Accurate excited states with quantum Monte Carlo: looking beyond conventions

Monika Dash

**ACCURATE EXCITED STATES WITH QUANTUM MONTE CARLO:
LOOKING BEYOND CONVENTIONS**

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Accurate Excited States with quantum Monte Carlo: Looking beyond conventions
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**ACCURATE EXCITED STATES WITH QUANTUM MONTE CARLO:
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DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
Prof. dr. T. T. M. Palstra,
on account of the decision of the graduation committee,
to be publicly defended
on Thursday 19th of November 2020 at 14:45

by

Monika Dash

born on December 31, 1991
in Rourkela, India

This doctoral dissertation is approved by:

Prof. dr. C. Filippi

Promotor

To my family

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Chapter 1

Introduction

1.1 Predictive modeling of excited states

The absorption of light by a photosensitive molecule (or chromophore) can trigger a series of physical and/or chemical responses both within the molecule and its environment which can extend over a range of spatial and temporal scales. For instance, upon photoabsorption, the chromophore present on the retina of our eyes undergoes a conformational change [1–8] which then drives a cascade of chemical reactions resulting in the activation of the optical nerve leading to vision. A process of equivalent complexity is at play in the working of organic photovoltaics (solar cells) where the energy from absorbed solar radiation is used to generate an electric current. In these devices, light-absorption causes the excitation of an electron in a photoactive electron-donating polymer leading to the formation of an exciton (bound electron-hole pair). If these excitons successfully diffuse to reach the donor-acceptor interface without recombining, they can separate into free charges after the acceptor receives the electron [9–12], resulting in a photocurrent. Clearly, these are extremely complex multiscale processes and accurately describing every involved step is far from trivial for any theoretical/computational model.

Modeling the initial steps in a photoexcitation process demands a quantum mechanical treatment and falls under the realm of first-principle electronic structure calculations. Despite great progress in the field, reliably describing the primary electronic excitation and possible subsequent structural relaxation in the excited state is in general not straightforward due to limitations of current available approaches in either accuracy or efficiency. In fact, recent years have witnessed a surge in theoretical efforts to truly establish the predictive power of available first-principle methods in characterizing excited states at least in the Franck-Condon region [13–22]. Some of these studies [17–19] have even gotten beyond what can be termed as the theoretical “gold standard” and have quite literally benchmarked the benchmarks! These investigations are of course carried out in the gas phase, are limited to small molecules, and are clearly not representative of a complex photoactive process like the ones described above.

One may ask whether it is indeed necessary to achieve this degree of accuracy in

the gas phase. The issue is that we cannot easily validate the reliability of a given quantum method to compute excited states if the system is embedded in a solvent, protein, or polymer matrix. The complexity of the full problem requires a multiscale description such as a quantum-in-classical approach and the number of “knobs” one can turn does not allow us to ascertain that we are truly predictive, namely, that we are getting the apparently correct answer for the correct reasons and not just accidentally agreeing with experimental observations.

In general, we have at our disposal several first-principle techniques to robustly compute ground-state structures and energies, even for some relatively large molecules, with density functional theory (DFT) being the most widely used approach [23]. On the other hand, finding a balanced description of the ground and excited states entails the task of solving the Schrödinger equation for multiple states with consistent accuracy. If we depart from the Franck-Condon region, we also require the robust computation of interatomic forces to correctly characterize the excited-state potential energy surface (PES) and, for instance, determine its minima, barriers, and conical intersections. In principle, the extension of DFT to excited states, time-dependent DFT (TD-DFT) [24,25], can be readily employed to compute not only vertical excitation energies but also optimal excited-state geometries even for fairly large systems [26–28]. However, the final results can be strongly dependent on the choice of the exchange-correlation functional [29–31] and also on the physical nature of the excitation, for instance, if the excited state demands a complex description of static correlation such as in multiconfigurational states. Furthermore, the applicability of TD-DFT to the conical intersection region is limited. In such cases, we can resort to multireference wave function methods and, to date, the most used approach for photochemical applications remains the complete-active-space self-consistent-field (CASSCF) method [32]. This is a full configuration-interaction (CI) calculation in a small user-defined “active” orbital space, performed simultaneously with the optimization of the orbitals. Here, the quality of the results can however strongly depend on the choice of the orbitals to correlate and the approach largely lacks dynamical correlation. Its perturbative extension cures this last limitation but becomes quickly prohibitive for realistic chromophores. These general difficulties are also reflected in the scarcity of reliable reference data for excited-state geometries or “difficult” features of the PES.

In this thesis, we focus on an alternative set of approaches for the description of excited states and work in the framework of quantum Monte Carlo (QMC) methods [33, 34]. These are a class of highly correlated techniques that provide an approximate, stochastic solution to the Schrödinger equation. Compared to traditional quantum chemistry methods, they offer a greater flexibility in the functional form of the wave function which can explicitly depend on the electron-electron separations, thanks to the stochastic nature of integration. Typically, one employs wave functions which are the product of determinantal expansions on single-particle orbitals multiplied by a correlation factor depending on the interparticle coordinates. Importantly, the most commonly used QMC variants, variational (VMC) and diffusion (DMC) Monte Carlo, scale quite favorably with the size of the system, namely, a mere $\mathcal{O}(N^4)$ where N is the number of electrons. The intrinsic parallelism of these algorithms

also makes them ideal candidates to exploit the use of modern supercomputing architectures. Finally, recent algorithmic developments within our group [35, 36] have enabled the computation of energy derivatives at the same cost per Monte Carlo step as the computation of the energy itself, even when working with large determinantal expansions containing as many as 200,000 determinants. We are therefore now in a unique position to optimize the geometry and the variational parameters in a self-consistent manner and explore the ingredients needed for the accurate computation of ground- and excited-state properties in QMC.

Despite the potential of this method, relatively little is in fact still known about the impact of the choice of the wave function on the QMC results. Investigations in the literature are routinely carried out with relatively simple ansatz such as a single determinant in the ground state using orbitals “borrowed” for instance from DFT. Even less is known about the predictive power of QMC for excited states where calculations are relatively few. For instance, early studies within our group have employed CASSCF wave functions, leading to encouraging results also for realistic chromophores [2, 37, 38]. Small CAS spaces were however often used or the wave functions were truncated to limit the computational cost in the belief/hope that either the variational optimization in the presence of a correlation function or the use of DMC (which stochastically projects a better approximation starting from a given wave function) would have cured the possible deficiency of a small expansion. Therefore, many questions are currently unanswered: Can we really “get by” with few determinants thanks to the explicit inclusion of a correlation factor depending on the interelectronic distances? What is the impact of variational optimization on QMC energies and gradients? Is the use of DMC necessary to improve on a wave function fully optimized at the variational level?

Figure 1.1: Prototypical molecules investigated in this thesis: (A) 1,3-*trans*-butadiene, (B) formaldehyde, (C) thioformaldehyde, (D) thiophene. We also study polymers of thiophene, 2,2'-bithiophene (2 units) and terthiophene (3 units).

Our goal here is to answer these questions and establish the competency of QMC in generating accurate excited-state properties. This will require a concomitant effort to develop a reliable computational protocol to generate compact and systematically improvable QMC wave functions for multiple states. To this aim, we focus on the description of the vertical excitation energy, the structural relaxation in the ground and excited states, and the adiabatic excitation energy of some small, yet theoretically

challenging prototypical molecules in the gas phase (see Fig. 1.1). As discussed below, these molecules are chosen because of the apparent difficulty encountered by other approaches or by QMC itself in accurately determining some of these properties. Furthermore, their small size allows us to truly assess the impact of the choice of the wave function and its optimization in obtaining converged QMC energies and gradients. Importantly, we explore and design here two different strategies to generate robust QMC wave functions. On the one hand, we investigate the use of a selected configuration-interaction approach (i.e. CIPSI – configuration interaction with perturbative selection done iteratively [39]) to perform a smart and automatic selection of the most important determinants for a given electronic state, and generate the determinantal expansions entering our wave functions. We also propose modifications to its standard selection scheme for the construction of QMC wave functions of consistent quality for multiple states at different molecular geometries, and for the accurate computation of vertical and adiabatic excitation energies. On the other hand, we look into the potential use of alternative compact multideterminant wave functions for excited states based on a local description of correlation. These strategies together with the low-scaling algorithms for simultaneous wave function and geometry optimization pave the way to the accurate and efficient QMC study of photoexcitation processes in larger molecular systems.

1.2 This Thesis

We begin this Thesis by presenting all theoretical methods employed during its course in **Chapter 2**. We primarily focus on the selected configuration-interaction, multi-reference perturbation theory, and the continuum quantum Monte Carlo approaches as they form the foundation of the majority of our investigations. In particular, we provide a step-by-step description of the CIPSI scheme for determinant selection along with the algorithmic tricks of its implementation within Quantum Package [40]. Since the optimization of the wave function is a key step in the QMC calculations, we also recount a comprehensive description of the different optimization techniques used in this dissertation. We end this Chapter with a brief overview of density functional theory.

In **Chapter 3**, we establish the competency of using compact CIPSI determinantal expansions in fully optimized QMC wave functions to compute optimal ground-state structures. To this aim, we study butadiene (C_4H_6 ; molecule A in Fig. 1.1), a small conjugated polyene whose bond length alternation (BLA – average difference between alternating single and double bond lengths) is theoretically difficult to estimate, being quite sensitive to the choice of quantum chemical method [41–49]. Even though we are here concerned about very small differences (about 10 mÅ), we are intrigued by recent findings within our group, where the use of a range of CASSCF determinantal components in QMC has led to a somewhat erratic variation of the BLA with the size of the active space as shown in Fig. 1.2. Even after considering expansions containing over 45000 determinants, it is not possible to determine a converged QMC estimate of this structural parameter. As shown in the same Fig-

Jastrow-CIPSI : QMC geometries with few determinants

Figure 1.2: Goals of Chapter 3 – Obtain accurate estimates of optimal ground-state structural parameters of butadiene with compact Jastrow-Slater expansions in QMC.

ure, the use of CIPSI wave functions, on the other hand, yields a much smoother, monotonic convergence of the BLA with increasing number of determinants in the QMC wave function. In fact, our final VMC geometry, even when computed in a minimally-augmented basis of double- ζ quality, is in very good agreement with the reference best theoretical estimates and this is already achieved using just a handful of determinants. This establishes both the higher quality of wave functions generated using the CIPSI selection scheme and the competency of VMC gradients to compute accurate ground-state geometries.

In **Chapter 4**, we extend the CIPSI-QMC protocol to model excited states. We

QMC-CIPSI : Excited states with chemical accuracy

Figure 1.3: Goals of Chapter 4 – Identify a robust protocol to obtain chemically accurate (1) ground- and excited-state geometries, and (2) vertical ($\Delta E_{\text{vertical}}$) and adiabatic ($\Delta E_{\text{adiabatic}}$) excitation energies with CIPSI-QMC.

are interested in computing QMC vertical and adiabatic excitation energies (see Fig. 1.3) as well as equilibrium ground- and excited-state VMC structures with chemical accuracy. This requires to design a strategy to construct CIPSI expansions that yield a balanced description of multiple states at different geometries, namely, not only in the Franck-Condon region but also as the molecule relaxes in the excited state. As test cases, we investigate the lowest-lying $n \rightarrow \pi^*$ excited states of formaldehyde (CH_2O) and thioformaldehyde (CH_2S) in the gas phase (molecules B and C in Fig. 1.1). Formaldehyde is interesting for our purposes since a recent study employing CIPSI wave functions in DMC required as many as 0.3 million determinants to obtain a vertical excitation energy within 0.08(3) eV of the extrapolated FCI estimate [17]. This is a surprisingly large number of determinants given the size of the molecule. Furthermore, its non-planar excited-state geometry computed with a range of highly-correlated methods sees a spread of about 80 mÅ in the CO bond length and 20 degrees in the out-of-plane angle [50]. Similarly, for thioformaldehyde, the use of CIPSI expansions in Ref. 51 has led to a disappointing 0.2 eV error in the VMC estimate of the vertical excitation energy compared to the best theoretical estimates [52]. This is clearly a source of concern for the performance of QMC and is worth revisiting.

Here, we find that generating CIPSI expansions targeting the same second-order perturbation energy correction for all states and geometries in a so-called iso-PT2 scheme leads to a balanced description of the ground- and excited-state PESs for both molecules. The PT2 energy ($E^{\text{PT}2}$) for a given expansion can be viewed as an estimate of the difference between the current CI energy and the FCI value. Therefore, if the second-order energy corrections of the ground ($E_{\text{GS}}^{\text{PT}2}$) and excited ($E_{\text{ES}}^{\text{PT}2}$) states are comparable, we expect to be describing both states in a consistent manner. Combining our iso-PT2 recipe with a full variational optimization of the corresponding QMC wave functions yields chemically accurate estimates of vertical excitation energies with relatively few determinants. In fact, we do not even need to carry out DMC calculations since the DMC excitation energies are compatible with the VMC ones, both agreeing with the best estimates. With our compact iso-PT2 CIPSI determinantal components, we obtain chemically-accurate equilibrium ground- and excited-state geometries and corresponding adiabatic excitation energies. Finally, we also test the procedure of matching the VMC energy variances of the ground and excited states to compute the vertical excitation energies [51, 53] since the variance is another measure of the quality of a wave function. However, we find this scheme to be much less robust than the aforementioned iso-PT2 strategy since it requires much larger determinantal expansions to yield chemical accuracy.

In **Chapter 5**, we consider a more complex excited state, namely, the lowest-lying $\pi \rightarrow \pi^*$ excited state of thiophene ($\text{C}_4\text{H}_4\text{S}$; molecule C of Fig. 1.1). This state is characterized by a highly multireference character and different electronic structure methods yield vertical excitation energies spanning a range of 0.5 eV as shown in Fig. 1.5. Furthermore, the ground and excited states are in the same symmetry class and the corresponding CIPSI expansions are therefore expressed on a common set of determinants, rendering their balanced description more difficult to achieve. Finally, the QMC wave functions of the ground and excited states must be optimized

Figure 1.4: Goals of Chapter 5 – (A) Modify the CIPSI selection scheme to obtain a balanced description of multiple wave functions of states of the same symmetry and (B) accurate estimates of the optimal excited-state geometries.

in a state-averaged fashion within energy minimization, a procedure which might in principle also impact the quality of the results.

For the molecules in Chapter 4, the states of interest belonged to two different symmetry classes, and it was relatively straightforward to ensure the iso-PT2 construction also when we were performing a common selection of the dominant CI determinants. For thiophene, the selected determinants contribute to both states and we therefore find it very difficult to match the PT2 corrections using the standard “old” scheme as shown in Fig. 1.4. In particular, the ground state is clearly converg-

Figure 1.5: Spread of vertical excitation energies of the lowest lying $\pi \rightarrow \pi^*$ excited state of thiophene computed with different correlated approaches.

ing much faster than the excited state since $E_{\text{ES}}^{\text{PT2}} < E_{\text{GS}}^{\text{PT2}}$, and is always closer to the full CI limit (i.e. $E^{\text{PT2}} = 0$). To improve the balance in the description of the two states, we should speed up the selection for the excited state and/or slow down the convergence of the ground state. We demonstrate that we can enforce an iso-PT2 construction for the two states if we simply bias the CIPSI selection in favor of the slower converging state as shown in Fig. 1.4A.

With our modified selection, we obtain accurate QMC vertical excitation energies with quite compact CIPSI expansions in close correspondence with the reference coupled cluster estimates as shown in Fig. 1.5. Somewhat surprisingly, this requires however the use of a basis set larger than the minimally-augmented double- ζ one, which has been found to be sufficient in the previous Chapters to model excited states in QMC. We believe that this basis sensitivity points to remaining difficulties in the CIPSI selection and the corresponding wave function convergence as further discussed in Chapter 6. Finally, we optimize the excited-state geometry of thiophene employing our CIPSI expansions and again succeed in obtaining very high-quality estimates of the structural parameters, as shown in Fig. 1.4B, reaffirming the ability of VMC to model complex excited states also when they are not the lowest in their symmetry class.

Our last Chapter, **Chapter 6**, is in fact the first study we undertook during the course of this dissertation. It focuses on an alternative strategy to model excited states in QMC, which remains however still open for further investigation. Here, we explore whether a local-orbital description allows us to build compact and transferable QMC wave functions for the study of the lowest-lying excited states of thiophene and its polymers as schematically depicted in Fig. 1.6. To start, we employ a recently developed scheme to generate compact ground- and excited-state expansions with the

Figure 1.6: Goals of Chapter 6 – Obtain compact and transferable local wave functions for the computation of vertical excitation energies of thiophene and its polymers. Different orbital representations are schematically shown.

use of orbitals localized on one or two atoms, the concept of “orbital domains”, and the inclusion of a description in terms of multiple resonance structures [54]. While this approach was successful in treating linear chromophores, we find that, for cyclic systems, it leads to wave functions of significant multi-configurational nature, causes greater difficulties in defining the domains to correlate, and requires the inclusion of higher-order excitations. Therefore, we explore an alternate formulation of a local description by restoring the delocalization of the active orbitals within each thiophene unit while retaining the localization of the remaining orbitals on one or two atoms (semi-local orbitals in Fig. 1.6). With this semi-local orbital representation, we obtain compact expansions and, with only a small subset of determinants, recover QMC vertical excitation energies in agreement with the ones computed with the full CAS space. We conclude the Chapter exploring the impact of the use of (semi)local orbitals on the CIPSI selection for thiophene and bithiophene, shedding light on some of the difficulties encountered with thiophene in the previous Chapter.

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Chapter 2

Theoretical Methods

2.1 Introduction

In this thesis, we identify and further develop an automated and efficient protocol for the computation of accurate ground- and excited-state energies and corresponding optimal geometries in the framework of quantum Monte Carlo (QMC) methods. To this aim, we explore the excited-state properties of a range of prototypical molecules with varying degrees of complexity ranging from small triatomic systems to polymers of thiophene that form a crucial component of the donor photo-active units of organic solar cells. We employ a wide range of correlated methods to assess the quality of our results and, in particular, benchmark our structural parameters and excitation energies against high-level coupled cluster (CC) methods.

In this chapter, we briefly describe the various theoretical methods employed in this dissertation, focusing primarily on QMC and on a selected configuration-interaction (sCI) method used to generate accurate and compact wave functions. We additionally review the formalism of the multi-configurational self-consistent field (MCSCF) method as well as its perturbative extensions, the coupled-cluster approach, density functional theory (DFT) and time-dependent (TD)DFT.

We perform all our calculations in the Born-Oppenheimer approximation [1] and neglect relativistic effects since the heaviest atom we consider is sulphur ($Z = 16$). The electronic Hamiltonian is then described in atomic units as:

$$\mathcal{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i) + \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (2.1)$$

The first term is the electronic kinetic energy operator and the second term is the external potential which is here the electron-nucleus Coulomb potential, $-Z/r$, where Z is the nuclear charge. The third term accounts for the electron-electron interaction and is not separable into one-electron operators like the first two terms. While density-functional-theory-based methods map the interacting problem into a non-interacting one with the use of approximate exchange-correlation functionals, higher-level correlated approaches attempt to describe this interaction explicitly and, in so doing, are generally more accurate and expensive at the same time. We will discuss

several such quantum chemical methods in detail in the following sections. Hereafter, we denote the coordinates of an electron by $\mathbf{x} = (\mathbf{r}, \sigma)$ representing the 3 spatial and 1 spin coordinate where $\sigma = \pm 1$.

2.2 The Hartree-Fock approximation

When one accounts for the antisymmetry of the electronic solution, the simplest approximation to the ground-state solution of the Schrödinger equation is the Hartree-Fock (HF) approximation [2–7], where one uses a non-interacting ansatz for the wave function of the N interacting electrons, namely, a single determinant of one-particle orbitals called a Slater determinant [8]:

$$\Psi_{\text{HF}}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Phi_1(\mathbf{x}_1) & \Phi_1(\mathbf{x}_2) & \cdots & \Phi_1(\mathbf{x}_N) \\ \Phi_2(\mathbf{x}_1) & \Phi_2(\mathbf{x}_2) & \cdots & \Phi_2(\mathbf{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \Phi_N(\mathbf{x}_1) & \Phi_N(\mathbf{x}_2) & \cdots & \Phi_N(\mathbf{x}_N) \end{vmatrix}.$$

The single-particle orbitals $\{\Phi_i\}$ are orthonormal spin-orbitals and are obtained via the minimization of the expectation value of $\mathcal{H}$ on Ψ_{HF} . If the spin-orbitals are written as a product of a spatial and a spin component, $\Phi_i(\mathbf{x}) = \phi_i(\mathbf{r})\chi_{s_i}(\sigma)$, the minimization leads to the so-called HF equations:

$$\hat{f}|\phi_i\rangle = \sum_{j=1}^N \epsilon_{ij} |\phi_j\rangle, \quad (2.2)$$

where the sum runs over the occupied orbitals and $\hat{f}$ is an effective one-electron operator, called the Fock operator, which has the following form for a system containing M nuclei:

$$(\hat{f}\phi_i)(\mathbf{r}) = \left(-\frac{1}{2}\nabla^2 - \sum_{I=1}^M \frac{Z_I}{|\mathbf{r} - \mathbf{r}_I|} \right) \phi_i(\mathbf{r}) + (\hat{v}_{\text{HF}}\phi_i)(\mathbf{r}), \quad (2.3)$$

where $\mathbf{r}_I$ denotes the position of a nucleus. The HF potential, $\hat{v}_{\text{HF}}$, describes an effective potential experienced by an electron in the field of the other electrons, and is the sum of two components, namely, a local Coulomb electrostatic potential (also called the Hartree potential), and a non-local exchange potential:

$$(\hat{v}_{\text{HF}}\phi_i)(\mathbf{r}) = v_{\text{Coul}}(\mathbf{r})\phi_i(\mathbf{r}) + (\hat{v}_{\text{x}}^{\text{HF}}\phi_i)(\mathbf{r}), \quad (2.4)$$

$$v_{\text{Coul}}(\mathbf{r}) = \sum_{j=1}^N \int \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.5)$$

$$(\hat{v}_{\text{x}}^{\text{HF}}\phi_i)(\mathbf{r}) = - \sum_{j=1}^N \delta_{s_i, s_j} \left[\int \frac{\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \phi_j(\mathbf{r}), \quad (2.6)$$

where the last potential accounts for exchange effects among electrons in orbitals with the same spin quantum number and also cancels the self-interaction term (of orbital ϕ_i with itself) coming from the Hartree potential.

The spatial components of the spin-orbitals are usually expanded as linear combinations of atomic orbitals (LCAO) centered on the nuclear positions,

$$\phi_i(\mathbf{r}) = \sum_{I=1}^M \sum_{j=1}^{N_{AO}^I} a_{ji}^I \eta_{jI}(\mathbf{r} - \mathbf{r}_I). \quad (2.7)$$

Most quantum chemistry codes employ a Gaussian atomic basis set to represent η :

$$\eta(\mathbf{r}) = x^a y^b z^c \exp(-\alpha r^2), \quad (2.8)$$

since this allows all integrals to be computed analytically.

The HF determinant is initially constructed from a guess of the spin-orbitals, followed by the computation of the effective potential ($\hat{v}_{\text{HF}}$) and the solution of the eigenvalue equations (Eq. 2.2). This yields a new set of spin-orbitals and the same procedure is repeated until convergence. This iterative process of solving a set of eigenvalue equations is called a self-consistent field (SCF) method. In practice, the minimization is performed with respect to the LCAO coefficients, a_{ji}^I .

2.3 Post Hartree-Fock quantum chemical methods

The HF wave function is the best non-interacting solution to an interacting multi-electron problem. The HF energy, E_{HF} , is of course higher than the exact energy, E , and the difference between the exact and HF energies is called the correlation energy, E_{corr} :

$$E_{\text{corr}} = E - E_{\text{HF}}. \quad (2.9)$$

To recover part of the missing E_{corr} , a possible option is to expand the wave function as a linear combination of Slater determinants constructed from a set of orthonormal single-particle orbitals (e.g. the occupied and virtual HF orbitals). The additional determinants have an occupation pattern (or configuration) different from the HF determinant, thereby leading to a so-called configuration interaction (CI) wave function:

$$\Psi_{\text{CI}} = c_0 \Psi_{\text{HF}} + c_1 \Psi_1 + c_2 \Psi_2 + \dots, \quad (2.10)$$

where the different configurations are excitations out of the reference HF determinant to a set of virtual orbitals. Therefore, we can rewrite Ψ_{CI} as

$$\Psi_{\text{CI}} = c_0 D_{\text{HF}} + \sum_{ac} c_{a \rightarrow c} D^{a \rightarrow c} + \sum_{abcd} c_{ab \rightarrow cd} D^{ab \rightarrow cd} + \dots, \quad (2.11)$$

where we denote the HF determinant as D_{HF} for consistency of notation. The determinant $D^{a \rightarrow c}$ represents a single excitation where the occupied orbital a in the HF

determinant is replaced by the virtual orbital c . Similarly, $D^{ab \rightarrow cd}$ denotes a double excitation from the occupied orbitals a and b to the virtual orbitals c and d . One can include higher excitations to further improve the quality of the wave function.

For a given expansion, the optimal CI coefficients, $\{c_i\}$, are obtained through the minimization of the energy, which leads to the secular equations

$$\sum_{j=1}^K \langle D_i | \mathcal{H} | D_j \rangle c_j^{(k)} = E_{\text{CI}}^{(k)} \sum_{j=1}^K \langle D_i | D_j \rangle c_j^{(k)}, \quad (2.12)$$

where $\langle D_i | D_j \rangle = \delta_{ij}$ as the orbitals are orthonormal. The solution of these equations yields an approximation not only to the ground-state wave function and energy, but also to the excited-state ones. The variational principle for the energy guarantees that the lowest energy, $E_{\text{CI}}^{(0)}$, is an upper bound to the exact ground-state energy of the system. For the other states, the Hylleraas-Undheim-MacDonald's theorem [9, 10] states that the approximate solutions with energies $E_{\text{CI}}^{(1)} \leq \dots \leq E_{\text{CI}}^{(k)}$ satisfy

$$E_k \leq E_{\text{CI}}^{(k)}, \quad (2.13)$$

where E_k are the exact energies of the eigenstates of the Hamiltonian, $\mathcal{H}$.

Given an atomic basis set and a corresponding equal number of molecular orbitals, the full CI (FCI) expansion includes all possible configurations obtained by exciting up to N electrons from the HF determinant to the virtual orbitals. In practice, FCI is only feasible for relatively small systems and basis sets since the number of determinants in the CI expansion grows exponentially with N . Typically, one is either forced to truncate the expansion to a low level of excitation including the most important contributions (e.g. CI singles and doubles, CISD, only includes single and double excitations) or use approaches such as selected CI where the expansion is built by selecting the most relevant determinants in the full CI space according to some energetic criterion. We will discuss one such approach in detail in Section 2.3.2.

In the multi-configurational SCF (MCSCF) method, one optimizes the LCAO coefficients, a_{ji} (Eq. 2.7), in addition to the linear parameters in the expansion. This is particularly important since energetically-higher orbitals from a starting HF calculation might be far from optimal and will be significantly modified in the SCF optimization. The complete active space SCF (CASSCF) approach is a particular type of MCSCF calculation which is often employed in this thesis. In a CAS calculation, the orbital set is divided in three groups: inactive, active, and virtual orbitals. The inactive orbitals remain doubly occupied and the virtual orbitals unoccupied, while the active orbitals constitute the so-called active space and are often chosen based on chemical intuition: if n electrons occupy m active orbitals, the active space is a $\text{CAS}(n, m)$ and all possible excitations of the n electrons in the m orbitals are allowed. In other words, one constructs a FCI expansion within the restricted active space and a CASSCF(n, m) calculation is then an energy optimization of the CI and orbital coefficients in the CAS expansion. The choice of a proper active space can significantly affect the quality of the results and is often the trickiest part in such calculations. We will discuss the implications of the choice of CAS spaces for different systems in this thesis.

For obtaining multiple states of the same symmetry, a state averaged (SA) MC-SCF approach is customarily employed to avoid root-flipping problems in the optimization. In a SA calculation, the weighted average of the energies of the states of interest is optimized:

$$E_{\text{SA}} = \sum_J w_J \frac{\langle \Psi^J | \mathcal{H} | \Psi^J \rangle}{\langle \Psi^J | \Psi^J \rangle}, \quad (2.14)$$

where $\sum_J w_J = 1$. The optimization yields a common set of orbitals and the orthogonality between the wave functions is maintained via the state-specific CI coefficients.

MCSCF or CASSCF calculations, however, recover only a small part of the correlation energy as only static correlations in a relatively small CI subspace are considered. One way to improve upon them is to use perturbation approaches as discussed in the next Section.

2.3.1 Perturbation theory

The Rayleigh-Schrödinger perturbation theory (RSPT) is often used to improve results obtained at a certain level of theory as, for instance, HF or MCSCF. In a perturbation approach, the total Hamiltonian of the system, $\mathcal{H}$, is partitioned into a zero-order Hamiltonian, $\mathcal{H}^{(0)}$, and a perturbation operator, $\mathcal{V}$, as

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{V}. \quad (2.15)$$

Correspondingly, the total wave function, $|\Psi_n\rangle$, for the electronic state n and its corresponding energy, E_n , can be written as the following expansions:

$$|\Psi_n\rangle = \sum_{i=0}^{\infty} |\Psi_n^{(i)}\rangle \quad (2.16)$$

$$E_n = \sum_{i=0}^{\infty} E_n^{(i)}, \quad (2.17)$$

where the superscript, i , indicates the order of the perturbation correction. To improve the convergence properties of the perturbation series, the zero-order wave function should provide a good description of the electronic state under consideration. This implies that the zero-order Hamiltonian should be as close as possible to the total Hamiltonian, thereby reducing the role of the perturbation. There are several choices for partitioning the total Hamiltonian, irrespective of which the following equations for the lowest-order corrections to the energy eigenvalues hold true (in the absence of degeneracies at zero order):

$$\begin{aligned} E_n^{(0)} + E_n^{(1)} &= \langle \Psi_n^{(0)} | \mathcal{H} | \Psi_n^{(0)} \rangle \\ E_n^{(2)} &= \langle \Psi_n^{(0)} | \mathcal{H} | \Psi_n^{(1)} \rangle. \end{aligned} \quad (2.18)$$

Using the expression of the first-order correction to the wave function,

$$|\Psi_n^{(1)}\rangle = - \sum_{k \neq n} |\Psi_k^{(0)}\rangle \frac{\langle \Psi_k^{(0)} | \mathcal{H} | \Psi_n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}}, \quad (2.19)$$

the second-order perturbation correction to the energy becomes

$$E_n^{(2)} = - \sum_{k \neq n} \frac{|\langle \Psi_k^{(0)} | \mathcal{H} | \Psi_n^{(0)} \rangle|^2}{E_k^{(0)} - E_n^{(0)}}. \quad (2.20)$$

The definition of perturbation theory is complete once we have decided on the zero-order wave function and Hamiltonian. If we are interested in the ground state and the zero-order wave function is chosen to be a HF determinant, the application of RSPT bears the name of Möller-Plesset perturbation theory (MP2) [11]. In this case, the zero-order Hamiltonian is defined as the sum of the Fock operators (Eq. 2.3) for all the electrons, $\mathcal{H}^{(0)} = \sum_i \hat{f}(i)$, and, assuming a set of canonical orbitals, the zero-order energy is given by the sum of the orbital energies.

If we instead use a MCSCF wave function as the zero-order wave function, we obtain the so-called multi-reference perturbation theory (MRPT). In this case, different choices of zero-order Hamiltonian result in different formulations of perturbation theory, which are often characterized by rather different properties. The general idea is to construct the other eigenstates of the zero-order Hamiltonian (also called perturbation functions) to include the excitations not present in the MCSCF wave function, which can then couple to the MCSCF wave function via the total Hamiltonian. The first-order wave function and second-order energy corrections are then computed following the usual equations (Eqs. 2.19 and 2.20).

The complete-active-space perturbation theory (CASPT2) is one of the most widely used perturbation approaches, particularly in the context of excited-state calculations [12, 13]. In this approach, the zero-order wave function is the CASSCF wave function of the state of interest and the perturbation functions are generated by single and double replacements in the CAS wave function. Only these replacements couple to the zero-order CAS wave function in the computation of the second-order energy. The resultant excited determinants include, for instance, excitations of one electron from the inactive to the active orbitals, or from the active to the virtuals, and other possible combinations. For MRPT, there is no unique definition of the zero-order Hamiltonian. Consequently, there have been multiple formulations of CASPT2 that differ in the choice of the zero-order Hamiltonian yielding the same zero-order CASSCF wave function. In this thesis, we employ a formulation of the zero-order one-body Hamiltonian for CASPT2 calculations that includes a shift in the denominators of Eq. 2.20 to prevent them from becoming too small. The shift depends on the occupation of the orbitals and a semi-empirical parameter, the so-called ionization potential-electron affinity (IPEA) shift, which is here set to the default value of 0.25 a.u. [14]. Excitation energies computed with the CASPT2 method without this shift have been shown to be consistently lower than the best theoretical estimates [15].

A partitioning of the Hamiltonian which we extensively use in this thesis is the Epstein-Nesbet partitioning [16, 17], where the full CI space is partitioned into a variational space $\mathcal{S}$ spanned by the determinants $\{|D_i\rangle\}$ and the remaining space spanned by the determinants $\{|\alpha\rangle\}$. The zero-order Hamiltonian $\mathcal{H}^{(0)}$ is chosen so

that its matrix elements are exact in $\mathcal{S}$ and diagonal on $|\alpha\rangle$, resulting in

$$\begin{aligned}\langle D_i | \mathcal{H}^{(0)} | D_j \rangle &= \langle D_i | \mathcal{H} | D_j \rangle \\ \langle D_i | \mathcal{H}^{(0)} | \alpha \rangle &= 0 \\ \langle \alpha | \mathcal{H}^{(0)} | \alpha \rangle &= \langle \alpha | \mathcal{H} | \alpha \rangle,\end{aligned}\tag{2.21}$$

so $\mathcal{H}^{(0)}$ is defined as

$$\mathcal{H}^{(0)} = \sum_{i,j \in \mathcal{S}} \langle D_i | \mathcal{H} | D_j \rangle | D_i \rangle \langle D_j | + \sum_{\alpha \notin \mathcal{S}} \langle \alpha | \mathcal{H} | \alpha \rangle | \alpha \rangle \langle \alpha |.\tag{2.22}$$

It therefore follows from the above definition that

$$\begin{aligned}\langle D_i | \mathcal{V} | \alpha \rangle &= \langle D_i | \mathcal{H} | \alpha \rangle \\ \langle D_i | \mathcal{V} | D_j \rangle &= 0.\end{aligned}\tag{2.23}$$

Let us now consider a CI wave function, $|\Psi^{(0)}\rangle = \sum_{i \in \mathcal{S}} c_i |D_i\rangle$, which diagonalizes $\mathcal{H}$ (and therefore $\mathcal{H}^{(0)}$) in the space $\mathcal{S}$ with variational energy $E^{(0)}$. The first-order perturbation correction to $E^{(0)}$ is zero by virtue of the last equality in Eq. 2.23 while the second-order energy correction, denoted here as E_{PT2} , is given by

$$E_{\text{PT2}} = \sum_{\alpha} \frac{|\langle \alpha | \mathcal{H} | \Psi^{(0)} \rangle|^2}{E^{(0)} - \langle \alpha | \mathcal{H} | \alpha \rangle} = \sum_{\alpha} \delta E_{\alpha}^{(2)},\tag{2.24}$$

where $\delta E_{\alpha}^{(2)}$ is the perturbation energy contribution of a determinant $|\alpha\rangle$ not present in $\mathcal{S}$. The Epstein-Nesbet perturbation theory is the method of choice in estimating the perturbation correction to second order in the configuration-interaction-using-a-perturbative-selection-done-iteratively (CIPSI) approach described below.

2.3.2 CIPSI

CIPSI is a selected CI method proposed by Huron, Rancurel, and Malrieu [18], where determinants to construct a multi-determinant wave function are perturbatively chosen *on the fly* from the entire set of determinants in a FCI space in an iterative fashion. This is in contrast to conventional CI approaches where the determinants in the expansion are chosen *a priori* based on an occupation or excitation criterion (e.g. CISD discussed in Sec. 2.3). The selection is performed based on the estimated energetic contribution of a determinant to the FCI wave function. At every CIPSI iteration, an external determinant $|\alpha\rangle$ is added to a reference set of determinants if its second-order energy correction is higher than a user-defined threshold. Although the selection criterion might differ from one selected CI method to another, the primary advantage of any such algorithm is that the most relevant determinants are considered first. Consequently, they often yield a much more accurate description of a given electronic state and a lower energy for an equivalent number of determinants in comparison to those obtained via a conventional CI approach.

A typical CIPSI selection process is described below through the definition of the initial reference wave function and its subsequent modifications. In this thesis, all CIPSI selections are performed in the basis of the orbitals optimized in a small CASSCF calculation for the electronic state(s) of interest. Since the orbitals are not optimized any further during the selection process itself, using such orbital basis is beneficial in ensuring that some important determinants are selected first and that the variational CI energy converges faster to the FCI limit. At the n^{th} iteration of the CIPSI selection, we have the following [19]:

1. The reference wave function $|\Psi^{(n)}\rangle$ is a variational expansion defined over a set of N_{det} “internal” determinants $\{|D_i\rangle\}^{(n)}$:

$$|\Psi^{(n)}\rangle = \sum_{i=1}^{N_{\text{det}}} c_i^{(n)} |D_i\rangle, \quad (2.25)$$

with energy $E_{\text{var}}^{(n)} = \langle \Psi^{(n)} | \mathcal{H} | \Psi^{(n)} \rangle$. Typically, at the start, $|\Psi^{(0)}\rangle$ is the HF configuration or a CIS expansion.

