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OF ICELAND**

**M.S. Thesis  
in Chemistry**

**Variational Density Functional Calculations of Rydberg  
Excited States with and without Self-Interaction  
Correction**

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**FACULTY OF PHYSICAL SCIENCES**



# Variational Density Functional Calculations of Rydberg Excited States with and without Self-Interaction Correction

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Thesis submitted in partial fulfillment of a  
*Magister Scientiarum* degree in Chemistry

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Variational Density Functional Calculations of Rydberg Excited States with and without  
Self-Interaction Correction  
(Variational DFT Calculations of Rydberg Excited States)

Thesis submitted in partial fulfillment of a *M.S.* degree in Chemistry

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## Abstract

Rydberg excited electronic states are reminiscent of the hydrogen atom orbitals in that the excited electron is most likely located far from the other electrons and the energy of successively higher states follows the Rydberg series. For some molecules, such as ethylene, the first excited state is already a Rydberg state, but more often this applies to the highly excited states. The calculation of such states is challenging because highly diffuse basis sets are needed and the commonly used density functional theory is not reliable because of the self-interaction error. In the present project, the orbitals are represented on a real space grid instead of the commonly used atomic orbitals and the calculations are carried out using orbital based explicit self-interaction correction. The orbitals are allowed to be complex functions since the correction breaks unitary invariance of the wave function. Calculations are carried out for several molecules and comparison made with experimental measurements.



# Ágrip

Örvuð rafeindaástönd af Rydberg gerð minna á svigrúm vetnisatómsins að því leiti að örvaða rafeindin er líklegast langt frá hinum rafeindunum og orka slíkra ástanda fylgir Rydberg röð. Fyrir sumar sameindir, t.d. etþýlen, er fyrsta örvaða ástandið Rydberg ástand en oftast á þetta við um ástönd með hærri orku. Reikningar á slíkum ástöndum eru erfiðir að því leiti að grunnföllin þurfa að ná langt frá kjörnunum og þéttifellaaðferðin sem oftast er notuð í reikningum á rafeindakerfi sameinda er ekki áreiðanleg vegna sjálfsvíxlverkunarinnar. Í verkefninu er grind í raunrúmi notuð til að lýsa svigrúmumunum í stað atómsvigrúma og leiðrétting gerð fyrir sjálfsvíxlverkunina í hverju svigrúmi. Tvinntöluföll eru notuð fyrir svigrúmin því með leiðréttingunni skiptir máli hvaða línuleg samtekt af svigrúmumunum er notuð til að lýsa bylgjufallinu. Reikningar eru gerðir fyrir ýmsar sameindir og samanburður gerður við mæligildi.





# Preface

My first experience with excited state calculations was during the summer of 2020 when I calculated a range of charge transfer excited states for several organic molecules. It was a part of a benchmark study into the effectiveness of direct optimisation methods compared to commonly used time dependant density functional theory methods. It was quite interesting for me to see the challenges involved in calculating excited states of molecules.

When I started work on my master's thesis in the autumn of 2022, I had the chance to work on a project where the ionization energy for excited states on a certain molecule had been measured. I was to perform calculations in order to correctly identify the excited states that were measured. As the measured states were Rydberg states, I was introduced to the Perdew-Zunger self-interaction correction (SIC) in order to get more accurate results for those states. I thought that this was an interesting method and I wanted to gain more understanding of it, so I decided to make my project about the use of SIC in calculations of excited states and to test it on some benchmark molecules.



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# Abbreviations

**PBE** Perdew-Burke-Ernzerhof (exchange correlation functional)

**TPSS** Tao, Perdew, Staroverov and Scuseria (exchange correlation functional)

**SIC** Self-interaction correction

**XC** Exchange correlation (functional)

**r2SCAN**

**DO** Direct optimization

**MOM** Maximum overlap method

**DFT** density functional theory

**TDDFT** Time dependent density functional theory

**SCF** Self consistent field

**ME** Mean error

**RMSE** Root mean square error

**GGA** Generalized gradient approximation

**meta-GGA** meta-generalized gradient approximation

**GMF** Generalized mode following

**CI** Configuration interaction

**CC** Coupled cluster



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# 1 Introduction

Density functional theory (DFT) is a frequently used method in computational modelling and studies of molecules and materials. This stems from the fact that it gives reasonable accuracy without being prohibitively heavy in computational load for general use. While it is mainly used in ground state calculations, there is ongoing development of applying it also in calculations of excited states.

The calculations of excited states is growing in importance, as fields such as ultrafast spectroscopy, solar energy conversion and photocatalysis are in rapid development. In these fields it is often desirable to model the dynamics of atoms after excitation. For this it is necessary to have a low-cost but relatively accurate method of describing the excited states. High level wave function approaches such as multireference and coupled cluster methods are known to give accurate results, but are too computationally expensive for general use, especially in larger system as the computational cost scales rapidly with size.

In recent years, time-dependent density functional theory (TDDFT) has been frequently used in calculations of electronic excitations, especially within the linear response approximation, as it is a computationally efficient method when compared to the higher level approaches. However, this level of theory is quite limited in accuracy as has been shown in many application studies. Among the states that TDDFT struggles to describe accurately are Rydberg states, where an electron is excited to an orbital which is diffuse in that it extends far away from the molecule.

In more recent times, attention has shifted to calculations using time independent DFT in order to describe excited states. Excited state DFT methods target solutions to the Kohn-Sham equations that have higher energy than the ground state. This is done by finding stationary points on the energy surface that describes the energy variation with respect to the electronic degrees of freedom. These methods have been shown to give good results in part because the orbitals are optimized for the excited states instead of working with the ground state orbitals. Furthermore, since the calculations are variational the atomic forces can be evaluated without needing the derivatives of the orbitals, and this opens practical avenues for performing simulations of the atomic dynamics.

Implicit in the DFT description of the electronic system in terms of the electron density rather than a wave functions is self interaction of the electrons. This stems from the fact that DFT describes the classical Coulomb interaction of the system in terms of the total electron density, thereby including interaction of each electron with itself, as can be most easily seen from the description of one-electron systems. A correction for this self interaction should be included in the exchange-correlation (XC) part of the energy functional. However, commonly used XC functionals are semi-local and do not completely cancel out this non-local error. This is especially important for Rydberg states, as the electrons that are in Rydberg orbitals do not have as significant overlap with the other electrons.

Self-interaction correction (SIC) functionals attempt to explicitly correct for this by optimizing the electronic orbitals while subtracting the estimated self interaction error from the total energy. This makes calculations using SIC dependent on the orbital densities, rather than just the total electron density [15].

In this project, the effect of using SIC with the semi-local Perdew-Burke-Ernzerhof (PBE) [21] functional is explored in calculations of excitations from the highest occupied molecular orbitals (HOMO) of ammonia, ethylene, formaldehyde and water molecules into valence and Rydberg excited states. Also, the improvement obtained in DFT results for these excited states by using the less local meta-GGA XC functionals is studied, by carrying out calculations using both the Tao, Perdew, Staroverov and Scuseria (TPSS) functional [22] and the recently developed r2SCAN functional [7].

The thesis is structured in the following way: First there is a discussion of the theory underlying the methods used. After that there is a brief overview of the implementation of the methods and how the results were obtained. Comments on the molecular structures used for the calculations, the timing and convergence rate of the calculations then follow. The results of the calculations of the excitation energy values are then presented, alongside the experimental values as well as theoretical best estimates coming from published higher level quantum chemistry calculations.

## 2 Theory

### 2.1 Schrödinger Equation

The Born-Oppenheimer approximation treats the atomic nuclei and electrons separately. Often this is ascribed to the different time scale of the motion of nuclei vs. that of the electrons due to the mass differences, but more fundamentally this relates to the difference in the excitation energy of nuclear motion vs. the energy of electronic excitations. The approximation breaks down when the difference between electronic levels becomes small (non-adiabatic effects). The Hamiltonian for electrons interacting with stationary nuclei in the absence of an external field is then:

$$\hat{H} = \sum_{i=1}^N \hat{v}(\mathbf{r}_i) + \hat{T} + \hat{V}_{ee} \quad (1)$$

Here,  $\hat{T}$  is the kinetic energy operator,  $\hat{v}(\mathbf{r}_i)$  the Coulomb interaction between the nuclei and the electrons, and  $\hat{V}_{ee}$  is the Coulomb electron-electron interaction. These are given by:

$$\hat{T} = \sum_{i=1}^N -\frac{1}{2} \nabla_i^2 \quad (2)$$

$$\hat{v}(\mathbf{r}_i) = \frac{1}{2} \sum_{a=1}^N \frac{Z_a}{|\mathbf{r}_i - \mathbf{R}_a|} \quad (3)$$

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i,j=1; i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (4)$$

Where  $\mathbf{r}_i$  is the coordinate of an electron,  $\mathbf{R}_a$  and  $Z_a$  the position and charge of nucleus  $a$ , and is  $N$  the total number of electrons in the system.

The time independent Schrödinger equation is given by:

$$\hat{H}|\psi\rangle = E|\psi\rangle \quad (5)$$

The ground state electronic energy can then be found by minimizing the expectation value of the Hamiltonian in equation (1) operating on wave functions  $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  that are properly anti-symmetric and normalized:

$$E_{GS} = \min_{\psi} \langle \psi | \hat{H} | \psi \rangle = \langle \psi_{GS} | \hat{H} | \psi_{GS} \rangle \quad (6)$$

Finding an exact solution to the ground state wave function is a challenging problem, even for small systems, and so various approximate theories need to be applied in order for the calculations to be done efficiently.

## 2.2 Density Functional Theory

The Hohenberg-Kohn theorem states that for a non-degenerate ground state, the energy of the system can be determined from the electron density given by:

$$\rho(\mathbf{r}_1) = N \int \dots \int d^3\mathbf{r}_2 \dots \mathbf{r}_N \psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (7)$$

This seemingly leads to a simplification of the problem of finding the ground state energy, as one can reduce the minimization of many-body wave functions to an energy minimization with respect to the electron density. The electron-electron interaction has the same form for all systems, while the specifics of a given system (such as a particular molecule) is in the electron-nuclei interaction. This can be emphasized by writing the functional as:

$$E_{GS} = \min_{\rho} E_v[\rho] = \min_{\rho} \left\{ \int v(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r} + F_{HK}[\rho] \right\} \quad (8)$$

where  $F_{HK}[\rho]$  is the Hohenberg-Kohn functional that contains all of the terms in the Hamiltonian that do not depend on the electron-nuclei interaction.

$$F_{HK}[\rho] = \langle \psi_{\rho}^{HK} | \hat{T} + \hat{V}_{ee} | \psi_{\rho}^{HK} \rangle. \quad (9)$$

As there are many different wave functions that have the same density, a separate minimization needs to be done to find the wave function that gives the lowest kinetic and electron-electron Coulomb interaction energy for a given density. This leads to the functional:

$$F[\rho] = \min_{\psi \rightarrow \rho} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle \quad (10)$$

Kohn-Sham density functional theory further separates the energy into the following terms:

$$E[\rho] = T_s[\rho] + \int d^3\mathbf{r} \rho(\mathbf{r}) \hat{v}(\mathbf{r}) + U[\rho] + E_{XC}[\rho] \quad (11)$$

Where  $T_s$  is the kinetic energy of the independent electrons,  $U$  is the Hartree energy describing the classical Coulomb interaction of the electrons:

$$U[\rho] = \frac{1}{2} \int \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (12)$$

and the exchange-correlation energy is a term which covers the difference between the actual  $F$  functional and the kinetic and Hartree terms, defined in the following way:



$$E_{XC} = F - U - T_s \quad (13)$$

Simplifying the problem into a system of non-interacting electrons subject to potential  $V_s$ , gives

$$V_s(\mathbf{r}) = v(\mathbf{r}) + \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{XC}[\rho(\mathbf{r})] \quad (14)$$

Then, by assuming that the ground state orbitals can be obtained through orbitals  $\phi_i$  that satisfy the single particle Schrödinger equations (that is to say, that the wave function can be expressed using a Slater determinant), the self consistent Kohn-Sham equations are obtained:

$$\left[ -\frac{1}{2}\nabla^2 + V_s(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad (15)$$

with the density then obtained through:

$$\rho(\mathbf{r}) = \sum_{i=1}^{\text{inf}} f_i |\phi_i|^2 \quad (16)$$

where  $f_i$  are the occupation numbers of the orbitals, with the sum of the occupation numbers being the number of electrons in the system considered,  $\sum_i^{\text{inf}} f_i = N$ .

