QUANTUM CHEMISTRY CALCULATIONS OF ENERGETIC AND SPECTROSCOPIC PROPERTIES OF $p$- AND $f$-BLOCK MOLECULES

Christopher South, B.S.

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APPROVED:

Angela K. Wilson, Major Professor
Thomas R. Cundari, Committee Member
Paul Marshall, Committee Member
Simone Raugei, Committee Member
Michael Richmond, Committee Member and Chair of the Department of Chemistry
David Holdeman, Dean of the College of Arts and Sciences
Victor Prybutok, Vice Provost of the Toulouse Graduate School

Quantum chemical methods have been used to model a variety of p- and f-block chemical species to gain insight about their energetic and spectroscopic properties. As well, the studies have provided understanding about the utility of the quantum mechanical approaches employed for the third-row and lanthanide species. The multireference ab initio correlation consistent Composite Approach (MR-ccCA) was utilized to predict dissociation energies for main group third-row molecular species, achieving energies within 1 kcal mol$^{-1}$ on average from those of experiment and providing the first demonstration of the utility of MR-ccCA for third-row species. Multireference perturbation theory was utilized to calculate the electronic states and dissociation energies of NdF$^{2+}$, providing a good model of the Nd-F bond in NdF$_3$ from an electronic standpoint. In further work, the states and energies of NdF$^+$ were determined using an equation of motion coupled cluster approach and the similarities for both NdF$^{2+}$ and NdF were noted. Finally, time-dependent density functional theory and the static exchange approximation for Hartree-Fock in conjunction with a fully relativistic framework were used to calculate the L$_3$ ionization energies and electronic excitation spectra as a means of characterizing uranyl (UO$_2^{2+}$) and the isoelectronic compounds NUO$^+$ and UN$_2$. 
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By

Christopher South
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CHAPTER 1

INTRODUCTION

A fundamental goal of quantum chemistry is to obtain thermochemical and kinetic data, such as enthalpies of formation and rate constants, for unknown systems to such accuracy as to reliably direct chemical design. The inherent difficulty of obtaining data capable of predicting chemical reactivity trends and reaction energies is in the large number of electronic interactions that have a direct effect on the electronic energies and must be taken into account to reach the level of accuracy desired. Additionally, the magnitude of the effects of electronic interactions such as electron correlation, core-valence correlation, and relativistic effects, among others, may vary wildly between systems. As a result, it is necessary to prioritize the most important effects and cancel errors between calculated energies where possible to obtain the most chemically accurate computed data. Further, the methods arising from the solution to Schrödinger’s equation must be confirmed to be reliable for molecules for which verifiable experimental data exists prior to being used to calculate properties for unknown species. Once the methods have been shown to be reliable for a wide array of systems and properties, they can then be used to predict chemical and electronic properties for systems for which these properties are not yet known. In this work, computational methods have been used to model a wide variety of properties such as bond energies, reaction enthalpies, and excitation energies, among others, for the purposes of method verification, prediction of reactivity, and molecule characterization.

In Chapter 2, the computational methods and means of mitigating errors in absolute and relative electronic energies for the following chapters are enumerated. These methods are then related to the types of problems they solve and how they are used to obtain quantitative and qualitative computational data. Computational methods ranging from pure \textit{ab initio} (from first
principles) methods to density functional theory are explained as well as the basis sets and functions used to model the wavefunctions. Further, methods designed to model electronic effects such as relativistic effects, static and dynamic electron correlation, and excited states are expanded upon. The final concepts explained in this chapter are techniques designed to reduce the innate cost of computational methods that are used to obtain computational data for larger molecules such as effective core potentials and composite computational methods.

Chapter 3 encompasses the research performed using the multi-reference correlation consistent composite approach (MR-ccCA) to calculate the quantitative spectroscopic rotational and vibrational constants and dissociation energies and potential energy curves for third-row main group diatomic molecules. The utility of MR-ccCA in the prediction of accurate thermochemical and spectroscopic data for lighter molecules has been demonstrated, and also produced continuous potential energy curves despite MR-ccCA being a composite method not explicitly designed to produce this behavior. The question remained, though, whether MR-ccCA would continue to describe heavier molecules with more complicated electronic states, which was investigated in this research. To this end, MR-ccCA was used on a set of seven diatomic molecules, each containing at least one third-row main group element (Ga-Kr). The resulting thermochemical and spectroscopic data obtained for their ground and excited states was compared to experiment to determine if MR-ccCA still retains its quantitative agreement with experiment for these systems.

Chapter 4 recounts work on calculating the excited states of NdF$_2^{2+}$ as an analog to the Nd-F bond in NdF$_3$ using multi-reference perturbation theory and spin-orbit coupling. The nature of bonding of lanthanide molecules is not well understood as examining the electronic structure of lanthanides is difficult, and it is known that the degenerate 4f orbitals can create a
complex excited state manifold. To investigate the nature of the bond in NdF₃, NdF²⁺, containing neodymium in the typical 3+ oxidation state for lanthanides, was investigated using multiconfigurational quasi-degenerate perturbation theory and spin-orbit coupling to calculate the bond strength and excited states and compared to those of NdF₃.

Chapter 5 is a continuation of the research in the previous chapter looking instead at neodymium in the less common 2+ oxidation state as NdF⁺ and determining through an equation of motion coupled cluster approach, whether NdF⁺ resembles NdF²⁺ or NdF chemically and electronically. Both NdF²⁺ and NdF with neodymium in the 3+ and 1+ oxidation states, respectively, have been examined electronically in computational studies and been found to have different electronic states as well as bond strengths. However, since the difference in atomic state of neodymium from 2+ to 1+ is the removal of a 4f electron, the effect the nearby 5d orbitals have on the electronic and thermochemical properties is unknown. Therefore, NdF⁺ with neodymium in the 2+ oxidation state was examined using an equation of motion coupled cluster approach and the electronic and thermochemical properties of NdF⁺ were compared to those of the remaining oxidation states and to experiment.

In Chapter 6, the excited states for uranyl (UO₂²⁺) and the isoelectronic molecules OUN⁺ and UN₂ were examined using time-dependent density functional theory and static exchange approximation Hartree-Fock theory. Uranyl compounds form a myriad of coordination complexes and tend to be very soluble in water, leading to possible concerns of groundwater contamination. As a result, characterization of these complexes is complicated in that the valence spectra will vary wildly between complexes. However, core level spectroscopy is highly element specific and sensitive to the core level environment. To gauge the utility of computational methods to calculate the diagnostic core level spectra for uranyl compounds, the
core level L₃ X-ray absorption near edge spectra were calculated for UO₂²⁺, OUN⁺, and UN₂. In addition, the effects of the ligands on the local electronic environment of uranium were investigated as were the types of electronic transitions involved in the electronic spectrum. The ionization energies were also calculated to gauge the effect of correlation and relaxation on the ionization energies and on how the ligand environment affects those quantities.
CHAPTER 2

COMPUTATIONAL THEORY

2.1 Schrödinger’s Equation

The foundation of quantum computational chemistry lies in the Schrödinger equation \(^1\textsuperscript{-4}\)

\[
\hat{H}\Psi = E\Psi
\]

(2.1)

expressed in the time-independent formalism where the Hamiltonian is expressed in atomic units as

\[
\hat{H} = \sum_i \frac{-1}{2} \nabla_i^2 - \sum_i \frac{1}{2m_i} \nabla_i^2 - \sum_i \sum_j Z_i Z_j \frac{1}{r_{ij}} + \sum_i \sum_{j \neq i} \sum_j \frac{1}{r_{ij}}
\]

(2.2)

where capital letters indicate nuclear coordinates, the lower case letters represent electronic coordinates, \(Z\) represents the integer nuclear charge of the specified atom, and \(r\) represents the distance between the particles denoted by the subscripts. The first two terms denote the kinetic energy of the electrons and nuclei, respectively, and the latter three denote the interaction potentials between the nuclei and electrons, the nuclei and the nuclei, and the electrons and the electrons. The Hamiltonian as it is expressed in Equation 2.2 requires a wavefunction that varies in the electronic and nuclear coordinates simultaneously in order to obtain a solution. Born and Oppenheimer posited that since electrons typically possess much higher velocities than the nuclei in a molecule that the electrons will respond to nuclear motion almost instantaneously, leading to the Born-Oppenheimer approximation.\(^1\) As a result, the nuclei (within the frame of reference of the electrons) can be approximated as stationary, reducing the total Hamiltonian to

\[
\hat{H} = \hat{H}_e + \hat{V}_{nn}
\]

(2.3)

where \(\hat{V}_{nn}\) is the constant nuclear-nuclear repulsion term calculated at a predetermined molecular geometry according to \(\langle \Psi | \hat{V}_{NN} | \Psi \rangle = V_{NN} \langle \Psi | \Psi \rangle\) and \(\hat{H}_e\) is
\[
\hat{H}_e = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}
\]  
(2.4)

where \( \hat{T}_e \) is the electronic kinetic energy, \( \hat{V}_{ne} \) is the nuclear-electronic attraction, \( \hat{V}_{ee} \) is the electron-electron repulsion, and the nuclear kinetic energy is zero due to the approximation of stationary nuclei. Due to this decoupling of electronic and nuclear degrees of freedom, the energy of the molecule can be expressed entirely by the electronic wavefunction. The electronic wavefunction, by the requirements of antisymmetry for fermions, is expressed as a Slater determinant:

\[
\Psi(n, r_2, ..., r_n) = \frac{1}{\sqrt{n!}} \det \begin{bmatrix}
\phi_1(n) & \phi_1(r_2) & \cdots & \phi_1(r_n) \\
\phi_2(n) & \phi_2(r_2) & \cdots & \phi_2(r_n) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_n(n) & \phi_n(r_2) & \cdots & \phi_n(r_n)
\end{bmatrix}
\]  
(2.5)

where \( \phi_i \) is the molecular orbital containing electron \( i \) with coordinates \( r_i \). The individual molecular orbitals are constructed as a linear combination of atomic orbitals (LCAO) as

\[
\phi(r) = \sum_i c_i \varphi_i(r)
\]  
(2.6)

where \( c_i \) is a variational parameter and \( \varphi_i \) is the atomic orbital. The atomic orbitals are constructed as a linear combination of basis functions according to

\[
\varphi(r) = \sum_i c_i \chi_i(r)
\]  
(2.7)

where \( \chi_i \) is the basis function and \( c_i \) is the optimized coefficient for the basis function, though not necessarily to normalize the function.

2.2 Basis Sets

The basis functions described in the previous section that are used to model the wavefunction take the form of hydrogen-like orbitals expressed as,
\[ \chi(r, \theta, \phi) = N R_{n^l}(r) Y_{\ell m_l}(\theta, \phi) \]  

(2.8)

where \( R_{n^l} \) is the radial portion of the basis function and \( Y_{\ell m_l} \) is the angular portion that takes the form of real linear combinations of spherical harmonic functions. For exact solutions of the hydrogen atom, the radial portion of these orbitals takes the form,

\[ R_{n^l}(r) = r^{n-l} e^{-r\zeta} \]  

(2.9)

where \( n \) is the principle quantum number, \( r \) is the radial extent from the center of the function, and \( \zeta \) is the exponent determining the rate of decay of the function with large values of \( \zeta \) decaying faster than smaller values. Unfortunately, these hydrogenic Slater type orbitals (STOs), when introduced into the integrals necessary to obtain the electronic energies, possess no analytical solutions for three- and four-center two electron integrals, thus requiring numerical integration to obtain results.\(^3\) Fortunately, a simple change of the radial function from an exponential to a Gaussian according to,

\[ R_{n^l} = r^{2n-2-l} e^{-r^2\zeta} \]  

(2.10)

where the additional variable \( l \) represents the angular momentum of the orbital, results in a functional form that is very easily analytically integrated. The tradeoff for using Gaussian functions in an atom centered basis set is that they do not accurately represent the electronic cusp at the nucleus. This problem can be remedied somewhat by approximating the Slater type orbital with a contracted linear combination of Gaussian type orbitals (GTOs) to more closely approximate the electronic cusp of the Slater type orbitals.

The precise design of basis sets can vary depending on the developer and their method for optimizing the electronic energy obtained from the functions. While basis sets that have more functions will obtain a lower energy for a variational method due to the larger number of variational parameters, the amount of electronic energy recovered may vary depending on the
types of functions included in the basis set. There are basis sets that, as a consequence of their construction, can produce energies that will systematically recover correlation energy. The correlation consistent basis sets were developed by Dunning and others after Dunning noticed that successive shells of correlating functions optimized on top of a minimal HF set would recover similar amounts of correlation energy. These functions can be grouped in such a way such that the first set of functions with similar correlation energy recovery corresponds to one of each angular momentum type function of the minimal basis plus one set with angular momentum plus 1. As an example, for carbon, the first zeta level of the basis set is a 3s2p1d set, the second zeta level is a 4s3p2d1f set, and so on. This trend continues for each successive level of valence correlating functions added, (that is, the zeta level), though each successive level recovers less correlation energy relative to the previous one. These correlation consistent basis sets, as a result, systematically recover electron correlation energy as the size of the basis set increases. Additionally, it has been shown that elements of the second-row main group are poorly described by the standard cc-pVnZ basis sets and require an additional optimized d-type set of orbitals in order to properly describe the polarization of the orbitals, leading to the cc-pV(n+d)Z basis sets.

Because of this systematic recovery of correlation energy, the energies obtained from smaller, less complete basis sets can be extrapolated to an energy corresponding to that from a complete basis set, resulting in very accurate data without the corresponding cost of the equivalent direct calculation. This is accomplished by modeling the energies by a function designed to approach a complete basis set energy limit with the correct convergence rate and limit. Such functions include the Feller exponential function

$$E_n = E_{CBS} + Ae^{-cn},$$

the Peterson dual exponential function
\[ E_n = E_{CBS} + A e^{-(n-1)} + B e^{-(n-1)^2}, \quad (2.12) \]

and the Schwartz inverse power functions\(^{15-17}\)

\[ E(l_{\text{max}}) = E_{CBS} + \frac{A}{l_{\text{max}}^3}, \]

\[ E(l_{\text{max}}) = E_{CBS} + \frac{A}{(l_{\text{max}} + 1/2)^4}, \quad (2.13) \]

among other functional forms,\(^{18,19}\) where \( n \) is the zeta level of the basis set, \( l_{\text{max}} \) is the highest angular momentum basis function in the basis set. \( E_{CBS} \) is the electronic energy at the complete basis set (CBS) limit, and \( A, B, \) and \( C \) are variable parameters required to solve the system of linear equations for \( E_{CBS} \).

The specific choice of basis set can also have an effect on the properties to be calculated due to how the specific basis set has been optimized and its purpose. For example, the Sapporo family of basis sets have been optimized for light elements to elements as heavy as the lanthanides similarly to how the cc-pVnZ sets were derived, but with optimized natural orbitals as opposed to correlating orbitals in addition to a Hartree-Fock set, and with a finite nucleus for the fourth and fifth row relativistic sets.\(^{20,21}\)

For elements that possess a large number of electrons, the computational expense for the calculation can be mitigated through the use of effective core potentials (ECPs).\(^{6,7,22-25}\) The cost of a method is directly related to the time it takes to calculate all the necessary integrals for the calculation and is, therefore, directly related to the number of integrals. The number of integrals scales exponentially with the number of basis functions, so the more electrons that need to be modeled, the more expensive the calculation is. Since the chemical bonding occurs only between valence electrons, the relatively inert chemical core electrons are not actively participating, but must still have integrals computed for them in an all electron basis set, taking a
very large amount of time for elements with many core electrons. To remedy this, ECPs are constructed through replacing the chemically inert core orbitals from a set of electronic orbitals that have been optimized by some method with a smooth, nodeless potential for each angular momentum type in the core and optimizing those potentials with respect to either the energy or the shape of the core orbitals they represent.\textsuperscript{6,7,22–25} The starting set of orbitals is typically optimized using fully relativistic methods to obtain an implicit account of relativity in the molecular calculations. The valence basis functions that describe the valence electrons and their chemical bonding and electron correlation are then optimized on top of the pseudopotential. The advantage of the pseudopotential is that it is much easier to integrate than the functions they replace and reduces the overall size of the system, in terms of the number of electronic integrals required to calculate, allowing for larger elements and molecules to be considered in calculations. Model core potentials (MCPs) are similar to ECPs in that they replace the core functions with a potential and are optimized the same way, except that their functional form preserves the nodal structure of the core orbitals allowing the valence basis to continue the appropriate radial node structure for the valence functions.\textsuperscript{26,27}

2.3 Hartree-Fock

Because the exact analytical solution cannot be calculated for more than a one electron system due to the coupling caused by electron-electron interaction, an issue known as the many body problem, additional approximations must be made in order to obtain any solution beyond one electron. Hartree, Fock, and Roothaan were instrumental in developing the equations necessary for the mean field approximation, the Hartree-Fock (HF) method.\textsuperscript{28–30} Hartree-Fock simplifies the electron repulsions by treating them as formally one electron being acted upon by the mean field of the other electrons. Through iterative solving of the secular equation
the optimal mean field energy for the molecule can be calculated. 

The $\mathbf{F}$ in Equation 2.14 is the Fock matrix with elements 

$$F_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu}^{ne} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left( \langle \mu\nu | \sigma\lambda \rangle - \frac{1}{2} \langle \mu\lambda | \sigma\nu \rangle \right)$$

in the instance where the wavefunction is constrained to be a singlet, where the subscript denotes the molecular orbitals, the operator notation indicates integrals over $\nu$ and $\mu$ using the specified operator. $P_{\lambda\sigma}$ is an element of the density matrix, formulated as 

$$P_{\lambda\sigma} = 2\sum_{a}^{a/2} C_{\lambda a}^{*} C_{\sigma a}^{a}$$

where $C_{\lambda a}$ is the coefficient corresponding to the $\lambda$ element of molecular orbital $a$. The remaining elements of Equation 2.14 are $\mathbf{C}$, the matrix of molecular orbital coefficients, $\mathbf{S}$, the overlap matrix between the molecular orbitals, and $\mathbf{e}$, the diagonal matrix containing molecular orbital energy eigenvalues. In the instance where the alpha and beta spin electrons are optimized separately, as in unrestricted Hartree-Fock, the Fock matrix is split into alpha and beta Fock matrices with the only change being in the exchange wherein only the alpha and beta electron density matrices are used in their respective matrices such that $F_{\mu\nu} = F_{\mu\nu}^{\alpha} + F_{\mu\nu}^{\beta}$ and 

$$P_{\alpha\sigma}^{\alpha} = P_{\beta\sigma}^{\beta} = 1/2 P_{\lambda\sigma}$$

The secular equation is solved through an initial guess of $\mathbf{C}$ (and, by extension, $\mathbf{P}$) which is transformed to the orthonormal basis through use of the inverse overlap matrix to obtain a new set of coefficients $\mathbf{C}$ used to calculate the energy and new density matrix $\mathbf{P}$. This process is repeated successively until the mean field is consistent with itself and the energy reaches a minimum by the variational principle. 

2.4 Single Reference Correlation Methods
The averaged electronic potential from Hartree-Fock is able to recover 99% of the total energy of a molecule.\textsuperscript{31,32} However, the remaining 1% of energy, the correlation energy, still contains a sizeable portion of the chemical information of a molecule. Therefore, post-Hartree-Fock methods that explicitly account for the correlated motion of the electrons are required to obtain accurate chemical properties. There are multiple ways to model electron correlation methods, among which are Rayleigh-Schrödinger perturbation theory,\textsuperscript{33} configuration interaction,\textsuperscript{34–36} and coupled cluster.\textsuperscript{37,38}

The premise behind Rayleigh-Schrödinger perturbation theory is the introduction of a small perturbation to the Hamiltonian
\begin{equation}
\hat{H} = \hat{H}_0 + \hat{V} \tag{2.17}
\end{equation}

where $\hat{H}_0$ is the unperturbed zeroth order Hamiltonian and $\hat{V}$ is the two particle perturbation operator. Additionally, the wavefunction is now expressed as a linear combination of perturbed wavefunctions
\begin{equation}
|\Psi\rangle = |\Psi_0\rangle + |\Psi_1\rangle + |\Psi_2\rangle + \ldots \tag{2.18}
\end{equation}

where $\Psi_0$ is the unperturbed wavefunction followed by the first, second, etc. order perturbed wavefunctions. When the unperturbed wavefunction takes the form of an optimized HF wavefunction, the method is then classified as Möller-Plessett perturbation theory. Collecting all the operators and wavefunctions of the same perturbation level gives a series of eigenvalue equations
\begin{align*}
E_0^{(0)} &= \langle \Psi_0 | \hat{H}_0 | \Psi_0 \rangle \\
E_0^{(1)} &= \langle \Psi_0 | \hat{V} | \Psi_0 \rangle \\
E_0^{(2)} &= \langle \Psi_0 | \hat{V} | \Psi_1 \rangle
\end{align*}
\[ E^{(3)}_0 = \langle \Psi_0 | \hat{V} | \Psi_2 \rangle \text{ etc.} \quad (2.19) \]

as defined by intermediate normalization
\[ \langle \Psi_0 | \Psi \rangle = 1. \quad (2.20) \]

When the equations are solved for the second order energy, an equation is obtained of the form
\[ E^{(2)}_0 = \sum_n \frac{\langle \Psi_0 | \hat{V} | n \rangle \langle n | \hat{V} | \Psi_0 \rangle}{E_0 - E_0^n} \quad (2.21) \]

where the summation runs over all eigenfunctions of \( \hat{H}_o \), \( n \) where \( n \neq \Psi_o \), and \( E_0^n \) are the eigenvalues of \( n \) from the \( \hat{H}_o \) operator.

The simplest electron correlation method is the configuration interaction (CI) method.\(^{34-36}\) Configuration interaction involves the excitation of electrons into virtual orbitals and mixing those orbitals with the ground state orbitals. The resultant optimized orbital is more diffuse than the previous one due to the ability of the orbital to now expand more due to the interelectronic repulsion and the additional variational parameter to be optimized in the orbital. In functional form, the wavefunction is expressed as
\[ |\Psi\rangle = c_0 |\Psi_0\rangle + \sum_{a,r} \frac{1}{n!} c_a^r |\Psi^r_a\rangle + \sum_{b>a,s>r} \frac{1}{2^n} c_{ab}^{rs} |\Psi^{rs}_{ab}\rangle + \ldots \quad (2.22) \]

where \(|\Psi_o\rangle\) is the reference wavefunction, \(|\Psi^{rst\ldots}_{abc\ldots}\rangle\) are the singly, doubly, etc. excited determinants of the HF ground state, and \( c_{ab}^{rs\ldots} \) are the coefficients associated with each particular singly, doubly, etc. excited determinant. Equation 2.22 can be written in a more compact way as
\[ |\Psi\rangle = c_0 |\Psi_0\rangle + c_S |S\rangle + c_D |D\rangle + \ldots \quad (2.23) \]

where the S, D, etc. indicate singly, doubly, etc. excited determinants in the expansion. When the expansion is performed over the entire set of electrons and possible determinants, the method
is termed full configuration interaction (full CI) and is formally exact within the basis set used to generate the determinants. However, full CI scales factorially with the number of electrons and basis functions and is not feasible for most chemical systems.\textsuperscript{3,39} Therefore, the CI expansion is typically truncated to some finite order of excitations. The CI matrix elements are then constructed according to

\[
\begin{bmatrix}
\langle \Psi_0 | \hat{H} - E | \Psi_0 \rangle & 0 & \langle \Psi_0 | \hat{H} - E | D \rangle & \cdots \\
0 & \langle S | \hat{H} - E | S \rangle & \langle S | \hat{H} - E | D \rangle & \cdots \\
\langle D | \hat{H} - E | \Psi_0 \rangle & \langle D | \hat{H} - E | S \rangle & \langle D | \hat{H} - E | D \rangle & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{bmatrix}
\tag{2.24}
\]

and diagonalized to obtain the correlation energy as the lowest eigenvalue of the CI matrix. The singles interactions with the ground state determinant are proven to be zero according to Brillouin’s Theorem.\textsuperscript{32} Unfortunately, when the CI expansion is truncated, the method is no longer size consistent as certain excitations which would be able to interact with the truncated excitation space (such as quadruples with the doubles) are no longer present.\textsuperscript{3}

A similar method to the CI method, though designed to maintain size consistency, is the coupled cluster (CC) method.\textsuperscript{37,38} The coupled cluster wavefunction is constructed using the cluster excitation operator

\[T = T_1 + T_2 + T_3 + \ldots \tag{2.25}\]

on the HF reference wavefunction where

\[T_i = \sum_{a,r} t_{a\ldots a_r} \hat{a}_r \ldots \hat{a}_a \ldots \tag{2.26}\]

and \(t_{a\ldots a_r}\) is the cluster amplitude of excitation order \(i\) and \(\hat{a}_r^{\dagger}\) and \(\hat{a}_a\) are the particle creation and annihilation operators associated with the creation of the excited determinant from the ground
state HF wavefunction. The cluster operator is expressed in an exponential form and applied to
the wavefunction to obtain the coupled cluster wavefunction

\[ e^T |\Psi_0\rangle = (1 + T + \frac{1}{2}T^2 + \frac{1}{6}T^3 + ...) |\Psi_0\rangle \]  \hspace{1cm} (2.27)

The coupled cluster energy is solved for in the same way as for CI by multiplying the HF
wavefunction on the left and using intermediate normalization to obtain

\[ E_{cc} = E_0 + (t_{ab}^r + t_{a}^r t_{b}^s - t_{a}^r t_{b}^s) \left( \langle \phi_a \phi_b | \phi_a \phi_b \rangle - \langle \phi_a \phi_b | \phi_a \phi_b \rangle \right) \]  \hspace{1cm} (2.28)

and the cluster amplitudes are solved for by projecting the coupled cluster wavefunction onto the
spaces of single, double, etc. excitations so that

\[ \langle \Psi_a^r | e^{-T} \hat{H} e^T | \Psi_0 \rangle = 0 \]

\[ \langle \Psi_{ab}^{rs} | e^{-T} \hat{H} e^T | \Psi_0 \rangle = 0, \text{ etc.} \]  \hspace{1cm} (2.29)

The amplitudes are solved iteratively until they are consistent with each other and the energy is
simply obtained from the \( t_1 \) and \( t_2 \) amplitudes obtained after their optimization in the presence of
the remaining amplitudes. Similar to full CI, it is too expensive to use the full cluster expansion
in coupled cluster, so the cluster operator is truncated at some finite order \( T = T_1 + T_2 \) for CCSD,
e.g.). However, unlike truncated CI, truncated CC is size consistent due to the inclusion of
disconnected single and double excitations to infinite order \( (T_1^n, T_2^n, \text{ and } T_1^n T_2^m) \). In fact, the
exponential ansatz for CC is so versatile that CCSD is equivalent to full CI for \( n \) noninteracting
two electron systems while for a CI expansion you would need CISD…2n for an equivalent
result.\(^3\) Triples contributions can be added in a perturbative fashion on top of CCSD in order to
recover some of the additional triples correlation energy necessary to accurately describe certain
chemical systems. The functional form of this perturbation is

\[ E_{ccSDT} = E_{ccSD} + E_T^{[4]} + E_{ST}^{[5]} \]
\[ E_T^{[41]} = \langle \Psi_0 | T_3^{[21]} \rangle \Psi_0 \]
\[ E_{ST}^{[5]} = \langle \Psi_0 | Z_3 \rangle \Psi_0 \]

where \( T_3^{[21]} \) is the contribution from connected triples, \( Z_3 \) is the contribution from disconnected triples, and \( V_N \) is a second order many body perturbation theory operator for the amplitudes.\(^{40}\)

CCSD(T) has been shown to be able to obtain an accuracy of up to 1 kcal mol\(^{-1}\) for main group elements, demonstrating the importance of including some manner of triples contributions in the method.\(^{41}\)

### 2.5 Multi-reference Methods and Other Static Correlation Methods

Each of the previous methods relies on the HF wavefunction to obtain their correlation energies. These methods are termed single reference as the HF method depends on only a single Slater determinant. Some chemical systems, such as radicals and open shell degenerate excited states, are very poorly described by only a single reference wavefunction and require a more flexible wavefunction in order to describe them.\(^{42}\) The simplest formulation of such a wavefunction is a linear combination of Slater determinants

\[ |\Phi\rangle = c_0 |\Psi_0\rangle + c_1 |\Psi_1\rangle + c_2 |\Psi_2\rangle + ... \]  \hspace{1cm} (2.31)

where \( \Psi_i \) are the Slater determinants and \( c_i \) is the determinant coefficient corresponding to its overall contribution to the multi-reference (that is, multi Slater determinant) wavefunction. The configurations can either be hand selected or generated by effectively running full CI within a limited window of molecular orbitals, termed an active space, to produce a complete active space\(^{43}\) (also known as a fully optimized reaction space).\(^{44}\) The simplest generalized multi-reference computational method is the multiconfigurational self-consistent field (MCSCF) method\(^{42,43,45,46}\) which operates exactly like HF, only with the CI coefficients and the orbital coefficients optimized simultaneously. While MCSCF does recover some correlation energy
relative to HF, it is primarily static correlation arising from (semi-)degenerate determinants. This is in contrast to dynamic correlation where electrons are excited to different spatial orbitals to calculate the interaction with the ground state determinant that is recovered in standard electron correlation methods.

