

Modelling the Electronic Structure of Intermetalloid Cluster Compounds



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Abstract

Intermetalloid clusters consist of a number of transition metal atoms surrounded by a larger number of p-block metal/metalloid atoms. The clusters are notable for how their transition metal and p-block units influence each other's structures, which frequently leads to novel bonding and structures in the two units. To understand the properties of intermetalloid clusters, bonding models are frequently employed. Existing bonding models explain a large number of intermetalloid clusters, though there are also compounds which do not conform well to existing models. Additionally, the current understanding of what causes an intermetalloid cluster to adhere to a particular bonding model is limited. As such, the bonding models of intermetalloid clusters are an active area of research. Furthermore, electronic structure methods are often used to gain insight into intermetalloid clusters from a theoretical standpoint. However, the clusters can push the limits of existing electronic structure methods, thereby presenting a need to develop methodologies using electronic structure methods to allow for accurate modelling of the properties of intermetalloid clusters.

This thesis presents contributions to both the development of bonding models for intermetalloid clusters and to the development of electronic structure methodologies suited to intermetalloid clusters. The first two chapters provide an introduction to the fields of electronic structure methods and intermetalloid clusters, as well as a review of the theoretical background underpinning the methods used in the thesis. Chapter three then presents a characterisation of the electronic structure of the newly synthesised $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$. It is argued that the compound can be described in terms of an existing bonding model which could not be applied to previously observed Cr_6 clusters. Chapter four develops an electronic structure methodology aiming to establish the global minima of two isoelectronic intermetalloid clusters: Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$. Doing so provides insight into the conditions under which M@Si_{14} compounds adopt structures described by different bonding models. Lastly, with the goal of increasing the proportion of the correlation energy of core electrons that may be calculated for intermetalloid

clusters, expressions for correlation-induced core orbital relaxation are derived within the Brueckner coupled-cluster theoretical framework as an alternative to the frozen core approximation. While it is found that the core orbital relaxation only captures a small portion of the core correlation energy, the investigation highlights how the core orbital relaxation is affected by double excitations, which has further implications for the development of approximations for core correlation in coupled-cluster methods.

Statement of Originality

Except when indicated otherwise, all work presented in this thesis is my own.

Aidan Manley

Publication Accompanying this Thesis

Please be aware that the work in chapter three of this thesis has been published in the Journal of the American Chemical Society (*J. Am. Chem. Soc.*, 2025, **147**, 24309–24316. DOI: 10.1021/jacs.5c00515).

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[†] Otherwise known as the Stanway Biker Crew (SBC).

Dedicated to Thomas Rae Manley

Thomas Rae Manley (17/5/1926–16/2/2020) was a professor of polymer chemistry at Newcastle Polytechnic (now Northumbria University). The family story goes that he tried to get my older cousins interested in chemistry when they were in school, to no avail. He had given up on piquing his grandchildren's interest in chemistry by the time I was studying but I ended up developing an interest in the subject independently. Later in life, I had the privilege of a few treasured conversations about chemistry with my grandad during my undergraduate degree and shortly before the start of this DPhil program. I would have loved to show you my thesis, Grandad.

Chapter 1

Introduction

*You know, it would be sufficient to really
understand the electron.*

Albert Einstein

1.1 Models of Electronic Structure

Quantum mechanical phenomena have long perplexed and fascinated both researchers and the general population. The deviation from Newtonian mechanics exhibited by sub-atomic particles has been studied for over 100 years and is still one of the most important areas of research today.

At the heart of this importance is the electron.

From semi-conductors and transistors to solar cells and life-saving drugs, the technology developed from a better understanding of the electron has shaped life in the 21st century. Crucially, electrons rarely exist in isolation. They are found surrounding the nuclei of atoms and their interactions with these particles determines the range of behaviours electrons can exhibit. How exactly electrons surround nuclei is known as the electronic structure of a system and this underpins how nuclei come together and form more complex species, leading to the vast majority of known matter. Understanding the electronic structure of matter is no simple task however and its pursuit has led to a large variety of models.

Ultimately, the development of the Schrödinger equation provided the most insight into the quantum mechanical nature of electrons. It is now considered a law of nature given how rarely it deviates from experiment. The equation is inherently complex however. It has dimensions of $3N$ for a N particle system given that only a particle's position or its momentum can be known at once. This differs from the $6N$ -dimensional nature of classical mechanics where both a particle's position and momentum can be known simultaneously. Quantum mechanics gains its complexity from the fact that the solutions to the Schrödinger equation have values at every point in the $3N$ -dimensional space whereas classical systems can be described by a single point in the $6N$ -dimensional space at any given instance. Furthermore, in interacting multi-electron systems, the Schrödinger equation cannot be solved exactly. An electron-electron interaction term in the equation prevents any analytical solutions from being found and as a result numerical

approximations are all that can be obtained. This constraint is what has shaped modern models of electronic behaviour and many of the concepts used to understand chemistry. For example, molecular orbital theory, possibly the most used chemical model besides Lewis structures, comes as a result of approximating solutions to the Schrödinger equation in the form of products of one-particle functions, known as orbitals, or molecular orbitals (MOs) when used specifically for a molecule. Means of calculating the electronic structure of a system are known as electronic structure methods. The most significant challenge facing modern electronic structure methods is electron correlation. This is often understood in terms of the correlation energy which can be defined as the difference between the exact energy and that of a Hartree-Fock (HF) calculation,

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}.$$

A HF calculation provides a mean-field model of electron–electron interactions in which the electrons adjust to the averaged field of all other electrons in a system. Electrons also obey Pauli’s principle in the HF model, which prohibits electrons of the same spin from occupying the same point in space. Pauli’s principle therefore introduces a statistical correlation between electrons (known as Fermi correlation), which highlights that the correlation energy does not capture the effect of the statistical correlation between electrons. Instead, the correlation energy accounts for the correlation which causes a deviation from the mean-field description of electronic structure via the Coulomb interaction.

Methods which calculate the electron correlation energy are known as post-Hartree-Fock methods. In the vast majority of these methods, it is assumed that the wavefunction takes a certain functional form, known as an *ansatz*. Various possible *ansätze* may be used but they are most commonly based on an expansion of the wavefunction in a series of terms known as Slater determinants (discussed further in section 2.1.2). Slater determinants are products of orbitals which have been antisymmetrised in order to satisfy Pauli’s principle. A Slater determinant expansion of the wavefunction utilises a set of orbitals defined for the system of interest (e.g. those found from a HF calculation) and is

formulated as a sum over a single “reference state”, which is a Slater determinant formed from a sub-set of the system’s orbitals (known as the occupied orbitals), and multiple “excited states”, which are Slater determinants formed from the same orbitals as the reference state except for a number of the reference orbitals which are replaced with orbitals not included in the reference state (referred to as unoccupied or virtual orbitals). The Slater determinant expansion of the wavefunction is able to systematically converge to the exact solution of the Schrödinger equation but the expansion is infinite, meaning it must be truncated for practical use. This fact shapes how post-HF methods are defined and developed. Possibly the most direct way of defining an electronic structure method using a Slater determinant expansion is known as configuration interaction (CI) theory. The *ansatz* of CI theory is a linear combination of Slater determinants and, in its conventional form, CI theory uses a system’s HF orbitals as its orbital set and the HF solution corresponding to the electronic state of interest as its reference state. Various levels of truncation to CI theory are defined in terms of the number of orbitals which have been replaced in the reference state to form the excited states included in the expansion. For example, CIS stands for CI theory including single excitations and therefore includes the reference state and all possible excited states where a single orbital in the reference state has been replaced. Likewise, CISD is CI theory with single and double excitations where doubly excited states are those where two of the orbitals in the reference state have been replaced. Increasing the order of excitation, i.e. CIS, CISD, CISDT, CISDTQ, etc. has been shown to provide results which systematically converge to the exact solution to the Schrödinger equation. Full configuration interaction theory (FCI) includes all possible orders of excitation[†] in the expansion, which results in the most accurate result possible within the finite orbital set chosen. However, the computational expense of FCI scales exponentially with system size¹ which means that only calculations on the smallest chemical systems, utilising small orbital sets are possible. CI methods truncated to lower orders of excitation are feasible however. For example, CISD scales² as $\mathcal{O}(O^2V^4)$, where O and V are the number of occupied and virtual orbitals respectively, and has been applied to routinely to systems in the past.^{3,4}

[†]The number of possible excitation orders is equal to the number of electrons in the system.

The use of CI theory has been largely superseded by a related method known as coupled-cluster (CC) theory. Coupled-cluster theory also utilises a Slater determinant expansion and exhibits the same systematic convergence with excitation order to the exact solution of the Schrödinger equation as CI theory. However, CC theory employs a non-linear combination of Slater determinant in its expansion, unlike the linear combination of Slater determinants featured in CI theory. This results in the CC expansion exhibiting size consistency[†] which is a property not featured in CI theory. Truncated coupled-cluster methods exhibit similar scaling to their CI counterparts and therefore have many of the same limitations. Despite this, coupled-cluster theory can achieve markedly accurate results in a truncated form known as CCSD(T), that is CCSD with triple excitations determined with a perturbative correction. As a result, CCSD(T) has become a common tool in the application of electronic structure methods and is even referred to as the gold standard due to its ability to approach chemical accuracy (1 kcal · mol⁻¹) at an affordable computational cost in a large number of systems.⁵ The computational expense of CCSD(T) scales² as $\mathcal{O}(O^3V^4)$, meaning its application is limited to medium-sized systems of roughly 20–30 atoms and smaller.⁶ Consequently, an active area of research is making approximations to CCSD(T) which reduce the scaling of its computational cost with system size. An effective example of such approximations are local correlation approximations, which are made in methods such as DLPNO-CCSD(T),⁷ PNO-CCSD(T),⁸ and LNO-CCSD(T).⁶ Such methods have been applied to systems containing hundreds of atoms^{9,10} but retain limitations in the size extensive nature of the error in local correlation approximations.¹⁰

Despite their potential for highly accurate and tractable calculations, CCSD(T) and its approximations have proved not to be the panacea in estimating the solutions of the Schrödinger equation. This is due to a property exhibited in some systems known as multi-reference character. Both CI and CC theory can be described as single-reference methods since they include terms in their Slater determinant expansion where excited states are generated by making orbital replacements in a single reference state. Such an

[†]An electronic structure method is size consistent if it finds that the energy of a system featuring infinitely separated sub-systems is the same as the sum of the energies of the isolated sub-systems.

approach is suited to systems where the electron correlation energy is dominated by dynamic correlation. Broadly, dynamic correlation may be thought of as the correlation due to electrons instantaneously adjusting to the positions of all other electrons. However, there are some systems which are strongly influenced by static correlation, which is electron correlation which causes a change in the average position of electrons in the system. In principle, any system can be modelled accurately with single-reference methods by including as many high-order excitations (CCSDTQ, CCSDTQP, etc.) as necessary to converge the correlation energy. However, beyond the CCSD(T) level, this quickly becomes computationally infeasible and means single-reference methods achieve their most accurate results in cases where dynamic correlation is dominant. Such problems lead to the development of multi-reference methods where excited states are generated by making replacements in multiple reference states and the orbital set is optimised over all the reference states used. Crucially, multi-reference methods account for higher orders of excitation by allowing all possible excitations within a sub-set of the orbitals known as the “active space”, typically denoted as (n_e, n_o) where n_e and n_o denote the number of electrons and number of orbitals in the active space respectively.[†] This approach is effective at capturing the static correlation in a system but quickly scales with the size of the active space, with the largest on record being (20,20).¹¹ In many systems, it is therefore not possible to include all valence electrons in the active space and how to define the active space to accurately model the static correlation in a system becomes an open question and an active area of research.^{12–14} Likewise, there is also a significant research effort which aims to make approximations which allow the maximum size of the active space to be increased, leading to methods such as DMRG,¹⁵ FCIQMC,¹⁶ and ASCI,¹⁷ among others.

There is not a rigorous distinction between static and dynamic correlation¹⁸ and both single- and multi-reference methods will capture amounts of the two forms of

[†]Typically, the electrons are the first n_e counting down from those in the occupied orbital with the highest energy. The orbitals may each accommodate two electrons and are typically the first n_o orbitals when counting up from the orbital of the lowest energy electron(s) included in the active space. For example, a (6,6) active space consists of the three orbitals containing the six highest energy electrons and the three lowest energy unoccupied orbitals.

correlation. Multi-reference methods generally will not account for a large portion of the dynamic correlation present¹⁹ and hence to achieve accurate results, corrections for dynamic correlation are employed,^{20,21} though these corrections retain limitations in their applicability.²² Similarly, coupled-cluster theory is known to account for moderate amounts of multi-reference character and steps have been made towards adapting coupled-cluster theory for a multi-reference formalism.²³ However, there is no commonly accepted method for implementing multi-reference coupled-cluster theory^{24,25} and the existing methods typically require system-specific knowledge to be applied effectively.²⁶

From the discussion in the present chapter, it can be seen that there is no single electronic structure method which may be applied indiscriminately to all chemical systems to achieve accurate results. As such, there is a need to assess the correlation present in each system of interest and decide which method is most suited to its study on a case-by-case basis. As one may expect, there are systems for which this status quo is a problem. For example, the bis(μ -oxo) and μ - η^2 : η^2 -peroxo isomers of $[\text{Cu}_2\text{O}_2]^{2+}$ have been modelled inaccurately by both single- and multi-reference methods. This inaccuracy has been ascribed to the two isomers exhibiting different amounts of static and dynamic correlation.²⁷ This means a method suited to either form of correlation will give results biased toward one of the isomers, complicating how a balanced treatment of both static and dynamic correlation in both the isomers can be obtained with a single method. In this case, benchmark results have been obtained using a combined approach of CCSD(T) and auxiliary-field quantum Monte Carlo calculations.²⁸ The $[\text{Cu}_2\text{O}_2]^{2+}$ system emphasises the broader point that, even with the vast number of electronic structure methods defined today, there are still some systems which require methodologies to be developed specifically for their study. Other notable examples of such systems include the Cr_2 dimer, particularly its dissociation,²⁹ and the iron-molybdenum enzyme co-factor.³⁰

The post-HF methods discussed so far have benefit in their potential for high accuracy across a variety of systems. However, as discussed previously, the methods boasting such accuracy come at a significant computational cost. This makes anything other than

energy calculations at a fixed geometry (“single point calculations”) prohibitive for systems larger than 10–15 atoms. For many systems of interest, it is desirable to calculate properties which require the gradient of the energy with respect to the nuclear positions, most notably a system’s geometry via a geometry optimisation which comes at a greater cost than single point calculations. HF theory has a computational cost where geometry optimisations are approachable for systems larger than 10–15 atoms but, since it neglects electron correlation, the method lacks accuracy in many systems. As such, when only considering wavefunction methods (i.e. methods which involve calculating the wavefunction in some form), a method which can perform geometry optimisations at a low cost while also accounting for electron correlation is missing. Fortunately, such a method can be found in density functional theory.

Density functional theory (DFT) is a formulation of molecular quantum mechanics which avoids calculation of the wavefunction entirely and hence the theory provides a departure from wavefunction methods. Instead, DFT calculates the energy, and subsequently all other properties, from the electron density — the probability of observing an electron at a given point in space. The electron density is a three-dimensional object regardless of system size and therefore offers a substantial memory benefit over the calculation of the $3N$ -dimensional wavefunction. Furthermore, the computational scaling of DFT is similar to that of HF meaning geometry optimisations can be performed for larger systems. Crucially, DFT is able to achieve greater accuracy than HF theory since it can account for electron correlation. Given that DFT is not a post-HF method, it does not calculate electron correlation directly. Rather, DFT can be shown to be a formally exact theory, meaning it is capable of calculating exact energies of molecular systems. However, it is not known how to calculate exact molecular energies using DFT since the mathematical form of an object known as the universal functional (see section 2.5.1) is unknown. Thus, implementations of DFT approximate the exact energy directly, unlike HF theory which systematically neglects the electron correlation energy, and therefore can account for the effects of electron correlation.

For practical use, DFT is reformulated into Kohn-Sham DFT (KS-DFT) where the unknown universal functional is re-packaged into an “exchange-correlation” functional. The form of the exchange-correlation functional is also unknown and hence approximate forms are implemented. There are a number of well-established approximate exchange-correlation functionals (frequently referred to as just “functionals”) and these can be assembled into a rough hierarchy (shown section 2.5.3), though the methods in this hierarchy do not produce results which follow a systematic convergence to the exact energy, as seen when increasing the excitation level in post-HF methods. In general, it is not known how the accuracy of an exchange-correlation functional can be increased or converged towards exact results. This makes how to improve exchange-correlation functionals an open question and a significant area of research.^{31–33} Currently, the accuracy of KS-DFT can generally be considered to be between that of HF and post-HF methods.³⁴ Overall, the combination of DFT’s accuracy and computational cost has made it the most used electronic structure method and has led to such widespread use that three of the top ten most cited papers of all time are those defining exchange-correlation functionals.³⁵

1.2 Intermetalloid Clusters

Having discussed the methods available for modelling electronic structure and their limitations, one can consider an area of interest for which electronic structure methods can provide insight. In particular, the present thesis applies a variety of electronic structure methods to study a class of compounds known as intermetalloid clusters. Typically, intermetalloid clusters are cluster compounds consisting of a number of transition metal atoms (referred to as the metal fragment) surrounded by a larger amount of p-block metal/metalloid atoms (referred to as the cage fragment).[†] Intermetalloid clusters are notable for how their metal and cage fragments influence each other's structures, which often produces structures of transition metals and p-block metals/metalloids unseen in other compounds. Some depictions of intermetalloid clusters discussed in the present section can be found in figure 1.1. The cage structures in intermetalloid clusters are often supported by the interstitial metal fragment. For example, icosahedral Ge₁₂ (featured in the compound second from bottom left in figure 1.1) is not observed in isolation⁴² but is observed⁴³ in Mn@Ge₁₂. Additionally, [Co₂@Sn₅Sb₇]³⁻ exhibits a structure comprised of two face-sharing square anti-prisms (top left of figure 1.1) which is supported by a strong interaction between the Co atoms and the cage of Sn and Sb.^{36,44} Novel geometries are also observed for the metal fragments. For example, a pentagonal Cr₅ motif has only been observed⁴⁵ as part of the intermetalloid clusters [Cr₅Sn₂Sb₂₀]⁴⁻ (top right in figure 1.1) and [(Cr₅)₂Sn₆Sb₃₀]⁶⁻. Furthermore, the structure of a metal fragment can vary depending on the nature of the cage fragment and *vice versa*. For instance, the In₁₀ cage of [Ni@In₁₀]¹⁰⁻ is a bi-capped square anti-prism (second from bottom right figure 1.1)⁴⁶ but in the isoelectronic

[†]Definitions of intermetalloid clusters vary in the literature. Authors have used the term synonymously with endohedral Zintl clusters,³⁶⁻³⁸ though some of such studies also refer to non-endohedral clusters as intermetalloid clusters e.g. ^{36,39}[Ni₂Ge₅(CO)₃]²⁻. Another study uses the term to refer to compounds featuring d- and f-block elements but no p-block metal/metalloid elements.⁴⁰ Ultimately, the term came from collecting together species which were perceived to share certain properties⁴¹ rather than any rigorous distinction from all other compounds. Hence, whether a cluster fits the technicalities of a definition is less important than whether a cluster exhibits properties informative to any areas of interest. In the present thesis, all clusters referred to as intermetalloid clusters are cluster compounds consisting of transition metal atoms surrounded by a larger number of p-block metal/metalloid atoms.

compound $[\text{Zn}@\text{In}_{10}]^{8-}$, the cage is a tetra-capped trigonal prism (bottom right figure 1.1).⁴⁷ The theoretical branch of intermetalloid cluster research aims to understand the interaction between metal and cage fragments and how the fragments influence each other's structures. Achieving such an understanding not only allows for the rationalisation of the observed structures of p-block and transition metal elements, but also can aid in the prediction of new intermetalloid clusters and in establishing how the structures in the clusters can be tuned to fit potential applications.

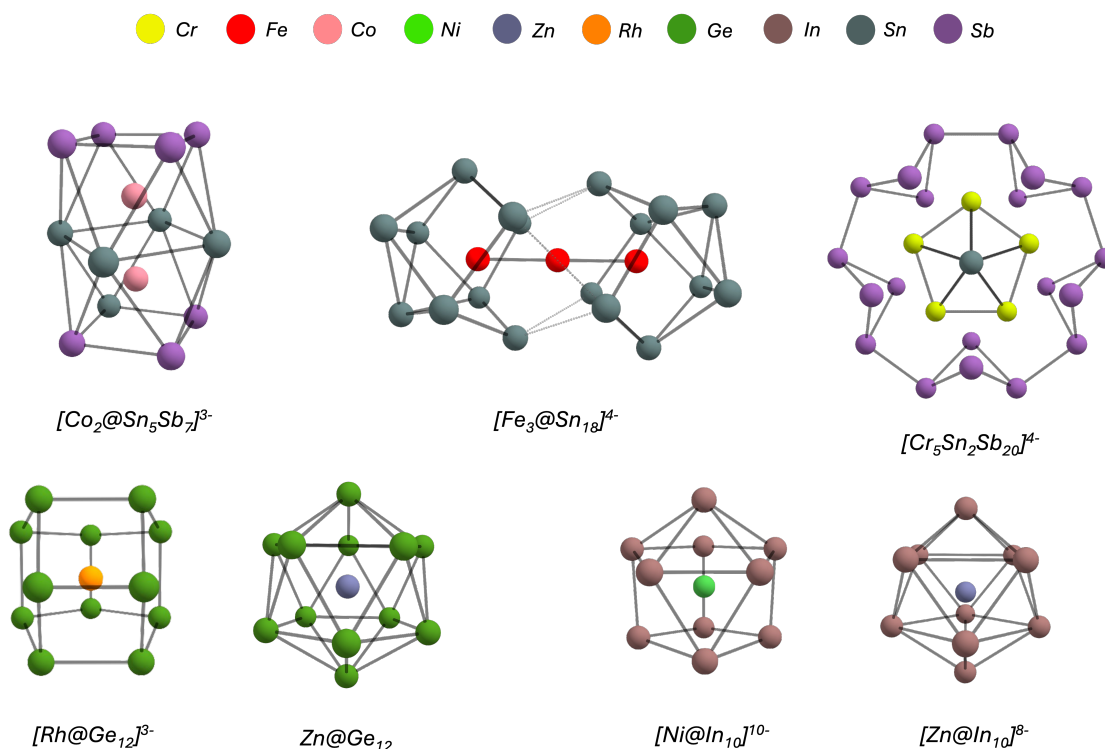


Figure 1.1: Selected examples of intermetalloid clusters.

Bonding models can be used to understand the structures of intermetalloid clusters. To detail two of the most common bonding models in the field of intermetalloid clusters, consider the isovalent compounds $\text{Zn}@\text{Ge}_{12}$ and $[\text{Rh}@\text{Ge}_{12}]^{3-}$. In $\text{Zn}@\text{Ge}_{12}$, the Ge_{12} cage takes an icosahedral structure but in $[\text{Rh}@\text{Ge}_{12}]^{3-}$ the cage takes a 3-connected structure (bottom left figure 1.1). Analysis of the Kohn-Sham molecular orbitals of $\text{Zn}@\text{Ge}_{12}$ shows the structure has 50 valence electrons associated with its cage and retains 10 d-electrons associated with its interstitial Zn atom.⁴⁸ This implies the cluster is electron-deficient or, in other words, that it does not have enough electrons to form

two-centre two-electron ($2c-2e^-$) bonds across all the edges of the icosahedral structure. Conversely, the Kohn-Sham MOs of $[\text{Rh@Ge}_{12}]^{3-}$ show 30 orbitals associated with either Ge–Ge bonding or Ge lone pairs, implying that there is an electron count of 60 associated with the cage.⁴⁸ Additionally, a sub-set of these orbitals feature Rh–Ge bonding character, which stabilises the 4d electrons of Rh. The cage is therefore considered electron-precise since the 60 electrons are enough for each Ge atom in the cage to be thrice-connected with $2c-2e^-$ bonds. The electron-deficient icosahedral structure of Zn@Ge_{12} can be understood in terms of the bonding model provided by Wade’s rules and the electron-precise structure of $[\text{Rh@Ge}_{12}]^{3-}$ can be understood in terms of the bonding model provided by the pseudo-element concept. These models are described in the subsequent paragraphs and it is then shown how the bonding models apply to each cluster.

Wade’s rules state that an n atom motif in a compound, will adopt a deltahedral structure with either no vertices missing, one vertex missing, or two vertices missing, denoted as *closo*, *nido*, or *arachno* respectively. The structure taken depends on the valence electron count associated with the motif: $4n + 2$ indicates a *closo* structure while $4n + 4$, and $4n + 6$ correspond to *nido* and *arachno* structures respectively. A common example is $[\text{B}_6\text{H}_6]^{2-}$ which has 26 valence electrons and hence an octahedral structure, and the *nido* version of this can be found in $[\text{B}_5\text{H}_5]^{4-}$ which has 22 valence electrons and a square-based pyramid geometry.

The pseudo-element concept is the idea that, when assigned formal charges, atoms will behave similarly to neutral elements with the same number of valence electrons, N_v . For example, in $[\text{Si}_4]^{4-}$, each silicon atom can be assigned a formal charge of -1 , meaning the pseudo-element concept suggests that each silicon atom will behave as pseudo-phosphorous and hence that $[\text{Si}_4]^{4-}$ will adopt the tetrahedral structure of P_4 , as is observed.⁴⁹ The valence electron count is the same for all elements of the pseudo-atom’s group so in general the structure expected from the pseudo-element concept is that of the element in the same period as the original element (e.g. $\text{Si}^- \approx \text{P}$ as above) in particular. Typically, “[behaving similarly]” is interpreted as following the

$8 - N_v$ rule, as seen in the example since each Si^- unit will form $8 - (4 + 1) = 3$, $2c-2e^-$ bonds in a tetrahedral arrangement. It may also be noted that all atoms of the same element do not need to be assigned the same formal charge.

To apply Wade's rules and the pseudo-element concept to $Zn@Ge_{12}$ and $[Rh@Ge_{12}]^{3-}$, formal charges need to be assigned to the interstitial metal and the cage. Based on the aforementioned analyses of the Kohn-Sham MOs, the formal charges of $Zn@Ge_{12}$ may be assigned as $Zn^{2+}@[Ge_{12}]^{2-}$. This associates the previously discussed 50-electron count with the Ge_{12} cage and matches the $4n + 2$ *closo* electron count required for the Wade's rules description of its icosahedral structure. Similarly, the formal charges of $[Rh@Ge_{12}]^{3-}$ may be assigned as $[Rh^{9+}@(Ge_{12})^{12-}]^{3-}$, indicating a 60-electron count at the cage. As previously mentioned, this electron count meets that required for all Ge atoms in the cage to form three $2c-2e^-$ bonds to other Ge atoms in the cage and therefore the cluster can be described in an electron-precise bonding model. Overall, the formal charges inferred from the analysis of Kohn-Sham MOs reflect the differences in the metal-cage interaction seen between the two compounds. The greater availability of the Rh 4d electrons means that it would populate the antibonding orbitals of the icosahedral structure and hence destabilise it compared to its 3-connected global minimum. In contrast, the 3d orbitals of Zn remain localised on the metal and hence do not destabilise the icosahedral structure and do not delocalise to the cage enough to stabilise the 3-connected structure as its global minimum.

While it is possible to understand the structures in intermetalloid clusters using bonding models, determining what causes a cluster to follow a particular bonding model is more complicated. In certain cases, properties in addition to electron count can be used to show to which bonding model a cluster will adhere. For example, one could use a property such as an effective nuclear charge of the metal to indicate when the Wade's rules or electron-precise structure will be adopted by the Ge_{12} cage in $Zn@Ge_{12}$ and $[Rh@Ge_{12}]^{3-}$. This approach could also be applied to show which structures are adopted in certain compounds where the electron count of the cage could imply multiple structures. For example, the cluster $[Ti@Si_{14}]^{2-}$ takes an *arachno* structure while the

isoelectronic $[\text{Fe}@\text{Si}_{14}]^{2+}$ takes a structure described by a fullerene-like bonding model,⁵⁰ despite both silicon cages being assigned the formal charge $[\text{Si}_{14}]^{6-}$. It was determined⁵⁰ that the metal's ability to donate electron density to the cage dictates which structure is adopted and hence the effective nuclear charge also correlates with the structure adopted by these clusters. It is not always possible to show when a particular bonding model applies by considering a single additional property of the cluster however. For example, it was found⁵¹ that total electron density transferred to the cage could not explain the structural preference of $[\text{Fe}@\text{Ge}_{10}]^{3-}$ for a pentagonal prism over the bi-capped square anti-prism seen for $[\text{Ni}@\text{Pb}_{10}]^{2-}$. Instead, it was demonstrated that the number of orthogonal d-orbitals available for bonding determined the structural preference for the pentagonal prism. Furthermore, not all known intermetalloid clusters are described well by typical bonding models. The compound $\text{Cr}@\text{Si}_{12}$ is a notable example of such a cluster.^{48,52–58} Its Si_{12} cage adopts a 3-connected hexagonal prism structure which, in principle, can be explained with an electron-precise bonding model. However, even if all the metal valence electrons are assigned to the cage, its electron count is 54, six short of the 60 required for an electron-precise count. The electron count of 54 does equal that required for a Wade's rule $n = 12$ *arachno* structure but of the possible $n = 12$ *arachno* structures,⁵⁹ the most similar to the hexagonal prism of $\text{Cr}@\text{Si}_{12}$ is a hexagonal anti-prism, which is not the compound's global minimum. Hence, the structure of $\text{Cr}@\text{Si}_{12}$ cannot be described by either an electron-precise or Wade's rules bonding model. More broadly, the examples discussed show that understanding which structures of the metal and cage fragments are adopted and when is complex. As such, establishing bonding models to explain the structures of intermetalloid clusters and determining when each model applies remains an active area of research.

Further studies developing the bonding models of intermetalloid clusters include, among others, a description of how the fusion of two E_{18} ($\text{E} = \text{Ge}, \text{Sn}$) cages is mediated by varying the interstitial metal fragment,⁶⁰ the reported synthesis of $[\text{Nb}@\text{Ge}_{13}]^{3-}$ and $[\text{Nb}@\text{Ge}_{14}]^{3-}$, which also demonstrated that the structures of both of the compounds

cannot be explained by either Wade's rules or electron-precise bonding models and instead the bonding in the structures can be considered intermediates between those of the two models.⁶¹ Additionally, a review establishes a relationship between the valence electron count and structures, spanning from electron-deficient structures with $4n + 2$ electron counts to electron-precise structures with $6n$ counts, for $n = 12$ endohedral intermetalloid clusters with a single interstitial metal atom.⁶² The review also highlights "missing links" in the series where there have been no compounds observed for a given electron count.

Having toured the bonding models of intermetalloid clusters, the application of electronic structure methods to intermetalloid clusters is discussed. Transition metals, metal-metal bonds, and weak interactions have all been noted as being modelled with varying degrees of accuracy by electronic structure methods.^{63–65} Given all of these features can be exhibited in intermetalloid clusters, it may be considered unsurprising that, for certain intermetalloid clusters, multiple electronic structure methods need to be considered in order to establish a methodology capable of modelling the cluster accurately. Most notably, there have been a number of cases where cluster properties have been inaccurately calculated with KS-DFT or have shown a significant dependence on the exchange-correlation functional used.^{50,66,67} In such cases, it is possible for post-HF methods to provide a resolution to the discrepancy.^{66,67} However, there are also intermetalloid clusters which push the limitations of the electronic structure methods available. For example, the limitations on the size of the active space in CASSCF methods has been noted as a challenge in modelling certain clusters, even when applying approximations through the RASSCF and GASSCF methods.⁶⁸ Such cases highlight the need to identify when electronic structure methods produce varying results for intermetalloid clusters and to develop methodologies capable of resolving these discrepancies.

The present thesis reports contributions to both the understanding intermetalloid clusters through bonding models and to the development of methodologies using electronic structure methods which may be used to gain insight into intermetalloid clusters. In

chapter three, it is shown that the structure of a newly synthesised intermetalloid cluster can be understood as a previously unseen manifestation of a pre-existing bonding model. Chapter four develops a methodology based on coupled-cluster methods in order to resolve a discrepancy in predicted global minima of two $M@Si_{14}$ intermetalloid clusters. Lastly, chapter five derives an approximation for the correlation of core electrons in Brueckner coupled-cluster theory, aiming to expand the proportion of the correlation energy of core electrons which can be calculated when applying electronic structure methods to intermetalloid clusters. Before these contributions are presented, the theoretical background of the methods used throughout the thesis is discussed in chapter two.

Chapter 2

Theoretical Background

2.1 The Molecular Many-Body Problem

The molecular many-body problem pertains to obtaining an accurate mathematical description of the behaviour of all the particles in a molecule. Molecules are many-body systems consisting of N_e electrons and N_n nuclei and both of these particles can be accurately modelled with quantum mechanics. Thus, the current chapter presents a quantum-mechanical formulation of the molecular many-body problem. There have been various formulations of quantum mechanics since its discovery. The current chapter presents a formulation which primarily follows Dirac's state space formulation⁶⁹ but also draws from more modern accounts such as that of Sakurai and Napolitano.⁷⁰ The state space formulation begins with the postulates of quantum mechanics, which in the present thesis, are considered to be the following.[†]

The Postulates of Quantum Mechanics

- I. The state of an isolated system at a fixed time, t , is represented by a vector contained in a vector space, $\mathcal{H}$, which admits complex-valued scalars. The vector space is referred to as the state space and a vector in the state space is known as a state vector.
- II. All physically observable quantities are described by Hermitian operators acting on the Hilbert space. Their eigenvalues must be the possible results of measurements of the quantity. Their eigenvectors form a basis for $\mathcal{H}$.
- III. The probability of measuring a possible measurement outcome is given by the square magnitude of the projection of the state vector onto measurement outcome's eigenvector.
- IV. When a particular outcome is measured, the state vector becomes the eigenstate of the measured outcome. This is known as wavefunction collapse.

[†]Occasionally, the state space defined in the postulates is referred to as a Hilbert space. Technically, the state space formulated in the present chapter does not conform to the axioms of a Hilbert space (e.g. the position eigenvectors used to expand a state vector in equation (2.1) require an infinite norm, meaning they cannot exist as vectors in a Hilbert space) and therefore the present thesis avoids referring to the state space as a Hilbert space. More broadly, one may raise concerns about the lack of rigorous formulation used in the state space approach. As set in stone as one may want the postulates of quantum mechanics to be, the behaviour certain mathematical objects encountered in the current chapter exhibit outside of a rigorous formulation leads to results which agree with experiment and as such their lack of mathematical rigour need not be a concern for the scientific endeavours of the present thesis.

To formulate the molecular many-body problem, a state vector capable of describing all properties of a molecular system is sought. For a single particle, the operator of any observable property can be constructed from the operators of three fundamental observables. In atomic units, these are: 3D position, $\mathbf{r} \in \mathbb{R}^3$, 3D momentum, $\mathbf{p} \in \mathbb{R}^3$, and spin, $s \in \{\frac{1}{2}, -\frac{1}{2}\}$ for electrons, and $S \in \{-I, -I+1, \dots, I\}$ for nuclei with nuclear spin I . Therefore, forming a state space which contains eigenvectors of all of these fundamental observables' operators for all electrons and nuclei in a system allows any molecular property to be calculated.

In order to derive the state space of a molecular system, first consider a single dimension of position for a single electron. The state space for this system is defined by the eigenvectors of a position operator, $|x\rangle$, which in turn are defined by: $\hat{x}|x\rangle = x|x\rangle$. It is then assumed an arbitrary vector in the state space for this system, $\mathcal{H}_x$, may be expressed as

$$|\psi\rangle = \int_{-\infty}^{\infty} \psi(x)|x\rangle dx, \quad (2.1)$$

where the $\psi(x)$ are the complex-valued expansion coefficients of the vector. The state space $\mathcal{H}_x$ is defined as the set of all possible vectors expressed in the manner of equation (2.1). A momentum operator can be defined in a similar manner to the position operator, $\hat{p}_x|p_x\rangle = p_x|p_x\rangle$. However, the position and momentum operators for the same dimension must satisfy the commutation relation $[\hat{x}, \hat{p}_x] = i\hbar$. This prevents the eigenvectors of the position and momentum operators forming a simultaneous eigenbasis for an electron's state space and therefore a state vector can be expressed in a position or momentum eigenbasis, but not both. Physically, this restriction corresponds to an inability to precisely know both the position and momentum of an electron simultaneously in a given dimension.

The position operators in each dimension all commute with each other and hence the tensor product of their state spaces, all defined in a manner equivalent to that of the $\hat{x}$ operator, can be taken to produce a space capable of describing the outcome of position measurements in three dimensions: $\mathcal{H}_{\mathbf{r}} = \mathcal{H}_x \otimes \mathcal{H}_y \otimes \mathcal{H}_z$. An arbitrary vector in this

space can be written as

$$|\psi\rangle = \int \psi(\mathbf{r})|\mathbf{r}\rangle d\mathbf{r},$$

where $|\mathbf{r}\rangle = |x, y, z\rangle = |x\rangle \otimes |y\rangle \otimes |z\rangle$.

Next, the spin of the electron is sought to be included in the state space. The state of a quantum mechanical spin can be described in terms of the eigenvectors of the spin-projection operator along an arbitrary axis, which is chosen to be $\hat{S}_z$ in this case. The spin-projection operator commutes with the position operator in all dimensions so the tensor product of the two spaces may be taken again. A general vector in the resultant space may be expressed as

$$|\psi\rangle = \sum_s \int \psi(\mathbf{x})|\mathbf{x}\rangle d\mathbf{r}, \quad (2.2)$$

in which $|\mathbf{x}\rangle = |\mathbf{r}\rangle \otimes |s\rangle$.

The position and spin operators of different particles all commute with each other so a general vector in the state space for the molecular case of N_e electrons and N_n nuclei can be defined as

$$|\Psi\rangle = \sum_{\{s_i\}} \sum_{\{S_K\}} \int \Psi(\tilde{\mathbf{x}}, \tilde{\mathbf{X}}) |\tilde{\mathbf{x}}, \tilde{\mathbf{X}}\rangle d\tilde{\mathbf{r}} d\tilde{\mathbf{R}},$$

where $\tilde{\mathbf{x}}$ and $\tilde{\mathbf{X}}$ are vectors containing the space-spin coordinates for the electrons and nuclei respectively and $\tilde{\mathbf{r}}$ and $\tilde{\mathbf{R}}$ are vectors containing the spatial coordinates for all electrons and nuclei respectively.

The energy of molecular systems is the primary quantity calculated in the present thesis. For the majority of calculations reported, the energy is assumed to be independent of time and relativistic effects. The operator corresponding to such an energy is the time-independent, non-relativistic Hamiltonian. Therefore, the primary concern of the present thesis may be considered to be finding solutions to the Schrödinger equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle, \quad (2.3)$$

in which $\hat{H}$ is the time-independent, non-relativistic Hamiltonian,

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ &= \hat{T}_e + \hat{T}_n + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}.\end{aligned}$$

$\hat{T}$ denotes a kinetic energy operator and hence $\hat{T}_e$ and $\hat{T}_n$ are the kinetic energy operators of the electrons and nuclei respectively. $\hat{V}$ denotes a potential energy operator and so $\hat{V}_{en}$ is the operator for the Coulomb attraction between the electrons and nuclei, $\hat{V}_{ee}$ is the operator for the Coulomb repulsion between electrons, and $\hat{V}_{nn}$ is operator for the Coulomb repulsion between nuclei.

The time-independent, non-relativistic Hamiltonian does not depend on any spin operators, hence

$$[\hat{H}, \hat{S}_z] = 0 \quad \& \quad [\hat{H}, \hat{S}^2] = 0 \quad (2.4)$$

and the same for nuclear spin,

$$[\hat{H}, \hat{I}_z] = 0 \quad \& \quad [\hat{H}, \hat{I}^2] = 0. \quad (2.5)$$

This means that eigenvectors of $\hat{H}$ will simultaneously be eigenvectors of all the spin operators in expressions (2.4) and (2.5). As a result, the eigenvectors of the Hamiltonian have a pure electronic and nuclear spin state. Therefore, a general eigenvector of $\hat{H}$ can be written as

$$|\Psi\rangle = \int \Psi(\tilde{\mathbf{x}}, \tilde{\mathbf{X}}) |\tilde{\mathbf{x}}, \tilde{\mathbf{X}}\rangle d\tilde{\mathbf{r}} d\tilde{\mathbf{R}}. \quad (2.6)$$

A solution to the molecular many-body problem can now be formulated in terms of computable functions. Projecting equation (2.3) onto the position eigenvector $|\tilde{\mathbf{x}}', \tilde{\mathbf{X}}'\rangle$ and evaluating the resultant inner products (in a manner that has been documented elsewhere⁷⁰) results in an expression that shows the coefficients of the general vector in (2.6) satisfy the Schrödinger equation,

$$\hat{H}\Psi(\tilde{\mathbf{x}}, \tilde{\mathbf{X}}) = E\Psi(\tilde{\mathbf{x}}, \tilde{\mathbf{X}}), \quad (2.7)$$

where

$$\hat{H} = -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \sum_K^{N_n} \frac{1}{2M_K} \nabla_K^2 - \sum_{iK} \frac{Z_K}{|\mathbf{r}_i - \mathbf{R}_K|} + \frac{1}{2} \sum_{ij} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{KL} \frac{Z_K Z_L}{|\mathbf{R}_K - \mathbf{R}_L|}$$

when expressed in atomic units. Equation (2.7) is the Schrödinger equation in the position representation and the coefficients are commonly referred to as the many-body wavefunction.

2.1.1 The Born-Oppenheimer Approximation

At this stage, solving the molecular many-body problem amounts to solving the time-independent, non-relativistic Schrödinger equation for a wavefunction and its energy. The wavefunction is a function of both the nuclear and electronic coordinates and simultaneously considering both the nuclei and electrons increases the complexity of solving the Schrödinger equation. The Born-Oppenheimer approximation offers a means to reduce this complexity by allowing the electrons and nuclei to be treated separately. The approximation has turned out to be greatly effective and is used in the vast majority of electronic structure calculations in the present day. It has also heavily influenced the way electronic structure and chemistry are understood with it underpinning concepts such as electronic states and potential energy surfaces. The approximation can break down in certain scenarios,⁷¹ but these will not be encountered in this thesis.

