COMPUTATIONAL THERMOCHEMISTRY FOR HEAVY ELEMENTS AND METHOD DEVELOPMENT IN QUANTUM ELECTRON-NUCLEAR DYNAMICS

By

Lucas Aebersold

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Chemistry – Doctor of Philosophy

2021

ABSTRACT

COMPUTATIONAL THERMOCHEMISTRY FOR HEAVY ELEMENTS AND METHOD DEVELOPMENT IN QUANTUM ELECTRON-NUCLEAR DYNAMICS

By

Lucas Aebersold

The focus of this thesis is in two main areas: computational approaches to heavy element thermochemistry and development of quantum electron-nuclear dynamic methods. Computational chemistry is important because it can be used to describe time-independent phenomena such as enthalpies of formation, geometries, activation energies, and much more. Furthermore, computational chemistry can describe many time-dependent phenomena as well such as electron-transfer rates, ionization effects, and ultrafast phenomena.

Methodologies for time-independent phenomena are well-developed, though there is still more that needs to be understood about lower parts of the periodic table. Existing methods often miss an important aspect for the description of these elements; ranging from the incorporation of certain relativistic effects to the treatment of static and dynamic correlation. For time-dependent phenomena that involve strong electron-nuclear coupling, methods are much less developed and restricted to two-electron systems. Including a quantum treatment of both the nuclei and electrons is an immense challenge for larger systems. Developing a general and efficient method is of great interest as it would provide more theoretical insight in the growing attosecond science field. In this dissertation, time-independent methods for heavy elements, namely the actinides and lanthanides are investigated. As well, the development of a time-dependent method with a quantum description of electron-nuclear dynamics is presented.

The overview is as follows, in Chapter 3 the performance of commonly used density functional theory (DFT) approaches are analyzed for a select set of lanthanide containing molecules. 22 different functionals were considered to gain insight on performance for prediction of thermochemical properties compared to experiment. for the prediction of enthalpies of formation and bond dissociation energies. The focus is specifically on determining the accuracy of relativistic effective core

potentials for these lanthanide species. The set of lanthanides, termed Ln54 set, includes lanthanide oxides, fluorides, and chlorides with the lanthanide formally in the +1, +2, and +3 oxidation state. In Chapter 4, a similar analysis as for the lanthanides was done for a series of actinide compounds. A dataset for enthalpies of formation from experiment encompassing a set of 66 actinide species consisting of Th, U, Np, Pu, or Am with oxide, halide or both ligands was compiled and used as a gauge. The study was expanded to include a variety of approach that account for relativistic effects, which are important for heavy element species. In Chapter 5 the impact of spin-orbit effects on DFT calculations was considered for the lanthanide oxide subset of the Ln54 dataset (along with YbF and LuF). A number of methods are considered, including spin-orbit DFT (SO-DFT) and full four-component Diract-Hartree-Fock calculations for spin–orbit coupling.

The following chapters 6, 7, and 8, development towards the multiconfigurational electronnuclear dynamics (MCEND) method and subsequent analysis of electron-nuclear dynamic effects. In Chapter 6 an overview of the motivation and methods for a quantum mechanical method for both electrons and nuclei is presented along with initial efforts on the method development. In Chapter 7 the first published work of our recent MCEND work is detailed. In this chapter, the dynamics of H₂ and LiH in strong laser fields is studied and insight is gained about how the electron and nuclear motion are coupled. Analysis is done of excitation spectra and coherence properties of the electronic and nuclear wavefunctions. In Chapter 8 the performance of the MCEND method is detailed for the diatomics: H₂, HeH⁺, BeH⁺, LiH, Li₂, and N₂. The ground-state equilibrium bond lengths and dipole moments, and time-dependent properties (electronic, vibrational, and high-harmonic spectra) are obtained with MCEND. The viability of MCEND is demonstrated, as well as the observation of nonadiabatic effects that arise in high-harmonic spectra, where electronic excitation displaces nuclear motion from equilibrium position. Isotope effects for H₂ are also analyzed for the spectra. Lastly, the future directions of the research are discussed in Chapter 9.

Copyright by LUCAS AEBERSOLD 2021

ACKNOWLEDGEMENTS

I would like to thank my advisor Angela K. Wilson for her continued support and understanding. Members of our group, both past and current, who both helped directly in my work, had useful discussions with or just made the day a little easier. I also thank Inga S. Ulusoy for her support and mentorship on the projects with the time-dependent methods. I am grateful for my friends and family for their support and care. Furthermore, I am grateful to the wonderful staff and professors and MSU, whose teaching and advice is deeply appreciated. And everyone else who supported me in either a big or small way to achieve this accomplishment.

TABLE OF CONTENTS

LIST OI	F TABI	LES viii
LIST OF	F FIGU	IRES xv
CHAPT	ER 1	OVERVIEW OF RESEARCH
CHAPT	ER 2	MOTIVATION AND METHODS FOR HEAVY ELEMENT THERMO-
0.1	T 1 <i>C</i>	CHEMISTRY
2.1	The f	-block
	2.1.1	Introduction
2.2	Densi	ty Functional Theory
	2.2.1	Basics of Density Functional Theory
	2.2.2	Functional Taxonomy 7
	2.2.3	DFT and the f -block
	2.2.4	Overview of Relativistic Effects
	2.2.5	Properties of f -elements $\dots \dots \dots$
2.3	Relati	vistic Quantum Mechanics
	2.3.1	Dirac Equation and Relativistic Hamiltonians
	2.3.2	Computational Methods
CHAPT	ER 3	EFFICACY OF DENSITY FUNCTIONALS AND RELATIVISTIC EF- FECTIVE CORE POTENTIALS FOR LANTHANIDE-CONTAINING
2.1		SPECIES: THE LN54 MOLECULE SET
3.1	Introd	luction
3.2	Comp	putational Methods
3.3	Resul	ts and Discussion
	3.3.1	Ln54HFa Set
	3.3.2	Ln54HFb Set
	3.3.3	Ln54D0 Set
	3.3.4	Ln54 Set
	3.3.5	Conclusions
CHAPT	ER 4	ACTINIDES
4.1	Introd	luction
4.2	Comp	utational Methods
4.3	Discu	ssion
	4.3.1	Geometries
	4.3.2	Enthalpies of Formation
	4.0.0	1
	4.3.3	Spin–Orbit Effects 49
	4.3.3	Spin–Orbit Effects 49 Regression Analysis 52
	4.3.3 4.3.4 4.3.5	Spin-Orbit Effects 49 Regression Analysis 52 Summary 55

CHAPT	TER 5 SPIN–ORBIT EFFECTS ON LANTHANIDES	57 57
5.1		57
СНАРТ	TER 6 INTRODUCTION TO QUANTUM DYNAMICS	60
6.1	Motivation	60
6.2	Time-dependent Schrödinger Equation	60
	6.2.1 Time-Dependent Methods	62
	6.2.2 Time-Independent Methods	62
63	Multiconfigurational Electron Nuclear Dynamics	63
0.5	6.3.1 The Electronic Basis	63
	6.3.2 Reconstruction of the MCEND Code	6 <i>1</i>
	0.5.2 Reconstruction of the MCEND Code	04
CHAPT	TER 7 COUPLED ELECTRON AND NUCLEAR MOTION IN STRONG LASER	
	FIELDS	66
7.1	Introduction	66
7.2	Multiconfiguration Electron-nuclear Dynamics	68
7.3	Results and Discussion	71
	7.3.1 H_2 Excitation Spectra	71
	7.3.2 LiH Excitation Spectra	76
	7.3.3 Nuclear Vibration of H_2 and LiH	81
	7 3 4 Born-Oppenheimer Potential and Coherence Properties	84
7.4	Summary	88
	·	
СНАРТ	TER 8 ELECTRON-NUCLEAR MULTICONFIGURATIONAL QUANTUM DY-	00
0.1	NAMICS OF SEVERAL DIATOMIC MOLECULES	90
8.1	Introduction	90
	8.1.1 Basis Representation	91
	8.1.2 Electron-nuclear Coupling and Diabatic Basis	92
	8.1.3 Integral Interpolation Routine	93
	8.1.4 Computational Details	94
8.2	Results and Discussion	95
	8.2.1 Correlation Energy	95
	8.2.2 Equilibrium Bond Length	98
	8.2.3 Dipole Moments	99
	8.2.4 High harmonic Generation	00
	8.2.5 Absorption Spectra 1	00
02		03
8.3		08
СНАРТ	TER 9 FUTURE DIRECTIONS	.09
APPEN		
1 21 1 L/1 V	DICES 1	12
	DICES	12
	DICES	.12 .13 .20
APF APF	DICES	12 13 30

LIST OF TABLES

Table 3.1:	MAD (kcal mol ⁻¹) values for the three Ln54 subsets computed with the Minnesota functionals: M06-L, M06, and M06-2X, which have increasing percentages of exact exchange, respectively.	30
Table 3.2:	Values for the B_1 diagnostic for multireference character using B1LYP/BLYP	32
Table 4.1:	Statistical properties computed for the enthalpies predicted by each functional, for the SEG, ANO, and AE basis sets. The statistics include the mean unsigned error (MUE), mean signed error (MSE), the range of errors noted (Min and Max), all in kcal mol ⁻¹ , and finally the standard deviation σ	47
Table 4.2:	Statistical properties computed for the enthalpies predicted by each functional at the SO-DFT level, for the SEG and ANO basis sets. Similar to Table 4.1, the statistics include the mean unsigned error (MUE), mean signed error (MSE), the range of errors noted (Min and Max), all in kcal mol ⁻¹ , and finally the standard deviation σ .	51
Table 4.3:	Linear regression analysis information for each functional at the two DFT/RECP levels of theory and the DFT/AE level of theory. A rank is given based on the overall R^2 in comparison to other functionals. In the table x is used to represent ΔH_{exp} .	54
Table 4.4:	Linear regression analysis information for each functional at the SO-DFT levels of theory and the DFT/AE level of theory. A rank is given based on the overall R^2 in comparison to other functionals. In the table x is used to represent ΔH_{exp} .	55
Table 5.1:	Calculated Δ_{SO} (kcal mol ⁻¹) for LnF and LnO molecules for 4c-DHF and DFT (TPSS), in comparison to literature 4c-DHF values.	58
Table 8.1:	Nuclear grid basis spanning from R_{\min} to R_{\max} at a spacing of ΔR using n_{grid} grid points, for the different diatomics. The grid points at which electronic basis functions are placed are denoted by $R_{sp,1}$ to $R_{sp,4}$. All values given in atomic units (a_0) .	95
Table 8.2:	Correlation energy as the difference between larger wave function expansion lengths relative to the smallest possible expansion length, in eV. The parent basis sets are given as ADZ (aug-cc-pVDZ), ATZ (aug-cc-pVTZ), and DZ (cc-pVDZ), with the number of remaining basis functions and number of parent basis functions in parenthesis.	96

Table 8.3:	Equilibrium bond lengths of the different diatomics in Å. The parent basis sets are given as ADZ (aug-cc-pVDZ), ATZ (aug-cc-pVTZ), and DZ (cc-pVDZ), with the number of remaining basis functions and number of parent basis functions in parenthesis. For comparison, bond lengths computed at the CCSD(T)/aug-cc-pVQZ (AQZ) level of theory are given as well (CCSD/aug-cc-pVQZ for H ₂ and HeH ⁺), along with available experimental r_e values taken from the NIST WebBook.	. 99
Table 8.4:	Dipole moments of the different diatomics in Debye (D). The parent basis sets are given as ADZ (aug-cc-pVDZ), ATZ (aug-cc-pVTZ) and DZ (cc-pVDZ), with remaining and parent basis functions as in Table 8.2. For comparison, the experimental dipole moments for HeH ⁺ and for LiH are given. No experimental value is available for BeH ⁺ , instead a CCSD(T)/aug-cc-pVQZ dipole moment is used for comparison. The error of the MCEND dipole moment value relative to the reference value is given in parenthesis.	. 100
Table A.1:	Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol ⁻¹) computed with each functional for the lanthanide trichlorides (Ln54HFa subset) with experimental values shown for comparison.	. 114
Table A.2:	Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol ⁻¹) computed with each functional for the lanthanide trifluorides (Ln54HFa subset) with experimental values shown for comparison.	. 115
Table A.3:	Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol ⁻¹) computed with each functional for the lanthanide trifluorides (Ln54HFa subset) with experimental values shown for comparison.	. 116
Table A.4:	Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol ⁻¹) computed with each functional for the lanthanide diffuorides (Ln54HFb subset) with experimental values shown for comparison.	. 117
Table A.5:	Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol ⁻¹) computed with each functional for the lanthanide dichlorides (Ln54HFb subset) with experimental values shown for comparison.	. 118
Table A.6:	Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol ⁻¹) computed with functional for the lanthanide fluorides (Ln54HFb subset) with experimental values shown for comparison.	. 119
Table A.7:	Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol ⁻¹) computed with each functional for the lanthanide monoxides (Ln54HFb subset) with experimental values shown for comparison.	. 120

Table A.8:	Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol ⁻¹) computed with each functional for the lanthanide monoxides (Ln54HFb subset) with experimental values shown for comparison.	121
Table A.9:	Calculated bond dissociation energies, (D_0) (kcal mol ⁻¹) computed with each functional for the lanthanide monofluorides (Ln54D0 subset) with experimental values used as a reference for the MSD/MAD calculations	122
Table A.10	: Calculated bond dissociation energies, (D_0) (kcal mol ⁻¹) computed with each functional for the lanthanide monofluorides (Ln54D0 subset) with experimental values used as a reference for the MSD/MAD calculations.	123
Table A.11	:Calculated bond dissociation energies, (D_0) (kcal mol ⁻¹) computed with each functional for the lanthanide monoxides (Ln54D0 subset) with experimental values shown for comparison.	124
Table A.12	:Calculated bond dissociation energies, (D_0) (kcal mol ⁻¹) computed with each functional for the lanthanide monoxides (Ln54D0 subset) with experimental values shown for comparison.	125
Table A.13	Experimental enthalpies of sublimation ΔH_{sub} (298 K) used in the calculation of the final enthalpies of formation for each lanthanide	126
Table A.14	:Molecules where the ionic assumption results in higher energy solutions. The following molecules have the lanthanide in the formally +2 oxidation state with the unpaired electrons occupying orbitals localized on the lanthanide corresponding to excited electronic states of the Ln^{2+} ions	128
Table B.1:	Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: ThO to ThBr.	131
Table B.2:	Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: ThBr ₂ to UF.	132
Table B.3:	Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: UF ₂ to UCl ₆ .	133
Table B.4:	Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: UBr to NpO ₂ .	134

Table B.5:	Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: NpF to PuF.	135
Table B.6:	Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: PuF ₂ to AmF ₃ .	136
Table B.7:	Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: ThO to ThBr.	137
Table B.8:	Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: ThBr ₂ to UF	138
Table B.9:	Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: UF ₂ to UCl ₆	139
Table B.10	: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: UBr to NpO ₂	140
Table B.11	: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: NpF to PuF	141
Table B.12	: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: PuF ₂ to AmF ₃	142
Table B.13	: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: ThO to ThBr.	143
Table B.14	: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: ThBr ₂ to UF.	144
Table B.15	: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: UF ₂ to UCl ₆ .	145

Table B.16: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: UBr to NpO ₂ .	146
Table B.17: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: NpF to PuF.	147
Table B.18: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: PuF ₂ to AmF ₃ .	148
Table B.19: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: ThO to ThBr.	149
Table B.20: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: ThBr ₂ to UF.	150
Table B.21: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: UF ₂ to UCl ₆	151
Table B.22: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: UBr to NpO ₂	152
Table B.23: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: NpF to PuF	153
Table B.24: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: PuF ₂ to AmF ₃ .	154
Table B.25: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: ThO to ThBr.	155
Table B.26: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: ThBr ₂ to UF.	156

Table B.27: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: UF ₂ to UCl ₆
Table B.28: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: UBr to NpO ₂
Table B.29: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: NpF to PuF
Table B.30: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: PuF ₂ to AmF ₃
Table B.31: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: ThO to ThBr
Table B.32: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: ThBr ₂ to UF
Table B.33: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: UF ₂ to UCl ₆
Table B.34: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: UBr to NpO ₂
Table B.35: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: NpF to PuF
Table B.36: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol ⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: PuF ₂ to AmF ₃
Table B.37: Zero-point energies from TPSS geometry optimization and determined multiplicity. Compounds ThO-UF2 167

Table B.38: Zero-point energies from TPSS geometry optimization and determined multi- plicity. Compounds $UF_3 - UI_4 \dots \dots$
Table B.39: Zero-point vibrational energies (ZPVE) from TPSS geometry optimization and determined multiplicity. Compounds NpO-AmF3determined multiplicity.
Table B.40: Experimental sublimation (vaporization for Br2) values for atoms and diatomicsused (Data from NIST and NEA).170

LIST OF FIGURES

Figure 3.1:	MSD (left blue bars) and MAD (right orange bars) values of $\Delta H_{\rm f}^{\circ}$ (kcal mol ⁻¹) with respect to experimental values for the Ln54HFa subset containing Ln in the +3 formal oxidation state. Functionals are listed in order of increasing complexity from the local density approximation (SVWN) to a double hybrid (B2PLYP).	 23
Figure 3.2:	Comparison of average predicted $\Delta H_{\rm f}^{\circ}$ enthalpies of formation of each functional class and experimental $\Delta H_{\rm f}^{\circ}$ for LnF ₃ . Experimental values are depicted as black squares connected with a solid line. Functional classes are connected with dashed lines, with values corresponding to the colored markers depicted in the legend.	 25
Figure 3.3:	MSD (left blue bars) and MAD (right orange bars) of $\Delta H_{\rm f}^{\circ}$ (kcal mol ⁻¹) with respect to experimental values for Ln54HFb subset containing Ln in the +1 and +2 formal oxidation states.	 26
Figure 3.4:	Average predicted $\Delta H_{\rm f}^{\circ}$ (kcal mol ⁻¹) of each functional class and experimental $\Delta H_{\rm f}^{\circ}$ for LnCl ₂ . Experimental values are depicted as black squares connected with a solid line. Functional classes are connected with dashed lines, with values corresponding to the colored markers depicted in the legend	 28
Figure 3.5:	Average predicted $\Delta H_{\rm f}^{\circ}$ of each functional class and experimental $\Delta H_{\rm f}^{\circ}$ for LnO. Experimental values are depicted as black squares connected with a solid line. Functional classes are connected with dashed lines, with values corresponding to the colored markers depicted in the legend.	 28
Figure 3.6:	Ln54D0 subset MSD (left blue bars) and MAD (right orange bars), in kcal mol^{-1} , for the calculated bond dissociation energies taken with respect to experimental values reported for each of the 25 lanthanide-containing diatomics composing the Ln54D0 set.	 29
Figure 3.7:	Averaged predicted D_0 (kcal mol ⁻¹) or in the case of LDA and DH average predicted of each functional class and experimental D0 for LnO. Experimental values are depicted as black squares connected with a solid line. Functional classes are connected with dashed lines, with values corresponding to the colored markers depicted in the legend	 30
Figure 3.8:	Comparison of the MADs (kcal mol^{-1}) for the (a) Ln54HFa, (b) Ln54HFb, and (c) Ln54D0 subsets of both the RECP calculations and the all-electron calculations from a prior study for all 22 tested density functionals	 34

Figure 4.1:	A comparison of functionals and the four basis sets, S97, SEG, ANO, and AE. MUEs for each actinide are given in the four panels in kcal mol^{-1} , the upper left shows the MUEs for all Th compounds. The lower left shows the MUEs for all U compounds, the upper right shows the results for the Np compounds and finally the lower right shows the combined MUE for the Pu and Am compounds.	44
Figure 4.2:	Mean unsigned errors in kcal mol^{-1} for the 18 functionals analyzed across the four basis sets for the overall molecule set.	46
Figure 4.3:	Comparison of the DFT and SO-DFT results for both SEG and ANO bases. MUE bars are shown in purple and the MSE bars are shown in cyan	50
Figure 4.4:	The error reduction of SO-DFT on the later actinides for the (SEG) and ANO basis.	52
Figure 6.1:	MCEND basis construction flow example for LiH	64
Figure 7.1:	Absorption spectra for H_2 using the aug-cc-pVDZ basis set at the (221) expansion length, for z (top) and x (bottom) polarization direction. Experimental transition frequencies are marked with black lines.	71
Figure 7.2:	Graphical representations of the MOs of H_2 before and after laser-pulse exci- tation in the z-polarization direction. The initial MOs resemble the σ and σ^* MOs, which then adapt to the optimal representation at each time step for the time-dependent Hamiltonian.	73
Figure 7.3:	Graphical representations of the MOs of H_2 before and after laser-pulse exci- tation in the <i>x</i> -polarization direction.	73
Figure 7.4:	Electronic and nuclear excitation peaks obtained from H_2 excitation in the <i>z</i> -direction run for 300 fs. The Savitzky-Golay filter (black line) is applied to the 300 fs spectrum. Experimental transition energies (cm ⁻¹) are overlayed as vertical lines. a) Energy region around the electronic excited states. b) Energy region close to the electronic ground state.	74
Figure 7.5:	Absorption spectra for LiH; experimental transition frequencies are marked with black lines. a) Excitation along z polarization direction with different expansion lengths. b) Excitation along x polarization direction with different expansion lengths.	77
Figure 7.6:	Absorption spectra for LiH; experimental transition frequencies are marked with black lines. The one-pulse spectrum is overlayed for comparison. a) Excitation along z polarization direction. b) Excitation along x polarization direction.	78

Figure 7.7:	Electronic and nuclear excitation peaks obtained from the two-pulse excitation of the (441) expansion length for LiH in the <i>z</i> -polarization direction overlayed with experimental transition energies. In the upper part a), the energy region around the first electronic excited state $({}^{1}\Sigma^{+})$ is shown. In the lower part b) the energy region close to the electronic ground state is shown 80
Figure 7.8:	Contour plot of the nuclear difference density $\Delta \rho_n(R, t)$ for H ₂ during the excitation with a <i>z</i> -polarized laser pulse. Positive values indicate a probability increase, while negative contour values indicate a probability decrease 82
Figure 7.9:	Contour plot of the nuclear difference density $\Delta \rho_n(R, t)$ for LiH during the a) UV/VIS-excitation using a pulse polarized along z and b) an IR pulse followed by an UV/VIS pulse to induce nuclear motion, both polarized along z 83
Figure 7.10:	Contour plot of the Born-Oppenheimer potential V_{BO} during the UV-excitation of H ₂ using a pulse polarized along z_1
Figure 7.11:	Contour plot of the Born-Oppenheimer potential V_{BO} during the IR+VIS- excitation of LiH using a pulse polarized along z
Figure 7.12:	Entropy <i>S</i> and purity $P = tr[\rho^2]$ of the electron-nuclear wave packet as calculated from the density matrix. The norm tr $[\rho]$ is shown as well to demonstrate the conservation of the norm. The raw data for <i>S</i> and <i>P</i> is overlayed with a filtered signal (Savitzky-Golay filter) for an enhancement of the dominant peaks. a) During the laser pulse excitation of H ₂ . b) During the two-pulse excitation of LiH
Figure 8.1:	Selected V_{en} diagonal matrix elements obtained through the cubic spline and Akima interpolation routine. The four explicitly sampled nuclear grid points are marked on the graph
Figure 8.2:	HHG spectra of H_2 , HD and D_2 (221/ATZ), for each given (expansion length/basis set) and <i>z</i> - (along molecular axis) and <i>x</i> - (perpendicular to molecular axis) polarization direction of the electric field
Figure 8.3:	HHG spectra of HeH ⁺ (221/ATZ), LiH (441/DZ), and BeH ⁺ (441/DZ), for each given (expansion length/basis set) and z - (along molecular axis) and x - (perpendicular to molecular axis) polarization direction of the electric field 103
Figure 8.4:	HHG spectra of Li ₂ (651/DZ) (top) and N ₂ (1471/DZ) (bottom), for each given (expansion length/basis set) and z- (along molecular axis) and x- (perpendicular to molecular axis) polarization direction of the electric field. $\dots \dots \dots$

Figure 8.5:	Absorption spectrum for BeH ⁺ (441/DZ) with laser pulse polarized perpendicular to the bond. The experimental transition energy is overlayed as a vertical line
Figure 8.6:	Absorption spectra of H ₂ , HD, D ₂ (ADZ/221) for <i>z</i> -polarization direction (top) and <i>x</i> -polarization direction (bottom). $\dots \dots \dots$
Figure A.1:	The average predicted $\Delta H_{\rm f}^{298\rm K}$ (kcal mol ⁻¹) for each functional class and the experimental $\Delta H_{\rm f}^{298\rm K}$ for LnCl ₃ plotted across the lanthanide series
Figure A.2:	The average predicted D_0 (kcal mol ⁻¹) of each functional class and experi- mental D_0 for LnF plotted across the lanthanide series
Figure A.3:	The MAD/MSD weighted averages of the three Ln54 subsets: Ln54HFa, Ln54HFb, and Ln54D0

CHAPTER 1

OVERVIEW OF RESEARCH

This thesis is comprised of two main areas: computational approaches to heavy element thermochemistry and development of quantum electron-nuclear dynamic methods. Computational chemistry is important because it can be used to describe time-independent phenomena such enthalpies of formation, geometries, activation energies, and much more. Furthermore, computational chemistry can describe many time-dependent phenomena as well, such as: electron-transfer rates, ionization effects, laser research. Computation is especially useful here, as it can guide experiments where it is difficult to study the molecules directly due to a wide number of reasons, from short-lived states to radioactivity.