Solving for the ground state can then be done self-consistently, by starting with a guess for the electron density, then using the density to solve for orbitals, which in turn give a new density that can be used to solve for orbitals again. This process is then carried on until convergence is reached.

Inherent in this approximation of the wave function being a Slater determinant is an error, as the actual wave function cannot be written as a single Slater determinant. This error however is placed along with other errors into the exchange-correlation functional  $E_{XC}$ . The exact functional may well not represent any simplification of the calculation, but this formulation of the problem has motivated the development of approximate analytical functional forms and various parametrizations have been presented. Among commonly used exchange-correlation (XC) functionals are the generalized gradient approximation (GGA) functionals (for example the Perdew-Burke-Ernzerhof (PBE) functional used in this study [21]), where the XC functional is a functional of the electron density  $\rho(\mathbf{r})$  and its gradient  $\nabla\rho(\mathbf{r})$ ; and meta generalized gradient approximation (meta-GGA) functionals (for example the Tao, Perdew Staroverov and Scuseria (TPSS) and (r2SCAN) functionals are of this type [22, 7]), where the laplacian of the electron density  $\nabla^2\rho(\mathbf{r})$  is also involved.

## 2.3 Self-Interaction Correction

The Hartree energy term described in equation (12) and the corresponding terms in the Kohn-Sham equations (15), applies a potential from all of the electrons to each electron. This includes the electron density of the electron considered. This is incorrect in reality, as

electrons should not be affected by a potential from themselves. In the case of a one-electron system, this would lead a non-zero Hartree energy due to the electron interacting with itself.

This self-interaction error is a part of the errors that the XC functionals are supposed to correct. But, the semi-local form of practical XC functionals means that they are incapable of fully subtracting out the non-local self interaction. One can, however, choose to perform this correction explicitly. Perdew and Zunger proposed such an orbital-by-orbital self-interaction correction (PZ-SIZ, below simply referred to as SIC). The functional for the SIC energy can then be described in the following way:

$$E_{SIC}[\rho] = E_{KS}[\rho] - \sum_i^N (U[\rho_i] + E_{XC}[\rho_i]) \quad (17)$$

Where  $E_{KS}$  is the Kohn-Sham energy described in equation (11) and  $\rho_i$  is the electron density associated with orbital  $i$ .

Applying this correction leads to a dependence on the orbital densities, making it an orbital density dependent (ODD) functional. The energy is therefore no longer unitary invariant with respect to the orbitals, i.e. different linear combinations of the orbitals give different values of the energy.  $|\xi\rangle = \mathbf{U}|\psi\rangle$  will not necessarily have the same SIC energy as  $|\psi\rangle$ . The corrected energy is then a function of both the orbitals and unitary transformations of those,  $E_{SIC}[\mathbf{U}, \psi]$ .

Minimizing this  $E_{SIC}$  for a given wave function then involves rotating the wave function so that the term  $\sum_i^N (U[\rho_i] + E_{XC}[\rho_i])$  is minimized. This can be done in an inner loop of the calculations, and the whole calculation can be viewed as a minimization of a single functional:

$$F_{SIC}[\psi] = \min_{\mathbf{U}} E_{SIC}[\mathbf{U}, \psi] \quad (18)$$

This functional can then be minimized to get a self consistent result [15, 13, 14].

The need for SIC in calculations of Rydberg states is important, as local and semi-local XC functionals do not give the  $-1/r$  curve expected from Coulomb interaction. SIC has previously been shown to get the shape of the potential curve far away from atomic nuclei correctly [8].

## 2.4 Spin Purification

The singlet excitations calculated here are single electron excitation to open-shell singlet states with two unpaired electrons. The singlet state resulting from an excitation from orbital  $r$  to orbital  $s$  will be denoted as  $|^1\Phi_r^s\rangle$ . The single determinants that are calculated using variational calculations by exciting an electron in the same spin channel ( $|\phi_r^s\rangle$ ), however, are not singlet states but rather mixed spin states, as they have an expectation value of  $\mathbf{S}^2 = 1$  for the total spin. The triplet states ( $|^3\Phi_r^s\rangle$ ) can however be described using a single determinant.

The pure singlet and triplet states can, however, be described using a linear combination of the single determinants with the unpaired electrons in differing spin channels:

$$|^1\Phi_r^s\rangle = \frac{1}{\sqrt{2}} (|\phi_r^s\rangle + |\phi_{\bar{r}}^{\bar{s}}\rangle) \quad (19)$$

$$|^3\Phi_r^s\rangle = \frac{1}{\sqrt{2}} (|\phi_r^s\rangle - |\phi_{\bar{r}}^{\bar{s}}\rangle) \quad (20)$$

Combining equations (19) and (20) we get:

$$|\phi_r^s\rangle = \frac{1}{\sqrt{2}} (|^1\Phi_r^s\rangle + |^3\Phi_r^s\rangle). \quad (21)$$

By taking the expectation value of the Hamiltonian with respect to  $|\phi_r^s\rangle$  as expressed in (21) and rearranging we get the following value for the energy of the singlet state:

$$\langle ^1\Phi_r^s | \mathbf{H} | ^1\Phi_r^s \rangle = 2\langle \phi_r^s | \mathbf{H} | \phi_r^s \rangle - \langle ^3\Phi_r^s | \mathbf{H} | ^3\Phi_r^s \rangle \quad (22)$$

Equation (22) can then be expressed using the energy values obtained for the mixed spin state ( $E_M$ ) and the triplet state ( $E_T$ ):

$$E_S = 2E_M - E_T. \quad (23)$$

Equation (23) is often referred to as Ziegler's rule [16].

This spin purification formula was used in this project in order to obtain excitation energy values for the singlet states. One should note however, that this assumes that the wave functions obtained in the mixed spin state and the triplet state are the same, which is not the case when the two are found variationally. This also means that the singlet state cannot be said to be found fully variationally. Ideally, the linear combination of the two states should be variationally optimized, not the two determinants separately. But, this has not yet been implemented.



## 3 Methods

### 3.1 General Parameters

All of the DFT calculations are performed using the Atomic Simulation Environment (ASE) and GPAW packages. The geometry optimizations carried out for comparison with results of Hartree-Fock theory, shown in tables 4.1 and 4.4, are however done using the ORCA software.

The DFT calculations are performed for molecules surrounded by vacuum and use the semilocal PBE, TPSS or r2SCAN exchange-correlation functionals. The orbitals are represented on a real space grid. The convergence criteria for the self consistent field cycle are (default in GPAW):

- Energy change over the last three cycles should be less than 0.5 meV per valence electron
- The change in density should be less than 0.0001 electrons per valence electrons
- The integrated value of the square of the residual of the Kohn-Sham equations should be less than  $4.0 \times 10^{-8}$  eV<sup>2</sup> per valence electron[1]

In some cases a small adjustment to the default criteria is made in that the convergence criterion for the residual is changed to  $1.0 \times 10^{-6}$  eV<sup>2</sup> per valence electron while the calculations fulfilled all of the other convergence criteria.

Unlike in the default settings, however, the unoccupied orbitals are also converged for the ground-state calculations, in addition to the occupied orbitals. The initial guess orbitals for an excited-state calculations are obtained from the ground-state orbitals by swapping the occupation numbers of an occupied orbital (electron donor) and an unoccupied orbital (acceptor). The excitation energy is calculated by subtracting the ground-state energy from the excited-state energy at the same geometry.

All of the DFT calculations are done using a cubic simulation cell with side lengths of 20 Å. The valence electrons were described using a uniform grid with a mesh size of  $\sim 0.15$  Å. All of the calculations of the wave functions, except for the ones using r2SCAN, are done on a real space grid. This was chosen as it is easier to obtain convergence with real space grid basis functions, by simply reducing the grid spacing, when compared to using linear combinations of atomic orbitals, where attaining convergence with respect to the basis set chosen can be difficult.

The calculations with r2SCAN are done using a plane wave expansion of the wave functions, with a cutoff energy of 340 eV for the plane waves. This is done in order for the calculations to converge, as convergence turns out to be quite difficult using a real space grid to represent the orbitals. The r2SCAN is known to be hard to converge because of rapidly varying terms that require an exceptionally smooth representation of the orbitals. The plane wave representation gives smoother orbitals than real space grid.

## 3.2 Direct Optimisation

Excited states of molecules can be described as solutions to the Kohn-Sham equations (equation (15)) with non-aufbau occupation of the orbitals. These solutions correspond to stationary points on the energy surface corresponding to the functional used. These stationary points typically correspond to saddle points since the system can lower its energy by sliding down to the ground state, which is represented by a minimum on the energy surface.

In order to find these solutions, the excited state wave function  $\Psi$  is expanded as a linear combination of some auxiliary orbitals  $\Phi$ :

$$\Psi = U\Phi \quad (24)$$

where  $U$  is a unitary matrix. The auxiliary orbitals may be chosen as the ground state orbitals or any set of orbitals that give an initial guess for the excited state. The energy of the excited state can then be denoted as a functional of both the rotation  $U$  and the auxiliary orbitals  $\Phi$

$$E[\Psi] = E[U\Phi] = F[U, \Phi]. \quad (25)$$

Then, the search for stationary points can be simplified in a similar manner as was explained for SIC above. A search for stationary points of the functional  $E$  can be done in two steps. In an inner loop the functional  $F$  is converged to a stationary point as desired, and in an outer loop the following functional is minimized:

$$L[\Phi] = \text{stat}_U F[U, \Phi]. \quad (26)$$

This reduces the number of dimensions the saddle point search is operated on. In GPAW this has been implemented using a quasi-Newton method for finding saddle points in the space of the unitary matrices  $U$  [12].

