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Master’s Thesis

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X-ray absorption spectroscopy by means of Lanczos-chain driven damped coupled cluster response theory

A novel method by which to calculate the near edge X-ray absorption fine structure region of the X-ray absorption spectrum has been derived and implemented. By means of damped coupled cluster theory at coupled cluster levels CCS, CC2, CCSD and CCSDR(3), the spectra of neon and methane have been investigated. Using methods incorporating double excitations, the important relaxation effects may be taken into account by simultaneous excitation of the core electron and relaxation of other electrons. An asymmetric Lanczos-chain driven approach has been utilized as a means to partially resolve the excitation space given by the coupled cluster Jacobian. The K-edge of the systems have been considered, and relativistic effects are estimated with use of the Douglas–Kroll scalar relativistic Hamiltonian. Comparisons have been made to results obtained with the four-component static-exchange approach and ionization potentials obtained by the ΔSCF-method.

The appropriate basis sets by which to describe the core and excited states have been determined. The addition of core-polarizing functions and diffuse or Rydberg functions is important for this description. Scalar relativistic effects accounts for an increase in excitation energies due to the contraction of the 1s-orbital, and this increase is seen to be 0.88 eV for neon. The coupled cluster hierarchy shows a trend of convergence towards the experimental spectrum, with an 1s → 3p excitation energy for neon of an accuracy of 0.40 eV at a relativistic CCSDR(3) level of theory. Results obtained at the damped coupled cluster and STEX levels of theory, respectively, are seen to be in agreement, with a mere relative energy shift.

Keywords computational physics, theoretical chemistry, molecular properties, X-ray absorption spectroscopy, coupled cluster, NEXAFS, damped response theory
To my Family.
Abstract

A novel method by which to calculate the near edge X-ray absorption fine structure region of the X-ray absorption spectrum has been derived and implemented. By means of damped coupled cluster theory at coupled cluster levels CCS, CC2, CCSD and CCSDR(3), the spectra of neon and methane have been investigated. Using methods incorporating double excitations, the important relaxation effects may be taken into account by simultaneous excitation of the core electron and relaxation of other electrons. An asymmetric Lanczos-chain driven approach has been utilized as a means to partially resolve the excitation space given by the coupled cluster Jacobian. The K-edge of the systems have been considered, and relativistic effects are estimated with use of the Douglas–Kroll scalar relativistic Hamiltonian. Comparisons have been made to results obtained with the four-component static-exchange approach and ionization potentials obtained by the ΔSCF-method.

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Chapter 1

Introduction

1.1 Quantum chemistry

The scientific branch of quantum chemistry utilizes the physical laws governing matter on a microscopic level on fields of chemistry, i.e. at a molecular level. This requires the laws and postulates of quantum mechanics for an accurate description, with possible inclusion of special relativity for even greater validity.

With the aid of quantum chemistry it is possible then to develop such methods by which chemical and molecular characteristics may be calculated, possible without the inclusion of extensive empirical knowledge [1, 2, 3]. These methods can be applied for a variety of chemical aspects, including, but not restricted to: molecular geometries and energies [4, 5], chemical reaction pathways and reaction rates [6], molecular properties and studies of systems too unstable for experimental measurements. Experimental data can thus be interpreted, optimal molecules designed and so on.

This project concerns the development of methods for the calculation of molecular properties. More precisely, we are interested in the possibility of theoretically calculating a molecules interaction with electromagnetic fields of X-ray frequency, in terms of photon absorption. We will now discuss some aspects of absorption spectroscopy in this frequency region.

1.2 X-ray absorption spectroscopy

The experimental study of matter on the microscopic level can be conducted in a variety of different manners, many including the interaction of the matter with a controlled field or particle flow. In the present project we are interested in the interaction with X-ray radiation, yielding X-ray absorption spectroscopy (XAS). As a result of the increasing radiation intensity and frequency accuracy achieved at high-technology synchrotron radiation facilities, this field of study has progressed relatively rapidly lately,
The use of X-ray radiation has the advantage of affecting the most strongly bound electrons, i.e. core electrons, in the molecule. The energies of such electrons are very different for different elements, and we thus have an experimental tool highly specific to different elements and local molecular structures. Surface structure, chemical composition and other aspects may then be treated.

We may further divide XAS into several subgroups, characterized by the physical processes stimulated. This study concerns the XAS spectrum just below an ionization edge, i.e. the excitation of an electron to the continuum. The edge is named by the principal quantum number of the resonant electron, i.e. K-edge, L-edge and so on. This region is designated the near-edge X-ray absorption fine structure (NEXAFS) region, and possesses features describing the excited states of the molecule. The region extending approximately 20–30 eV [7] above the edge is designated the extended X-ray adsorption fine structure (EXAFS) region. The combination of those two frequency regions yields the X-ray absorption fine structure (XAFS) region. See references [8, 9, 10, 11, 12] for more material.

Following excitation, the molecule will rapidly experience de-excitation into the core. This very short lifetime of the excited state will yield a Lorentzian broadening of the absorption spectrum. Further, the resolution of the instrument and molecular vibrations will result in a Gaussian and asymmetrical broadening, respectively [9]. The movement of the molecules may also affect the spectrum through Doppler shifts [13]. Of these features, the finite lifetime of the excited state will prove to be of importance for this theoretical treatment.

The theoretical consideration of X-ray absorption spectroscopy has a number of difficulties, e.g. strong relaxation effects following excitation and the embedded nature of the core states. A number of theoretical models exists [14, 15, 16, 17, 18], and this project investigates the behaviour of a novel model.
Chapter 2

Theory

2.1 Basis of electronic structure theory

The study of quantum chemistry is a study of large systems composed of charged particles influencing each other, mainly as a result of Coulomb interactions and the Pauli principle governing half-integer spin particles (fermions) [1, 2, 19]. Due to the small size of the systems of interest, the theoretical description utilizes a quantum mechanical framework, possibly with the inclusion of relativistic effects [20]. We will now consider some basics of quantum mechanics important for electronic structure theory.

2.1.1 Quantum mechanical wave equation

Disregarding relativistic effects, the behaviour of chemical systems can be described by the Schrödinger equation

\[ i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle, \]

for a many-particle wave function \( |\Psi\rangle \) with the Hamiltonian operator \( \hat{H} \). If the Hamiltonian is time-independent, a separation of variables yields the time-independent Schrödinger equation, where the right-hand-side becomes the energy of the system, \( E \), times the wave function.

The many-particle wave function does not in itself represent an observable, i.e. an entity that can be explicitly observed. It does, however, contain all information concerning the system it describes, in accordance to the fundamental postulates of quantum mechanics [19]. From this a number of observables may be obtained, e.g. probability densities and dipole moments.

This wave equation gives a correct description only in a nonrelativistic setting. If relativistic effects, such as scalar relativistic shifts and spin effects, are to be described for a more accurate description, other methods need to be considered. The relativistic quantum mechanical wave equation is given for spin-1/2 as the
four-component *Dirac equation*, given in the form

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) = c \left( \tilde{\beta} mc - i\hbar \tilde{\alpha} \cdot \nabla \right) \Psi(\vec{r}, t).$$ (2.2)

Here the wave function $\Psi$ is a four-component entity and $\tilde{\alpha}$ and $\tilde{\beta}$ are $4 \times 4$-matrices [20]. If relativistic effects are small, they can also be added unto the nonrelativistic framework.

### 2.1.2 Many-particle systems

The Hamiltonian associated with a chemical system consisting of $N$ electrons and $M$ nuclei is given as

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{A=1}^{M} \frac{1}{2m_{A}} \nabla_{A}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} Z_{A} r_{iA} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A} Z_{B}}{R_{AB}},$$ (2.3)

expressed in atomic units, units convenient when considering electronic structure [2, 3]. The first two terms describe the kinetic energy of the electrons and nuclei, the third term the Coulomb attraction between the electrons and the nuclei and the last two terms describe the electron-electron and nucleus-nucleus Coulomb repulsion, respectively.

The subsequent many-particle problem can only be solved analytically for two-body systems, so approximate solutions are sought. Quantum chemistry deals largely with the development of proper approximate methods to describe the systems of interest.

As a first approximation, the movement of the electrons and nuclei are separated, yielding a problem where the electrons are considered in the field of static nuclei. This is known as is the *Born–Oppenheimer approximation*, and relies on the fact that a single proton is approximately 1835 times heavier than a single electron [21], and thus moves more slowly. This yield the *electronic Hamiltonian* for the electrons, with the second and fifth term contributing only with a fixed constant for a specific nuclei configuration

$$\hat{H}_{\text{elec}} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}.$$ (2.4)

The nuclei are then treated in the field of the electrons. Note here that this electronic Hamiltonian in no way incorporate the vibrational states or rotations of the system. A general molecule will, for any temperature, occupy a rovibronic state, i.e. a vibrational, rotational and electronic state. The effect from this is that molecular properties will be broadened and quantum mechanical transition rules may be circumvented by the vibronic state, yielding a small possibility of electronically forbidden transitions.
2.1 Basis of electronic structure theory

2.1.3 Electronic wave functions

A many-particle wave equation can be constructed by a direct product of single-particle wave functions. For a molecular system, the single-particle wave functions of interest describes the electrons, and an approximate wave function for a single electron in such a system is known as a \textit{(spin) orbital}, and is a function of spin $\omega$ and spatial coordinates $\vec{r}$,

$$\chi = \chi(\vec{x}) = \chi(\vec{r}, \omega).$$  \hfill (2.5)

Each orbital may be divided into a product of a spin and spatial function:

$$\chi(\vec{x}) = \left\{ \begin{array}{ll} \psi(\vec{r}) \cdot \alpha(\omega) \\ \psi(\vec{r}) \cdot \beta(\omega) \end{array} \right.$$ \hfill (2.6)

where the spatial functions (spatial orbitals) form an orthonormal basis

$$\langle \psi_i(\vec{r}) | \psi_j(\vec{r}) \rangle = \delta_{ij},$$ \hfill (2.7)

and the spin functions have the following properties,

$$\langle \alpha | \alpha \rangle = 1, \quad \langle \beta | \beta \rangle = 1, \quad \langle \alpha | \beta \rangle = 0, \quad \langle \beta | \alpha \rangle = 0.$$ \hfill (2.8)

As the Pauli principle states that each fermion wave function can only be occupied by zero or one fermion, this means that a many-particle wave function describing a system of electrons must be antisymmetric with respect to interchanging two electrons [1, 3],

$$\Psi(\vec{x}_1, \ldots, \vec{x}_i, \ldots, \vec{x}_j, \ldots, \vec{x}_N) = -\Psi(\vec{x}_1, \ldots, \vec{x}_j, \ldots, \vec{x}_i, \ldots, \vec{x}_N).$$ \hfill (2.9)

A mathematical function that satisfies this antisymmetry property is the determinant, as interchanging two rows yields a change of sign. A general $N$-electron wave function can then be formed by a superposition of determinants, each of those having the form of a Slater determinant,

$$|\Psi\rangle = \Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \cdots & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \end{vmatrix}$$ \hfill (2.10)

Should a linear combination of all possible Slater determinant for a specific one-electron basis be treated and the expansion coefficient be found variationally, the exact solution to the Schrödinger equation is given in this basis [1]. However, this is possible only for very small systems and other approaches must be used for an approximate solution.
2.2 Hartree–Fock theory

This thesis considers electronic structure theories using a wave function approach. Other approaches are possible, see e.g. [2]. A wave function approach has the advantage of generally needing no parametrizations from experiment or other calculations, and are thus examples of \textit{ab initio} methods. The simplest wave function approach is given by the Hartree–Fock model, which will be considered in this section.

2.2.1 Hartree–Fock approximation

The Hartree–Fock (HF) approximation forms an approximate electronic wave function as a single Slater determinant. This construction of the wave function and the Hamiltonian from Eq. 2.4 gives a ground-state HF wave function as obtain by the variational principle

\[ E_{HF} = \min_{\lambda} \langle \Psi(\lambda) | \hat{H} | \Psi(\lambda) \rangle \geq E_0, \]  

(2.11)

where the energy of the trial wave functions is minimized by varying the set of parameters \( \lambda \) associated with the construction of the spin orbitals in the determinant. Note that these molecular orbitals are orthonormal.