2. The set of determinants $\{|\alpha\rangle\}$ “external” to this reference space $\{|D_i\rangle\}^{(n)}$ is given by all possible single and double excitations out of the internal configurational space. For each $|\alpha\rangle$, the perturbative correction, $\delta E_{\alpha}^{(2)}$, can be computed using the expression for the summand in Eq. 2.24, where $E^{(0)} = E_{\text{var}}^{(n)}$.

As described below, a subset of the most relevant $\{|\alpha\rangle\}$, which we denote by $\{|\alpha_*\rangle\}^{(n)}$, is generated and selected based on a threshold on their second-order energy contribution and added to the current internal space so that

$$\{|D_i\rangle\}^{(n+1)} = \{|D_i\rangle\}^{(n)} \cup \{|\alpha_*\rangle\}^{(n)}. \quad (2.26)$$

The net perturbative correction, $E_{\text{PT2}}^{(n)}$, at iteration n is then given by

$$E_{\text{PT2}}^{(n)} = \sum_{\alpha_*} \delta E_{\alpha_*}^{(2)}. \quad (2.27)$$

3. The new reference wave function at iteration $n + 1$, $|\Psi^{(n+1)}\rangle$, is then constructed by diagonalizing the many-body Hamiltonian, $\mathcal{H}$, in the new reference space $\{|D_i\rangle\}^{(n+1)}$ and the new $c_i^{(n+1)}$ coefficients are obtained.
4. Steps 2–3 are then either repeated or the selection process is terminated based on some criterion, for instance, if the target number of determinants has already been reached or if E_{PT2} is such that E_{var} can be reliably extrapolated to the full CI energy, E_{FCI} .

When a selection is performed to describe more than one state, each state, k , is characterized by a wave function $\Psi_k^{(n)}$ and corresponding variational energy $E_{\text{var},k}^{(n)}$ at

iteration n . Then, a common set of the most relevant $\{|\alpha\rangle\}$ are generated and chosen from the external space based on their energy contribution:

$$e_\alpha = \sum_{k=1}^{N_{\text{states}}} w_k \delta E_{\alpha,k}^{(2)}, \quad (2.28)$$

which is now computed as the weighted sum of the energy contribution of a given $|\alpha\rangle$ to all N_{states} of interest. Using the reweighting factor w_k is crucial to ensure that all states have similar PT2 corrections. For sufficiently large expansions, the PT2 correction can be viewed as an estimate of the current error in the variational energy with respect to the FCI value. Consequently, wave functions of different states with similar PT2 corrections are expected to have comparable quality and yield a reasonable estimate of the excitation energies already at the CI level.

To this aim, in Chapter 4, we follow the suggestion of Angeli *et al.* [20] and assign w_k to be equal to the inverse of $\max(|c_{k,i}^{(n)}|^2)$ where $|c_{k,i}^{(n)}|$ is the largest absolute determinant coefficient in the reference wave function of state k at the n^{th} selection iteration. In the applications presented in Chapter 4, the ground state is a closed-shell and the excited state an open-shell singlet, both having single-reference character with the dominant configuration state function (CSF) comprising a single determinant in the ground state and two determinants in the excited state. Since the expansion is performed in the basis of the determinants and not of the CSFs, reweighting the energy contributions by w_k recovers the balance for the different states. As a consequence, we observe that multiple states resulting from the common expansion have approximately equivalent net PT2 corrections at every CIPSI iteration.

Unfortunately, we find that one needs to further modify these weights when the states belong to the same symmetry or if one of the states has a significantly higher multi-configurational character than the others. For states of different symmetry, one can alternatively perform the CIPSI expansions separately until when they have comparable net PT2 corrections. Such a procedure is however not possible if the states have the same symmetry and, in this case, we introduce and discuss possible modifications of w_k in Chapter 5.

Construction of the external determinant space

We will now discuss how the external determinant set $\{|\alpha\rangle\}$ is constructed and the most relevant $\{|\alpha_*\rangle\}$ are isolated in practice.

The construction of a set of external determinants, not present in the current internal space $\mathcal{S} \equiv \{|D_i\rangle\}^{(n)}$, can in principle be done by looping over all internal determinants and generating all possible *unique* single and double excitations out of them while simultaneously computing their second-order energy contribution, $\delta E_\alpha^{(2)}$. Such a procedure is however challenged by the requirement to store all values of $\delta E_\alpha^{(2)}$ in memory simultaneously since their number scales as $\mathcal{O}(N_{\text{det}} \times N^2 \times N_{\text{bas}}^2)$, where N_{det} is the total number of determinants in $\mathcal{S}$, N is the number of electrons, and N_{bas} is the total number of one-electron basis functions [21].

In Chapters 3 and 4, we therefore employ a modified CIPSI algorithm that significantly reduces the number of external determinants generated at a given iteration as well as the cost of computing their second-order energy correction without any considerable loss in accuracy. The determinants in the reference space $\mathcal{S}$ are first sorted in order of decreasing weight such that $c_i^2 \geq c_{i+1}^2$ and then the following modifications are made:

1. We use “generators” to construct the external set, $\{|\alpha\rangle\}$.

We do not generate single and double excitations out of every determinant in the reference space $\mathcal{S}$ but only use a subset of them. This subset of determinants, $\{|D_g\rangle\}$, are called the “generators” and are identified by collecting all determinants whose weights add up to meet the following condition:

$$\sum_{i \in [1, N_{\text{det}})} c_i^2 \leq 0.99. \quad (2.29)$$

It is important to note that an $|\alpha\rangle$ can already be contained in the reference space or can be generated by more than one generator. To avoid this, at every selection iteration, one checks and discards an $|\alpha\rangle$ generated by $|D_i\rangle$ if this is already in $\mathcal{S}$ or connected to any of the generators $|D_{j < i}\rangle$.

Quite often, only a relatively small subset of internal determinants are sufficient to meet the condition in Eq. 2.29. It is expected that the excluded determinants, $\{|D_i\rangle\} - \{|D_g\rangle\}$, will account for less than 1% of the correlation energy and that the $|\alpha\rangle$ generated by them will have a very small second-order energy contribution, lower than the selection threshold. This will, however, not be the case when we are very close to CIPSI convergence, typically when $|E_{\text{PT2}}|$ is less than 1% of $|E_{\text{FCI}} - E_{\text{HF}}|$.

2. We use “selectors” to compute $\delta E_\alpha^{(2)}$.

We do not need to compute extremely accurate values of $\delta E_\alpha^{(2)}$ as small differences are unlikely to have a substantial effect on the selection of the most relevant external determinants. Therefore, connections of a determinant $|\alpha\rangle$ to $\{|D_i\rangle\}$ with small coefficients $|c_i|$ can be neglected in the computation of its energy contribution. The subset of the internal connected determinants, $\{|D_s\rangle\}$, sufficient to compute reliable estimates of $\delta E_\alpha^{(2)}$ are called the set of “selectors”.

This subset is obtained by truncating the reference wave function by again defining a threshold on the norm of the wave function, which is typically larger than the threshold on the generators (i.e. $\{|D_i\rangle\} \supset \{|D_s\rangle\} \supset \{|D_g\rangle\}$). In particular, we consider

$$\sum_{s \in [1, N_{\text{det}})} c_s^2 \leq 0.999, \quad (2.30)$$

and approximate $\langle \alpha | \mathcal{H} | \Psi^{(n)} \rangle$ as

$$\langle \alpha | \mathcal{H} | \Psi^{(n)} \rangle \approx \sum_{D_s} c_s \langle \alpha | \mathcal{H} | D_s \rangle. \quad (2.31)$$

Employing a larger threshold on the selectors than the generators ensures that the PT2 energy contribution of an $|\alpha\rangle$ obtained out of the last generators (with smallest $|c_i|$) is reliably estimated since such an $|\alpha\rangle$ might have many connections with determinants in $\{|D_s\rangle\} - \{|D_g\rangle\}$.

While working with generators/selectors significantly accelerates the selection process, it systematically introduces a bias in the estimate of E_{PT2} which is computed as a sum of approximate perturbative corrections (using Eq. 2.31 in Eq. 2.24) of the external determinants selected at each iteration ($\delta E_\alpha^{(2)}/e_\alpha$). Defining generators using Eq. 2.29, we are only able to access the singles and doubles excitations out of determinants accounting for 99% of the reference wave function. We asymptotically miss out on some small contributions and consequently converge to a biased FCI wave function. This has the effect of introducing a size-consistency error in the extrapolated FCI energies.

From Chapter 5 onward, E_{PT2} is therefore computed by stochastically sampling the $\delta E_\alpha^{(2)}$ contributions. The concept of using selectors in calculating these contributions is entirely removed. The idea of using generators is retained but these are now drawn stochastically using Monte Carlo (MC) sampling from the complete reference space $\mathcal{S}$ with probabilities proportional to their weights. For each drawn determinant, all possible single and double excitations are built and their net second-order energy contribution is computed. This new algorithm, called the stochastic PT2 sampling method [21], besides being demonstrably cheaper and more accurate than the previous approach succeeds in removing the bias in E_{PT2} introduced by the aforementioned approximations. In detailing this sampling method, we will first introduce a partitioning of the external determinantal space $\{|\alpha\rangle\}$ that is instrumental for the efficiency of the MC sampling algorithm.

The external determinant set $\{|\alpha\rangle\}$ is partitioned into N_{det} (the number of determinants in $\mathcal{S}$) subsets $\{|\alpha_i\rangle\}$ such that

$$\{|\alpha\rangle\} = \bigcup_{i=1}^{N_{\text{det}}} \{|\alpha_i\rangle\}, \quad \text{where} \quad \{|\alpha_i\rangle\} \cap \{|\alpha_j\rangle\} = \emptyset \quad \forall \quad i \neq j. \quad (2.32)$$

Each $\{|\alpha_i\rangle\}$ contains all *unique* single and double excitations that can be generated out of an internal determinant $|D_i\rangle$ which do not already exist in $\mathcal{S}$ or in $\{|\alpha_{j<i}\rangle\}$. Note that the internal determinants are still ordered in decreasing order of their weights, i.e. $c_i^2 \geq c_{i+1}^2$. Correspondingly, the net PT2 contribution of $\{|\alpha\rangle\}$ can also be decomposed as a sum of the PT2 contributions of the different $\{|\alpha_i\rangle\}$ partitions:

$$E_{\text{PT2}} = \sum_{i=1}^{N_{\text{det}}} e_i, \quad (2.33)$$

where

$$e_i = \sum_{|\alpha\rangle \in \{|\alpha_i\rangle\}} \frac{|\langle \alpha | \mathcal{H} | \Psi^{(n)} \rangle|^2}{E_{\text{var}}^{(n)} - \langle \alpha | \mathcal{H} | \alpha \rangle}. \quad (2.34)$$

By construction, $\{|\alpha\rangle\} \in \{|\alpha_i\rangle\}$ are not connected to any $|D_{j<i}\rangle$ with a non-zero coefficient. Therefore, we can rewrite Eq. 2.34 as:

$$e_i = \sum_{|\alpha\rangle \in \{|\alpha_i\rangle\}} \frac{|\langle\alpha|\mathcal{H}|\Psi_i^{(n)}\rangle|^2}{E_{\text{var}}^{(n)} - \langle\alpha|\mathcal{H}|\alpha\rangle}, \quad (2.35)$$

where

$$\Psi_i^{(n)} = \sum_{m=i}^{N_{\text{det}}} c_m |D_m\rangle. \quad (2.36)$$

Accordingly, Eq. 2.33 can now be written as,

$$E_{\text{PT2}} = \sum_{i=1}^{N_{\text{det}}} \sum_{|\alpha\rangle \in \{|\alpha_i\rangle\}} \frac{|\langle\alpha|\mathcal{H}|\Psi_i^{(n)}\rangle|^2}{E_{\text{var}}^{(n)} - \langle\alpha|\mathcal{H}|\alpha\rangle}. \quad (2.37)$$

An important point to note from the definition of e_i is the fact that their absolute value decays rapidly with increasing values of i [21] owing to the manner in which $\{|\alpha_i\rangle\}$ are constructed. With increasing values of i , (1) the number of determinants involved in the sum of Eq. 2.35 decreases thereby making the computation of e_i faster, (2) the magnitude of the denominator of Eq. 2.35 increases, and (3) the norm of the wave function $\Psi_i^{(n)}$ decreases.

To obtain unbiased estimates of E_{PT2} , we want to sample the e_i contributions stochastically using MC. To this aim, we need to recast Eq. 2.33 into a suitable form:

$$E_{\text{PT2}} = \sum_{i=1}^{N_{\text{det}}} p_i \left(\frac{e_i}{p_i} \right), \quad (2.38)$$

which can then be rewritten as a MC estimator:

$$E_{\text{PT2}} = \left\langle \frac{e_i}{p_i} \right\rangle_{p_i}. \quad (2.39)$$

Here, p_i is an arbitrary probability distribution. The optimal choice for p_i given by a zero-variance condition would be

$$p_i^{\text{opt}} = \frac{e_i}{E_{\text{PT2}}}. \quad (2.40)$$

Garniron *et al.* note that the magnitude of e_i is related to the norm of the truncated wave function $\Psi_i^{(n)}$ [19, 21] and, therefore, choose the probability distribution p_i as

$$p_i = \frac{\langle\Psi_i^{(n)}|\Psi_i^{(n)}\rangle}{\sum_{j=1}^{N_{\text{det}}} \langle\Psi_j^{(n)}|\Psi_j^{(n)}\rangle} = \frac{\sum_{m=i}^{N_{\text{det}}} c_m^2}{\sum_{j=1}^{N_{\text{det}}} \sum_{k=j}^{N_{\text{det}}} c_k^2}. \quad (2.41)$$

Furthermore, they also observe from their MC simulations that summing all c_m^2 terms in the numerator of Eq. 2.41 or only a subset of it does not significantly alter the

statistical fluctuations. In the actual code implementation, the numerator is restricted only to the leading coefficient so that

$$p_i = \frac{c_i^2}{\sum_{j=1}^{N_{\text{det}}} c_j^2}. \quad (2.42)$$

Therefore, this probability distribution is sampled, the corresponding internal determinant $|D_i\rangle$ is drawn and all unique single and double excitations are generated out of it, the value e_i/p_i is computed and added to the average to estimate E_{PT2} . In practice, the value e_i is computed only the first time the generator $|D_i\rangle$ is drawn. It is then stored in memory and retrieved if the same generator is drawn again. This is done since the number of e_i is always small enough to fit in memory. Doing so makes the algorithm extremely efficient since the vast majority of the computational time is in fact spent in the computation of the e_i values.

The first few determinants $|D_i\rangle$ (smallest i) are often the ones responsible for the most significant contributions to E_{PT2} . It is therefore advantageous to remove these determinants from the stochastic sampling process. The net contribution of the external determinants that are generated out of these dominant determinants is computed and stored as the so-called deterministic component of E_{PT2} . The remaining generators are stochastically sampled, therefore resulting in a so-called hybrid stochastic-deterministic scheme. Starting from the deterministic component, the average is updated at every MC step by adding to it the e_i contribution of every newly drawn generator while keeping track of all previous draws. As discussed in Ref. [21], several additional tricks are introduced to further improve the efficiency of the algorithm.

Selection of most relevant determinants $|\alpha_*\rangle$

In all Chapters, a threshold is used to determine the most relevant determinants in the external space based on their PT2 contribution ($\delta E_\alpha^{(2)}/e_\alpha$ in Chapters 3 and 4, and e_i for Chapters 5 and 6) since we want to expand the wave function by a predefined amount at every iteration. In Chapter 3, we employ a fixed energy threshold on $|\delta E_\alpha^{(2)}|$ to obtain $|\alpha_*\rangle$. However, if this threshold is set too low, it can allow rather unimportant determinants to come into the wave function at an earlier iteration than more relevant ones. This can be particularly undesirable when we want to obtain compact wave functions for QMC.

To address this issue, a dynamic threshold is used in the following Chapters. The initial selection threshold is set to zero and an empty buffer array is created which is typically twice the size of the internal space (i.e. $2N_{\text{det}}$). $|e_\alpha|$ (or $|e_i|$) contributions are added until the buffer is filled. Once the buffer is full, it is sorted in decreasing order of these energy contributions. The selection threshold is then set to the value at position $N_t = N_{\text{det}}$. The remaining buffer between N_t and $2N_{\text{det}}$ is emptied and the buffer is continued to be filled based on the new selection threshold. The buffer is sorted again, the threshold is changed to the value at $N_t = N_t + 1$, and the process is repeated. Once all external contributions (from the generators or the MC sampling)

have passed through this procedure, the highest N_{det} contributors are selected and added to the current reference space. The dynamic threshold, therefore, ensures that only the most relevant determinants are selected first. The size of the buffer can of course be modified according to the preference of the user. A smaller buffer causes the size of the wave function to grow slowly from one iteration to the next and helps exercise a better control on the quality of the wave function at any given iteration.

The CIPSI expansions are used to construct the Slater components of the corresponding quantum Monte Carlo wave functions, which we discuss in detail in Section 2.4.

2.3.3 Coupled Cluster Theory

Coupled cluster (CC) methods are another class of post-HF approaches that we extensively use in this thesis, in particular, to obtain reference ground- and excited-state structures as well as excitation energies. These use an exponential ansatz of the wave function:

$$|\Psi_{\text{CC}}\rangle = e^{\hat{T}} |\Psi_{\text{HF}}\rangle, \quad (2.43)$$

where $\hat{T} = \hat{T}^1 + \hat{T}^2 + \hat{T}^3 + \dots$ is the excitation operator written as the sum of single ($\hat{T}^1$), double ($\hat{T}^2$), triple ($\hat{T}^3$) and so on excitations. As an example, we can write the operator for the single-excitation class, $\hat{T}^1$, as follows:

$$\hat{T}^1 = \sum_i \sum_a t_a^i \hat{a}_a^\dagger \hat{a}_i, \quad (2.44)$$

where t_a^i are unknown excitation amplitudes. Often one truncates CC calculations based on the order of excitations such as CCS, CCSD [22], CCSDT [23, 24], similarly to their corresponding CI counterparts like CIS, CISD, CISDT. An important difference, however, between CC and CI methods is that CC is size-consistent and this is true for any truncation of the coupled-cluster expansion because of the exponential ansatz. Nevertheless, while truncated CI methods are variational and yield an upper bound to the energy, the energy estimator of a truncated CC wave function (Eq. 2.45) is not and it might recover more than 100% of the correlation energy. This non-variational character, however, does not seem to affect the energies of small molecules close to equilibrium and, therefore, these approaches often serve as benchmark standards.

The CC energy and excitation amplitudes are calculated from the coupled-cluster equations which, for example in CCSD (coupled cluster singles and doubles), are given by:

$$\langle \Psi_{\text{HF}} | e^{-\hat{T}} \mathcal{H} e^{\hat{T}} | \Psi_{\text{HF}} \rangle = E_{\text{CCSD}} \quad (2.45)$$

$$\langle \Psi_i^a | e^{-\hat{T}} \mathcal{H} e^{\hat{T}} | \Psi_{\text{HF}} \rangle = 0 \quad (2.46)$$

$$\langle \Psi_{ij}^{ab} | e^{-\hat{T}} \mathcal{H} e^{\hat{T}} | \Psi_{\text{HF}} \rangle = 0. \quad (2.47)$$

where $\hat{T} = \hat{T}_1 + \hat{T}_2$.

There are several available routes to approximate the CC equations in order to reduce the computational cost. For instance, CCSD which scales as N^6 can be approximated with CC2 [25–27] that offers a reduced scaling of N^5 ; CCSDT which scales as N^8 can be approximated with CCSD(T) [28–31] that scales as N^7 . CCSD(T) is often referred to as the “gold standard” for small systems with low static correlation, and introduces the triple excitations via perturbation theory on top of a CCSD calculation. In Chapter 3, we employ CCSD(T) to obtain an optimal ground-state geometry and corresponding energy of 1,3-*trans*-butadiene, and test the performance of our QMC wave functions against these results.

Another approximation to the CCSDT level of theory is CC3 [32], which also offers a N^7 scaling and has similar level of accuracy and robustness to CCSD(T) with respect to static correlation. It, however, bears the advantage of being well-suited for the computation of time-dependent properties. In a recent effort, CC3 excitation energies of over 40 small and medium sized molecules were benchmarked against highly accurate extrapolated FCI energies [33, 34] and were found to be compatible within a maximum deviation of 0.04 eV. Therefore, whenever possible, we employ CC3 in the computation of reference vertical and adiabatic excitation energies as well as optimal ground- and excited-state geometries in Chapters 4 and 5.

Excited states are computed in the CC method using the so-called equation-of-motion coupled-cluster (EOM-CC) ansatz. The excited state wave function, $|\Psi_{CC}^{ES}\rangle$, is written as the action of an excitation operator $\hat{R}$ (with unknown amplitudes) on the ground-state CC wave function, $|\Psi_{CC}^{GS}\rangle$:

$$|\Psi_{CC}^{ES}\rangle = \hat{R} |\Psi_{CC}^{GS}\rangle = \hat{R} e^{\hat{T}} |\Psi_{HF}\rangle. \quad (2.48)$$

Rearranging the excited state Schrödinger equation (using that $\hat{R}$ and $\hat{T}$ commute), we obtain:

$$e^{-\hat{T}} \mathcal{H} e^{\hat{T}} \hat{R} |\Psi_{HF}\rangle = E_{CC}^{ES} \hat{R} |\Psi_{HF}\rangle, \quad (2.49)$$

where $e^{-\hat{T}} \mathcal{H} e^{\hat{T}} = \bar{\mathcal{H}}$ is the effective EOM-CC Hamiltonian. The CC excitation energy, $\Omega = E_{CC}^{ES} - E_{CC}^{GS}$, is then computed as an eigenvalue of the following equation:

$$(\bar{\mathcal{H}} - E_{CC}^{GS}) \hat{R} |\Psi_{HF}\rangle = \Omega \hat{R} |\Psi_{HF}\rangle \quad (2.50)$$

The Hamiltonian $\bar{\mathcal{H}}$ is non-Hermitian since $e^{\hat{T}}$ is nonunitary and therefore its each root is associated with two eigenvectors corresponding to different bra and ket states: $\langle \tilde{\Psi} | = \langle \Psi_{HF} | \hat{L} e^{-\hat{T}}$ and $|\Psi\rangle = e^{\hat{T}} \hat{R} |\Psi_{HF}\rangle$, where $\hat{L}$ is the deexcitation operator. The ket states $|\Psi\rangle$ are the excited state wave functions (as shown in Eq. 2.48) [35]. In practice, the operators $\hat{R}$ are truncated to the same degree as the coupled-cluster operator. For example, in EOM-CCSD, $\hat{R}$ includes only the single and double excitations.

2.4 Quantum Monte Carlo Methods

The primary focus of this thesis is the development and application of efficient wave functions for continuous quantum Monte Carlo methods [36], particularly, the zero-temperature variational (VMC) and diffusion (DMC) Monte Carlo variants which

we employ to compute optimal excitation energies as well as ground- and excited-state equilibrium structures of various organic molecular systems. Similar to the different approaches listed above, QMC methods are also wave function methods that bear potential to outperform them in accuracy and computational cost when dealing with highly correlated problems and/or large molecules. However, in contrast to the deterministic nature of the previously mentioned traditional quantum chemistry methods, QMC solves the electronic Schrödinger equation stochastically. Owing to the use of sampling MC techniques, we exercise significant flexibility in the choice of the functional form of the many-body wave function, that can also explicitly include a dependence on interelectronic distances. We additionally benefit from a favorable scaling with the number of electrons (N^4). Furthermore, their inherent parallel nature makes them ideal candidates for use on modern massively parallel supercomputing architectures.

2.4.1 Variational Monte Carlo

Variational Monte Carlo, or VMC, is the simplest variant of quantum Monte Carlo methods that employs classical Monte Carlo to estimate the multidimensional integrals involved in the computation of expectation values of quantum mechanical operators. Doing so circumvents the need to have any major restrictions on the functional form of the wave function as long as it is “computable”.

To illustrate the method for the stochastic computation of expectation values, let us suppose that we have an initial trial wave function Ψ_T [37] and that we are interested in computing the expectation value of the Hamiltonian, $\mathcal{H}$, to obtain an estimate of the variational energy E_V . We can do so using the following equation:

$$E_V = \frac{\int \Psi_T^*(\mathbf{R}) \mathcal{H} \Psi_T(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R}) d\mathbf{R}} = \int \frac{|\Psi_T(\mathbf{R})|^2}{\int |\Psi_T(\mathbf{R}')|^2 d\mathbf{R}'} \frac{\mathcal{H} \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} d\mathbf{R}, \quad (2.51)$$

where $\mathbf{R}$ denotes the $3N$ electronic coordinates. We can rewrite Eq. 2.51 in the following form:

$$E_V = \int \rho(\mathbf{R}) E_L(\mathbf{R}) d\mathbf{R}, \quad (2.52)$$

where the new terms $\rho(\mathbf{R})$ and $E_L(\mathbf{R})$ are defined as follows:

$$\rho(\mathbf{R}) = \frac{|\Psi_T(\mathbf{R})|^2}{\int |\Psi_T(\mathbf{R}')|^2 d\mathbf{R}'} \quad (2.53)$$

$$E_L(\mathbf{R}) = \frac{\mathcal{H} \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}. \quad (2.54)$$

Clearly, $\rho(\mathbf{R})$ is a positive quantity and integrates to one. It can therefore be interpreted as a normalized probability distribution. Hereafter, we will refer to the quantity E_L as the local energy.

Figure 2.1: Local energy (E_L ; circles) and the running average (E_V ; green line) in a typical VMC run (shown here: ground state of thiophene). The root-mean-square fluctuation of the local energy, σ_V , is also shown.

To compute the integral in Eq. 2.52, we can employ classical Monte Carlo techniques and sample a set of configurations $\{\mathbf{R}_m\}$ in the $3N$ dimensional space of the electrons that are distributed according to the distribution $\rho(\mathbf{R})$. The expectation value of $\mathcal{H}$ can then be estimated as the average of the local energy, $E_L(\mathbf{R})$, evaluated on the sampled configurations:

$$E_V = \langle E_L \rangle_\rho \approx \frac{1}{M} \sum_{m=1}^M E_L(\mathbf{R}_m). \quad (2.55)$$

This relation between the local energy (E_L) and the average variational energy (E_V) in a typical VMC run is shown in Fig. 2.1, where σ_V denotes the standard deviation (the square root of the variance) which measures the spread of the local energies around E_V :

$$\sigma_V^2 = \int \rho(\mathbf{R}) (E_L(\mathbf{R}) - E_V)^2 d\mathbf{R}. \quad (2.56)$$

The error on the estimate of the average energy decays as $\sigma_V/\sqrt{M}$. If the chosen trial wave function is an exact eigenstate of the Hamiltonian, σ_V^2 will be zero and a single configuration will be sufficient to obtain the exact variational energy.

For the realistic molecular systems studied here, it is not feasible to compute the normalization of the trial wave function. Therefore, instead of direct sampling techniques, we employ the Metropolis algorithm [38] to generate a set of configurations $\{\mathbf{R}_m\}$ distributed according to $\rho(\mathbf{R})$ since it allows us to sample an arbitrary probability distribution without knowing its normalization. In this thesis, we employ the VMC algorithm described in Ref. 39, which uses a non-symmetrical transition

matrix in the Metropolis algorithm and has been appropriately modified to deal with non-local pseudopotentials.

The trial wave functions used in our QMC calculations are of the so-called Jastrow-Slater form, and are written in a spin-assigned form as

$$\Psi_T(\mathbf{r}_1, \dots, \mathbf{r}_N) = \mathcal{J}(\mathbf{r}_1, \dots, \mathbf{r}_N) \sum_k d_k D_k^\uparrow(\mathbf{r}_1, \dots, \mathbf{r}_{N_\uparrow}) D_k^\downarrow(\mathbf{r}_{N_\uparrow+1}, \dots, \mathbf{r}_N), \quad (2.57)$$

where $D_k^\uparrow$ and $D_k^\downarrow$ are Slater determinants of single particle orbitals for the up- and down-spin electrons, respectively. In this thesis, as Slater component, we use multi-determinantal expansions obtained either from a CASSCF calculation or a CIPSI selection scheme. The Jastrow factor, $\mathcal{J}$, explicitly depends on the interelectron distances and can include electron-electron, electron-nucleus as well as electron-electron-nucleus correlation terms. Through this factor, we can impose Kato's cusp conditions at the inter-particle coalescence points, i.e. where the interparticle distances go to zero. At the electron-electron and electron-nuclear coalescence points, one encounters divergent $1/r$ and $-Z/r$ potentials and, to ensure that the local energy stays finite, one requires that the wave function satisfies the cusp conditions so that the kinetic energy has an equal and opposite divergence to the potential. For two electrons of opposite spin, the cusp condition at the coalescence point is

$$\left. \frac{1}{\Psi} \frac{\partial \hat{\Psi}}{\partial r_{ij}} \right|_{r_{ij}=0} = \frac{1}{2}, \quad (2.58)$$

and, for the coalescence of an electron with a nucleus of charge Z positioned at the origin is

$$\left. \frac{1}{\Psi} \frac{\partial \hat{\Psi}}{\partial r_i} \right|_{r_i=0} = -Z, \quad (2.59)$$

with $\hat{\Psi}$ the spherical average of the wave function. These conditions can also be extended to the case of like-spin electrons where the wave function goes to zero at the electron-electron coalescence point. The absence of terms such as the Jastrow factor in the wave function of conventional CI-type methods makes them converge more slowly with the number of Slater determinants, partly because of the difficulty in describing the electron-electron cusp conditions.

The functional form of the Jastrow factor used in this thesis is:

$$\mathcal{J} = \prod_{I,i} \exp \{A(r_{iI})\} \times \prod_{i<j} \exp \{B(r_{ij})\} \times \prod_{I,i<j} \exp \{C(r_{iI}, r_{jI}, r_{ij})\}, \quad (2.60)$$

where $A(r_{iI})$, $B(r_{ij})$, and $C(r_{iI}, r_{jI}, r_{ij})$ are fifth-order polynomials of the interparticle distances. To distinguish between different atom types, we employ different polynomial parameters for each atom in the A and C factors, which contain the electron-nucleus distances. To ensure that the Jastrow factor is well behaved at large interparticle separations, the arguments of A and B are scaled as $\bar{r} = (1 - e^{-\kappa r})/\kappa$ so that $\bar{r}$ approaches $1/\kappa$ as the interparticle distance goes to infinity. The argument

of C is instead scaled as $e^{-\kappa r}$. To satisfy the electron-electron cusp conditions, the two-body $B(r_{ij})$ function includes a $b_1 \bar{r}_{ij}/(1 + b_2 \bar{r}_{ij})$ term with $b_1 = 1/2$ and $1/4$ for opposite- and like-spin electrons, respectively. Since we employ pseudopotentials, we do not need to impose the electron-nucleus cusp conditions. In this thesis, we primarily work with a two-body Jastrow factor, $\mathcal{J}_{2\text{-body}}$, which only includes A and B terms, and sometimes consider the C terms to test the impact of higher-order correlations on the results.

The quality of the initial trial wave function, Ψ_T , is crucial for any QMC calculation. At the variational level, it directly impacts the quality of the expectation values computed with it, as well as the statistical efficiency of the Monte Carlo sampling. Furthermore, it affects the results obtained with projector Monte Carlo techniques such as DMC, which we will discuss later. Capturing the correct physics with an appropriate wave function and, subsequently, optimizing it within VMC are key steps of a QMC calculation. The construction of the Slater component of Ψ_T is often based on chemical intuition, which at times might not be sufficient or correct. Furthermore, when dealing with relatively large molecules or when correlating a large number of orbitals in a CASSCF calculation, we often use arbitrary thresholds on the CI coefficients to limit the number of determinants in the wave function. This can be particularly problematic since it is difficult to guarantee an accurate and balanced description of different regions of the potential energy surface. To avoid such issues, we have carried out several investigations on how to construct the Slater component in an accurate and, yet, compact manner, namely, by resorting to a local-orbital representation [40] and, more recently, by automating the selection of relevant determinants via the CIPSI algorithm [41, 42].

Once a satisfactory Slater description is obtained, we always optimize the CI and LCAO coefficients together with the parameters of the Jastrow factor. This is necessary because the determinants were selected in the absence of the Jastrow factor and, therefore, the optimal coefficients might be different from their initial values. In the course of this thesis, we employ one of the following methods to optimize the parameters of a trial QMC wave function within energy minimization: (a) the stochastic reconfiguration (SR) method [43, 44] in a low-memory conjugate-gradient implementation [45], (b) the linear optimization method [46], which is an extension of the super-CI optimization method of MCSCF to arbitrary wave functions in the VMC framework, or (c) a new “mixed-SR-Davidson” method where we alternate between the optimization of the non-linear (orbital and Jastrow) parameters with the SR method and the computation of the corresponding optimal linear CI coefficients with a memory-efficient Davidson diagonalization scheme [47, 48]. While (a) is primarily employed in state-specific energy minimization calculations and (c) is only used for state-average optimizations, (b) serves both purposes. We will now discuss these wave function optimization methods in detail.

Wave function optimization in VMC

As stated above, we optimize all (Jastrow, CI, and orbital) parameters in a QMC wave function at the variational level in energy minimization. For this purpose, we

need to compute the derivatives of the wave function as well as the operation of the Hamiltonian on these derivatives efficiently. In particular, when dealing with excited states, we often have to optimize multi-determinant expansions, whose size increases with the degree of correlation. In order to study excited states for realistic molecular systems, we need to have low-cost and memory-efficient algorithms to compute these derivatives. To this aim, recent research in the group has led to the formulation of a simple analytical method to compute the derivatives of the wave function and of the local energy at the same cost of computing the energy itself per MC step [49, 50]. Furthermore, this scaling is the same for both single- and multi-determinant wave functions. These developments have facilitated the various investigations conducted in this thesis where we successfully optimize tens of thousands of variational parameters, also together with the molecular geometries, in VMC [41, 42].

Here, we briefly discuss the different methods to optimize the wave function employed in the course of this thesis: the stochastic reconfiguration (SR), linear, and mixed-SR-Davidson methods. We follow an energy minimization route, which has been shown to be more robust and faster in targeting the desired energy eigenstates of a given Hamiltonian as compared to variance minimization techniques, where one may lose the state of interest in favor of the lowest-variance state [48].

Stochastic Reconfiguration (SR) method

The Stochastic reconfiguration method has been employed as a simple and stable method for the optimization of ground-state wave functions. It is similar in approach to the Newton method where one follows the downhill gradient of the energy to reach the variational minimum spanned by the given wave function and its derivatives. In this thesis, we also use the SR method for excited states when the required state is the lowest in its symmetry class. We detail the method below and present its low-memory implementation introduced by Neuscamman *et al.* [45] in VMC.

Suppose we have an initial trial wave function, Ψ_T , that contains N_p variational parameters $\{p_i\}$. For simplicity of notation, we denote by Ψ the trial wave function and by $\Psi_i = \partial_i \Psi$ its derivatives with respect to a parameter p_i . At an optimization iteration, the SR method computes the parameter variations using the following equation:

$$\bar{\mathbf{S}} \delta \mathbf{p} = -\frac{\tau}{2} \mathbf{g}, \quad (2.61)$$

where $\mathbf{g}$ is the gradient of the energy with respect to p_i ,

$$g_i = 2 \left[\frac{\langle \Psi_i | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} - E_V \frac{\langle \Psi_i | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right] \equiv \partial_i E_V, \quad (2.62)$$

and $\bar{\mathbf{S}}$ is defined as

$$\bar{S}_{ij} = \frac{\langle \Psi_i | \Psi_j \rangle}{\langle \Psi | \Psi \rangle} - \frac{\langle \Psi_i | \Psi \rangle \langle \Psi | \Psi_j \rangle}{\langle \Psi | \Psi \rangle^2} \equiv S_{ij} - S_{i0} S_{0j}, \quad (2.63)$$

where $\mathbf{S}$ is the overlap matrix of the wave function derivatives. Using an appropriately small positive value for τ , Eq. 2.61 is solved and the $\delta \mathbf{p}$ values are used to update the parameters in an iterative fashion until convergence.