To derive the Born-Oppenheimer approximation, it is first assumed that the wavefunction can be separated into a product of a function of nuclear coordinates and a function of electronic coordinates with parametric dependence on the nuclear coordinates,

$$\Psi(\tilde{\mathbf{x}}, \tilde{\mathbf{X}}) \approx \Psi_e(\tilde{\mathbf{x}}; \tilde{\mathbf{X}}) \Psi_n(\tilde{\mathbf{X}}). \quad (2.8)$$

Substituting the right-hand side of (2.8) into the Schrödinger equation in the position

representation, equation (2.7), yields

$$\Psi_n \hat{T}_e \Psi_e + \hat{T}_n \Psi_e \Psi_n + \hat{V} \Psi_e \Psi_n = E \Psi_e \Psi_n. \quad (2.9)$$

The nuclear kinetic energy term can then be expanded as

$$\begin{aligned} \hat{T}_n \Psi_e \Psi_n &= -\frac{1}{2M_K} \nabla_K^2 [\Psi_e(\tilde{\mathbf{x}}; \tilde{\mathbf{X}}) \Psi_n(\tilde{\mathbf{X}})] \\ &= -\frac{1}{2M_K} [2 \nabla_K \Psi_e(\tilde{\mathbf{x}}; \tilde{\mathbf{X}}) \cdot \nabla_K \Psi_n(\tilde{\mathbf{X}}) + \Psi_e(\tilde{\mathbf{x}}; \tilde{\mathbf{X}}) \nabla_K^2 \Psi_n(\tilde{\mathbf{X}}) + \Psi_n(\tilde{\mathbf{X}}) \nabla_K^2 \Psi_e(\tilde{\mathbf{x}}; \tilde{\mathbf{X}})], \end{aligned} \quad (2.10)$$

and it can be further approximated that the terms which contain any derivative of the electronic wavefunction with respect to the nuclear coordinates are negligible. The basis for this approximation is that the motion of the electrons is assumed to be much faster than that of the nuclei and hence that the electronic wavefunction is largely unaffected by the kinetic energy of the nuclei. Setting these terms to zero means that only the second term in equation (2.10) remains and hence the substitution $\hat{T}_n \Psi_e \Psi_n \approx \Psi_e \hat{T}_n \Psi_n$ can be made in expression (2.9), which leads to

$$\Psi_n \hat{T}_e \Psi_e + \Psi_e \hat{T}_n \Psi_n + \hat{V} \Psi_e \Psi_n = E \Psi_e \Psi_n. \quad (2.11)$$

Using the fact that the potential energy operator can be expressed as $\hat{V} = V(\tilde{\mathbf{x}}, \tilde{\mathbf{X}})$, expression (2.11) can be written as

$$\Psi_e \hat{T}_n \Psi_n + [\hat{T}_e \Psi_e + V(\tilde{\mathbf{x}}, \tilde{\mathbf{X}}) \Psi_e] \Psi_n = E \Psi_e \Psi_n. \quad (2.12)$$

The bracketed term in equation (2.12) can be recognised as the action of a Hamiltonian on a wavefunction for a system of electrons moving in the potential resulting from a number of nuclei in fixed positions. This Hamiltonian is known as the electronic Hamiltonian and is defined as $\hat{H}_e = \hat{T}_e + V(\tilde{\mathbf{x}}, \tilde{\mathbf{X}})$. The electronic Hamiltonian can be

used to write the electronic Schrödinger equation:

$$\hat{H}_e \Psi_e(\tilde{\mathbf{x}}; \tilde{\mathbf{X}}) = E_e(\tilde{\mathbf{X}}) \Psi_e(\tilde{\mathbf{x}}; \tilde{\mathbf{X}}). \quad (2.13)$$

Inputting the right-hand side of (2.13) back into equation (2.12) and then dividing Ψ_e out of the expression results in the nuclear Schrödinger equation,

$$[\hat{T}_n + E_e] \Psi_n(\tilde{\mathbf{X}}) = E \Psi_n(\tilde{\mathbf{X}}). \quad (2.14)$$

Equation (2.14) can be viewed simply as the Schrödinger equation for a system of nuclei moving in the potential E_e . The eigenvalue on the right-hand side of (2.14) is still the total energy of the system under the Born-Oppenheimer approximation. In most electronic structure calculations, the nuclear equation is not solved and only the solutions to electronic Schrödinger equation are determined, as is the case for all calculations reported in this thesis. However, the nuclear Schrödinger equation does see use when the rotational or vibrational motion of the nuclei are of interest.

2.1.2 The Slater Determinant Expansion of the Many-Body State

Having reduced the molecular many-body problem to finding a solution of the electronic Schrödinger equation, one could attempt to solve the electronic Schrödinger equation directly. This is a partial differential equation so in principle can be approached with standard methods. However, it is known that the electron–electron repulsion term in the Hamiltonian prevents analytical solutions from being obtained. Moreover, attempting a numerical solution by finding Ψ on a grid would quickly become impossible. A back of the envelope calculation, often reported to be by Douglas Hartree (though the original source has proved elusive), shows that even just the wavefunction of an iron atom stored using $10 \times 10 \times 10$ grids for the spatial dimensions would require more numbers to be stored than the estimated number of atoms in the solar system.[†] Hence, formulations of

[†]Fe has 26 electrons, the wavefunction requires $3N_e = 78$ dimensions and hence 10^{78} numbers to store. Estimates for atoms in the solar system are on the scale of 10^{60} .

the electronic Schrödinger equation that lend themselves to practical computation are needed to obtain a solution to the molecular many-body problem.

Far and away the most common formulation of the electronic Schrödinger equation for practical computation is the Slater determinant expansion of the many-body state. The expansion is found by first considering operators with countably infinite eigenspectra that are also comprised of position and momentum operators. A number of these operators have been established and they are generally model Hamiltonians e.g. that of the simple harmonic oscillator. Since such operators act on the same space as the position and momentum operators, their eigenvectors can provide a countably infinite basis for the state space. In the case of a single electron, the eigenproblem of such an operator can be written as

$$\hat{H}|\phi_i\rangle = \varepsilon_i|\phi_i\rangle,$$

where $|\phi\rangle = |\phi\rangle \otimes |s\rangle$ and further $|\phi\rangle \in \mathcal{H}_{xyz}$. The presence of $|s\rangle$ ensures $|\phi\rangle$ is simultaneously an eigenvector of $\hat{S}_z$ and $\hat{H}$. Hence a state vector for a single electron may be expressed in the countably infinite eigenbasis,

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle.$$

Similarly, a state vector in a N_e -electron state space can be expressed as

$$|\Psi\rangle = \sum_{i,j,\dots} c_{ij\dots} |\phi_i\rangle_1 \otimes |\phi_j\rangle_2 \otimes \dots \otimes |\phi_{N_e}\rangle_{N_e} \quad (2.15)$$

$$= \sum_{i,j,\dots} c_{ij\dots} |\phi_i \phi_j \dots \phi_{N_e}\rangle, \quad (2.16)$$

in which the indices on each vector in (2.15) denote the sub-space for each electron, and the sub-space occupied by each single-particle eigenvector is implied by the ordering of the single-particle eigenvectors in equation (2.16).

Electrons are indistinguishable from one another, meaning the state of an individual electron within a many-body system cannot be known. For example, in a system of two

electrons where it is known that the possible states for each electron are $|\varphi_1\rangle$ and $|\varphi_2\rangle$, a measurement of the eigenvalues of these states will simply return either ε_1 or ε_2 with no information about which electron it came from. The indistinguishability of electrons is enforced in expansion (2.16) via the Pauli principle. The Pauli principle states that the many-body state may change by no more than a phase factor when two particles are interchanged among the states they occupy. In particular, for fermions (and therefore electrons), the phase factor must be such that the many-body state is antisymmetric under the interchange of any two particles among their states. In the two-electron example, this means the coefficients in expansion (2.6) have to satisfy $c_{12} = -c_{21}$. Hence, when normalised, the state vector is

$$|\Psi\rangle = \sqrt{\frac{1}{2}} \left(|\varphi_1 \varphi_2\rangle - |\varphi_2 \varphi_1\rangle \right).$$

In cases where there are more than two electrons, it is convenient to define an antisymmetrising operator, $\hat{A}$ which acts on a product state to produce its corresponding antisymmetric combination of product states. The antisymmetrisation operator can be defined as

$$\hat{A} = \frac{1}{N_e!} \sum_{\{\mu\}} (-1)^{p_\mu} \hat{\pi}_\mu,$$

where $\{\mu\}$ is the set of $N_e!$ permutations of the single-particle states among the electrons' sub-spaces. The operator $\hat{\pi}_\mu$ acts on a product state to produce permutation μ e.g. $\hat{\pi}_{321}|\varphi_1 \varphi_2 \varphi_3\rangle = |\varphi_3 \varphi_2 \varphi_1\rangle$. The quantity $(-1)^{p_\mu}$ is the parity of permutation μ . This is equal to 1 if there is an even number of interchanges of single-particle eigenvectors among electron sub-spaces made in the operand to produce permutation μ and -1 if there is an odd number of interchanges.

Using the antisymmetrising operator, expansion (2.6) can be enforced to obey Pauli's principle,

$$|\Psi\rangle = \sum_{i,j,\dots} c_{ij\dots} \hat{A} |\varphi_i \varphi_j \dots \varphi_{N_e}\rangle. \quad (2.17)$$

Note that the antisymmetrising operator ensures that terms where $i = j$ are non-existent.

Consequently, only terms where a different spin orbital occupies each electron's sub-space are present in the summation. Equation (2.17) is the sought Slater determinant expansion of the many-body state, in which the $\hat{A}|\varphi_i\varphi_j\ldots\varphi_{N_e}\rangle$ terms in the summand are known as a Slater determinants. Note that expansion (2.17) does not necessarily satisfy the condition that $[\hat{H},\hat{S}^2] = 0$. In general, it is not possible to ensure that $[\hat{H},\hat{S}^2] = 0$ with a single Slater determinant. It is however possible to construct linear combinations of Slater determinants, known as configuration state functions, which are eigenvectors of $\hat{S}^2$ and therefore satisfy this condition. In practice, not all methods using expansion (2.17) enforce $[\hat{H},\hat{S}^2] = 0$ but some do employ configuration state functions for this purpose.

2.2 Configuration Interaction Theory

The Slater determinant expansion of the many-body state sees use in the electronic structure method configuration interaction (CI) theory. As discussed in section 1.1, CI theory forms a Slater determinant expansion by first determining a set of molecular orbitals and selecting a sub-set of these to construct a Slater determinant known as the reference state. The orbitals constituting the reference state are known as the occupied orbitals and the unused orbitals are known as the virtual or unoccupied orbitals. The Slater determinant expansion is then formed from the reference state by replacing a sub-set of the occupied orbitals in the reference state with virtual orbitals to construct new determinants which are then added to the reference state in a linear expansion. The process of replacing occupied orbitals in the reference state with virtual orbital orbitals is known as excitation, which is classified according to how many replacements have been made. For example, single excitations have one occupied orbital replaced with one virtual orbital, double excitations replace two occupied orbitals with two virtual orbitals and so on.

The ground-state energy and expansion coefficients of the CI expansion can be determined using variational theorem, which states that the energy calculated from a

normalised trial wavefunction cannot be lower than the exact ground-state energy. This means the Slater determinant expansion can be inserted into the energy expression

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle},$$

and the coefficients optimised to give the lowest energy possible. If the expansion uses an infinite set of molecular orbitals and all possible excited Slater determinants are included, this calculation approaches[†] the exact ground-state energy. In practice, it is impossible to use an infinite molecular orbital set, thus finite sets are used. Including all possible excited determinants within a finite molecular orbital set to determine the ground-state energy is known as full configuration interaction (FCI) theory. This gives the closest possible energy to the ground-state energy for the set of molecular orbitals. As the world would have it, FCI calculations are intractable for all but the smallest molecules (such as H₂O) using small sets of molecular orbitals. Consequently, CI calculations in practice often restrict the maximum excitation level. For example, CISD includes only singly and doubly excited determinants in its expansion.

2.3 Hartree-Fock Theory

Hartree-Fock theory is the result of restricting the Slater determinant expansion of the many-body state to a single Slater determinant and optimising the orbitals to minimise the energy calculated. To derive the theory, the Slater determinant is assumed to be comprised of orthonormal orbitals and is expressed in terms of the antisymmetrising operator, and a normalisation constant,

$$|\Psi\rangle = \sqrt{N_e!} \hat{A} |\varphi_1 \varphi_2 \dots \varphi_{N_e}\rangle. \quad (2.18)$$

[†] Provided the expansion does not converge to an excited electronic state.

Inserting expression (2.18) into the equation for the expectation value of the Hamiltonian results in a formula for the HF energy,

$$\begin{aligned} E_{\text{HF}} &= \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \\ &= \sum_i \langle \varphi_i | \hat{h}_1 | \varphi_i \rangle + \frac{1}{2} \sum_{ij} \langle \varphi_i \varphi_j | \frac{1}{r_{12}} | \varphi_i \varphi_j \rangle - \frac{1}{2} \sum_{ij} \langle \varphi_i \varphi_j | \frac{1}{r_{12}} | \varphi_j \varphi_i \rangle. \end{aligned}$$

Since orthonormal orbitals have been assumed, the orbitals must be minimised under the constraint that orbitals remain orthonormal. Hence the method of Lagrange multipliers is employed. The relevant Lagrangian is

$$L[\varphi] = E_{\text{HF}} - \sum_{ij} \varepsilon_{ij} (\langle \varphi_i | \varphi_j \rangle - \delta_{ij}),$$

whose stationary points can be found by solving the equation

$$\begin{aligned} \delta L &= \langle \delta \varphi_k | \hat{h}_1 | \varphi_k \rangle + \\ &\sum_j \left(\langle \delta \varphi_k \varphi_j | \frac{1}{r_{12}} | \varphi_k \varphi_j \rangle - \langle \delta \varphi_k \varphi_j | \frac{1}{r_{12}} | \varphi_j \varphi_k \rangle \right) - \sum_j \varepsilon_{kj} \langle \varphi_k | \varphi_j \rangle + \text{h.c.} = 0, \end{aligned} \quad (2.19)$$

in which h.c. denotes the Hermitian conjugate. Equation (2.19) is most commonly expressed in terms of the Fock operator, which, in the position representation, is defined as

$$\hat{f} = \hat{h}_1 + \sum_j \int \varphi_k^*(\mathbf{x}_2) \frac{1}{r_{12}} (1 - \hat{\pi}_{12}) \varphi_j(\mathbf{x}_2) d\mathbf{x}_2$$

and allows equation (2.19) to be written as

$$\hat{f} \varphi_k(\mathbf{x}_1) = \sum_j \varepsilon_{kj} \varphi_j. \quad (2.20)$$

It can then be shown that there exists a set of spin orbitals for which the matrix of Lagrange multipliers is diagonal,⁷² meaning equation (2.20) can be written as an eigenvalue equation,

$$\hat{f} \varphi_k(\mathbf{x}_1) = \varepsilon_k \varphi_k(\mathbf{x}_1). \quad (2.21)$$

Equation (2.21) is the canonical form of the Hartree-Fock equations. Notably, the Fock operator depends on the orbitals being found. This means solutions to equation (2.21) must be obtained self-consistently, that is to initially guess a set of orbitals, calculate a new operator, solve the eigenvalue problem to obtain a new set of orbitals, and repeat until the solutions have converged to a desired degree of precision. This algorithm is sometimes known as the self-consistent field (SCF) algorithm.

2.4 Coupled-Cluster Theory

2.4.1 Initial Considerations

As with CI theory, coupled-cluster theory is a wavefunction method which employs a Slater determinant expansion. Coupled-cluster theory also introduces a non-linear parametrisation of the Slater determinant expansion coefficients. This results in an alternative description of the correlation of electrons, which features desirable properties not seen in CI theory such as size consistency.

Coupled-cluster theory is conveniently derived with the use of occupation number representation, which provides an alternative to representing Slater determinants with the antisymmetrisation operator.⁷³ Briefly, occupation number vectors have a 1:1 mapping with Slater determinants. When a Slater determinant is expressed as the determinant of a matrix, as done in the right-hand side of expression (2.22), an occupation number vector shows the number of particles present in each orbital of the Slater determinant, in the order they appear down its diagonal (typically in order of eigenvalue). For example

$$|1_1 1_2\rangle \leftrightarrow \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_2(\mathbf{x}_1) \\ \varphi_1(\mathbf{x}_2) & \varphi_2(\mathbf{x}_2) \end{vmatrix}, \quad (2.22)$$

and the occupation number vector $|1_1 1_2\rangle$ indicates the orbitals φ_1 and φ_2 are occupied by one electron each. As with CI theory, coupled-cluster theory employs a reference state

from which the other determinants are generated. This is done with creation and annihilation operators which are defined by their respective actions on occupation number vectors,

$$\hat{c}_p^\dagger |\text{ref}\rangle = \hat{c}_p^\dagger |1 \dots (N_e)_1 \dots 0_p \dots\rangle = |1 \dots (N_e)_1 \dots 1_p \dots\rangle = |\text{ref}, p\rangle$$

and

$$\hat{c}_p |\text{ref}, p\rangle = |\text{ref}\rangle,$$

in which $|\text{ref}\rangle$ denotes the reference state, along with their anticommutation relations,

$$\{\hat{c}_p^\dagger, \hat{c}_q\} = \delta_{pq} \quad \& \quad \{\hat{c}_p^\dagger, \hat{c}_q^\dagger\} = \{\hat{c}_p, \hat{c}_q\} = 0,$$

which ensure the antisymmetric properties of the wavefunction are maintained when creation/annihilation operators are used consecutively.

Excited determinants are generated via excitation operators, $\hat{\tau}$, which annihilate a particle in one state and create a particle in another (and hence are guaranteed to conserve particle number). The symbol γ is used to indicate an excitation of an arbitrary order. For example, $\hat{\tau}_\gamma$ may equally refer to a single, $\hat{\tau}_i^a$, double, $\hat{\tau}_{ij}^{ab}$, or triple, $\hat{\tau}_{ijk}^{abc}$ excitation and so on. Hence, the action of an excitation operator may be written as

$$\hat{\tau}_\gamma |\text{ref}\rangle = |\gamma\rangle,$$

where $|\gamma\rangle$ corresponds to an excited determinant. The excitation process can equally be expressed in terms of creation and annihilation operators, for example in the case of a double excitation,

$$\hat{\tau}_{ij}^{ab} |\text{ref}\rangle = \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_i \hat{c}_j |\text{ref}\rangle = |_{ij}^{ab}\rangle. \quad (2.23)$$

CI theory may also be generated using excitation operators but coupled-cluster theory differs from CI theory in how the excitation operators are used to generate its Slater

determinant expansion. The coupled-cluster *ansatz* is written as a product,

$$|\Psi\rangle = \prod_{\gamma} (1 + t_{\gamma} \hat{\tau}_{\gamma}) |\text{ref}\rangle, \quad (2.24)$$

where the t_{γ} are constants known as the excitation amplitudes. Note this *ansatz* is intermediately normalised, meaning the amplitudes are defined such that the reference state always has a coefficient of one. The product form of (2.24) ensures that, in a system where n electrons are being excited in total, excited determinants of order n will appear in the expansion. This means that the coupled-cluster wavefunction includes determinants which span the full CI space, regardless of the excitation order employed. The coefficients of the Slater determinants in the coupled-cluster *ansatz* are not all single constants like their CI counterparts. Instead, a number of the Slater determinants have coefficients which are products of excitation amplitudes. For example, in the case of a closed-shell, two-state system, the CCS expansion (that is coupled-cluster with only single excitations) is

$$|\Psi\rangle = |\text{ref}\rangle + t_{1\alpha}^{2\alpha} |1\alpha\rangle + t_{1\beta}^{2\beta} |1\beta\rangle + t_{1\alpha}^{2\alpha} t_{1\beta}^{2\beta} |1\alpha 1\beta\rangle.$$

Notice that a doubly excited determinant is produced, despite the coupled-cluster *ansatz* only explicitly including single excitation operators. Additionally, the coefficient of the doubly excited state is a product of the amplitudes for the two single excitations.

Physically, the use of a product of excitation amplitudes corresponds to allowing the particles to occupy the two states independently of each other. The probability amplitude for the double excitation occurring is the same as the probability amplitude for both single excitations occurring simultaneously and independently, which is equal to the product of the two single excitation amplitudes. In contrast, the CIS (configuration interaction with only single excitations) expansion for the same system,

$$|\Psi\rangle = |\text{ref}\rangle + t_{1\alpha}^{2\alpha} |1\alpha\rangle + t_{1\beta}^{2\beta} |1\beta\rangle,$$

introduces a correlation between the particles since it prevents both excitations from

occurring at once i.e. the wavefunction only contains contributions from when one particle has been excited and the other remains unexcited. The excitations are not independent since both particles cannot be excited at once.

The correlation introduced by truncated CI methods is what prevents these methods from exhibiting size consistency in the energy. For example, consider a case where the states in the previous paragraph's example correspond to the states of a system of two non-interacting atoms, one with an α electron and the other with a β electron. Both electrons are superimposed across their individual atom's ground and first excited states. The electrons' superpositions should be independent of each other since their sub-systems are non-interacting. However, the CIS expansion does not include contributions to the overall wavefunction from the state where both electrons are excited at the same time. This prevents the total CIS energy from equalling the sum of the individual sub-systems' energies. The CCS energy does equal the sum of sub-systems' energies however, as is correct, and therefore the CCS energy is size consistent.

2.4.2 General Formulation

The solutions to the coupled-cluster equations can be formulated by first recognising that, when the product of excitation operators in equation (2.24) is expanded, the terms can be collected and expressed as an exponential operator,

$$\prod_{\gamma} (1 + t_{\gamma} \hat{t}_{\gamma}) = \exp \left(\sum_{\gamma} t_{\gamma} \hat{t}_{\gamma} \right).$$

The argument of the exponential operator is often denoted $\hat{T}$ and further broken down by order of excitation,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n = \sum_{\gamma_1} t_{\gamma_1} \hat{t}_{\gamma_1} + \sum_{\gamma_2} t_{\gamma_2} \hat{t}_{\gamma_2} + \dots + \sum_{\gamma_n} t_{\gamma_n} \hat{t}_{\gamma_n}. \quad (2.25)$$

The truncation of this series can be used to define the different coupled-cluster methods with, for example, CCSD employing $\hat{T} = \hat{T}_1 + \hat{T}_2$, CCSDT using $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$, and so on. Using the complete $\hat{T}$, the exponential form of the *ansatz* can be placed in the Schrödinger equation to give the compact expression

$$\hat{H}e^{\hat{T}}|\text{ref}\rangle = Ee^{\hat{T}}|\text{ref}\rangle. \quad (2.26)$$

Since the coupled-cluster Slater determinant expansion contains enough Slater determinants to span the full state space, solving (2.26) variationally (as is done with CI methods), has the same computational cost as FCI, despite the coefficients of the coupled-cluster *ansatz* not all being independent. Therefore, the solutions to (2.26) are instead found tractably by projecting both sides of the equation onto the states $\{\langle\text{ref}|e^{-\hat{T}}\rangle \oplus \{\langle\gamma|e^{-\hat{T}}\rangle\}$. Doing so generates a non-linear system of equations, represented in expressions (2.27) and (2.28), with one equation present for the energy and an equation present for each amplitude to be determined. Note the $e^{-\hat{T}}$ operator is not technically necessary but does simplify the expressions found.

$$\langle\text{ref}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\text{ref}\rangle = E \quad (2.27)$$

$$\langle\gamma|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\text{ref}\rangle = 0 \quad (2.28)$$

Hence it can be seen that the projection involving the reference state determines the energy while the projections involving the excited states put conditions on the amplitudes.

The task then becomes casting equations (2.27) and (2.28) into forms which can be evaluated numerically. This is a laborious but well-documented⁷⁴ process so only an outline is given in the present section. It has been found that the action of the exponential operators and the Hamiltonian can be expressed using what is known as a Baker-Campbell-Hausdorff (BCH) expansion. The expansion terminates at its fifth term

in this case to give

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{6}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{24}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}]. \quad (2.29)$$

Expression (2.29) usefully removes the infinite expansions of the exponentials and can be substituted into equations (2.27) and (2.28) to lead to a system of equations which can be evaluated numerically. The form of the expressions for the amplitudes depends on the excitation order and the expressions are large even at a low order. As such, only the determination of the energy expression is continued in the present section.

Recognising the non-zero terms in (2.27) after substitution of the BCH expansion leaves

$$E = \langle \text{ref} | \hat{H} + \hat{H}\hat{T}_1 + \hat{H}\hat{T}_2 + \frac{1}{2}\hat{H}\hat{T}_1^2 | \text{ref} \rangle, \quad (2.30)$$

where there are notably no excitations higher than second order even when $\hat{T}$ is not truncated. In principle, the matrix elements in (2.30) can be evaluated directly using the creation and annihilation operators. However, this approach leads to particularly long derivations (especially in the case of the amplitude equations) so it is common to cast the creation and annihilation operators into ‘normal order’ and apply Wick’s theorem to identify all the terms which contribute to each matrix element. Diagrammatic techniques can also be used to further aid the derivation. The final energy expression is

$$E = E_{\text{ref}} + \sum_{ia} f_{ia} t_i^a + \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}, \quad (2.31)$$

which features Fock matrix elements, $f_{ia} = \langle \varphi_i | \hat{f} | \varphi_a \rangle$, and electron repulsion integrals in physicists’ notation, $\langle ij || ab \rangle$.[†] Thus, with similar expressions for the amplitude equations, the amplitudes can be determined using any algorithm for solving systems of non-linear equations. The amplitudes may then be input into expression (2.31) to determine the coupled-cluster ground-state energy of a system. As previously

[†]In particular, $\langle ij || ab \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle = \langle \varphi_i \varphi_j | \frac{1}{r_{12}} | \varphi_a \varphi_b \rangle - \langle \varphi_i \varphi_j | \frac{1}{r_{12}} | \varphi_b \varphi_a \rangle$, remembering that the ordering of the single electron eigenvectors implies the electron sub-space in which they exist e.g. $\langle \varphi_i \varphi_j | \frac{1}{r_{12}} | \varphi_a \varphi_b \rangle = \langle \varphi_i |_1 \otimes \langle \varphi_j |_2 \left(\frac{1}{r_{12}} \right) | \varphi_a \rangle_1 \otimes | \varphi_b \rangle_2$.

mentioned, expression (2.31) is valid for all orders of excitation in coupled-cluster theory and it can be further noted that the second term, involving the sum of off-diagonal Fock matrix elements, is zero in the case of canonical coupled-cluster theory, which is defined by its use of a Hartree-Fock Slater determinant as its reference state. For reasons which will become clear in the next section, the second term in equation (2.31) is also zero in the case of a variant of coupled-cluster theory known Brueckner coupled-cluster theory.

2.4.3 Brueckner Coupled-Cluster Theory

Thouless' theorem states that the single excitations in coupled-cluster theory are equivalent to orbital rotations.⁷⁵ The proof of Thouless' theorem is omitted in the present section but to gain an impression of its validity, consider the CCS expansion of a system with two electrons with opposite spins in the position representation,

$$\begin{aligned}\Psi(\mathbf{x}_1, \mathbf{x}_2) &= \varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) + t_1^3\varphi_3(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) + t_2^4\varphi_1(\mathbf{x}_1)\varphi_4(\mathbf{x}_2) + t_1^3t_2^4\varphi_3(\mathbf{x}_1)\varphi_4(\mathbf{x}_2) \\ &= [\varphi_1(\mathbf{x}_1) + t_1^3\varphi_3(\mathbf{x}_1)] \cdot [\varphi_2(\mathbf{x}_2) + t_2^4\varphi_4(\mathbf{x}_2)]\end{aligned}\quad (2.32)$$

$$= \varphi'_1(\mathbf{x}_1)\varphi'_2(\mathbf{x}_2).\quad (2.33)$$

The factorisation leading to equation (2.32) demonstrates how the coupled-cluster expansion resulting from single excitations can be factored into products of linear combinations of orbitals. Thouless' theorem provides the validation for writing the product of the linear combinations of orbitals in (2.32) as a product of only two orbitals in (2.33), meaning the linear combinations in (2.32) can be considered rotations of the reference orbitals. Note that the rotated orbitals have single excitation amplitudes of zero and hence all Slater determinants resulting from single excitations may be removed from the coupled-cluster expansion if the reference orbitals are varied such that their single excitation amplitudes are non-existent.

The formulation of coupled-cluster theory which rotates the reference orbitals under the

requirement that all single excitation amplitudes are zero is known as Brueckner coupled-cluster (BCC) theory. BCC theory uses the same product of excitation operators to determine its Slater determinant expansion as canonical coupled-cluster theory but only double excitation operators and above are used to determine the expansion explicitly. Hence the equivalent of CCSD(T) in Brueckner coupled-cluster theory is to include orbital rotations, double excitations, and perturbative triple excitations. This method sees use in chapters four and five of the present thesis and is denoted BCCD(T). Since CCSD(T) and BCCD(T) account for the same excitations in their Slater determinant expansions, they may be thought to produce similar results. However, it is seen in chapter four that this is not always the case.

2.5 Density Functional Theory

2.5.1 General Formulation

The probability of finding a single electron at a given position in a many-body system, also known as the electron density, can be found with the expression

$$\rho(\mathbf{r}) = N_e \sum_{\{\sigma_i\}} \int \Psi^*(\mathbf{x}_1, \dots, \mathbf{x}_{N_e}) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_{N_e}) d\mathbf{r}_2 \dots d\mathbf{r}_{N_e}. \quad (2.34)$$

Two theorems show that it is possible to calculate the energy of a molecular system solely from the electron density, and furthermore that the electron density can be determined without the wavefunction. Doing so (remarkably) eliminates the need for wavefunctions entirely. The two theorems are known as the Hohenburg-Kohn theorems and form the basis of density functional theory. The first theorem, HK1, is stated as follows.⁷⁶

- **HK1:** The ground-state expectation value of any observable can be written as a

unique functional of the ground-state density i.e.

$$\langle \hat{O} \rangle = O[\rho]$$

The validity of HK1 can be seen by first considering the system-dependence of the molecular electronic Hamiltonian, seen in equation (2.13). It can be noticed that the total kinetic energy and electron–electron repulsion terms vary depending on how many electrons are in the system. The electron–nuclei attraction term also varies with the number of electrons but additionally depends on the positions and identities of the nuclei. This term can be written in terms of the external potential, $v_{\text{ext}}(\mathbf{r})$,

$$\hat{V}_{\text{ne}} = - \sum_{iK} \frac{Z_K}{|\mathbf{r}_i - \mathbf{R}_K|} = \sum_i v_{\text{ext}}(\mathbf{r}_i).$$

Hence, for a constant number of electrons, $v_{\text{ext}}(\mathbf{r})$ is the only part of the Hamiltonian which depends on the specific system. Changes in the external potential change the operation of the Hamiltonian on a vector by more than a multiplicative or additive constant, which leads to different wavefunctions being obtained with different external potentials. This should be expected as a change in external potential is equivalent to a change in system. Thus, for a given number of electrons, there is a mapping from the external potential of a system to the wavefunctions of the same system. Additionally, the expectation value of any observable in its ground-state is a functional of the ground-state wavefunction. Therefore, there exists a map from the ground-state wavefunction to the ground-state expectation value of any observable. Consequently, the external potential can be mapped to the ground-state expectation value of any observable,

$$v_{\text{ext}}(\mathbf{r}) \mapsto \hat{H} \mapsto \Psi \mapsto \langle \hat{O} \rangle.$$

HK1 then goes to show that there is a unique mapping between the density and the external potential. This is done via a *reductio ad absurdum* proof which is omitted from the present chapter but can be readily found elsewhere.⁷⁶ Since the proof shows there is

a unique mapping between the density and external potential, there must also be a mapping between the density and the ground-state expectation value of an observable. That is to say that any ground-state expectation value can be found solely in terms of the ground-state density i.e. $\langle \hat{O} \rangle = O[\rho]$.

Given that the external potential can be known from the density, the energy functional can be written as

$$E[\rho] = \langle \Psi[\rho] | \hat{T} | \Psi[\rho] \rangle + \langle \Psi[\rho] | \hat{V}_{ee} | \Psi[\rho] \rangle + \int v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \quad (2.35)$$

$$= F[\rho] + \int v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}. \quad (2.36)$$

Noticing that the map between density and the wavefunction is not dependent on the particular system and given the forms of the kinetic energy and electron–electron repulsion operators also do not depend on the particular system, the functional $F[\rho]$ is identical for all systems and as such is described as universal. The form of the universal functional is not known and therefore must be approximated with reference to experimental data and/or other electronic structure methods.

The second theorem, HK2, may be stated as⁷⁶

- **HK2:** Any energy calculated from a valid density is greater than or equal to the exact ground-state energy.

HK2 comes as a result of variational theorem. Quite simply, the *reductio ad absurdum* proof in HK1 that shows each density corresponds to only one wavefunction means that any valid trial wavefunction[†] can be found from a valid trial density. Since any trial wavefunction not equal to the exact ground-state wavefunction has a higher energy than that of the ground-state wavefunction, any trial density which is not the ground-state density also has a higher energy than the true ground-state energy.

[†]Valid meaning it does not contain any impermissible features such as discontinuities. The wavefunction is normalised for the purposes of variational theorem.

2.5.2 Kohn-Sham DFT

At this point, it is possible to attempt to find ground-state energies and densities by minimising the result of (2.36) with respect to the possible trial densities. However, solely proving that the energy can be written as a unique functional of the density does not give any information about the exact form the functional takes. As shown in (2.36), the external potential contribution to the functional is known but the form of the universal functional is not.

One approach to this problem is to attempt to approximate the universal functional, which is the basis of orbital-free density functional theory.⁷⁷ However, this approach has not received widespread use and instead, DFT finds use through Kohn-Sham DFT (KS-DFT). KS-DFT expresses contributions to the universal functional in terms of quantities whose form is known and a correction term. In particular, KS-DFT postulates that a sizeable portion of the electron–electron repulsion term can be captured using the expression for the Coulomb energy, identical to that seen in Hartree-Fock theory,

$$V_{ee}[\rho] = J[\rho] + (V_{ee}[\rho] - J[\rho]), \quad (2.37)$$

in which $J[\rho]$ is the Coulomb energy,

$$J[\rho] = \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'.$$

Similarly, the kinetic energy is separated into a contribution from a system of non-interacting particles and a correction term,

$$T[\rho] = T_s[\rho] + (T[\rho] - T_s[\rho]), \quad (2.38)$$

where

$$T_s[\rho] = T_s[\{\varphi_i\}] = -\frac{1}{2} \sum_i \int \varphi_i^*(\mathbf{x}) \nabla^2 \varphi_i(\mathbf{x}) d\mathbf{x},$$

and the $\{\varphi_i\}_{i=1}^{N_e}$ are solutions to a Schrödinger equation for non-interacting electrons, which is later seen in equation (2.40). Importantly, the calculation of $T_s[\rho]$ requires orbitals and therefore a departure from the sole use of the electron density in DFT. This is not an issue however since any electron density can be found from the orbitals of a single Slater determinant wavefunction,

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_e} |\varphi_i(\mathbf{x})|^2,$$

and therefore all other terms in the energy expression can be found from the orbitals of a single Slater determinant. Incorporating expressions (2.37) and (2.38) into the energy functional gives

$$\begin{aligned} E[\rho] &= T_s[\rho] + J[\rho] + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]) \\ &= T_s[\rho] + J[\rho] + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{\text{xc}}[\rho]. \end{aligned} \quad (2.39)$$

The correction terms have been collected into a single functional in equation (2.39), denoted the exchange-correlation functional, $E_{\text{xc}}[\rho]$.

Overall, KS-DFT changes the problem from finding approximations for the universal functional to finding approximations for $E_{\text{xc}}[\rho]$. This has turned out to be a more fruitful endeavour and has led to the widespread use of KS-DFT. With the *a posteriori* knowledge that useful approximations to the exchange-correlation functional can be found, all that is needed to calculate the ground-state energy is the set of orbitals which map to the ground-state density. Similar to orbital-free DFT, these orbitals can be found by using HK2 and minimising the energy functional under the constraint the orbitals are normalised. The Lagrangian for this procedure is

$$L[\{\varphi_i\}] = T_s[\rho] + J[\rho] + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{\text{xc}}[\rho] - \sum_i^{N_e} \varepsilon_i \int (\varphi_i^*(\mathbf{x})\varphi_i(\mathbf{x}) - 1)d\mathbf{x},$$

and requiring the Lagrangian to be stationary with respect to variations of each orbital

gives

$$\frac{\delta L}{\delta \varphi_i^*} = -\frac{1}{2}\nabla^2 \varphi_i(\mathbf{x}) + v_{\text{ext}}(\mathbf{r})\varphi_i(\mathbf{x}) + \frac{\delta}{\delta \varphi_i^*}(J[\rho] + E_{\text{xc}}[\rho]) - \varepsilon_i \varphi_i(\mathbf{x}) = 0.$$

The chain rule can then be applied to the derivatives of the exchange-correlation and Coulomb functionals to express the functional derivatives in terms of the density,

$$-\frac{1}{2}\nabla^2 \varphi_i(\mathbf{x}) + v_{\text{ext}}(\mathbf{r})\varphi_i(\mathbf{x}) + \frac{\delta J[\rho]}{\delta \rho} \varphi_i(\mathbf{x}) + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \varphi_i(\mathbf{x}) - \varepsilon_i \varphi_i(\mathbf{x}) = 0,$$

which leads to the final expression

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_J(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right) \varphi_i(\mathbf{x}) = \varepsilon_i \varphi_i(\mathbf{x}), \quad (2.40)$$

in which the Coulomb and exchange-correlation potentials have been defined as

$$v_J(\mathbf{r}) = \frac{\delta J[\rho]}{\delta \rho} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad \text{and} \quad v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho}.$$

Hence the minimisation procedure shows that the stationary points of the energy functional can be found from the solutions to N_e simultaneous differential equations, all taking the form of equation (2.40), which are known as the Kohn-Sham equations. It can be additionally noted that these equations are eigenvalue equations of a Hermitian operator and are therefore guaranteed to give orthogonal solutions. In a similar manner to Hartree-Fock theory, it can be seen that the Coulomb and exchange-correlation potentials both depend on the density and therefore depend on the solutions to the Kohn-Sham equations. Thus, the equations must be solved in a self-consistent manner and hence KS-DFT programs use the same SCF method as seen in Hartree-Fock programs.

Besides its benefits in the combination of its accuracy and computational expense discussed in section 1.1, KS-DFT is also notable for showing that a complete description of the electronic structure of a system can be explained entirely in terms of molecular orbitals. This contrasts earlier molecular orbital methods such as HF or extended Hückel theory where it cannot be shown that the MO description can be used to find the exact

energy of the system.

2.5.3 Exchange-Correlation Functionals

The final piece of the KS-DFT puzzle is the aforementioned approximation for the exchange-correlation functional. There have been a multitude of these defined since the publication of KS-DFT and as such many different approaches to the approximation exist. Many of the commonly used functionals are expressed in terms of the exchange-correlation energy per electron, ϵ_{xc} ,

$$E_{xc}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}[\rho] d\mathbf{r}.$$

The unknown is now ϵ_{xc} . The various ways of approximating this have been arranged biblically in a “Jacob’s ladder”⁷⁸ towards chemical accuracy. Each step up the ladder increases the quantities employed in calculating ϵ_{xc} and roughly corresponds to an increase in accuracy and computational cost. Note that LDA stands for local density approximation and GGA refers to the generalised gradient approximation.

Ladder Rung	Functional Type	Quantities Used
Chemical Accuracy		
5	Double-Hybrid	$\rho, \nabla\rho, \tau$, HF-ex, virtual orbitals
4	Hybrid	$\rho, \nabla\rho, \tau$, HF-ex
3	Meta-GGA	$\rho, \nabla\rho, \tau$
2	GGA	$\rho, \nabla\rho$
1	LDA	ρ
Hartree World		

Note: τ – kinetic energy density, HF-ex – Hartree-Fock exchange.

Table 2.1: An illustration of the Jacob’s ladder hierarchy of exchange-correlation functionals.

Crucially, this hierarchy is not rigorous and a more accurate result cannot be guaranteed by using functionals further up the ladder.

2.6 Potential Energy Surfaces

Since the Born-Oppenheimer approximation fixes the nuclear positions, a map from the molecular geometry of a system to its energy can be defined. The nuclear positions are treated as continuous variables so this map forms a surface, or more generally a manifold, known as a potential energy surface (PES). Because a molecular system admits multiple possible energies at any particular nuclear configuration (corresponding to ground and excited electronic states), the mapping is multi-valued. It is possible to define an arrangement of nuclear positions which gives the lowest energy possible for a particular electronic state, thus providing a link between electronic structure and geometry, similar to earlier methods such as VSEPR.

The process of finding minima on a PES is known as geometry optimisation. General algorithms such as Quasi-Newton optimisation can be used to carry out this process. Such algorithms give no information as to whether their result is the global or local minimum on the PES. Additionally, certain algorithms are not guaranteed to find a minimum and could result in other stationary points. Because of this, the Hessian matrix at a position on a PES is often calculated to characterise the nature of the stationary point found.

2.7 Computational Considerations

2.7.1 Basis Sets

Both HF theory and KS-DFT are single-determinant methods whose solutions are found by solving an eigenvalue problem. One could take a direct approach to solving these problems and employ a discrete set of points in $\mathbb{R}^3$ and a method such as finite differences to determine the values of the eigenfunctions at each point, alongside the eigenvalues of each eigenfunction.⁷⁹ However, this turns out to be computationally

intractable for all but a number of systems which have certain properties that can be exploited to reduce the number of discrete points needed.⁸⁰ Instead, the approach used ubiquitously in electronic structure programs is to expand the unknown eigenfunctions as a linear combination of known basis functions. As is shown in the derivation leading to equation (2.41), this allows the coefficients of the linear expansion and the eigenvalues to be cast into a matrix eigenvalue problem, which can be solved by standard methods such as the QR algorithm.⁸¹

$$\begin{aligned}
\hat{O}\phi_i(\mathbf{r}) &= \lambda_i\phi_i(\mathbf{r}) \\
&= \hat{O}\sum_k c_{ki}\chi_k(\mathbf{r}) = \lambda_i\sum_k c_{ki}\chi_k(\mathbf{r}) \\
\Rightarrow \sum_k \int \chi_l(\mathbf{r})\hat{O}\chi_k(\mathbf{r})d\mathbf{r} \cdot c_{ki} &= \lambda_i\sum_k c_{ki} \int \chi_l(\mathbf{r})\chi_k(\mathbf{r})d\mathbf{r} \\
&= \sum_k O_{lk}c_{ki} = \lambda_i\sum_k S_{lk}c_{ki} \\
&\equiv \mathbf{O}\mathbf{c} = \lambda\mathbf{S}\mathbf{c}
\end{aligned} \tag{2.41}$$

For electronic structure calculations, a suitable basis set needs to be defined for the case where the eigenfunctions of interest are molecular orbitals. Molecular orbitals are three-dimensional, square-integrable functions. Thus, in principle, a complete set of functions which form a basis for the space of all possible three-dimensional, square-integrable functions is sought, though note there are some complications in the nature of the completeness of such sets of functions.⁸² In any case, the linear combination of functions required for a complete expansion of a MO contains an infinite number of functions and therefore any practical computation implements a truncated linear combination. The truncation is defined such that the expansion of basis functions achieves a pre-defined target level of convergence towards the exact MOs and eigenvalues.

Along with selecting basis functions with the necessary properties to converge to the MOs, it is desirable that these functions also reach the target convergence using as few functions as possible in order to reduce the computational cost of calculations. This can

be achieved by using basis functions which already resemble the target eigenfunctions and thus will contribute more to the linear combination representing the eigenfunction, which reduces the number of basis functions needed to reach the target level of convergence. For an eigenfunction of an arbitrary operator, it cannot be generally expected that information about the eigenfunctions' form will be known *a priori*. Fortunately, the electronic structure of molecular systems is a well-studied topic and as such it is known that there is only a small change in the distribution of electrons close to a nucleus in an atom compared to a molecule.⁸³ This observation underpins the linear combination of atomic orbitals (LCAO) approach to constructing basis sets for electronic structure calculations.