We now attempt to find a scheme by which we can solve for the Hartree–Fock ground state in an iterative manner. As the electronic Hamiltonian in Eq. 2.4 contains terms including only one- and two-electron interactions, one- and two-electron operators are constructed as

\[ \hat{O}_1 = \sum_{i=1}^{N} \hat{h}(i) \quad \text{and} \quad \hat{O}_2 = \sum_{i=1}^{N} \sum_{j=1}^{N} \hat{g}(i,j). \]  

(2.12)

If the operators are spin-independent, as for a nonrelativistic consideration, the corresponding expectation values for a closed-shell system becomes

\[ \langle \Psi | \hat{O}_1 | \Psi \rangle = 2 \sum_{k=1}^{N/2} \hat{h}_{kk}, \]  

\[ \langle \Psi | \hat{O}_2 | \Psi \rangle = \sum_{i>j}^{N/2} (2 \langle \chi_i \chi_j | \hat{g} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \hat{g} | \chi_j \chi_i \rangle) = \sum_{i>j}^{N/2} (2J_{ij} - K_{ij}), \]  

(2.14)

where \( h_{kk} \) are one-electron integrals, and

(2.15)

where \( J_{ij} \) and \( K_{ij} \) are known as the Coulomb and exchange integral, respectively. The Coulomb integral arises from the Coulomb repulsion between different electrons, while the exchange integral is a correction due to correlation of electrons with parallel spin [3]. With the operators

\[ \hat{J}_j \chi_i(\vec{x}_1) = \left[ \int \frac{|\chi(\vec{x}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_2 \right] \chi_i(\vec{x}_1), \]  

\[ \hat{K}_j \chi_i(\vec{x}_1) = \left[ \int \frac{\chi^*(\vec{x}_2) \chi_i(\vec{x}_1)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_2 \right] \chi_j(\vec{x}_1), \]  

(2.16)
the integrals can be given as simple expectation values

\begin{align}
J_{ij} &= \langle \chi_i | \hat{J}_j | \chi_i \rangle, \\
K_{ij} &= \langle \chi_i | \hat{K}_j | \chi_i \rangle.
\end{align}

(2.17) (2.18)

The HF ground state can now be obtained by solving a set of effective one-electron Schrödinger equations for the spin orbitals, with the Hamiltonian replaced by the Fock operator

\[ \hat{f} = \hat{h} + \sum_i \left( \hat{J}_i - \hat{K}_i \right) = \hat{h} + \hat{v}_F, \]

(2.19)

where \( \hat{v}_F \) is the effective two-electron Fock potential. If the Fock operator is diagonalized we obtain a set of special Hartree–Fock equations, to which the solutions corresponds to the canonical orbitals,

\[ \hat{f} |\Psi_i\rangle = \epsilon_i |\Psi_i\rangle. \]

(2.20)

These orbitals are unique for the system, and possesses some properties, such as certain symmetries of the molecule.

### 2.2.2 Electron correlation

As Hartree–Fock treats electronic interaction as arising from one electron interacting with static nuclei and a mean-field from the other electrons, any electronic correlations due to the dynamic behaviour of the electrons are disregarded. This is the main flaw of HF and accurate correlated calculations thus utilizes other methods, commonly taking HF results as a starting point \([1, 2]\). The correlation energy is defined as

\[ E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}, \]

(2.21)

where \( E_{\text{exact}} \) is the exact ground state energy for the system.

### 2.2.3 Orbital energies and ionization potential

If the canonical orbitals are obtained as from Eq. 2.20, the eigenvalues \( \epsilon_i \) corresponds approximately to the ionization potential, \( \text{IP} \), of the respective orbital \( i \) as by Koopmann’s theorem \([1, 3]\). The ionization potential is the energy required to excite an electron to the continuum, resulting in a free electron and an ionized molecule. As the other electrons are considered unaffected here, this description lacks the relaxation effects of the remaining electrons following excitation. This approximation thus becomes progressively more inaccurate for the more strongly bound electrons, such as the core, due to the increasingly important relaxation effects.

An improved description of excitation energies is given by the \( \Delta \text{SCF} \) method \([1]\). The ionization potential of one electron is approximated as the difference in
energy for the ground state system, and an ionic system where the orbital $i$ of interest is forced to be unoccupied and the other orbitals are allowed to relax

$$\text{IP}^\Delta_{\text{SCF}} = E^{N-1}_{0,i} - E^N_{0,i}. \quad (2.22)$$

This method uses Hartree–Fock methods, and thus suffers the lack of electron correlations.

### 2.3 Static-exchange approach

For the description of relaxation effects following excitation, the static-exchange (STEX) approach has been developed [22], and later generalized into a fully relativistic method [17].

In the STEX method the relaxation of the excited state is taken into account by an explicit optimization of the ionic state with a core hole. The excitation processes is considered as the promotion of an electron to a virtual orbital, corresponding to an eigenvector of the one-electron Hamiltonian describing this electron in the electrostatic field generated by the frozen ion. A STEX Hamiltonian is then constructed and transformed such that the STEX states are given by a diagonalization. The $\Delta$SCF IP is calculated, and by adding this result unto the eigenvalues of the states, the frequency of excitations are retrieved. The transition strengths may then be given by forming a transition matrix from the (non-orthogonal) ground and final states. By a Lorentzian broadening to incorporate the finite lifetime of the excited states, we can thus calculate a spectrum.

The STEX method utilizes the Hartree–Fock method for the calculation of electronic structure, and thus suffers the same lack of electron correlation. The orbital relaxation of the remaining electrons is somewhat overestimated, as the system lacks the screening of the excited electron. Further, utilizing STEX for large systems is inefficient, due to the state-specific nature of the approach and resulting need to consider one ionic state for each possible excitation of relevant energy.

### 2.4 Coupled cluster theory

This project utilizes an approach for the calculation of electronic structure that generally takes a HF state as reference state and improve the description of the system from this: the coupled cluster, CC, method. By the use of excitation operators the electronic correlation effects are incorporated as excitations to virtual states, and the wave function is given as a sum of Slater determinants.

Coupled cluster has proven to be highly successful in terms of static behaviour, and contains some of the most accurate $ab\initio$ electronic wave function methods in quantum chemistry [4]. Standard CC methods will be considered here, as well as two methods with approximate excitations, derived with application in response theory in mind. First some aspects of second quantization will be reviewed, as this is of importance for the excitations.
2.4 Coupled cluster theory

2.4.1 Second quantization

Quantum mechanics may be described in terms of second quantization, in which we describe wave functions in terms of creation and annihilation operators [19]. Consider a wave function of a system of fermions with \( M \) possible states

\[ | k \rangle = | k_1, k_2, \ldots, k_M \rangle, \tag{2.23} \]

where \( k_i \) is the occupation of state \( i \). Due to the Pauli principle, the only possible values of \( k \) is 0 and 1. A creation operator \( \hat{a}_i^\dagger \) and an annihilation operator \( \hat{a}_i \) is introduced, by which we can operate onto this system according to

\begin{align*}
\hat{a}_i^\dagger | k_1, \ldots, k_i, \ldots, k_M \rangle &= \begin{cases} 
\Gamma^k_i | k_1, \ldots, 1_i, \ldots, k_M \rangle & \text{if } k_i = 0 \\
0 & \text{if } k_i = 1
\end{cases}, \tag{2.24} \\
\hat{a}_i | k_1, \ldots, k_i, \ldots, k_M \rangle &= \begin{cases} 
\Gamma^k_i | k_1, \ldots, 0_i, \ldots, k_M \rangle & \text{if } k_i = 1 \\
0 & \text{if } k_i = 0
\end{cases}. \tag{2.25}
\end{align*}

The phase factor is given as,

\[ \Gamma^k_i = \prod_{j=1}^{i-1} (-1)^{k_j}, \tag{2.26} \]

yielding +1 if there are an even number of fermions in all orbitals \( j < i \) and -1 otherwise.

With this it is possible to construct excitation operators \( \hat{\tau} \) of some order, constructed according to

\[ \hat{\tau}_i^a = \hat{a}_i^\dagger \hat{a}_i, \quad \hat{\tau}_{ij}^{ab} = \hat{a}_i^\dagger \hat{a}_i \hat{a}_j^\dagger \hat{b}_j, \tag{2.27} \]

for the single and double excitations and analogous for higher-order excitations [1]. The effects of the operators are such as

\[ \hat{\tau}_i^a | k_0 \rangle = \hat{a}_i^\dagger \hat{a}_i | \ldots, 1_i, \ldots, 0_a, \ldots, \rangle = \Gamma^k_i \Gamma^k_i | \ldots, 0_i, \ldots, 1_a, \ldots, \rangle = | k_{ij}^{ab} \rangle. \tag{2.28} \]

where \( | k_0 \rangle \) is a reference state.

2.4.2 Coupled cluster method

The coupled cluster approach utilizes an excitation operator

\[ \hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N, \tag{2.29} \]

where \( N \) is the number of electrons in the system [1]. The separate excitation operator \( \hat{T}_i \) here is an excitation operator that simultaneously excites \( i \) electrons from occupied to unoccupied orbitals.
If given in this form where all possible excitations of the system is included, the coupled cluster method yields an exact description of the \(N\)-electron many-particle wave function. However, this is only possible for very small systems, and a truncation of the expansion is by necessity employed in most cases. The truncation determines the model in the CC hierarchy: including only single excitations yield the single excited coupled cluster, CCS, while including both single and double excitations yields the single and double excited coupled cluster, CCSD [23] and so on. For practical purposes the inclusion of triple excitations are generally unfeasible, and such effects may rather be introduced in an approximate manner \([1, 2]\).

The effects of the excitation operators follows section 2.4.1, and is for single excitation and double excitation given as

\[
\hat{T}_1 |\Psi_0\rangle = \sum_{i} \sum_{a} t_i^a a_i^a |\Psi_0\rangle = \sum_{i} t_i^a |\Psi_i^a\rangle ,
\]

\[
\hat{T}_2 |\Psi_0\rangle = \sum_{i>j} \sum_{a>b} t_{ij}^{ab} t_{ij}^{ab} |\Psi_0\rangle = \sum_{i>j} t_{ij}^{ab} |\Psi_{ij}^{ab}\rangle ,
\]

where \(t_i^a\) and \(t_{ij}^{ab}\) are the expansion coefficients, or coupled cluster amplitudes. To avoid double-counting we impose the conditions of \(i, j\) and \(a, b\) in Eq. 2.31. The CC wave function is obtained by use of the exponential ansatz, where we operate on a reference wave function by an exponential operator

\[
|CC\rangle = e^{\hat{T}} |\Psi_0\rangle = e^{\hat{T}} |0\rangle .
\]

The reference wave function is usually taken in the form of a HF wave function. The expansion of the exponential yields

\[
e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \ldots
\]

\[
= 1 + \hat{T}_1 + \left( \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right) + \left( \hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{1}{6} \hat{T}_1^3 \right) + \ldots
\]

where operating with the different subgroups gives the reference state, single excited states, double excited states and so on. Note here that the reference wave function is static, and systems are more accurately described if they are dominated by a single electronic configuration [24].

As can be seen, excited states of a higher order includes simultaneous excitations of lower order. So the doubly excited states includes not only the connected double excitations \(\hat{T}_2\), but also the disconnected simultaneous single excitations \(\hat{T}_1^2\). This results in an approach that is size-extensive, i.e. yields consistent results for arbitrary number of non-interacting molecules. Further, disconnected excitations may be most important for higher-order excitations, e.g. the \(\hat{T}_2^2\) terms are more important for quadruple excitations than \(\hat{T}_4\) [4, 23], so the system may be well described at a low order of truncation.

The coupled cluster wave ground state can in principle be solved by use of the variational principle, analogous to Eq. 2.11. However, due to the non-linear nature
of the coupled cluster ansatz, this is quite complicated and only possible for small systems. The procedure by which coupled cluster is solved is by projecting the Schrödinger equation onto a Hartree–Fock state \( |0\rangle \) and a manifold of the excited states

\[
\hat{\tau}_n |0\rangle = |n\rangle.
\]  

(2.34)

This manifold consists of all single excited states for CCS, all single and double excited states for CCSD and so on.

For convenience, we choose to multiply the time-independent Schrödinger equation 2.1 by the exponential operator \( e^{-\hat{T}} \) from the left, resulting in what can be regarded as an effective, non-Hermitian Hamiltonian

\[
\hat{H}_T = e^{-\hat{T}} \hat{H} e^{\hat{T}},
\]  

(2.35)

called the similarity-transformed Hamiltonian. The Schrödinger equation becomes

\[
e^{-\hat{T}} \hat{H} e^{\hat{T}} |0\rangle = E |0\rangle.
\]  

(2.36)

Project this equation onto the Hartree–Fock state and the manifold of excited states yields

\[
\langle 0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle = E,
\]  

(2.37)

\[
\langle n | e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle = 0,
\]  

(2.38)

which corresponds to the coupled cluster equations and may be solved for the coupled cluster ground state energy and amplitudes. Further, from Eqs. 2.1 and 2.37 it is trivial to show that the an effect of the exponential operator is

\[
\langle 0 | e^{-\hat{T}} = \langle 0 |.
\]  

(2.39)

If the reference state used is an optimized HF state, it can be shown that one-particle excitation operators doesn’t contribute to the electronic energy in a connected manner, as following Brillouin’s theorem [1]:

\[
\langle 0 | \hat{H} \hat{T}_1 | 0 \rangle = 0.
\]  

(2.40)

Using this, the fact that the Hamiltonian is a two-particle operator and Eqs. 2.33, 2.37 and 2.39, we obtain a new expression for the coupled cluster energy:

\[
E = \langle 0 | e^{-\hat{T}} \hat{H} \left( 1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \ldots \right) | 0 \rangle
\]  

(2.41)

\[
= \langle 0 | \hat{H} \left( 1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right) | 0 \rangle,
\]  

as the higher-order excitation operators yields states that are orthogonal to the reference state. So the energy of a coupled cluster method depends explicitly on only the single and double excitations, while any higher excitations contribute in the coupling of amplitudes as given by Eq. 2.38.
2.4.3 Approximate coupled cluster excitation methods

The full inclusion of higher order excitations yields computationally demanding calculations, with CCSD scaling as $m^6$ and CCSDT as $m^8$ for a system described by $m$ basis functions. It is thus desirable to find methods by which we can include approximate higher-order excitations at a lower computational cost. The approximate methods for inclusion of double excitations CC2 [25] and triple excitations CCSDR(3) [26], developed for the calculation of molecular properties, have been utilized in this work.

The CC2 method utilizes perturbation theory to determine the order of contribution from the different excitations. Single excitation equations (Eq. 2.38 with the excitation manifold consisting solely of single excitations, $\langle n_1 |$) remains the same as for CCSD. For double excitation equations, only contributions of lowest non-vanishing order (this being first order) are retained. What is obtained is a subset of the CCSD equations, solved iteratively with a scaling of $m^5$.