Static correlation is vital in describing chemical systems such as radicals and electronically excited states as well as for potential energy surfaces where MO energies approach near degeneracy along the surface. However, accurate thermochemical properties still require dynamic correlation in order to achieve the level of accuracy desired in the calculation. Both Rayleigh-Schrödinger perturbation theory and CI have been modified to operate with multi-reference wavefunctions. Rayleigh-Schrödinger perturbation theory has been implemented in several ways, but among the more commonly used methods are the complete active space perturbation theory (CASPT) method and the multiconfigurational quasidegenerate perturbation theory (MCQDPT) method. Both methods calculate the energy using the same equation as in the single reference Rayleigh-Schrödinger perturbation theory in equation 2.21, but with the difference that the methods vary in the zeroth order Hamiltonian $\hat{H}_0$.

The multi-reference wavefunction $\Psi_\theta$ is not necessarily an eigenfunction of the Fock operator, and so the Fock operator is projected onto selected excitation subspaces in order to enforce $\hat{H}_\theta$ as a valid operator on the wavefunction. For CASPT2, the zeroth order Hamiltonian is projected onto the external single and double excitations from the reference wavefunction. For CASPT2, the zeroth order Hamiltonian can be further modified by adding a term to the Fock operator designed to correct for the preference of high spin configurations over low spin through the $g_\alpha$ operators. MCQDPT2 uses a more general projection onto the internal orthogonal
CASCI space as well as the external singles and doubles space.\textsuperscript{47–49} The second order perturbed energy is then calculated iteratively as in the single reference case.

In similar fashion, truncated CI can also be modified to correlate a multi-reference wavefunction.\textsuperscript{51} An important factor in modifying CI to operate on a multi-reference wavefunction is the potential for double counting excited determinants. Redundant determinants resulting from excitations of different reference determinants must be removed prior to optimizing the correlation coefficients in order to ensure the wavefunction possesses no linear dependencies. The wavefunction is then simply solved as in the single reference case through diagonalizing the CI matrix.

CCSD(T) can also be modified to describe some level of static correlation through renormalizing the left hand side (LHS) vectors of the perturbed triples, termed the completely renormalized coupled cluster (CR-CC) method.\textsuperscript{52–55} The functional form of CR-CCSD(T) is

\[
E_{\text{CR-CCSD(T)}} = E_{\text{CCSD}} + \frac{N_{\text{CR(T)}}}{D^\text{(T)}}
\]

\[
N_{\text{CR(T)}} = \langle \Psi_0 | T_{312}^\dagger M_3(2) | \Psi_0 \rangle + \langle \Psi_0 | Z_3^\dagger M_3(2) | \Psi_0 \rangle
\]

\[
D^\text{(T)} = \langle \Psi_{\text{CCSD(T)}} | e^{T_{1}^\dagger T_{2}} | \Psi_0 \rangle
\]

where \( T_{312} \) and \( Z_3 \) are defined as in CCSD(T), \( M_3(2) \) is the coupled cluster moment responsible for renormalizing the LHS vectors, and \( \langle \Psi_{\text{CCSD(T)}} | \) is the CCSD(T) wavefunction. CR-CCSD(T) is able to accurately describe static correlation involved in single bond breaking processes through correcting the perturbed triples through use of an energy denominator designed to renormalize the wavefunction as a whole. While CR-CCSD(T) has been shown to work for single bond breaking processes and simple radicals, it is still inadequate for multiple bond breaking.\textsuperscript{56,57}
2.6 Density Functional Theory

Wavefunction based methods are not the only way to solve the Schrödinger equation as Hohenberg and Kohn state in their proof\textsuperscript{58} that all values and properties of interest that can be produced from a wavefunction can also be obtained from its square, that is, the electron density, forming the basis for density functional theory (DFT). Unfortunately, the nature of the exact form of the density functional is unknown, so the functional must be approximated. This is done through splitting the functional into portions which can be solved exactly and then modeling the remainder of the correlation and exchange with some functional.\textsuperscript{59} In functional form, this is expressed as

$$E[\rho] = T_s[\rho] + v_{\text{ext}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

(2.33)

where $T_s[\rho]$ is the kinetic energy of noninteracting electrons. $v_{\text{ext}}[\rho]$ and $J[\rho]$ are the functionals for the interaction of the density with an external potential generated by the nuclei and the averaged Coulomb repulsion functional of independent electrons with the density, respectively. Finally, $E_{\text{xc}}[\rho]$ is the unknown exchange-correlation functional designed to account for everything that the previous terms have approximated. The first three terms are known exactly and it is by modifying the exchange-correlation functional in order to properly model the physical property of molecules that different DFT methods are developed. In order to describe the density, Kohn and Sham placed the electrons in orbitals and used those to create an initial density.\textsuperscript{59} The orbitals are then optimized in a self-consistent fashion to obtain a minimum energy density.

2.7 Excited State Methods

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As formulated, DFT and single reference wavefunction theory methods are formally ground state methods. However, if the methods were instead formulated within the time-dependent Schrödinger equation

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

then the wavefunction can be modeled in response to an electromagnetic perturbation which would allow the molecule to transition between electronic states. In functional form, this is expressed as a linear response function as

\[ \langle \langle P; Q \rangle \rangle = \lim_{\epsilon \to 0} \sum_{n \neq 0} \left( \frac{\langle \Psi_n | P | \Psi_n \rangle \langle \Psi_n | Q | \Psi_0 \rangle}{E - E_n + i\epsilon} - \frac{\langle \Psi_0 | Q | \Psi_n \rangle \langle \Psi_n | P | \Psi_0 \rangle}{E + E_n + i\epsilon} \right) \]  

where \( \Psi_0 \) is our electronic ground state, \( \Psi_n \) is our excited state, and \( E_{n0} = E_n - E_0 \). P and Q are operators for the desired transitions related to the properties P and Q, E is the excitation energy, and \( \epsilon \) is a positive infinitesimal value designed to prevent singularities in the calculation. For dipole allowed transitions, P and Q would both be the position operator related to the dipole in length representation. The excitation energies are obtained by calculating the property integrals and modifying the energy E until the singularities are found, at which point the excitation energy between states n and 0 will be the value E. This linear response method can be applied to any single reference method with notable examples as time dependent DFT and equation of motion coupled cluster. 

Another means of calculating excited state transition energies for single reference methods is through the static exchange (STEX) approximation. STEX is a HF based method that approximates the excited states of a molecule as an electron being acted upon by the ionized molecule according to
\[ H_j = h + \sum_{i \neq j}^{\text{occ}} (2J_i - K_i) + J_j + K_j \]  

where \( J \) is the Hartree-Fock Coulomb operator, \( K \) is the Hartree-Fock exchange operator, \( h \) is the one electron operator, and \( j \) is the orbital of the ionized electron. The STEX approximation contains an exact account of the electronic relaxation energy in the ionized molecule, so the closer the excited state approximates the ion, the more accurate the approximation becomes. As a result, the STEX approximation is particularly useful for core excited states and weakly bound excited states due to the high influence of electron relaxation in the former and the similarity of the approximate static exchange system to the actual system in the latter.

2.8 Relativistic Methods

Each of the previous methods, in their standard usage, make an unspoken approximation that the speed of light is infinite, that is, that relativity does not have a significant effect on the atom. However, as the nuclear charge increases and the electrons orbit the nucleus faster, the worse this approximation becomes. To be strictly accurate, the velocity of the electrons needs to be relativistically adjusted relative to the speed of light in order to obtain a correct description of the electronic wavefunction for heavy elements. There are many ways to calculate the effects of relativity on the molecule.\(^{66-73}\) The most rigorous way is through the Dirac Hamiltonian.\(^{66}\) The Dirac Hamiltonian is derived through the introduction of the relativistic energy of a free particle in the Schrödinger equation and is formulated in its ultimate form as

\[
\hat{H} = \begin{bmatrix}
\hat{V} & c(\sigma \cdot \hat{\pi}) \\
c(\sigma \cdot \hat{\pi}) & \hat{V} - 2mc^2
\end{bmatrix}
\]  

where \( \hat{V} \) is \( \hat{V}_{\text{ne}} \), \( \sigma \) is the vector of Pauli spin matrices. \( \hat{\pi} \) is the canonical momentum operator where the momentum is expressed as \( \hat{\pi} = \hat{p} + q\hat{A} \) where \( A \) is the vector potential of the magnetic
field generated by the nucleus of the atom and \( q \) is the charge of the nucleus. The energies have also been shifted by \( mc^2 \) (particle rest energy) in order to maintain the same zero point for the electronic energy solutions. The wavefunction the Hamiltonian operates on is different from the standard nonrelativistic wavefunction in that it both requires an explicit account of the spin of all electrons and requires a set of “positronic” functions, called the small component, which are related to the electronic functions, the large component by the kinetic balance,

\[
\Psi_s = \frac{c(\sigma \cdot \hat{p})}{2mc^2 - \hat{V} + E} \Psi_L
\]

(2.38)

where \( E \) is the energy of the electronic (positive energy) solutions of the molecule and is typically omitted for an approximate solution of \( \lim_{\epsilon \to \infty} \Psi_s = \frac{(\sigma \cdot \hat{p})}{2m} \Psi_L \). Inclusion of two electron repulsion between all types of functions results in the Dirac-Coulomb Hamiltonian and is the basis for the most rigorous fully relativistic computational methods, Dirac-Hartree-Fock, which is solved iteratively as for the non-relativistic case.\(^{72}\)

One downside to full four-component calculations is that the inclusion of the spin and small component increases the number of integrals that must be calculated, adding to the computational cost. Fortunately, there are several methods, such as Douglas-Kroll-Hess,\(^{69,74}\) infinite order two component (IOTC),\(^{73}\) and the Pauli Hamiltonian,\(^{67}\) which can eliminate the small components to produce an effective one component scalar relativistic Hamiltonian.\(^{69,72-76}\)

This is done by applying some unitary transformation to the Dirac Hamiltonian such that the small component terms are eliminated and omitting or eliminating the terms dependent on electron spin though expanding the transformed operators using the Dirac identity

\[
(\sigma \cdot \vec{x})(\sigma \cdot \vec{y}) = \vec{x} \cdot \vec{y} + i(\vec{x} \times \vec{y}) \cdot \sigma
\]

One such Hamiltonian produced from such a transformation is the Douglas-Kroll-Hess (DKH) Hamiltonian.\(^{69,74-76}\) The DKH Hamiltonian is produced by first
applying the free particle Foldy-Wouthuysen transformation\textsuperscript{68} and applying additional successive unitary transformations on the remaining odd ordered matrices. To infinite order, the transformation is exact and produces the relativistically transformed terms on the diagonal and the upper left diagonal component corresponding to the large component is retained. In practice, the transformation is truncated at some finite order of transformed matrix and only the even ordered diagonal terms corresponding to the positive energy solutions are considered. The infinite order two component (IOTC) Hamiltonian is similar to DKH, starting from the free particle Foldy-Wouthuysen transformation, though rewriting the second formal transformation that fully decouples the components through an iterative and numerical procedure that is formally exact.\textsuperscript{73}

For a separate account of the effects of electron spin on state energies, the Breit-Pauli spin-orbit operator\textsuperscript{67}

\[
h_{so} = \frac{\sigma \cdot [\nabla \hat{V}] \times \hat{p}_j}{4m^2c^2} \tag{2.39}
\]

is derived from applying the approximate small component coupling of

\[
\Psi_j = \frac{(\sigma \cdot \hat{p})}{2mc} \Psi_L \tag{2.40}
\]

in a unitary transformation of the Dirac Hamiltonian. This operator is more commonly presented in the form

\[
h_{so} = \sum_A \frac{Z_A e^2}{4m^2c^2 r_{ia}^3} \sigma \cdot I_{ia} \tag{2.41}
\]

where $Z_A$ is the charge of nucleus $A$, $r_{ia}$ is the distance between the nucleus $A$ and electron $i$, and $I_{ia}$ is the angular momentum vector for relative motion of the nucleus $A$ with respect to the electron $i$. This operator is exact for spin-orbit, with the accuracy of the splitting dependent on
the method employed to calculate the energies and is used in a multiple state formalism to
calculate the splitting and spin-orbit interactions between multiple spin-angular-momentum
states.

2.9 Composite Methods

Another complication in obtaining highly accurate electronic energies is the inherently
high cost of rigorous computational methods combined with large basis sets, with most methods
scaling exponentially with the number of basis functions. Additionally, for larger molecules,
the inherent cost for the desired level of accuracy may be beyond the capability of the available
computational resources available. In order to remedy this, computational methods have been
developed which consist of sequential additive terms to a base energy, termed composite
methods. There are many formulations for composite methods and these typically consist of
a base energy computed as a cheap method and a larger sized basis set. Afterwards, additional
calculations are performed wherein one electronic effect in the method, such as basis set
polarization, diffuse basis functions, computational method, etc., is altered from a fixed reference
and the difference in energy from the reference is added to the base energy to account for the
specific variable that has been changed. The final energy obtained from this process is designed
to be an approximation to the energy obtained by the method that consists of the sum of the
electronic effects considered, that is, the most expensive method and basis set, allowing for
accurate thermochemical energies to be calculated for much more computationally expensive
chemical systems than would normally be possible.

One such example is the multi-reference correlation consistent composite approach
(ccCA) developed by Wilson et al., a variant of the correlation consistent composite
approach\textsuperscript{77–81} explicitly designed to obtain chemical accuracy for molecules with significant static correlation. The total equation for the MR-ccCA equation can be expressed as,

\[ E_{\text{MR-ccCA}} = E_\infty + \Delta E_{\text{CC}} + \Delta E_{\text{CV}} + \Delta E_{\text{DK}} + \Delta E_{\text{SO}} + \text{ZPE} \]  (2.42)

where \( E_\infty \) is the base energy of MR-ccCA, \( \Delta E_{\text{CC}} \) is the higher level correlation term, \( \Delta E_{\text{CV}} \) is the core-valence correlation term, \( \Delta E_{\text{DK}} \) is the scalar relativistic term, \( \Delta E_{\text{SO}} \) is the spin-orbit term, and ZPE is the zero-point energy obtained at the optimized geometry, typically calculated at the CASSCF/CASPT2 level. The base energy of MR-ccCA is CASPT2 based and takes advantage of the correlation consistent basis sets by extrapolating the CASPT2 energies to the CBS limit according to

\[ E_\infty = E(\text{CASPT2/aug-cc-Z}) \]  (2.43)

using the Peterson or Schwartz 3 or 4 extrapolations. The next term, \( \Delta E_{\text{CC}} \) is designed to account for higher level correlation such as from Davidson corrected MRCISD,\textsuperscript{51,102} multi-reference averaged coupled pair functional (MR-ACPF),\textsuperscript{103} or multi-reference averaged quadratic coupled cluster (MR-AQCC)\textsuperscript{104} and is formulated as,

\[ \Delta E_{\text{CC}} = E("\text{MRCC}"/cc - \text{pVTZ}) - E(\text{CASPT2/cc - pVTZ}). \]  (2.44)

The core-valence correlation term \( \Delta E_{\text{CV}} \) is designed to account for the correlation energy of the electrons contained in the principle electron shell below the valence electrons already correlated and is given as,

\[ \Delta E_{\text{CV}} = E(\text{CASPT2(fc1)/aug - cc - pCVTZ}) - E(\text{CASPT2(fc)/aug - cc - pVTZ}) \]  (2.45)

where fc denotes that the frozen core approximation of omitting correlation of all but the valence electrons and fc1 denotes the inclusion of an additional principle shell of electrons in the correlation. The core correlation functions in the aug-cc-pCVTZ are included in order to
properly describe the tighter semi-core electronic orbitals. The scalar relativistic effects are accounted for in the $\Delta E_{DK}$ term which is represented as,

$$\Delta E_{DK} = E(CASPT2(DK)/cc - pVTZ - DK) - E(CASPT2/cc - pVTZ)$$

(2.46)

where the DK in the method indicates that second order Douglas-Kroll-Hess is used to account for scalar relativistic effects and the DK in the basis set indicates the use of basis sets optimized for second order Douglas-Kroll-Hess orbitals. The final term is $\Delta E_{SO}$ and represents the molecular and atomic spin-orbit coupling contribution for the molecule which can either be taken from experimental data, or calculated using the Breit-Pauli spin-orbit operator according to,

$$\Delta E_{SO} = E(CASSCF(SO)/aug - cc - pVTZ) - E(CASSCF/aug - cc - pVTZ)$$

(2.47)

where the SO indicates that the energy corresponds to a particular total angular momentum state of the molecule as opposed to the total angular momentum averaged state. The sum total of these terms are able to predict thermochemical properties such as reaction enthalpies within a chemical accuracy of $\pm 1$ kcal mol$^{-1}$ for main group species with respect to reliable experiments.
CHAPTER 3
MR-ccCA: A ROUTE FOR ACCURATE GROUND AND EXCITED STATE POTENTIAL ENERGY CURVES AND SPECTROSOCPIC PROPERTIES FOR THIRD-ROW DIATOMIC MOLECULES*

3.1 Introduction

*Ab initio* composite methods have long been used to mitigate the cost of high accuracy computations through a series of additive calculations designed to account for various electronic correlation, relativity and basis set incompleteness effects applied to a reference energy calculated at a lower level of theory in order to approximate a desired level of theory (see, e.g., Ref. [78,79,84,89,91,97,98,105–128]). Currently, there are a number of composite methods in widespread use. The most widely used methods are the Gaussian-n (Gn) methods developed by Pople and coworkers. Other families of composite methods include the high accuracy extrapolated *ab initio* thermochemistry (HEAT) methods developed by Stanton et al., the Weizmann-n (Wn) methods developed by Martin et al., the CBS methods developed by Petersson et al., the Feller-Peterson-Dixon (FPD) method developed by Feller, Peterson, and Dixon, and the multicoefficient composite methods developed by Truhlar and coworkers. Another composite method is the correlation consistent Composite Approach, developed by Wilson and coworkers. The single reference implementation of the ccCA method is MP2-based and designed to approximate CCSD(T,fc1)-DK/aug-cc-pCV∗∗Z-DK; coupled cluster with single and double excitations correlating the valence and one additional shell of electrons using the second order Douglas-Kroll-Hess Hamiltonian extrapolated to the basis set limit with diffuse core-valence basis sets. The ccCA

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method has been shown to obtain “chemical accuracy” of 1 kcal mol$^{-1}$ from reliable experimental energies on average, and without the need for an empirical high-level correction, which is needed in methods such as the Gaussian-n methods.$^{77-79,127}$

While these methods are widely used, due to the restriction of integer orbital occupation from a Slater determinant, single reference wavefunction methods are unable to accurately account for orbital degeneracy effects such as those which arise along the potential energy surface of a molecule toward dissociation. Multi-reference wavefunction methods are able to account for these orbital degeneracies which occur during bond breaking and forming processes by using a linear combination of Slater determinants as the wavefunction to be solved. Such a multi-reference wavefunction has the flexibility to describe fractional orbital occupation, enabling an explicit account of the orbital degeneracies.

As multi-reference wavefunction methods can be computationally costly in terms of computer time, memory and disk space requirements, multi-reference composite methods have been developed. Currently in existence are multi-reference composite methods based on internally contracted multi-reference configuration interaction (MRCI)$^{138}$ the Gaussian-n methods,$^{139}$ the Weizmann-n methods,$^{86}$ and the correlation consistent composite approach.$^{82,100,101,140}$ The multi-reference Gaussian-n (MR-Gn) methods substitute the multi-reference analogues of the single reference methods into the substituent calculations of the method (e.g., HF to CASSCF), but retain the empirical high level correction, which has been shown to be absolutely integral to the performance of the single reference method.$^{78,100,101,140}$ However, the MR-Gn methods were only tested on systems of a single reference nature, leaving no quantitative data as to how the method will perform on systems with multi-reference character.
The multi-reference Weizmann-n (Wn-CAS) methods are based primarily on the multi-reference average coupled pair functional (MR-ACPF) method, and include no parameterization.\textsuperscript{86} The WnCAS methods are known to provide very accurate energies. For example, they were used to calculate the dissociation energies of hydroxyl radical and anion to within 0.02 eV of the experimental value, of which, the former has since been revised to coincide exactly with the W2CAS value.\textsuperscript{141} However, since the WnCAS methods are based on MR-ACPF as the lowest level of theory in their calculations and employ up to aug-cc-pV5Z basis sets for the CBS extrapolation, they are very computationally expensive and can only be utilized for the smallest of systems.\textsuperscript{86,100,101,140}

The multi-reference correlation consistent Composite Approach (MR-ccCA) can be applied to near degenerate systems without the comparatively high cost of MR-Wn to MR-ccCA or the empirically derived parameters included in MR-Gn.\textsuperscript{82,100,101,140} MR-ccCA, like its single-reference counterpart, has achieved an accuracy of \( \approx 1 \) kcal mol\(^{-1}\) or less on the average for heats of formation and reaction enthalpies of main group molecules.\textsuperscript{82,100,101,140} Oyedepo and Wilson used MR-ccCA to calculate the rotational barrier of the ethylene molecule\textsuperscript{140} and obtained a value within 0.7 kcal mol\(^{-1}\) of the estimated experimental barrier.\textsuperscript{142} Oyedepo \textit{et al.} has also used MR-ccCA to calculate total atomization energies and enthalpies of formation of silicon compounds and produced enthalpies of formation and total atomization energies which were either close to or within the error for the experimental energies as well as achieving energies similar to those from previous theoretical studies.\textsuperscript{101}

Diatom ic molecules provide useful systems as a gauge for the performance of methodologies, as diatomics have been widely studied with both experimental and theoretical methods (see, e.g., [\textit{6,7,39,89,90,121,143–176}]), and frequently have well-established thermochemical
and spectroscopic properties. Ruedenberg et al. used first-row diatomics as a point of comparison when developing his full configuration interaction correlation energy extrapolation by intrinsic scaling (full CI-CEEIS) method before extending the method to larger, more complicated molecules such as cyanogen. Cleland et al. used another variant of full CI, full CI quantum Monte Carlo (full CI-QMC) on a series of first-row main group diatomics, and obtained dissociation energies on par with both experiment (a mean absolute deviation (MAD), of 0.6 kcal mol\(^{-1}\) from experiment) while Ruedenberg’s full CI-CEEIS method slightly outperformed full CI-QMC (a mean absolute deviation of 0.5 kcal mol\(^{-1}\) from experiment). Peterson and coworkers regularly use much more extensive methods to benchmark basis sets on third-row diatomic molecules to ensure that results obtained through their use are valid, and had obtained results, at their most accurate, deviating on the order of 0.1 kcal mol\(^{-1}\). More recently, Jie-Min and Qiang performed an extensive multi-reference configuration interaction calculation including scalar relativistic effects on four electronic states of As\(_2\) (the ground state and three excited states), examining the spectroscopic constants as well as the transition energies between the states and achieved deviations of less than 1 kcal mol\(^{-1}\) for the transition energies with the exception of the transition energy of the highest state.

In recent work, Jiang and Wilson have used MR-ccCA to calculate potential energy curves for the ground states of first-row main group diatomic molecules, C\(_2\), N\(_2\), and O\(_2\), and their excited states and demonstrated the ability of MR-ccCA to produce dissociation energies with a MAD of 1.06 kcal mol\(^{-1}\) from experiment. Jiang and Wilson also have used MR-ccCA to study the excited states of C\(_2\), N\(_2\), and O\(_2\), resulting in the potential energy curves generated by the composite MRCI method (deviating from experimental values with maximum signed deviations of 0.0003 Å for \(r_e\), 0.58 cm\(^{-1}\) for \(\omega_e\), and 0.7 kcal mol\(^{-1}\) for \(D_e\)) for the ground state and
the B $^1\Lambda_g$ and B$'$ $^1\Sigma^+_g$ excited states with MAD’s of 0.0007 Å for the bond lengths, 0.7 kcal mol$^{-1}$ for the dissociation energies and 3.5 cm$^{-1}$ for the harmonic vibrational frequencies.$^{82}$ The values for the transition energies are also in good agreement with experiment with deviations of 70 cm$^{-1}$ and -4 cm$^{-1}$, respectively, for the composite MRCI method and -278 cm$^{-1}$ and -122 cm$^{-1}$ from MR-ccCA.

The smooth, continuous nature of the diatomic potential energy curves that result from the use of MR-ccCA is particularly interesting, since MR-ccCA was not explicitly constructed to produce smooth curves nor would this necessarily be expected since the magnitude of each term of the composite method varies along the potential energy curve. There is no guarantee that the summation of the lower level curves calculated within MR-ccCA will include a consistent description of the electron correlation along the potential energy curve. Thus, the resultant curve cannot necessarily be expected to possess the smooth behavior that a single, high accuracy calculation will possess. However, for the first-row molecules studied by Jiang and Wilson,$^{82}$ no such inconsistency in the potential energy curves was observed.

