as candidate molecules for singlet fission, is difficult with DFT [12, 13]. Also for excited state processes that involve electron transfer between chromophores or molecules, the use of DFT is not without problems. One of the methods, that is particularly suitable to describe photophysical processes like electron or excitation transfer in a cluster of molecules in terms of molecular states, is the nonorthogonal configuration interaction - fragments (NOCI-Fragments) method [14, 15]. The method is aimed at being sufficiently accurate to for example describe photophysical processes in solids, while maintaining a chemical interpretation of the cluster wavefunctions in terms of molecular states. In this method, the wavefunction for a cluster of molecules is expanded in so-called many-electron basis functions (MEBFs), which are spin-adapted, antisymmetrized products of molecular wavefunctions. Typically these molecular wavefunctions used to build the MEBFs are configuration specific, complete active space self-consistent field (CASSCF) wavefunctions, in which the orbitals are optimized for each different electronic state that may be relevant in the description of the studied process in the molecular cluster [13, 16, 17]. Hence, the method includes intramolecular static correlation effects and orbital relaxation effects, while the cluster wavefunctions can be straightforwardly interpreted in terms of molecular states (diabatic states).

The NOCI-Fragments approach has been used to explore the singlet fission [18–20] probability in molecular clusters [21–23]. Of relevance in these studies are the direct and charge-transfer mediated couplings between the diabatic S_0S_1 and 1TT states. It was noticed in these previous studies that the use of CASSCF wavefunctions leads to incorrect relative energies for the MEBFs (as the excitation energies are of CASSCF quality) and the omission of the contribution of the dynamic electron correlation to the molecular energies leads to incorrect relative energies of the relevant electronic states of the cluster. In specific cases it may even lead to an incorrect ordering of states and less accurate electronic couplings between the diabatic states. Clearly, to further improve upon the description of singlet fission and in general of the NOCI-Fragments method, dynamic correlation effects beyond CASSCF have to be included. Fortunately, it is reasonable to expect that only the dynamic correlation between electrons on the same one molecule plays a role and that the dynamic correlation between electrons on different molecules is negligible. The inclusion of dynamic correlation in NOCI-Fragments may also help to

understand better some phenomena in the fields of core-level spectroscopy and magnetic interactions.

Correlation effects in NOCI approaches can be incorporated following the approach of Yost and Head-Gordon [24, 25], Kähler and Olsen [26, 27], but this has the disadvantage for our NOCI-Fragments approach that the diabatic character of the MEBFs is lost, as in this correlation treatment intermolecular excitations are allowed. The diabatic character of the MEBFs can be maintained while incorporating the relevant intra-molecular dynamical correlation effects, if one would use dynamically correlated molecular wavefunctions in constructing the MEBFs. A straightforward, but computationally costly, way is to improve the CASSCF wavefunctions for each molecular electronic state with a singles and doubles CI (CISD). However, except for very small cases, the number of configurations in a MEBF would exceed practical limits. Hence, an alternative way to include electron correlation effects, while maintaining the diabatic character of the MEBFs, is sought for. Burton and Thom [28] did this through the use of multiple Hartree-Fock solutions to construct multireference wavefunctions and adding a perturbative correction to include dynamic correlation. The method however is not practical when it comes to handling systems of interest to our NOCI-Fragments approach, like potential singlet fission candidates.

A straightforward way to incorporate the effect of dynamic correlation on the NOCI-Fragments energy is to replace the CASSCF energy of the MEBF by its dynamically correlated energy in the Hamiltonian, as is extensively done when spin-orbit coupling is included in the description of the electronic structure of molecular magnets [29–31] through the state interaction method of Malmqvist et al. [32] implemented in Molcas [33]. This approach translates in our implementation to shifting the energy of the MEBFs towards energies that include the effects of dynamic correlation. This shifting of the diagonal is also common practice in the AIFDEM method [34], a method closely related to the NOCI-Fragments approach. In this way, the effect of dynamic correlation is accounted for in the energies, but not in the wavefunctions and the MEBFs. However, the final cluster wavefunctions can be affected, as they follow from diagonalization of the (nonorthogonal) CI matrix.

A second option to include the effects of dynamic correlation in the MEBFs is to map the effect of the dynamic correlation onto the smaller CI space over which we expand our MEBF. This can be done with the help of effective Hamiltonian theory and has been implemented previously by Neese and co-workers [35]. This way we are able to have a dynamic correlation ‘dressed’ CAS-wavefunction (DCDCAS) that can be used to build the MEBFs that are required for our NOCI-Fragments procedure. Changes due to dynamic correlation in the molecular wavefunctions are then incorporated in our MEBFs; the diagonal elements of the Hamiltonian matrix in the MEBF basis should still be shifted towards the DCDCAS energy.

In this Chapter, we explore both aforementioned ways to include dynamic correlation in the NOCI-Fragments approach; we are particularly interested in what the effects of dynamic correlation are on the two suggested pathways of singlet fission, the ‘direct’ and ‘charge-transfer’ (CT) mediated. We calculate electronic couplings for both these pathways and also study the effect of dynamic correlation on the final cluster wavefunctions. We start with a presentation of the theory, followed with a discussion of the results of the effect of dynamic correlation, and we finally conclude with recommendations on how to

include dynamic correlation effects in the NOCI-Fragments approach, in particular for the study of the singlet fission probability.

4.2. CORRECTION TO THE NONORTHOGONAL HAMILTONIAN

ASSUME we use a CASSCF wavefunction to describe each molecule in our cluster. So each electronic state ‘ κ ’ of each molecule ‘ Ξ ’ is described by some wavefunction Ψ_{κ}^{Ξ} . A many-electron basis function (MEBF) is a spin-adapted, antisymmetrized product of these molecular wavefunctions. For example, in a dimer used to study the singlet fission process we can have $\Xi = A, B$ and $\kappa = S_0, S_1, T_1$, giving us the following MEBFs: $\Psi_{S_0}^A \Psi_{S_0}^B, \Psi_{S_0}^A \Psi_{S_1}^B, \Psi_{T_1}^A \Psi_{T_1}^B$, etc. For brevity, let us change notation and write the MEBFs in this list as; Ψ_1, Ψ_2, Ψ_3 , etc. The MEBFs here are neither normalized nor restricted to be orthogonal to one another. The Hamiltonian matrix written using these MEBFs will then look like,

$$\mathbf{H} = \begin{bmatrix} \langle \Psi_1 | \hat{H} | \Psi_1 \rangle & \langle \Psi_1 | \hat{H} | \Psi_2 \rangle & \dots & \langle \Psi_1 | \hat{H} | \Psi_n \rangle \\ \langle \Psi_2 | \hat{H} | \Psi_1 \rangle & \langle \Psi_2 | \hat{H} | \Psi_2 \rangle & \dots & \langle \Psi_2 | \hat{H} | \Psi_n \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \Psi_n | \hat{H} | \Psi_1 \rangle & \langle \Psi_n | \hat{H} | \Psi_2 \rangle & \dots & \langle \Psi_n | \hat{H} | \Psi_n \rangle \end{bmatrix} \quad (4.1)$$

The corresponding overlap matrix is,

$$\mathbf{S} = \begin{bmatrix} \langle \Psi_1 | \Psi_1 \rangle & \langle \Psi_1 | \Psi_2 \rangle & \dots & \langle \Psi_1 | \Psi_n \rangle \\ \langle \Psi_2 | \Psi_1 \rangle & \langle \Psi_2 | \Psi_2 \rangle & \dots & \langle \Psi_2 | \Psi_n \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \Psi_n | \Psi_1 \rangle & \langle \Psi_n | \Psi_2 \rangle & \dots & \langle \Psi_n | \Psi_n \rangle \end{bmatrix} \quad (4.2)$$

Prior to the NOCI procedure, we perform the calculations to obtain the correlated energies for the different molecular electronic states that include both static and dynamic electron correlation e.g., using CASPT2 [36, 37], NEVPT2, MRCI etc. The shift (δE_i) for a particular MEBF i that is a product of the molecular wavefunctions Ψ_k^A and Ψ_l^B is then roughly the sum of the correlation energies (ϵ) that are obtained for the corresponding molecular electronic states of the molecules,

$$\delta E_i = \epsilon_k^A + \epsilon_l^B. \quad (4.3)$$

Since the Hamiltonian is not expressed in an orthogonal basis, we cannot perform a straightforward ‘shift’ of the energies of the MEBFs (the diagonal Hamiltonian matrix elements). The reason is that applying a shift on the diagonal matrix elements of a matrix expressed in a nonorthogonal basis introduces an additional, unphysical change in the energy differences of the NOCI states (see appendix). For this reason we first transform the NOCI matrix to an orthogonal basis by a symmetric orthogonalization [38], where this unphysical energy shift is not present. First, we diagonalize the overlap matrix,

$$\mathbf{s} = \mathbf{U}^\dagger \mathbf{S} \mathbf{U} \quad (4.4)$$

and form the orthogonalizing transformation $\mathbf{S}^{-\frac{1}{2}}$,

$$\mathbf{S}^{-\frac{1}{2}} = \mathbf{U} \mathbf{s}^{-\frac{1}{2}} \mathbf{U}^\dagger. \quad (4.5)$$

The matrix $\mathbf{S}^{-\frac{1}{2}}$ is used to orthogonalize the Hamiltonian matrix,

$$\mathbf{H}' = (\mathbf{S}^{-\frac{1}{2}})^\dagger \mathbf{H} (\mathbf{S}^{-\frac{1}{2}}) \quad (4.6)$$

giving us the final orthogonalized Hamiltonian matrix,

$$\mathbf{H}' = \begin{bmatrix} \langle \Psi'_1 | \hat{H} | \Psi'_1 \rangle & \langle \Psi'_1 | \hat{H} | \Psi'_2 \rangle & \dots & \langle \Psi'_1 | \hat{H} | \Psi'_n \rangle \\ \langle \Psi'_2 | \hat{H} | \Psi'_1 \rangle & \langle \Psi'_2 | \hat{H} | \Psi'_2 \rangle & \dots & \langle \Psi'_2 | \hat{H} | \Psi'_n \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \Psi'_n | \hat{H} | \Psi'_1 \rangle & \langle \Psi'_n | \hat{H} | \Psi'_2 \rangle & \dots & \langle \Psi'_n | \hat{H} | \Psi'_n \rangle \end{bmatrix} \quad (4.7)$$

where the vector,

$$\Psi' = \mathbf{S}^{-\frac{1}{2}} \times \Psi. \quad (4.8)$$

The Hamiltonian $\mathbf{H}'$ is now written in the basis of the orthogonalized MEBFs $\Psi'_1, \Psi'_2, \Psi'_3, \dots, \Psi'_n$ with each being a linear combination of the original nonorthogonal MEBFs. For example,

$$\Psi'_\mu = c_{\mu 1} \Psi_1 + c_{\mu 2} \Psi_2 + c_{\mu 3} \Psi_3, \dots, c_{\mu n} \Psi_n \quad (4.9)$$

where $c_{\mu i}$ are elements of the orthogonalizing transformation matrix ($\mathbf{S}^{-\frac{1}{2}}$), i.e., coefficients for each original nonorthogonal MEBF that make up the orthogonal MEBF Ψ'_μ . Both bases, primed and unprimed, span the same space.

The relative importance of each original, nonorthogonal MEBF in the orthogonal MEBF cannot be determined directly as the square of the coefficients in this equation. The nonorthogonality of the MEBFs makes that the sum of the squares does not necessarily equal one. The Gallup-Norbeck scheme [39] provides a robust and easy recipe for determining the weights of mutually nonorthogonal basis states, which are calculated using the inverse overlap matrix ($\mathbf{S}^{-1}$) and results in only positive valued weights, unlike the Chirgwin and Coulson scheme [40]. The Gallup-Norbeck weight $\omega_{\mu i}^{GN}$ for the i th original nonorthogonal MEBF in the μ th orthonormal MEBF is,

$$\omega_{\mu i}^{GN} = \frac{N_\mu^{GN} \cdot c_{\mu i}^2}{(\mathbf{S}^{-1})_{ii}} \quad (4.10)$$

where the normalization constant of the μ -th orthogonal MEBF is given by

$$N_\mu^{GN} = \frac{1}{\sum_i c_{\mu i}^2 / (\mathbf{S}^{-1})_{ii}}. \quad (4.11)$$

The shift can now be applied to the diagonal elements of the orthogonalized matrix $\mathbf{H}'$ to give us $\mathbf{H}''$,

$$(\mathbf{H}'')_{\mu\mu} = (\mathbf{H}')_{\mu\mu} + \sum_i (\omega_{\mu i}^{GN} \cdot \delta E_i) \quad (4.12)$$

$\mathbf{H}''$ now contains the matrix elements in the orthogonal basis, and can be diagonalized to obtain the final NOCI energies and wavefunctions. To calculate the electronic couplings

between states and the excitation energies to diabatic states, we transform the matrix back to the original nonorthogonal basis.

$$\mathbf{H}_{\text{corr}} = (\mathbf{S}^{-\frac{1}{2}}) \mathbf{H}'' (\mathbf{S}^{-\frac{1}{2}})^\dagger \quad (4.13)$$

We now have the Hamiltonian matrix (in the basis of the nonorthogonal MEBFs) which contains the dynamic correlation energy contribution.

4.3. DYNAMIC CORRELATION DRESSED WAVEFUNCTION

NUMEROUS determinants with small coefficients are included in the CI-expansion of a correlated wavefunction. This means that the Hilbert space that contains the determinants in a correlated wavefunction is very large. The effect on the wavefunction brought about by these determinants can be mimicked using a shorter CI-expansion through **effective Hamiltonian theory**. Here, we model a system using only a part of the Hilbert space while having the rest as an ‘effective’ term included in the Hamiltonian [41]. This has the advantage that we retain the quality of the full space in a space with a much smaller dimension. In addition, this also provides a better physical picture of the underlying chemical concepts.