Methodologies for time-independent phenomena are well-developed, but there is still more that needs to be understood about lower parts of the periodic table. Existing methods often miss an important aspect for the description of these elements; ranging from the incorporation of certain relativistic effects to the treatment of static and dynamic correlation. For time-dependent phenomena that involve strong electron-nuclear coupling, methods are much less developed and restricted to two-electron systems. Including a quantum treatment of both the nuclei and electrons is an immense challenge for larger systems. Developing a general and efficient method is of great interest as it would provide more theoretical insight in the growing attosecond science field. In this dissertation, time-independent methods for heavy elements, namely the actinides and lanthanides are investigated. Then, work on the development of a time-dependent method with a quantum description of electron-nuclear dynamics is presented.

In Chapter 3 the performance of density functional theory (DFT) approaches—some of the most widely used quantum mechanical approaches—are analyzed for a select set of lanthanide containing molecules. 22 different functionals were considered to gain insight about their performance and how it compares to experiment for the prediction of enthalpies of formation and bond dissociation energies. This study focused on determining the accuracy of relativistic effective core potentials

for these lanthanide species. The set of lanthanides, termed Ln54 set, includes lanthanide oxides, fluorides, and chlorides with the lanthanide formally in the +1, +2, and +3 oxidation state.

In Chapter 4, a similar analysis was done for a series of actinide compounds. Until now, there has been limited evaluation on the performance of DFT for actinide compounds. However, DFT use for actinide calculations is common, thus it is important to give a broad analysis on the performance. A dataset for enthalpies of formation from experiment encompassing a set of 66 actinide species consisting of Th, U, Np, Pu, or Am with oxide, halide or both ligands was compiled and used as a gauge. The study was expanded to include a variety of approach that account for relativistic effects, which are important for heavy element species. In Chapter 5 the impact of spin-orbit effects on DFT calculations was considered for the lanthanide oxide subset of the Ln54 dataset. Without spin-orbit correction, the errors for all density functionals (Chapter 3) are large. Here, a number of methods are considered, including spin-orbit DFT (SO-DFT) and full four-component Diract-Hartree-Fock calculations for spin–orbit coupling.

The following chapters 6, 7, and 8, development towards the multiconfigurational electronnuclear dynamics (MCEND) method and subsequent analysis of electron-nuclear dynamic effects. In Chapter 6 an overview of the motivation and methods for a quantum mechanical method for both electrons and nuclei is presented along with initial efforts on the method development. In Chapter 7 the first published work of our recent MCEND work is detailed. In this chapter, the dynamics of H₂ and LiH in strong laser fields is studied and insight is gained about how the electron and nuclear motion are coupled. Analysis is done of excitation spectra and coherence properties of the electronic and nuclear wavefunctions.

Chapter 8 details the performance of the MCEND method for the diatomics: H_2 , HeH^+ , BeH^+ , LiH, Li₂, and N₂. With this method, ground-state equilibrium bond lengths and dipole moments, and time-dependent properties (electronic, vibrational, and high-harmonic spectra) are obtained. The viability of the new method is demonstrated. The nonadiabatic effects that arise in high-harmonic spectra, where electronic excitation displaces nuclear motion from equilibrium position, are observed. Isotope effects for H_2 are also analyzed for the spectra. Lastly, the future directions of the research

are discussed in Chapter 9.

CHAPTER 2

MOTIVATION AND METHODS FOR HEAVY ELEMENT THERMOCHEMISTRY

2.1 The *f*-block

2.1.1 Introduction

Located at the bottom of the periodic table are the f-elements, composed of the lanthanide and actinide series. These are some of the most difficult elements to address, both experimentally and theoretically. Motivations for work on the actinide and lanthanide compounds arise from their key role in catalysis, energy production, medicine, lighting materials, high-performance alloys, magnets and military applications.¹ Another area where f-element species play a vital role is in the nuclear fuel industry. Here, the treatment of nuclear waste produced from power plants, for example, is an ongoing area of importance by the Department of Energy. This spent nuclear fuel contains a variety of radiotoxic elements, which can have half-lives of up to hundreds of thousands of years.²

Understanding the thermochemistry of the heavy elements is important in making processes such as nuclear waste separation more efficient and safe, improving existing and developing new catalysts, and better modes of recycling the critical elements (most of which are lanthanides) from consumer products including cars, cell phones, and display devices. Experimental work with compounds containing these heavy elements can be difficult and expensive due to a number of reasons, including the danger of radioactivity and short half-lives for some of these species. Thus, understanding these compounds via computation has become a major focus of research.

There are many theoretical challenges in heavy element chemistry. The complexity in modeling heavy elements arises from a number of factors, including the high number of core electrons, the multireference character of the partially filled f-orbitals, and increasingly significant relativistic effects. As well, identifying a methodology that can address these challenges without becoming cost prohibitive (in terms of computational cost) is also important.

2.2 Density Functional Theory

2.2.1 Basics of Density Functional Theory

One of the most popular electronic structure methods in use for the *f*-elements is density functional theory (DFT), due to its efficiency. For larger molecular systems, often it is the only feasible quantum mechanical calculation that can be performed. In Hartree-Fock and post-HF methods, electronic properties are derived from the wavefunction. However, in DFT, the ground-state electronic energy is fully determined from the electron density. That is, there is a one-to-one mapping from the ground-state electron density of a system to its energy.³ This is advantageous over wavefunction theory because the electron density is the square of the wavefunction, integrated over N - 1 electron coordinates, where each spin density depends on just the three spatial coordinates, independent of the number of electrons. Thus, as the wavefunction complexity increases exponentially with the number of electrons, the electron density remains independent. The challenge is that the functional connecting the density to the ground state energy is of an unknown form. The goal of DFT methods is to design functionals that approximate the functional connecting the electron density to the energy.⁴

DFT methods are based on the work of Kohn and Sham⁵, where they proposed adding orbitals to the scheme. The basic idea in the Kohn-Sham formalism is to separate the kinetic energy functional into two parts: an exact term and a more approximate term. This exact term corresponds to a fictional non-interacting system of a uniform electron gas. The approximate term corresponds to a real interacting system. When this separation is done, the exchange-correlation (EC) and kinetic energy terms only make up a small portion of the total energy, which becomes the unknown function. Mathematically, if we express the Hamiltonian operator in the form operator of the form

$$H_{\lambda} = T + V_{ext}(\lambda) + \lambda V_{ee} \tag{2.1}$$

where the external potential operator V_{ext} is equal to V_{ne} for $\lambda = 1$. For an intermediate form of λ , an assumption is made that $V_{ext}(\lambda)$ will give the same density as the real system, where λ equals 1. The fictional non-interacting ($\lambda = 0$) system, will result in the exact solution to the Schrödinger equation equation, with a Slater determinant made of molecular orbitals (MOs). Note, however, that this Slater determinant is not equivalent to the one in Hartree-Fock theory. The exact kinetic energy will be given by

$$T_{S} = \sum_{i=1}^{N_{elec}} \left\langle \phi_{i} \right| - \frac{1}{2} \nabla^{2} |\varphi_{i}\rangle$$
(2.2)

Another approach to get the exact kinetic energy is to consider natural orbitals (NOs), the eigenvectors of the density matrix. The exact kinetic energy can be calculated from these NOs when they come from the exact density matrix. The NO approach is very similar to the Hartree-Fock scheme, however there is not an exact cancellation of the exchange term with the Coulomb term, in DFT. This is a result of the exchange term having a different functional form than the Coulomb term.⁴

The difference between the exact kinetic energy and the one calculated by assuming noninteracting orbitals is small. The remaining kinetic energy is absorbed into the EC term and a general DFT energy expression can be written as

$$E_{xc}[\rho] = (T[\rho] - T_{S}[\rho]) + (E_{ee}[\rho] - J[\rho])$$
(2.3)

The first term in eq. (2.3) is the classical kinetic correlation energy, while the last contains both potential correlation and exchange energy. Since the exchange-correlation energy is roughly a factor of ten smaller than the kinetic energy, the accuracy of Kohn-Sham theory is much more resilient to functional inaccuracies than an orbital-free version of the theory. However, by introducing orbitals into the KS scheme, it no longer retains the three variable dependence and while it now an independent particle model of 3N variables, it will still be less complicated than many-body wavefunction methods. In terms of accuracy, DFT performs much better than Hartree-Fock theory, but unlike post-HF methods, more complex functionals do not systematically improve results—a major issue in modern DFT methods. Furthermore, DFT methods fail to describe many important phenomena, like van der Waals interactions and H₂ dissociation.⁴

2.2.2 Functional Taxonomy

Approximations. For the remaining $E_{xc}(\rho)$ term and its functional derivative, there is still no explicit form of the expression that is known. Thus, methods for approximating this energy term are required. The first approximation to this energy, discussed previously, was purposed by Kohn and Sham, and is the local spin-density approximation (LSDA).⁵ The $E_{xc}(\rho)$ term takes the form

$$E_{xc}^{\text{LDA}} = \int \varepsilon_{xc}^{\text{UEG}}(\rho)$$
(2.4)

where $\varepsilon_{xc}^{\text{UEG}}(\rho)$ is the exchange-correlation (EC) energy per unit volume of a uniform electron gas, having the local value $\rho(r)$ of the density. This is the simplest functional and results in approximately the right answer to the property of interest (e.g. energy or geometry) but not accurate enough to describe properties to be within experimental uncertainties. The next DFT advance was the introduction of generalized gradient approximations (GGAs), which use both the density and the gradient of the density.⁶ GGAs greatly improve bond dissociation energies and generally improve transition-state barriers. However, there is not a single universal form of the GGA, unlike the LSDA, giving rise to many varieties including BLYP, BP86, and PBE. Along similar lines, to improve upon the Kohn-Sham kinetic energy density a Laplacian can be incorporated, giving rise to the meta GGAs (mGGAs). The next level of functionals are the hybrid GGAs (HGGAs), which include a fraction of exact exchange analogous to the way the exchange in HF theory is removed, though it should be clarified that it is not the Hartree-Fock exchange itself that is being removed, but an analogous term.

The principal behind HGGAs, is that if only a small fraction of the exact exchange is included, then static correlation can be mimicked, increasing the accuracy. The increase in accuracy is possible because the EC term is non-local, depending not only on the electron density but also on the density matrix. The non-local nature of the EC term has implications for other approximations used in modern DFT—implications such as the reduced effectiveness of density fitting approximation. This reduction of effectiveness provided the motivation for developing the mGGAs, which was to achieve similar accuracy as for the hybrid functionals while bypassing this penalty.⁷

Parameterization. All density functional approximations include some degree of parameterization, either to other theoretical calculations or to experimental results. Common functionals that contain no empirical parameterization include LSDA, PBE, TPSS and TPSSH. These are not fit to any molecule properties and will therefore meet as many exact conditions as possible. Fit parameters are based on theoretical methods, such as Quantum Monte Carlo simulations. In general, this allows functionals to have rather systematic errors, such as for the overbinding in the LSDA. For entirely new systems, this systematic nature is actually desirable, as results from these functionals can be considered as controlled extrapolations from the known systems. This allows their reliability to be at the very least understood, if not predicted, beforehand.⁷

For the functionals that include a few empirical parameters, such as BLYP, B3LYP, BP86, and the Minnesota class of functionals. The empirical parameters employed in these functionals result in drastically reduced the errors for similar systems as to the systems to which the parameters were fit. This fitting to parameters can allow DFT to reach levels of thermochemical accuracy for many early main group systems. The downside to parameter fitting, however, is that errors are no longer systematic. Thus, for new systems, these functionals may be far less reliable and predictable in the prediction of electronic properties.⁷

In practical DFT calculations, the EC functional is not the only approximation used, in fact there are several more that are of concern. Most DFT calculations are performed with finite basis sets and discrete integration grids for numerical evaluation of EC contributions, which can confound the determination of error sources in the method.⁷ Errors of approximate functionals can actually be partially negated by disregarding relativistic effects. In the heavier elements, bond strengths are stronger, for example in the 5*d* metals, bond are 10 kcal mol⁻¹ stronger.⁸ When these effects are neglected, the overestimation of bond strength that is typical in the LSDA and GGA functionals is offset by some amount.⁹ This can give the impression of enhanced performance but for the wrong reasons.

Other properties in transition metals, like the ground state, spin-state splittings, and exchange couplings can also be severely affected by the type of EC functional. For functionals with no EC term,

low-spin states are stabilized substantially, while the Hybrid functionals and HF theory will favor the higher spin states. The increase in energy difference between the high spin and low spin energy states has been found to increase linearly with the amount of exact-exchange in hybrid functionals. An optimum range for mixing has even been suggested to be around 10 to 15% for certain transition metal complexes.⁸

2.2.3 DFT and the *f*-block

There are some advantages of the Kohn-Sham DFT approach for the *f*-elements. In LSDA especially, since the electronic structure problem is reduced to single particle-like equations, the Coulomb and kinetic energy terms are much easier to evaluate. LSDA in particular can work quite well for strongly inhomogeneous systems, which may be due to the Coulomb interaction being much larger, so the EC functional only has to account for a minor amount of energy in comparison. LSDA, however, neglects the nonlocality of the true EC functional, which puts a limit on the accuracy of the results that can be obtained.⁷ In the LSDA, when the problem is reduced to a set of single-particle-like equations, the kinetic energy and Coulomb interaction are easily evaluated. In particular, LSDA works fairly well for 3*d* transition metals like Fe, Co, and Ni. However, for the *f*-block, LSDA does not fare as well, due to the orbital degrees of freedom and multiplet configurations.^{4,8,10} To summarize, the main issues with LSDA are the less valid approximations made to EC term and the lack of a description for spatially localized electrons. Also, it is important to state that there are no widely implemented DFT functionals (if any at all) adjusted to the *f*-block.

2.2.4 Overview of Relativistic Effects

The Schrödinger equation is a nonrelativistic formulation and will yield inaccurate properties, like energies, from the wavefunction for elements that show significant relativistic effects. Relativistic effects have an impact on all of the elements, though for the first two rows, the effects are usually small enough to disregard. From the third row and beyond, however, the effects become increasingly important and for the f-series, accounting for relativity is essential for any electronic structure

calculation. For an understanding, let us first briefly discuss Einstein's theory of special relativity. Special relativity requires that all fundamental laws of physics be the same in all inertial reference frames. This requires that the speed of light remain the same in all inertial reference frames, which leads to the counter-intuitive phenomenon of length contraction, mass-velocity dependence, and time-dilation, the latter of which is important in time-dependent phenomena.¹¹

For atoms, the mass-velocity dependence will have a major impact on its electronic properties, such as the energy and geometry, for example. Considering an electron, the relativistic mass increase can be written as¹¹

$$m = m_0 / \left(1 - (\nu/c)\right)^{1/2} \tag{2.5}$$

where m_0 is the rest mass and v the speed of the electron, the effective Bohr radius,

$$a_0 = (4\pi\varepsilon_0)(\hbar^2/me^2)$$
 (2.6)

will decrease for inner electrons with large average speeds. For example, in a 1*s* shell at the nonrelativistic limit, the electron will have an average speed of about *Z* (nuclear charge) au. For a heavy element like mercury, the 1*s* electron will have a v/c of 80/137 = 0.58. This corresponds to a decrease in the radial extent of 23%. Because all *s*-shells must remain orthogonal to each other, this forces them to experience a similar contraction. In fact, it is even possible for higher *s*-shells to have a larger percentage of relativistic effects than the 1*s* shell. The 6*s*-shell in the gold atom is a good example of this, where the overall percent contraction of the 6*s* is greater than the 1*s*.¹² Similar but smaller contraction also occur for *p* electrons, though for the heaviest *p*-block this effect reverses and little to no contraction is present.¹¹ Additional relativistic effects include the orbital angular momentum quantum number l > 0 (*p*, *d*, *f*) experiencing the spin-orbit splitting into¹³

$$\mathbf{j} = \mathbf{l} + \mathbf{s} \tag{2.7}$$

$$j = l \pm 1/2$$
 (2.8)

Also, the effective potential for the d and f electrons, which usually do not come close enough to the nucleus, will be more efficiently screened as an additional effect of the contraction of the s

and p shells. This screening of the potential reduces the pull on the electrons, causing an increase in the radial extent and overall energy, leading to a more distributed radial wavefunction over a longer region. The main effects of relativity on the atomic orbital can be summarized into: (1) direct relativistic effects—the contraction of the *s* and *p* shells, (2) indirect relativistic effects—the expansion of the *f* and *d* shells, and (3) spin-orbit (SO) coupling. All three of these effects are approximately on the same order of magnitude and scale in proportion to Z^2 .^{13,14}

2.2.5 Properties of *f*-elements

Relativity plays a big part in understanding the chemistry of the *f*-block elements, as the effects on the orbitals dictate much of their chemistry. Both the lanthanide and actinide series contain open *f*-shell configurations and possess unique qualities as a result. Furthermore, it must also be noted that comparing the lanthanide series with the actinide series is not as straightforward as it is with the main group series and even transition metal series. The lanthanides exhibit the "lanthanide contraction".^{11,15} This term specifically refers to the lower than expected decrease in atomic radii of the lanthanide elements. All the lanthanides have very similar atomic radii, which is especially true in their +3 oxidation state, leading to very similar chemical behavior.

This is a result of the destabilization of the 4f-orbital due to increased screening of nuclear charge by the *s*- and *p*- orbitals. Note, this is mainly a result of the nature of the 4f-orbital itself, and relativity only accounts for about 10% of this contraction.¹¹ However, the 4f-orbital is still not thought to extend far enough from the core to participate in covalent bonding interactions with other ligands directly. As a result, the interactions that lanthanides have with other ligands are usually assumed to be ionic in nature. There are cases where this might not necessarily hold true, but for the majority of lanthanide compounds, the ionic description is widely supported.¹⁵ A major consequence of this ionic picture and similar radial extent is that lanthanides are very difficult to separate from each other. Because the lanthanides have widespread use and importance, there is a significant scientific focus on effective methods of separation.

Beyond the non-scalar effects, vector effects also have a large effect on the electronic properties,

with spin-orbit (SO) coupling being the most important. SO coupling will raise the spin and orbital degeneracy of any open-shell electronic states, leading to a large number of low-lying electronic states. The interactions of the increased electron correlation, scalar, and vector relativistic effects will increase the multireference nature of the atoms and molecules, making conventional electronic structure methods inadequate to describe these compounds.¹⁶

Lanthanides. The chemistry of lanthanides deviates from the *d*-block metals in quite a few ways. Most chemistry of the lanthanides will generally occur in the (+3) oxidation state, though +2 and +4 states are common among a few lanthanide species. In transition metals, crystal field effects play a dominant role in describing the coordination geometry, however, in lanthanides ligand steric effects are far more influential on the coordination geometry.¹⁵ Compared to other *d*-block metals, the lanthanides have very small crystal-field splittings and very sharp electronic spectra. As for ligand binding, lanthanides tend to bind with anionic ligands whose donor atoms have high electronegativity (e.g. O, F).¹⁵ Interactions between lanthanide and oxygen or lanthanide and nitrogen are quite different from oxygen and nitrogen interactions with transition metals. Transition metals and early actinides will form strong double and triple bonds with O and N, however, the lanthanides will not form these strong bonds with O and N.¹⁵ Another impact on the properties of lanthanide compounds results from the reduced participation of the 4*f*-orbital in bonding. This results in any bound ligands having minimal effect on the spectroscopic and magnetic properties, enabling a variety of unique applications, for example in development of strong magnets.

Actinides. Directly below the lanthanides, the actinides consist of elements 89–103, and only the first few are naturally occurring and elements heavier than Pu must be artificially synthesized. The valence shells occupied at this point are the 5*f*, 6*d*, 7*s*, 7*p*, all of which are separated very well in space, yet energetically remain very close. This spatial separation can account for some of the unique chemical properties of the actinides; uranium serves as a good example. Specifically, the ground state for uranium which has the configuration of $5f^36d^17s^2$, some of which are very close energetically. This causes complications when describing chemical bonding, as several of

these states will be competing to contribute to the bonding picture. Describing this with electronic structure methods then becomes extremely difficult. Furthermore, SO coupling will confound the chemical picture, as it impacts the degeneracy of shells with angular momentum number greater than zero. This leads to energetically lower and higher sub-shells, which alter the possible occupied states. 13,16 As previously mentioned, the lanthanide 4f-shell does not have enough radial extent to contribute much to chemical bonding, however in actinides the indirect effects cause the 5f-shell and 6d-shell to have enough radial extent to form stable covalent interactions. This results in a much higher range of possible oxidation states than for the lanthanides, with +4 and +6 being the most common.

2.3 Relativistic Quantum Mechanics

2.3.1 Dirac Equation and Relativistic Hamiltonians

The standard equation in the formulation of quantum mechanics is the Schrödinger equation, which in the time-independent domain can be expressed as

$$\mathscr{H}\Psi = E\Psi \tag{2.9}$$

Where \mathcal{H} is the molecular Hamiltonian, that describes the total energy, and Ψ is the wavefunction of the system. In the nonrelavistic formulation it broken up into five terms:

$$\mathcal{H} = \hat{H}_{mol} = \hat{T}_n + \hat{T}_e + V_{nn} + V_{en} + V_{ee}$$
(2.10)

which include the kinetic energy operators \hat{T} for electrons and nuclei, potential terms (V), for electronelectron repulsion, nuclear-nuclear repulsion and electron-nuclear attraction. A time-dependent variant also exist and is discussed in depth in Chapter 6.