As the total amount of the electron correlation increases for diatomic molecules beyond the first-row, the absolute amount of electron correlation energy recovered from electronic structure methods greatly increases, though it remains in similar proportions of the total electronic energy as that of first-row diatomics. As the constituent calculations within MR-ccCA do not necessarily handle electron correlation with similar levels of consistency along the potential energy curve and, thus, can lead to discontinuities in the composite curve’s shape, increases in the magnitude of the electron correlation energy recovered from the calculations can amplify this effect. Therefore, MR-ccCA may not be effective or suitable for the determination of potential energy curves of diatomics containing heavier elements.
In this work, MR-ccCA has been used to consider the viability of the method in the determination of the potential energy curve and spectroscopic properties for heavier elements - specifically, diatomics that include third-row species: Se$_2$, As$_2$, Br$_2$, SeS, AsP, HBr, and BrN. Dissociation energies and vibrational and rotational constants were computed for these molecules and compared with experimental values to assess the quality of the MR-ccCA predictions. Additionally, several of the lowest excited states for As$_2$ were determined as well as their spectroscopic properties and transition energies ($T_e$).

3.2 Methodology

3.2.1 MR-ccCA Composition

Though MR-ccCA has been described elsewhere,$^{82,100,101,140}$ a description is provided here for clarity, particularly as a number of choices of composite steps can be made within the approach. The MR-ccCA reference energy, $E_\infty$, is the energy obtained via extrapolation of the second order complete active space perturbation theory (CASPT2)$^{47,177}$ electronic energies obtained using the double, triple, and quadruple zeta levels of the correlation consistent basis sets to the complete basis set (CBS) limit. Unless otherwise stated, a full valence active space is used in all calculations. In functional form, the energy is

$$E_\infty = E(CASPT2/\text{aug}-\text{cc} - pV\infty Z)$$

(3.1)

with “$\infty$” indicating extrapolation to the CBS limit. As recommended in prior MR-ccCA studies,$^{82,140}$ the CASSCF and CASPT2 correlation energies that comprise the total CASPT2 energy are extrapolated separately to the CBS limit, so that the CASPT2 reference energy is

$$E_\infty = E(\text{CASSCF}/\text{aug}-\text{cc} - pV\infty Z) + E(\text{CASPT2(corr)}/\text{aug}-\text{cc} - pV\infty Z)$$

(3.2)

which can also be expressed as

$$E_\infty = E_{\text{CBS}}(\text{CASSCF}) + E_{\text{CBS}}(\text{CASPT2(corr)})$$

(3.3)
where \( E_{CBS} \) indicates that the energy has been extrapolated to the basis set limit.

The CASSCF energy is extrapolated using a simple exponential form developed by Feller and others\(^{13,18}\)

\[
E_n = E_{CBS} + Ae^{-Cn}
\]

(3.4)

where \( n \) is the zeta level of the basis set used, \( E_n \) is the energy at the zeta level \( n \), \( E_{CBS} \) is the complete basis set energy, and \( A \) and \( C \) are variables used to construct the fit.

For the correlation energy, there are several different extrapolation schemes that have been used within MR-ccCA which all obtain similar levels of accuracy for dissociation energies and reaction enthalpies, differing on the order of hundredths of kcal mol\(^{-1}\).\(^{82,100,101,140}\) The extrapolation scheme developed by Peterson and coworkers\(^{14}\) is a three point extrapolation which takes the form

\[
E_n = E_{CBS} + Be^{-(n-1)} + Ce^{-(n-1)^2}
\]

(3.5)

where \( B \) and \( C \) are unknown variables in Eqn. 3.5, and \( n \) is the zeta level of the basis set. The Schwartz extrapolations, which are both two point extrapolations, take the form of inverse power functions according to Eqns. 3.6 and 3.7\(^{15–18,178}\)

\[
E_n = E_{CBS} + \frac{A}{l_{\max}^3}
\]

(3.6)

\[
E_n = E_{CBS} + \frac{A}{\left( l_{\max} + \frac{1}{2} \right)^4}
\]

(3.7)

where \( l_{\max} \) is the highest angular momentum function within the basis set and \( A \) is the additional unknown for this function. Finally, since the Peterson extrapolation (Eqn. 3.6) tends to overestimate the CBS limit and the inverse cubic Schwartz extrapolation (Eqn. 3.7) tends to underestimate the CBS limit,\(^{77}\) the arithmetic mean of the two limits (dubbed “PS3”) has been
used to correct for this behavior and obtain more accurate results. This behavior has been demonstrated for both single-reference and multi-reference cases.

The first addition to the reference energy is the term describing electron correlation beyond the CASPT2 level of theory, $\Delta E_{CC}$, with the functional form

$$\Delta E_{CC} = E("MRCC"/cc - pVTZ) - E(CASPT2/cc - pVTZ)$$

(3.8)

where “MRCC” represents one of three methods in the general MR-ccCA formulation. The first “MRCC” method is MRCISD with an additional term accounting for disconnected quadruple excitation contributions developed by Langhoff and Davidson, known as MRCI+Q. Another method that has been used to account for higher-level correlation within the composite scheme is the multi-reference average coupled pair functional (MR-ACPF). MR-ACPF is an extension of the coupled pair functional (CPF) method designed to eliminate exchange principle violating (EPV) terms in the calculation. The final option for the electron correlation term is the multi-reference averaged quadratic coupled cluster (MR-AQCC) method. The MR-AQCC method also eliminates the EPV terms, though in a functionally different manner than the MR-ACPF method and is meant to correct the deficiencies in calculating excited state properties arising from MR-ACPF. For the purposes of this research, MRCI+Q was chosen as the “MRCC” method with which to obtain the electron correlation energy correction based on the more general applicability of the method to excited state calculations and its wide implementation in computational codes.

The second additive term, $\Delta E_{CV}$, is designed to account for core-core and core-valence electron coupling, and includes the correlation energy neglected through use of the frozen core approximation, as opposed to the use of the full core. The addition is formulated as

$$\Delta E_{CV} = E(CASPT2(fc:1)/aug – cc – pCVTZ) - E(CASPT2/aug – cc – pVTZ)$$

(3.9)
where 'fc1' denotes an extra principle level of electrons that are included in the CASPT2 calculation (e.g. for sulfur, the 2s and 2p are included in fc1, but not the 1s), and the aug-cc-pCVTZ basis set includes an additional set of tight functions meant to better describe the core electronic orbitals.

Relativistic effects are included in the MR-ccCA formulation through two terms. The term for scalar relativistic effects, $\Delta E_{SR}$ is formulated as

$$
\Delta E_{SR} = E(\text{CASPT2}/\text{cc}-p\text{VTZ}) - E(\text{CASPT2}/\text{cc}-p\text{VTZ}) - E(\text{DK}/\text{cc}-p\text{VTZ})
$$

where 'DK' indicates the use of the second order Douglas-Kroll-Hess (DKH) Hamiltonian. The corresponding DK-recontracted correlation consistent relativistic all electron basis sets were used to calculate the DK2 electronic energy. The other relativistic additive term applied to MR-ccCA accounts for spin-orbit coupling effects, $\Delta E_{SO}$. Experimental spin-orbit splitting values can be used for the molecule at the equilibrium geometry as well as for the desired products, allowing for the proper description of reaction enthalpies and Gibbs free energies. However, spin-orbit effects for thermochemical properties and energies at non-equilibrium geometries cannot be accounted for in this way. For non-equilibrium systems, spin-orbit coupling must be calculated explicitly at that molecular geometry using a spin-orbit operator. In MOLPRO, the spin-orbit operator is implemented as the Breit-Pauli spin-orbit operator. Given that potential energy curves are non-equilibrium constructs, the spin-orbit term for each point along the curves was calculated at the CASSCF/cc-pVTZ level according to

$$
\Delta E_{SO} = E(\text{CASSCF}/\text{cc}-p\text{VTZ}) - E(\text{CASSCF}/\text{cc}-p\text{VTZ})
$$

where BP indicates the use of the Breit-Pauli spin-orbit operator to obtain the spin-orbit splitting energies. Thus, the complete formulation of MR-ccCA is

$$
E_{MR-ccCA} = E_\infty + \Delta E_{CC} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO}.
$$
3.2.2 Research Specifics

A set of diatomic molecules (Se₂, As₂, Br₂, SeS, AsP, HBr, BrN) was selected based on the availability of experimental data against which to compare. Potential energy curves (PEC's) were obtained by calculating single-point MR-ccCA energies at intervals of 0.05 Å along the potential energy curve from 2.0 Å to 10.0 Å for Se₂ (X³Σ⁻₉₀g⁺), As₂ (X³Σ⁺₉₀g⁺), and Br₂ (X³Σ⁺₉₀g⁺), 1.7 Å to 10.0 Å for SeS (X³Σ⁻₉₀g⁺) and AsP (X³Σ⁺₉₀g⁺), 1.6 Å to 9.0 Å for BrN (X³Σ⁻₉₀g⁺), and 1.2 Å to 5.2 Å for HBr (X³Σ⁺₉₀g⁺). Additional fine analysis was performed around the minimum energy (ten points on either side of the minimum at intervals of 0.01 Å) to capture the fine curvature of the PEC for use in Dunham analysis¹⁸² to calculate the vibrational and rotational diatomic constants. A Dunham potential was fit to the data using fourth, fifth, or sixth order polynomials, depending on which order resulted in the lowest average error, to ensure that an accurate polynomial fit is obtained. The fitted functions were used to calculate the diatomic constants and dissociation energies for the molecules under consideration. The zero-point energy (ZPE) was calculated from the harmonic (ωₑ) and anharmonic (ωₑₓₑ) vibrational diatomic constants according to

\[
ZPE = \frac{1}{2} \omegaₑ - \frac{1}{4} \omegaₑ \chiₑ
\]  

(3.13)

and added to the spectroscopic dissociation energy, Dₑ, to obtain the thermodynamic dissociation energy, Dₒ.

The tight-d augmented Dunning correlation consistent basis sets (cc-pV(n+d)Z) were used for the second-row main group elements, as they achieve better convergence of physical properties for compounds containing these atoms.⁹ Finally, the g3 modified zeroth-order
Hamiltonian for CASPT2 developed by Andersson was used in all CASPT2 calculations. All ground state calculations were performed using MOLPRO09. The excited states for As₂ were calculated using state specific CASSCF, CASPT2, and MRCI+Q calculations implemented within MOLCAS7.4. The active space choice remains the full valence active space from the ground state calculation. The lowest seven calculated states (five unique electronic states, including the ground state) were used as the basis for the spin-orbit calculation. In total, 12 unique spin-orbit states (19 states total with seven doubly degenerate states) were obtained and analyzed using a sixth order Dunham potential to obtain their spectroscopic constants and transition energies.

The potential energy curve and spectroscopic properties for Br₂ were calculated with two additional virtual orbitals in the active space since the full valence active space produces too few configurations to accurately describe the bond dissociation region of the potential energy curve. These orbitals had A_g and B_{1u} symmetry (from Abelian D_{2h} symmetry for Br₂) corresponding to unoccupied \( d_{x^2} \) and \( d_{x^2-y^2} \) orbitals and were included within the active space to improve the quality of the multi-reference wavefunction.

3.3 Results and Discussion

3.3.1 Ground State Potential Energy Curves

For each of the seven molecules considered, the PEC’s for each constituent calculation of MR-ccCA and the overall MR-ccCA PEC exhibit the uniform smooth behavior expected for dissociation curves of diatomic molecules. Figure 3.1 illustrates the smooth behavior for each of the component curves associated within the calculation of the selenium dimer PEC while Figure 3.2 exhibits the overall composite curve produced by MR-ccCA. In contrast, the potential energy curve obtained for Br₂ exhibited a strong discontinuity at the CASPT2 level when
calculated in the standard valence space. Adding two additional virtual orbitals in the active space served to eliminate the discontinuity in the curve, indicating that the discontinuity is related to the omission of significant configuration state functions in the first calculation which do not arise within the original full valence active space. The full valence active space contained only ten configuration state functions (CSF) requiring additional CSF’s to properly describe the wavefunction.

In the absence of spin-orbit coupling, an artificial maximum in the Br$_2$ curve is reached before the curve tapers to a plateau. The difference in energy between the maximum and the dissociation limit is on the order of microhartrees, so the overall effect of the artificial maximum is negligible. Inclusion of spin-orbit coupling (with no symmetry) within the MR-ccCA energy rectifies this behavior. Similar behavior is observed in the curves for HBr and BrN, though in each case, the curve at the CASPT2(g3,fc1) level was either smooth throughout or had shifted the maximum to a much longer internuclear distance. A possible source of this behavior is incomplete cancellation of error in the spin-orbit correction, which might be rectified by loosening symmetry constraints and allowing the spin-orbit curve to optimize freely.

The calculated and experimental diatomic constants and dissociation energies are shown in Table 3.1. On the whole, MR-ccCA obtains a MAD of 3.1 kcal mol$^{-1}$ (0.13 eV) for the dissociation energies of the seven molecules studied. Compared to experiment,$^{152}$ the largest outlier of the computed dissociation energies occurs with BrN which results in a dissociation energy 18.1 kcal mol$^{-1}$ (0.784 eV) below the experimental value.$^{152}$ However, it is of note that the experimental value has been called into question$^{153}$ with the argument that the Birge-Sponer extrapolation method to the dissociation limit utilized in the experiment produced a dissociation energy that was 15 kcal mol$^{-1}$ too high. When the experimental dissociation energy of BrN is
removed from the statistical analysis, a MAD of 0.484 kcal mol\(^{-1}\) (0.0210 eV) is obtained for MR-ccCA.

In a previous study, a CCSD(T)/aug-cc-pV\(\infty\)Z calculation was performed on BrN and did not include core-core/core-valence or scalar relativistic coupling explicitly as the core remained frozen in all calculations, nor was the spin-orbit splitting explicitly calculated from first principles. The core-core/core-valence coupling was estimated to be 1 kcal mol\(^{-1}\). The \(D_e\) of BrN determined by extrapolation to the CCSD(T)/aug-cc-pV\(\infty\)Z limit was found to be 52.0 kcal mol\(^{-1}\) (2.26 eV) (vibrational ZPE included).\(^{153}\) However, the application of spin-orbit coupling lowers the dissociation energy to 48.5 kcal mol\(^{-1}\) (2.10 eV). Scalar relativistic effects were not explicitly taken into account. However, when the scalar relativistic term calculated within MR-ccCA is applied to the value for the dissociation energy from this CCSD(T) calculation, a \(D_o\) value of 48.9 kcal mol\(^{-1}\) (2.12 eV) for BrN is obtained. This value is within 0.09 kcal mol\(^{-1}\) (0.004 eV) of the MR-ccCA value. When the MAD for MR-ccCA is compared with this theoretical dissociation energy for BrN, a MAD of 0.415 kcal mol\(^{-1}\) (0.0180 eV) is obtained. The remaining diatomic constants calculated by MR-ccCA agreed well with experiment,\(^{152}\) differing on the order of wavenumbers.

When compared to other theoretical computations on these seven diatomic molecules, MR-ccCA performs either comparably or superior to prior theoretical studies, as shown in the tabulated results (Table 3.2). In the case of Se\(_2\), a first-order CI (FOCI) calculation was performed with a full valence active space and relativistic effective core potentials (RECP’s) on Se\(_2\) for the lowest 18 electronic states and obtained values of \(r_e=2.224\) Å, \(\omega_e=357\) cm\(^{-1}\), and \(D_o=66.6\) kcal mol\(^{-1}\) (2.89 eV).\(^{154}\) For the spin-orbit correction, a relativistic CI method using a Slater type orbital basis was employed. The all-electron calculations using MR-ccCA improve on the
FOCI results significantly, especially in the case of the $D_o$ value, due to both the inclusion of core-core/core-valence corrections and the elimination of error due to a finite basis set through extrapolation to the CBS limit, as well as electron correlation far beyond that of first order CI.

A similar approach was utilized for $\text{As}_2$, though the spin-orbit correction was not performed since spin-orbit effects are negligible for $\text{As}_2$ at equilibrium and at dissociation.\textsuperscript{155} The FOCI calculation resulted in 2.164 Å for $r_e$, 394 cm$^{-1}$ for $\omega_e$, and an estimate of 90.9 kcal mol$^{-1}$ (3.94 eV) for $D_o$, which was obtained by extrapolation of the predissociated $^1\Sigma_u^+$ bonds into $^4\text{S}$ and $^2\text{D}$ atomic states. MR-ccCA calculations on the same molecule improve on the diatomic constants relative to experimental results.

A more extensive calculation on $\text{As}_2$ was performed using CCSD and contracted atomic natural orbital basis sets,\textsuperscript{156} albeit only for the ground state, to retrieve the diatomic constants for the molecule. The results obtained for the diatomic constants ($r_e=2.107$ Å and $\omega_e=447$ cm$^{-1}$) are in agreement with MR-ccCA results, but deviate with regards to the dissociation energy ($D_o=71.0$ kcal mol$^{-1}$ (3.08 eV)). This low dissociation energy was attributed by Scuseria\textsuperscript{156} to the omission of connected triples in the coupled cluster calculations that would recover more correlation energy from the molecule (we note from our calculation a difference of $\approx 9.5$ kcal mol$^{-1}$ when perturbative triples are included). Additionally, while the prior study accounts for core-core/core-valence interactions by correlating the 3s, 3p, and 3d electrons, this prior work does not account for scalar relativistic effects which should be important for $\text{As}_2$.

An extensive calculation on $\text{As}_2$ was performed wherein a composite approach based on a reference energy which was extrapolated to the CBS limit at the CCSD(T) level using basis sets through cc-pV6Z was used. Additional correlation terms containing coupled cluster levels up to 5 in addition to a full CI calculation with a cc-pVDZ basis set were also used in order to account
for higher order electron correlation.\textsuperscript{121} Error analysis of the extrapolated curves was performed using the average energy of five separate CBS extrapolation schemes. Experimental spin-orbit and ZPE corrections were applied to $D_e$ to obtain the appropriate thermochemical data. Additionally, scalar relativistic effects were taken into account through the use of the second order DKH2 Hamiltonian. Core-valence effects were also explicitly calculated by including an additional shell of electrons in the correlation treatment. The calculated values are $r_e=2.0998 \pm 0.0006 \ \text{Å}$, $\omega_e=430.4 \pm 0.3 \ \text{cm}^{-1}$, and $D_o=92.0 \pm 0.3 \ \text{kcal mol}^{-1}$ (3.99 \pm 0.01 \text{eV}), in good agreement with the MR-ccCA results, though MR-ccCA does produce a dissociation energy and equilibrium bond length that are closer to experiment.\textsuperscript{171}

CASPT2 calculations were performed on Se$_2$, As$_2$, and Br$_2$ using a custom made ANO-RCC basis set constructed for each element and a full valence active space.\textsuperscript{157} The spin-orbit coupling in the molecule was calculated at the minimum and the dissociation limit to include in the description of the dissociation energies for the molecules. The calculated values obtained were $r_e=2.180 \ \text{Å}$, $\omega_e=384 \ \text{cm}^{-1}$, and $D_o=79.1 \ \text{kcal mol}^{-1}$ (3.43 eV), for Se$_2$, $r_e=2.133 \ \text{Å}$, $\omega_e=413 \ \text{cm}^{-1}$, and $D_o=86.9 \ \text{kcal mol}^{-1}$ (3.77 eV) for As$_2$, and $r_e=2.298 \ \text{Å}$, $\omega_e=317 \ \text{cm}^{-1}$, and $D_o=41.5 \ \text{kcal mol}^{-1}$ (1.80 eV) for Br$_2$. The results for Se$_2$ are in close agreement with both experiment and the calculated MR-ccCA results. For As$_2$, and Br$_2$, the MR-ccCA values produce a significant improvement of up to 3.9 kcal mol$^{-1}$ (0.17 eV) for the dissociation energy.

An intensive calculation on SeS has been performed using MRCI+Q and aug-cc-pV5Z basis sets on several states of SeS.\textsuperscript{158} Additional terms accounting for basis set incompleteness, relativity (spin-orbit and scalar relativistic), and core-core/core-valence interactions, were calculated using MRCI+Q with the same basis sets. The resultant curve generated constants ($r_e=2.0283 \ \text{Å}$, $\omega_e=557.19 \ \text{cm}^{-1}$, $\omega_ex_e=1.5144 \ \text{cm}^{-1}$, $B_e=0.179429 \ \text{cm}^{-1}$, $\alpha_e=0.00077141 \ \text{cm}^{-1}$) in
good agreement with experiment and MR-ccCA (differing at most by 7.69 cm\(^{-1}\) in the case of \(\omega_e\)), indicating that MR-ccCA is comparable to the level of theory in this prior study.

Calculations on SeS were also performed using both MRCI and CCSD(T) using an ANO basis.\(^{159}\) Scalar relativistic effects were handled through the use of the DKH Hamiltonian. Spin-orbit effects were not calculated, so the results reference an average of the \(\Omega\) components of the electronic states to first order. In the case of MRCI, the calculations produced results of \(r_e=2.047\ \text{Å}, \omega_e=547.8\ \text{cm}^{-1}, \omega_{ex}=1.6\ \text{cm}^{-1}, B_e=0.1762\ \text{cm}^{-1}, \alpha_e=0.00078\ \text{cm}^{-1},\) and \(D_o=88.6\ \text{kcal mol}^{-1}\ (3.84\ \text{eV}).\) The CCSD(T) results are similar at \(r_e=2.044\ \text{Å}, \omega_e=557.7\ \text{cm}^{-1}, \omega_{ex}=1.7\ \text{cm}^{-1}, B_e=0.1767\ \text{cm}^{-1}, \alpha_e=0.00074\ \text{cm}^{-1},\) and \(D_o=88.6\ \text{kcal mol}^{-1}\ (3.84\ \text{eV}).\) In both cases, the results closely match those calculated with MR-ccCA and those obtained from experiment,\(^{172}\) differing by only 0.7 kcal mol\(^{-1}\) (0.03 eV) from the experimental value.

For AsP, an MRCI calculation was performed with a cc-pV5Z basis on arsenic and a cc-pCV5Z basis on phosphorous.\(^{160}\) A full valence active space was used, and an exponential-like curve was fit to the energies obtained, which was used to calculate the diatomic constants. The diatomic constants obtained (\(r_e=2.0194\ \text{Å}, \omega_e=598.60\ \text{cm}^{-1}, \omega_{ex}=1.98\ \text{cm}^{-1}, B_e=0.1925\ \text{cm}^{-1}, \alpha_e=0.0008\ \text{cm}^{-1}, D_o=98.0\ \text{kcal mol}^{-1}\ (4.25\ \text{eV})) are in close agreement with those calculated with MR-ccCA. The \(D_o\) value is 2.4 kcal mol\(^{-1}\) (0.10 eV) lower than the MR-ccCA value (3.8 kcal mol\(^{-1}\) (0.16 eV) lower than experiment),\(^{176}\) which may be due to the neglect of core-core/core-valence and scalar relativistic interactions in the previous study.

The diatomic constants of Br\(_2\) were calculated\(^{161}\) by using a specialized pseudopotential, the modified Phillips-Kleinman pseudopotential, which uses a valence nominal basis (3s3p + 1d polarization), for chemical bonding in the valence region. The method used to obtain the energies is a specialized form of MCSCF called the optimized valence configuration (OVC).
method,\textsuperscript{186} which achieves significant agreement of the constants with experiment ($r_c=2.3390$ Å, $\omega_e=302$ cm$^{-1}$, $\omega_e\chi_e=1.3$ cm$^{-1}$, $\alpha_e=0.00037$ cm$^{-1}$, $D_o=43.8$ kcal mol$^{-1}$ (1.90 eV)). MR-ccCA achieves higher accuracy data than these prior calculations, within 0.41 kcal mol$^{-1}$ of the experimental dissociation energy ($D_o=45.02$ kcal mol$^{-1}$ (1.952 eV)), and more accurately models the other diatomic constants ($r_c=2.28$ Å, $\omega_e=321.8$ cm$^{-1}$, $\omega_e\chi_e=1.17$ cm$^{-1}$, $B_e=0.0816$ cm$^{-1}$, $\alpha_e=0.00033$ cm$^{-1}$) in comparison to the method in this previous study.

A more recent calculation on Br$_2$ was performed wherein a fully relativistic four component Hamiltonian was used in conjunction with both CISD and CCSD(T) methods and cc-pVTZ basis sets.\textsuperscript{162} Since the full four component Hamiltonian was used, there was exact treatment of both scalar and spin-orbit relativistic effects in the calculation. The CISD results are $r_c=2.292$ Å, $\omega_e=335$ cm$^{-1}$, and $D_o=22.3$ kcal mol$^{-1}$ (0.946 eV), which are 23.6 kcal mol$^{-1}$ (1.02 eV) below the experimental dissociation energy. The CCSD(T) results are an improvement, giving values of $r_c=2.315$ Å, $\omega_e=312$ cm$^{-1}$, and $D_o=39.2$ kcal mol$^{-1}$ (1.68 eV), which, while an improvement over the CISD calculation, still falls short of both the MR-ccCA and experimental dissociation energies.\textsuperscript{171}

A more extensive calculation was performed on Br$_2$ as well as HBr wherein a composite approach was used with a reference energy of CCSD(T) extrapolated to the CBS limit using up to aug-cc-pV6Z basis sets and included higher order correlation contributions of up to full CI with a double zeta basis.\textsuperscript{89} Error analysis was performed based on the average of five CBS extrapolated energies using five separate extrapolation methods. Scalar relativistic effects were calculated though the use of the DKH2 Hamiltonian and core-valence calculations included an extra principle shell of electrons in both cases when applicable. The ZPE and atomic spin-orbit contributions were both obtained from experiment. The results obtained are $r_c=2.2807$ Å and
$D_o=45.39 \pm 0.3 \text{ kcal mol}^{-1} (1.968 \pm 0.013 \text{ eV})$ for Br$_2$ and $r_e=1.4139 \text{ Å}$ and $D_e=86.47 \pm 0.2 \text{ kcal mol}^{-1} (3.750 \pm 0.009 \text{ eV})$ for HBr, both of which are within 0.05 kcal mol$^{-1}$ (0.002 eV) of the experimental dissociation energies and 0.37 kcal mol$^{-1}$ (0.016 eV) of the MR-ccCA dissociation energies.

For the HBr molecule, fully relativistic calculations were performed to obtain the diatomic constants using both aug-cc-pVDZ and aug-cc-pVTZ basis sets. Of the methods used, the most extensive was a full Dirac-Coulomb CCSD(T) calculation using the aug-cc-pVTZ basis set, which produced values of $r_e=1.419 \text{ Å}$, $\omega_e=2645 \text{ cm}^{-1}$, and $D_o=88.1 \text{ kcal mol}^{-1} (3.66 \text{ eV})$. The most comparable calculation to MR-ccCA, however, is the full Dirac-Coulomb CISD+Q calculation using an aug-cc-pVTZ basis set ($r_e=1.419 \text{ Å}$, $\omega_e=2646 \text{ cm}^{-1}$, $D_o=87.2 \text{ kcal mol}^{-1} (3.62 \text{ eV})$). In either case, MR-ccCA is able to perform similarly to both methods, obtaining a value even closer to experiment than these previous calculations and within 0.05 kcal mol$^{-1}$ (0.002 eV) of the experimental dissociation energy.