Similar methods as CC2 can be utilized for an inclusion of approximate triple excitation contributions, designated CC3 [27]. This yields an iterative method of scaling $m^7$, and is thus relatively computationally demanding. It is possible to define a perturbational correction to the CCSD excitation energies that is of same order of accuracy as CC3, but at a lower computational cost. This corresponds to the CCSDR(3) method, which is a non-iterative correction to CCSD eigenvectors that incorporate lowest order triple corrections.

Benchmark studies on valence excitations have shown that CCSDR(3) gives results close to those obtained by CC3 [28], and is thus a cost-efficient alternative. Further, basis set effects on CC2 and CCSDR(3) are seem to be similar [29], and CC2 may perform better than CCSD for certain systems [30].

2.5 Basis functions

The many-particle wave function, e.g. Eq. 2.9, describing the molecular system requires one-electron trial wave functions to be constructed. For an exact description we would need a complete basis set of such functions, but this is only possible for small systems. Truncation of the basis set is thus needed, and the optimal manner of doing such varies between different systems of interest and is thus important to consider.

A simple way to proceed is to use atomic centered orbitals, as the linear combination of atomic orbitals (LCAO) [1]. The molecular orbitals (MOs) $\psi$ are then formed by a linear superposition of atomic centered orbitals $\phi$, designated atomic orbitals (AOs).

$$\chi_i = \sum_{\nu} c_{i\nu} \phi_{\nu},$$

(2.42)

here $c_{i\nu}$ are the MO-coefficients associated with AO $\nu$ and MO $i$. The atomic orbitals consist of a product of an angular part, normally a solid harmonic [1], and a radial part. The radial part is usually of the form

$$R(r) \propto e^{-\xi r^2},$$

(2.43)
2.6 Exact state response theory

called Gaussian type orbitals (GTOs). The parameter $\xi$ is a coefficient optimized for each AO. This form is easier to use in calculations than the physically more accurate behaviour $e^{-\xi r}$, and by using several GTOs the same accuracy is attained at a lower computational cost. Some orbitals can further be approximated as a pre-determined linear combination of several GTOs:

$$R^{CGTO} = \sum_i c_i R^{PGTO}_i,$$

where $R^{CGTO}$ is a contracted GTO formed by a set of primitive GTOs $R^{PGTO}$. This is usually done for the core orbitals, as they are affected weakly by molecular bonds. The number of variational parameters and subsequently the flexibility of the calculation is thus lowered, but this can be relaxed at need.

A systematic family of correlation-consistent basis sets has been developed by Dunning and co-workers, with a systematic evaluation and behaviour towards the basis set limit. The basic form of those are a correlation-consistent polarized valence X-zeta basis, cc-pVXZ [31]. They are constructed such as to achieve fast convergence of the correlation energy, and are of great importance for any electron correlated methods. Without those or some other set of additional orbitals, a coupled cluster calculation has insufficient virtual space to excite to, and may be no more accurate than uncorrelated methods. The polarization of the orbitals, important for asymmetric electron density following molecular bonds, is achieved by adding functions of large angular momentum. By the value of X, the cardinal number, the number of basis functions are determined for the valence. The core is described by a minimal basis.

To account for effects of the core and long-range effects, additional basis functions may be required. The basis set is thus augmented with functions with desired properties, such as core-polarizing functions for a better description of core effects [32], or diffuse functions for better description of excited states molecular properties and effects such as long-range van der Waals-interactions [33].

If the molecular states are of a character similar to atomic Rydberg character, it is possible to use a set of Rydberg function [34]. Those are not element-specific and can be centered at a point of interest, such as the center-of-charge.

Note that we have two different ways by which to improve the description of the molecular system: by using a better method to construct the many-particle wave function, or by using a more extensive basis set. This corresponds to the description of the $N$-electron space and the one-electron space, respectively.

2.6 Exact state response theory

For the purpose of determining molecular properties, response theory is utilized. Exact states will first be considered, i.e. states for which the true eigenstates of the unperturbed Hamiltonian is available and the full $N$-electron Hilbert space is spanned, as the results from this will be useful for approximate state response theory. The quasi-energy formalism is utilized as it will be used for coupled cluster response function, and relaxation is incorporated in a density matrix framework by which we obtain equations valid for resonance energies.
The theory in this section mainly follows [35] and partially [36]. Damped response theory can be found in [37, 38].

2.6.1 Standard response theory

When an external field is applied to a molecular system the system interacts with this field; the system responds to the applied perturbation. If such field is of sufficiently small field strength, i.e. sufficiently small intensity, the system will change only slightly and we can use perturbation theory with the perturbed Hamiltonian

\[ \hat{H}(t) = \hat{H}_0 + \hat{V}(t), \] (2.45)

where is \( \hat{H}_0 \) the unperturbed Hamiltonian and \( \hat{V}(t) \) the external field [19].

If the perturbing field is taken as a non-oscillating, static field, i.e. \( \hat{V}(t) = \hat{V}_\alpha F_\alpha \) for a field direction \( \alpha \), the system is reduced to a time-independent case. The time-independent Schrödinger equation can then be utilized in order to obtain ground and excited state energies. For this case the energy is well-defined, as opposed to the case of a time-dependent field where the interaction between the field and the system yields ill-defined energies. The energy of the static case can be considered by a Taylor expansion at zero perturbing field strength

\[ E = E_0 + F_\alpha \frac{\partial E}{\partial F_\alpha} \bigg|_{F_\alpha=0} + F_\alpha F_\beta \frac{1}{2} \frac{\partial^2 E}{\partial F_\alpha \partial F_\beta} \bigg|_{F_\alpha=F_\beta=0} + \ldots, \] (2.46)

with implied summation over indices. The molecular properties are now identified as the different field derivatives of different orders and different perturbing fields, as the observables changes in the system for the perturbing field. For example, the polarizability may be obtained through the second derivative of the energy with respect to an perturbing electric field, at zero field strength. If the field is time-dependent, other methods must be utilized, and this will now be discussed.

We consider a field that is periodic at the time of interest. The field is not assumed to be fully periodic, as this would imply that it has always been present for the system and the system has thus never completely resided in the reference state. We are instead interested in a perturbation that has been adiabatically turned on at a time long past, so that the system has lost all memory of the process of switching on the field. The form of the perturbation operator is the chosen as

\[ \hat{V}_{\alpha}(t) = \sum_\omega \hat{V}_\alpha^{\omega} F_{\alpha}^{\omega} e^{-i\omega t} e^{\epsilon t}. \] (2.47)

where \( F_{\alpha}^{\omega} \) is the Fourier amplitude of the field along a molecular axis \( \alpha \). The small positive \( \epsilon \) gives the adiabatical switch on as \( t \to \infty \), while ensuring that the last term differs negligible from unity at times close to \( t = 0 \). The summation is understood to be over both positive and negative frequencies, and due to the real nature of the perturbation we have \( F_{\alpha}^{-\omega} = [F_{\alpha}^{\omega}]^* \) and \( \hat{V}_{\alpha}^{-\omega} = [\hat{V}_{\alpha}^{\omega}]^\dagger = \hat{V}_{\alpha}^{\omega} \).

The time-dependent molecular properties may now be defined through the time-dependent expectation value of an observable, corresponding to an operator
2.6 Exact state response theory

\( \hat{\Omega} \). We first expand the wave function in orders of the perturbation

\[
|\psi(t)\rangle = |\psi(0)\rangle + |\psi(1)\rangle + |\psi(2)\rangle + \ldots,
\]

(2.48)

and the expectation value of the operator may then be expanded as

\[
\langle \psi(t)|\hat{\Omega}|\psi(t)\rangle = \langle \psi(0)|\hat{\Omega}|\psi(0)\rangle + \langle \psi(1)|\hat{\Omega}|\psi(0)\rangle + \langle \psi(0)|\hat{\Omega}|\psi(1)\rangle + \langle \psi(2)|\hat{\Omega}|\psi(0)\rangle + \langle \psi(1)|\hat{\Omega}|\psi(1)\rangle + \langle \psi(0)|\hat{\Omega}|\psi(2)\rangle + \ldots,
\]

(2.49)

rewritten for simplicity

\[
\langle \psi(t)|\hat{\Omega}|\psi(t)\rangle = \langle \hat{\Omega}^{(0)} \rangle + \langle \hat{\Omega}^{(1)} \rangle + \langle \hat{\Omega}^{(2)} \rangle + \ldots,
\]

(2.50)

where the different terms to the right are again understood as the correction of the expectation value of given order. By use of the perturbation operator in Eq. 2.47, we may now rewrite Eq. 2.49 as

\[
\langle \psi(t)|\hat{\Omega}|\psi(t)\rangle = \langle 0|\hat{\Omega}|0\rangle + \sum_{\omega_1} \langle \langle \hat{\Omega}; \hat{V}_{\omega_1}^{\beta} \rangle \rangle F_{\omega_1}^{\beta} e^{-i\omega_1 t} e^{\epsilon t}
\]

\[
+ \frac{1}{2} \sum_{\omega_1, \omega_2} \langle \langle \hat{\Omega}; \hat{V}_{\omega_1}^{\beta}, \hat{V}_{\omega_2}^{\gamma} \rangle \rangle F_{\omega_1}^{\beta} F_{\omega_2}^{\gamma} e^{-i(\omega_1 + \omega_2) t} e^{2\epsilon t}
\]

\[
+ \ldots,
\]

(2.51)

explicitly giving the expressions for the first-, second- and third-order properties. We express the linear response function as \( \langle \langle \hat{\Omega}; \hat{V}_{\omega_1}^{\beta} \rangle \rangle \), collecting all expectation values that are linear in the the perturbation. In an analogous manner, \( \langle \langle \hat{\Omega}; \hat{V}_{\omega_1}^{\beta}, \hat{V}_{\omega_2}^{\gamma} \rangle \rangle \) collects all first-order non-linear terms and are thus designated as first-order non-linear response functions, and so on for higher-order terms.

2.6.2 Quasi-energy formalism

The quasi-energy formalism may be utilized in order to obtain molecular properties. The wave function is first reformulated as a product of two time-dependent functions

\[
\psi(t) = e^{-i\phi(t)} \tilde{\psi}(t),
\]

(2.52)

a choice that is made unique by requiring \( \phi(t) \) to be a real function and the phase of the projection of \( \tilde{\psi}(t) \) onto ground state \( \psi_0 \) zero. Compare this to the time-evolution of the unperturbed system, which is given by variable separation in the Schrödinger equation 2.1 as

\[
|\psi(t)\rangle = e^{-iE_0 t / \hbar} |0\rangle
\]

(2.53)
with $|0\rangle$ as the ground state wave function. Using the above product of functions in the Schrödinger equation yields
\[
\left(\hat{H} - i\hbar \frac{\partial}{\partial t}\right) \tilde{\psi}(t) = \hbar \dot{\phi}(t) \tilde{\psi}(t) = Q(t) \tilde{\psi}(t),
\] (2.54)
where $Q(t)$ is the time-dependent quasi-energy. This can be explicitly given by a projection, such that
\[
Q(t) = \langle \tilde{\psi} | \left(\hat{H} - i\hbar \frac{\partial}{\partial t}\right) | \tilde{\psi}(t) \rangle.
\] (2.55)

The requirements for Eq. 2.52 and the definition of $Q(t)$ in Eq. 2.54 yield that, in the absence of perturbing fields:
\[
\tilde{\psi}(t) = \psi_0, \quad \phi(t) = E_0 t/\hbar, \quad Q(t) = E_0.
\] (2.56, 2.57, 2.58)

For the phase-isolated wave function, phase function and quasi-energy, respectively. We also define the time-averaged quasi-energy as
\[
Q_T = \frac{1}{T} \int_t^{t+T} Q(t') dt'.
\] (2.59)

If we consider times when only the fundamental frequencies remains to be accounted for, the time-averaged quasi-energy will have no dependencies on time. With a perturbation of the form in Eq. 2.47, collecting all amplitudes of all frequencies along molecular axis $\alpha$ as $F^{\omega}_{\alpha}$, we obtain the following derivative with respect to the perturbing field
\[
\frac{dQ_T}{dF^{\omega}_{\alpha}} = \frac{1}{T} \int_t^{t+T} \langle \tilde{\psi}(t') | \frac{\partial \hat{H}}{\partial F^{\omega}_{\alpha}} | \tilde{\psi}(t') \rangle dt' = \frac{1}{T} \int_t^{t+T} \langle \tilde{\psi}(t') | V^{\omega}_{\alpha} | \tilde{\psi}(t') \rangle e^{-i\omega t'} e^{et'} dt',
\] (2.60)
which is the Hellmann–Feynman theorem. By use of expansions of the time-averaged quasi-energy in amplitudes of the perturbing field, molecular properties may be identified. This will not be treated here, but instead we will consider a density matrix formalism in which relaxation can be incorporated.

### 2.6.3 Damped response theory

The inclusion of resonance frequencies in the external field can be addressed by considering the physical processes that influence an excited state. In the absence of any fields or external interactions an excited state will eventually de-excite into the ground state, the excited state thus has a finite lifetime and experiences spontaneous relaxation. Now, if the system is allowed to interact with other molecules,
e.g. by collisions, the lifetime may be lowered as the system now can be relaxed through radiative and non-radiative relaxation channels. A (weak) perturbing field affecting a ground state, on the other hand, may both influence the population of the different states of the system by absorption and stimulated emission. With decay rates following from the spontaneous processes, the resulting population of excited states remains small, and it is thus possible to apply perturbation theory on the system. Incorporating such relaxation effects directly into the Schrödinger equation is not easily done, even if non-Hermitian contributions are addressed. The effects will instead be incorporated in a phenomenological manner.