In considering special relativity, the Dirac equation for a single electron is the equivalent of the Schrödinger equation in nonrelativistic quantum mechanics. The Dirac equation includes scalar-relativistic and SO coupling effects, requiring four coordinates—one time and three spatial coordinates—and has solutions that are wavefunctions with four components (bispinors). Any method that incorporates the Dirac equation in some way is usually referred to as a 4-component (4c) method. However, for many electron systems there is not a direct analogue of the Dirac equation; instead, there is an approximately relativistic many-electron equation, the Dirac-Coulomb-Breit equation.¹⁶ This equation resembles the Schrödinger equation equation, and is usually expressed as¹⁷

$$\mathcal{H}^{R} = \mathcal{H}^{NR} - \underbrace{\frac{p_{i}^{4}}{8m^{3}c^{2}}}_{\text{mass-velocity}} + \underbrace{\frac{1}{4m^{2}c^{2}}\boldsymbol{\sigma} \cdot [(\nabla V) \times \mathbf{p}_{i}]}_{\text{spin-orbit}} + \underbrace{\frac{1}{8m^{2}c^{2}}(\nabla^{2}V)}_{\text{Darwin}}$$
(2.11)

Here, the one-electron part of the Hamiltonian is replaced by Dirac operators and a retardation term (the Darwin term) is added to the two-electron part. Taking out the Darwin term gives the Dirac-Coulomb equation, but the wavefunction solutions will still retain all 4 components from the Dirac equation.¹⁶

Implementing these equations is not straightforward, as the energy spectrum of the Dirac and the Dirac-Breit equation spans a continuum at negative energies that extends to $-\infty$, making them unsuitable to variational schemes. Practical implementations invoke a 'no-pair approximation' and implicitly project out the negative-continuum states. This leads to a 4c Hamiltonian bound from below. Current implementations of 4c methods are based on Hartree-Fock (termed Dirac-Fock), configuration interaction (CI), multiconfigurational self-consistent field (MCSCF), coupled cluster (CC), and density functional theory (DFT) methods. In practice, however, the 1- and *N*-particle basis set requirements restrict the highly accurate, generally applicable 4c multireference electron correlation methods (MRCI and MRCC) to molecules with only a few atoms.¹⁶

There are a number of transformation and elimination techniques that alter the Hamiltonian to project out the negative energy solutions, reducing the number of components in the wavefunction to two (spinors). In common use are the Douglas-Kroll-Hess¹⁸ (DKH) Hamiltonian, and the zero/first-order regular approximations (ZORA/FORA). The resulting methods are called 2-component (2c) electronic structure methods. The 2c methods include any spin-dependent terms, and will exactly reproduce the positive energy spectrum of the Dirac-Breit equation in the limit of an infinite-order unitary transformation. There are implementations of 2c SCF, CI, MCSCF, and CC as well as 2c

DFT for ground state energies and gradients and 2c TD-DFT for the calculation of excited states including SO coupling.

Removing vector effects by not including the SO coupling term results in the scalar-relativistic Hamiltonians, (such as the scalar DKH approximation) where the wavefunctions include only a single component, thus called 1c methods. Another economical alternative are relativistic effective core potentials (RECPs) with and without SO coupling terms. They constitute parameterized potentials which reproduce either experimental or computed data.¹⁹ Scalar-relativistic electronic structure methods are usually implemented as extensions to nonrelativistic quantum chemistry software packages.

Because 1c methods are unable to describe SO-coupling and 4c methods are computationally limited by their high cost, 2c methods are often the method of choice. 2c methods can be further divided into methods that incorporate SO coupling in the orbital optimization step and methods that use a basis of real, spin-averaged MOs which address SO coupling effects during the treatment of correlation. Both methods are equivalent in the limit of full CI, however, the latter method is more approximate for treatments that have incomplete electron correlation. This treatment of electronic correlation can be described in an MO-based formalism, where spin polarization is not present at the MO optimization stage. This must be recovered in a correlation step by use of a singly excited configuration state function (CSF) for a wavefunction expansion. That said, a MO-basis still works well across the periodic table.¹⁶

2.3.2 Computational Methods

Douglas-Kroll-Hess The most popular all-electron method in computational use is the DKH method, generally the second and third order expansions.²⁰ In this formalism, the Dirac Hamiltonian is utilized, and the four components are decoupled into two sets of two components by means of a unitary transformation

$$H_{\rm DKH} = U H_D U^{-1} = \begin{bmatrix} H^+ & 0 \\ 0 & H^- \end{bmatrix}$$
 (2.12)

The element H⁺ relates to the electronic energies and the H⁻ element relates to the positronic energies. The positronic energies are disregarded and only the H⁺ is used without affecting the electronic energies. Further approximations can be made by removing spin components, but this will neglect spin-orbit effects. ^{16,19} In computational implementations, this is usually the route taken, and the transformation of the two-electron interaction and often the SO-coupling terms are not included. Advantages of the DKH method are that it is variationally stable, and often gives better results than Breit-Pauli based methods. As for disadvantages, the operators are very complicated, and matrix elements cannot be computed analytically and must rely on numerical methods, which can be particularly problematic in the calculation of higher-order derivatives.^{21,22}

Pseudopotentials There exists another popular method that is used extensively in relativistic cases that uses a valence only approach as opposed to the previously discussed all-electron methods. These methods treat the core and valence electrons distinctly and at various levels. One such way is to use atomic orbitals for the core electrons, known as the frozen core approach, then model the core electrons with one of the many possible potentials. The effective core potential (ECP) is the most frequently used computational chemistry approach to account for relativistic effects. In the creation of the ECP, nodeless pseudo-orbitals that resemble the true valence orbitals in the bonding region are made.

$$\psi_{\nu}(\mathbf{r}) \to \tilde{\psi}_{\nu}(\mathbf{r}) = \begin{cases} \psi_{\nu}(r) & (r \ge r_{C}) & \text{original orbital in outer region} \\ f_{\nu}(r) & (r < r_{C}) & \text{smooth polynomial in inner region} \end{cases}$$
(2.13)

The idea behind RECPs is that the core electrons do not have much effect on the chemistry of the atom and can be replaced by a simple one-electron operator. The valence electrons are explicitly treated in the calculation. To account for relativity, these potentials are parameterized, usually from all-electron calculations with the DHF method or to experimental values for properties like enthalpies, dissociation energies, or geometries, to name a few. The Fock operator is split into two terms, one that accounts for the valence electrons and the other that represents the effective core potential. ECP's are useful in calculations, as they can reproduce intermolecular overlap integrals

very well and can result in accurate structures. The absolute correlation energy may be overestimated, however, relative to correlation calculations done with orbitals not modified for an RECP.

Approaches for the creation of the potentials include using standard non-relativistic quantum chemistry techniques, where the effects of the relativistic core are projected to the valence region by the pseudopotential. Another important method is to fit matrix elements of the valence Hamiltonian, which attempts to reproduce the low-energy atomic spectrum using correlated calculations. This approach is used by the German School^{23–25} of pseudopotential developers, whose models see extensive use in the literature, providing very good accuracy. For actinide and lanthanide calculations, these particular potentials have largely become the most commonly used approach.¹⁹

CHAPTER 3

EFFICACY OF DENSITY FUNCTIONALS AND RELATIVISTIC EFFECTIVE CORE POTENTIALS FOR LANTHANIDE-CONTAINING SPECIES: THE LN54 MOLECULE SET

The following is a reprint of the journal article²⁶ taken with permission from ACS. The majority of the calculations and analysis in this project were done by Lucas Aebersold. Stephen Yuwono aided in calculations, and discussions. The B_1 diagnostic calculations were done by George Schoendorff.

3.1 Introduction

The accurate prediction of the thermodynamic properties for lanthanide-containing species is of great importance due to the use of lanthanide-containing species in many fields such as nuclear energy, national defense, electronic industries, and catalysis. However, the electronic structure of lanthanides and lanthanide-containing compounds makes the effective computational study of such species difficult. In particular, complexities arise from the high number of core electrons, the multireference character of the partially filled f-orbitals, and increasingly significant relativistic effects. These complexities limit any quantum chemical methods that rely on all electron approaches, as the computational cost quickly becomes prohibitive for many practical applications involving the lanthanides.

The large number of electrons in lanthanides makes computationally efficient methods, such as density functional theory (DFT), of significant interest. DFT is a common choice across the periodic table, generally known for its lower computational scaling in comparison to ab initio correlated methods, typical ability to predict ground state structures, and, overall, ability to predict energetic properties with qualitative accuracy (though there are numerous exceptions), and is widely used even for *d*-block^{27–29} and *f*-block species. ^{30–32} However, an important and often overlooked potential problem with DFT is that many of the density functionals are parameterized with respect to properties of main group elements, with very little, if any, parameterization based on *d*-block or *f*-block molecules.⁴ This naturally raises questions as to the efficacy of the utilization of DFT for
lanthanides.

Another important concern with the use of DFT for lanthanide-containing species arises due to the multireference character of the partially filled *f*-orbitals in lanthanides. For example, the low-lying excited states of NdF have been shown to have multiple crossing points with the ground state near the equilibrium geometry.³³ DFT approaches are largely implemented as single-reference methods, and in molecules like NdF it is very likely that DFT calculations may converge to one of the low-lying excited states rather than to the ground state.³⁴ This problem can be alleviated by using multireference methods such as complete active space SCF (CASSCF),³⁵ but multireference methods usually scale combinatorially with the size of the active space making them generally more computationally demanding than many wave function based single reference approaches. Because DFT ultimately depends upon the total electronic density rather than orbitals, static correlation effects can be captured though in an unpredictable manner.⁴ For the lanthanides, a treatment of relativistic effects is essential due to the high nuclear charges. This can be done using a number of different approaches explicitly using a Douglas-Kroll approximation-based method, ^{18,21,36} zeroth-order relativistic approximation (ZORA),^{37,38} or infinite order two component approach,^{39,40} etc. Alternatively, relativistic effects can be incorporated implicitly via the use of a relativistic pseudopotential such as a model potential or a relativistic effective core potential (RECP).⁴¹ RECPs treat a pre-defined number of the core electrons using a pseudopotential while simultaneously accounting for the scalar and sometimes even vector relativistic effects as the potentials as fit to high level relativistic calculations. This allows the use of an RECP to lower the computational cost dramatically in contrast to the use of an all-electron basis set because of the reduced number of electrons to be addressed explicitly within calculations. The efficacy of using ECP on *d*-block transition metals in combination with an all-electron basis has been shown in a previous study.⁴² Consequently, RECPs also have been a popular choice for the calculation of lanthanide-containing molecules. 43-48 However, a question regarding the accuracy of calculations utilizing RECPs naturally arises because even though 4f orbitals are treated as a part of the valence region, the radial extent of the 4f orbitals makes them more core-like in nature. The fact that the 5s and 5p outer core orbitals have a larger radial expectation value than the 4f orbitals

indicates the importance of core-valence correlation which can be lost if the outer core electrons are treated with a pseudopotential.

In this study, the performance of DFT used in conjunction RECPs for the prediction of thermodynamic properties of lanthanide-containing molecules was assessed with respect to experimental data.^{49–54} The average experimental uncertainties of the Ln54 set are 2.0 kcal mol⁻¹, 4.9 kcal mol⁻¹, and 4.7 kcal mol⁻¹ for the Ln54HFa, Ln54HFb, and Ln54D0 subsets, respectively. Of particular interest is the performance of RECPs in comparison to all-electron methods. The performance of DFT for the prediction of thermodynamic properties for a set of 54 lanthanide-containing species, called the Ln54 set, has been evaluated in a previous study.⁵⁵ The study provided insight as to functional performance when combined with the third-order Douglas-Kroll (DK3) treatment of all-electron basis sets. However, all-electron calculations of lanthanide-containing species can be of limited use as compared to RECP in larger molecules. Herein, the calculated results using DFT and RECPs are reported and compared to both experiment and to the results from the prior study that used all-electron basis sets with explicit treatment of relativistic effects.⁵⁵

3.2 Computational Methods

Density functional calculations were performed with the NWChem software package.⁵⁶ The Stuttgart relativistic small core (RSC) segmented/ECP set was used for lanthanide atoms (La-Lu)^{24,57}. The cc-pVTZ correlation consistent basis set was utilized for O and F,⁵⁸ whereas the DK recontracted set, cc-pV(T+d)Z-DK, was utilized for Cl^{59–62} as this allows for a direct comparison with the prior study that used all electron basis⁵⁵. Single point calculations were performed using geometries and thermal corrections obtained from the prior study to further aid a direct comparison to quantify the effects of using a relativistic pseudopotential as opposed to an all electron basis set with explicit relativistic corrections.⁴⁹ The enthalpies of formation were then calculated using the atomistic approach.⁵⁵ The geometries used correspond to the PBE0 optimized geometries from the prior all electron study as this functional provides reasonable agreement with the experimental geometries⁶³. The relatively flat potential energy surfaces of the molecules in the Ln54 set results in

computed thermodynamic properties that are relatively insensitive to small variations (see Tables A.9-A.12 in the supplementary material). The functionals considered span different levels of complexity: the local density approximation (LDA), of which the SVWN functional was utilized;^{64,65} generalized gradient approximations (GGAs) including the BP86,^{66,67} BLYP,^{66,68} PW91⁶⁹ PBE,⁷⁰ B97-D,⁷¹ and SSB-D functionals;^{72,73} meta-GGAs (mGGA) including the TPSS⁷⁴ and M06-L functionals;⁷⁵ hybrid GGAs (HGGA) consisting of the PBE0,⁷⁶ B3LYP,^{64,68,77} BHLYP,^{68,78}, B3P86,^{67,77} B97-1,^{79,80} MPW1K,⁸¹ and X3LYP functionals;^{65,66,68,69} hybrid meta-GGA (HmGGAs) including the TPSSH,⁸² M06, and M06-2X;⁸³ range-separated hybrids (RSH) including CAM-B3LYP⁸⁴ and M11;⁸⁵ and double hybrids (DH) in which B2PLYP functional was the chosen.^{71,86} All calculations were done using restricted open-shell DFT except for B2PLYP in order to allow for a direct comparison with prior work. Unrestricted open-shell DFT was instead used for B2PLYP due to the unavailability of restricted open-shell MP2 in NWChem.

The energies were calculated for the experimentally determined ground state configurations of the lanthanide species. For molecules where the experimental ground state configuration data is unavailable, an ionic assumption of the molecules was used as a starting guess, where the anions were treated as closed shells and the spin density was associated with the lanthanide cations. For example, NdF was assumed to be Nd⁺F⁻, thus the unpaired electrons are localized on the neodymium atom.^{87,88} However, if lower energy configurations corresponding to a non-ionic view were found for a molecule, than that value was used, rather than forcing an ionic state.

The molecule set used in this study is referred to as the Ln54 set and has 54 lanthanide-containing molecules with known enthalpies of formation or bond dissociation energies.⁵⁵ There are three subsets within the Ln54 set: Ln54HFa consisting of 15 molecules containing formally Ln(III) with known experimental $\Delta H_{\rm f}^{\circ}$ values. Ln54HFb consisting of 31 molecules containing formally Ln(I) and Ln(II) with known experimental values; and Ln54D0 consisting of 25 diatomic molecules with experimentally known D_0 values. The data is compared by evaluating the mean signed deviation

(MSD) and mean absolute deviation (MAD), defined as,

$$MSD = \frac{1}{N} \sum_{i}^{N} x_{i}^{calc} - x_{i}^{exp}$$
(3.1)

$$MAD = \frac{1}{N} \sum_{i}^{N} \left| x_{i}^{\text{calc}} - x_{i}^{\exp} \right|$$
(3.2)

It should be noted that in reference 32, all MSD signs were reversed as a result from subtracting x_i^{exp} from x_i^{calc} . When comparing data from this previous study, all MSDs are updated to reflect the proper definition.

Another definition that will be used as a benchmark throughout this paper is the lanthanide chemical accuracy, defined as $5.0 \text{ kcal mol}^{-1}$ in the all-electron study. This was established as the target accuracy for thermochemical calculations of lanthanide-containing compounds to account for the average experimental uncertainty for the Ln54 set.

3.3 Results and Discussion

3.3.1 Ln54HFa Set.

The Ln54HFa subset of molecules includes lanthanide atoms formally in the +3 oxidation state. The mean absolute deviation (MAD) and mean signed deviation (MSD) from experiment of the Ln54HFa set were plotted for each functional (Figure 3.1). Overall, the MSDs are equal in sign and magnitude to the MADs, showing that the functionals generally predict a higher $\Delta H_{\rm f}^{\circ}$ than experiment. The functionals with the lowest MADs are SVWN (26.5 kcal mol⁻¹), M06-L (26.2 kcal mol⁻¹), and BHLYP (26.0 kcal mol⁻¹). The MSDs for these same functionals are 24.1, 23.5, and 22.7 kcal mol⁻¹, respectively. The GGA functionals result in the poorest predictions in terms of MAD, ranging from PW91 (37.9 kcal mol⁻¹) to SSB-D (49.6 kcal mol⁻¹). Despite the high MADs, it is important to note that the GGA functionals, particularly those without dispersion corrections, predict enthalpies of formation that are higher than experiment. However, it is also noteworthy that the MADs of the Ln54HFa set using the tested functionals are always above the lanthanide chemical accuracy. The relative magnitudes of the MSDs compared with the MADs indicate that

this is systematic behavior. On the other hand, the range separated hybrid M11 and the double hybrid B2PLYP have low MSD-to-MAD ratios, indicating their predications are not systematic. A high MSD-to-MAD ratio indicates that there is a systematic deviation in the calculated enthalpies of formation. This is the definition of systematic deviation referred to for the rest of this study. On the contrary, a low MSD-to-MAD ratio means that some of the calculated data points are higher and some of the data points are lower than experimental values throughout the subset. This indicates that the deviation is not systematic, thereby decreasing the predictive power of the tested method outside the test set.



Figure 3.1: MSD (left blue bars) and MAD (right orange bars) values of $\Delta H_{\rm f}^{\circ}$ (kcal mol⁻¹) with respect to experimental values for the Ln54HFa subset containing Ln in the +3 formal oxidation state. Functionals are listed in order of increasing complexity from the local density approximation (SVWN) to a double hybrid (B2PLYP).

With the Ln54HFa set, the most extreme deviations occurred for lanthanides with significant multireference character, i.e., when the lanthanide is neither in a closed-shell nor half-filled configuration ([Xe], [Xe]4 f^7 , and [Xe]4 f^{14}). To show this behavior explicitly, the computed enthalpies of formation were plotted along with the experimental values for the species that comprise the Ln54HFa set (LnF₃ and LnCl₃). The plot for LnF₃ is shown in Figure 3.2 and a similar plot for LnCl₃ is

provided in the supplementary materials (Figure ??) as well as values for each of the computed enthalpies of formation. The average enthalpies of formation for each functional class are used to clarify the distinction between the different types of functionals. The accuracy achieved using the DFT functionals decreases drastically for compounds that possess multireference character due to the partially filled f shell. While common implementations of density functional theory are single determinant methods, some degree of static correlation is accounted for by pure functionals albeit in an unpredictable manner.⁸⁹ This likely contributes large variations in MSD and MAD among the functionals for the species with multireference character. Furthermore, the values predicted with the DFT functionals deviate highly from each other as can be seen in Figure 3.2. When looking at the predicted values for La to Gd, all of the functionals produce deviations that are all in a similar range, i.e., the predicted values are more precise in that the different functionals predict similar values though computed enthalpies of formation also become less accurate with respect to the experimental values as the *f*-shell is filled. Then, for Gd and Ho, the functionals predict vastly different enthalpies. There also seems to be a relationship between error prediction and exact exchange – predicted errors are higher among functionals containing more exact exchange. This effect of exact exchange continues to be prevalent in the later subsets.



Figure 3.2: Comparison of average predicted $\Delta H_{\rm f}^{\circ}$ enthalpies of formation of each functional class and experimental $\Delta H_{\rm f}^{\circ}$ for LnF₃. Experimental values are depicted as black squares connected with a solid line. Functional classes are connected with dashed lines, with values corresponding to the colored markers depicted in the legend.

3.3.2 Ln54HFb Set.

The results for the Ln54HFb subset are provided in Figure 3.3. The Ln54HFb consists of molecules with the lanthanide formally in the +1 and +2 oxidation states. In contrast to the Ln54HFa set, the MADs for the Ln54HFb subset are smaller and range from 20 to 30 kcal mol⁻¹. The best performing functionals are SVWN, TPSS, and TPSSH each with MADs of 20.8, 21.9, and 21.6 kcal mol⁻¹, respectively. The poorest performance is for the M06-2X functional with an MAD of 31.9 kcal mol⁻¹. The lanthanide chemical accuracy is not achieved in the Ln54HFb set, just as observed in the Ln54HFa set. Furthermore, of note is that GGA functionals no longer predict consistently higher MADs than other functional classes as was observed with the Ln54HFa set. Although the reduction in error compared with the Ln54HFa subset is most prominent for the GGA, all of the MADs are lower by some extent. This indicates that the formal oxidation state of the lanthanide must be considered before selecting an appropriate functional. However, the performance

of the various functionals in the Ln54HFb subset is not better than with the Ln54HFa subset. The MSDs of the Ln54HFb subset were noticeably smaller in magnitude than the corresponding MADs. This indicates that the functionals do not produce a systematic error when computing enthalpies of formation. So, despite the increase in accuracy in the Ln54HFb set compared to the Ln54HFa set, there is a loss in precision.



Figure 3.3: MSD (left blue bars) and MAD (right orange bars) of $\Delta H_{\rm f}^{\circ}$ (kcal mol⁻¹) with respect to experimental values for Ln54HFb subset containing Ln in the +1 and +2 formal oxidation states.

To highlight the differences in signed error that occur for the Ln54HFb set, plots of calculated and experimental enthalpies of formation of LnCl₂ and LnO are shown in Figures 3.4 and 3.5, respectively. Though it appears from the signed errors that most functionals predict enthalpies of formation that are higher than experiment, there are two notable exceptions. The errors obtained with the BHLYP and MPW1K functionals indicate that they predict enthalpies of formation that are lower than experiment for both GdO and GdCl₂ (see supplemental Tables A4-A7). In both figures, the same trend in accuracy and precision occurs around the Ln species dominated by single-reference character as was shown with the Ln54Ha subset.

3.3.3 Ln54D0 Set.

The Ln54D0 subset consists of diatomic molecules with experimentally known bond dissociation energies. The MADs and MSDs for the calculated bond dissociation energies of the LnO and LnF diatomics are shown in Figure 3.6. The best performing functionals are SVWN, PBE, and PW91 with MADs of 21.0, 22.9, and 23.5 kcal mol⁻¹, respectively. In the previous subsets, the top performing functionals are within 1 kcal mol⁻¹ difference of MAD from each other. Yet, in the Ln54D0 subset, this difference is larger, as the MAD of SVWN is approximately 2 kcal mol⁻¹ lower than PBE. Additionally, SVWN is the only functional that retains a positive MSD, whereas the rest of the functionals have negative MSDs that are typically much smaller in magnitude than the MADs. This indicates that SVWN systematically predicts overbinding, which is consistent with previous observations for LDA calculations.⁹⁰ Additionally, the same trends in the accuracy of the computed bond dissociation energies with respect to the other functionals are present. These same trends were also present for both of Ln54HFa/b subsets (Figure 3.7), i.e. the best agreement with experiment occurs for molecules that can be described with single determinant.



Figure 3.4: Average predicted $\Delta H_{\rm f}^{\circ}$ (kcal mol⁻¹) of each functional class and experimental $\Delta H_{\rm f}^{\circ}$ for LnCl₂. Experimental values are depicted as black squares connected with a solid line. Functional classes are connected with dashed lines, with values corresponding to the colored markers depicted in the legend.



Figure 3.5: Average predicted $\Delta H_{\rm f}^{\circ}$ of each functional class and experimental $\Delta H_{\rm f}^{\circ}$ for LnO. Experimental values are depicted as black squares connected with a solid line. Functional classes are connected with dashed lines, with values corresponding to the colored markers depicted in the legend.