Calculations were also performed on HBr, using MRCI+Q and a pseudopotential on bromine. The valence basis sets were of aug-cc-pV5Z quality, and a full valence active space was used to obtain the configuration state functions for the calculation. Spin-orbit effects were accounted for at the CASSCF level using the Breit-Pauli spin-orbit operator implemented in MOLPRO. The MR-ccCA dissociation energy is 2.8 kcal mol$^{-1}$ (0.12 eV) closer to the experimental dissociation energy than the dissociation energy obtained this prior study ($D_o=83.8 \text{ kcal mol}^{-1} (3.63 \text{ eV})$).

3.3.2 As$_2$ Excited States

The As$_2$ excited state data is listed in Table 3 and the curves are shown in Figure 3.3. Figures 3.4-3.7 are close-ups of the curves to highlight the spin-orbit splittings of the states.
spin-orbit states exhibit the characteristic splitting patterns which are expected of the specific states (all the spin-orbit states are doubly degenerate, corresponding to the positive and negative $m_j$ components of the electronic state, with the exception of $\Sigma$ states with $J=0$, which possess only one component). The $^1\Sigma_g^+$ state does not exhibit any kind of spin-orbit splitting given its distinct lack of spin and orbital angular momentum even as far out as the $^4S + ^4S$ dissociation limit. The next highest state, the $^3\Sigma_u^+$ state (Figure 3.4), does exhibit significant spin-orbit splitting into the $1_u$ and $0_u^-$ states (in order of ascending energy) with a splitting of 116 cm$^{-1}$ (0.33 kcal/mol).

The high energy $^3\Sigma_u^-$ state (Figure 3.5) exhibits a similar splitting, but with opposite ordering of states, into $0_u^+$ and $1_u$ states with a splitting of 117 cm$^{-1}$ (0.34 kcal/mol). The calculated $^3\Delta_u$ state (Figure 3.6) splits into three doubly degenerate states, $3_u$, $2_u$, and $1_u$, with splittings of 114 cm$^{-1}$ (0.33 kcal/mol) between the three states. Finally, the $^3\Pi_g$ state (Figure 3.7) splits into three states $0_g$, $1_g$, and $2_g$, with splittings of 614 and 617 cm$^{-1}$ (1.76 kcal/mol) between the former and latter pairs of states, respectively. Oddly, there appears to be an interaction between the ground state and the $^3\Pi_{g,0_g}$ states that raises one of the states 61 cm$^{-1}$ (0.17 kcal/mol) in energy. This might indicate a very weak coupling between the ground state and the $^3\Pi_{g,0_g}$ state, or it could be an artifact in the spin-orbit calculation.

In terms of the spectroscopic constants (excepting $T_e$), MR-ccCA maintains very good agreement with the experimental values$^{165}$ with a maximum deviation of $\approx 7$ cm$^{-1}$. The bond lengths agree exceptionally well with the experimental values when they exist, differing within $10^{-2}$ Å. Spin-orbit coupling does not appear to have a significant effect on the spectroscopic
constants (again, excepting $T_e$) for the calculated electronic states, but rather seems to produce a vertical shift near the minimum and an eventual tapering off to the dissociation limit.

The transition energies calculated using MR-ccCA differ on average by 461 cm$^{-1}$ (1.32 kcal/mol) from the experimental energies, with the largest deviation originating from the difference between the $^1\Sigma^+_{g^*,0g^*}$ and $^3\Delta_{u,1u}$ states with a value of 681 cm$^{-1}$ (1.95 kcal/mol). However, this large deviation is offset by a deviation of only 109 cm$^{-1}$ (0.31 kcal/mol) arising from the $^3\Sigma^-_{u,0u^*}$ state transition energy. MR-ccCA significantly improves on the results obtained in the previous study, which obtained an average deviation of 1486 cm$^{-1}$ (4.25 kcal/mol). A more recent paper obtained theoretical transition energies for the $^3\Delta_{u,1u}$ and $^1\Sigma^+_{g^*,0g^*}$ states with deviations of 193 cm$^{-1}$ (0.55 kcal/mol) and 233 cm$^{-1}$ (0.67 kcal/mol) from the experimental gas phase energies, which is more accurate than MR-ccCA for the first value but less accurate with regard to the second.

A similar electronic structure calculation for a collection of electronic states of As$_2$ was performed using a relativistic pseudopotential and triple zeta valence basis set with polarization for arsenic in conjunction with a full valence CASSCF/CIS calculation. The ordering of states from these calculations matches those obtained with MR-ccCA. Interestingly, both theories predict the presence of a $^3\Pi_g$ state lower in energy than the $^3\Sigma^-_{u,0u^*}$ state, the former of which is not observed in the gas phase. Heimbrook et al., performed a similar experiment in which As$_2$ was isolated in a neon matrix, and managed to isolate a strange peak which they posited might be a $^3\Sigma^-_{u^*}$ state. However, given the lifetime of the state in the neon matrix (30 ms) and the observed transition energy of the state lining up very well with the transition energy of the $^3\Pi_g$
state, it is possible that this state relaxes too quickly for detection in the gas phase and is not
directly observed in those conditions.

3.4 Conclusion

MR-ccCA has produced quantitatively accurate thermochemical data for all the
molecules considered reaching an overall accuracy of less than 1 kcal mol\(^{-1}\) for the dissociation
energies \(D_o\). It is worth noting that this specific set of molecules is quite small. Therefore,
application of the statistical results obtained from the calculations is limited. However, future
work in this area should include adopting a larger set of molecules and obtaining more extensive
thermochemical data for MR-ccCA.

The performance of MR-ccCA is either comparable or superior to previous theoretical
and experimental results for the systems studied. In the case of the most recent theoretical
calculations for the set of diatomics in this study, MR-ccCA agrees very closely with the
spectroscopic constants obtained from these methods, differing on the order of wavenumbers.\(^{89,121,153,158,160,163,164}\) MR-ccCA also compares well with experiment, again
differing on the order of wavenumbers with the experimentally derived spectroscopic
constants.\(^{152,171,172,174,176}\) Additionally, MR-ccCA results in dissociation energies which agree
well with the experimental energies on the average obtaining a MAD value of 0.415 kcal mol\(^{-1}\)
when the theoretical value for the dissociation energy of BrN is considered in place of the
experimental dissociation energy and a MAD of 0.484 kcal mol\(^{-1}\) when the BrN experimental
value is omitted.

MR-ccCA is also able to determine excited state potential energy curves that exhibit the
same uniform convergence to the dissociation limit as the calculated ground states. The
spectroscopic constants generated from these curves are in excellent agreement with established
experimental results and similar theoretical calculations. The ordering of the \text{As}_2 \text{ electronic states calculated with MR-ccCA matches the ordering of the experimentally observed states indicating the utility of MR-ccCA as a predictive computational method. Finally, the MR-ccCA calculations suggest the existence of a low-lying $^3\Pi_g$ state for \text{As}_2 \text{ that has yet to be fully characterized experimentally due to its short lifetime in the gas phase.}

**Figure 3.1** Potential energy curves from each of the individual calculations within MR-ccCA for Se$_2$. Energies are vertically translated to the same zero point for the purpose of comparison. In the figure, REF = CASPT2/aug-cc-pV\text{\infty}Z; TZ = CASPT2/cc-pVTZ; ATZ = CASPT2/aug-cc-pVTZ; CC = MRCI+Q/aug-cc-pVTZ; DK = CASPT2-DK2/cc-pVTZ-DK; CV = CASPT2(fc1)/aug-cc-pCVTZ; SO = CASSCF(BP)/cc-pVTZ
Figure 3.2 The calculated MR-ccCA potential energy curve for the selenium dimer.
Table 3.1 Table of calculated diatomic constants and experimental values for the constituent calculations within MR-ccCA\textsuperscript{d} for the ground electronic states of Se\textsubscript{2}, SeS, BrN (X 3Σ\textsuperscript{−} \textsubscript{g,0,0}) and As\textsubscript{2}, AsP, Br\textsubscript{2}, and HBr (X 3Σ\textsuperscript{+} \textsubscript{g,0,0}).

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**CC** = MRCI+Q/aug-cc-pVTZ  
**DK** = CASPT2-DK2/cc-pVTZ-DK  
**CV** = CASPT2(fc1)/aug-cc-pCVTZ  
**SO** = CASSCF(BP)/cc-pVTZ

\(^{a}\) All experimental constants, unless otherwise noted, were obtained from Reference 174  
\(^{b}\) Reported values adjusted for zero-point energy  
\(^{c}\) Reference 172  
\(^{d}\) Reference 171  
\(^{e}\) Reference 176  
\(^{f}\) Reference 152  
\(^{g}\) 1 kcal mol\(^{-1}\) = 0.0434 eV
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\(^a\) Reported values adjusted for zero point energy  
\(^b\) Additional correction for scalar relativistic effects obtained from MR-ccCA calculation for purpose of comparison  
\(^c\) Reference 153  
\(^d\) Reference 154  
\(^e\) Reference 157  
\(^f\) Reference 155  
\(^g\) Reference 156  
\(^h\) Reference 121  
\(^i\) Reference 158  
\(^j\) Reference 159  
\(^k\) MRCI/ANO basis  
\(^m\) CCSD(T)/ANO basis
\textsuperscript{m} Reference 160
\textsuperscript{n} Reference 161
\textsuperscript{o} Reference 89
\textsuperscript{p} Reference 162
\textsuperscript{q} Dirac-Coulomb CCSD/cc-pVTZ
\textsuperscript{r} Dirac-Coulomb CISD/cc-pVTZ
\textsuperscript{s} Reference 163
\textsuperscript{t} Dirac-Coulomb CISD+Q/aug-cc-pVTZ
\textsuperscript{u} Dirac-Coulomb CCSD(T)/aug-cc-pVTZ
\textsuperscript{v} Reference 164
\textsuperscript{w} Error estimates derived from an average of CBS extrapolated energies
Figure 3.3 Graph of electronic excited state curves with spin-orbit splitting for As$_2$ calculated with the MR-ccCA method.
Figure 3.4 Graph of the region near the calculated equilibrium bond length of the $^3\Sigma_u^+$ spin-orbit states in As$_2$. The zero point of the energy is the minimum of the $^1\Sigma_g^+$ state.
Figure 3.5 Graph of the region near the calculated equilibrium bond length of the $^{3}\Sigma_{u}^{-}$ spin-orbit states in As$_2$. The zero point of the energy is the minimum of the $^{1}\Sigma_{g}^{+}$ state.
Figure 3.6 Graph of the region near the calculated equilibrium bond length of the $^3\Delta_u$ spin-orbit states in As$_2$. The zero point of the energy is the minimum of the $^1\Sigma_g^+$ state.
Figure 3.7 Graph of the region near the calculated equilibrium bond length of the $^3\Pi_g$ spin-orbit states in As$_2$. The zero point of the energy is the minimum of the $^1\Sigma^+_g$ state.
Table 3.3 Table of spectroscopic constants for the electronic excited states of As₂.

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<th>𝜔ₑₓₑ(cm⁻¹)</th>
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²Constants obtained from MOLPRO ground state calculation
ᵇReference 155
\(^{c}\) Reference 151
\(^{d}\) Reference 166
\(^{e}\) Reference 165
\(^{f}\) Splitting caused by minor interaction with ground state
CHAPTER 4

A NEOTERIC NEODYMIUM MODEL: GROUND AND EXCITED ELECTRONIC STATE ANALYSIS OF NdF\(^{2+}\)†

4.1 Introduction

Rare earth elements, particularly the lanthanides, are ubiquitous in modern technology. They can be found in strong permanent magnets, photovoltaic devices, medical technology, and catalysts. Neodymium in particular has a wide range of uses stemming from its unique magnetic properties and catalytic applications.\(^ {187}\) Its magnetic properties are often applied to electronic devices such as headphones, cell phones, and hard drives to make them smaller and more efficient. Likewise, neodymium has found uses in the energy industry in both traditional and clean technologies as a catalyst or as a component of turbines, respectively.\(^ {188}\) The pervasiveness of neodymium and other rare earth elements in modern technology has thus lead to a surge in interest in their study.

Lanthanides are unique in that the 4f shell is essentially part of the chemical core. As such, lanthanides can maintain exceptionally high spin states that lead to numerous magnetic and electrical applications. While low oxidation states of the lanthanides are known, it is most common for lanthanides to be found in the 3+ oxidation state which results in a \(f^n\) configuration with \(n=0\) for La and \(n=14\) for Lu.\(^ {189,190}\) The lanthanide trihalides, \(\text{LnX}_3\), are prototypical examples of Ln(III) compounds. The structure of \(\text{LnX}_3\) has been studied experimentally via electron diffraction, IR spectroscopy, and molecular beam deflection methods,\(^ {191–193}\) and it has

† This entire chapter is reproduced with permission from G. Schoendorff, C. South, and A. K. Wilson, “A Neoteric Neodymium Model: Ground and Excited Electronic State Analysis of NdF\(^{2+}\)” J. Phys. Chem. A. 2013, 117, 10881-10888 http://pubs.acs.org/articlesonrequest/AOR-Yb4f3SHh5ZJW7TwTDc9K copyright 2013 American Chemical Society. This is an unofficial adaptation of an article that appeared in an ACS publication. ACS has not endorsed the content of this adaptation or the context of its use.
been shown that the bond lengths of the trihalides follow the lanthanide contraction trend observed with the ionic radius of $\text{Ln}^{3+}$ which is a direct result of the core-like behavior of the f electrons.\textsuperscript{190,194} While there is disagreement regarding the X-Ln-X bond angle, the prevailing idea is that LnX$_3$ is planar with D$_{3h}$ symmetry rather than pyramidal with C$_{3v}$ symmetry. Experimentally all of the trifluorides have been predicted to be planar with D$_{3h}$ symmetry with the exception of PrF$_3$, GdF$_3$, and HoF$_3$ which have C$_{3v}$ symmetry and F-Ln-F bond angles of 102.6, 108.4, and 107.7 degrees, respectively.\textsuperscript{191} Computational studies suggest that the trifluorides of the early lanthanides may prefer a pyramidal structure, though it is posited that this may be an artifact of the single reference post-HF methods employed (MP2 and DFT).\textsuperscript{192} In all cases, the out-of-plane motion bending mode of the lanthanide trihalides tends to be less than 100 cm$^{-1}$ regardless of the level of theory employed.

Thermodynamic properties for many of the trihalides also have been measured. Enthalpies of formation for LnX$_3$ (X = Cl, Br, I) are known in the solid state,\textsuperscript{195} and the enthalpies of formation also have been measured for many of the trichlorides in the gas phase.\textsuperscript{196–198} Lanthanide fluorides are less thoroughly studied, although the bond dissociation energies of NdF$_3$, NdF$_2$, and NdF have been measured via Knudsen effusion cell mass spectroscopy.\textsuperscript{199}

From a computational standpoint, the study of lanthanide complexes are complicated by the large number of core electrons, by relativistic effects due to the high nuclear charge, and by the multiconfigurational nature of the partially filled 4f shell and quasidegenerate 6s and 5d shells. Pseudopotentials alleviate the need for a large number of core electrons and an explicit description of scalar relativistic effects, and have been successfully employed for lanthanide studies.\textsuperscript{22,200–203} For species wherein the lanthanide is formally 3+, e.g. f$^n$ metals, an (n,7) active space is frequently sufficient to describe the multiconfigurational nature of the
However, the choice of active space is not necessarily clear for species with low oxidation states where the 6s and 5d orbitals may play a role. In addition to the near degeneracy of the localized lanthanide valence orbitals, other molecular orbitals may also be needed to accurately describe bond breaking and bond forming processes, and an evaluation of suitable active spaces will be necessary for each molecule. It has even been observed that the 4f orbitals can participate in molecular bonding, such as in LuF₃ even though the lanthanide is formally in the +3 state.

NdF²⁺ has been observed as an incidental finding in a recent experimental study. Presently, however, NdF²⁺ is examined as a model for NdF₃. While the bond length for the dication will be shorter than the observed bond length for NdF₃ due to the high positive charge on the molecule, a study of NdF²⁺ can provide a qualitative picture of the nature of the Nd-F interaction. Furthermore, the short bond length that results from the high molecular charge can help elucidate the potential role of the 4f shell in bonding. A variety of active spaces are employed to investigate the contribution of the 6s, 5d, and 4f shells on the ground state and low-lying excited states of NdF²⁺, and potential energy curves are calculated for some of the low-lying electronic states. Equilibrium bond lengths, electronic energy levels, and crossing points are presented at the MCSCF and MCQDPT2 levels of theory to examine the effect of dynamical correlation. Spin-orbit effects are also examined within the L-S coupling scheme and the potential energy curves for each of the resultant terms is presented.

4.2 Computational Details

All calculations were performed using GAMESS. Model core potentials (MCPs) were used for both neodymium and fluorine in conjunction with polarized valence basis sets of double-ζ quality with additional diffuse s and p functions centered on fluorine. The double-ζ
MCP explicitly treats the 5s, 5p, 4f, 5d, and 6s shells. The valence basis set for Nd is split-valence plus polarization, i.e. \( \text{Nd} \ (8811/6121/315/622)/[4s4p3d3f] \), and the contraction scheme for the F MCP valence basis is \((31/31/2)/[2s2p1d]\).\(^{27,210-212}\) Triple-\(\zeta\) MPC valence basis sets that include g functions on the lanthanide were also tested and found to offer no appreciable difference in the computed results. Scalar relativistic effects at the level of Cowan and Griffin’s quasi-relativistic Hartree-Fock (QRHF)\(^{213}\) were included implicitly through the use of the model core potentials. Furthermore, MCPs allow for valence orbitals with the proper nodal structure as opposed to the nodeless pseudo-orbitals implemented for use with effective core potentials (ECPs).

MCSCF calculations were performed using fully optimized reaction space (FORS)\(^{214-216}/\) complete active space self-consistent field (CASSCF)\(^{217}\) type wave functions with a variety of active spaces for \(\text{NdF}^{2+}\). As \((n,7)\) active spaces spanning only the 4f orbitals with \(n\ f\) electrons are commonly used for lanthanides, a \((3,7)\) active space was used in the present work. Other studies have suggested that 6s and 5d orbitals may play a significant role in bonding to halides.\(^{206,218}\) Therefore larger active spaces \([(9,16)\) and \((5,8)\)] were also examined to describe the Nd-F bond and investigate the role of the 6s and 5d orbitals on the electronic structure of \(\text{NdF}^{2+}\). The \((9,16)\) active space consists of the 6s, 4f, and 5d orbital sets on Nd and the 2p orbital set on F. The \((5,8)\) active space consists of the seven 4f orbitals on Nd and the 2p\(_z\) orbital on fluorine, where the \(z\)-axis is defined as the internuclear axis. The Nd 5p sub-valence orbitals and the Nd 4f orbitals have a similar radial extent and may be expected to play a role in the chemistry of Nd\(^{3+}\). However, the Nd 5p orbitals were not considered for inclusion in the active space due to the large difference in orbital energies. Application of the extended Koopmans’ theorem\(^{219}\) to the Nd\(^{3+}\) ion shows that the 5p orbitals are 210.3 kcal/mol lower in energy than the 4f orbitals.
MCSCF optimized orbitals were used for subsequent multiconfigurational quasi-degenerate perturbation theory (MCQDPT2) and spin-orbit MCQDPT2 (SO-MCQDPT2) calculations with the (5,8) active space. Intruder states were removed by the application of denominator shifts of 0.02 a.u. and 0.10 a.u. to the MCQDPT2 and SO-MCQDPT2 calculations, respectively. In the MCQDPT2 calculations, the Nd 4f electrons and the F 2p electrons were correlated (9 correlated electrons). Low-lying quartet states were examined with each of the active spaces described above. Additionally, doublet and sextet states were calculated with the (5,8) active space. Dunham analyses were performed on 7th order polynomial fits to \textit{ab initio} energies obtained with the (5,8) active space near the minimum of each of the potential energy curves. A total of 15 data points were taken for the polynomial fits over the range of 1.55 Å to 2.25 Å at intervals of 0.05 Å in order to capture the anharmonic portion of the curve. Analyses including additional points taken at intervals of 0.001 Å around the minimum did not show significant deviation (≤ 0.02 cm\(^{-1}\)) from the values obtained using only 0.05 Å intervals, suggesting that the potential energy minimum region is sufficiently well described by the more highly separated data points. The dissociation limit used to calculate the dissociation energies was assumed to be the limit of the \(6\text{H}\) state (\(6\text{H}_{5/2}\) for SO-MCQDPT2) for the \(4\text{I}\) states corresponding to the homolytic dissociation products Nd\(^{2+}\) and F\(^{-}\), with all unpaired electrons in the alpha spin state. Based on the negligible spin-orbit coupling of the \(4\Delta\) and \(4\Phi\) states and the rather high energy crossing of the \(6\text{H}\) state with the \(4\Gamma\) state, the dissociation limit for the excited quartet states was chosen to be the energy at 2.7 Å on the respective quartet potential energy curves. Term symbols were assigned according to the SO-MCQDPT2 and MCQDPT2 energies obtained with the (5,8) active space.
The NdF₃ quartet was also examined for comparison with NdF²⁺. The geometry was frozen at 2.09 Å in accordance with the experimental bond length. A (5,8) active space spanning the Nd 4f orbitals and a single F p orbital directed along the Nd-F bond was employed for a direct comparison with NdF²⁺. The other two fluoride fragments were constrained to be F⁻ with Nd-F distances of 2.09 Å and F-Nd-F angles of 120°. MCQDPT2 and SO-MCQDPT2 calculations were performed with the optimized MCSCF orbitals in the same manner as described for NdF²⁺.

4.3 Results

MCSCF calculations were performed on the NdF²⁺ dication. Initially, a (9,16) active space was chosen that includes the Nd 6s, 4f, and 5d orbitals as well as the F 2p orbitals. It was found that the Nd 5d orbitals remained essentially unoccupied for the entire range of internuclear distances examined (1.4 – 3.5 Å). The largest d occupation was 0.03 e⁻ and occurred near 2.5 Å. The 6s orbital was even less significant. The 6s orbital occupation never exceeded 0.02 e⁻ for the range of internuclear distances examined. Furthermore, since the z-axis was defined as the internuclear axis, the F 2px and 2py orbitals cannot form σ bonds with Nd. Both of these orbitals remain doubly occupied and localized on F at all internuclear distances. The occupation of the F 2px and 2py orbitals, together with the low d orbital occupation on Nd indicates that the F 2px and 2py orbitals do not back-donate to the dπ orbitals on Nd. Thus, the (9,16) active space is unnecessarily large for NdF²⁺ and all multi-reference calculations of NdF²⁺ discussed herein use either the (5,8) active space that includes the Nd 4f orbitals and the F 2pz orbital or the (3,7) active space that spans only the Nd 4f orbital set.

Figure 4.1 shows the ground state curves obtained with the (3,7) active space and with the (5,8) active space. The ground state is ⁴I in both cases, and it is doubly degenerate. The
curves are nearly parallel near the equilibrium bond geometry, and the equilibrium distance varies by only 0.007 Å, with the (3,7) active space producing the shorter Nd-F bond. Thus the (3,7) active space is sufficient to describe properties of NdFx such as optimized geometries and frequencies (within the harmonic oscillator approximation). However, the shape of the curves diverges in the region near 2.4 Å where the (5,8) curve goes through an inflection point, while the (3,7) curve remains concave upward. The inflection point on the (5,8) curve corresponds to a region where the dominant configurations no longer have the F 2p\(_{z}\) orbital doubly occupied. Since the spin multiplicity is constrained to be a quartet, the F 2p\(_{z}\) orbital retains the beta electron and the alpha electron is transferred to the 4f manifold of Nd. This process cannot occur with the (3,7) active space since the F 2p\(_{z}\) orbital is constrained to be doubly occupied at all internuclear distances. Thus, the (5,8) active space allows for homolytic dissociation (Nd\(^{2+}\) + F\(^{-}\)) while the (3,7) active space forces heterolytic dissociation (Nd\(^{3+}\) + F\(^{-}\)), a process that is not stable in the gas phase in the absence on an external field to stabilize the charge separation. The natural orbital occupation numbers highlight differences between the two active spaces along the ground state potential energy curves (Table 1). In Table 4.1, it is clear that the F 2p\(_{z}\) orbital is always doubly occupied with the (3,7) active space, whereas the F 2p\(_{z}\) orbital occupation varies gradually from 1.99 electrons at 1.6 Å to 1.90 electrons at 2.6 Å with the (5,8) active space. Likewise, the Nd 4f orbitals react to the variation in F 2p\(_{z}\) occupation. In the case of the (3,7) active space, electrons are simply transferred from the bulk of the Nd 4f set to the 4f\(_{z^3}\) orbital (orbital f(7) in Table 4.1). However, the electrons are transferred from the F 2p\(_{z}\) orbitals to the Nd 4f\(_{z^3}\) orbital (orbital f(7) in Table 4.1) when the (5,8) active space is used. All the remaining f orbitals maintain an occupation of 0.5 electrons for all internuclear distances when the (5,8) active space is used. In both cases, there is a relatively large change in the Nd 4f\(_{z^3}\) orbital
occupation between 2.6 Å and 2.8 Å where the occupation is 0.33 electrons with the (3,7) active space and 0.26 electrons with the (5,8) active space.

Potential energy curves for NdF\(^{2+}\) obtained at the MCSCF level of theory with the (5,8) active space is shown in Figure 4.2. Four quartet states are shown, but each of the quartet states is also doubly degenerate. The MCSCF quartet states, in order of increasing energy at the equilibrium distance, \(r_e\), are \(X^4\)\(\Pi\), \(A^4\)\(\Phi\), \(B^4\)\(\Delta\), and \(C^4\)\(\Gamma\) and their energies relative to the ground state (\(X^4\)\(\Pi\)) are 7.1 kcal/mol, 14.1 kcal/mol, and 30.6 kcal/mol, respectively. Inclusion of dynamic correlation via MCQDPT2 calculations does not change the ordering of the quartet states, but the energy differences relative to the ground state of the \(A^4\)\(\Phi\), \(B^4\)\(\Delta\), and \(C^4\)\(\Gamma\) states are lowered to 5.6 kcal/mol, 10.5 kcal/mol, and 22.5 kcal/mol, respectively, and the ground state energy is lowered by 14.5 kcal/mol relative to the MCSCF ground state energy. Four doublet states are also shown, and these states are all doubly degenerate as well. The doublet states (\(a^2\)\(\Phi\), \(b^2\)\(\Pi\), \(c^2\)\(\Gamma\), and \(d^2\)\(\Delta\)) are much higher in energy than the quartet states, which should be expected according to Hund’s rule. The MCSCF energy differences between the doublet states and the quartet ground state are 50.1 kcal/mol, 55.3 kcal/mol, 55.5 kcal/mol, and 57.0 kcal/mol for the \(a^2\)\(\Phi\), \(b^2\)\(\Pi\), \(c^2\)\(\Gamma\), and \(d^2\)\(\Delta\) states, respectively. As with the quartet states, inclusion of dynamic correlation via MCQDPT2 calculations lowers the doublet states relative to the ground state energy. The MCQDPT2 energies of the doublet states at \(r_e\) are 44.6 kcal/mol, 46.6 kcal/mol, 48.2 kcal/mol, and 49.8 kcal/mol for the \(a^2\)\(\Phi\), \(b^2\)\(\Pi\), \(c^2\)\(\Gamma\), and \(d^2\)\(\Delta\) states, respectively. In addition to lowering the relative energies of the doublet states, the energy gap between the lowest and highest doublet states closes by approximately 2 kcal/mol.