As it proves to be well-suited for this task [35], this will be done in the density matrix formalism. Consider the Schrödinger equation for a bra-vector

$$\frac{\partial}{\partial t} \langle \psi(t) | = - \frac{1}{i \hbar} \langle \psi(t) | \hat{H} ,$$

and for a ket-vector as given in Eq. 2.1. Introducing a density operator as

$$\hat{\rho} = \sum_n p(n) |\psi_n(t)\rangle \langle \psi_n(t)| ,$$

for the statistical ensemble of system configurations \(n\) with corresponding probabilities \(p(n)\). We will now consider ensembles that can be described by a single wave function, i.e. pure states. The equation-of-motion for the density operator is then given as

$$\frac{\partial}{\partial t} \hat{\rho} = \frac{1}{i \hbar} [\hat{H}, \hat{\rho}] ,$$

which is known as the Liouville equation. This equation may now be modified as to, phenomenologically, include relaxations of the system. For a matrix element of the density operator, this modification is made such that the Liouville equation becomes a damped counterpart

$$\frac{\partial}{\partial t} \rho_{mn} = \frac{1}{i \hbar} [\hat{H}, \hat{\rho}]_{mn} - \gamma_{mn}(\rho_{mn} - \rho_{mn}^{eq})$$

where we introduce a damping term \(\gamma_{mn}\) that corresponds to the rate of \(\rho\) decaying into the equilibrium value \(\rho_{mn}^{eq}\). We further assume that electronic excitations by thermal or other effects are negligible, and the equilibrium is thus the ground state yielding equilibrium values \(\delta_{n0}\delta_{m0}\).

As the diagonal elements of the density operator can, for a pure state, be regarded as the population of the different states, the diagonal elements of the damping matrix can be understood as the inverse of the average lifetime. We now have a way by which the lifetimes, obtained by experiment or other means, can be phenomenologically addressed for the system.

The expectation value of a operator in the density matrix formalism is then given as the simple trace

$$\langle \hat{\Omega} \rangle = \text{Tr}(\hat{\rho} \hat{\Omega}) = \text{Tr}(\hat{\Omega} \hat{\rho}) .$$

By use of perturbation theory, the density operator can be expanded in orders of the perturbation

$$\rho_{mn}(t) = \rho_{mn}^{(0)} + \rho_{mn}^{(1)} + \rho_{mn}^{(2)} + \ldots ,$$
with a zeroth-order value given by the ground state nature of the unperturbed system

$$\rho_{mn}^{(0)} = \delta_{n0} \delta_{m0}. \quad (2.67)$$

With a Hamiltonian as given in Eq. 2.45, the unperturbed Hamiltonian gives

$$[\hat{H}_0, \hat{\rho}]_{mn} = \hbar \omega_{mn} \rho_{mn}, \quad (2.68)$$

and the damped Liouville equation 2.64 can be solved in order $N$ by time integration

$$\rho_{mn}^{(N)} = e^{-(i\omega_{mn} + \gamma_{mn})t} \int_{-\infty}^{t} \frac{1}{i\hbar} [\dot{V}, \rho_{mn}^{(N-1)}] e^{(i\omega_{mn} + \gamma_{mn}t')dt'} \quad (2.69)$$

The perturbation operator is given in Eq. 2.47, and we obtain the first-order response as equal to

$$\rho_{mn}^{(1)} = \frac{1}{i\hbar} \sum_{\omega} \left[ \frac{\langle m|\hat{V}_\omega|0\rangle \delta_{n0}}{i\omega_{mn} - i\omega + \gamma_{mn} + \epsilon} - \frac{\langle 0|\hat{V}_\omega|n\rangle \delta_{m0}}{-i\omega_{n0} - i\omega + \gamma_{n0} + \epsilon} \right] F^\omega_{\alpha\beta} e^{-i\omega t} e^{\epsilon t}. \quad (2.70)$$

The first-order correction of the expectation value of an operator can now be identified this first-order density operator and Eq. 2.65 as

$$\langle \hat{\Omega}^{(1)} \rangle = \text{Tr}(\hat{\rho}^{(1)} \hat{\Omega}) = \sum_{mn} \rho_{mn}^{(1)} \Omega_{mn} \quad (2.71)$$

$$= -\frac{1}{\hbar} \sum_{\omega} \left[ \frac{\langle 0|\hat{\Omega}|n\rangle \langle n|\hat{V}_\omega|0\rangle - \langle 0|\hat{V}_\omega|n\rangle \langle n|\hat{\Omega}|0\rangle}{\omega_{n0} - \omega - i\gamma_{n0} - i\epsilon} + \frac{\langle 0|\hat{V}_\omega|n\rangle \langle n|\hat{\Omega}|0\rangle}{\omega_{n0} + \omega + i\gamma_{n0} + i\epsilon} \right] F^\omega_{\alpha\beta} e^{-i\omega t} e^{\epsilon t}. \quad (2.72)$$

The frequency $\omega$ runs over both positive and negative values. Now consider a reasonable laser detuning, by which it is possible to let $\epsilon = 0$. We also assume a global lifetime $\gamma_{mn} = \gamma$, for simplicity. By comparison to Eq. 2.51, the linear response function is found to be equal to

$$\langle \langle \hat{\Omega}; \hat{V}_\omega \rangle \rangle = -\frac{1}{\hbar} \sum_{\omega} \left[ \frac{\langle 0|\hat{\Omega}|n\rangle \langle n|\hat{V}_\omega|0\rangle}{\omega_{n0} - \omega - i\gamma} + \frac{\langle 0|\hat{V}_\omega|n\rangle \langle n|\hat{\Omega}|0\rangle}{\omega_{n0} + \omega + i\gamma} \right] F^\omega_{\alpha\beta} e^{-i\omega t} e^{\epsilon t}. \quad (2.73)$$

A standard response function, lacking relaxation, can simply be obtained by letting the damping term $\gamma = 0$. This yields a real equation with divergencies at resonance frequencies, due to the terms in the denominator. In other words, by letting the frequency $\omega \to \omega + i\gamma$, we obtain a complex response function which allows for calculations including excitation frequencies.

The polarizability is given by the linear response function with the electric dipole moment operator as the operator of perturbation and the operator of interest

$$\alpha_{\alpha\beta}(-\omega; \omega) = \alpha^I_{\alpha\beta}(-\omega; \omega) + i\alpha^R_{\alpha\beta}(-\omega; \omega) = -\langle \langle \hat{\mu}_\alpha; \mu_\beta \rangle \rangle. \quad (2.73)$$
with this, the absorption cross-section, and thus spectrum of a system, can be obtained by the imaginary part of the polarizability

\[
\sigma(\omega) = \frac{4\pi\omega}{3c} \sum_{\beta=x,y,z} \alpha_{\beta\beta}^{1}(-\omega;\omega) \tag{2.74}
\]

for all Cartesian component \(\beta\) of the electric dipole moment operator. This imaginary part can be given from Eq. 2.72 as

\[
\alpha_{\alpha\beta}^{1} = \frac{\gamma}{\hbar} \sum_{n} \left[ \frac{\langle 0|\hat{\mu}_{\alpha}|n\rangle\langle n|\hat{\mu}_{\beta}|0\rangle}{(\omega_{0n} - \omega)^2 + \gamma^2} - \frac{\langle 0|\hat{\mu}_{\beta}|n\rangle\langle n|\hat{\mu}_{\alpha}|0\rangle}{(\omega_{0n} + \omega)^2 + \gamma^2} \right]. \tag{2.75}
\]

The resonance term of this equation is seen to be

\[
f(\omega;\omega_{0n},\gamma) = \frac{A}{\pi} \frac{\gamma}{(\omega_{0n} - \omega)^2 + \gamma^2} \quad \text{with} \quad A = \pi \frac{\langle 0|\hat{\mu}_{\alpha}|n\rangle\langle n|\hat{\mu}_{\beta}|0\rangle}{\hbar}, \tag{2.76}
\]

which is equivalent to a Lorentzian function with amplitude \(A/(\pi\gamma)\) and a half-width at half-maximum of \(\gamma\).

In other words, the inclusion of phenomenological damping by a finite lifetime \(\gamma\) yields a Lorentzian broadening, as is the effect of the lifetime of excited states for absorption processes.

### 2.7 Damped coupled cluster response theory

We will now consider response theory utilizing approximate states as obtained by the coupled cluster method. A Lagrangian formalism using quasi-energy will be used, and relaxation incorporated again by the addition of a finite lifetime. The asymmetric Lanczos-chain method by which to determine eigenvalues of a large matrix will also be considered, as this is necessary for a computationally tractable approach. Damped coupled cluster linear response functions as solved by the Lanczos-chain method will finally be given, which is the method of obtaining X-ray absorption spectrum studied in this thesis.

The theory in this section mainly follows [35] and [36].

#### 2.7.1 Coupled cluster response theory

Response theory using approximate states as from coupled cluster methods can be given in the quasi-energy formalism, described in section 2.6.2. The definition of the coupled cluster quasi-energy is obtained from the equation

\[
\left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) e^{\mathcal{T}(t)} |0\rangle = Q(t) e^{\mathcal{T}(t)} |0\rangle, \tag{2.77}
\]

and as the time-derivative of the phase-isolated coupled cluster state is orthogonal to the Hartree–Fock states, the quasi-energy is equal to

\[
Q(t) = \langle 0|\hat{H} e^{\mathcal{T}(t)} |0\rangle, \tag{2.78}
\]
analogous to the definition of the coupled cluster energy as given in Eq. 2.37. It should be noted that the projection by which the quasi-energy is obtained does not guarantee that the value obtained is real, as opposed to the situation when an expectation value is given (i.e. variational methods).

In a similar manner, the projection unto the the excited states manifold in Eq. 2.38 can be used in the quasi-energy formalism to yield the time-dependent amplitudes
\[
\langle 0 | e^{-\hat{T}(t)} \left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) e^{\hat{T}(t)} | 0 \rangle = 0. \tag{2.79}
\]

In the time-dependent coupled cluster approach we then solve the quasi-energy equation with constraints given by the equation for the time-dependent amplitudes. The constraints that the amplitude equations results in can be incorporated by use of variational Lagrangian methods, where equations of motion must fulfill the variational conditions
\[
\delta L_T = 0, \tag{2.80}
\]
imposed here for a time-averaged Lagrangian. The coupled cluster Lagrangian can be found to be equal to
\[
L(t) = Q(t) + \sum_n \lambda_n(t) \langle n | e^{-\hat{T}(t)} \left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) e^{\hat{T}(t)} | 0 \rangle, \tag{2.81}
\]
with the time-dependent Lagrangian multipliers \( \lambda_n \) associated with the constraints given by a specific excited determinant \( n \).

The response functions are obtained as the derivatives of the time-averaged Lagrangian with respect to the perturbing field, such that the zeroth-order and linear response function in coupled cluster response theory is identified as
\[
\langle \hat{V}_{\omega_1} \rangle = \left. \frac{dL_T}{dF_{\omega_1}} \right|_{F_{\omega_1}=0}, \quad \langle \langle \hat{V}_{\omega_1} ; \hat{V}_{\omega_2} \rangle \rangle = \left. \frac{d^2L_T}{dF_{\omega_1} dF_{\omega_2}} \right|_{F_{\omega_1}=0}. \tag{2.82}
\]

In order to evaluate these field derivatives, the derivative of the time-averaged Lagrangian with respect to the perturbing field, such that the zeroth-order and linear response function in coupled cluster response theory is identified as
\[
\langle \hat{V}_{\omega_1} \rangle = \left. \frac{dL_T}{dF_{\omega_1}} \right|_{F_{\omega_1}=0}, \quad \langle \langle \hat{V}_{\omega_1} ; \hat{V}_{\omega_2} \rangle \rangle = \left. \frac{d^2L_T}{dF_{\omega_1} dF_{\omega_2}} \right|_{F_{\omega_1}=0}. \tag{2.82}
\]

In order to evaluate these field derivatives, the derivative of the time-averaged Lagrangian with respect to the Lagrangian multipliers and the amplitudes are first considered. The variational condition yields for the multipliers
\[
\left. \frac{\partial L_T}{\partial \lambda_n^{(0)}} \right|_{F_{\omega_1}=0} = \langle n | e^{-\hat{T}^{(0)}} \hat{H}_0 \hat{T}^{(0)} | 0 \rangle = 0 \tag{2.83}
\]
which is identical to Eq. 2.79. Superscripts again designate the \( N \):th order correction with respect to the perturbation. For the coupled cluster amplitudes the following is obtained
\[
\left. \frac{\partial L_T}{\partial t_n^{(0)}} \right|_{F_{\omega_1}=0} = \langle 0 | \hat{H}_0 \hat{T}_n^{(+)} | CC \rangle + \sum_n \lambda_n^{(0)} \langle k | e^{-\hat{T}^{(0)}} [\hat{H}_0, \hat{T}_n^{(+)}] | CC \rangle, \tag{2.84}
\]
where \( | CC \rangle = e^{\hat{T}} | 0 \rangle \) and \( \hat{T}_n^{(+)} \) is the excitation operator corresponding to amplitude \( t_n \), as earlier. The time-dependent amplitude is given as
\[
t_n(0) = t_n^{(0)} + \sum_{\omega_1} t_n^{(1)} e^{-i\omega_1 t} + \ldots. \tag{2.85}
\]
The derivative with respect to coupled cluster amplitudes in Eq. 2.84 can be rewritten in matrix form, such that

$$\tilde{\lambda}^{(0)} = -\tilde{\kappa}^{[1]} \left[ A^{[2]} \right]^{-1},$$

with

$$\tilde{\kappa}^{[1]}_n = \langle 0 | \hat{H}_0 \hat{\tau}^\dagger_0 | \text{CC} \rangle$$ and $$A^{[2]}_{\kappa n} = \langle k | e^{-T^{(0)}} [\hat{H}_0, \hat{\tau}^\dagger_0] \text{CC} \rangle.$$ (2.87)