Among all three sets, a correlation between exact exchange and a subsequent increase in error is present. To show this trend, the MADs for each Ln54 subset of the M06-L, M06, and M06-2X functionals are compared in Table 3.1. These particular functionals differ only in the amount of exact exchange used allowing for a direct comparison of the effects of exact exchange to be made. From the table, there is indeed a clear increase in MAD error as the percentage of exact exchange is increased, which is in line with previous observations from the all-electron DFT study.⁴⁹ Further supporting this correlation is the fact that both the 4f orbitals and the outer core electrons that are treated explicitly with the small core ECP are highly localized on the lanthanide in the molecules. The inclusion of exact exchange introduces non-locality in the functional. It is also shown that the effect is more significant in the Ln54HFa set than in the Ln54HFb subset. The correlation with exact exchange was observed with the all electron calculations, but it is less pronounced when the core electrons are removed with the ECP.



Figure 3.6: Ln54D0 subset MSD (left blue bars) and MAD (right orange bars), in kcal mol⁻¹, for the calculated bond dissociation energies taken with respect to experimental values reported for each of the 25 lanthanide-containing diatomics composing the Ln54D0 set.



Figure 3.7: Averaged predicted D_0 (kcal mol⁻¹) or in the case of LDA and DH average predicted of each functional class and experimental D0 for LnO. Experimental values are depicted as black squares connected with a solid line. Functional classes are connected with dashed lines, with values corresponding to the colored markers depicted in the legend.

 B_1 Diagnostic. The B_1 diagnostic is a DFT-based multireference diagnostic that relies on the energies obtained with the BLYP and B1LYP functionals (Eq. 3.3).⁹

$$B_1 = \frac{BE_{BLYP} - BE_{B1LYP/BLYP}}{n}$$
(3.3)

Table 3.1: MAD (kcal mol^{-1}) values for the three Ln54 subsets computed with the Minnesota functionals: M06-L, M06, and M06-2X, which have increasing percentages of exact exchange, respectively.

Functional	exact exchange	Ln54 Subset					
		Ln54HFa	Ln54HFb	Ln54D0			
M06-L	0.00%	26.2	26.7	31.1			
M06	27.00%	32.9	28.2	35			
M06-2X	54.00%	38.9	31	40.8			

In equation 3.3, the B_1 value is a difference in bond energies (BE) obtained with the BLYP functional and the B1LYP functional at the BLYP geometry while *n* is the number of bonds being broken. Thus, the B_1 diagnostic is scaled to be the energy difference per bond. It has been

suggested that a 10 kcal mol⁻¹ threshold could be used to determine if a molecule has significant multireference character, but it is at best simply a guideline. Lanthanide containing molecules often exhibit significant multireference character that is largely due to the incomplete occupation of the 4fshells that occurs for species that do not have a $4f^0$, $4f^7$, or $4f^{14}$ occupation. This is often the cause of multireference character arising in lanthanide complexes where the lanthanide is formally in the +3 oxidation state as the 5d and 6s orbitals remain unoccupied as is the case with the molecules in the Ln54HFa set. The B_1 values for each molecule in the Ln54 set are shown in Table 3.2. It can clearly be seen that the trihalide species with lanthanides near the ends or middle of the series have low B_1 diagnostic values while those in the intermediate regions of the lanthanide series tend to have the largest B_1 values that exceed the 10 kcal mol⁻¹ guideline. Additional static correlation effects arise when the lanthanide is in a low formal oxidation state. In the +2 and +1 oxidation states, the 5d and 6s orbitals can be occupied. This leads to covalent bonds as well as near degeneracies due to the partially filled 5d and 4f shells. Despite this, the dihalide species tend to have low B_1 diagnostic values with only two exceptions - SmCl₂ and TbCl₂. The lanthanide monoxides, however, have far higher B_1 diagnostic values suggesting significant multireference character particularly for the latter half of the lanthanide series. The lanthanide monofluorides typically have B_1 values that exceed 10 kcal mol⁻¹ as well with the exceptions being LaF, EuF, GdF, TbF, TmF, and YbF. This can be rationalized based on the electronic configurations of the Ln⁺ species. La+ has a $5d^2$ ground state, so the static correlation arises primarily from the incomplete 5d shell, though some of this should be alleviated due to ligand field splitting. Eu⁺ has a $4f^7 6s^1$ ground state so that both the 4f and 6sshells remain half-filled. Likewise, the remaining species—Gd⁺, Tb⁺, Tm⁺, and Yb⁺—all either preferentially populate the 6s orbital over the 5d in the ground state, or population of the 6s orbital corresponds to a low-lying excited state that may be significant in a molecular environment.

Ln	LnF3	LnCl3	LnF ₂	LnCl ₂	LnF	LnO
La	7.4	1.2	8.7	2.2	9.8	16.3
Ce	4	2.2		0.4		11.2
Pr	20.2	29.4		2.9	10.7	8.6
Nd	24.9	49.6		2.1	39.8	10.3
Sm			4	97.8		14.5
Eu			7.1	0.3	7.3	21.6
Gd	1.2	2.4		0.4	6.1	13.4
Tb	5.5			158.4	4.6	17.5
Dy	15.2				195.7	36.6
Но	0.4			0.1	11.2	23.3
Er	20.3			1.6	51.2	65.1
Tm					4.7	115.6
Yb					8.4	318.3
Lu	5.7				26.3	18.5

Table 3.2: Values for the B_1 diagnostic for multireference character using B1LYP/BLYP.

3.3.4 Ln54 Set.

For the overall Ln54 set, the choice of an RECP to treat relativity for lanthanide compounds, as opposed to an all-electron approach that still considers every single electron, is examined. To show the comparison between the predictions made using RECPs versus those made using all-electron basis sets and the third-order Douglas-Kroll approach, MADs obtained from the RECP and the previous all electron study ⁵⁵ were plotted for each Ln54 subset (Figure 3.8). Each subset comparison is depicted in Figures 3.8a–c, with Ln54HFa (top), Ln54HFb (center), and Ln54D0 (bottom), respectively. For LDA (SVWN), both methods give approximately the same MADs of 20 kcal mol⁻¹. However, for the GGA functional class there is a clear increase in the RECP MAD predictions compared to those of the all-electron basis set. This difference is most pronounced in the Ln54HFa and Ln54HFb subsets where the RECP MADs are 7.6 to 13.6 kcal mol⁻¹ larger than the results obtained previously with all-electron basis sets and an explicit treatment of relativistic effects.⁵⁵ The significant differences between the RECP and all-electron energies may result from the

replacement of the core electrons with a smooth polynomial and the nuclear charge with an effective nuclear charge in the ECP. This effectively results in the loss of most of the highly localized core leading to the most notable decreased performance with the semi-local GGA functionals. Another notable observation is that the difference in MADs are consistently more than 10 kcal mol⁻¹ in all subsets for B97-D and SSB-D, which could be attributed to the empirical dispersion correction utilized in the functional.



Figure 3.8: Comparison of the MADs (kcal mol^{-1}) for the (a) Ln54HFa, (b) Ln54HFb, and (c) Ln54D0 subsets of both the RECP calculations (red circles) and the all-electron calculations from the prior study⁵⁵ (blue triangles) for all 22 tested density functionals.

The superior performance of the all-electron approach over the RECP treatment is less pronounced when increasing the functional complexity beyond the GGAs. The differences between

the MADs does not favor either approach over the other. Often, the MAD values are nearly the same for some functionals, e.g. TPSSH, where the values are within 2 kcal mol^{-1} for each subset. In other cases, a functional will perform better with an RECP in one subset, but in another it will perform better with an all electron basis set. A good illustration of this occurs in the B3P86 where the MAD value obtained with an RECP for the Ln54HFa subset is 5 kcal mol⁻¹ lower than the MAD obtained with an all electron basis set with explicit treatment of relativistic effects. However, the opposite trend is observed for the Ln54b subset. As for the Ln54D0 subset, the MADs are within 0.1 kcal mol^{-1} of each other between the two approaches preventing a definitive conclusion. The only difference between the two approaches is how the core electrons and relativistic effects are handled. The scalar relativistic effects affect the core directly while the valence orbitals are mostly affected indirectly in response to the changes in the core. To illustrate the effect of relativistic treatment, consider the 6s orbital since it is the most diffuse valence orbital and as an s orbital the valence orbital most affected by relativistic effects. With the PBE functional the radial expectation value, $\langle R \rangle$, of the 6s orbital for Yb is 3.6598 au with the all electron set and 3.5858 au with the RECP-a difference of only 0.0740 au. Thus, the removal of the core electrons is by far the most significant difference between the two approaches. It then can be seen that the change in the density has a significant impact on the performance local and semi-local density functionals in particular. This is to be expected as the core is highly localized and its removal results in a more delocalized density. Yet the outer core electrons remain localized on the lanthanide resulting in improved performance of the local and semi-local functionals when compared to the hybrid and double hybrid functionals nonetheless.

In conclusion, the local and semi-local functionals performed best for the Ln54 set. The nonlocal hybrid and double-hybrid functionals resulted in the poorest performance, and predicted the energetic properties of the Ln54 set in an inconsistent manner, i.e. there was less systematic error for the non-local functionals. In general, the performance of the hybrid functionals decreased as more exact exchange was included. The general lack of systematic deviations for the hybrid and double hybrid functionals is most notable for the lanthanide compounds known to have significant multireference character. Due to the difference in sign between the MSD in the Ln54HFa/b and the Ln54D0 set the MSD of the combined Ln54 set is small relative to the MAD due to cancellations. However, SVWN generally produces a systematic error with a positive deviation in all Ln54 subsets in contrast to the rest of the functionals. SVWN also has the lowest overall MAD at 22.1 kcal mol⁻¹ and a MSD of 13.5 kcal mol⁻¹. The PBE and TPSS functional are comparable with SVWN with MADs of 27 kcal mol⁻¹ and 25 kcal mol⁻¹, respectively, though the smaller MSDs in comparison to their MADs associated with these functionals indicates less systematic energy predictions. The computed energy could be an overestimate or underestimate from the true value without any clear indication as to which, unlike SVWN which will in most cases overestimate energies. Finally, when examining the performance of the functionals in each class, it is clear that the functionals with a minimum of parameterization typically perform the best, i.e. SVWN, PBE, TPSS and TPSSH for the LDA, GGA, mGGA, and HmGGA functionals, respectively. Parameterization appears to negatively impact the quality of the results obtained with each functional, though this should be expected as no functional has been parameterized for use with lanthanides.

3.3.5 Conclusions.

A range of density functionals spanning multiple functional forms has been assessed for their ability to predict enthalpies of formation and bond dissociation energies of the Ln54 molecule set. The effect of the use of a relativistic ECP was examined and contrasted with the results obtained using all electron basis sets and an explicit treatment of relativistic effects.⁵⁵ SVWN is shown to be the best performing functional for the Ln54HFa, Ln54HFb, and Ln54D0 subsets and for the overall Ln54 set. The MAD and MSD for SVWN is 22.1 kcal mol⁻¹ and 13.5 kcal mol⁻¹, respectively, for the combined Ln54 molecule set. The lanthanide chemical accuracy, defined to be 5.0 kcal mol⁻¹, is not achieved using DFT and RECP throughout the Ln54 set. It has also been shown that the errors obtained with the SVWN functional tend to be systematic in contrast to the errors obtained with other functionals. The systematic deviation obtained with SVWN combined with its relatively low MAD makes it a favorable choice to use for predictive calculations of thermodynamic

properties of lanthanide-containing molecules. A comparison between the use of RECPs and allelectron basis sets yields the same observation that the local functionals typically perform better than non-local functionals for the computation of thermodynamic properties when lanthanides are involved. However, GGAs with RECPs are the most sensitive to the removal of the core electrons when compared with the performance of GGAs when all electrons are treated explicitly. This is due to the loss of some of the locality of the density due to the replacement of the highly localized core of the lanthanides. Finally, hybrid and double hybrid functionals perform roughly the same for the prediction of thermodynamic properties when either RECPs or all electron basis sets are used, though the non-local character of the hybrid and double hybrid functionals leads to their poor performance overall for the Ln54 molecule set.

CHAPTER 4

ACTINIDES

All calculations in this chapter were carried out by Lucas Aebersold.

4.1 Introduction

Actinide compounds are of interest in many applications, with the use of actinide oxides in nuclear fuel cycles being one of the most common.^{20,91} Other applications in medicine, energy production and catalysis are widespread, and include actinide use in cancer therapy, smoke detectors, heart pacemakers, power sources, missiles, and actinide-doped materials to achieve properties such as luminescence. While there are many uses of actinides, there are also significant ongoing environmental challenges, in terms of the nuclear waste generated as a byproduct towards its many applications. Transuranic elements, which contribute the most heat to underground storage facilities, have half-lives on the order of tens-to-ten thousands of years. Separating these species from the waste makes their transmutation into species that decay much faster more feasible and also facilitates potential reuse.² Thermochemistry is an essential key to the nuclear separation process, the design of new actinide-based catalysts and applications, and improvement of existing processes.

In addressing actinide species, computational chemistry provides a vital route towards describing their thermochemistry, in part, due to the inherent difficulties of experimental work with such compounds.⁹² However, computational methods have their own challenges. Calculations on *f*-block species are inherently difficult due to the preponderance of nearly-degenerate states, the influence of relativistic effects, and the need to account for high levels of electron correlation, which all pose significant demands on electronic structure methods. Combining the methodological requirements for *f*-block species makes even small molecule calculations costly in terms of computer time, memory, and disk space.

There are several routes that can be used to account for relativistic effects, with Hamiltonians that incorporate various levels of relativistic effects. One of the most accurate methods for the treatment

of relativistic effects is the four-component Dirac-Hartree-Fock (DHF) method. A drawback of the method, however, is that it is computationally demanding, largely restricted to very small molecules, and careful analysis is required to collect meaningful results. More approximate two-component methods such as Douglas-Kroll-Hess (DKH) and zeroth-order regular approximation (ZORA) allow the inclusion of effects such as scalar relativistic contraction and spin-orbit coupling, while enabling a significant reduction of computational effort relative to DHF-based approaches.

As molecule size increases, even these approximate methods can become too computationally costly, and instead, scalar relativistic corrections are considered in a one-component representation, incorporating effects of relativity within relativistic effective core potentials (RECPs).⁹³ These Hamiltonians can be used with standard wavefunction based methods and density functional based methods. As molecules get bigger in terms of the number of electrons, the computational cost soars. Thus, rather than using ab initio methods (CCSD, MRCC, etc.) Kohn-Sham density function approaches become more favorable. This is especially the case for heavy elements due to the efficiency of DFT approaches relative to *ab initio* approaches, enabling molecules of larger size to be investigated, while accounting for electron correlation.

Most density functional approaches, however, were designed for the study of main group species, largely with parameterization based upon properties of main group species, with only a limited number of functionals incorporating any transition metal chemistry data in their parameterization, and, of those, very little transition metal data is used. This suggests that significant examination of property prediction be done to help ensure the utility and relevance of the functionals in this regime of the periodic table.

In considering a broad perspective of functional performance across the periodic table, for main group energetics, overall, the root mean square deviation of over 1,000 energies from experiment is $\sim 2-4$ kcal mol⁻¹, generally depending upon functional class.⁹⁴ For 3*d* transition metals, this deviation increases, overall, so that the best functionals for a set of ~ 200 enthalpies of formation different from experiment with a root mean squared deviation (RMSD) of 6–9 kcal mol⁻¹. It is important to note as well, however, that reported experimental uncertainties for these different energy

sets also increase across the periodic table.^{26,95} Nevertheless, there is still a need to take stake of the performance.

In recent work on the lanthanides, it was observed that overall, there is a deviation in the enthalpies of formation and dissociation energies for the Ln54 set, a set of 54 lanthanide energies from experiment, of $\sim 1 \text{ eV}$.^{26,96} This is a sizable error, especially considering the small molecules that were investigated. While there are *ab initio* methods that markedly reduce this error, the computational demands can quickly become daunting. In the present study, the impact of functional and basis set choice, as well as the impact of spin-orbit effects, on the energy predictions for actinides, is considered.

4.2 Computational Methods

Density functional calculations were performed on a set of actinide compounds and their constituent atoms. The actinides chosen are based on our compilation of 66 actinide energies from experiment—which we call the An66 set. 18 commonly used functionals were used, representing several families of functionals, some of which have performed the best in prior DFT studies of transition metal or lanthanide species, including: the local spin density approximation (LSDA) SVWN^{64,65}]; the generalized gradient approximations (GGA) [BP86^{97,98}, BLYP^{68,97}, PW91⁶⁹, and PBE⁹⁹]; meta-corrected GGAs (mGGAs) [TPSS⁷⁴ and M06-L⁷⁵]; a variety of hybrid GGAs with various levels of exact exchange [B3P86^{78,98}, X3LYP^{65,68,69,97}, B97-1^{80,100}, B3LYP^{68,78}, PBE0¹⁰¹, MPW1K⁸¹, BHLYP^{68,78}]; meta-hybrids [TPSSH¹⁰², M06⁸³ and M06-2X⁸³]; and the double hybrid functional B2PLYP.^{71,86} All calculations were performed with the NWChem⁵⁶ computational suite of software.

The effects of all-electron methods and relativistic effective core potential methods were analyzed. For the RECP calculations, three basis sets from the Stuttgart family of RECPs were considered for each actinide atom. All RECP basis sets used the same small core pseudopotential fit to the quasi-relativistic Wood-Boring results for many electrons (ECP60MWB). $^{103-105}$ The first basis set, the Stuttgart 1997 RSC (S97) is a (12s11p10d8f)/[8s7p6d4f] segmented contracted basis set, that is less demanding computationally with respect to other commonly used RECP basis.¹⁰⁴ However, as noted by Cao et al.¹⁰⁴ the basis set has specific drawbacks. Thus, for geometry optimization the (14s13p10d8f6g)/[6s6p5d4f3g] segmented contracted atomic natural orbital (SEG) basis, given by Cao and co-workers¹⁰⁶ was used for all actinide compounds.

Additionally, the pVQZ quality (14s13p10d8f6g)/[6s6p5d4f3g] general contracted atomic natural orbital (ANO) basis¹⁰⁴ was used for single point energies. For the lighter ligands O, F, Cl the cc-pVTZ basis sets (cc-pV(T+d)Z for Cl) were used^{107,108}. For the heavier ligands Br and I, relativistic effects should be addressed, thus the small-core Stuttgart-Köln ECP10MDHF and ECP28MDHF pseudopotentials with the cc-pVTZ-PP basis sets were employed.¹⁰⁹

Geometry optimization was performed with the TPSS⁷⁴ meta-GGA functional using the unrestricted Kohn-Sham formalism. The TPSS functional was selected, based on its effectiveness in systems with many degenerate states.^{8,74,99} The optimized structures were used in the ANO and AE calculations. As such, optimizations with other basis sets were not considered. For molecules that have available experimentally determined states (i.e., actinide oxides), the DFT calculations were aligned with those states.²⁰ To determine the ground state multiplicity of compounds with no experimental reference, calculations were done across a range of likely multiplicities and states. The orbital vectors were checked, and rotations done if needed to identify the lowest energy state possible. This state was used as the ground state for all calculations. Vibrational frequencies were calculated with NWChem's built in numeric methods, and no imaginary frequencies were present for the final optimized structures.

In prior studies on small lanthanides, in general, functional choice for the geometry optimization results in small differences in the overall prediction of the computed enthalpies of formation (considering the magnitude of error).^{26,96} For example, in a previous DFT study of the lanthanides, structures optimized with SVWN, PBE, TPSS, M06-2X, and PBEO resulted in enthalpies of formation and bond dissociation energies that differed, largely by less than a single kcal mol⁻¹.⁹⁶ Thus, the structures optimized with TPSS were utilized in single-point calculations for all of the other functionals and basis sets for each compound. Spin–orbit DFT (SO-DFT) calculations were performed using NWChem's SO-DFT method for the SEG and ANO basis with the small-core Stuttgart RECPs. For the all-electron calculations, the third-order Douglas-Kroll-Hess method²², as implemented in NWChem¹¹⁰, was used. The cc-pVTZ-DK basis sets^{109,111,112} are used for of the all atoms. Third-order Douglas-Kroll-Hess was used as it has been shown to be more accurate than second-order DKH.^{111,113,114} For the all-electron calculations, DKH and ZORA are common choices. Here, the DKH method was selected as prior work suggested ZORA and DKH have similar performance.¹¹⁵

To assess the predictive capability of the functionals, a set of experimental enthalpies of formation, $\Delta H_{\rm f}^{298\rm K}$, for 66 actinide compounds was utilized (An66). The energies were taken from Nuclear Energy Agency (NEA)^{116,117} data and a recent 2014 review/survey of actinide oxides⁵³. The set of compounds includes a variety of oxides, halides, and oxohalides for actinides Th, U, Np, Pu, and Am. The thorium compounds included were: ThX_n where X = F, Cl, or Br, and n = 1–4, as well as ThO_n (n = 1,2)⁵³, ThOF, and ThI₄. For uranium the 26 compounds included were: UX_n where X = O (n = 1–3)⁵³, F (n = 1–6), Cl (n = 1–6), Br (n = 1–5), and I (n = 1–4). Additionally, the oxohalides UOF₄, UO₂F₂, and UO₂Cl₂ were included. For neptunium 9 compounds included were NpX_n where X = F (n = 1–4, 6), Cl (n = 3, 4), and O (n = 1, 2)⁵³. Plutonium compounds consisted of PuX_n where X = F (n = 1–4, 6), Cl (n = 3, 4), Br (n = 3), I (n = 3), and O (n = 1–3)⁵³. Lastly, two Am compounds were considered AmO and AmF₃.

The enthalpies were computed using a thermodynamic cycle. Linear regression analysis of computed values versus experimental values, along with mean unsigned errors (MUE) and mean signed errors (MSE) were used to assess the performance of the functionals.

4.3 Discussion

4.3.1 Geometries

The geometries of the compounds, the vibrational modes, and thermokinetic constants can be found in the supplemental material in Appendix B

4.3.2 Enthalpies of Formation

To analyze the utility of the basis sets, the all-electron DKH3 basis, the generally contracted ANO RECP basis, the segmented contracted RECP basis, and 1997 Stuttgart RECP basis are compared using several different metrics. The error from the experiment value, that is, the computed value subtracted from the experimental value was taken for each compound. The mean signed errors (MSE) and mean unsigned errors (MUE) with respect to experiment were computed for the data set as a whole and also for subsets of the data. In addition, the minimum error (most negative), maximum error (most positive), and standard deviation are also reported. To attain a better idea of the overall consistency—the distribution of the error and accuracy of the energies across a span of molecules—of the functionals, linear regression statistics, including the R^2 , slope and intercept values, were utilized. The analysis here was done by considering each subset of compounds—Th, U, and Np species, and a subset including Pu and Am compounds together due to the limited numbers of Am species.

For the actinide subsets, the MUEs in the energies for each functional and basis set are shown in Fig. 4.1. For the thorium compounds, the MUEs were the best overall, with values ranging from 5 to 10 kcal mol⁻¹, with the exception of SVWN, whose error is approximately 23 kcal mol⁻¹ for each basis. Spin–orbit coupling does not drastically affect most of the thorium species considered, likely due to the singlet nature of ThX₂, ThX₄, and ThO compounds—where X can be O, F, Cl, Br, and I. Other molecules in the set are doublets. There is also little difference arising from energies determined using the all-electron basis sets and the RECP basis sets.

The uranium compounds make up the majority of the An66 set and the trends exhibited are more complicated than for the thorium compounds. As shown in the lower left panel of Fig. 4.1, the MUEs for each functional and the respective basis set begin to diverge in the sense that there are substantial differences in the MUEs, depending upon functional. For example, the MUE of the TPSS functional is the highest at 19.6 kcal mol⁻¹ for the AE basis set, yet the MUEs for the S97, SEG, and ANO are 12.7, 12.1, and 9.9 kcal mol⁻¹, respectively. An increase in the MUE for functionals with higher amounts of exact exchange occurs for all basis sets, such as B3LYP (23%), PBE0 (25%), to



MPW1K (46%), to BHLYP (50%). However, the Minnesota functionals, M06 and M06-2X—which have 26 % and 54 % exact exchange, respectively—do not result in such an increase for uranium.