In VMC, we compute the gradient $\mathbf{g}$ and the overlap matrix $\mathbf{S}$ by sampling the distribution ρ , where $\rho(\mathbf{R}) = \Psi(\mathbf{R})^2 / \langle \Psi | \Psi \rangle$:

$$\begin{aligned} S_{ij} &= \frac{\langle \Psi_i | \Psi_j \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int \Psi_i(\mathbf{R}) \Psi_j(\mathbf{R}) d\mathbf{R}}{\int \Psi(\mathbf{R})^2 d\mathbf{R}} \\ &= \int \frac{\Psi_i(\mathbf{R})}{\Psi(\mathbf{R})} \frac{\Psi_j(\mathbf{R})}{\Psi(\mathbf{R})} \rho(\mathbf{R}) d\mathbf{R} \approx \frac{1}{M} \sum_{k=1}^M \frac{\Psi_i(\mathbf{R}_k)}{\Psi(\mathbf{R}_k)} \frac{\Psi_j(\mathbf{R}_k)}{\Psi(\mathbf{R}_k)}. \end{aligned} \quad (2.64)$$

The computational cost of this matrix scales as $\mathcal{O}(MN_p^2)$ and its storage also becomes increasingly difficult with the increase in the number of variational parameters. If we use a conjugate gradient (CG) method to solve the SR equations (Eq. 2.61), we only need to repeatedly compute the action of $\mathbf{S}$ on a trial vector of parameter variations [45]:

$$\begin{aligned} \sum_{j=1}^{N_p} S_{ij} \delta p_j &= \sum_{j=1}^{N_p} \left(\frac{1}{M} \sum_{k=1}^M \frac{\Psi_i(\mathbf{R}_k)}{\Psi(\mathbf{R}_k)} \frac{\Psi_j(\mathbf{R}_k)}{\Psi(\mathbf{R}_k)} \right) \delta p_j \\ &= \frac{1}{M} \sum_{k=1}^M \frac{\Psi_i(\mathbf{R}_k)}{\Psi(\mathbf{R}_k)} \sum_{j=1}^{N_p} \frac{\Psi_j(\mathbf{R}_k)}{\Psi(\mathbf{R}_k)} \delta p_j, \end{aligned} \quad (2.65)$$

where we swapped the order of the sums in the last line. If we compute and store the $M \times N_p$ matrix of ratios $\Psi_i(\mathbf{R}_k)/\Psi(\mathbf{R}_k)$, we can reduce the overall computational cost of solving the SR equations to $\mathcal{O}(N_{\text{CG}} M N_p)$, where N_{CG} is the number of conjugate gradient steps. Furthermore, if we exploit the inherent parallelism of Monte Carlo algorithms, we can significantly reduce the memory requirements per core of storing the ratios along the MC path. We note that N_{CG} has been found to be typically orders of magnitude smaller than the number of parameters in recent optimization tests performed with large determinantal expansions [41, 50].

The SR method is simple and has been used to optimize a very large number of parameters. It is found to require a large number of iterations to converge but is very robust to noise and one can perform shorter runs in the first part of the optimization. When dealing with excited states that are not the lowest states in their respective symmetry classes, the following two methods have instead been extensively used in this thesis.

Linear method

For the linear parameters of a Jastrow-Slater wave function, one can simply solve the following generalized eigenvalue equations:

$$\sum_j H_{ij} c_j = E \sum_j S_{ij} c_j, \quad (2.66)$$

where, here, $H_{ij} = \langle \mathcal{J} D_i | \mathcal{H} | \mathcal{J} D_j \rangle$ and $S_{ij} = \langle \mathcal{J} D_i | \mathcal{J} D_j \rangle$. The solution of this eigenvalue problem gives access not only to the ground state but also to higher roots. We note that, in a Monte Carlo run, the matrix $\mathbf{H}$ will not be symmetric for a finite

sample and it has been shown by Nightingale and Melik-Alaverdian [51] that the method benefits from reduced fluctuations if one does not symmetrize the Hamiltonian matrix.

Such a linear optimization method can be extended to the non-linear parameters, starting from the linearization of the wave function with respect to the parameter variations and minimizing the energy in the basis of the wave function and its derivatives [46]. We must then solve the generalized eigenvalue equations in this basis and iterate until convergence. In a standard implementation of the approach, we are often restricted to a rather small number of variational parameters due to the memory requirements involved in the diagonalization and storage of the Hamiltonian and overlap matrices. In general, we find that, while the linear method converges faster with numbers of iterations than the SR approach, it is more sensitive to noise and, therefore, requires much longer VMC runs to obtain reliable variations in the parameters.

When dealing with multiple states of the same symmetry, we usually express the Jastrow-Slater wave functions as

$$\Psi^I = \sum_k c_k^I \mathcal{J} D_k, \quad (2.67)$$

which share the same Jastrow factor and orbitals, but have different linear CI coefficients. While one can find the optimal CI coefficients by solving Eq. 2.66, for the non-linear (Jastrow and orbital) parameters, we seek a compromise for the description of the different states and minimize the state-average energy,

$$E^{\text{SA}} = \sum_I w_I \frac{\langle \Psi^I | \mathcal{H} | \Psi^I \rangle}{\langle \Psi^I | \Psi^I \rangle}, \quad (2.68)$$

where $\sum_I w_I = 1$. As described in Ref. [52], it is possible to generalize the linear approach also to the optimization of the state-average energy.

Mixed-SR-Davidson method

Since the SR method is more robust to noise, in particular when optimizing orbital coefficients, we use a combination of the linear method for the CI coefficients in a low-memory implementation, and the SR method for the optimization of the state-average energy when optimizing Jastrow-Slater wave functions of multiple states. We refer to this procedure as the Mixed-SR-Davidson method.

We first perform a few steps of optimization of the non-linear Jastrow and orbital parameters, following the gradient of the state-average energy,

$$g_i^{\text{SA}} = \sum_I w_I g_i^I, \quad (2.69)$$

where g_i^I is the gradient for state I , computed using Eq. 2.62. The overlap matrix of Eq. 2.63 is extended to a state-average description by similarity to the SR approach as

$$\bar{S}_{ij}^{\text{SA}} = \sum_I w_I \bar{S}_{ij}^I. \quad (2.70)$$

Then, we optimize of the linear CI coefficients using Eq. 2.66. To avoid computing and storing the full Hamiltonian and overlap matrices, we employ a subspace diagonalization technique called the Davidson approach and compute only a small subset of the lowest energy eigenvalues. The process of alternating few SR optimization steps of the non-linear parameters with one step of Davidson diagonalization of the CI matrix is iterated until convergence and allows us to work with a rather large number of variational parameters.

2.4.2 Diffusion Monte Carlo

VMC is a powerful approach that allows us to greatly advance our understanding of the system of interest by easily exploring what type of correlation is important. Upon complete optimization of all possible variational parameters, VMC yields high-quality wave functions that are often sufficient to accurately describe a given electronic state. When this is not the case, it is possible to further improve on the VMC results with the use of projector Monte Carlo techniques. These approaches represent a stochastic implementation of the power method for finding the dominant eigenstates of a matrix or integral kernel. The idea behind any projection Monte Carlo method is to construct an operator, the projection operator, that inverts the spectrum of the Hamiltonian $\mathcal{H}$ and projects out the ground state by its repeated application on a trial wave function.

Diffusion Monte Carlo (DMC) is one such method that we use in this thesis. The projection operator in DMC is $e^{-\tau(\mathcal{H}-E_T)}$ where E_T is a trial energy, whose role will become apparent soon, and τ the so-called time-step. To understand the effect of the application of the DMC projection operator on a trial wave function Ψ , let us expand Ψ on the eigenstates of $\mathcal{H}$, Ψ_i , with eigenvalues E_i . We then obtain:

$$\begin{aligned} \lim_{n \rightarrow \infty} e^{-n\tau(\hat{H}-E_T)}|\Psi\rangle &= \lim_{n \rightarrow \infty} \sum_i e^{-n\tau(E_i-E_T)}|\Psi_i\rangle\langle\Psi_i|\Psi\rangle \\ &\approx e^{-n\tau(E_0-E_T)}|\Psi_0\rangle\langle\Psi_0|\Psi\rangle, \end{aligned} \quad (2.71)$$

since the coefficients of the higher eigenstates decay exponentially faster relative to the ground state. If we adjust E_T to be equal to E_0 , the projection will yield the exact ground state Ψ_0 of the Hamiltonian. The starting wave function must of course have a non-zero overlap with the ground-state one.

To understand how the projection is performed in practice, let us write its operation on the trial wave function in integral form, namely, in the position representation:

$$\Psi(\mathbf{R}', t + \tau) = \int G(\mathbf{R}'|\mathbf{R}, \tau)\Psi(\mathbf{R}, t)d\mathbf{R}, \quad (2.72)$$

where we introduce the Green's function G defined as:

$$G(\mathbf{R}'|\mathbf{R}, \tau) = \langle\mathbf{R}'|e^{-\tau(\mathcal{H}-E_T)}|\mathbf{R}\rangle. \quad (2.73)$$

We can compute the integral of Eq. 2.72 using Monte Carlo if we can sample the Green's function and the trial wave function. Unfortunately, electrons are fermions

and $\Psi(\mathbf{R})$ is antisymmetric. Therefore, it is not possible to interpret the wave function as a probability distribution. For the moment, we will assume that we are working with a bosonic system and return to this issue later.

Since the exact functional form of G is unknown, we use the Trotter-Suzuki theorem to approximate it in the limit of small time steps τ as:

$$e^{-\tau(\hat{T}+\hat{V})} = e^{-\tau\hat{T}}e^{-\tau\hat{V}} + \mathcal{O}(\tau^2). \quad (2.74)$$

In the so-called *short-time approximation*, we can therefore write the following:

$$\begin{aligned} \langle \mathbf{R}' | e^{-\tau\hat{H}} | \mathbf{R} \rangle &\approx \langle \mathbf{R}' | e^{-\tau\hat{T}} e^{-\tau\hat{V}} | \mathbf{R} \rangle = \int d\mathbf{R}'' \langle \mathbf{R}' | e^{-\tau\hat{T}} | \mathbf{R}'' \rangle \langle \mathbf{R}'' | e^{-\tau\hat{V}} | \mathbf{R} \rangle \\ &= \langle \mathbf{R}' | e^{-\tau\hat{T}} | \mathbf{R} \rangle e^{-\tau\hat{V}(\mathbf{R})}, \end{aligned} \quad (2.75)$$

and, correspondingly, the Green's function of Eq. 2.73 can be rewritten as

$$G(\mathbf{R}' | \mathbf{R}, \tau) = (2\pi\tau)^{-3N/2} \exp \left[-\frac{(\mathbf{R}' - \mathbf{R})^2}{2\tau} \right] \exp \left[-\tau (\hat{V}(\mathbf{R}) - E_T) \right] + \mathcal{O}(\tau^2). \quad (2.76)$$

Therefore, to perform the DMC projection, we start by sampling a trial wave function to generate a set of so-called “walkers” and then move each walker from the initial configuration $\mathbf{R}$ to $\mathbf{R}'$ by diffusion, namely, by sampling a displacement from the positive Gaussian distribution in the first part of Eq. 2.76. The second exponential term in the Green's function is a positive factor that guides a branching process. This term decides the survival probability of the walkers and populates regions where $\hat{V}(\mathbf{R}) < E_T$ and depopulates those where $\hat{V}(\mathbf{R}) > E_T$. The value of E_T is adjusted to ensure that the total walker population is maintained around a target value. We evolve the walkers until a stationary distribution is attained and the energy of the system is converged within the desired statistical accuracy. We must remember that this expression for the Green's function is valid only in the limit of $\tau \rightarrow 0$. Therefore, in practice, we perform DMC calculations for different values of τ and simply extrapolate the results to zero time-step.

The direct sampling of this Green's function is however problematic since the potential can vary significantly between configurations and even diverge, leading to large changes in walker population. Therefore, to overcome these issues, one introduces the trial wave function, Ψ_T , to guide the sampling in the so-called *importance sampling* algorithm [53]. Therefore, we rewrite Eq. 2.72 in terms of the probability distribution $f(\mathbf{R}, t) = \Psi_T(\mathbf{R})\Psi(\mathbf{R}, t)$ as

$$f(\mathbf{R}', t + \tau) = \int \tilde{G}(\mathbf{R}' | \mathbf{R}, \tau) f(\mathbf{R}, t) d\mathbf{R}, \quad (2.77)$$

where the importance-sampled Green's function is given by:

$$\tilde{G}(\mathbf{R}' | \mathbf{R}, \tau) = \Psi_T(\mathbf{R}') \langle \mathbf{R}' | e^{-\tau(\hat{H} - E_T)} | \mathbf{R} \rangle / \Psi_T(\mathbf{R}). \quad (2.78)$$

For small τ , the importance-sampled drift-diffusion-branching Green's function becomes:

$$\tilde{G}(\mathbf{R}'|\mathbf{R}, \tau) \approx (2\pi\tau)^{-3N/2} \exp \left[-\frac{(\mathbf{R}' - \mathbf{R} - \tau\mathbf{V}(\mathbf{R}))^2}{2\tau} \right] \times \exp \left[-\tau([E_L(\mathbf{R}) + E_L(\mathbf{R}')]/2 - E_T) \right], \quad (2.79)$$

where $\mathbf{V}(\mathbf{R})$ is the quantum drift velocity defined as

$$\mathbf{V}(\mathbf{R}) = \frac{\nabla \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}, \quad (2.80)$$

and $E_L(\mathbf{R})$ is the local energy for the trial wave function Ψ_T . Comparing the Green's functions in Eqs. 2.79 and 2.76, we note the following important differences: (1) the Gaussian term includes the quantum drift velocity $\mathbf{V}(\mathbf{R})$ that pushes the walkers to regions where the wave function is large and, (2) the branching term depends on the local energy $E_L(\mathbf{R})$ instead of the bare potential $\hat{V}(\mathbf{R})$. If we have a trial wave function approaching the eigenstate of the Hamiltonian, the local energy becomes constant and equal to the eigenvalue. Therefore, using a good initial Ψ_T ensures that the fluctuations in the exponential branching term are small. When we use a Jastrow-Slater wave function as Ψ_T , we have already imposed the necessary cusp conditions and consequently also eliminated the instabilities that could arise from divergences of the Coulomb potential.

There is still another issue we need to address: until now, we have assumed that the system is bosonic but electrons are fermions. The bosonic ground state is lower in energy than the fermionic one and, therefore, the projection operator in DMC will yield the former. This is the so-called *fermionic sign problem*. To circumvent this issue, we work in the *fixed-node approximation*, namely, we find the best solution with the same nodes (zeros) as a given trial wave function. To this aim, in the simple DMC algorithm, one can simply kill the walkers that attempt to cross the nodes. When using the drift-diffusion-branching Green's function, one automatically finds the fixed-node solution in the limit of tau that goes to zero. The fixed-node solution will be exact only if the nodes of the trial wave function are exact. In general, it provides an upper bound to the exact energy.

Even though DMC is designed to project out the ground state, in this thesis, we have also used it to compute the excited states of a given Hamiltonian. When the excited state is the lowest state in its symmetry class, then, it is equivalent to a ground-state problem and DMC will yield a variational solution. For cases where the excited state is not the lowest state in its symmetry class, all what we know is that we obtain the correct solution for the exact nodes. In general, we might lose variationality but, in practice, unless we have a really poor trial wave function, we find that we approach the correct solution from above by gradually improving the excited-state trial wave function.

2.5 Density Functional Theory

Density functional theory (DFT) [54] is an alternative to wave-function-based approaches and is the method of choice for large molecular systems, owing to its favorable scaling with system size. In this thesis, we mainly employ it to obtain preliminary estimates of optimal ground-state structures as well as excitation energies using time-dependent DFT.

The DFT formalism differs from the wave function methods as it works with the 3-dimensional electronic density, $\rho(\mathbf{R})$. DFT has its roots in the Hohenberg-Kohn (HK) theorem [55], which states that for a given ground-state electronic density, one can uniquely determine the external potential and, consequently, the complete wave function together with all its expectation values. This allows one to write the ground-state energy as a functional of the density, which is minimum at the ground-state density. However, the functional is not known and needs to be approximated.

In practice, one employs the Kohn-Sham (KS) formulation [56] that maps the fully interacting system onto a fictitious non-interacting system with the same ground-state density, ρ . This results in the following simple single-particle Kohn-Sham equations:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}([\rho]; \mathbf{r}) \right] \phi_i = \epsilon_i \phi_i, \quad (2.81)$$

where $\rho(\mathbf{r})$ is computed via the occupied single-particle orbitals ϕ_i as:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_{\text{occ}}} |\phi_i(\mathbf{r})|^2, \quad (2.82)$$

and the effective KS potential, v_{eff} , is given by

$$v_{\text{eff}}([\rho]; \mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}([\rho]; \mathbf{r}). \quad (2.83)$$

The first term is the external potential, the second term the Hartree potential, while the third term is the exchange-correlation potential which is the functional derivative of the exchange-correlation functional, $\delta E_{\text{xc}}[\rho]/\delta\rho$. This functional enters in the expression of the total energy as

$$\begin{aligned} E = & -\frac{1}{2} \sum_{i=1}^{N_{\text{occ}}} \int \phi_i \nabla^2 \phi_i d\mathbf{r} + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} \\ & + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[\rho]. \end{aligned} \quad (2.84)$$

Equation (2.84) is exact in principle. The exchange-correlation functional is however unknown and needs to be approximated in an actual DFT calculation. There are several approximations available in the literature [57] for the exchange-correlation functional, which can be mainly classified into one of the following types: the local

density approximation (LDA), generalized gradient approximation (GGA), hybrid, meta-hybrid, and long-range corrected (LC) functionals.

LDA has the simplest functional form where the exchange-correlation energy per electron at a point of density $\rho(\mathbf{r})$ in an inhomogeneous system is replaced by the exchange-correlation energy per electron of a uniform electron gas, $\epsilon_{xc}^{\text{hom}}$, of the same density ρ . The corresponding total exchange-correlation energy is given by:

$$E_{xc}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}^{\text{hom}}(\rho(\mathbf{r})) d\mathbf{r}. \quad (2.85)$$

GGA improves upon LDA by introducing a dependence on the gradient of electronic density (and possibly higher derivatives) resulting in considerably better estimates of energies and structural parameters. Generally speaking, a GGA functional can be written as

$$E_{xc}^{\text{GGA}}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}^{\text{GGA}}(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|, \nabla^2 \rho(\mathbf{r})) d\mathbf{r}. \quad (2.86)$$

Hybrid functionals also introduce an explicit dependence on the KS orbitals by mixing a portion of exact exchange from the HF theory, given by:

$$E_x^{\text{HF}}[\rho] = -\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \delta_{s_i, s_j} \iint \frac{\phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}) \phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (2.87)$$

where the exchange energy is a functional of the density via the KS orbitals. For example, in this thesis, we employ the hybrid B3LYP [58, 59] functional to compute ground-state geometries which has the following form:

$$E_{xc}^{\text{B3LYP}}[\rho] = (1 - h_1) E_x^{\text{LDA}}[\rho] + h_1 E_x^{\text{HF}} + h_2 E_x^{\text{B88}}[\rho] + h_3 E_c^{\text{LYP}}[\rho] + (1 - h_3) E_c^{\text{LDA}}, \quad (2.88)$$

where $h_1 = 0.2$, $h_2 = 0.72$ and $h_3 = 0.81$. Here, E_x^{B88} is the GGA exchange Becke functional [60] and $E_c^{\text{LYP}}[\rho]$ is the GGA correlation Lee-Yang-Parr functional [61].

The extension of DFT to the treatment of excited states is called time-dependent (TD) DFT which, because of its favorable scaling of $\mathcal{O}(N^3)$, is the most widely used method to compute excitation properties of large molecular systems. Analogous to the HK theorem, here, the Runge-Gross theorem [62] defines a unique map between the external time-dependent potential $v_{\text{ext}}(\mathbf{r}, t)$ and the time-dependent electronic density $\rho(\mathbf{r}, t)$. The time-dependent many-body Schrödinger equation is similarly translated to single-particle KS equations for a non-interacting system that reproduces the exact electronic time-dependent density of the real system. The corresponding exchange-correlation energy functional needs to be approximated and one adopts the so-called adiabatic approximation, which amounts to the use of the ground-state exchange-correlation functional and its approximations. In practice, approximate TDDFT struggles to treat non-trivial excited states that possess a strong multi-configurational or charge-transfer character [63–65]. The treatment of charge-transfer states can be ameliorated with the use of so-called range-separated functionals. In this thesis, we employ TDDFT either to optimize excited-state geometries or to compute vertical excitation energies, whose quality is assessed against the results of wave-function-based approaches.

2.6 Software

We list here the codes employed in this thesis. Additional computational details specific to the calculations are discussed in the respective Chapters.

- **Ground-state DFT and TDDFT:** The **Gaussian Package** [66] for the optimization of ground- and excited-state molecular geometries as well as the computation of vertical excitation energies. These codes employ Gaussian basis sets and a range of exchange and correlation functionals.
- **CASSCF and CASPT2:** We employ **GAMESS** [67, 68] for ground- and excited-state CASSCF calculations. The resulting wave functions serve as the starting point of subsequent CIPSI and QMC calculations. CASPT2 energies as well as CASSCF and CASPT2 geometries (ground and excited state) are computed with the **MOLCAS** code [69]. Both codes use Gaussian basis sets.
- **Coupled Cluster (CCSD(T), CC3):** The **PSI4** [70], **Gaussian** [71] and **Dalton** [72] codes are used for CCSD(T) and CC3 excitation energy computations as well as ground-state geometry optimizations.
- **Selected CI (CIPSI): Quantum Package** [73] is an open-source code that we use to obtain compact CIPSI determinantal expansions for subsequent use in QMC.
- **Local orbitals: Cost Package** [74], **MOLCAS** [69] and **GAMESS** [67, 68] are used for the formulation of different local orbital descriptions.
- **Quantum Monte Carlo (QMC):** Our in-house **CHAMP** [75] code is used for all the QMC calculations. It can perform VMC and DMC calculations and optimizes the wave function and structural parameters for molecular systems by energy minimization.

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Chapter 3

Perturbatively selected configuration-interaction wave functions for efficient geometry optimization in quantum Monte Carlo [†]

We investigate the performance of a class of compact and systematically improvable Jastrow-Slater wave functions for the efficient and accurate computation of structural properties, where the determinantal component is expanded with a perturbatively selected configuration interaction scheme (CIPSI). We concurrently optimize the molecular ground-state geometry and full wave function – Jastrow factor, orbitals, and configuration interaction coefficients– in variational Monte Carlo (VMC) for the prototypical case of 1,3-trans-butadiene, a small yet theoretically challenging π -conjugated system. We find that the CIPSI selection outperforms the conventional scheme of correlating orbitals within active spaces chosen by chemical intuition: it gives significantly better variational and diffusion Monte Carlo energies for all but the smallest expansions, and much smoother convergence of the geometry with the number of determinants. In particular, the optimal bond lengths and bond-length alternation of butadiene are converged to better than one mÅ with just a few thousand determinants, to values very close to the corresponding CCSD(T) results. The combination of CIPSI expansion and VMC optimization represents an affordable tool for the determination of accurate ground-state geometries in quantum Monte Carlo.

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3.1 Introduction

Quantum Monte Carlo methods are a class of *ab initio* approaches which solve the interacting Schrödinger equation stochastically. The most widely used variants of QMC are the variational (VMC) and diffusion Monte Carlo (DMC). Thanks to their favorable scaling with the number of particles and the ease of parallelization, they have often been employed to benchmark electronic properties, in particular, total energies of relatively large molecules as well as solids. Recently, it has been shown [1, 2] that it is possible to compute derivatives of the energy at the same computational cost per Monte Carlo step as evaluating the energy itself, also when employing large determinantal expansions in the commonly used Jastrow-Slater QMC wave functions. Consequently, one can compute all derivatives necessary for the optimization of the structure of a system very efficiently and, simultaneously, of the variational parameters in the wave function, as was demonstrated on the structural optimization of short polyenes with expansions comprising over 200,000 determinants [2]. These developments also allow us to thoroughly explore the sensitivity of QMC calculations to the choice of the Slater expansion, namely, the set of orbitals which one must correlate and the truncation of the active space. It was shown that an instructed guess of the orbitals based on chemical intuition can lead to significant variations in VMC energies and structures of a molecule as small as butadiene even when employing large expansions in the presence of a Jastrow correlation factor [2].

To overcome the limitations of an *a priori* approach in the choice of the orbital set and achieve a compact description of the determinantal component in QMC, a promising alternative is to employ a selected CI algorithm such as the CIPSI (configuration interaction using a perturbative selection done iteratively) method. CIPSI was originally introduced by Huron *et al.* in 1973 [3] and continually tested [4–10], improved [10–13], and assessed in comparison to full-CI (FCI) expansions [10, 14, 15] in combination with a variety of orbital descriptions [16]. In the last few years, there has been renewed interest in the development of selected CI approaches [17–22] to accurately calculate the ground- and excited-state energies of small molecules, establishing the competence of these approaches for benchmarking applications. The use of these expansions has however only been marginally explored within the QMC framework [23–28], where it was shown to yield very good DMC energies at the price of employing large CIPSI wave functions. Good selection in multideterminantal expansions is also likely to improve the accuracy and efficiency in the phaseless auxiliary-field Monte Carlo method [29].

Here, we complement the perturbatively selected CIPSI determinants with a Jastrow factor and VMC optimization of the full wave function (Jastrow parameters, orbitals and CI coefficients), and investigate the ability of the resultant Jastrow-CIPSI wave functions to obtain accurate molecular geometries in VMC, as well as corresponding VMC and DMC energies, with relatively compact expansions. We focus on the butadiene molecule, where an accurate estimation of the bond length alternation (BLA) is theoretically quite challenging, demanding a proper description of correlation effects, both static and dynamic. As mentioned above, significant variations in energies and structural parameters were observed in VMC when correlating different

sets of σ and π orbitals in a fully optimized Jastrow-Slater wave function [2]: with a large expansion comprising over 45,000 determinants in a restricted active space, good agreement with coupled cluster with singles, doubles, and perturbative triples in the complete basis set limit (CCSD(T)/CBS) was obtained in the bond lengths. This number of determinants is however surprisingly large for the description of the ground state of such a small system. Indeed, we find here that a determinantal description with CIPSI yields a much smoother convergence in the structural parameters and QMC energies when the size of the expansion is systematically incremented. Correspondingly, very accurate values for these physical properties are already obtained with only a few thousand determinants.

To construct the CIPSI component of the QMC trial wave functions, we follow two different schemes: one where we systematically “expand” the wave function by adding important determinants at every step, and the other where we first generate an extremely large wave function and subsequently “truncate” it to obtain requisite sizes. For a fixed size of the CI expansion, the “truncation” scheme is expected to be more accurate than the “expansion” one since the overlap of the wave function with the FCI wave function is larger. The difference can be important in systems where the CI coefficients change dramatically with the number of determinants in the wave function [30], but generation of the large wave function to initiate “truncation” might not be entirely feasible for larger systems where the “expansion” scheme would therefore represent a computationally less expensive route. For small systems such as butadiene, however, we can employ both strategies and, consequently, draw an assessment of their relative performance. Here, we find that the truncation scheme provides a faster and smoother convergence of the bond lengths of butadiene, while the convergence of the VMC energies is comparable for both schemes. We note that we are looking at extremely small variations in the structural parameters (well below mÅ) when comparing and establishing the convergence. Finally, while we primarily employ multi-configurational self consistent field (MCSCF) canonical orbitals in the CIPSI algorithm and as starting orbitals in QMC, we additionally test the use of natural orbitals. Rather peculiarly, expansions with natural orbitals commensurate in size with those with canonical orbitals consistently converge to slightly higher VMC energies.

In section 3.2, we describe the CIPSI algorithm and the functional form of the Jastrow-Slater wave functions and, in Section 3.3, we report the computational details. The numerical results obtained for the structural optimization of butadiene and a comparison with our previous Jastrow-CAS results [2] are given in Section 3.4.

3.2 Methods

CIPSI is an iterative CI selection algorithm that allows us to perturbatively select determinants from the FCI space. Starting with an initial reference wave function, additional determinants are added to the expansion based on their effective second-order energy contribution which is required to be greater than a fixed or an iteratively modifiable threshold. Selection iterations can be performed until a target number of

determinants is reached or until some other selection criterion is met [31]. In the process, the quality of the wave function is systematically improved and converges towards the FCI solution.

A step-by-step description of the CIPSI algorithm is provided in Refs.23, 25, 26, 32. The scheme is briefly reiterated here. The reference wave function is composed of a linear combination of Slater determinants, D_i , spanning a space, S :

$$\psi_{\text{CIPSI}} = \sum_{D_i \in S} c_i D_i. \quad (3.1)$$

Typically, this reference wave function is initially the single determinant with the lowest energy, which is also the case here. At every iteration, the many-body Hamiltonian, $\mathcal{H}$, is diagonalized in the reference space S to obtain the variationally minimized energy E^{ref} and the corresponding c_i coefficients. Then, all the determinants D_j outside of this reference space that are connected to S by $\mathcal{H}$ are generated, and their individual contributions to the energy are estimated with the Epstein-Nesbet [33, 34] perturbation theory,

$$\delta E_j^{(2)} = \frac{|\langle D_j | \mathcal{H} | \psi_{\text{CIPSI}} \rangle|^2}{E^{\text{ref}} - \langle D_j | \mathcal{H} | D_j \rangle}. \quad (3.2)$$

If $|\delta E_j^{(2)}|$ is greater than a given threshold, determinant D_j is selected for the next iteration. Summing all these contributions gives $E^{\text{PT}2}$, namely, the second-order perturbative energy correction to E^{ref} , and the CIPSI energy of the current iteration is given by

$$E^{\text{CIPSI}} = E^{\text{ref}} + E^{\text{PT}2}. \quad (3.3)$$

Finally, all the selected determinants are added to the reference space S for the next iteration.

For the generation of different lengths of the CIPSI component of the QMC wave function, one could either follow (a) an “expansion” scheme where we repeat the above process as many times as necessary, thereby systematically increasing the size of the wave function, or (b) a “truncation” scheme after generating a very large CIPSI wave function, typically to a point where the CIPSI energy (Eq. 3.3) is reasonably converged. The large wave function created for the second scheme can contain millions of determinants and one needs to reorder them in decreasing order of the absolute value of their CI coefficients and then truncate the expansion, keeping their coefficients the same as in the large CIPSI wave function. This strategy is said to be a better starting point for VMC optimization as the determinant coefficients are from a near FCI calculation [26]. We use complete active space SCF (CASSCF) orbitals for the majority of these calculations, however, (c) the use of natural orbitals obtained from a large CIPSI calculation is another aspect of our investigation.

In the expansion scheme, we choose to impose that the wave function is an eigenstate of the $\mathbf{S}^2$ operator. Therefore, after each selection, we apply all possible spin flips on the selected determinants keeping the number of α and β electrons unchanged. All spin-flipped determinants which are not already present in the set

of selected determinants are added. This larger set of determinants spans the same space as all the configuration state functions to which the selected determinants belong. Consequently, when the Hamiltonian is diagonalized in this larger basis of determinants, the eigenfunctions are also eigenfunctions of $\mathbf{S}^2$. Note that, in the truncated scheme, the truncation is made in the determinant space, so the truncated wave functions are not eigenfunctions of $\mathbf{S}^2$. Hence, the comparison of the two schemes is not exactly one to one.

After generating the CIPSI expansion, we introduce a positive Jastrow correlation factor $\mathcal{J}$ and construct the Jastrow-CIPSI wave function as

$$\psi = \mathcal{J}\psi_{\text{CIPSI}} = \mathcal{J} \sum_{i=0}^{N_{\text{det}}} c_i D_i, \quad (3.4)$$

where $\mathcal{J}$ explicitly describes the two-body electron-electron and electron-nucleus ($\mathcal{J}_{2\text{-body}}$) and three-body electron-electron-nucleus ($\mathcal{J}_{3\text{-body}}$) correlations [35] while imposing the electron-electron cusp conditions. N_{det} represents the number of determinants in the CIPSI wave function spanning the space S .

3.3 Computational Details

The QMC calculations are carried out with the program package CHAMP [36]. We employ scalar-relativistic energy-consistent Hartree-Fock pseudopotentials and the cc-pVTZ Gaussian basis set specifically constructed for our pseudopotentials [37, 38]. In particular, we perform all calculations with the cc-pVTZ basis set and test the convergence of the results with the cc-pVQZ basis set. To generate the Slater component of the QMC wave functions, CIPSI calculations are performed in Quantum Package [39] using canonical orbitals obtained from a CAS(10,10) MCSCF calculation for the ground state of butadiene carried out with the program GAMESS(US) [40, 41].

All parameters (Jastrow, orbital, and CI coefficients) are variationally optimized in VMC using the stochastic reconfiguration method [42] in a conjugate gradient implementation [43]. Most calculations are performed with a two-body Jastrow factor and the impact of the electron-electron-nucleus terms on the energy is tested for a few cases. Exploiting the low-numerical-scaling computation of energy and wave function derivatives [2], the ground-state geometry of butadiene is simultaneously optimized with the wave function following the path of steepest descent and an appropriate rescaling of the inter-atomic forces. To avoid spikes in forces, an improved estimator of the inter-atomic forces is used in all calculations, which is obtained by sampling the square of a modified wave function close to nodes [44]. In the DMC calculations, we treat the pseudopotentials beyond the locality approximation [45] and use an imaginary time step of 0.015 a.u. We perform a careful study which shows that this time step yields DMC energies converged to better than 0.1 mHartree for a simple Jastrow-CIPSI wave function with only two determinants and is therefore appropriate for all wave functions of higher quality considered in this work.

We employ Gaussian09 [46] to perform CCSD(T) geometry optimization in combination with our pseudopotentials and in all-electron calculations in the frozen core (FC) approximation with the cc-pVXZ ($X = D, T, Q$, and 5) and aug-cc-pVXZ ($X = D, T$, and Q) basis sets. For CCSD(T) geometry optimization without the FC approximation, we use the PSI4 code [47] with the cc-pCVXZ, cc-pwCVXZ, and corresponding augmented ($X = D, T$, and Q) basis sets. The results of these optimizations and their extrapolations to the CBS limit are detailed in Appendix 3.7.

3.4 Results and discussion

We investigate the merits of the choice of a CIPSI expansion to describe the Slater component of a QMC wave function when optimizing the ground-state geometry of butadiene over the conventional CAS description. We start all structural optimizations with the Jastrow-CIPSI wave functions from the same initial MP2/cc-pVQZ optimized geometry and, as described above, variationally optimize the Jastrow parameters, CI coefficients, and orbitals simultaneously with the geometry in VMC. Post convergence of the VMC energy and stabilization of the bond lengths, we perform 40 additional iterations and average these geometries. A final VMC and DMC energy calculation is done on this average geometry with the wave function obtained in the last iteration. We validated our approach of averaging the last 40 geometries by using the optimized wave function with 5114 determinants in Table 3.1 and re-optimizing it on top of the symmetrized average geometry. It yields an optimal VMC energy of -26.29957(24) Hartree which is equivalent to that reported in Table 3.1 within statistical error.

With the “truncation” scheme, an initial CIPSI wave function is constructed including as many as 1.17 million determinants and then truncated to generate a set of determinantal expansions of increasing size. The results are summarized in Table 3.1 and illustrated in Figures. 3.1 and 3.2, where the final VMC and DMC energies, and corresponding structural parameters are plotted against the size of the CIPSI expansions. We also compare our results with previous QMC calculations [2] of the structural optimization of butadiene, which employed various CAS expansions: a CAS(4,4), CAS(4,16), and CAS(4,20) correlating 4 π electrons in the orbitals constructed from the $2p_z$, $3p_z$, $3d_{xz}$, $3d_{yz}$, and $4p_z$ atomic orbitals; a CAS(10,10) consisting of 6 σ and 4 π electrons in 10 bonding and antibonding orbitals; a truncated RAS(10,22) that includes single and double excitations in additional 12 π and δ orbitals over the CAS(10,10) space. Since the cc-pVTZ and cc-pVQZ basis sets yield VMC and DMC energies compatible to better than 2 and 0.2 mHartree, respectively, and structural parameters differing by less 0.4 mÅ (see Table 3.2), we can directly compare our cc-pVTZ calculations with the results obtained with the optimization of Jastrow-CAS wave functions in the cc-pVQZ basis.

As shown in Figure 3.1, a CIPSI wave function with roughly 100 determinants yields a VMC energy which is only about 1 and 4 mHartree higher than the energies of the CAS(10,10) and RAS(10,22) expansions consisting of 15,912 and 45,644 Slater determinants, respectively. Unlike the Jastrow-CAS case, where the energies

Table 3.1: Optimal ground-state structural parameters (Å) of butadiene and corresponding VMC and DMC energies (a.u.) with increasing number of CIPSI determinants obtained in the truncation scheme. The total number of optimized parameters in the wave function is listed. The statistical error is given in brackets.

No. det	No. param	C-C	C=C	BLA	VMC	DMC
1	749	1.45595(28)	1.32415(11)	0.13180(30)	-26.24310(32)	-26.30426(28)
2	782	1.44596(20)	1.33025(14)	0.11571(29)	-26.24912(32)	-26.30681(14)
8	822	1.45244(28)	1.33245(15)	0.11999(50)	-26.25644(31)	-26.31044(26)
128	1594	1.45778(12)	1.33564(20)	0.12214(20)	-26.26562(30)	-26.31223(24)
1024	5514	1.45632(22)	1.33493(08)	0.12139(25)	-26.28829(26)	-26.31908(20)
2048	7726	1.45626(15)	1.33456(09)	0.12170(17)	-26.29386(25)	-26.32147(16)
5114	12147	1.45549(08)	1.33434(11)	0.12115(07)	-26.29980(24)	-26.32424(09)
15469	24818	1.45491(06)	1.33406(08)	0.12085(10)	-26.30880(22)	-26.32873(22)
32768	44265	1.45487(25)	1.33414(21)	0.12072(37)	-26.31194(12)	-26.32928(20)

Table 3.2: Basis-set dependence of the optimal structural parameters (Å) and VMC and DMC energies (a.u.) computed with the cc-pVTZ and cc-pVQZ basis sets and CIPSI expansions of comparable sizes obtained with the truncation scheme, truncated from 1.17 and 4.9 million determinants respectively.

Basis	No. det	No. param	C-C	C=C	BLA	E _{VMC}	E _{DMC}
cc-pVTZ	5114	12147	1.45549(08)	1.33434(11)	0.12115(07)	-26.29980(24)	-26.32424(09)
cc-pVQZ	5000	21582	1.45576(15)	1.33475(06)	0.12102(14)	-26.30154(22)	-26.32408(21)

are scattered around a relatively flat value, CIPSI expansions of increasing size yield a monotonic decrease in the VMC energy, with our largest considered expansion of 32,768 determinants amounting to an energy which is about 40 mHartree lower than the best RAS(10,22) value. In fact, the VMC energy obtained with our largest CIPSI expansion is within 5 mHartree of the seemingly converged DMC energy obtained with the Jastrow-CAS wave functions. Therefore, a smart selection of determinants from the approximate FCI space helps us attain much lower VMC energies in comparison to CAS expansions over conventionally used active-space definitions, which instead lead to the inclusion of many determinants with little contribution to the energy.