In the context of our correlated wavefunction that has to be described in a more compact way, let us start with a Hamiltonian acting on a Hilbert space of dimension m giving m eigenvalues (for example, in a CASSCF type description, which does not include dynamic correlation). This reduced space has eigenvalues E_i and eigenvectors Ψ_i .

$$H|\Psi_i\rangle = E_i|\Psi_i\rangle \quad (4.14)$$

A more complete description, with dynamic correlation included, is obtained from the Hilbert space spanned by the wavefunctions Φ_i with energies E'_i ,

$$H|\Phi_i\rangle = E'_i|\Phi_i\rangle \quad (4.15)$$

This can be obtained through the use of a lengthy (full-)CI expansion. Alternatively, the whole space can be split into subspaces and project the ‘outer’ space ($\mathbb{S}'$) into the smaller space ($\mathbb{S}_0$) conveniently chosen to have the same dimension (and maximum overlap) with the smaller Hilbert space defined in Eq. 4.14. We represent this division as,

$$\mathbb{S} = \mathbb{S}_0 \oplus \mathbb{S}'. \quad (4.16)$$

We project m eigenfunctions of H in $\mathbb{S}$ into m eigenfunctions of H in $\mathbb{S}_0$ as schematically shown in Fig. 4.1. This is done using the projection operator $\mathbf{P}_0$,

$$\mathbf{P}_0 = \sum_{i=1}^m |\Psi_i\rangle\langle\Psi_i|. \quad (4.17)$$

Figure 4.1 | Projection of m eigenfunctions of H in $\mathbb{S}$ into m eigenfunctions of H in $\mathbb{S}_0$ giving us the space spanned by $|\tilde{\Psi}_i\rangle$.

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This results in a set of nonorthogonal functions $\tilde{\Psi}_i$ that contain the full description of the system for this limited subset of eigenstates. These are then orthogonalized,

$$\tilde{\Psi}_i^\perp = S^{-\frac{1}{2}} \tilde{\Psi}_i \quad (4.18)$$

and these orthogonalized vectors are used to construct the effective Hamiltonian H_{eff} ,

$$H_{eff} = \sum_{i=1}^m |\tilde{\Psi}_i^\perp\rangle E'_i \langle \tilde{\Psi}_i^\perp| \quad (4.19)$$

Diagonalization of H_{eff} gives m of the (original) n E'_i eigenvalues. H_{eff} acts only on the reduced space (space spanned by $\tilde{\Psi}_i$). The eigenvalues of the effective Hamiltonian are equal to the eigenvalues of the full eigenspace. The wavefunction is of dimension m but is a projection of an n dimensional wavefunction on the model space. The DCDCAS (Dynamic Correlation Dressed Complete Active Space) method [35] uses intermediate Hamiltonian theory [42]. Here, the model space $\mathbb{S}_0$ is the CAS, and the dynamic correlation is added as a 'dressing' from a NEVPT2 (n-electron valence state perturbation theory) [43–45] calculation.

4.4. COMPUTATIONAL INFORMATION

THE molecules we studied were benzene, pyridine, naphthalene, anthracene, tetracene, and pentacene. These were chosen as they belong to the class of organic molecules which have been of interest to our research on singlet fission [13, 16, 17, 46]. The geometry of the pyridine molecule was optimized using DFT with B3LYP/6-311G**. The molecular geometries of benzene, naphthalene, and anthracene were optimized with BP86/def2-TZVP while those of tetracene and pentacene were optimized using B3LYP/def2-TZVP.

CASSCF and CASPT2 calculations on benzene, naphthalene, tetracene, and pentacene were performed using ANO-RCC bases (C:5s4p2d1f, H:3s2p1d) with OpenMOLCAS [33]. For anthracene, a smaller ANO-s (C:3s2p1d; H:2s1p) basis was used. The CAS (only π orbitals) chosen for naphthalene and anthracene were (6,6), (8,8), and (10,10). In benzene only a CAS(6,6) was performed. The CASPT2 calculation used no level shift, and IPEA shift=0.25. These calculations were done on each molecule for 5 electronic states, viz., $S_0, S_1, T_1, D_1^+, D_1^-$. For the NOCI calculation, a CAS(6,6) wavefunction was used to describe

each electronic state for all molecules except naphthalene for which CAS(8,8) monomer wavefunctions were computed to describe the monomer electronic states.

We generated the benzene dimer necessary for our NOCI-Fragments calculations by shifting one of the monomers $\Delta x = 2.25$ Å and $\Delta y = 1.25$ Å relative to the other, keeping $\Delta z = 3.0$ Å. The pyridine dimer was formed by placing the second unit at a perpendicular distance (along z -axis) of 4 Å to the first and sliding it by 7 Å along the x -axis and 5 Å along the y -axis and subsequently varying the angle between the molecular planes of the two molecules as shown in Figure 4.2. The naphthalene and anthracene molecules were shifted $\Delta x = 1.50$ Å, $\Delta y = 1.35$ Å, and $\Delta x = \Delta y = 1.97$ Å respectively, to generate the corresponding dimers.

Figure 4.2 | Ball and stick diagrams of the (a) naphthalene dimer shifted by $\Delta x = 1.50$ Å $\Delta y = 1.35$ Å while increasing the inter-molecular distance Δz from $\Delta z = 3.00$ Å to 3.75 Å in steps of 0.25 Å, and (b) slip stack arranged pyridine dimer with the angle between the molecular planes of the dimers being varied.

The shifts along the x - and y -axis were chosen such as to maximize the coupling between the S_0S_1 and 1TT MEBFs for a fixed perpendicular distance of 3.00 Å for benzene, naphthalene and anthracene. The displacements of the larger acenes (tetracene and pentacene) were chosen in line with the results for the smaller ones, as an optimization of Δx and Δy is computationally very costly. The many-electron basis functions (MEBFs) generated for the NOCI were: S_0S_0 , S_1S_0 , S_0S_1 , 1TT , $D_1^+D_1^-$, $D_1^-D_1^+$. The electronic coupling is calculated between the S_0S_1 and 1TT states. The values of couplings between $S_0S_1 - ^1TT$ and $S_1S_0 - ^1TT$ were found to be similar for these arrangements, and hence are not studied separately. The Δz was then increased in steps of 0.25 Å to see the effect of the distance on the electronic coupling. The NOCI calculations were performed using the GNOME algorithm[47] implemented in the massively parallel, GPU-accelerated GronOR program [15]. We studied two types of couplings based on the different pathways in singlet fission; direct and CT-mediated. Using the procedure outlined from equation 4.4 to 4.13 we calculate the direct and CT mediated couplings. The process of evaluating couplings between diabatic states has been adapted from [16]. The S_0S_1 , S_1S_0 and 1TT MEBFs are dressed with the effect of the CT MEBFs for the CT-mediated coupling.

We obtain a 6×6 Hamiltonian matrix using these MEBFs that contains on the diagonal the energies of the diabatic states. The correlation energy shift ($E_{\text{CASPT2}} - E_{\text{CASSCF}}$) is introduced in the NOCI Hamiltonian matrix using the process outlined in section 4.2. The various shifts done used energies from CASPT2 (or NEVPT2) on CAS(6,6), CAS(8,8), etc. type wavefunctions. Throughout the rest of this work they are referred to as CASPT2(6,6), CASPT2(8,8), or NEVPT2(6,6) etc. The shifting was done using a subroutine that is part of GronOR. This utilized LAPACK routines for standard diagonalization and matrix inversion. The symmetric orthogonalization procedure was written in FORTRAN and utilized the above LAPACK routines. We also calculated the electronic couplings with the shifts of the diagonal Hamiltonian matrix elements but without the Gallup-Norbeck weights. The couplings turned out to be very similar (within hundredths of an meV) to the values when GN weights were used and hence are not shown separately. The NEVPT2 and DCD-CAS(2) calculations were performed using Orca [48]. The DCD-CAS(2) wavefunction is written out in terms of electronic configurations (grouping together the CSFs and determinants by their orbital occupation), as opposed to determinants in the Molcas CASSCF wavefunction. Therefore an intermediate step was taken to convert the wavefunction expressed in electronic configurations as a list of determinants. In most cases this is not especially difficult, except for those configurations that have contributions from more than one CSF for example the electronic configuration $\phi_a^1 \phi_b^1 \phi_c^1 \phi_d^1$ consists of two CSFs;

$$\begin{aligned} \Psi_{\text{CSF}_1} = & \frac{1}{6} \left(\phi_1^\alpha \phi_2^\alpha \phi_3^\beta \phi_4^\beta + \phi_1^\beta \phi_2^\beta \phi_3^\alpha \phi_4^\alpha \right) \\ & - \frac{1}{12} \left(\phi_1^\alpha \phi_2^\beta \phi_3^\alpha \phi_4^\beta + \phi_1^\alpha \phi_2^\beta \phi_3^\beta \phi_4^\alpha + \phi_1^\beta \phi_2^\alpha \phi_3^\alpha \phi_4^\beta + \phi_1^\beta \phi_2^\alpha \phi_3^\beta \phi_4^\alpha \right) \end{aligned} \quad (4.20)$$

and

$$\Psi_{\text{CSF}_2} = \frac{1}{4} \left(\phi_1^\alpha \phi_2^\beta \phi_3^\alpha \phi_4^\beta - \phi_1^\alpha \phi_2^\beta \phi_3^\beta \phi_4^\alpha - \phi_1^\beta \phi_2^\alpha \phi_3^\alpha \phi_4^\beta + \phi_1^\beta \phi_2^\alpha \phi_3^\beta \phi_4^\alpha \right) \quad (4.21)$$

in the case of a singlet wavefunction, where α and β represent the two one-electron spin states. In these cases we assumed that the relative importance of the contributing CSFs is equal to that of the corresponding ‘undressed’ CASSCF wavefunction. The effect of this choice on the final result is small as the configurations with more than one CSF have small weights in the DCD-CAS wavefunction in the cases that we have studied.

4.5. RESULTS AND DISCUSSION

4.5.1. SHIFTING OF DIAGONAL

RESULTS of the calculations done on the naphthalene molecule are shown in this section. The data on the other acenes in our study, viz, anthracene, tetracene, and pentacene showed similar trends and they can be found in the supplementary information. We performed CASPT2 calculations on different monomer electronic states of each of the molecules. We compare the CASSCF and CASPT2 energies of S_0 , S_1 , T_1 , D_1^+ , and D_1^- for CAS(6,6), CAS(8,8), CAS(10,10) in table 4.1. The table shows that both the CASSCF and CASPT2 relative energies do not change significantly with increasing active space for all states except S_1 . The CASPT2 energy of the latter states appears to be converged

with a CAS(8,8) reference wavefunction, but the CASSCF energy at this level is still quite different from the full- π active space with 10 orbitals and 10 electrons. Nevertheless, we have used the CAS(8,8) wavefunction in the GronOR calculations as best compromise between accuracy and computational efficiency. For the other molecules, the CAS(6,6) relative energies of the S_1 state (and the others as well) are more similar to the largest CAS results, and hence, we have used the simpler CAS(6,6) wavefunctions in those cases.

Table 4.1 | CAS(6,6), (8,8), (10,10) and corresponding CASPT2 relative energies (eV) for the $S_0, S_1, T_1, D_1^+,$ and D_1^- monomer states of naphthalene w.r.t the ground state S_0 .

State	CAS(6,6)	CASPT2(6,6)	CAS(8,8)	CASPT2(8,8)	CAS(10,10)	CASPT2(10,10)
S_0	0.00	0.00	0.00	0.00	0.00	0.00
S_1	6.38	5.02	5.24	4.25	4.31	4.27
T_1	3.50	3.34	3.32	3.22	3.10	3.23
D^+	7.51	8.27	7.56	8.19	7.41	8.18
D^-	1.91	0.64	2.28	0.50	2.28	0.47

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MEBFs of type $S_0S_0, S_1S_0, S_0S_1, {}^1TT, D_1^+D_1^-, D_1^-D_1^+$ were formed as spin-adapted, antisymmetrized products of the constituent monomer wavefunctions. We performed a 6×6 NOCI calculation using these MEBFs. We look at the variation of the direct electronic coupling matrix element (γ) for perturbatively corrected MEBFs using the correction obtained from CASPT2(6,6), CASPT2(8,8), and CASPT2(10,10) calculations over different intermolecular distances along the z -axis. The dynamic correlation was included by shifting the diagonal matrix elements in the NOCI matrix as explained in the theory section. Table 4.2 shows the absolute values of the direct electronic coupling when energy shifts from CASPT2(6,6), (8,8), and (10,10) are applied to the NOCI Hamiltonian, together with the unshifted values, for different inter-molecular distances.

Table 4.2 | Absolute values of the direct electronic coupling γ (in meV) of the unshifted CAS(6,6) Hamiltonian, and the Hamiltonian shifted with CASPT2 energies of CASPT2(6,6), (8,8), and (10,10) for a naphthalene dimer, as function of the inter-molecular distance.

Distance [$\text{\AA}$]	Unshifted		Shifted	
	CAS(6,6)	CASPT2(6,6)	CASPT2(8,8)	CASPT2(10,10)
3.00	13.9	14.1	14.0	14.1
3.25	7.2	7.3	7.3	7.3
3.50	3.6	3.7	3.7	3.7
3.75	1.8	1.8	1.8	1.8

At each inter-molecular distance, the difference in electronic coupling between unshifted and (the most) shifted case was no more than one tenth of an meV. These changes in γ are negligible and these results suggest that the direct electronic singlet fission coupling is unaffected by applying a diagonal shift. However, the energies of the molecular states and in consequence the MEBFs are affected considerably by the shift, and this

influences the energies and the compositions of the final cluster wavefunctions. The final NOCI energies and wavefunctions from the unshifted and shifted NOCI Hamiltonians are shown in table 4.3. In the unshifted case, the energies of the different types of MEBFs (S_0S_1/S_1S_0 ; 1TT and $D_1^+D_1^-/D_1^-D_1^+$) are well separated, and hence, the final NOCI wavefunctions do not show large mixing between these groups of MEBFs. However, the S_0S_1 and S_1S_0 are combined in almost equal parts in root 2 and 3 and describe so-called excitonic resonant states [49]. A similar effect is observed for the CT-dominated roots, which therefore can be labeled as charge resonance states. While the interaction between the S_0S_1 and S_1S_0 MEBFs is small, leading to degenerate NOCI solutions, there is a finite interaction between the CT MEBFs, which results in a splitting of 0.14 eV for the highest two roots.