Figure 4.1: A comparison of functionals and the four basis sets, S97, SEG, ANO, and AE. MUEs for each actinide are given in the four panels in kcal mol^{-1} , the upper left shows the MUEs for all Th compounds. The lower left shows the MUEs for all U compounds, the upper right shows the results for the Np compounds and finally the lower right shows the combined MUE for the Pu and Am compounds.

Relative to the MUEs for uranium and thorium compounds, for neptunium compounds, there is an increase in the MUEs for nearly all functional and basis set selections. For the HGGAs MUEs are higher for the AE basis than for the RECP basis sets, but for the meta HGGAs this is not the case. The TPSSH functional results in the lowest MUEs of the functionals for all basis sets, with values of 8.1, 10.5, 7.8, and 8.7 kcal mol⁻¹ for S97, AE, SEG, and ANO sets, respectively. The RECP MUE values of TPPSH are similar regardless of the RECP used. The large errors in energies for the SVWN functional observed for the uranium and thorium compounds are smaller for Np, with MUE's of ~17 kcal mol⁻¹. To note, for thorium and uranium compounds, SVWN predicted far more negative enthalpies of formation than the other functionals and experiment. However, for Np, functionals other than SVWN result in MUEs that are higher than the experimental enthalpy. With SVWN's tendencies to predict enthalpies that are more negative than for the other functionals, the resulting MUE is closer to experiment. The predictions arising from the Minnesota functionals, M06 and M06-2X, are not as good for the neptunium compounds as for uranium and thorium compounds, as most MUEs range from ~20 to 30 kcal mol⁻¹.

For the plutonium and americium compounds, the MUE values are also large, and the differences arising from the basis sets choice are more evident. In contrast to the Np compounds, the AE basis set for nearly every functional results in the lowest MUE. Though the AE MUE values for Pu and Am are actually similar to the Np values, there is a large increase in the MUEs for the RECP basis sets. The TPSSH functional provides MUEs of 15.5, 10.3, 12.2 and 13.7 kcal mol⁻¹ for the S97, AE, SEG, and ANO basis sets, respectively. The TPPSH values do not show much fluctuation across the plutonium and americium compounds, as for the SVWN and Minnesota (M06) functionals with exact exchange. The M06 and M06-2X functionals experience a large decrease in performance, having MUEs in the range of 40 to 50 kcal mol⁻¹, the highest of all functionals across the actinide series. Plutonium oxides are known to have significant multireference character¹¹⁸, which can be problematic for DFT approaches, in general, and as demonstrated for actinides by a prior study on AtO^{+ 119}. This may explain the particularly high MUEs observed, especially for the functionals with higher percentages of exact exchange. Prior studies have shown that higher percentages of exact exchange in functionals leads to poorer predictions of energetics for systems with significant multireference character.^{26,119}



Figure 4.2: Mean unsigned errors in kcal mol^{-1} for the 18 functionals analyzed across the four basis sets for the overall molecule set.

	MUE				MSE			Min		Max			σ		
	SEG	ANO	AE	SEG	ANO	AE	SEG	ANO	AE	SEG	ANO	AE	SEG	ANO	AE
SVWN	25.2	23.2	25.1	-21.0	-18.3	-21.6	-90.3	-85.4	-96.6	25.2	22.8	21.7	20.7	19.5	21.4
BP86	12.0	10.7	12.1	0.2	2.4	-0.8	-35.4	-32.4	-41.9	43.3	39.5	39.3	10.2	9.7	10.5
BLYP	11.9	12.1	12.1	6.1	8.8	5.2	-25.8	-20.3	-33.2	46.1	41.8	41.8	11.1	11.1	10.9
PW91	12.9	11.3	12.8	-3.3	-1.0	-4.7	-42.9	-38.1	-50.1	39.6	35.2	34.9	10.4	9.8	11.3
PBE	12.6	11.2	12.3	-1.3	0.9	-2.6	-39.0	-35.3	-45.6	42.6	38.7	38.1	10.4	9.9	11.0
TPSS	11.0	9.2	14.9	-4.7	-2.4	-9.0	-41.0	-36.0	-46.8	33.4	26.4	29.8	8.8	7.9	10.4
M06-L	11.6	10.9	11.4	1.7	3.3	-2.9	-32.9	-29.1	-36.1	40.1	36.5	28.5	9.6	9.5	8.5
B3P86	11.9	11.4	13.0	-2.5	-0.2	-3.9	-21.9	-19.4	-28.6	33.1	32.0	29.0	7.2	7.9	7.8
X3LYP	11.6	12.0	11.6	3.9	6.4	2.6	-20.6	-17.3	-21.0	37.5	44.0	36.8	9.2	10.7	9.2
B97-1	11.6	12.1	13.1	2.7	4.7	1.5	-22.0	-19.3	-22.6	38.9	39.9	40.6	9.3	10.7	9.4
B3LYP	11.4	12.1	11.6	4.3	6.9	2.7	-20.4	-16.7	-20.8	37.9	45.7	34.7	9.4	11.1	9.2
PBE0	11.5	11.6	12.4	-0.2	2.9	-1.5	-21.1	-18.4	-24.3	35.3	40.8	36.2	8.6	9.9	8.3
MPW1K	12.7	13.6	13.5	0.5	3.3	-0.7	-21.6	-21.7	-26.0	53.3	60.0	54.4	9.7	12.2	10.6
BHLYP	14.9	16.3	15.3	6.0	9.0	5.5	-20.3	-17.4	-22.3	64.9	72.0	73.0	13.3	16.5	15.1
TPSSH	10.7	10.4	11.9	-4.8	-2.8	-6.4	-28.4	-23.6	-35.5	31.8	26.8	27.2	7.1	6.7	8.1
M06	17.0	17.6	12.8	13.1	15.0	5.9	-18.9	-12.6	-21.3	51.0	52.9	51.7	14.2	14.4	10.6
M06-2X	17.2	20.1	17.4	10.1	10.5	10.9	-21.6	-19.8	-26.0	84.1	90.8	72.6	18.5	20.8	19.3
B2PLYP	13.4	12.7	15.4	-2.5	1.1	-4.6	-41.0	-37.7	-51.4	35.7	58.6	60.4	8.9	10.4	12.5

Table 4.1: Statistical properties computed for the enthalpies predicted by each functional, for the SEG, ANO, and AE basis sets. The statistics include the mean unsigned error (MUE), mean signed error (MSE), the range of errors noted (Min and Max), all in kcal mol⁻¹, and finally the standard deviation σ .

To give an overall summary of performance, the total MUEs for all compounds are given in Figure 4.2. In Table 4.1 the MUE, MSE, range (minimum and maximum), and the standard deviations for all of the enthalpies computed for the An66 set for each functional and the AE, SEG, and ANO basis sets are provided.

For the AE basis set, the lowest MUE is achieved by M06-L and B97-1 with values of 11.4 and 11.6 kcal mol⁻¹, respectively. The MSE for B97-1 was 1.5 kcal mol⁻¹ while the MSE of M06-L was -2.9 kcal mol⁻¹, indicating that the enthalpy predictions did not strongly overestimate or underestimate the experimental values.

For the SEG basis set, the lowest MUE is achieved by TPSSH and TPSS, with values of 10.8 and 11.0 kcal mol⁻¹, respectively, and MSE values of -4.3 and -4.7 kcal mol⁻¹, respectively. The TPSSH value is slightly lower than what was determined using the AE basis set, (11.9 kcal mol⁻¹). However, the TPSS MUE is much lower than the MUE for the AE basis of 14.9 kcal mol⁻¹. The source of the larger MUE for the AE's can be attributed to the uranium compounds, where the MUE for the uranium AE was ~20 kcal mol⁻¹, compared to other compounds where the MUE was ~13 kcal mol⁻¹ (Fig. 4.2).

For the ANO basis sets, the lower MUE is achieved by TPSS and TPSSH with values of 9.2 and 10.4 kcal mol⁻¹, respectively. The MSEs for both however, are -2.4 and -2.8 kcal mol⁻¹, indicating the tendency to equally predict enthalpies that are more positive or more negative than experiment. However, the range of TPSSH is 10 kcal mol⁻¹ lower than that of the segmented sets, and the standard deviation is 6.7, which is the lowest SD for any of the functionals when paired with the ANO basis set. Of all the basis sets, the meta-GGAs and the meta-hybrid TPSSH perform the best, overall, regardless of the choice of basis. Slight improvements in MUE occur in transitioning from AE to SEG to ANO for TPSS and TPSSH. The functionals that do the poorest are those with the highest percentages of exact exchange (>40%), including BHLYP, MPW1K, and M06-2X; or SVWN, the most basic functional.

The reported experimental uncertainties of the NEA and Kovács et al⁵³ recommended values have been reported at the 95% confidence interval.⁵³ The average of the uncertainties is approximately 4

kcal mol⁻¹, thus in considering thermochemical accuracy in the computationally predicted energies, any method that can attain a MUE of ~4 kcal mol⁻¹ is of greatest interest.

4.3.3 Spin–Orbit Effects

SO-DFT calculations were performed on the An66 set, using the SEG and ANO basis sets from the Stuttgart RECP family. The summary statistics are reported in the supplemental information and in Figure 4.3, total MUEs and MSEs for DFT and SO-DFT with the SEG and ANO basis are provided. As shoown in Figure 3, there seems to be a limited difference between the overall DFT and SO-DFT MUE values in considering the entire set of molecules. However, in closer examination of each actinide, more substantial changes are noted for some of the molecule types. Generally there is an increase in the MSE for SO-DFT, however, the errors relative to experiment are more similar from one molecule to the next than for DFT. In this sense, SO-DFT enhances the functional reliability. In terms of basis sets, TPSSH with the ANO set had the lowest MUE of 9.8 kcal mol⁻¹ For the thorium compounds the SO effects were not significant, and for uranium compounds, overall, the SO effects impact the MUE by about ± 1 kcal mol⁻¹. For Np, Pu, and Am the effects of SOC are more important, (Fig. 4.4), as demonstrated by the large reductions to the MUE that occurs for all functionals except SVWN when SO-DFT is used. For the Am compounds, SOC is necessary in order to achieve the lowest MUE for the functionals, with reductions in the MUE ranging from approximately 10-30 kcal mol⁻¹, as shown in Figure 4.4.



Figure 4.3: Comparison of the DFT and SO-DFT results for both SEG and ANO bases. MUE bars are shown in purple and the MSE bars are shown in cyan.

	MUE MSE		Mi	in	Μ	[ax	σ			
	SEG	ANO	SEG	ANO	SEG	ANO	SEG	ANO	SEG	ANO
SVWN	27.9	23.3	-26.2	-21.3	-101.4	-87.5	16.7	18.0	22.9	20.3
BP86	12.1	9.8	-5.7	-0.8	-48.6	-39.6	29.9	32.4	10.7	9.0
BLYP	10.3	9.5	0.2	5.1	-39.2	-25.5	34.7	37.5	9.4	9.4
PW91	13.7	10.9	-9.2	-4.2	-56.3	-45.4	26.2	28.1	12.1	9.9
PBE	13.0	10.5	-7.3	-2.3	-52.2	-42.6	29.1	31.6	11.4	9.5
TPSS	13.0	9.9	-10.4	-6.3	-54.7	-41.2	21.3	20.0	10.7	8.7
M06-L	11.3	9.7	-4.7	-0.3	-47.9	-36.8	28.2	31.5	9.7	9.0
B3P86	11.6	9.9	-6.9	-1.9	-33.0	-18.8	18.4	23.6	6.7	6.3
X3LYP	9.8	10.2	-1.1	4.6	-23.0	-16.8	25.9	37.6	6.3	8.7
B97-1	10.9	10.3	-2.2	2.8	-22.7	-18.7	26.3	32.0	6.7	8.3
B3LYP	9.9	10.3	-0.5	5.0	-22.8	-16.6	26.1	45.4	6.3	9.4
PBE0	10.6	9.5	-4.2	0.6	-23.9	-18.3	24.4	32.2	6.1	7.1
MPW1K	11.6	12.7	-2.7	2.8	-23.8	-19.3	41.0	52.7	8.1	10.3
BHLYP	13.3	15.3	2.9	9.0	-21.5	-17.8	54.6	67.0	12.0	15.7
TPSSH	12.2	10.1	-9.7	-5.8	-42.9	-31.4	19.5	20.4	8.4	7.4
M06	14.0	16.0	9.4	14.1	-20.2	-14.6	41.2	42.8	10.4	10.9
M06-2X	17.1	19.1	2.7	7.6	-36.5	-31.2	67.6	80.8	13.7	17.3

Table 4.2: Statistical properties computed for the enthalpies predicted by each functional at the SO-DFT level, for the SEG and ANO basis sets. Similar to Table 4.1, the statistics include the mean unsigned error (MUE), mean signed error (MSE), the range of errors noted (Min and Max), all in kcal mol⁻¹, and finally the standard deviation σ .



Figure 4.4: The error reduction of SO-DFT on the later actinides for the (SEG) and ANO basis.

4.3.4 Regression Analysis

Regression analysis shows the overall consistency, i.e. the distribution of the error and accuracy of the functionals across the wide span of molecules. The combined linear regression tests for all compounds computed with the RECP for the ANO and SEG basis sets with and without SO-DFT are listed in Tables 4.3 and 4.4. The experimental enthalpies of formation are compared against the computed enthalpies of formation utilizing a linear fit with least-squares regression:

$$\Delta H_{exp} = m \Delta H_{calc} + b \tag{4.1}$$

where *m* is the slope and *b* the *y*-intercept. In an ideal situation the slope is 1 and the intercept 0, with a very high R^2 value (> 0.990). A functional is considered consistent if it maintains a high R^2 value from one basis set to the next (e.g., for ANO and then for SEG) while having similar slopes and intercepts. The functionals are ranked in Table 4.3 by the R^2 .

Overall, TPSSH resulted in the highest R^2 values for the AE and SEG basis sets, and the second highest for the ANO basis. The highest R^2 for the ANO basis set was for TPSS with a slope of 0.99354. TPSS had the second highest R^2 value for the SEG basis set, however, for the AE basis set, its ranking was seventh. M06-L had the second highest ranking for the AE basis set, and seventh for the SEG basis. In addition to TPSSH, B3P86 had greater consistency (similar performance) across the basis sets, evidenced by its ranking of third, fifth, and third for AE, SEG, and ANO basis sets, respectively. The lowest scoring functional was M06-2X, which scored last for all three basis sets, with an R^2 of 0.96591 for the AE basis.

For the SO-DFT calculations, the TPSSH functional has the highest R^2 values for both the SEG and ANO basis sets, with values of 0.99460 and 0.99432, respectively. B3P86 ranked second overall for the SEG basis and third for the ANO basis. TPSS ranked second with the ANO basis, but only sixth for the SEG basis. For the R^2 of the SEG basis, TPSS has a value of 0.99208 for DFT, and 0.99299 for SO-DFT. Thus, the accuracy did improve with use of SO-DFT, however, for other functions the improvements were much better. Overall, these results demonstrate the importance of SO-DFT for most functionals.

In considering aspects beyond how well the data fits a linear trend, the intercepts should be considered. For example, for the ANO basis, TPSSH had a slope of 0.999 and an intercept of -3.0 for DFT and a slope of 1.004 and intercept of -5.2 for SO-DFT. The negative *y*-intercept suggests an additive systematic deviation, i.e., all values are shifted from experiment by about -5.2 kcal mol⁻¹. This implies that, considering this shift, a direct comparison with experiment and TPSSH values can, at the very least, provide qualitative trends.

		<i>R</i> ²		ΔH	$\Delta H_{exp} = m \Delta H_{calc} + b$				
	AE	SEG	ANO	AE	SEG	ANO	AE	SEG	ANO
SVWN	0.98123	0.98048	0.98250	1.081x - 9.5	1.078x - 9.4	1.080x - 6.5	16	17	16
BP86	0.98861	0.98867	0.99069	1.012x + 1.0	1.003x + 0.7	1.004x + 3.0	10	10	6
BLYP	0.98917	0.98942	0.99108	1.005x + 6.0	0.995x + 5.4	0.995x + 8.0	8	9	4
PW91	0.98858	0.98833	0.99012	1.023x - 1.3	1.014x - 1.2	1.013x + 1.0	11	12	7
PBE	0.98845	0.98803	0.98989	1.017x - 0.1	1.008x - 0.1	1.007x + 2.0	12	14	8
TPSS	0.98924	0.99208	0.99354	1.018x - 6.4	1.010x - 3.2	1.007x - 1.4	7	2	1
M06-L	0.99159	0.99006	0.99119	1.018x - 0.2	1.014x + 3.8	1.012x + 5.1	2	7	3
B3P86	0.99037	0.99121	0.99097	1.010x - 2.5	0.993x - 3.6	0.996x - 0.9	3	3	5
X3LYP	0.99018	0.99049	0.98982	1.001x + 2.8	0.983x + 1.3	0.985x + 4.2	4	5	9
B97-1	0.98793	0.99003	0.98880	0.995x + 0.8	0.983x + 0.2	0.986x + 2.6	13	8	12
B3LYP	0.99007	0.99067	0.98968	0.997x + 2.3	0.981x + 1.5	0.985x + 4.6	5	4	10
PBE0	0.98970	0.99044	0.98954	1.000x - 1.5	0.982x - 2.9	0.987x + 1.0	6	6	11
MPW1K	0.98634	0.98826	0.98494	0.998x - 1.0	0.973x - 3.5	0.978x + 0.1	14	13	15
BHLYP	0.97998	0.98332	0.97868	0.993x + 4.4	0.967x + 1.0	0.973x + 4.9	17	16	17
TPSSH	0.99245	0.99332	0.99328	1.008x - 5.2	0.996x - 5.3	0.999x - 3.0	1	1	2
M06	0.98907	0.98521	0.98631	1.009x + 7.3	0.980x + 10	0.985x + 13	9	15	14
M06-2X	0.97449	0.97537	0.96591	0.996x + 10	0.958x + 3.8	0.966x + 5.4	18	18	18
B2PLYP	0.98538	0.98867	0.98799	1.037x + 1.0	1.010x - 1.1	1.010x + 2.6	15	11	13

Table 4.3: Linear regression analysis information for each functional at the two DFT/RECP levels of theory and the DFT/AE level of theory. A rank is given based on the overall R^2 in comparison to other functionals. In the table *x* is used to represent ΔH_{exp} .
	<i>R</i> ²		$\Delta H_{exp} = m \Delta H_{calc} + b$		Rank	
	SEG	ANO	SEG	ANO	SEG	ANO
SVWN	0.98294	0.98574	1.090x - 12.9	1.080x - 9.5	16	15
BP86	0.99017	0.99197	1.019x - 2.8	1.008x + 0.3	11	10
BLYP	0.99120	0.99294	1.010x + 1.7	0.999x + 4.9	9	5
PW91	0.98988	0.99147	1.030x - 4.7	1.019x - 1.4	13	12
PBE	0.98969	0.99129	1.024x - 3.6	1.013x - 0.4	14	13
TPSS	0.99299	0.99407	1.028x - 6.2	1.011x - 4.7	6	2
M06-L	0.99219	0.99225	1.031x - 0.1	1.014x + 1.8	8	7
B3P86	0.99411	0.99371	1.012x - 5.1	0.998x - 2.2	2	3
X3LYP	0.99376	0.99260	1.000x - 1.1	0.988x + 2.9	4	6
B97-1	0.99270	0.99218	1.003x - 1.9	0.989x + 1.2	7	8
B3LYP	0.99358	0.99215	1.001x - 0.3	0.988x + 3.2	5	9
PBE0	0.99385	0.99345	1.000x - 4.1	0.989x - 1.0	3	4
MPW1K	0.99098	0.98797	0.990x - 4.3	0.974x - 1.0	10	14
BHLYP	0.98548	0.98156	0.984x + 0.5	0.969x + 4.4	15	16
TPSSH	0.99460	0.99432	1.018x - 7.1	1.004x - 5.2	1	1
M06	0.99004	0.99189	0.998x + 9.1	0.987x + 12.2	12	11
M06-2X	0.97804	0.97162	0.985x + 0.4	0.966x + 2.5	17	17

Table 4.4: Linear regression analysis information for each functional at the SO-DFT levels of theory and the DFT/AE level of theory. A rank is given based on the overall R^2 in comparison to other functionals. In the table x is used to represent ΔH_{exp} .

4.3.5 Summary

In conclusion, a study of the enthalpies of formation computed by a variety of DFT functionals for different basis sets and the impact of SOC effects on the predictions is presented. In prior work on lanthanides, the AE approaches resulted in much lower MUEs than the RECP's, 26,96 whereas in this study, not only are the differences not as pronounced, but, AE's do not always result in the lower MUEs. In fact, the analysis shows the AE and RECP basis sets result in enthalpies of formation with differences usually within ~2-3 kcal mol⁻¹ of one another, though largely for Np, Pu, and Am, there are a number of functionals that result in differences of ~5-10 kcal mol⁻¹, depending upon functional. The closer overall performance between AE's and RECP's is useful, as RECP's are much more computationally efficient, which is particularly important, considering the cost of the DKH method.

In the earlier lanthanide study, SVWN resulted in the lowest MUE in most cases and gave very consistent deviations from experiment. The performance for the actinides was similar for SVWN itself, but for the other functionals, significant improvements were shown for many of the molecules with MUEs of ~10 kcal mol⁻¹, even without the inclusion of SOC which his less than half the errors encountered for lanthanides, overall. With that said, the lanthanide studies differed in a number of key ways: the availability of experimental data allowed the entire series to be detailed for lanthanides, which was not possible for the actinides. It is established that lanthanide bonding, is overall, more ionic in nature than early actinide bonding. As such, it is not surprising that there is substantial improvement (though still not ideal) for actinides, with performance that is more akin to that of transition metals. For future actinide studies utilizing DFT, this study suggests that TPSS and TPSSH are among the better functionals for the computation of thermochemical energies. Given, the degrading performance for B3LYP, BP86, PBE, and PBE0 for actinides beyond uranium, reliance on these functionals is not recommended.

There is a stark increase in error for the Pu compounds for almost all of the functionals in comparison to the other actinide compounds. However, the most consistent errors in terms of MUE, are produced by TPSSH, where little difference in the MUE is seen among each group of actinides. This is demonstrated by the linear regression results, where TPSSH was the most consistent across all the compounds for RECP and AE. For the Np, Pu, and Am compounds, there is a deterioration of performance for the more parameterized functionals and those with higher percentages of exact exchange.

CHAPTER 5

SPIN-ORBIT EFFECTS ON LANTHANIDES

5.1 Lanthanide Oxides

In the actinide study, it was noted that incorporating spin-orbit effects via SO-DFT can have an impact on the accuracy of the predicted enthalpies, and should be considered. Thus, it is worth revisiting the lanthanides to examine the impact of spin-orbit effects, particularly given the poorer DFT predictions for lanthanides than for actinides. Furthermore, methods that go beyond SO-DFT in terms of accounting for spin-orbit effects should also be used to ensure accuracy. To investigate the spin–orbit impact on the lanthanides, the LnO and LnF molecules from the Ln54 dataset were selected and calculations were done at the four-component Dirac-Hartree-Fock (4c-DHF) level with the Dyall triple- ζ basis sets¹²⁰ using the DIRAC19¹²¹ software program. The 4c-DHF calculations were compared to the spin-free variations of the calculations to determine the magnitude of the spin–orbit coupling. For further comparison, SO-DFT calculations using TPSS optimized geometry (without SOC) for LnO and LnF molecules using the cc-pVTZ-DK3 basis set.¹²² The SO-TPSS calculations also used the cc-pVTZ-DK3 basis set, and the SOC value was obtained as the difference between SO-TPSS and TPSS energies.