The matrix $$A^{[2]}$$ is the nonsymmetric coupled cluster Jacobian. The response functions as from Eq. 2.82 can now be evaluated, and the zeroth-order is equal to

$$\langle \hat{V}_{\omega} \alpha \rangle = \frac{dL_T}{dF_{\alpha}^{\omega_1}} \bigg|_{F_{\omega} = 0} = \frac{\partial L_T}{\partial F_{\alpha}^{\omega_1}} \bigg|_{F_{\omega} = 0} + \sum_n \left[ \frac{\partial L_T}{\partial t^{(1)}_n} \frac{\partial t^{(1)}_n}{\partial F_{\alpha}^{\omega_1}} + \frac{\partial L_T}{\partial \lambda^{(1)}_n} \frac{\partial \lambda^{(1)}_n}{\partial F_{\alpha}^{\omega_1}} \right] \bigg|_{F_{\omega} = 0}$$

$$= \frac{\partial L_T}{\partial F_{\alpha}^{\omega_1}} \bigg|_{F_{\omega} = 0} = \left[ \langle 0 | \hat{V}_{\omega}^{\alpha_1} e^{-\hat{T}^{(0)}} \hat{\tau} | 0 \rangle + \sum_n \lambda^{(0)}_n \langle n | e^{-\hat{T}^{(0)}} \hat{\tau} \hat{V}_{\omega}^{\alpha_1} e^{-\hat{T}^{(0)}} | n \rangle \delta_{\omega_1} \right]$$

where the evaluation is made at zero field strength and the variational condition ensures that the sum in the first row is zero. The zeroth-order multipliers in this expression is give in the matrix equation 2.86.

Continuing with the linear response function, we introduce a permutation operator $$P_{\alpha, \beta}$$, which permutes the field amplitudes $$F_{\alpha}^{\omega_1}$$ and $$F_{\beta}^{\omega_2}$$. With this the expression of the response function can be made symmetric, and through cancellation of terms and implicit summation over indices:

$$\langle \hat{V}_{\omega}^{\alpha_1} ; \hat{V}_{\omega}^{\alpha_2} \rangle = \frac{d^2L_T}{dF_{\alpha}^{\omega_1} dF_{\beta}^{\omega_2}} \bigg|_{F_{\omega} = 0}$$

$$= \sum P_{\alpha, \beta} \left[ \frac{\partial^2 L_T}{\partial F_{\alpha_1}^{\omega_1} \partial t^{(1)}_n \partial F_{\beta_1}^{\omega_2}} \bigg|_{F_{\omega} = 0} + \frac{1}{2} \frac{\partial t^{(1)}_m}{\partial F_{\alpha_1}^{\omega_1}} \frac{\partial^2 L_T}{\partial t^{(1)}_m \partial t^{(1)}_n} \bigg|_{F_{\omega} = 0} \right].$$

The field derivative of the first-order amplitudes at zero field strength can be evaluated by repeated use of the variational condition in Eq. 2.80, and this yields

$$\frac{d}{dF_{\alpha}^{\omega_1}} \left[ \frac{\partial^2 L_T}{\partial \lambda^{(1)}_m (\omega_2)} \right] = \frac{\partial^2 L_T}{\partial F_{\alpha_1}^{\omega_1} \partial \lambda^{(1)}_m} + \frac{\partial^2 L_T}{\partial \lambda^{(1)}_m \partial t^{(1)}_n} \bigg|_{F_{\omega} = 0}$$

$$\Rightarrow \frac{\partial t^{(1)}_n (\omega_1)}{\partial F_{\alpha_1}^{\omega_1}} \bigg|_{F_{\omega} = 0} = - \left[ \frac{\partial^2 L_T}{\partial \lambda^{(1)} \partial t^{(1)}} \bigg|_{F_{\omega} = 0} \right]^{-1} \frac{\partial^2 L_T}{\partial F_{\alpha_1}^{\omega_1} \partial \lambda^{(1)}} \bigg|_{F_{\omega} = 0},$$

where the last row is given in matrix and vector form. The element of the matrix in this equation is given as

$$\frac{\partial^2 L_T}{\partial \lambda^{(1)}(\omega_1) \partial t^{(1)}(\omega_1)} \bigg|_{F_{\omega} = 0} = \left[ A^{[2]}_{mn} - \hbar \omega_2 \delta_{mn} \right] \delta_{\omega_1 + \omega_2},$$
and reformulating Eq. 2.90 such as
\[ (A^{[2]} - \hbar \omega_2 I)\tilde{t}^F(\omega) = -\xi^F, \]  
(2.92)
where \( \tilde{t}^F(\omega) \) is the vector of field derivatives of response amplitudes, i.e. the left-hand side of Eq. 2.86, and
\[ \tilde{\xi}^F = \left. \frac{\partial^2 L_T}{\partial F_\omega \partial \lambda_m^{(1)}(\omega_1)} \right|_{F_\omega = 0} = \langle m|e^{-T^{(0)}\hat{V}\omega_1}|CC\rangle \delta_{\omega_1 + \omega_2}. \]  
(2.93)
The poles of the response function are given by the singularities of the matrix in Eq. 2.92, so that a diagonalization of the Jacobian \( A^{[2]} \) yields the excitation energies [35].

Relaxation in the coupled cluster approach is achieved in an analogous manner as for the exact state, given in Eq. 2.64. This is equivalent with replacing the frequency with a damped, complex counterpart such that \( \omega \rightarrow \omega + i\gamma \). The dampening factor is again chosen with a global value \( \gamma \). This yields a damped equation from which the absorption spectrum in principle can be solved:
\[ (A^{[2]} - \hbar(\omega + i\gamma) I)\tilde{t}^F(\omega + i\gamma) = -\xi^F. \]  
(2.94)
However, all regions are not of physical significance, and this equation would be computationally challenging as a result of the large number of possible excitation. The asymmetric Lanczos-chain method can be applied for a more feasible approach.

### 2.7.2 Lanczos-chain method

The **Lanczos-chain method** is a way to obtain a tri-diagonal form of a large matrix in an iterative manner. This can yield an exact representation of the original matrix or an approximation, depending on the truncation of the method. The method is described in [39] and as implemented in a symmetrical setting in [40].

Consider a nonsymmetric matrix \( A \) of dimension \( n \). We now seek a transformation of this matrix as follows
\[ T^{(m)} = P^{(m)}A Q^{(m)}, \]  
(2.95)
where \( T^{(m)} \) is of dimension \( m \) and has an asymmetric tri-diagonal form such that
\[ T^{(m)} = \begin{pmatrix} \alpha_1 & \gamma_1 & 0 \\ \beta_1 & \alpha_2 & \cdots \\ 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \alpha_{m-1} & \gamma_m \\ 0 & \cdots & \cdots & \beta_m & \alpha_m \end{pmatrix}. \]  
(2.96)
The transformation matrices \( P^{(m)} \) and \( Q^{(m)} \) are of dimension \( n \times m \) and imposed to bi-orthonormal
\[ P^{(m),T} = Q^{(m), -1} \quad \Rightarrow \quad P^{(m),T} Q^{(m)} = I. \]  
(2.97)
If the dimension of the tri-diagonal matrix is equal to that of the original matrix, i.e. \( m = n \), we obtain a complete transformation of \( A \) given as

\[
A Q^{(n)} = Q^{(n)} T^{(n)} \quad \text{and} \quad A^T P^{(n)} = P^{(n)} T^{(n)}^T.
\] (2.98)

By labeling the columns in \( Q^{(n)} \) as \( \bar{q}_1, \bar{q}_2, \ldots, \bar{q}_n \), and analogous for \( P^{(n)} \), it is trivial to show that

\[
A \bar{q}_i = \gamma_{i-1} \bar{q}_{i-1} + \alpha_i \bar{q}_i + \beta_i \bar{q}_{i+1},
\] (2.99)

\[
A^T \bar{p}_i = \beta_{i-1} \bar{p}_{i-1} + \alpha_i \bar{p}_i + \gamma_i \bar{p}_{i+1},
\] (2.100)

for all \( i = 1, \ldots, n-1 \), with the requirement that \( \gamma_0 \bar{q}_0 = \beta_0 \bar{p}_0 = 0 \). It is now possible to rearrange this so that we obtain an iterative procedure by which to construct the matrices

\[
\beta_i \bar{q}_{i+1} = \bar{r}_i = (A - \alpha_i I) \bar{q}_i - \gamma_i \bar{q}_{i+1},
\] (2.101)

\[
\gamma_i \bar{p}_{i+1} = \bar{r}_i = (A^T - \alpha_i I) \bar{p}_i - \beta_i \bar{p}_{i+1},
\] (2.102)

and with the bi-orthogonality condition from Eq. 2.97 we get

\[
\bar{p}^T_i \bar{q}_j = \left( \frac{s_i}{\gamma_i} \right) \left( \frac{\bar{r}_i}{\beta_i} \right) = \delta_{ij}
\] (2.103)

There is no unique way of determining the values of \( \beta_i \) and \( \gamma_i \), and we choose to define those as

\[
\beta_i = \sqrt{|s_i^T \bar{r}_i|} \quad \Rightarrow \quad \gamma_i = \frac{s_i^T \bar{r}_i}{\sqrt{|s_i^T \bar{r}_i|}} = \pm \beta_i
\] (2.104)

If we now terminate the iterative procedure given by Eqs. 2.101 and 2.102 at a value \( m < n \), an error is introduced for the transformation in Eq. 2.98, yielding for matrix \( Q^{(m)} \)

\[
A Q^{(m)} = Q^{(m)} T^{(m)} + E^{(m)},
\] (2.105)

where

\[
E^{(m)} = \beta_m \bar{q}_{m+1} e^{(m)T}_m.
\] (2.106)

Here \( e^{(m)}_m \) is a unit vector with value 1 in element \( m \).

Disregarding this error, we construct an approximate vector \( A^{(m)} \) as

\[
A^{(m)} Q^{(m)} = Q^{(m)} T^{(m)}.
\] (2.107)

The tri-diagonal matrix \( T^{(m)} \) may now be diagonalized with left and right eigenvectors

\[
T^{(m)} R^{(m)} = R^{(m)} \Omega^{(m)},
\] (2.108)

\[
L^{(m)} T^{(m)} = \Omega^{(m)} L^{(m)},
\] (2.109)
2.7.3 Damped coupled cluster response theory with the Lanczos-chain method

Consider the linear response function, as given in Eq. 2.89. For simplicity, let \( \langle \langle \hat{V}_\omega \rangle \rangle = \langle \langle A; B \rangle \rangle \), where \( A \) and \( B \) in this case will correspond to electric dipole operators of Cartesian coordinates, and let \( \omega' = \omega + i\gamma \). It can be shown that the linear response function is given as [36]

\[
\langle \langle A; B \rangle \rangle = C^{\pm \omega'} \left[ \eta^A_{\mu} t^B_{\mu}(\omega') + \eta^A_{\mu} t^B_{\mu}(-\omega') + t^A_{\mu}(-\omega') F_{\mu \nu} t^B_{\nu}(\omega') \right],
\]

where

\[
\eta^A_{\mu} = \langle 0 | [A, \hat{T}^\dagger]|CC \rangle + \sum_n \lambda^{(0)}_k \langle k | e^{-iT} [A, \hat{T}^\dagger]|CC \rangle,
\]

\[
F_{\mu \nu} = \langle 0 | [\hat{H}_0, \hat{T}^\dagger]|CC \rangle + \sum_n \lambda^{(0)}_k \langle k | e^{-iT} [\hat{H}_0, \hat{T}^\dagger]|CC \rangle.
\]

and the symmetrization operator is included to ensure real values of the linear response function lacking relaxation, given as

\[
C^{\pm \omega} f(\omega) = \frac{1}{2} \left[ f(\omega) + f^*(\omega) \right].
\]

As can be seen, the calculation of the linear response function in this formalism involves contributions of the form

\[
c_{AB}(\omega') = \tilde{\eta}^A(A^{[2]} - \hbar \omega' I)^{-1} \tilde{\xi}^B = N_\eta N_\xi \tilde{\eta}^A(A^{[2]} - \hbar \omega' I)^{-1} \tilde{\xi}^B,
\]

with normalization factors \( N_\eta \) and \( N_\xi \). Choosing the normalized vectors as initial vectors of construction of the (complete) \( P = P^{(n)} \) and \( Q = Q^{(n)} \) transformation matrices from section 2.7.2

\[
\tilde{q}_1 = \tilde{\xi}^B = Q \tilde{e}_1^{(n)},
\]

\[
\tilde{p}^T_1 = \tilde{\eta}^A = e_1^{(n), T} P^T.
\]

and designating \( A^{[2]}(\omega') = A^{[2]} - \hbar(\omega + i\gamma) I \) and \( T(\omega') = T - \hbar(\omega + i\gamma) I \), Eq. 2.117 is seen to be equal to

\[
c_{AB}(\omega') = N_\eta N_\xi P^T A^{[2]}(\omega') Q \tilde{e}_1^{(n)} = N_\eta N_\xi e_1^{(n), T} T^{-1} e_1^{(n)}.
\]
The bi-orthogonal eigenvectors to the tri-diagonal matrix, as given in Eqs. 2.108 and 2.109 yields (in full space)

\[ T(\omega') = T - \hbar(\omega + i\gamma)I = R(\Omega - \hbar\omega'I)^{-1}L. \]  