Equilibrium bond lengths for each of the quartet and doublet states are shown in Table 4.2. At the MCSCF level the equilibrium bond lengths are approximately the same for each state.
and range from 1.905 Å to 1.912 Å. Inclusion of dynamic correlation shortens the bond slightly; the MCQDPT2 bond lengths vary between 1.900 Å and 1.905 Å. For comparison, the bond lengths of NdF₃ and NdF₄⁻ are 2.09 Å[191] (or 2.15 Å[225]) and 2.63 Å[226] respectively. At rₑ the F 2pₓ orbital is doubly occupied in all of the dominant configuration state functions (CSFs), i.e. all CSFs with a coefficient greater than 0.07. The quartet states differ from each other by permutations of f orbital occupations localized solely on Nd, and therefore the quartet potential energy curves are all roughly parallel to each other. The F 2pₓ orbital is doubly occupied near rₑ for all dominant CSFs for the doublet states. The doublet states differ from each other by permutations of f occupations, and they differ from the quartet states by a spin flip, i.e., there is a beta electron in one of the f orbitals. The potential energy well is relatively flat for all of the quartet and doublet states.

The remaining potential energy curve depicted in Figure 4.2 is a doubly degenerate ⁶H state. The ⁶H state corresponds to a singly occupied F 2pₓ orbital and four singly occupied Nd 4f orbitals with all unpaired electrons having parallel spin, thus the sextet state leads to the homolytic dissociation products, Nd²⁺ + F⁻. The ⁴I state crosses the ⁶H state at 2.509 Å (2.432 Å at the MCQDPT2 level of theory), and this intersystem crossing involves a spin flip of the electron that remains in the F 2pₓ orbital. Dissociation to the homolytic products via crossover to the ⁶H state produces dissociation energies of 56.9 kcal/mol and 47.6 kcal/mol at the MCSCF and MCQDPT2 levels of theory, respectively.

Spin-orbit coupling (SOC) constants obtained at the SO-MCQDPT2 level of theory are shown in Table 4.3. The SOC constants presented correspond to calculations performed at an internuclear distance of 1.9 Å, but calculation of the SOC constant over the full range of internuclear distances considered shows a variation by up to 20% in the SOC constant. Thus, the
SOC constants can only be taken as a guide as to the strength of the coupling between states. The $^4I$ ground state exhibits coupling with the $^6H$ state on the order of 200 cm$^{-1}$. Therefore, intersystem crossing and the spin flip needed to dissociate to the heterolytic products can occur. This is also true of the intersystem crossing between the $^4\Gamma$ and the $^6H$ states. The $^4\Phi$ and $^4\Delta$ do not couple with the $^6H$ state and the crossing is forbidden. However, there is strong coupling between the $^4\Phi$ and the higher quartet states, so transitions within the quartet excited state manifold are to be expected. The $^4\Delta$ state and the doublet states also exhibit strong coupling, although the coupling between to the $^2\Gamma$ is orders of magnitude weaker than the coupling to other doublet states. Within the doublet excited state manifold, the coupling between the states presented herein is generally non-negligible, although the coupling strength varies by 1 – 3 orders of magnitude. Most significantly with respect to the doublet states, however, is the absence of coupling to the $^6H$ state. It is likely that the doublets dissociate to an excited repulsive quartet state, although such a state was not found in this study.

The effect of spin-orbit coupling on the potential energy curves for each state was examined. Figure 4.3 illustrates how each of the states is split upon inclusion of spin-orbit coupling at the SO-MCQDPT2 level of theory, and the transition energies at the equilibrium bond length are presented in Table 4.4. The ordering of states predicted in the present study largely parallels the ordering of states determined experimentally$^{227}$ and theoretically$^{228}$ for the free Nd$^{3+}$ ion. The $X^4I_{9/2}$ ground state is separated from the first excited state ($A^4I_{11/2}$) by 1764 cm$^{-1}$, and the next state higher state ($B^4\Phi_{3/2}$) is 3301 cm$^{-1}$ above the ground state. Beyond the second excited state ($B^3\Phi_{3/2}$), the separation between quartet states ($^4I, ^4\Phi$, and $^4\Delta$) is quite small. The $^4\Gamma$ states are separated from the lower quartet states and seem to lie in a distinct band within the excited state manifold. However, it is likely there are higher quartet states that also exist in
this region, but no attempt was made to isolate such high-energy quartet states. The doublet states also appear in a relatively narrow band that spans less than 4000 cm\(^{-1}\) between the lowest and highest doublet states presented here. The lowest doublet state is the \(a^2\Pi_{1/2}\), which is 17565 cm\(^{-1}\) above the ground state at equilibrium. Notably, while SOC may impact the relative ordering of the states, especially within the doublet manifold, the general shape of the potential energy curves remains unaltered and the equilibrium bond lengths correspond to those obtained at the MCQDPT2 level of theory, i.e. SOC does not affect the equilibrium geometry.

The spectroscopic constants obtained from the Dunham analysis of the ground state at the MCSCF, MCQDPT2 and SO-MCQDPT2 levels of theory are reported in Table 4.5. Dunham analysis results for additional states are provided in the supplementary material. Electron correlation has a significant effect on the potential energy curves, lowering the dissociation energy (\(D_e\)) by 9.3 kcal/mol and raising \(\omega_e\) by 5 cm\(^{-1}\). Spin-orbit effects raise the \(D_e\) by 2.0 kcal/mol while leaving the remaining diatomic constants unaltered, indicating limited contribution of spin-orbit effects on the curvature of the PEC. The zero-point energy (\(D_e - D_0\)) of the \(X^4\Pi_{9/2}\) state is \(~1\) kcal/mol, whereas the first excited state, \(A^4\Pi_{11/2}\) is 5 kcal/mol above the ground state. So, even accounting zero-point energy, the ground state is moderately separated from the excited states. Higher in the potential energy manifold, the states are much closer in energy. Inclusion of zero-point energy and higher vibrational levels can make the excited state manifold resemble a continuum. The polynomial fits were also used to determine the crossing points at the MCSCF, MCQDPT2, and SO-MCQDPT2 levels of theory. Tables of the crossing points are included in the supplementary material.

Calculations on the NdF\(_3\) quartet were also performed for comparison. Ideally, a (21,22) active space spanning the Nd 4f, 5d, 6s, and F 2p orbital sets should be used. Such an active
space is prohibitively expensive, so a series of active spaces was employed to determine a suitable, yet practical, active space. A (9,16) active space spanning the Nd 4f, 5d, and 6s orbitals as well as the three F p orbitals directed along the bonding axes was employed to determine the 5d and 6s occupations. At the bond distance examined, the F p orbitals remain doubly occupied and the three unpaired electrons lie exclusively in the Nd 4f orbitals. Thus, Nd in NdF$_3$ is truly Nd$^{3+}$ at the experimental equilibrium geometry. A (21,16) active space was considered that spans the Nd 4f orbital set as well as the complete F 2p sets. The F 2p orbitals remain doubly occupied in this situation, thus reaffirming that the Nd-F bond in NdF$_3$ is primarily ionic. Finally, a (5,8) active space was employed that is analogous to the (5,8) active space used for the study of NdF$_{2+}$ spanning the Nd 4f orbital set and a single F p orbital directed along the Nd-F bond.

Calculations on NdF$_3$ show that there are additional quasi-degenerate states in the excited state manifold when compared to NdF$_{2+}$. The appearance of these states can be attributed to the threefold increase in the number of equivalent Nd-F bonds. However, the lowest electronic state is suitably separated from the higher electronic states and can be used to provide a direct comparison with NdF$_{2+}$. State averaging over the doubly degenerate ground state in the SO-MCQDPT2 calculation provides results in close agreement with the levels that result from the $^4$I ground state of NdF$_{2+}$. The NdF$_{2+}$ $^4$I state splits into the $^4$I$_{9/2}$, $^4$I$_{11/2}$, $^4$I$_{13/2}$, and $^4$I$_{15/2}$ levels at 0 cm$^{-1}$, 1764 cm$^{-1}$, 3301 cm$^{-1}$, and 5291 cm$^{-1}$, respectively. The analogous levels that result for NdF$_3$ are 0 cm$^{-1}$, 1551 cm$^{-1}$, 3094 cm$^{-1}$, and 5949 cm$^{-1}$. The agreement between the NdF$_{2+}$ model and NdF$_3$ is within 1 kcal/mol for the lower levels and 2 kcal/mol for the highest level. However, both models predict a 4 – 5 kcal/mol separation between the ground and first excited states.

4.4 Conclusions
NdF$^{2+}$ was studied using multi-reference methods. It was determined that a (3,7) active space that spans the 4f orbital set on Nd is not sufficient to describe NdF$^{2+}$ at long internuclear distances since heterolytic dissociation to the ionic product, Nd$^{3+}$ and F$^-$, is enforced. A large active space that includes the 4f and 5d orbitals on Nd as well as the 2p orbital set on F is unnecessarily large. Examination of the orbital occupations at a range of internuclear distances (1.4 Å – 3.5 Å) suggested that a (5,8) active space that consists of the Nd 4f orbitals set and the F 2p$_z$ orbital is the minimum active space required to adequately describe the homolytic dissociation of NdF$^{2+}$.

Homolytic dissociation of NdF$^{2+}$ occurs via a state crossing between the $^4$I ($^4$I$^9/2$) state and the $^6$H ($^6$H$^5/2$) state. Dissociation by this method leads to a dissociation energy of ~ 47 – 59 kcal/mol depending on the level of theory employed. Inclusion of dynamic correlation via perturbation theory lowers sextet states relative to the quartet states and thus leads to dissociation energies ~ 47 kcal/mol. Inclusion of spin-orbit coupling via SO-MCQDPT2 raises the dissociation energy for the $^4$I$^9/2$ ground state to ~ 49 kcal/mol. The SOC constant for coupling between the $^4$I and $^6$H states is on the order of 200 cm$^{-1}$, indicating that dissociation via the intersystem crossing is allowed. Stronger coupling exists among higher quartet states and also among the high-energy doublet states, but the doublet states do not couple to the $^6$H state.

The (5,8) active space is shown to be suitable to describe the lowest levels of NdF$_3$ as well as NdF$^{2+}$. The similarity of the energetic separation of the low-lying excited states for these two species indicates the potential utility of the dicaticionic diatomic in describing the nature of the NdF bond. Furthermore, it is evident from the results presented here that the nature of the Nd-F bond in both NdF$^{2+}$ and NdF$_3$ is primarily ionic rather than covalent at the equilibrium bond distance.
Figure 4.1 The $^4$I ground state curves calculated at the MCSCF level with a (3,7) active space and with a (5,8) active space.
Figure 4.2  Potential energy curves obtained with a (5,8) active space at the MCSCF level of theory. Relative energies are in kcal/mol, and the zero of the energy scale is set to the lowest point on the MCSCF ground state potential energy curve.
Figure 4.3 Potential energy curves obtained for the spin-orbit states at the SO-MCQDPT2 level of theory with a (5,8) active space. Points at 0.05 Å increments in the internuclear distance are shown, although 0.001 Å increments were used near the equilibrium distance. Relative energies are in kcal/mol, and the zero of the energy scale is set to the lowest point on the MCSCF (5,8) ground state potential energy curve.
Table 4.1 Natural orbital occupation numbers for the F 2p$_z$ and Nd 4f orbitals for the (3,7) active space and the (5,8) active space (in parentheses) for the ground state at internuclear distances ranging from 1.6 Å – 2.8 Å. Orbital f(7) is the Nd 4f$_{x^2-y^2}$ orbital directed along the internuclear axis.

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<td>Nd f(2)</td>
<td>0.57 (0.50)</td>
<td>0.58 (0.50)</td>
<td>0.58 (0.50)</td>
<td>0.50 (0.50)</td>
<td>0.50 (0.50)</td>
<td>0.50 (0.50)</td>
<td>0.50 (0.50)</td>
<td></td>
</tr>
<tr>
<td>Nd f(3)</td>
<td>0.57 (0.50)</td>
<td>0.58 (0.50)</td>
<td>0.58 (0.50)</td>
<td>0.50 (0.50)</td>
<td>0.50 (0.50)</td>
<td>0.50 (0.50)</td>
<td>0.50 (0.50)</td>
<td></td>
</tr>
<tr>
<td>Nd f(4)</td>
<td>0.43 (0.50)</td>
<td>0.42 (0.50)</td>
<td>0.42 (0.50)</td>
<td>0.50 (0.50)</td>
<td>0.50 (0.50)</td>
<td>0.50 (0.50)</td>
<td>0.50 (0.50)</td>
<td></td>
</tr>
<tr>
<td>Nd f(5)</td>
<td>0.43 (0.50)</td>
<td>0.42 (0.50)</td>
<td>0.42 (0.50)</td>
<td>0.33 (0.50)</td>
<td>0.33 (0.50)</td>
<td>0.33 (0.50)</td>
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</tr>
<tr>
<td>Nd f(6)</td>
<td>0.33 (0.50)</td>
<td>0.33 (0.50)</td>
<td>0.33 (0.50)</td>
<td>0.33 (0.50)</td>
<td>0.33 (0.50)</td>
<td>0.33 (0.50)</td>
<td>0.33 (0.50)</td>
<td></td>
</tr>
<tr>
<td>Nd f(7)</td>
<td>0.02 (0.01)</td>
<td>0.03 (0.02)</td>
<td>0.03 (0.02)</td>
<td>0.33 (0.03)</td>
<td>0.33 (0.05)</td>
<td>0.33 (0.10)</td>
<td>0.33 (0.26)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2 Equilibrium distance (Å) for bound states calculated using the (5,8) active space at the MCSCF and MCQDPT2 levels of theory.

<table>
<thead>
<tr>
<th></th>
<th>MCSCF</th>
<th>MCQDPT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>X$^4$I</td>
<td>1.907</td>
<td>1.901</td>
</tr>
<tr>
<td>A$^4$Φ</td>
<td>1.912</td>
<td>1.905</td>
</tr>
<tr>
<td>B$^4$Δ</td>
<td>1.907</td>
<td>1.902</td>
</tr>
<tr>
<td>C$^4$Γ</td>
<td>1.905</td>
<td>1.901</td>
</tr>
<tr>
<td>a$^2$Φ</td>
<td>1.909</td>
<td>1.903</td>
</tr>
<tr>
<td>b$^2$Π</td>
<td>1.908</td>
<td>1.902</td>
</tr>
<tr>
<td>c$^2$Γ</td>
<td>1.905</td>
<td>1.900</td>
</tr>
<tr>
<td>d$^2$Δ</td>
<td>1.905</td>
<td>1.900</td>
</tr>
</tbody>
</table>

Table 4.3. Spin-orbit coupling constants (in cm$^{-1}$) computed at the SO-MCQDPT2 level of theory.

<table>
<thead>
<tr>
<th></th>
<th>X$^4$I</th>
<th>A$^4$Φ</th>
<th>B$^4$Δ</th>
<th>C$^4$Γ</th>
<th>a$^2$Φ</th>
<th>b$^2$Π</th>
<th>c$^2$Γ</th>
<th>d$^2$Δ</th>
<th>e^6H</th>
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</thead>
<tbody>
<tr>
<td>X$^4$I</td>
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<td>3</td>
<td>3</td>
<td>0</td>
<td>1</td>
<td>27</td>
<td>0</td>
<td>0</td>
<td>207</td>
</tr>
<tr>
<td>A$^4$Φ</td>
<td>1955</td>
<td>3302</td>
<td>2983</td>
<td>1927</td>
<td>0</td>
<td>83</td>
<td>683</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>B$^4$Δ</td>
<td>1318</td>
<td>1</td>
<td>374</td>
<td>1153</td>
<td>84</td>
<td>3135</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$^4$Γ</td>
<td>2563</td>
<td>1320</td>
<td>8</td>
<td>2742</td>
<td>84</td>
<td>228</td>
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<tr>
<td>a$^2$Φ</td>
<td>161</td>
<td>2</td>
<td>1196</td>
<td>187</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b$^2$Π</td>
<td>1971</td>
<td>24</td>
<td>635</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c$^2$Γ</td>
<td>2059</td>
<td>138</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d$^2$Δ</td>
<td>1886</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e^6H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3246</td>
</tr>
</tbody>
</table>
Table 4.4 SO-MCQDPT2 transition energies (cm$^{-1}$) at the ground state ($^{4}\text{I}_{9/2}$) equilibrium bond length for NdF$^{2+}$ (1.901 Å).

<table>
<thead>
<tr>
<th>SO-MCQDPT2</th>
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</tr>
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<tbody>
<tr>
<td>$X^{4}\text{I}_{9/2}$</td>
<td>0</td>
</tr>
<tr>
<td>$A^{4}\text{I}_{11/2}$</td>
<td>1764</td>
</tr>
<tr>
<td>$C^{4}\text{I}_{13/2}$</td>
<td>3527</td>
</tr>
<tr>
<td>$F^{4}\text{I}_{15/2}$</td>
<td>5291</td>
</tr>
<tr>
<td>$B^{4}\Phi_{3/2}$</td>
<td>3301</td>
</tr>
<tr>
<td>$D^{4}\Phi_{5/2}$</td>
<td>4175</td>
</tr>
<tr>
<td>$E^{4}\Phi_{7/2}$</td>
<td>5049</td>
</tr>
<tr>
<td>$H^{4}\Phi_{9/2}$</td>
<td>5924</td>
</tr>
<tr>
<td>$G^{4}\Lambda_{1/2}$</td>
<td>5418</td>
</tr>
<tr>
<td>$I^{4}\Delta_{3/2}$</td>
<td>6008</td>
</tr>
<tr>
<td>$J^{4}\Delta_{5/2}$</td>
<td>6598</td>
</tr>
<tr>
<td>$K^{4}\Delta_{7/2}$</td>
<td>7187</td>
</tr>
<tr>
<td>$L^{4}\Gamma_{5/2}$</td>
<td>8785</td>
</tr>
<tr>
<td>$M^{4}\Gamma_{7/2}$</td>
<td>9931</td>
</tr>
<tr>
<td>$N^{4}\Gamma_{9/2}$</td>
<td>11077</td>
</tr>
<tr>
<td>$O^{4}\Gamma_{11/2}$</td>
<td>12223</td>
</tr>
<tr>
<td>$c^{2}\Phi_{5/2}$</td>
<td>18141</td>
</tr>
<tr>
<td>$d^{2}\Phi_{7/2}$</td>
<td>18369</td>
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<tr>
<td>$b^{2}\Gamma_{7/2}$</td>
<td>18040</td>
</tr>
<tr>
<td>$g^{2}\Gamma_{9/2}$</td>
<td>20952</td>
</tr>
<tr>
<td>$a^{2}\Pi_{1/2}$</td>
<td>17565</td>
</tr>
<tr>
<td>$f^{2}\Pi_{3/2}$</td>
<td>20352</td>
</tr>
<tr>
<td>$e^{2}\Delta_{3/2}$</td>
<td>18718</td>
</tr>
<tr>
<td>$h^{2}\Delta_{5/2}$</td>
<td>21385</td>
</tr>
<tr>
<td>$i^{6}\text{H}_{5/2}$</td>
<td>38224</td>
</tr>
<tr>
<td>$j^{6}\text{H}_{7/2}$</td>
<td>38999</td>
</tr>
<tr>
<td>$k^{6}\text{H}_{9/2}$</td>
<td>39774</td>
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<tr>
<td>$l^{6}\text{H}_{11/2}$</td>
<td>40549</td>
</tr>
<tr>
<td>$m^{6}\text{H}_{13/2}$</td>
<td>41324</td>
</tr>
<tr>
<td>$n^{6}\text{H}_{15/2}$</td>
<td>42097</td>
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</tbody>
</table>
Table 4.5  Spectroscopic constants for the ground state of NdF$^{2+}$ ($^4$I for MCSCF and MCQDPT2 and $^4$I$_{9/2}$ for SO-MCQDPT2). The constants were obtained by a Dunham analysis of the ground state potential energy curves for each level of theory employed. All values are reported in cm$^{-1}$ except for $D_e$ and $D_0$, which are reported in kcal/mol.

<table>
<thead>
<tr>
<th></th>
<th>$\omega_e$</th>
<th>$\omega_e x_e$</th>
<th>$B_e$</th>
<th>$\alpha_e$</th>
<th>$D_e$</th>
<th>$D_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCSCF</td>
<td>709.1</td>
<td>2.13</td>
<td>0.2767</td>
<td>0.00117</td>
<td>56.9</td>
<td>55.9</td>
</tr>
<tr>
<td>MCQDPT2</td>
<td>714.1</td>
<td>2.14</td>
<td>0.2783</td>
<td>0.00117</td>
<td>47.6</td>
<td>46.5</td>
</tr>
<tr>
<td>SO-MCQDPT2</td>
<td>714.0</td>
<td>2.13</td>
<td>0.2783</td>
<td>0.00117</td>
<td>49.6</td>
<td>48.6</td>
</tr>
</tbody>
</table>
CHAPTER 5

DISSOCIATION ENERGY AND ELECTRONIC STRUCTURE OF THE LOW VALENT LANTHANIDE COMPOUND NdF$^{2+}$

5.1 Introduction

Due to the importance of lanthanides in solid state magnets, luminescent phosphors, and catalysts among other uses, there is a corresponding interest in understanding the physical properties behind the metal-ligand interactions of lanthanide compounds in order to direct materials and catalyst design. Lanthanide chemistry is primarily dominated by lanthanides in the +3 oxidation state, which corresponds to the loss of three electrons from some combination of those in the 6s, 5d, and, in some cases, 4f orbitals, leaving only the compact 4f electrons to dictate the chemical and physical properties of the compound, resulting in highly ionic bonding. Therefore, the bulk of lanthanide chemistry arises from the distribution of the remaining unpaired electrons among the 4f orbitals and transitions between the resulting states. This is especially true for lanthanides near the middle of the series as these elements tend to have diverse and densely packed excited electronic state manifolds owing to the distribution of electrons among the nearly degenerate 4f orbitals.

Studies have been performed on low valent lanthanide compounds using various levels of theory ranging from ligand field theory, semi-empirical methods, and ab initio quantum chemistry and density functional theory (DFT). Ligand field theory has been a useful model for the electronic structure of highly ionic lanthanide complexes in the +3 oxidation state. However, in the +2 and +1 oxidation states, one or both of the additional electrons relative to the +3 state will occupy a 4f, 5d, or 6s orbital, which will change how the lanthanide non-integer.
will bond to its ligands, leading to the possibility of bonds with a slightly more covalent character in contrast to the entirely ionic +3 state. Ren et al. utilized a combined ligand field and DFT (CLDT) method to calculate the dissociation energies and spin-orbit energy levels of LnF molecules and achieved good agreement on the order of $10^2$ cm$^{-1}$ with experimental multiplet resolved energies of PrF, SmF, and YbF.$^{244}$ Mucklejohn utilized the diatomic molecular constants of barium and lanthanide monohalides LnX(X=F-I) to calculate the enthalpies of formation of the lanthanide halides across the entire series and reported agreement for the molar entropies of the barium monohalides with experiment within 1.2 J mol$^{-1}$ K$^{-1}$. However, Mucklejohn obtained limited agreement with experiment with respect to the molar enthalpies of formation for the same set of molecules, reporting errors between 3.3 kJ mol$^{-1}$ and 48 kJ mol$^{-1}$. $^{245}$ DFT and CCSD(T) calculations were also performed on selected LnF molecules (YbH, YbF, GdF, EuF, and NdF) by Wahlgren et al.$^{246}$ who observed that CCSD(T) gave the best agreement with experiment as compared with BLYP, BP, BP86, and B3LYP for bond dissociation energies and bond lengths, though B3LYP with a small core Stuttgart pseudopotential performed the best among the DFT functionals chosen.

Recent work on lanthanide fluorides has focused on the determination of thermochemical, geometric, and electronic properties using highly correlated and multi-reference \textit{ab initio} methods for lanthanide complexes.$^{202,218,246,250,254-256}$ NdF$^{2+}$ was examined using complete active space SCF (CASSCF) and second-order multiconfigurational quasi-degenerate perturbation theory (MCQDPT2) and was found to have a very dense set of roughly parallel electronic states,$^{255}$ similar to that found with PrF$^{2+}$ and PmF$^{2+}$. $^{257}$ The observed states were the result of permutations of 4f orbital occupations that resembled the low-lying electronic states of NdF$_3$, thereby demonstrating the utility of NdF$^{2+}$ as a simplified model of the Nd-F bond in
Neutral NdF was analyzed using both CASSCF and equation of motion completely renormalized coupled cluster (EOM-CR-CCSD(T)) and was shown to possess a very different electronic structure than NdF$^{2+}$ owing to the contributions from the neodymium 5d and 6s orbitals.

The current work focuses on NdF$^+$, where neodymium is formally in the less common +2 oxidation state. There is very little experimental or theoretical data on NdF$^+$, as with most other lanthanides, with the noted exception of one experimental paper that reports a dissociation energy of 131 ± 10 kcal mol$^{-1}$ for NdF$^+$. The bare Nd$^{2+}$ ion has an electron configuration of [Xe]4f$^4$, implying that the ion will bind ligands in an ionic fashion, and the electronic state distribution may possibly resemble that of either NdF$^{2+}$ or NdF depending on how the ligand field affects the 4f, 5d, and 6s orbital energies. If ionic character dominates in NdF$^+$, i.e. Nd$^{2+}$F$^-$, then it is likely that the ground electronic state is a quintet state. However, if the ligand field allows promotion of an electron from the 4f to the 6s or 5d shells, then many potential quasi-degenerate configurations are accessible, leading to the possibility of a triplet ground state. Thus, both triplet and quintet states must be considered. As a result, the energies and geometries obtained from the calculations are compared to the previous studies on NdF$^{2+}$ and NdF to determine the similarities of the electronic structure and thermochemical properties of NdF$^+$ to its lower and higher oxidation state analogues.

5.2 Methodology

Equation of motion completely renormalized coupled cluster with single, double, and perturbative triple excitations (EOM-CR-CCSD(T))$^{52,54,55,258}$ was used to obtain potential energy curves for the lowest two quintet and triplet states of NdF$^+$ in each irreducible representation of C$_{2v}$ symmetry using the NWChem$^{259}$ computational chemistry software package. The Sapporo-
DKH3-TZP-2012\textsuperscript{21} all electron basis set on Nd and the Sapporo-TZP-2012 basis set on F\textsuperscript{20} to model the orbitals of NdF\textsuperscript{+}. Points along the potential energy curves were calculated at intervals of 0.05 Å in the range of 1.7-2.3 Å for the quintet and triplet curves. The dissociation limit was computed at 10.0 Å corresponding to (\textsuperscript{6}I)Nd\textsuperscript{+} + (\textsuperscript{2}P)F. All of the valence electrons were correlated in addition to the sub-valence neodymium 5s and 5p electrons. An additional calculation for the ground state correlating all electrons was also performed to ascertain the effect of core correlation on the dissociation energy. Relativistic effects were included through the an implementation of the third-order Douglass-Kroll-Hess Hamiltonian that includes the $\hat{p}\hat{V}\hat{p}$ cross-product terms\textsuperscript{69,76,260,261} thereby incorporating vector as well as scalar relativistic effects, though the results remain J-averaged due to the neglect of the odd terms. Equilibrium bond lengths and spectroscopic constants were calculated through fitting an 8th order Dunham type potential\textsuperscript{182} to the data for the quintets using all the available data points.