	4c-DHF V3Z	SO-TPSS	Lit.
LaO	0.19	0.22	0.16
CeO	0.20	0.22	
PrO	0.54	0.56	
NdO	1.66 ^a	0.85	
SmO	0.71	0.79	
EuO	0.45	0.25	
GdO	0.36	0.27	
HoO		2.77	
ErO		2.55	
TmO		3.68	
YbO	0.77	2.45	
LuO	0.63	0.68	0.63
YbF	0.15	1.38	
LuF	0.25	0.20	0.23

Table 5.1: Calculated Δ_{SO} (kcal mol⁻¹) for LnF and LnO molecules for 4c-DHF and DFT (TPSS), in comparison to 4c-DHF level values from prior work.¹²³

^{*a*} Tentative value

The results are provided in Table 5.1. For the oxides the SO coupling results in values usually less than a kcal mol⁻¹, which would not account for the very large errors with respect to experiment observed in the lanthanide DFT studies described earlier in this dissertation.²⁶ For HoO, ErO, and TmO, only SO-DFT values are provided for the SO coupling, though the DFT calculations have great difficulty converging to the correct state. DFT may be unable to adequately describe the ground state energy, if contributions from lower-lying excited states are too great. This would require a multireference approach. Overall, for the LnO molecules, SO-DFT does result in predicted spin-orbit effects that are mostly in agreement with the 4c DHF results, with NdO and Ybo being exceptions. With NdO the 4c-DHF calculation had convergence issues and must be revisited to ensure it has in the correct state. The ground state for YbO is also a singlet with the f-shell filled, which DFT is adequate to describe as shown in Chapter 3. Singlets also have very little SOC contributions, and usually SOC is not as significant

Interestingly, SO-DFT predicts larger SO-coupling values around 2-3 kcal mol⁻¹ for HoO-TmO. If it is the case the SO-DFT values for the SOC are accurate, this would help with getting more accurate energies for these species. Values for YbF and LuF are also shown for 4c-DHF and SO-DFT, the LuF values is in agreement with the 4c-DHF with a difference of 0.05 kcal mol⁻¹. The YbF value for SO-DFT is, however, is about 1 kcal mol⁻¹ larger than the 4c-DHF, similar to YbO. Thus, further investigation on the SOC values for YbF and YbO must be carried out.

CHAPTER 6

INTRODUCTION TO QUANTUM DYNAMICS

6.1 Motivation

The previous chapters have been focused on methods of solving the time-*independent* Schrödinger equation, where time is not a factor. However, there are many applications that require time-evolution of the wavefunction. For example, charge transfer reactions that are initiated by light involve the movement of electrons from one molecule or molecular site to another. These processes underlie many important physical phenomena such as DNA repair, sensory protein activation, and photosynthesis.¹²⁴ Being able to monitor these electronic processes in real time provides the pathway to understand their fundamental chemistry and learn how to direct or even control chemical reactions.¹²⁴

Furthermore, the rise of attosecond spectroscopy has driven the need for the development of additional theoretical methodologies. In attosecond science, there is often strong electron-nuclear coupling that must be described at the quantum level. This encourages the development of a method that can describe nuclear and electron dynamics at the same quantum mechanical level, as opposed to mixed classical-quantum methods that are often used now.

6.2 Time-dependent Schrödinger Equation

In time-dependent systems, the Schrödinger equation takes a new form, where there is explicit time-dependence, and can be written as:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) = \mathcal{H}\Psi(\mathbf{r}, \mathbf{R}, t)$$
 (6.1)

where **r** and **R** are the positions of the electrons and nuclei respectively. The Hamiltonian \mathcal{H} consists of five terms:

$$\mathcal{H} = \hat{H}_{mol} = \hat{T}_n + \hat{T}_e + V_{nn} + V_{en} + V_{ee} \tag{6.2}$$

where \hat{T}_n and \hat{T}_e is the kinetic energy of the nuclei and electrons, respectively; V_{nn} is the nuclearnuclear repulsion and V_{ee} is the electron-electron repulsion. The final term is the electron-nuclear coupling term (V_{en}). The time-dependent Schrödinger equation with this Hamiltonian is extremely difficult to solve and infeasible for more than two electrons. Thus, the equation is often simplified to make it easier to solve. Because the timescale of the nuclear motion is about 100 times that of the electron, in most cases, the electronic phenomena occurs by the time nuclear motion sets in. This leads to one of the most common approximations used for both time-independent and time-dependent quantum mechanics, the Born-Oppenheimer approximation (BOA). In the BOA the nuclear and electronic motion are decoupled, leading to a parametric dependence of the nuclear position on the wavefunction. This allows the V_{en} term to be calculated only at any single, R and the T_n term is removed.

The BOA has proven to be very useful, especially in the time-dependent domain, which is the focus in the following chapters. But there are cases where the approximation breaks down, for example in strong-laser fields, conical intersections, and generally where many electronic states are energetically close. This is especially true in attosecond excitation, where the interaction of the molecule with the laser pulse usually matches the interaction the strength of the electrons and nuclei, which can lead to bond softening or hardening, Auger decay, and interatomic Coulombic decay ^{125–127}, to name a few. In those examples, the electronic and nuclear degrees of freedom (DOF) are coupled, and the BOA is insufficient to describe them. Electronic excitation in strong fields, generally, can create a time-dependent potential that drives the nuclei from the equilibrium bond length. ^{128–130} This can also happen the other way, by initiating nuclear motion, electronic processes can initiated and enhanced. This dual action is explored in chapters 7 and 8. Where the multiconfigurational electron-nuclear dynamics method (MCEND), currently in development by the Wilson group, is able to successfully describe both electronic influence of the nuclei and vice versa for LiH and H₂.

6.2.1 Time-Dependent Methods

There have been other efforts to describe electron-nuclear coupling, many of these approaches use a mix of classical and quantum methods. Often in dynamics, electrons are treated quantum mechanically, but nuclei are treated classically. Other methods, like the multiconfigurational time-dependent Hartree (MCTDH)^{131,132} method, use a pre-constructed electronic potential energy surface.

A traditional way to include electron-nuclear coupling explicitly without the prior construction of a PES, is through the Born-Huang expansion of the electron-nuclear wavefunction as a product sum of electronic and nuclear parts. Another way is via an exact solution of the electron-nuclear Schrödinger equation, and have been done in a few studies ^{133–135}, but computational limitations make applications to systems with more than two-electrons unfeasible. Electron and nuclear dynamics can be treated on the same footing as the END (electron-nuclear dynamics)^{136,137} approach. In END the wavefunction is as a product of an electronic part (a Thouless determinant) and a nuclear part. In the END approach, the nuclear part is approximated with classical dynamics and extensions that incorporate higher levels of electron correlation and nuclear quantum effects have been implemented. ^{138,139} Density-based methods have also been proposed in the literature ^{140–142}, but nuclei are also approximated classically.

6.2.2 Time-Independent Methods

Nuclei have previously been incorporated into the quantum picture in time-independent electronic structure methods. An example of this is the nuclear-electronic orbital (NEO) method ¹⁴³, which uses a similar Hamiltonian to the one used in MCEND, but only hydrogen nuclei are described quantum mechanically. Several implementations of NEO have been introduced including Hartree-Fock, MCSCF, coupled cluster, and CI variants; all of these variants use a Gaussian type orbital representation for the nuclear orbitals. The NEO method is related to earlier work from Tachikawa and co-workers ^{144,145}, who used smaller nuclear basis sets composed of GTOs. These nuclear molecular orbitals were constructed similar to electronic molecular orbitals, but which can also

describe permanents (Hartree products) for bosons in addition to the standard determinants for fermions. Adamowicz and coworkers $^{146-148}$ has similarly used explicit correlated Gaussian basis functions in a nonadiabatic approach for calculations on H₂, LiH and their isotopes.

Furthermore, Gaussian functions have not been shown to be adequate to describe translational and rotational wavefunctions in nuclear orbital methods.¹⁴⁹ This inadequacy results from a more strict requirement of basis set completeness for rotational descriptions and also the lack of an electron-nuclear cusp.¹⁵⁰ Work from Nakai¹⁴⁹ using nuclear GTOs, showed inaccuracies in energy spectra resulting from contamination of the translational and rotational motions. In the same work, however, Nakai introduced a way to remove the translational and rotational contamination using variational techniques.

6.3 Multiconfigurational Electron Nuclear Dynamics

One of the first generalized methods to have a quantum description of both the electrons and the nuclei was developed by Nest¹⁵¹ and called the multiconfigurational electron-nuclear dynamics method (MCEND). This method is the foundation that is built upon in the work of this dissertation. In the MCEND method, the wavefunction is written as a sum of products of determinants for the electrons and Hartree products for the nuclei. The equations of motion (EOM) for wave functions and coefficients are obtained through the time-dependent variational principle (TDVP). The method is general and in theory can be implemented to any system. The theory of the MCEND method is detailed in greater depth in Chapters 7 and 8. In summary, the method utilizes a wavefunction that is the product sum of nuclear permanents and electronic determinants. This allows the coupling of nuclear and electronic motion via the V_{en} term in our Hamiltonian.

6.3.1 The Electronic Basis

The electronic basis sets used in the MCEND method must be specially constructed The details about the construction are provided in Chapter 8 and the original MCEND paper¹⁵²; however, a brief overview is described here, with graphical aids. The $\langle V_{en} \rangle_{\mu\nu}$ matrix elements are interpolated for the grid points not explicitly calculated using an Akima interpolation.¹⁵³ The basis sets used in this work are derived from correlation-consistent sets, namely the cc-pV*n*Z set, where *n* represents the ζ level (double, triple, etc.) A larger resulting molecular orbital (MO) basis set is constructed over the grid points. The process is illustrated graphically in Fig. 6.1 for LiH.



Figure 6.1: MCEND basis construction flow example for LiH

In the construction of this larger basis, linear dependencies become an issue for code stability. Canonical orthogonalization is used to remove these dependencies. The eigenvalues of the basis functions formed from the overlap matrix $S_{\mu\nu}$ with threshold smaller than 0.1 are removed. The reason for this strict threshold is that in real-time calculations, the numerical stability of the Runge-Kutta integrator becomes unstable. This is a limitation of the current static basis set implementation; alternate methods are being looked into for future use. For the current work, the static basis set do produce meaningful and useful results.

6.3.2 Reconstruction of the MCEND Code

Initially, the original MCEND code required significant updates, as much of the base code had been written in an older style of FORTRAN77. There were numerous issues with memory leaks and stability that made computation with larger basis sets and longer real time runs impossible. The code was overhauled and this fixed many memory problems, while also making it much faster. There were still major bottlenecks in the code, and implementation of parallelization was necessary. OpenMP was chosen to do this, and was successfully implemented into the existing code. The result was a dramatic speed up and allowed longer real time runs to be done in a timely manner. Specific details of performance and speed improvements are given in Chapter 8. Furthermore, the code relied on getting two-electron integrals from a modified version of the GAMESS computational software. For usability and portability, this was overhauled to include an easier way to get the two-electron integral values. The PSI4 software suite ¹⁵⁴ was selected as it could be linked and called by Python code, which can in turn link to Fortran routines via the use of the F2Py library. This allowed for a more user-friendly program, as numerically demanding routines written in Fortran and Python can handle other tasks like parsing inputs and processing resulting data. This is an important step to make the future code accessible to others when it is ready for general use.

CHAPTER 7

COUPLED ELECTRON AND NUCLEAR MOTION IN STRONG LASER FIELDS

About this chapter: The following work is reprinted from *Physical Review* A^{155} with permission from the American Physical Society, © 2019 American Physical Society. The calculations and analysis for this project were done by Lucas Aebersold. Dr. Inga Ulusoy provided helpful discussions and advice for this project. This work has been submitted for publication, though parts of the introduction and the methods section has been omitted, d as Chapters 6 and 7 have already discussed background and theory in depth.

7.1 Introduction

Experimental efforts to initiate and monitor electronic motion in molecules have achieved tremendous progress in the past two decades: From the first generation of attosecond pulse trains in 2001^{156,157}, through the first imaging of single-electron wave functions¹⁵⁸ and generation of laser pulses with pulse durations of only six attoseconds¹⁵⁹, to the observation and control of electron migration in iodoacetylene¹⁶⁰, and, very recently, the acceleration of chemical reactions¹⁶¹. Attosecond science has begun to receive more attention from the chemistry and molecular physics community. One pertinent goal of chemists, the control of chemical reactions, seems viable through charge-directed chemistry. This field is inspired by early experiments of Weinkauf et al. 128-130; initially, an electronic wave packet is created either through ionization or electronic excitation. This electronic wave packet leads to non-stationary electron dynamics through charge migration^{162–164}. resulting in an electron-nuclear potential that changes on a femtosecond to attosecond time scale. Through this modulating potential, nuclear motion can be initiated and, ideally, be driven to trigger a desired process such as a specific fragmentation of a molecule or even chemical reactions. Conversely, the motion of the nuclei can facilitate and enhance electronic processes, such as charge-resonance enhanced ionization (CREI)^{133,165–168}, the generation of even harmonics for centrosymmetric molecules 169 , or in chemical reactions 161 .

Attosecond spectroscopy is very closely connected with strong-field physics, as attosecond laser pulses are commonly generated through the electronic response to strong incident laser fields (typically around 10^{14} W/cm²), such as in high harmonic generation (HHG). Recent combined experimental and theoretical approaches ^{170,171} demonstrate that the electron-nuclear dynamics in H₂ and H₂⁺ exhibit very strong electron-nuclear coupling in electric fields. The phase of the overlapping eigenstates that compose the initiated wave packet leads to very complex dynamics; these can only be understood in a fully quantum mechanical description of both electronic and nuclear degrees of freedom.

It is shown here that the molecular response to strong laser fields entails both nuclear and electronic excitations (even on a timescale of a few tenths of fs), which can be coupled to each other, forming molecular rather than electronic or vibrational excitations. In the spirit of vibronic or excitonic states, these initiated wave packets generate signatures in the potential, resembling quantum beating. Furthermore, absorption spectra are obtained in which both electronic and nuclear transition energies are encoded, and provide excellent agreement with experimental data.

The multiconfiguration electron-nuclear dynamics method (MCEND)^{152,172,173} is employed, where the electron-nuclear wave function is described as a sum of products of determinants for the electrons and Hartree products for the nuclei. Both the determinants and the Hartree products are time-dependent, as are the state coefficients that signify the population of each product. Similar as in the multi-configuration time-dependent Hartree method (MCTDH)¹³² for nuclear dynamics, and the multi-configuration time-dependent Hartree-Fock method (MCTDHF)^{174–176} for electron dynamics, the equations of motion (EOM) for wave functions and coefficients are obtained through the time-dependent variational principle (TDVP). This leads to a very efficient, though non-linear, description of the time evolution of the electron-nuclear system, and allows the simulation of systems that cannot be treated by solving the time-dependent Schrödinger equation directly. Such exact calculations have been carried out by Bandrauk and co-workers^{133–135} and in the framework of exact factorization (XF) techniques^{177–179}. Another approach that treats electron and nuclear dynamics on the same footing is the END (electron-nuclear dynamics)¹³⁶ approach, where extensions to including electron

correlation and nuclear quantum effects have been proposed^{138,139}. Furthermore, there are densitybased methods available that allow a simultaneous evolution of electronic and nuclear degrees of freedom (DOF)^{140–142}, but these also treat the nuclei classically. Other extensions of MCTDH(F), similar in spirit to MCEND, have been proposed,^{180,181} which utilize a different partitioning of electronic and nuclear subspaces to facilitate the evaluation of the EOMs. A formulation within a mean–field configuration interaction (CI) scheme is also available¹⁸².

7.2 Multiconfiguration Electron-nuclear Dynamics

In the MCEND method, the molecular wave function is represented as a sum over products of determinants $\Phi_{J_{\ell}}(\mathbf{r}, t)$ for the electrons and Hartree products $\Phi_{J_n}(\mathbf{R}, t)$ for the nuclei

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{J_e}^{\text{ord}} \sum_{J_n} A_{J_e J_n}(t) \Phi_{J_e}(\mathbf{r}, t) \Phi_{J_n}(\mathbf{R}, t)$$
(7.1)

$$\Phi_{J_e}(\mathbf{r},t) = |\varphi_{j_1^e}(\mathbf{r}_1,t)\varphi_{j_2^e}(\mathbf{r}_2,t)\dots\varphi_{j_{N_e}^e}(\mathbf{r}_{N_e},t)|$$
(7.2)

$$\Phi_{J_n}(\mathbf{R},t) = \prod_k^{N_k} \varphi_{j_k^n}(R_k,t)$$
(7.3)

with composite index $J_e = (j_1^e, j_2^e, \dots, j_{N_e}^e)$ and $J_n = (j_1^n, j_2^n, \dots, j_{N_k}^n)$. The spin orbitals (SOs) $\varphi_{j_i^e}$ and single-particle functions (SPFs) $\varphi_{j_k^n}$ constitute the single-particle basis and are time-dependent, adapting to the optimal representation at each time step. The MCEND molecular Hamiltonian is expressed as

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_e(\mathbf{r}) + \hat{T}_n(\mathbf{R}) + V_{ee}(\mathbf{r}) + V_{en}(\mathbf{r}, \mathbf{R}) + V_{nn}(\mathbf{R}).$$
(7.4)

Here, $\hat{H}_e(\mathbf{r}) = \hat{T}_e(\mathbf{r}) + V_{ee}(\mathbf{r})$ is defined as the electronic Hamiltonian (where $V_{en}(\mathbf{r}, \mathbf{R})$ is not contained in $\hat{H}_e(\mathbf{r})$, contrary to the usual definition), and $\hat{H}_n(\mathbf{R}) = \hat{T}_n(\mathbf{R}) + V_{nn}(\mathbf{R})$ is the nuclear Hamiltonian. The coupling between electronic and nuclear DOF is contained in $V_{en}(\mathbf{r}, \mathbf{R})$. The time-dependence of the SOs, SPFs, and coefficients $A_{J_eJ_n}(t)$ that relate the single-particle to the

many-particle basis, are obtained from the TDVP:

$$i\dot{A}_{J_eJ_n} = \sum_{L_e}^{\text{ord}} \sum_{L_n} \langle \Phi_{J_e} \Phi_{J_n} | \hat{H} | \Phi_{L_e} \Phi_{L_n} \rangle A_{L_eL_n}$$

$$= \sum_{L_e}^{\text{ord}} \langle \Phi_{J_e} | \hat{H}_e | \Phi_{L_e} \rangle A_{L_eL_n} + \sum_{L_n} \langle \Phi_{J_n} | \hat{H}_n | \Phi_{L_n} \rangle A_{L_eL_n}$$

$$(7.5)$$

$$+\sum_{L_e}^{\text{ord}}\sum_{L_n} \langle \Phi_{J_e} \Phi_{J_n} | V_{en} | \Phi_{L_e} \Phi_{L_n} \rangle A_{L_e L_n},$$
(7.6)

$$i\dot{\varphi}_{j_i^e} = (1 - P^e) \left(\rho^e\right)^{-1} \langle \hat{H}_e + V_{en} \rangle \varphi_{j_i^e}, \tag{7.7}$$

$$i\dot{\varphi}_{j_k^n} = (1 - P^n) \left(\rho^n\right)^{-1} \left[\hat{H}_n + \langle V_{en} \rangle\right] \varphi_{j_k^n}.$$
(7.8)

The projection operators P^e and P^n project onto the space spanned by the SOs and SPFs so that $P^e = \sum_{i=1}^{N_e} |\varphi_{j_i^e}\rangle\langle\varphi_{j_i^e}|$ and $P^n = \sum_{k=1}^{N_k} |\varphi_{j_k^n}\rangle\langle\varphi_{j_k^n}|$. The reduced electronic and nuclear density matrices are given by ρ^e and ρ^n , and $\langle \hat{H}_e + V_{en}\rangle$ and $\langle V_{en}\rangle$ are the mean fields ¹⁷². No nuclear rotational terms are included in the Hamiltonian, which is supported by the alignment of the molecular axis in strong fields as in the applications targeted here. The MCEND wave function is very flexible, and can be systematically improved by adding molecular orbitals (MOs) and SPFs. The naming convention follows the one in electronic structure theory, with (number of electrons, number of MOs, number of SPFs).

Using a wave function obtained from a propagation in imaginary time as initial state, the absorption spectrum of a molecule can be generated with MCEND by employing a time-dependent Hamiltonian. The electric field coupling is described in the semiclassical dipole approximation in the length gauge. By computing the autocorrelation function, $\langle \Psi(\mathbf{r}, \mathbf{R}, t = 0) | \Psi(\mathbf{r}, \mathbf{R}, t) \rangle$, and taking its inverse Fourier transform after the laser pulse has been switched off, the frequency components of the time-dependent electron-nuclear wave function can be resolved. Here, the molecule is excited using a short, non-resonant laser pulse, so that a superposition state is generated that contains components of the accessible eigenstates of the molecule. The frequency components of the autocorrelation function (and their weights) then provide insights into the energies of the eigenstates and transition moments from the ground state. Such absorption spectra are computed for H₂ and LiH, where the

laser pulse takes the following form

$$\mathbf{E}(t) = \mathbf{E}_0 \sin^2\left(\frac{\pi t}{2\sigma}\right) \cos(\omega_0 t),\tag{7.9}$$

with \mathbf{E}_0 the initial pulse height for a specific orientation along the *x*, *y*, or *z* direction, 2σ the pulse width, and ω_0 the carrier frequency. For very short pulses, the vector potential would need to be included as to avoid non-zero-area pulses.

The approach here does not describe electronic and vibrational continuum states (the primitive basis that is used at this point does not allow a treatment of continuum states). For one, the electronic basis is chosen as a Gaussian basis distributed on a grid; and Gaussian basis functions lead to a trapping of charge rather than allowing charge to occupy the highly delocalized continuum states. Furthermore, the grid basis that represents the primitive nuclear basis in principle can describe dissociation, but would need to be extended much further in range than what is included in the calculation (and, ideally, be capped with a complex absorbing potential). However, the laser pulse parameters were chosen such that the intensity lies at or below 10^{-14} W/cm², as this is generally considered a threshold beyond which ionization and dissociation channels are fully accessible for a molecular system. Below this threshold, tunnel-ionization, and similarly, dissociation, also take place, but at a much lower percentage. For example, the possibility to generate high-harmonic spectra necessarily implies that negative charge can be moved far away from the molecule through tunnel-ionization. For the electron-nuclear spectra presented here, the parameters were chosen such to minimize these effects; this becomes apparent from considering the nuclear difference density as shown above, which is well contained on the nuclear grid, thus signifying that, if at all, dissociative channels do not contribute significantly to the dynamics. For the electronic degrees of freedom, such an estimate is much harder to obtain; here, due to the charge trapping, ionization would appear as noise in the spectra. For H₂, it appears that this is not the case, while for LiH, we cannot fully exclude contributions from ionization.

7.3 Results and Discussion

7.3.1 H₂ Excitation Spectra

The absorption spectrum of H₂ (laser pulse parameters: $2\sigma = 2.8$ fs, $\omega = 0.416 E_h$ (109.5 nm), $I = 10^{14}$ W/cm², z direction (along the molecular axis); and $2\sigma = 1.4$ fs, $\omega = 0.555 E_h$ (80.9 nm), $I = 10^{14}$ W/cm², x direction) is shown in Fig. 7.1 for a (221) expansion length. The laser pulse parameters are chosen such that the frequency is off-resonant with a specific transition, while being high enough to lie in the vicinity of the electronic excited states. Through the finite pulse length, additional frequency components are included in the laser pulse. The expansion length signifies the use of two time-dependent MOs (four SOs) for two electrons, and one SPF to describe the vibrational DOF.