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Consider for example the wavefunctions 4, 5, 6 in the unshifted case (Table 4.3): these correspond to the 1TT , and the plus and minus combinations of the $D_1^+D_1^-$ and $D_1^-D_1^+$ MEBFs (based on their CI coefficients in the wavefunction). Wavefunction 4 is ‘pure’ in the sense that the largest contributor is just the 1TT MEBF, with small contributions from the charge transfer states. Upon applying the CASPT2(6,6) shift, considerable mixing occurs between the 1TT MEBF and the charge transfer states, and concomitantly, the minus combination of the charge transfer states, state 6, gains a significant 1TT character. The 1TT MEBF has a coefficient of 0.71 in wavefunction 4, and a coefficient of 0.70 in wavefunction 6. The charge transfer states have coefficients of 0.45 and 0.52 in wavefunctions 4 and 6, respectively. The other charge transfer state 5 shows zero weight for the 1TT MEBF because of the inversion symmetry with respect to the midpoint between the two fragments.

Table 4.3 | NOCI energies (ΔE in eV) and wavefunctions (written in terms of the MEBFs; 1- S_0S_0 , 2- S_0S_1 , 3- S_1S_0 , 4- 1TT , 5- $D_1^+D_1^-$, 6- $D_1^-D_1^+$) for unshifted CAS(6,6), and shifted with CASPT2 on CAS(6,6), CAS(8,8), and CAS(10,10) wavefunctions of a dimer of two naphthalene molecules, separated by $\Delta z = 3.00$ Å.

	State	1	2	3	4	5	6
unshifted	ΔE	0.00	4.13	4.13	5.01	6.03	6.17
	S_0S_0	-0.996	0.000	-0.024	0.040	0.000	0.099
	S_0S_1	0.003	0.712	-0.685	-0.075	0.096	-0.102
	S_1S_0	-0.003	0.689	0.707	0.075	0.096	0.102
	1TT	0.008	0.001	-0.056	0.950	0.000	-0.309
	$D_1^+D_1^-$	0.036	0.081	-0.094	0.182	-0.703	0.677
	$D_1^-D_1^+$	-0.036	0.077	0.096	-0.182	-0.703	-0.677
CASPT2(6,6)	ΔE	0.00	3.90	3.91	4.85	5.12	5.48
	S_0S_0	-0.994	-0.037	0.000	0.088	0.000	-0.080
	S_0S_1	0.004	-0.684	0.691	-0.157	-0.147	0.098
	S_1S_0	-0.004	0.682	0.693	0.157	-0.147	-0.098
	1TT	0.008	-0.063	0.000	0.712	0.000	0.700
	$D_1^+D_1^-$	0.046	-0.154	0.130	0.454	0.696	-0.520
	$D_1^-D_1^+$	-0.046	0.154	0.130	-0.454	0.696	0.520
CASPT2(8,8)	ΔE	0.00	3.16	3.16	4.61	4.88	5.25
	S_0S_0	-0.993	0.000	-0.031	0.095	0.000	-0.082
	S_0S_1	0.006	0.703	-0.692	-0.105	-0.105	0.074
	S_1S_0	-0.006	0.695	0.700	0.105	-0.105	-0.074
	1TT	0.009	0.000	-0.031	0.705	0.000	0.710
	$D_1^+D_1^-$	0.049	0.088	-0.101	0.472	0.702	-0.517
	$D_1^-D_1^+$	-0.049	0.087	0.102	-0.472	0.702	0.517
CASPT2(10,10)	ΔE	0.00	3.18	3.18	4.60	4.85	5.24
	S_0S_0	-0.993	0.000	0.032	0.099	0.000	0.078
	S_0S_1	0.006	0.705	0.689	-0.111	-0.108	-0.071
	S_1S_0	-0.006	0.693	-0.701	0.111	-0.108	0.071
	1TT	0.009	0.000	0.032	0.673	0.000	-0.740
	$D_1^+D_1^-$	0.050	0.092	0.104	0.494	0.702	0.495
	$D_1^-D_1^+$	-0.050	0.090	-0.106	-0.494	0.702	-0.495

Although the shift has a negligible effect on the direct electronic coupling, there is still a considerable change in the wavefunction. This observation prompted us to examine the charge-transfer (CT) mediated coupling for singlet fission. As shown in the theory chapter 2, there are two alternative pathways for the formation of the 1TT state. There is the direct pathway where the CT MEBFs do not play a role and the CT mediated pathway where there is a significant contribution from the CT configurations, known as the superexchange path for its analogy with the role of the CT in the coupling between localized magnetic moments.

To examine the latter mechanism, we first let the individual S_0S_1 , S_1S_0 , and 1TT MEBFs interact with the two CT MEBFs in three separate NOCI calculations, to obtain three new MEBFs that include the CT states. Subsequently, the Hamiltonian matrix is transformed to the basis of these new MEBFs, and the electronic coupling is evaluated again, but now between the diabatic states that are dressed with the effect of the CT MEBFs.

Table 4.4 shows the CT-mediated couplings for the naphthalene dimer for various shifts and inter-molecular distances. First and foremost, it can be seen that the charge transfer mediated coupling is much larger than the direct coupling, independent of the fact that shifts are applied to include the effect of dynamic correlation. The second interesting observation is that contrary to the direct coupling, the shifting of the diagonal matrix elements does lead to changes in the values of the CT mediated coupling.

The CT mediated electronic coupling is sensitive for the applied shift, which is particularly visible at an intermolecular distance of 3.00 Å: it decreases by 10 meV for the CASPT2(6,6) shift, then increases again by 9 meV for the CASPT2(8,8) shift, and ultimately decreases again by 5 meV when the CASPT2(10,10) shift is applied. At other inter-molecular distances, the shifts have a more uniform effect, and they consistently lead to an increase in CT-mediated coupling.

Table 4.4 | Absolute values of CT-mediated coupling (in meV) of unshifted Hamiltonian, Hamiltonian shifted using energies from CASPT2(6,6), (8,8), and (10,10) for a naphthalene dimer as function of the inter-molecular distance.

Distance [Å]	unshifted	CASPT2(6,6)	CASPT2(8,8)	CASPT2(10,10)
3.00	53.9	43.1	52.3	47.6
3.25	27.3	40.3	45.0	41.0
3.50	13.2	36.3	36.0	38.9
3.75	6.2	18.5	18.4	20.9

The CT-mediated electronic couplings and final cluster wavefunctions vary due to the inclusion of dynamic correlation, because this inclusion changes the energy differences between the MEBFs, and therefore affects the mixing of the MEBFs. The change in electronic coupling also depends on the interaction matrix elements between the MEBFs and hence it is difficult to systematically increase or decrease the electronic coupling in a straightforward manner.

As a last example, we have studied a dimer that does not have inversion symmetry. We have calculated the electronic coupling in a slip-stack arrangement of the pyridine

dimer as a function of the angle between the planes containing the monomers as shown in Fig. 4.2b. A CASPT2(6,6) shift was applied and the comparison between the direct and CT-mediated electronic coupling for increasing interplanar angle is shown in table 4.5. As expected, only the CT-mediated electronic couplings are affected by the shift. Note that maximum electronic coupling is found at different angles for the direct and the charge-transfer mediated electronic couplings. The direct electronic coupling has its maximum absolute value around 40°, and the CT-mediated electronic coupling at 15°.

Table 4.5 | Absolute values of direct and CT-mediated electronic couplings (in meV) for a pyridine dimer as function of the angle between the monomer fragments.

Angle [deg]	Direct		CT-mediated	
	unshifted	shifted	unshifted	shifted
0	0.2	0.2	1.9	6.2
5	0.04	0.03	2.2	6.8
10	0.4	0.3	2.2	7.2
15	0.7	0.7	2.1	7.6
20	1.4	1.4	1.3	7.0
25	2.1	2.1	0.3	6.5
30	2.7	2.7	1.0	5.7
35	3.2	3.2	2.3	4.7
40	3.4	3.4	3.4	3.4
45	3.1	3.1	3.8	2.2

The wavefunctions obtained after applying the shift on the Hamiltonian matrix for each angle (in the supplementary information) show the extent of delocalization of the CT-states. Although the energies of the 1TT and charge transfer MEBFs come very close (within 0.3 and 0.5 eV with $D_1^+ D_1^-$ and $D_1^- D_1^+$ respectively), the NOCI wavefunctions seem to be very localized and do not show the mixing as was found for the acenes, where the cluster possesses an inversion center, causing the delocalization of the final NOCI wavefunction over the two constituting fragments.

Thus, the CT-mediated electronic coupling is shown to be sensitive to inclusion of dynamic correlation corrections to the energies of the MEBFs, while the direct electronic coupling is not significantly affected. However, the molecular wavefunctions that are used to build the MEBFs also change due to inclusion of dynamic correlation. To assess the significance of these changes in the CASSCF wavefunctions on the electronic couplings, we have replaced the CASSCF molecular wavefunctions by DCD-CAS(2) wavefunctions, which effectively contain dynamic correlation effects.

4.5.2. DYNAMIC CORRELATION DRESSED WAVEFUNCTION

The suitability of DCD-CAS(2) wavefunctions as the monomer wavefunctions to construct the MEBFs required for the NOCI-Fragments methods was tested for a dimer of benzene molecules. At first, we present the relative energies of the states that were obtained

using CAS(6,6) followed by CASPT2, using the ANO-RCC basis, and using the CAS(6,6), NEVPT2 [43–45] (which is employed in DCD-CAS(2) to complement the small model space spanned by the eigenvectors of the CASSCF and DCD-CAS(2) methods using the def2-TZVP basis set, for the benzene molecule (Table 4.6). The excitation energies obtained using the ANO-RCC basis set are virtually identical to those using the def2-TZVP basis set. The CASPT2, NEVPT2, and DCD-CAS(2) excitation energies are also very similar, indicating that the basis set and correlation treatments do not introduce any significant differences.

Table 4.6 | CAS(6,6), CASPT2, relative energies (in eV) using the ANO-RCC basis, and CAS(6,6), NEVPT2, and DCD-CAS(2) relative energies using def2-TZVP basis for the benzene molecule.

State	ANO-RCC		def2-TZVP		
	CAS(6,6)	CASPT2	CAS(6,6)	NEVPT2	DCD-CAS(2)
S_0	0.00	0.00	0.00	0.00	0.00
S_1	5.06	5.05	5.07	5.33	5.30
T_1	3.95	4.23	3.95	4.43	4.45
D_1^+	8.39	9.44	8.39	9.31	9.32
D_1^-	3.32	1.74	3.33	1.75	1.82

In Table 4.7 a comparison is given of the electronic couplings evaluated using MEBFs constructed from molecular CAS(6,6) wavefunctions, DCD-CAS(2) wavefunctions, and DCD-CAS(2) wavefunctions in which a shift has been applied in order to obtain the correct DCD-CAS(2) energies. The electronic coupling does not vary significantly with chosen wavefunction (CASSCF/DCD-CAS(2)) or when a shift is applied in the DCD-CAS(2) case. The electronic couplings evaluated using the MEBFs constructed using the CAS(6,6) shown here are essentially the ‘unshifted’ cases that have been discussed in the previous Tables 4.2, 4.8. The small differences are caused by the change of basis. The electronic coupling decreases steeply with increasing distance, as expected, but for all three methods, the changes are similar.

Table 4.7 | Direct $S_0S_1 -^1 TT$ electronic couplings (in meV) for a benzene dimer as function of the inter-molecular distance. Comparison between electronic couplings evaluated using MEBFs that were constructed from CAS(6,6), DCD-CAS(2), and DCD-CAS(2) shifted towards the DCD-CAS(2) energy differences.

Distance [Å]	CAS(6,6)	DCD-CAS(2)	
		unshifted	shifted
3.00	16.0	16.4	16.3
3.25	8.7	9.0	9.0
3.50	4.5	4.8	4.8
3.75	2.3	2.5	2.5

4.6. CONCLUSION AND OUTLOOK

THE NOCI-Fragments method is particularly suitable to study charge and energy transfer processes, such as singlet fission. The relevant quantities necessary for such a study are the vertical excitation energies and the electronic couplings between the diabatic states. To obtain reliable estimates of the excitation energies, the inclusion of dynamic correlation is required. The inclusion of dynamic correlation may also influence the electronic couplings between diabatic states. We include the effects of dynamic correlation in the NOCI-Fragments approach in two alternative ways, which are: 1) performing a shift of the energies of the MEBFs by the dynamical correlation energies (obtained from CASPT2 or NEVPT2), and 2) using a correlation dressed CAS molecular wavefunctions (DCD-CAS(2)) to construct the MEBFs.

The study shows that relative excitation energies of the MEBFs in NOCI-Fragments show marked differences (especially the energies of the CT MEBFs were affected) after dynamic correlation was included, but the effect on the direct electronic coupling for singlet fission is small. As a consequence of the significant change in energy of the CT MEBFs, the CT-mediated electronic couplings, together with the final cluster NOCI wavefunctions vary significantly. The use of correlation dressed wavefunctions, such as DCD-CAS(2) to construct the MEBFs does not further change the electronic couplings (direct nor CT-mediated). Hence, for the study of electronic couplings for singlet fission, CASSCF wavefunctions are suitable to construct the MEBFs and the effect of dynamical correlation can be introduced as a correction to the energies of the MEBFs. This correction is especially required for the study of the role of the charge transfer states in the singlet fission process.