(2.121)

This can be utilized in Eq. 2.120 to yield

\[ c_{AB}(\omega') = N_\eta N_\xi \bar{\epsilon}_1^{(n)} R(\Omega - \hbar\omega'I)^{-1}L\bar{\epsilon}_1^{(n)} = N_\eta N_\xi \sum_j \frac{L_{j1}R_{1j}}{\hbar(\omega_j - \omega - i\gamma)}. \]  

(2.122)

Further, the last term in Eq. 2.113 is simplified by first rewriting the amplitude vector as

\[ t^A(\omega') = N_\xi (A^{[2]} - \hbar\omega'I)^{-1}\bar{\xi}^B = -N_\xi Q R(\Omega - \hbar\omega'I)^{-1}LP^T\bar{\xi}^B \]

\[ = -N_\xi Q R(\Omega - \hbar\omega'I)^{-1}L\bar{\epsilon}_1^{(n)}, \]  

(2.123)

where we in the last row make use of the definition of starting vectors from Eqs. 2.118 and 2.119 and the bi-orthogonality condition yielding Eq. 2.103. This gives, in matrix form

\[ N_\eta N_\xi \bar{\epsilon}_1^{A,T}(\omega) = N_\xi^2 \sum_{jk} (QRQR)^{jk} \frac{L_{j1}L_{k1}}{\hbar^2(\omega - \omega_j + i\gamma)(\omega + \omega_k + i\gamma)}. \]  

(2.124)

The linear response equation can then be written in the following simple form, where the \( \hbar \) terms are accounted for through the numerical constants:

\[ \langle A; B \rangle = N_\eta N_\xi \sum_j \left[ \frac{L_{j1}R_{1j}}{\omega - \omega_j + i\gamma} - \frac{L_{j1}R_{1j}}{\omega + \omega_j + i\gamma} \right] \]

\[ + N_\xi^2 \sum_{jk} (QRQR)^{jk} \frac{L_{j1}L_{k1}}{(\omega - \omega_j - i\gamma)(\omega - \omega_k + i\gamma)}. \]  

(2.125)

This response equation can be split into a real and an imaginary part. Since we are interested in the imaginary part of the response function, we identify this as

\[ Im\langle A; B \rangle = \gamma N_\eta N_\xi \sum_j \left[ \frac{L_{j1}R_{1j}}{(\omega - \omega_j)^2 + \gamma^2} + \frac{L_{j1}R_{1j}}{(\omega + \omega_j)^2 + \gamma^2} \right] \]

\[ + N_\xi^2 \sum_{jk} (QRQR)^{jk} \frac{L_{j1}L_{k1}(2\omega + \omega_k - \omega_j)}{(\omega - \omega_j - i\gamma)(\omega - \omega_k + i\gamma)}. \]  

(2.126)

This equation yields the imaginary part of the polarizability, and by use of Eq. 2.74 we are then able to calculate the cross-section and thus the spectrum of the system.

The above equation yields the spectrum of the system, with lifetime broadening included directly. It may, however, be of interest to study the excitations directly, e.g. the oscillator strength and nature of excited states. For this purpose, the left and right eigenvectors of the Jacobian can be obtained through the Lanczos-chain method as in Eqs. 2.111 and 2.112. The weights of the different coupled
cluster excitations can then be identified and the nature of the excited states given. Further, the oscillator strength can be obtained as the residues of the linear response function in Eq. 2.125

\[
f_{0 \rightarrow j} = \frac{2}{3} \omega_j N \xi \left[ L_{j1}R_{1j} - N^2 \sum_k (Q R Q R)_{jk} L_{j1}L_{k1} \right]. \tag{2.127}
\]

Note that we have so far considered the case where the Lanczos-chain method is used to span the full space. If the method is truncated by a choice of chain length \( m < n \), the expressions given above will be approximately correct. The chain length must then be chosen such as ensuring that the Lanczos-chain method is converged in the frequency region of interest, i.e. all excitations of energy of interest have been found with correct values. This convergence can be studied visually, by comparing two calculations of chain lengths \( j \) and \( k \) (where \( j < k \)). A better method is achieved by use of an error function, calculated as

\[
e_{j,k}(\omega_1, \omega_2) = \frac{\omega_2}{\omega_1} \left| \int_{\omega_1}^{\omega_2} \sigma^{(j)}(\omega) - \sigma^{(k)}(\omega) \, d\omega \right|
\]

(2.128)

where \( \sigma^{(j)} \) and \( \sigma^{(k)} \) is the absorption spectra calculated with the different chain lengths in the frequency interval \( \omega_1 \) to \( \omega_2 \). The values of \( j \) and \( k \) should be sufficiently different so that the spectra will change if not converged.
Chapter 3

Computational details

This project has mainly concerned calculations made with a locally modified version of the quantum chemical program DALTON [41]. All the coupled cluster calculations has utilized this program, mainly using the coupled cluster method CCSD [23]. The CC levels of theory CCS and CC2 [25] have also been used for comparison, as well as CCSDR(3) [26] corrections to the CCSD results. In order to account for relativistic effects, the Douglas–Kroll scalar relativistic Hamiltonian has been used [42, 43]. This may account for purely scalar relativistic effects by corrections of the one-electron integrals. This approach is made necessary as correlation effects and relativistic effects are not additive, so that shifts obtained by STEX cannot be used.

Calculation using the four-component STEX [17] approach have been done in the relativistic quantum chemical program DIRAC [44]. Fully relativistic, scalar relativistic and nonrelativistic settings have been considered, the last two utilizing Dyall’s spin-free Hamiltonian [45] and the Lévy-Leblond Hamiltonian [46], respectively. As STEX gives excitation energies with corresponding moments, a Lorentzian broadening have been used for visualization of the results.

The correlation-consistent basis sets developed by Dunning and co-workers have been utilized, designated as cc-pVXZ [31]. These basis sets have also been augmented with diffusee functions [33] and core-polarizing functions [32]. Further, Rydberg basis functions [34] have been used. These are given with low angular momentum and quantum numbers that vary with half-integer steps.
Chapter 4

Results and discussion

4.1 Neon

The K-edge of neon has been extensively studied with the present method, and the conclusions are illustrated in this section. Neon has a clean spectrum with no vibronic features and relatively simple excited states, and is thus suitable for a investigation of theoretical models. The excitations of interest are transitions from 1s to 3p, 4p, 5p, 6p and 7p [47]. The ionization potential of the core electron has been experimentally determined as 870.17 eV [48].

4.1.1 Static-exchange approach

Ionization potential

The 1s ionization potential (IP) has been determined by means of the ∆SCF method and, for comparison, we also report 1s-orbital energies for the ground and ionized state, respectively. Results are given in Table 4.1. The qaug-cc-pVQZ (qQZ) basis set provides benchmark values for this approach, and we note that the smaller basis set taug-cc-pVTZ (tTZ) overestimated the IP by 0.57 eV, in comparison. Furthermore, we investigate the relativistic effect as due to the relativistic contraction of the 1s-orbital. The relativistic calculations are performed at the four-component Dirac–Coulomb level of theory, and it is seen that the relativistic effects on the neon 1s IP amounts to 1.13 eV at a qQZ level. For a nonrelativistic calculation using the taug-cc-pVTZ basis set, we see a cancellation of errors due to the use of a limited basis set and the neglect of scalar relativistic effects for the 1s-orbital.

Decontracting the basis set and relativistic effects

The effect of using fully uncontracted basis sets has been investigated to evaluate the resulting enhanced flexibility. This decontraction can be expected to be most important for relativistic calculations, as the basis set contraction coefficients are optimized for the nonrelativistic case.
Table 4.1. Ionization potential and Hartree–Fock $1s$-orbital energies for neon, all results are given in eV.

<table>
<thead>
<tr>
<th></th>
<th>Nonrelativistic</th>
<th>Relativistic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$tTZ^a$</td>
<td>$qQZ^b$</td>
</tr>
<tr>
<td>Ionization potential</td>
<td></td>
<td></td>
</tr>
<tr>
<td>∆SCF</td>
<td>869.30</td>
<td>868.82</td>
</tr>
<tr>
<td></td>
<td>870.52</td>
<td>869.95</td>
</tr>
<tr>
<td>1s-orbital energy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ground state</td>
<td>-891.96</td>
<td>-891.83</td>
</tr>
<tr>
<td></td>
<td>-893.22</td>
<td>-893.05</td>
</tr>
<tr>
<td>ionized state</td>
<td>-1011.95</td>
<td>-1011.50</td>
</tr>
<tr>
<td></td>
<td>-1013.35</td>
<td>-1012.92</td>
</tr>
</tbody>
</table>

$^a$taug-cc-pVTZ. $^b$qaug-cc-pVQZ.

The results are given in Fig. 4.1, and we see a resulting shift of the $1s \rightarrow 3p$ transition energy in the X-ray absorption spectra that is largest for the smaller basis set: 0.50 eV. Smaller shifts are observed for nonrelativistic and relativistic calculations with the $qQZ$ basis set: 0.15 and 0.12 eV respectively. Note that the shifts in the ionization potentials are very similar: 0.50, 0.16, and 0.11 eV, respectively. These effects are attributed to the reduced screening and subsequent contraction of the $1s$-orbital in ionized state as compared to ground state, as this is better described in a decontracted basis set. We remark the smaller shift in energy for a uncontracted basis set in the relativistic case, contrary to expectation.

We note the appearance of peaks above the IP. These features arise from the use of an incomplete basis set consisting of localized atomic orbitals, and as such has no physical meaning. They will be present for all calculations and should be disregarded. The unphysical features can also be investigated by analyzing the nature of the excited states through the approximate eigenvectors, obtained from Eqs. 2.111 and 2.112. There may, however, exist features such as excitations to $σ^*$-orbitals above the IP for other systems [9].

Relativistic effects amount to an energy shift of the X-ray adsorption spectra and the IP of 1.13 and 1.17 eV for contracted and uncontracted $qQZ$ basis sets, respectively. The nature of the relativistic effects have been studied using STEX with a contracted qaug-cc-pCVTZ basis set at a fully relativistic, scalar relativistic and nonrelativistic level of theory. The resulting ionization potentials and $1s \rightarrow 3p$ excitation energies can be found in Table 4.2. We observe a relativistic shift of 1.24 eV for the excitation energy, and 1.16 eV for the ionization potential. Using scalar relativistic methods, these energy shifts are almost fully obtained, with a discrepancy of a 0.3 and 0.2 meV for the excitation energy and IP, respectively. We thus conclude that relativity has a pure scalar effect for this system, and incorporating this will yield a correct description.
Figure 4.1. Neon $K$-edge X-ray absorption spectra obtained using nonrelativistic (NR) and relativistic (REL) STEX approaches. Vertical dashed lines indicate the ionization potential (IP). Obtained using contracted and uncontracted basis sets qaug-cc-pVQZ and taug-cc-pVTZ.

Table 4.2. Neon $1s \rightarrow 3p$ excitation energy and ionization potential (IP) obtained by STEX calculations using fully relativistic, spin-free scalar relativistic and nonrelativistic methods. The basis set is qaug-cc-pCVTZ, and energies are expressed in eV.

<table>
<thead>
<tr>
<th>Method</th>
<th>$1s \rightarrow 3p$</th>
<th>IP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relativistic</td>
<td>867.0394</td>
<td>869.9887</td>
</tr>
<tr>
<td>Scalar relativistic</td>
<td>867.0397</td>
<td>869.9889</td>
</tr>
<tr>
<td>Nonrelativistic</td>
<td>865.8786</td>
<td>868.8278</td>
</tr>
</tbody>
</table>

Description of the nucleus

The STEX spectrum and $\Delta$SCF ionization potential have been obtained for a nucleus treated as a point-charge and as a Gaussian charge distribution. Resulting shifts in energy are below level of interest, and it is thus sufficient to consider the nuclei as point charges.
4.1.2 Convergence of the Lanczos-chain method

The convergence of the Lanczos-chain method for the calculation of CCSD spectra has been investigated in terms of chain length $J$. The result with the basis set taug-cc-pCVTZ is seen in Fig. 4.2, and a similar study using taug-cc-pVTZ has been performed. We report a need of a chain length $J$ of approximately 600 for a converged spectrum in the given frequency region, while smaller chain lengths may yield no absorption peaks or incorrect excitation energies and transition moments. The $1s \rightarrow 3p$ excitation is obtained before the less intense features, as is expected for the Lanczos-chain method.

By comparison to calculations using the basis set taug-cc-pVTZ, we report a requirement of approximately half the chain length as for the system with core-polarizing functions. This is due to the linear scaling of the dimension of the $A^{[2]}$-matrix with respect to the excitation space, see Eq. 2.87.

![Graph showing the convergence of the Lanczos-chain method](image)

**Figure 4.2.** Neon K-edge X-ray absorption spectra as obtained for different Lanczos-chain lengths $J$, at the CCSD/taug-cc-pCVTZ level of theory. The error $\epsilon_{j,k}$ is calculated from Eq. 2.128 for the interval 865.1 to 873.5 eV.

4.1.3 Basis set selection

The damped coupled cluster response method sets several demands on the basis sets used. Not only should they be correlation-consistent, but we also require a good description of the excited states and the relaxation of the core and valence
electrons. For this purpose the description of the excited states have been studied using diffuse functions and Rydberg functions. The description of the core (and partially the valence) has been examined by use of core-polarizing functions and an uncontracted basis set.