The computed absorption spectra for H_2 are shown in Fig. 7.1



Figure 7.1: Absorption spectra for H₂ using the aug-cc-pVDZ basis set at the (221) expansion length, for *z* (top) and *x* (bottom) polarization direction. Experimental transition frequencies ¹⁸³ are marked with black lines.

There are many features that can be observed in the calculated absorption spectra, where the

experimental peak positions are indicated with intensity set to an arbitrary height for better visibility. For one, there is a large cluster of peaks close to the ground-state energy; and one centered around 100,000 cm⁻¹ (*z*) and 120,000 cm⁻¹ (*x*). The peaks at higher energies correspond to electronic states that have been populated in the wave packet. The positioning of the peaks is in excellent agreement with the experimental values¹⁸³. However, very noticeable is that there are many smaller peaks located around the excited electronic states at almost equidistant energies from the center peak at E = 90,700 cm⁻¹ (*p* = *z*), E ≈ 110,000 cm⁻¹ (*p* = *x*), and also from the ground state peak at E = 0.0 cm⁻¹. These peaks result from *nuclear* excited states—vibrational excitations—that have been induced in the diatomic. As H₂ is a homonuclear diatomic with a zero dipole moment, these vibrational excitations cannot be directly induced through the laser pulse. They are a consequence of the electron-nuclear coupling and therefore induced nonadiabatically through the motion of the electrons, through Raman or other processes. The energy spacing of the peaks is in the range of vibrational transition frequencies, ranging from about 1000 cm⁻¹ to ≈ 4500 cm⁻¹.

The MOs for H₂ during the excitation are shown in Fig. 7.2 and 7.3. At time t = 0 fs, the MOs clearly resemble the σ and σ^* MOs of H₂. Through the laser pulse excitation, electron motion is induced in the diatomic and the time-adaptable MOs rotate in Hilbert space, adapting to an optimal representation at the single-particle level of the electron-nuclear wave function. As such, their shape changes as is shown in Fig. 7.1 and 7.2, and differs for different polarization directions of the laser pulse.

The electronic excitations that are observed in the spectrum—such as transitions to the ${}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{g}$ states—lead to an effective mixing of the MOs, for example, with the $\sigma_{p_{z}}$ and $\pi_{p_{x}/y}$ orbitals. It should be noted that these MOs are somewhat analogous to time-independent MCSCF MOs in that they do not diagonalize the one-particle reduced density matrix (they are not natural orbitals and as such exhibit fractional occupancies). The multiconfigurational wavefunction includes determinants in which both electrons are in the lower-lying MO, singly excited determinants, and the doubly-excited determinant in which both electrons are excited into the higher-lying MO. As the MOs are time-dependent and adapt to the time-dependent Hamiltonian at each time step, their character changes from pure σ to containing contributions of the higher-lying one-particle states such as the π orbitals.



Figure 7.2: Graphical representations of the MOs of H₂ before and after laser-pulse excitation in the *z*-polarization direction. The initial MOs resemble the σ and σ^* MOs, which then adapt to the optimal representation at each time step for the time-dependent Hamiltonian.



Figure 7.3: Graphical representations of the MOs of H_2 before and after laser-pulse excitation in the *x*-polarization direction.

The detailed absorption spectrum of H₂ (laser pulse parameters: $2\sigma = 2.8$ fs, $\omega = 0.416$ E_h (109.5 nm), $I = 10^{14}$ W/cm², z-direction (along the molecular axis); $2\sigma = 1.4$ fs, $\omega = 0.555$ E_h (80.9 nm), $I = 10^{14}$ W/cm², x-direction) is shown in Fig. 7.4 for a (221) expansion length.



Figure 7.4: Electronic and nuclear excitation peaks obtained from H₂ excitation in the *z*-direction run for 300 fs. The Savitzky-Golay filter (black line) is applied to the 300 fs spectrum. Experimental transition energies (cm⁻¹) are overlayed as vertical lines. a) Energy region around the electronic excited states. b) Energy region close to the electronic ground state.

Different possible transitions are marked in the Figure together with reference values from the experiment ^{183,184}. The raw spectrum from a 300 fs propagation is overlayed with a filtered spectrum,

using a Savitzky-Golay filter with a window length of 17 points (1770 cm^{-1}) and polynomial order of three. Both electronic and vibrational transitions are obtained in the spectrum, although the laser pulse frequency targets electronic excitation (UV) and, a direct excitation of vibrations in H₂ is not possible, as it has a zero dipole moment. However, vibrational transitions are induced indirectly through Raman-type processes. In the higher-energy region, the 0-0 transition from the $X^{1}\Sigma_{g}^{+}(S_{0})$ ground to the first singlet excited state, $B^{1}\Sigma_{u}^{+}(S_{1})$, and from the $E^{1}\Sigma_{g}^{+}(S_{2})/F^{1}\Sigma_{g}^{+}(S_{2})$ $(S_3) \leftarrow X^1 \Sigma_g^+$ transition is indicated by a vertical solid line in red $(v_{0-0}, B^1 \Sigma_u^+ \leftarrow X^1 \Sigma_g^+)$ and green $(v_{0-0}, E^1 \Sigma_g^+ / F^1 \Sigma_g^+ \leftarrow X^1 \Sigma_g^+$, denoted as $v_{0-0}^{S_n}$). In the following the focus is on vibrational transitions in the ground and $B^{1}\Sigma_{u}^{+}$ -state only, as the complexity increases rapidly when more electronic states are considered. The v_{1-1} and $v_{2-2} B^1 \Sigma_u^+ \leftarrow X^1 \Sigma_g^+$ transitions are marked with solid red lines, at energies lower than the v_{0-0} transition as the vibrational energy levels are closer in energy for the excited state (the H₂ bond in this state is weaker). At all of these transition energies, peaks can be found in the simulated spectrum, where the v_{0-0} transition from ground to first excited state results in the highest intensity. Furthermore, in the simulated spectrum there are peaks occurring at energies that correspond to v_{0-n} transitions from electronic ground to first excited state, with n = [1, 7] (dashed line); a peak at the v_{1-2} transition energy (dotted line); and a small peak at the v_{1-0} transition. In the energy region close to the ground state, peaks for vibrational excitations in the electronic ground state can be found (from the vibrational ground state v_0 to vibrationally excited states, v_n). Similarly, vibrational transitions in the first electronic excited state also lie in this energy region (from $v_0^{S_1}$ to $v_n^{S_1}$), and also transitions in higher-lying electronic states. Furthermore, there is a peak at the $C^1\Pi_u \leftarrow B^1\Sigma_u^+$ transition energy which does not originate from the nuclear part of the wave function, as has been confirmed through a Fourier transform of electronic and nuclear position expectation value (this peak is only obtained in the electronic part). The excellent agreement of peak positions with experimental values is providing a high level of confidence for these calculations, in that not only qualitative, but also quantitative predictions towards the electron-nuclear dynamics can be made.

Through the laser-pulse excitation of the electrons, an electronic wave packet is generated, that

induces a modulating potential which drives the nuclei from their equilibrium position. As such, a nuclear wave packet is generated that is a superposition of vibrationally excited states (ground state, first vibrational state, and higher-lying states), in the electronic ground state, and also in the electronic excited state(s). The peaks that are observed in the spectrum originate in vibrational transitions in the electronic ground state, and electronic excited states. The magnitude of the peaks is related to the transition dipole moments between the electronic states, and the overlap of the nuclear eigenstate functions in the respective vibrational states, $\langle \phi_{initial}^n | \phi_{final}^n \rangle$ (Franck-Condon factors), and the energy difference between the electronic states.

7.3.2 LiH Excitation Spectra

As a second example, a similar calculation was carried our for LiH ($\omega_0 = 0.110 E_h$ (414 nm), $I = 1.405 \times 10^{13}$ W/cm², $2\sigma = 2.8$ fs). The resulting spectra are shown in Fig. 7.5 a) and b). Experimental electronic excitation energies ^{183,185} are indicated with black lines. The spectra were generated for three different expansion lengths: (421), (431), and (441). The agreement of the (441) transition energies with the experimentally observed transitions is excellent, both for *z* and *x* polarization direction, where, depending on the relative polarization of electric field and molecule, different excitations can be observed. The (431) expansion length yields results in close agreement with the experiment, and can be chosen as a compromise between accuracy and computational demand. The (421) expansion length, in which the electron-electron interaction is represented through mean-field interaction only with no correlation effects, the agreement with experiment is poor as expected.

Comparing to the H_2 spectra, it is very noticeable that for LiH, very little to no nuclear vibration is initiated, neither through the laser pulse nor electronic motion.



Figure 7.5: Absorption spectra for LiH (cc-pVDZ basis set); experimental transition frequencies are marked with black lines 183,185 . **a**) Excitation along *z* polarization direction with different expansion lengths. **b**) Excitation along *x* polarization direction with different expansion lengths.

In order to generate an electron-nuclear spectrum, a two-pulse excitation is carried out: first, LiH is irradiated using an infrared (IR) laser pulse to initiate nuclear motion, directly followed by the same laser pulse used prior to obtain the electronic spectrum. The resulting spectra are shown in Fig. 7.6, for the (441) expansion length and z/x polarization direction of the second pulse (parameters of the first pulse: $\omega = 0.010 E_h$ (4,556 nm), $I = 1.86 \times 10^{13}$ W/cm² (z - z) and I = 2.19×10^{13} W/cm² (z - x), $2\sigma = 60.8$ fs). The agreement of the calculated excitation energies with experimental transition energies is excellent. Two characteristics are very noticeable: Many small peaks at a similar energy spacing can be found in the spectra, which at least partially originate in nuclear excitations. Secondly, for b), where the second laser pulse was polarized in *x* direction, we also obtain excitation into the ${}^{1}\Sigma^{+}$ electronic state, which did not occur without nuclear motion. Inducing nuclear motion therefore in turn induces a population transfer into the ${}^{1}\Sigma^{+}$ excited state.



Figure 7.6: Absorption spectra for LiH (cc-pVDZ basis set, (441) expansion length); experimental transition frequencies are marked with black lines^{183,185}. The one-pulse spectrum is overlayed for comparison. **a**) Excitation along *z* polarization direction. **b**) Excitation along *x* polarization direction.

An in-depth analysis of the two-pulse excitation spectrum is shown in Fig. 7.7, for the (441) expansion length and z polarization direction of both pulses. Many small peaks at a similar energy spacing can be found in the spectrum; however for many of these it remains inconclusive if these represent real features in the electron-nuclear dynamics. The spacing between the small peaks is roughly 420–550 cm⁻¹, which is in the range of the experimental vibrational transition energies between the vibrational states in the ${}^{1}\Sigma^{+}$ state. But, as these features are very small, only peaks are discussed that exhibit substantial intensity and that are reproduced through different propagation times, and Fourier transforms of electronic and nuclear expectation values.

Different experimental vibrational and electronic transition energies ^{183,185} are marked on Figure

7.7. In the higher energy region, the v_{0-0} transition energy coincides with the largest peak (~27,000 cm⁻¹), and several possible transitions lie around it; such as the v_{1-1} and v_{0-1} transitions. In the lower-energy region, the vibrational transition energies in the electronic ground state and ${}^{1}\Sigma^{+}$ excited state are marked as v_{0} and $v_{0}^{S_{1}}$ to v_{n} and $v_{n}^{S_{1}}$, and so on for transitions from vibrational excited states. For LiH, no electronic transitions between the singlet excited states are observed in the spectrum (${}^{1}\Pi \leftarrow {}^{1}\Sigma^{+}$) but only transitions from the electronic ground state.



Figure 7.7: Electronic and nuclear excitation peaks obtained from the two-pulse excitation of the (441) expansion length for LiH in the *z*-polarization direction overlayed with experimental transition energies^{183,185}. In the upper part a), the energy region around the first electronic excited state (${}^{1}\Sigma^{+}$) is shown. In the lower part b) the energy region close to the electronic ground state is shown.

7.3.3 Nuclear Vibration of H₂ and LiH

The two above examples illustrate quite different electron-nuclear coupling effects. In the first example—H₂—the electronic motion leads to an uptake of nuclear motion, and to the appearance of many electronic and vibrational transitions in the spectra. In the second example—LiH—the induced nuclear motion influences the electronic excitations, and not only electronic and vibrational peaks are seen in the spectra, but also transitions that were previously not observed, such as the ${}^{1}\Sigma^{+}$ excitation for the *x* polarization direction. The nuclear vibration can also be visualized through the nuclear difference density.

The nuclear difference density in the grid basis, $\Delta \rho^n(R, t)$, which is the difference of the nuclear density at time *t* and initial time, can be obtained from

$$\Delta \rho^{n}(R,t) = \rho^{n}(R,t) - \rho^{n}(R,0), \qquad (7.10)$$

with the nuclear density on the grid given as

$$\rho^{n}(R,t) = \sum_{k}^{n_{\text{SPF}}} \sum_{l}^{n_{\text{SPF}}} \sum_{j=1}^{J_{\text{max}}} \phi_{k}^{n*}(R,t) A_{J,k}^{*}(t) A_{J,l}(t) \phi_{k}^{n}(R,t).$$
(7.11)

The sums here run over all SPFs k and l, and all their respective configurations J, k and J, l for a total number of configurations J_{max} .

Such a nuclear density difference is shown in Fig. 7.8 for H₂. Already from the beginning of the propagation, just after the laser pulse has been switched off at about 3 fs, nuclear vibration sets in. Initially, the nuclei are moved further apart and move back to the equilibrium position; but around 32 fs, the nuclei start to move also further in, resulting in a vibration that leads to a shortening and stretching of the H₂ bond. The vibrational period obtained with MCEND is 11.0 fs, which is close to the experimental vibrational period of H₂ (the fundamental vibrational excitation $v_0 = 4162.6$ cm⁻¹ has a vibrational period of ≈ 8 fs).



Figure 7.8: Contour plot of the nuclear difference density $\Delta \rho_n(R, t)$ for H₂ during the excitation with a *z*-polarized laser pulse. Positive values indicate a probability increase, while negative contour values indicate a probability decrease.

The difference density for LiH after laser pulse excitation with an UV/VIS wavelength is shown in Figure 7.9 a) and results in very little nuclear motion, thus confirming the absence of vibrational peaks in the above spectra. For the two-pulse excitation, where an IR pulse is followed by an UV/VIS pulse, the uptake of vibrational motion is clearly visible in the difference density, shown in Fig. 7.9 b). Here, the nuclear motion sets in around 20 fs, and quickly builds up, with the nuclei moving in and out from the equilibrium position, resulting in a shortening and stretching of the bond and an oscillating nuclear contribution to the dipole moment.



Figure 7.9: Contour plot of the nuclear difference density $\Delta \rho_n(R, t)$ for LiH during the a) UV/VISexcitation using a pulse polarized along *z* and b) an IR pulse followed by an UV/VIS pulse to induce nuclear motion, both polarized along *z*.

7.3.4 Born-Oppenheimer Potential and Coherence Properties



Figure 7.10: Contour plot of the Born-Oppenheimer potential V_{BO} during the UV-excitation of H₂ using a pulse polarized along *z*.

Monitoring the different energy contributions to the total energy allows a reconstruction of a timevarying "Born-Oppenheimer potential" which contains the overall potential energy contributions that can trigger nuclear motion. The Born-Oppenheimer (BO) potential is defined here as

$$V_{\rm BO}(t) = \langle T_e \rangle + \langle V_{ee} \rangle + \langle V_{en} \rangle + \langle V_{nn} \rangle \tag{7.12}$$

in analogy with the definition of potential energy surfaces. It should be noted at this point that the time-dependence of the BO potential results from the implicit time-dependence of its constituent terms; while the electronic kinetic energy, electron-electron interaction, etc., are defined as usual in a molecular Hamiltonian, their expectation values, of course, change over time due to the explicit time-dependence of the wave function. As such, the time-dependence of $V_{BO}(t)$ results from the time-dependence of the electron-nuclear wave packet.

The time-dependent BO potential is plotted against the nuclear distance expectation value R and time in Fig. 7.10. As the expectation values during the propagation are calculated at a time step of 0.01 fs, it is possible to generate an interpolated surface, although technically there is only one point for each t and R. The equilibrium bond distance before the laser pulse, which is the optimal

bond distance for this basis set and expansion length as obtained through a propagation in imaginary time, is $R_0 = 0.763$ Å. Looking at the BO potential versus bond distance, the equilibrium distance no longer corresponds to a minimum in the potential. Instead, the minimum has been shifted to larger bond lengths at around R = 0.84 - 0.90 Å. As the potential energy curves of the H₂ excited states are more repulsive with minimum bond lengths further out than the ground state, this overall behaviour stems from the superposition of electronic ground and excited states that shifts the energy landscape. Also, for the first 40 fs, the BO potential does not reach any minima as deep as around 50 fs—although the bond lengths sampled during the propagation are the same. This reflects that not only the energetics, but also the phase of the wave packet plays a significant role in the dynamics. Through the onset of nuclear motion, the electronic wave function loses coherence rapidly. The continuing modulation of the electronic wave function through the nuclear vibration, however, leads to recurrences of coherence in the electron-nuclear wave function, and, also if the electronic ground state is significantly populated, to the reappearance of minima in the BO potential.

The time-dependent BO potential for LiH after the two-pulse excitation is shown in Fig. 7.11, and exhibits several minima at bond lengths further out from the equilibrium bond length (around R = 1.392 Å) and one minimum closer to the equilibrium bond length between t = 110 - 125 fs. Again, these minima occurring at certain times during the propagation are attributed to coherence and quantum transport effects: when the electronic part of the electron-nuclear wave packet mostly corresponds to the electronic ground state (around the equilibrium distance) versus electronic excited states (slightly elongated bond), and coherence is gained through the recurrence of resonances, then the BO potential exhibits dips that appear periodically, similar to quantum beats.



Figure 7.11: Contour plot of the Born-Oppenheimer potential V_{BO} during the IR+VIS-excitation of LiH using a pulse polarized along *z*.

The coherence of a wave packet can be quantified through the density matrix $\rho^{186,187}$. The density matrix contains the populations of the individual states on its diagonal, while the off-diagonal elements signify the mixing of the states. In a coherent wave packet, the phase of the wave packet has no destructive interference, and the trace of the density matrix squared—the purity *P*—is equal to one. Decoherence of an initially coherent wave packet can be introduced through fluctuations of the environment, through which the purity is reduced, resembling a mixed state. Another measure of the mixture of a state is the von Neumann entropy *S*, given as

$$S = -\mathrm{tr}\left[\rho \ln \rho\right] \tag{7.13}$$

If the nuclei in electron-nuclear dynamics are treated as classical particles, quantum coherence effects as well as effects from the spatial delocalization of the nuclear wave function are not present in the dynamics. Here however, electrons and nuclei are treated on the same footing, and the electron-nuclear density matrix reflects the coherence and decoherence of the *molecular* wave packet. For H_2 , initially an electronic wave packet is generated, but then the nuclear motion sets in quickly, leading to dephasing and a fast decoherence of the electronic wave packet in a few fs (Fig. 7.12). This is reflected in the quick rise of the entropy and lowering of the purity at the beginning of the propagation. However, throughout the propagation, the nuclear motion continuously modulates

the electronic wave packet, while the electron dynamics modulate the nuclear motion–leading to recurrences of coherence as the purity increases around 38 fs and 120 fs, and the entropy decreases. These coherence gains are also visible in the BO potential as potential wells whenever the electronic wave packet mostly corresponds to the ground state.

For the two-pulse excitation in LiH, the underlying process is slightly different: in the first 60.8 fs, LiH is vibrationally excited with an IR laser pulse; coherence is maintained initially but then much reduced at around 25 fs. This is when the nuclear motion sets in fully (see above), and results from the electronic wave packet following the nuclei; though instantaneously, the following is not necessarily coherent during the rapid change of nuclear positions. At several instances throughout the propagation, entropy is reduced and purity gained. The change is not as dramatic as for H₂, and there are many more fluctuations obtained. The broad minimum in the BO potential around t = 110 fs coincides with one of these oscillations. So far, at this point we can conclude that several factors play a role in the occurrence and recurrence of the "dips" in the BO potential, one of them certainly is the coherence of the electron-nuclear wave packet, another the predominant population of one of the electronic states, and also the position of the nuclei, as we have shown throughout the two-pulse scheme that a small nuclear excitation can impact the electronic motion significantly.



Figure 7.12: Entropy *S* and purity $P = tr[\rho^2]$ of the electron-nuclear wave packet as calculated from the density matrix. The norm tr $[\rho]$ is shown as well to demonstrate the conservation of the norm. The raw data for *S* and *P* is overlayed with a filtered signal (Savitzky-Golay filter) for an enhancement of the dominant peaks. a) During the laser pulse excitation of H₂. b) During the two-pulse excitation of LiH.

7.4 Summary

Simulations of the fully coupled electron-nuclear dynamics of H_2 and LiH in strong laser fields demonstrated the high level of correlation between electronic and nuclear degrees of freedom. Excitation spectra of both diatomics contain signatures of the coupled motion, where for H_2 , the electronic excitation directly initiated nuclear motion. In the case of LiH, nuclear motion was induced using a laser pulse, and then the electronic response was probed using a second pulse. Electronic transitions that are not observed under electronic excitation only for certain polarization directions could be obtained as a direct consequence of electron-nuclear coupling.

The time-dependent signatures of the potential that the nuclei experience due to electronic motion show recurring patterns that resemble quantum beating. The coherence properties of the electronnuclear wave packets predominantly influence the occurence of these minima in the potential.

Further investigations toward coupled electron-nuclear dynamics are needed to investigate the impact and magnitude of coherence effects, and their role in processes that exhibit, for example, quantum beating, or other vibronic and excitonic states ^{188–191}. This is also important with respect to attosecond dynamics, as the experimental driving field for the generation of high harmonic radiation typically lies in the IR range ¹⁹², and the molecular response to the driving field can entail nuclear effects as well as the electronic motion ¹⁷¹.

CHAPTER 8

ELECTRON-NUCLEAR MULTICONFIGURATIONAL QUANTUM DYNAMICS OF SEVERAL DIATOMIC MOLECULES

The calculations and analysis for this project were done by Lucas Aebersold. Dr. Inga Ulusoy provided helpful discussions and advice for this project. Code implementation of Akima interpolation, was done by Lucas Aebersold.

8.1 Introduction

The Born-Oppenheimer approximation (BOA)¹⁹³ is fundamental to the understanding of chemical processes, where the electrons are assumed to follow the nuclear motion instantaneously, thus readily adapting to a changing environment. A deviation from the BOA, that is, nonadiabaticity, occurs when the nuclear motion can no longer be treated separately from the electronic motion, effectively leading to a coupling of nuclear and electronic momenta. This often happens in photophysical or photochemical processes, or more generally, when the electronic states lie close together, or the electron(s) does not follow the nuclei as closely as in weak electron-nuclear interactions, for example.¹⁹⁴ We present here an approach, the multiconfiguration electron-nuclear dynamics method (MCEND)^{152,155,172,173} that goes beyond the BOA and treats electrons and nuclei on an equal footing. Using this methodology, we investigate the extent to which nonadiabatic effects can be observed in optical spectra of HD, D₂ and BeH⁺, and in high-harmonic spectra of these and several additional diatomic molecules. The presented methodology can be used to investigate nonadiabatic effects after strong-field excitation.

In the BOA, a potential energy surface (PES) is defined as the sum of the electronic kinetic, electron-electron repulsion, electron-nuclear attraction and nuclear-nuclear repulsion energy terms, and provides the multidimensional energy surface on which the nuclei reside. From this representation, additional excited-state surfaces can be included in the framework, allowing the electronic part of the molecular wave function to change between these states, 'switching' fully or partially
from one state to the other. Such 'switching' can either be represented through surface-hopping approaches $^{195-204}$, or coupled dynamics mediated through conical intersections $^{205-207}$. Alternatively, instead of a parametric dependence as in the Born-Oppenheimer approximation, a conditional dependence of the electronic part of the wave function on the nuclear positions can be employed, resulting in the exact factorisation (XF)^{177,179} or time-dependent Born-Oppenheimer approach (TD-BOA)¹⁷⁸.