4

4.7. APPENDIX: SHIFTING IN NOCI VS CI

Consider a trial wavefunction (Ψ) written in terms of two normalized basis functions (Φ),

$$\Psi = c_1 \Phi_1 + c_2 \Phi_2 \quad (4.22)$$

We can construct the secular equations to solve for the c_i ,

$$(H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 = 0 \quad (4.23)$$

$$(H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 = 0 \quad (4.24)$$

where $S_{ij} = \int \Phi_i \Phi_j d\tau$ and $H_{ij} = \int \Phi_i \hat{H} \Phi_j d\tau$. The secular determinant,

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad (4.25)$$

Since the basis functions are real and H is hermitian we can take $S_{12} = S_{21} \equiv S$ and $H_{12} = H_{21} \equiv V$, and $S_{11} = S_{22} = 1$ because they are normalized. Thus we get,

$$\begin{vmatrix} H_{11} - E & V - ES \\ V - ES & H_{22} - E \end{vmatrix} = 0 \quad (4.26)$$

Solving this for E , we obtain two NOCI energies $E_{1,2}^{\text{NOCI}}$,

$$E_{1,2}^{\text{NOCI}} = \frac{1}{S^2} \left[H_{11} + \frac{1}{2}\Delta - VS \pm \sqrt{S^2(H_{11} + \frac{\Delta}{2})^2 + (1-S^2)(\frac{\Delta}{2})^2 - 2SV(H_{11} + \frac{\Delta}{2}) + V^2} \right] \quad (4.27)$$

where $\Delta = H_{22} - H_{11}$. We see here that the splitting of NOCI energies ($E_2 - E_1$) depends on Δ , V , and also H_{11} . Hence, we can not arbitrarily shift H_{11} . Comparing this to the case of an energy expansion for a CI wavefunction (taking overlap terms to be zero in the NOCI energy equation),

$$E_{1,2}^{\text{CI}} = H_{11} + \frac{\Delta}{2} \pm \frac{1}{2} \sqrt{\Delta^2 + 4V^2}. \quad (4.28)$$

This shows no dependence of the splitting on H_{11} . Therefore, we can also choose an arbitrary value for the H_{11} , as long as we keep the Δ unchanged.

4.8. SUPPLEMENTARY INFORMATION

Table 4.8 | $S_0S_1 -^1 TT$ Direct and CT-mediated coupling (in meV) for a naphthalene dimer as function of the inter-molecular distance.

	Distance [Å]	Direct		CT-mediated	
		unshifted	shifted	unshifted	shifted
CAS(6,6)	3.00	13.9	14.1	53.9	43.1
	3.25	7.2	7.3	27.3	40.3
	3.50	3.6	3.7	13.2	36.3
	3.75	1.8	1.8	6.2	18.5
CAS(8,8)	3.00	13.9	14.0	53.9	52.3
	3.25	7.2	7.3	27.3	45.0
	3.50	3.6	3.7	13.2	36.0
	3.75	1.8	1.8	6.2	18.4
CAS(10,10)	3.00	-13.9	14.0	53.9	47.6
	3.25	7.2	7.3	27.3	41.0
	3.50	3.6	3.7	13.2	38.9
	3.75	1.8	1.8	6.2	20.9

Next we do the same comparisons for anthracene, but using CAS(6,6), CAS(10,10), and CAS(14,14).

Table 4.9 | $S_0S_1 -^1 TT$ coupling (in meV) for a anthracene dimer as function of the inter-molecular distance. Molecules are displaced by $\Delta x = \Delta y = 1.97 \text{ \AA}$.

Distance [Å]	unshifted	CAS(6,6)	CAS(10,10)	CAS(14,14)
3.0	20.12	20.01	20.03	20.06
3.25	11.04	10.98	10.99	11.01
3.50	5.88	5.84	5.85	5.86
3.75	3.05	3.03	3.04	3.04

Table 4.10 | CASSCF and CASPT2 relative energies for monomer states of anthracene.

State	CAS(6,6)	PT2	CAS(10,10)	PT2	CAS(14,14)	PT2
S_0	0.0	0.0	0.0	0.0	0.0	0.0
S_1	4.8	3.8	5.0	3.8	5.3	3.6
T_1	2.9	2.3	2.5	2.5	2.4	2.4
D_1^+	6.8	7.5	6.7	7.6	6.7	7.4
D_1^-	1.3	0.2	1.4	0.2	1.6	0.3

Table 4.11 | NOCI energies (ΔE in eV) and wavefunctions (written in terms of the MEBFs; S_0S_0 , S_0S_1 , S_1S_0 , 1TT , $D_1^+D_1^-$, $D_1^-D_1^+$) for unshifted, and shifted with CASPT2 on CAS(6,6), CAS(10,10), and CAS(14,14) wavefunctions of anthracene at 3.00 Å.

	State	1	2	3	4	5	6
unshifted	ΔE	0.00	4.61	4.68	5.63	5.84	6.09
	S_0S_0	-0.997	-0.016	0.000	-0.074	0.000	-0.054
	S_0S_1	0.016	0.623	0.612	-0.302	-0.357	-0.151
	S_1S_0	-0.016	-0.623	0.612	0.302	-0.357	0.152
	1TT	0.002	-0.087	0.000	-0.585	0.000	0.807
	$D_1^+D_1^-$	0.029	-0.291	0.316	-0.493	0.635	-0.418
	$D_1^-D_1^+$	-0.029	0.291	0.316	0.493	0.635	0.418
CASPT2(6,6)	ΔE	0.00	3.64	3.72	4.63	5.00	5.13
	S_0S_0	-0.996	-0.009	0.000	0.060	0.000	-0.085
	S_0S_1	0.019	0.642	0.636	0.214	-0.313	-0.207
	S_1S_0	-0.019	-0.642	0.636	-0.214	-0.313	0.207
	1TT	0.003	-0.089	0.000	0.818	0.000	0.569
	$D_1^+D_1^-$	0.036	-0.249	0.271	0.340	0.655	-0.569
	$D_1^-D_1^+$	-0.036	0.249	0.271	-0.340	0.655	0.569
CASPT2(8,8)	ΔE	0.00	3.68	3.76	4.85	5.10	5.31
	S_0S_0	-0.996	0.006	0.000	-0.074	0.000	0.070
	S_0S_1	0.019	-0.651	0.644	-0.228	-0.296	0.158
	S_1S_0	-0.019	0.651	0.644	0.228	-0.296	-0.158
	1TT	0.002	0.067	0.000	-0.690	0.000	-0.721
	$D_1^+D_1^-$	0.035	0.231	0.253	-0.455	0.662	0.491
	$D_1^-D_1^+$	-0.035	-0.231	0.253	0.455	0.662	-0.491
CASPT2(10,10)	ΔE	0.00	3.49	3.56	4.59	4.83	5.05
	S_0S_0	-0.995	0.010	0.000	-0.080	0.000	0.070
	S_0S_1	0.020	-0.642	0.633	-0.253	-0.318	0.160
	S_1S_0	-0.020	0.642	0.634	0.253	-0.318	-0.160
	1TT	0.003	0.075	0.000	-0.662	0.000	-0.746
	$D_1^+D_1^-$	0.038	0.252	0.276	-0.465	0.653	0.471
	$D_1^-D_1^+$	-0.038	-0.252	0.275	0.465	0.653	-0.471

Table 4.12 | $S_0S_1 -^1 TT$ CT-mediated coupling (in meV) for a anthracene dimer as function of the inter-molecular distance.

	Distance [Å]	Direct		CT-mediated	
		unshifted	shifted	unshifted	shifted
CAS(6,6)	3.00	20.1	20.0	23.6	72.9
	3.25	11.0	11.0	23.7	70.7
	3.50	5.9	5.8	22.7	63.7
	3.75	3.0	3.0	20.1	34.5
CAS(10,10)	3.00	20.1	20.0	23.6	51.8
	3.25	11.0	11.0	23.7	47.8
	3.50	5.9	5.9	22.3	44.0
	3.75	3.0	3.0	20.1	41.9
CAS(14,14)	3.00	20.1	20.1	23.6	42.0
	3.25	11.0	11.0	23.7	39.3
	3.50	5.9	5.9	22.3	36.2
	3.75	3.0	3.0	20.1	34.0

Table 4.13 | $S_0S_1 -^1 TT$ CT-mediated coupling (in meV) for a tetracene dimer as function of the inter-molecular distance.

	Distance [Å]	Direct		CT-mediated	
		unshifted	shifted	unshifted	shifted
CAS(6,6)	3.00	8.4	8.5	55.1	32.4
	3.25	4.3	4.4	31.6	29.1
	3.50	2.1	2.1	16.3	26.4
	3.75	1.0	1.0	7.7	25.4
CAS(10,10)	3.00	8.4	8.5	55.1	45.6
	3.25	4.3	4.4	31.6	42.6
	3.50	2.1	2.2	16.3	44.4
	3.75	1.0	1.0	7.7	21.1
CAS(14,14)	3.00	8.4	8.5	55.1	87.4
	3.25	4.3	4.3	31.6	48.8
	3.50	2.1	2.2	16.3	23.6
	3.75	1.0	1.0	7.7	10.4

Table 4.14 | $S_0S_1 - ^1TT$ CT-mediated coupling (in meV) for a pentacene dimer as function of the inter-molecular distance. CASPT2 done on CAS(8,8) wavefunction.

Distance [Å]	Direct		CT-mediated	
	unshifted	shifted	unshifted	shifted
3.00	20.0	20.1	65.0	70.5
3.25	10.7	10.8	39.1	40.8
3.50	5.6	5.6	21.8	21.8
3.75	2.8	2.8	11.3	11.0

We observe the change in the direct $S_0S_1 - ^1TT$ coupling from NOCI with unshifted and CASPT2(6,6) shifted Hamiltonian in two steps. First we use the ANO-RCC basis for our CASSCF and CASPT2 calculations on the monomers and the couplings hence obtained from the subsequent NOCI at different inter-molecular distances are in table 4.15. The couplings for benzene dimer varies little through the inclusion of dynamic correlation. This comes as no surprise since we saw that the difference in relative energies with and without PT2 for the S_0 , S_1 and T_1 states is low. The largest differences can be observed in the CT-states.

Table 4.15 | Direct $S_0S_1 - ^1TT$ coupling (in meV) for a benzene dimer for different inter-molecular distances. One molecule is placed relative to the other by $\Delta x = 2.25$ Å and $\Delta y = 1.25$ Å; CASSCF wavefunctions got using ANO-RCC basis.

Distance [Å]	unshifted	CASPT2(6,6)
3.00	15.1	15.3
3.25	8.0	8.1
3.50	4.1	4.2
3.75	2.1	2.1

We compare the final NOCI wavefunction for the benzene dimer. Table 4.16 shows the NOCI wavefunctions of an unshifted and CASPT2(6,6) shifted benzene dimer. The energy difference between the 1TT and CT-states are similar to what we saw in naphthalene, but the mixing between them is much smaller. The 1TT state has a coefficient of 0.93 and the CT-states have 0.23 in shifted wavefunction 4, and wavefunction 6 is predominantly a CT-state with weights 0.67 for CT and 0.36 for 1TT states respectively. The final NOCI wavefunctions of the case where a CASPT2(6,6) is used and where a DCD-CAS(2) wavefunction is used, with the same basis set, can provide a better insight into whether shifting the diagonal can produce the same effect as using a dynamic correlation dressed wavefunction. That is a conclusive test to find if we have to change the wavefunction to include dynamic correlation in NOCI-Fragments.

Table 4.16 | NOCI energies (ΔE in eV) and wavefunctions (written in terms of the MEBFs S_0S_0 , S_0S_1 , S_1S_0 , 1TT , $D_1^+D_1^-$, $D_1^-D_1^+$) for unshifted, and shifted with CASPT2 on CAS(6,6) wavefunctions of benzene when ANO-RCC basis was used.

	State	1	2	3	4	5	6
unshifted	ΔE	0.00	4.96	4.99	7.73	8.48	8.62
	S_0S_0	-0.999	0.000	-0.004	-0.029	0.000	0.065
	S_0S_1	0.000	0.707	-0.705	0.029	0.018	-0.054
	S_1S_0	0.000	0.707	0.705	-0.029	0.018	0.054
	1TT	-0.003	0.000	0.010	0.931	0.000	0.367
	$D_1^+D_1^-$	0.016	0.013	-0.039	-0.234	-0.708	0.667
	$D_1^-D_1^+$	-0.016	0.013	0.039	0.234	-0.707	-0.667
CAS(6,6)	ΔE	0.00	4.94	4.97	7.83	7.95	8.55
	S_0S_0	-0.995	0.000	-0.022	0.050	0.000	0.104
	S_0S_1	0.006	0.705	-0.702	-0.042	0.069	-0.074
	S_1S_0	-0.006	0.703	0.703	0.042	0.069	0.074
	1TT	0.009	0.000	-0.018	0.933	0.000	-0.361
	$D_1^+D_1^-$	0.041	0.052	-0.059	0.225	-0.706	0.668
	$D_1^-D_1^+$	-0.041	0.052	0.060	-0.225	-0.706	-0.668

Finally, we compare the direct and CT-mediated couplings for different inter-molecular distances in table 4.17. This further goes on to show that even the small change in wavefunction because of the shift as seen on table 4.16 impacts the coupling largely. Though it may be inconclusive to draw parallels between the extent of change in the wavefunction and its effect on the electronic couplings, we can say with certainty that the CT-mediated couplings are affected by the inclusion of dynamic correlation.

Table 4.17 | $S_0S_1-^1TT$ CT-mediated coupling (in meV) for a benzene dimer as function of the inter-molecular distance. CASPT2 done on CAS(6,6) wavefunction using ANO-RCC basis.

Distance [Å]	Direct		CT-mediated	
	unshifted	shifted	unshifted	shifted
3.00	15.1	15.3	73.4	56.7
3.25	8.0	8.1	37.5	28.6
3.50	4.1	4.2	18.0	13.9
3.75	2.0	2.1	8.4	6.6

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5

NOCI FOR CONDENSED PHASE

ABSTRACT

The applicability of nonorthogonal configuration interaction (NOCI) - Fragments had so far been limited to molecular clusters isolated in vacuum. This chapter provides the framework to perform NOCI calculations including effects of the environment in which the cluster is embedded. The two prominent effects of the surrounding environment, Pauli repulsion and polarization of the molecular fragments are studied. The effect of delocalization and localization of the excitations on the electronic couplings between diabatic states involved in singlet fission of a molecular cluster is also analyzed through a simple model. The study led to the conclusion that the (squared) local electronic coupling matrix element is a crucial parameter for the singlet fission process, both when the process involves localized and when it involves delocalized initial and final states.