The LCAO approach involves placing a set of basis functions at the position of each nucleus in the molecule and defining the basis set expansion of the MOs as the total linear combination of these nucleus-centred functions. The basis functions are also optimised to resemble the atomic orbitals of the elements at each nuclear position. Note however that the basis functions are not formally the atomic orbitals of the atoms in the molecule,^{84,85} though they are often referred to as atomic orbitals (AOs). Because of the efficiency AO basis functions obtain in representing MOs, the LCAO approach is used in nearly all molecular electronic structure programs and, through its widespread use, has also influenced perspectives on electronic structure and chemistry. For example, the Woodward-Hoffmann rules,⁸⁶ which provide information about the viability pericyclic reactions, are explained using ideas about the interactions of linear combinations of p-orbitals used to express the MOs of the reactants.⁸⁷

An implementation of the LCAO approach still requires a set of known functions for placement at each nuclear position. As previously mentioned, LCAO approach is based on the observation that the distribution of electrons close to a nucleus does not differ greatly between atoms and molecules. Since no analytic solutions are available for the atomic orbitals of multi-electron elements, the exact atomic orbitals cannot be known prior to any calculations. Thus, a natural choice for the basis functions are the eigenfunctions of the hydrogenic Schrödinger equation, the only system with atomic

orbitals that can be obtained analytically. However, there turns out to be a number of practical difficulties which limits the use of these eigenfunctions as a LCAO basis set.⁸⁸

A more practical set of functions which is able to capture significant features of the hydrogenic eigenfunctions is the set of Slater-type orbitals (STOs). In spherical polar coordinates, these take the form

$$\chi^{\text{STO}}(r, \theta, \phi) = Ar^{n-1}e^{-\zeta r}Y_{lm}(\theta, \phi),$$

where A is a normalisation constant, n , l , and m are the principle, angular momentum, and magnetic quantum numbers respectively, Y_{lm} is a spherical harmonic function, and ζ is a constant.

The Slater-type orbitals feature the same exponential decay in r as seen for hydrogenic orbitals and exhibit the cusp at the nucleus in their s-orbitals as is also seen in the hydrogenic orbitals. Additionally, the STOs do not suffer from the same practical issues mentioned for the hydrogenic orbitals. These features have led to their use in practical calculations, most notably in the Amsterdam Density Functional (ADF) program.⁸⁹ Although, the use of STOs is not widespread. This is due to the computational difficulty in evaluating two-electron repulsion integrals when the basis functions involved are located on three or four different atomic centres.^{90†} As such, Gaussian-type orbitals (GTOs) were suggested as an alternative to STOs.⁹¹ The form of a GTO in spherical polar and cartesian coordinates is displayed in equation (2.42) and equation (2.43) respectively.

$$\chi^{\text{GTO}}(\mathbf{r}) = Ar^{2(n-1)-l}e^{-\zeta r^2}Y_{lm}(\theta, \phi) \quad (2.42)$$

$$= Ax^{l_x}y^{l_y}z^{l_z}e^{-\zeta r^2} \quad (2.43)$$

Note that l_x , l_y , and l_z are all positive integers whose sum determines the type of the GTO. For example, when $l_x + l_y + l_z = 2$, the GTO is d-type and resembles a d-orbital.

[†]In chemists' notation, these integrals are written $(\mu\nu|\sigma\lambda)$ where μ , ν , σ , and λ refer to LCAO basis functions located across a total of three or four different nuclear positions.

GTOs do not have the same issues as the STOs in the evaluation of molecular integrals due to Gaussian product theorem⁹² and hence are more appealing computationally. This computational appeal comes at the expense of missing some of the desirable physical features of STOs, notably GTOs exhibit an exponential decay in r^2 with increasing distance between the electron and nucleus and do not feature a cusp at the nucleus for s-orbitals. Despite these limitations, GTOs see far wider use than STOs, in large part due to the possibility of mitigating their limitations through the use of contracted GTOs (CGTOs). Equation (2.44) displays the general form of a contracted GTO.

$$\chi^{\text{CGTO}}(\mathbf{r}) = a \sum_k b_k \chi_k^{\text{GTO}}(\mathbf{r}) \quad (2.44)$$

Note that the Gaussian functions under the sum are referred to as primitive Gaussian functions. The coefficients and exponents of the primitive Gaussian functions are optimised to resemble the atomic orbitals of the given element and are fixed during an electronic structure calculation. The coefficient ahead of all of the primitive functions, a , is the only coefficient in the CGTO optimised during an electronic structure calculation. While the use of contracted GTOs improves their viability for use as LCAO basis functions, CGTOs are unable to converge to features present in the hydrogenic orbitals such as the cusp at the nucleus in s-orbitals, even with an infinite Gaussian expansion.⁹³ Nevertheless, through the use of contracted orbitals, GTOs have become the most used type of basis set in electronic programs, including the aptly named Gaussian,⁹⁴ ORCA,⁹⁵ TURBOMOLE,⁹⁶ and many others.

The finite nature of practical basis sets means that, rather than the infinite number of eigenfunctions that exist theoretically, the number of eigenfunctions obtained in a calculation is equal to the number of basis functions used in the calculation. In the language of LCAO bases, this fact is stated as the number of molecular orbitals is equal to the number of atomic orbitals.⁹⁷ Consequently, methods which invoke a single occupation of orbitals, such as HF and KS-DFT, produce a set of orbitals where N_e are occupied and there are a finite number of unoccupied/virtual orbitals. In post-HF methods, such as configuration interaction theory and coupled-cluster theory, the finite

set of virtual orbitals defines the number of Slater determinants which can be generated and therefore the level of convergence achieved in their calculation of the correlation energy. Hence the basis set chosen for a post-HF calculation defines both the convergence of the orbitals and the convergence of the correlated wavefunction. The orbitals and correlated wavefunction do not exhibit the same rate of convergence with respect to basis set^{98,99} and as such, a basis set suited to single-determinant methods may not also be suitable for post-HF methods.

2.7.2 The Frozen Core Approximation

The frozen core approximation can refer to either of two methods for reducing the computational cost of a calculation. One method is implemented in methods which determine a set of molecular orbitals, such as HF and KS-DFT, and refers to omitting the optimisation of the LCAO coefficients of the core orbitals in the calculation of a set of molecular orbitals.¹⁰⁰ The other method is implemented in post-HF methods and refers to omitting excitations from core orbitals in determining the correlation energy.^{101–103} Past the second row of the periodic table, the number of core electrons of an element exceeds the number of valence electrons and hence applying either form of the frozen core approximation can lead to significant reductions in computational cost. In many scenarios, the frozen core approximation is necessary for a tractable calculation. For example, the calculations on M@Si₁₄ clusters presented in chapter four of this thesis could not be completed if all the electrons in the compound were included in the calculation of the correlation energy. Fortunately, employing either form of the frozen core approximation often leads to little loss in accuracy. The reason for this is the same in both cases: when compared to the core electrons, the valence electrons undergo a much more significant change from their atomic electronic structure when placed in a molecular environment. As a result of this, most properties of compound systems are dominated by contributions from the valence electrons and the contributions from core electrons can often be neglected. However, cases do exist where the frozen core

approximation leads to notable errors¹⁰² and thus it cannot be applied indiscriminately to all calculations.

2.8 Relativistic Effects

The special theory of relativity can be formed from two postulates: all physical laws are identical in all inertial frames of reference and the observed speed of light in a vacuum is constant regardless of the motion of the observer or the light source.^{104†} Requiring that the laws of nature are the same across all reference frames is equivalent to requiring that the laws of nature are invariant under a Lorentz transformation. Schrödinger equations in general are not Lorentz invariant¹⁰⁷ and further, a fully relativistic form of the Schrödinger equation has not been discovered for the many-body case.¹⁰⁸ In lieu of such an equation, relativistic effects are accounted for in electronic structure calculations by making adaptations to the molecular Hamiltonian. Changes can be made to both the one- and two-electron contributions to the molecular Hamiltonian, though the most common methods only make changes to the one-electron contribution, as is the case for all methods used in this thesis.

Relativistic effects in the one-electron contribution to the molecular Hamiltonian are most often accounted for with use of the Dirac equation. The time-dependent Dirac equation provides a Lorentz invariant adaptation of the Schrödinger equation for spin- $\frac{1}{2}$ single-particle systems. The time-independent Dirac equation is derived from the time-dependent case but does not fully satisfy Lorentz invariance. Nonetheless, it has come to be considered to be sufficient for achieving chemical accuracy.¹⁰⁹ For an electron in an electric field (as, for example, is the case for an electron moving in a molecule) the time-independent Dirac equation is

$$(c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + \hat{V}) \psi = E\psi. \quad (2.45)$$

[†]It has been debated whether or not the second postulate is necessary. For example, see a proposal shortly after the original formulation¹⁰⁵ or a more modern perspective.¹⁰⁶

The terms in equation (2.45) require some explanation. The speed of light, c , is included explicitly but note that $c = 1$ in atomic units. The mass of the particle, m , is also explicitly included in the equation, but it is also true that $m = 1$ in atomic units if the particle studied is an electron. The momentum operator in three dimensions, $\mathbf{p} = -i\nabla$, is present, as is the potential energy operator, $\hat{V}$. The quantity $\boldsymbol{\alpha}$ arranges three 4×4 matrices in a vector and β is also a 4×4 matrix. These quantities are defined as

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_x \\ \alpha_y \\ \alpha_z \end{pmatrix}, \quad \alpha_\mu = \begin{pmatrix} 0 & \sigma_\mu \\ \sigma_\mu & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} 0 & 0 \\ 0 & -2\mathbf{I} \end{pmatrix},$$

in which $\mu \in \{x, y, z\}$, $\mathbf{0}$ and $\mathbf{I}$ are the 2×2 zero and identity matrices respectively, and the σ_μ are the Pauli spin matrices, defined as

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Note additionally that $\boldsymbol{\alpha} \cdot \mathbf{p} = \sum_\mu \alpha_\mu \hat{p}_\mu$, which may be considered an abuse of notation.

From the definition of the terms in (2.45), it can be seen that the Dirac Hamiltonian is a 4×4 matrix operator, as opposed to the non-relativistic Hamiltonian which is scalar operator. Hence the eigenvectors of (2.45), ψ , are four-component vectors. In general, two of the components describe “positive energy solutions” which are solutions above $-2mc^2$ in energy and the other two components describe “negative energy solutions” which are solutions below $-2mc^2$ in energy. The pair of components associated with the positive energy solutions describe the motion of an electron and its spin, as is also done by equation (2.2). Similarly, the negative energy solutions describe the motion of a positron, the electron’s antimatter counterpart, and its spin. Given this thesis is concerned with electronic structure, only the positive energy solutions are desired. So-called two-component methods aim to construct operators which produce only the positive energy solutions of the four-component Dirac equation. These operators can then be used in place of the one-electron Hamiltonian in electronic structure calculations.

Two-component methods collect the first two components of the eigenvector together in a two-dimensional vector known as the large component. Likewise, the last two components are collected in a two-component vector known as the small component. In mathematical terms, this is written

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix}.$$

It is then possible to separate the Dirac equation given in expression (2.45) into coupled equations in terms of ψ_L and ψ_S :

$$c(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_S + \hat{V}\psi_L = E\psi_L \quad (2.46)$$

$$c(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_L + (\hat{V} - 2mc^2)\psi_S = E\psi_S. \quad (2.47)$$

Note $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)^T$. Two-component methods construct the desired operators by either eliminating the small component of the wavefunction from equations (2.46) and (2.47) or by casting the equations into a matrix equation and performing a unitary transformation to remove the off-diagonal elements and hence obtain an equation which can be solved for the large component and its eigenvalues only — see equations (2.52) and (2.53). These two approaches are equivalent¹¹⁰ and both produce Hamiltonians which can be used in the eigenvalue equation to return the positive energy solutions only.¹¹¹ The present section covers both of these approaches in deriving the relativistic Hamiltonians used in chapters three, four, and five in this thesis. First, the zeroth-order regular approximation (ZORA) Hamiltonian is derived via elimination of the small component and then the exact two-component (X2C) Hamiltonian is derived using the unitary rotations to eliminate off-diagonal elements in the matrix form of the Dirac equation.

To derive the ZORA Hamiltonian, equation (2.47) is rearranged to make ψ_S the subject

and then expressed in a form which lends itself to series expansion,

$$\psi_S = (E + 2mc^2 - \hat{V})^{-1} c(\boldsymbol{\sigma} \cdot \mathbf{p}) \psi_L \quad (2.48)$$

$$\begin{aligned} &= (2mc^2 - \hat{V})^{-1} \left(1 + \frac{E}{2mc^2 - \hat{V}} \right)^{-1} c(\boldsymbol{\sigma} \cdot \mathbf{p}) \psi_L \\ &= (2mc^2 - \hat{V})^{-1} \hat{K} c(\boldsymbol{\sigma} \cdot \mathbf{p}) \psi_L. \end{aligned} \quad (2.49)$$

Substituting equation (2.49) back into (2.46) gives an expression solely in terms of the large component,

$$\left[c(\boldsymbol{\sigma} \cdot \mathbf{p})(2mc^2 - \hat{V})^{-1} \hat{K} c(\boldsymbol{\sigma} \cdot \mathbf{p}) + \hat{V} \right] \psi_L = E \psi_L. \quad (2.50)$$

In principle, the goal of formulating a Hamiltonian which solely returns the positive energy solutions of the Dirac equation has been achieved with equation (2.50). However, the energy dependence of $\hat{K}$ means that the Hamiltonian seen in square brackets in equation (2.50) will be different for each solution of the Dirac equation. The energy dependence of $\hat{K}$ also means this Hamiltonian depends on its own eigenvalue. Thus, equation (2.50) does not lend itself to practical computation. As such, an energy-independent approximation to the coupling between the small and large components can be introduced by expanding $\hat{K}$ in powers of $\{1 + [E/(2mc^2 - \hat{V})]\}^{-1}$. Applying this expansion and also performing a renormalisation procedure to account for the fact that ψ_L is not normalised, results in the zeroth-order regular approximation.¹¹² Equation (2.51) presents the ZORA for the case of an electron moving at a distance r from the centre of the field of a single nucleus,¹¹³

$$\left(\frac{c^2 \mathbf{p}^2}{2mc^2 - \hat{V}} + \frac{2c^2}{(2mc^2 - \hat{V})^2} - \frac{Z\mathbf{s} \cdot \mathbf{l}}{r^3} + \hat{V} \right) \psi_L = E \psi_L. \quad (2.51)$$

Note $\mathbf{s} = (1/2)\boldsymbol{\sigma}$ and $\mathbf{l}$ is the angular momentum operator, $\mathbf{l} = \mathbf{r} \times \mathbf{p}$. The third term in equation (2.51) is a correction for spin-orbit coupling and necessarily produces a two-component eigenvector. Relativistic effects are primarily incorporated into calculations in this thesis as scalar relativistic effects. These are relativistic effects which

are obtained from a scalar operator and hence have eigenvectors which consist of a single component. Thus, for the scalar relativistic ZORA, used for example in chapter three, only the first two terms of equation (2.51) are included in the ZORA Hamiltonian.

An alternative to ZORA used in chapters four and five of this thesis is the exact two-component (X2C) approach.[†] As previously mentioned, instead of eliminating the small component from the system of equations, the X2C Hamiltonian is discussed here by using a unitary transformation to decouple equations (2.46) and (2.47) and hence obtain an equation which can be solved to return only the large component of the wavefunction. Put in mathematical terms, the Dirac Hamiltonian may be cast into matrix form,

$$\mathbf{H}_D = \begin{pmatrix} \hat{V} & c(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c(\boldsymbol{\sigma} \cdot \mathbf{p}) & \hat{V} - 2mc^2 \end{pmatrix}, \quad (2.52)$$

and the goal is to find a unitary transformation which results in

$$\mathbf{U} \mathbf{H}_D \mathbf{U}^\dagger = \begin{pmatrix} \mathbf{h}_L & 0 \\ 0 & \mathbf{h}_S \end{pmatrix}. \quad (2.53)$$

It turns out that the unitary transformation can be formulated as¹¹⁵

$$\mathbf{U} = \begin{pmatrix} \frac{1}{\sqrt{1+\hat{X}^\dagger \hat{X}}} & \frac{\hat{X}^\dagger}{\sqrt{1+\hat{X}^\dagger \hat{X}}} \\ \frac{-\hat{X}^\dagger}{\sqrt{1-\hat{X} \hat{X}^\dagger}} & \frac{1}{\sqrt{1+\hat{X} \hat{X}^\dagger}} \end{pmatrix}, \quad (2.54)$$

where the coupling operator, $\hat{X}$, is defined by equation (2.55),

$$\psi_S = \hat{X} \psi_L. \quad (2.55)$$

Equation (2.55) is notably a coupling between the small and large component, an exact expression for which was seen previously in equation (2.48). Of course, attempting to eliminate the off-diagonal elements of (2.52) by using equation (2.48) directly leads to a

[†]Many papers contribute to the development of the X2C approach but see for example the first reported X2C calculation.¹¹⁴

retelling of the problem encountered in the discussion of the ZORA approximation: the coupling operator depends on the energy sought and consequently does not lend itself to practical computation. It has been shown however that an energy-independent expression for the coupling operator exists.¹¹⁵ There is no closed-form analytic expression for the exact coupling operator but it can be determined via solution of the full four-component Dirac equation. In particular, by first obtaining ψ_L and ψ_S from the solution of the full four-component Dirac equation, $\hat{X}$ can be found from equation (2.55). Hence the unitary transformation of $\mathbf{H}_D$ can be performed and $\mathbf{h}_L$ obtained, ready for use in an electronic structure calculation. Notably, the X2C approach only includes the nuclear–electron attraction term in its potential energy operator and neglects the electron–electron repulsion. Doing so significantly reduces the computational expense in solving the four-component Dirac equation and hence underpins the viability of X2C as a correction for relativistic effects.¹¹¹

The implementation of relativistic effects changes the nature of the orbitals an electronic structure calculation produces. As such, it cannot be expected that the same cost:accuracy ratio obtained with basis sets optimised to resemble non-relativistic atomic orbitals will be obtained if these basis sets are used in relativistic calculations. Thus, relativistic calculations require the use of basis sets which have been optimised to resemble the atomic orbitals obtained using relativistic Hamiltonians.

2.9 Explicit Correlation

Explicitly correlated methods seek to increase the rate at which wavefunction methods converge to the complete basis set (CBS) limit by including functions which contain an explicit dependence on the interelectronic distance in the wavefunction *ansatz*. The basis for this approach is the observed linear dependence of the wavefunction on the interelectronic distance in the vicinity of electron–electron coalescence points, which require a large basis set of molecular orbitals, dependent on a single electron coordinate,

to model accurately.¹¹⁶ Analyses have shown that Slater determinant expansions converge to the CBS limit of the correlation energy as $(\ell_{\max} + 1)^{-3}$, where $\ell_{\max}$ is the largest angular momentum quantum number associated with a function in the basis set.¹¹⁷ In contrast, methods using explicitly correlation show a convergence rate^{117,118} of $(\ell_{\max} + 1)^{-7}$. This difference in convergence behaviour has led to explicitly correlated methods being considered to achieve an accuracy of roughly 1–2 cardinal numbers higher than a regular calculation in the same basis.¹¹⁹

Functions with an explicit dependence on interelectronic distance are known as geminals. When considered for Slater determinant wavefunction *ansatz*, a geminal can be written in the general form

$$|w^{xy}\rangle = \hat{Q}_{12}f(r_{12})|\overline{\varphi_x\varphi_y}\rangle. \quad (2.56)$$

The indices x and y are used to refer to the orbitals from which the geminal is constructed. Additionally note $|\overline{\varphi_x\varphi_y}\rangle$ is a Slater determinant: $|\overline{\varphi_x\varphi_y}\rangle = \hat{A}|\varphi_x\varphi_y\rangle$, the quantity $f(r_{12})$ is a function of interelectronic distance, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and $\hat{Q}_{12}$ is the strong orthogonality operator. The strong orthogonality operator ensures that, in cases where excitations replace two orbitals in the reference state with a geminal, the resulting vector does not occupy the space spanned by the conventional doubly excited determinants.¹¹⁹ There are multiple forms of the strong orthogonality operator which may be implemented. All methods used in this thesis were formulated with the “*ansatz* 2” form of the operator, which is defined as

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2)(1 - \hat{V}_1\hat{V}_2),$$

where the $\hat{O}_\mu$ and $\hat{V}_\mu$ are projection operators which project onto the space of all occupied orbitals and the active virtual orbitals respectively i.e.

$$\hat{O}_\mu = \sum_k |\varphi_k\rangle_\mu \langle \varphi_k|_\mu \quad \text{and} \quad \hat{V}_\mu = \sum_a |\varphi_a\rangle_\mu \langle \varphi_a|_\mu.$$

Explicitly correlated methods employ a basis set in addition to the orbital basis used to represent the MOs and to define the occupied and virtual spaces. This additional basis set is known as the complementary auxiliary basis set (CABS) and, when used in conjunction with the orbital basis, it forms a complete basis set for the space of one-electron vectors. The result of using CABS in practice is a set of virtual orbitals in addition to the conventional virtuals present from the orbital basis. The set of all virtual orbitals (due to the orbital basis and the CABS) are indexed with the symbols α and β throughout the present section. A geminal can be expressed in the basis set of all virtual orbitals¹¹⁶ by inserting the resolution of the identity into (2.56),

$$\begin{aligned}
|w^{xy}\rangle &= \left(\sum_{\alpha>\beta} |\overline{\varphi_\alpha\varphi_\beta}\rangle \langle \overline{\varphi_\alpha\varphi_\beta}| \right) \hat{Q}_{12}f(r_{12})|\overline{\varphi_x\varphi_y}\rangle \\
&= \sum_{\alpha>\beta} \langle \overline{\varphi_\alpha\varphi_\beta} | \hat{Q}_{12}f(r_{12}) | \overline{\varphi_x\varphi_y} \rangle |\overline{\varphi_\alpha\varphi_\beta}\rangle \\
&= \sum_{\alpha>\beta} w_{\alpha\beta}^{xy} |\overline{\varphi_\alpha\varphi_\beta}\rangle.
\end{aligned} \tag{2.57}$$

Explicit correlation is exclusively used in coupled-cluster methods in this thesis. Geminals can be incorporated into coupled-cluster theory by including additional excitations where a pair of occupied orbitals are replaced by a geminal. This can be achieved by defining an excitation operator in a similar manner as seen in equation (2.23) in the discussion of canonical coupled-cluster theory. Hence, an excitation operator, $\hat{\tau}_{ij}^{xy}$, which replaces orbitals i and j of a Slater determinant with a geminal constructed from the orbitals x and y can be defined as

$$\hat{\tau}_{ij}^{xy}|\text{ref}\rangle = \sum_{\alpha>\beta} w_{\alpha\beta}^{xy} \hat{c}_\alpha^\dagger \hat{c}_i \hat{c}_\beta^\dagger \hat{c}_j |\text{ref}\rangle. \tag{2.58}$$

Note that equation (2.58) is expressed in second quantisation notation. The full set of explicitly correlated coupled-cluster equations can then be defined by including the

geminal excitations in an additional cluster operator. This cluster operator is defined as

$$\hat{T}_{2'} = \sum_{\substack{i>j \\ x>y}} c_{xy}^{ij} \hat{\tau}_{ij}^{xy},$$

where the c_{xy}^{ij} are excitation coefficients. This cluster operator is included in the exponential *ansatz* in the same manner as the canonical cluster operators. Hence, in the case of truncation to single and double excitations only, the explicitly correlated coupled-cluster Schrödinger equation can be written

$$\hat{H} e^{\hat{T}_1 + \hat{T}_2 + \hat{T}_{2'}} |\text{ref}\rangle = E e^{\hat{T}_1 + \hat{T}_2 + \hat{T}_{2'}} |\text{ref}\rangle. \quad (2.59)$$

As seen for the derivation of the canonical coupled-cluster equations in section 2.4.2, the ground-state solution of equation (2.59) can be found with the use of a similarity-transformed Hamiltonian and the projection of equation (2.59) onto the reference and excited Slater determinants. Applying this method to equation (2.59) results in the CCSD-F12 equations given in equations (2.60)–(2.63).

$$E_{\text{CCSD-F12}} = E_{\text{CCSD}} + \langle \text{HF} | [\hat{H}, \hat{T}_{2'}] | \text{HF} \rangle \quad (2.60)$$

$$\Omega_{\gamma_1, \text{CCSD}} + \langle \gamma_1 | [\tilde{\hat{H}}, \hat{T}_{2'}] | \text{HF} \rangle = 0 \quad (2.61)$$

$$\Omega_{\gamma_2, \text{CCSD}} + \langle \gamma_2 | [\tilde{\hat{H}}, \hat{T}_{2'}] + [[\hat{H}, \hat{T}_{2'}], \hat{T}_2] + \frac{1}{2} [[\hat{H}, \hat{T}_{2'}], \hat{T}_{2'}] | \text{HF} \rangle = 0 \quad (2.62)$$

$$\langle \gamma_{2'} | \tilde{\hat{\Phi}} + [\tilde{\hat{H}}, \hat{T}_2 + \hat{T}_{2'}] + \frac{1}{2} [[\hat{H}, \hat{T}_2 + \hat{T}_{2'}], \hat{T}_2 + \hat{T}_{2'}] | \text{HF} \rangle = 0 \quad (2.63)$$

Note in residual (2.63) the additional states $\langle \gamma_{2'} | = \langle \gamma_{xy}^{ij} | = \langle \text{HF} | (\hat{\tau}_{ij}^{xy})^\dagger$ are due to the excitations from the reference state into the geminal functions. Additionally, a tilde over an operator indicates it has been similarity transformed with the exponential *ansatz*, i.e. $\tilde{\hat{O}} = e^{-\hat{T}} \hat{O} e^{\hat{T}}$. These equations allow for the coefficients of the geminal excitations, c_{xy}^{ij} , to be determined alongside the conventional excitation amplitudes which appear in the canonical CCSD equations.

The CCSD-F12 methods used in this thesis make use of the SP approach to reduce computational cost. This approach involves the inclusion of an additional operator, $\hat{S}_{xy}$ in the general form of the geminal which ensures that certain conditions for electron coalescence are met. The geminal using the SP operator can be written¹¹⁶

$$|w^{xy}\rangle = \hat{Q}_{12}f(r_{12})\hat{S}_{xy}|\overline{\varphi_x\varphi_y}\rangle, \quad (2.64)$$

which leads to an altered definition of $w_{\alpha\beta}^{xy}$,

$$w_{\alpha\beta}^{xy} = \langle \overline{\varphi_\alpha\varphi_\beta} | \hat{Q}_{12}f(r_{12})\hat{S}_{xy} | \overline{\varphi_x\varphi_y} \rangle.$$

The action of $\hat{S}_{xy}$ is defined as

$$\hat{S}_{xy}\varphi_x(\mathbf{x}_1)\varphi_y(\mathbf{x}_2) = \left(\frac{3}{8}\phi_x(\mathbf{r}_1)\phi_y(\mathbf{r}_2) + \frac{1}{8}\phi_x(\mathbf{r}_2)\phi_y(\mathbf{r}_1) \right) \sigma_x(s_1)\sigma_y(s_2).$$

Utilising the form of the geminals given in equation (2.64) allows the coefficients of the geminals to be determined prior to solving the CCSD-F12 equations. In particular, their values are given by¹²⁰

$$c_{xy}^{ij} = \delta_{ix}\delta_{jy} - \delta_{iy}\delta_{jx}. \quad (2.65)$$

Consequently, residual (2.63) does not need to be included in the coupled CCSD-F12 equations. Additionally, the energy may therefore be determined using a Lagrangian,

$$\begin{aligned} E_{\text{CCSD-F12-SP}} &= L_{\text{CCSD-F12-SP}} \\ &= E_{\text{CCSD-F12}} + \\ &\quad \sum_{\substack{i>j \\ x>y}} c_{xy}^{ij} \langle \text{HF} | (\hat{\tau}_{ij}^{xy})^\dagger \tilde{\Phi} + [\tilde{H}, \hat{T}_2 + \hat{T}_{2'}] + \frac{1}{2} [[\hat{H}, \hat{T}_2 + \hat{T}_{2'}], \hat{T}_2 + \hat{T}_{2'}] | \text{HF} \rangle, \end{aligned} \quad (2.66)$$

in which, $\hat{\Phi}$ denotes the fluctuation potential, defined as $\hat{\Phi} = \hat{H} - \hat{f}$. The computational cost of the computing the additional terms present in CCSD-F12 theory is significant due to the many-electron integrals which arise from these terms.¹²¹ Hence, like most

practical uses of explicitly correlated methods, the investigations in the present thesis utilise an implementation of CCSD-F12 which makes further approximations to reduce the computational cost of calculations: CCSD(F12*). In particular, CCSD(F12*) achieves near-identical results to another approximate CCSD-F12 method, CCSD(F12), which in turn is considered to achieve accuracy close to CCSD-F12.¹²² CCSD(F12) neglects certain higher order terms from the CCSD-F12 equations and CCSD(F12*) removes further terms from the CCSD(F12) equations based on an analysis of the importance of the most computationally demanding terms.¹²⁰ The resultant CCSD(F12*) equations can be written in the forms given in equations (2.67)–(2.69).¹¹⁶

$$\begin{aligned}
E_{\text{CCSD(F12*)}} = & E_{\text{CCSD}} + \langle \text{HF} | [\hat{\Phi}_{\text{N}}, \hat{T}_{2'}] | \text{HF} \rangle + \\
& \sum_{\substack{i>j \\ x>y}} c_{xy}^{ij} \langle \text{HF} | (\hat{\tau}_{ij}^{xy})^\dagger \hat{Q}^{(0)} \frac{1}{2} [[\hat{H}, \hat{T}_1], \hat{T}_1] | \text{HF} \rangle + \\
& \sum_{\substack{i>j \\ x>y}} c_{xy}^{ij} \langle \text{HF} | (\hat{\tau}_{ij}^{xy})^\dagger \hat{\Phi} + [\hat{f}_{\text{N}}^{(0)}, \hat{T}_{2'}] + [\hat{H}, \hat{T}_1 + \hat{T}_2] | \text{HF} \rangle
\end{aligned} \tag{2.67}$$

$$\Omega_{\gamma_1, \text{CCSD}} + \langle \gamma_1 | [\hat{H}, \hat{T}_{2'}] | \text{HF} \rangle + \langle \gamma_1 | [[\hat{H}, \hat{T}_1], \hat{Q}_{12}^{(0)} \hat{T}_{2'}] | \text{HF} \rangle = 0 \tag{2.68}$$

$$\begin{aligned}
\Omega_{\gamma_2, \text{CCSD}} + \langle \gamma_2 | [\hat{H}, \hat{T}_{2'}] | \text{HF} \rangle + \langle \gamma_2 | [[\hat{H}, \hat{T}_1 + \hat{T}_2], \hat{Q}_{12}^{(0)} \hat{T}_{2'}] | \text{HF} \rangle + \\
\langle \gamma_2 | \frac{1}{2} [[\hat{H}, \hat{T}_1], \hat{T}_1], \hat{Q}_{12}^{(0)} \hat{T}_{2'}] | \text{HF} \rangle = 0
\end{aligned} \tag{2.69}$$

Note that an operator subscripted with N indicates is a normal-ordered operator, defined as $\hat{\mathcal{O}}_{\text{N}} = \hat{\mathcal{O}} - \langle \text{HF} | \hat{\mathcal{O}} | \text{HF} \rangle$. Additionally, $\hat{Q}_{12}^{(0)}$ is a modified projection operator defined as $\hat{Q}_{12}^{(0)} = 1 - \hat{P}_1 \hat{P}_2$, where $\hat{P}_\mu = \hat{\mathcal{O}}_\mu + \hat{V}_\mu$, and $\hat{f}_{\text{N}}^{(0)}$ is the zeroth-order normal-ordered Fock operator.[†] The SP approach is also used for the CCSD(F12*) method which is reflected in the presence of just two residuals in the CCSD(F12*) equations. The overall result of the approximations leading to the CCSD(F12*) equations is a method capable of accuracy similar to CCSD-F12 and exhibits the same scaling of computational expense with the number of correlated electrons and basis set size as canonical CCSD for the

[†]The order of perturbation refers to that defined within Møller-Plesset perturbation theory, in which the Hamiltonian is partitioned as $\hat{H} = E^{(0)} + \hat{f}_{\text{N}}^{(0)} + \hat{f}_{\text{N}}^{(1)} + \hat{\Phi}_{\text{N}}$. The zeroth order Fock operator can be written as¹¹⁶ $\hat{f}_{\text{N}}^{(0)} = \hat{f}^{(0)} - \langle \text{HF} | \hat{f}^{(0)} | \text{HF} \rangle$.

iterative solution of the coupled-cluster equations, and an additional small overhead cost.¹²⁰

Chapter 3

Characterisation of the Electronic Structure of $[\text{Cr}_6@ \text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$

3.1 Introduction

The synthesis of novel intermetalloid clusters offers the opportunity to directly establish which intermetalloid clusters can exist and to test and develop bonding models. One group of structural motifs which has gained attention in the synthesis of new intermetalloid clusters is annular arrangements of “butterfly” Pn_4 units (Pn — pnictogen element), which have been observed as cage structures surrounding transition metal atoms, an example of which is shown in figure 3.1. Only a few examples of cages of butterfly units have been documented in the literature. For arrangements of butterfly units entrapping a single atom, the series $[\text{LnSb}_{12}]^{3-}$ where $\text{Ln}=\text{Y}, \text{La}, \text{Ho}, \text{Er}, \text{Lu}$ ¹²³ and $[\text{AnBi}_{12}]^{x-}$ where $\text{An}:x = \text{Th}:4, \text{U}:3$ ^{124,125} have been reported. For butterfly units entrapping multiple atoms, there only appears to be the triangular Pd_3 cluster surrounded by three butterfly units in $[\text{Pd}_3\text{Sn}_8\text{Bi}_6]^{4-}$, and the pentagonal Cr_5 surrounded by five butterflies in $[\text{Cr}_5\text{Sb}_{20}\text{Sn}_2]^{4-}$, documented in the literature.^{45,126} Additionally, the study which reported the encapsulated Cr_5 unit⁴⁵ demonstrated it was possible to capture two Cr_5 units using a larger cage of butterfly units.

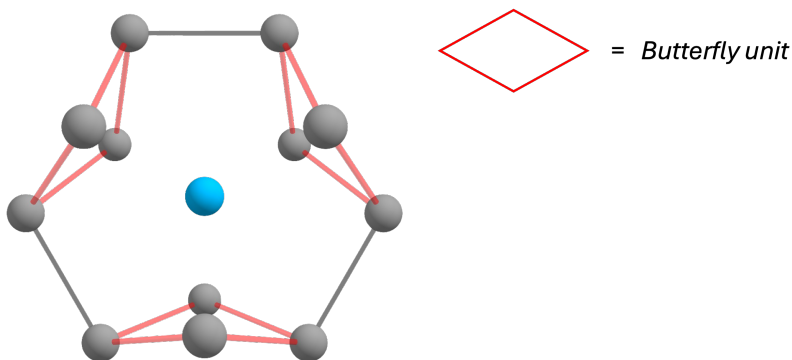


Figure 3.1: An example of a cluster, $[\text{Th}@\text{Bi}_{12}]^{4-}$, surrounded by three butterfly units.

The reported compounds show that the number of butterfly units surrounding the metal fragment can be varied to accommodate different sizes of metal atom clusters. Having observed this trend, the experimental contributors to the publication accompanying the present work¹²⁷ also noted the pseudo-element equivalence between Sb and Sn^- and hypothesised that the reduction in charge which comes with the use of Sn^- may be able

to stabilise metal atom clusters with a greater positive charge than the clusters reported previously. The result of this hypothesis was their synthesis of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$, a compound containing an octahedron of Cr atoms, capped by two ethylenediamine (en) ligands and surrounded by a four-membered butterfly ring, with each butterfly unit comprised of two Sn and Sb atoms. The geometry of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ was characterised using X-ray Diffraction (XRD) techniques, leading to the structure depicted in the figure 3.2. Notably, the XRD structure is displayed with the Sb atoms occupying the facial sites of the Cr_6 octahedron and the Sn atoms occupying crystallographic sites in the equatorial plane of the compound (henceforth referred to as the facial, E_{fac} , and equatorial, E_{eq} , sites respectively). However, it has been recognised that XRD experiments cannot reliably distinguish between Sn and Sb atoms due to their similar nuclear charge and number of electrons.^{128,129} Therefore, any facial site could be occupied by a Sn or Sb atom and equally, any equatorial site could be occupied by a Sn or Sb atom. To resolve this uncertainty, the present work employs KS-DFT to model the experimental data and propose a distribution of the Sn and Sb atoms over the facial and equatorial sites of the compound. Additionally, the KS-DFT model is used to suggest the electronic state of the compound.

The present study also aims to characterise the electronic structure of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ to establish whether the structure of the compound can be understood in terms of existing bonding models. Ahead of the analysis presented in section 3.4.3, one can note the central Cr_6 octahedral motif has been previously observed¹³⁰ in members of the $\text{M}_6\text{E}_8\text{L}_6$ series (e.g. $\text{M} = \text{Cr}, \text{Mo}, \text{Co}, \text{Nb}$; $\text{E} = \text{S}, \text{Se}, \text{Te}, \text{Cl}, \text{OMe}$; $\text{L} = \text{PR}_3, \text{CO}, \text{Cl}$). The electronic structure of this series has been studied,^{131–133} and shows diversity despite the similar geometries of the compounds. In particular, three electron counts associated with the M_6 motif are commonly found in the series: 20, 24 and 38. The 20-electron species are considered electron-deficient as they lack the electrons required to form $2c-2e^-$ bonds along all 12 edges of the octahedral motif. Likewise, 24-electron species are considered electron-precise, and the 38-electron compounds are electron-rich, existing through additional population of $\text{M}-\text{M}$ antibonding orbitals. The members of this series

where $M = \text{Cr}$ all show a 20-electron count which, in the sub-series where $M = \text{Cr}$ and $E = \text{S, Se, or Te}$ and $L = \text{PEt}_3$, have $\text{Cr}-\text{Cr}$ bond lengths varying from 2.59–2.60 Å when $E = \text{S}$ to 2.82–2.86 Å when $E = \text{Te}$.¹³⁴ Curiously, the present chapter's subject has $\text{Cr}-\text{Cr}$ bond lengths which are markedly shorter at 2.45–2.49 Å, possibly indicating a difference in electronic structure.

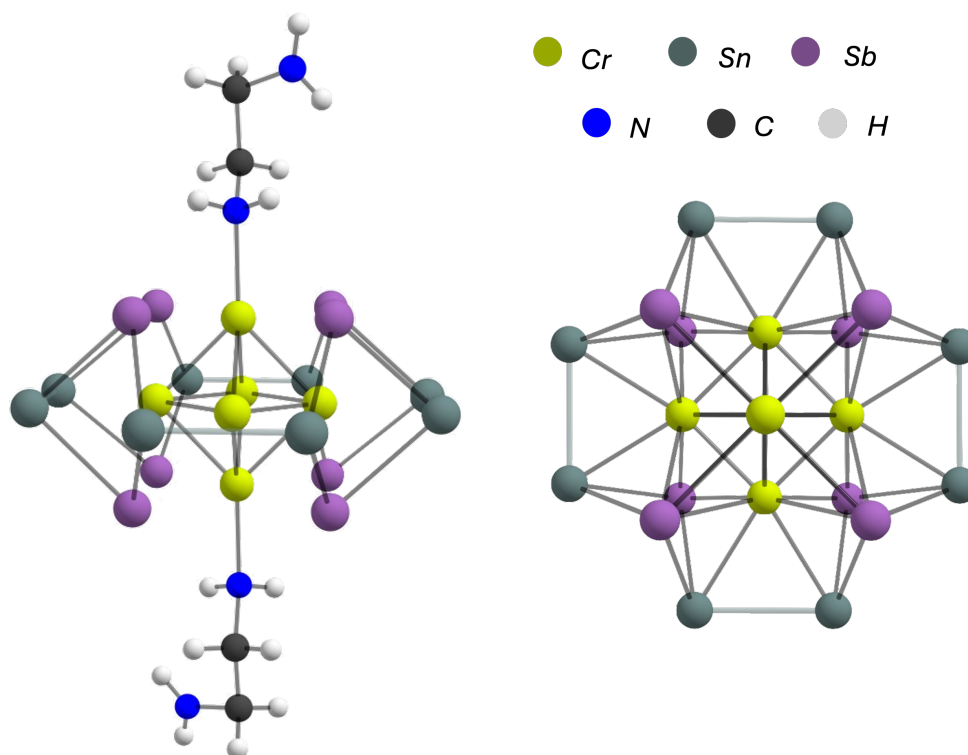


Figure 3.2: The empirically determined crystal structures of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$. Note that *en* refers to an ethylenediamine ligand. The *en* ligands were removed from the structure on the right for clarity.

3.2 Experimental Data

Experimental data characterising $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ is provided by contributors to the publication accompanying the present study.¹²⁷ Full details of the experimental methodology can be found in the publication and a summary of the conclusions drawn from the experimental data is given in the current section. As discussed in section 3.1, the X-ray diffraction data represented in figure 3.2 reveals the location of the Cr, N, and

C atoms in $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ but cannot show which of the compound's equatorial and facial sites are occupied by Sn and which are occupied by Sb. As such, electrospray ionisation mass spectrometry (ESI-MS) and energy dispersive X-ray (EDX) spectroscopy is used to gain further information about the atoms occupying the E_{eq} and E_{fac} sites.

The ESI-MS shows significant fragmentation but a peak at $m/z = 1401.8384$ can be assigned to $[\{[\text{K}(18\text{-C-}6)]_2\text{Cp}\}[\text{Cr}_4\text{Sn}_8\text{Sb}_8]^{2-}]^+$ which may indicate a $\{[\text{K}(18\text{-C-}6)]_2\text{Cp}\}^+$ cation ionically bound to a $[\text{Cr}_4\text{Sn}_8\text{Sb}_8]^{3-}$ anion. This could be explained by two, presumably axial, Cr(en) groups leaving $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ without additional charge, which would support equal amounts of Sn and Sb distributed over the equatorial and facial sites. The EDX data indicates a Sn:Sb ratio of 7.9:8.4 when normalised to give the six Cr atoms observed in the XRD experiments. Notably the ratio can vary to 7:9 when the 3σ distribution of the measurements is considered so unequal proportions of Sn and Sb cannot be ruled out with this data alone. On balance, the 8:8 ratio is considered most likely given the close ratio suggested by the EDX and the 8:8 ratio implied by the fragment observed in the ESI-MS. Additionally, this ratio might be expected since atoms in the facial and equatorial positions would be expected to exhibit significantly different interactions and hence lead to a preference for a particular element at each site. Evidence for the different interactions can be found in the calculations provided in section 3.4.2.

Finally, electron paramagnetic resonance (EPR) spectroscopy experiments show a single absorbance in the observed spectrum, possibly indicating one unpaired electron in the compound. The measured EPR spectrum is presented in figure 3.4.

3.3 Methodology

All calculations reported in the current chapter were performed in version 2024.101 of the Amsterdam Density Functional (ADF) program.¹³⁵

$[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ was synthesised in a $\{[\text{K}(18\text{-C-}6)]_2\text{Cp}\}_3\{[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]\}$

crystalline system. This system is modelled by first approximating it as a single molecule of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ in a positive background charge to account for the presence of the $\{[\text{K}(\text{18-C-6})]_2\text{Cp}\}^+$ cations. The properties of the system are then calculated using KS-DFT. In particular, unrestricted Kohn-Sham DFT is used for open-shell systems and restricted KS-DFT is used for closed-shell systems.