This method for optimizing  $E$  for excited states was used in the present study along with the maximum overlap method (MOM) to converge on a solution for the desired occupation numbers. There, the overlap between the initial guess for the excited state orbitals  $|\phi_i\rangle$  that are occupied, and the orbitals  $|\phi_k^{(m)}\rangle$  at iteration number  $m$  of the wave function operation, is used to determine the occupation numbers of the new orbitals in each step. The overlap between two states is given by:

$$O_{i,k}^{(m)} = \langle \phi_i | \phi_k^{(m)} \rangle. \quad (27)$$

The occupation numbers chosen are then the ones that give the highest value of the following projection:

$$P_k^{(m)} = \left( \sum_{i=1}^N |O_{i,k}^{(m)}|^2 \right)^{1/2} \quad (28)$$

This is used in order to try to prevent the calculations from falling down to another solution or even the ground state [9]. This has also been implemented in GPAW.

When DO is used with SIC, it results in a three-loop optimization [12].

### 3.3 Methods Considered

Four different molecules were considered in this study: ammonia, ethylene, formaldehyde and water. A total of 36 Rydberg state and 4 valence state excitations were calculated.

Calculations using five different functionals were compared: (1) PBE functional, (2) PBE functional with SIC and real valued orbitals ( $SIC_R$ ), (3) PBE functional with SIC and complex valued orbitals ( $SIC_C$ ), (4) TPSS functional, and (5) the newly developed r2SCAN functional.

Often when SIC is used, it is scaled by 1/2, which generally gives better results for the ground state [13, 14]. Here however, only full SIC will be considered, as it is only with full SIC that the potential curve for electrons far away from the atom nuclei has the correct form [8].





## 4 Results

### 4.1 Molecular geometries

A comparison was made of the optimal structure obtained for the molecules when the ground state energy is minimized using PBE, SIC<sub>R</sub>, SIC<sub>C</sub>, TPSS, and r2SCAN, as well as using Hartree-Fock theory for NH<sub>3</sub> and H<sub>2</sub>O. The resulting bond lengths and angles of each structure obtained by relaxation can be seen in tables 4.1, 4.2, 4.3 and 4.4; alongside experimental values from [11].

*Table 4.1. Molecular geometry of ammonia obtained using the various functionals.*

Bond lengths [Å] Angles [deg]	Exp. <sup>a</sup>	PBE	SIC <sub>R</sub>	SIC <sub>C</sub>	1/2 SIC <sub>C</sub>	HF	TPSS	r2SCAN
N-H	1.012	1.022	1.005	0.994	1.006	1.008	1.017	1.048
H-N-H angle	106.7	106.4	106.8	111.9	109.3	107.6	106.5	102.1
				113.7	109.9			
				111.7	109.8			

<sup>a</sup>. From reference [11]

For ammonia the symmetry was broken when using complex orbital SIC. The same also happened when using complex SIC scaled by 1/2. It is well documented that SIC calculations can lead to symmetry breaking and that seems to be the case here [15].

*Table 4.2. Molecular geometry of ethylene obtained using the various functionals.*

Bond lengths [Å] Angles [deg]	Exp. <sup>a</sup>	PBE	SIC <sub>R</sub>	SIC <sub>C</sub>	1/2 SIC <sub>C</sub>	TPSS	r2SCAN
H-C	1.082	1.092	1.076	1.073	1.082	1.085	1.093
C-C	1.329	1.333	1.321	1.331	1.332	1.331	1.332
H-C-C angle	117.2	116.6	116.4	118.2	117.4	116.5	116.8

<sup>a</sup>. From reference [11]

The structures of ethylene and formaldehyde were relatively consistent for all the functionals, with bond angles at most 1° off the experimental values. The bond lengths show slightly greater variation, with H-C and C-O bond lengths calculated using SIC functionals showing the greatest deviation from the experimental values (largest error about 0.03 Å).

For the H<sub>2</sub>O molecule, all the structures obtained retain the C<sub>2v</sub> symmetry. Here, however, there is great variation in the bond angle, with the values spanning a range of 8°. The bond lengths show a similar variation as with the other molecules of about 0.03 Å.

Table 4.3. Molecular geometry of formaldehyde obtained using the various functionals.

Bond lengths [ $\text{\AA}$ ] Angles [deg]	Exp. <sup>a</sup>	PBE	SIC <sub>R</sub>	SIC <sub>C</sub>	1/2 SIC <sub>C</sub>	TPSS	r2SCAN
C-H	1.116	1.118	1.088	1.093	1.104	1.109	1.118
C-O	1.212	1.209	1.191	1.186	1.196	1.209	1.225
H-C-O angle		122	121.4	121.8	121.8	122	121.9
H-C-H angle	116.5	115.9	117.3	116.5	116.3	116.1	116.3

<sup>a</sup>. From reference [11]

Table 4.4. Molecular geometry of the water molecule obtained using the various functionals.

Bond lengths [ $\text{\AA}$ ] Angles [deg]	Ex. <sup>a</sup>	PBE	SIC <sub>R</sub>	SIC <sub>C</sub>	1/2 SIC <sub>C</sub>	HF	TPSS	r2SCAN
H-O	0.9575	0.972	0.95	0.958	0.954	0.943	0.969	0.982
H-O-H angle	104.51	104.2	105.2	110.2	107.4	105.9	104.3	102.3

<sup>a</sup>. From reference [11]

PZ-SIC is known for over-correcting when there are significant overlaps between the orbitals [15, 12]. This causes the bond lengths to contract when compared with the structures calculated without SIC. This can be seen to various degrees for all of the molecules. When comparing the structures with respect to having real or complex orbitals with SIC the results are mixed. In some cases the bonds are lengthened with complex orbitals, while in other cases they are shortened even further.

Overall the most dramatic changes in structure were in ammonia and water molecules. Here, the bond angles are increased significantly when using SIC functionals, especially with complex orbitals, compared to the other values and have quite a large error when compared to the experimental values. The results of the Hartree-Fock calculations for these molecules show a similar increase in the bond angles, but to a smaller degree than with complex SIC. Calculations with full SIC have previously been shown to give similar results as Hartree-Fock calculations in certain situations.

This points to relaxation with SIC using complex orbitals being an unreliable functional for determining the structure of molecules. As is shown below, the structure has a significant effect on the calculated excitation energy values, and for the ammonia and water molecules the values from the structures obtained using complex SIC have significant systematic errors.

Also shown in the tables with the molecular geometries are the results obtained using complex wave function PBE with SIC scaled by 1/2. The values for both the bond lengths and bond angles obtained using this functional are all roughly in the middle between the PBE calculations without SIC and the full SIC values.

SIC scaled with 1/2 and using real orbitals with PBE gives relatively good estimates for the molecular structures, as the experimental values for the bond lengths and angles are in many

Table 4.5. Excitation energy values (in eV) of the HOMO  $\rightarrow$  LUMO excitation in an ammonia molecule, using different functionals and differing structures. The relative energy of the ground state compared to the optimised geometry is also presented.

Structure Functional	Ground state energy w.r.t. optimised structure	mixed spin	singlet	triplet
<b>Experimental</b>				
PBE	0.006	6.281	6.424	6.139
SIC <sub>R</sub>	0.003	6.002	6.142	5.861
SIC <sub>C</sub>	0.049	6.196	6.347	6.045
<b>PBE</b>				
PBE	0.000	6.253	6.399	6.107
SIC <sub>R</sub>	0.019	5.987	6.131	5.844
SIC <sub>C</sub>	0.081	6.166	6.318	6.014
<b>SIC<sub>R</sub></b>				
SIC <sub>R</sub>	0.000	6.027	6.165	5.889
<b>SIC<sub>C</sub></b>				
SIC <sub>C</sub>	0.000	5.911	6.061	5.760

cases in between the values obtained using real wave function PBE calculations with and without SIC. SIC scaled by 1/2 has also been shown to give good results for ground state calculations, as the scaling seems to fix the over-correction that SIC does to a certain degree [15, 12]. This however was not done in this study, but rather the experimental structures were generally used when presenting results of excitation energy from SIC calculations.

Interestingly, r2SCAN seemed to have the opposite error when compared to the SIC calculations using PBE. There, the bond lengths tended to be lengthened when compared to other functionals, and the bond angles in ammonia and water decreased significantly. This might mean that using r2SCAN is not an optimal functional for determining molecular geometry, especially considering the computational cost and time required for calculations using that functional compared to other functionals that are cheaper and generally give good results for molecular geometry.

## 4.2 Effect of Molecular Structure on Excitation Energy Values

In tables 4.5 and 4.6 the excitation energy values for ammonia and water using the PBE functional, with and without SIC, with the different molecular geometries given above are shown. The relative energy of the ground state for each structure using the different functionals, compared to their respective optimised structures are also shown.

The difference in energy is small (less than 0.05 eV) for the PBE and SIC<sub>R</sub> functionals, while the SIC<sub>C</sub> functional seems to be somewhat more sensitive to changes in geometry. This stems largely from the fact that the SIC<sub>C</sub> geometry for both water and ammonia differ much more from the structures obtained by other functionals, as can be seen in tables 4.1 and 4.4.

Table 4.6. Excitation energy values of the HOMO  $\rightarrow$  LUMO excitation of a water molecule, using different functionals and differing structures. The relative energy of the ground state is also presented.

Structure Functional	Ground state energy w.r.t. optimised structure	mixed spin	singlet	triplet
<b>Experimental</b>				
PBE	0.010	7.277	7.454	7.100
SIC <sub>R</sub>	0.004	6.739	6.887	6.591
SIC <sub>C</sub>	0.028	7.284	7.458	7.111
<b>PBE</b>				
PBE	0.000	7.161	7.342	6.980
SIC <sub>R</sub>	0.027	6.645	6.795	6.495
SIC <sub>C</sub>	0.048	7.140	7.264	7.015
<b>SIC<sub>R</sub></b>				
SIC <sub>R</sub>	0.000	6.790	6.937	6.643
<b>SIC<sub>C</sub></b>				
SIC <sub>C</sub>	0.000	7.409	7.585	7.233

The difference in excitation energy values stems partially from the lowering of the ground state, but to a larger degree from changes in the energy of the excited state. For the two SIC functionals, the excitation energy is reduced both due to increased energy of the ground state and lowering of the energy of the excited state.

The energy surface of the Rydberg states can be approximated with the energy surface of the cations of the molecules, as the excited electron is far enough away in order to not have a significant effect on the optimal location of the atom cores. This is not to say that the energy surfaces are completely the same, however, similar trends can be seen. Both for the water and ammonia molecules, ionization leads to increased bond lengths, and this is expected to lower the energy of the Rydberg state.

As can be seen from the data presented here, the bond lengths are shortened in the order:

$$PBE > Experimental > SIC, \quad (29)$$

as seen in tables 4.1 and 4.4.

For the PBE functional, the lowering of the ground state energy involved in changing from the experimental structure to the PBE relaxed structure, as the bond lengths are increased, is less than the lowering of the energy of the excited states, resulting in a lower excitation energy when lengthening the bond, as is seen with the other functionals.