The behavior of DMC parallels the VMC results with the energy of the Jastrow-CAS wave functions being lowered by about 8 mHartree when the size of the wave function is increased from 1 to 20 determinants, and stagnating afterwards as shown in Figure 3.1. The Jastrow-CIPSI wave function yields a DMC energy which is comparable with the Jastrow-CAS case when the CIPSI expansion has only about 100 determinants, while the largest CIPSI expansion gives a DMC energy 12 mHartree lower than the truncated RAS(10,22) case. We also note that the estimate of the FCI limit in the current basis set on the initial geometry is about -26.275 Hartree (see SI) and, therefore, as much as 37 and 54 mHartree higher than our best VMC and DMC energies. Our best DMC energies are also superior to the CCSD(T) optimized values obtained with a quintuple- ζ basis set (see Appendix 3.6).

Importantly, the use of CIPSI expansions (in combination with a Jastrow factor

Figure 3.1: Convergence of the VMC and DMC energies on the optimal geometry with the number of determinants in the CIPSI expansion (red). Previous results [2] obtained with Jastrow-CAS wave functions are also presented (blue).

and the optimization of all wave function parameters) is not only beneficial in terms of the quality of the final total energies: the smooth and monotonic convergence of the VMC and DMC energies with the number of determinants demonstrates the effectiveness of such an approach in identifying energetically relevant determinants in a systematic manner. These important excitations are not easily accessible through manual selection as demonstrated by the energy plateau one reaches in constructing very large expansions based on an *a priori* choice of an apparently reasonable set of active orbitals. Besides being completely automated, this feature of the CIPSI scheme is also crucial for obtaining a smooth convergence of the structural properties (to better than 1 mÅ) with the number of determinants as discussed next.

In Figure 3.2, we illustrate the variation of the carbon-carbon single and double bonds and of the bond length alternation (BLA) obtained with the Jastrow-CIPSI expansions. The convergence of the bond lengths and BLA is smooth with the increase in the size of the wave function. While the double bond is already converged to better than 0.5 mÅ with little over 2000 determinants, the single bond and, consequently, the BLA show a somewhat slower convergence and reach the same level of accuracy with about 5114 determinants. We stress however that we are here looking at extremely small differences while establishing the degree of convergence. For all practical purposes, the BLA is already converged to better than 1 mÅ within the limits of statistical error with just over 1000 determinants, again proving the ability of CIPSI expansions to obtain optimal geometry descriptions with a very small set of determinants. Besides overcoming the non-uniform convergence of the structural parameters when expanding the wave function on different active spaces, these calculations also confirm the need for a rather subtle multireference description for such conjugated systems [48, 49]. The converged single bond length is in excellent agreement with

Figure 3.2: Convergence of the single bond (C-C), double bond (C=C), and bond length alternation (BLA) (Å) with the number of determinants in the CIPSI wave function (red). Previous results [2] obtained with a Jastrow-CAS wave function are presented in blue.

the CCSD(T)/CBS value of 1.455 Å obtained with the same pseudopotentials used in the QMC calculations (see SI). Our double bond is instead less than 0.003 Å smaller than the corresponding CCSD(T)/CBS value, consequently resulting in a difference of about 0.002 Å on the BLA.

To investigate the impact of the inclusion of three-body terms in the Jastrow factor, we add them to the CIPSI wave functions with 2048 and 5114 determinants and reoptimize all wave function parameters on the fixed average geometries we have determined with the two-body Jastrow factor. These optimizations result in the VMC and DMC energies presented in Table 3.3. While there is an expected gain in the VMC energies, the DMC energies are equivalent within the statistical error of 0.2 mHartree to the energies obtained with a two-body Jastrow factor. Consequently, given the quality of our determinantal component, a two-body Jastrow recovers most

of the missing dynamical correlation contribution and is sufficient for our purposes.

Table 3.3: Effect of the inclusion of three-body Jastrow terms ($\mathcal{J}_{3\text{-body}}$) on the total VMC and DMC energies (a.u.). ΔE denotes the gain in energy with respect to the values obtained with a two-body Jastrow factor ($\mathcal{J}_{2\text{-body}}$). The structures optimized with the two-body Jastrow factor are used.

No. det	E_{VMC}	E_{DMC}	ΔE_{VMC}	ΔE_{DMC}
2048	-26.29908(15)	-26.32162(20)	-0.00522(29)	-0.00015(26)
5114	-26.30333(23)	-26.32412(16)	-0.00353(33)	0.00012(18)

All results presented so far have been obtained by selecting the CIPSI determinants out of a much larger CIPSI wave function according to the “truncation” scheme. The VMC energies obtained with the “expansion” scheme where one constructs CIPSI expansions of increasing size are compared with the “truncation” scheme in Figure 3.3. Both schemes lead to very comparable convergence in the energy as a

Figure 3.3: Optimal ground-state VMC energies obtained with Jastrow-CAS and Jastrow-CIPSI wave functions constructed with the “expansion” and “truncation” schemes.

function of the number of determinants in the Jastrow-CIPSI wave function and to compatible converged structural parameters. However, as can be seen in Figure 3.4, the variation of the bond lengths and BLA is not as smooth as in the truncation case. In particular, the calculation with 5114 determinants following the “expansion” strategy breaks the monotonicity of the geometry convergence with the single bond being smaller than that obtained with 2424 and 15,469 determinants, and the double bond longer than the values obtained in the other two cases. This difference probably arises from the added requirement of having an eigenstate of $\mathbf{S}^2$ in the expansion scheme. In fact, if we follow the expansion scheme without this requirement and construct a

wave function of 5114 determinants, we obtain an optimal VMC single and double bonds of 1.45564(26) and 1.33496(11) Å respectively, and, a BLA of 0.12068(26) Å. The VMC energy converges to -26.29960(24) a.u. These results are in good agreement with the corresponding values obtained with the truncation scheme.

Figure 3.4: Convergence of the structural parameters (Å) of butadiene with the number of determinants obtained with Jastrow-CIPSI wave function and the “expansion” scheme (red). Previous results [2] obtained with Jastrow-CAS wave functions are presented in blue.

Finally, we explore a potentially better orbital description in terms of natural orbitals obtained from a CIPSI calculation instead of the canonical orbitals resulting from a CAS(10,10) self-consistent calculation as done above. To this aim, we determine the natural orbitals for a very large CIPSI wave function of 2 million determinants and construct three expansions of roughly 2000, 5000, and 15,000 determinants with the truncation scheme. The number of variational parameters in these wave functions is much higher than corresponding ones in the canonical case, since the package used to generate the natural orbitals from CIPSI wave functions lacks the symmetry information of the resultant orbitals. Counter-intuitively, we consistently obtain higher VMC energies compared to the expansions generated with canonical

orbitals. The reason behind this observation is unclear. The bond lengths and BLA obtained with 5000 determinants are in excellent agreement with the corresponding values for the truncated canonical set of comparable size but the other test cases do not provide as compatible values. The results of these calculations are given in Table 3.4.

Table 3.4: Optimal ground-state structural parameters of butadiene (Å) and corresponding VMC energies (a.u.) with increasing number of determinants for CIPSI expansions over natural orbitals. The cc-pVTZ basis set is used.

No. det	No. param	C-C	C=C	BLA	E _{VMC}
2048	11851	1.45453(37)	1.33444(11)	0.12009(31)	-26.28733(26)
5000	18320	1.45536(14)	1.33444(09)	0.12091(20)	-26.29437(25)
15000	39325	1.45562(10)	1.33417(11)	0.12145(12)	-26.30379(23)

3.5 Conclusion

We demonstrated the excellent performance of compact perturbatively-selected CIPSI determinantal expansions in obtaining significantly lower VMC and DMC energies as compared to conventional active space definitions for the challenging case of butadiene. With the use of these wave functions, we were able to obtain converged ground-state structural parameters with the use of only a few thousand determinants. We tested two different schemes for the selection of the CIPSI expansions either by constructing a large CIPSI wave function and then truncating it (“truncation” scheme), or by considering successive sets of determinants in the CIPSI construction (“expansion” scheme). We found that the two representations are rather equivalent in terms of energy but that the truncation scheme possibly leads to a somewhat smoother convergence of the structural parameters with the size of the CIPSI expansion. CCSD(T) calculations with the same pseudopotentials yield a CBS estimate of the carbon-carbon single bond in very good agreement with our converged value but a double bond and corresponding BLA smaller by about 0.002 Å. We do not expect any significant change in the bond lengths upon inclusion of additional determinants, in view of their weak variations observed over a wide range of the number of determinants already considered.

Our study therefore shows that the automated selection of determinants from a CIPSI wave function is an extremely suitable and less cumbersome alternative for the fast optimization of ground-state geometries in QMC than a choice based on correlating electrons in active spaces constructed from energetically low-lying orbitals. The latter results in large expansions with many determinants which contribute little to the energy and to the convergence of the structural parameters. The use of CIPSI-based wave functions in combination with the low-scaling algorithms for simultaneous wave function and geometry optimization opens the way to the accurate and efficient QMC optimization of large molecular systems.

3.6 Appendix: Full CI extrapolation of CIPSI energies

Figure 3.5: Full CI extrapolation of the variational CI (E^{ref}) energy with respect to perturbation correction, $E^{\text{PT}2}$, obtained with canonical and natural orbitals. We use the BFD pseudopotentials and the corresponding cc-pVTZ basis set.

We extrapolate the variational CI energy of the CIPSI expansions to the full CI limit, i.e. to $E^{\text{PT}2} = 0$ obtained with both canonical MOs and natural MOs. In the fitting procedure, the values of $E^{\text{PT}2}$ are quite large, so a quadratic fit is used. We consider points where $E^{\text{PT}2} < -0.4$ a.u., and impose that the two extrapolated curves (natural and canonical) cross at $E^{\text{PT}2} = 0$ a.u. The extrapolated FCI energy is -26.2753 a.u., in good agreement with the CCSD(T)/cc-pVTZ value of -27.2773 a.u. (see Table 3.5 below).

3.7 Appendix: CCSD(T) calculations and CBS extrapolation

As shown in Table 3.5, we perform CCSD(T) geometry optimization using our pseudopotentials and the corresponding cc-pVXZ ($X = \text{D, T, Q, and 5}$) and aug-cc-pVXZ ($X = \text{D, T, and Q}$) basis sets. We also optimize the geometry in all-electron calculations in the frozen core (FC) approximation with the all-electron cc-pVXZ and aug-cc-pVXZ basis sets. Finally, full all-electron calculations (no FC) are also carried out with the basis sets, cc-pCVXZ and aug-cc-pCVXZ, and cc-pwCVXZ and aug-cc-pwCVXZ.

For the pseudopotential and FC cases where we have a reasonable number of data points, we extrapolate the bond lengths to the complete basis set (CBS) limit and use a five parameter fit as a combination of two three-parameter exponential fits [50] for

the cc- and aug-cc- basis sets according to the following equation

$$f(X) = (a + b e^{-cX})\delta_{\text{cc-}} + (a + d e^{-eX})\delta_{\text{aug-cc-}}, \quad (3.5)$$

where X is the cardinality of the basis set. We employ Mathematica [51] to perform the fit.

In the all-electron calculations, the use of augmentation appears to slow down the convergence of the bond lengths and lead to a seemingly smaller BLA. The same observation also holds for the pseudopotential case and the carbon-carbon bond length. The use of pseudopotentials leads to a somewhat larger BLA, bringing the CCSD(T) result in even better agreement with our QMC calculations.

We also report previous calculations [50], where the CBS limit with a three-parameter exponential fit is computed on the CCSD(T) bond lengths obtained in the FC approximation with the aug-cc-pVXZ basis sets with $X = D, T$, and Q . The core-valence correlation error is then extrapolated (again in a three-parameter exponential fit) on the differences with the values computed without the FC approximation and with the cc-pwCVXZ basis set (with $X = D, T$, and Q). The addition of a CCSDT(Q)(FC)/cc-pVDZ correction leads to a lengthening of the double bond and a consequent shortening of the BLA.

Table 3.5: Optimal CCSD(T) ground-state structural parameters of butadiene and corresponding energies.

Basis	C-C	C=C	BLA	Energy
Burkatzki-Filippi-Dolg pseudopotentials				
cc-pVDZ	1.4743	1.3605	0.1138	-26.11741
cc-pVTZ	1.4575	1.3399	0.1176	-26.27737
cc-pVQZ	1.4561	1.3375	0.1186	-26.30670
cc-pV5Z	1.4546	1.3367	0.1179	-26.32791
aug-cc-pVDZ	1.4679	1.3579	0.1100	-26.14781
aug-cc-pVTZ	1.4570	1.3400	0.1170	-26.28746
aug-cc-pVQZ	1.4569	1.3381	0.1188	-26.31379
CBS limit	1.4556	1.3371	0.1185	–
All-electron calculations with FC				
cc-pVDZ	1.4725	1.3585	0.1140	-155.53877
cc-pVTZ	1.4612	1.3439	0.1173	-155.69593
cc-pVQZ	1.4587	1.3412	0.1175	-155.74073
cc-pV5Z	1.4580	1.3407	0.1173	-155.75411
aug-cc-pVDZ	1.4733	1.3609	0.1124	-155.56506
aug-cc-pVTZ	1.4608	1.3447	0.1161	-155.70597
aug-cc-pVQZ	1.4591	1.3417	0.1174	-155.74455
All-electron calculations with no FC				
cc-pwCVDZ	1.4688	1.3541	0.1147	-155.67785
cc-pwCVTZ	1.4570	1.3396	0.1174	-155.89914
cc-pwCVQZ	1.4552	1.3379	0.1174	-155.96010
aug-cc-pwCVDZ	1.4704	1.3577	0.1127	-155.69915
aug-cc-pwCVTZ	1.4571	1.3407	0.1164	-155.90786
cc-pCVDZ	1.4689	1.3546	0.1143	-155.70116
cc-pCVTZ	1.4581	1.3407	0.1174	-155.89970
cc-pCVQZ	1.4554	1.3381	0.1173	-155.95485
aug-cc-pCVDZ	1.4708	1.3581	0.1126	-155.72248
aug-cc-pCVTZ	1.4580	1.3418	0.1162	-155.90907
Other calculations				
CCSD(T)/CBS ^a	1.4548	1.3377	0.1171	
CCSD(T)/CBS-corr ^b	1.4549	1.3389	0.1160	

^a Ref. 50; ^b Ref. 50, including a CCSDT(Q)(FC)/cc-pVDZ correction.

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Chapter 4

Excited states with selected configuration interaction-quantum Monte Carlo: chemically accurate excitation energies and geometries[†]

We employ quantum Monte Carlo to obtain chemically accurate vertical and adiabatic excitation energies, and equilibrium excited-state structures for the small, yet challenging, formaldehyde and thioformaldehyde molecules. A key ingredient is a robust protocol to obtain balanced ground- and excited-state Jastrow-Slater wave functions at a given geometry, and to maintain such a balanced description as we relax the structure in the excited state. We use determinantal components generated via a selected configuration interaction scheme which targets the same second-order perturbation energy correction for all states of interest at different geometries, and we fully optimize all variational parameters in the resultant Jastrow-Slater wave functions. Importantly, the excitation energies as well as the structural parameters in the ground and excited states are converged with very compact wave functions comprising few thousand determinants in a minimally augmented double- ζ basis set. These results are obtained already at the variational Monte Carlo level, the more accurate diffusion Monte Carlo method yielding only a small improvement in the adiabatic excitation energies. We find that matching Jastrow-Slater wave functions with similar variances can yield excitations compatible with our best estimates; however, the variance-matching procedure requires somewhat larger determinantal expansions to achieve the same accuracy, and it is less straightforward to adapt during structural optimization in the excited state.

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4.1 Introduction

Quantum Monte Carlo (QMC) methods are first-principle approaches that approximately solve the Schrödinger equation in a stochastic manner. The two most commonly used variants, namely, variational (VMC) and diffusion Monte Carlo (DMC) typically employ so-called Jastrow-Slater wave functions where a determinant expansion is multiplied by a Jastrow factor which explicitly depends on the inter-particle distances and accounts for a significant portion of electronic correlation. Because of the presence of the Jastrow factor, much shorter expansions are often needed to describe the Slater component and obtain accurate VMC results, which can then be further improved with the use of DMC. Thanks to the favorable scaling with system size, these methods have been routinely employed to compute the electronic properties, particularly total energies, of relatively large molecules and solids [1–5].

Recent methodological advances have reduced the cost per Monte Carlo step of computing energy derivatives to the one of the energy itself also for large multi-determinant wave functions [6, 7]. This has enabled us not only to simultaneously optimize geometry and wave function with as many as 200,000 determinants but also to explore the dependence of the results on different lengths and types of Slater expansions, foraying into QMC wave function choices beyond conventional small-active-space definitions. Capitalizing on these developments, our recent thorough investigation [8] of constructing the Slater component by an automated determinant selection through a selected configuration interaction (CIPSI) approach [9–21] has lead to accurate predictions of the ground-state energies and structural parameters of butadiene with relatively short Slater expansions. Relevant determinants could be systematically introduced into the wave function that would not have been chosen otherwise based on a manual, intuitive selection.

These developments also open very interesting prospects for the application of QMC to geometry relaxation in the excited state, where most electronic structure methods either lack the required accuracy or are computationally quite expensive due to their scaling with system size. To date, there are very few studies to assess the ability of QMC to predict excited-state geometries [22–25], while most of the relatively limited literature on excited-state QMC calculations is primarily concerned with vertical excitation energies [26–42]. Importantly, all these studies are characterized by the use of very different wave functions ranging from the simple ansatz of a CI singles wave function to complete active space (CAS) expansions, sometimes truncated or only partially optimized in the presence of the Jastrow factor due to the limitations previously faced in sampling and optimizing large numbers of determinants. In this work, we want to overcome this empiricism in the application of QMC to excited states and a) identify the most efficient protocol to obtain a balanced and robust description of the ground and excited states in VMC at a given geometry; b) extend this protocol to the optimization of the geometry as well as the computation of energy differences between different potential energy surfaces at distinct geometries; c) demonstrate the competence of VMC in determining accurate vertical excitation energies, optimal excited-state structures, and adiabatic excitations.

To this aim, we focus on the low-lying singlet $n \rightarrow \pi^*$ excitation of formaldehyde

and thioformaldehyde, and compute these excited-state properties employing relatively compact wave functions containing between a few thousand to about 45,000 determinants obtained through different CIPSI selection schemes. These molecules are small but theoretically challenging: a recent VMC study reported an error as large as 0.2 eV on the vertical excitation energy of thioformaldehyde [39], and DMC calculations without a Jastrow factor required wave functions with as many as hundred thousand determinants to achieve high accuracy for formaldehyde [38]. Here, we obtain VMC vertical excitation energies within chemical accuracy (~ 0.04 eV) of the extrapolated full CI (FCI) estimates for both molecules with expansions as small as a few thousand determinants in combination with a minimally augmented double- ζ basis set. These excellent results are obtained using CIPSI expansions constructed to yield a comparable second-order perturbation (PT2) correction in the ground and excited states, and fully reoptimized in the presence of the Jastrow factor. Matching the energy variance of the Jastrow-Slater wave functions of the two states [39, 43] to estimate the excitation energy appears to be a more delicate procedure which, in the case of formaldehyde, recovers VMC excitation energies within 0.05 eV of our best estimates for determinantal expansions comprising at least 7000 determinants.

When optimizing the structure, we follow two different selection routes to maintain a balanced treatment of the wave function while changing the geometry: we construct the determinantal component targeting a roughly constant value of either the perturbation correction or the variance of the CIPSI expansions. We find that both schemes are viable to obtain robust VMC geometries, also in the more demanding case of formaldehyde where different correlated methods give a range of variations in the prediction of the CO bond and the out-of-plane angle in the excited state as large as 80 mÅ and 20° , respectively [44]. With just a minimal basis, we obtain optimal VMC structures converged with fewer than a thousand determinants and in excellent agreement with the coupled cluster estimates, namely, with deviations smaller than a couple of degrees in the angles and 3 and 10 mÅ in the ground- and excited-state bond lengths, respectively. Finally, we compute the difference between the variational minima of the VMC ground- and excited-state potential energy surfaces to evaluate the adiabatic excitation energies. For both molecules, irrespective of the determinant selection mode, we obtain VMC and DMC estimates within better than 0.05 eV of the corresponding coupled cluster values.

We describe the CIPSI selection scheme employed to obtain a balanced description of multiple states in Section 4.2 and present the computational details in Section 4.3. The VMC and DMC vertical excitation energies of formaldehyde and thioformaldehyde are given in Section 4.4 and the results of the VMC structural relaxation in the ground and excited states in Section 4.5. We conclude in Section 4.6 by summarizing the most important outcomes of our investigation and the future prospects of the applicability of our approach.

4.2 Methods

The wave functions used in the QMC calculations are of the Jastrow-Slater form, namely, the product of a determinantal component and a positive Jastrow correlation function,

$$\Psi = \mathcal{J} \sum_k^{N_{\text{det}}} c_k D_k, \quad (4.1)$$

where N_{det} is the total number of determinants and the Jastrow factor $\mathcal{J}$ depends here on the electron-nucleus and electron-electron distances, explicitly ensuring that the electronic cusp conditions are satisfied.

To construct the determinantal part of the wave function, we employ the CIPSI selected CI algorithm that iteratively allows us to identify energetically important determinants from the FCI space. When one is interested in multiple electronic states, it is important to obtain a description of the CI subspace which leads to a uniform and balanced treatment of all states of interest. To ensure a consistent quality of the wave functions, the selection of the determinants for the multiple states is done in a single run even if the states belong to different symmetry classes. In practice, starting from an initial reference subspace $\mathcal{S}$ typically given by the CI singles wave functions of all states, at every iteration, we expand the space by selecting among all singly- and doubly-excited determinants those which contribute the most to a state-average PT2 energy contribution.

If we represent a newly selected determinant with $|\alpha\rangle$, we then compute its second-order energy contribution using Epstein-Nesbet perturbation theory [45, 46] as

$$\delta E_n^{(2)} = \frac{|\langle \alpha | \mathcal{H} | \Psi_n \rangle|^2}{\langle \Psi_n | \hat{\mathcal{H}} | \Psi_n \rangle - \langle \alpha | \mathcal{H} | \alpha \rangle}, \quad (4.2)$$

and the corresponding CI coefficients as

$$c_{\alpha,n} = \frac{\langle \Psi_n | \hat{\mathcal{H}} | \alpha \rangle}{\langle \Psi_n | \hat{\mathcal{H}} | \Psi_n \rangle - \langle \alpha | \hat{\mathcal{H}} | \alpha \rangle}, \quad (4.3)$$

where n denotes a state and Ψ_n is the current CI wave function in the space $\mathcal{S}$. As suggested by Angeli *et al.* [47], the selection criterion for a determinant $|\alpha\rangle$ in the external space is based on the energy contribution

$$e_\alpha = \sum_n^{N_{\text{states}}} w_n \delta E_n^{(2)}, \quad (4.4)$$

where w_n is the inverse of the maximum $c_{k,n}^2$ with the index k running over the determinants in the current subspace $\mathcal{S}$. The determinant $|\alpha\rangle$ is added to $\mathcal{S}$ if its energy contribution e_α is higher than a threshold, which is automatically adjusted in such a way that the number of determinants in $\mathcal{S}$ is doubled at each iteration. In the applications presented in this work, the ground state is a closed-shell and the excited state an open-shell singlet, both having single-reference character with the dominant configuration state function (CSF) comprising a single determinant in the ground state

and two determinants in the excited state. Since the expansion is performed in the basis of the determinants and not of the CSFs, reweighting the energy contributions by w_n recovers the balance for the different states. As a consequence, we find that that multiple states resulting from the expansion have approximately equivalent net PT2 corrections at every CIPSI iteration. For sufficiently large expansions, the PT2 correction can be viewed as an estimate of the current error in the variational energy with respect to the FCI value and, therefore, wave functions of different states with similar PT2 corrections will have comparable quality and yield a reasonable estimate of the excitation energies already at the CI level.

The many-body Hamiltonian, $\mathcal{H}$, is diagonalized in the subspace $\mathcal{S}$ at every iteration to determine the current CI coefficients. One keeps expanding until the wave function has a required number of determinants or until another chosen criterion is met as for instance a desired total PT2 correction or variance of the CI wave functions as further discussed below in the Results sections [8, 48–51]. Additionally, we impose that the selected wave functions are spin-adapted, namely, eigenfunctions of the $\hat{S}^2$ operator: all determinants corresponding to the spatial occupation patterns currently present in $\mathcal{S}$ are added to the reference space before the Hamiltonian is diagonalized [52, 53]. Although wave functions for all the states are obtained through this common selection process, determinants of one symmetry character do not contribute, of course, to a state of a different character. Therefore, we separate these determinants based on space symmetry prior to proceeding with the VMC optimization.

In what we name the “expansion” scheme, we simply use subsequent wave functions of increasing length generated according to the CIPSI algorithm we just described. While the “expansion” scheme is more easily transferable to larger systems where one could experience difficulty in obtaining a large expansion to then truncate, we will also present some tests with wave functions generated from a “truncation” scheme. After having introduced a large number of determinants in the reference space and obtained the wave functions for both states by diagonalizing the Hamiltonian, we project the wave functions in a common subspace of determinants as follows: for each group of determinants, $\mathcal{P}$, of the internal space sharing the same spatial occupation pattern, we compute the quantity

$$d(\mathcal{P}) = \sum_{k \in \mathcal{P}} \sum_n^{N_{\text{states}}} c_{kn}^2, \quad (4.5)$$

All the individual spatial occupation patterns of the internal space are sorted in decreasing order of $d(\mathcal{P})$ values, and the truncated determinant space is built by taking the union of the first patterns of the list. This guarantees that the truncated wave functions are spin-adapted and that the final determinants kept after truncation are the most important for all states of interest.

4.3 Computational Details

All QMC computations are carried out with the program package CHAMP [54]. We employ scalar-relativistic energy-consistent Hartree-Fock pseudopotentials and the correlation-consistent Gaussian basis sets specifically constructed for these pseudopotentials [55, 56]. For the majority of our calculations, we use a minimally augmented double- ζ basis set denoted here as maug-cc-pVDZ and constructed by augmenting the cc-pVDZ basis with s and p diffuse functions on the heavy atoms. Basis-set convergence tests are performed with the fully augmented aug-cc-pVTZ pseudopotential basis. In both cases, the diffuse functions are taken from the corresponding all-electron Dunning’s correlation-consistent basis sets [57]. The Jastrow factor includes two-body electron-electron and electron-nucleus correlation terms [58].

We optimize all wave function parameters (Jastrow, orbital, and CI coefficients) by energy minimization in VMC using the stochastic reconfiguration (SR) method [59] in a conjugate gradient implementation [60]. We optimize the ground and excited states separately since the two states have different symmetries both at the ground- and the excited-state optimal structures. We relax the geometry in Z-matrix coordinates and simply follow the direction of steepest descent, appropriately rescaling the interatomic forces and using an approximate constant diagonal hessian. After convergence, we perform additional optimization steps and average the last 40 structures to estimate the structural parameters presented below. To remove occasional spikes in the forces, we use an improved estimator of the forces obtained by sampling the square of a modified wave function close to the nodes [61]. In the DMC calculations, we treat the pseudopotentials beyond the locality approximation using the T-move algorithm [62] and employ an imaginary time step of 0.02 a.u. Through careful time step extrapolation tests performed with the shortest wave function in Table 4.1, we identify that this time step yields DMC excitation energies converged to better than 0.01 eV for the smallest wave function in formaldehyde and is therefore appropriate for all wave functions of higher quality considered in this work [63].

The CIPSI calculations are performed with Quantum Package [64] using orbitals obtained from small complete active space self-consistent field (CASSCF) calculations in the program GAMESS(US) [65, 66]. As explained above, the CIPSI expansions are constructed to be eigenstates of $\hat{S}^2$ and the selected determinants are subsequently mapped into the basis of configuration state functions, thereby effectively reducing the number of optimization parameters for QMC.

4.4 Vertical excitation energies

We begin our investigation by computing the lowest singlet vertical excitations energies of $n \rightarrow \pi^*$ character of formaldehyde (CH_2O) and thioformaldehyde (CH_2S) (see Fig. 4.1). In the ground state, both molecules possess C_{2v} symmetry and the relevant ground (S_0) and excited (S_1) states belong to the A_1 and the A_2 irreducible representation, respectively. The QMC vertical excitation energies are computed on the ground-state structures optimized at the iterative approximate coupled clus-

Figure 4.1: Schematic representation of the molecules considered in this work: formaldehyde (CH₂O) and thioformaldehyde (CH₂S). The orbitals involved in the $n \rightarrow \pi^*$ excitation of formaldehyde is also illustrated.

ter singles, doubles and triples (CC3) level with an aug-cc-pVTZ basis and without the frozen-core approximation [38, 67]. Importantly, as we show below, the CC3 geometries are identical to the optimal ground-state structures obtained at the VMC level.

4.4.1 Formaldehyde

The lowest $n \rightarrow \pi^*$ excited state of formaldehyde has been the subject of a recent DMC investigation [38], where Jastrow-free CIPSI wave functions with as many as 300,000 determinants were employed to recover a vertical excitation energy within 0.08(3) eV of the best theoretical estimate of 3.97 eV [67]. In fact, calculations involving about 9000 and 75,000 determinants yielded excitation energies about 0.2 and 0.1 eV higher, respectively, than the reference value. Given the size of the molecule and the single-reference character of the excitation, the large number of determinants required to recover a satisfactory result is rather surprising and warrants an investigation where we generate optimal wave functions in the presence of the Jastrow factor prior to the DMC step.

Here, we revisit the VMC and DMC computation of this vertical excitation energy with compact CIPSI expansions in the Jastrow-Slater wave functions, containing between 1000 and 40,000 determinants. These determinant components are the result of subsequent expansions at the CIPSI level constructed to achieve a balanced description of the two states of interest at each step by selecting determinants that yield comparable PT2 contributions for both states as discussed above. The determinants corresponding to A_1 and A_2 symmetry are then isolated and the Jastrow-Slater

wave functions are separately fully optimized by energy minimization in VMC. The resulting VMC and DMC total and vertical excitation energies are listed in Table 4.1 and plotted in Figure 4.2.

Figure 4.2: Convergence of the VMC and DMC energies of the ground and excited states (top) and of the excitation energy (bottom) of the $n \rightarrow \pi^*$ excitation of formaldehyde with the combined number of determinants in the CIPSI expansions. The maug-cc-pVDZ basis is used. We also show the extrapolated FCI and CC3 values obtained with the aug-cc-pVTZ basis set [67].

The VMC vertical excitation energies computed with the maug-cc-pVDZ basis are already within 0.05 eV of the CC3/aug-cc-pVTZ value with about 1000 and 2400 determinants in the ground and the excited state, respectively. Further increasing the size of the wave functions by a factor of 10, we observe a rapid convergence to within ~ 0.02 eV of the CC3 value. The DMC calculations with the VMC optimized wave

Table 4.1: VMC and DMC ground- and excited-state energies, and vertical excitation energies (eV) of formaldehyde obtained with fully optimized Jastrow-CIPSI wave functions, where a series of increasing determinantal expansions are obtained with the “expansion” scheme.

Basis	No. det		No. param		VMC			DMC		
	S0	S1	S0	S1	E(S0)	E(S1)	ΔE	E(S0)	E(S1)	ΔE
maug-cc-pVDZ	343	436	848	614	-22.88852(32)	-22.74015(33)	4.037(13)	-22.91702(26)	-22.76903(26)	4.027(10)
	580	1124	946	961	-22.89762(32)	-22.74929(31)	4.036(12)	-22.92182(25)	-22.77393(24)	4.024(09)
	994	2360	1104	1357	-22.90177(30)	-22.75459(27)	4.005(11)	-22.92362(23)	-22.77635(23)	4.008(09)
	1703	4182	1375	1937	-22.90512(25)	-22.75753(25)	4.016(10)	-22.92530(22)	-22.77772(22)	4.016(08)
	2747	7110	1762	2805	-22.90717(25)	-22.76046(24)	3.992(09)	-22.92675(22)	-22.77947(22)	4.008(08)
	3050	8320	1874	3141	-22.90719(20)	-22.76051(20)	3.991(08)	-22.92642(18)	-22.77916(17)	4.007(07)
	5932	16871	2915	5550	-22.90852(20)	-22.76233(20)	3.978(08)	-22.92687(18)	-22.77997(17)	3.997(07)
aug-cc-pVTZ	10854	29786	4681	9177	-22.90961(20)	-22.76303(20)	3.989(08)	-22.92728(14)	-22.78072(16)	3.988(06)
	675	912	3237	2256	-22.90151(19)	-22.75361(19)	4.024(07)	-22.92260(16)	-22.77499(16)	4.017(06)
	1488	3214	3592	3474	-22.91364(17)	-22.76638(17)	4.007(06)	-22.92778(14)	-22.78068(13)	4.015(05)
	3058	7672	4210	5050	-22.92021(15)	-22.77242(15)	4.021(06)	-22.93112(12)	-22.78359(12)	4.014(05)
	5849	15338	5222	7401	-22.92050(16)	-22.77333(14)	4.005(06)	-22.93136(11)	-22.78360(10)	4.021(04)
	12987	31710	7731	12040	-22.92188(15)	-22.77466(14)	4.006(06)	-22.93145(11)	-22.78393(13)	4.014(05)

functions gain about 17-30 mHartrees for the range of expansions studied, so the gain is uniform for both states. Consequently, the gap is quite stable also at the DMC level and consistently compatible within statistical error (to better than 0.02 eV) with the corresponding VMC values. A similar behavior is observed when employing the fully-augmented triple- ζ basis set with the VMC excitation energy being rather stable as a function of the expansion size and in agreement within statistical error with the corresponding DMC value. From these calculations, we can therefore make three important observations: a) the weighted CIPSI algorithm used here yields an automated, balanced determinant selection of the two states; b) in combination with VMC optimization, we obtain reliable estimates for the vertical excitation energy with rather small and compact Jastrow-Slater wave functions; c) to estimate the excitation energy, there is no need to perform a DMC calculation as the main correlation effects on the energy difference have already been captured at the VMC level.

The extrapolated FCI estimate of the excitation energy computed with the same pseudopotential maug-cc-pVDZ basis set is 3.99 eV (see Figure 4.8) in perfect agreement with the all-electron value of 3.99 eV obtained with the corresponding aug-cc-pVDZ basis set. In the all-electron calculations, the use of the larger aug-cc-pVTZ only reduces the FCI value to 3.98 eV, that can be further corrected for basis set and frozen-core errors to yield the best theoretical estimate of 3.97 eV [67]. Our results of 3.99 and 4.02 eV obtained with the maug-cc-pVDZ and aug-cc-pVTZ, respectively, are in excellent agreement with the reference value.

So far, we have obtained a balanced description of both states by selecting determinants in the CIPSI expansion that yield comparable net PT2 contribution to both states at every step. In Figure 4.3, we plot the resulting excitations energies together with the estimates obtained as difference of the fits of the ground- and excited-state VMC energies against the number of total determinants as $E_{\text{EX}}^{\text{fit}}(N_{\text{det}}) - E_{\text{GS}}^{\text{fit}}(N_{\text{det}})$ (see Appendix 4.8). Although we optimize our wave functions separately for the two states in VMC, we use the total number of determinants as common index since the determinants were obtained from the same CIPSI selection [68]. Furthermore, since we now have at hand multiple wave functions for the ground and excited states, we can alternatively follow another physically appropriate approach to compute the excitation energy by matching the variances of the states of interest [39, 43]. To do so, we fit the VMC energies separately for the ground and the excited states against the corresponding variances (see Figure 4.11) and then subtract the two fits as $E_{\text{EX}}^{\text{fit}}(\sigma^2) - E_{\text{GS}}^{\text{fit}}(\sigma^2)$. The resulting variance-matched excitation energies are plotted in Figure 4.3, where smaller variances correspond to larger expansions.

For our fully optimized Jastrow-CIPSI wave functions, both schemes to estimate the excitation energy yield reasonable values, which become of course more compatible for the larger expansions. The excitation energies computed by fitting the energies against the number of determinants display a clear and fast convergence, and are closer to the extrapolated FCI estimate over the whole range of expansions explored here. For the variance-matching scheme, the fit at high variances deviate from the FCI value by 0.08-0.12 eV and, only beyond about 7000 determinants and a variance of about 0.31 a.u, the fit starts giving reasonable estimates within 0.05 eV of our best estimate. Therefore, to make a reliable variance-matched prediction, one

needs to employ larger wave functions containing several thousand determinants. We note that we are not in a regime [69] where a reliable estimate of the exact energy can be obtained by linear extrapolation to zero variance.

Figure 4.3: VMC vertical excitation energies (circles) of formaldehyde obtained with the “expansion” scheme. The excitation energy is also estimated as the difference of the fits of the energies against the total number of determinants (bottom x-axis) and against the variance of the two states (top x-axis). We also show the extrapolated FCI and CC3 values obtained with the aug-cc-pVTZ basis set [67].