5.3 Results and Discussion

The potential energy curves computed with EOM-CR-CCSD(T) are shown in Figure 5.1. All of the B\textsubscript{1}/B\textsubscript{2} states in each spin multiplicity examined and the triplet A\textsubscript{1}/A\textsubscript{2} states were found to be doubly degenerate in C\textsubscript{2v} symmetry. There are two possible candidates for the ground state of NdF\textsuperscript{+}, the doubly degenerate X\textsuperscript{5}(B\textsubscript{1}/B\textsubscript{2}) state, or the singly degenerate X\textsuperscript{5}A\textsubscript{2} state as shown by the vertical excitation energies between the states from the lowest energy minimum (Table 5.1). There is a separation of 0.18 kcal mol\textsuperscript{-1} between the doubly degenerate \textsuperscript{5}(B\textsubscript{1}/B\textsubscript{2}) state and the single \textsuperscript{5}A\textsubscript{2} state that is far smaller than the typical accuracy of 1 kcal mol\textsuperscript{-1} expected from coupled cluster methods of this order, making a definite determination of the ground state between these two candidates impossible. The A\textsuperscript{5}A\textsubscript{1} state is shown to be within 1 kcal mol\textsuperscript{-1} of the C\textsuperscript{5}A\textsubscript{2} state indicating a possible degeneracy between these electronic states as well.
Figure 5.1 Graph of calculated quintet and triplet potential energy curves for NdF⁺.

Table 5.1 Vertical excitation energies from the minimum of the lowest energy $X^5(B_1/B_2)$ state.

<table>
<thead>
<tr>
<th>State</th>
<th>Transition energy (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^5A_2$</td>
<td>0.176</td>
</tr>
<tr>
<td>$A^5A_1$</td>
<td>21.0</td>
</tr>
<tr>
<td>$B^5(B_1/B_2)$</td>
<td>21.3</td>
</tr>
<tr>
<td>$C^5A_2$</td>
<td>21.5</td>
</tr>
<tr>
<td>$a^3(A_1/A_2)$</td>
<td>24.1</td>
</tr>
<tr>
<td>$D^5A_1$</td>
<td>30.4</td>
</tr>
<tr>
<td>$b^3(A_1/A_2)$</td>
<td>41.7</td>
</tr>
</tbody>
</table>

The triplet states could not be calculated past 2.023 Å due convergence issues with the coupled cluster amplitudes. When an unrestricted reference is used, the spin contamination beyond this point on the potential energy curve is substantial, with an $<S^2>$ value of greater than 3, i.e. spin contamination in excess of 150% of the exact value for a triplet. This indicates that the triplet states have significant multi-reference character at internuclear distances greater than 2.023 Å, implying that the triplets are strongly correlated, for which coupled cluster is poorly suited to describe. Figure 5.2 illustrates what happens to the triplet PECs at longer
internuclear distances. This is characteristic of strongly correlated systems where higher-order excitations are required.

**Figure 5.2** Triplet EOM-CCSD(T) curves illustrating the catastrophic failure of coupled cluster.

In addition, the triplet reference is an exceptionally poor descriptor of homolytic dissociation for NdF\(^{+}\) since it is clear from the reference state the triplet states undergo a heterolytic dissociation pathway to ionic products. The tendency of the low spin state to dissociate heterolytically is analogous to the low-spin quartet states of neutral NdF\(^{2+}\). Since the heterolytic dissociation pathway is unfavorable in the gas phase, and the triplets are separated from the ground state by over 20 kcal mol\(^{-1}\), the triplets do not have a significant contribution to the dissociation energy of the molecule, even at high temperatures. Septet states were also considered as a possible route to dissociation due to similar high spin states playing a pivotal role
in the dissociation of NdF\textsuperscript{2+}, but were found to be even higher in energy than the triplet states, at ~ 166.0 kcal mol\textsuperscript{-1} from the lowest energy state, and so were not considered further.

**Table 5.2** Diatomic constants for the quintet electronic states obtained from 8\textsuperscript{th} order Dunham potentials.

<table>
<thead>
<tr>
<th>State</th>
<th>(r_e) (Å)</th>
<th>(\omega_e) (cm\textsuperscript{-1})</th>
<th>(\omega_e\chi_e) (cm\textsuperscript{-1})</th>
<th>(B_e) (cm\textsuperscript{-1})</th>
<th>(\alpha_e) (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X^5(B_1/B_2))</td>
<td>2.023</td>
<td>576.2</td>
<td>1.84</td>
<td>0.2457</td>
<td>0.00112</td>
</tr>
<tr>
<td>(X^5A_2)</td>
<td>2.022</td>
<td>576.0</td>
<td>1.84</td>
<td>0.2461</td>
<td>0.00112</td>
</tr>
<tr>
<td>(A^5(A_1/A_2))</td>
<td>2.018</td>
<td>578.8</td>
<td>2.38</td>
<td>0.2471</td>
<td>0.00159</td>
</tr>
<tr>
<td>(B^5(B_1/B_2))</td>
<td>2.019</td>
<td>577.9</td>
<td>1.94</td>
<td>0.2467</td>
<td>0.00106</td>
</tr>
<tr>
<td>(C^5(A_2/A_1))</td>
<td>2.018</td>
<td>573.0</td>
<td>1.54</td>
<td>0.2470</td>
<td>0.00143</td>
</tr>
<tr>
<td>(D^5A_1)</td>
<td>1.962</td>
<td>621.7</td>
<td>1.53</td>
<td>0.2612</td>
<td>0.00097</td>
</tr>
</tbody>
</table>

Results of the Dunham analysis are shown in Table 5.2. As shown in Figure 5.1, the curves for most of the quintets are very similar to each other, with equilibrium bond distances differing by only a few hundredths of an Angstrom between the states. However, the \(D^5A_1\) curve is a notable exception, possessing an equilibrium bond length of 1.962 Å, significantly shorter than any of the other quintet states. Additionally, the differences between the harmonic vibrational and rotational constants also indicate that the curvature of the \(D^5A_1\) state is significantly different from that of the others. Analysis of the large coupled cluster singles amplitudes involving 4f to 5d transitions for the \(D^5A_1\) state confirm that the change in geometry is directly related to the involvement of the 5d orbitals since all of the other large amplitudes for all remaining calculated states involve either permutations among 4f orbitals, or 4f to 6s transitions.

As shown in a previous paper on NdF\textsuperscript{2-},\textsuperscript{256} the level of electron correlation can have a significant effect on the dissociation energy of the molecule. It was found in that study that while correlating the 5s and 5p neodymium orbitals can be useful, the dissociation energy still differs from the experimental value, requiring further electron correlation to obtain experimentally accurate results. To ensure the dissociation energy of NdF\textsuperscript{+} is within
experimental accuracy, all of the core electrons were correlated and the molecule was forced to remain as a supermolecule calculated with the atoms at an internuclear separation of 10 Å to ensure strict size consistency. The dissociation energy of NdF\(^+\), calculated from the lowest energy quintet X\(^5\)(B\(_1\)/B\(_2\)) state using the supermolecule approach is 134.5 kcal mol\(^{-1}\), in excellent agreement with the experimental value of 131 ± 10 kcal mol\(^{-1}\).\(^{199}\) When zero point energy is included, the bond dissociation energy, D\(_0\), becomes 133.7 kcal mol\(^{-1}\), which is in even better agreement with experiment. When the dissociation energy is compared to those for the other oxidation states of neodymium (Table 3), NdF\(^+\) appears to be more chemically similar to NdF than NdF\(^{2+}\) in terms of its binding to fluorine in that there is a dependence on the 5d and 6s orbitals and the presence of a dissociative low energy high spin state in NdF\(^{2+}\). A similar dissociative state for NdF\(^+\) has not yet been found, so all thermochemical data is based on the dissociation limit of the quintet state, as in NdF. However, NdF\(^+\) appears slightly more similar to NdF\(^{2+}\) in terms of its excited electronic states due to the mostly parallel excited states in the quintets. There are some aberrations though, namely the D\(^5\)A\(_1\) state, that hint at the 5d orbitals now becoming a contributor to the excited state spectrum, but most of the quintet states do lie parallel to each other implying that these excitations primarily involve nonbonding, local orbitals, i.e. the 4f orbitals.

**Table 5.3** Comparison of dissociation energies of multiple oxidation states of NdF.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>D(_0) (kcal mol(^{-1}))</th>
<th>Expt. (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdF</td>
<td>131.9(^a)</td>
<td>130.3 ± 3.0(^c)</td>
</tr>
<tr>
<td>NdF(^+)</td>
<td>133.7</td>
<td>131 ± 10(^c, d)</td>
</tr>
<tr>
<td>NdF(^{2+})</td>
<td>48.6(^b)</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 256  
\(^{b}\)Reference 255  
\(^{c}\)Reference 199  
\(^{d}\)Gas phase Knudsen cell effusion performed at 1383-1520° K
Examination of the $t_1$ and $t_2$ amplitudes indicates that both the $^5A_2$ and $^5(B_1/B_2)$ candidates for the ground state exhibit ionic character in the region around the equilibrium geometry with both states having the spin density localized on Nd. This indicates that the molecule is dominated by Nd$^{2+}$F$^-$ character with Nd resembling the [Xe] 4f$^4$ configuration of Nd$^{2+}$. Yet, both states have a single large amplitude corresponding to excitation from an 4f orbital to the 6s orbital, and the states differ only in which 4f orbital from which the electron is excited. While this might appear to suggest NdF$^+$ has some covalent Nd$^+$ F character, the spin density is still localized on Nd indicating Nd$^{2+}$ character rather than Nd$^+$. As the internuclear distance is increased, the spin density of fluorine increases while the Nd 4f orbitals are correlated with the 5d and 6p orbitals such that overlap with the F 2p is maintained. This allows donation of an electron from a 2p orbital on fluorine to Nd such that homolytic dissociation is achieved.

5.4 Conclusion

The electronic structure and physical properties of NdF$^+$ have been examined using the completely renormalized equation of motion coupled cluster method. It was found that the nature of the ground state of NdF$^+$ resembles neutral NdF, while the excited state manifold is more like NdF$^{2+}$. The lowest energy states in NdF$^+$ are the $X'^5A_1$ state and degenerate $X^5(B_1/B_2)$ state. Given the small separation in energy between these states, a definitive assignment of the ground state is not possible in this case. Most of the quintet states remain parallel with the main exception showing significant bond shortening relative to the others, indicating a change in the bonding character in this state. Chemically, NdF$^+$ behaves much more like NdF than NdF$^{2+}$ both in the nature of the ground state and in the fact that the low spin states lead to heterolytic dissociation. Moreover, NdF$^+$ possesses a dissociation energy that is only 1.8 kcal mol$^{-1}$ higher.
in energy than that of NdF, implying that the bonding character between the two molecules is remarkably similar.
CHAPTER 6

4-COMPONENT RELATIVISTIC CALCULATIONS OF L_3 IONIZATION AND EXCITATIONS FOR THE ISOELECTRONIC SPECIES UO_2^{2+}, OUN^{+} AND UN_2$\S$

6.1 Introduction

Uranyl compounds are of great interest due to their unique coordination chemistry as well as their potential impact on the environment. Uranium has been shown to readily form a myriad of coordination complexes in three separate oxidation states (IV, V, and VI), though it tends to prefer the IV and VI oxidation states, resulting in its rich chemistry.$^{262-265}$ Because uranium (along with thorium, actinium, and protactinium) is one of the few actinide elements that is stable and safe enough to be characterized in a laboratory, this allows for the physical effects of the f orbitals on the electronic structure, geometry and thermochemistry to be determined experimentally, giving much insight on the electronic structure of uranyl coordination complexes.$^{266-276}$

The electronic properties of uranyl coordination complexes, as well as the nature of the compounds themselves, have been determined through electronic spectroscopy and X-ray diffraction methods. X-ray absorbance and photoelectron spectroscopy have been frequently used to provide knowledge about the electronic structure of the deep core, which results in an element-specific electronic spectrum.$^{268}$ X-ray absorbance near edge spectroscopy (XANES) has been used to probe low-lying unoccupied core-ionized states of the uranyl complexes, returning energetics of the energy levels of the low-lying virtual orbitals, as well as information on the oxidation state of the molecule.$^{268,270,275,276}$ Walshe and coworkers used both high resolution XANES spectroscopy as well as extended X-ray absorbance fine structure (EXAFS) spectroscopy to characterize uranyl

$\S$ This entire chapter is reproduced from C. South, A. Shee, D. Mukherjee, A. K. Wilson, and T. Saue, “4-Component Relativistic Calculations of L_3 Ionization and Excitations for the Isoelectronic Species UO_2^{2+}, OUN^{+} and UN_2.” Phys. Chem. Chem. Phys. DOI:10.1039/c6cp00262e with permission from the PCCP Owner Societies.
peroxides and uranyl oxohydroxides in their mineral forms and provided the first experimental crystal structure of metastudtite, as well as subtle differences in the core spectra of the mineral forms studied. Given the highly local nature of the atomic core orbitals, the orbitals will be heavily affected by changes in the local electronic environment, such as relaxation effects which may be caused by changes in the formal oxidation state.

While uranium is not strongly radioactive (an alpha emitter with a half-life of over 44 billion years), it still presents a significant long term health risk, especially in a solvated form such as uranyl. Computational modeling of uranium complexes circumvents this risk and has been used to model the thermochemistry and electronic structure of uranium coordination complexes.

Analogous to experiment, computational chemistry can be used to calculate electronic transitions, allowing for the creation of electronic spectra from calculated excitation energies. Multi-reference computational methods have been used to directly solve for electronic states and transitions between states in the molecule. Réal et al. compared preexisting CASPT2 electronic transitions of uranyl to intermediate Hamiltonian Fock space coupled cluster (IHFSCC) excitations and found that the two methods perform similarly for low level excitations, but the methods deviate from each other for higher excitation energies. However, multi-reference methods scale unfavorably with the size of the system, and as a result, can only be utilized for the smallest of molecular systems. A commonly used alternative to multi-reference methods for the simulation of molecular spectra is time-dependent DFT (TDDFT), which have been used to great effect to calculate the electronic transitions in uranyl complexes. Tecmer et al. performed TDDFT calculations to simulate the UV-Vis spectrum of uranyl as well as the isoelectronic analogues OUN⁺ and UN₂. They found that among the functionals used, CAMB3LYP, M06, and PBE0 gave the lowest mean errors relative to IHFSCC, performing similarly to CASPT2 overall. The complex
polarization propagator (CPP) method\textsuperscript{297–302} is similar to time-dependent methods, but explicitly accounts for the linewidth of the peaks \textit{via} an imaginary damping factor which, when graphed, generates the spectrum. At the Hartree–Fock level, the static exchange approximation (STEX)\textsuperscript{64,303,304} models core excitations as an electron being acted upon by the core-ionized molecule, the latter of which is optimized separately in order to give a complete account of the orbital relaxation in the molecule.

Accounting for relativistic effects is of great importance in calculations on actinide elements, especially in the calculation of properties of deep core orbitals as spin–orbit is incredibly strong for these orbitals. The most direct means of accounting for relativity is the full four-component Dirac–Coulomb (DC) Hamiltonian. The DC Hamiltonian gives a full account of the one-electron relativistic effects in a molecule, whereas the fully relativistic two-electron interaction is truncated, but includes the instantaneous Coulomb interaction as well as spin–own orbit interaction.\textsuperscript{72} It has been used to calculate properties of uranyl and its complexes.\textsuperscript{281,285,286} Relativistic effective core potentials (RECPs) are another means of accounting for relativistic effects for heavy atoms, and have been used frequently to recover these effects and to simplify the costly calculations involved.\textsuperscript{24,25,273,279,284,286,287,293,296,305,306} Dolg and Cao developed a relativistic small core pseudopotential for uranium constructed from Dirac–Coulomb–Breit (DCB) orbitals, compared it to all-electron DKH calculations with perturbative spin–orbit (+BP), and noted that the vertical excitation energies agreed well with the values obtained at the all-electron level, at far reduced computational cost.\textsuperscript{24} However, since the chemical core is simplified and treated by a simple function, part of the core-level description is lost and no core-level properties (such as core-ionization energies) can be calculated. The large and small component of the wave function can also be decoupled yielding two (or one) component Hamiltonians for the purpose of reducing computational
cost relative to the full four-component calculation.\textsuperscript{283,284,286,289,290,294} The eXact 2-Component relativistic Hamiltonian (X2C)\textsuperscript{307–309} has been used by Réal et al. to calculate relativistic effects for uranyl compounds and has resulted in similar effectiveness to Dirac–Coulomb in the calculation of vertical excitation energies.\textsuperscript{286} Klooster et al.\textsuperscript{310} have reported calculations of X-ray photoelectron spectra, including U\textsuperscript{5+} using the analogous normalized elimination of the small component (NESC) Hamiltonian. Calculations on uranium compounds including scalar relativistic effects through the Darwin and mass-velocity terms have also been reported.\textsuperscript{290,292}

Two isoelectronic homologues of uranyl have been synthesized, OUN\textsuperscript{+} and UN\textsubscript{2}, and have been characterized using experimental and theoretical methods.\textsuperscript{284,292,293,295,305,311} Both of these molecules possess uranium in the +VI formal oxidation state and, analogous to uranyl, have also been shown to have linear structures.\textsuperscript{278,284,287,290,292,293,295,305,306,312,313} The geometries and valence electronic spectra for these molecules have been determined computationally. However, less is known about the core spectra of these molecules from a theoretical standpoint.

Therefore, to classify and characterize these new molecules, we have in the present work simulated the uranium L\textsubscript{3} edge XANES spectrum for UO\textsubscript{2}\textsuperscript{2+}, OUN\textsuperscript{+} and UN\textsubscript{2} using restricted excitation window (REW) TDDFT, the CPP method, as well as STEX. We have also investigated the position of the uranium L\textsubscript{3} ionization threshold using both wave function and density functional methods. The paper is outlined as follows: in Section 6.2 we present the theory behind the methods employed in this work. In Section 6.3 we provide computational details and then, in Section 6.4, present and discuss our results. In Section 6.5 we provide conclusions and perspectives.

6.2 Theory

6.2.1 Core Ionization

Koopmans’ theorem\textsuperscript{314} provides a reasonable estimate of valence ionization energies,
although it is based on the difference of Hartree–Fock energies between the ionized and the parent state, using the orbitals of the parent state. There are accordingly two major sources of error, that is, (i) lack of orbital relaxation of the core-ionized state and (ii) lack of electron correlation:

\[ IP_i(M) = -\varepsilon_i(M) + A_{relax} + A_{corr} . \]

The relaxation contribution \( \Delta_{relax} \) (\( -\Delta_{relax} \) is denoted the contraction error by Koopmans\(^{314} \)) will be negative since orbital relaxation lowers the energy of the core-ionized state. The correlation contribution \( \Delta_{corr} \) is, on the other hand, expected to be positive since there is one more electron to correlate in the parent state (see for instance ref. 315). In practice, for valence ionizations, the two contributions are found to be of the same order of magnitude, thereby providing fortunate error cancellation, as illustrated for the HOMO (1b\(_1\)) ionization of the water molecule in Table 6.1. For core ionizations, on the other hand, the Koopmans estimate is known to be poor\(^{316} \) since the correlation contribution is typically an order of magnitude smaller than the relaxation contribution, as seen in Table 6.1 for the 1a\(_1\) (oxygen 1s) ionization energy.

**Table 6.1** Valence and core ionization energies (in eV) of gaseous water obtained using the dyall.ae3z basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>1b(_1)</th>
<th>1a(_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.(^{317,318})</td>
<td>12.61</td>
<td>539.7</td>
</tr>
<tr>
<td>Koopmans</td>
<td>13.84</td>
<td>560.1</td>
</tr>
<tr>
<td>( \Delta )HF</td>
<td>11.05</td>
<td>539.6</td>
</tr>
<tr>
<td>( \Delta )MP2</td>
<td>12.75</td>
<td>540.5</td>
</tr>
<tr>
<td>( \Delta_{relax} )</td>
<td>-2.79</td>
<td>-20.5</td>
</tr>
<tr>
<td>( \Delta_{corr} )</td>
<td>1.70</td>
<td>0.9</td>
</tr>
</tbody>
</table>

In the present work the correlation contribution is calculated by \( \Delta \)MP2. The core-ionized state is first obtained by a Kramers restricted average-of-configuration Hartree–Fock (HF) calculation\(^{319} \) starting from the orbitals of the parent state. Convergence is straightforward and obtained by first reordering the orbitals such that the target core orbital is in the position of the open
shell and then kept there by overlap selection. This method has been used since the molecular \( \Delta \text{SCF} \) calculations of Bagus and Schaefer,\textsuperscript{320,321} but has more recently been rediscovered under the name Maximum Overlap Method by Gill and co-workers.\textsuperscript{322} For the \( \Delta \text{MP2} \) calculation we have employed the RELCCSD module of DIRAC\textsuperscript{323} which uses a Kramers unrestricted formalism\textsuperscript{324} and thereby allows simple open-shell calculations. However, since the incoming molecular orbitals are optimized under Kramers restriction, the reconstructed Fock matrix for the core-ionized state is not diagonal and will have a non-zero occupied-virtual (ov) block. We have therefore extended the MP2 algorithm to handle this case. We start from the electronic Hamiltonian normal-ordered with respect to the Fermi vacuum defined by the current (Kramers restricted) orbital set

\[ H_N = \sum_{pq} f_{pq}^{\dagger} a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} V_{pqrs}^{pr} a_p^\dagger a_s^\dagger a_r a_q; \quad V_{pqrs}^{pr} = \langle pr \| qs \rangle. \]

Following Lauderdale et al.,\textsuperscript{325} we then define the zeroth-order Hamiltonian to be the diagonal blocks (oo and vv) of the Fock matrix. Setting up perturbation theory in a coupled cluster (CC) framework we subsequently derive the non-canonical MP2 energy

\[ E^{\text{ncMP2}} = \sum_{ai} f_{ai} t_{i}^{a(1)} + \sum_{ij} \sum_{ab} V_{ab} t_{ij}^{ab(1)}. \]  

(6.1)

Here and in the following we employ indices \( i, j, k, l \) for occupied orbitals, \( a, b, c, d \) for virtual orbitals and \( p, q, r, s \) for general orbitals. The equations of the first-order CC amplitudes are

\[ \sum_{b} f_{b} t_{i}^{b(1)} = \sum_{j} t_{j}^{a(1)} f_{i} = -f_{i}^{a} \]

\[ \sum_{c} \left( f_{c} t_{ij}^{ac(1)} + f_{c} t_{ij}^{bc(1)} \right) - \sum_{k} \left( f_{jk} t_{ik}^{ac(1)} + f_{jk} t_{ik}^{bc(1)} \right) = -V_{ij}^{ab}. \]

Starting from these, one may show that the non-canonical MP2 energy is invariant under separate rotation of occupied and virtual orbitals. The equation for the first-order \( T_{1} \)-amplitudes may be recognized as the Sylvester equation and can therefore be solved in a direct fashion, but we have for
convenience chosen to use the existing iterative scheme in RELCCSD for the solution of the amplitude equations.

6.2.2 Core Excitation

In this work we are exploring three different methods for the calculation of core excitation spectra: restricted excitation window time-dependent density functional theory (REW-TDDFT), complex polarization propagator (CPP) and the static exchange approximation (STEX). In this section we give a brief presentation and comparison of these methods.

A common starting point for the three methods is the frequency-dependent linear response function which in the exact state formalism\(^{326-328}\)

\[
\langle\langle A; B \rangle\rangle_\omega = -\frac{1}{\hbar} \sum_{m=0} A_m^* B_m \frac{B_m^* A_m}{\omega_m - \omega} + \frac{B_m^* A_m}{\omega_m + \omega}
\]  \hspace{1cm} (6.2)

involves an explicit sum over the excited states \(|m\rangle\) of the zeroth-order Hamiltonian. In the above expression \(\hbar \omega_m = E_m - E_0\) are excitation energies with respect to the unperturbed ground state \(|0\rangle\) and \(P_m = \langle m|\hat{H}_P|0\rangle\), \((P = A, B)\) the corresponding transition moments with respect to property operator \(\hat{H}_P\). In the present work we restrict ourselves to the electric dipole approximation, so that both property operators are limited to components of the electric dipole operator, although the short wave length of X-ray radiation may require the inclusion of terms beyond this approximation.\(^{329,330}\)

It is clear from the above expression that a scan of the linear response function through a frequency window will display poles corresponding to excitations in the range allowed by the property operators \(\hat{H}_A\) and \(\hat{H}_B\) and whose transition moments can be extracted from the residues. The singularities are unphysical, though, in that they correspond to infinitely long lifetimes of the excited states. This feature may be amended by the introduction of inverse lifetimes \(\gamma_m\) through the
substitution $\omega_m \rightarrow \omega_m - i \gamma_m$ in the above expression (6.2). The response function then becomes generally complex, with the real part corresponding to refractive properties such as polarizabilities and the imaginary part associated with absorption processes.