For ethylene and formaldehyde, the structures did not change as dramatically as for ammonia and water molecules. The trends in excitation energy were similar as for ammonia and water, and can be explained in a similar way.

Table 4.7. The rate of failure of the excited state calculations where the calculations did not manage to converge to any state.

Functional	# of calculations	# of failed calculations	Failure rate [%]
PBE	80	0	0.0
SIC <sub>R</sub>	120	1	0.83
SIC <sub>C</sub>	120	1	0.83
TPSS	40	8	20
r2SCAN	40	1	2.5

### 4.3 Convergence of Calculations

In general, the calculations converged without significant problems. Table 4.7 shows the rate of failure using the different functionals, where the calculations simply did not converge to any state. There was only one instance of failure in each of the SIC, SIC<sub>C</sub> and r2SCAN functionals, while the TPSS calculations had for some reason difficulty in handling the excited states of ethylene and has therefore a much higher failure rate.

A greater problem for convergence however, were issues relating to the use of the DO-MOM method. Calculations of excited states could often fall down to a lower excited or ground state, and in some cases even, the calculations converged to a higher excitation. The rate of missing excitation values in the results presented further below is shown in table 4.8. This type of collapse was especially prominent with r2SCAN and the SIC functionals.

Table 4.8. The number of excited states for which a converged solution was not found; whether due to failed convergence of the calculations, or due to a collapse to a different state.

Functional	# of states	# of missing states	Missing excited states [%]
PBE	76	5	6.6
SIC <sub>R</sub>	38	10	26.3
SIC <sub>C</sub>	38	10	26.3
TPSS	38	8	21.0
r2SCAN	38	18	47.4

When calculations failed to converge or collapsed to different states, different approaches were used to try to get better convergence. In the case where calculations using complex orbitals using SIC failed to converge, while the calculations using real valued functions did, I developed a method to copy the wave functions from the real valued solution and rotating the wave function in the complex plane to use as an initial guess in the complex value calculations. This rotation should in theory be enough to get the wave function to converge to another solution other than the real valued one.

However, when doing these rotations, in some cases the real valued solution seemed to be degenerate and the calculations ended up converging to a state with the same energy, but with significant imaginary components in the orbitals.

Another method I used in order to achieve convergence to the correct states when either the mixed spin solution or the triplet state converged, but the other did not, was to use the

solutions given there as an initial guess. When the triplet state converged, the wave functions describing the orbitals in the spin channel where the excited electron in the triplet state was, were copied over to the other spin channel and the occupation numbers redefined and the result used as an initial guess. When the mixed spin state converged while the triplet state did not, then the same total wave function was used as an initial guess, just with revised occupation numbers.

In other cases the wave functions acquired using other methods were copied and used as an initial guess, but this was only possible when using the same geometry. These methods to try to get convergence to the correct state had varying degrees of success.

## 4.4 Timing of Calculations

A systematic difference in the number of steps required to reach convergence in the calculations with or without SIC was not noted when comparing ground state calculations. The functional that converged using the fewest steps varied between the molecules and the molecular geometries. In the cases where there is a dramatic difference in the number of steps required between the various functionals, the reason is mainly related to difficulty in reducing the residual of the Kohn-Sham equations enough to fit the convergence criterion. That is to say, all the functionals using PBE seem to get down to  $10^{-5} eV^2/e^-$  at roughly the same number of steps, but reducing it further needed varying amounts of steps. My impression is that the calculations using SIC were slightly more prone to needing more steps to further reduce the residuals, than the calculations without SIC.

*Table 4.9. Timing of calculations of the ground state of the ammonia molecule.*

Timing of calculations	PBE	SIC <sub>R</sub>	SIC <sub>C</sub>	TPSS	r2SCAN
# of steps	28	25	32	26	20
Total [s]	69	115	395	77	1074
SCF cycle [s]	64	109	388	72	1061
SIC e/g grid [s]		58	204		

The total time of the calculations of the ground state of ammonia using the different functionals are shown in table 4.9. Also shown are specifically the time taken for initial localization, the time for the SCF cycle, and the time needed for the SIC energy gradient calculations. For the calculations using the TPSS and r2SCAN functionals, initial localization was not used.

As expected, the main difference between the calculations using PBE with and without SIC comes from the time used in the extra inner loop where the orbitals are optimized for SIC. Also of note is that the complex orbital calculations took almost four times as long as the real valued calculations, as mathematical operations such as multiplication, division etc. using complex numbers require four real number operations of the same type.

The table shows that the r2SCAN calculations are computationally the heaviest and dwarf the cost of using SIC. As SIC calculations using meta-GGA functionals were not done in this project, it remains to be seen whether the time taken for the SIC calculations scale exactly as the general calculation times between different functionals, but calculations using TPSS do seem feasible, while the cost of SIC calculations using r2SCAN may be excessively high.

Table 4.10. Excitation energy values obtained using DO-MOM compared to differences between orbital energy eigenvalues in the ground state. All energy values are in eV.

Molecule	State	$\Delta\epsilon$ PBE	DO-MOM PBE	Experimental
$H_2O$	3s	6.32	7.45	7.40
	3p <sub>y</sub>	7.55	8.91	9.10
$C_2H_4$	3s	5.81	6.85	7.09
	3p <sub>y</sub>	6.51	7.92	7.97

## 4.5 Direct Optimization Compared to Orbital Eigenvalues

Table 4.10 shows the excitation energy values resulting from DO-MOM calculations of water and formaldehyde molecules, compared with the difference between the eigenvalue of the highest occupied orbital and the targeted orbital in the ground state. For both molecules, the eigenvalue of the 3p<sub>y</sub> state is positive, which would mean that an electron placed in that orbital would be pushed away from the molecule. By using DO-MOM to converge on an excited state solution brings the excitation energy much more in line with experimental results, when compared with taking simply the difference between the eigenvalues of the orbitals. This shows that while orbital energy values obtained in ground state DFT calculations are not good indicators of excitation energy, the variational calculations of excited states with non-aufbau orbital occupation numbers can give excitation energy in good agreement with experimental estimates.

## 4.6 Effect of Self-Interaction Correction

Table 4.11 shows the energy contribution from each term in the calculation of the ground state and the mixed spin HOMO  $\rightarrow$  LUMO excited state of the ammonia molecule. It is clear that the use of SIC in variational calculations has a large effect, as it leads to convergence to another electron density, evidenced by the differing, potential, kinetic and XC energy contributions. These solutions are higher in energy than the solutions calculated without SIC.

The use of complex orbitals with SIC allow the calculations to converge to a solution that is lower in energy, both in the ground state and in the excited state. Here one should note that the real valued orbital results are also solutions to the calculations using complex wave functions. Generally, the lowering of the ground state is larger than the lowering of the excited state when switching to complex orbitals, resulting in larger excitation energy values.

## 4.7 Excitation Energy Values

The excitation energy values obtained using the optimized ground state structure of the four molecules considered, with the PBE functional with and without SIC, are given in tables A.1, A.3, A.5 and A.7. The excitation energy values obtained using the different functionals in the

Table 4.11. Energy contributions of the ground state and the HOMO  $\rightarrow$  LOMO mixed spin excited state of ammonia using the experimental molecular geometry.

Energy contribution	PBE	SIC <sub>R</sub>	SIC <sub>C</sub>
<b>Ground</b>			
Kinetic	+20.45	+14.21	+14.14
Potential	-23.07	-16.51	-16.61
XC	-17.25	-17.32	-17.17
Local	+0.26	+0.24	+0.26
SIC		+2.52	+2.03
Total energy	-19.61	-16.86	-17.35
<b>Mixed spin state</b>			
Kinetic	+19.85	+12.48	+12.69
Potential	-20.45	-13.43	-13.64
XC	-12.98	-12.40	-12.41
Local	+0.25	+0.24	+0.25
SIC		+2.25	+1.95
Total energy	-13.33	-10.85	-11.15
<b>Excitation energy</b>	6.28	6.00	6.20

optimized geometry for each functional are given in tables A.2, A.4, A.6 and A.8. The results presented in the tables are shown in figures 4.1, 4.3, 4.6 and 4.8.

Interestingly, even when the excitation is to an orbital that has a positive eigenvalue in the ground state PBE calculation, the variational calculation using the DO-MOM method and uncorrected PBE functional converges without any problem on a bound excited state. Values were obtained using PBE for all of the excitations considered, except for a couple in ethylene where the calculations converged on a different state than was desired.

The calculations using SIC with complex orbitals, with the single exception of the singlet valence excitation in ethylene, give larger excitation energy when compared to calculations using real valued orbitals and SIC. Generally this also lead to similar or higher excitation energy values than were obtained without SIC.

The excitation energy values obtained using only PBE were at times remarkably close to the experimental values, but in general tended to be slightly too low. The use of SIC with complex orbitals in most cases raised the excitation energy and gave closer agreement with the experimental values in the cases where the calculations without SIC were lower than the experimental values.

For water and ammonia, the real valued SIC calculations give a lower excitation energy than PBE without SIC. For ethylene and formaldehyde however, the results are a bit more mixed. The Rydberg states in ethylene are lowered in energy, while the valence states are raised in energy. For formaldehyde, the Rydberg states were either unaltered or slightly raised in energy, while the singlet valence state lowered in energy and the triplet state was raised.



### 4.7.1 Ammonia

In ammonia, the excitation energy for the degenerate singlet  $3p_{xy}$  state was underestimated by all of the functionals, except for the calculations using r2SCAN. The results from that calculation must be taken with a grain of salt however, as the geometry did change significantly during relaxation, and it remains to be seen if the functional would give the same result with the experimental geometry.

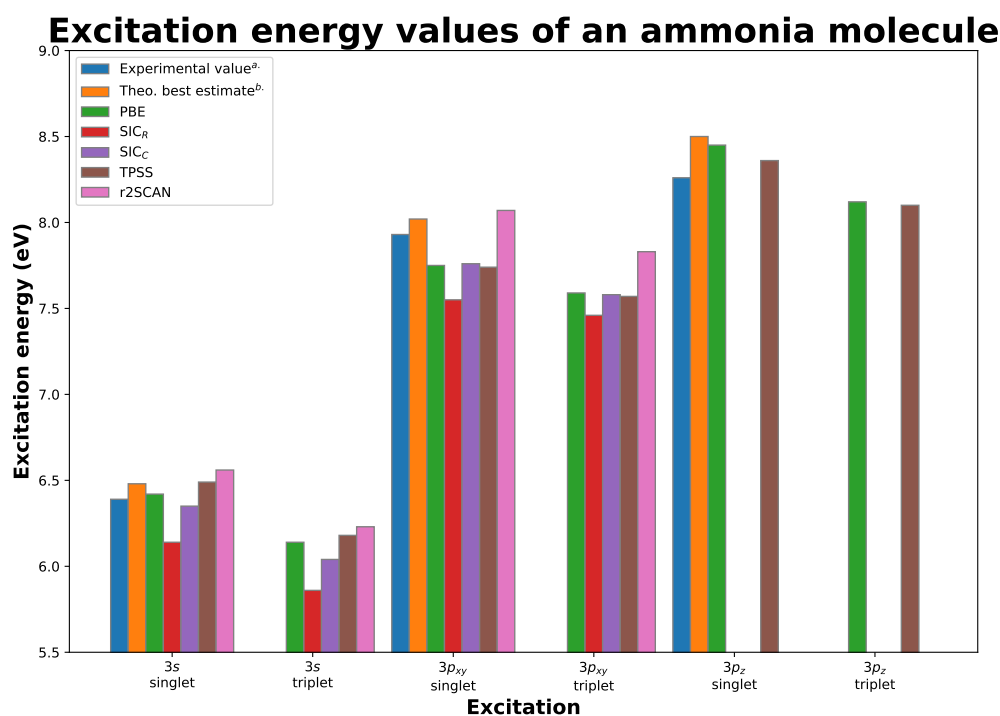


Figure 4.1. Energy values for excitations from HOMO to different Rydberg states in an ammonia molecule, calculated using different functionals. The experimental structure is used for the PBE, SIC<sub>R</sub> and SIC<sub>C</sub> functionals, while the optimised structures are used with the TPSS and r2SCAN functionals.