5.1. INTRODUCTION

THEORETICAL chemistry is dedicated to the development and implementation of methods to accurately describe properties of molecules and extended systems, and their application to understand chemical and physical phenomena [1–3]. The tools developed often provide valuable insights that are otherwise difficult to obtain or are inaccessible through experiments. There exist several theoretical and computational methods based on quantum mechanics that range from high cost, high accuracy to low cost, low accuracy. Conventionally the study of molecular properties has been carried out in vacuum because the complete (quantum mechanical) description of the molecule(s) and the environment is often not feasible. But, studying molecular properties in vacuum is sometimes far from the description of materials in solids or solution, because we miss the essential physics that is associated with the interaction of the molecules with the environment. To bridge the gap between a description of an isolated molecule in vacuum where not all physics is described and a computationally expensive quantum mechanical description of the molecules in condensed phase, we make use of approximate ways to include the effect of an environment in the system.

In the case of an ordered system in the condensed phase, this is often approached by using DFT based methods; lattice (periodic) DFT calculations can be done with standard quantum chemical packages yielding chemical accuracy for many interesting ground state properties [4, 5]. In other cases, for example when the molecules exist in solution (as in the study of enzymatic reactions or homogeneous catalysis) or when there is a need for a higher level of theory to describe the electronic properties (like calculation of diabatic couplings in singlet fission) we can make use of an embedding which mimics the effect of the environment. One way to do this is using the hybrid quantum mechanical/molecular mechanics (QM/MM) method where the environment is treated classically and the effect is used as a force field in the quantum mechanically described molecule [6, 7].

Our study of NOCI-Fragments [8, 9] can be used for calculating accurate electronic coupling matrix elements and wavefunctions expressed in a few key diabatic states. The diabatic states are expressed using many-electron basis functions (MEBFs). Over the years, we have improved on the method to be more computationally feasible through the use of a reduced common molecular orbital basis [10]. We also studied the effect of dynamic correlation on NOCI energies and wavefunctions (see Chapter 4). As an application of NOCI-Fragments, our focus has been on a better understanding of the singlet fission process [11–13]. We hence evaluated the coupling between the singlet excited S_0S_1 and the multi-excitonic 1TT states, along with the vertical excitation energies for the relevant states. Singlet fission happens in a crystal or in solution, thus a study of singlet fission would be incomplete if only carried out in vacuum. Here, we try to simulate such an environment and explore possible effects that may be encountered when electronic couplings are evaluated using NOCI-Fragments. We also show here a model study that shows that the electronic coupling does not depend on choosing a localized or a delocalized starting point.

In condensed phase, the electrostatic effects of nearby nuclei and electron clouds on our test system can be mimicked by the use of a frozen density embedding (FDE) [14–17]. ‘Frozen’ (non-reactive) fragments, typically described using a Hartree-Fock wavefunction

or DFT electron density is placed around the ‘active’ molecule. The number of such fragments and their relative coordinates can be varied to simulate the effect of the crystal structure. This representation covers the Coulombic part of the interaction and can also describe the exchange interaction between the two electron clouds. But there is more than this purely static representation, as the environment can react to changes in the electron distribution of the ‘active’ fragment. This can be effectively included in our calculation by using a polarizable field around the molecule. One way to do this is to use the discrete (also known as direct) reaction field method [18–20]. In this chapter, we discuss the possible effects of a FDE and a basic implementation of DRF on the principal outcomes of a typical NOCI-Fragments calculation. The insights gained here will be used in future work involving charge and energy transfer using NOCI-Fragments.

The chapter is organized as follows; in the theory section, we discuss briefly how we use the FDE and DRF in a NOCI-Fragments calculation. We then present evidence for our claim that the delocalization effects are less prominent than intuitively might be thought in a charge/energy transfer process. In the results section, that follows the computational details section, we show the proof of principle by performing a NOCI in the presence of a frozen embedding for a dissociation curve of an alkali halide. We take LiF as the example and calculate the energies of the four lowest states ($1^1\Sigma^+$, $2^1\Sigma^+$, and $1^1\Pi$) using NOCI-Fragments. We compare the potential energy curve obtained from NOCI calculations in which the fragment wavefunctions were optimized in vacuum to the curve where the fragment wavefunctions were optimized in the presence of a frozen representation of the other fragment. We then take the benzene dimer as test case for singlet fission materials. Results are compared for fragment wavefunctions optimized in vacuum versus wavefunctions obtained with a frozen embedding or taking polarization into account. We investigate the effect of FDE and DRF at different interdimer distances and compare the NOCI energies of the states with the CASSCF energies. The last section summarizes the conclusions drawn from the calculations and outlines the procedure to include static and polarization environment effects to improve the accuracy of the calculated electronic couplings in future calculations on more realistic singlet fission systems.

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5.2. INCLUSION OF ENVIRONMENTAL EFFECTS

THE theory behind the evaluation of matrix elements between nonorthogonal MEBFs in NOCI-Fragments was presented in Chapter 2. In most of the applications of the NOCI-Fragments procedure, the calculations were limited to those molecules that are directly involved in the charge/energy transfer process. Also, in our studies of singlet fission, we have studied a pair of molecules with a singlet excited state (a linear combination of $S_0^A S_1^B$ and $S_1^A S_0^B$), which evolves to a coupled triplet-triplet state $T_1^A T_1^B$. Singlet fission is known to happen in molecular crystals and in solution. The molecules around this ‘active’ pair can then be described using a frozen density representation of their electronic clouds. We add the orbitals of the embedding molecule to the active molecule. The CASSCF wavefunctions required for NOCI-Fragments are then generated while excluding the orbitals of the embedding fragments from the optimization procedure.

Figure 5.1 | The orbitals of benzene molecules A and B are each optimized in the presence of Hartree-Fock orbitals of two (one above and one below) other benzene molecules. The Hartree-Fock orbitals (within the dashed lines) are used to mimic a frozen embedding for a dimer that we study using NOCI-Fragments.

The FDE treatment provides a wavefunction that contains the electrostatic and exchange effects of a frozen description of the environment. It does not however account for the effect on the wavefunction due to the presence of polarizable electron distributions around the system. A discrete (or direct) reaction field (DRF) can be used for this purpose. DRF describes the environment as a classical force field with atomic point charges and polarizabilities as parameters. The polarizabilities are extracted from fitting molecular polarizabilities obtained from experiment or in our case, calculated using CASSCF calculations performed in OpenMolcas [21].

We calculate the effect of the environment polarization by placing two isotropic polarizabilities on the two neighbouring benzene molecules, previously used for generating the frozen embedding. The different fragment CASSCF wavefunctions are brought to self-consistency with the dipoles induced on these neighboring fragments, which means that the resulting wavefunction contains the information of the polarization caused by the dipoles. In subsection 5.4.3 we discuss this effect on the excitation energies and electronic couplings in NOCI-Fragments. In addition to these changes in the wavefunctions of the fragments, the induced dipoles also cause an electrostatic interaction, which is significantly larger for the MEBFs with a permanent dipole, e.g., the charge-transfer (CT) states in the studies of singlet fission, than for those MEBFs where the number of electrons remains constant on the fragments. A rigorous treatment of this effect would require the implementation of DRF in GronOR, which is beyond the scope of this thesis. Hence we assume that the effect can be accurately approximated by a procedure analogous to the one that we applied for the dynamic electron correlation. The (de-)stabilization of the MEBF by the interaction with the induced dipoles in the environment is assumed to be approximately the same as the sum of the effects on the fragment functions that constitute the MEBF. Hence, we apply a shift on the MEBF energy to simulate the energy

effect of electrostatic interaction of the MEBF with the induced dipoles on the neighboring molecules.

5.2.1. EFFECT OF DELOCALIZATION ON ELECTRONIC COUPLING

In their DFT study of singlet fission in pentacene crystals, Zimmerman *et al.* used a cluster of 10 pentacene molecules to model the excitation process [22]. Using a natural transition orbital (NTO) analysis to ascertain the wavefunction character and spatial spread of the exciton, they found that the S_1 state was delocalized predominantly over four pentacene molecules. This immediately raises the question whether the calculation of the coupling between the excited singlet and the 1TT state using only two molecules is of any use at all. We provide an answer to this problem using a simple theoretical model showing that the delocalization does indeed affect the electronic coupling. We first consider the case where one photon is absorbed by a dimer AB . In the localized description we assume that the absorption of the photon leads directly or indirectly either to $A = S_1^A S_0^B$ or to $B = S_0^A S_1^B$ and then to $T_1^A T_1^B$. For each of these two transitions the coupling matrix element is γ and the squared matrix element (SME), which is proportional to the transition probability, is γ^2 . Both transitions are equally likely and the average SME is also γ^2 . In the delocalized description we take into consideration the interaction between A and B , which we choose to be negative. We neglect the overlap between wavefunctions on different molecules. We now assume that the absorption of the photon leads, directly or indirectly, to the delocalized excited S_1 type state of lowest energy, which is $(A + B)/\sqrt{2}$. The SME with the state $T_1^A T_1^B$ is $2\gamma^2$. Note that the SME for the complementary delocalized state $(A - B)/\sqrt{2}$, is 0 which makes the average over all two delocalized states equal to the average over the localized states, namely γ^2 .

Let us now take three fragments A, B, C in a stack, with negative nearest neighbor interactions, β , for the S_1 states and, similarly, negative interactions β' between nearest neighbor 1TT states. Again, we assume the fragment wavefunctions to be mutually orthogonal (and normalized). In a fully localized description the S_1 states can be represented as,

$$\Phi_1 = S_1^A S_0^B S_0^C \quad (5.1)$$

$$\Phi_2 = S_0^A S_1^B S_0^C \quad (5.2)$$

$$\Phi_3 = S_0^A S_0^B S_1^C \quad (5.3)$$

The localized singlet-coupled triplets can be represented as,

$$\Phi_4 = T_1^A T_1^B S_0^C \quad (5.4)$$

$$\Phi_5 = S_0^A T_1^B T_1^C \quad (5.5)$$

where we only consider states where the triplets are adjacent. For simplicity we introduce a shorter notation where 'A' represents the S_1 excitation on molecule A with the other two molecules in the ground state (here it is: $\Phi_1 = A = S_1^A S_0^B S_0^C$), and similarly states where two fragments are involved like $T_1^A T_1^B$ are represented as AB (corresponding to $\Phi_5 = T_1^A T_1^B S_0^C$) and so on. Taking into consideration that the 1TT state must involve the centre where the $S_0 \rightarrow S_1$ transition took place, we have a non-zero interaction matrix

element γ only in these cases:

$$\langle A|\hat{H}|AB\rangle = \gamma \quad (5.6)$$

$$\langle B|\hat{H}|AB\rangle = \langle B|\hat{H}|BC\rangle = \gamma \quad (5.7)$$

$$\langle C|\hat{H}|BC\rangle = \gamma \quad (5.8)$$

This results in a average value of SME equal to $2\gamma^2/3$. The delocalized singlet excited states are,

$$S_1 = \begin{cases} \frac{1}{2}(A + \sqrt{2}B + C) \\ \frac{1}{2}(A - \sqrt{2}B + C) \\ \frac{1}{\sqrt{2}}(A - C) \end{cases} \quad (5.9)$$

and the triplets form the combinations

$${}^1TT = \begin{cases} \frac{1}{\sqrt{2}}(AB + BC) \\ \frac{1}{\sqrt{2}}(AB - BC) \end{cases} \quad (5.10)$$

The interaction matrix element between the lowest energy delocalized S_1 and 1TT states,

$$\begin{aligned} \frac{1}{2} \cdot \frac{1}{\sqrt{2}} \langle A + \sqrt{2}B + C | \hat{H} | AB + BC \rangle &= \frac{1}{2\sqrt{2}} (\langle A | \hat{H} | AB \rangle + \sqrt{2} \langle B | \hat{H} | AB \rangle \\ &+ \sqrt{2} \langle B | \hat{H} | BC \rangle + \langle C | \hat{H} | BC \rangle) = \frac{1 + \sqrt{2}}{\sqrt{2}} \gamma \end{aligned} \quad (5.11)$$

The other possibilities are

$$\frac{1}{2} \cdot \frac{1}{\sqrt{2}} \langle A + \sqrt{2}B + C | \hat{H} | AB - BC \rangle = 0 \quad (5.12)$$

$$\frac{1}{2} \cdot \frac{1}{\sqrt{2}} \langle A - \sqrt{2}B + C | \hat{H} | AB + BC \rangle = \frac{1 - \sqrt{2}}{\sqrt{2}} \gamma \quad (5.13)$$

$$\frac{1}{2} \cdot \frac{1}{\sqrt{2}} \langle A - \sqrt{2}B + C | \hat{H} | AB - BC \rangle = 0 \quad (5.14)$$

$$\frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} \langle A - C | \hat{H} | AB + BC \rangle = 0 \quad (5.15)$$

$$\frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} \langle A - C | \hat{H} | AB - BC \rangle = \gamma \quad (5.16)$$

This gives us an average SME of $2\gamma^2/3$. The value for averaged SME is $2\gamma^2/N$ for a stack of N S_1 states, both in the local and the delocalized case, because the transformation matrices from localized to delocalized wavefunctions are unitary. So, the average SMEs do not depend on the degree of delocalization of the singlet excited state over the chromophores.

More interesting are the transition probabilities from the lowest energy delocalized S_1 state, because this is the most probable initial state for singlet fission. The SME to the lowest delocalized singlet 1TT is $2.91\gamma^2$ in the case of the stack of three molecules. Likewise we find $3.33\gamma^2, 3.67\gamma^2, 3.81\gamma^2$ for transitions from lowest delocalized S_1 to the

lowest delocalized 1TT state in stacks of four, six, and eight molecules, respectively [23]. For extremely long stacks the energies of the S_1 and 1TT states form bands of width 4β and $4\beta'$ respectively and the SME approaches $4\gamma^2$. Transitions from the lowest S_1 to other delocalized 1TT states are also possible, but their SME is much smaller. So we find that the local SME γ^2 is a crucial parameter for the SF process, both when the process involves localized and when it involves delocalized initial and final states. The prefactor varies from 2 for a stack of only two molecules to 4 for very long stacks. We shall see that this result is important in the following sections because it shows that a model system of two interacting chromophores in the environment of frozen fragments, with the NOCI performed using only the two interacting molecules gives information that is relevant for any stack length. The simple model presented here establishes that there is no necessity to go beyond localized calculations of the charge/energy transfer process to obtain reliable couplings.