Finally, while the “expansion” scheme represents the most practical route to generate the determinantal component in a Jastrow-CIPSI wave function for larger systems, given the small size of formaldehyde, we can also investigate the effect of using the “truncation” scheme where a large CIPSI expansion is truncated either to yield wave functions with a similar norm for all states (Table 4.2, truncation from 40,000 total determinants) or to include the most relevant patterns (Table 4.3, truncation from 3.15 million total determinants) as discussed in Section 4.2. We find that both truncated wave functions yield energetically equivalent estimates of the vertical excitation energies at the VMC and DMC levels as those obtained with comparable expansion sizes with the “expansion” scheme of Table 4.1. We note that the “truncation” scheme should be applied to a relatively large expansion since, during the CIPSI iterations, the largest coefficients vary much at the beginning but tend to stabilize as the size of the expansion grows. If the size of the initial expansion is such that the determinants kept after truncation have converged coefficients relative to the largest coefficient, then truncating the wave function will be independent of the size of the starting expansion and, therefore, will be equivalent to truncating the FCI wave function. In general, fully reoptimizing the trial wave functions appears to yield accurate and robust estimates of the excitation energies of formaldehyde for both the

“expansion” and the “truncation” scheme.

4.4.2 Thioformaldehyde

This small molecule has been the subject of many recent investigations [39, 70–72] and is a variant of formaldehyde, wherein the O atom is replaced by a S atom. Interestingly, the very recent study by Flores *et. al* [39] employed Jastrow-CIPSI wave functions to compute the excitation energy of the $n \rightarrow \pi^*$ transition but obtained a VMC excitation energy of 2.07(2) eV, that is, about 0.2 eV lower than the reference extrapolated stochastic-heat-bath CI value of 2.31(1) eV on their geometry. They optimized all wave function parameters, albeit in variance minimization. In view of our success with the computation of the vertical excitation energy of formaldehyde at the VMC level, it is somewhat puzzling that the simple substitution of oxygen with sulfur would worsen so much the performance of the method. Therefore, we revisit here the same molecule using fully optimized Jastrow-CIPSI wave functions and both the CIPSI selection procedure of multiple states with similar PT2 energy correction and the variance-matching scheme.

We summarize our QMC results obtained from the CIPSI “expansion” scheme and the maug-cc-pVDZ basis set in Table 4.4 and also present them in Figure 4.4. As in the case of formaldehyde, we find that we are able to obtain a stable estimate of the vertical excitation energy both at the VMC and DMC level with relatively little effort. The excitation energy is essentially the same within statistical error at both the VMC and the DMC level when increasing the total number of determinants from 800 to 44,000. The use of larger expansions yields of course a gain in the total energies, which is however less than 1 and 0.5 mHartree in VMC and DMC, respectively, when doubling the expansion size between the last two entries of Table 4.4. Computation of the DMC energies on top of the final VMC optimized wave functions uniformly lowers the energies of both states by about 18-20 mHartrees, thereby unaltering the energy separation between them. Therefore, the CIPSI selection scheme combined with wave function optimization ensures a balanced description of the two states and yields a VMC excitation energy of 2.23 eV in excellent agreement with the CC3 value of 2.23 eV and the extrapolated FCI estimate of 2.22 eV obtained with a larger aug-cc-pVTZ basis [70].

In Figure 4.5, we plot the excitation energies obtained for the different CIPSI expansions together with the two estimates one obtains by computing the difference of the fits of the ground- and excited-state energies against the total number of determinants and against the variances of the two states as done for formaldehyde. We find that both estimates are compatible well within 0.05 eV over the whole range of expansion sizes/variances. We therefore do not reproduce the large error of 0.2 eV reported in Ref. [39], which cannot therefore be due to the use of the variance-matching recipe with reoptimized Jastrow-CIPSI wave functions.

Table 4.2: VMC and DMC total energies (a.u.) and vertical excitation energies (eV) computed with Jastrow-CIPSI wave functions obtained with truncation scheme (a) starting from the largest expanded wave function of Table 4.1 (about 40,000 total determinants). The maug-cc-pVDZ basis set is used.

% CIPSI weight	No. det.		No. param.		VMC			DMC		
	S0	S1	S0	S1	E(S0)	E(S1)	ΔE	E(S0)	E(S1)	ΔE
95	266	566	512	640	-22.88776(26)	-22.74379(25)	3.918(10)	-22.91641(19)	-22.77052(18)	3.970(7)
96	578	1210	737	878	-22.89430(25)	-22.74959(25)	3.956(10)	-22.92003(18)	-22.77347(17)	3.988(7)
97	1187	2674	1016	1195	-22.89902(24)	-22.75419(24)	3.941(09)	-22.92275(17)	-22.77616(16)	3.989(6)
98	2186	5072	1369	1644	-22.90490(23)	-22.75822(23)	3.991(09)	-22.92512(16)	-22.77798(15)	4.004(6)
99	4264	10212	2023	2563	-22.90657(23)	-22.76038(23)	3.978(08)	-22.92586(19)	-22.77928(15)	3.989(6)
100	10854	29786	4681	9177	-22.90961(20)	-22.76303(20)	3.989(08)	-22.92728(14)	-22.78072(16)	3.988(6)

Table 4.3: VMC and DMC total energies (a.u.) and vertical excitation energies (eV) computed with Jastrow-CIPSI wave functions obtained with truncation scheme (b) starting from a very large CIPSI expansion containing about 3.15 million total determinants. The maug-cc-pVDZ basis set is used.

No. det.		No. param.		VMC			DMC		
				S0	S1	E(S0)	E(S1)	ΔE	E(S0)
1590	3474	1224	1660	-22.90178(18)	-22.75450(18)	4.008(07)	-22.92426(16)	-22.77583(16)	4.039(06)
3242	7700	1861	2863	-22.90637(18)	-22.75952(18)	3.996(07)	-22.92601(16)	-22.77866(16)	4.009(06)
4403	10636	2284	3688	-22.90756(17)	-22.76034(17)	4.006(07)	-22.92688(15)	-22.77938(15)	4.014(06)
5801	14158	2788	4671	-22.90820(17)	-22.76134(17)	3.996(07)	-22.92702(15)	-22.78000(15)	4.000(06)
9311	23032	4038	7151	-22.90909(14)	-22.76197(14)	4.003(05)	-22.92683(15)	-22.77980(16)	4.001(06)

Table 4.4: VMC and DMC ground- and excited-state energies, and vertical excitation energies (eV) of thioformaldehyde obtained with fully optimized Jastrow-CIPSI wave functions obtained with the “expansion” scheme. The maug-cc-pVDZ basis set is used.

No. det		No. param		VMC			DMC		
S0	S1	S0	S1	E(S0)	E(S1)	ΔE	E(S0)	E(S1)	ΔE
353	475	854	607	-17.04424(26)	-16.96212(25)	2.234(10)	-17.06968(25)	-16.98671(24)	2.258(9)
702	1488	995	1044	-17.04998(25)	-16.96814(24)	2.227(09)	-17.07246(23)	-16.99023(23)	2.237(9)
1165	2702	1168	1461	-17.05239(24)	-16.97019(24)	2.237(09)	-17.07284(22)	-16.99086(22)	2.231(9)
1834	4692	1419	2034	-17.05388(23)	-16.97100(23)	2.255(09)	-17.07394(22)	-16.99171(22)	2.237(9)
2500	6316	1662	2514	-17.05494(23)	-16.97260(23)	2.241(09)	-17.07434(21)	-16.99211(22)	2.238(8)
3432	8338	1997	3112	-17.05622(23)	-16.97313(23)	2.261(09)	-17.07482(22)	-16.99219(22)	2.248(8)
5712	14562	2810	4848	-17.05698(22)	-16.97497(22)	2.232(08)	-17.07542(22)	-16.99314(26)	2.239(9)
14218	30142	5650	9162	-17.05780(15)	-16.97590(19)	2.236(07)	-17.07566(18)	-16.99345(26)	2.237(8)

Table 4.5: Optimal VMC ground-state bond lengths ($\text{\AA}$) and bond angles (deg) of formaldehyde obtained using Jastrow-CIPSI wave functions with the maug-cc-pVDZ basis. The VMC energy (a.u.) is averaged over the last 40 iteration of geometry optimization. We also list the CC3/aug-cc-pVTZ and the experimental values.

No. det.	No. par.	CO	CH	H-C-H	$\langle E_{\text{VMC}} \rangle$
580	946	1.20754(08)	1.09871(9)	117.09(6)	-22.89824(4)
2747	1762	1.20791(13)	1.09952(6)	116.85(3)	-22.90716(4)
5932	2915	1.20819(08)	1.09952(3)	117.05(3)	-22.90867(3)
CC3 [44]		1.208	1.100	116.4	
Expt. [73]		1.208	1.116	116.3

Figure 4.4: Convergence of the VMC and DMC energies with the number of CIPSI determinants of the ground and excited states (top) and of the excitation energy (bottom) of the $n \rightarrow \pi^*$ excitation of thioformaldehyde. The maug-cc-pVDZ basis is used. We also show the extrapolated FCI and CC3 values obtained with the aug-cc-pVTZ basis set [67].

4.5 Optimal excited-state structures and adiabatic excitation energies

Upon relaxation of formaldehyde in the first singlet excited state, the oxygen atom moves out of the plane. The optimal excited-state structure therefore possesses C_s symmetry with the symmetry plane being perpendicular to the initial molecular plane and passing through the CO bond. The excited-state optimization therefore follows

Figure 4.5: VMC vertical excitation energies (circles) of thioformaldehyde obtained with the “expansion” scheme. The excitation energy is also estimated as the difference of the fits of the energies against the total number of determinants (bottom x-axis) and against the variance of the two states (top, x-axis). We also show the extrapolated FCI and CC3 values obtained with the aug-cc-pVTZ basis set [67].

the A'' state as the symmetry of the molecule is lowered from C_{2v} to C_s . In the first singlet excited state, thioformaldehyde remains instead planar and preserves C_{2v} symmetry so that the excited state maintains A_2 character.

4.5.1 Formaldehyde

Figure 4.6: Optimal ground (S_0) and excited (S_1) state minimum structures of formaldehyde. o.o.p denotes the ‘out of plane’ angle of the S atom from the initial molecular plane.

We first optimize the structure of formaldehyde in the ground state for some of the Jastrow-Slater CIPSI wave functions that we have used to compute the vertical excitation energies of Table 4.1. Similar to our previous findings for butadiene [8],

we obtain an accurate geometry in the ground state with relatively short expansions. As shown in Table 4.5, the optimal bond lengths and bond angles computed with the compact aug-cc-pVDZ basis are within 1 mÅ and 1° of the corresponding CC3/aug-cc-pVTZ values already with the smallest wave function considered. Energetically, we gain about 1 mHartree upon structure optimization with the smallest wave function of 580 determinants and the average VMC energies of the two larger cases are identical to the initial energies on top of the starting CC3 geometry.

To relax the geometry in the excited state, we can simply start from the ground-state structure, with the oxygen slightly displaced out of plane, and use the same excited-state expansion as in the calculation of the vertical excitation. Even though such a wave function misses all determinants of B_2 character which will acquire non-zero weight as the molecule moves out of plane, this quick procedure gives us already a good estimate of the excited-state geometry with a CO bond of about 1.334 Å and an out-of-plane angle of 31.5°. These structural parameters compare very favorably with the corresponding values obtained in CC3 and a full valence CASPT2 calculation [44]. We stress that the excited-state geometry of formaldehyde has been found to depend significantly on the level of theory, with highly-correlated methods spanning differences of as much as 0.08 Å in the CO bond length and 20 degrees in the out-of-plane angle subtended by this bond on the HCH plane [44].

Starting from such an out-of-plane excited-state geometry, we generate a series of CIPSI expansions of symmetry A'' and continue the structural relaxation in the excited state to further investigate the dependence of the resultant geometry on the complexity of the wave function. Since we also want to compute the adiabatic excitation energy, we have to evaluate differences of the ground/excited-state energies on the ground/excited-state optimal geometries. To obtain a balanced description, we therefore generate the CIPSI wave functions at different geometries either targeting a given value of the PT2 correction or of the CI variance for all four states. For convenience, we shall hereafter refer to them as the iso-PT2 and the iso-variance procedure, respectively. The results of these calculations are shown in Table 4.6.

We perform four iso-PT2 optimization tests. Starting from a VMC geometry of Table 4.5, we generate four ground-state wave functions targeting different values of PT2 correction and further optimize the structure with these wave functions. We follow a similar procedure for the excited state starting from an out-of-plane VMC excited-state geometry obtained using the wave functions employed to compute the vertical excitation energies. For the ground state, the resulting bond lengths and angles remain within 1 mÅ and 1°, respectively, of the CC3 values for all four wave functions. In the excited state, the CO bond undergoes a marginal lengthening and the out-of-plane angle slightly increases by 2-3° becoming closer to the CC3 angle. The adiabatic excitation energies are computed as differences between iso-PT2 ground and excited-state energies on the corresponding equilibrium structures, and are highly stable irrespective of the size of the wave function: the VMC values lie between 3.55-3.56 eV and the DMC ones are somewhat higher and compatible within statistical error with the CC3 estimate. The iso-variance tests yield very similar results as the iso-PT2 ones and the procedure is therefore also a viable route to compute excited-state structures and adiabatic energies. The results of these calculations are

Table 4.6: Optimal VMC ground- and excited-state bond lengths ($\text{\AA}$) and bond angles (deg), and VMC and DMC adiabatic excitation energies (eV) of formaldehyde obtained using Jastrow-CIPSI wave functions with targeted PT2 correction (iso-PT2). The VMC energy (a.u.) is averaged over the last 40 iterations of geometry optimization. o.o.p denotes the out of plane angle of the CO bond.

State	δE_{PT2}	No. det.	No. par.	CO	CH	H-C-H	o.o.p	$\langle E_{\text{VMC}} \rangle$	$\Delta E_{\text{adia}}^{\text{VMC}}$	$\Delta E_{\text{adia}}^{\text{DMC}}$
S0	0.20	515	1183	1.20663(05)	1.09851(03)	116.84(4)	-0.098(25)	-22.89892(5)		
	0.15	1184	1496	1.20795(08)	1.09832(05)	116.96(6)	0.075(15)	-22.90411(6)		
	0.10	2784	2208	1.20752(19)	1.09947(05)	117.00(5)	0.073(54)	-22.90723(5)		
	0.07	4799	2946	1.20710(14)	1.09959(10)	117.01(8)	-0.030(29)	-22.90805(4)		
	CC3 [44] Expt. [73]			1.208 1.208	1.100 1.116	116.4 116.3	0.000 0.000			
S1	0.20	1088	1363	1.33948(07)	1.08468(02)	119.83(03)	32.916(055)	-22.76787(5)	3.566(2)	3.612(9)
	0.15	3106	2037	1.33971(36)	1.08630(06)	119.03(20)	34.778(051)	-22.77342(5)	3.556(2)	3.614(8)
	0.10	8058	3520	1.33606(21)	1.08647(12)	119.34(17)	34.027(233)	-22.77626(3)	3.564(2)	3.597(8)
	0.07	15278	5589	1.33597(15)	1.08645(08)	119.56(09)	33.294(070)	-22.77746(3)	3.553(1)	3.592(8)
	CC3 [44, 70] Expt. [74–76]			1.326 1.321–1.323	1.089 1.092–1.103	118.3 118.1–121.5	36.8 20.5–34		3.602	

Table 4.7: Same as Table 4.6 using Jastrow-CIPSI wave functions with targeted CI variance (iso-variance).

State	σ_{CI}^2	No. det.	No. par.	CO	CH	H-C-H	o.o.p	$\langle E_{\text{VMC}} \rangle$	$\Delta E_{\text{adia}}^{\text{VMC}}$	$\Delta E_{\text{adia}}^{\text{DMC}}$
S0	0.80	515	1183	1.20663(05)	1.09851(03)	116.84(4)	-0.098(025)	-22.89892(5)		
	0.60	1459	1605	1.20761(14)	1.09886(04)	116.98(5)	-0.091(023)	-22.90489(6)		
	0.40	3755	2566	1.20732(23)	1.09886(05)	116.99(4)	-0.057(235)	-22.90761(6)		
S1	0.80	782	1167	1.33888(11)	1.08562(06)	119.40(07)	34.061(104)	-22.76474(6)	3.651(2)	3.652(8)
	0.60	3106	2037	1.33971(36)	1.08630(06)	119.03(20)	34.778(051)	-22.77342(5)	3.577(2)	3.624(8)
	0.40	9820	4031	1.33713(31)	1.08641(06)	119.23(11)	33.522(079)	-22.77682(6)	3.563(2)	3.611(8)

shown in Table 4.7.

4.5.2 Thioformaldehyde

Figure 4.7: Optimal ground (S0) and excited (S1) state minimum structures of thioformaldehyde. The C–S bond lengthens in plane upon excitation from the ground to excited state.

For thioformaldehyde, we investigate the VMC convergence of the ground-state optimization again with three ground-state wave functions used in the computation of the vertical excitation energies. As shown in Table 4.8, we are able to obtain converged bond lengths and bond angles within less than 3 mÅ and 1° of the CC3 values already with the smallest set of 702 determinants and a maug-cc-pVDZ basis. Energetically, we gain much less than 1 mHartree in all three cases upon optimization starting from the CC3 structure.

In the first singlet excited state, unlike its oxygen counterpart, thioformaldehyde remains planar and the excited state does not change character. We therefore start by simply relaxing the structure with one of the excited-state wave functions employed in the estimation of the vertical excitation energy. To proceed in the structural optimization, we then generate new CIPSI expansions following the iso-PT2 scheme and matching the PT2 corrections used in the corresponding ground-state calculations. As shown in Table 4.8, despite testing a large range of expansions, there is no significant variation in the length of the CS bond, which is 10 mÅ longer than the CC3 value. The adiabatic excitation energy is again rather stable across all cases and within 0.01-0.04 eV of the CC3 estimate.

4.6 Discussion

We have demonstrated the excellent performance of QMC in the accurate computation of the vertical excitation energies of two small but theoretically challenging systems, formaldehyde and thioformaldehyde. Using fully optimized Jastrow-CIPSI wave functions where the determinantal components are constructed to yield a similar PT2 correction for both states, we are able to obtain VMC excitation energies compatible within less than 0.02 eV of the extrapolated FCI values using relatively compact expansions of a few thousand determinants and a minimally augmented double- ζ basis. Performing DMC calculations on top of the fully optimized VMC wave functions leads to a uniform gain across both states, thereby not affecting the

Table 4.8: Optimal VMC ground- and excited-state bond lengths (Å) and bond angles (deg), and VMC and DMC adiabatic excitation energies (eV) of thioformaldehyde obtained using Jastrow-CIPSI wave functions with targeted PT2 correction (iso-PT2). The VMC energy (a.u.) is averaged over the last 40 iterations of geometry optimization. o.o.p denotes the out of plane angle of the SO bond.

State	δE_{PT2}	No. det.	No. par.	CS	CH	H-C-H	o.o.p	$\langle E_{VMC} \rangle$	ΔE_{adia}^{VMC}	ΔE_{adia}^{DMC}
S0	0.17	702	995	1.62218(14)	1.08427(04)	116.869(53)	-0.042(50)	-17.05044(4)		
	0.10	2500	1662	1.62250(16)	1.08469(05)	116.862(32)	0.070(36)	-17.05570(4)		
	0.07	5712	2810	1.62200(11)	1.08464(06)	116.786(34)	-0.058(46)	-17.05715(6)		
	0.045	14218	5650	1.62207(10)	1.08480(07)	116.756(26)	-0.041(53)	-17.05817(3)		
	CC3 [44]			1.619	1.083	116.1	0.000			
S1	Expt. [73, 77, 78]			1.611-1.614	1.093-1.096	116.2-116.9	0.000			
	0.17	858	764	1.72393(27)	1.07879(07)	121.309(163)	-0.024(46)	-16.97123(4)	2.155(2)	2.152(6)
	0.10	3982	1820	1.72514(04)	1.07895(04)	121.388(27)	-0.106(79)	-16.97809(5)	2.112(2)	2.131(6)
	0.07	8418	3110	1.72309(07)	1.07909(05)	121.149(26)	0.115(79)	-16.97998(4)	2.100(2)	2.119(6)
	0.045	16866	5475	1.72182(09)	1.07921(03)	121.144(28)	0.041(85)	-16.98090(3)	2.103(1)	2.112(6)
CC3 [44, 70]				1.709	1.078	120.2	0.0		2.112	
	Expt. [73, 77, 79, 80]			1.682-1.708	1.077-1.093	116.8-121.6	0.0-8.9			

VMC estimate of the excitation. If we compute the excitation energy by matching instead wave functions with similar variances, we obtain a less robust procedure in the case of formaldehyde, where relatively large expansions of about 7000 determinants are required to recover results within 0.05 eV of our best estimates.

Next, we have investigated the ability of QMC to obtain accurate ground- and excited-state structures. In the ground state, we easily obtain geometries in excellent agreement with those produced by other high-level correlated approaches such as CC3 and full valence CASPT2, using quite compact Jastrow-CIPSI wave functions. The maximum deviation is a meager 3 mÅ in the CS bond of thioformaldehyde. During the relaxation of the excited-state structure, we regenerate the determinantal component in our Jastrow-CIPSI wave functions following two different determinant selection schemes: i) keeping a roughly constant PT2 energy correction during the optimization and ii) targeting a fixed value of the CI energy variance. Like the vertical excitation energies, the excited-state structural parameters show relatively low sensitivity to the size of the wave function and both selection schemes yield similar structures with no clear distinction in the convergence properties. The largest deviation with respect to the CC3 bond lengths is of about 10 mÅ when using the double- ζ basis. Geometrical relaxation of the excited state additionally allows us to estimate the adiabatic excitation energies, which we find to be compatible within less than 0.05 eV of the CC3 values for all wave function sizes.

To summarize, the use of a CIPSI selection scheme targeting similar PT2 corrections for the states of interest in combination with the full optimization of the Jastrow-Slater wave function enables us to obtain extremely stable and accurate estimates of the vertical excitation energies already at the VMC level, namely, without the need of DMC. This can be achieved with relatively compact wave functions, demonstrating the accuracy of the “expansion” scheme, which is viable also for larger systems. Furthermore, our iso-PT2 protocol to regenerate the wave function during relaxation along a potential energy surface leads to consistent and high-quality structures for both ground and excited state and to accurate adiabatic excitation energies. Our robust estimates of the structural parameters and the vertical and adiabatic excitation energies with moderate Slater expansions open important prospects for the use of VMC structural optimization with Jastrow-CIPSI wave functions as an efficient and reliable approach to characterize excited-state potential energy surfaces.

4.7 Appendix: Full CI extrapolation of CIPSI energies

We extrapolate here the ground- and excited-state variational CI energies of the CIPSI expansions of formaldehyde and thioformaldehyde to the full CI (FCI) limit.

For formaldehyde, these expansions are obtained with CAS(2,2) ground-state orbitals and the maug-cc-pVDZ basis set. The CI energies are fitted with a quadratic polynomial over the data points with $E(\text{PT2}) > -0.3$ a.u. and are shown in Figure 4.8. The FCI estimate is obtained for $E(\text{PT2}) = 0$. The extrapolated FCI energies are -22.8001 and -22.6534 a.u. for the ground and the excited state, respectively, and the corresponding gap equals 3.99 eV. For both states, the VMC energy obtained with the shortest expansion (see Table 4.1) is already about 90 mHartrees lower than the corresponding FCI estimate.

Figure 4.8: FCI extrapolation of the ground- and excited-state variational CI energies of formaldehyde with respect to the perturbation correction, $E(\text{PT2})$. We use CAS canonical orbitals and the BFD pseudopotentials with the corresponding maug-cc-pVDZ basis set.

For thioformaldehyde, we fit the CI energies of the CIPSI expansions for the ground and excited states obtained with CAS(4,3) ground-state orbitals and the maug-cc-pVDZ basis set. We employ a quadratic fit and the data points with $E(\text{PT2}) > -0.3$ a.u. as shown in Figure 4.9. The extrapolated FCI energies are -16.9528 and -16.8705 a.u. for the ground and excited state, respectively. These extrapolated values give a FCI energy gap of 2.24 eV. For both states, the VMC energy obtained with the shortest expansion (see Table 4.4) is already about 100 mHartrees lower than the corresponding FCI estimate.

Figure 4.9: FCI extrapolation of the ground- and excited-state variational CI energies of thioformaldehyde with respect to the perturbation correction, $E(\text{PT2})$. We use CAS canonical orbitals and the BFD pseudopotentials with the corresponding maug-cc-pVDZ basis set.

4.8 Appendix: Fits of VMC energies against number of determinants and VMC variance

As shown in Figure 4.10, we separately fit the ground- and excited-state VMC energies obtained in the “expansion” scheme against the total number of determinants using the power-law formula $E(N_{\text{det}}) = A + B(N_{\text{det}})^C$. As the determinants of both states are selected together in the CIPSI generation, the number of determinants in the figure is the size of the determinant space in which the CI Hamiltonian is diagonalized to obtain both states. Note that, as the states have different symmetries, the number of non-zero determinant coefficients for each state is different. These fits are used to obtain the extrapolated value of the vertical excitation energy to the total number of determinants in the FCI space (as shown in Figure 4.3).

We also fit the VMC energies against the corresponding VMC variances for the ground and excited states with a linear polynomial as illustrated in Figure 4.11. In subtracting the ground-state fit from the excited-state one, we match the variances of the two states and subtract the values of the ground- and excited-state energies corresponding to the same variance. Equal values of energy variance is a measure of a consistent description of both states and represents another possible procedure to estimate the vertical excitation energy as illustrated in Figure 4.3.

Fits of the ground- and excited-state VMC energies of thioformaldehyde as a function of the total number of determinants (Figure 4.12) and of the corresponding VMC variances (Figure 4.13). The procedure is similar to the one adopted in the case of formaldehyde.

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Figure 4.10: Fits of (left) ground-state and (right) excited-state VMC energies of formaldehyde as a function of the total number of determinants for both states.

Figure 4.11: Fits of (left) ground-state and (right) excited-state VMC energies of formaldehyde as a function of the corresponding VMC variances.

Figure 4.12: Fits of (left) ground-state and (right) excited-state VMC energies of thioformaldehyde as a function of the total number of determinants for both states.

Figure 4.13: Fits of (left) ground-state and (right) excited-state VMC energies of thioformaldehyde as a function of the corresponding VMC variances.

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Chapter 5

Modeling excited states with QMC-CIPSI: the case study of thiophene[†]

We present here a modification of the CIPSI selection scheme to extend its application to the QMC computation of excited states that belong to the same symmetry class as the ground state. We focus on the lowest-lying bright $\pi \rightarrow \pi^*$ excited state of thiophene, whose accurate computation is additionally complicated by its significant multireference character. For this system, we illustrate the difficulties of the old selection algorithm in selecting determinants which yield a balanced description of the ground and excited states, and propose a modification of the weights in the energy threshold to generate wave functions with matched second-order perturbation correction and configuration interaction variances for the two states. Importantly, we also establish the robustness of the modified criterion since, for the given system, the externally modified weights are insensitive to the choice of basis set and orbitals. We find that the new scheme improves the prediction of the VMC vertical excitation energies which are now within 0.05 eV of the best theoretical value for expansions containing only a thousand determinants, albeit with the use of large augmented triple- ζ basis. Finally, we relax the ground- and excited-state structures in VMC and obtain bond lengths which are accurate to better than 10 mÅ also with very small basis sets.

5.1 Introduction

The interaction of light with electrons in a material can give rise to complex photo-induced processes. A particular example is the class of π -conjugated donor polymers in organic solar-cell devices that upon photo-excitation transfer electrons to an acceptor molecule guiding the flow of an electronic current in the device. Thiophene is a molecule that forms the backbone of several such polymers and has been

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shown to improve the working efficiency of polymeric solar cells [1–10]. The accurate and efficient computation of electronic excited states for thiophene and similar systems is paramount to understand their electronic properties and guide the design of efficient polymer blends for high-performance devices. Thiophene has, consequently, been the subject of several rather recent theoretical investigations [11–20], which have demonstrated the theoretical complexity inherent in the description of its lowest-lying, bright excited state: the accurate prediction of this state is difficult for traditional *ab-initio* methods, with different levels of theory spanning a range of about 0.5 eV on the same ground-state geometry. Its multireference character calls in fact for the use of highly correlated electronic structure methods.

The accurate computation of a vertical excitation energy relies on the good quality of the ground-state geometry and the balanced description of the states involved in the excitation process. Quite recently, we have demonstrated the ability of quantum Monte Carlo (QMC) methods to yield highly reliable ground- and excited-state structures as well as vertical (absorption) and adiabatic (fluorescence) excitation energies for two small, yet theoretically challenging molecules, formaldehyde and thioformaldehyde [21, 22]. To this aim, we have explored the use of a selected configuration interaction (sCI) method, namely CIPSI, in generating high-quality, compact wave functions to constitute the Slater component of the Jastrow-Slater QMC wave functions. The performance of these determinantal expansions, selected in an automated manner, was extensively tested for the computation of excitation energies and molecular geometries, and found to be superior in comparison to conventional active space descriptions. Capitalizing on our ability to efficiently compute energy derivatives, we were able to optimize a rather large number of variational parameters and demonstrate that a handful of CIPSI determinants is already sufficient to provide well converged excitation energies and geometries.

The excited states investigated so far belonged however to a different symmetry class than the ground state and possessed a largely single-reference character. Their treatment was consequently relatively simple since the excited states could, in principle, be treated as the ground state in a different symmetry. This difference in symmetry character aided the CIPSI selection of determinants since determinants relevant for one state had zero contribution to the other and, hence, obtaining a balanced description for both states was possible with the rather straightforward reweighting scheme used for the second-order perturbation energy (PT2) contributions as illustrated in the previous Chapter [22]. However, the same scheme is found to be insufficient when dealing with non-trivial excited states (of the same symmetry as lower-lying states) such as the aforementioned excited state of thiophene, and needs to be modified further.

Here, we propose the simple but effective modification of multiplying the default selection weights by unequal additional weights for the different states during the CIPSI selection, assigning a higher factor to the state (here the excited state) showing a slower rate of convergence with the default scheme. We find that, by doing so, we slow the selection procedure for the ground state and succeed in constructing balanced expansions with well-matched PT2 corrections and configuration-interaction (CI) variances of the involved states. For thiophene, the ideal distribution of the ad-

ditional weights is found to be always close to 40% for the ground state and 60% for the excited state, irrespective of the basis set size and orbital basis. The resulting wave functions yield a converged estimate of the VMC vertical excitation energy already with rather compact expansions containing a few thousand determinants. For this excited state of thiophene, we find however that the excitation energy computed using these CIPSI expansions is somewhat sensitive to the choice of basis set and we need to employ the aug-cc-pVTZ basis to obtain estimates within 0.05 eV of the best coupled cluster (CC) values. Also for thiophene, we show that matching the VMC variances to compute the excitation energy [23, 24] is a less robust procedure since the resulting estimates worsen with the size of basis sets.

Finally, we relax the ground-state geometry in VMC with CIPSI wave functions and obtain bond lengths within less than 5 mÅ of the reference complete active space second-order perturbation theory (CASPT2) and CC values. For the excited state, we determine the optimal VMC geometries following the second state and generating CIPSI expansions with similar PT2 corrections along the path, both for the ground and excited states as in the so-called iso-PT2 scheme of Chapter 4. The resulting optimal excited-state structural parameters are in excellent agreement with the CASPT2 estimates, namely, within 10 mÅ for the bond lengths and 1° for the bond angles.

This chapter is organized as follows: We describe the modified CIPSI selection procedure for multiple states of the same symmetry in Section 5.2, and present the computational details in Section 5.3. The construction procedure of the wave functions with the modified selection scheme is detailed in Section 5.4.1. We present the QMC vertical excitation energies in Section 5.4.2 and the optimal ground- and excited-state VMC structures in Section 5.5. We conclude in Section 5.6.

5.2 Methods

In this work, we consider excited states that are not the lowest in their symmetry class. In the QMC calculations, we describe them together with the lower-energy states of the same symmetry via a set of Jastrow-Slater wave functions with different CI coefficients but the same Jastrow and orbital parameters:

$$\Psi_n = \mathcal{J} \sum_{k=1}^{N_{\text{det}}} c_k^n D_k \quad (5.1)$$

where N_{det} is the total number of determinants and the index n denotes an electronic state. We use a Jastrow factor which describes electron-nucleus and electron-electron correlations ($\mathcal{J}_{2\text{-body}}$), and ensures that the Kato's cusp conditions are satisfied at the inter-particle coalescence points.

To ensure that the common non-linear (Jastrow and orbital) parameters offer a reasonable description of all states of interest, we optimize them by minimizing the state-average (SA) energy [25] defined as

$$E^{\text{SA}} = \sum_{n=1}^{N_{\text{states}}} w_n^{\text{QMC}} \frac{\langle \Psi_n | \mathcal{H} | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle}, \quad (5.2)$$

where the weights, w_n^{QMC} , sum up to one and are kept fixed during the optimization. Orthogonality between the states is maintained through the (linear) CI coefficients whose optimal values are obtained by solving a generalized eigenvalue problem in the basis of the determinants multiplied by the Jastrow factor.

As described in Ref. [26], we alternate a number of optimization steps of the non-linear parameters with a step of optimization of the linear coefficients. For the former, we follow the down-hill gradient of the SA energy in a scheme inspired by the stochastic reconfiguration approach for a single state [27], and solve the relevant equations in a low-memory conjugate-gradient implementation [28]. For the latter, we use a memory-efficient Davidson diagonalization method that allows the computation of the lowest energy eigenvalues without explicit construction of the entire Hamiltonian and overlap matrices [28, 29]. Combining this optimization scheme with the fast generation of the quantities needed in the QMC estimators [30, 31], we can optimize QMC wave functions for ground and excited states containing large determinantal expansions and several thousand parameters.

To construct the determinantal component of these wave functions, we employ an improved CIPSI approach that allows us to iteratively select the most important determinants required for the balanced description of multiple electronic states. Starting from an initial reference subspace, $\mathcal{S}$, given by the union of determinants describing the states of interest, an external determinant $|\alpha\rangle$ is selected based on its weighted second-order perturbation (PT2) energy contribution obtained via the Epstein-Nesbet partitioning of the Hamiltonian [32, 33],

$$e_\alpha = \sum_{n=1}^{N_{\text{states}}} w_n \delta E_{\alpha,n}^{(2)}, \quad (5.3)$$

where

$$\delta E_{\alpha,n}^{(2)} = \frac{|\langle \alpha | \mathcal{H} | \Psi_n^{\text{CIPSI}} \rangle|^2}{\langle \Psi_n^{\text{CIPSI}} | \mathcal{H} | \Psi_n^{\text{CIPSI}} \rangle - \langle \alpha | \mathcal{H} | \alpha \rangle}, \quad (5.4)$$

and Ψ_n^{CIPSI} is the current reference CIPSI wave function for state n . In this partitioning scheme, the first-order energy correction is zero by definition. The determinant $|\alpha\rangle$ is added to $\mathcal{S}$ if its energy contribution e_α is higher than a threshold, and the threshold is automatically adjusted so that the number of determinants in $\mathcal{S}$ is increased by a certain percentage at every iteration.

We have recently shown that the use of CIPSI expansions with similar net PT2 energy contributions results in a balanced description of the relevant states, since we can view the PT2 correction as the error of the CIPSI expansion with respect to the corresponding FCI limit. When employed in QMC, these expansions were found to yield accurate QMC estimates of the excitation energies also for relatively small numbers of determinants [22].

When interested in the lowest-energy states of different symmetries, one can in principle perform the expansion separately for each state until the corresponding perturbation energy contribution is equal to a target value. Alternatively, one can generate the expansions using one set of orbitals for all states and enlargening the

union space, $\mathcal{S}$, through a single threshold. Following this last scheme, we were able to obtain matched PT2 corrections [22] by simply choosing the weights in the selection step (Eq. 5.3) as:

$$w_n^{\text{cmax}} = \frac{1}{\max(c_{k,n}^2)}, \quad (5.5)$$

where the index k runs over all determinants in the current Ψ_n^{CIPSI} . Such a choice is motivated by the fact that we perform the CIPSI selection in the basis of determinants and not of configuration state functions (CSFs) [34]. The resulting expansions for states of different symmetry have different sizes since they do not share any common determinant (determinants of a given symmetry have zero coefficients in the expansion for a state belonging to a different symmetry class).

Here, we are interested in describing states of the same symmetry, where the states are expanded on the same set of determinants and a CSF may have a different but non negligible overlap with all states of interest. In this case, we find that the use of the simple weights (Eq. 5.5) does not yield expansions with similar net PT2 contribution. To improve this balance, we explore a simple modification to the selection scheme where we multiply the weights of the old criterion with user-inputed weights, w_n^{SA} , as

$$w_n = w_n^{\text{cmax}} \times w_n^{\text{SA}}. \quad (5.6)$$

In Appendix 5.8.1, we also discuss alternative modifications of the weights to impose explicitly that the CI variances and/or the second-order energy corrections for different states are well matched.

5.3 Computational details

All QMC calculations are performed with the program package CHAMP [35]. We employ scalar-relativistic energy-consistent Hartree-Fock (HF) pseudopotentials and correlation consistent Gaussian basis sets that have been specifically constructed for these pseudopotentials [36, 37]. We use a minimally augmented double- ζ (maug-cc-pVDZ) basis set, where the basis on the heavy atoms are augmented with s and p diffuse functions. Basis-set convergence tests are performed with the fully augmented triple (aug-cc-pVTZ) basis set. All diffuse functions are obtained from the corresponding all-electron Dunning's correlation-consistent basis sets [38]. While we employ a two-body Jastrow factor including electron-electron and electron-nucleus terms for most calculations, additional tests are performed to quantify the effect of three-body electron-electron-nucleus correlations on the excitation energies [39].