<sup>a</sup>. Experimental values from [10]

<sup>b</sup>. Theoretical best estimate from [2]

For the other two singlet excitation energy values, the calculations using PBE without SIC seem to be in reasonable agreement with the experimental values. For the  $3p_z$  state, it seems however that the calculations converged to a slightly different mixed spin state in the experimental geometry, compared with the calculations with the optimized structure. This has resulted in a difference in the estimated excitation energy for the singlet state. Using SIC with complex wave functions gives similar results.

### 4.7.2 Ethylene

Special comment has to be made about the  $\pi \rightarrow \pi^*$  in ethylene. The singlet state is significantly higher in energy than the triplet state. This high energy results from the anti-bonding orbital having the same symmetry as the  $3d_{xz}$  Rydberg state and therefore mixing with it. This can be seen in figure 4.4 which shows the orbitals of the valence excited state obtained through the

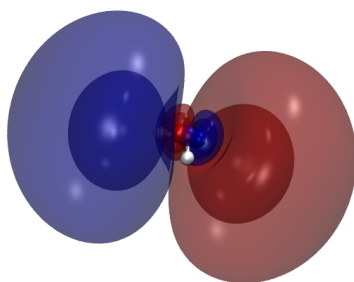


Figure 4.2. The  $3p_{xy}$  orbital in an ammonia molecule calculated using the PBE functional for the experimental structure. The isosurfaces shown are 0.1, 0.025 and  $0.00625 \text{ \AA}^{-3/2}$ . The red surfaces are positive isosurfaces and the blue surfaces are negative.

SIC<sub>R</sub> functional. The singlet state shown in 4.4a is more diffuse than the triplet state shown in 4.4b due to this mixing. This mixing is also the cause of the valence excitation being higher in energy than the  $3s$  Rydberg state.

The theoretical best estimates from various sources give the value of this  $\pi \rightarrow \pi^*$  at around 8.0 eV, which is higher than the experimental value given as 7.60 eV ([6] however gives a value of 7.68 eV). This is seemingly because of problems overcoming biases in the selection of basis sets in CI and CC calculations [6].

Out of the functionals considered, the calculations using SIC as well as the calculation using the r2SCAN functional give the correct order of the singlet states, with the valence state higher in energy than the  $3s$  Rydberg state. The TPSS functional gives the energy values quite close to each other, while PBE gives an excitation energy for the valence excitation that is too low.

The results from the direct optimization using SIC with real wave functions are quite close to previous theoretical best estimates, using configuration interaction (CI) and coupled cluster (CC) calculations. The calculations using SIC with complex wave functions however, are closer to the experimental values, especially the value given in [11].

For the triplet  $\pi \rightarrow \pi^*$  state in ethylene however, the excitation energy is closest to the experimental value in the TPSS calculations. The r2SCAN functional gives a lower excitation energy for this state, while the PBE calculation seem to be in agreement with the theoretical best estimates, but when using SIC with complex wave functions, the energy of this state is raised even higher.

### 4.7.3 Formaldehyde

The excitation energy values of formaldehyde were overall best estimated using SIC with complex wave functions, out of the functionals considered. However the error for many of the states are comparatively large when compared to the other molecules considered. This

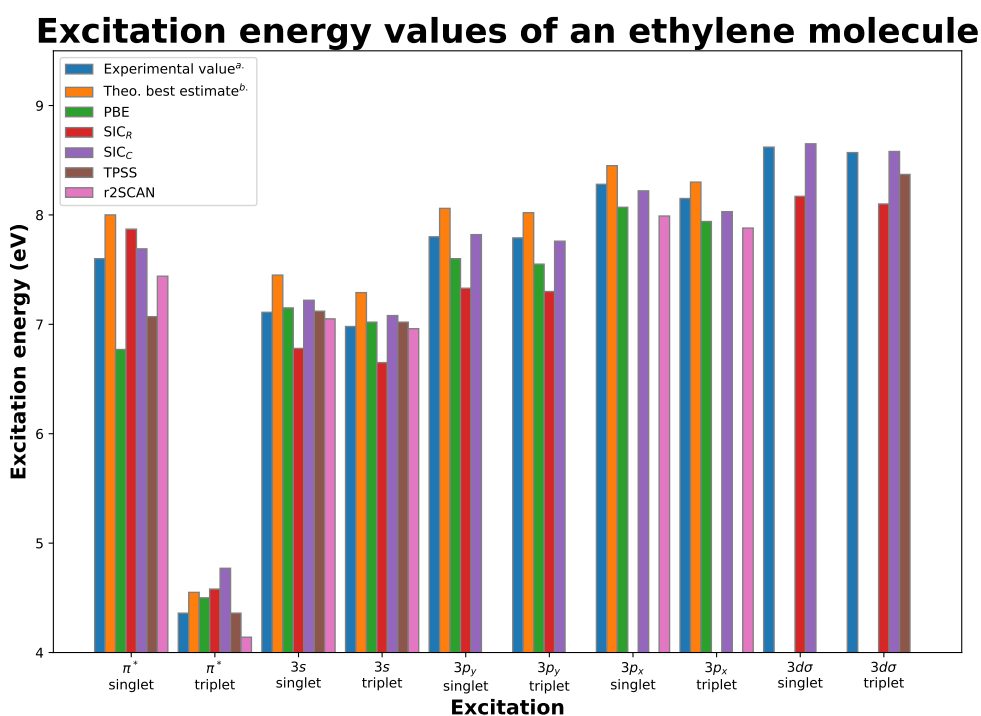


Figure 4.3. Energy values for excitations from HOMO to different valence and Rydberg states in an ethylene molecule, calculated using different functionals. The experimental structure is used for the PBE, SIC<sub>R</sub> and SIC<sub>C</sub> functionals, while the optimised structures are used with the TPSS and r2SCAN functionals.

<sup>a</sup>. Experimental values from [24]

<sup>b</sup>. Theoretical best estimate from [6]

is especially noticeable in the value for the  $\pi \rightarrow \pi^*$  singlet excitation. The energy for that excitation is underestimated to various degrees in all of the functionals considered. The causes of this need to be further investigated.

The calculations using the TPSS functional resulted in 3p Rydberg orbitals that were very skewed. The alignment of the orbitals were shifted off the axes by varying degrees, and was especially prominent for the 3p<sub>x</sub> state (The singlet 3p<sub>x</sub> state here was ignored when plotting the errors in figure 4.10). This may be the result of some unintended mixing between different Rydberg states and could explain the higher error using TPSS for formaldehyde than for other molecules.

#### 4.7.4 Water

Calculations of the water molecule showed the same trends as for the other molecules. Calculations using SIC with complex orbitals resulted in excitation energy values that were in closest agreement with the experimental values. Calculations using the r2SCAN functional were particularly prone to falling to another state, resulting in only the 3s orbital being described using the functional.

As with all of the molecules, the higher-level calculations used as theoretical best estimates



(a) Mixed spin state

(b) Triplet state

Figure 4.4. The  $\pi^*$  anti-bonding orbital of an ethylene molecule calculated using the  $SIC_R$  functional on the experimental structure. (a) shows the mixed spin state whereas (b) shows the triplet state. The isosurfaces shown are 0.1, 0.025 and  $0.00625 \text{ \AA}^{-3/2}$ . The red surfaces are positive isosurfaces and the blue surfaces are negative. The mixed spin state shows more of a Rydberg character compared to the triplet state.

resulted in excitation energy values that are too high, however, this is most prominent for the water molecule, with the values for the  $3p$  orbitals displaying particularly bad agreement with experimental values. The calculations performed here using the various functionals did not, however, show a greater error than for the other molecules considered.

#### 4.7.5 Errors

Figure 4.10 shows the range of errors of the values obtained using the different functionals when compared to the experimental values, as well as the mean error for each functional. Table 4.12 shows the mean error (ME), root mean square error (RMSE) and the mean absolute error (MAE) of all of the calculated excitation energy values, compared with the experimental values where they exist.

This figure and table shows that using PBE with complex orbitals and SIC gave the lowest errors overall. This was especially true for the Rydberg states considered, but it was only for PBE and PBE with SIC using complex orbitals that there was a significant decrease in RMSE and MAE when excluding the valence excitations. Using SIC with real valued orbitals, however, gave worse results than without SIC. This highlights the importance of using complex orbitals when implementing SIC.

The meta-GGA functionals considered here did not give significantly better results overall than the PBE functional, but this might be explained by the fact that there are comparatively fewer excitation values obtained using these functionals, so outliers might have a larger effect on the overall picture. This needs to be explored further. In figure 4.10, however, the range of the errors from r2SCAN is shown to have a slightly smaller spread than PBE. Using SIC with this functional might improve results significantly, as it does with PBE.

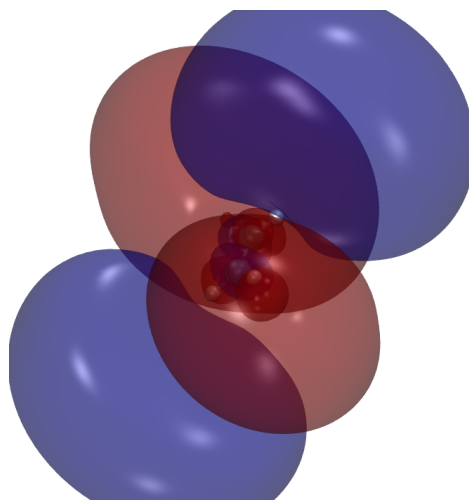


Figure 4.5. The  $3d\delta$  orbital in an ethylene molecule calculated using the PBE functional for the experimental structure. The isosurfaces shown are 0.1, 0.025 and  $0.00625 \text{ \AA}^{-3/2}$ . The red surfaces are positive isosurfaces and the blue surfaces are negative.

Table 4.12. Errors of all of the excitation energy values calculated with the different functionals. The experimental structure is used for the PBE,  $SIC_R$  and  $SIC_C$  functionals, while the optimised structures are used with the TPSS and r2SCAN functionals. All values are in eV.