5.3. COMPUTATIONAL DETAILS

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To test the effect of a frozen embedding on NOCI-Fragments, we first studied the dissociation curve of the LiF molecule, which is a well-known test case to study the strong correlation from a multi-reference description. We looked at the potential energy curve of the ionic and covalent descriptions of LiF. The Li, F, Li^+ , and F^- fragments were described using complete active space self-consistent field (CASSCF) wavefunctions. CAS(1,1) for Li, CAS(2,1) for Li^+ , CAS(5,3) for F, and CAS(2,1) for F^- , meaning that the wavefunctions are essentially Hartree-Fock (HF) wavefunctions. All CASSCF calculations are performed with OpenMolcas [21] using the ANO-RCC basis (Li:4s3p2d, F:4s3p2d). The F fragment was represented by the lowest three doublet configuration state functions of the atomic 2P state obtained from a state-averaged CASSCF. Each fragment is optimized with and without the presence of a frozen representation by means of a Hartree-Fock wavefunction of the other atom. We made antisymmetrized products of the fragment wavefunctions to construct many-electron basis functions (MEBFs) of type: Li^+F^- , and 3 LiF combinations (two of $^1\Sigma^+$ and the $^1\Pi$) which were then used for the 4×4 NOCI. All NOCI calculations were performed using the GNOME code [24] in GronOR [8, 9].

We then extended our study to benzene, due to its resemblance to the acenes that have been the focus of singlet fission [11–13] based studies in our group [25–27]. In a manner analogous to the LiF embedding, we prepared a benzene dimer in a stack of other benzene molecules. The two interacting benzene fragments were placed with their molecular planes parallel to the xy plane, and only the z -coordinates differed by a distance of 3.00 Å which was incremented in steps of 0.25 Å. The wavefunction for each of the two fragments was optimized in the presence of two other benzene molecules to mimic the environment felt by a benzene molecule in a (hypothetical) stack of benzene molecules. The wavefunctions for the benzene fragments were of type CAS(6,6) using the basis ANO-RCC (C:4s3p1d;H:3s1p). We generated the ground (S_0), first excited singlet (S_1), first excited triplet (T_1), lowest cationic (D_1^+), and anionic state (D_1^-). The spin singlet MEBFs used in the 6×6 NOCI are $|S_0S_0\rangle$, $|S_1S_0\rangle$, $|S_0S_1\rangle$, $|^1TT\rangle$, $|D_1^+D_1^-\rangle$, $|D_1^-D_1^+\rangle$.

Polarizabilities for the reaction field were calculated for the benzene molecule with the ANO-RCC basis comprised of the basis functions (C:5s4p2d1f;H:3s2p1d) from the

second derivative of the energy with respect to the applied field through the FFPT (finite field perturbation theory) module in OpenMOLCAS. CASPT2 energies to calculate the polarizabilities showed only minimal differences with those calculated using CASSCF energies. Table 5.1 shows the x -, y -, and z -components of the polarizabilities that were averaged to obtain an isotropic polarizability for benzene.

Table 5.1 | x -, y - and z -components of polarizabilities for benzene molecule.

	Polarizability
x	68.95
y	68.95
z	35.14

The molecule is oriented along the z -axis giving a different value of polarizability along the z -direction. The isotropic polarizability is therefore overestimated for that direction. In more elaborate treatments one might consider to use an anisotropic polarizability.

5.4. RESULTS AND DISCUSSION

5.4.1. LiF DISSOCIATION

Figure 5.2 shows the asymptotic energy differences ΔE_∞ of the two lowest $^1\Sigma^+$ and the $^1\Pi$ adiabatic states of LiF with the ground state energy of Li + F at 50 Å. In line with the nomenclature used in previous studies on this subject [28–32], we refer to the Li^+F^- configuration as ‘ionic’ (where charge transfer has taken place) and the three LiF configurations as ‘covalent’ configurations. The dotted curves represent the energies obtained when the atomic fragments were optimized in the presence of a frozen embedding and the solid curves for fragments optimized in vacuum.

At the shorter interatomic distances, the lowest $^1\Sigma^+$ state (dark blue and maroon-dashed curves) is strongly dominated by the ionic configuration and show a characteristic minimum due to the attractive Coulomb interactions between the two oppositely charged fragments. Upon increasing the interatomic distance, the energies of the two $^1\Sigma$ states approach each other and the two states undergo an avoided crossing around 4 Å. In this region, the character of both states changes dramatically; with increasing interatomic distance the $^1\Sigma^+$ states changes rather abruptly from a state dominated by the ionic configuration to a mostly covalent electronic state, while the $^2\Sigma^+$ state changes from covalent to ionic. Comparing the energies without and with embedding, we can see that the effect of a frozen embedding in the energies is sizeable.

Figure 5.2 | Relative energies of $1\Sigma^+$ and the $1\Pi^-$ LiF states with respect to the ground state energy at 50 Å. Solid curves are the energies obtained for vacuum optimized fragment wavefunctions and the dotted lines when the fragment wavefunctions are optimized in the presence of a frozen representation of the other fragment.

The most striking difference is that the total energy at equilibrium distance is lowered by 0.5 eV due to the frozen density embedding, leading to a 0.5 eV larger dissociation energy. Also, there are some differences in the equilibrium bond length, avoided crossing point, and the direct electronic coupling at the avoided crossing (Table 5.2). The contributions of each state to the NOCI wavefunction can be seen in Table 5.3 and the differences in weights of the ionic and covalent states before and after the avoided crossing are clearly seen.

Table 5.2 | Equilibrium bond length R_e (Å), point at which avoided crossing occurs R_c (Å), dissociation energy $E_{dissociation}$ (eV), and direct coupling (γ) at avoided crossing (eV) for LiF in vacuum and with a frozen embedding.

	Vacuum	Embedding
R_e	1.7	1.6
R_c	4.2	4.0
$E_{dissociation}$	3.3	3.8
γ	0.4	0.2

From Table 5.2 we can observe that the equilibrium bond length and the point of avoided crossing do not vary much due to the embedding. The dissociation energy is 0.5 eV different. The embedded calculation can offer a more realistic picture of the bonding. This is because, due to the presence of the charged, embedding, fragment, the orbitals of the other fragment are more ‘drawn’ to the position where the bonding takes place, giving rise to a better overlap, and hence, better bonding. The effective coupling of the covalent and ionic curves γ calculated using NOCI shows a reduction of

0.2 eV, which is consistent with the higher quality of the MEBFs when obtained using a frozen embedding. Extensive studies of alkali metal - halide bond dissociation have been performed previously [30, 33, 34]. Most studies focus on locating the point of avoided crossing and employ methods like CASSCF or CASPT2 to obtain accurate enough descriptions of the avoided crossings. The position of the avoided crossing in itself is relevant for studies of the quantum dynamics of the system. Since the system is strongly correlated, a multideterminantal CASSCF type wavefunction may be insufficient to describe the physics since it does not include dynamic correlation. This results in the position of the crossing point to be underestimated as at larger internuclear distances there is a larger contribution from dynamic correlation to the ionic state. Our study is currently focused on studying the difference in the descriptions with and without a frozen embedding, hence we do not compare the potential energy curves with dynamic correlation included although it is currently possible to do so (see Chapter 4). Mayhall *et al.* [35] studied the dissociation of LiH using a spin-flip NOCI (SF-NOCI) strategy. This approach is similar to NOCI-Fragments in the use of nonorthogonal orbitals, but the configurations for each state are selected as combinations of α and β -strings from a high-spin reference and variationally optimized, which is in contrast to NOCI-Fragments where all determinants arising from our choice of active space are used in the molecular wavefunction.

Table 5.3 | NOCI excitation energies ΔE (in eV) and Gallup-Norbeck (GN) weights of the MEBFs (Li^+F^- , LiF) for the LiF states ($1^1\Sigma^+$, $2^1\Sigma^+$) at equilibrium bond length R_e , crossing point R_c , and a point after the crossing, 5.00 Å.

State	Vacuum		Embedding	
	R_e		R_e	
	$1^1\Sigma^+$	$2^1\Sigma^+$	$1^1\Sigma^+$	$2^1\Sigma^+$
ΔE	0.00	5.14	0.00	5.47
GN(Li^+F^-)	0.988	0.084	1.000	0.003
GN(LiF)	0.012	0.916	0.000	0.997

State	R_c		R_c	
	$1^1\Sigma^+$	$2^1\Sigma^+$	$1^1\Sigma^+$	$2^1\Sigma^+$
ΔE	0.00	0.91	0.00	0.40
GN(Li^+F^-)	0.176	0.786	0.420	0.575
GN(LiF)	0.823	0.214	0.580	0.424

State	After crossing (5.0 Å)		After crossing (5.0 Å)	
	$1^1\Sigma^+$	$2^1\Sigma^+$	$1^1\Sigma^+$	$2^1\Sigma^+$
ΔE	0.00	1.16	0.00	0.95
GN(Li^+F^-)	0.018	0.969	0.001	0.990
GN(LiF)	0.982	0.030	0.999	0.010

Table 5.3 shows the NOCI energies and Gallup-Norbeck weights [36] for the vacuum and embedded LiF (placed along the z axis), expanded using 4 MEBFs (1 ionic, 3 covalent). The GN-weights of the covalent part is expressed as a sum of the three MEBFs ($\text{Li}(^2\text{S}) \times \text{F}(^2\text{P})$). The GN-weights at the equilibrium bond length R_e , crossing point R_c , and a point after the crossing show the characteristic variation of their ionic/covalent contributions. At the equilibrium bond length R_e the largest contribution to the ground state is expected to be from the ionic state in the NOCI wavefunction. This can be seen in Table 5.3 where the lowest singlet state has the highest contribution from Li^+F^- . State $2^1\Sigma^+$ has the covalent LiF configuration showing maximum contribution. Moving to the avoided crossing R_c , we see the weights of the MEBFs making up the states in the NOCI change. Close to the avoided crossing point of the states which were previously nearly pure-ionic or covalent are not so pure anymore. Moving further along the coordinate axis to 5 Å, we see from the weights that the character of the states has now been reversed. The state which had a dominant ionic character now has a high covalent contribution from LiF and the previously covalent state is dominated by the ionic contribution. The Li^+F^- state has a higher energy of 0.95 eV and shows an almost-pure ionic character. From the results shown in Figure 5.2 and Tables 5.2 and 5.3, we conclude that a non-negligible effect on the NOCI wavefunction and energies is seen due to the presence of a frozen embedding.

We now turn to a pair of molecules instead of atoms to see the effect of FDE. We do this with a stack of benzene molecules.

5.4.2. FROZEN EMBEDDING ON STACKED BENZENE FRAGMENTS

We start the discussion of the results with a comparison of the excitation energies obtained with NOCI using vacuum optimized fragment wavefunctions (see Figure 5.3 a) with a frozen embedding (b), and (c) using state-averaged CASSCF(12,12). Subfigures 5.3(a), (b) show the NOCI-Fragments energies of the NOCI states made of the MEBFs $|S_0S_1\rangle$, $|S_1S_0\rangle$, $|^1TT\rangle$, $|D_1^+D_1^-\rangle$, and $|D_1^-D_1^+\rangle$, subfigure (c) shows the state-averaged CASSCF energies of the 12 lowest energy spin singlet states. The two lowest excited states of the NOCI-Fragments show a significant splitting at small distances, which tends to zero as the distance between the two fragments increases. These states are dominated by the $\pm$ combinations of S_0S_1 and S_1S_0 . The splitting is mostly caused by the interaction between the S_0S_1 and S_1S_0 MEBFs, which (as expected) becomes smaller upon increasing fragment distance. Before comparing these energies with the CASSCF results we first remark that the CASSCF energies are not the state specific energies as in NOCI-Fragments, but instead the twelve lowest state-averaged energies. The lowest excited state (blue curve) and the second excited state (orange curve) converge to the same energy in all three cases (≈ 5.00 eV) and can therefore be considered to describe the same molecular electronic states, although its character in terms of electronic configurations is not easily extracted from the CASSCF calculation. The differences between the three approaches are small along the whole curve and only at very small (rather unphysical) fragment distances a small effect of the frozen density embedding can be observed: The lowest excitation energy is 2.04 eV for the vacuum optimized fragments and 2.20 eV for the embedded ones. The second excited state, characterized as the linear combination of S_0S_1 and S_1S_0 in the NOCI-Fragments calculation, also shows basically the same trend in the three approaches.

(a) NOCI in vacuum

(b) NOCI + frozen embedding

(c) State-average CASSCF

Figure 5.3 | Vertical excitation energies (eV) of the benzene dimer as function of the intermolecular distance (Å) obtained using (a) NOCI-Fragments energies (vacuum), (b) NOCI-Fragments performed in presence of a frozen fragment, and (c) state-averaged CASSCF. The subfigures (a) and (b) contain the NOCI-states; $S_0S_1 \pm S_1S_0$ (blue and orange), 1TT (yellow), CT (green and maroon). Subfigure (c) contains the twelve lowest roots of the SA-CASSCF.

The other NOCI curves in (a) and (b) represent the excitation energy to the state with almost 100% 1TT character (yellow), and the CT states (green and maroon) and they are also qualitatively (and actually also quantitatively) very similar with and without embedding. A comparison with CASSCF is more complicated as it is extremely difficult to distinguish a state with a large 1TT contribution among the many singlet excited states of almost equal energy. The only straightforward point of comparison is the gap between the $S_0S_1 \pm S_1S_0$ states and the next singlet state at large fragment distance. This gap is 1.48, 1.48 and 0.52 eV for (a),(b), and (c), respectively. Again very small differences are observed.