We optimize all parameters of the Jastrow-Slater wave function in VMC as described above. We employ equal weights in the state-average energy and a guiding wave function $\Psi_g^2 = \sum_n |\Psi_n|^2$ in the sampling to ensure a reasonable overlap with all states of interest [25]. In the VMC geometry optimization, we relax the structure without symmetry constraints and simply follow the path of steepest descent for the root of interest by appropriately rescaling the interatomic forces and using an approximate constant diagonal Hessian. After convergence, we perform 40 additional

optimization steps to estimate the optimal average structural parameters. In the DMC calculations, we treat the pseudopotentials beyond the locality approximation using the T-move algorithm [40] and employ an imaginary time step of 0.02 a.u. This time step yields DMC excitation energies converged to better than 0.01 eV also for the simplest wave function employed here.

The CIPSI calculations are carried out with Quantum Package [41] using orbitals obtained from complete active space self-consistent field (CASSCF) calculations performed with the program GAMESS(US) [42, 43]. The CIPSI expansions are constructed to be eigenstates of $\hat{S}^2$ and are mapped into the basis of configuration state functions (CSFs), effectively reducing the number of optimization parameters in VMC. The Dalton package [44, 45] is used to compute the reference ground-state geometry and vertical excitation energies within the iterative approximate coupled cluster singles, doubles, and triples (CC3) approach. All QMC vertical excitation energies are computed on the fixed ground-state structure optimized at the CC3 level with an aug-cc-pVTZ basis and the frozen-core approximation.

5.4 Vertical excitation energies

We are interested in the lowest-lying, bright $\pi \rightarrow \pi^*$ singlet excited state of the thiophene molecule (C_4H_4S) shown in Fig. 5.1. This state belongs to the same symmetry class, A_1 , of the ground state and needs to be optimized in a state-averaged manner when following energy minimization. The accurate computation of this excited state is further challenged by its significant multi-reference character since the wave function contains two dominant single excitations along with a rather considerable contribution from double excitations with four unpaired electrons [16]. This can be readily verified in a CASSCF calculation with the minimal CAS(6,5) active space correlating six electrons in five π and π^* orbitals, which yields two dominant transitions between the HOMO-1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1 levels, accounting for almost 60% and 20% of the wave function, respectively. The higher-order double excitations with four unpaired electrons make up for another 7%. The ground state, on the other hand, is single reference, dominated by the HF determinant which alone accounts for more than 90% of the wave function in the same calculation.

The nature of this excited state leads to difficulties in estimating the corresponding vertical excitation energy, which we find to span a range of about 0.5 eV (between 5.65 and 6.11 eV) across different levels of theory. While TDDFT in combination with different exchange-correlation functionals places a $\pi \rightarrow \pi^*$ state of B_2 symmetry lower than the A_1 state by about 0.1 eV or less, all tested wave function methods (CASPT2, the n -electron valence perturbation theory – NEVPT2, QMC, and CC3) correctly identify our state of interest as the energetically lowest singlet excited state and are therefore qualitatively compatible with experimental observations [16, 46–48] despite yielding very different excitation energies.

Figure 5.1: Schematic representation of thiophene (C_4H_4S). Yellow, blue, and white denote sulphur, carbon, and hydrogen, respectively. The ground-state structure has C_{2v} symmetry and the ground and targeted excited states belong to the fully symmetric A_1 irreducible representation.

5.4.1 Construction of CIPSI expansions

For the ground and excited states, we construct CIPSI expansions of increasing length from subsequent CIPSI iterations. Unless otherwise specified, we generate the CIPSI expansions using orbitals from a minimal CASSCF(6,5) calculation, correlating 6 electrons in 5 π orbitals, and the maug-cc-pVDZ basis set.

We first adopt the simple reweighting scheme (Eq. 5.5) that we successfully used for states of different symmetry and plot the resulting differences between the PT2 corrections and CI variances of the ground and excited states in Fig. 5.2 (“cmax”; black curves). We find that the convergence of the ground state is much faster than that of the excited state: for all expansions, the ground-state PT2 corrections are smaller in absolute value than the corresponding quantities for the excited state, and the same holds for the CI variances. This is consistent with the observation that partitioning the determinants in each expansion based on the relative contribution to each state gives an insufficient number of “excited-state” determinants, namely, about 1.3-1.6 times more determinants contributing to the excited than to the ground state (see Table 5.4 in Appendix 5.7) compared to a significantly higher ratio of about 2.4-2.9 in our previous calculations with matched PT2 corrections (iso-PT2) [22]. Therefore, all indications are that the description of the states is unbalanced in favor of the ground state.

If we modify the selection criterion by introducing the state-average weights, w_n^{SA} (Eq. 5.6), and place a larger weight on the excited state, it is possible to uniformly achieve a more even description of the two states. In Fig. 5.2, we show the PT2 corrections and CI variances for sets of expansions generated with different choices of the state-average weights (“cmax $\times$ SA”). All these choices represent an improvement on the bare “cmax” scheme and the use of 0.425 and 0.575 as w_n^{SA} for the ground and the excited state, respectively, leads to optimally matched PT2 corrections and CI variances (iso-variance) for all expansion sizes. As shown in Table 5.4, partitioning the determinants based on their dominant relative contributions

Figure 5.2: Difference of the PT2 corrections (top) and CI variances (bottom) between the ground and the excited state for different reweighting schemes in the selection criterion, namely, w^{cmax} and $w^{\text{cmax}} \times w^{\text{SA}}$, and different choices of state-average weights, w^{SA} .

to the two states reveals that the ratio between “excited-state” and “ground-state” determinants is now increased to about 1.9-2.1. Furthermore, an inspection of the CI energies obtained with both schemes in Table 5.5 shows that, for comparable sizes of the expansion, the modified selection criterion slows down the convergence of the ground state and, to a lesser extent, speeds up the excited state. The CI excitation energy is also significantly reduced from about 6.6 eV with the old criterion to 5.9 eV for the larger expansions considered here. For comparison, the CC3/aug-cc-pVTZ excitation energy is 5.65 eV.

Importantly, we find that the ideal weights depend rather weakly on the orbital basis employed in the determinant selection (see Fig. 5.2 and 5.7) and also on the

basis set (see Fig. 5.8), being always very close to 0.4 and 0.6.

As discussed in Appendix 5.8.1, alternative modifications of the weights to directly match the PT2 corrections and/or CI variances during the CIPSI selection were not as successful since they did not yield consistently good wave functions over the complete range of expansions. Also in these schemes, the addition of state-average weights to favor the excited state is found to be essential to obtain CIPSI wave functions which offer a balanced description of both states.

5.4.2 Vertical excitation energy

We now explore the quality of the VMC and DMC vertical excitation energies of thiophene obtained employing Jastrow-Slater wave functions fully optimized at the VMC level. We construct the determinantal components using CIPSI expansions obtained in combination with either the old “cmax” or the new “cmax $\times$ SA” scheme. For comparison, we also build Jastrow-Slater wave functions using traditional CAS expansions and three different active spaces: the minimal CAS(6,5), a CAS(10,9) correlating two additional occupied σ and two unoccupied σ^* orbitals on the C–S bonds as in Ref. [15], and a CAS(10,14) that further includes the five 3d orbitals of the S atom. For the largest active space, the expansions are truncated with a threshold of 5×10^{-4} on the CSF coefficients and the union of the CSFs of the ground and excited states is retained.

In Table 5.1, we list the VMC and DMC total and excitation energies obtained with the maug-cc-pVDZ basis set as well as the reference CC3 values computed with the BFD pseudopotentials. As expected, increasing the size of the active space in the Jastrow-CAS wave functions lowers the corresponding total energies, particularly, in VMC. However, in all three cases, the VMC excitation energies are compatible with each other within statistical errors, they are rather comparable to their DMC counterparts, and are about 0.2 eV higher than the CC3/aug-cc-pVTZ value of 5.65 eV. Clearly, the orbitals included beyond the minimal expansion are not sufficient and larger active spaces are needed to ameliorate the estimate of the excitation energy.

We now consider the Jastrow-CIPSI results generated with expansions of increasing size. As also shown in Fig. 5.3, the VMC excitation energies corresponding to the “cmax” selection gradually widens to settle around a value of 5.9 eV with the largest wave functions tested here. Therefore, while the total ground- and excited-state VMC energies are lowered by as much as 30 mHartree with respect to the corresponding values computed with CAS components of similar size, the excitation energy is not improved. Performing DMC calculations for the optimal Jastrow-CIPSI wave functions decreases the excitation energy, which remains however more than 0.1 eV higher than the CC3 reference. Therefore, while both VMC and DMC substantially improve on the starting CIPSI excitation energy of about 6.6 eV (see Table 5.5), the bias of the CIPSI selection towards the ground state is reflected in the QMC overestimation of the excitation energy.

When we use the expansions obtained with the “cmax $\times$ SA” reweighting scheme in Jastrow-Slater wave functions and reoptimize all parameters, we observe that the convergence of the ground state is somewhat slowed down with respect to “cmax”

Table 5.1: VMC and DMC total (a.u.) and vertical excitation (eV) energies of thiophene obtained with different expansions in fully optimized Jastrow-Slater wave functions. The maug-cc-pVDZ basis set is used.

WF	No. det	No. param	E(S0)	VMC E(S1)	ΔE	E(S0)	DMC E(S1)	ΔE
(6,5)	52	471	-35.26385(46)	-35.04801(46)	5.873(18)	-35.34545(31)	-35.13112(32)	5.832(12)
(10,9)	3996	1891	-35.26751(46)	-35.05182(46)	5.869(18)	-35.34588(31)	-35.13231(31)	5.811(12)
(10,14) ^a	16446	4041	-35.27293(32)	-35.05742(32)	5.864(12)	-35.34758(30)	-35.13309(30)	5.837(12)
CIPSI	211	899	-35.26797(32)	-35.05597(32)	5.769(12)	-35.34588(31)	-35.13491(31)	5.741(12)
cmax	1087	2065	-35.28171(31)	-35.06584(31)	5.874(12)	-35.35044(29)	-35.13737(29)	5.798(11)
	2797	2906	-35.28741(30)	-35.07297(31)	5.835(12)	-35.35291(28)	-35.14166(29)	5.748(11)
	5389	4057	-35.29131(30)	-35.07635(31)	5.849(12)	-35.35464(28)	-35.14215(28)	5.782(11)
	10289	6080	-35.29733(29)	-35.08126(30)	5.880(11)	-35.35499(27)	-35.14350(27)	5.755(10)
	22081	10090	-35.30217(29)	-35.08512(30)	5.906(11)	-35.35818(26)	-35.14546(27)	5.788(10)
	32022	13225	-35.30425(29)	-35.08717(30)	5.907(11)	-35.35865(26)	-35.14632(27)	5.778(10)
CIPSI	216	968	-35.26834(32)	-35.05731(32)	5.742(12)	-35.34592(30)	-35.13526(30)	5.732(12)
cmax $\times$ SA	1037	2002	-35.27964(31)	-35.06666(31)	5.795(12)	-35.35012(29)	-35.13830(29)	5.764(11)
	2614	2823	-35.28546(31)	-35.07232(31)	5.800(12)	-35.35233(28)	-35.14119(29)	5.745(11)
	5605	4106	-35.28966(30)	-35.07607(31)	5.812(12)	-35.35339(28)	-35.14222(28)	5.746(11)
	11003	6326	-35.29416(30)	-35.08053(30)	5.813(12)	-35.35514(28)	-35.14387(28)	5.749(11)
	22100	9943	-35.29870(29)	-35.08536(30)	5.805(11)	-35.35597(26)	-35.14492(27)	5.743(11)
	31039	12795	-35.30047(29)	-35.08700(30)	5.809(11)	-35.35743(27)	-35.14570(27)	5.761(10)
CC3(BFD)/maug-cc-pVDZ								5.741
CC3(BFD)/aug-cc-pVDZ								5.678
CC3(BFD)/aug-cc-pVTZ								5.650

^a A threshold of 5×10^{-4} is used on the CSF coefficients.

Figure 5.3: VMC (filled circles) and DMC (empty circles) vertical excitation energies of thiophene versus the number of determinants (bottom x-axis) for CIPSI determinantal expansions generated with the “cmax” and “cmax $\times$ SA” schemes with state-average weights 0.425 and 0.575. The excitation energy is also estimated as the difference of the fits of the energies against the variance of the two states (top x-axis).

expansions of comparable size, while the VMC excited-state energies are largely unaffected. This leads to reduced VMC excitation energies, which converge to about 5.8 eV for expansions with only 1000 determinants. The VMC correction on the CIPSI excitation energy is now smaller and the same holds for the improvement of DMC upon VMC. Nevertheless, the DMC excitation energies are still about 0.1 eV higher than the CC3/aug-cc-pVTZ reference.

In Fig. 5.3, we also estimate the excitation energies by matching the variances of the two states as in Chapter 4. To this aim, we linearly fit the VMC ground- and excited-state energies separately against their corresponding variances and then compute the excitation energy as $E_{\text{ES}}^{\text{fit}}(\sigma^2) - E_{\text{GS}}^{\text{fit}}(\sigma^2)$. Matching the variances starting from either the “cmax” or the “cmax $\times$ SA” results leads to estimates of the excitation energies within less than 0.05 eV of the CC3 reference for all expansion sizes. This is somewhat surprising and different than what we have found for formaldehyde and thioformaldehyde [22] and described in the previous Chapter, where using CIPSI expansions with matched PT2 corrections always leads to results superior to those obtained by matching the variances in VMC. We will return to this point below.

In search of the culprit: Jastrow factor and basis set

To better understand whether the difficulties encountered in obtaining an accurate VMC excitation energy resides in the CIPSI selection or in other ingredients of the calculation, we test the addition of three-body (electron-electron-nuclear) terms in

the Jastrow factor and reoptimize the Jastrow-CIPSI wave functions. The absolute VMC energies of both states are uniformly lowered (about 12-14 and 7 mHartrees for the CAS and CIPSI expansions, respectively) and the effect on the DMC energies is also uniform but smaller, being less than 1 mHartree for all cases. Consequently, the impact on the VMC and DMC excitation energies is negligible and these findings confirm that we can proceed in further calculations without including these higher-order correlations in the Jastrow factor.

The basis set usually has a small impact on the excitation energies at the QMC level but we are here concerned about relatively small energy differences. We therefore construct new CIPSI expansions with the larger aug-cc-pVTZ basis set and the “ $c_{\max} \times SA$ ” scheme where the optimal weight for an iso-PT2 and iso-variance selection are now 0.4 and 0.6 for the ground and excited state, respectively. As shown in Fig. 5.4, the resulting VMC and DMC excitation energies are red-shifted relative to comparable expansions in the smaller maug-cc-pVDZ basis, and lie within less than 0.05 eV of our best CC3 reference value.

If we estimate the vertical excitation energies by matching the VMC variances for the wave functions generated with the aug-cc-pVTZ basis set, we find that the slope of the estimated excitation energies versus the variance changes sign with respect to the same fit for the smaller basis, and the excitations fall further below the CC3 reference as shown in Fig. 5.4. Therefore, while the adoption of the iso-PT2 “ $c_{\max} \times$

Figure 5.4: VMC (filled circles) and DMC (empty circles) vertical excitation energies of thiophene versus the number of determinants (bottom x-axis) for CIPSI determinantal expansions generated with the maug-cc-pVDZ (maug-D) and aug-cc-pVTZ (aug-T) basis sets and the “ $c_{\max} \times SA$ ” scheme. The excitation energy is also estimated as the difference of the fits of the energies against the variance of the two states (top x-axis). The lines of the fit difference are solid over the range of variances used to perform the energy fits.

SA" reweighting scheme yields a consistent decrease of the excitation energies with increasing basis set, we observe a somewhat less regular and predictable behavior when matching the variances and, for thiophene, a deterioration of the prediction in going from the smaller to the larger basis set.

We also note that the reduction in the VMC vertical excitation energy when the basis set size is increased from maug-cc-pVDZ to aug-cc-pVTZ mirrors the corresponding behavior of the CC3 excitation energies. All-electron coupled-cluster calculations with analogous basis sets (constructed as the pseudopotential ones as regards augmentation) display a similar variation with the size of the basis set. We therefore conclude that the QMC dependence on the basis is not due to the intrinsic quality of the pseudopotential basis set but, most likely, to the fact that a larger basis is indeed required to guide a better CIPSI selection. This remains a matter which requires further investigation and analysis, and on which we will return in the next Chapter.

5.5 Optimal excited-state structures

We begin by optimizing the structure of thiophene in the ground state using some of the ground-state wave functions previously employed to compute the vertical excitation energies in Table 5.1. We find that all Jastrow-Slater wave functions yield very accurate VMC geometries with differences of less than 5 mÅ in the bond lengths with respect to the reference values as shown in Table 5.2. In particular, the use of CIPSI expansions yields slightly longer carbon-carbon bonds than the CAS counterparts, providing a better agreement with both the CASPT2 and coupled cluster values.

Table 5.2: Optimal VMC ground-state bond lengths (Å) and angles (deg) of thiophene using CAS and "cmax $\times$ SA" CIPSI expansions and the maug-cc-pVDZ basis. The CC results are obtained either in all-electron calculations with the frozen-core (FC) approximation or with the BFD pseudopotentials.

WF	No. det	C–C	C=C	C–S
(6,5)	52	1.4260(1)	1.3660(2)	1.7165(1)
(10,9)	3996	1.4258(1)	1.3660(2)	1.7206(1)
(10,14)	16446	1.4261(3)	1.3658(2)	1.7250(1)
CIPSI	1037	1.4281(2)	1.3662(1)	1.7201(2)
cmax $\times$ SA	2614	1.4282(2)	1.3681(2)	1.7202(1)
	5605	1.4290(2)	1.3669(1)	1.7218(1)
	11003	1.4279(4)	1.3676(4)	1.7223(4)
MS-CASPT2(10,8)/6-31G** [15]		1.430	1.372	1.720
CCSD(T)/aug-cc-pVTZ (BFD)		1.425	1.368	1.717
CCSD(T)/aug-cc-pVTZ (FC)		1.430	1.372	1.728
CC3/aug-cc-pVTZ (FC)		1.430	1.372	1.729

Figure 5.5: Optimal S0 (ground-state) and S1 (excited-state) structures of thiophene.

The excited-state global minimum is the S-puckered structure of symmetry C_s shown in Fig. 5.5 as obtained in previous studies employing the ADC(2) [18], DFT-MRCI [14], and MS-CASPT2 [15] approaches. It is interesting to note that TDDFT predicts instead a C-puckered minimum with the S-puckered structure actually being a transition state [17]. Since the excited state has the same symmetry as the ground state also when the molecular symmetry is lowered from C_{2v} to C_s , we need to follow the path of steepest descent for the second root in optimizing the excited-state structure. In VMC, we do not impose any symmetry constraints and start from a slightly distorted geometry, where we optimize the wave function containing 5605 determinants of Table 5.1. In the subsequent steps, we generate CIPSI wave functions targeting the same PT2 corrections (iso-PT2) along the whole minimization path for both the ground and the excited state.

The final converged structural parameters are shown in Table 5.3: the optimized VMC geometry is S-puckered in agreement with previous correlated calculations, with an elongation of all bonds, in particular of the former C=C and the C–S bonds. The VMC bond lengths and angles obtained with Jastrow-CIPSI wave functions are within 10 mÅ and 1° of the corresponding CASPT2 values, respectively. The Jastrow-CAS wave functions, on the other hand, yield a somewhat wider spread of values particularly for the C–S bond as well as a non-monotonic variation of the δ_{CCCS} angle with the size of the active space.

5.6 Summary and next steps

In this work, we present a systematic investigation on how to obtain balanced CIPSI expansions for multiple states that belong to the same symmetry class, focusing on a case, the lowest-energy bright state of thiophene, where the targeted excited state has a significant multi-reference character. For states of different symmetries, we had shown that CIPSI expansions satisfying the iso-PT2 and iso-variance conditions for the different states would yield accurate excitations energies. Here, we demonstrate that the use of unequal selection weights in the energy threshold allows us to obtain CIPSI expansions characterized by equal PT2 energies and CI variances for the states of interest [22]. To this aim, we assign a higher weight to the state which shows a slower rate of convergence within the default “cmax” scheme. For thiophene, we

Table 5.3: Optimal VMC excited-state bond lengths ($\text{\AA}$) and bond angles (deg) of thiophene using CAS and “cmax $\times$ SA” CIPSI wave functions with the maug-cc-pVDZ basis. Correlated results from the literature are listed.

WF	No. det	C–C	C=C	C–S	δ_{CCCS}
(6,5)	52	1.4403(2)	1.4252(1)	1.7451(1)	24.25(3)
(10,9)	3996	1.4421(1)	1.4218(4)	1.7603(2)	23.62(8)
(10,14)	16446	1.4327(3)	1.4162(1)	1.7738(3)	26.58(2)
CIPSI	1663	1.4396(7)	1.4161(6)	1.7626(5)	24.84(2)
cmax $\times$ SA	3752	1.4388(7)	1.4151(3)	1.7655(4)	25.58(3)
	8304	1.4383(1)	1.4144(2)	1.7709(1)	25.75(2)
	15815	1.4422(7)	1.4112(4)	1.7725(6)	26.01(7)
MS-CASPT2(10,8)/6-31G** [15]		1.448	1.423/1.416	1.782/1.778	26.7
ADC(2)/cc-pVTZ [18]		1.422	1.419	1.796	28.2
DFT-MRCI/TZVP [14]		1.436	1.394	1.799	27.4

identify a range of weights which leads to iso-PT2 and iso-variance expansions and show that these weights depend weakly on the basis set size and the choice of orbitals.

The more balanced description of the states obtained via the “cmax $\times$ SA” expansions is evidenced by the fact that the corresponding CIPSI estimates of the excitation energy are significantly improved and, in parallel, the corresponding Jastrow-CIPSI wave functions yield smaller corrections on these bare CI values. We note that, in practice, the new selection criterion slows down the convergence of the ground state at every iteration and, to a lesser extent, accelerates the one of the excited state, making the quality of the two CI wave functions more similar. Nevertheless, the DMC excitation energies computed on top of final VMC wave functions with Slater components from either scheme are about 0.1 eV higher than our best CC3 reference. While higher-order (electron-electron-nucleus) correlations in the Jastrow factor do not have a measurable impact, using a larger aug-cc-pVTZ basis set brings both the VMC and DMC excitation energies within 0.05 eV of the CC3 value. We additionally note that matching the VMC variances to estimate the excitation energies, at least in the range spanned by the wave functions tested here, is a less robust approach, yielding estimates which deteriorate with increasing size of basis sets.

Structural relaxation in the ground state with our Jastrow-CIPSI wave functions and the minimal basis set yields VMC bond lengths which are compatible within less than 5 m $\text{\AA}$ with the best reference values. In general, these wave functions predict longer and more accurate C–C and C–S single bonds than Jastrow-CAS counterparts of similar size. In the excited state, the Jastrow-CIPSI wave functions yield estimates of VMC bond lengths and angles within less than 10 m $\text{\AA}$ and 1 $^\circ$ of the reference values. The Jastrow-CAS wave functions display a somewhat larger spread of values for the different expansion sizes.

The results presented here support our simple recipe for modifying the reweighting criterion in the CIPSI selection to generate balanced wave functions for multiple states of the same symmetry. Furthermore, recently, this scheme has been applied

to generate ground- and excited-state expansions for a protonated Schiff base model, enabling the accurate determination of its lowest excitation energy both in VMC and DMC [26]. That said, the observed dependence of the QMC excitation energy of thiophene on the basis set calls for further investigations, especially if we consider that this excited state is clearly problematic at the CIPSI level: it displays a very slow convergence towards a regime where the excitation energy can be reliably extrapolated to the full CI limit as further elaborated in the next Chapter. In this context, it would be interesting to explore how orbital optimization during the CIPSI selection process affects the convergence and the selection of important determinants.

5.7 Appendix: Partitioning of CSFs between the states

In Table 5.4, we partition the full set of CSFs of the CIPSI expansions into ground-state ($N_{\text{csf}}^{\text{GS}}$) and excited-state ($N_{\text{csf}}^{\text{ES}}$) ones according to a very simple algorithm: if a CSF has a larger coefficient in the ground than in the excited state, it is assigned to the ground state and vice versa. For the cases of formaldehyde and thioformaldehyde in the previous Chapter, the ratio $N_{\text{csf}}^{\text{ES}}/N_{\text{csf}}^{\text{GS}}$ was in the range of 2.4–2.9. For thiophene, if we ignore the smallest expansions with 211 determinants, the same ratio ranges between 1.32 and 1.63 when the standard “cmax” selection criterion is adopted, even though the targeted excited state is expected to have stronger multideterminant character than those studied for the other two molecules. When using the “cmax $\times$ SA” scheme to generate iso-PT2 and iso-variance expansions, the ratio grows to values between 1.85 and 2.08.

Table 5.4: Partitioning the CSF space between ground and excited states based on the weight contribution to the individual states. The maug-cc-pVDZ basis set is used.

No. dets.	Partitioned CSFs		$N_{\text{csf}}^{\text{ES}}/N_{\text{csf}}^{\text{GS}}$
	GS	ES	
cmax			
211	28	63	2.25
1087	180	237	1.32
2797	401	572	1.43
5389	736	1095	1.49
10289	1341	2039	1.52
22081	2682	4295	1.60
32022	3776	6163	1.63
cmax $\times$ SA			
216	30	66	2.20
1037	138	256	1.86
2614	302	590	1.95
5605	640	1215	1.90
11003	1168	2351	2.01
22110	2208	4623	2.09
31039	3075	6395	2.08

5.8 Appendix: Construction of CIPSI expansions

5.8.1 Alternate reweighting schemes

We explore here alternative schemes to modify the “cmax” reweighting criterion, namely, by multiplying the “cmax” weights by a numerical weight that forces the

matching of the CI variances (σ_{CI}^2) and/or the PT2 energy correction (E^{PT2}) of both states.

The CI variance of a state n at a given CIPSI selection iteration is computed as follows:

$$\begin{aligned}\sigma_{\text{CI},n}^2 &= \langle \Psi_n^{\text{CIPSI}} | \mathcal{H}^2 | \Psi_n^{\text{CIPSI}} \rangle - \langle \Psi_n^{\text{CIPSI}} | \mathcal{H} | \Psi_n^{\text{CIPSI}} \rangle^2 \\ &\approx \sum_{i \in \text{FCI}} \langle \Psi_n^{\text{CIPSI}} | \mathcal{H} | i \rangle \langle i | \mathcal{H} | \Psi_n^{\text{CIPSI}} \rangle - \langle \Psi_n^{\text{CIPSI}} | \mathcal{H} | \Psi_n^{\text{CIPSI}} \rangle^2 \\ &= \sum_{\alpha} |\langle \alpha | \mathcal{H} | \Psi_n^{\text{CIPSI}} \rangle|^2,\end{aligned}\quad (5.7)$$

where, in the first term of the second line, we have inserted an identity operator in the full CI space. Therefore, this approximate expression of the CI variance goes to zero as the CIPSI wave function approaches the FCI limit.

When matching the CI variances of the states, Eq. 5.6 is modified as

$$w_n = w_n^{\text{cmax}} \times w_n^{\text{var}}, \quad (5.8)$$

where the additional weight, w_n^{var} , is computed at iteration i as follows:

$$w_n^{\text{var}}(i) = z_n(i-2) \times z_n(i-1) \times z_n(i), \quad (5.9)$$

with

$$z_n(i) = \begin{cases} 1 & \text{for } i \leq 1, \\ \exp \left[4 \times \left(\frac{N_{\text{states}} \sigma_{\text{CI},n}^2(i-1)}{\sum_{k=1}^{N_{\text{states}}} \sigma_{\text{CI},k}^2(i-1)} - 1 \right) \right] & \text{otherwise} \end{cases}. \quad (5.10)$$

We also impose that $0.5 \leq z_n(i) \leq 1.5$.

When we want to match the PT2 or the renormalized PT2 (rPT2) energy corrections of both states, we introduce a different weight, $w_n^{\text{PT2/rPT2}}$, which multiplies w_n^{cmax} :

$$w_n = w_n^{\text{cmax}} \times w_n^{\text{PT2/rPT2}}, \quad (5.11)$$

where the new factor is computed by replacing $\sigma_{\text{CI},n}^2$ with $E_n^{\text{PT2/rPT2}}$ in Eq. 5.10. The rPT2 energy correction is essentially a damped value of E^{PT2} for small expansions, namely, $E^{\text{rPT2}} = Z E^{\text{PT2}}$ where $0 \leq Z \leq 1$ [41]. In the range of short expansion lengths, the sum $E^{\text{ref}} + E^{\text{PT2}}$ (Eq. 3.3) usually overestimates the FCI energy yielding a rather pronounced non-linear behavior of the CIPSI energy. Using the sum $E^{\text{ref}} + E^{\text{rPT2}}$ instead leads to a much more linear behavior of the energy and provides an easier extrapolation to the FCI limit. Finally, if we impose both variance and PT2 energy matching, we modify the weights as

$$w_n = w_n^{\text{cmax}} \times (w_n^{\text{var}} \times w_n^{\text{PT2/rPT2}})^{0.5}. \quad (5.12)$$

In Fig. 5.6, we show the quality of CIPSI expansions obtained from these alternate reweighting schemes. While matching the CI variance (iso-variance) and/or rPT2 corrections (iso-rPT2) can improve the balance of the states beyond “cmax”, this is not consistent for the different expansion sizes. Clearly, only introducing the additional state-average weights, w^{SA} , of 0.425 and 0.575 ensures consistency in the quality of the expansions of the two states.

Figure 5.6: Difference of the PT2 corrections (top) and CI variances (bottom) between the ground and the excited states for different reweighting schemes in the selection criterion. For all schemes including w^{SA} , the state-average weights of 0.425 and 0.575 are used for the ground and the excited state, respectively. The maug-cc-pVDZ basis set is used. Note that the colors and symbols for the “cmax” and “cmax $\times$ SA” schemes are different here than in Fig. 5.2.

5.8.2 Dependence of the state-average weights on the choice of orbitals and basis set

Figure 5.7: Difference of the (top) PT2 corrections and (bottom) CI variances for different CASSCF orbitals and choices of state-average weights. The maug-cc-pVDZ basis set is used.

In Fig. 5.7, we investigate the impact of the use of different CASSCF orbitals on the choice of weights, w_n^{SA} , which yield balanced (iso-PT2 and iso-variance) CIPSI expansions. The maug-cc-pVDZ basis is used.

In addition to the default CAS(6,5) orbitals used in the expansions of Fig. 5.2, we employ CAS(10,9) and CAS(10,14) optimized orbitals as well as CAS(6,12) orbitals where the virtual $3p_z$ orbitals of the four carbon atoms and the $3d_{xz}$, $3d_{yz}$, and $4p_z$ orbitals of the sulphur atom are included on top of the CAS(6,5) space (the molecule is in the xy -plane). Irrespective of the orbitals, we find that the optimal weight distribution is around 0.4 and 0.6 for ground and excited state, respectively.

In Fig. 5.8, we show the difference of the PT2 corrections and CI variances for the larger aug-cc-pVTZ basis set and different choices of state-average weights. We use the CAS(6,5) optimized orbitals in the expansions. The values of 0.4 and 0.6 for the weights give balanced expansions also for this size of the basis set.

5.8.3 CI energies and variances, and PT2 corrections

In Table 5.5, we list the CI energies and variances, and the PT2 energy corrections for the CIPSI expansions used in the computation of the vertical excitation energies in Table 5.1 (maug-cc-pVDZ basis set) and Fig. 5.4 (aug-cc-pVTZ basis set). We also report the CI excitation energies (ΔE_{CI}). The results are presented for both the “cmax” and “cmax $\times$ SA” selection schemes.

Table 5.5: CI energies (E_{CI}), PT2 corrections (E^{PT2}) and CI variances (σ_{CI}^2) of the ground- (S0) and excited-state (S1) CIPSI expansions (in a.u.). The CI excitation energy (ΔE_{CI}) is also listed in eV. The maug-cc-pVDZ and aug-cc-pVTZ basis sets are used.

WF	No. det	E _{CI}		ΔE _{CI}	E ^{PT2}		σ ² _{CI}		Δσ ² _{CI}
		S0	S1		S0	S1	S0	S1	
maug-cc-pVDZ basis set									
CIPSI	211	-34.43266	-34.21240	5.993	-0.70960	-0.70256	1.87049	1.87102	0.00053
cmax	1087	-34.46642	-34.23896	6.189	-0.65700	-0.66795	1.80760	1.83113	0.02353
	2797	-34.49461	-34.26313	6.299	-0.61417	-0.63302	1.74865	1.78590	0.03725
	5389	-34.52433	-34.28930	6.396	-0.57174	-0.59632	1.68834	1.73468	0.04634
	10289	-34.55887	-34.31902	6.527	-0.52615	-0.55605	1.61846	1.67556	0.05710
	22081	-34.60662	-34.36445	6.590	-0.46766	-0.49583	1.51545	1.57014	0.05469
	32022	-34.63282	-34.39021	6.602	-0.43760	-0.46448	1.45716	1.51237	0.05521
CIPSI	216	-34.43046	-34.21534	5.854	-0.71325	-0.70135	1.87563	1.86752	-0.00811
cmax × SA	1037	-34.45731	-34.24055	5.898	-0.67150	-0.66759	1.82666	1.82811	0.00145
	2614	-34.47912	-34.26441	5.842	-0.63664	-0.63243	1.78100	1.78308	0.00208
	5605	-34.51119	-34.29424	5.904	-0.59013	-0.59029	1.71621	1.72344	0.00723
	11003	-34.54451	-34.32755	5.904	-0.54431	-0.54388	1.64807	1.65060	0.00253
	22100	-34.58550	-34.36973	5.872	-0.49248	-0.49094	1.56108	1.55991	-0.00117
	31039	-34.60970	-34.39332	5.888	-0.46400	-0.46296	1.50824	1.51038	0.00214
aug-cc-pVTZ basis set									
CIPSI	222	-34.46082	-34.24477	5.879	-0.87321	-0.86209	2.97208	2.96683	-0.00525
cmax	1015	-34.48113	-34.26248	5.950	-0.83990	-0.83800	2.93774	2.94411	0.00637
	2665	-34.50216	-34.27954	6.058	-0.80482	-0.81433	2.89120	2.91678	0.02558
CIPSI	203	-34.46000	-34.24438	5.867	-0.87465	-0.86277	2.97293	2.96744	-0.00549
cmax × SA	1019	-34.47751	-34.26353	5.823	-0.84476	-0.83669	2.94238	2.94212	-0.00026
	2608	-34.49538	-34.28098	5.834	-0.81553	-0.81178	2.90412	2.91260	0.00848
	5051	-34.51093	-34.29712	5.818	-0.79074	-0.78778	2.87286	2.88301	0.01015
	10755	-34.53466	-34.32017	5.836	-0.75472	-0.75402	2.82308	2.83567	0.01259
	21716	-34.55993	-34.34654	5.807	-0.71915	-0.71668	2.77149	2.77860	0.00711
	31581	-34.57706	-34.36291	5.827	-0.69690	-0.69512	2.73794	2.74485	0.00691

Figure 5.8: Difference of the PT2 corrections (top) and CI variances (bottom) between the ground and the excited state for different state-average weights in the $w^{\text{cmax}} \times w^{\text{SA}}$ selection criterion. The aug-cc-pVTZ basis set is used.

5.9 Appendix: QMC results in the aug-cc-pVTZ basis set

We report below the VMC and DMC total and excitation energies computed with fully optimized Jastrow-CIPSI wave functions and the aug-cc-pVTZ basis set.

Table 5.6: VMC and DMC ground- and excited-state energies (a.u.), and vertical excitation energies (eV) of thiophene obtained with different expansions in fully optimized Jastrow-Slater wave functions. The aug-cc-pVTZ basis set is used.

WF	No. det	No. param	VMC			DMC		
			E(S0)	E(S1)	ΔE	E(S0)	E(S1)	ΔE
CIPSI	203	3719	-35.28232(29)	-35.07161(30)	5.734(11)	-35.35344(29)	-35.14294(29)	5.728(11)
$c_{\max} \times SA$	1019	7442	-35.29270(28)	-35.08212(29)	5.730(11)	-35.35744(28)	-35.14760(28)	5.710(11)
	2608	11780	-35.29933(28)	-35.08871(28)	5.731(11)	-35.36007(27)	-35.15046(27)	5.704(10)
	5051	14656	-35.30375(27)	-35.09326(28)	5.728(11)	-35.36164(26)	-35.15294(27)	5.679(10)
	10755	19674	-35.30913(27)	-35.09948(27)	5.705(10)	-35.36438(22)	-35.15464(22)	5.707(09)
	21716	27056	-35.31278(21)	-35.10256(21)	5.720(08)	-35.36435(51)	-35.15556(50)	5.681(19)
	31581	33363	-35.31600(26)	-35.10596(27)	5.715(10)	-35.36534(46)	-35.15666(44)	5.678(17)
CC3(BFD)/maug-cc-pVDZ								5.741
CC3(BFD)/aug-cc-pVDZ								5.678
CC3(BFD)/aug-cc-pVTZ								5.650

5.10 Appendix: Comparison with other methods

Table 5.7: Vertical excitation energies (eV) of thiophene computed on the CC3(FC)/aug-cc-pVTZ geometry with different methods.