Functional	All states			Rydberg states only		
	ME	RMSE	MAE	ME	RMSE	MAE
PBE	-0.19	0.3	0.23	-0.16	0.25	0.2
$SIC_R$	-0.38	0.46	0.42	-0.42	0.45	0.37
$SIC_C$	-0.01	0.21	0.14	-0.005	0.13	0.10
TPSS	-0.25	0.37	0.27	-0.23	0.37	0.26
r2SCAN	-0.22	0.3	0.26	-0.19	0.29	0.24

## Excitation energy values of a formaldehyde molecule

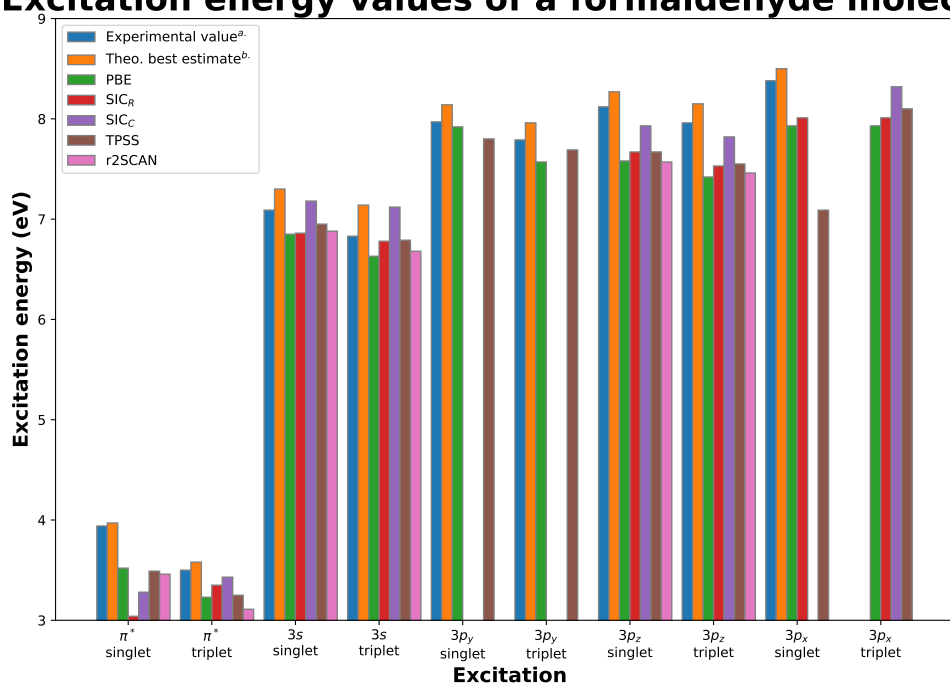


Figure 4.6. Energy values for excitations from HOMO to different valence and Rydberg states in a formaldehyde molecule, calculated using different functionals. The experimental structure is used for the PBE, SIC<sub>R</sub> and SIC<sub>C</sub> functionals, while the optimised structures are used with the TPSS and r2SCAN functionals.

<sup>a</sup>. Experimental values from [5] and [28]

<sup>b</sup>. Theoretical best estimate from [18]

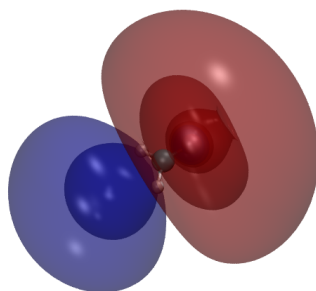


Figure 4.7. The  $3p_z$  orbital in a formaldehyde molecule calculated using the PBE functional for the experimental structure. The isosurfaces shown are 0.1, 0.025 and  $0.00625 \text{ \AA}^{-3/2}$ . The red surfaces are positive isosurfaces and the blue surfaces are negative.

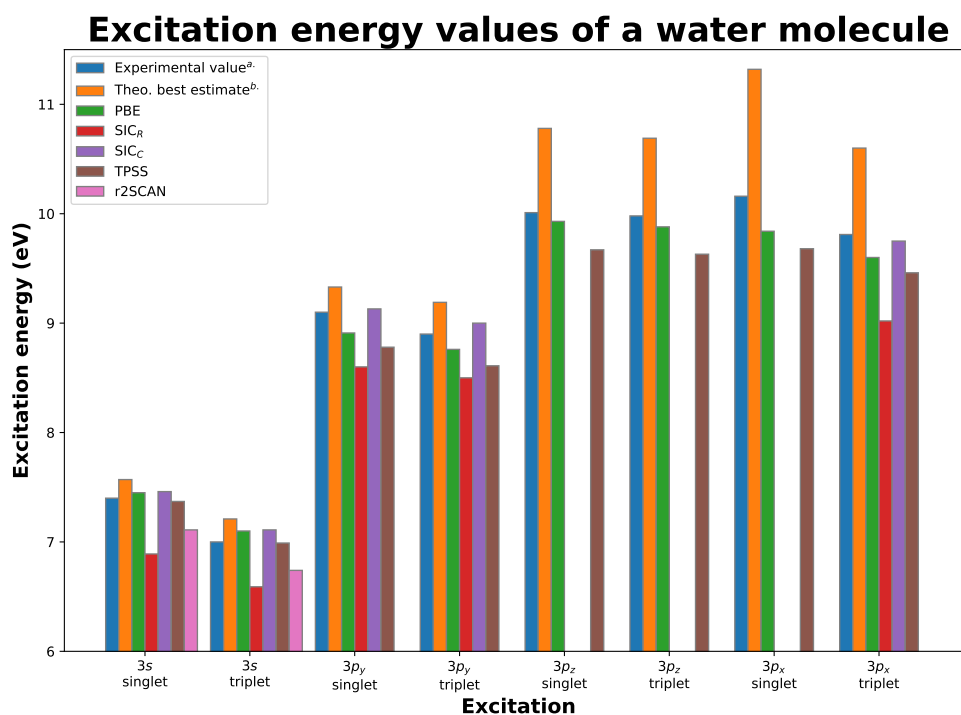


Figure 4.8. Energy values for excitations from HOMO to different Rydberg states in a water molecule, calculated using different functionals. The experimental structure is used for the PBE, SIC<sub>R</sub> and SIC<sub>C</sub> functionals, while the optimised structures are used with the TPSS and r2SCAN functionals.

<sup>a</sup>. Experimental values from [4]

<sup>b</sup>. Theoretical best estimate from [17]

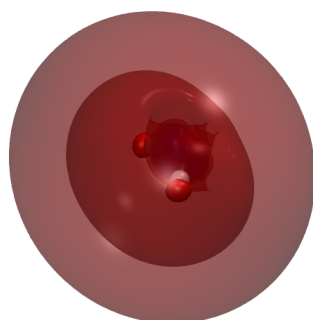


Figure 4.9. The 3s orbital in a water molecule calculated using the PBE functional for the experimental structure. The isosurfaces shown are 0.1, 0.025 and 0.00625 Å<sup>-3/2</sup>. The red surfaces are positive isosurfaces and the blue surfaces are negative.

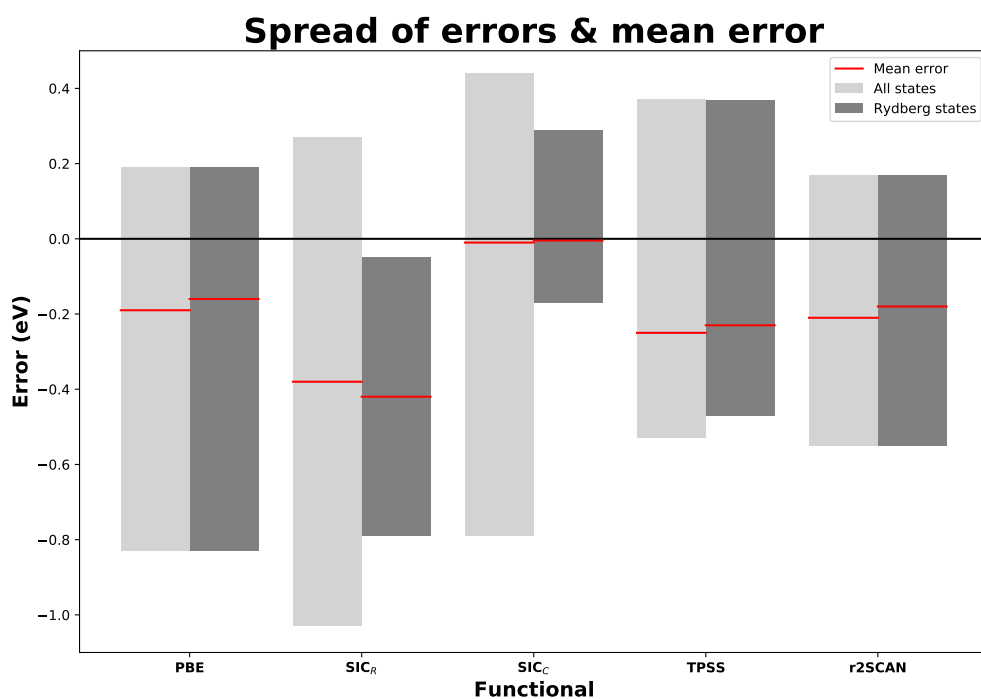


Figure 4.10. The range of errors from the different functionals when compared to the experimental values. The red lines show the mean error. The experimental structure is used for the PBE, SIC<sub>R</sub> and SIC<sub>C</sub> functionals, while the optimised structures are used with the TPSS and r2SCAN functionals.



## 5 Discussion

The excitation energy values calculated using the  $\text{SIC}_C$  functional are often in remarkably good agreement with the experimental estimates, especially for Rydberg states. Even for some valence excitations, it is necessary to include SIC in order to obtain a value for the excitation energy in agreement with experimental results. Using complex orbitals while using SIC was also shown to be important, as using SIC with real valued orbitals gave worse results than using PBE without SIC. This is consistent with what has been shown earlier for total energy of atoms [13] and binding energy of molecules [14].

A particular note must again be repeated regarding the valence excitation in ethylene, to the antibonding  $\pi^*$  orbital, as it has been much discussed over the years. The singlet excitation has proven quite difficult to describe accurately in calculations due to mixing with a Rydberg state that has the same symmetry and is close in energy. Calculations tend to either overestimate the amount of mixing, resulting in orbitals that are too diffuse, or to underestimate it [6]. The current theoretical best estimates for the excitation energy to this state from the ground state lie at around 7.9 to 8.0 eV. This is higher than the experimental values of between 7.6 and 7.7. The  $\text{SIC}_C$  functional however, gives a value for the excitation energy that is quite close to the experimental value.

This definitely needs to be explored further, as it does seem that the  $\text{SIC}_C$  functional gives a better result than higher level theory calculations give. The accuracy of the functional in this case might be a coincidence, but it might also possibly be explained partially from a choice of basis sets. For calculations at a higher level of theory, it is generally necessary to use linear combinations of atomic orbital-like wave functions as a basis set. For the calculation of this state at a higher level of theory, it seems like the problem is overcoming a bias from the choice of basis sets. Using a basis set of orbitals that are diffuse results in a too diffuse excited state. On the other hand, using basis sets that are not diffuse enough leads to an underestimation of the mixing with the Rydberg state. The calculations in this project were mostly done using a real space grid representation of the wave functions. This allows for a higher degree of freedom for the calculations to converge on a correct form. There is then no constraint on the extent to which the Rydberg state can mix in, as can be the case in an atomic basis set with limited set of diffuse functions.