The zeroth-order regular approximation (ZORA)^{112,136–138} is applied to all calculations presented in the current chapter to estimate the impact of relativistic effects. The frozen core approximation is also used in all calculations. Specifically, the 1s orbital of C and N, the [Ar] orbitals of Cr and the [Kr] orbitals of Sn and Sb were frozen. ADF makes use of Slater-type basis sets⁸⁹ rather than the more common Gaussian functions and additionally offers Slater-type bases optimised for the simultaneous use of the ZORA method and the frozen core approximation. Such bases were used in all calculations reported in this chapter. The bases were all of triple-zeta quality and included an additional set of polarisation functions. Note that the present chapter uses the notation [functional]/[basis set], e.g. PBE/TZP, to denote methodology throughout.

The present chapter provides the positive background charge through the conductor-like screening model (COSMO)¹³⁹ with a dielectric constant, ϵ , of 100. This COSMO model is applied to all calculations reported in section 3.4. COSMO has been adopted in a number of studies on transition metals in crystal phases^{140–143} and it has been noted outright for improving results in certain studies.^{141,142} One study notes its results are largely insensitive to the choice of dielectric constant¹⁴¹ and indeed certain studies choose a value of infinity,^{140,142} or that of water ($\epsilon_{\text{H}_2\text{O}} = 78.39$), even when the system of interest does not contain any H_2O molecules.^{141,143} Thus, the present study employs a dielectric constant similar to that of water but rounded to avoid any inadvertent implication that there is significance in using the value of water in particular. An approach using point charges to model the positive background charge is also trialled in the present investigation, the details of which can be found in appendix section A1.1. It is found that there is only a small difference in the point charge model compared to the COSMO method, with the point charges expanding the calculated bond lengths in

$[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ by 0.01–0.04 Å. As such, the point charge model is not used for any calculations presented in the current chapter, though does see use in section A1.4 of the appendix.

All calculations in the present chapter are geometry optimisations which include the aforementioned ZORA treatment of relativistic effects and the COSMO positive background charge. All points on the potential energy surface found through converged geometry optimisations were characterised using the harmonic approximation.¹⁴⁴

The treatment of the en ligands in this study requires additional attention. Using the geometry extracted from the crystal data as the initial guess in a geometry optimisation and employing the PBE/TZP methodology results in a structure with two imaginary frequencies ($27i\text{ cm}^{-1}$ and $32i\text{ cm}^{-1}$) associated with rotation about the Cr–N bonds. This result is expected since there is unlikely to be a large energetic barrier to rotation about the Cr–N bonds, meaning the potential energy surface is near-flat with respect to this rotation. This makes it difficult to converge to the bonds' optimal angle of rotation. It can also be noted that the energies of the nine reported conformers of the en ligand are near-identical, with them spanning a range of only¹⁴⁵ $1.5\text{ kcal} \cdot \text{mol}^{-1}$. Additionally, given the distance of the bulk of the en ligand from the $[\text{Cr}_6\text{Sn}_8\text{Sb}_8]^{3-}$ unit of the compound, it is expected that the conformation of the en ligands will have very little effect on any energy differences of interest to the present study. Therefore, it is most likely that the conformation of the en ligands and rotation about the Cr–N bonds can be chosen without affecting the conclusions of the present study. As such, the en conformations and Cr–N rotation angle are chosen to allow the compound to transform as the highest symmetry point group possible: C_{2v} or C_{2h} . The C_{2v} point group is chosen and defined such that the mirror planes are the equatorial plane and one of the two planes which intersects a $\text{Cr}_{\text{eq}}\text{--Cr}_{\text{ax}}\text{--Cr}_{\text{eq}}\text{--Cr}_{\text{ax}}$ cycle (the choice of which is essentially arbitrary given the approximate D_{4h} symmetry of the $[\text{Cr}_6\text{Sn}_8\text{Sb}_8]^{3-}$ centre of the compound). This definition of the C_{2v} symmetry of the compound is applied to all calculations presented for $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ in the current chapter, except when otherwise indicated. The C_{2v} symmetry constraint prevents rotations about the Cr–N bonds and hence all converged

geometries using the C_{2v} point group also have two small imaginary frequencies (see table 3.1), similar to those from the symmetry-unconstrained calculation discussed at the start of the current paragraph. The restriction to the C_{2v} point group also limits the compound's range of possible geometries beyond the restrictions of the rotation about the Cr–N bonds and the conformations of the en ligand. Hence, if the symmetry constraint is preventing a compound from adopting the structure of a stationary point, it is feasible that an optimised geometry is not at a stationary point on the PES. However, since the position of each converged geometry on the PES is characterised, imaginary modes which break the symmetry of the compound will be present if the constraint is preventing the compound from optimising further. In such cases, further analysis is conducted to determine the significance of any further structural optimisation.

Various functionals were trialled for the present study. It has been stated previously⁶² that the results spanned by well-established GGA and hybrid functionals, such as PBE¹⁴⁶ and B3LYP^{147,148} respectively, will typically be representative of the range of calculated properties that can be expected from realistic exchange-correlation functionals. As such, the present study trialled the B3LYP and PBE functionals, and additionally the meta-GGA functional TPSS. The B3LYP/TZP optimisation did not produce a converged geometry[†] for $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$. Examination of the geometry throughout the optimisation shows the structure tending towards a strong distortion of the experimental geometry, for example $\text{Cr}_{\text{eq}}-\text{Cr}_{\text{eq}} = 2.57\text{--}2.64 \text{ \AA}$ (cf. the experimental value of $2.45\text{--}2.49 \text{ \AA}$). As such, B3LYP and other hybrid functionals are not considered further in the present study. Additionally, the TPSS/TZP optimisation did not produce a converged geometry since the SCF cycle failed to converge after a number of iterations of the geometry. TPSS and meta-GGAs are therefore also not investigated further. The PBE functional did produce a converged geometry with bond lengths generally close to those from experiment. Hence, two more GGA functionals, BLYP,^{149,150} and OPBE,^{151,152} are considered in the present study in order to represent the range of results which can be found from GGAs. These functionals produced results which could

[†]The calculation was halted after 35 iterations of the Quasi-Newton geometry optimisation algorithm.

rationalise the experimental data and hence were used for the primary investigation in this chapter, presented in section 3.4. The results of the three GGA functionals show the same qualitative features and only vary numerically to a moderate degree. Hence only the results obtained using the PBE functional are presented in section 3.4 and the full results from the three functionals are displayed in appendix table A1.2.

As mentioned in section 3.1, the electronic state of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ is investigated and as such it is desirable to test the agreement of multiple electronic states with the experimental data. ADF can automatically find an electronic state by populating the orbitals at each step of the SCF cycle according to the Aufbau principle until a certain SCF iteration, after which it then occupies the orbitals which bear the most spatial resemblance to those occupied on the previous iteration. The program additionally offers the option to find different electronic states through specifying which orbitals of a given set of MOs (e.g. those from the initial guess orbitals or a completed calculation) should be occupied. However, it is still possible that the SCF cycle causes the final occupied orbitals to deviate from those initially specified. This turns out to be an issue in the case of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$. Given a doublet spin state and using PBE/TZP methodology, the automatic option resulted in a $^2\text{A}_1$ state and all attempts to specify a different orbital occupation either converged to the $^2\text{A}_1$ state or resulted in an unconverged SCF cycle. An alternative to specifying a particular set of orbitals to be occupied is to only specify the number of occupied orbitals transforming as each irreducible representation (irrep) of the molecule's point group. This does not require any specific orbitals to be occupied, only requires that there is a particular number of occupied orbitals transforming as a given irrep. The $^2\text{A}_1$ state found with the automatic option has a singly occupied a_1 orbital and hence other states can be found by doubly occupying this a_1 orbital and requiring that an orbital of another irrep is singly occupied. Doing so led to one electronic state for each irrep of the C_{2v} point group producing a converged geometry optimisation: $^2\text{A}_1$, $^2\text{A}_2$, $^2\text{B}_1$, and $^2\text{B}_2$, which are the electronic states considered in this chapter.

Table 3.1 shows all imaginary frequencies computed for the four electronic states considered in the present study. All four states show the expected small imaginary

frequencies ($24i-59i\text{ cm}^{-1}$) associated with rotations about the Cr–N bonds. The 2A_1 state has no further imaginary frequencies which indicates the energy of the compound cannot be minimised further with respect to geometric change to its $[Cr_6Sn_8Sb_8]^{3-}$ centre. This state also localises its radical in a Sn–Sn bonding orbital (see discussion in section 3.4.1) and, when necessary, is referred to as the Sn radical state. The 2A_2 state shows two large imaginary frequencies associated with distortions of the $[Cr_6Sn_8Sb_8]^{3-}$ centre. All attempts to follow these frequencies converged to the 2A_1 state which puts up a barrier to investigating the 2A_2 state in the present study. Given this barrier and the size of the state's imaginary frequencies, it is possible that the 2A_2 state is not a stable state. Furthermore, given the insight into the experimental data provided by the three other electronic states (discussed in section 3.4.1), it is considered unlikely that the 2A_2 state will provide further insight into the compound's properties of interest. Thus, the 2A_2 state is not considered further in the present study. The 2B_1 state can exhibit two imaginary frequencies associated with the distortion of the $[Cr_6Sn_8Sb_8]^{3-}$ unit, however these vary with functional to the point of vanishing entirely when the OPBE functional is used. Given the moderate size of these frequencies and that the frequencies feasibly may also vary with other factors in the computational model such as basis set or model of the positive background charge, the 2B_1 is considered a stable state within the margin of error of the computational model and is used to aid in the interpretation of the experimental data discussed in section 3.4.1. Finally, the 2B_2 state contains a single large imaginary frequency which distorts the $[Cr_6Sn_8Sb_8]^{3-}$ centre of the compound along the Cartesian axis perpendicular to the mirror plane intersecting a $Cr_{eq}-Cr_{ax}-Cr_{eq}-Cr_{ax}$ cycle. Note also that the 2B_2 state singly occupies a b_2 orbital localised on the Cr_6 unit. In principle, the large imaginary frequency can be followed within the C_{2v} point group, though this requires a re-definition of the compound's axes which necessarily means the singly occupied b_2 orbital transforms as a_1 . This causes convergence issues as the state can no longer be distinguished by irrep from the Sn radical 2A_1 state mentioned at the start of the current paragraph. Consequently, all attempts to converge the 2B_2 -equivalent state with a singly occupied and Cr_6 -localised a_1 orbital converged to the Sn radical state. However, it is found that replacing the en ligands with F^- anions provides a minor

stabilisation to the singly occupied b_2 orbital of the 2B_2 state and allows convergence to the 2B_2 -equivalent state when the axes are re-defined. This allows the effect of removing the large imaginary frequency to be approximated. A discussion of the approximation is presented in section A1.4 and it is estimated that removal of the large imaginary frequency only leads to a small change in the geometry and energy of the 2B_2 state. Therefore, the results with the large imaginary frequency still present are discussed in section 3.4.1 for simplicity.

		Cr–N /cm ⁻¹	[Cr ₆ Sn ₈ Sb ₈] ³⁻ /cm ⁻¹
2A_1	PBE	42i, 44i	–
	BLYP	37i, 53i	–
	OPBE	34i, 40i	–
2B_1	PBE	11i, 27i	71i, 88i
	BLYP	38i, 52i	22i, 32i
	OPBE	25i	–
2B_2	PBE	40i, 43i	647i
	BLYP	50i, 59i	440i
	OPBE	42i, 47i	534i
2A_2	PBE	24i	148i, 489i

Table 3.1: The imaginary frequencies computed for each of the four electronic states of [Cr₆Sn₈Sb₈(en)₂]³⁻ considered in the present study. Results from each of the functionals trialled are shown. The frequencies under the heading Cr–N indicate frequencies associated with rotations about the Cr–N bonds and frequencies under the [Cr₆Sn₈Sb₈]³⁻ heading are associated with distortions of [Cr₆Sn₈Sb₈]³⁻ centre of [Cr₆Sn₈Sb₈(en)₂]³⁻. All values are in cm⁻¹.

3.4 Results and Discussion

3.4.1 Determination of the Electronic State

As mentioned in section 3.2, the arrangement of the eight Sn and eight Sb atoms among the facial and equatorial crystallographic sites is unknown. To investigate the possible electronic states of [Cr₆Sn₈Sb₈(en)₂]³⁻, the arrangement depicted in figure 3.2 is used, in

which the Sn atoms occupy the equatorial sites and the Sb atoms occupy the facial sites. The possible site occupations of the Sn and Sb atoms are then investigated in section 3.4.2. Geometrically optimising the 2A_1 , 2B_1 , and 2B_2 electronic states mentioned in section 3.3 using the PBE/TZP methodology described in the same section leads to the bond lengths and relative energies presented in table 3.2. The experimental geometric data is also included in table 3.2 for comparison.

E.S.	Rel. E	Cr _{eq} -Cr _{eq}	Cr _{eq} -Cr _{ax}	Cr _{eq} -Sb	Cr _{ax} -Sb	Cr _{eq} -Sn	Sn-Sn	Sn-Sb
Exp.	-	2.453(2)-	2.480(2)-	2.739(2)-	2.778(1)-	2.787(1)-	2.9293(7)-	2.9106(8)-
		2.457(1)	2.482(2)	2.754(2)	2.790(1)	2.809(2)	2.9353(9)	2.9262(8)
2A_1	0.00	2.38-2.39	2.42	2.78-2.79	2.77-2.80	2.89-2.91	3.04	2.97-2.98
2B_1	+4.78	2.37	2.46	2.79-2.80	2.81-2.83	2.90-2.92	2.96	2.97-2.98
2B_2	+0.80	2.44-2.45	2.36-2.47	2.78-2.80	2.81-2.84	2.85-2.93	2.97-2.99	2.96-2.99

Table 3.2: Experimental (Exp.) bond lengths of $[Cr_6Sn_8Sb_8(en)_2]^{3-}$ presented alongside the bond lengths and relative energies (Rel. E) calculated for three electronic states (E.S.) of $[Cr_6Sn_8Sb_8(en)_2]^{3-}$ using the PBE/TZP methodology. Note that the subscripts eq and ax denote equatorial and axial positions respectively. All bond lengths are reported in Å and all energies are reported in kcal·mol⁻¹.

Certain calculated bond lengths exhibit much larger ranges than their experimental counterparts. However, the lack of larger ranges in the experimental bond lengths does not necessarily evidence against the electronic states found to have larger ranges in their bond lengths with the KS-DFT model. This is because the KS-DFT model calculates data for a single molecule whereas the experimental data is an average over all unit cells in the experimental crystal sample. Hence, when considered over multiple unit cells, certain bond lengths found in the single-molecule calculations may be expected to average and therefore reduce in range. For example, this averaging would be expected in the case of the Cr_{eq}-Cr_{ax} (where the subscripts eq and ax denote equatorial and axial positions respectively) and Cr_{eq}-Sn lengths in the 2B_2 state. The range in these lengths is due to four of the eight Cr_{eq}-Cr_{ax} lengths exhibiting an elongation with respect to the other four lengths, depictions of which can be found in appendix figure A1.4. Notably, all four of the elongated Cr_{eq}-Cr_{ax} lengths are in the same plane. There are two planes in the compound which contain four Cr_{eq}-Cr_{ax} lengths and feasibly the lengths in either

plane could exhibit the elongations. The energy of the compound is the same regardless of which plane's bond lengths are elongated and therefore a crystal sample of the 2B_2 state is expected to contain instances of the compound where the elongated bond lengths are in different planes. Thus, an average of the $Cr_{eq}-Cr_{ax}$ (and consequently the $Cr_{eq}-Sn$) lengths found in a single molecule would be expected from XRD data resulting from the 2B_2 state.

The geometric differences between the three states can be rationalised by considering which orbital the states singly occupy. The singly occupied orbital of each state is displayed alongside its spin density in figure 3.3. As mentioned in section 3.3, the three states only differ in the orbital they singly occupy and all of their other orbitals are equivalent. Therefore, the orbital singly occupied in one state is doubly occupied in the two others. The 2B_1 and 2B_2 states both singly occupy a MO localised on the Cr_6 cluster, while the radical in the 2A_1 state occupies a $Sn-Sn$ σ bonding orbital. Thus, the $Sn-Sn$ bond length is larger in the 2A_1 state compared to 2B_1 and 2B_2 states. All other bond lengths in the 2A_1 state show small ranges, reflecting the near- D_{4h} symmetry of the $[Cr_6Sn_8Sb_8]^{3-}$ unit maintained in this state. The singly occupied orbitals of the 2B_1 and 2B_2 states are strongly resemblant and might be considered equivalent orbitals in different orientations since both transform as t_{2u} in O_h symmetry. The singly occupied orbitals in both of the 2B states exhibit eight $Cr-Cr$ bonding interactions. The bonding interactions in the 2B_1 state are along all eight of $Cr_{eq}-Cr_{ax}$ lengths whereas the bonding interactions in the 2B_2 state occur along all four $Cr_{eq}-Cr_{eq}$ lengths and the four $Cr_{eq}-Cr_{ax}$ lengths which intersect a mirror plane of the compound. Consequently, the 2B_1 state has larger $Cr_{eq}-Cr_{ax}$ lengths than both the 2A_1 and 2B_2 state while its $Cr_{eq}-Cr_{eq}$ length is similar to that of the 2A_1 state. Likewise, the 2B_2 state shows longer $Cr_{eq}-Cr_{eq}$ lengths than the other two states and shows a range in the $Cr_{eq}-Cr_{ax}$ lengths since it has only lost electron density from a sub-set of the bonding interactions that occur along these lengths.

Due to the physical differences between the states discussed in the previous paragraph, if the dominant electronic state in the experiment features a Cr_6 -localised radical, as is the case for the two 2B states, it would be expected that the 2A_1 state would underestimate

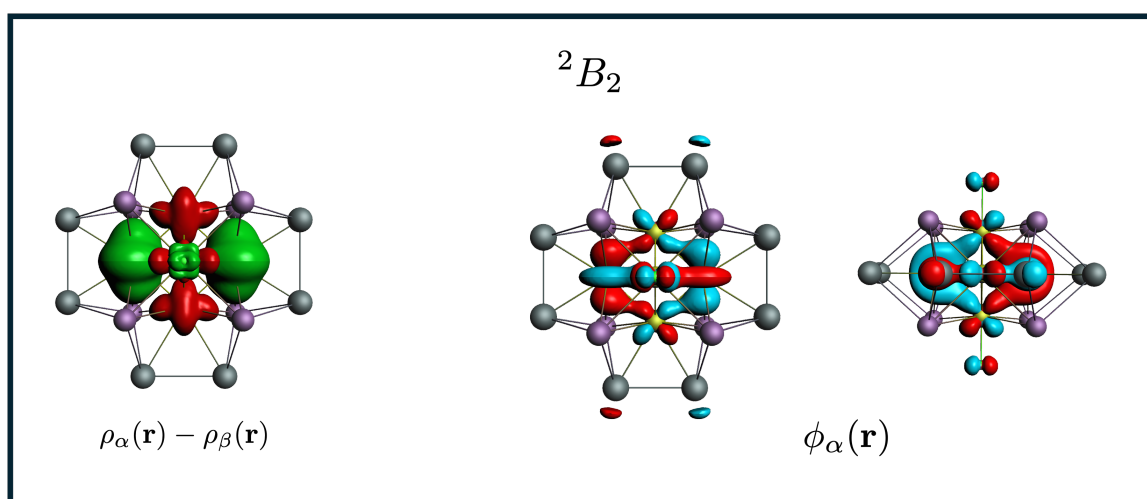
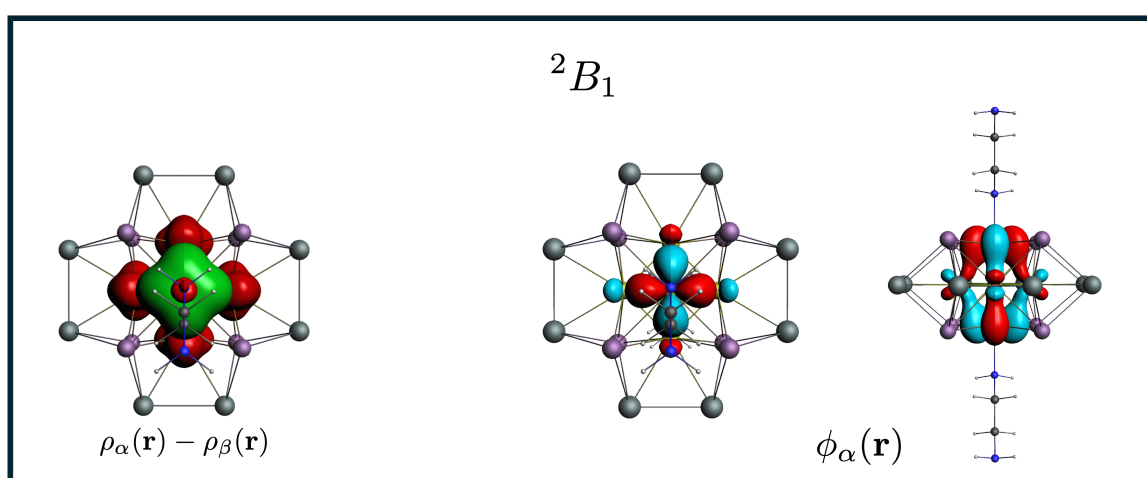
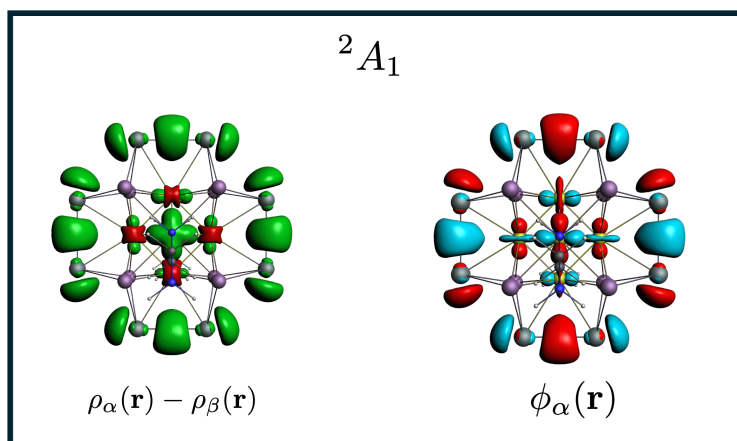


Figure 3.3: Spin densities($\rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$) and corresponding singly occupied molecular orbitals ($\phi_\alpha(\mathbf{r})$) for the three discussed states. Note the 2B_2 results use a F^- ligand rather than *en* for clarity. The spin density and singly occupied orbital for the 2B_2 with the *en* ligand can be found in appendix figure A1.1

the Cr–Cr lengths and overestimate the Sn–Sn bond length. This trend is observed with the 2A_1 state underestimating both Cr–Cr lengths and overestimating the Sn–Sn bond length across all functionals tested. Furthermore, the two 2B states agree with the experimental Sn–Sn length when the OPBE functional is used and both have at least one Cr–Cr bond length in agreement with experiment when all functionals are considered. This demonstrates that the longer Cr–Cr lengths and shorter Sn–Sn lengths observed in the experiment can be associated with an electronic state that localises the unpaired electron on the Cr_6 centre of the compound. Therefore, it can be hypothesised that the 2A_1 state is not the dominant state in the experiment and an electronic state with a Cr_6 -localised radical, such as either of the 2B states, is dominant.

Despite both 2B states obtaining agreement with experiment in at least one Cr–Cr length, neither state shows conclusive agreement with both experimental Cr–Cr lengths. The 2B_1 state underestimates the experimental value for $Cr_{eq}-Cr_{eq}$ across all tested functionals but it is in agreement with experiment for the $Cr_{eq}-Cr_{ax}$ length. The 2B_2 state agrees with experiment for the $Cr_{eq}-Cr_{eq}$ length when the PBE and BLYP functionals are used but its range for the $Cr_{eq}-Cr_{ax}$ length only obtains experimental agreement with its upper bound. However, it is feasible that the experimental values are within the error of the computational model. Results in appendix section A1.4 show the Cr–Cr lengths are moderately sensitive to the model of the positive background charge with, for example, the $Cr_{eq}-Cr_{eq}$ range in the 2B_2 state increasing to 2.47–2.48 Å when the point charge model is used. Additionally, factors not considered in the computational model such as the aforementioned averaging over unit cells or the possibility of multiple electronic states being present in the experiment could explain the discrepancies with experiment seen for the 2B states. In any case, the results from the 2B states demonstrate how a Cr_6 -localised radical can achieve agreement with the experimental Cr–Cr bond lengths whilst also agreeing with the experimental Sn–Sn length. Hence, the hypothesis that the electronic state of $[Cr_6Sn_8Sb_8(en)_2]^{3-}$ contains a Cr_6 -localised radical is considered to be supported by the data in table 3.2.

The measured EPR spectrum of $[Cr_6Sn_8Sb_8(en)_2]^{3-}$, displayed in figure 3.4, provides a

further test of the hypothesis that the compound's electronic state features a Cr_6 -localised radical. EPR g -factors are calculated for the $^2\text{A}_1$ and $^2\text{B}_2$ states for comparison with experiment. The $^2\text{B}_1$ state is not expected to have distinguishable g -factors from the $^2\text{B}_2$ state with respect to the uncertainty of the experiment and therefore is not included in the comparison. The spectrum shows an isotropic signal which is centred around the point $g = 2.21$ (3049 Gauss). The g -factors for the $^2\text{A}_1$ state are calculated to be 2.05, 2.06, and 3.80 which imply an axial signal with absorption features at approximately 3280 and 1770 Gauss. Some coalescence of the peaks may be expected but there does not appear to be a significant absorption near 1770 Gauss. In contrast, the g -values for the $^2\text{B}_2$ state are 1.96, 2.06, 2.16 which are expected to give only a single peak, centred near the average of 3277 Gauss ($g = 2.06$). This is consistent with the experimental data, given the limitations of the model used. Therefore, the comparison of computational and EPR data also supports an electronic state with a Cr_6 -localised radical.

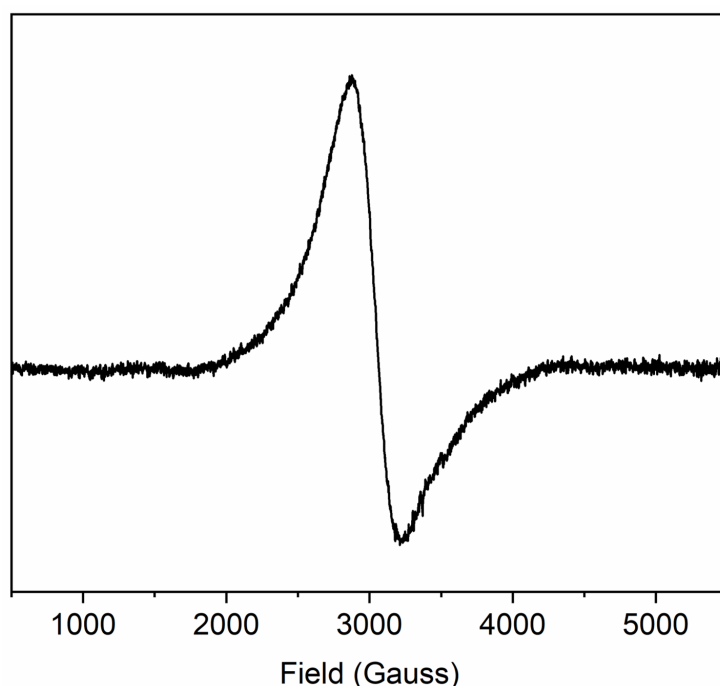


Figure 3.4: The measured EPR spectrum of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$. This figure is adapted from reference.¹²⁷

Overall, the experimental data discussed in the current section supports the hypothesis that the electronic state of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ features a Cr_6 -localised radical. It can be

noted that the electronic state calculated to be the lowest energy across all functionals is the 2A_1 state which does not feature a Cr_6 -localised radical. However, the 2B_2 state is calculated to be only $0.80 \text{ kcal} \cdot \text{mol}^{-1}$ higher in energy when the PBE functional is used. Furthermore, removing the large imaginary frequency in the 2B_2 state is, as per the discussion in section A1.4, is estimated to reduce the energy of the state by $0.55 \text{ kcal} \cdot \text{mol}^{-1}$. This means the calculated energy difference between the 2B_2 and 2A_1 may be considered to be as little as $0.25 \text{ kcal} \cdot \text{mol}^{-1}$. Such a small energy difference is considered within the margin of error of KS-DFT calculations and hence 2B_2 state is still considered a possibility. Given the experimental agreement obtained by both states with a Cr_6 -localised radical and that the 2B_2 state cannot be ruled out on an energetic basis, the 2B_2 state is considered to be the dominant electronic state for the purpose of further analyses.

3.4.2 The Site Occupation of the Sn and Sb Atoms

With the electronic state assumed to be 2B_2 , the ambiguity of the occupation of the equatorial and facial sites by Sn and Sb can be addressed.

As previously mentioned, XRD alone is unable to distinguish between atoms of Sn and atoms of Sb. Thus, any of the equatorial or facial crystallographic sites of $[Cr_6Sn_8Sb_8(en)_2]^{3-}$ could be occupied by a Sn or a Sb atom. If the 8:8 ratio of Sn:Sb outlined in section 3.2 is taken to be true, various occupations of the sites can be geometrically optimised using the KS-DFT methodology described in section 3.3. Doing so allows the geometries resulting from different site occupations to be compared with the experimental data, and enables the relative energies of different site occupations to be established. In lieu of testing all possible site occupations, four are sampled to understand the impact of site occupation on the energy and geometry of $[Cr_6Sn_8Sb_8(en)_2]^{3-}$. These include: (a) eight Sn atoms occupying the equatorial sites and eight Sb atoms occupying the facial sites, (b) eight Sb atoms occupying the equatorial sites and eight Sn atoms occupying the facial sites, (c) four Sn and four Sb atoms in the

equatorial sites, and four Sn and four Sb atoms in the facial sites, with the distribution among the sites being symmetric under a C_2 rotation about an axis which intersects opposing Cr_{eq} units, and (d) seven Sb atoms and one Sn atom in the facial sites along with seven Sn atoms and a Sb atom adjacent to the facial Sn atom in the equatorial sites. Depictions of all of these site occupations can be found in figure 3.5.

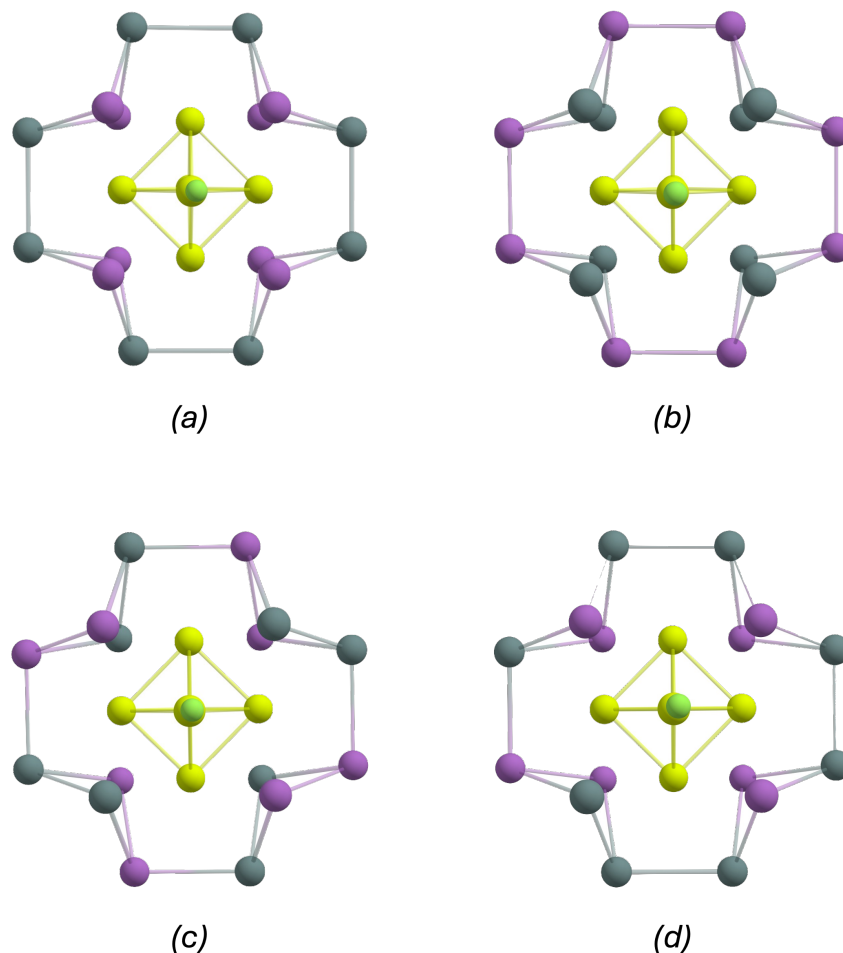


Figure 3.5: The four trialled site occupations of Sn and Sb among the facial and equatorial crystallographic sites.

In the calculations performed for the four site occupations, the en ligands are replaced by F^- which leads to an electronic structure with a spin density resembling that of the 2B_2 state in all the optimised structures. Additionally, pilot testing showed that small variations in the initial guess geometry could lead to a variation in the energy of the optimised structures of up to $4 \text{ kcal} \cdot \text{mol}^{-1}$. As such, three initial guess geometries were trialled for each site occupation: the experimental geometry, the experimental geometry

with a small random displacement of ± 0.05 Å applied to each atom, and the C_{2v} -symmetrised experimental geometry with the same small displacement then applied.[†] In all cases, the latter of these gave the lowest energy solution, the data from which is displayed in table 3.3. The converged geometries providing the data given in table 3.3 were all confirmed to be local minima using the harmonic approximation.¹⁴⁴

S.O.	Rel. E	Cr _{eq} -Cr _{eq}	Cr _{eq} -Cr _{ax}	Cr _{eq} -E _{fac}	Cr _{ax} -E _{fac}	Cr _{eq} -E _{eq}	E _{eq} -E _{eq}	E _{eq} -E _{fac}
Exp.	-	2.453(2)-	2.480(2)-	2.739(2)-	2.778(1)-	2.787(1)-	2.9293(7)-	2.9106(8)-
		2.457(1)	2.482(2)	2.754(2)	2.790(1)	2.809(2)	2.9353(9)	2.9262(8)
(a)	0	2.42-2.48	2.36-2.48	2.79-2.82	2.83-2.85	2.85-2.93	3.00-3.02	2.96-2.99
(b)	+20.8	2.46	2.32-2.39	2.90-2.91	2.90	2.77-2.83	2.95-2.98	2.98-3.00
(c)	+21.8	2.41-2.51	2.32-2.44	2.75-2.93	2.82-2.91	2.75-2.94	2.95-2.96	2.95-3.03
(d)	+5.88	2.39-2.55	2.33-2.49	2.76-2.91	2.83-2.89	2.78-2.95	2.98-3.02	2.94-3.00

Table 3.3: The relative energies (Rel. E) and bond lengths of the four trialled site occupations (S.O.) of Sn and Sb atoms among the equatorial and facial sites, labelled according to figure 3.5. Computational data was obtained using the PBE/TZP methodology. Energies are in kcal·mol⁻¹. Bond lengths are in Å.

Site occupation (b) overestimates the Cr_{eq}-E_{fac} and Cr_{ax}-E_{fac} bond lengths, beyond the range that the results discussed in section 3.4.1 suggested could be overturned by changing functional. Additionally, site occupation (b) underestimates the Cr_{eq}-Cr_{ax} bond length significantly, also beyond the range that may be expected to be overturned by a different choice of functional. Hence it is concluded that site occupation (b) does not fit the experimental data and is therefore not considered to be the dominant site occupation in the experiment.

The geometric data for site occupations (a), (c), and (d) is less conclusive. The range of the Cr-Cr lengths contains the experimental Cr-Cr lengths in all of three of these site occupations except for Cr_{eq}-Cr_{ax} in site occupation (c). Therefore, it cannot be ruled out that an average over unit cells could explain the experimental data. Furthermore, all other bond lengths show similar agreement with experiment when the variation with functional is considered. As such, the relative energies of the site occupations are considered for further insight. For all site occupations, the placing Sb atoms in the

[†]In the case of structure (b) a random displacement ± 0.1 Å is used since a displacement of ± 0.05 Å did not lead to a local minimum.

equatorial sites and Sn atoms in the facial sites raises the energy. The energy is size extensive so the trend in the relative energies, $(a) < (d) < (b) \approx (c)$, is partially explained by the number of Sn atoms in facial sites and Sb atoms in equatorial sites following the order $(a) < (d) < (c) < (b)$. However, the relative energies do not show a linear increase with the amount of Sn in the equatorial sites and Sb atoms in the facial sites. This complicates the determination of the lowest-energy site occupation. Site occupation (d) shows the energy increase due to a single Sn atom in a facial site and a single Sb atom in an equatorial site, which is close to, but possibly not out of, the range in which a change in functional could be expected to eliminate this increase in energy. However, given that PBE has been found to provide reasonable agreement with the experimental data thus far, and its trends in the relative energies of the electronic states are also seen in other functionals, it is considered likely that there is at least some energy increase associated with the placement of Sn and Sb atoms in the facial and equatorial sites respectively. Thus, overall structure (a) is considered most likely to be the dominant species in the experiment.

3.4.3 Analysis of Stabilising Interactions

With the electronic state and site occupation of the Sn and Sb atoms previously discussed, the bonding characteristics of the 2B_2 state of $[Cr_6Sn_8Sb_8(en)_2]^{3-}$ may be analysed in further detail. For greater clarity when analysing the molecular orbitals, the en ligands of the compound are replaced with F^- ions to allow symmetrisation to the D_{4h} point group. Thus, $[Cr_6Sb_8Sn_8F_2]^{5-}$ is the compound discussed in the present section. In the D_{4h} point group, the Cr_6 -localised radical occupies an e_u orbital and therefore the relevant electronic state in D_{4h} symmetry has the term symbol 2E_u .

$[Cr_6Sb_8Sn_8F_2]^{5-}$ shares a number of geometric features with compounds in the $M_6E_8L_6$ series (previously mentioned in section 3.1), which are all closed-shell species transforming with O_h symmetry. Compounds in the $M_6E_8L_6$ series contain a central M_6 octahedron with an E species on each of its faces. The compounds also have a total of six

L species distributed across sites on opposing sides of the M_6 motif along the three axes which pass through the vertices of the M_6 octahedron. The electronic structure of $M_6E_8L_6$ compounds has been studied previously and provides a reference point from which the bonding characteristics of $[Cr_6Sb_8Sn_8F_2]^{5-}$ may be understood. In particular, it was shown¹³² that the bonding in $M_6E_8L_6$ compounds can be described in terms of the frontier orbitals of square-pyramidal ME_4L units. Each M has five σ interactions with the surrounding E and L species and there are four metal frontier orbitals on each unit. When the ME_4L units are combined to give the $M_6E_8L_6$ compound, the metal orbitals are shown to give rise to 12 M–M bonding combinations. In total, six M–L, eight M–E, and 12 M–M bonding interactions are expected in the orbitals of the $M_6E_8L_6$ compounds. Two common electron counts associated with the M_6 cluster in this series are 20 and 24, examples of which can be found in $Cr_6Te_8(CO)_6$ and $[Mo_6Cl_{14}]^{2-}$ respectively.

The Kohn-Sham MOs[†] of $Cr_6Te_8(CO)_6$ and $[Mo_6Cl_{14}]^{2-}$ reveal that the compounds can be understood as $[(Mo_6)^{12+}(Cl^-)_{14}]^{2-}$ and $(Cr_6)^{16+}(Te^{2-})_8(CO)_6$. This means the E species in both compounds can be considered electron donors with a complete outer-shell of electrons. The E atoms form eight M–E σ interactions to the central M_6 cluster in both cases, as expected from the aforementioned analyses in the literature. There are therefore also 16 orbitals associated with E_8 lone pairs in the two compounds. In principle all 16 of these MOs are available for additional M–E π interactions and indeed these interactions are observed in a number of the 16 MOs. The two compounds also show the expected six M–L σ interactions.[‡] $[Mo_6Cl_{14}]^{2-}$ occupies the 12 expected M_6 bonding orbitals but $Cr_6Te_8(CO)_6$ only occupies 10 of these. The M_6 bonding orbitals which $Cr_6Te_8(CO)_6$ does not occupy are doubly degenerate, transforming as e_g , and are found in its virtual orbital set. The majority of the orbitals mentioned for $Cr_6Te_8(CO)_6$ and $[Mo_6Cl_{14}]^{2-}$ show a strong resemblance and the differences between the two sets of MOs appear to be minor. Therefore, the significant difference in the

[†]The PBE/TZP methodology is used to provide a set of Kohn-Sham molecular orbitals for each of these compounds.

[‡]One may also note, in the case of $[Mo_6Cl_{14}]^{2-}$, the L species is Cl^- and hence one also finds 12 orbitals associated with L_6 lone pairs. Additionally, the L species of $Cr_6Te_8(CO)_6$, CO, shows the M–L σ interaction through its usual two-electron donation.

electronic structure of the two compounds appears to be that $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ occupies the e_g M–M bonding orbitals whereas $\text{Cr}_6\text{Te}_8(\text{CO})_6$ does not. Consequently, it seems the cause of the different electron counts in $\text{Cr}_6\text{Te}_8(\text{CO})_6$ and $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ can be explained by the effect the occupation of this M–M e_g orbital has on the compounds.

The e_g M–M bonding orbital, displayed in figure 3.6, shows an antibonding M–E π^* interaction as well as M–M bonding interactions. It can therefore be expected that the occupation of the e_g orbital will simultaneously strengthen the M–M interactions and weaken the M–E π interactions in the compounds. Hence, it seems reasonable to conclude that if the e_g orbital were occupied in $\text{Cr}_6\text{Te}_8(\text{CO})_6$, the strengthening of the M–M bonds would be outweighed by the weakening of the M–E π interaction, which makes the population of the e_g orbital unfavourable and therefore rationalises the compound's 20-electron count. Equally, for $[\text{Mo}_6\text{Cl}_{14}]^{2-}$, it may be said that the strengthening of the M–M bonds outweighs the weakening of the M–E π interactions, making occupation of the M–M e_g orbital favourable, which leads to the compound's 24-electron count.

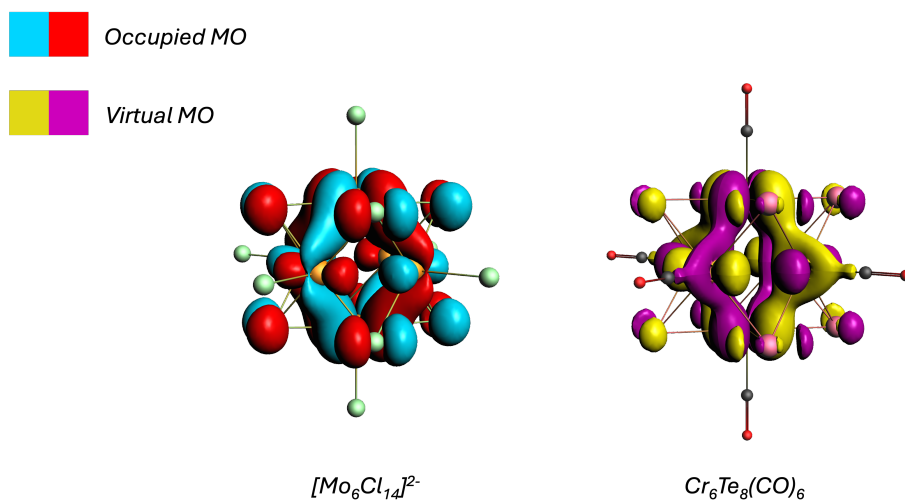


Figure 3.6: The e_g M–M bonding orbitals in $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ and $\text{Cr}_6\text{Te}_8(\text{CO})_6$ showing the simultaneous M–M bonding and M–E antibonding character. Isosurfaces are at a value of 0.025.