Finally, we inspect the SA-CASSCF(12,12) wavefunction of the excited states plotted in Figure 5.3 to determine the character of these states and distinguish between local excited and charge-transfer states. Pairwise rotations were performed on the orbitals from the CASSCF calculations to obtain strictly localized orbitals for the benzene dimer. From the weights of contributions to each, we could then determine the local excitations (6 electrons in the top benzene and 6 in the bottom) and the CT excitations (asymmetric distribution of electrons). Table 5.4 shows the weights of the neutral, the charge transfer and double charge transfer configurations in the eleven excited states considered. Note that these weights are the sum of thousands of mostly very small contributions; the CAS(12,12) has approximately 250000 CSFs. The analysis was made for an inter-molecular distance of 3 Å. The weights clearly show that among these eleven states no pure CT states can be found, roots 6 and 7 are almost 50-50 mixtures of local excitations and CT states and also roots 2 and 4 have significant contributions from the CT configurations. This mixed character makes the interpretation of the results much more difficult than in the NOCI approach where each state can be clearly identified from the GN-weights in the short expansion. One may have to include many more roots in the state-averaged optimization of the CASSCF to reach the pure CT states, but this would not only increase the computational effort, but also deteriorate the description of each individual state.

Table 5.4 | Weights of local, CT, and double charge-transfer (DCT) configurations of the 12 lowest states considered in the state averaged CASSCF(12,12)..

	Local	CT	Double CT
GS	98.82	0.13	
root2	84.89	12.24	
root3	97.50	0.05	
root4	62.62	35.56	
root5	86.88	9.54	0.09
root6	51.58	45.59	
root7	51.59	45.59	
root8	84.47	11.77	
root9	84.43	11.84	
root10	82.99	10.93	0.06
root11	82.99	10.98	0.06
root12	88.07	6.24	0.03

Having established that the NOCI relative energies of the lowest four neutral singlet states are comparable to those obtained with CASSCF(12,12), we now turn to a more quantitative analysis of the effect of the frozen embedding. Table 5.5 shows the vertical excitation energies at different distances of the six states from a NOCI-Fragments calculation of a stacked benzene dimer in vacuum and when the fragment wavefunctions are optimized in the presence of a frozen density embedding (FDE). The energies are calculated with regard to the ground state energy. The frozen fragment is a Hartree-Fock representation of a benzene molecule that mimics the effect of a non-interacting environment on the interacting species. In this case, we can see the effect of FDE is rather modest (<0.2 eV energy difference between vacuum and FDE) on all states. The potential energy surface of the ground state in vacuum and with FDE turned out to be also very similar.

Table 5.5 | Vertical excitation energies of five lowest excited NOCI-Fragments singlet states Ψ_n , where $n = [2, 6]$ of the benzene dimer w.r.t the corresponding ground state Ψ_1 .

Distance	Vacuum					FDE				
	Vertical excitation energies									
	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6
3.00	4.35	4.96	7.43	8.28	8.46	4.23	4.82	7.37	8.24	8.40
3.25	4.64	4.98	7.63	8.41	8.51	4.59	4.91	7.58	8.38	8.47
3.50	4.80	4.98	7.73	8.55	8.60	4.75	4.92	7.74	8.59	8.63
3.75	4.89	4.99	7.79	8.70	8.72	4.84	4.93	7.79	8.73	8.74
4.00	4.94	4.99	7.81	8.84	8.84	4.89	4.94	7.82	8.87	8.87

The addition of benzene fragments above and below the active benzene molecules

as frozen embedding of each of the interacting fragments has a very small effect on the excitation energies. But the description of their effect is not complete because the frozen density effectively accounts only for the description of Pauli repulsion. The reaction of the environment to the change in electron density is not captured by the current description. Induced dipoles can be placed in the surrounding to mimic roughly the effect of a polarizable environment. This effect of such an ‘approximate’ field of induced dipoles is studied in the next section.

5.4.3. POLARIZABLE ENVIRONMENT FOR NOCI-FRAGMENTS

Table 5.6 shows the z -component of the induced dipoles on the two neighboring benzene molecules for the S_0 , S_1 , T_1 , D_1^+ , and D_1^- fragment states due to the polarizable field. It can be seen that the magnitude is largest in the D_1^+ and D_1^- states. It is hence reasonable to estimate that the largest effect on the wavefunction due to the polarizabilities can be seen in the CT-states. This is illustrated in the part of Table 5.6 showing the vertical excitation energies ΔE_{vacuum} and $\Delta E_{\text{dipoles}}$ corresponding to the energies in vacuum and in presence of DRF. We can observe from here that the effect of the polarizable environment is more pronounced in the cationic and anionic states. The induced dipoles in the CT-states of 1.25 D and 1.91 D bring about a difference of 0.27 eV and 0.42 eV between vertical excitation energies of the D_1^+ and D_1^- states.

Table 5.6 | Induced dipoles (μ_1, μ_2 in Debye) on the electronic states of neighboring benzene molecules due to DRF and the corresponding vertical excitation energies ΔE (in eV) in vacuum and with dipoles.

	S_0	S_1	T_1	D_1^+	D_1^-
μ_1 (D)	-0.38	-0.25	-0.25	1.25	-1.91
μ_2 (D)	0.38	0.25	0.25	-1.25	1.91
ΔE_{vacuum} (eV)	0.00	5.06	3.92	8.36	3.50
$\Delta E_{\text{dipoles}}$ (eV)	0.00	5.08	3.93	8.19	3.08

Table 5.7 shows the change in vertical excitation energies of the NOCI eigenstates using MEBFs constructed from fragment wavefunctions optimized in vacuum and with the polarizable field. Note that in the NOCI-Fragments calculations, only the wavefunction generated with the field present is used, and that in the actual NOCI calculation this field is not present anymore. Comparing the energies in vacuum and in DRF we see negligible energy differences in this test case showing that the changes in the fragment wavefunctions caused by the presence of induced dipoles in the surrounding is minimal for this arrangement of benzene molecules.

Table 5.7 | Vertical excitation energies of S_0S_1 , S_1S_0 , 1TT , $D_1^+D_1^-$, and $D_1^-D_1^+$ states of benzene dimer w.r.t the ground state S_0S_0 with and without polarized wavefunctions.

Distance	Vacuum					Polarized wavefunctions				
	Vertical excitation energies									
	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6
3.00	4.38	4.98	7.42	8.30	8.47	4.37	4.98	7.42	8.27	8.44
3.25	4.67	5.00	7.62	8.43	8.52	4.66	4.99	7.62	8.41	8.49
3.50	4.83	5.01	7.72	8.57	8.61	4.83	5.00	7.72	8.55	8.59
3.75	4.92	5.01	7.78	8.71	8.73	4.92	5.01	7.78	8.70	8.71
4.00	4.97	5.01	7.81	8.85	8.86	4.96	5.01	7.81	8.84	8.84

The fact that the excitation energies in vacuum reported in Tables 5.5 and 5.7 are slightly different is due to the symmetry restrictions that were imposed in the CASSCF calculations with the frozen embedding. Without these restrictions, the unpaired electron in the D_1^- fragment state ends up in a diffuse orbital mostly localized in the plane of the benzene molecule to reduce the repulsion of the frozen densities above and below the molecule. Imposing the symmetry restrictions of the D_{2h} point group, the highest Abelian subgroup of the real D_{6h} symmetry, enables us to confine the extra electron in the π -orbitals of the molecule. Unfortunately, no symmetry restrictions can be imposed when an external field with polarizabilities is used. The wavefunctions nevertheless converged to the desired state.

As explained above, the polarization of the fragment wave functions is not the only effect caused by the dipoles in the environment. These dipoles themselves also have a direct electrostatic interaction with the electron distribution of the cluster, especially when the cluster has a permanent dipole, as is the case for the CT MEBFs. In the next section, we discuss how the approximate inclusion of this effect affects the NOCI results.

5.4.4. DRF ELECTROSTATIC EFFECTS

We include the effect of the electrostatic interactions caused by the dipoles on the neighbouring molecules through a shift in the energies of the NOCI Hamiltonian. The shift is defined as the difference between the fragment CASSCF energies in the absence and presence of DRF (Table 5.6). This effectively includes the electrostatic interaction between the electron clouds of the embedding and the interacting fragments. Table 5.8 shows a significant lowering of the energies of the CT states in comparison to vacuum when the electrostatic interactions are accounted for. The NOCI state with large contributions from the $|D_1^+D_1^- \rangle$ and $|D_1^-D_1^+ \rangle$ MEBFs shows a reduction of around 0.6 eV from its value in vacuum. The other states dominated by $|S_0S_1 \rangle$, $|S_1S_0 \rangle$, and $|^1TT \rangle$ MEBFs show differences of around 0.1 eV on average. This makes the inclusion of electrostatic effects caused by a polarizable environment relevant not only directly for the calculation of the excitation energies of CT states in a NOCI calculation, but also indirectly for properties such as the charge-transfer mediated coupling discussed in the previous chapter.

Table 5.8 | Vertical excitation energies of S_0S_1 , S_1S_0 , 1TT , $D_1^+D_1^-$, and $D_1^-D_1^+$ states of benzene dimer w.r.t the ground state S_0S_0 with and without Hamiltonian shifted with DRF energies.

Distance	Vacuum					DRF electrostatic				
	Vertical excitation energies									
	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6
3.00	4.38	4.98	7.42	8.30	8.47	4.28	4.97	7.45	7.70	7.95
3.25	4.67	5.00	7.62	8.43	8.52	4.61	4.99	7.64	7.82	7.96
3.50	4.83	5.01	7.72	8.57	8.61	4.79	4.99	7.75	7.96	8.03
3.75	4.92	5.01	7.78	8.71	8.73	4.89	5.00	7.80	8.11	8.14
4.00	4.97	5.01	7.81	8.85	8.86	4.94	5.00	7.83	8.25	8.26

Table 5.9 lists the NOCI vertical excitation energies and wavefunctions for the benzene model at 3.00 Å for the 6 NOCI states expressed in terms of the MEBFs $|S_0S_0\rangle$, $|S_0S_1\rangle$, $|S_1S_0\rangle$, $|^1TT\rangle$, $|D_1^+D_1^- \rangle$, $|D_1^-D_1^+ \rangle$ before and after including the shift on the diagonal to mimic the effect of the dipole interactions, showing the variations in the wavefunctions due to the electrostatic effects.

Table 5.9 | NOCI energies (ΔE in eV) and wavefunctions (written in terms of the MEBFs; $|S_0S_0\rangle$, $|S_0S_1\rangle$, $|S_1S_0\rangle$, $|^1TT\rangle$, $|D_1^+D_1^- \rangle$, $|D_1^-D_1^+ \rangle$) for vacuum and DRF electrostatic wavefunctions of a dimer of two benzene molecules, separated by 3.00 Å.

	State	1	2	3	4	5	6
Vacuum	ΔE	0.00	4.35	4.96	7.43	8.28	8.46
	S_0S_0	-1.000	0.000	-0.000	0.017	0.000	0.000
	S_0S_1	0.000	0.653	-0.711	0.000	-0.000	-0.284
	S_1S_0	0.000	-0.653	-0.711	0.000	-0.000	0.284
	1TT	-0.008	-0.000	-0.000	-1.000	-0.000	-0.000
	D^+D^-	0.000	-0.178	-0.004	-0.000	0.713	-0.688
	D^-D^+	0.000	0.178	-0.004	-0.000	0.713	0.688
DRF electrostatic	ΔE	0.00	4.29	4.97	7.45	7.69	7.94
	S_0S_0	-1.000	0.000	0.000	-0.017	0.000	0.000
	S_0S_1	0.000	0.638	0.711	-0.000	-0.001	-0.317
	S_1S_0	0.000	-0.638	0.711	0.000	-0.001	0.317
	1TT	-0.008	-0.000	0.000	1.000	-0.000	-0.000
	D^+D^-	0.000	-0.212	0.005	0.000	0.713	-0.678
	D^-D^+	0.000	0.212	0.005	0.000	0.713	0.678

Not unexpectedly, the energy and wavefunction of the NOCI roots 1, 3 and 4 are virtually the same before and after applying the DRF shift. These states are strongly

dominated by the $|S_0S_0\rangle$, $|S_1S_0\rangle$, $|S_0S_1\rangle$ and $|^1TT\rangle$ MEBFs, exactly the ones that are only weakly affected by the dipoles on the neighbouring molecules. NOCI states 2, 5 and 6 do show significant changes: All three are lowered in energy and the contribution of the MEBFs $|D^+D^-\rangle$ and $|D^-D^+\rangle$ increases in state 2, while state 6 shows an increased contribution of $|S_0S_1\rangle$ and $|S_1S_0\rangle$. This means that the stabilization of the CT MEBFs due to dipoles induced on the environment can have a direct effect on the charge-transfer mediated coupling between S_0S_1 and 1TT , and have an impact on the understanding of the singlet fission mechanism.

Although benzene is not a system that fulfils the energetic requirements of singlet fission, it can still be illustrative to calculate the electronic coupling between S_0S_1 and 1TT in the different computational settings discussed so far. Unfortunately, the geometry of the benzene stack used in the above-described calculations leads to a strictly zero $S_0S_1 - ^1TT$ coupling, and therefore, we report here the $S_0S_1 - D_1^+D_1^-$ coupling in the different representations of the benzene stack. This is the largest of all couplings and beforehand one of the most likely to be affected by changes in material model. In table 5.10 we compare the electronic coupling matrix element between the S_0S_1 and $D_1^+D_1^-$ states at various distances for the benzene dimer in vacuum, in the presence of a frozen embedding, with DRF polarization, and with DRF electrostatic effects included. We saw in the previous tables that the excitation energies of the CT-states varied due to the presence of the DRF electrostatic field, but with FDE, and DRF polarization the excitation energies remained largely unchanged. Apart from the expected reduction in electronic coupling for increasing fragment distance, we do not observe any significant dependency of the coupling on the representation of the material. Neither adding a frozen embedding, nor using dipole polarised fragment wavefunctions, nor including the effect of the induced dipole - fragment interactions does lead to a difference in the coupling. This is not completely unexpected since the coupling is entirely determined by the wavefunction of the MEBFs involved in the coupling and not on their energies. The latter was shown above to change under certain circumstances but we have not found evidence that the wavefunctions become strongly polarized by the changes in the environment that we have studied here.