There are also various other states where the excitation energy values given as theoretical best estimates are significantly higher than the experimental values. This is to some extent present in ethylene, but is most prominent for water and ammonia.

There were however, some states where the use of SIC performed worse than without, or did not improve on a relatively inaccurate result. For example when looking at the excitations in formaldehyde, the  $\text{SIC}_C$  results showed a larger error from the experimental value than for other molecules. It should be noted however that for the TPSS functional a similar effect of the error being higher with formaldehyde compared to the other molecules is seen. The causes of this remain to be identified.

Another outlier was the doubly degenerate  $E$  state in ammonia, corresponding to an excitation to the degenerate  $3p_{xy}$  orbitals. The degeneracy might be a possible cause for the error being relatively large. In order to determine this, the functional needs to be tested out on more excitations, to see if there are some states that the SIC functionals have a larger problem describing.

Overall though, the  $SIC_C$  functional provided quite accurate results. As noted, the computational cost of SIC calculations scale in the same way as general DFT, and therefore are a good option for calculations of excited states and their dynamics. For open shell singlet states, the energy surface of the mixed spin state is generally assumed to be similar enough to the singlet state so that it can be used for dynamics in that state. One should perhaps be careful with this, as for example in the valence excitation of ethylene there was a significant difference in energy between the singlet state and the mixed spin state.

Another point of concern with regards to using the  $SIC_C$  functional for molecular dynamics is the symmetry breaking that can occur when relaxing structures. For the water and ammonia molecules the geometries changed significantly during relaxation, as shown in tables 4.1 and 4.4. It has previously been well documented that using SIC for relaxations can lead to problems [15]. It has also been shown that when using SIC for ground state calculations, scaling SIC by 1/2 generally leads to better results. A future point of study would be to investigate how SIC behaves with excited states, and perhaps do a comparison between relaxed excited state structures and experimental measurements of those structures.

Recently, a new method to converge on excited state solutions has been developed, called general mode following (GMF) [25]. There, convergence on an  $n$ -th order saddle point on the electronic energy surface is obtained by inverting components of the gradient in the direction of the eigenvectors of the  $n$  lowest eigenvalues of the Hessian matrix. This has been shown to lead to better results and more reliable convergence than the maximum overlap method (MOM). This has however, not yet been implemented for real space grid and plane wave calculations and could therefore not be used in the present project. This will however need to be explored in future work, as there seems to be more reliable convergence to excited states than when using MOM.

Use of the meta-GGA functionals did not improve the results consistently when compared to the results obtained using PBE. In the majority of cases TPSS gave a similar result as PBE, while in a few cases it gave results that were closer to experimental values. A problem with the comparison here is that the calculations were not performed on the same structure, but in tables A.2, A.4, A.6 and A.8, the values were obtained having relaxed the structure using each functional. For a proper comparison, these calculations need to be repeated on the same structure.

Another field to consider in the future is the use of SIC with the meta-GGA functionals. Analysis of the computational time showed that the time needed for ground state calculations did not increase much between PBE and TPSS. Therefore, the use of SIC with TPSS seems feasible in terms of computational cost. The use of SIC with the r2SCAN functional, on the other hand, might be quite costly computationally, as the r2SCAN functional is already quite computationally heavy.

## 6 Conclusion

This study of different methods has investigated the accuracy of different functionals when calculating excitation energy values for Rydberg states. The calculations make use of the direct optimization method as well as MOM to give variationally optimized orbitals for the excited states. The results have been presented along with an analysis of various aspects. Directions for subsequent research in this field have also been discussed and presented.

The variational optimization of the excited states manages to give excitation energy values relatively well even when the orbital energy values in the ground state calculations are far from giving a reasonable estimate. The use of self-interaction correction with complex orbitals tends to improve the results and remarkably close agreement with experimental estimates is obtained in many cases, especially for high energy Rydberg states. At the same time, it is also clear that using the self-interaction correction for geometry optimization can cause problems, especially with the risk of symmetry breaking.

More testing needs to be done using this method, to see whether it gives good results for other molecules and excitations as well as considering what features condition the quality of the calculations. Using SIC should also in the future be attempted using meta-GGA functionals.



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# A Excitation Energy Values

Table A.1. Vertical excitation energy values for an ammonia molecule (in eV) using PBE, and using PBE with SIC implemented with either real or complex orbitals for the experimentally determined structure. The energy values for the mixed spin solution before spin purification are also shown in parentheses.

Excited state	Ex. <sup>a</sup>	Ex. <sup>b</sup>	Th. <sup>c</sup>	Th. <sup>d</sup>	PBE	SIC <sub>R</sub>	SIC <sub>C</sub>
3s singlet	6.39	6.38	6.48	6.66	(6.28) 6.42	(6.00) 6.14	(6.20) 6.35
3s triplet				6.37	6.14	5.86	6.04
3p <sub>xy</sub> singlet	7.93	7.90	8.02	8.21	(7.67) 7.75	(7.51) 7.55	(7.67) 7.76
3p <sub>xy</sub> triplet					7.59	7.46	7.58
3p <sub>z</sub> singlet	8.26	8.14	8.50	8.65	(8.28) 8.45		(8.09)
3p <sub>z</sub> triplet					8.12		
ME <sup>e</sup>					0.012	-0.45	-0.11
RMSE <sup>e</sup>					0.15	0.49	0.12
MAE <sup>e</sup>					0.13	0.45	0.11

<sup>a</sup> From reference [10]

<sup>b</sup> From reference [27]

<sup>c</sup> CCSD(T) calculations with aug-cc-pVTZ basis set from reference [2]

<sup>d</sup> Extrapolated full CI results with aug-cc-pVQZ basis set from reference [19]

<sup>e</sup> Errors are compared to the experimental values given in the first column.

Table A.2. Vertical excitation energy values (in eV) of an ammonia molecule using PBE, TPSS and r2SCAN for the relaxed ground state structure obtained from each functional. The mixed spin energy values before spin purification are also shown in parentheses.

Excited state	Ex. <sup>a</sup>	Ex. <sup>b</sup>	Th. <sup>c</sup>	Th. <sup>d</sup>		PBE	TPSS	r2SCAN
3s singlet	6.39	6.38	6.48	6.66	(6.25)	6.40	(6.33) 6.49	(6.39) 6.56
3s triplet				6.37		6.11	6.18	6.23
3p <sub>xy</sub> singlet	7.93	7.90	8.02	8.21	(7.65)	7.73	(7.65) 7.74	(7.95) 8.07
3p <sub>xy</sub> triplet						7.57	7.57	7.83
3p <sub>z</sub> singlet	8.26	8.14	8.50	8.65	(8.13)	8.12	(8.23) 8.36	
3p <sub>z</sub> triplet						8.13	8.10	
ME <sup>e</sup>						-0.11	0.0033	0.16
RMSE <sup>e</sup>						0.14	0.14	0.16
MAE <sup>e</sup>						0.11	0.13	0.15

<sup>a</sup>. From reference [10]

<sup>b</sup>. From reference [27]

<sup>c</sup>. CCSD(T) calculations with aug-cc-pVTZ basis set from reference [2]

<sup>d</sup>. Extrapolated full CI results with aug-cc-pVQZ basis set from reference [19]

<sup>e</sup>. Errors are compared to the experimental values given in the first column.

Table A.3. Vertical excitation energy values (in eV) of an ethylene molecule using PBE, and using PBE with SIC implemented with either real or complex orbitals for the experimentally determined structure. The mixed spin energy values before spin purification are also shown in parentheses.

Excited state	Ex. <sup>a.</sup>	Th. <sup>b.</sup>	Th. <sup>c.</sup>	PBE	SIC <sub>R</sub>	SIC <sub>C</sub>
$\pi^*$ singlet	7.60	8.00	7.93	(5.64) 6.77	(6.22) 7.87	(6.23) 7.69 <sup>d.</sup>
$\pi^*$ triplet	4.36	4.55	4.54	4.50	4.58	4.77 <sup>d.</sup>
3s singlet	7.11	7.45	7.43	(7.09) 7.15	(6.72) 6.78 <sup>e.</sup>	(7.15) 7.22
3s triplet	6.98	7.29	7.28	7.02	6.65 <sup>e.</sup>	7.08
3p <sub>y</sub> singlet	7.80	8.06	8.10	(7.57) 7.60	(7.31) 7.33	(7.79) 7.82
3p <sub>y</sub> triplet	7.79	8.02	8.00	7.55	7.30	7.76
3p <sub>z</sub> singlet		8.11		(7.75)		
3p <sub>z</sub> triplet		8.04			7.35	
3p <sub>x</sub> singlet	8.28	8.45		(8.01) 8.07	(7.65)	(8.12) 8.22
3p <sub>x</sub> triplet	8.15	8.30		7.94		8.03
3d $\sigma$ singlet	8.62			(8.40)	(8.14) 8.17	(8.61) 8.65
3d $\sigma$ triplet	8.57				8.10	8.58
3d $\delta$ singlet	8.90	9.16		(8.77)		
3d $\delta$ triplet		9.15				
3d <sub>xy</sub> singlet	9.33	9.47				
3d <sub>xy</sub> triplet		9.28				
ME <sup>f.</sup>				-0.18	-0.26	0.059
RMSE <sup>f.</sup>				0.34	0.39	0.16
MAE <sup>f.</sup>				0.24	0.38	0.10
ME (Rydberg states) <sup>f.</sup>				-0.13	-0.42	0.0074
RMSE (Rydberg states) <sup>f.</sup>				0.18	0.43	0.074
MAE (Rydberg states) <sup>f.</sup>				0.16	0.42	0.06

<sup>a.</sup> From reference [24]

<sup>b.</sup> Best composite CI results from reference [6]

<sup>c.</sup> Extrapolated full CI results with aug-cc-pVTZ basis set from reference [19]

<sup>d.</sup> These values are taken from the structure relaxed with SIC<sub>R</sub>, as the value for the triplet calculation in the experimental structure converged to a different state.

<sup>e.</sup> These values are taken from the structure relaxed with SIC<sub>C</sub>, as the value for the triplet calculation in the experimental structure converged to a different state.

<sup>f.</sup> Errors are compared to the experimental values given in the first column.

Table A.4. Vertical excitation energy values (in eV) of an ethylene molecule using PBE, TPSS and r2SCAN for the relaxed structures from each functional. The mixed spin energy values before spin purification are also shown in parentheses.