**Excited states**

The effect of multiple augmentation has been studied at nonrelativistic CCSD and STEX levels of theory, using single to quadruple sets of diffuse functions. The results are given in Fig. 4.3, and we see similar behaviour of the two methods, with a relative shift of 1.54 eV for the $1s \rightarrow 3p$ excitation energy. Single augmentation yields an unreliable spectrum, and at least double augmentation is required to obtain an absorption peak at correct photon energy. By further increasing augmentation with larger sets of diffuse functions the less intense peaks appear: triple augmentation gives $1s \rightarrow 4p$ and quadruple augmentation gives also $1s \rightarrow 5p$ excitations. Once the correct absorption peaks are obtained, they remain at the same photon energy and approximately the same intensity, see Table 4.3 for CCSD excitation energies. Here excitation energies using pentuple augmentation are also reported, as constructed in an even-tempered manner [2]. It is suggested that a basis set augmented with few diffuse functions can be used to obtain good results for the most intense peaks, if a large basis is unfeasible.

**Table 4.3.** Neon excitation energies (eV) obtained by CCSD calculations, using the basis sets cc-pVTZ augmented with double, triple, quadruple and pentuple sets of diffuse functions.

<table>
<thead>
<tr>
<th>Excitation</th>
<th>daug</th>
<th>taug</th>
<th>qaug</th>
<th>paug</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s \rightarrow 3p$</td>
<td>867.90</td>
<td>867.90</td>
<td>867.90</td>
<td>867.90</td>
</tr>
<tr>
<td>$1s \rightarrow 4p$</td>
<td></td>
<td>869.58</td>
<td>869.58</td>
<td>869.58</td>
</tr>
<tr>
<td>$1s \rightarrow 5p$</td>
<td></td>
<td></td>
<td>870.18</td>
<td>870.18</td>
</tr>
</tbody>
</table>

As the excited states for neon are of Rydberg character, a cost-efficient way to describe these would be by use of Rydberg functions. These have the advantage of possessing variable angular momentum, as the excited states of this system are of low angular momentum. By including functions of low angular momentum, we can thus improve the description of the excited states while maintaining the computational cost, as compared to only using diffuse functions. This option has been explored by comparing results for a qaug-cc-pCVTZ basis set to a aug-cc-pCVT basis with additional Rydberg ($6s6p$) functions. The result is given in Fig 4.4, and we note the appearance the $1s \rightarrow 6p$ and $1s \rightarrow 7p$ excitations for the basis set including Rydberg functions. These features arise due to the improved description by additional s-functions of the Rydberg basis set. A quadruply augmented basis set instead possess a larger number of functions of d- and f-character. The excitation energies obtained shows a slight difference in excitation energies: 0.02 eV for the $1s \rightarrow 3p$ excitation, and 0.01 eV for $1s \rightarrow 5p$.

We thus conclude that the description of the system is enhanced when using additional Rydberg functions as opposed to only diffuse functions.
Figure 4.3. Neon $K$-edge X-ray absorption spectra obtained at the nonrelativistic CCSD and STEX levels of theory, with basis set cc-pVTZ augmented with diffuse functions. Vertical dashed lines indicate $\Delta$SCF ionization potential (IP).

Core states

Using core-polarizing functions yields a better description of core and core-valence correlation effects. While this is often unnecessary for chemical bonds, equilibrium geometries and other molecular characteristics, these functions may better incorporate the core relaxation effects following excitation of a core electron.

We have studied the addition of core-polarizing functions to the basis set at a CCSD qaug-cc-pVTZ level, and we observe a shift in energy of 0.25 eV of the $1s \rightarrow 3p$ excitation. This is illustrated in Fig. 4.5, where the total energy of the calculations is included. We also report the total energies of calculations with no excitation from the HF core orbitals, i.e. a frozen core. The total correlation energy amounts to 7.83 and 9.24 eV at a qaug-cc-pVTZ and qaug-cc-pVTZ level of theory, respectively. Subtracting the energy difference of calculations using a frozen and relaxed core yields 7.47 and 7.50 eV, and we interpret this as the valence correlation energy. The energy difference between frozen and relaxed core is interpreted as core-valence and core correlation energy. The core and core-valence correlation energies thus requires a core-polarized basis set to be properly
Figure 4.4. Neon K-edge X-ray absorption spectra obtained at the CCSD levels of theory, for different basis sets where the lower spectrum has Rydberg (6s6p) functions.

described.

To some surprise, we note a relative energy shift of 1.15 eV when comparing the excited states with and without core-polarizing functions. As this state lacks a core electron, no core correlation effects are present, and the core-valence correlation and core relaxation effects would not be expected to be of this size.

Decontracting the basis set

As the core orbitals in a contracted basis set is described mainly by contracted basis functions, we can expect improved core correlation and relaxation effects if the basis set is decontracted. This has been studied using aug-cc-pVTZ with Rydberg (6s6p) functions, with and without core-polarizing functions. The resulting spectra are seen in Fig. 4.6, and we observe a progressive increase in excitation energy for the larger basis sets. The 1s $\rightarrow$ 3p excitation energy are increase by 0.21, 0.04 and 0.10 eV. For comparison, a calculation using a pCVQZ basis yields corresponding energy 0.01 eV lower than the uncontracted pCVTZ value. These results can be compared to STEX in Section 4.1.1, where a energy shift of 0.50 eV is obtained at a taug-cc-pVTZ level. This is contrary to what could be expected, as electron
correlated methods are expected to be more sensitive to the choice of basis set than HF. Note that the STEX calculations have a different description of the excited states, but this effect is not expected to be significant, see Fig. 4.4.

The addition of core-polarizing functions thus yields an improved description of the relaxation of the core, and this can further be improved by decontracting the basis set. However, it is deemed unfeasible to use an uncontracted basis set as an effect of the large chain length required, and a quadruple zeta basis set is also considered to costly. We thus conclude that an aug-cc-pCVTZ basis set with Rydberg (6s6p) functions is a suitable choice for neon.

4.1.4 Ionization potential

The ionization potential of the neon $K$-edge has been pursued with the present method. This identification is of importance mainly because this is an important physical feature, available for experimental measurement. It can also be used as a means by which to infere which features in a calculated spectrum are unphysical.
Figure 4.6. Neon K-edge X-ray absorption spectra obtained at the CCSD levels of theory, using single augmented basis sets with added Rydberg (6s6p) functions. The basis sets are used in contracted and fully uncontracted form.

Attempts has been made by which the coefficients ξ of the basis functions are rescaled, as this could be expected to distort the eigenvalues of the unphysical features while leaving those of the physical features intact due to optimization procedures. An uncontracted taug-cc-pVTZ basis set has been used, and the result is given in Fig 4.7. We note approximately equal shifts for all features, so this approach is not a possibility. The reason for this is currently not known.

4.1.5 Level of coupled cluster theory

The performance of the coupled cluster hierarchy CCS, CC2, CCSD and CCSDR(3) has been examined. As a consequence of the different approximations, mainly concerning the neglect of double excitations for CCS, the chain length required for convergence differs greatly. At a CCS level it is possible to span the whole excitation space at reasonable computational cost, while this is not the case for CC2 and CCSD. Further note that the CCSDR(3) method yields only a correction to CCSD excitation energies, while the oscillator strengths remains the same. The CCSDR(3) utilizes the approximate eigenvectors as obtained for CCSD by
Results and discussion

Photon energy [eV] \( \sigma(\omega) \) [arb. units] 

Default coefficients
Scaled with factor 0.9801
Scaled with factor 1.201

**Figure 4.7.** Neon K-edge X-ray absorption spectra obtained at a CCSD level of theory with uncontracted basis set taug-cc-pVTZ. The atomic orbital coefficients have been rescaled with given factors.

Eqs. 2.111 and 2.112, thus requiring the roots to be well converged.

The resulting X-ray adsorption spectra in Figure 4.8 show that the \( 1s \rightarrow 3p \) excitation energy is corrected toward the experimental energy for each level, with an overshoot for up to CCSDR(3). This method in turn underestimates the correction towards experimental value. The spectra are shifted so as the \( 1s \rightarrow 3p \) excitation energies match that of CCSDR(3).

The CCS calculations gives an excitation energy corresponding to \( 1s \rightarrow 3p \) of 21.23 eV too high energy, and corresponding values for CC2 and CCSD are -2.68 and 1.13 eV, respectively. CCSDR(3) reduces this discrepancy to -0.40 eV. As the CCS method lacks double excitations and thus the possibility of describing relaxation effects by such, the large error in excitation energy is deemed to be due to relaxation effects. These results are neglecting (scalar) relativistic effects, expected to shift the transition energy upwards. As a result of the different spectral profiles of the methods it is concluded that at least a CCSD level of theory is necessary for excitation energies of correct relative energies.
Figure 4.8. Neon K-edge X-ray absorption spectra as obtained with coupled cluster methods CCS, CC2, CCSD and CCSD corrected with the CCSDR(3) method. The basis set aug-cc-pCVTZ with added Rydberg (6s6p) functions is adopted. The dotted vertical line indicates the experimental 1s → 3p transition energy [47]. CCS, CC2 and CCSD spectra has been shifted so that the 1s → 3p peaks coincide with that of CCSDR(3).
4.1.6 Scalar relativistic effects

As the relativistic effects of interest for this system are scalar in nature, as shown in Table 4.3, including only such effects yields results compatible with a fully relativistic setting. This has been done using the second-order Douglas–Kroll scalar relativistic Hamiltonian for a CCSD calculation, using the basis set aug-cc-pCVTZ with Rydberg \((6s6p)\) functions. The resulting shift is reported to amount to 0.88 eV, as can be compared to the shift of 1.13 eV from STEX.

4.1.7 Comparison to experiment

The calculated X-ray absorption spectra are compared to the experimental spectrum from [47]. We consider CCSDR(3) calculations with and without the Douglas–Kroll Hamiltonian. For comparison, fully relativistic STEX results using an uncontracted basis set is also reported.

The experimental and coupled cluster spectra are given in Fig 4.9, and a comparison of all excitation energies in Table 4.4. We also report the \(T^2\)-contribution of the CCSD calculation using Douglas–Kroll, giving a measure of the importance of double excitation for the different transitions.

It is seen that nonrelativistic and relativistic CCSDR(3) yields excitations of 0.44–0.52 too low and 0.34–0.40 eV too high energies, respectively. Meanwhile, STEX yields results of 0.05–0.12 eV too low energy. The profiles of the spectra is similar for all methods. The pre-edge region, i.e. the energy interval from the \(1s \rightarrow 3p\) absorption peak to the ionization potential, is given by experiment as 3.05 eV. With a ∆SCF IP of 869.93 eV for the STEX calculation, the corresponding pre-edge region is obtained as 2.93 eV. This discrepancy is an effect of the lack of screening from the excited electron.

Table 4.4. Neon K-edge excitations and excitation energies for CCSDR(3) calculations with (REL) and without (NR) the scalar relativistic Douglas–Kroll Hamiltonian. Compared to relativistic STEX with a uncontracted basis set and experiment from [47]. Also including \(T^2\)-contribution for CCSD calculations with the DK Hamiltonian. Energies are expressed in eV and contributions in %.

<table>
<thead>
<tr>
<th>Excitation</th>
<th>NR</th>
<th>REL</th>
<th>Expt.</th>
<th>STEX</th>
<th>(T^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s (\rightarrow) 3p</td>
<td>866.64</td>
<td>867.52</td>
<td>867.12</td>
<td>867.00</td>
<td>8.00</td>
</tr>
<tr>
<td>1s (\rightarrow) 4p</td>
<td>868.20</td>
<td>869.08</td>
<td>868.69</td>
<td>868.58</td>
<td>7.99</td>
</tr>
<tr>
<td>1s (\rightarrow) 5p</td>
<td>868.77</td>
<td>869.65</td>
<td>869.27</td>
<td>869.15</td>
<td>7.99</td>
</tr>
<tr>
<td>1s (\rightarrow) 6p</td>
<td>869.04</td>
<td>869.92</td>
<td>869.56</td>
<td>869.43</td>
<td>7.99</td>
</tr>
<tr>
<td>1s (\rightarrow) 7p</td>
<td>869.29</td>
<td>870.17</td>
<td>869.73</td>
<td>869.68</td>
<td>7.99</td>
</tr>
</tbody>
</table>

Basis set aug-cc-pCVTZ with Rydberg \((6s6p)\) functions.
Figure 4.9. Neon K-edge X-ray absorption spectra obtained for nonrelativistic (NR) CCSDR(3) and CCSDR(3) with scalar relativistic effects incorporated by means of the Douglas–Kroll Hamiltonian (REL). Compared to experiment from [47].
4.2 Methane

The $K$-edge NEXAFS spectrum of methane has been studied using the present method, although not at a CCSDR(3) level of theory. The experimental spectrum is taken from [49], and a number of other studies have been examined [50, 51, 52]. The excitations of interest are the dipole allowed 1s to np and nd transitions, the weaker vibronic allowed ns transition ($n \geq 3$), with vibrational broadenings. The present method cannot incorporate vibrational broadening or dipole forbidden transitions, so results will lack some features.

The geometry of the molecule is given from experiment as tetrahedral with a C–H bond length of 1.086 eV [53].

4.2.1 Static-exchange approach

Ionization potential

The 1s ionization potential (IP) has been determined by the $\Delta$SCF method, parallel to the case of neon in Section 4.1.1. The ground and ionized state 1s-orbital energies are again reported for comparison. The basis sets have been chosen as cc-pVTZ and cc-pVQZ, augmented with triple (tTZ) or quadruple (qQZ) sets of diffuse functions on carbon, respectively.