Having investigated the origins of the 20- and 24-electron counts in $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ and $\text{Cr}_6\text{Te}_8(\text{CO})_6$, the electronic structure of $[\text{Cr}_6\text{Sb}_8\text{Sn}_8\text{F}_2]^{5-}$ can be compared to that of $\text{M}_6\text{E}_8\text{L}_6$ compounds. The 12 M–M bonding, eight M–E σ , and six M–L σ MOs

expected of the $M_6E_8L_6$ series are all found occupied in $[Cr_6Sb_8Sn_8F_2]^{5-}$, confirming the similarity of the bonding in $[Cr_6Sb_8Sn_8F_2]^{5-}$ and $M_6E_8L_6$ compounds. All 12 M–M bonding orbitals are occupied (one singly) in $[Cr_6Sb_8Sn_8F_2]^{5-}$, meaning its electronic structure is most similar to those of 24-electron clusters. This is curious as all of the $M_6E_8L_6$ compounds where $M = Cr$ exhibit a 20-electron count. The reason for this appears to be due to $[Cr_6Sb_8Sn_8F_2]^{5-}$ featuring weaker M–E π interactions. After the 12 M–M bonding, eight M–E σ , and six M–L σ MOs, there are 16 MOs remaining in the valence space[†] of $[Cr_6Sb_8Sn_8F_2]^{5-}$, all of which are associated with the Sn_8Sb_8 unit. These 16 MOs include orbitals localised on the Sn atoms and Sn–Sb σ orbitals, as well as orbitals localised on the Sb atoms which are available for π bonding with the Cr_6 cluster. In comparison, $[Mo_6Cl_{14}]^{2-}$ and $Cr_6Te_8(CO)_6$ both have 16 MOs associated with the E_8 lone pairs alone, all of which are in principle available for M–E π bonding. Hence there are fewer orbitals in $[Cr_6Sb_8Sn_8F_2]^{5-}$ available for M–E π bonding. Moreover, some of the orbitals showing M–E π character in $Cr_6Te_8(CO)_6$ show visibly less amplitude between the M and E species in $[Cr_6Sb_8Sn_8F_2]^{5-}$, an example of which is depicted in figure 3.7. Thus, it may be hypothesised that the M–E π interactions are weaker in $[Cr_6Sb_8Sn_8F_2]^{5-}$ than in $Cr_6Te_8(CO)_6$ and therefore that the weakening of the M–E π interactions that occurs on occupation of the M–M e_g orbitals (which transform as $a_{1g} \oplus b_{1g}$ in D_{4h} symmetry) is less significant in $[Cr_6Sb_8Sn_8F_2]^{5-}$. Consequently, it is postulated that the stabilisation from strengthening the M–M interaction is large enough for the occupation of the M–M e_g orbitals, and hence the adoption of a 23-electron count, to become favourable in $[Cr_6Sb_8Sn_8F_2]^{5-}$.

Evidence for the weaker M–E π interactions can be seen in the experimental Cr–Cr and Cr– E_{fac} bond lengths of $[Cr_6Sb_8Sn_8(en)_2]^{3-}$ and $Cr_6E_8(PEt_3)_6$ species, displayed in table 3.4. The Cr– E_{fac} lengths of $[Cr_6Sb_8Sn_8(en)_2]^{3-}$ are markedly longer than those of $Cr_6Te_8(CO)_6$, despite the E_{fac} species of the two compounds being adjacent on the periodic table. Given that the $[Cr_6Sb_8Sn_8(en)_2]^{3-}$ and $Cr_6E_8L_6$ compounds also exhibit equivalent sets of M–E σ interactions, the longer Cr– E_{fac} bond lengths of

[†]Not including the 5s orbitals of Sn and Sb nor the orbitals of F^- not involved in σ donation.

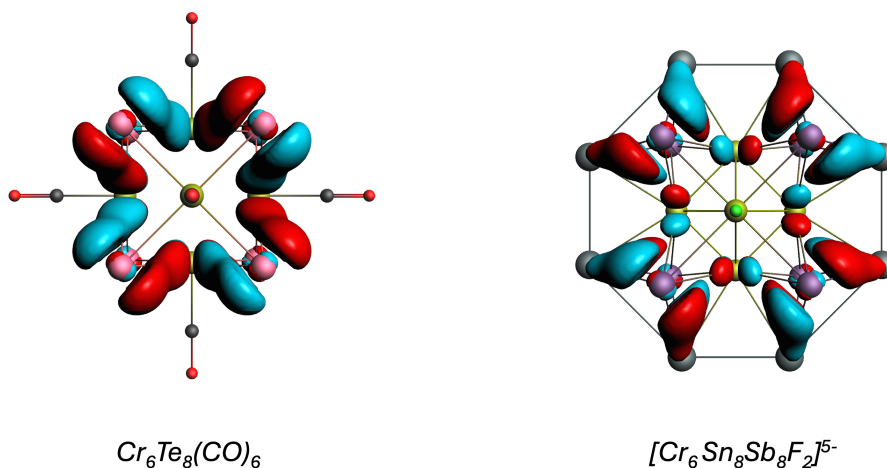


Figure 3.7: A member of the e_u M–E π bonding orbitals in $\text{Cr}_6\text{Te}_8(\text{CO})_6$ and its equivalent in $[\text{Cr}_6\text{Sn}_8\text{Sb}_8\text{F}_2]^{5-}$, illustrating the reduction in orbital amplitude between in the M and E species in the latter compound. Isosurfaces are at a value of 0.03.

$[\text{Cr}_6\text{Sb}_8\text{Sn}_8(\text{en})_2]^{3-}$ support the hypothesis that this compound features weaker M–E π interactions. Additionally, the Cr–Cr bonds are significantly shorter in $[\text{Cr}_6\text{Sb}_8\text{Sn}_8(\text{en})_2]^{3-}$ than in any of the $\text{Cr}_6\text{E}_8\text{L}_6$ compounds, in line with the hypothesis that additional M–M bonding orbitals are populated in $[\text{Cr}_6\text{Sb}_8\text{Sn}_8(\text{en})_2]^{3-}$.

Compound	Cr–Cr	Cr–E _{fac}	ref.
$[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$	2.45–2.49	2.73–2.79	127
$\text{Cr}_6\text{S}_8(\text{PEt}_3)_6$	2.59–2.60	2.33–2.35	134
$\text{Cr}_6\text{Se}_8(\text{PEt}_3)_6$	2.67–2.71	2.43–2.45	134
$\text{Cr}_6\text{Te}_8(\text{PEt}_3)_6$	2.82–2.86	2.65–2.67	134

Table 3.4: Selected experimental bond lengths of Cr_6 species. All bond lengths are in Å.

In summary, it appears that the cyclic Sn_8Sb_8 ligand in $[\text{Cr}_6\text{Sb}_8\text{Sn}_8(\text{en})_2]^{3-}$ reduces the π donor strength at the E_{fac} sites in comparison to $\text{Cr}_6\text{E}_8\text{L}_6$ species and causes a 23-electron Cr_6 cluster to become favourable in $[\text{Cr}_6\text{Sb}_8\text{Sn}_8(\text{en})_2]^{3-}$. Furthermore, the occupation of the Kohn-Sham MOs suggests that $[\text{Cr}_6\text{Sb}_8\text{Sn}_8(\text{en})_2]^{3-}$ can be assigned the formal charges $[(\text{Cr}_6)^{13+}(\text{Sb}_8\text{Sn}_8)^{16-}(\text{en})_2]^{3-}$. This means that, alongside the near-electron-precise count of $(\text{Cr}_6)^{13+}$, the $(\text{Sb}_8\text{Sn}_8)^{16-}$ fragment may be considered electron-precise with respect to the bonds shown on the cage in figure 3.2. Therefore,

$[\text{Cr}_6\text{Sb}_8\text{Sn}_8(\text{en})_2]^{3-}$ can be largely understood in terms of an electron-precise bonding model. It may also be noted that, prior to the synthesis of $[\text{Cr}_6\text{Sb}_8\text{Sn}_8(\text{en})_2]^{3-}$, researchers had commented on the lack of a 24-electron Cr_6 cluster and speculated its existence.^{132,133} To the best of this researcher's knowledge, $[\text{Cr}_6\text{Sb}_8\text{Sn}_8(\text{en})_2]^{3-}$ provides the first instance of a Cr_6 cluster which occupies all 12 M–M bonding orbitals expected of a 24-electron cluster and is associated with an electron count greater than 20.

3.5 Conclusion

Through modelling of XRD and EPR empirical data using KS-DFT, it is concluded that the newly synthesised $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ adopts a doublet spin state with its radical localised to the central Cr_6 motif. Furthermore, it could not be inferred from the experimental data whether crystallographic sites in the compound's equatorial plane and sites at the faces of the Cr_6 octahedron were occupied by Sn or Sb atoms. The KS-DFT model was therefore used to establish that the Sn atoms occupy the crystallographic sites in the equatorial plane of the compound while the Sb atoms occupy the sites at the faces of the Cr_6 octahedron.

Additionally, the bonding in $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ was characterised and it was argued that the structure of the compound can be largely understood in terms of an electron-precise bonding model. The Sb_8Sn_8 cage adopts an electron-precise count and the Cr_6 octahedron is associated with an electron count one short of that required for an electron-precise count. Such a near-electron-precise count is unprecedented for Cr_6 clusters given that the previously observed Cr_6 clusters are from the $\text{M}_6\text{E}_8\text{L}_6$ series where they adopt an electron-deficient count of 20. The larger electron count in $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ was suggested to be driven by the compound's weaker π donor strength in the E_{fac} positions, which provides insight into what causes octahedral M_6 fragments in intermetalloid clusters to adhere to electron-precise or electron-deficient bonding models.

Chapter 4

A Coupled-Cluster Investigation into the Relative Stability of Isoelectronic M@Si₁₄ Compounds

4.1 Introduction

Endohedral intermetalloid clusters comprised of a cage fragment and a single interstitial transition metal atom serve as useful systems for understanding the stabilising interactions in intermetalloid cluster compounds. One advantage of studying these endohedral clusters is that the single metal atom can be varied within a cage structure to establish relationships between the properties of the metal atom and the properties of the cage. The underlying cause for said relationships can often be inferred from theoretical data, which may lead to insights into how bonding models can be developed for the compounds. For example, by collecting together structures with the same number of cage atoms and a single interstitial metal, authors were able to identify⁶² that the structures of a series of $[M@E_{12}]^q$ ($M/E/q = \text{Au/Pb/3-}, \text{Ni/Pb/2-}, \text{Co/Ge/3-}, \text{Mn/Pb/3-}$) clusters could be explained as distortions from an icosahedral geometry, where the distortions are driven by the ability of the interstitial metal to donate electron density to the four-fold degenerate LUMO of a perfectly icosahedral cage. A notable series of intermetalloid clusters with a single interstitial atom is the isoelectronic series $[M@Si_{14}]^q$ ($M = \text{Ti-Fe}, q = Z_M - 24$).[†] Interestingly, the electron count of the Si_{14} cage remains constant across this series, yet the global minimum of the compounds changes when later transition metals are the interstitial atom. The change in global minimum is particularly significant in this series since the global minimum of the compounds featuring earlier transition metals present is described by a different bonding model to the global minimum of compounds featuring later transition metals, meaning the minima in the series cannot all be understood as distortion from a parent structure, as was the case for the aforementioned $[M@E_{12}]^q$ compounds. While it is known the global minimum of the $M@Si_{14}$ series changes when later transition metals are the interstitial atom, it is not known for which metal exactly the global minimum changes. As such, the goal of the present study is to develop a methodology using electronic structure methods capable of determining the global minima of the $M@Si_{14}$ series. Before reviewing the possible approaches to this problem, the interactions underpinning the different global

[†] Z_M – Atomic number of the metal atom.

minima of the compounds and the available experimental data are summarised.

In the motivating study for the present work, it is demonstrated that the global minima of the $M@Si_{14}$ series are determined by the extent to which the metal d-orbitals are able to interact with the Si_{14} cage.⁵⁰ In particular, a structure referred to as an arachno structure, shown on the left in figure 4.1, is the global minimum when an early transition metal is the interstitial element and their d-orbitals are able to form a significant interaction with the cage. However, when later transition metals are present, the nuclear charge of the metal becomes more positive and hence the d-orbitals of the metal are more contracted. In principle, this contraction reduces the ability of the d-orbitals to interact with the cage, and indeed, a higher nuclear charge at the metal correlates with a destabilisation of the arachno isomer. As the interstitial transition metal becomes later, a fullerene-like structure, shown on the right of figure 4.1, eventually becomes the global minimum. The fullerene-like (henceforth referred to as just “fullerene”) structure also becomes less stable as the contraction of the d-orbitals increases but not as greatly as the arachno structure. This trend has been explained in terms of the Kohn-Sham orbitals of each compound.⁵⁰ The stability of the arachno isomer is related to three of its orbitals which feature both M–Si and Si–Si bonding interactions. To be both M–Si and Si–Si bonding, the d-orbitals need to be able to delocalise onto the cage. Therefore, it may be expected that the stability of the arachno isomer is strongly related to the ability of its metal’s d-electrons to delocalise onto the Si_{14} cage. Consequently, it would also be expected that the arachno isomer is most stable when earlier transition metals are present. The fullerene isomer features a back-bonding interaction between its metal and the Si_{14} cage. The back-bonding strengthens the M–Si interaction at the expense of donating electron density to Si–Si π^* antibonding orbitals and therefore weakening Si–Si π interactions. The trend in the fullerene isomer’s stability with respect to the identity of the metal atom can hence be rationalised: as the interstitial metal becomes later, its d-orbitals become more contracted and both the M–Si bonding interaction and the Si–Si antibonding interactions weaken. The competing destabilisation from weakening the M–Si bonding interaction and stabilisation from weakening the Si–Si antibonding interactions leads to

the fullerene isomer destabilising more slowly than the arachno isomer as the transition metal becomes later.

The relationship between the ability of the metal d-electrons to interact with the Si_{14} cage and the global minima of the M@Si_{14} species was established using KS-DFT and, while the relationship is observed across multiple functionals, some functionals differ on the point in the series where the fullerene structure becomes the global minimum. Going from early to late transition metals, the PBE functional calculates the arachno isomer to be the most stable until $[\text{Mn@Si}_{14}]^+$ where it calculates the fullerene isomer to be marginally more stable. In contrast, the B3LYP functional only calculates the arachno structure to be the global minimum for $[\text{Ti@Si}_{14}]^{2-}$ and computes the fullerene isomer as the global minimum in the rest of the series.

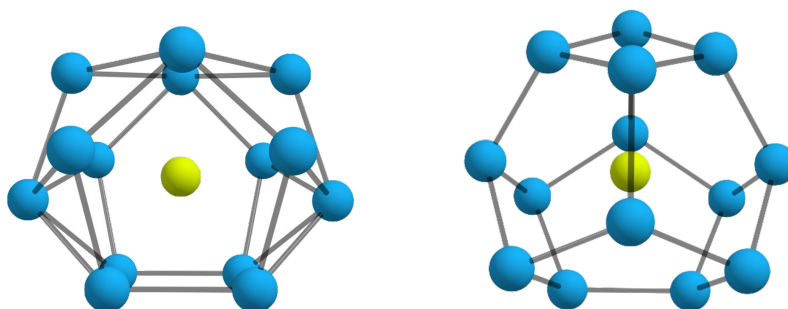


Figure 4.1: The geometries of the arachno (left) and fullerene-like (right) isomers of the M@Si_{14} , exemplified in the Cr@Si_{14} system.

Clearly, the PBE and B3LYP functionals vary in their models of the interaction between the metal d-electrons and the silicon cage. The qualitative difference in the functional's calculations of the global minima in the series suggests that one or both of the functionals is demonstrating unphysical behaviour. As such, there is a need to develop a methodology which can resolve this discrepancy to show which isomer is the global minimum for the two compounds. Furthermore, such a methodology may also indicate the origin of any unphysical behaviour produced by either functional and hence provide useful information about which intermetaloid clusters the functionals are suited to modelling. As stated previously, the goal of the present chapter is to establish a method capable of determining the global minima in the M@Si_{14} series and in particular, the

present investigation focuses on determining the global minima of the Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$ clusters.

In establishing a methodology, any indication of which of the two functionals is qualitatively correct in their prediction of the global minima of Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$ is useful to know. Without a rigorous hierarchy of DFT functionals, neither PBE nor B3LYP can be shown to be more accurate and as such information from other sources is sought. One such source is experimental data. Unambiguous structural data from experiment is elusive for endohedral silicon clusters since these have been primarily synthesised in the gas phase.^{153–155} Nonetheless, Infra-red multi-photon dissociation (IR-MPD) experiments have been performed on $[\text{Mn@Si}_{14}]^+$, which indicate that the fullerene isomer and a bicapped hexagonal prism structure are plausible global minima within the ambiguity of the experiment.¹⁵⁶ Although, no results for the arachno geometry were reported in the study. Experimental data has also been reported for Cr@Si_{14} . The photoelectron spectrum of the reduced version of the compound, $[\text{Cr@Si}_{14}]^-$, has been measured and compared with results from DFT in two studies.^{157,158} Both studies found functionals which favour the arachno isomer (PBE and BP86) gave the closest agreement with experiment, though the one of the studies notes that results from the B3LYP functional are also in agreement.¹⁵⁷ In both cases, the simulated spectra of the arachno and fullerene isomers of $[\text{Cr@Si}_{14}]^-$ appeared to be consistent with experiment and hence neither study provides a basis to remove either isomer from consideration. Overall, the experimental data is limited for both compounds and it remains plausible that either the arachno or the fullerene structure could be the global minimum of either Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$.

It may also be noted that a number of authors have either stated that the global minimum of Cr@Si_{14} is the arachno isomer or that functionals favouring the arachno isomer such as PBE or BP86 are suitable for this cluster.^{58,157–159} While these claims may turn out to be true, their supporting evidence retains some limitations. For example, one study argues for the use of PBE based on the experimental agreement it obtains for other Cr@Si_n compounds⁵⁸ and does not report results from alternative functionals. Another

study¹⁵⁷ cites an investigation¹⁶⁰ showing PBE gives results consistent with experimental electron detachment energies for a number of MSi_n compounds, not including Cr@Si_{14} . These bases for functional choice are not unreasonable and there appears to be a level of agreement among researchers on the global minimum of Cr@Si_{14} . However, the rationales for this conclusion lack data from functionals which favour the fullerene isomer and therefore do not formally rule out the fullerene isomer as a plausible global minimum of Cr@Si_{14} . Thus, the present study errs on the side of caution and does not use the consensus in the literature as a basis to treat the arachno isomer as the true global minimum of Cr@Si_{14} .

A route to determining the global minima of Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$ without experimental validation might be found in wavefunction methods. As may be seen from the discussion in chapters one and two, wavefunction methods are based entirely on physical principle and consequently the performance of their models can often be rationalised and information can be gained about the confidence that should be placed in the results from a given method. The most significant considerations when employing wavefunction methods are the treatment of static and dynamic correlation, and the computational cost of the calculation. The degree of static and dynamic correlation in a system cannot be known *a priori*, and thus one should consider multiple methods which vary in their capability of modelling either form of correlation.

One might consider a method such as CASPT2 which is primarily suited to modelling static correlation and contains a perturbative correction to capture dynamic correlation. Indeed, CASPT2 has been applied to the fullerene geometry of $[\text{Mn@Si}_{14}]^+$ previously using a (14,15) active space.¹⁶¹ However, it may not be possible to perform a comparable calculation for the arachno isomer. The electronic structures of the arachno and fullerene isomers are significantly different and it is possible that an active space that leads to results comparable between the two compounds would need to include all valence orbitals and electrons, meaning a (64,64) active space. This is much larger than the largest CASSCF active space on record, (20,20),¹¹ and is also likely out of the range to which variants such as GASSCF and RASSCF could extend. It is possible that

alternative methods such as DMRG could approach the necessary size of active space but such methods would require a large amount of computational resource to do so.¹⁶²

Additionally, DMRG may not be able to accurately model large amounts of dynamic correlation, though methods have been proposed to mitigate this issue.¹⁶³

Single-reference wavefunction methods may also be considered for determining the global minima of Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$. As discussed in the introductory chapter, coupled-cluster methods are considered the gold standard for modelling dynamic correlation and have been shown to tolerate moderate amounts of multi-reference character in a system.¹⁶⁴ Additionally, a sizeable amount of research has gone into developing multi-reference character diagnostics for coupled-cluster theory, which aid in determining if a system is suited to being modelled with single-reference wavefunction methods. Therefore, if the isomers of Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$ contain small to moderate amounts of static correlation, it may be expected that the most accurate results will be obtained from coupled-cluster methods. In principle, both multi-reference and single-reference wavefunction methods may provide insight into how the global minima in the M@Si_{14} series can be determined. The present study focuses on the role of dynamic correlation and applies coupled-cluster calculations to Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$. In particular CCSD(T) and its equivalent in Brueckner coupled-cluster theory, BCCD(T), are used. These methods differ in the reference state they employ and hence their comparison may provide insight into whether single-reference methods are suitable for the M@Si_{14} systems.

4.2 Methodology

Due to the high cost of performing coupled-cluster calculations on the systems of interest, geometry optimisations are not performed using coupled-cluster methods. Instead, all the geometries used in the present study were those previously obtained

using KS-DFT with the PBE functional[†] in the motivating study for this work,⁵⁰ all of which were local minima. All calculations reported in the present study are single point coupled-cluster calculations performed at these DFT-optimised geometries. Of course, the choice to use the geometries obtained with the PBE functional is arbitrary and as such the sensitivity of the calculations to the geometry used is also investigated by performing single point coupled-cluster calculations at the geometries obtained with the B3LYP functional, the results of which are reported in section 4.3.3. Additionally note that, except when indicated otherwise, calculations are performed in the C_{2v} point group for both the arachno and fullerene isomers.

There are various factors (e.g. core-valence correlation, non-Born-Oppenheimer effects, relativity, etc.) that may impact an energy difference calculated for the arachno and fullerene isomers which may be accounted for in a coupled-cluster model. Most often, a coupled-cluster calculation quickly becomes intractable as the number of factors for which it accounts increases. However, the expense of including multiple factors in a model can be reduced with the use of a composite method. Composite methods involve performing a base calculation to account for a sub-set of factors and then the impact of additional factors is estimated via additive corrections. The additive corrections are found by subtracting the base calculation from a calculation which incorporates all the same factors as the base calculation as well as an additional factor. This difference isolates the impact the additional factor has on the energy and therefore can be considered a correction term. Both calculations used to find an additive correction are performed at a lower computational cost, most often by using a smaller basis set than employed for the base calculation. This reduction in computational cost makes calculations which incorporate factors in addition to those included in the base calculation feasible. A variety of composite methods have been established in the literature^{165–170} and are typically formulated as

$$E = E_{\text{CBS}} + \Delta E_{\text{CV}} + \Delta E_{\text{SR}} + \Delta E_{\text{SO}} + \Delta E_{\text{ZPVE}} + \Delta E_{\text{DBOC}}. \quad (4.1)$$

[†]Using the ADF program and TZP Slater-type basis sets for Cr and Mn, and DZP Slater-type basis for the silicon atoms.

The terms in scheme (4.1) are defined as the following:

- E_{CBS} — The complete basis set (CBS) limit of a calculation including the valence correlation energy.
- ΔE_{CV} — Correction for the correlation of core electrons. Often referred to as the core-valence correlation correction since this is typically the dominant effect but does also include core-core correlation.
- ΔE_{SR} — Correction for scalar relativistic effects.
- ΔE_{SO} — Correction for spin-orbit coupling.
- ΔE_{ZPVE} — Correction for zero-point vibrational energy.
- ΔE_{DBOC} — Diagonal Born-Oppenheimer Correction.

The study presented in the current chapter employs a truncated version of scheme (4.1) since the size of the systems of interest prohibits the calculation of all of the scheme's terms. Thus, the three terms most often recognised as being the largest, E_{CBS} , ΔE_{CV} , and ΔE_{SR} ,¹⁶⁵ are computed. Notably, these are also all the factors accounted for in the KS-DFT calculations from the motivating study.⁵⁰ The employed scheme is therefore written

$$E = E_{\text{CBS}} + \Delta E_{\text{CV}} + \Delta E_{\text{SR}}. \quad (4.2)$$

Since coupled-cluster methods are used to calculate all the terms in scheme 4.2, the composite method used bears some similarities to existing schemes in the literature^{165,170} but does differ in places and hence the level of accuracy reported for these schemes cannot be claimed for the calculations reported in the present study. The details about how each term was calculated can be found in subsections 4.2.2–4.2.4 of the present section.

The present investigation uses a development copy of TURBOMOLE version 7.6 to perform all the reported calculations. Initial CCSD(T)[†] calculations showed large t_1

[†]CCSD(T)/cc-pVTZ with a [Ne] frozen core for Si and [Ne]3s² for the metal.

amplitudes for both isomers of Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$. This is sometimes taken as an indication of multi-reference character, most notably with the use of the popular T_1 diagnostic.¹⁷¹ However, since single excitations are equivalent to orbital rotations in the reference state, large t_1 amplitudes do not necessarily imply multi-reference character. To further investigate the large rotations, Brueckner coupled-cluster (BCC) calculations are used in addition to the canonical CCSD(T) to eliminate the t_1 amplitudes and show the effect of a reference state with a T_1 diagnostic of zero on the energy difference. Hence, the composite scheme detailed in (4.2) is calculated for each isomer using both CCSD(T) and BCCD(T).

For any system, multiple coupled-cluster solutions exist and it is possible that a completed calculation does not produce the ground state of the system. For a CCSD(T) calculation, it might be assumed that using lowest energy HF solution as the reference state will also result in the lowest energy coupled-cluster solution, however this is not always true.¹⁷² Indeed, there are cases encountered in the current chapter where using excited HF solutions as the reference state results in a lower coupled-cluster energy (see section 4.3.2). This shows it is necessary for the current study to probe for multiple coupled-cluster solutions in each system of interest. Evidently, this can be done by varying the reference state but it should also be noted that there is not a 1:1 mapping from reference states to coupled-cluster solutions¹⁷³ i.e. the same reference state can result in different coupled-cluster solutions depending on the initial amplitudes used in the calculation. This illustrates that the initial guess t_1 and t_2 amplitudes may also need to be varied to find all coupled-cluster solutions of interest. However, as with most electronic structure programs, TURBOMOLE offers no control over the initial guess amplitudes used in a coupled-cluster calculation. Moreover, how to vary the amplitudes in a practical manner to probe for solutions is not a well-established procedure. Hence the present study limits probing for different coupled-cluster solutions to changing the reference state only. It may also be noted that all truncated coupled-cluster calculations exhibit an inherent dependence on their reference state¹⁷⁴ and therefore if a difference is found between the energies calculated when using different reference states, this does

not necessarily imply a different coupled-cluster solution has been found.

To investigate multiple HF solutions for use as different reference states in CCSD(T) calculations, the various options for initial guess orbitals available in TURBOMOLE are trialled. The options are either extended Hückel theory orbitals or the orbitals from a core Hamiltonian calculation. These initial guesses led to two HF solutions being found for every system considered in the present study. The composite scheme in equation (4.2) was calculated in full for each of these reference states using CCSD(T).

Additionally, scheme (4.2) was calculated using each HF state as the initial state for BCCD(T) calculations. As discussed in chapter two, BCCD(T) calculations change the reference state to ensure that $t_1 = 0$, and therefore do not retain the initial reference state input into the calculation as CCSD(T) does. However, it is possible a system admits multiple BCCD(T) solutions,^{172,175} hence utilising multiple HF solutions as the initial states serves as a means for varying the initial conditions in a BCCD(T) calculation to investigate the possibility of multiple BCCD(T) solutions. One of the HF solutions found for the fullerene isomer of Cr@Si₁₄ was 275 kcal · mol⁻¹ higher in energy than the other HF solution found for this system and did not produce a converged CCSD(T) calculation when used as a reference state. This HF solution was therefore omitted from the present study. All of the remaining HF solutions found for a given isomer had the same number of MOs transforming as each irreducible representation of the C_{2v} point group. As such, the HF solutions are labelled according to their HOMO–LUMO gap in eV.

4.2.1 Computational Details

As previously mentioned, all calculations reported in the present chapter were performed using a development copy of TURBOMOLE version 7.6. Additionally, all calculations in the present chapter used correlation consistent basis sets. These are referred to by the abbreviation ccXZ for cc-pVXZ where X is the cardinality of the basis. In the case of augmented correlation consistent basis sets, the abbreviation a-ccXZ denotes aug-cc-pVXZ when referring to chromium or manganese, and aug-cc-pV(X+d)Z when

referring to silicon.

TURBOMOLE allows for canonical and Brueckner coupled-cluster calculations to be performed in abelian point groups. The highest symmetry abelian point group for both the arachno and fullerene isomer is C_{2v} , hence all conventional CCSD(T) and BCCD(T) calculations are performed in C_{2v} symmetry. Explicit correlation^{120,176,177} is also used in this study which does not permit the use of symmetry and hence all explicitly correlated calculations are performed in the C_1 point group.

Coupled-cluster calculations in TURBOMOLE are performed using the resolution of the identity (RI) approximation¹⁷⁸ and therefore use auxiliary basis sets. Calculations without explicit correlation used the RI auxiliary bases synonymous with those used for the orbital sets. Calculations with explicit correlation used the (a-)ccQZ RI basis set for all elements. Explicitly correlated calculations also employed a complementary auxiliary basis set (CABS) and a RI-JK auxiliary set.¹⁷⁹ For all elements, the (a-)ccTZ RI auxiliary basis sets were used as the CABS. The RI-JK bases used for silicon are the ccQZ and a-ccQZ bases. Note a RI-JK aug-cc-pV(Q+d)Z basis set was not available for silicon so the RI-JK aug-cc-pVQZ set was used instead. The RI-JK def2-QZVPD is used for chromium and manganese since no options were available from the correlation consistent basis set family.

Lastly, TURBOMOLE offers a level shift which can be applied to the eigenvalues of the Fock-like matrix¹⁷⁷ from which the Brueckner orbitals are determined. For all Brueckner calculations (both with and without explicit correlation) reported in the present study, a level shift of 0.7 was applied to aid in convergence to the solutions of the BCCD equations.

4.2.2 The CBS Limit of the Total Energy Including Valence Correlation

The base energy used in scheme (4.2) is an estimation of the CBS limit of the total energy where only the valence electrons are correlated, E_{CBS} . For all systems, the valence shell is chosen to include the 3d and 3p electrons of the metal atom and the 3s and 3p of silicon atoms. The remaining electrons are not included in the correlation treatment when calculating E_{CBS} and thus are treated as the frozen core of the system. There is not a single commonly accepted method for estimating E_{CBS} documented in the literature. The two most common approaches are extrapolation methods and explicit correlation methods. Both have been shown to be effective in providing estimations of E_{CBS} but are formulated on different bases and therefore show a degree of variation in their estimates. Neither method can be shown to provide more accurate estimates and therefore both are used in the present study to provide a rough knowledge of the error in their estimations.

Extrapolation methods are based on the idea that the total energy follows a certain monotonic convergence to the CBS limit when particular basis sets are used. It has been shown that the reference and correlation energies converge at different rates to their respective CBS limits and as such different extrapolation formulae exist for the two energies. In the present study, the convergence expression⁹⁸

$$E^{\text{ref}}(X) = E_{\text{CBS}}^{\text{ref}} + Ae^{-\alpha\sqrt{X}} \quad (4.3)$$

is used, in which $E^{\text{ref}}(X)$ is the reference energy at basis set cardinality X , $E_{\text{CBS}}^{\text{ref}}$ is the reference energy at the CBS limit, A is a constant, and the parameter in the exponent is selected to be $\alpha = 5.04$, in accordance with reported data for correlation consistent basis sets.¹⁸⁰ The convergence of the reference energy shown in equation (4.3) is used alongside the model behaviour

$$E^{\text{corr}}(X) = E_{\text{CBS}}^{\text{corr}} + BX^{-3}, \quad (4.4)$$

suggested for the correlation energy in correlation consistent basis sets,¹⁸¹ in which $E^{\text{corr}}(X)$ is the correlation energy at basis set cardinality X , $E_{\text{CBS}}^{\text{corr}}$ is the correlation energy at the CBS limit, and B is a constant. Alternative formulae are documented in the literature^{182,183} though there is no single one accepted as the standard. The present study employs two-point extrapolations to determine the CBS energies in formulae (4.3) and (4.4). In particular, extrapolations employing triple- and quadruple-zeta basis sets are used, the results from which are denoted (a-)cc(T,Q)Z.

As discussed in section 2.9 and unlike extrapolation methods, explicitly correlated methods are based on the idea that the rate of convergence to the CBS limit can be increased by including terms with an explicit dependence on the interelectronic distance in the wavefunction *ansatz*. In theory, explicitly correlated coupled-cluster methods converge to the CBS limit at a rate of¹⁸⁴ X^{-7} and the implementations used in practice achieve results with an accuracy of roughly 1-2 cardinal numbers higher than a regular coupled-cluster calculation in the same basis.¹¹⁹ Due to their accelerated convergence, explicitly correlated coupled-cluster calculations see use as a CBS limit approximation. The present study uses the CCSD(F12*)(T) and BCCD_(F12*)(T) implementations of explicitly correlated coupled-cluster theory. The BCCD_(F12*)(T) method¹⁷⁷ employs the same approximations as CCSD(F12*)(T) (discussed in section 2.9) but only treats the Brueckner orbitals with explicit correlation once they have converged through the regular BCCD algorithm. This avoids the high cost of re-evaluating the additional integrals needed for explicit correlation at each iteration of the BCCD algorithm. BCCD_(F12*)(T) has been shown to give accurate results. For example, it was able to calculate electron affinities and ionisation energies of first row transition metals and small organic molecules to within 1 kcal · mol⁻¹ of experimental values, demonstrating similar performance to CCSD(F12*)(T).¹⁷⁷

A degree of confidence can be associated with cases where E_{CBS} values from explicitly correlated and extrapolated methods agree since the two methods have different sources of error, making it less likely that they would agree unless both methods are providing accurate results. The error in extrapolated methods is due to the true convergence of a

particular system’s energy to E_{CBS} deviating from the employed model convergence. In contrast, the error in explicitly correlated methods is due to basis set incompleteness and the approximations used in the implementation of explicit correlation. To aid further in estimating the error in calculated values of E_{CBS} , both augmented and non-augmented basis sets are trialled in the two CBS limit estimation methods. The augmented basis sets are larger than their non-augmented counterparts though, as detailed in section 2.4, the coupled-cluster equations are not solved variationally and therefore it cannot be said rigorously that lower energy results (most often obtained from larger basis sets) are closer to the CBS limit. Therefore, the variation with basis set can also be incorporated into the estimation of the error of each E_{CBS} method. The results of all testing to establish a method for estimating E_{CBS} are reported in section 4.3.1.

4.2.3 Correction for the Correlation of Core Electrons

The correction for the correlation of core electrons is calculated from the equation

$$\Delta E_{\text{CV}} = E_{\text{cc-pwCVTZ, 3s2p correlated}} - E_{\text{cc-pVTZ, valence only}}. \quad (4.5)$$

Expression (4.5) corrects for the energy change due to the correlation of the Si 2p and Cr 3s electrons in addition to the valence electrons. The scaling of the computational cost of coupled-cluster methods means that the cc-pwCVTZ set is the largest affordable basis set for the ΔE_{CV} correction. This computational expense also means that no core electrons in addition to the Si 2p and Cr 3s electrons, such as the Si 2s electrons, may be correlated. Because correction (4.5) is determined with respect to a calculation in the cc-pVTZ basis, the correction is also influenced by calculating the valence orbitals and their correlation in the cc-pwCVTZ basis rather than the cc-pVTZ basis. This influence is expected to be small in comparison to the size of the correction and there are examples of established composite methods defining ΔE_{CV} corrections with respect to valence-correlated calculations in both core-correlated and valence-only basis sets.^{165,170}

4.2.4 Correction for Scalar Relativistic Effects

There are various corrections available for the scalar relativistic effects, some of the most common schemes can be related to each other formally¹⁸⁵ and no single method has been established as the standard. In the present study, the X2C Hamiltonian¹⁸⁶ is used. It has been noted that the ΔE_{SR} correction is rarely sensitive to basis set size or the level of theory used,¹⁶⁵ hence the relativistically adapted and triple-zeta-quality cc-pVTZ-DK basis set is used. The correction is defined as

$$\Delta E_{\text{SR}} = E_{\text{CCSD(T)/ccTZ-DK}} - E_{\text{CCSD(T)/ccTZ}}.$$

The X2C Hamiltonian changes the one-electron contribution to the molecular Hamiltonian and so is applied to both the HF reference state calculations as well as the valence correlation in the coupled-cluster calculations. Thus, the correction is the energy change due to the use of the X2C Hamiltonian on all electrons, with the valence electrons being correlated.

The use of the X2C Hamiltonian makes a large difference to the energy of the reference states and hence leads to changes in the HOMO–LUMO gaps. For clarity, the relativistic reference states used in each calculation of scheme (4.2) are still labelled according to their non-relativistic counterparts’ HOMO–LUMO gaps. The relativistic reference state used in each calculation of scheme (4.2) is confirmed to be equivalent to the reference state used for all other contributions to scheme (4.2) by inspection of the orbitals. In all cases except those of the $[\text{Mn@Si}_{14}]^+$ fullerene isomer, the orbitals of the non-relativistic reference state are used as the initial guess orbitals in a X2C HF calculation to obtain the state’s relativistic counterpart. In the cases of the $[\text{Mn@Si}_{14}]^+$ fullerene isomer, the relativistic version of one of its reference states, labelled the 5.1 eV state, was obtained by using the non-relativistic orbitals of its other reference state, labelled the 4.7 eV state, as the initial guess orbitals in the X2C HF calculation. The relativistic orbitals obtained from using the orbitals of the non-relativistic 5.1 eV state as the initial guess orbitals in a X2C HF calculation bear the most resemblance to the orbitals of the 4.7 eV state, but

some visible differences are present in some of the orbitals. Therefore, the relativistic reference state obtained from the 5.1 eV state's initial guess is tentatively assigned to the 4.7 eV state but the observed differences are noted in the reported results.

4.3 Results and Discussion

4.3.1 Estimation of E_{CBS}

The current section aims to establish a method for estimating E_{CBS} which may be applied to all of the systems considered in the present study. The current section also aims to estimate the error associated with the E_{CBS} approximations. It is expected that an estimate of E_{CBS} will vary with both the estimation method and the electronic structure of the system. Hence, to establish the E_{CBS} estimation method and an approximation of its error, explicitly correlated and extrapolated methods are used to calculate the isomer energy difference of Cr@Si_{14} . The isomer energy difference is calculated for each reference state of the compound's isomers to test how the error changes when different electronic structures are present. The established method of estimating E_{CBS} is assumed to give similar accuracy for the calculations performed on the $[\text{Mn@Si}_{14}]^+$ systems and is used for their study.

The E_{CBS} estimations found for the Cr@Si_{14} systems are presented in table 4.1. The two HF solutions found for the arachno isomer of Cr@Si_{14} are labelled as the 5.5 eV state and the 6.2 eV state in accordance with their HOMO–LUMO gaps. Note that 6.2 eV state solution had a HF energy $8.26 \text{ kcal} \cdot \text{mol}^{-1}$ lower than that of the 5.5 eV state. However, when used as CCSD(T) reference states, the 5.5 eV state produces lower energy E_{CBS} estimations than the 6.2 eV state. As mentioned in section 4.2, only one of the HF reference states of the fullerene isomer of Cr@Si_{14} produced a converged CCSD(T) calculation. This is labelled the 5.1 eV state and only results using this reference state are reported for the fullerene isomer in table 4.1.

		CCSD(T)		CCSD(F12*)(T)	
		cc(T,Q)Z	a-cc(T,Q)Z	ccTZ	a-ccTZ
Fullerene	5.1 eV	0	0	0	0
Arachno	5.5 eV	-2.71	-3.11	-2.12	-3.30
	6.2 eV	-0.94	-1.35	-2.10	-3.00

Table 4.1: The relative values of E_{CBS} estimations obtained from each reference state found for Cr@Si_{14} . The E_{CBS} values are relative to those obtained from the fullerene 5.1 eV reference state. All energies are in $\text{kcal}\cdot\text{mol}^{-1}$.

Firstly, when using the 5.5 eV reference state, the range of values found with the extrapolated calculations is contained within the larger range of values found with the CCSD(F12*)(T) method. The E_{CBS} estimations from the 5.5 eV state are therefore in agreement and hence a level of confidence may be associated with the possibility that the true CBS limit is within the total range of results found from the extrapolated and explicitly correlated methods. Conversely, when using the 6.2 eV reference state, the range of values obtained with each E_{CBS} method do not overlap at all. The lack of overlap implies the E_{CBS} methods are in disagreement rather than there being any discrepancy as a result of the basis sets. It might be argued that the disagreement among the methods therefore needs to be factored into the estimation of the error the E_{CBS} results, however it is also notable that the CCSD(F12*)(T) results from the 6.2 eV state are near-coincident with those from the 5.5 eV state. This could be nothing more than a coincidence and the different electronic structure calculated using the 6.2 eV state results in a greater disagreement between the methods than seen for the electronic structure calculated using the 5.5 eV state. Alternatively, the near-coincident results could be due to the 6.2 eV reference state converging to the same coupled-cluster solution found for the 5.5 eV state when using CCSD(F12*)(T). In principle this is possible. It has been demonstrated previously that coupled-cluster calculations using the same reference state can converge to different solutions to the CCSD equations.¹⁷³ Hence the 6.2 eV reference state may have converged to the 5.5 eV solution when used with CCSD(F12*)(T) but to a different solution when used with the extrapolated method.

It is not well-established how to characterise a coupled-cluster solution, though in some cases it is possible to use contextual information to differentiate between solutions.¹⁷³ In this case, few contextual clues are available besides the coincidence of the E_{CBS} estimations so the cause of disagreement between the extrapolated and explicitly correlated results when using the 6.2 eV reference state cannot be demonstrated from this data. The present study therefore chooses to use the results from the 5.5 eV state to estimate the error in the E_{CBS} approximations. Note also that, in the event the disagreement in the E_{CBS} results obtained with 6.2 eV state is due to the uncertainties in the E_{CBS} estimations, the error in the E_{CBS} would be $2.06 \text{ kcal} \cdot \text{mol}^{-1}$. It is seen later in the present study that even if the error is this large, the conclusions of the present investigation do not change.

As previously mentioned, the agreement in the results from the extrapolated and explicitly correlated methods when using the 5.5 eV state provides a degree of confidence that the true E_{CBS} value is within (or at least close to) the range of results obtained by the two methods. It can also be argued that an additive scheme of CCSD(F12*)/(a-)ccTZ and (T)/(a-)ccQZ values achieves greater convergence than the 5.5 eV state's CCSD(F12*)(T) results. This argument is presented in section A2.1 and leads to a smaller range of -2.68 to $-3.52 \text{ kcal} \cdot \text{mol}^{-1}$, which notably still contains the range of results from the extrapolation method and therefore maintains the degree of confidence in the E_{CBS} value. Because of this degree of confidence, the value of E_{CBS} when using the 5.5 eV state can be reasonably approximated as the midpoint of the -2.68 to $-3.52 \text{ kcal} \cdot \text{mol}^{-1}$ range. Equally, the error in the result can be taken as this range, meaning the E_{CBS} contribution to the isomer energy difference could be approximated as $\Delta E_{\text{CBS}} = -3.10 \pm 0.42 \text{ kcal} \cdot \text{mol}^{-1}$.