Within the framework of Hartree–Fock and Kohn–Sham methods we may employ an exponential parametrization of orbitals (and thereby density and energy)

$$\varphi_i (\kappa) = \sum_a \varphi_a \exp[-\kappa] ; \quad \kappa_{pq} = -\kappa_{qp}^*$$

which allows for unconstrained optimization and straightforward identification of redundancies.331–334 In the present case we restrict ourselves to closed-shell references in which only rotations between occupied and virtual orbitals, with amplitudes $\kappa_{ai}$, are non-redundant; all other amplitudes may therefore be set to zero. At the SCF level of theory the frequency-dependent linear response function may be formulated as

$$\langle \langle A; B \rangle \rangle_{ai} = E_B^{[1]} X_B(\omega) ,$$

where the vector $X_B(\omega)$ contains the first-order orbital rotation amplitudes

$$X_B(\omega) = \begin{bmatrix} K(\omega) \\ K^*(-\omega) \end{bmatrix} ; \quad K_{ai}(\omega) = \kappa_{ai}^{(1)}(\omega) .$$

It is a solution of the linear response equation

$$(E_0^{[2]} - \hbar \omega S^{[2]}) X_B(\omega) = -E_B^{[1]} ,$$

where appears the property gradient

$$E_B^{[1]} = \begin{bmatrix} g \\ g^* \end{bmatrix} ; \quad g_{ai} = -\langle \varphi_a | \hat{H}_B | \varphi_i \rangle$$

as well as the generalized metric $S^{[2]}$ and the electronic Hessian $E_0^{[2]}$, with structures

$$S^{[2]} = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} ; \quad E_0^{[2]} = \begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} ;$$
Further discussion of the SCF linear response formalism can be for instance be found in ref. 326, 335 and 336. Since the SCF linear response function does not contain any sum over states, its complex extension cannot be obtained by the introduction of state-specific inverse lifetimes $\gamma_m$. It is therefore common practice to employ a single damping parameter $\gamma$ which can be interpreted as an imaginary extension of the perturbing frequency $\omega \rightarrow \omega + i\gamma$. A relativistic implementation of complex response, including spin–orbit interaction, has been reported by Devarajan et al. However, it is based on the zeroth order regular approximation (ZORA), which may not be very accurate for core excitations, as pointed out by the authors themselves. In the present contribution we employ the complex response implementation of the DIRAC code, which can be used with the more accurate 4-component Dirac–Coulomb and eXact 2-Component (X2C) Hamiltonians. Working within the electric dipole approximation the isotropic oscillator strength $f^{iso}$, including a Lorentzian linewidth defined by the damping parameter $\gamma$, is obtained directly by a scan of the imaginary part of the isotropic electric dipole polarizability $\alpha^{iso}$ through the desired frequency window

$$f^{iso}(\omega) = \frac{2m\omega}{\pi\varepsilon^2} \text{Im}\{\alpha^{iso}(\omega + i\gamma)\}.$$ 

Alternatively, excitation energies can be found by TDDFT (or TDHF), that is, by solving the generalized eigenvalue problem

$$(E_0^{(2)} - \hbar\omega_m S^{(2)})X_m = 0.$$ 

An inconvenience with this approach is that excitation energies are typically found by a “bottom-
up” approach, which becomes highly impractical for core excitations. A solution is to restrict the occupied orbitals entering the orbital rotation amplitudes \( \{ \kappa_{ai} \} \) to the desired core orbitals. This is referred to as the “restricted excitation window”\(^{338}\) or “restricted channel”\(^{339}\) approach. In the present work we employ the relativistic adiabatic TDDFT implementation reported by Bast et al.,\(^{328}\) where restrictions are possible both on occupied and virtual orbitals, such that the extension to REW-TDDFT is straightforward.

Transition moments are found by contracting the eigenvectors \( X_m \) with the corresponding property gradient

\[
P_m = X_m^\dagger(\omega) E_P^{[1]}.
\]

The isotropic oscillator strength associated with excitation \( m \) is then obtained as

\[
f_m^{iso} = \frac{2m\omega_m}{3\hbar c^2} \sum_{\alpha=x,y,z} |\mu_{m,\alpha}|^2.
\]

Cumulated isotropic oscillator strengths, including a Lorentzian broadening \( \Delta^L \), are then obtained as

\[
f^{iso}(\omega) = \sum_m f_m^{iso} \Delta^L(\omega, \omega_m, \gamma);
\]

\[
\Delta^L(\omega, \omega_m, \gamma) = \frac{1}{\gamma \pi} \left[ \frac{\gamma^2}{(\omega - \omega_m)^2 + \gamma^2} \right].
\]

The resulting simulated spectra obtained by complex response and REW-TDDFT are expected to be identical to the extent that no other occupied orbitals are involved in the excitation processes with the selected frequency window (channel coupling) and to the extent that the REW-TDDFT calculation includes a sufficient number of excitations to cover the frequency window. In passing we note that upon a change of energy units the Lorentz-broadened oscillator strengths are scaled down by the same factor as the energy is scaled up, in order to conserve the integrated oscillator strength.

A third method investigated in the present work is the static exchange approximation.
(STEX). The name originated in the context of early theoretical investigations of the scattering of electrons by hydrogen atoms.\textsuperscript{340,341} The two-electron wave function of the system was expanded in products of hydrogen atom orbitals and orbital of the projectile electron.\textsuperscript{342} The static exchange approximation was obtained by restricting the atomic orbital in this expansion to the ground state 1s orbital of the target hydrogen atom, thus neglecting polarization of the atomic charge density during collision, yet retaining exchange effects, shown by Morse and Allis in 1933 to have some importance upon scattering with slow electrons.\textsuperscript{343} This is apparently the first STEX calculation. A further development was the observation by Hunt and Goddard\textsuperscript{344} that the optimal virtual orbital $\varphi_a$ in the otherwise frozen $N$-electron singly-excited determinant $\Phi_a$ is obtained by diagonalization of the orbital-specific Fock operator

$$\hat{F}^{(N-1)} = \hat{h} + \sum_{j \neq i} (\hat{J}_j - \hat{K}_j)$$

where $\hat{J}_j$ and $\hat{K}_j$ are the usual Coulomb and exchange operators, respectively. The diagonalization is carried out in the space of virtual orbitals, thus keeping the occupied orbitals frozen. The assumption that the other occupied orbitals are hardly modified upon excitation is an instance of the STEX approximation, as pointed out by Langhoff.\textsuperscript{345–347} The so-called improved virtual orbitals (IVO) generated in this manner contrasts with the canonical virtual HF orbitals generated from the usual Fock operator

$$\hat{F}^N = \hat{F}^{(N-1)} + (\hat{J}_i - \hat{K}_i)$$

and which are more appropriate for the $(N + 1)$-electron system. Not surprisingly then, the orbital-specific Fock operator $\hat{F}^{(N-1)}$ is also the conventional Fock operator for the $(N - 1)$-electron system obtained by removal of the occupied orbital $\varphi_i$ from the system. Based on the above observations, Ågren and co-workers\textsuperscript{64,303} proposed to extend the IVO approach to core excitations and notably to
build the STEX operator \( \hat{F}^{(N-i)} \) using the occupied orbitals of the corresponding core-ionized system, thus capturing orbital relaxation essentially missing in TD-DFT/HF. Transition moments are calculated between the parent ground state and the core excited states, the latter built from the core-ionized orbitals. Since two non-orthogonal orbital sets are used, special techniques, such as a cofactor expansion,\textsuperscript{348} must be used. In the present work we are using the 4-component relativistic STEX implementation of Ekström et al.\textsuperscript{65}

The core excitation energies obtained by a STEX calculation can be reproduced by a REW-TDHF calculation using the orbitals of the core-ionized system and invoking the Tamm–Dancoff approximation (TDA), that is, setting \( B = 0 \) in the electronic Hessian (6.3). If excitations are restricted to a single (core) orbital \( \varphi_i \) the elements of the remaining \( A \) block can be expressed as

\[
A_{ai,bi} = \langle \tilde{\Phi}_i^a | \hat{H}^N | \tilde{\Phi}_i^b \rangle - \delta_{ab} \langle \tilde{\Phi}_0^a | \hat{H}^N | \tilde{\Phi}_0^b \rangle = \tilde{F}_{ab}^N - \delta_{ab} \tilde{F}_{ii}^{N-i} - \langle \tilde{a}_i^a | \tilde{b}_i^b \rangle
\]

In the above expression we employ the tilde symbol to indicate quantities calculated in the orbitals of the core-ionized system. Upon diagonalization of the \( A \) block, we obtain the eigenvalues of the orbital-specific Fock operator \( \hat{F}^{(N-i)} \) shifted by \( \tilde{F}_{ii}^{N-i} \), which can be recognized as the negative of the core ionization energy, calculated in the frozen orbitals of the core-ionized system, contrary to Koopmans’ theorem, who uses the frozen orbitals of the parent system. It is corrected by rather using the ionization energy obtained by \( \Delta \)SCF.

6.2.3 Projection Analysis

In order to elucidate the electronic structure of the title species as well as to assign the simulated core excitation spectra we have performed projection analysis.\textsuperscript{349} This method is akin to Mulliken population analysis, but the strong basis-set dependence of the latter method is avoided by
expanding molecular orbitals in pre-calculated orbitals of the atoms constituting the molecule

\[ |\psi_i\rangle = \sum_{A_j} |\psi^A_{ij}\rangle c^A_{ji} + |\psi^{\text{pol}}_{ji}\rangle, \quad (6.5) \]

where indices \( A \) and \( j \) refer to atoms and atomic orbitals (AOs), respectively. Charges and populations of atoms in the molecule are subsequently calculated in analogous manner to Mulliken population analysis, but starting from molecular orbitals given as linear combinations of true and well-defined atomic orbitals, rather than in terms of atom-centered basis functions. The atoms are calculated in their proper basis and by default in their ground state configuration, either by average-of-configuration at the HF level or by using fractional occupation at the DFT level. In order to make the projection analysis chemically meaningful, the expansion in eqn (6.5) is normally limited to AOs occupied in the atomic ground state configuration. However, for the assignment of the calculated core excitation spectra these orbitals, in the case of uranium, were supplemented by selected improved virtual orbitals, as discussed in Section 7.4.3. In either case, the selected set of AOs is not guaranteed to fully span a given molecular orbital. The orthogonal complement \( |\psi^{\text{pol}}_{ji}\rangle \), which we denote the polarization contribution, can be eliminated using the Intrinsic Atomic Orbital scheme of Knizia.\textsuperscript{350}

6.3 Computational Details

Reference geometries were optimized at the scalar-relativistic CCSD(T) level using the MOLPRO 09\textsuperscript{351} package and numerical gradients. For uranium we employed a relativistic small core potential (ECP60MDF) with a (14s13p10d8f6g)/(6s6p5d4f3g) quadruple zeta level valence ANO basis set developed by Dolg and Cao,\textsuperscript{24} and the (11s6p3d2f)/(5s4p3d2f) aug-cc-pVTZ basis sets\textsuperscript{8,352} for oxygen and nitrogen.

All other calculations were carried out with the DIRAC code\textsuperscript{353} and are, unless otherwise stated, based on the 4-component Dirac–Coulomb Hamiltonian using the simple Coulombic
correction\textsuperscript{354} to avoid the explicit calculation of two-electron integrals involving the small components only. For uranium we employed the dyall.v3z basis set\textsuperscript{355} (large component 33s29p20d13f4g2h) and for oxygen and nitrogen the cc-pVTZ basis set\textsuperscript{8} (large components 10s5p2d1f). For MP2 calculations we switched to the slightly larger dyall.ae3z basis (large component 33s29p20d13f7g3h) for uranium. All basis sets were uncontracted and the small components generated by restricted kinetic balance. A finite nucleus model in the form of a Gaussian charge distribution was employed.\textsuperscript{356}

Uranium 2p ionization energies were calculated by \( \Delta \text{SCF} \) calculations,\textsuperscript{316} both at the Kramers-restricted Hartree–Fock and Kohn–Sham level, the latter using the BLYP,\textsuperscript{357–359} B3LYP,\textsuperscript{360,361} PBE,\textsuperscript{362} PBE0\textsuperscript{363} and CAM-B3LYP\textsuperscript{364} functionals. Convergence of the core excited states was straightforward using initial reordering of orbitals followed by selection of orbitals based on overlap with starting orbitals during the SCF cycles.

The uranium L\textsubscript{3} edge XANES spectrum of the selected molecules was simulated by REW-TDDFT, CPP and STEX calculations, the former two using the CAM-B3LYP\textsuperscript{364} functional. Transition moments have been calculated within the electric dipole approximation, more specifically in the length gauge, that is, as integrals over the electric dipole operator. The nature of the excitations was determined from the excitation amplitudes combined with Mulliken and projection analysis\textsuperscript{349} of the involved molecular orbitals. In the REW-TDDFT and STEX calculations finite linewidths of the individual peaks were introduced by Lorentzian functions of half-width at half-maximum (HWHM) \( \gamma = 0.0367 \text{ Eh} \) \((\sim 1 \text{ eV})\). The same value of \( \gamma \) was taken as damping parameter in the CPP calculations.

6.4 Results and Discussions

6.4.1 Molecular and Electronic Structures
Prior to the calculation of core ionization and excitation energies we optimized the geometries of the title species and investigated their electronic structures by projection analysis.\textsuperscript{349} In Table 6.2 we report our calculated bond lengths for the isoelectronic series together with selected literature values. Wei et al.\textsuperscript{284} reported bond lengths for NUO\textsuperscript{+} and UN\textsubscript{2} calculated at the CCSD(T) level using the aug-cc-pVTZ basis set\textsuperscript{8} for the ligands. For uranium the authors employed the relativistic small core potential ECP60MWB with the accompanying (12s11p10d8f)/[8s7p6d4f] valence basis, although it was developed for SCF calculations.\textsuperscript{25} Jackson et al.\textsuperscript{287} reported bond distances for UO\textsubscript{2}\textsuperscript{2+} with the same computational setup, except that they added two g functions to the valence basis. Switching to the larger segmented valence basis set (14s13p10d8f6g)/[10s9p5d4f3g] developed by Cao and co-workers\textsuperscript{365,366} and further augmentation by h and i functions was found to have only a small effect on calculated bond lengths. More recently, Tu et al. reported bond lengths for the entire isoelectronic series with basically the same computational setup.\textsuperscript{312} They reproduce the uranyl bond length reported by Jackson et al.,\textsuperscript{287} and get slightly shorter bond distances than reported by Wei et al.\textsuperscript{284} for the other species. We have optimized bond lengths for the isoelectronic species using the more recent ECP60MDF core potential with the accompanying valence basis\textsuperscript{24} and interestingly get somewhat longer bond lengths, closer to those reported by Gagliardi and Roos\textsuperscript{306} at the CASPT2 level with ANO basis sets. Particularly noteworthy is that the U–N bond in the nitridooxouranium cation is shorter than the U–O bond, although experiment suggest that that the former is weaker than the latter (bond dissociation energies BDE[OU\textsuperscript{+}–N] = 4.44 ± 1.27 eV vs. BDE[NU\textsuperscript{+}–O] = 7.66 ± 1.70 eV).\textsuperscript{292}

\begin{table}[h]
\centering
\begin{tabular}{lcccccc}
\hline
Bond & CCSD(T) & CCSD(T) & CCSD(T)\textsuperscript{312} & CASPT2\textsuperscript{306} & PBE\textsuperscript{295} \\
\hline
UO\textsubscript{2}\textsuperscript{2+} & U–O & 1.704 & 1.6898\textsuperscript{287} & 1.689 & 1.705 \\
OUN\textsuperscript{+} & U–O & 1.748 & 1.743\textsuperscript{284} & 1.731 & 1.746 & 1.761 \\
 & U–N & 1.696 & 1.703\textsuperscript{284} & 1.681 & 1.695 & 1.698 \\
UN\textsubscript{2} & U–N & 1.736 & 1.743\textsuperscript{284} & 1.731 & 1.735 & 1.739 \\
\hline
\end{tabular}
\caption{Calculated bond lengths (in Å) for the title species}
\end{table}
### Table 6.3 Charge and electronic configuration of uranium in the title compounds obtained by projection analysis at the HF level

<table>
<thead>
<tr>
<th>Molecule</th>
<th>QU</th>
<th>Atomic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2^{2+}$</td>
<td>+2.84</td>
<td>$5f^{2.28}6p^{5.67}6d^{1.20}7s^{0.04}$</td>
</tr>
<tr>
<td>NUO$^+$</td>
<td>+2.12</td>
<td>$5f^{2.52}6p^{5.67}6d^{1.60}7s^{0.10}$</td>
</tr>
<tr>
<td>UN$_2$</td>
<td>+1.45</td>
<td>$5f^{2.68}6p^{5.66}6d^{2.01}7s^{0.23}$</td>
</tr>
</tbody>
</table>

We have also investigated the electronic structure of the title compounds by projection analysis$^{349}$ at the HF level using the pre-calculated atomic orbitals occupied in the electronic ground state of the constituent atoms. Polarization contributions have been eliminated by polarizing the atomic orbitals in the molecule according to the Intrinsic Atomic Orbital scheme of Knizia,$^{350}$ yet conserving overlap between atomic orbitals on different centers. The charge and electronic configuration of uranium in the three molecules are given in Table 6.3. Concerning the electronic configurations, one in particular notes the 6p-hole,$^{367}$ primarily arising from overlap between the 6p$_{3/2}$ orbital with the ligands, and which is basically identical for the three species. The calculated atomic charges, which do not suffer from the strong basis set dependence of Mulliken charges, are far from the formal oxidation state +VI of uranium in these molecules, in agreement with previous theoretical and experimental studies.$^{368}$ The uranium charge furthermore reduces according to the total molecular charge, as expected. The ligand charge is -0.42e and in -0.73e in UO$_2^{2+}$ and UN$_2$, respectively. In NOU$^+$ the charge on oxygen and nitrogen is -0.63e and -0.49e, respectively. The calculated dipole moment of NUO$^+$ is -1.43 D, when the uranium atom is placed at the origin with the nitrogen atom along the positive axis. Interestingly, for certain initial start guesses the HF SCF procedure converges to a solution 0.2 Eh higher in energy and with atomic charges very slightly modified ($Q_U = +2.16e$, $Q_O = -0.70e$, $Q_N = -0.45e$), but enough to switch the sign of the calculated dipole moment (+1.55 D).

Canonical orbitals are quite suitable for the description of electron detachment and excitation...
processes, such as XPS and XAS, respectively. However, in order to “see” chemical bonds one needs to rotate the occupied molecular orbitals to form localized ones,\textsuperscript{369,370} although there is no unique localization criterion. In Table 6.4 we present a projection analysis of bonding orbitals obtained by Pipek–Mezey localization.\textsuperscript{371} The bonding orbitals are identified as localized molecular orbitals with significant contributions from both the uranium center and a (single) ligand. Approximate orbital eigenvalues have been calculated as expectation values of the converged Fock operator. For each ligand we find three such bonding orbitals, of which two are almost degenerate and with $\omega = 1/2$ and $3/2$, respectively. Based on our analysis we conclude that each ligand is bound to the central uranium atom by triple ($\sigma, \pi$) bonds, where the $\pi$ bond has been split by spin–orbit interaction into $\pi_{1/2}$ and $\pi_{3/2}$, and where the metal center contributes $df$ hybrid atomic orbitals.

**Table 6.4** Projection analysis of Pipek-Mezezy localized bonding orbitals in the title compounds at the HF level. $\langle \epsilon \rangle$ refers to the expectation value (in $E_h$) of the converged Fock operator. X refers to the ligand.

<table>
<thead>
<tr>
<th></th>
<th>$\omega$</th>
<th>$\langle \epsilon \rangle$</th>
<th>U6p$_{3/2}$</th>
<th>U5f$_{5/2}$</th>
<th>U5f$_{7/2}$</th>
<th>U6d$_{3/2}$</th>
<th>U6d$_{5/2}$</th>
<th>U7s$_{1/2}$</th>
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<th>X2s$_{1/2}$</th>
<th>X2p$_{1/2}$</th>
<th>X2p$_{3/2}$</th>
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<tr>
<td>UO$_2^{2+}$</td>
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<td>0.19</td>
<td>0.18</td>
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<td>0.08</td>
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<td>0.12</td>
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<td>0.12</td>
<td>0.09</td>
<td>0.08</td>
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<td>O</td>
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<td>0.35</td>
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<td>0.09</td>
<td>0.00</td>
<td>O</td>
<td>0.00</td>
<td>1.16</td>
<td>0.43</td>
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<td>0.09</td>
<td>0.28</td>
<td>0.00</td>
<td>N</td>
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<td>0.00</td>
<td>1.24</td>
</tr>
<tr>
<td>UN$_2$</td>
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<td>0.19</td>
<td>0.16</td>
<td>0.10</td>
<td>0.09</td>
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<td>O</td>
<td>0.00</td>
<td>0.00</td>
<td>1.33</td>
</tr>
</tbody>
</table>

6.4.2 Uranium 2p binding energy

In Table 6.5 we report relaxation $\Delta_{\text{relax}}$ and correlation $\Delta_{\text{corr}}$ contributions to the uranium 2p ionization energies of the title species, for uranium using the dyall:ae3z basis set which include correlation functions for all occupied orbitals. The calculations are based on the default Hamiltonian of the DIRAC package, that is, the 4-component relativistic Dirac–Coulomb Hamiltonian with a
simple Coulomb correction, thus avoiding the calculations of two-electron integrals (SS|SS) containing small component basis functions only. At the HF level the uranium 2p orbitals are split by 3838 eV due to spin–orbit interaction, and the 2p_{3/2} orbital further split by a mere 0.3 eV due to the molecular field. As illustrated by Fig. 6.1, the ΔHF uranium 2p binding energies are a linear function, all with slope 13.4 eV e⁻¹, of the atomic charges reported in Table 6.3, thus demonstrating the chemical shift of X-ray photoelectron spectroscopy as well as the usefulness of the atomic charges obtained from projection analysis.

We have defined Δcorr as the difference between the ionization energy (IP) obtained at the ΔMP2 and ΔHF level, that is,

$$\Delta_{\text{corr}} = IP(\text{ΔMP2}) - IP(\text{ΔHF}),$$

but it should be emphasized that due to the non-canonical nature of the orbitals of the core-ionized states, there will be non-zero $T_1$ contributions to the MP2 energy, that are more properly associated with relaxation (see eqn (6.1)). However, these contributions are negligible in the calculations reported in Table 6.5, as will be discussed and demonstrated below. Table 6.5 shows that the correlation contribution Δcorr is an order of magnitude smaller than the relaxation contribution Δrelax and that the Koopmans estimate gives errors on the order of 75 eV. What is striking, though, is that the correlation contribution has the same sign as the relaxation contribution that is, it is negative. If we consider the canonical MP2 energy expression
\[ E_{\text{MP}2} = \sum_{i<j} e_{ij} ; \quad e_{ij} = \sum_{a,b} \frac{|\langle ij | ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \]

with \( N_o \) occupied and \( N_v \) virtual orbitals for the parent state, then the core-ionized state has \((N_o - 1)\) fewer pair energies \( \varepsilon_{ij} \), all of them negative in the parent state. In addition, the remaining pair energies has \( N_v \) new contributions containing the now virtual core orbital, such that denominators may be zero or even positive. Indelicato and co-workers,\(^{374-376} \) in the framework of many-body perturbation theory, makes a distinction between contributions to the ionization energy for which \(|\varepsilon_i + \varepsilon_j| > |\varepsilon_h|\), where \( \varepsilon_h \) is the energy of the virtual core orbital, say \( b \), and contributions for which \(|\varepsilon_i + \varepsilon_j| < |\varepsilon_h|\) and refer to them as core–core and Auger effects, respectively. Core–core contributions only occur if there are core orbitals lower in energy than the ionized one. The denominator is generally negative, but may change sign if the second virtual orbital, say \( a \) is bound, which are precisely the orbitals associated with pre-edge structure in X-ray absorption spectroscopy. The denominator of Auger effect contributions, on the other hand, starts off positive with increasing energy of the second virtual orbital, but eventually become negative for sufficiently high-lying virtuals. Such contributions were observed by Nooijen and Bartlett\(^ {377} \) to lead to convergence problems in coupled-cluster calculations of core-ionized states and were therefore ignored. In the present non-canonical MP2 calculations we do not make a distinction between Auger and core–core contributions, but simply monitor contributions to the pair correlation energy of positive sign. For the 1a_1 ionization energy of water the total contribution is quite small (0.13 eV), whereas we obtain 3.43 eV for the uranium 2p_{3/2,3/2} ionization of uranyl.
**Figure 6.1** Shifted ΔHF uranium 2p ionization energies of the title species (in eV) as a function of the uranium charge (in a.u.) from projection analysis.

![Graph showing ionization energies](image)

### Table 6.6
Relaxation and correlation contributions (in eV) to core ionization energies of water and uranyl. See text for further details

<table>
<thead>
<tr>
<th>Molecule</th>
<th>IP</th>
<th>Orbital set</th>
<th>$\Delta_{\text{relax}}$</th>
<th>$\Delta_{\text{corr}}$</th>
<th>$\Delta_{\text{corr}(T_1)}$</th>
<th>$\Delta_{\text{corr}(T_2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>1a$_1$</td>
<td>Relaxed</td>
<td>-20.51</td>
<td>0.92</td>
<td>-0.17</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Frozen</td>
<td>0.00</td>
<td>-34.58</td>
<td>-35.50</td>
<td>0.92</td>
</tr>
<tr>
<td>UO$_2^{2+}$</td>
<td>2p$_{3/2,3/2}$</td>
<td>Relaxed</td>
<td>-64.54</td>
<td>-5.17</td>
<td>-0.28</td>
<td>-4.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Frozen</td>
<td>0.06</td>
<td>-103.91</td>
<td>-106.08</td>
<td>2.17</td>
</tr>
</tbody>
</table>

The above discussion confirms the expectation that the correlation contribution should be positive. However, a negative contribution, arising from a strong coupling of correlation and
relaxation, cannot be excluded. To investigate this, we carried out non-canonical MP2 calculations on core-ionized uranyl as well as water using the molecular orbitals of the parent state. The results are shown in Table 6.6. Using the orbitals of the parent state (denoted “frozen” in the table) the relaxation contribution $\Delta_{\text{relax}}$ is by definition zero, to within numerical noise. The correlation contribution $\Delta_{\text{corr}}$, on the other hand, becomes negative for both water and uranyl. However, when decomposing $\Delta_{\text{corr}}$ further into $T_1$ and $T_2$ contributions, according to the non-canonical MP2 expression of eqn (6.1), one observes that the $T_1$-contribution, which can be associated with relaxation, is completely dominating. For water the $T_2$-contribution $\Delta_{\text{corr}}(T_2)$ remains positive and is basically the same as when using relaxed orbitals. For uranyl, on the other hand, the $T_2$-contribution using frozen orbitals is positive, leading us to conclude that the negative correlation contribution obtained with the relaxed orbitals is indeed due to a strong coupling of correlation and relaxation.

We now turn to the effect of extensions to the default Hamiltonian of the DIRAC package. In Table 6.7 we report the effect of explicit inclusion of the (SS|SS) class of integrals ($\Delta\Delta\text{DOSSSS}$). Although the effect is sizable, causing a reduction of binding energies on the order of 18 and 6 eV for uranium 2p$_{1/2}$ and 2p$_{3/2}$ orbitals, respectively, it is constant for all three isoelectronic species, and thus does not contribute to the chemical shift. Even more important is the effect of the inclusion of the Gaunt two-electron interaction, but again the chemical shift is not affected, and so we have ignored these both (SS|SS) integrals and the Gaunt term in the subsequent calculations. In passing we note that the Gaunt term reduces the spin–orbit splitting of the uranium 2p manifold by about 40 eV, which makes sense, since the Gaunt term contains the spin-other-orbit interaction.\textsuperscript{72}

We have also investigated the performance of a selection of DFT functionals for the calculation of uranium 2p binding energies of the title species. These are reported in Table 6.7 relative to the HF binding energies. To the extent that the difference between HF and DFT binding
energies can be interpreted as pure correlation contributions, we note that these are significantly larger in magnitude than the correlation contributions extracted from the ΔMP2 calculations. It should be noted that the core-ionized species have been calculated under Kramers restriction such that spin polarization, which is expected to reduce ionization energies, is missing. The GGA functionals PBE and BLYP reduce both uranium 2p\(_{1/2}\) and 2p\(_{3/2}\) binding energies, whereas the global hybrid functionals PBE0 and B3LYP, as well as the long-range corrected hybrid CAMB3LYP, decrease the 2p\(_{3/2}\) binding energies and increase the 2p\(_{1/2}\) ones. No DFT functional has a performance similar to MP2.