Excited state	Ex. <sup>a</sup>	Th. <sup>b</sup>	Th. <sup>c</sup>	PBE	TPSS	r2SCAN
$\pi^*$ singlet	7.60	8.00	7.93	(5.60) 6.74	(5.72) 7.07	(5.79) 7.44
$\pi^*$ triplet	4.36	4.55	4.54	4.47	4.36	4.14
3s singlet	7.11	7.45	7.43	(7.06) 7.12	(7.07) 7.12	(7.00) 7.05
3s triplet	6.98	7.29	7.28	6.99	7.02	6.96
3p <sub>y</sub> singlet	7.80	8.06	8.10	(7.64)	(7.62)	(7.53)
3p <sub>y</sub> triplet	7.79	8.02	8.00			
3p <sub>z</sub> singlet		8.11		(7.53) 7.56		(7.63) 7.65
3p <sub>z</sub> triplet		8.04		7.51		7.60
3p <sub>x</sub> singlet	8.28	8.45		(7.99) 8.05		(7.94) 7.99
3p <sub>x</sub> triplet	8.15	8.30		7.92		7.88
3d $\sigma$ singlet	8.62			(8.40) 8.43		
3d $\sigma$ triplet	8.57			8.36	8.37	
3d $\delta$ singlet	8.90	9.16		(8.71) 8.73		
3d $\delta$ triplet		9.15		8.70		
3d <sub>xy</sub> singlet	9.33	9.47				
3d <sub>xy</sub> triplet		9.28				
ME <sup>d</sup> .				-0.20	-0.14	-0.17
RMSE <sup>d</sup> .				0.33	0.25	0.19
MAE <sup>d</sup> .				0.22	0.16	0.17
ME (Rydberg states) <sup>d</sup> .				-0.14	-0.052	-0.16
RMSE (Rydberg states) <sup>d</sup> .				0.17	0.11	0.20
MAE (Rydberg states) <sup>d</sup> .				0.15	0.083	0.16

<sup>a</sup>. From reference [24]

<sup>b</sup>. Best composite CI results from reference [6]

<sup>c</sup>. Extrapolated full CI results with aug-cc-pVTZ basis set from reference [19]

<sup>d</sup>. Errors are compared to the experimental values given in the first column.

Table A.5. Vertical excitation energy values (in eV) of a formaldehyde molecule using PBE, and using PBE with SIC implemented with either real or complex orbitals for the experimentally determined structure. The mixed spin energy values before spin purification are also shown in parentheses.

Excited state	Ex. <sup>a</sup>	Ex. <sup>b</sup>	Th. <sup>c</sup>	Th. <sup>d</sup>	Th. <sup>e</sup>	PBE	SIC <sub>R</sub>	SIC <sub>C</sub>
$\pi^*$ singlet	3.94	4.07	3.98	3.88	3.97	(3.38) 3.53	(3.20) 3.04	(3.36) 3.28
$\pi^*$ triplet	3.50	3.50		3.50	3.58	3.23	3.35	3.43
3s singlet	7.09	7.11	7.12		7.30	(6.74) 6.85	(6.82) 6.85	(7.15) 7.18 <sup>f</sup>
3s triplet	6.83	6.83			7.14	6.63	6.78	7.12 <sup>f</sup>
3p <sub>y</sub> singlet	7.97	7.97	7.94	8.11	8.14	(7.75) 7.92		
3p <sub>y</sub> triplet	7.79	7.79			7.96	7.57		
3p <sub>z</sub> singlet	8.12	8.14	8.16		8.27	(7.50) 7.58	(7.60) 7.67	(7.88) 7.93
3p <sub>z</sub> triplet	7.96	7.96			8.15	7.42	7.53	7.82
3p <sub>x</sub> singlet	8.38	8.37	8.38		8.50	(7.93) 7.93	(8.01) 8.01	
3p <sub>x</sub> triplet						7.93	8.01	8.32
ME <sup>g</sup>						-0.34	-0.39	-0.14
RMSE <sup>g</sup>						0.38	0.49	0.36
MAE <sup>g</sup>						0.34	0.39	0.26
ME (Rydberg states) <sup>g</sup>						-0.32	-0.31	0.0036
RMSE (Rydberg states) <sup>g</sup>						0.37	0.35	0.19
MAE (Rydberg states) <sup>g</sup>						0.32	0.31	0.18

<sup>a</sup>. From reference [5] and [28]

<sup>b</sup>. From reference [24]

<sup>c</sup>. Multi-reference averaged quadratic CC linear response theory calculations (MR-AQCC/LRT) from reference [20]

<sup>d</sup>. Best estimates from reference [26]

<sup>e</sup>. Extrapolated full CI results with aug-cc-pVTZ basis set from reference [19]

<sup>f</sup>. These values are taken from the structure relaxed with SIC<sub>C</sub>, as the value for the triplet calculation in the experimental structure converged to a different state.

<sup>g</sup>. Errors are compared to the experimental values given in the first column.

Table A.6. Vertical excitation energy values (in eV) of a formaldehyde molecule using PBE, TPSS and r2SCAN for the relaxed structures from each functional. The mixed spin energy values before spin purification are also shown in parentheses.

Excited state	Ex. <sup>a</sup>	Ex. <sup>b</sup>	Th. <sup>c</sup>	Th. <sup>d</sup>	Th. <sup>e</sup>	PBE	TPSS	r2SCAN
$\pi^*$ singlet	3.94	4.07	3.98	3.88	3.97	(3.39) 3.55	(3.37) 3.49	(3.28) 3.46
$\pi^*$ triplet	3.50	3.50		3.50	3.58	3.24	3.25	3.11
3s singlet	7.09	7.11	7.12		7.30	(6.73) 6.85	(6.87) 6.95	(6.78) 6.88
3s triplet	6.83	6.83			7.14	6.62	6.79	6.68
3p <sub>y</sub> singlet	7.97	7.97	7.94	8.11	8.14	(7.64) 7.75	(7.75) 7.80	
3p <sub>y</sub> triplet	7.79	7.79			7.96	7.54	7.69	
3p <sub>z</sub> singlet	8.12	8.14	8.16		8.27	(7.49) 7.57	(7.61) 7.67	(7.51) 7.57
3p <sub>z</sub> triplet	7.96	7.96			8.15	7.42	7.55	7.46
3p <sub>x</sub> singlet	8.38	8.37	8.38		8.50	(7.92) 7.92	(7.59) 7.09	
3p <sub>x</sub> triplet						7.92	8.10	
ME <sup>f</sup> .						-0.35	-0.37	-0.38
RMSE <sup>f</sup> .						0.37	0.51	0.41
MAE <sup>f</sup> .						0.35	0.37	0.38
ME (Rydberg states) <sup>f</sup> .						-0.35	-0.37	-0.36
RMSE (Rydberg states) <sup>f</sup> .						0.38	0.54	0.40
MAE (Rydberg states) <sup>f</sup> .						0.35	0.37	0.36

<sup>a</sup>. From reference [5] and [28]

<sup>b</sup>. From reference [24]

<sup>c</sup>. Multi-reference averaged quadratic CC linear response theory calculations (MR-AQCC/LRT) from reference [20]

<sup>d</sup>. Best estimates from reference [26]

<sup>e</sup>. Extrapolated full CI results with aug-cc-pVTZ basis set from reference [19]

<sup>f</sup>. Errors are compared to the experimental values given in the first column.

Table A.7. Vertical excitation energy values (in eV) of a water molecule using PBE, and using PBE with SIC implemented with either real or complex orbitals for the experimentally determined structure. The mixed spin energy values before spin purification are also shown in parentheses.

Excited state	Ex. <sup>a</sup>	Ex. <sup>b</sup>	Th. <sup>c</sup>	Th. <sup>d</sup>	Th. <sup>e</sup>	PBE	SIC <sub>R</sub>	SIC <sub>C</sub>
3s singlet	7.40	7.42	7.81	7.57	7.70	(7.28) 7.45	(6.74) 6.89	(7.28) 7.46
3s triplet	7.00	7.20	7.14	7.21	7.33	7.10	6.59	7.11
3p <sub>y</sub> singlet	9.10	9.20	9.30	9.33	9.47	(8.83) 8.91	(8.55) 8.60	(9.07) 9.13
3p <sub>y</sub> triplet	8.90	8.90	9.42	9.19	9.30	8.76	8.50	9.00
3p <sub>z</sub> singlet	10.01		10.72	10.78		(9.91) 9.93	(9.19)	(9.74)
3p <sub>z</sub> triplet	9.98		10.61	10.69		9.88		
3p <sub>x</sub> singlet	10.16		11.26	11.32		(9.72) 9.84		
3p <sub>x</sub> triplet	9.81	9.79	10.52	10.60		9.60	9.02	9.75
ME <sup>f</sup>						-0.11	-0.52	0.047
RMSE <sup>f</sup>						0.17	0.54	0.078
MAE <sup>f</sup>						0.15	0.52	0.073

<sup>a</sup>. From reference [4]

<sup>b</sup>. From reference [23]

<sup>c</sup>. Multireference CC calculation with quadruples correction with aug-cc-pVTZ basis set from reference [3]

<sup>d</sup>. Multireference CC calculations with aug-cc-pVTZ basis set from reference [17]

<sup>e</sup>. Extrapolated full CI results with aug-cc-pVQZ basis set from reference [19]

<sup>f</sup>. Errors are compared to the experimental values given in the first column.

Table A.8. Vertical excitation energy values (in eV) of a water molecule using PBE, TPSS and r2SCAN for the relaxed structures obtained from each functional. The mixed spin energy values before spin purification are also shown in parentheses.

Excited state	Ex. <sup>a</sup>	Ex. <sup>b</sup>	Th. <sup>c</sup>	Th. <sup>d</sup>	Th. <sup>e</sup>	PBE	TPSS	r2SCAN
3s singlet	7.40	7.42	7.81	7.57	7.70	(7.16) 7.34	(7.18) 7.37	(6.92) 7.11
3s triplet	7.00	7.20	7.14	7.21	7.33	6.98	6.99	6.74
3p <sub>y</sub> singlet	9.10	9.20	9.30	9.33	9.47	(8.72) 8.79	(8.69) 8.78	
3p <sub>y</sub> triplet	8.90	8.90	9.42	9.19	9.30	8.64	8.61	
3p <sub>z</sub> singlet	10.01		10.72	10.78		(9.85) 9.88	(9.65) 9.67	
3p <sub>z</sub> triplet	9.98		10.61	10.69		9.83	9.63	
3p <sub>x</sub> singlet	10.16		11.26	11.32		(9.67) 9.79	(9.57) 9.68	
3p <sub>x</sub> triplet	9.81	9.79	10.52	10.60		9.55	9.46	
ME <sup>f</sup>						-0.19	-0.27	-0.28
RMSE <sup>f</sup>						0.22	0.31	0.28
MAE <sup>f</sup>						0.20	0.27	0.28

<sup>a</sup>. From reference [4]

<sup>b</sup>. From reference [23]

<sup>c</sup>. Multireference CC calculation with quadruples correction with aug-cc-pVTZ basis set from reference [3]

<sup>d</sup>. Multireference CC calculations with aug-cc-pVTZ basis set from reference [17]

<sup>e</sup>. Extrapolated full CI results with aug-cc-pVQZ basis set from reference [19]

<sup>f</sup>. Errors are compared to the experimental values given in the first column.