The results are given in Table 4.5, and we note a discrepancy of the IP of 0.16 eV. Comparing this to the case of neon, it appears as if the basis sets for methane behaves more evenly. Experimental value of the IP is given as 290.74 eV [49], and the $\Delta$SCF method gives values above this. Relativistic effects for this system amount to 0.13 eV, significantly smaller than before as a result of the different masses of neon and carbon.

Further, it is seen that the 1s-orbital energy of ground and excited state is lower for tTZ, consistent with the case of neon. This may appear odd considering the fact that better methods should lower the energy, but this fact is true for the total energy while the orbital energy can both be raised and lowered. For the nonrelativistic case the total energy is in fact lowered by 0.07 eV for the better basis set.

<table>
<thead>
<tr>
<th>Ionization potential</th>
<th>Nonrelativistic</th>
<th>Relativistic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>tTZ$^a$</td>
<td>qQZ$^b$</td>
</tr>
<tr>
<td>$\Delta$SCF</td>
<td>291.00</td>
<td>290.84</td>
</tr>
<tr>
<td>1s-orbital energy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ground state</td>
<td>-304.91</td>
<td>-304.88</td>
</tr>
<tr>
<td>ionized state</td>
<td>-374.71</td>
<td>-374.45</td>
</tr>
</tbody>
</table>

$^a$cc-pVTZ with triple augmentation of carbon. $^b$cc-pVQZ with quadruple augmentation of carbon.
Decontracting the basis set

The effects of decontracting the basis set have been studied at a STEX level, utilizing the same basis sets as previously. The results are given in Fig. 4.10, and we observe a shift of the $1s \rightarrow 3p$ peak of 0.20 and 0.07 eV for nonrelativistic tTZ and qQZ, respectively. Corresponding shift for a relativistic calculations using qQZ amounts to 0.06 eV.

We also note a scalar relativistic shift of this peak of 0.13 and 0.14 eV for the contracted and uncontracted qQZ basis sets, respectively. This is in line with the shift of 0.13 eV for the IP using a contracted basis set.

![Graph showing X-ray absorption spectra](image)

**Figure 4.10.** Methane $K$-edge X-ray absorption spectra as obtained using nonrelativistic (NR) and relativistic (REL) STEX approaches. Vertical dashed lines indicate the ionization potential (IP). Calculated with contracted and uncontracted basis sets cc-pVTZ and cc-pVQZ, with carbon augmented with triple and quadruple sets of diffuse functions, respectively.
4.2.2 Convergence of the Lanczos-chain method

The convergence of the Lanczos-chain method have been studied for methane. The results for a calculation using the basis set cc-pCVTZ with triple augmentation on carbon are given in Fig. 4.11. We observe a greatly increased demand of the chain length as compared to the case of neon, resulting from the larger basis set for the present system (147 contracted basis functions as oppose to 91 for similar basis sets). Notice the emergence of a single peak appearing at an intermediate energy of two true peaks for an insufficient value of $J$.

![Figure 4.11. Methane K-edge X-ray absorption spectra as obtained for different Lanczos-chain lengths $J$, at the CCSD level of theory with basis sets cc-pCVTZ and taug-cc-pCVTZ on hydrogen and carbon, respectively. The error $e_{j,k}$ is calculated from Eq. 2.128 for the interval 283.5 to 298.9 eV.](image)

4.2.3 Basis set selection

As the excitation of interest for this system are transitions of a $1s$ electron to $np$ and $nd$ excited states, the description of orbitals of carbon atomic character are of interest. The basis functions centered at hydrogen can thus be expected to be of less importance.
Excited states

The augmentation of diffuse functions on hydrogen may be used to construct orbitals of desired symmetry, such as $s$-functions from different atoms giving a $p$-like combination. However, this is estimated as a cost-inefficient description, as multiple augmentations on carbon or Rydberg functions is likely to yield the same description, without the inclusion of many diffuse functions of high angular momentum. Further, as the number of basis functions quickly grows with the level of augmentation, and linear dependencies may arise between different functions, we will focus at augmentation of carbon. The possibilities of linear dependencies of functions centered at different atoms are lower for tight core and valence functions, due to the low overlap of such.

The investigation of different augmentation of carbon by diffuse functions has been done using a cc-pVTZ basis set. The result is seen in Fig. 4.12, and we observe the need of at least triple augmentation for proper fine structure, similar to the case of neon.

![Figure 4.12](image)

**Figure 4.12.** Methane $K$-edge X-ray absorption spectra at a CCSD level of theory, using the basis set cc-pVTZ with different augmentations by diffuse functions on carbon.
Core states

For a proper description of the core states, we consider again a basis set with core-
polarizing functions. Due to the large number of basis functions for the system,
it is in this case not possible to compare the results obtained in this manner to a
uncontracted basis set, as is done in Section 4.1.3. The effects are deemed to be
similar for the two systems.

The first excitation energies for calculation using a cc-pVTZ basis set with
triple augmentation of carbon and inclusions of core-polarizing functions are re-
ported in Table 4.6. A shift of 0.53 eV are seen when adding core-polarizing
functions on carbon, and no difference is observed when adding core-polarizing
functions also on hydrogen. This is expected, as hydrogen has no core electrons
and the core-polarized basis set only have different values of AO-coefficients $\xi$.

Table 4.6. Methane 1s $\rightarrow$ 3p excitation energies (eV) obtained at a CCSD level of
theory using different basis sets.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Hydrogen</th>
<th>1s $\rightarrow$ 3p</th>
</tr>
</thead>
<tbody>
<tr>
<td>taug-cc-pVTZ</td>
<td>cc-pVTZ</td>
<td>288.73</td>
</tr>
<tr>
<td>taug-cc-pCVTZ</td>
<td>cc-pVTZ</td>
<td>289.26</td>
</tr>
<tr>
<td>taug-cc-pCVTZ</td>
<td>cc-pCVTZ</td>
<td>289.26</td>
</tr>
</tbody>
</table>

4.2.4 Level of coupled cluster theory

The performance of the coupled cluster methods CCS, CC2 and CCSD have been
studied for methane. No CCSDR(3) corrections are available due to technical
problems for this system.

The basis set is chosen as aug-cc-pCVTZ on carbon, aug-cc-pCVDZ on hydro-
gen, and with additional Rydberg (3s3p3d) functions centered at carbon. This
basis should be capable of describing the np and nd excited states, and the re-
striction of only a double zeta basis on hydrogen are deemed to have no significant
effect.

The resulting spectra are seen in Fig. 4.13, where the CCS and CC2 spectra
are shifted so as the 1s $\rightarrow$ 3p excitation energies coincide with CCSD. Included
is also the experimental 1s $\rightarrow$ 3p excitation energy. The CCS results are seen
to be 11.76 eV too high in energy, while CC2 and CCSD are 1.77 and 1.22 eV
too high, respectively. Compare this to 21.23, -2.68 and 1.13 eV, as obtained for
neon. We see that the discrepancy for the two systems are similar for CCSD,
different with opposite sign for CC2 and have quite different value for CCS. From
the last results we conclude that the relaxation energy is lower for this system.
The resulting spectral profiles are again highly different, and we conclude that at
least CCSD is necessary for a good description of this molecule.
Figure 4.13. Methane $K$-edge X-ray absorption spectra as obtained with coupled cluster methods CCS, CC2 and CCSD. The basis set is given by aug-cc-pCVTZ for carbon, aug-cc-pCVDZ for hydrogen and additional Rydberg (3$s$3$p$3$d$) functions. The dotted vertical line indicates the experimental $1s \rightarrow 3p$ transition energy [49]. CCS and CC2 spectra has been shifted so that the $1s \rightarrow 3p$ peaks coincide with that of CCSD.
4.2.5 Comparison to experiment

Calculated relativistic and nonrelativistic X-ray absorption spectra using the previously given basis set at a CCSD level are compared to experiment [49]. The results are given in Fig. 4.14, where the designation of the experimental peaks are included for clarity. Excitation energies are provided in Table 4.7. We again remark the neglect of vibrational features for the present method. Further, by comparing the spectra it is clear that the experimental lifetime of the excited states are lower than the value used in the calculations.

While not reported in the Table, a feature at approximately 290.45 eV and with an oscillator strength of the order $10^{-3}$ as compared to adjacent peaks is found. This feature has a $T_2$-contribution of 83.8% and involves excitation from the valence orbitals, but not the core. It is thus inferred as an unphysical peak. Its emergence at an energy assumed to be below the edge is somewhat inconvenient, as this implies a need of analyzing the nature of all peaks at frequencies of interest.

Scalar relativistic effects are observed to account for a shift of 0.10 eV for coupled cluster, and the nonrelativistic and relativistic calculations yields 1.22–1.47 and 1.32–1.57 eV too high excitation energies, respectively.

<table>
<thead>
<tr>
<th>Excitation energy</th>
<th>NR</th>
<th>REL</th>
<th>Expt.</th>
<th>$T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s \rightarrow 3p$</td>
<td>289.22</td>
<td>289.32</td>
<td>288.00</td>
<td>11.90</td>
</tr>
<tr>
<td>$1s \rightarrow 3d$</td>
<td>290.01</td>
<td>290.11</td>
<td>288.70</td>
<td>12.28</td>
</tr>
<tr>
<td>$1s \rightarrow 4p$</td>
<td>290.68</td>
<td>290.78</td>
<td>289.21</td>
<td>12.17</td>
</tr>
<tr>
<td>$1s \rightarrow 4d$</td>
<td>290.89</td>
<td>290.99</td>
<td>289.46</td>
<td>12.36</td>
</tr>
<tr>
<td>$1s \rightarrow 5p$</td>
<td>291.22</td>
<td>291.33</td>
<td>289.99</td>
<td>12.30</td>
</tr>
<tr>
<td>$1s \rightarrow 5d$</td>
<td>291.39</td>
<td>291.49</td>
<td>290.08</td>
<td>12.30</td>
</tr>
</tbody>
</table>

Basis set aug-cc-pCVTZ with Rydberg (6s6p) functions.

Table 4.7. Methane K-edge excitations and excitation energies for CCSD calculations with (REL) and without (NR) the scalar relativistic Douglas–Kroll Hamiltonian, compared to experiment in [49]. Also including $T_2$-contribution for CCSD calculation with the DK Hamiltonian. Energies are expressed in eV and contributions in %.
Figure 4.14. Methane $K$-edge X-ray absorption spectra obtained for nonrelativistic (NR) CCSD and CCSD with scalar relativistic effects incorporated by means of the Douglas–Kroll Hamiltonian (REL). Compared to experiment from [49].
Chapter 5

Conclusions

A damped coupled cluster method by which to calculate the near-edge X-ray absorption fine structure region of the X-ray absorption spectrum has been derived and investigated through the application on the K-edge of neon and methane. By use of a damped response method the finite lifetime of the excited states can be incorporated. A complex linear response function is obtained, from which resonance states and transition moments can be directly computed. Comparisons are made for calculations using CCS, CC2, CCSD and CCSDR(3), the last by which CCSD results are corrected with approximate triple corrections. The use of coupled cluster methods at a level that incorprates double excitations are desirable, due to the importance of relaxation effects of the systems following excitation.

As the unsymmetric coupled cluster Jacobian is of a size that is generally too large to be spanned completely, an asymmetric Lanczos-chain driven approach has been utilized as a means by which the spectrum is iteratively converged. Due to the nature of the Lanczos-chain method, an insufficient chain length may result in a spectrum with excitation peaks of incorrect energy. It is also possible to obtain intense features of correct energies, while smaller features are not yet present.

Comparison have been made with spectra obtained by four-component relativistic STEX calculations, and corresponding ionization potentials by the ∆SCF method. The relativistic effects are seen to be scalar in nature, and such effects can thus be incorporated in a nonrelativistic setting through the Douglas–Kroll scalar relativistic Hamiltonian. Due to the non-additive nature of relativistic and electron correlation effects, relativistic shifts for a CC calculation cannot be evaluated at a STEX level.

The choice of basis set it shown to be of great importance, as a proper description needs to be achieved while maintaining a moderate number of basis functions. A basis set with an insufficient description of the core is seen to yield too low excitation energies. If the description of the excited states are insufficient, excitation features might not appear, or do so at an incorrect energy. Increasing the flexibility of the basis set by decontracting all basis functions is seen to be an appropriate, if not always strictly necessary, action at a STEX level. However, this decontraction yields a great number of eigenvectors with large eigenvalues for damped
coupled cluster, and is as a result untractable for all systems save the very smallest. Augmenting the basis set with core-polarizing functions yields results similar to decontracting the basis set, due to the improved descriptions of mainly the core states in both cases. Proper descriptions of the states are thus achieved by use of core-polarizing functions and, for the systems treated, a combination of augmentation by diffuse functions and Rydberg functions. Unphysical features arise as a result of the use of localized basis functions, and weak such features are observed at a photon energy in the NEXAFS region of methane.

For neon, nonrelativistic and relativistic results of 0.48 eV too low and 0.40 eV too high are obtained at a CCSDR(3) level. These values refers to the excitation energies of the first transition, and corresponding results for methane at a CCSD level are 1.22 and 1.32 eV too high. Further, the relaxation effects are seen to be large, of the order of 21 and 12 eV for neon and methane, respectively. These effects are largely accounted for at a CC level including double excitations. The approximate inclusion of double excitation by CC2 have proven to yield incorrect spectral profiles, and at least a CCSD level of theory is necessary.
Bibliography