Table 6.7 Ionization energies (in eV) obtained using the dyall.v3z basis set for uranium

<table>
<thead>
<tr>
<th>Method</th>
<th>(\Delta HF)</th>
<th>(\Delta DOSSSS)</th>
<th>(\Delta Gaunt)</th>
<th>(\Delta PBE)</th>
<th>(\Delta BLYP)</th>
<th>(\Delta PBE0)</th>
<th>(\Delta B3LYP)</th>
<th>(\Delta CAMB3LYP)</th>
</tr>
</thead>
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<tr>
<td>(2p_{1/2})</td>
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<td>19.37</td>
</tr>
<tr>
<td>(2p_{3/2})</td>
<td>17238.87</td>
<td>-5.86</td>
<td>-68.91</td>
<td>-58.12</td>
<td>-15.35</td>
<td>-15.29</td>
<td>-22.34</td>
<td>-22.12</td>
</tr>
<tr>
<td>(2p_{2/3})</td>
<td>17239.01</td>
<td>-5.86</td>
<td>-68.91</td>
<td>-56.05</td>
<td>-15.29</td>
<td>-15.29</td>
<td>-22.28</td>
<td>-22.06</td>
</tr>
</tbody>
</table>

No experimental uranium L\(_{2}\) or L\(_{3}\) binding energies are available for the title species. The 2p\(_{1/2}\) and 2p\(_{3/2}\) binding energies of metallic uranium are 20 948 and 17 166 eV, respectively, relative to the Fermi level.\(^{378}\) If we add the (SS|SS) and Gaunt contributions as corrections, then the MP2 ionization energies for UN\(_2\), in which uranium has the smallest charge, agree to within 10 eV with the cited experimental numbers. If we instead linearly extrapolate the MP2 ionization energies to zero uranium nuclear charge at the HF level and add the cited corrections, we underestimate the experimental numbers by about 30 eV.

6.4.3 Uranium L\(_{3}\) Edge XANES Spectra

In this section we present and analyze simulated uranium L\(_{3}\) edge XANES spectra of the title species. A good discussion of the electronic structure of actinyls has been given by Denning.\(^{379}\)
Here focus will be on the bound virtual orbitals. We start by considering the calculated uranium L₃ edge XANES spectrum for uranyl obtained by the STEX method. In Fig. 6.2 we compare the spectra obtained with three different basis sets. These are local Gaussian basis sets which are not appropriate for the description of continuum states, as can be seen from the lack of any convergence of the spectra with respect to basis sets beyond the L₃ edge. Such artifacts have been observed previously, and it was suggested by Ekström and Norman that the meaningful energy range of a simulated spectrum in a local basis can be ascertained by exponent scaling. In the present case, a zoom into the pre-edge region of the spectrum, as shown in Fig. 6.3 suggests that the spectrum is not fully converged for quasi-bound states in the vicinity of the ionization threshold. Convergence in this region would probably require a rather extensive set of diffuse functions. In the following we shall therefore focus on the first three peaks of the spectrum.
Figure 6.2  UO$_2^{2+}$ uranium L$_3$ edge XANES spectra simulated by STEX using different basis sets and a Lorentzian broadening of ~1 eV. The vertical line indicates the ionization threshold obtained at the $\Delta$HF level (the value changes less the 0.1 eV with the indicated basis sets).
Figure 6.3 $\text{UO}_2^{2+}$ uranium L$_3$ edge XANES spectra simulated by STEX using different basis sets and a Lorentzian broadening of $\sim 1$ eV: zoom of the pre-edge region.
Figure 6.4 Comparison of UO$_2^{2+}$ uranium L$_3$ edge XANES spectra obtained by STEX and REW-TDHF, in both cases adding a Lorentzian broadening of ~1 eV. The REW-TDHF calculations has been carried out within the Tamm-Dancoff approximation and using the orbitals of the core-ionized state. The vertical line indicates the ionization threshold obtained at the ΔHF level. The REW-TDHF and STEX excitation energies are both corrected by the difference between the ground state energy calculated in ground state and core-ionized orbitals.

We shall also compare the performance of the three different methods discussed in Section 6.2.2. We start by demonstrating numerically that the STEX excitation energies can be obtained by using a REW-TDHF calculation within the Tamm–Dancoff approximation and using the orbitals of the core-ionized state. In Fig. 6.4 the uranium L$_3$ edge XANES spectrum for uranyl calculated by the two methods is displayed. As discussed in Section 6.2.2 both the STEX and the TDHF/TDA excitation energies have been corrected as

$$\hbar \omega_m \rightarrow \hbar \omega_m + E_0 - \tilde{E}_0$$

where $E_0$ and $\tilde{E}_0$ are the energies of the parent state calculated in the parent and core-ionized orbitals,
respectively. The same correction is applied to the oscillator strengths, eqn (6.4). The excitation energies are indeed seen to match perfectly, whereas the REW-TDHF/TDA Lorentz-broadened oscillator strengths are systematically smaller than the STEX ones.

Table 6.8 Estimated ionization potential of uranium 2p_{3/2} orbital (in eV) based on excitation to a tight ghost function placed 100 \( a_0 \) away from uranium, compared to the negative orbital energy \( -\varepsilon_{2p_{3/2}} \) (averaged over the \( m_j \) components). All results have been obtained with the CAM-B3LYP functional

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Estimated IP (U2p_{3/2}) in eV</th>
<th>( -\varepsilon_{2p_{3/2}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO_{2}^{2+}</td>
<td>17104.31</td>
<td>17104.41</td>
</tr>
<tr>
<td>OUN^{+}</td>
<td>17095.03</td>
<td>17095.13</td>
</tr>
<tr>
<td>UN_{2}</td>
<td>17087.25</td>
<td>17087.34</td>
</tr>
</tbody>
</table>

A direct comparison of STEX on the one hand and CPP and REW-TDDFT on the other hand is complicated by the fact that the latter spectra are significantly shifted with respect to the experimental L\textsubscript{3} edge due to the combined effect of missing orbital relaxation and self-interaction errors.\textsuperscript{382} In order to align the spectra we have therefore considered the position of the L\textsubscript{3} ionization threshold within a linear response regime. We may consider the process of ionization as an extreme case of a charge-transfer excitation in which the separation between donor and acceptor tends towards infinity. Following the arguments of Dreuw \textit{et al.},\textsuperscript{383} it then becomes clear that the excitation energy reduces, for any DFT functional, to the energy difference between the acceptor and donor orbital. Since this excitation energy is also equal to the difference between the ionization potential of the donor and the electron affinity of the acceptor we are led to the conclusion that within TDDFT (and TDHF) the ionization threshold is \textit{de facto} given by Koopmans’ theorem, that is, as the negative of the donor orbital. We have tested this conclusion numerically by forcing an excitation from the selected core orbital to a remote tight ghost function placed 100 \( a_0 \) away from the uranium atom along the molecular axis and then subtracting the ghost orbital eigenvalue from the resulting excitation energy. The results are given in Table 6.8 and clearly confirms the validity of our
conclusion. On the other hand, it should be emphasized that the meaning of orbital eigenvalues is different in Hartree–Fock and exact Kohn–Sham theory.\textsuperscript{384–386}

**Figure 6.5** \( \text{UO}_2^{2+} \) uranium \( L_3 \) edge XANES spectra simulated by STEX, CPP(CAM-B3LYP), and REW-TDDFT(CAM-B3LYP), including a Lorentzian broadening of ~1 eV. The two latter spectra have been shifted by 152.63 eV according to (6.6).
Figure 6.6  OUN$^+$ uranium L$_3$ edge XANES spectra simulated by STEX, CPP(CAM-B3LYP) and REW-TDDFT(CAM-B3LYP), including a Lorentzian broadening of $\sim$1 eV. The two latter spectra have been shifted by 151.73 eV according to (6.6).
As a consequence we have shifted the excitation energies obtained with CPP and REW-TDDFT according to

$$h\omega_m \rightarrow h\omega_m + IP_i(\Delta HF) + \epsilon_i^{KS}$$  \hspace{1cm} (6.6)$$

From Fig. 6.5–6.7 it is seen that these shifts, on the order of 150 eV, clearly bring the CPP and REW-TDDFT spectra into the same energy region as the STEX one. The CPP and REW-TDDFT spectra agree perfectly, as they should (cf. Section 6.2.2); the slight deviation observed towards higher photon energies in Fig. 6.6 is simply due to an insufficient number of excitations calculated at the REW-TDDFT level. For uranyl the CPP and REW-TDDFT spectra are seen to match the STEX one very well, but the agreement deteriorates as the molecular charge is reduced along the isoelectronic series. For OUN\(^+\) we note in particular new pre-edge features with respect to
STEX. It should be pointed out, however, that the uranium 2p\textsubscript{3/2} natural width is 7.43 eV,\textsuperscript{387} although the experimental energy resolution can be reduced down to about 4 eV using partial fluorescence yield techniques.\textsuperscript{271,388} This still means that the above-mentioned pre-edge structures of the theoretical spectrum cannot be resolved by present-day experiment.

Amongst the three methods STEX offers perhaps the most straightforward assignment of spectra. This is because XANES spectroscopy, in an orbital picture, probes bound virtual orbitals which, as discussed in Section 6.2.2, have been optimized by calculating the core-ionized state. As an illustration we may note that in the dyall.v3z basis a HF calculation on the uranyl ground state gives 41 bound also virtual orbitals (Kramers pairs) whereas for OUN\textsuperscript{+} this number is reduced to 15 and for UN\textsubscript{2} there are none. In contrast, the corresponding numbers for the uranium 2p\textsubscript{3/2}-ionized state are 46, 35 and 15, respectively. We have been able to carry out a detailed assignment of the STEX uranium L\textsubscript{3} XANES spectra using projection analysis.\textsuperscript{349} For the ligands we have used the ground state orbitals. For uranium the ground state occupied orbitals were supplemented by the bound improved virtual orbitals generated by freezing the ground state orbitals and then recalculating the virtual orbitals for the 2p\textsubscript{3/2}-ionized state. The first peak of the uranyl STEX spectrum (cf. Fig. 6.5) is thereby found to be dominated by excitations to uranium 6d orbitals, but also virtual orbitals of uranium 7s character. These virtual orbitals have essentially no ligand character. The second peak is assigned as excitations to virtual orbitals dominated by uranium 6d, but about 25% ligand character. The third and final peak before the ionization threshold is dominated by excitations to uranium 7d orbitals. Moving to OUN\textsuperscript{+} the molecular charge is reduced by one unit and the number of peaks before the ionization threshold to two; both are dominated by excitations to uranium 6d orbitals, but the second peak also has some ligand character (23% nitrogen and 6% oxygen). Finally, for neutral UN\textsubscript{2} there is a single peak before the ionization threshold dominated by excitations to
uranium 6d and with no ligand character. The same assignment basically carries over to the CPP and REW-TDDFT spectra, but with less precision since the virtual orbitals are less optimal. The extra features of the second peak of the OUN\(^+\) spectrum (cf. Fig. 6.6) appears to be due to a larger splitting of the \(\omega = 3/2\) and \(\omega = 5/2\) components of the uranium 6d\(_{5/2}\) orbitals.

6.5 Conclusions and Perspectives

In the present work we have studied the processes of ionization and excitation out of the uranium 2p\(_{3/2}\) orbital in the isoelectronic species UO\(_2\)^{2+}, OUN\(^+\) and UN\(_2\) at the 4-component relativistic level. Molecular geometries were reoptimized at the CCSD(T) level using small-core scalar relativistic pseudopotentials and correlation-consistent basis sets, and the electronic structure studied by projection analysis in localized orbitals. Using the extracted uranium atomic charges we find a perfectly linear chemical shift of uranium 2p\(_{3/2}\) ionization energies obtained by \(\Delta\text{HF}\). We confirm the failure of Koopmans’ theorem for core ionization due to the dominance of relaxation contributions over correlation ones. More unexpected is that the correlation contribution \(\Delta\text{corr}\) is negative for all three species, meaning that the parent state has less correlation energy than the core-ionized state. Our analysis suggests that this is due to a strong coupling of relaxation and correlation. Uranium 2p\(_{3/2}\) ionization energies calculated by \(\Delta\text{SCF}\) using different DFT functionals do not agree very well with our \(\Delta\text{MP2}\) values, but this situation might improve by the introduction of spin polarization in a Kramers unrestricted formalism.

To describe core excitations we have investigated three methods and shown how they are related. In particular, we show how STEX excitation energies, but not intensities, can be reproduced by TDHF calculations within the Tamm–Dancoff approximation. We also show that for the same Lorentz broadening REW-TDDFT and CPP give identical spectra. The CPP method has a certain ease of application in that the spectrum is directly simulated by scanning the desired frequency
region, without any worry about the appropriate number of excitations to include. On the other hand, CPP lacks some flexibility in that spectra are only simulated for one specific damping parameter and would therefore have to be recalculated if another value was chosen. Although Koopmans’ theorem fails for core excitations, it is the correct approximation of ionization potentials in the linear response regime, and this observation has allowed us to introduce shifts (cf. eqn (6.6)), on the order of 150 eV, to align REW-TDDFT and CPP uranium L3 XANES spectra with the STEX ones. Since orbital relaxation dominates over electron correlation for core excitations, the ionization threshold of STEX spectra are in the vicinity of experimental ones. The interpretation of STEX spectra is furthermore more straightforward in that the virtual orbitals of the core-ionized state are optimal. We accordingly obtain a detailed assignment of our calculated STEX spectra using projection analysis, notably with improved virtual orbitals of the uranium atom. On the other hand, it has been claimed (see for instance ref. 389) that REW-TDDFT (and thus CPP) gives better relative peak positions and intensities than STEX compared to experiment due to the inclusion of electron correlation. In the present work no direct comparison with experiment was made. In future work we plan to address this issue in detail. It should also be pointed out that the molecules in the present study are closed shell in their parent state, which is rather the exception in the domain of f-elements. As pointed out by Roemelt et al.,390 TDDFT (and therefore also CPP and STEX) has simply not enough parameters to handle the general open-shell case. A challenge for the future is therefore to develop cost-effective methods for the simulation of X-ray spectra of actinide species.
CHAPTER 7

CONCLUSIONS

Computational methods ranging from single reference DFT to multi-reference excited state CASPT2 have been employed on a variety of chemical systems from third-row main group compounds to the actinide complexes. The cumulative results of this whole body of research as it relates to the calculated free energies, dissociation energies, diatomic constants, and ionization energies follows.

The multi-reference correlation consistent Composite Approach, MR-ccCA, predicted continuous potential energy curves for third-row molecules despite MR-ccCA being constructed as a summation of energies. Additionally, the dissociation energies and diatomic constants for each molecule were found to be less than 1 kcal mol\(^{-1}\) on the average different from reliable experiment or rigorous computational theory. Finally, the excited states of the arsenic dimer were calculated with MR-ccCA, and their ordering was found to be in good agreement with well-established experiment and theory.

NdF\(^{2+}\) was investigated and found to be a suitable model of the Nd-F bond in NdF\(_3\) based on comparisons between the electronic structures of both NdF\(^{2+}\) and NdF\(_3\). The dissociation energy of NdF\(^{2+}\) was found to be \(\sim 49\) kcal mol\(^{-1}\) due to an allowed spin-orbit state crossing to a dissociative sextet state. Both the NdF\(^{2+}\) and NdF\(_3\) compounds show ionic bonding character.

The NdF\(^+\) molecule, containing neodymium in the 2+ oxidation state, was also examined, but found to differ from NdF\(^{2+}\) in bond energy. The dissociation energy of NdF\(^+\) was found to be 133.7 kcal mol\(^{-1}\), much more similar to NdF in which the dissociation was 131.9 kcal mol\(^{-1}\). However, the excited states of NdF\(^+\) more closely resembled those for NdF\(^{2+}\) than NdF, mostly lying parallel to the ground state that correspond to permutations of electrons among the 4f
orbitals. There is a state that deviates from this trend, though, and possesses a bond length that is shorter by ~ 0.06 Å. This state had significant contributions from the 5d orbitals, implying that the 5d orbitals are beginning to have an effect on the bonding of electronic states in NdF+.

The calculations on uranyl and its isoelectronic homologues, UNO+ and UN2, revealed that the L3 edge core ionization energies and excited states are both sensitive to the electronic charge distribution around the central uranium atom. Examining the ionization energies more closely, it was found that the relaxation and correlation energy had the same sign, whereas they normally cancel out, implying that there is a strong coupling of the electron correlation and relaxation for the core electrons. The STEX spectra possessed ionization energies that were the closest to the experimental energies, so the remaining TD-DFT and CPP spectra were shifted to coincide with this ionization limit for the purposes of comparison. The uranyl spectra were all very similar, differing only in relative peak intensity and peak position between STEX and CPP(TD-DFT). The UNO+ and UN2 results showed a difference between the STEX and CPP(TD-DFT) spectra. A shoulder peak appeared in the CPP UNO+ spectrum but not the STEX while in the UN2 spectrum, a peak appeared in the STEX spectrum, but not in the CPP spectrum. Projection analysis of the excitations showed primarily uranium core to d type transitions prior to the ionization of the molecule and that as the charge on the molecule decreases, fewer core excited valence states remain bound, explaining the decreasing number of peaks from uranyl to UN2.

While these projects have been published, there still remain unanswered questions that can be addressed through further research on the topics. Regarding the MR-ccCA calculations on third-row molecules, a larger molecule set would add weight to the mean absolute deviation of the calculated energies with experiment. Additionally, further excited states can be calculated.
for yet more molecules, particularly those with more complicated excited state manifolds and for molecules whose excited states play a direct role in dissociation mechanics, such as for Br$_2$.

On further work for lanthanide diatomics, it would be interesting to note the similarities and differences between lanthanide molecules that naturally are able to assume a 2+ oxidation state versus those that do not. It would also be worthwhile to examine different lanthanide bond types, such as Ln-O or Ln-C in order to isolate electronic effects that may play a role between a ligand and the central lanthanide in a catalyst, for example.

The effect, though, that is most deserving of a comprehensive study in the future is the stabilizing correlation contribution to the ionization energy observed in the uranyl project. It is not currently known which elements the correlation effect can be observed with or if the molecular environment has a direct effect on it. Additionally, since all of the calculations that this effect was observed in were fully relativistic, it is not known whether scalar relativity or spin-orbit effects play a direct role in the correlation stabilization. A study that isolates these effects and elucidates trends for this novel correlation effect should be undertaken.
APPENDIX A

A NEOTERIC NEODYMIUM MODEL: GROUND AND EXCITED ELECTRONIC STATE

ANALYSIS OF NdF^{2+} SUPPLEMENTARY INFORMATION
Table A1. Diatomic constants of the quartet MCSCF states of NdF$^{2+}$ obtained through Dunham analysis$^a$

<table>
<thead>
<tr>
<th>State</th>
<th>$r_e$ (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$\omega_{ex}$ (cm$^{-1}$)</th>
<th>$\omega_{ey}$ (cm$^{-1}$)</th>
<th>$B_e$ (cm$^{-1}$)</th>
<th>$\alpha_e$ (cm$^{-1}$)</th>
<th>$D_e$ (eV)$^a$</th>
<th>$D_o$ (eV)$^a$</th>
<th>$D_o$ (kcal/mol)</th>
<th>$D_o$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X$^4\Pi$</td>
<td>1.907</td>
<td>709.1</td>
<td>2.13</td>
<td>0.00</td>
<td>0.2767</td>
<td>0.00117</td>
<td>2.47</td>
<td>56.9</td>
<td>2.43</td>
<td>55.9</td>
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<td>706.6</td>
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<td>B$^4\Delta$</td>
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<td>707.9</td>
<td>2.12</td>
<td>0.00</td>
<td>0.2766</td>
<td>0.00117</td>
<td>3.30</td>
<td>76.1</td>
<td>3.25</td>
<td>75.0</td>
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<td>709.9</td>
<td>2.13</td>
<td>0.00</td>
<td>0.2772</td>
<td>0.00117</td>
<td>3.30</td>
<td>76.1</td>
<td>3.26</td>
<td>75.1</td>
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</tbody>
</table>

$^a$Unless otherwise noted, the dissociation limit is taken as the energy at 2.7 Å along the same state’s curve  $^b$Dissociation limit taken as the asymptotic limit of the repulsive $e^6H$ state

Table A2. Diatomic constants of the quartet MCQDPT2 states of NdF$^{2+}$ obtained through Dunham analysis

<table>
<thead>
<tr>
<th>State</th>
<th>$r_e$ (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$\omega_{ex}$ (cm$^{-1}$)</th>
<th>$\omega_{ey}$ (cm$^{-1}$)</th>
<th>$B_e$ (cm$^{-1}$)</th>
<th>$\alpha_e$ (cm$^{-1}$)</th>
<th>$D_e$ (eV)$^a$</th>
<th>$D_o$ (eV)$^a$</th>
<th>$D_o$ (kcal/mol)</th>
<th>$D_o$ (kcal/mol)</th>
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</thead>
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<tr>
<td>X$^4\Pi$</td>
<td>1.901</td>
<td>714.1</td>
<td>2.14</td>
<td>0.00</td>
<td>0.2783</td>
<td>0.00117</td>
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<td>711.6</td>
<td>2.14</td>
<td>0.00</td>
<td>0.2772</td>
<td>0.00118</td>
<td>3.31</td>
<td>76.3</td>
<td>3.26</td>
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<td>712.6</td>
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<td>0.00</td>
<td>0.2782</td>
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<td>C$^4\Gamma$</td>
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<td>76.7</td>
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</table>

$^a$Unless otherwise noted, the dissociation limit is taken as the energy at 2.7 Å along the same state’s curve  $^b$Dissociation limit taken as the asymptotic limit of the repulsive $e^6H$ state
Table A3. Diatomic constants of the quartet SO-MCQDPT2 states of NdF\(^{2+}\) obtained through Dunham analysis

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<th>(\omega_e) ((\text{cm}^{-1}))</th>
<th>(\omega_x) ((\text{cm}^{-1}))</th>
<th>(\omega_y) ((\text{cm}^{-1}))</th>
<th>(B_e) ((\text{cm}^{-1}))</th>
<th>(\alpha_e) ((\text{cm}^{-1}))</th>
<th>(D_e) ((\text{eV})^a)</th>
<th>(D_o) ((\text{kcal/mol}))</th>
<th>(D_o) ((\text{kcal/mol})^a)</th>
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</thead>
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<td>714.0</td>
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<td>0.00</td>
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<td>0.00118</td>
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<td>0.00118</td>
<td>3.37</td>
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\(^a\)Unless otherwise noted, the dissociation limit is taken as the energy at 2.7 Å along the same state’s curve  
\(^b\)Dissociation limit taken as the asymptotic limit of the repulsive \(^i\)H\(_{5/2}\) state.
**Table A4.** Crossing points of the MCSCF curves of NdF\textsuperscript{2+} in Å. Crossing points were obtained by 5\textsuperscript{th} order polynomial fits to the \textit{ab initio} potential energies curves with the (5,8) active space.

|   | X\textsuperscript{4}I | A\textsuperscript{4}Φ | B\textsuperscript{4}Δ | C\textsuperscript{4}Γ | a\textsuperscript{2}Φ | b\textsuperscript{2}Π | c\textsuperscript{2}Γ | d\textsuperscript{2}Δ | e\textsuperscript{6}Η |
|---|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------
| X\textsuperscript{4}I | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| A\textsuperscript{4}Φ | --- | --- | --- | --- | --- | --- | --- | --- | 2.509 |
| B\textsuperscript{4}Δ | --- | --- | --- | --- | --- | --- | --- | --- | 2.467 |
| C\textsuperscript{4}Γ | --- | --- | --- | --- | --- | --- | --- | --- | 2.418 |
| a\textsuperscript{2}Φ | --- | --- | --- | --- | --- | --- | --- | --- | 2.319 |
| b\textsuperscript{2}Π | --- | 1.857 | 1.526 | 2.191 |
| c\textsuperscript{2}Γ | --- | --- | --- | --- | 2.189 |
| d\textsuperscript{2}Δ | --- | --- | --- | --- | 2.181 |
| e\textsuperscript{6}Η | --- | --- | --- | --- | --- |

**Table A5.** Crossing points of MCQDPT2 curves of NdF\textsuperscript{2+} in Å. Crossing points were obtained by 5\textsuperscript{th} order polynomial fits to the \textit{ab initio} potential energies curves with the (5,8) active space.

|   | X\textsuperscript{4}I | A\textsuperscript{4}Φ | B\textsuperscript{4}Δ | C\textsuperscript{4}Γ | a\textsuperscript{2}Φ | b\textsuperscript{2}Π | c\textsuperscript{2}Γ | d\textsuperscript{2}Δ | e\textsuperscript{6}Η |
|---|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------
| X\textsuperscript{4}I | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| A\textsuperscript{4}Φ | --- | --- | --- | --- | --- | --- | --- | --- | 2.432 |
| B\textsuperscript{4}Δ | --- | --- | --- | --- | --- | --- | --- | --- | 2.403 |
| C\textsuperscript{4}Γ | --- | --- | --- | --- | --- | --- | --- | --- | 2.370 |
| a\textsuperscript{2}Φ | --- | --- | --- | --- | --- | --- | --- | --- | 2.301 |
| b\textsuperscript{2}Π | --- | 1.529 | --- | --- | --- | --- | --- | --- | 2.178 |
| c\textsuperscript{2}Γ | --- | --- | --- | --- | --- | --- | --- | --- | 2.169 |
| d\textsuperscript{2}Δ | --- | --- | --- | --- | --- | --- | --- | --- | 2.161 |
| e\textsuperscript{6}Η | --- | --- | --- | --- | --- | --- | --- | --- | --- |
Table A6. Crossing points of SO-MCQDPT2 quartet curves of NdF\(^{2+}\) in Å. Crossing points were obtained by 5\(^{th}\) order polynomial fits to the \textit{ab initio} potential energies curves with the (5,8) active space.

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<th>F(^4)I(_{15/2})</th>
<th>B(^4)\Phi(_{3/2})</th>
<th>D(^4)\Phi(_{5/2})</th>
<th>E(^4)\Phi(_{7/2})</th>
<th>H(^4)\Phi(_{9/2})</th>
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<th>I(^4)\Delta(_{3/2})</th>
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Table A7. Crossing points of SO-MCQDPT2 doublet curves of NdF$^{2+}$ in Å. Crossing points were obtained by 5th order polynomial fits to the \textit{ab initio} potential energies curves with the (5,8) active space.

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<th>$a^2\Pi_{1/2}$</th>
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<th>$g^2\Gamma_{9/2}$</th>
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Table A8. Crossing points of SO-MCQDPT2 quartet and doublet curves with sextet curves of NdF$^{2+}$ in Å. Crossing points were obtained by 5th order polynomial fits to the \textit{ab initio} potential energies curves with the (5,8) active space.

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<th>$l^6\Pi_{11/2}$</th>
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<td>$f^2\Pi_{3/2}$</td>
<td>2.132</td>
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<td>$b^2\Gamma_{7/2}$</td>
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<td>$g^2\Gamma_{9/2}$</td>
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<td>2.154</td>
<td>2.165</td>
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<td>$e^2\Delta_{3/2}$</td>
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<td>2.196</td>
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<td>$h^2\Delta_{5/2}$</td>
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<td>2.138</td>
<td>2.149</td>
<td>2.159</td>
<td>2.170</td>
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