Level of theory	Vertical excitation energy (eV)
B3LYP/aug-cc-pVTZ	5.701
CASSCF(6,5)/aug-cc-pVTZ	6.109
MS-CASPT2(6,5)/aug-cc-pVTZ	5.692
NEVPT2(6,5)/aug-cc-pVTZ	5.908
VMC-CAS(6,5)/aug-cc-pVTZ (BFD)	5.857(12)
DMC-CAS(6,5)/aug-cc-pVTZ (BFD)	5.800(11)
VMC-CIPSI/aug-cc-pVTZ (BFD)	5.715(10)
DMC-CIPSI/aug-cc-pVTZ (BFD)	5.678(17)
CC3/aug-cc-pVTZ (FC)	5.598
CC3/aug-cc-pVTZ (BFD)	5.650

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Chapter 6

Excited states of thiophene and its polymers with a local description of correlation

We investigate different local correlation schemes with the aim to construct compact and accurate Jastrow-Slater expansions for the computation of the lowest $\pi \rightarrow \pi^*$ excitation of thiophene and its polymers. We begin by exploring the applicability of the localization approach based on orbital domains and multi-resonance structures, which was recently developed within our group and successfully applied to the excited states of retinal models of increasing length. We find that, for cyclic systems such as thiophene-based stretches, this scheme requires the inclusion of higher classes of excitations and, therefore, relatively large expansions. If we delocalize the π orbitals on individual thiophene units while leaving the σ and virtual orbitals localized on one or two atoms, we recover compact Jastrow-Slater wave functions for bithiophene, which reproduce the targeted excitation energy obtained with a complete-active-space (CAS) expansion in VMC. The wave function for terthiophene is readily generated by the addition of one thiophene unit. In the previous Chapters, we have however demonstrated the superior performance of CIPSI with respect to CAS wave functions, whose generation is based on chemical intuition and, generally, limited to minimal sizes. Our preliminary investigation on the use of (semi)local orbitals within CIPSI indicates that the ground- and excited-state wave functions of thiophene and bithiophene converge to the full CI limit significantly faster than in the case of fully delocalized orbitals. The results also shed some light on the difficulties of VMC-CIPSI observed in the previous Chapter, to describe the lowest $\pi \rightarrow \pi^*$ excitation energy of thiophene.

6.1 Introduction

A reliable protocol for the generation of computationally efficient wave functions must be systematically scalable with the size of the system. In the previous Chapters, we have developed a CIPSI-based approach to construct compact multi-determinant

wave functions for the accurate QMC computation of ground- and excited-state structures as well as excitation energies of small, prototypical molecules. However, as the size of the system increases, such a construction scheme is bound to incur difficulties due to the intrinsic exponential scaling of a configuration interaction ansatz. Here, we aim to identify a viable route to construct size-extensive QMC wave functions for excited states of larger molecular systems, in particular, the polymers of thiophene. Such wave functions should have the desirable feature to be automatically extendable from one thiophene molecule to its polymeric chains.

We focus on the lowest-lying $\pi \rightarrow \pi^*$ excitations of thiophene, its dimer (2,2'-bithiophene), and trimer (terthiophene). We begin our investigation by following the recent suggestion by Zulfikri *et al.* [1] who limit the size of the determinantal expansion by elaborating a coupling scheme between electrons within domains of orbitals localized on one or two atoms, combined with the use of multiple Lewis resonance structures. While the approach was successfully used to treat charge-transfer excited states of π -conjugated protonated Schiff base (PSB) retinal "linear" chromophores, we encounter severe difficulties in directly applying it to our cyclic systems. We therefore investigate a range of possible modifications to the approach and identify an alternative local orbital description, which can be straightforwardly extended in polymeric thiophene chains.

Most of the work presented here predates the findings of the previous Chapters and focuses on how a localization scheme is able to reproduce the results of small CAS expansions with a subset of the determinants. In the course of this Thesis, we have however gathered enough evidence that CAS-based wave functions are not always sufficient to yield accurate excitation energies in QMC. Therefore, we conclude this Chapter by presenting a few exploratory calculations on the use of such a localized description as the orbital basis for CIPSI selection.

The chapter is organized as follows. We review the localization scheme of Ref. [1], and present the classification of the determinants in excitation classes and its application to the thiophene molecule in Section 6.3. We discuss alternative localization strategies and their extension to larger systems in Sections 6.4 and 6.5. We conclude with some preliminary results on the use of a local orbital basis within CIPSI for thiophene and bithiophene in Section 6.6.

6.2 Computational details

In this Chapter, we use B3LYP/cc-pVTZ ground-state geometries for all molecules, which are computed using the Gaussian09 package [2]. In the previous Chapter, a coupled cluster structure was used for thiophene but obtaining geometries at the same level of theory for the larger bithiophene and terthiophene is computationally too expensive. Hence, we consistently use here B3LYP structures for all thiophene stretches.

The QMC calculations are carried out with the CHAMP program [3] and scalar-relativistic energy-consistent Hartree-Fock (HF) pseudopotentials [4, 5]. We always employ the corresponding maug-cc-pVDZ basis set and a two-body Jastrow factor

containing electron-electron and electron-nucleus terms. The CIPSI calculations are performed with the Quantum Package [6, 7]. The coupled cluster energies are computed with the PSI4 code [8] and the multi-state CASPT2 calculations with the Molcas8.2 package [9, 10].

Localized orbitals centered on one atom or bond are constructed through a series of steps. We perform a CASSCF calculation with a minimal CAS(6,5) and CAS(12,10) over the π orbitals for thiophene and bithiophene, respectively, and localize the inactive σ orbitals with the Pipek-Mezey scheme [11, 12] within Molcas. We then generate HF orbitals localized on one or two atoms using the DOLO module [13] of the Cost package [14]. To construct a full set of local orbitals, we carry out another CASSCF calculation, starting from the DOLO π and virtual orbitals, and the occupied CASSCF local σ orbitals which are kept frozen. This last step is performed with GAMESS(US) [15, 16] for ease of interfacing with our CHAMP code.

The construction of linear scaling generalized valence bond (LGVB) orbitals is done with the program package GAMESS(US) by optimizing the active orbitals for an expansion comprising doubles configurations as further elaborated in Section 6.4.

To construct semi-local orbitals for bithiophene and terthiophene, we begin by generating local HF orbitals centered on one or two atoms using DOLO. Starting from these orbitals, we perform a CASSCF(6,5) calculation in Molcas to delocalize the π orbitals centered on one ring while keeping all the core σ orbitals and the π orbitals located on the other rings frozen. Next, we freeze these delocalized π orbitals together with all the σ orbitals, and delocalize the π orbitals on another thiophene ring via a CASSCF(6,5) calculation. This process is repeated until all the relevant π orbitals are delocalized on top of their respective rings. Since the virtual orbitals delocalize in this process, we combine the local inactive σ and active π orbitals with the localized HF virtual orbitals that were initially built with the localization procedure in DOLO. We then perform a CASCI($6n, 5n$) calculation (n is the number of thiophene rings) on these final orbitals to obtain a complete orthogonal orbital set and the initial wave function for our QMC calculations. Note that, in all the above localization procedures, we work in C1 symmetry.

6.3 Localized orbitals on one and two atoms

Local approaches have been primarily employed in the study of the ground states of non-metallic systems with the argument that electron correlation is a local phenomenon. Within QMC, Fracchia *et al.* developed a scheme to localize molecular orbitals on one/two atomic centers and generate determinants by correlating electron pairs located on adjacent bonding orbitals and their corresponding anti-bonding orbitals (i.e. in a CAS(4,4) active space) [17–19]. Electrons located on separated orbitals are not correlated and, consequently, the number of determinants in the wave function scales linearly with the size of the system. While this scheme was apt to treat the ground-state potential energy surface of a variety of systems, Zulfikri *et al.* [1] quickly established that the same is not applicable to excited states since electrons in spatially well-separated orbitals can also correlate strongly as, for instance,

in charge-transfer excitations. Additionally, one needs to treat all states of interest in an equivalent manner in choosing which orbitals to correlate. In general, developing local schemes for excited states remains an open and active research area in computational chemistry [20–41].

To develop a local description of excited states in QMC, Zulfikri *et al.* propose to borrow the concept of orbital domains from local coupled-cluster methods [22, 27, 29, 42, 43] and apply it to the localized orbitals of an active space. To this aim, for each doubly-occupied reference configuration in the CASSCF expansion, an occupied orbital and the set of orbitals coupled to it by large single-electron transitions are grouped in an orbital domain. Only dominant domains are kept and higher-order excitations are constructed within and from the union of these domains. The resulting excitations are further classified into so-called excitation classes based on the nature of transition. In building a Slater expansion for QMC, the determinants of the different excitation classes are sequentially added based on the net contribution of each class to the total CASSCF wave function. To further improve the description of the states of interest (in particular, the excited states), Zulfikri *et al.* also account for the presence of multiple Lewis resonance structures in the molecule. For a given representation of the delocalized orbitals in the active space, multiple sets of equivalent local orbitals corresponding to the different Lewis structures are generated together with the corresponding domains and excitation classes. While these set of orbitals are equivalent if the complete CAS space is treated, this is not the case if we retain only a subset of the determinants as we do when using the concept of domains. The resulting multiple-resonance Jastrow-Slater wave functions are therefore a linear combination of classes of excitations built from the domains of all the different Lewis structures. Dynamic correlation is then recovered through the Jastrow factor and, eventually, through DMC.

We now begin our application of the localized correlation scheme of Ref. [1] to the lowest, bright $\pi \rightarrow \pi^*$ excited state of thiophene, which was the subject of the previous Chapter. As already explained, this state has a non-negligible multi-reference character and belongs to the same symmetry class as the ground state, needing therefore to be computed in a state-averaged fashion. The minimal active space required to describe this state is shown in Fig. 6.1 (panel A) and comprises 6 electrons distributed in 5 π orbitals, thus a CAS(6,5). At the CASSCF level with fully delocalized orbitals, the most important contributions to the excited-state wave function are single excitations from HOMO–1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1 that account for 57% and 21% of the wave function respectively. There is also a net contribution of about 7% from double excitations among these four levels.

In addition to the standard delocalized representation, one can construct equivalent sets of localized π orbitals by unitary transformation, which correspond to the five different Lewis resonance structures shown in the top panel of Fig. 6.1. These different local descriptions might be more suitable for different geometries or electronic states of the thiophene molecule, and all resonance structures will be visited at different points of the excited-state potential energy surface. The third and fourth structures, however, have opposite charges on adjacent atoms and are therefore unlikely to be stable or contribute to either the ground or the excited state. Conse-

Figure 6.1: Resonance structures of thiophene: (A) Active delocalized π orbitals obtained from a CASSCF(6,5) calculation, and (B-C) unitary transformed sets of localized orbitals for two Lewis resonance structures. Structures 2 and 2' are mirror images of each other, where the mirror plane is perpendicular to the plane of the molecule and passes through the S atom.

quently, we are left with only three dominant resonance structures: Res-1, Res-2, and Res-2', where Res-2 and Res-2' are mirror images of each other. The resonance structure Res-1 (panel B of Fig. 6.1) is the dominant representation at the ground-state equilibrium. An analysis of the electronic dipole moment of the molecule upon excitation indicates a transfer of electron density from the sulphur atom towards the ring. Therefore, Res-2 and Res-2' are expected to contribute to the description of the excited state. The local CASSCF orbitals of the Res-1, Res-2, and Res-2' rep-

representations are centered on either an atom or a bond, and are constructed using the Pipek-Mezey scheme [11, 12] for the σ orbitals and the DOLO module [13] of the Cost package [14] for active π and virtual orbitals as detailed in Section 6.2.

We recall that, if we include all possible excitations in the active space, all these different orbital representations will recover the exact same amount of electronic correlation. Here, we want however a compact determinantal expansion for our QMC calculations and, for each resonance structure, will therefore select only a small subset of determinants corresponding to the most important excitation classes to include in the final multi-resonance Jastrow-Slater wave function. We must stress that we can easily combine determinants expressed on multiple sets of orbitals thanks to the inherent flexibility of QMC which enables us to employ an over-complete orbital set.

Having described the different local-orbital representations for thiophene, we will now expand on the concept of orbital domains and check whether the subset of electronic configurations generated with them can recover sufficient weights of the target CASSCF wave functions of both the ground and the excited state. As an example, we will focus on the Res-1 representation (panel B of Fig. 6.1) and compute the optimal CASSCF(6,5) wave function, correlating the lone pair on S (orbital 1), two bonding orbitals (orbitals 2,3) and two anti-bonding orbitals (orbitals 4,5). If one defines a reference configuration as a configuration in the ground state consisting of doubly-occupied localized bonding orbitals, there is only one such configuration for the Res-1 representation, namely, 22200. We build the domains by considering single excitations out of this reference and ensuring that all active orbitals are involved at least once. This procedure results in the following list of domains:

- a) {1 : 4,5}
- b) {2 : 5}
- c) {3 : 4}

where the number before the colon represents the doubly-occupied orbital in the reference from which the single excitation takes place, and the number after the colon indicates the orbital to which the electron is excited. Note that the two excitations in domain (a) arise because of symmetry reasons, and the single excitations from the lone pair on the S atom to the two adjacent anti-bonding orbitals contribute equally in both the ground and excited states. We then construct the higher-order excitations by coupling these domains and categorize them into the different classes listed in Table 6.1, following the nomenclature of Ref. [1]. One can of course construct further excitation classes and also couple more than two domains recovering more (or all) configurations in the CAS(6,5) active space.

We present the relative contributions of the excitation classes to the ground and excited state CASSCF(6,5) wave functions in the Res-1 representation in Table 6.2. The X0 and X1 classes are composed of the reference and the most important single excitations constituting the orbital domains, respectively. The X3 class made of the bonding-antibonding doubles is generally found to be important for the description of the ground state [17] and is always included even though, in this case, it cannot be constructed from the orbital domains since the singles which yield X3 (2 $\rightarrow$ 4 and 3 $\rightarrow$ 5) have negligible weight. The X2 class composed of important singles from the least dominant domains is not present because of the symmetry of the transitions. All

Table 6.1: Description of excitation classes. The X4–X7 excitations are built from the orbital domains (adapted from Ref. [1]).

Class	Description
X0	References (all doubly-occupied bonding)
X1	Important singles in dominant domains to build the doubles
X2	Important singles in other domains
X3	Bonding-antibonding doubles
X4	Doubles to adjacent antibonding
X5	Doubles (4 unpaired electrons)
X6	Doubles (2 unpaired electron in bonding orbitals)
X7	Doubles (2 unpaired electron in empty orbitals)
X8	Triples (bonding-antibonding doubles plus X1 singles)

other classes are generated by combining the domains as described in Table. 6.1.

As shown in Table 6.2, the local Res-1 representation yields wave functions, which are strongly multi-configurational. In the ground state, the reference only accounts for about 56% of the total weight and contributes by as much as 22% to the excited state. The single excitations appear to be stabilizing the ground more than the excited state, comprising 29% and 12% of the wave function, respectively, and are therefore not the most dominant class for the excited state. Instead, the X5 class of excitations with 4 unpaired electrons accounts for the largest weight of 49% in the excited state. The situation is therefore rather different from what was encountered for the retinal chromophores, where X0 and X1 were accounting for more than 80% of the wave functions of the ground and excited state, respectively. Therefore, the relative importance of the different excitation classes is very different for our cyclic system. If we include all X0-X8 classes with 20 of the 27 possible configuration state functions (CSF) (41 of the 52 possible determinants) of the CAS(6,5) wave function, we recover about 98% and 91% of the total CASSCF wave functions but are still far from a balanced description of both states.

Before exploring the use of multiple resonances, we investigate how the analysis based on CASSCF weights translates to VMC and whether the relative importance of the excitation classes changes upon optimization of the Jastrow-Slater wave function. Importantly, we can assess the quality of the corresponding vertical excitation energy in VMC. When optimizing the orbitals in the Jastrow-Slater wave function, we must however ensure that these remain localized, failing which, the purpose of localizing the orbitals and classifying the excitations is defeated. In principle, if the Slater component accounts for all relevant excitations to describe a state appropriately, one would expect that the orbitals do not change dramatically and remain localized. In general, to prevent delocalization, we can impose additional restrictions on orbital mixing during optimization. To this aim, we employ the “threshold on orbital mixing” (TM) strategy which is based on spatial considerations [1]. Basically, a user-defined threshold is set on a measure that determines the extent of localization of the orbitals on individual atoms, and an orbital is mixed with another if they share

Table 6.2: CASSCF(6,5) weight distribution (in %) of configurations with localized Res-1 orbitals computed on top of the S0 B3LYP/cc-pVTZ geometry.

	Type	Domain	CSF	Det	Configuration (1,2,3,4,5)	Weight (%)	
			(N)	(N)		S0	S1
X0	ref		1	1	22200	56.19	21.96
X1	S	a	1	2	12210	9.94	2.42
	S	a	1	2	12201	9.94	2.42
	S	b	1	2	21201	4.76	3.51
	S	c	1	2	22110	4.75	3.50
Sub			4	8		29.39	11.85
X3	D	-	1	1	20220	2.47	1.68
	D	-	1	1	22002	2.47	1.68
Sub			2	2		4.94	3.36
X4	D	b	1	1	20202	0.02	0.05
	D	c	1	1	22020	0.02	0.05
	D	a	1	1	02220	0.12	0.33
	D	a	1	1	02202	0.12	0.33
Sub			2	2		0.26	0.77
X5	D	a+b	2	6	11211	1.79	9.51
	D	a+c	2	6	12111	1.79	9.51
	D	b+c	2	6	21111	2.36	29.56
Sub			6	18		5.94	48.58
X6	D	a+b	1	2	11202	0.27	0.85
	D	a+c	1	2	12120	0.27	0.85
Sub			2	4		0.54	1.70
X7	D	a	1	2	02211	0.52	1.51
Sub			1	2		0.52	1.51
X8	T	a+X3	1	2	12012	0.04	0.17
	T	a+X3	1	2	10221	0.07	0.62
Sub			2	4		0.11	0.79
Total			20	39		97.89	90.52

at least one atom according to this threshold. An added benefit of the TM approach is its scaling to larger systems where the number of orbitals to mix (i.e. the orbital parameters) would increase significantly. Such a scheme is successful if the orbitals remain localized without the excitation energy being affected.

In Table 6.3, we list the results of our VMC calculations with the Res-1 representation and different excitation classes in Jastrow-Slater wave functions, which are optimized with various TM parameters. The reference total and excitation energies are those obtained from a VMC optimization with the delocalized CAS(6,5) active space which we are targeting as determinantal component¹. We note that the use of

¹We note that the VMC total energies and excitation energies are different from those of the previous Chapter since we are here using a B3LYP/cc-pVTZ ground-state geometry for thiophene.

Table 6.3: VMC total and excitation energies of thiophene computed with Res-1 localized orbitals and different excitation classes. The TM threshold on orbital mixing is reported together with the nature of the final optimal orbitals. The S0 B3LYP/cc-pVTZ geometry and the maug-cc-pVDZ basis set is used.

Thr. mixing (no. param.)	Determinants (N)	S0 (a.u.)	S1 (a.u.)	ΔE (eV)	Delocalized/ Localized
0.00 (909)	X0+X1 (9)	-35.2552(4)	-35.0284(4)	6.172(14)	Delocalized
0.00 (913)	X0+X1+X3 (11)	-35.2625(4)	-35.0340(4)	6.218(14)	Delocalized
0.10 (356)		-35.2621(4)	-35.0199(4)	6.591(14)	Localized
0.20 (314)		-35.2621(4)	-35.0182(4)	6.636(14)	Localized
0.00 (917)	X0+X1+X5 (27)	-35.2575(4)	-35.0410(4)	5.890(14)	Localized
0.15 (326)		-35.2574(4)	-35.0403(4)	5.909(14)	Localized
0.20 (318)		-35.2572(2)	-35.0402(2)	5.905(09)	Localized
0.00 (919)	X0+X1+X3+X5 (29)	-35.2653(4)	-35.0460(4)	5.966(14)	Localized
0.10 (362)		-35.2647(3)	-35.0458(3)	5.957(10)	Localized
0.15 (328)		-35.2646(2)	-35.0457(2)	5.957(09)	Localized
0.20 (320)		-35.2650(2)	-35.0462(2)	5.952(09)	Localized
0.00 (483)	CAS(6,5) (52)	-35.2668(4)	-35.0482(4)	5.948(14)	Delocalized

this CAS expansion does not lead to a very accurate VMC estimate of the vertical excitation energy of thiophene as shown in the previous Chapter. After having assessed which ingredients are needed to construct a local and compact wave function transferable to larger polymers and of CAS quality, we will discuss extensions beyond CAS expansions.

As in the case of the PSB molecules, when using just the reference and the single excitations (X0 and X1) the orbitals delocalize but, for thiophene, this persists even after the addition of the X3 class. For a determinantal component comprising the X0–X3 classes, the use of the TM criterion in the optimization allows us to maintain the orbitals localized but the resulting excitation energy is blue-shifted by more than 0.6 eV with respect to the reference value. We know however that the X5 class is very important to stabilize the excited states since these excitations have the largest weight for the excited state at the CASSCF level. The inclusion of X5 with X0 and X1 leads to balanced estimates of the ground- and excited-state energies, being both about 8 mHartree higher than the corresponding reference, and a vertical excitation energy which is now within 0.05 eV of the delocalized CAS value. Adding the X3 determinants maintains the excitation energy in agreement with the CAS value and further improves the quality of the total energies which are now within 2 mHartree of the reference. With these dominant classes, we have however already included 29 of the 52 determinants in the active space. We note that, in the presence of the X5 determinants, the orbitals remain localized and, in this case, restricting orbital mixing with a non-zero TM value does not affect the excitation energy (nor the energies) and is of practical use to reduce the number of variational optimization parameters.

If we were only interested in the excitation energies, we could be reasonably satisfied since we were able to obtain good estimates with a subset of determinants. We expect however that this subset will not be transferable to different configura-

tions of the potential energy surface, especially in the excited state. To ensure this transferability, we should consider excitations also out of the Res-2 and Res-2' representations and construct a multi-resonance Jastrow-Slater wave function. As shown in Appendix 6.9, an analysis of the CASSCF(6,5) weights with the Res-2 orbitals on a geometry which stabilizes this Lewis structure indicates that the X5 remain important, accounting for about 32% of the excited-state wave function. If we were to also include the Res-2 representation, we will need to add an almost equivalent number of configurations to the existing Res-1 set. Furthermore, we also have to consider Res-2' together with Res-2 for symmetry reasons. This means that we would end up with the undesirable situation of having more determinants (and parameters to optimize) than in a delocalized representation.

6.4 Degree of orbital localization

Figure 6.2: LGVB1 orbitals: Localized orbitals with longer tails.

Localizing orbitals on one/two atoms for this excited state of thiophene leads to a representation of the wave function which is highly multi-configurational. Before looking for other ways to build compact and efficient expansions for QMC, we investigate to what extent our findings are tied to the degree of localization of the initial orbitals. To this aim, we construct localized orbitals which are still largely localized on an atom or bond but have small tails on adjacent atoms. This can be easily done for the Res-1 representation, following the work by Fracchia *et al.* [17–19] and constructing what they called linear scaling generalized valence bond (LGVB) orbitals, (more specifically, LGVB1 orbitals). These are obtained by minimizing the energy in a MCSCF calculation which includes all possible bonding-antibonding pair doubles configurations. The localization of orbitals emerges naturally from this calculation.

Typically, for an N (even) number of electrons, a LGVB1 wave function is composed of $N/2+1$ determinants: the reference (HF) and all bonding-antibonding doubles. However, in our case, we retain the previous localized σ orbitals and include the following configurations: 22200, 20220, 22002, 02220, 02202, where the numbering of the orbitals is shown in Fig. 6.2: since the lone pair on the S atom strongly correlates with the anti-bonding orbitals on the carbon-carbon bonds, we also include

two extra CSFs for double excitations between them. As can be seen in Fig. 6.2, the resultant optimized active orbitals primarily differ from the Res-1 orbitals as the lone pair of S has acquired tails on the adjacent C atoms, and the anti-bonding orbitals also have a small contribution on the S and the adjacent C atom. We now construct a new set of localized orbitals by i) starting from the LGVB1 orbitals as new active orbitals and ii) retaining the previous σ and virtual orbitals localized on individual atoms or bonds. Upon performing a CASSCF(6,5) active space with this new orbital set, the degree of localization is preserved for all orbitals. We then construct the dominant domains, which are the same as found previously, and the corresponding excitation classes. We list the classes with largest weights in Table 6.4.

Table 6.4: CASSCF(6,5) weight distribution (in %) of configurations with LGVB1 π orbitals computed on top of the S0 B3LYP geometry.

	Type	Domain	CSF	Det	Configuration (1,2,3,4,5)	Weight (%)	
			(N)	(N)		S0	S1
X0	ref		1	1	22200	91.92	0.50
X1	S	a	1	2	12210	0.03	7.93
	S	a	1	2	12201	0.03	7.93
	S	b	1	2	21201	0.17	27.07
	S	c	1	2	22110	0.17	27.07
Sub			4	8		0.40	70.00
X3	D	-	1	1	20220	2.82	1.52
	D	-	1	1	22022	2.82	1.52
Sub			2	2		5.64	3.04
X5	D	a+b	2	6	11211	0.14	0.84
	D	a+c	2	6	12111	0.14	0.84
	D	b+c	2	6	21111	1.03	20.43
Sub			6	18		1.33	22.11
Total			13	29		99.29	95.65

Clearly, the weight distribution is much less scattered through the different classes than in the case of the DOLO-generated orbitals of Table 6.2. The single excitations (X1) account for 70% of the excited-state wave function compared to the previous 12%, while the X1 class does no longer contribute to the ground state. The X5 class remains important particularly for the excited state but its total weight is more than halved. The weights of the X3 excitations are very similar to before. Combining only these classes, we are now able to recover 99% and 96% of the ground and excited states, respectively, against 96% and 86% with the more localized orbitals. Even though the balance of CASSCF weights in the initial wave functions is improved, we find however that the use of these semi-localized orbitals and corresponding determinants in Jastrow-Slater wave functions does not alter the conclusions drawn above. As shown in Table 6.5, the inclusion of the X0, X1, X3, and X5 classes and subsequent optimization in VMC preserves the localized nature of the orbitals (also without the use of the TM threshold) and leads to wave functions whose total and

excitation energies are in very close agreement with the values we had previously found with the more localized initial orbitals in Table 6.2.

Table 6.5: VMC total and excitation energies of thiophene computed with semi-localized LGVB1 orbitals and different thresholds on orbital mixing. The nature of final optimized orbitals is also indicated. The S0 B3LYP/cc-pVTZ geometry and the maug-cc-pVDZ basis set is used.

Thr. mixing (no. param)	Determinants (N)	S0 (a.u.)	S1 (a.u.)	ΔE (eV)	Delocalized/ Localized
0.00 (919)	X0+X1+X3+X5 (29)	-35.2655(7)	-35.0454(7)	5.989(26)	Localized
0.15 (328)		-35.2554(4)	-35.0354(4)	5.986(14)	Localized
0.20 (320)		-35.2553(4)	-35.0349(4)	5.997(14)	Localized
0.00 (483)	CAS(6,5) (52)	-35.2668(4)	-35.0482(4)	5.948(14)	Delocalized

6.5 Bithiophene and Terthiophene

For thiophene, the above localization strategies yield wave functions that recover the full-CAS VMC estimates of vertical excitation energies with a subset of determinants but might not be transferable to different parts of the excited-state potential energy surface where other localization patterns are needed. On the other hand, if we add contributions from multiple Lewis representations, the final number of optimization parameters will exceed those present in a standard delocalized representation thereby defeating part of the purpose of using local orbitals. Thiophene is however a small system and has relatively few parameters in the delocalized space to begin with, while the same is not true for its polymers where we might benefit from the above localization techniques. Hence, we investigate the application of a local description of correlation to the lowest lying bright $\pi \rightarrow \pi^*$ singlet excited states of 2,2'-bithiophene (2 units of thiophene) and terthiophene (3 units).

The ground-state structure of bithiophene is non-planar, has a *trans* geometric configuration with two thiophene rings connected by a single C–C bond, and possesses C_2 symmetry. The lowest-lying $\pi \rightarrow \pi^*$ singlet excited state is the lowest state of B symmetry, different from the ground state which belongs to the A class. We note that, when working with local orbitals, these no longer belong to the irreducible representation of C_2 and we must work in C_1 , performing state-average calculations. The minimal active space correlating the most relevant orbitals is composed of 12 electrons distributed in 10 active π orbitals, CAS(12,10). At the CASSCF(12,10) level with fully delocalized orbitals, this state has significant contributions from the following transitions: HOMO $\rightarrow$ LUMO (40%), HOMO-2 $\rightarrow$ LUMO (24%) and HOMO $\rightarrow$ LUMO+1 (7%) (see orbitals highlighted in Fig. 6.3).

We transform the delocalized CAS(12,10) orbitals into an equivalent DOLO and LGVB1 localized sets where the orbitals are centered on one or two atoms. We then perform an analysis of the CASSCF wave function in these representations and classify the different configurations into excitation classes. In both cases, we observe

Figure 6.3: 2,2'-bithiophene: Orbitals localized on individual thiophene units.

that the wave function is again extremely multi-configurational with several configurations contributing with small but comparable weights. Furthermore, the X5 class continues to remain important especially for the excited state. As shown in Table 6.6, the inclusion of X0, X1, X3, and X5 recovers a smaller percentage of the reference wave functions than in the case of thiophene (see Table 6.2). This holds not only for the DOLO representation but, especially in the excited state, also when using the LGVB1 orbitals (73% versus 96% in thiophene). An analogous analysis performed on other Lewis resonance structures (with the corresponding “optimal” geometries) reveals similar weight distribution across the different excitation classes: the X5 class stays important and contributes between 16 and 18% for both states. Therefore, irrespective of the choice of local orbital bases, the description of the excited state is much more multiconfigurational compared to the delocalized reference, rendering the construction of the corresponding wave function even more problematic than in the case of thiophene (especially in the definition of the domains due to the presence of many single excitations with comparable and small weights in both states).

We will therefore abandon the above approach and seek to identify a new definition of orbital localization apt for a compact description of the excited states of thiophene polymers. To this aim, we now allow delocalization of the active orbitals within each thiophene ring but restrict them from spreading across bridging bonds (see Fig. 6.3). Consequently each thiophene ring now acts as a repeatable unit. We

Table 6.6: CASSCF(12,10) weight distribution (in %) of configurations with localized DOLO and LGVB1 π orbitals (orbitals of Fig. 6.2 on two thiophene units) computed on top of the S0 B3LYP geometry.

	Type	CSF (N)	Det (N)	DOLO		LGVB1	
				S0	S1	S0	S1
X0	Ref	1	1	32.95	0.00	83.75	0.00
X1	S	10	20	29.11	21.02	0.05	58.06
X3	D	4	4	5.87	0.04	10.45	1.14
X4	D	6	6	1.56	0.13	0.14	0.63
X5	D	64	192	12.18	30.77	2.32	14.17
Total		85	223	81.67	51.96	96.71	74.00

leave the doubly occupied σ and unoccupied virtual orbitals localized on one or two atoms as before. Essentially, as shown in Fig. 6.3 for bithiophene, our starting orbitals are not the (de)localized orbitals of the minimal CAS(12,10) space but two sets of 5 delocalized orbitals. As the size of the polymer grows, we can generate the orbital space by simply adding an equivalent set of orbitals every time a new thiophene is added to the polymer. In so doing, we can circumvent optimizing large CAS wave functions, a calculation which becomes quickly unfeasible beyond a CAS(18,15) (3 thiophene units). Furthermore, we do not need to consider multiple resonance structures to access different parts of the ground- and excited-state potential energy surfaces since the delocalized π description should be sufficient to account for all scenarios. The complete procedure to obtain such an orbital representation is detailed in Section 6.2.

Starting from the “local” representation of Fig. 6.3, we perform a CASCI(12,10) calculation to construct orbital domains following the same strategy as before. We correlate orbitals connected by dominant single excitations until all active orbitals are involved at least once. In addition to identifying important excitations between individual orbitals, we also check whether the domains represent inter-ring (Cross unit) or intra-ring (Within unit) excitations (see Fig. 6.4 and Table 6.7). This information will be particularly valuable when constructing domains for larger units, say terthiophene, where we will simply adopt the same recipe in analyzing the large CASCI(18,15) wave function.

Figure 6.4: 2,2'-bithiophene: Inter-ring ($C_{R \rightarrow L} / L \rightarrow R$) and intra-ring ($W_{R/L}$) excitations.

From the domains listed in Table 6.7 (orbital labels shown in Fig. 6.3), we can see that only the orbitals that are the HOMO of the individual thiophenes (orbitals 1 and 4) have a significant correlation with the anti-bonding orbitals on the adjacent ring via single excitations. The bonding orbitals delocalized over the C atoms (orbitals 2 and 5) and the lone pair on S (orbitals 3 and 6) are primarily correlated with their corresponding anti-bonding orbitals within the same ring. Using these domains, we construct higher-order excitations and identify the most relevant excitation classes at the CASCI level for both states, which we list together with their net contribution in Table 6.8.

Even though the net contribution of the X0–X5 classes to the total wave functions is not so dissimilar to the LGVB1 case, the distribution of weights with this

Table 6.7: Orbital domains for 2,2'-bithiophene using the orbitals localized on the thiophene units.

Orbital domains	Excitation description
{1 : 7, 8, 9, 10}	$W_L, W_L, C_{L \rightarrow R}, C_{L \rightarrow R}$
{2 : 7}	W_L
{3 : 7}	W_L
{4 : 7, 8, 9, 10}	$C_{R \rightarrow L}, C_{R \rightarrow L}, W_R, W_R$
{5 : 9}	W_R
{6 : 9}	W_R

Table 6.8: CASCI(12,10) weights distribution (in %) of configurations with π orbitals delocalized on individual thiophene units. The B3LYP/cc-pVTZ geometry is used.

	Type	CSF	Det	Weight (%)	
		(N)	(N)	S0	S1
X0	Ref	1	1	84.29	0.00
X1	S ($W_{L/R}$)	8	16	0.01	52.51
	S ($C_{R \rightarrow L/L \rightarrow R}$)	4	8	0.03	13.41
X3	D	4	4	1.34	4.21
X4	D	4	4	6.46	3.88
X5	D	70	210	3.20	5.10
Total		91	243	95.33	79.11

semi-local orbital representation is much less scattered among the different excitation classes in comparison to what is obtained with either the DOLO or the LGVB1 orbitals. The X0 and X1 classes are clearly dominant for the ground and the excited state, respectively. The single excitations within individual rings ($W_{L/R}$) accounting for a four-times higher weight than the single excitations across rings ($C_{R \rightarrow L/L \rightarrow R}$). Furthermore, the X5 excitations which were extremely important for thiophene and also for bithiophene appear to have a much smaller role here, at least at the CASCI level, and yield a comparable contribution to both states. On the other hand, X4 acquires weight, while it was unimportant in thiophene. We stress that the weight analysis is not performed on a CASSCF(12,10) but on a CASCI(12,10) wave function with orbitals which were “manually” prepared as described in the Computational Details Section. Therefore, while these weights give us a good indication of the largest classes, we need to verify the relevance of X4 and X5 at the VMC level, where we reoptimize the orbitals in the Jastrow-Slater wave functions.

In Table 6.9, we list the VMC total and excitation energies obtained with the semi-local orbital representation, together with the corresponding values from a delocalized CAS(12,10) calculation. We recall that the latter are not necessarily the best theoretical estimates available (our CASPT2(12,10)/maug-cc-pVDZ excitation energy is about 4.6 eV) but represent the target of the current calculations, where we want to recover the CAS results with a subset of determinants. We find that including

Table 6.9: VMC total and excitation energies of bithiophene computed with active orbitals localized on individual thiophene units and different thresholds on orbital mixing. The nature of the optimized orbitals is also indicated. The S0 B3LYP/cc-pVTZ geometry and the maug-cc-pVDZ basis set are used.

Thr. mixing (no. param.)	Determinants (N)	S0 (a.u.)	S1 (a.u.)	ΔE (eV)	Delocalized/ Localized
0.00 (5646)	X0+X1+X3 (29)	-69.3289(5)	-69.1480(5)	4.922(18)	Localized
0.05 (1848)		-69.3122(5)	-69.1302(5)	4.953(18)	Localized
0.10 (1572)		-69.3098(5)	-69.1279(5)	4.949(18)	Localized
0.00 (5650)	X0+X1+X3+X4 (33)	-69.3376(5)	-69.1479(5)	5.161(18)	Localized
0.05 (1852)		-69.3201(5)	-69.1302(5)	5.168(18)	Localized
0.10 (1576)		-69.3176(5)	-69.1277(5)	5.167(18)	Localized
0.00 (5807)	X0+X1+X3+X5 (239)	-69.3350(5)	-69.1495(5)	5.046(18)	Localized
0.05 (1959)		-69.3180(5)	-69.1320(5)	5.059(18)	Localized
0.10 (1642)		-69.3177(5)	-69.1312(5)	5.073(18)	Localized
0.00 (5730)	X0+X1+X3+X5'' (41)	-69.3349(5)	-69.1498(5)	5.037(18)	Localized
0.05 (1890)		-69.3172(5)	-69.1314(5)	5.057(18)	Localized
0.10 (1614)		-69.3163(5)	-69.1300(5)	5.067(18)	Localized
0.00 (9802/9702)	Delocalized (22100/22000)	-69.3457(5)	-69.1598(5)	5.058(17)	Delocalized

the X0, X1, and X3 classes yields an excitation energy about 0.1 eV lower than the reference, and the addition of X4 improves only the ground-state energy, increasing the excitation above the reference by the same amount. The inclusion of X5 instead of X4 leads to a smaller/larger gain in the energy of the ground/excited state and, consequently, an excitation energy compatible within statistical error with the delocalized reference. When the wave function comprises both X4 and the most relevant X5 determinants (see discussion below), we severely unbalance the description of the two states in favor of the ground state. Therefore, we only retain the X0, X1, X3, and X5 classes in further calculations. Even though one needs to include the large X5 for a balanced description of the two states as in the case of the DOLO or LVGB1 orbitals, the delocalization of the orbitals on the thiophenes will allow us to proceed without the inclusion of additional resonance representations when transferring this wave function to geometries very different from the optimal ground-state one.