The approach used to estimate ΔE_{CBS} with the 5.5 eV reference state required multiple calculations with a significant computational cost. As such, when finding E_{CBS} for all systems of interest to the present study, it is desirable to use a method with a lower computational cost that can achieve results close to the ΔE_{CBS} estimation. For the results using the 5.5 eV state, a suitable choice is CCSD(F12*)(T)/a-ccTZ which requires a

single calculation and gives a ΔE_{CBS} value only $0.2 \text{ kcal} \cdot \text{mol}^{-1}$ below the midpoint of the uncertainty. This is the method chosen to estimate E_{CBS} for all systems included in the present study.

For the Brueckner coupled-cluster calculations, the expense of quadruple-zeta bases is prohibitive, in part due to the need to calculate new integrals at every iteration of the algorithm used to solve the BCCD equations. Given the error demonstrated in the canonical coupled-cluster E_{CBS} calculations, it is expected the $\text{BCCD}_{(\text{F12}^*)}(\text{T})$ method will provide an adequate level of accuracy in estimating E_{CBS} . To investigate this briefly, $\text{BCCD}_{(\text{F12}^*)}(\text{T})$ calculations are performed in the ccTZ and a-ccTZ basis sets as was done for the $\text{CCSD}(\text{F12}^*)(\text{T})$ method. As discussed in section 4.2, it is possible to find multiple Brueckner coupled-cluster solutions and these are probed for by performing BCC calculations using all found HF reference states as initial reference states. The results of these calculations are displayed in table 4.2 and additional $\text{BCCD}(\text{T})$ computations in the ccTZ and a-ccTZ bases without explicit correlation are also presented for comparison.

		BCCD(T)		BCCD _(F12*) (T)	
		ccTZ	a-ccTZ	ccTZ	a-ccTZ
Fullerene	5.1 eV	0	0	0	0
Arachno	5.5 eV	-7.51	-9.36	-6.44	-6.92
	6.2 eV	-7.42	-9.24	-6.35	-6.67

Table 4.2: Relative values of E_{CBS} using $\text{BCCD}(\text{T})$ theory for each Cr@Si_{14} reference state. Energies are in $\text{kcal} \cdot \text{mol}^{-1}$.

Firstly, the two initial reference states give very similar results when the same method and basis set are used. It is therefore taken to be that the two initial reference states converge to the same BCC solution. Additionally, the calculations without explicit correlation vary by about $1.8 \text{ kcal} \cdot \text{mol}^{-1}$ with the basis set used, but when explicit correlation is used, the variation with basis set drops to under $0.5 \text{ kcal} \cdot \text{mol}^{-1}$. In contrast, the canonical coupled-cluster results maintained a roughly $1 \text{ kcal} \cdot \text{mol}^{-1}$

variation with basis set when explicit correlation was used. The smaller variation with basis set seen in the $\text{BCCD}_{(\text{F12}^*)}(\text{T})$ calculations may be taken as a rough indication that the $\text{BCCD}_{(\text{F12}^*)}(\text{T})$ results have reached a higher level of convergence than their $\text{CCSD}(\text{F12}^*)(\text{T})$ counterparts. Given that $\text{CCSD}(\text{F12}^*)(\text{T})$ is deemed to provide a E_{CBS} estimation of reasonable accuracy at a seemingly lower level of convergence, it is expected that the $\text{BCCD}_{(\text{F12}^*)}(\text{T})$ E_{CBS} estimations are achieving at least a similar level of accuracy to the $\pm 0.42 \text{ kcal} \cdot \text{mol}^{-1}$ uncertainty approximated for the canonical coupled-cluster calculations. It can be seen later in the chapter (e.g. section 4.3.5) that whether the $\text{BCCD}_{(\text{F12}^*)}(\text{T})/\text{ccTZ}$ or $\text{BCCD}_{(\text{F12}^*)}(\text{T})/\text{a-ccTZ}$ is chosen to provide the E_{CBS} estimations for all the systems in the present study does not make a difference to the study's conclusions. Therefore, the computationally cheaper $\text{BCCD}_{(\text{F12}^*)}(\text{T})/\text{ccTZ}$ is chosen to provide the estimations.

In conclusion, the $\text{CCSD}(\text{F12}^*)(\text{T})/\text{a-ccTZ}$ and $\text{BCCD}_{(\text{F12}^*)}(\text{T})/\text{ccTZ}$ methods are chosen to provide the E_{CBS} estimates for all systems in the present study. The error of both methods was approximated to be $\pm 0.42 \text{ kcal} \cdot \text{mol}^{-1}$. For the purposes of further analyses, this error is considered to be $\pm 0.5 \text{ kcal} \cdot \text{mol}^{-1}$ to reflect the approximate nature of the methods used to estimate this error.

4.3.2 Relative Energies of the Reference States

Composite scheme (4.2) is calculated for all HF reference states found for both isomers of the two compounds. The relative energies of the results found for each reference state for each contribution to the composite scheme are displayed in table 4.3. Since only one of the HF states found for the fullerene isomer of Cr@Si_{14} produced a converged $\text{CCSD}(\text{T})$ calculation, only the relative energies of the results found from HF states of the arachno isomer are included in table 4.3 for Cr@Si_{14} . Additionally note that the E_{CBS} result from the 6.2 eV HF state of the Cr@Si_{14} arachno isomer was obtained using the a-cc(T,Q)Z extrapolation method in light of ambiguity in the coupled-cluster solution found using explicitly correlated methods with this reference state, discussed in section

4.3.1.

		E_{CBS}	ΔE_{CV}	ΔE_{SR}	Total
CCSD(T)					
Cr@Si ₁₄ :					
Arachno	5.5 eV	0	0	0	0
	6.2 eV	+1.76 ^a	+8.34	-1.13	+8.97
[Mn@Si ₁₄] ⁺ :					
Arachno	5.5 eV	0	0	0	0
	5.1 eV	+1.24	-0.257	+0.168	+1.15
Fullerene	5.1 eV	0	0	0	0
	4.7 eV	+1.68	+0.106	+7.92 ^b	+9.71
BCCD(T)					
Cr@Si ₁₄ :					
Arachno	5.5 eV	0	0	0	0
	6.2 eV	+0.0889	-0.0747	-6.52 × 10 ⁻³	+0.157
[Mn@Si ₁₄] ⁺ :					
Arachno	5.5 eV	0	0	0	0
	5.1 eV	-5.43 × 10 ⁻³	-0.0416	+4.84 × 10 ⁻⁴	-9.11 × 10 ⁻³
Fullerene	5.1 eV	0	0	0	0
	4.7 eV	-0.137	+0.106	+0.298	+0.267

^aResult obtained with a-cc(T,Q)Z extrapolation.^bCorrection tentatively assigned to this state.

Table 4.3: The relative values of each contribution to scheme 4.2 calculated using each of the HF reference states found. All energies are in kcal·mol⁻¹.

In the CCSD(T) results, the use of 6.2 eV reference state for the arachno isomer of Cr@Si₁₄ leads to a total energy significantly higher than that resulting from the 5.5 eV reference state. This is largely due to a much higher ΔE_{CV} value when using the 6.2 eV state, the underlying reason for which remains a curiosity. The CCSD(T) results from the 4.7 eV reference state of the [Mn@Si₁₄]⁺ fullerene isomer show a similarly large

difference with respect to the results from the 5.1 eV reference state. This is due to the much higher energy ΔE_{SR} correction of the 4.7 eV reference state. However, this correction is only tentatively assigned to this state as, while the orbitals bear the most resemblance to the non-relativistic orbitals of the 4.7 eV state, there did not appear to be near-identical matches for all of the orbitals, as was seen for the other reference states. Only $1.15 \text{ kcal} \cdot \text{mol}^{-1}$ separates the CCSD(T) results of the reference states of the arachno isomer of $[\text{Mn}@\text{Si}_{14}]^+$. This is within the range where a change in other factors such as geometry (discussed in section 4.3.3) could lead to either reference state giving the lower energy results. Hence it is considered that the results from the CCSD(T) 5.5 eV and 5.1 eV reference states in the $[\text{Mn}@\text{Si}_{14}]^+$ arachno isomer are within each other's margin for error. The calculated electronic structures from the two reference states likely do not differ greatly from one another given their similar energies, and thus the 5.5 eV state is chosen for calculation of the isomer energy difference. For the BCCD(T) calculations, the use of different initial reference states is shown to make little difference to the components of the composite scheme and the total energy. This applies to all cases and evidences the idea that there is not a significant difference in the electronic structures calculated from the different initial reference states when using BCCD(T). Thus, the initial states associated with the lower calculated energies are used for computing the isomer energy difference.

Overall, the lowest energy results are obtained from the arachno 5.5 eV state and the fullerene 5.1 eV state for both $\text{Cr}@\text{Si}_{14}$ and $[\text{Mn}@\text{Si}_{14}]^+$. As such, these states are used to calculate the present study's best estimates of the isomer energy differences, which are presented later in table 4.5. Choosing these states has the additional benefit of retaining a consistent frozen core across all calculations for a given isomer.

4.3.3 Sensitivity to Geometry

All calculations in section 4.3.2 used geometries optimised with the PBE functional. These geometries cannot be guaranteed to be minima on the potential energy surface

(PES) of the composite scheme (4.2) and therefore the energies calculated using the scheme may change if the composite scheme's true minima were used in the calculations. Thus, there is a degree of uncertainty associated with the geometries used for the calculation of scheme (4.2). Geometry optimisations using scheme (4.2) are not possible in the present study but the geometries of the clusters optimised with the B3LYP functional (reported in the present study's motivating work⁵⁰) may also be trialled to estimate the uncertainty with respect to geometry present in scheme (4.2). Since a geometry optimisation procedure minimises the energy of a compound with respect to its geometry, lower calculated energies are closer to the energy of the true PES minimum. However, in the present study, the geometries producing the lowest energies are not used for the best estimate of the isomer energy difference. This is because, on the PES of scheme (4.2), the energy gap between a minimum and a geometry found using DFT is not known and this gap may vary depending on the system. Therefore, the energy difference between results from the two DFT geometries for a given system is used as a rough estimate of the variation of the energy found via scheme (4.2) with respect to geometry. The geometries optimised with B3LYP and PBE may be considered to provide a representative sample of the range of plausible minima since the B3LYP functional tended to favour the fullerene isomer for both compounds while the PBE functional tended to favour the arachno isomer.

It is assumed that the E_{CBS} contribution to scheme (4.2) is the most sensitive to changes in geometry and additionally that the difference between a result in the ccTZ basis and its CBS limit estimation will remain constant across geometries. Hence the energies of each reference state of both isomers of both compounds are calculated using CCSD(T)/ccTZ and BCCD(T)/ccTZ. Additionally, since the results in section 4.3.2 indicated all the initial reference states tested lead to the same BCC solution, only the 5.5 eV and 5.1 eV reference states for the arachno and fullerene isomers respectively are used for the BCCD(T) calculations.

The range of energies found using each reference state is presented in figure 4.2, in which energies are displayed relative to the lowest energy calculated in each compound.

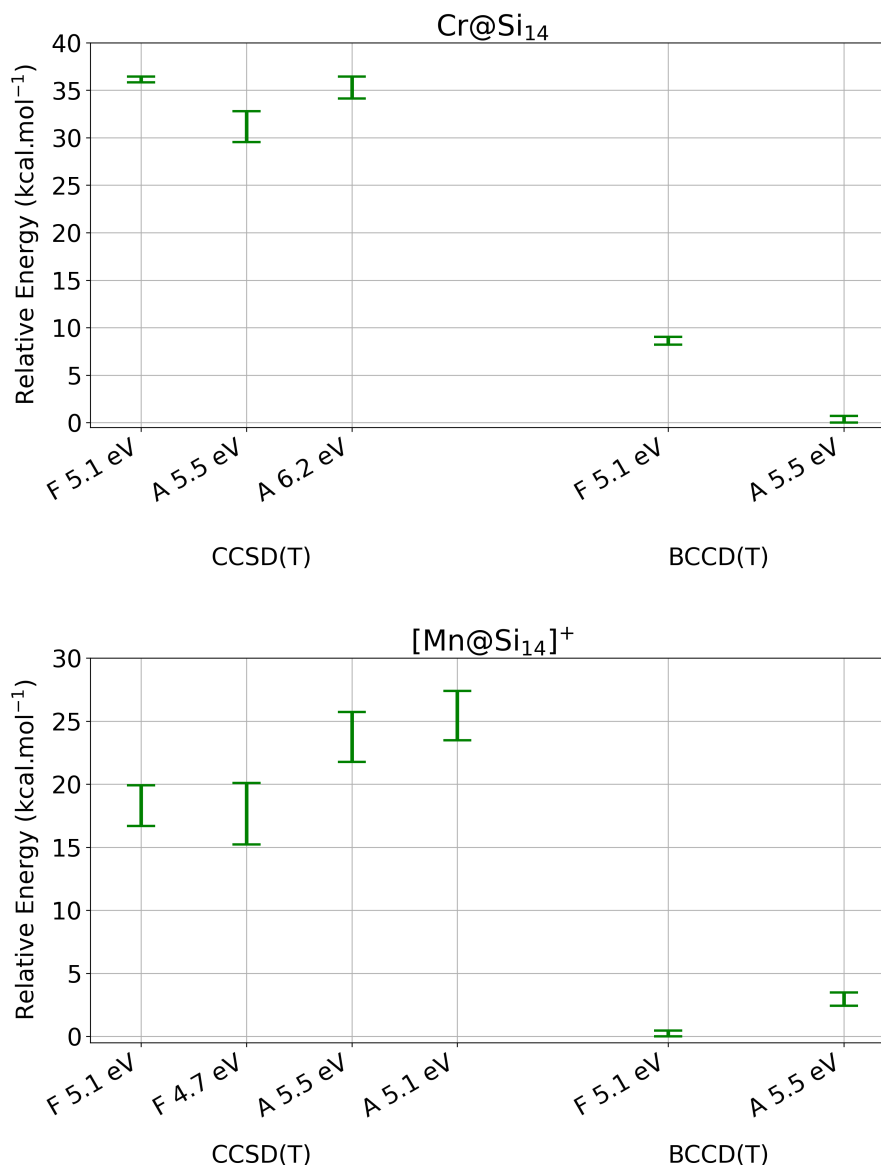


Figure 4.2: The range of energies calculated from the PBE and B3LYP geometries for each reference state found in each compound using CCSD(T) and BCCD(T) in the ccTZ basis set. Energies are displayed as values relative to the lowest energy calculated for each compound. A and F refer to the arachno and fullerene isomers respectively.

The BCCD(T) energies span smaller ranges than the CCSD(T) energies in both compounds. This is curious and implies the use of BCCD(T) reduces the dependence of the clusters' energies on geometry. Furthermore, it may be noted that the size of the energy ranges follows the broad trend: $[\text{Mn@Si}_{14}]^+ \text{ CCSD(T)} > \text{Cr@Si}_{14} \text{ CCSD(T)} > [\text{Mn@Si}_{14}]^+ \text{ BCCD(T)} \approx \text{Cr@Si}_{14} \text{ BCCD(T)}$. This ordering correlates with the degree of metal–cage delocalisation discussed in section 4.3.5 since both CCSD(T) and $[\text{Mn@Si}_{14}]^+$ were associated with reducing the level of metal–cage delocalisation.

Therefore, a cluster’s sensitivity to geometry may be related to the level of metal–cage delocalisation present.

For the estimation of the error due to geometry in scheme (4.2), when CCSD(T) is used, the results in figure 4.2 suggest errors of up to 3 kcal · mol^{−1} for Cr@Si₁₄ and up to 5 kcal · mol^{−1} for [Mn@Si₁₄]⁺. When using BCCD(T), the results suggest errors of up to only 1 kcal · mol^{−1} for both compounds.

4.3.4 Multi-reference Character Diagnostics

A set of multi-reference character diagnostics are computed to aid in determining the level of error introduced to the reported coupled-cluster calculations by static correlation. The diagnostics are calculated using the 5.5 eV arachno reference state and 5.1 eV fullerene reference state for both compounds, which are the reference states used for the present study’s best estimates of the isomer energy differences. It was found that the diagnostics do not vary significantly across the contributions to scheme (4.2) and hence only the diagnostics found from the E_{CBS} contribution are reported. The set of calculated diagnostics are presented in table 4.4.

The T_1 and D_1 diagnostics^{171,187} are both calculated solely from the t_1 amplitudes and thus only take non-zero values in the CCSD(T) calculations. Their definitions are given in expression (4.6).

$$T_1 = \frac{\|\mathbf{t}_1\|}{\sqrt{N_{e,\text{corr}}}} \quad D_1 = \sqrt{\lambda_{\text{max}}(\mathbf{t}_1 \cdot \mathbf{t}_1^T)} \quad (4.6)$$

Note that $\|\mathbf{t}_1\|$ is the norm of the vector of the singles amplitudes, $N_{e,\text{corr}}$ is the number of electrons included in the correlation treatment, λ_{max} is a function which returns the largest eigenvalue of its input, and $\mathbf{t}_1 \cdot \mathbf{t}_1^T$ is the outer product of the $\mathbf{t}_1$ vector with itself and therefore returns a matrix. The T_1 and D_1 diagnostics have recommended maximum values of 0.05 and 0.15 respectively,¹⁶⁴ beyond which it has been suggested that coupled-cluster methods will give results with significant errors due to multi-reference character. All the reported T_1 and D_1 values in table 4.4 are far above these suggested

		D_1	T_1	$\max(t_2)$	$ \mathbf{t}_2 $	%TAE[(T)]
Cr@Si₁₄ :						
CCSD(F12*)(T) a-ccTZ	Arachno	0.359	0.0843	0.0720	0.730	12.0
	Fullerene	0.363	0.0881	0.0614	0.734	11.1
BCCD _(F12*) (T) ccVTZ	Arachno	0.000	0.000	0.0273	0.716	15.7
	Fullerene	0.000	0.000	0.0667	0.721	14.9
[Mn@Si₁₄]⁺:						
CCSD(F12*)(T) a-ccTZ	Arachno	0.610	0.114	0.0572	0.761	12.2
	Fullerene	0.554	0.114	0.0631	0.760	11.3
BCCD _(F12*) (T) ccVTZ	Arachno	0.000	0.000	0.0373	0.720	16.2
	Fullerene	0.000	0.000	0.0856	0.723	15.0

Table 4.4: Multireference character diagnostics calculated from the E_{CBS} results of the arachno and fullerene isomers of Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$. Values were found using the 5.5 eV arachno reference state and 5.1 eV fullerene reference state in both Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$ and in the CCSD(T) and BCCD(T) methods.

maximums, indicating a large degree of orbital rotation via single excitations is occurring in all the systems considered. Curiously, the D_1 values of both of the $[\text{Mn@Si}_{14}]^+$ isomers approach twice those of their Cr@Si_{14} counterparts, and their T_1 values exceed those of the Cr@Si_{14} isomers by 0.03. This indicates a larger degree of orbital rotation occurs in both of the $[\text{Mn@Si}_{14}]^+$ compounds. The T_1 and D_1 diagnostics are necessarily zero in all BCCD(T) calculations but BCC theory is not generally regarded as a panacea for modelling multi-reference systems.¹⁸⁸ Hence the T_1 and D_1 diagnostics cannot be regarded as reliable indicators of multi-reference character in isolation. Moreover, large D_1 and $\max(|t_1|)$ values and have been shown to be present in some systems in which single-reference coupled-cluster methods demonstrated high accuracy.¹⁸⁹ Another study considered such results and additionally noted a lack of

correlation of the T_1 and D_1 diagnostics with the errors in geometry optimisations, leading the authors to suggest that these metrics should be removed as diagnostics in single-reference coupled-cluster methods altogether.¹⁹⁰

The $\max(|t_2|)$ metric is simply the doubles amplitude with the highest magnitude. The intermediate normalisation of coupled-cluster theory means that this represents the largest ratio between the reference state and a doubly excited state present in the coupled-cluster wavefunction. The values in table 4.4 range between 0.03 and 0.09 and so do not appear indicate that there is a doubles excitation that is comparable in amplitude to the reference. It should be noted that this is not always a reliable indicator of whether the CCSD(T) method will give accurate results. One paper reports $\max(|t_2|) = 0.07$ for the Ti_2 dimer which correlated with an error of $35 \text{ kcal} \cdot \text{mol}^{-1}$ in its bond dissociation energy.¹⁶⁴ Hence using $\max(|t_2|)$ as a sole diagnostic is precarious. Though it can also be noted in cases such as bond breaking, $\max(|t_2|)$ varies with bond length as may be expected. In such known multi-reference cases, it will reach values of 1 or more as excited states become comparable in amplitude to the reference.[†]

Curiously, when using BCCD(T), the $\max(|t_2|)$ for the arachno isomer of both compounds decreases significantly but the same is not true for the fullerene isomers. This might not be considered typical behaviour since the $\max(|t_2|)$ has been observed as remaining close to invariant to the choice of reference orbitals in a study on diatomics.¹⁷⁴ This could be an indication that the reference determinant has greater weighting in the coupled-cluster expansion when BCCD(T) is used. This idea appears to be further evidenced by the decrease seen in the norm of the vector of t_2 amplitudes, $\|\mathbf{t}_2\|$, on use of Brueckner orbitals. Furthermore, the fullerene isomer of $[\text{Mn}@\text{Si}_{14}]^+$ does not show the same decrease in $\max(|t_2|)$ on use of Brueckner orbitals and instead its $\max(|t_2|)$ increases by a similar amount to the decrease seen in the $\max(|t_2|)$ of its arachno isomer when the BCCD(T) method is used. The same increase in $\max(|t_2|)$ is not observed in the fullerene isomer of $\text{Cr}@\text{Si}_{14}$ where its $\max(|t_2|)$ remains about the same as that of

[†]For example, $\max(|t_2|)=1.17$ for CuH at a bond distance of $9\text{\AA}$ in an all-electron CCSD(T)/cc-pwCVTZ-DK calculation using the X2C Hamiltonian.

the arachno isomer. The $||t_2||$ of both compounds' fullerene isomers does still decrease on use of BCCD(T) however, so the increase in $\max(|t_2|)$ may not indicate that the Brueckner reference state is contributing less to the coupled-cluster wavefunction.[‡]

Diagnostics based on the (T) correction are often used as an indication of significant excitations of a higher order than the singles and doubles. The present study calculates the %TAE[(T)] diagnostic which has been shown to correlate with multi-reference character in a number of studies.^{164,191} These studies have particularly focused on CCSD(T) calculations and have produced a guidance value of <10% to indicate single-reference character. This puts the CCSD(T) calculations reported in table 4.4 on the borderline. Care must be taken in interpreting the %TAE[(T)] value however since the bulk of the testing data has been performed on small, often diatomic, molecules. Recent studies have pointed out that %TAE[(T)] is a size extensive quantity^{192,193} and demonstrate further that, even if significant multi-reference character is present, the %TAE[(T)] value can be reduced by the introduction of interactions without a large (T) contribution to the system of interest. This makes the interpretation of %TAE[(T)] ambiguous in the case of Cr@Si₁₄ and [Mn@Si₁₄]⁺ since both clusters are larger than the systems for which the guidance values were determined. Nevertheless, the clusters' borderline %TAE[(T)] values do demonstrate that the diagnostic does not reach overwhelming multi-reference values. For example, Ni₂ and V₂ have %TAE[(T)] values of 132% and 354% respectively, which correlates with their respective errors in their bond dissociation energy of¹⁶⁴ 29 kcal · mol⁻¹ and 53 kcal · mol⁻¹.

%TAE[(T)] values are also displayed for the BCCD(T) calculations, which are about 4% larger than their CCSD(T) counterparts in all cases. It is unclear if the same guidance values used for CCSD(T) should also apply to BCCD(T) calculations since the (T)

[‡]Note that, since the augmented and non-augmented basis sets are different sizes and therefore lead to different numbers of amplitudes, $||t_2||$ can be affected by the difference in the basis set used for the calculation. The BCCD(T) calculations presented in table 4.4 use the smaller ccTZ bases, while the CCSD(T) calculations used the a-ccTZ basis set so this fact must be considered. However, for the Cr@Si₁₄ system, it was found that $||t_2||$ varied from 0.75–0.76 between the ccTZ and a-ccTZ basis sets for both isomers. Similarly, when using BCCD(T), $||t_2||$ varies from 0.71–0.72 between ccTZ and a-ccTZ basis sets for both isomers. This indicates that difference in the $||t_2||$ values reported for the BCCD(T) and CCSD(T) calculations in table 4.4 is due to the difference in the Brueckner and canonical coupled-cluster calculations rather than their different bases.

correction is defined differently in the two methods. Notably, the CCSD(T) correction consists of two terms which are most often oppositely signed and therefore cancel to a degree and reduce the value of (T).¹⁹⁴ In BCCD(T), the (T) correction contains a single term, which is negative, and hence does not undergo the same cancellation. This may explain the higher values of the %TAE[(T)] diagnostic seen for the BCC calculations. It has also been noted that the Brueckner orbitals tend to be more appropriate for the (T) correction¹⁷³ so the larger %TAE[(T)] values may not be a cause for concern. In any case, the near flat 4% increase with respect to the CCSD(T) values seems to suggest the behaviour of the Brueckner (T) correction is similar to that of the CCSD(T) calculations. It can also be noted that %TAE[(T)] diagnostic does not vary to a large extent between the compounds.

Overall, the multi-reference character diagnostics illustrate an ambiguous picture of the multi-reference character of the Cr@Si₁₄ and [Mn@Si₁₄]⁺ clusters. However, only the metrics associated with single excitations were inarguably outside of the ranges suggested to indicate single-reference character. The rest of the diagnostics are either borderline or within the range of recommended values. Therefore, while the exact error associated with multi-reference character is not known for these systems, it seems unlikely that the CCSD(T) and BCCD(T) calculations will produce unreasonable results, as seen when coupled-cluster methods are applied to well-known multi-reference systems such as Cr₂. Thus, it is considered that there may be a degree of error associated with multi-reference character in the systems considered in the present study, which is difficult to quantify but is also unlikely to cause large changes to the results obtained in this study.

4.3.5 Overall Results and Physical Interpretation

The present study's best estimates of the energy difference between the arachno and fullerene isomers of Cr@Si₁₄ and [Mn@Si₁₄]⁺ are reported in table 4.5. The estimates are calculated using scheme (4.2). The 5.5 eV reference state of the arachno isomer and

the 5.1 eV reference state of the fullerene isomer are used for both Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$ and in both the CCSD(T) and BCCD(T) methods. Note that the contributions to the energy difference are calculated as $E(\text{arachno}) - E(\text{fullerene})$ and therefore negative values indicate the arachno isomer has the more negative contribution and positive values indicate the fullerene isomer has the more negative contribution.

	ΔE_{CBS}	$\Delta \Delta E_{\text{CV}}$	$\Delta \Delta E_{\text{SR}}$	Total
CCSD(T):				
Cr@Si_{14}	−3.30	−5.16	−1.85	−10.3
$[\text{Mn@Si}_{14}]^+$	+9.64	−5.46	−2.42	+1.77
BCCD(T):				
Cr@Si_{14}	−6.44	−4.72	−2.30	−13.5
$[\text{Mn@Si}_{14}]^+$	+3.58	−4.69	−2.21	−3.32

Table 4.5: The contributions to the isomer energy difference from each term of the composite method defined in (4.2). Negative values indicate the arachno isomer is more stable and positive values indicate the fullerene isomer is more stable. All values are in $\text{kcal}\cdot\text{mol}^{-1}$

The arachno structure of Cr@Si_{14} is calculated as the most stable using both CCSD(T) and BCCD(T) by a wide margin. However, the most stable isomer of $[\text{Mn@Si}_{14}]^+$ varies depending on whether the CCSD(T) or BCCD(T) scheme is used. The isomer energy differences are also much smaller in magnitude for $[\text{Mn@Si}_{14}]^+$. The ΔE_{CV} and ΔE_{SR} corrections are similar in value across the methods and compounds, hence the differences seen are primarily due to the ΔE_{CBS} contribution. As such, the ΔE_{CBS} contributions are investigated further via their breakdown into the reference energy, single and double excitations energy, and perturbative triples energy. These results are displayed in figure 4.3.

In all cases, the arachno isomer becomes more stable with respect to the fullerene isomer as the the order of the correlation treatment increases. This suggests that, the introduction of correlation to the calculations causes the relative stabilisation of the arachno isomer. Comparing the HF and Brueckner orbitals provides more information

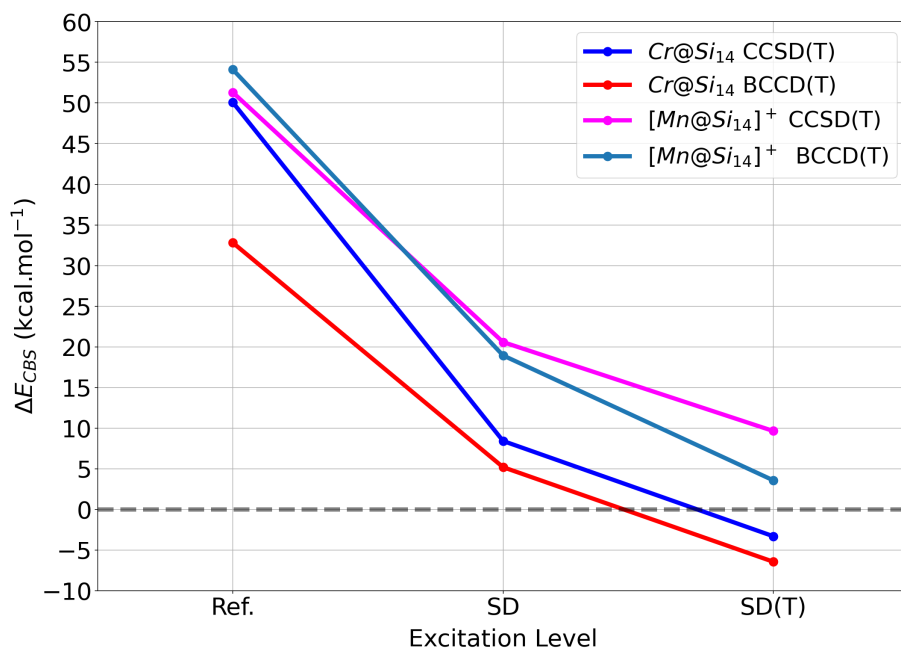


Figure 4.3: The E_{CBS} contribution to the isomer energy (ΔE_{CBS}) when only including the reference state (Ref.) in the calculation, when the reference state, single, and double excitations are included (SD), and when the reference state, single, double and perturbative triple excitations are included, SD(T). The ΔE_{CBS} values are shown for $Cr@Si_{14}$ and $[Mn@Si_{14}]^+$ using both the CCSD(F12*)(T)/a-ccTZ and BCCD(F12*)(T)/ccTZ methods (shortened to CCSD(T) and BCCD(T) respectively in the legend).

about the trend. Brueckner orbitals can be thought of as being representative of the correlation in a system since the Brueckner reference determinant is the determinant which has the most overlap with the total wavefunction^{195,196} and, in the case of BCCD(T), it is determined in response to the double excitations. Therefore, the comparison of the HF and Brueckner orbitals may be indicative of the difference electron correlation makes to the electronic structure of the clusters. As exemplified in figure 4.4, the Brueckner orbitals of all systems for which results are reported in table 4.5 are visibly more delocalised than their HF counterparts. Specifically, the orbitals show increased delocalisation between the cage and the metal. Thus, it may be that the increased delocalisation between the cage and the metal present in the Brueckner orbitals indicates that the correlation treatment is causing an increased level of delocalisation in the correlated wavefunction. This would further imply that the relative stabilisation of the arachno isomer which occurs when correlation is introduced to the calculations is

associated with the increased delocalisation between the cage and the metal indicated by the Brueckner orbitals. Therefore, it may be hypothesised that the correlation treatment causes an increase in electron delocalisation between the cage and the metal, which in turn leads to a relative stabilisation of the arachno isomer. This hypothesis is in line with the findings from the motivating study, which concluded that an increased ability of the metal d-orbitals to interact with the cage (which leads to increased metal–cage delocalisation) stabilised the arachno isomer.⁵⁰

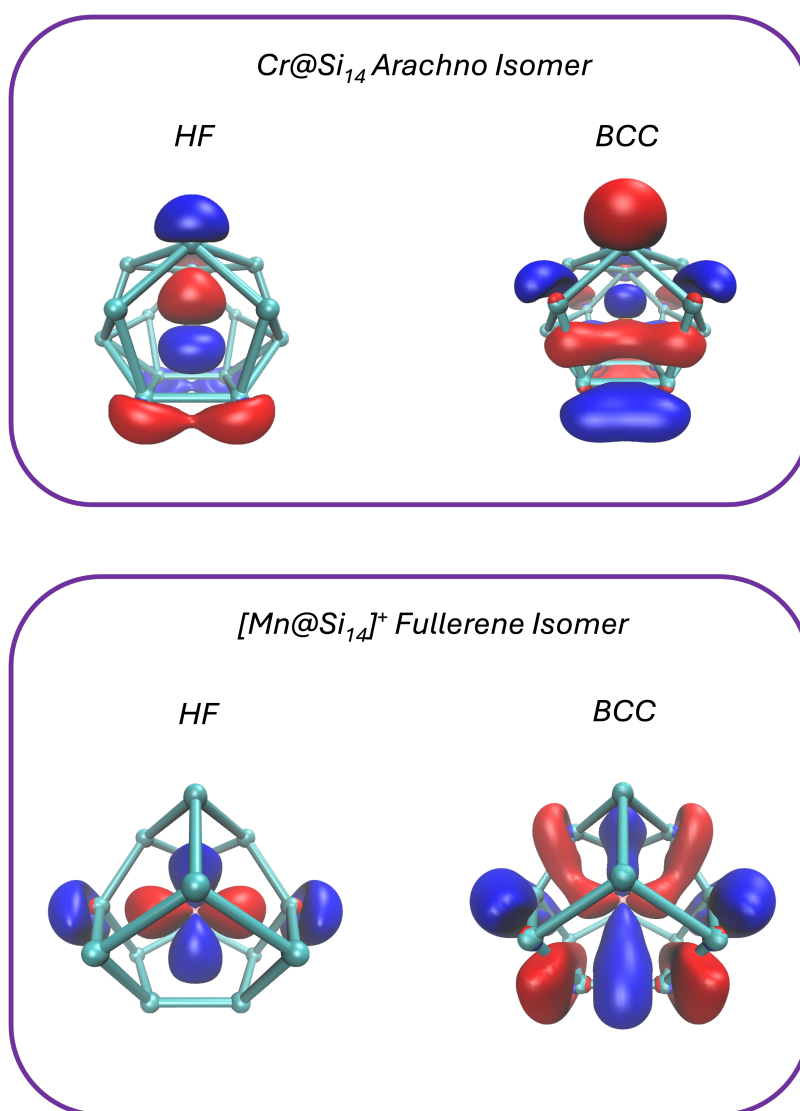


Figure 4.4: Examples of increased delocalisation seen in the Brueckner coupled-cluster (BCC) orbitals with respect to HF orbitals.

The trends in figure 4.3 also show that the relative stabilisation of the $[\text{Mn@Si}_{14}]^+$ arachno isomer that occurs on the introduction of correlation is not as large as that seen

for its Cr@Si_{14} counterpart. The principal difference between the $[\text{Mn@Si}_{14}]^+$ and Cr@Si_{14} species is that there is higher nuclear charge at the metal atom in $[\text{Mn@Si}_{14}]^+$. Given Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$ are isoelectronic, the higher nuclear charge means that the d-orbitals of manganese in $[\text{Mn@Si}_{14}]^+$ are more localised on the metal compared to those of chromium in Cr@Si_{14} . Therefore, if the coupled-cluster correlation treatment causes a greater delocalisation[†] between the cage and the metal, this metal–cage delocalisation might be expected to be reduced in $[\text{Mn@Si}_{14}]^+$. The Brueckner orbitals appear to evidence this implication since, while the Brueckner orbitals of the fullerene isomers of $[\text{Mn@Si}_{14}]^+$ and Cr@Si_{14} are near identical, three Brueckner orbitals of the Cr@Si_{14} arachno isomer show significant metal–cage delocalisation not present in its $[\text{Mn@Si}_{14}]^+$ counterpart. Depictions of these orbitals can be found in figure 4.5. If the Brueckner orbitals are again interpreted as being reflective of the correlated wavefunction, this shows that while the correlation treatment appeared to cause more delocalisation in $[\text{Mn@Si}_{14}]^+$ with respect to the HF treatment, it seems to be to a lesser degree to the delocalisation seen for Cr@Si_{14} . This difference may also explain why the Cr@Si_{14} Brueckner reference states exhibit an isomer energy difference with a near $20 \text{ kcal} \cdot \text{mol}^{-1}$ stabilisation of the arachno isomer with respect to the $[\text{Mn@Si}_{14}]^+$ reference states. Furthermore, if the coupled-cluster correlation treatment causes increased metal–cage delocalisation, it would be expected that when applied to $[\text{Mn@Si}_{14}]^+$, the counteraction of the localisation of the d-orbitals due to Mn^+ , causing the reduction of the metal–cage delocalisation discussed in the previous paragraph, would cause a lesser relative stabilisation of the $[\text{Mn@Si}_{14}]^+$ arachno isomer. This is the trend observed and therefore provides further confidence in the hypothesis that the coupled-cluster correlation treatment acts to increase the delocalisation of valence electrons between the metal and the cage.

[†]In particular that the delocalisation of the metal d-orbitals due to correlation outweighs the localisation of these orbitals due to the higher nuclear charge of manganese.

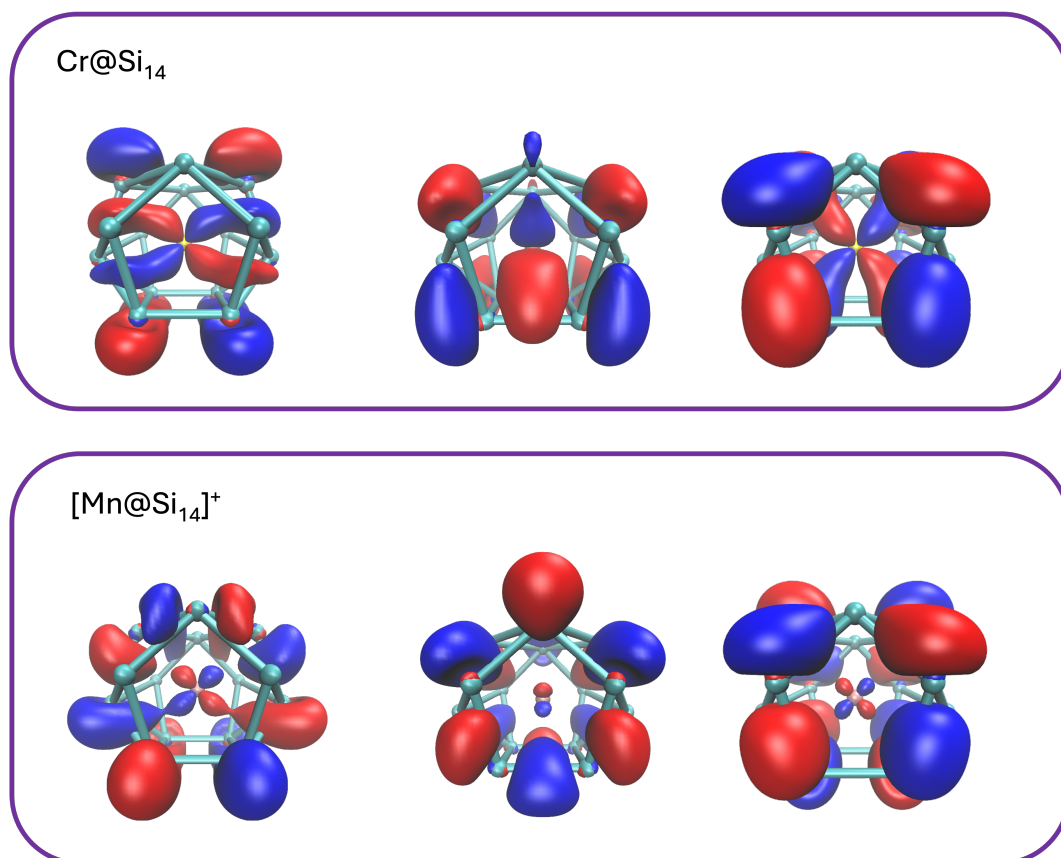


Figure 4.5: Equivalent Brueckner coupled-cluster orbitals in the Cr@Si₁₄ and [Mn@Si₁₄]⁺ arachno isomers showing different bonding characteristics.

From the analysis of the ΔE_{CBS} contributions given in the present section, particularly the comparison of the HF and Brueckner orbitals, it can be hypothesised that the HF method “overlocalises” the electrons and does not accurately model the metal–cage delocalisation, leading to its strong relative stabilisation of the fullerene isomer. This hypothesis is supported by the fact that, although there is a degree of uncertainty associated with the CCSD(T) and BCCD(T) schemes, it is unlikely that the coupled-cluster methods are misrepresenting the effect of correlation to such a degree that would make the approximately $50 \text{ kcal} \cdot \text{mol}^{-1}$ change in the isomer energy difference that their correlation treatment causes incorrect. The apparent inaccuracy of HF in these systems may partly explain why the coupled-cluster results are in closer agreement with the PBE functional than the B3LYP functional. The B3LYP functional includes 20% HF exchange (compared to none in the PBE functional) and for both Cr@Si₁₄ and [Mn@Si₁₄]⁺ it calculates the fullerene isomer to be the most stable by >10

$\text{kcal} \cdot \text{mol}^{-1}$, similar to the strong relative stabilisation of the fullerene isomers found by HF theory.

Having discussed the ΔE_{CBS} contribution, the other contributions to the isomer energy difference are considered. The $\Delta\Delta E_{\text{CV}}$ contribution is very similar across the compounds, providing approximately $5 \text{ kcal} \cdot \text{mol}^{-1}$ stabilisation to the arachno isomer in all cases. This invariance implies the CV correction is insensitive to the interstitial element of the cluster. Furthermore, the correction is due to correlating the Si 2p metal 3s electrons so it can be hypothesised that the insensitivity of $\Delta\Delta E_{\text{CV}}$ to the interstitial metal is because the CV correction is dominated by the correlation of the cage electrons, rather than the correlation metal 3s electrons. The final term, $\Delta\Delta E_{\text{SR}}$, is the smallest and also shows little variance across the methods and compounds. It provides an approximately $2 \text{ kcal} \cdot \text{mol}^{-1}$ stabilisation to the arachno isomer in all cases.

Finally, the accuracy of the results is discussed. Since it is suspected that the HF treatment induces an overlocalisation in the systems, it may be that the Brueckner reference state provides a more faithful representation of the system. This is also evidenced in the reduction of $\|t_2\|$ discussed in section 4.3.4 which occurs upon the use of Brueckner orbitals. All truncated coupled-cluster calculations contain a reference dependence so a closer representation of the true system in the reference state can lead to a quicker convergence of the coupled-cluster expansion to the exact solution of the Schrödinger equation and hence more accurate results. Therefore, it is considered that the BCCD(T) scheme is likely providing more accurate results than the CCSD(T) scheme.