Table 5.10 | Absolute values of diabatic electronic coupling (in meV) between S_0S_1 and D^+D^- states of benzene dimer.

Distance	Vacuum	FDE	DRF (Pol)	DRF (elec)
3.00	640.2	631.0	641.5	640.2
3.25	461.0	455.6	462.3	461.0
3.50	330.0	324.9	331.2	329.8
3.75	234.9	231.8	236.1	235.0
4.00	166.5	164.4	167.5	166.5

5.5. THE CONCLUSION AND OUTLOOK

In this chapter, we have explored various ways to include the effect of the environment in our NOCI-Fragments calculations. Through this, we could get an insight into how the calculations were affected by the inclusion of Coulomb and Pauli interactions from the neighboring molecules and by the polarization of the environment. This is closer to the process of charge or electron transfer that takes place under experimental conditions where the fragments are in a crystal or in solution.

From these initial calculations it seems that the addition of a frozen density does not have a large effect on the quantities of interest of our NOCI-Fragments study, *viz.* the electronic coupling between the diabatic states and vertical excitation energies. The effect of polarization of the environment due to the induced dipoles was seen on the excitation energies. As predicted, the effect was more profound on the charge transfer states than the other electronic excited states. This effect may need to be taken into consideration while modeling the singlet fission process in solution/crystals. The electrostatic effect due to the induced dipoles also turns out to be relevant in this study. We modeled this by shifting the energies of the diagonal of the NOCI Hamiltonian matrix (expectation energies of diabatic states) using the molecular energies in the presence of the reaction field. We observed considerable changes in the NOCI energies because of this 'DRF shift'. The change is predominantly observed in the CT-states. The direct coupling terms obtained from the NOCI with a DRF shift were similar to the couplings obtained in vacuum. We predict that in the CT-mediated pathway of singlet fission, we would discover considerable changes in the magnitude of electronic couplings. Through these preliminary tests on small molecules, we were able to get an idea of how the effect of an environment can be incorporated in NOCI-Fragments. Conclusive statements and definitive trends in the behavior can only be obtained from a more extensive study of various chromophores, starting with the family of acenes. This remains as part of the next phase in this study. We also conclude from the model study performed that there is no significant effect of the extent of delocalization of excitations on the electronic coupling between the states. The electronic coupling between the $S_0S_1 -^1 TT$ states in singlet fission can hence be calculated from the simple model containing two chromophores.

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SUMMARY

A theoretical study of electron transfer (ET) and excitation energy transfer (EET) processes can provide a more nuanced understanding of the underlying physics that may not always be accessible through experiments. The focus of this thesis is the development of nonorthogonal configuration interaction (NOCI) - Fragments, an electronic structure method that has shown promise for the study of ET and EET phenomena. The main aspects of NOCI-Fragments are: the possibility to retain the diabatic nature of the involved molecular states, a compact expansion of the NOCI wavefunction in terms of many-electron basis functions (MEBFs) which are spin-adapted antisymmetrized products of molecular (multiconfigurational) wavefunctions, direct accessibility of electronic coupling between diabatic states, the inclusion of static correlation effects. Singlet fission (SF) is a widely studied EET process due to the promise it holds to improve organic photovoltaic efficiency and was chosen as a suitable application to be investigated using NOCI-Fragments. The developmental work was done in collaboration with Oak Ridge Laboratory, USA, and implemented in the software GronOR, freely available and interfaced with OpenMolcas and GAMESS-UK.

In chapter 1 the methods currently used by the scientific community to study ET and EET are briefly discussed. NOCI is introduced as a viable option that can give an unbiased description of the ground and excited state wavefunctions in a molecular cluster. Chapter 2 contains the theoretical aspects on NOCI-Fragments like the evaluation of matrix elements between Slater determinants that have orbital sets nonorthogonal to each other, the procedure to make the MEBFs from complete active space self-consistent field (CASSCF) molecular wavefunctions, and the parallel implementation in GronOR. The number of two-electron integrals increases rapidly with the system size when expressed in the standard atom-centered basis sets. Moreover, the number of determinant pairs that need to be evaluated in the calculation of the matrix elements between the different MEBFs also grows very fast when longer wavefunction expansions are used for the fragment wavefunctions. This turns out to be a computational bottleneck for even the most advanced supercomputers if molecules containing more than a few dozen atoms are used. We address this issue in chapter 3 with the creation of a reduced common molecular orbital (MO) basis to express the two-electron integrals. This addition significantly reduces the number of two-electron integrals that need to be handled in the calculation of the NOCI Hamiltonian and overlap matrices. We show in the chapter that the results obtained with this basis do not show a significant loss of accuracy in calculating relevant quantities like electronic couplings and vertical excitation energies. We also show a significant reduction in wallclock time with almost no loss in accuracy when Hamiltonian matrix elements over determinant pairs with small weights are neglected in the NOCI.

The molecular wavefunctions that were used in NOCI-Fragments are CASSCF type wavefunctions which only account for so-called static electron correlation effects and not dynamical electron correlation. Fully correlated wavefunctions can provide us relative

energies between states that are comparable to the experimentally observed values. In chapter 4 two methods to incorporate the effect of dynamic electron correlation into the NOCI energies and the NOCI wavefunctions are presented. In the first approach, the diagonal Hamiltonian matrix elements of the NOCI matrix, corresponding to the MEBF energies, are shifted using the molecular energies from multiconfigurational second-order perturbation theory implementations such as CASPT2 and NEVPT2. In the second approach, a dynamic correlation dressed complete active space (DCD-CAS(2)) wavefunction is used instead of a CASSCF wavefunction in the NOCI procedure. The results on test molecules benzene, pyridine, and naphthalene are reported, showing that dynamic correlation does not affect the direct coupling between the MEBFs, but has a significant effect on the relative MEBF energies. Consequently, the charge-transfer mediated electronic couplings between the excited singlet and the 1TT state are found to vary when dynamic correlation is accounted for.

Chapter 5 provides the initial framework to perform NOCI calculations including the effects of the environment in which the molecular cluster is embedded. This step is being taken to be able to mimic the effect of condensed-phase environments where ET and EET processes take place. The applicability of NOCI-Fragments had been so far limited to molecular clusters isolated in vacuum which could possibly lead to an unrealistic description of the actual physics. The two prominent effects of the surrounding environment, Pauli repulsion, and polarization of the molecular fragments are studied. The effect of delocalization and localization of the excitations on the electronic couplings between diabatic states involved in singlet fission of a molecular cluster is also analyzed through a simple model. The study leads to the conclusion that the (squared) local electronic coupling matrix element is a crucial parameter for the singlet fission process, both when the process involves localized and when it involves delocalized initial and final states.

Taken together, the work done in the thesis makes it possible for NOCI-Fragments to: study large molecular systems that are relevant for ET and EET processes, using CASSCF wavefunctions with reasonably large active spaces as the initial molecular wavefunctions, include dynamical correlation effects within each molecule, and include effects of the environment. The advancements from this thesis will prove useful in providing a clearer and realistic view of some photophysical phenomena.

SAMENVATTING

Een theoretische studie van processen voor elektronenoverdracht (ET) en excitatie-energieoverdracht (EET) kan een genuanceerder begrip opleveren van de onderliggende fysica die niet altijd toegankelijk is via experimenten. De focus van dit proefschrift is de ontwikkeling van Niet-Orthogonale Configuratie Interactie (Nonorthogonal configuration Interaction; NOCI) met Fragmenten, een elektronenstructuur methode die veelbelovend is gebleken voor de studie van ET- en EET-verschijnselen. De belangrijkste aspecten van NOCI-Fragments zijn: de mogelijkheid om de diabatische aard van de betrokken moleculaire toestanden te behouden, een compacte expansie van de NOCI-golffunctie in termen van veel-elektronenbasisfuncties (MEBFs) die spin-aangepaste antisymmetrische producten van moleculaire (multiconfiguratie) golffuncties zijn, directe toegang tot de elektronische koppeling tussen diabatische toestanden, en het in rekening brengen van statische elektronencorrelatie. *Singlet fission* (SF) is een veel bestudeerd EET-proces vanwege zijn potentie om de efficiëntie van zonnecellen op basis van organische materialen te verbeteren en werd gekozen als een geschikte toepassing om te onderzoeken met behulp van NOCI-Fragments. De verdere ontwikkeling van de rekenmethode werd gedaan in samenwerking met Oak Ridge National Laboratory, VS, en geïmplementeerd in de software GronOR, vrij beschikbaar en gekoppeld aan OpenMolcas en GAMESS-UK.

In hoofdstuk 1 worden de methoden die momenteel door de wetenschappelijke gemeenschap worden gebruikt om ET en EET te bestuderen kort besproken. NOCI wordt geïntroduceerd als een haalbare optie die een onbevooroordeelde beschrijving kan geven van de golffuncties van de grond en aangeslagen toestanden in een molecuair cluster. Hoofdstuk 2 behandelt de theoretische aspecten van NOCI-Fragments, zoals de evaluatie van Hamilton matrix elementen tussen Slater-determinanten waarvan de moleculaire orbitalen onderling niet orthogonaal zijn, de procedure om de MEBF's te construeren met de complete active space self-consistent field (CASSCF) golffuncties (*complete active space self-consistent field wavefunctions*) en de parallele implementatie van de rekenmethode in GronOR. Het aantal twee-elektronen integralen neemt snel toe met de systeemgrootte wanneer deze worden uitgedrukt in standaard atoomgecentreerde basisfuncties. Bovendien groeit het aantal determinantenparen dat moet worden geëvalueerd bij de berekening van de matrixelementen tussen de verschillende MEBF's ook erg snel wanneer langere golffunctie-expansies worden gebruikt voor de fragmentgolffuncties. Dit blijkt een computationeel knelpunt te zijn voor zelfs de meest geavanceerde supercomputers als er moleculen worden gebruikt die meer dan enkele tientallen atomen bevatten. We behandelen dit probleem in hoofdstuk 3 met de creatie van een gereduceerde gemeenschappelijke moleculaire orbitaal (MO) basis waarin de twee-elektronen integralen worden uitgedrukt. Deze toevoeging vermindert het aantal integralen dat moet worden verwerkt bij de berekening van de NOCI Hamilton en overlap matrices aanzienlijk. We laten in het hoofdstuk zien dat de resultaten die met deze basis zijn verkregen geen significant verlies aan nauwkeurigheid veroorzaken bij het berekenen van relevante

grootheden zoals elektronische koppelingen en verticale excitatie-energieën. We laten ook een significante vermindering van de rekentijd zien zonder significant verlies aan nauwkeurigheid wanneer de bijdragen van determinantenparen met kleine gewichten worden verwaarloosd in de NOCI.

De moleculaire golffuncties die werden gebruikt in NOCI-Fragments zijn golffuncties van het CASSCF-type die alleen zogenaamde statische elektronencorrelatie in rekening brengen en niet dynamische elektronencorrelatie. Volledig gecorreleerde golffuncties kunnen ons relatieve energieën geven tussen toestanden die vergelijkbaar zijn met de experimenteel waargenomen waarden. In hoofdstuk 4 worden twee methoden gepresenteerd om het effect van dynamische elektronencorrelatie op de NOCI-energieën en de NOCI-golffuncties op te nemen. In de eerste benadering worden de diagonale matricelementen van de NOCI-matrix, overeenkomend met de MEBF-energieën, verschoven met behulp van de moleculaire energieën van multiconfiguratie-implementaties van tweede-orde-storingsrekening, zoals CASPT2 en NEVPT2. In de tweede benadering wordt een golffunctie gebruikt met de dynamische correlatie effecten ingebouwd (genaamd DCDCAS(2)) in plaats van een CASSCF-golffunctie in de NOCI-procedure. De resultaten op testmoleculen benzeen, pyridine en naftaleen worden gerapporteerd, waaruit blijkt dat dynamische correlatie geen invloed heeft op de directe koppeling tussen de MEBF's, maar wel een significant effect heeft op de relatieve MEBF-energieën. Dienovereenkomstig blijken de door ladingsoverdracht gemedieerde elektronische koppelingen tussen het aangeslagen singlet en de 1TT -toestand te veranderen wanneer rekening wordt gehouden met dynamische correlatie.

Hoofdstuk 5 biedt het eerste raamwerk om NOCI-berekeningen uit te voeren, om de effecten van de omgeving waarin het moleculaire cluster is ingebed in rekening te brengen. Deze stap wordt genomen om het effect van gecondenseerde fase-omgevingen waar ET- en EET-processen plaatsvinden na te kunnen bootsen. De toepasbaarheid van NOCI-fragmenten was tot nu toe beperkt tot moleculaire clusters geïsoleerd in vacuüm, wat mogelijk zou kunnen leiden tot een onrealistische beschrijving van de feitelijke fysica. De twee prominente effecten van de omgeving, Pauli-afstoting en polarisatie van de moleculaire fragmenten worden bestudeerd. Het effect van delokalisatie en lokalisatie van de excitaties op de elektronische koppelingen tussen diabatische toestanden die betrokken zijn bij singlet fission wordt ook geanalyseerd via een eenvoudig model. De studie leidt tot de conclusie dat het (gekwadrateerde) lokale elektronische koppelingsmatricelement een cruciale parameter is voor het singlet fission proces, zowel wanneer het proces gelokaliseerde als wanneer het gedelokaliseerde begin- en eindtoestanden betreft.

Alles bij elkaar maakt het werk dat in het proefschrift is beschreven het voor NOCI-Fragments mogelijk om: grote moleculaire systemen te bestuderen die relevant zijn voor ET- en EET-processen, gebruik te maken van CASSCF-golffuncties met redelijk grote actieve ruimtes als de initiële moleculaire golffuncties, dynamische correlatie-effecten binnen elk molecuul mee te nemen in de beschrijving, en effecten van de omgeving te bestuderen. De resultaten en conclusies uit dit proefschrift zullen nuttig zijn om een duidelijker en realistischer beeld te krijgen van sommige fotofysische verschijnselen.

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