Finally, we make two important observations that can further help us to control the computational cost when going to larger polymer stretches: (1) employing a TM criterion to reduce the variational parameters does not alter the excitation energies, and (2) using a very small subset of the most relevant X5 determinants (denoted as X5''), we recover the same ground- and excited-state energies as with the full X5 class. In particular, two configurations (4 CSFs and 12 determinants) corresponding to excitations within the same ring account for most of the X5 contributions.

We will now look at the lowest singlet $\pi \rightarrow \pi^*$ excited state of terthiophene whose ground-state structure is non-planar and C_s symmetric. The ground and excited states have A' and A'' symmetry, respectively. We again delocalize the active orbitals within individual thiophene rings (see Fig. 6.5) and simply extend the orbital domains of bithiophene by correlating the same set of π and π^* orbitals within and between adjacent rings, without performing any additional CAS(18,15) wave func-

Figure 6.5: Terthiophene: Orbitals localized on individual thiophene units.

tion analysis. Inter-ring correlations therefore only exist between the left (L) and the middle (M) ring and between the middle (M) and the right (R) ring. The resulting orbital domains are listed in Table 6.10.

Table 6.10: Orbital domains for terthiophene constructed by extending the domains of bithiophene. L: Left, M: Middle, R: Right rings.

Orbital domains	Excitation description
{1 : 10, 11, 12, 13}	$W_L, W_L, C_{L \rightarrow M}, C_{L \rightarrow M}$
{2 : 10}	W_L
{3 : 10}	W_L
{4 : 10, 11, 12, 13, 14, 15}	$C_{M \rightarrow L}, C_{M \rightarrow L}, W_M, W_M, C_{M \rightarrow R}, C_{M \rightarrow R}$
{5 : 12}	W_M
{6 : 12}	W_M
{7 : 12, 13, 14, 15}	$C_{R \rightarrow M}, C_{R \rightarrow M}, W_R, W_R$
{8 : 14}	W_R
{9 : 14}	W_R

It is now easy to count the number of determinants for a wave function comprising the X0, X1, X3, and X5'' excitation classes built from these orbital domains. There is one reference configuration/determinant (X0) and, from the orbital domains, we obtain 20 single excitations (X1), that is, 40 determinants. Each ring has two

bonding-antibonding doubles adding upto a total of 6 such configurations (or 6 determinants). For the dominant $X5''$, each ring contributes 2 CSFs, resulting in a total of 6 CSFs or 18 determinants. Therefore, our final wave function will only contain 33 CSFs and 65 determinants.

With this very compact wave function, we compute the VMC excitation energy and compare it with reference CASPT2 and CCSD values from literature (see Table 6.11). The close agreement between this preliminary result and the reference data is encouraging but we need to recall that we are here aiming for the energies obtained with the full minimal CAS space. Therefore, additional calculations are needed to ensure that this excitation energy is indeed converged with the number of excitation classes and compatible with the corresponding VMC-CAS(18,15) reference. We further note that the number of variational parameters is already over 12000 with this small set of 65 determinants. In the case of thiophene and bithiophene, a threshold-mixing criterion could significantly reduce the number of orbital parameters without altering the excitation energies, particularly after including determinants from the $X5$ class. This needs of course to be verified also in the case of terthiophene. Employing a threshold-mixing criterion is clearly increasingly important as we scale up to larger systems.

Table 6.11: VMC total and excitation energies of terthiophene computed with active orbitals localized on individual thiophene units. The nature of the final optimized orbitals is also indicated. The S0 B3LYP/cc-pVTZ geometry and the maug-cc-pVDZ basis set is used.

Thr. mixing (no. param.)	Determinants (N)	S0 (a.u.)	S1 (a.u.)	ΔE (eV)	Delocalized/ Localized
0.00 (12464)	$X0+X1+X3+X5''$ (65)	-103.3934(6)	-103.2442(6)	4.061(23)	Localized
CASPT2(18,15)/6-31G* [44]				4.03	Delocalized
CCSD/6-311+G* [44]				4.15	

6.6 CIPSI selection with local orbital basis

The calculations for bithiophene and terthiophene indicate that, by transforming the orbital space into a (semi)local representation, we can construct compact wave functions, which have in principle the necessary features to be scalable and transferable to larger polymers. That said, the procedure of selecting relevant determinants by constructing orbital domains is somewhat tedious and, while it can be automatized, it is system-specific and requires close scrutiny when analyzing the relevant classes of excitations in order to maintain the number of VMC calculations to a minimum. Furthermore, we have been targeting the CAS-based energies, while we know from previous Chapters that such description of correlation might be insufficient if we strive to obtain very accurate theoretical estimates and/or if do not have a clear understanding of which orbitals need to be correlated. In such cases, the CIPSI procedure of determinant selection that we explored in the previous Chapters could come to our

rescue. In this Section, we will investigate the convergence behavior of CIPSI expansions on (semi)local orbitals (against traditional delocalized orbitals) for thiophene and bithiophene, and perform VMC calculations on thiophene to assess how the use of a local orbital set affects the CIPSI selection and the resulting VMC excitation energy.

Thiophene

Figure 6.6: Convergence of the CI energies with number of determinants for the (top) ground and (bottom) excited states of thiophene for three orbital sets: (red) DOLO orbitals, (green) delocalized minimal CAS(6,5) active space with localized occupied σ and virtual orbitals, and (black) full delocalized orbitals. The expansions obtained with the “ $c_{\max} \times SA$ ” selection criterion and optimal SA weights are also shown for the semi-local and fully delocalized cases. The maug-cc-pVDZ basis set and the B3LYP/cc-pVTZ ground-state structure are employed.

In Fig. 6.6, we plot the convergence of the variational CI energy against the number of determinants of the ground- and excited-state CIPSI expansions for thiophene. We employ three different sets of orbitals: (1) the DOLO orbitals of the Res-1 representation (see Fig. 6.1), (2) the CASSCF(6,5) orbitals where the π orbitals are delocalized and the occupied σ and all virtual orbitals are localized on one or two atoms, and (3) fully delocalized orbitals. With the first two (semi)local representations, the ground- and excited-state CI energies clearly converge significantly faster than the fully delocalized case. The mixed representation (2) is particularly useful for the excited state since it reaches lower variational energies, also compared to representation (1), already for expansions with less than 50000 determinants. This observation further supports the choice we have made for thiophene polymers to delocalize the relevant π orbitals on individual thiophene units while keeping the σ and virtual orbitals localized.

For the semi-local and delocalized orbital sets, we also plot the energies of expansions obtained with the “ $\text{cmax} \times \text{SA}$ ” selection, where we use the optimal weights of (0.3,0.7) and (0.425, 0.575), respectively. We recall that these values of the weights for the delocalized orbitals were shown to be ideal for a balanced (iso-PT2 and iso-variance) description of both states in the previous Chapter. Also in the semi-local description, the use of additional weights slows down the convergence of the ground state, while only marginally accelerating the convergence of the excited state as compared to the “ cmax ” criterion. The superior performance of the semi-local approach holds for both the “ cmax ” and the “ $\text{cmax} \times \text{SA}$ ” selection.

If we inspect the convergence of the CI energies versus the corresponding rPT2 corrections [7], we can better assess how close the expansions are to the FCI limit, keeping in mind that the larger CIPSI expansions yield smaller magnitudes of the $E(\text{rPT2})$ correction, being close to the FCI description. In such analysis, using different criteria in the CIPSI selection simply yields overlying curves. As shown in Fig. 6.7, we find that the range of $E(\text{rPT2})$ corrections are shifted significantly closer to zero for the semi-local representation (green curves) compared to the delocalized one (black curves) for similar expansion sizes, once again asserting the faster convergence of local-orbital expansions to the FCI limit. Interestingly, the curves in the local representation clearly display a change in slope when reaching absolute PT2 corrections smaller than about 0.15 a.u. , a change which is more substantial for the excited state. Therefore, by extrapolating the energies to the FCI limit (zero PT2 correction), one obtains very different excitation energies when performing a linear fit with the data before or after the “kink” in the curves. The estimates differ by as much as 0.5 eV and the one obtained with the larger expansions is in much better agreement with the CC3/aug-cc-pVDZ value of 5.7 eV. The CI energies computed with the fully delocalized orbitals also display a similar behavior but for much larger expansions: the slope changes at about 6.6 million determinants (against 180000 with the semi-local orbitals) and, due to the lack of sufficient data points, it is not possible to reliably extrapolate the energies to the FCI limit.

In the calculations with delocalized orbitals in the previous Chapter, we used relatively short CIPSI expansions from the first part of the CI-energy curves, when constructing the determinantal component of QMC wave functions. The resulting

Figure 6.7: CI energies versus PT2 corrections for the (top) delocalized and (bottom) semi-local orbitals. The line fits of different parts of the curves are also shown together with the extrapolated estimates of the excitation energy.

VMC excitation energies were somewhat larger than the best available reference and comparable excitation energies were obtained with expansions between 5000 and 30000 determinants. The use of CIPSI wave functions beyond the “kink” was not tested since, with delocalized orbitals, this implies expansions beyond 6.6 million determinants. As shown in Table 6.12, if we use CIPSI wave functions of similar size in the semi-local representation, we obtain lower ground- and excited-state VMC energies (by about 15–17 mHartree) but compatible excitation energies to the values computed with the delocalized orbitals.² In particular, we find that VMC improves

²We recall again that we are here using a B3LYP ground-state geometry, while in the previous

Table 6.12: VMC total (a.u.) and vertical excitation (eV) energies of thiophene obtained with fully optimized Jastrow-CIPSI wave functions. The expansions are obtained with the “ $c_{\text{max}} \times \text{SA}$ ” criterion and different optimal weights for the two set of orbitals. The maug-cc-pVDZ basis set and B3LYP/cc-pVTZ ground-state structure are employed.

Orbitals	No. det	No. param	E(S0)	E(S1)	ΔE
Deloc.	5222	4098	-35.2905(4)	-35.0735(4)	5.904(17)
Semi-Loc. ^a	5562	11632	-35.3076(6)	-35.0887(6)	5.915(26)
Semi-Loc. ^b	5000	14996	-35.3073(8)	-35.0880(8)	5.967(31)
CC3/aug-cc-pVDZ(BFD)					5.678

^a Expansion scheme.

^b Truncated from an expansion containing 4.01 million determinants.

on the CIPSI excitation energies of 6.07 and 6.12 eV computed with delocalized and semi-local orbitals, respectively, bringing them to a value of about 5.9 eV, which remains however higher than the CC3/aug-cc-pVDZ reference of 5.7 eV. We note that the use of semi-local orbitals leads to the loss of symmetry and a significantly larger number of orbital parameters, which could however be reduced with the use of a threshold mixing as described above.

With the semi-local orbital basis, testing CIPSI wave functions beyond the “kink” requires expansions of more than 0.18 million determinants. Considering the small size of thiophene, one would hope that fewer determinants are needed to reach accurate excitation energies in quantum Monte Carlo. Therefore, we investigate whether truncating very large expansions beyond the “kink” (i.e. 4 million determinants) leads to different Slater components than the ones obtained by expanding the CIPSI wave function and stopping at a small number of determinants. As shown in Table 6.12, we find that the nature of an expansion of about 5000 determinants obtained by truncation is not different than the one obtained via expansion: the total and excitation energies obtained with semi-local orbitals and the two schemes are equivalent within statistical error.

Bithiophene

In Fig. 6.8, we plot the CI energies of CIPSI expansions performed with delocalized and semi-local orbitals against the number of determinants and, also for this molecule, observe a much faster convergence to the FCI limit using a local description. Nevertheless, we do not further explore the performance at the VMC level of the CIPSI expansions with the semi-local orbitals since this orbital set was generated “manually” as described in the Computational Details Section: for a fair comparison with the CIPSI selection on delocalized CASSCF(12,10) orbitals, one would ideally employ semi-local orbitals optimized at the same level of theory.

Chapter we were employing a CC3 geometry. Therefore, the VMC excitation energies in Table 6.12 are somewhat different than those in Table 5.1.

Figure 6.8: Convergence of the ground- and excited-state CI energies of bithiophene with respect to the number of determinants. (black) Delocalized and (green) semi-local orbitals are used.

We only note that we obtain VMC excitation energies in good agreement with the CASPT2(12,10)/maug-cc-pVDZ estimate of 4.6 eV when employing balanced (iso-PT2) CIPSI wave functions of up to 11000 and 20000 determinants for the ground and excited states, respectively. The generation of optimal semi-local orbitals and the comparison with the delocalized description will be the subject of further investigations beyond this Thesis.

6.7 Summary and prospects

We explore the use of a local correlation scheme to obtain compact and transferable wave functions to describe the low-lying $\pi \rightarrow \pi^*$ excited states of thiophene and its polymers. To this aim, we first adopt the protocol recently devised and applied to “linear” retinal models by Zulfikri *et al.*, combining the use of local orbitals with the concepts of orbital domains, excitation classes, and multiple Lewis structures [1]. While we do succeed in obtaining vertical excitation energies compatible with a delocalized VMC reference by using only a subset of the CAS determinants, we have to include higher excitation classes for cyclic thiophene. Consequently, the adoption of a multi-resonance representation to achieve transferability to different parts of the potential energy surface would lead to sizable expansions and number of optimization parameters. Allowing the orbitals to marginally delocalize on adjacent atoms via the use of an LGVB1 orbital set does not ameliorate the problem.

Next, we modify the definition of local orbitals for thiophene polymers and delocalize the active orbitals within each thiophene ring. The inactive σ and virtual orbitals are kept localized on one or two atoms. Consequently, each thiophene ring acts as a repeatable unit to be added as we increase the length of the polymer. With the active π orbitals delocalized within each unit, we construct the determinantal

space by retaining the concept of orbital domains. Even though we need to include excitation classes beyond what was required in Ref. [1] for linear molecules, we obtain the targeted VMC excitation energy using less than 0.5% of the number of CAS determinants for bithiophene, and have a description which naturally encompasses the multiple resonance structures one encounters in different parts of the excited-state potential energy surface. Analyzing the most relevant excitations for bithiophene, we then automatically construct the determinant set for terthiophene, which yields VMC estimates of the excitation energy compatible with data from literature. Further calculations to establish the corresponding delocalized VMC reference and to reduce the number of optimization parameters via threshold mixing criterion are needed.

Finally, we present some exploratory investigation on the impact of the use of a local orbital basis on the CIPSI construction. For thiophene and bithiophene, we find that the CIPSI expansions converge much faster towards the FCI limit if we employ a (semi)local orbital basis. Interestingly, for thiophene, the use of local orbitals allows us to observe a clear change of slope of the CI curves as a function of PT2 contribution and, therefore, to establish that the extrapolated FCI value is significantly different than what is obtained fitting the first part of the CI curves. This finding could explain the observations in the previous Chapter, where we performed calculations with delocalized orbitals and relatively small expansions, finding some difficulties in obtaining accurate VMC excitation energies for thiophene (e.g. a stronger dependence on the basis set). If we use semi-local orbitals and CIPSI expansions of similar size (i.e. before the “kink” in the CI curves) in our Jastrow-Slater wave functions, we obtain lower total energies but similar excitation energies in VMC compared to the delocalized case. Unfortunately, if we generate a very large CIPSI expansion well beyond the change in slope and truncate it, the nature of the surviving determinantal component is not too dissimilar than what was obtained by expansion, yielding comparable results at the VMC level. Directly testing the use of CIPSI wave functions on semi-local orbitals closer to the FCI limit is in principle possible for thiophene but does not represent a viable route for larger systems. We remark again that, given the observed dependence of CIPSI on the orbital set, it would be important to explore how orbital optimization during the CIPSI selection process affects not only the convergence but also the selection of important determinants for subsequent use in quantum Monte Carlo.

6.8 Appendix: Geometry dependence of the vertical excitation energy

In Chapter 5, we use a CC3/aug-cc-pVTZ ground-state geometry to compute the vertical excitation energies of thiophene. Obtaining ground-state structures at the same level of theory is however not practically feasible for the larger polymers of thiophene. Since we are here investigating how to build compact and transferable wave functions as we add more thiophene units, we want to employ geometries consistently generated for all thiophene stretches and, therefore, resort to B3LYP/cc-pVTZ

for this purpose.

Figure 6.9: Ground-state geometries of thiophene obtained with (left) CC3/aug-cc-pVTZ and (right) B3LYP/cc-pVTZ.

For thiophene, the maximum absolute difference between the bond lengths obtained at the CC3/aug-cc-pVTZ and B3LYP/cc-pVTZ level is less than 0.01 Å where the largest difference is for the C=C bond as shown in Fig. 6.9. Nevertheless, since these small structural differences can have a non-negligible impact on the vertical excitation energy, we compute the CC3, CASPT2, and QMC excitation energies on both geometries. As shown in Table 6.13, we find that the use of the B3LYP geometry leads to a consistent blue-shift of the excitation energy (about 0.06 eV) for all approaches, with respect to the corresponding quantities evaluated on the CC3 geometry. Therefore, although the B3LYP structure might not be optimal, we can be assured that this only yields a consistent, small energy shift.

Table 6.13: Impact of ground-state geometry on the vertical excitation energies (eV) of thiophene.

Method	Vertical excitation energy (eV)	
	CC3 geometry	B3LYP geometry
CC3/aug-cc-pVDZ (FC)	5.644	5.701
CC3/aug-cc-pVTZ (FC)	5.598	5.655
MS-CASPT2(6,5)/aug-cc-pVTZ (FC)	5.692	5.740
VMC-CAS(6,5)/aug-cc-pVTZ (BFD)	5.857(12)	5.911(12)
DMC-CAS(6,5)/aug-cc-pVTZ (BFD)	5.800(11)	5.880(11)

6.9 Appendix: Analysis of a CASSCF(6,5) wave function with the Res-2 representation

A geometry corresponding to the Res-2 resonance structure is obtained by performing a constrained geometry optimization with B3LYP/cc-pVTZ, where the C=C and C=S bonds are kept fixed. The C=C bond length is set to the value in the ground-state B3LYP geometry and the C=S bond to 1.6 Å following literature data [45].

An analysis of a localized CASSCF(6,5) wave function on this geometry yields the domains:

- a) {1 : 4,5}
- b) {2 : 4}
- c) {3 : 4}

where the orbitals and the numbering are shown in Fig. 6.1. The corresponding excitation classes are presented in Table 6.14.

Table 6.14: CASSCF(6,5) weight distribution (in %) of configurations with localized Res-2 orbitals computed on top of the Res-2 B3LYP/cc-pVTZ geometry.

	Type	Domain	CSF	Det	Configuration (1,2,3,4,5)	Weight (%)	
			(N)	(N)		S0	S1
X0	ref		1	1	22200	21.07	1.10
X1	S	a	1	2	12210	51.07	13.58
	S	a	1	2	12201	7.81	19.76
	S	b	1	2	21210	0.13	4.33
	S	c	1	2	22110	1.78	5.46
Sub			4	8		60.79	43.13
X3	D	b	1	1	20220	0.13	0.58
	D	(3$\rightarrow$5)	1	1	22002	0.32	0.25
Sub			2	2		0.45	0.89
X4	D	a	1	1	02220	6.54	4.41
	D	a	1	1	02202	0.13	0.78
	D	c	1	1	22020	0.03	0.04
Sub			3	3		6.70	5.23
X5	D	a+b	2	6	11211	0.62	3.58
	D	a+c	2	6	12111	1.75	28.76
Sub			4	12		2.37	32.34
X6	D	a+b	1	2	11220	0.52	5.13
	D	a+c	1	2	12120	0.15	0.78
	D	b+c	1	2	21120	0.12	0.07
Sub			3	6		0.79	5.98
X7	D	a	1	2	02211	4.16	4.48
Sub			1	2		4.16	4.48
X8	T	a+X3	1	2	10221	0.13	0.51
	T	a+X3	1	2	12012	1.59	1.00
	T	b+X3	1	2	21012	0.02	0.03
Sub			3	6		1.74	1.54
Total			21	40		98.07	94.69

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List of publications

- **M. Dash**, S. Moroni, A. Scemama and C. Filippi,
“Perturbatively Selected Configuration-Interaction Wave Functions for Efficient Geometry Optimization in Quantum Monte Carlo”
J. Chem. Theory Comput. **14**, 4176 (2018). (Chapter 3)
- **M. Dash**, J. Feldt, S. Moroni, A. Scemama and C. Filippi
“Excited States with Selected Configuration Interaction–Quantum Monte Carlo: Chemically accurate excitation energies and geometries”
J. Chem. Theory Comput. **15**, 4896 (2019). (Chapter 4)
- **M. Dash**, A. Scemama and C. Filippi,
“Modeling excited states with QMC-CIPSI: the case study of thiophene”
In preparation. (Chapter 5)

Summary and Outlook

Accurate Excited States with Quantum Monte Carlo: Looking beyond conventions

The development of accurate computational methods for the predictive modeling of excited states is a very active field of research in quantum chemistry. Despite significant progress, there still exists a serious theoretical vacuum in the availability of efficient techniques that can provide a reliable description, particularly when one is interested in features of the potential energy surface (PES) outside the Franck-Condon region. In this thesis, we explore the somewhat unconventional use of the highly-correlated quantum Monte Carlo (QMC) methods in this direction. In particular, we want to assess the predictive power of QMC methods in obtaining robust and accurate estimates of excitation energies as well as ground- and excited-state geometries. To this aim, we investigate these properties in the gas phase for a range of small prototypical molecules which are challenging for standard electronic structure methods. These studies are possible thanks to the following recent methodological advances that we either employ or achieve during the course of this dissertation.

Systematic strategy to construct many-body wave functions: A QMC calculation makes use of an initial “trial” wave function, which is often written as the product of a so-called Jastrow correlation factor that explicitly depends on inter-electronic distances and a Slater component taken from other, sometimes much less accurate, quantum chemical methods. Historically, the Slater component for an excited state has been constructed using the HOMO and LUMO orbitals from a density functional theory (DFT) calculation or chosen to be a linear combination of multiple determinants obtained from a small complete-active-space-self-consistent-field (CASSCF) calculation. To truly attest the predictive power of QMC and ensure that the physical quantities computed with these wave functions are not accidentally in agreement with available best estimates, we must have a way to systematically enhance the wave function quality and verify that the converged quantities are insensitive to any further improvement in the description of say static correlation (via the increase in size of the determinantal expansion). This is difficult to do by simply building DFT determinants using different exchange-correlation functionals which might yield very different values for the quantities of interest. The choice of a CASSCF expansion on the other hand will heavily depend on the chemical intuition of the user: it is not straightforward to realize whether a larger wave function is indeed a better description of a given electronic state compared to a shorter expansion obtained from

a different set of active orbitals. To circumvent these issues, we explore two unconventional routes to build many-body wave functions for QMC. In Chapters 3–6, we make use of a selected configuration-interaction (CI) scheme called CIPSI (CI with perturbative selection done iteratively) which iteratively selects the most important determinants from the full CI space in an automated fashion, ensuring a systematic improvement of wave function quality. To accurately compute excited states, it is crucial to have a balanced description of all involved states. In this thesis, we propose a simple strategy to generate extremely well-balanced CIPSI expansions for multiple states, also when working with different molecular geometries. We demonstrate its proficiency in obtaining high-quality excited-state properties and extend it to deal with non-trivial excited states that belong to the same symmetry class. In Chapter 6, which was in fact the first study that we undertook, we follow an alternative route to model excited states using (semi)-local orbitals which are correlated with a scheme based on the concept of orbital domains of local coupled cluster methods. Here, the wave function quality is iteratively improved by adding classes of determinants in decreasing order of importance, that are constructed by combining the orbital domains. This allows us to clearly identify the important ingredients (excitations) of an excited-state wave function but this scheme is not fully general (and therefore predictive) since the domains span a pre-defined active space and the QMC wave function can at best recover a corresponding Jastrow-CAS description. We also test the use of our (semi)-local orbitals as the basis for CIPSI selection and observe a faster convergence of the CI energies (for all states) as opposed to when the same is performed on standard delocalized orbitals.

Self-consistent wave function optimization in variational Monte Carlo (VMC): A common recipe in the application of QMC methods is to select a trial wave function and perform a diffusion Monte Carlo (DMC) calculation on it without any optimization of the determinantal parameters. The results of these calculations are then used to validate the quality of estimates obtained with other lower-level methods. This simple recipe has facilitated a better qualitative understanding of the physics of many systems. Similarly, using simple wave functions has enabled the applicability of QMC methods to rather large molecular clusters containing over a hundred atoms. One might however ask whether the addition of a Jastrow factor in VMC or the subsequent use of DMC is sufficient to compensate for possible inadequacies of the trial wave function. Furthermore, what is the impact of variational optimization on the quality and the ideal size of a QMC wave function? We have answered these questions thanks to the current capabilities of VMC to concomitantly optimize all variational parameters — Jastrow parameters, determinant, and orbital coefficients. Importantly, these optimization algorithms are efficient also when dealing with large wave functions containing tens of thousands of determinants and are sufficiently robust to perform both state-specific and state-average excited-state optimizations. Furthermore, we can render QMC a fully “self-consistent” method by optimizing not only the wave function but also the molecular geometries in the ground and excited states. In all our investigations, we optimize the orbitals in VMC and find this to be quite important when working with some complicated excited states or truncated CASSCF wave functions. Doing so also helps in the more accurate computation of

the interatomic forces, and consequently geometries.

To summarize, our work here represents the first steps in establishing QMC as a reliable, predictive method for the accurate computation of molecular excited states, while truly assessing the impact of the ingredients of a many-body wave function on different physical properties. Combining the strengths of CIPSI selection and VMC optimization, we demonstrate the excellent performance of QMC in this respect and make two important observations: (a) there is no further need of a DMC calculation on top of our optimized VMC wave functions since the two approaches yield compatible estimates of excitation energies, and (b) converged excitation energies and geometries can be computed with significantly shorter CIPSI expansions if the wave function is optimized in VMC. Therefore, we can recommend the use of such a CIPSI-QMC optimization protocol to generate theoretical benchmarking data for excitation energies and structural parameters of molecules in the gas phase, of course being cautious that all required states are correctly and consistently captured.

We also clearly demonstrate that it is no longer needed to borrow different components of a calculation (such as the ground-state structure or an orbital set) from other methods since we can now simultaneously optimize them in VMC. While we have tested and significantly pushed the use of CI-based wave functions in QMC, we do realize that our CIPSI-QMC approach will encounter difficulties as we scale up to larger system sizes owing to the factorial scaling of CI approaches. In such situations, one might need to seek drastically different formulations of the Slater component. An active direction of research in QMC is indeed the search of novel functional forms for the many-body wave function. Important work has for instance been done in the development of sophisticated pairing wave functions such as antisymmetrized geminal products or the more general Pfaffians [1] (and references therein), and in the application of backflow transformations [2,3] or even in the combination of both [4]. Particularly interesting are some pioneering studies which use artificial neural networks to construct QMC trial wave functions without having to depend on the chemical intuition of the user [5,6]. Although their promise of their applicability to large systems must still be assessed, these are some very exciting developments for future research. We finally note that the majority of these efforts are at the moment primarily concerted around modeling ground states; their application to excited states remains completely open.

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Samenvatting en Vooruitblik

Nauwkeurige aangeslagen toestanden met Quantum Monte Carlo: Voorbij de conventies

De ontwikkeling van nauwkeurige computationele methoden voor de voorspellende modellering van aangeslagen toestanden is een zeer actief onderzoeksgebied in de kwantumchemie. Ondanks de aanzienlijke vooruitgang bestaat er nog steeds een aanzienlijk theoretisch vacuüm in de beschikbaarheid van efficiënte technieken die een betrouwbare beschrijving kunnen geven, vooral wanneer men geïnteresseerd is in kenmerken van het potentiële energieoppervlak (PES) buiten het Franck-Condon gebied. In dit proefschrift onderzoeken we het wellicht onconventionele gebruik van de sterk gecorreleerde kwantum Monte Carlo (QMC) methoden voor deze toepassing. In het bijzonder willen we de voorspellende kracht van QMC-methoden beoordelen bij het verkrijgen van robuuste en nauwkeurige schattingen van excitatie-energieën en van de geometrie van grond- en aangeslagen toestanden. Daartoe onderzoeken we deze eigenschappen voor een reeks prototypische kleine moleculen in de gasfase die een uitdaging vormen voor standaard elektronenstructuurmethoden. Deze studies zijn mogelijk dankzij de volgende recente methodologische vooruitgang die we in de loop van dit proefschrift toepassen of bereiken.

Systematische strategie om veel-deeltjes golffuncties te construeren: Een QMC-berekening maakt gebruik van een “test”-golffunctie, die vaak wordt geschreven als het product van een zogenaamde “Jastrow” correlatiefactor die expliciet afhankelijk is van interelektronische afstanden en een Slater component die afkomstig is van andere, soms veel minder nauwkeurige, kwantumchemische methoden. Historisch gezien is de Slater-component voor een aangeslagen toestand geconstrueerd met behulp van HOMO en LUMO orbitals afkomstig uit een dichtheidsfunctionaliteitstheorie (DFT) berekening of gekozen als een lineaire combinatie van meerdere determinanten verkregen uit een kleine complete-active-space-self-consistent-field (CASSCF) berekening. Voor het bevestigen van het voorspellend vermogen van QMC en ervoor te zorgen dat de met deze golffuncties berekende fysische grootheden niet per ongeluk in overeenstemming zijn met de beschikbare beste schattingen, moeten we een manier hebben om de kwaliteit van de golffunctie systematisch te verbeteren en te verifiëren dat de geconvergeerde grootheden ongevoelig zijn voor verdere verbetering van de beschrijving van bijvoorbeeld de statische correlatie (via een grotere determinanten expansie). Dit is moeilijk te doen door eenvoudigweg DFT-determinanten te bouwen met behulp van verschillende exchange-

correlatie functionalen die zeer verschillende waarden voor de fysische grootheden van interesse kunnen opleveren. Daarentegen zal de keuze van een CASSCF expansie sterk afhangen van de chemische intuïtie van de gebruiker: het is niet eenvoudig vast te stellen of een grotere golffunctie inderdaad een betere beschrijving geeft van een bepaalde elektronische toestand in vergelijking met een kortere expansie verkregen uit een andere set van actieve orbitalen. Om deze kwesties te omzeilen verkennen we twee onconventionele routes om veel-deeltjes golffuncties voor QMC te bouwen. In hoofdstukken 3-6 maken we gebruik van een zgn. selected configuratie-interactie (CI) schema genaamd CIPSI (CI met iteratieve selectie via storingsrekening) dat op een geautomatiseerde manier iteratief de belangrijkste determinanten uit de volledige CI-ruimte selecteert waardoor een systematische verbetering van de kwaliteit van de golffuncties wordt gegarandeerd. Voor de nauwkeurige berekening van aangeslagen toestanden is een evenwichtige beschrijving van alle betrokken toestanden van cruciaal belang. In dit proefschrift stellen we een eenvoudige strategie voor om uiterst evenwichtige CIPSI-expansies voor meerdere toestanden te genereren, ook wanneer er gewerkt wordt met verschillende moleculaire geometrieën. We tonen aan dat hiermee met hoge kwaliteit eigenschappen van aangeslagen toestanden kunnen worden verkregen en we breiden het uit om niet-triviale aangeslagen toestanden te behandelen die tot dezelfde symmetrieklasse behoren. In hoofdstuk 6, dat eigenlijk de eerste studie was die we ondernamen, volgen we een alternatieve route om geëxciteerde toestanden te modelleren. Hierin wordt gebruik gemaakt van (semi)-lokale orbitalen die gecorreleerd zijn met een schema dat gebaseerd is op het concept van orbitaal domeinen uit lokale coupled cluster methoden. De kwaliteit van de golffunctie wordt zo iteratief verbeterd door het toevoegen van klassen van determinanten die worden geconstrueerd door het combineren van de orbitaal domeinen in volgorde van afnemende belangrijkheid. Dit stelt ons in staat om de belangrijke ingrediënten (excitatie) van een golffunctie voor een aangeslagen toestand duidelijk te identificeren. Echter dit schema is niet volledig algemeen (en daarmee voorspellend) omdat de domeinen een vooraf gedefinieerde actieve ruimte beslaan en de QMC-golffunctie kan in het beste geval een overeenkomstige Jastrow-CAS beschrijving krijgen. We testen ook het gebruik van onze (semi)-lokale orbitalen als basis voor CIPSI-selectie en observeren hiermee een snellere convergentie van de CI-energieën (voor alle toestanden) in tegenstelling tot wanneer hetzelfde wordt uitgevoerd op standaard gede-lokalisierde orbitalen.

Zelf-consistente golffunctie-optimalisatie in variationele Monte Carlo (VMC): Een veel voorkomende procedure bij de toepassing van QMC-methoden is het selecteren van een test-golffunctie en het daarop uitvoeren van een diffusie Monte Carlo (DMC) berekening zonder enige optimalisatie van de golffunctieparameters. De resultaten van deze berekeningen worden vervolgens gebruikt om de kwaliteit van schattingen te valideren die met andere lagere niveau methoden zijn verkregen. Deze eenvoudige procedure heeft een beter kwalitatief begrip van de fysica van vele systemen mogelijk gemaakt. Op dezelfde manier heeft het gebruik van eenvoudige golffuncties de toepasbaarheid van QMC-methoden op vrij grote moleculaire clusters met meer dan honderd atomen mogelijk gemaakt. Men kan zich echter afvragen of de toevoeging van een Jastrow-factor in VMC of het latere gebruik van DMC vol-

doende is om eventuele tekortkomingen van de test-golffunctie te compenseren. Wat is bovendien de impact van variationele optimalisatie op de kwaliteit en de ideale lengte van de Slater expansie van een QMC-golffunctie? We hebben deze vragen beantwoord dankzij de huidige mogelijkheden van VMC om alle variationele parameters - Jastrow parameters, determinant en orbital coëfficiënten - gelijktijdig te optimaliseren. Belangrijk is dat deze optimalisatiealgoritmen ook efficiënt zijn bij het omgaan met grote golffuncties die tienduizenden determinanten bevatten en dat ze voldoende robuust zijn om zowel toestandspecifieke als toestandsgemiddelde optimalisaties uit te voeren van aangeslagen toestanden. Bovendien kunnen we QMC een volledig “zelfconsistente” methode maken door niet alleen de golffunctie te optimaliseren, maar ook de moleculaire geometrieën in de grond en aangeslagen toestanden. In al onze onderzoeken optimaliseren we de orbitalen met VMC en vinden we dit heel belangrijk bij het werken met enkele gecompliceerde aangeslagen toestanden of afgekapte CASSCF-golffuncties. Dit helpt ook bij het nauwkeuriger berekenen van de interatomaire krachten, en dus ook van de geometrieën.

Samenvattend representeert ons werk hier de eerste stappen om QMC te vestigen als een betrouwbare, voorspellende methode voor de nauwkeurige berekening van moleculaire aangeslagen toestanden waarin de impact van de ingrediënten van een veel-deeltjes golffunctie op verschillende fysische eigenschappen daadwerkelijk wordt beoordeeld. Door de sterke punten van CIPSI-selectie en VMC-optimalisatie te combineren, demonstreren we de uitstekende prestaties van QMC in dit opzicht en doen we twee belangrijke observaties: (a) er is geen verdere behoefte aan een DMC-berekening bovenop onze geoptimaliseerde VMC-golffuncties aangezien de twee benaderingen overeenkomstige schattingen van excitatie-energieën opleveren, en (b) geconvergeerde excitatie-energieën en geometrieën kunnen worden berekend met beduidend kortere CIPSI-expansies als de golffunctie in VMC wordt geoptimaliseerd. Daarom kunnen we het gebruik van een dergelijk CIPSI-QMC optimalisatieprotocol aanbevelen om theoretische benchmarkgegevens te genereren voor excitatie-energieën en structurele parameters van moleculen in de gasfase, waarbij we er natuurlijk op moeten letten dat alle vereiste toestanden correct en consistent worden verkregen.

We laten ook duidelijk zien dat het niet langer nodig is om verschillende onderdelen van een berekening (zoals de grondtoestand geometrie of een orbitaal set) te gebruiken van andere methoden, omdat we deze nu tegelijkertijd kunnen optimaliseren in VMC. Hoewel we het gebruik van CI-gebaseerde golffuncties in QMC hebben getest en de mogelijkheden ervan hebben verkend, realiseren we ons dat onze CIPSI-QMC aanpak op problemen zal stuiten als we opschalen naar grotere systemen vanwege de factoriële schaalvergroting van CI-benaderingen. In dergelijke situaties kan het nodig zijn om drastisch andere formuleringen van de Slater-component te zoeken. Een actieve onderzoeksrichting in QMC is het zoeken naar nieuwe functionele vormen voor de veel-deeltjes golffunctie. Er is bijvoorbeeld belangrijk werk verricht in de ontwikkeling van geavanceerde paar-golffuncties zoals antisymmetrische geminaal producten of de meer algemene Pfaffians, en in de toepassing van ‘backflow’ transformaties of zelfs in de combinatie van beide. Bijzonder interessant zijn enkele baanbrekende studies die gebruik maken van kunstmatige neurale netwerken om

QMC test-golffuncties te construeren zonder afhankelijk te zijn van de chemische intuïtie van de gebruiker. Hoewel de belofte van toepasbaarheid ervan op grote systemen nog steeds moet worden beoordeeld, zijn dit enkele zeer spannende ontwikkelingen voor toekomstig onderzoek. We merken ten slotte op dat het merendeel van deze inspanningen op dit moment vooral rond het modelleren van de grondtoestanden wordt gedaan; de toepassing ervan op aangeslagen toestanden blijft volledig open.

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