The largest unknown source of error is the degree of multi-reference character. As discussed previously, the multi-reference character diagnostics do not give a clear indication of the error due to multi-reference character. However, it was also noted that the error due to multi-reference character was unlikely to be large and hence reach the order of tens of $\text{kcal} \cdot \text{mol}^{-1}$, as has been reported for compounds showing strong indications of multi-reference character in their diagnostics. Other than multi-reference

character, there are sources of error due to the assumptions of the composite method and the geometry chosen. Discussions in sections 4.3.1 and 4.3.3 indicate there is a variation in the CCSD(T) ΔE_{CBS} contribution of up to 3–4 kcal · mol⁻¹ in the Cr@Si₁₄ results and 5–6 kcal · mol⁻¹ in the [Mn@Si₁₄]⁺ results when the error in the CBS estimation method and the geometry are considered. The variation of ΔE_{CBS} with CBS method and geometry was smaller in the BCCD(T) calculations at up to 1–2 kcal · mol⁻¹ for both compounds. It has been reported previously that the error present in the ΔE_{SR} and ΔE_{CV} contributions would generally be expected to be less than that of the E_{CBS} contribution.¹⁹⁴ The assumption of the additivity of the ΔE_{CV} and ΔE_{SR} corrections has not been tested in the present study, however this assumption is used in most composite schemes which are able to achieve sub-kcal · mol⁻¹ accuracy. The same accuracy may not be expected here since the accuracy is reported for calculations using larger basis sets and smaller systems, nonetheless, the assumption of the additivity of the ΔE_{CV} and ΔE_{SR} corrections does not seem likely to be a significant source of error.

Overall, both the CCSD(T) and BCCD(T) results for the Cr@Si₁₄ isomer energy difference appear to be out of the range where the isomer energy difference could be overturned by factors such as multi-reference character and thus the arachno isomer is predicted to be lowest energy isomer of Cr@Si₁₄ based on the data reported in the present study. The CCSD(T) result for the [Mn@Si₁₄]⁺ isomer energy difference is within the margin of error which could overturn the lowest energy isomer and the BCCD(T) result, while larger in magnitude, is on the limit of what might be expected to be overturned. This leaves it ambiguous whether the arachno or fullerene structure is the global minimum of [Mn@Si₁₄]⁺. A greater knowledge of the error due to multi-reference character in this system seems to be necessary to establish the level of confidence which should be placed in the results from the coupled-cluster methods. Nevertheless, the results for the [Mn@Si₁₄]⁺ compound are of note since the BCCD(T) scheme predicts the arachno isomer as the lowest energy, which was not done by either the B3LYP or PBE DFT functionals, which furthers the variation with methodology seen in the [Mn@Si₁₄]⁺ system.

4.4 Conclusion

A methodology based on a composite scheme using coupled-cluster methods has been developed to investigate the proposed global minima of Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$. Composite schemes using both CCSD(T) and BCCD(T) methods were calculated and it was found that, while the arachno isomer of Cr@Si_{14} was the lowest energy using both CCSD(T) and BCCD(T), the methods differed in their prediction of the lowest energy $[\text{Mn@Si}_{14}]^+$ isomer. It was deemed that BCCD(T) was more likely providing a closer representation of the system for both compounds but even with this considered, the energy difference calculated was too small to put its result beyond the margin of error. In general, the results from both coupled-cluster methods were closer in agreement with the PBE functional than the B3LYP functional.

Brueckner orbitals provided insight into the impact of the coupled-cluster treatment of electron correlation on the isomer energy difference and indicated that the correlation increased delocalisation between the cage and metal. This correlated with a relative stabilisation of the arachno isomer with a lesser stabilisation being obtained in the case of $[\text{Mn@Si}_{14}]^+$, in line with what may be expected as a result of its more contracted d-orbitals. More broadly, the results reported in the present study provide insight into the conditions under which a M@Si_{14} cluster will adopt a structure described by a Wade's rules or a fullerene-like bonding model.

Chapter 5

Implementation and Investigation of the Correlation Induced Relaxation of Core Orbitals in Brueckner Coupled-Cluster Theory

5.1 Introduction

As discussed in the introductory chapter and seen in previous chapters, wavefunction methods are an invaluable tool in understanding the electronic structure of intermetalloid cluster compounds. However, the computational expense of wavefunction methods can limit the range of systems to which they can be applied and thus approximations which reduce the computational cost of wavefunction methods are frequently employed. One such approximation is the frozen core approximation, which was previously discussed in section 2.7.2.

For wavefunction methods, the frozen core approximation amounts to neglecting the correlation of core electrons. The effectiveness of the approximation is rooted in a broad truth in the assumption that the valence electrons of a compound have the greatest impact on energy differences of chemical interest. When this is true, the correlation energy from core electrons can be neglected without a significant loss in accuracy. However, there are systems in which the correlation of core electrons does make a significant impact on energy differences. This was seen in chapter three of the present thesis where the correlation of the Cr 3s and Si 2p electrons was enough to overturn the energy difference between the two isomers of $[\text{Mn}@\text{Si}_{14}]^+$. In this case, it was intractable to increase the number of core electrons in the correlation treatment but ideally the Si 2s electrons also would have been correlated. Thus, approximations accounting for the correlation of core electrons but still retaining an accessible computational cost, ideally similar to that which of the frozen core approximation, are a desirable tool to expand the number of core electrons which can be correlated in a calculation. Unsurprisingly, it does not take long to find studies investigating such approximations across a variety of electronic structure methods.^{197–199} The purpose of the present study is to derive and investigate a novel approximation for the correlation of core electrons. In particular, the present study focuses on such approximations within the Brueckner coupled-cluster (BCC) theoretical framework given the use of the BCCD(T) method in the previous chapter.

When occupied orbitals are left inactive in the coupled-cluster theoretical framework,

they simply remain as they are in the single determinant reference state. Since a HF calculation typically provides the initial guess for the Brueckner reference state, applying the frozen core approximation in BCC theory most frequently means the core orbitals remain as HF orbitals. This is in contrast to the active occupied orbitals in a BCC calculation which, as detailed in section 2.4.3 rotate to satisfy the $t_1 = 0$ requirement. There are no formal requirements for how one should define the inactive orbitals in BCC theory, which opens the door to altering them in order to approximate correlation effects. Departures from the HF treatment of core orbitals are difficult to find in the literature however and do not appear to have attracted much research attention. The examples which do exist include a study that performed a BCCD(T) calculation which included a portion of the core electrons in its active space and then used the resulting core orbitals as the frozen core in a calculation which only correlated the valence electrons and used a larger basis set.²⁰⁰ Also, in the program used in the present study, TURBOMOLE, a Fock core correction is available¹⁷⁷ where the core orbitals relax in the mean-field of the valence Brueckner orbitals, though this correction has not been formally investigated. It was also noted in one study that the HF treatment of frozen core orbitals causes issues in cases where spin contamination is present,²⁰¹ demonstrating an alternative motivation for the investigation of non-HF treatments of the inactive Brueckner orbitals. The present study continues the investigation into alternative definitions of the inactive orbitals in BCC theory and derives a way of altering the inactive orbitals in order to approximate the correlation of core electrons.

In the standard formulation of BCCD(T), the active occupied orbitals rotate under the $t_1 = 0$ requirement in response to the correlation introduced via double excitations (which also occur from the active orbitals). As previously mentioned, the inactive occupied orbitals do not rotate nor do their electrons participate in double excitations. The current chapter modifies the standard formulation of BCC theory to require that the inactive occupied orbitals rotate to satisfy the $t_1 = 0$ requirement but still omit any double excitations. To satisfy this requirement, the inactive orbitals rotate in response to the correlation of the active electrons. Therefore, the rotation of the inactive orbitals

under the $t_1 = 0$ requirement is an example of correlation-induced orbital relaxation. Since correlation-induced orbital relaxation is the first order of correlation treatment in BCCD(T), it can be postulated that implementing it for the inactive orbitals will capture a portion of their correlation energy and hence that it may provide a useful approximation for the correlation of core electrons. Furthermore, implementing solely correlation-induced orbital relaxation for the inactive orbitals isolates the effect of this order of correlation treatment and therefore can provide insight into its role in the BCCD(T) description of the correlation of core electrons. It may also be noted that requiring $t_1 = 0$ of the inactive orbitals is equivalent to only allowing single excitations from inactive orbitals in the CCSD(T) method. Throughout the present chapter enforcing the $t_1 = 0$ condition on inactive orbitals is referred to as Inactive orbital Correlated Relaxation (ICR).

Outside of Brueckner coupled-cluster theory, the correlation-induced relaxation of orbitals is a well-known element of the treatment of correlation in wavefunction methods, particularly for valence orbitals. For example, correlation-induced orbital relaxation underpins the changes in reference orbitals seen in multi-reference methods such as CASSCF and RASSCF. Correlation-induced relaxation is also discussed in single-reference systems approachable with coupled-cluster theory, where it is occasionally referred to as dynamic correlation-induced orbital relaxation. For example, significant correlation-induced orbital relaxation has been noted as a source of error for local coupled-cluster approximations which attempt to achieve results comparable to CCSD(T).^{202–204} However, examples of the correlation-induced relaxation of core orbitals are hard to find. A single example is found in the case of a model Fe(II) porphyrin system.^{205,206} CASSCF methods showed the Fe 3s orbital visibly gaining bonding character to surrounding nitrogen atoms which a ROHF calculation was unable to show.

To test the effectiveness of ICR as an approximation for the correlation of core electrons, the present chapter probes properties of systems which show a large contribution from the correlation of core electrons. Many examples of such systems can be found in the

realm of first row transition metal compounds where their core correlation is dominated by their 3s and 3p electrons. For example, there are reported instances of the binding energies,²⁰⁷ spin state energetics,^{22,208} and bond dissociation energies²⁰⁹ of transition metal compounds being sensitive to the treatment of their 3s and 3p electrons. Hence, in part for their large core correlation contribution and in part for their relevance to intermetalloid clusters, the current chapter focuses its testing on the properties of first row transition metal compounds. In particular, three spin state energy gaps (frequently referred to as just “spin gaps”) which have been previously shown to have a large contribution from the correlation of the 3s and 3p orbitals are investigated: ${}^6A'_1 \rightarrow {}^2E'_2$ in MnL_2 where $L = 1,3$ -diaminopropane,²² ${}^6A_g \rightarrow {}^2B_{2g}$ in $MnCp_2$,²² and ${}^5A_g \rightarrow {}^3E_g$ in the aforementioned model Fe(II) porphyrin system.²⁰⁵ Additionally, the ionisation energy and bond dissociation curves are found for two smaller and simpler systems, ScH and CuH, to allow for a clearer analysis of the effects of ICR.

5.2 Theory and Implementation

5.2.1 Theory

General Formulation of ICR

The present section derives a general expression for ICR for use in BCCD(T) theory. Since ICR is not affected by the perturbative triples correction, the ICR expression is derived solely within the BCCD theoretical framework. The formulation of ICR requires both that the inactive occupied orbitals satisfy the $t_1 = 0$ requirement and that no double excitations occur from the inactive orbitals. Thus, all doubles residuals from the inactive occupied orbitals are non-existent, as is the case in the standard formulation of BCCD theory. However, a singles residual which is not included in the standard formulation is required to rotate the inactive orbitals to satisfy the $t_1 = 0$ condition.

As discussed previously, the BCCD equations can be obtained by setting the t_1

amplitudes in the CCSD residuals to zero. Doing this for the CCSD singles residual gives

$$\Omega_i^a = f_{ia} + \sum_{kc} f_{kc} t_{ik}^{ac} + \frac{1}{2} \sum_{kcd} \langle ka || cd \rangle t_{ki}^{cd} - \frac{1}{2} \sum_{klc} \langle kl || ci \rangle t_{kl}^{cd} = 0. \quad (5.1)$$

As in chapter two, indices a, b, c , and d refer to active virtual orbitals, indices i, j, k , and l refer to active occupied orbitals, the quantities f and t refer to Fock matrix elements and coupled-cluster amplitudes respectively, and physicists' notation has been used for the electron repulsion integrals. The residual in equation (5.1) defines the rotation of an active occupied orbital, i . If i is instead treated as an inactive occupied orbital, m , all that is needed to adapt (5.1) into an expression for ICR is to set all double excitations involving an inactive occupied orbital to zero. Doing so results in

$$\Omega_m^a = f_{ma} - \frac{1}{2} \sum_{klc} \langle kl || cm \rangle t_{kl}^{ca} = 0. \quad (5.2)$$

Requiring the inactive occupied orbitals to satisfy condition (5.2) ensures their single excitations have zero amplitude and hence defines the ICR method implemented in the present chapter.

Spin Conditions

As detailed in chapter two, the exact wavefunction satisfies various conditions on the spin present in a system. Inexact wavefunctions do not necessarily satisfy the same conditions but often are enforced to do so. In the present study, the unrestricted BCCD (UBCCD) model wavefunction is used for open-shell systems and the restricted BCCD (RBCCD) model is used for closed shell systems. The unrestricted model only requires spin polarisation to be preserved in the system, which is equivalent to requiring the BCCD wavefunction to be an eigenvector of the $\hat{S}_z$ operator. It can be shown directly that a sufficient condition for this is

$$[\hat{S}_z, \hat{T}_i] = 0; \quad i = 1, 2, \quad (5.3)$$

provided that the reference state is also an eigenvector of $\hat{S}_z$. Note that $\hat{T}_i$ is the cluster operator, previously defined in equation (2.25). Since both ROHF and UHF states are eigenvectors of $\hat{S}_z$, both ROHF-UBCCD and UHF-UBCCD open-shell calculations are possible under condition (5.3). Conditions on the allowed amplitudes are derived from (5.3), so if a spin-orbital, $\varphi(\mathbf{x}) = \phi(\mathbf{r})\sigma(s)$, is indexed by i_σ , it can be shown that an arbitrary singles amplitude, $t_{i_\sigma}^{a\tau}$, must satisfy $\sigma = \tau$, and a doubles amplitude, $t_{i_\sigma j_\mu}^{a\tau b\nu}$, satisfies $\sigma + \mu = \tau + \nu$ to preserve spin polarisation.²¹⁰ Of course, the t_1 amplitudes are non-existent in Brueckner coupled-cluster theory, so the effect of the spin polarisation condition in this case is to eliminate all residuals corresponding to excitations with singles amplitudes which do not satisfy $\sigma = \tau$. Both UBCCD and RBCCD are subject to condition (5.3). Therefore, to formulate ICR for the two methods, equation (5.2) is first adapted to satisfy equation (5.3). This results in the UBCCD residual, from which the necessary restricted spin conditions are applied to formulate the RBCCD case.

Note in the following derivation, when spin orbitals indexed by i_σ appear in chemists' integrals, they refer only to the spatial component of the orbital. Additionally, a sum over all spin-orbitals is chosen to be represented as $\sum_\sigma \sum_{i_\sigma} = \sum_{i_\alpha} + \sum_{i_\beta}$. The result of applying the spin-polarisation condition, (5.3), to residual (5.2) can therefore be formulated as

$$\Omega_{m_\sigma}^{a\sigma} = f_{m_\sigma a_\sigma} - \frac{1}{2} \sum_{\substack{k_\lambda \lambda \\ l_\mu \mu \\ c_\nu \nu}} \langle k_\lambda l_\mu || c_\nu m_\sigma \rangle t_{k_\lambda l_\mu}^{c_\nu a_\sigma}. \quad (5.4)$$

The term containing the sum, henceforth referred to as the ‘‘H’’ term, as is done in TURBOMOLE, can be further developed by utilising chemists' integral notation,

$$\Omega_{m_\sigma}^{a\sigma, H} = -\frac{1}{2} \sum_{\substack{k_\lambda \lambda \\ l_\mu \mu \\ c_\nu \nu}} [(k_\lambda c_\nu | l_\mu m_\sigma) \langle \lambda | \nu \rangle \langle \mu | \sigma \rangle - (k_\lambda m_\sigma | l_\mu c_\nu) \langle \lambda | \sigma \rangle \langle \mu | \nu \rangle] t_{k_\lambda l_\mu}^{c_\nu a_\sigma}.$$

Then recognising the non-vanishing spin cases leads to

$$\Omega_{m_\sigma}^{a_\sigma, H} = -\frac{1}{2} \left(\sum_{\substack{k_\lambda \lambda \\ l_\sigma c_\lambda}} (k_\lambda c_\lambda | l_\sigma m_\sigma) t_{k_\lambda l_\sigma}^{c_\lambda a_\sigma} - \sum_{\substack{l_\mu \mu \\ k_\sigma c_\mu}} (k_\sigma m_\sigma | l_\mu c_\mu) t_{k_\sigma l_\mu}^{c_\mu a_\sigma} \right).$$

Since k and l both refer to the active occupied orbitals, if they have the same spin index they are indices for the same set of orbitals and hence can be interchanged. Making the interchanges $k_\sigma \leftrightarrow l_\sigma$ and $l_\mu \leftrightarrow k_\mu$ in the second term results in

$$\Omega_{m_\sigma}^{a_\sigma, H} = -\frac{1}{2} \left(\sum_{\substack{k_\lambda \lambda \\ l_\sigma c_\lambda}} (k_\lambda c_\lambda | l_\sigma m_\sigma) t_{k_\lambda l_\sigma}^{c_\lambda a_\sigma} - \sum_{\substack{k_\mu \mu \\ l_\sigma c_\mu}} (l_\sigma m_\sigma | k_\mu c_\mu) t_{l_\sigma k_\mu}^{c_\mu a_\sigma} \right).$$

In a similar manner, it can be recognised that the spin indices λ and μ are indices for identical sets and hence the interchange $\mu \leftrightarrow \lambda$ can be made in the second sum. This allows the expression to be brought under a single summation. Additionally, utilising electron swap symmetry, $(pq|rs) = (rs|pq)$, in the second integral allows a factorisation of the summand, resulting in

$$\Omega_{m_\sigma}^{a_\sigma, H} = -\frac{1}{2} \sum_{\substack{k_\lambda \lambda \\ l_\sigma c_\lambda}} (k_\lambda c_\lambda | l_\sigma m_\sigma) [t_{k_\lambda l_\sigma}^{c_\lambda a_\sigma} - t_{l_\sigma k_\lambda}^{c_\lambda a_\sigma}]. \quad (5.5)$$

One then obtains the final ICR formulation of the UBCCD residual by substituting equation (5.5)'s expression for the H term back into equation (5.4),

$$\Omega_{m_\sigma}^{a_\sigma} = f_{m_\sigma a_\sigma} - \frac{1}{2} \sum_{\substack{k_\lambda \lambda \\ l_\sigma c_\lambda}} (k_\lambda c_\lambda | l_\sigma m_\sigma) [t_{k_\lambda l_\sigma}^{c_\lambda a_\sigma} - t_{l_\sigma k_\lambda}^{c_\lambda a_\sigma}]. \quad (5.6)$$

The amplitudes in residual (5.6) already satisfy the doubles spin polarisation condition and hence the condition does not need to be applied directly in this case.

The ICR implementation of RBCCD additionally requires that the wavefunction is an eigenvector of the $\hat{S}^2$ operator, which leads to similar conditions as seen for the $\hat{S}_z$

operator. These conditions can be expressed in the following spin-free expressions for the closed shell amplitudes,

$$t_{i\sigma j\sigma}^{a\sigma b\sigma} = t_{ij}^{ab} - t_{ji}^{ab}$$

$$t_{i\sigma j\tau}^{a\sigma b\tau} = t_{ij}^{ab}$$

$$t_{i\tau j\sigma}^{a\sigma b\tau} = -t_{ji}^{ab}.$$

Note the non-subscripted indices refer to spatial orbitals (not to be confused with those in equation (5.2) where they refer to spin-orbitals). Applying these amplitude expressions to equation (5.6) gives the residual

$$\Omega_{ma} = f_{ma} - \sum_{klc} (kc|lm) [2t_{kl}^{ca} - t_{lk}^{ca}], \quad (5.7)$$

which is the form of the ICR-adapted RBCCD residual implemented in TURBOMOLE in the present study. The spin magnitude conditions are specifically applied to closed shell systems in the present study's implementation of ICR so only RHF-RBCCD calculations may be performed with the ICR method.

Symmetry Conditions

As has been demonstrated previously for coupled-cluster singles residuals, when a system exhibits point group symmetry, certain terms of the residual can be determined *a priori* to be zero. In residual (5.2), the Fock operator is invariant under all symmetry operations and therefore, for a Fock matrix element to be non-zero, the direct product of the irreducible representations (irreps) of the two orbitals must transform as the totally symmetric irreducible representation (TSIR) of the system's point group. For the H term, equation (5.5) is referred to, for which the relevant conditions are that the direct product of the irreps in of the orbitals in the integral must transform as the TSIR, which in this case is written

$$\Gamma_{k_\lambda} \otimes \Gamma_{l_\sigma} \otimes \Gamma_{c_\lambda} \otimes \Gamma_{m_\sigma} = \Gamma_{\text{TSIR}},$$

and that the doubles amplitudes are only non-zero if the direct product of all four spatial orbitals' irreps contains the TSIR,^{211,212} which is written as

$$\Gamma_{k_\lambda} \otimes \Gamma_{l_\sigma} \otimes \Gamma_{c_\lambda} \otimes \Gamma_{a_\tau} = \Gamma_{\text{TSIR}}$$

when applied to (5.5). Comparing both symmetry conditions further implies that

$$\Gamma_{m_\sigma} = \Gamma_{a_\tau}. \quad (5.8)$$

Thus, when (5.8) is coupled with expression (5.9),

$$\Gamma_{m_\sigma} = \Gamma_{k_\lambda} \otimes \Gamma_{l_\sigma} \otimes \Gamma_{c_\lambda}, \quad (5.9)$$

these are sufficient conditions for the integrals in the H term to be non-zero. These are the conditions implemented in the ICR algorithm developed in the present study.

5.2.2 Implementation

In its algorithm for solving the BCCD equations, TURBOMOLE employs a Fock-like matrix to carry out the orbital rotations in the reference state,

$$\begin{pmatrix} \mathbf{F}_{ii} & \boldsymbol{\Omega}_{ia} \\ \boldsymbol{\Omega}_{ai} & \mathbf{F}_{aa} \end{pmatrix}, \quad (5.10)$$

where $\mathbf{F}_{ii}$ and $\mathbf{F}_{aa}$ are the occupied-occupied and virtual-virtual blocks of the Fock matrix and $\boldsymbol{\Omega}_{ia}$ is the matrix of orbital rotation residuals. Diagonalisation of matrix (5.10) ensures that its off-diagonal elements are zero via rotation of the orbitals and therefore that the requirement for the residuals to be zero is satisfied. When a frozen core

is used, the matrix becomes

$$\begin{pmatrix} \mathbf{F}_{mm} & 0 & 0 \\ 0 & \mathbf{F}_{ii} & \mathbf{\Omega}_{ia} \\ 0 & \mathbf{\Omega}_{ai} & \mathbf{F}_{aa} \end{pmatrix}.$$

Thus, to adapt the Fock-like matrix for ICR, the matrix of the ICR residuals derived in the previous section is formed and then added to the core-virtual block of this matrix,

$$\begin{pmatrix} \mathbf{F}_{mm} & 0 & \mathbf{\Omega}_{ma} \\ 0 & \mathbf{F}_{ii} & \mathbf{\Omega}_{ia} \\ \mathbf{\Omega}_{am} & \mathbf{\Omega}_{ai} & \mathbf{F}_{aa} \end{pmatrix}. \quad (5.11)$$

The present study implements ICR in a development copy of TURBOMOLE version 7.6 using FORTRAN 90. The implementation first calculates the H term of the UBCCD or RBCCD residuals and stores them in a matrix. This H term matrix is formed through matrix multiplication of the amplitudes and integrals which constitute the H term. The H term matrix is then added to core-virtual block of an existing Fock matrix and the core-active occupied Fock matrix elements are then set to zero to form matrix (5.11). The Fock-like matrix is then diagonalised in the coupled-cluster iterations via pre-existing routines in TURBOMOLE.

5.3 Computational Details

All calculations were performed using a development version of TURBOMOLE 7.6.

All calculations employed the X2C Hamiltonian to model scalar relativistic effects. The cc-pwCVTZ-DK²¹³ set was used for all elements, except hydrogen where the cc-pVTZ-DK set²¹⁴ was used. Additionally, the RI fitting cc-pwCVTZ sets^{215,216} were used for auxiliary basis sets for all elements, except H which used the cc-pVTZ RI fitting set.²¹⁷ The main basis used, cc-pwCVTZ-DK, is optimised to account for both relativistic effects and core correlation effects. In particular, this basis set contains

additional “wC” functions which are Gaussian functions weighted to efficiently account for core-valence correlation at the expense of core-core correlation. Core-valence correlation tends to be the larger contributor to molecular properties, hence this weighting has been shown to achieve greater convergence of calculated molecular properties for a given basis set cardinality.²¹⁸

In the case of the main group elements, the cc-pwCVTZ-DK basis has not been defined in the literature. It is possible to construct a version of the basis set for these elements however. As can be confirmed by inspection of the basis sets, the cc-pVTZ-DK and cc-pwCVTZ-DK sets differ only in the inclusion of the wC functions. All other functions in the sets are identical. The cc-pwCVTZ and cc-pwCVTZ-DK sets contain all the same contracted Gaussian functions and hence the wC functions can be identified in the cc-pwCVTZ basis and added to the cc-pVTZ-DK set to create a cc-pwCVTZ-DK basis set. This procedure has been implemented by authors previously¹⁸⁹ and is used in the present study to define the cc-pwCVTZ-DK basis set used for the main group elements encountered. As previously mentioned, the contracted Gaussian functions common to both the cc-pVTZ-DK and cc-pwCVTZ-DK sets are identical, meaning only the added wC functions in the constructed sets vary from the form they would take had they been optimised in the same manner as the transition metals’ cc-pwCVTZ-DK bases.

For calculations on transition metal spin state complexes, geometries were taken from the original papers.^{22,205} In the case of the ionisation energies, the geometry of the neutral and ionised species were optimised using UKS-DFT and the PBE functional in the cc-pwCVTZ-DK set with the X2C hamiltonian. Since the geometry of both the neutral and ionised species are optimised, the present study reports adiabatic ionisation energies. The equilibrium geometries used in the bond dissociation calculations were determined with the same KS-DFT methodology as the ionisation energy calculations. In all calculations employing the frozen core approximation, Hartree-Fock orbitals are used as the inactive orbitals.

For bond dissociation calculations at bond lengths equal to or greater than 2 Å, a level

shift of 1.0 was applied to the Fock-like matrix described in section 5.2.2 on each coupled-cluster iteration. This was necessary to achieve convergence of the Brueckner coupled-cluster calculations at larger bond lengths. Additionally, it proved to be unreliable to converge coupled-cluster calculations at bond lengths greater than 9 Å and hence reported D_e values may not be fully converged. This is not a concern for the conclusions of the present study however.

5.4 Results and Discussion

5.4.1 Ionisation Energies

First, the role of correlation-induced core orbital relaxation (henceforth referred to as just core relaxation) in the ionisation energy (IE) of the diatomic compounds ScH and CuH is probed using the ICR and all-electron treatments. For the ICR and frozen core calculations, the [Ar] core of the metal is set as inactive. For the purposes of the present discussion, the energy changes due to the all-electron (ae) and ICR treatment of the core orbitals, with respect to the frozen core (fc) treatment are denoted as $\Delta_{\text{ICR}} = E_{\text{ICR}} - E_{\text{fc}}$ and $\Delta_{\text{ae}} = E_{\text{ae}} - E_{\text{fc}}$. The same symbol is also occasionally used in context to refer to change in the energy difference of interest e.g. $\Delta_{\text{ae}} = \text{IE}_{\text{ae}} - \text{IE}_{\text{fc}}$.

The results of the ionisation energy calculations are displayed in table 5.1. The total energies from each method, relative to the frozen core values, are presented under the headings of each compound. The ionisation energies of the ICR and all-electron methods are also presented relative to the frozen core value. Note that the relative values of the total energies are not reported for the all-electron BCCD and BCCD(T) calculations. Since the all-electron treatment is the only method which includes double excitations from the core orbitals, the change in total energy is large with respect to the frozen core and ICR BCCD/BCCD(T) values and does not solely reflect the effects of core relaxation. However, the effects of core relaxation in all-electron calculations are

captured solely in the reference energy since the orbitals from which the reference energy is calculated have adapted in response to the double excitations. Therefore, the relative values of the reference energies from the all-electron calculations of each compound are also reported.

	ScH	[ScH] ⁺	IE	CuH	[CuH] ⁺	IE
Ref.:						
fc	–	–	118.6	–	–	182.2
Δ_{ICR}	–0.03	–1.66	–1.63	–0.315	–1.11	–0.792
Δ_{ae}	+2.98	–0.095	–3.07	+2.53	+1.13	–1.401
BCCD:						
fc	–	–	144.8	–	–	209.4
Δ_{ICR}	–0.05	–1.66	–1.61	–0.258	–0.944	–0.686
Δ_{ae}	–	–	–1.27	–	–	–0.06
BCCD(T):						
fc	–	–	146.0	–	–	214.5
Δ_{ICR}	–0.05	–1.65	–1.60	–0.160	–0.954	–0.794
Δ_{ae}	–	–	+1.84	–	–	+0.231

Table 5.1: Total energies of the neutral and first ionised forms of ScH and CuH presented alongside the first (adiabatic) ionisation energies of ScH and CuH. All energies are calculated using BCCD(T) with frozen core, ICR, and all-electron treatments of core correlation. The total and ionisation energies are displayed relative to frozen core values. The reference (Ref.), BCCD, and BCCD(T) total energies and ionisation energies are displayed for each species. All values are reported in kcal·mol^{–1}.

For both systems, it can be seen that the change in ionisation energy across the all-electron, ICR, and frozen core methods is not significant comparison to the total ionisation energy, showing that core correlation has a small impact of on the ionisation energies of ScH and CuH. Nonetheless, the reference energy contributions are of particular interest for probing the effect of core orbital relaxation since the core relaxation present in an all-electron calculation is captured entirely at the reference level and thus can be compared directly to the ICR. Interestingly, while both the ICR and the all-electron core relaxation have negative contributions to the ionisation energy, the all-electron core relaxation increases the total reference energy of the neutral and ionised

species[†] while the ICR decreases it. This implies there is a difference in the nature of the core orbital relaxation depending on whether excitations from the core orbitals are included. The ICR and all-electron core orbitals did not show a clear visible difference but the data shown indicates there is a difference nonetheless.

The correlation from higher order excitations of the core electrons, shown by the all-electron BCCD and BCCD(T) ionisation energies, is seen to have an opposing effect on the ionisation energy to the all-electron core relaxation. The ΔIE_{ae} becomes more positive when double excitations are included at the BCCD level and the (T) correction leads to an additional positive contribution which provides a relative stabilisation to the neutral species in the BCCD(T) calculation. The influence of the all-electron core relaxation on the higher order excitations is not known, though this trend does demonstrate that the inclusion of double and perturbative triple excitations involving core orbitals affects the ionisation energy of these systems in a different manner to the core orbital relaxation. This is an important point for the consideration of ICR as an approximation for core orbital correlation in itself. The ΔIE_{ICR} remains roughly constant at all levels of correlation, while the higher order excitations from the core orbitals have a different qualitative impact on the energy difference of interest. As such this reduces the use of ICR by itself as a general approximation core correlation effects.

Lastly on this topic, all the treatments of core correlation contribute more to the ionisation energy of ScH than they do to the ionisation energy of CuH. This is true for the reference, BCCD, and BCCD(T) ionisation energies. In principle, this variation with compound could provide insight into how the core relaxation behaves with differing nuclear charge and amounts of valence electrons at the metal, though it is difficult with the available analysis tools to see how exactly the correlation is causing the orbitals to relax. It can be hypothesised that correlation is causing the amount of electron density at the metal centre to reduce in the ionised species relative to the neutral species. This may then explain why the core relaxation provides a relative stabilisation to the ionised species. Noting then that scandium's electron affinity²¹⁹ of $4.3 \text{ kcal} \cdot \text{mol}^{-1}$ is much

[†]With the slight exception of $[\text{ScH}]^+$.

lower than hydrogen's²²⁰ at $17.4 \text{ kcal} \cdot \text{mol}^{-1}$ while that of copper is larger than both²²¹ at $28.4 \text{ kcal} \cdot \text{mol}^{-1}$, it may be the case that copper is much more able to attract electron density to itself in a hydride system than scandium is, leading to a smaller change in electron density due to correlation on ionisation. This hypothesis is hard to confirm, though it is possible to test the core relaxation in systems where it is known that correlation reduces the electron density at the metal centre. Examples of such systems can be found in cases of bond dissociation and hence the bond dissociation of ScH and CuH is calculated and discussed in the next section.

5.4.2 Bond Dissociation Curves

In a typical $2c-2e^-$ bond dissociation, it can be expected that, as the bond length increases, a RHF model will increasingly overestimate the electron density at each nucleus. This is because the two electrons behave independently of each other in a RHF model and as such the amplitudes of configurations where the electrons are in close proximity are not accurately reduced. Correlated methods remove the independence of the electrons and allow configurations which separate the two electrons to increase in amplitude. Thus, bond dissociation processes may provide insight into whether the reduction of electron density through correlation does induce relaxation of the core orbitals. The situation is more complicated than a standard $2c-2e^-$ bond for ScH and CuH since more than just the bonding orbital is populated. Nonetheless, the effect of correlation should be similar.

Core relaxation in the all-electron and ICR cases is shown as a function of bond length in figure 5.1 via the values of Δ_{ICR} and Δ_{ae} in reference energy. Barring the Δ_{ICR} curve of CuH, the curves in figure 5.1 show an increasingly negative contribution from core orbital relaxation as the bond length increases until $4 \text{ \AA}$. At this point, the contribution becomes more positive as the bond length increases but not as sharply as the negative contribution seen prior. Notably, $4 \text{ \AA}$ is the point where the gradients of the bond dissociation curves (shown in figure 5.2) start to decrease sharply. This trend could be

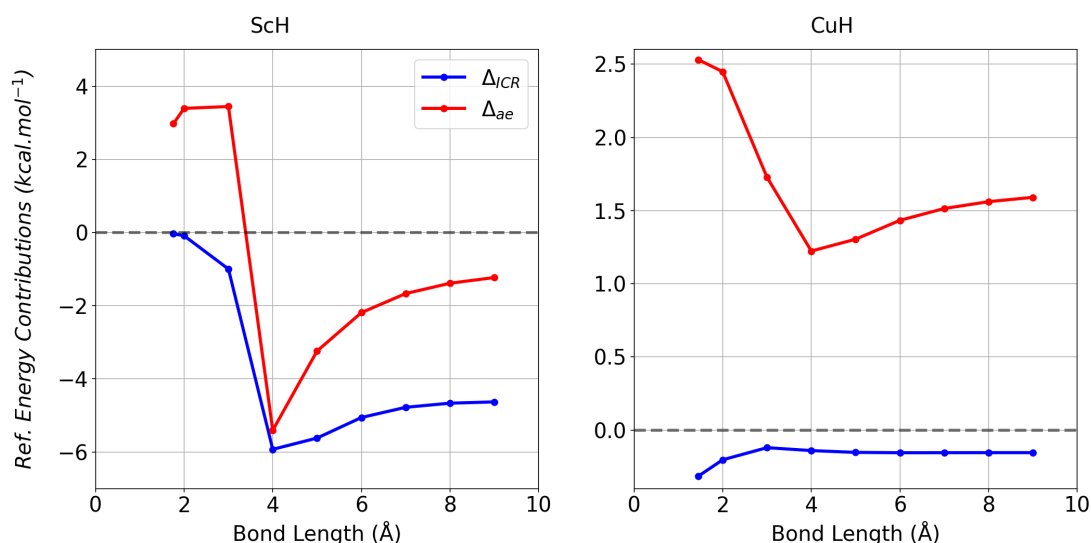


Figure 5.1: The values of Δ_{ICR} and Δ_{ae} in the reference energy as a function of bond length for the dissociation of ScH and CuH.

the result of the expected decrease in electron density around the core orbitals as the bond starts to separate and once the bond length reaches larger values, there may be less change in the electron density due to correlation, leading to other factors slowing the increase of positive energetic contributions due to core relaxation.

The difference between the all-electron core relaxation and ICR seen in the ionisation energies is also evident in the ScH graphs. The Δ_{ae} is positive at equilibrium while Δ_{ICR} is negative. However, both respond similarly when the bond length is increased and become near coincident at 4 Å. This implies that the changes in field causing the ICR trend also becomes dominant in the all-electron relaxation. This seems feasible as the all-electron relaxation residual, eq. (5.2), contains all the same terms as the ICR in alongside its terms which include double excitation amplitudes from the core orbitals. The all-electron relaxation remains more positive throughout the dissociation, which evidences the idea that the terms unique to the all-electron relaxation residual are acting in opposition to those present in the ICR residual.

In the CuH dissociation, the ICR shows different behaviour to the other relaxations seen in the present study. The ICR increases slightly in its negative contribution as the bond

length increases and then quickly plateaus as the bond length becomes larger. This trend only covers a small range of values and the Δ_{ICR} does not have a large magnitude initially: Δ_{ICR} is $-0.31 \text{ kcal} \cdot \text{mol}^{-1}$ at equilibrium and $-0.15 \text{ kcal} \cdot \text{mol}^{-1}$ at the longest bond length. The Δ_{ae} on the other hand shows similar behaviour to the ScH system. The reason for the difference in the Δ_{ICR} and Δ_{ae} behaviours is unknown, though the fact the Δ_{ae} in CuH shows similar behaviour to its ScH counterpart despite the relatively small effect of the ICR is interesting. Since Δ_{ICR} is insignificant in CuH, this shows that the terms unique to the all-electron relaxation residual induce the same relaxation behaviour seen in ScH for both the ICR and the all-electron relaxation. The terms unique to the all-electron residual still provide a positive contribution to the reference energy with respect to the frozen core in CuH so this may suggest that, in the ScH case, the terms unique to the all-electron relaxation and the terms in the ICR residual exhibit the same trend in core relaxation with increasing bond length and it is just that the terms unique to the all-electron relaxation are providing a more positive contribution to the reference energy. This could explain why the gap between ICR and all-electron relaxation progressively widens past 4 Å: both the terms in ICR residual and the terms unique to the all-electron residual could be providing positive contributions to the energy and the gap between the two relaxations widens since the all-electron relaxation contains both of these terms.

Turning to the contribution of core correlation to the dissociation energy, illustrated in figure 5.2, it can first be seen that ICR provides a stabilisation for the dissociating fragments of ScH with respect to the equilibrium geometry. As a result, the bond dissociation of ScH is $2.2 \text{ kcal} \cdot \text{mol}^{-1}$ lower when ICR is used instead of a frozen core. Contrastingly, in CuH, the difference between the ICR and frozen core bond dissociation energies is vanishingly small at $0.1 \text{ kcal} \cdot \text{mol}^{-1}$.

Curiously, in the dissociation of ScH, the all-electron contribution is much greater in magnitude than the frozen core and ICR contributions for both BCCD and BCCD(T). Additionally, at larger bond lengths, the all-electron contribution destabilises the compound with BCCD but stabilises it with BCCD(T). The same behaviour is seen in

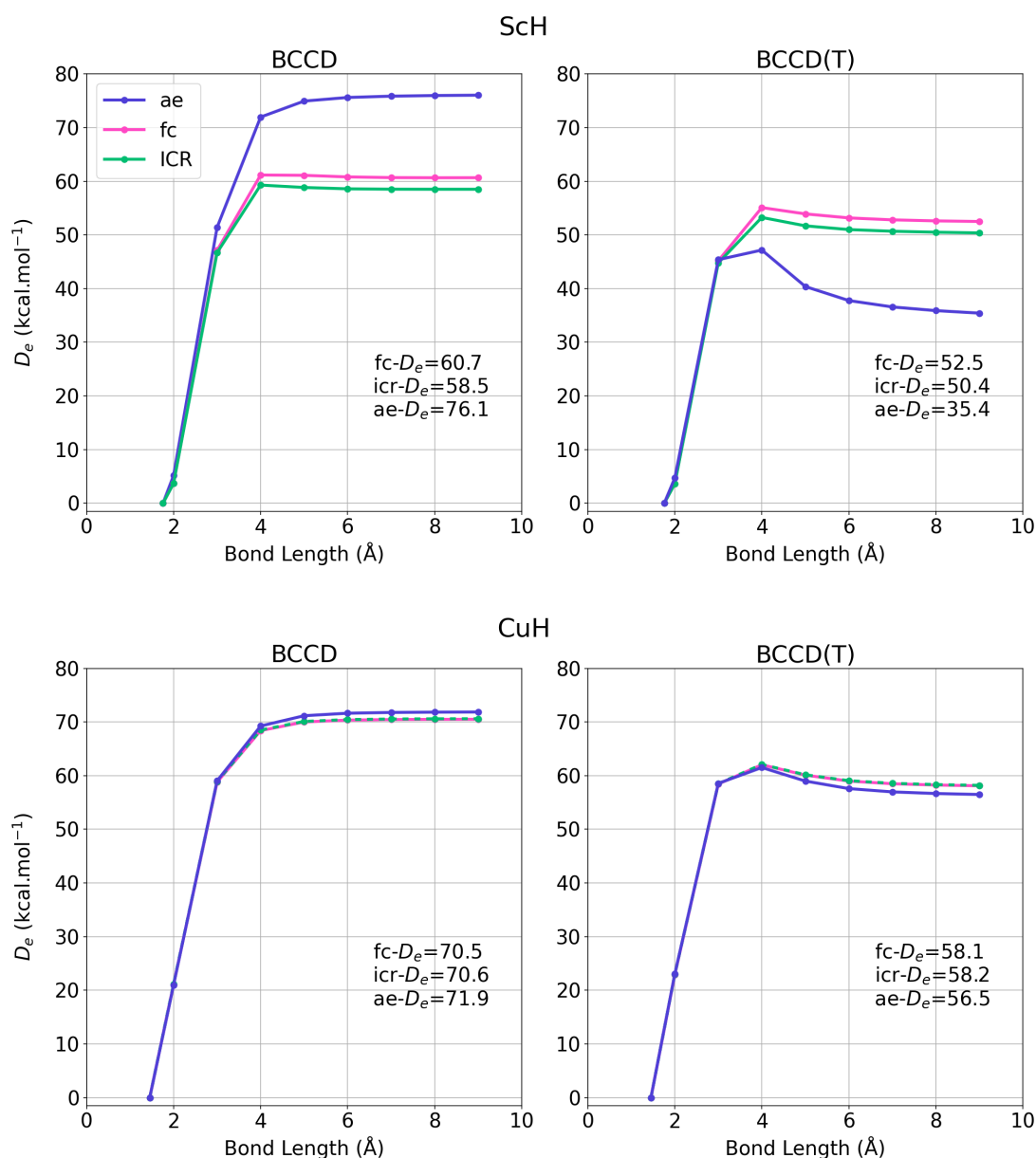


Figure 5.2: Bond dissociation curves for ScH and CuH. Note that convergence of the coupled-cluster equations proved unreliable for distances greater than 9Å so reported D_e values are not confirmed to be fully at the dissociation limit. Lower-case letters in front of D_e indicate the core treatment used in the determination of the quantity.

CuH but to a much lesser degree. Despite the previously discussed differences in their contributions to the reference energy, the ICR and all-electron core relaxation have similarly sized contributions to the dissociation energy, differing by no more than 2.5 kcal · mol⁻¹ in their reference energy contribution to D_e at a particular bond length.

Therefore, the difference in D_e seen in the all-electron curves is predominantly due to the higher order excitations from the core orbitals.

Bond dissociation systems are inherently multi-reference so the values reported in the current section may not align closely with experiment. However, the present section's results do further demonstrate that systems can exhibit significant core correlation effects which are not approximated closely by core relaxation, via ICR or all-electron core relaxation.

5.4.3 Spin States of Transition Metal Complexes

For all but the bond dissociation of ScH, the systems studied thus far do not show a significant impact of core correlation on the energy difference investigated. To test ICR in some systems which do exhibit properties which are sensitive to core correlation, three spin gaps in transition metal complexes identified with CCSD(T) as having a large contribution from the correlation of metal 3s3p electrons are tested. These include two manganese systems²² which are notable simply for their large value of Δ_{sp} , that is the amount the energy difference between the spin states changes when the 3s and 3p orbitals on the metal are included in the correlation treatment. Also included is an Fe(II) model porphyrin system.^{205,206} While this system exhibits a lower Δ_{sp} value, a visible difference between the Fe 3s orbitals obtained from ROHF and CASSCF(32,34) wavefunctions has been documented previously.²⁰⁶ The calculated spin gaps are reported in table 5.2. Note that Δ_{ae-cr} is the amount of the spin gap that is due to the all-electron core relaxation, which is found using the difference between the all-electron and frozen core reference energy contributions. Additionally, lower case letters in front of a method's name indicate the core treatment: 3s3p-BCCD(T) is BCCD(T) with the 3s and 3p orbitals on the metal active, fc indicates a frozen core calculation and icr indicates the use of inactive orbital correlated relaxation. Also note that, in table 5.2, ΔE refers to the energy gap between the two spin states.

	MnCp ₂	MnL ₂	Fe(por)
	${}^6A'_1 \rightarrow {}^2E'_2$	${}^6A_g \rightarrow {}^2B_{2g}$	${}^5A_g \rightarrow {}^3E_g$
fc-BCCD(T) ΔE	7.35	43.36	−1.56
icr-BCCD(T) ΔE	6.68	42.79	−1.81
3s3p-BCCD(T) ΔE	0.38	37.59	−3.85
$\Delta_{\text{ae-cr}}$	−0.513	−0.345	+0.273
Δ_{ICR}	−0.673	−0.574	−0.249
Δ_{sp}	−6.97	−5.77	−2.29
Δ_{ICR} as a % of Δ_{sp}	9.66%	9.95%	10.9%
Δ_{ICR} as a % of ΔE	176%	1.53%	6.46%
Literature CCSD(T) ΔE	−0.5	38.4	−2.7
Literature CCSD(T) Δ_{sp}	−7.8	−5.4	−2.2

L=1,3 diaminopropane
por=porphyrin model detailed in²⁰⁵

Table 5.2: Energy differences between the spin states of each complex indicated in their respective columns. The contributions to this value for each core treatment are also documented. All values are in kcal·mol^{−1}.

The BCCD(T) results for the ΔE and Δ_{sp} agree with the literature CCSD(T) values by up to approximately 1 kcal · mol^{−1} in all cases. A minor difference is expected due to the use of BCCD(T) rather than CCSD(T), and in the case of MnCp₂ and MnL₂, the second order Douglas-Kroll-Hess Hamiltonian was used with ANO-RCC basis sets rather than the cc-pwCVTZ-DK with the X2C Hamiltonian. It can also be noted that the ICR affects all inactive orbitals while the methods correlating the 3s3p electrons leave the rest of the core orbitals frozen. These differences in methodology are not expected to contribute significantly to the differences in results discussed in the subsequent paragraphs so the comparisons shown in table 5.2 are treated as fair.

All the spin gaps discussed in the present section involve the pairing of electrons to transition from their initial state to their final states. In the two Mn compounds, all five d-orbitals are singly occupied in the initial state and then two electrons are paired to produce the final doublet state. In the Fe compound, the initial state singly occupies four

of the Fe d-orbitals and doubly occupies the remaining d-orbital. In the final state, a further up-down pair is formed to give a triplet state. It can also be noted that the production of two electron pairs in the final state correlates with a larger Δ_{sp} value, seen for the two Mn complexes compared to Fe(por). This broad trend was noted with reference to more examples previously.²²

The Δ_{ICR} is negative for all the spin gaps, meaning the relaxation is greater in the lower (and final) spin states. This is independent of the overall ΔE between the states, which heavily favours the high spin state in MnL_2 , the lower spin state in Fe(por), and the difference between the two states is marginal in $MnCp_2$. It is difficult to isolate the cause for this pattern, however, it has been noted that ROHF tends to have a bias towards higher spin states due to its inclusion of Fermi but not Coulomb correlation.²² It can then be hypothesised that if Fermi correlation is the dominant correlation in the higher spin states, a ROHF reference will more accurately represent a higher spin state than a lower spin state. Hence the inactive 3s3p orbitals may be expected to experience more similar fields at the ROHF and BCCD(T) levels, and therefore undergo less relaxation when correlation is included in the calculation. Likewise, the paired electrons' higher dependence on Coulomb correlation could mean the ROHF orbitals are less representative of the correlated system and therefore undergo a larger change when the orbitals are allowed to relax in the correlated system.

The Δ_{sp} is notably also always negative and so Δ_{ICR} provides a stabilisation in the same direction as the Δ_{sp} , in contrast to what was seen previously for the ionisation and dissociation energies. Comparing the Δ_{sp} and the Δ_{ae-cr} contributions shows that the double excitations from the 3s and 3p orbitals also stabilise the lower spin states with respect to the higher spin states. Notably, the ICR is more negative than the all-electron core relaxation. Similar to the ionisation energies discussed previously, the all-electron relaxation in general increases the energy of the individual spin states with respect to the frozen core, while the ICR lowers it. The data showing this can be found in appendix table A3.5. This is likely indicative of the oppositely signed contributions from the different terms present in the two orbital relaxation residuals discussed in section 5.4.2.

Overall, this means that the ICR comes closer to the Δ_{sp} value than the all-electron core relaxation, though since Δ_{ICR} only makes up about 10% of the Δ_{sp} of each spin gap, ICR still demonstrates limited use as an approximation for core correlation.

The Fe(por) system has benefited from specific investigation into how the correlation of its 3s3p orbitals affects the spin gap calculated for its $^5A_g \rightarrow ^3E_g$ transition. As part of the investigations reported in the literature, a number of approaches to finding the correlation-induced core orbital relaxation have been tested. A selection of these which are suited to comparison with the ICR method are included in table 5.3 and compared against the BCCD results from the present chapter to establish how ICR performs in comparison. The core treatments include ICR alongside its equivalent in canonical coupled-cluster theory, T_1^{sp} , which includes single excitations from the core orbitals. Additionally, orbitals from a CASSCF(32,34) calculation (henceforth referred to as the CAS orbitals) are used in place of the HF orbitals in a CCSD calculation to provide core relaxation. Notably, the Fe 3s core orbital shows bonding interactions with the surrounding ligands in the CAS orbitals whereas the ROHF Fe 3s orbital resembles the atomic case and does not contain any significant bonding interactions. The bonding interactions present in the CAS orbitals can be considered a visible example of core relaxation.

In addition to the different treatments of core relaxation, each approach used a different method to calculate the valence correlation. The valence correlation methods included CCSD, BCCD, and DCSD. The DCSD method is the distinguishable cluster approach with single and double excitations.^{222,223} This approach employs a CCSD wavefunction which has been adapted to improve its description of static correlation in certain scenarios.[†] The Fe(por) system was reported to benefit from being treated with higher

[†]The DCSD approach removes certain terms from the CCSD expansion of the wavefunction based on the idea that they will cancel with terms from higher orders of excitations in the complete expansion of the wavefunction. Specifically, in bond breaking scenarios, there are terms associated with electron exchange between isolated molecular fragments which are present in truncated coupled-cluster expansions but cancel with terms from higher orders of excitation in the complete coupled-cluster expansion. These terms are removed from the CCSD expansion to give the DCSD wavefunction. In test cases, DCSD shows a large improvement over CCSD in describing the static correlation present in bond breaking and also achieves greater accuracy in calculating a set of reaction energies.²²³

orders of excitation and orbitals determined with a multi-reference method, with the most extensive treatment found in part using CCSDTQ with CASSCF(40,38) orbitals and excitations restricted to the same (40,38) active space.²⁰⁶ Here, BCCD and CCSD are single reference methods, and while DCSD is not a multi-reference method, it might be expected to show an improvement over CCSD and BCCD in describing static correlation.

	BCCD			CCSD ^a			DCSD ^a			DCSD ^a		
	ROHF	ICR	Δ_{cr}	ROHF	CAS	Δ_{cr}	ROHF	T_1^{sp}	Δ_{cr}	ROHF	CAS	Δ_{cr}
ΔE_{nosp}	5.0	4.8	-0.25 (20%)	4.0	3.5	-0.5 (29%)	1.8	0.2	-1.6 (70%)	1.8	1.2	-0.6 (26%)
ΔE_{sp}	3.7	3.7		2.3	2.3		-0.5	-0.5		-0.5	-0.5	
Δ_{sp}	-1.3	-1.0		-1.7	-1.2		-2.3	-0.7		-2.3	-1.7	

^a data taken from²⁰⁶

Table 5.3: A comparison of calculations of the spin gap of the Fe(por) compound. The core treatments are displayed in the middle column of each method. Note that CAS denotes the CASSCF(32,34) orbitals determined in²⁰⁶ and the core treatment T_1^{sp} refers to including single excitations from the 3s and 3p orbitals in the calculation. Δ_{cr} is the core relaxation contribution to the spin gap. The bracketed numbers are Δ_{cr} as a percentage of Δ_{sp} . All energies are in $\text{kcal}\cdot\text{mol}^{-1}$.

The icr-BCCD, CAS-CCSD, and CAS-DCSD all give similar magnitudes of Δ_{cr} which in turn make up similar percentages of Δ_{sp} . None of these three methods are able to capture a significant proportion of Δ_{sp} with their treatments of core relaxation, despite the CAS orbitals containing visibly relaxed Fe 3s orbitals. Notably, the icr-BCCD orbitals did not show the same visible relaxation in the Fe 3s orbital and instead resembled the ROHF case. Despite this, the core relaxation contribution to the spin gap is only $0.25 \text{ kcal}\cdot\text{mol}^{-1}$ smaller when using the icr-BCCD orbitals compared to CAS orbitals with the similar CCSD treatment of the valence correlation. In contrast, the T_1^{sp} -DCSD core relaxation contribution is the largest in magnitude and makes up 70% of its Δ_{sp} , the first instance seen in the current investigation where core relaxation accounts for the majority of the 3s3p correlation. Given that the CAS-DCSD did not see the same level of core relaxation and that icr-BCCD has an equivalent treatment of core relaxation

to T_1^{sp} -DCSD, it can be suggested that the heightened core relaxation observed in the T_1^{sp} -DCSD method is due to the combination of the T_1^{sp} core treatment and the DCSD valence treatment.

Overall, the Fe(por) spin gap exemplifies a case where the majority of the core correlation calculated by a method can be captured by a core correlation treatment equivalent to ICR, and as such can serve as an approximation of the core correlation with moderate accuracy. This is in contrast to the systems studied in the previous sections where the ICR contribution to the energy differences of interest was oppositely signed with respect to the total core correlation contribution.

5.5 Conclusion

The present chapter reports a derivation and implementation of correlation-induced core orbital relaxation in the BCCD(T) method, which was termed inactive orbital correlated relaxation (ICR). The subsequent investigation has shown how the nature of the core orbital relaxation depends on whether double excitations from the core orbitals are included in the coupled-cluster wavefunction. ICR and all-electron core relaxation were demonstrated to lead to oppositely signed contributions to the majority of the ionisation and bond dissociation energies tested but also to lead to contributions of the same sign when applied to the spin gaps of transition metal complexes. Additionally, it was found that a method equivalent to ICR, T_1^{sp} , was able to capture the majority of the core correlation contribution to a spin gap when used in conjunction with a DCSD treatment of valence correlation. Further results suggested that it was specifically the combination of DCSD and T_1^{sp} which allowed the greater core relaxation, highlighting the importance of an appropriate valence correlation method along with the treatment of core relaxation.

As an approximation for core correlation in general, ICR did not significantly improve the estimations for any of the quantities calculated in this investigation and had a small effect in general. To further develop approximations of core correlation, one might

consider implementing ICR in BDCD, the Brueckner coupled-cluster equivalent of DCSD, given the effectiveness of the T_1^{sp} -DCSD method in the Fe(por) system. More broadly, investigation into ways of approximating the double excitations from core orbitals may prove useful as double excitations tended to have a much larger effect on the energy differences calculated in this study than core relaxation.

Chapter 6

Conclusion

This thesis has reported three contributions to knowledge related to the modelling of the electronic structure of intermetalloid cluster compounds. Contributions to both the development of the bonding models of intermetalloid clusters and to the development of electronic structure methodologies suited to modelling intermetalloid clusters have been presented. The first contribution, presented in chapter three, examined a Cr_6 cluster encapsulated in an array of butterfly-like Sn_2Sb_2 units with KS-DFT to determine its electronic state. It was shown that a near-electron-precise count of 23 could be associated with the Cr_6 metal fragment, an electron count unprecedented in previously observed Cr_6 clusters. Secondly, a methodology using coupled-cluster theory was developed with the goal of determining whether the global minima of Cr@Si_{14} and $[\text{Mn@Si}_{14}]^+$ adhere to a Wade's rules or fullerene-like bonding model. The inclusion of electron correlation appeared to increase delocalisation between the Si_{14} cage and the interstitial metal, leading to a relative stabilisation of the Wade's rules arachno structure. The stabilisation was large enough in Cr@Si_{14} to conclude the arachno isomer was more stable, in line with previous claims. The situation for $[\text{Mn@Si}_{14}]^+$ was less clear with the arachno isomer calculated as the lower energy but within the margin of error of the computational method employed. Finally, correlation-induced core orbital relaxation was implemented in a BCCD(T) program with the aim of increasing the proportion of the electron correlation energy that may be calculated in certain intermetalloid clusters. Investigation into the behaviour of this relaxation showed that core orbital relaxation in Brueckner coupled-cluster theory is influenced by the double excitations from the core orbitals in addition to the field of the correlated valence electrons.

The field of intermetalloid clusters will continue to develop with new compounds being synthesised and characterised, followed by theoretical studies which establish and develop bonding models, and fill holes in experimental data. As touched on in this thesis, establishing what causes clusters to adhere to a particular bonding model remains a complicated task and an area where there is room for development. One may hope to work towards an understanding of the bonding in intermetalloid clusters which allows the design of novel clusters where their properties may be tuned to fit potential

applications. Intermetalloid clusters will also undoubtedly continue to push the limits of theoretical methods and inspire the development of new methodologies and electronic structure calculations. A challenge experienced in this thesis related to both developing bonding models and methodologies using electronic structure methods is a lack of analysis tools which can provide clear insight into the nature of the electron correlation present in a system. For example, cases of bond breaking proved to be a useful test case in chapter five precisely because the correlation in these systems was broadly understood. In contrast, only so much could be learnt about the results obtained in the other systems trialled in chapter five because it could not be seen from the tools available how the correlation in the system was acting. Furthermore, the effect of correlation had to be inferred from comparison of Brueckner and Hartree-Fock orbitals in chapter four, allowing only a broad trend to be established. Analysis tools for electronic structure calculations are difficult to develop as they require navigating the $3N_e$ -dimensional space which houses the wavefunction. This is not only a computational task but a conceptual one, and any breakthroughs in this area may require new ways of understanding electron correlation, similar to how MO theory provided a new way of understanding electronic structure. Nevertheless, being better able to understand electron correlation would allow more to be learnt from each calculation and no doubt lead to developments in both theoretical methods and in our understanding of the electronic structure of matter.

It really would be enough to *really* understand the electron.

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Appendix

A1 Characterisation of the Electronic Structure of



A1.1 Investigation into the Use of Point Charges as the Positive Background Charge

Point charges can be used as an alternative to the COSMO method to provide a positive background charge for the single molecule KS-DFT calculations of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$. The use of point charges is trialled in this investigation by placing a set of point charges in the positions of all K^+ ions within a distance of 15 Å from the centre of the $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ compound in the crystallographic data. Importantly, this placement of the point charges means that $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ cannot be symmetrised to the C_{2v} point group, removing the ability to choose to which of the ${}^2\text{A}_1$, ${}^2\text{B}_1$, or ${}^2\text{B}_2$ states the calculation converges. Hence, the $[\text{Cr}_6\text{Sn}_8\text{Sb}_8\text{F}_2]^{5-}$ system is used, which converges to the ${}^2\text{B}_2$ state when symmetry restrictions are not applied.

Geometry optimisations of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8\text{F}_2]^{5-}$ are performed using point charges values of 0.1, 0.5 and 1.0 a.u. with the PBE/TZP methodology discussed in section 3.3. Additionally, the Sn atoms were placed in the E_{eq} sites and the Sb atoms are placed in the E_{fac} sites for these calculations. The optimisation using a point charge value of 0.5 a.u. leads to a structure with a large imaginary frequency ($914i \text{ cm}^{-1}$) distorting the $[\text{Cr}_6\text{Sn}_8\text{Sb}_8]^{3-}$ centre of the compound and the optimisation using 1.0 a.u. point charges leads to results which contained atoms significantly displaced from their crystallographic positions. The optimisation using 0.1 a.u. point charges only leads to small imaginary ($3i \text{ cm}^{-1}$ and $5i \text{ cm}^{-1}$) frequencies associated with rocking the compound as a whole, with negligible changes in bond length. As such, only the data from a point charge value of 0.1 a.u. is considered. This data is presented in table A1.1 alongside data from the COSMO model for comparison. When compared to the COSMO model, the 0.1 a.u. point charges cause a general expansion of 0.01–0.04 Å of the bond lengths.

	Cr _{eq} -Cr _{eq}	Cr _{eq} -Cr _{ax}	Cr _{eq} -Sb	Cr _{ax} -Sb	Cr _{eq} -Sn	Sn-Sn	Sn-Sb
Exp.	2.453(2)-	2.480(2)-	2.739(2)-	2.778(1)-	2.787(1)-	2.9293(7)-	2.9106(8)-
	2.457(1)	2.482(2)	2.754(2)	2.790(1)	2.809(2)	2.9353(9)	2.9262(8)
COSMO	2.42-2.48	2.36-2.48	2.79-2.82	2.83-2.85	2.85-2.93	3.00-3.02	2.96-2.99
Point Charges	2.47-2.49	2.37-2.46	2.81-2.83	2.87-2.88	2.87-2.95	3.01-3.04	2.99-3.02

Table A1.1: A comparison of selected bond lengths in Å calculated from geometry optimisations of $[Cr_6Sn_8Sb_8F_2]^{5-}$ in different positive background charges using the PBE/TZP methodology. COSMO refers to the COSMO method, implemented as described in section 3.3. In this table, point charges refers to the use of point charges of value 0.1 a.u. in the position of K^+ crystallographic sites, as described in the present section. The XRD-measured bond lengths (Exp.) are also included for reference.

A1.2 Geometric data and Relative Energies of Electronic States with Different Functionals

E.S.	Rel. E	Cr _{eq} -Cr _{eq}	Cr _{eq} -Cr _{ax}	Cr _{eq} -Sb	Cr _{ax} -Sb	Cr _{eq} -Sn	Sn-Sn	Sn-Sb
Exp.	-	2.453(2)-	2.480(2)-	2.739(2)-	2.778(1)-	2.787(1)-	2.9293(7)-	2.9106(8)-
		2.457(1)	2.482(2)	2.754(2)	2.790(1)	2.809(2)	2.9353(9)	2.9262(8)
PBE:								
2A_1	0.00	2.38-2.39	2.42	2.78-2.79	2.77-2.80	2.89-2.91	3.04	2.97-2.98
2A_2	8.09	2.41-2.42	2.40-2.48	2.77-2.78	2.79-2.82	2.87-2.93	2.95-2.97	2.98-2.99
2B_1	4.78	2.37	2.46	2.79-2.80	2.81-2.83	2.90-2.92	2.96	2.97-2.98
2B_2	0.80	2.44-2.45	2.36-2.47	2.78-2.80	2.81-2.84	2.85-2.93	2.97-2.99	2.96-2.99
OPBE:								
2A_1	0	2.34–2.35	2.38–2.39	2.72–2.73	2.70–2.73	2.84–2.86	2.99–3.00	2.92–2.93
2B_1	4.31	2.34	2.44	2.73–2.74	2.75–2.77	2.85–2.87	2.92	2.92–2.93
2B_2	1.32	2.41–2.42	2.33–2.44	2.72–2.74	2.75–2.77	2.79–2.88	2.92–2.95	2.91–2.95
BLYP:								
2A_1	0	2.41	2.43–2.44	2.85–2.86	2.86–2.89	2.96–2.99	3.10	3.02
2B_1	7.5	2.38–2.39	2.48	2.86–2.87	2.88–2.91	2.97–2.99	3.00	3.02–3.03
2B_2	4.63	2.46–2.48	2.37–2.48	2.85–2.87	2.89–2.94	2.92–3.01	3.01–3.04	3.01–3.04

Table A1.2: Relative energies (Rel. E) and selected bond lengths calculated for possible electronic states (E.S.) of $[Cr_6Sn_8Sb_8(en)_2]^{3-}$ using the PBE, OPBE and BLYP functionals. The experimental (Exp.) bond lengths are also included. Energies are in kcal·mol⁻¹. Bond lengths are in Å.

A1.3 The Spin Density of the 2B_2 State with en Ligands and its Primary Contributing Orbitals

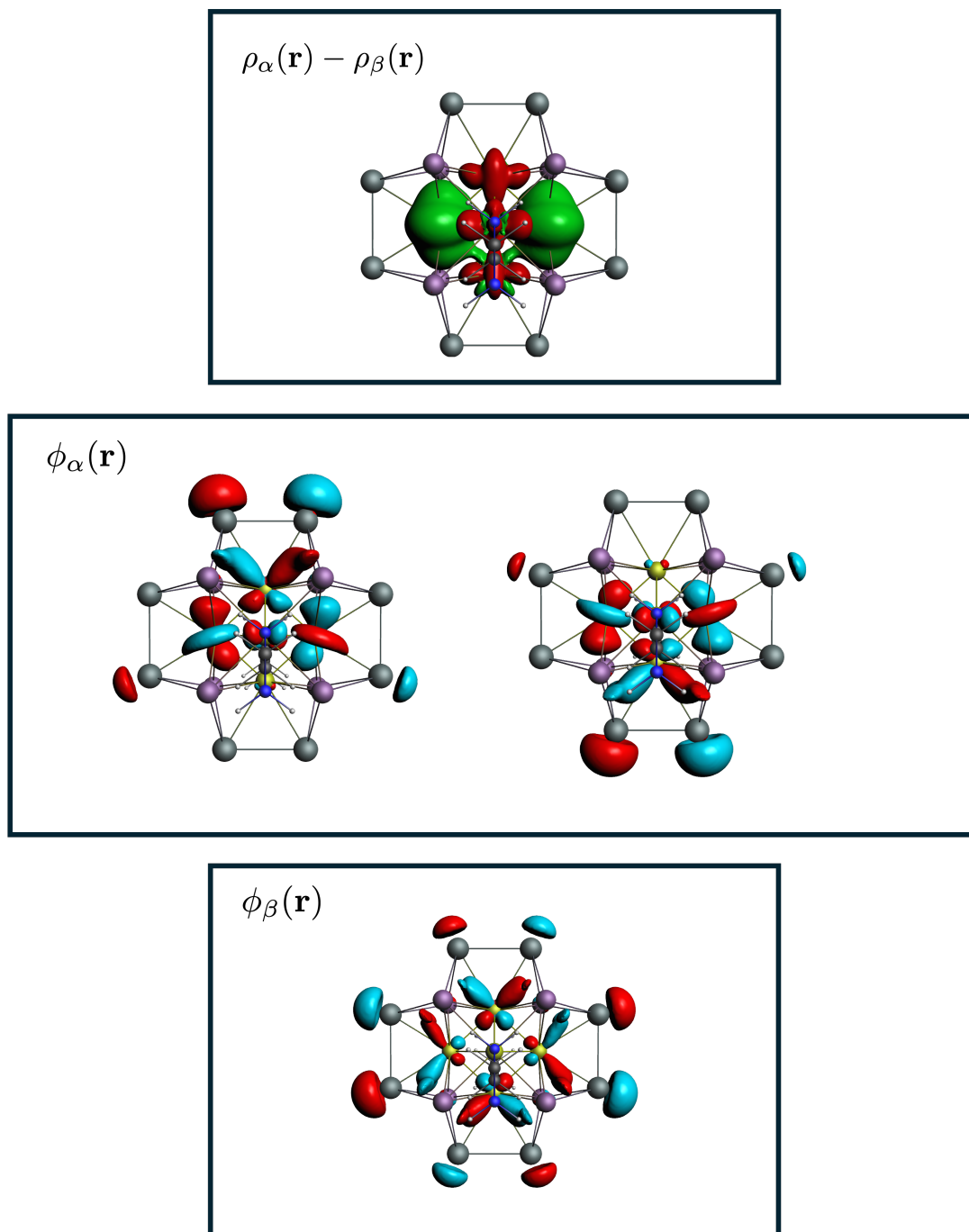


Figure A1.1: The spin density of the 2B_2 state of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ alongside the spatial components of the alpha and beta spin orbitals which make the primary contributions to the spin density of this state.

A1.4 Investigation into the Imaginary Mode Perturbing the [Cr₆Sn₈Sb₈]³⁻ centre of [Cr₆Sn₈Sb₈(en)₂]³⁻ in its ²B₂ Electronic State

The present section seeks to estimate the impact of removing the large imaginary frequency associated with distorting the [Cr₆Sn₈Sb₈]³⁻ centre of [Cr₆Sn₈Sb₈(en)₂]³⁻ in its ²B₂ state. As stated in section 3.3, all attempts to remove this frequency led to convergence to the Sn radical ²A₁ state but replacing the en ligands of [Cr₆Sn₈Sb₈(en)₂]³⁻ with F⁻ allowed convergence to the equivalent of the ²B₂ state in [Cr₆Sn₈Sb₈F₂]⁵⁻, without the imaginary mode present. The equivalent of the ²B₂ state in [Cr₆Sn₈Sb₈F₂]⁵⁻ is formally a ²A₁ state and therefore is referred to as the Cr₆ radical state in the present section to distinguish it from the Sn radical ²A₁ state. Note that, since there are no imaginary frequencies associated with rotations about Cr–N bonds in [Cr₆Sn₈Sb₈F₂]⁵⁻, the Cr₆ radical state is a local minimum when the imaginary frequency perturbing the [Cr₆Sn₈Sb₈]³⁻ centre is removed.

To obtain an estimate for the changes in energy and geometry which occur on removal of the imaginary frequency, a [Cr₆Sn₈Sb₈F₂]⁵⁻ structure with the imaginary frequency present is also needed. Such a structure can be obtained by calculating the Cr₆ radical state in the D_{2h} point group, in which the state is formally denoted ²B_{2u} and the imaginary frequency is 166i cm⁻¹ when using the PBE/TZP methodology. The D_{2h} symmetry restriction of [Cr₆Sn₈Sb₈F₂]⁵⁻ provides constraints on the [Cr₆Sn₈Sb₈]³⁻ centre similar to (but not exactly the same as) those of the C_{2v} restriction of [Cr₆Sn₈Sb₈(en)₂]³⁻ and, as can be seen from tables A1.2 and A1.3, the Cr₆ radical state in D_{2h} symmetry has a similar geometry to that obtained from the C_{2v} symmetry restriction on the ²B₂ state of [Cr₆Sn₈Sb₈(en)₂]³⁻. Ergo, the changes due to the removal of the large imaginary frequency in [Cr₆Sn₈Sb₈(en)₂]³⁻ can be estimated from the differences between the ²B_{2u} state of [Cr₆Sn₈Sb₈F₂]⁵⁻ in D_{2h} symmetry and the Cr₆ radical ²A₁ state of [Cr₆Sn₈Sb₈F₂]⁵⁻ in C_{2v} symmetry. The impact of the F⁻ ligand on the [Cr₆Sn₈Sb₈]³⁻ centre is expected to be approximately constant across the configurations

of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8\text{F}_2]^{5-}$ with and without the imaginary frequency present and therefore is not considered in the estimation. Table A1.3 displays the geometries and relative energies of the ${}^2\text{B}_{2u}$ and ${}^2\text{A}_1$ states.

E.S.	Rel. E	$\text{Cr}_{\text{eq}}\text{--}\text{Cr}_{\text{eq}}$	$\text{Cr}_{\text{eq}}\text{--}\text{Cr}_{\text{ax}}$	$\text{Cr}_{\text{eq}}\text{--}\text{Sb}$	$\text{Cr}_{\text{ax}}\text{--}\text{Sb}$	$\text{Cr}_{\text{eq}}\text{--}\text{Sn}$	Sn--Sn	Sn--Sb
Exp.	-	2.453(2)-	2.480(2)-	2.739(2)-	2.778(1)-	2.787(1)-	2.9293(7)-	2.9106(8)-
		2.457(1)	2.482(2)	2.754(2)	2.790(1)	2.809(2)	2.9353(9)	2.9262(8)
${}^2\text{B}_{2u}$	0.00	2.45	2.36-2.45	2.79-2.81	2.85	2.86-2.92	2.98-3.01	2.97-2.99
${}^2\text{A}_1$	-0.55	2.43-2.48	2.36-2.48	2.79-2.82	2.83-2.85	2.85-2.92	2.99-3.02	2.96-3.00

Table A1.3: A comparison of the geometries and relative energies (Rel. E) of the Cr_6 radical electronic states (E.S.) of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8\text{F}_2]^{5-}$ with (${}^2\text{B}_{2u}$) and without (${}^2\text{A}_1$) its largest imaginary frequency present. Experimental (Exp.) bond lengths are also presented for reference. All results are calculated using the PBE/TZP methodology, all energies are in $\text{kcal}\cdot\text{mol}^{-1}$, and all bond lengths are in $\text{\AA}$.

The geometric distortion in $[\text{Cr}_6\text{Sn}_8\text{Sb}_8\text{F}_2]^{5-}$ which removes the imaginary frequency is depicted in figure A1.4 alongside the spin densities of the Cr_6 radical state with (D_{2h}) and without (C_{2v}) the imaginary frequency present. The primary difference is in the $\text{Cr}_{\text{eq}}\text{--}\text{Cr}_{\text{eq}}$ bond lengths where two of these elongate towards the area of larger spin density and the other two shorten. It may also be noted that the distortion is sensitive to the model of the positive background charge employed. The point charge model discussed in section A1.1 produces a geometry where the range of the $\text{Cr}_{\text{eq}}\text{--}\text{Cr}_{\text{eq}}$ bond lengths reduces to near the point of vanishing since all four of these bond lengths elongate in the point charge model. The full set of bond lengths using the point charge model can be found in table A1.1.

Table A1.3 shows that the removal of the large imaginary frequency reduces the energy of the electronic state by $0.55 \text{ kcal}\cdot\text{mol}^{-1}$. As discussed in the first paragraph of the current section, it may therefore be approximated that the removal of the large imaginary frequency in the ${}^2\text{B}_2$ state of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8(\text{en})_2]^{3-}$ causes a reduction of $0.55 \text{ kcal}\cdot\text{mol}^{-1}$ in the energy of the ${}^2\text{B}_2$ state.

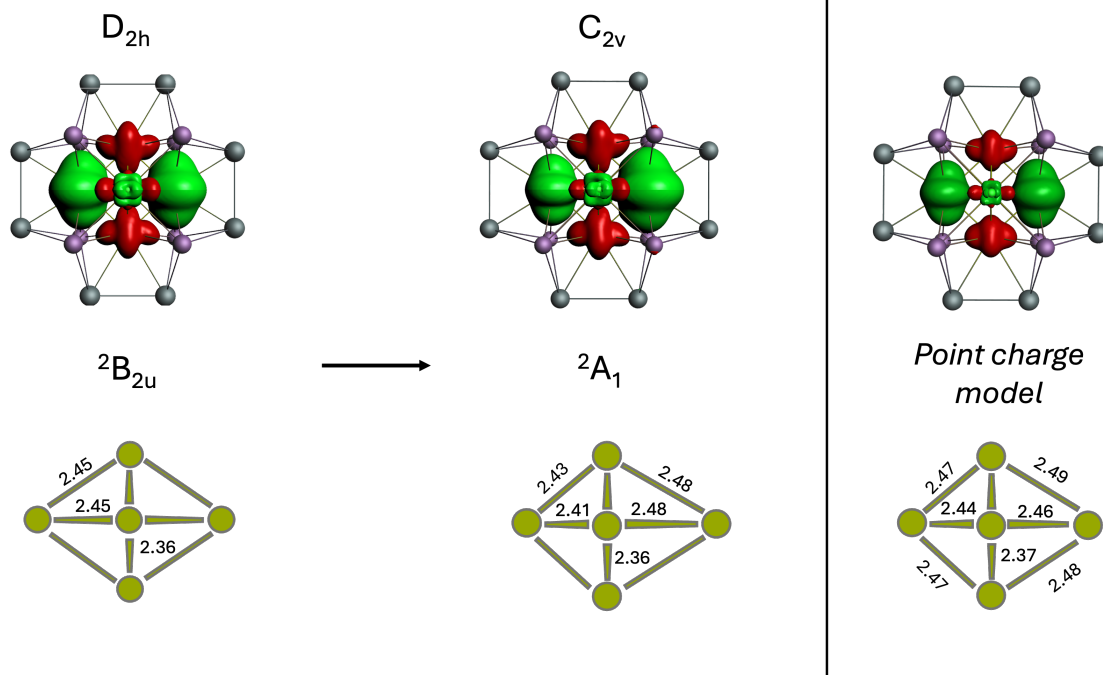


Figure A1.2: A representation of the change in the structure of the Cr_6 unit which occurs in the 2B_2 state of $[\text{Cr}_6\text{Sn}_8\text{Sb}_8\text{F}_2]^{5-}$ upon removal of its large imaginary frequency perturbing the $[\text{Cr}_6\text{Sn}_8\text{Sb}_8]^{3-}$ unit of the compound. The Cr_6 unit is displayed in a top-down view where four Cr atoms in the equatorial plane are visible. The change in the Cr_6 unit is approximated in the $[\text{Cr}_6\text{Sn}_8\text{Sb}_8\text{F}_2]^{5-}$ compound where the large imaginary frequency is present in the ${}^2B_{2u}$ state in D_{2h} symmetry and removed in the 2A_1 state in C_{2v} symmetry. A model using point charges to provide the positive background charge is also displayed to show how the change in the Cr_6 unit is influenced by the model of the positive background charge.

A2 A Coupled-Cluster Investigation into the Relative Stability of Isoelectronic $\text{M}@\text{Si}_{14}$ Isomers

A2.1 Analysis of the Convergence of CCSD and (T) Contributions to Isomer Energy Difference of $\text{Cr}@\text{Si}_{14}$ with respect to the Arachno 5.5 eV Reference State

In a CCSD(F12*)(T) calculation, the explicit correlation treatment only changes the way the CCSD contribution energy is calculated and does not change the way the perturbative triples correction is computed. In general, a CCSD(F12*) total energy is expected to be converged to a level equivalent to that of a CCSD calculation in a basis of approximately

1.5 cardinal numbers higher than that of the basis used in a CCSD(F12*) calculation. The increased convergence of the CCSD(F12*) contribution can be observed in calculations on Cr@Si_{14} by considering the difference in the CCSD energies when calculated in the ccXZ and a-ccXZ sets. The difference between the results obtained with augmented and non-augmented basis sets can be used as a rough measure of convergence since the size of the gap between the bases is expected to become increasingly small as the CBS limit is approached. A plot of the energy difference between results obtained in the non-augmented and augmented basis sets against the basis set cardinality is shown in figure A2.3

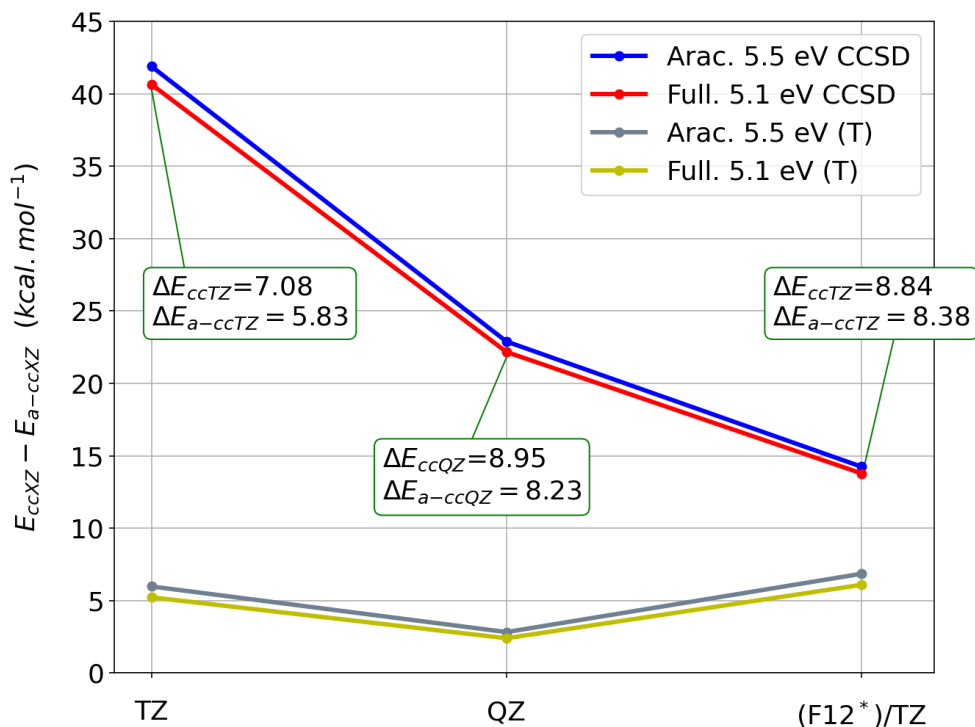


Figure A2.3: The difference between the CCSD total energies calculated in the ccXZ and a-ccXZ basis sets for the isomers of Cr@Si_{14} using the 5.5 eV arachno and 5.1 eV fullerene reference states. The differences are given for $X=T, Q$ for the canonical coupled-cluster calculations and for $X=T$ in the explicitly correlated CCSD(F12*) calculations. Also shown is the difference between the (T) corrections calculated in the ccXZ and a-ccXZ basis sets for the same systems. Again, results are found for $X=T, Q$ for canonical coupled-cluster calculations, and only for $X=T$ for the explicitly correlated CCSD(F12*)(T) calculations. The isomer energy differences using CCSD with each basis set ($\Delta E_{(a-)ccXZ}$) are also shown in the green boxes in kcal·mol⁻¹.

It can be seen that the energy gap between the basis sets decreases, first going from

CCSD/TZ to CCSD/QZ and then to CCSD(F12^{*})/TZ, as expected from previous reports. However, the reduction in this energy gap only correlates with a small change between the isomer energy differences calculated with CCSD/QZ and CCSD(F12^{*})/TZ. Nonetheless, the reduction of the energy gap between the non-augmented and augmented basis sets suggests a more converged E_{CBS} estimation of the CCSD energy may be obtained from the CCSD(F12^{*}) calculations.

Since the (T) correction in CCSD(F12^{*})(T) does not benefit from the same apparent increase in basis set as the single and double excitations, it is possible that the lower convergence of its (T) correction compared to that of the CCSD(T)/ccQZ calculation means the error in the (T) correction of the CCSD(F12^{*})(T) calculation is larger than the error in the CCSD/ccQZ calculation. This would mean that a more accurate E_{CBS} estimation could be obtained by an additive scheme where the (T) from CCSD(T)/ccQZ is added to the CCSD(F12^{*}) result,

$$E_{\text{CBS}} = E_{\text{CCSD(F12}^*)} + E_{\text{(T)/QZ}}. \quad (\text{A2.1})$$

To analyse the convergence of the (T) correction, the difference between the (T) corrections found in the augmented and non-augmented basis sets is also plotted in figure A2.3. This difference indicates a similar level of convergence of the (T) correction is obtained using the ccTZ basis in both CCSD(T) and CCSD(F12^{*})(T), despite the higher level of convergence in the CCSD contribution indicated in the CCSD(F12^{*})(T) calculations. Conversely, the (T) correction in the CCSD(T)/ccQZ calculations is indicated to have a higher level of convergence, even though the CCSD amplitudes from which it was calculated were indicated to be less converged. This evidences the idea that the (T) correction is affected more by the basis set used than the convergence of the CCSD amplitudes it is calculated from. Thus, there is reason to believe that the additivity scheme given in equation (A2.1) could provide a more accurate E_{CBS} estimation. The isomer energy differences from this scheme are displayed in table A2.4, alongside the results from the extrapolated method, seen also in table 4.1.

		CCSD(T)		CCSD(F12*)+(T)QZ	
		cc(T,Q)Z	a-cc(T,Q)Z	ccXZ	a-ccXZ
Fullerene	5.1 eV	0	0	0	0
Arachno	5.5 eV	-2.71	-3.11	-2.68	-3.52

Table A2.4: Comparison of the relative values of E_{CBS} obtained from the extrapolation method and from scheme (A2.1) for the isomers of Cr@Si_{14} . All values are in $\text{kcal}\cdot\text{mol}^{-1}$.

The span of the results from scheme (A2.1) is less than from the CCSD(F12*)(T) results displayed in table 4.1 and the range from scheme (A2.1) still contains the results from the extrapolated method. If the range of the results from scheme (A2.1) is taken as the error in E_{CBS} and its midpoint taken as the E_{CBS} estimate, the E_{CBS} contribution to the isomer energy difference is $\Delta E_{\text{CBS}} = -3.10 \pm 0.42 \text{ kcal}\cdot\text{mol}^{-1}$. This indicates a reduced error compared to the equivalent CCSD(F12*)(T) result of $\Delta E_{\text{CBS}} = -2.71 \pm 0.59 \text{ kcal}\cdot\text{mol}^{-1}$.

A3 Implementation and Investigation of the Correlation Induced Relaxation of Core Orbitals in Brueckner Coupled-Cluster Theory

A3.1 Spin States of Transition Metal Complexes

	BCCD(T)			BCCD			Reference		
	MnCp ₂	MnL ₂	Fe(por)	MnCp ₂	MnL ₂	Fe(por)	MnCp ₂	MnL ₂	Fe(por)
Initial state Δ_{sp}	-258.69	-257.67	-265.08	-250.89	-250.31	-257.43	1.36	1.00	-0.12
Final state Δ_{sp}	-265.65	-263.44	-267.38	-254.50	-253.61	-258.72	0.85	0.65	0.15
Initial state Δ_{ICR}	-0.74	-0.75	-2.01	-0.73	-0.74	-2.01	-0.70	-0.71	-2.07
Final state Δ_{ICR}	-1.41	-1.32	-2.26	-1.42	-1.34	-2.27	-1.40	-1.37	-2.35

Table A3.5: The differences due to ICR (Δ_{ICR}) and the correlation of 3s3p electrons (Δ_{sp}) in the total energies of the spin states of each of the compounds discussed in section 5.4.3. All values are in kcal · mol⁻¹.