In the following, details about the method and applications of the method to several diatomic molecules are presented. Ground-state properties, high-harmonic spectra and absorption spectra are described with respect to the occurrence of nonadiabatic effects and signatures.

8.1.1 Basis Representation

The primitive basis for the nuclear DOF is a grid basis with grid points $\{\alpha_k\}$, expressed in internal coordinates; for the diatomics studied here, the interatomic distance *R* is used. For the evaluation of the electron-nuclear coupling potential, the interatomic distance needs to be converted into Cartesian positions of the atoms *A*, $R_A(\alpha)$ (see below).

As the nuclei move during the propagation, the choice of the electronic basis is not trivial. While quantum chemistry approaches most often use an atom-centred basis such as Gaussian-type orbitals (GTOs), explicitly time-dependent methods such as MCTDHF often utilize a grid basis. However, an electronic grid basis is computationally more expensive than a GTO basis, and not as generalized as standard GTO basis sets. We use a combination of both types of basis representations, namely GTOs positioned at specified nuclear grid points. With this approach, an atom-centred travelling basis is avoided, as this can lead to complications due to linear dependencies in the basis set, while the computational cost is kept comparatively low. The electronic integrals for the electronic kinetic energy, electron-electron repulsion and electron-nuclear attraction are evaluated only once in the beginning of the calculation. Except for the electron-nuclear attraction integrals, the integrals are independent of the nuclear position; for the latter, an interpolation routine is used and described below.

Linear dependencies in the GTO basis introduce numerical instabilities for larger MCEND wave functions ¹⁷². Thus, the electronic basis is orthogonalized initially, and linearly dependent basis functions are removed from the basis, resulting in a smaller molecular basis set than the parent GTO basis set. The number of orthogonalized basis functions n_{ortho} , and non-orthogonal parent basis functions n_{parent} are denoted as ($n_{\text{ortho}}/n_{\text{parent}}$) in the following. At this point, several calculations are carried out to ensure that the propagation is stable for the selected basis set and MCEND expansion length. A linear dependence threshold is enforced for the orthogonalized new basis set, for all basis sets below a threshold of 0.1 for the eigenvalue of the overlap matrix was used.

8.1.2 Electron-nuclear Coupling and Diabatic Basis

The electron-nuclear coupling occurs in the EOMs of coefficients and SOs (SPFs). In the former, the expression that needs to be evaluated is

$$\left\langle \Phi_{J_e} \Phi_{J_n} \middle| \sum_{A,i}^{N_A,n_e} \frac{-Z_A}{|R_A(\alpha) - r_i|} \middle| \Phi_{L_e} \Phi_{L_n} \right\rangle = \sum_p \left\langle \Phi_{J_n}(\alpha_p) \middle| \Phi_{L_n}(\alpha_p) \right\rangle \cdot \left\langle \Phi_{J_e} \middle| \sum_{A,i}^{N_A,n_e} \frac{-Z_A}{|R_A(\alpha_p) - r_i|} \middle| \Phi_{L_e} \right\rangle$$
(8.1)

The first term on the right-hand side of Eq. 8.1 corresponds to a weight of the particular grid point, and the second term can be transformed into the AO basis, resulting in the familiar one-electron integrals of the electron-nuclear attraction, $\langle \mu | \frac{-Z_A}{|R_A(\alpha_p) - r_i|} | \nu \rangle$. The evaluation of Eq. 8.1 can be carried out under consideration of the Slater-Condon rules, which reduces the computational effort significantly.

The EOMs for the SOs and SPFs result in a similar expression for the electron-nuclear coupling

term. Here, the term enters in the mean-fields, i.e., for the electronic part

$$\langle \mu | \langle \hat{H}_{mol} \rangle^{e} | \nu \rangle = \left\langle \Phi^{e}_{J_{\text{SHD}}} \Phi_{J_{n}} \mu \right|^{N_{A}, n_{e}} \frac{-Z_{A}}{|R_{A}(\alpha) - r_{i}|} \left| \nu \Phi^{e}_{L_{\text{SHD}}} \Phi_{L_{n}} \right\rangle = \sum_{p} \left\langle \Phi_{J_{n}}(\alpha_{p}) | \Phi_{L_{n}}(\alpha_{p}) \right\rangle \cdot \left\langle \mu \Big| \frac{-Z_{A}}{|R_{A}(\alpha_{p}) - r_{1}|} \Big| \nu \right\rangle \delta_{J_{\text{SHD}}, L_{\text{SHD}}}$$
(8.2)

with single-hole determinants $\Phi_{J_{\text{SHD}}}$ and $\Phi_{L_{\text{SHD}}}$ ^{152,208}. Only electron 1 is included in the expression as the projector P_e eliminates all other electrons from Eq. 8.2.

A similar expression is obtained for the SPFs, however for only one nuclear DOF as is the case here, no nuclear mean-fields need to be evaluated. The electronic basis as used here is thus a diabatic basis, as the coupling between electrons and nuclei is included in the potential, and not the kinetic energy term.

8.1.3 Integral Interpolation Routine

The electronic integrals are evaluated only once in the beginning of the calculation. The overlap (**S**), electronic kinetic energy (**T**), and electronic position integrals (**x**, **y**, **z**), and the two-electron integrals (\mathbf{V}_{ee}) are independent of the nuclear positions. Only the electron-nuclear attraction (\mathbf{V}_{en}) depends on the actual atomic positions and is evaluated at the four to six selected interatomic distances and then interpolated on the finer nuclear grid. The selected atoms are placed at a specific nuclear grid point and ghost atoms are placed at the other remaining 3–5 grid points. Previously, a cubic spline interpolation was used to interpolate the \mathbf{V}_{en} matrix elements onto the finer nuclear grid (see Fig. 8.1). However, the interpolated curves for some of the matrix elements exhibited rather high oscillations¹⁷², typical of spline interpolation methods. To improve upon this, we have implemented the Akima method of interpolation¹⁵³ which uses a piece-wise function composed of several polynomials and applies them to successive intervals of the points. Each slope of the curve is calculated locally with each polynomial representing a piece of the curve between two points determined by both the points and their derivatives. In this way, no general functional form

for the entire data set is assumed, resulting in reduced oscillations between the explicitly sampled points. A comparison of both the cubic spline and Akima interpolation scheme is shown in Fig. 8.1 for selected diagonal V_{en} matrix elements. The Akima interpolation leads to a better agreement of calculated and experimental bond lengths for the considered diatomics as compared to the spline interpolation routine.



Figure 8.1: Selected V_{en} diagonal matrix elements obtained through the cubic spline and Akima interpolation routine. The four explicitly sampled nuclear grid points are marked on the graph.

8.1.4 Computational Details

Four nuclear grid points at which electronic basis functions are placed are used in all the following calculations. Basis sets with more sampling grid points (resulting in more ghost atoms, and as such, more basis functions) have also been generated but do not show large deviations for the properties calculated here. The EOMs are solved using an eighth-order Runge-Kutta integrator with an adaptive time step. The one- and two-electron integrals were constructed using PSI4¹⁵⁴. The parent basis sets used are Dunning's correlation consistent basis sets^{209–211} as denoted. The ground state electron-nuclear wave function for the different diatomics is obtained through a 10–20 fs imaginary time propagation. Ground-state properties including correlation energies, bond lengths,

and dipole moments are obtained as expectation values of this wave function. The ground-state wave function also serves as an initial state in the calculation of electronic, vibrational and high-harmonic spectra. All coupled cluster results were computed with the NWCHEM software package version 6.8^{56} .

The nuclear grid range and grid spacing for all diatomics are given in Table 8.1.

Table 8.1: Nuclear grid basis spanning from R_{\min} to R_{\max} at a spacing of ΔR using n_{grid} grid points, for the different diatomics. The grid points at which electronic basis functions are placed are denoted by $R_{sp,1}$ to $R_{sp,4}$. All values given in atomic units (a_0) .

	H ₂	HeH ⁺	LiH	BeH ⁺	Li ₂	N ₂
$R_{sp,1}$	0.7243	0.9520	1.5118	1.7006	3.3826	1.5000
$R_{sp,2}$	1.4283	1.4800	3.0236	3.2120	5.0456	2.2000
$R_{sp,3}$	3.0123	2.1840	5.2912	5.1012	7.8046	3.4000
$R_{sp,4}$	4.5523	3.1520	7.5589	7.3684	10.5635	5.0500
$R_{\rm min}$	0.6803	0.7760	0.9449	0.7559	2.8346	1.4500
<i>R</i> _{max}	4.7283	3.328	8.1231	7.7462	10.6592	5.2000
ΔR	0.0440	0.0440	0.1889	0.1889	0.1701	0.0500
<i>n</i> grid	92	58	38	38	46	75

8.2 Results and Discussion

The results for the diatomics are listed and discussed in the following, where we start with equilibrium properties and then discuss the obtained spectra.

8.2.1 Correlation Energy

The MCEND framework with its systematically improvable wavefunction enables the calculation of correlation energies. The correlation energy is defined as the difference between the total energy for a given expansion length and the smallest possible expansion (the MCEND wavefunction that includes only one product of determinant and Hartree product). For example, for H₂, this corresponds to the ground-state energy difference for expansion length (221) relative to (211), $E_{corr} = E_{221} - E_{211}$ (two electrons in two MOs with one SPF for the nuclei, versus the smallest possible wave function for this diatomic, which is two electrons in one MO with one SPF for the nuclei). The correlation energy that is gained upon increasing the MCEND expansion length is given in Table 8.2.

Table 8.2: Correlation energy as the difference between larger wave function expansion lengths relative to the smallest possible expansion length, in eV. The parent basis sets are given as ADZ (aug-cc-pVDZ), ATZ (aug-cc-pVTZ), and DZ (cc-pVDZ), with the number of remaining basis functions and number of parent basis functions in parenthesis.

Correlation energy recovery (eV)							
	Wa	ve functi	ion expa	nsion ler	ngth		
	2 11	221	222				
H ₂ (ADZ (27/72))	0.000	0.463	0.464				
H_2 (ATZ (66/184))	0.000	0.492	0.492				
HeH ⁺ (ADZ (24/72))	0.000	0.544	0.569				
HeH ⁺ (ATZ (60/184))	0.000	0.557	0.564				
	421	431	432	441	442		
LiH (DZ (32/76))	0.0	0.399	0.404	0.551	0.583		
LiH (DZ (59/76))	0.0	0.268	0.278	0.440	0.506		
BeH ⁺ (DZ (31/76))	0.0	0.418	0.423	0.602	0.607		
	631	641	642	651	652		
Li ₂ (DZ (48/112)	0.0	0.369	0.369	0.653	0.653		
	1471	1481	1482				
$N_2 (DZ (56/112))$	0.0	0.990	0.990				

The correlation energy can be compared to the one calculated using standard electronic-structure methods. For this, we have computed MRCI and CCSD(T) energies at the same bond distances as for MCEND. The correlation energy obtained with the electronic-structure methods is by a factor of 2 (H_2) to 1.3 (Li_2) larger than the MCEND correlation energy; the deviation between these two approaches decreases with increasing number of electrons. This deviation can be ascribed to the smaller derived basis sets in MCEND that are also not optimized to reproduce wave function properties as the standard basis sets have been.

It is noticeable that the largest correlation energy is gained upon addition of the first MO beyond

the minimum number of MOs (i.e., (211) to (221) and (421) to (431)). Adding more MOs and thus increasing the number of accessible configurations significantly increases correlation energy, but not as much as for the first MO (i.e., (431) to (441) and (641) to (651)). For LiH, addition of the first MO beyond the minimal wave function expansion length results in a correlation energy of 0.399 eV for the smaller DZ basis set. Addition of one more MO ((441) vs. (431)) leads to an additional correlation energy gain of 0.152 eV.

The addition of SPFs to the wave function leads to minor gains in correlation energy, i.e. (221) to (222), (431) to (432), (441) to (442), and (1481) to (1482), for the different diatomics. A comparison of different basis sets for H_2 , HeH⁺ and LiH, and linear dependency threshold for LiH (cc-pVDZ (56/76) basis set) shows that the correlation energy gain upon adding determinants/SPFs to the wave function is consistent, with similar amounts of correlation energy recovered for the largest expansion length. The higher-quality parent basis sets (ATZ vs. ADZ) and the sets using a lower linear-dependency threshold (thus retaining more primitive basis functions) tend to recover correlation energy more quickly.

As a compromise between accuracy and computational efficiency, expansion lengths with one or two virtual MOs (beyond the minimal number of MOs) are recommended. The addition of virtual SPFs does not impact the ground-state energies significantly. Higher-quality parent basis sets also lead to a faster convergence of correlation energy while also increasing the number of primitive basis functions in the calculation.

The computational demand of MCEND calculations is very reasonable—the timings for LiH (cc-pVDZ (32/76)) with one OpenMP thread are: (421) 0.76 min, (431) 2.4 min, (432) 5.3 min, (441) 12.7 min, (442) 37.7 min, which is very feasible. The relative timings, with respect to the smallest expansion length (421) are thus (431) factor of 3.2, (432) factor of 7.0, (441) factor of 16.7, (442) factor of 49.6. Even for N₂ with 14 electrons, a 10 fs propagation for the 1471 expansion length took 1.8 hours on 8 CPUs. The timings are obtained on Intel(R) Xeon(R) CPUs (E5-2640 (v4) at 2.40 GHz), using the Intel Fortran compiler version 17.0 with MKL and FFTW3 libraries.

8.2.2 Equilibrium Bond Length

The equilibrium bond lengths are given in Table 8.3. Largely, the changes in the bond length with increasing expansion length are very small, in the range of mÅ. The MCEND bond lengths, overall, are close to the reference bond lengths that are obtained from coupled cluster theory and experimental bond lengths.

Comparing the obtained bond lengths for different basis sets for H_2 and HeH^+ , the triple- ζ basis set, leads to a significant improvement in comparison with the reference values. For all diatomics, an increasing MCEND wave function expansion length does not impact the equilibrium distance significantly.

For the lighter diatomics, such as H_2 and HeH^+ , the grid sampling at different interatomic distances leads to a relatively uniform positioning of both atoms. However, for heteronuclear diatomics where the mass difference between atoms is much more significant, one of the atom types will be positioned more closely on the nuclear grid than the other in the integral sampling, leading to more linear dependencies in the basis functions on that atom. This results in an imbalanced removal of basis functions, and ultimately to a poorer description of the diatomic due to the bias, such as for LiH and BeH⁺. These two diatomics exhibit slightly larger deviations of the MCEND compared to the experimental/CCSD(T) bond length, at ~0.1–0.2 Å. Still, overall, the bond lengths for the other diatomics are in very good agreement with the reference bond lengths.

Table 8.3: Equilibrium bond lengths of the different diatomics in Å. The parent basis sets are given as ADZ (aug-cc-pVDZ), ATZ (aug-cc-pVTZ), and DZ (cc-pVDZ), with the number of remaining basis functions and number of parent basis functions in parenthesis. For comparison, bond lengths computed at the CCSD(T)/aug-cc-pVQZ (AQZ) level of theory are given as well (CCSD/augcc-pVQZ for H₂ and HeH⁺), along with available experimental r_e values taken from the NIST WebBook.²¹²

	Wave f	unction	expansic	on length/	bond length		
	211	221	222			CCSD/AQZ	Exp.
H ₂ (ADZ (27/72))	0.755	0.763	0.763			0.742	0.741
H ₂ (ATZ (66/184))	0.752	0.758	0.758			0.742	0.741
HeH ⁺ (ADZ (24/72))	0.881	0.882	0.884			0.775	
HeH ⁺ (ATZ (60/184))	0.782	0.785	0.786			0.775	
	421	431	432	441	442	CCSD(T)/AQZ	Exp.
LiH (DZ (32/76))	1.387	1.390	1.389	1.389	1.388	1.570	1.596
LiH (DZ (59/76))	1.496	1.496	1.496	1.496	1.495	1.570	1.596
BeH ⁺ (DZ (31/76))	1.401	1.403	1.403	1.403	1.403	1.309	
	631	641	642	651	652	CCSD(T)/AQZ	
Li ₂ (DZ (45/112)	2.628	2.628	2.628	2.628	2.628	2.622	2.673
	1471	1481	1482			CCSD(T)/AQZ	
N ₂ (DZ (56/112))	1.137	1.137	1.137			1.096	1.098

8.2.3 Dipole Moments

The dipole moments obtained for different expansion lengths of the MCEND wave function are given in Table 8.4. The agreement with the reference values from experiment is excellent, with deviations in the range of mD for HeH⁺ and LiH. For BeH⁺, no experimental value is available to our knowledge, and a comparison with coupled cluster theory (CCSD(T)) results in a deviation of ~0.8 D. One reason for this discrepancy lies in the slightly too long equilibrium bond length; and it appears that the dipole moment is more sensitive to a balanced description of both atoms in the re-orthogonalized basis. Additionally, it should be noted that the MCEND dipole moment values are vibrationally averaged as the nuclear contribution to the molecular dipole moment is of a quantum-mechanical nature.

The main improvement of the MCEND dipole moment is obtained when including more spin orbitals in the MCEND wave function, accounting for electron correlation (going from (211) to (221) for HeH⁺, and from (421) to (431) for LiH). This is expected, as the impact of electron correlation on the electronic structure is significant. The addition of further SOs does not change the dipole-moment value significantly. Interestingly, the addition of an SPF to the wave function affects the dipole moment for LiH, while this impact is not observed for HeH⁺ and BeH⁺.

Table 8.4: Dipole moments of the different diatomics in Debye (D). The parent basis sets are given as ADZ (aug-cc-pVDZ), ATZ (aug-cc-pVTZ) and DZ (cc-pVDZ), with remaining and parent basis functions as in Table 8.2. For comparison, the experimental dipole moments for HeH⁺²¹³ and for LiH²¹⁴ are given. No experimental value is available for BeH⁺, instead a CCSD(T)/aug-cc-pVQZ dipole moment is used for comparison. The error of the MCEND dipole moment value relative to the reference value is given in parenthesis.

	Wave	function exp	bansion leng	gth/dipole m	oment	
	211	221	222			ref.
HeH ⁺ (ATZ)	1.806	1.729	1.735			1.709 ^a
$\Delta_{\rm ref.}$	(0.097)	(0.020)	(0.026)			
	421	431	432	441	442	ref.
LiH (DZ)	6.197	5.872	5.872	5.997	5.996	5.880
$\Delta_{\rm ref.}$	(0.317)	(-0.008)	(-0.008)	(0.117)	(0.116)	
BeH ⁺ (DZ)	3.021	2.823	2.855	2.787	2.819	3.590
$\Delta_{\rm ref.}$	(-0.569)	(-0.767)	(-0.735)	(-0.803)	(-0.771)	

a at 0.767 Å

8.2.4 High-harmonic Generation

Using the MCEND approach, high harmonic spectra can also be generated. For this, the targeted molecule is irradiated with a strong infrared (IR) laser pulse, and the power spectrum is then obtained from the Fourier transform of the electronic dipole moment squared. The laser pulse takes the following form

$$\boldsymbol{E}(t) = \boldsymbol{E}_0 \sin^2\left(\frac{\pi t}{2\sigma}\right) \cos(\omega_0 t), \tag{8.3}$$

where E_0 is the initial pulse height with a specific polarization direction along the *x*, *y*, or *z* axis, 2σ is the pulse width, and ω_0 is the carrier frequency.

The power spectrum for H₂, HD, and D₂ for different polarization directions of the laser pulse (*x*: perpendicular to the molecular axis; *z*: parallel to the molecular axis) is shown in Fig. 8.2. The laser pulse parameters are $I = 10^{14}$ W/cm², $\omega_0 = 1.55$ eV, and laser pulse duration of 20 cycles (≈ 53 fs).



Figure 8.2: HHG spectra of H_2 , HD and D_2 (221/ATZ), for each given (expansion length/basis set) and *z*- (along molecular axis) and *x*- (perpendicular to molecular axis) polarization direction of the electric field.

The high harmonic spectrum for H_2 and D_2 exhibits peaks at the odd harmonics, as expected for a centrosymmetric molecule. For HD, there is no such constraint for the *z*-polarization direction, and the peaks at even harmonics are clearly visible. In all spectra, the peaks flatten off around the 25th harmonic for the *z*-polarization direction, and the 13th harmonic for the *x*-polarization direction. For higher orders, small oscillations are obtained, which is a result of the Gaussian basis set that does not allow for ionisation²¹⁵. In the harmonic spectra especially for the *z*-polarization direction, the appearance of shoulders on the lower-energy side of the peaks is very noticeable starting from the seventh order. These are attributed to the electron-nuclear coupling, as it has been predicted previously that nuclear motion leads to a red-shift of the high harmonics²¹⁶. For higher harmonics, around order 20 (211)/24 (221), small peaks appear at even harmonics, which could be a consequence of the electron-nuclear coupling¹⁶⁹. Isotope effects are not observed in the spectra.

The HHG spectra of HeH⁺, LiH, and BeH⁺ are shown in Fig. 8.3. The laser pulse parameters for HeH⁺ are $I = 10^{14}$ W/cm², $\omega_0 = 1.55$ eV, and laser pulse duration of 53 fs. For LiH and BeH⁺, a different laser pulse frequency was chosen, as with a frequency of 1.55 eV, no harmonic generation was observed. The laser pulse parameters for LiH are thus $\omega_0 = 3.1$ eV, $I = 8.7 \times 10^{11}$ W/cm², and pulse duration of 26.7 fs. The pulse parameters for BeH⁺ are $\omega_0 = 3.1$ eV, $I = 7.9 \times 10^{12}$ W/cm², and laser pulse duration of 26.7 fs.

For HeH⁺, only odd harmonics are observed for the *x*-polarization direction, while the even harmonics appear in the spectrum for the *z*-polarization direction. Only three resonances are observed, indicating that the electrons are tightly bound, which is expected for this cationic state. The peaks themselves appear symmetric, and nonadiabatic effects due to nuclear motion seem to be absent.

For LiH, the high-harmonic spectra are not very smooth, with many smaller peaks in between the even and odd harmonics. This can be attributed to electronic excitations during the HHG process, mostly for the *z*-polarization direction (see Supplemental Material). Also, more harmonics can be observed for the *x*-polarization direction than for the *z*-polarization direction. This is due to a slight nuclear vibration, which destroys the coherence between the tightly bound part of the wave function and the tail that has extended out (see Supplemental Material). This effect—electronic excitation and thus induced nuclear motion uptake during the HHG process—is a manifestation of electron-nuclear coupling that can be observed for LiH and excitation parallel to the bond.

The high-harmonic spectra for BeH^+ are similar to the LiH ones, except that fewer and less pronounced harmonics are observed, in line with the positive charge of the diatomic and the more tightly bound electronics. Nuclear motion does not play a role in the spectra, with the *z*-polarization direction leading to a smooth and regular spectrum.



Figure 8.3: HHG spectra of HeH⁺ (221/ATZ), LiH (441/DZ), and BeH⁺ (441/DZ), for each given (expansion length/basis set) and z- (along molecular axis) and x- (perpendicular to molecular axis) polarization direction of the electric field.

The HHG spectra of Li_2 and N_2 are shown in Fig. 8.4. The laser pulse parameters for Li_2 are the same as for BeH⁺, and for N₂, the parameters are the same as for H₂ and HeH⁺.

For Li₂, almost exclusively the odd harmonics are observed in the spectra, with some very slight deviation around the second harmonic for the *z*-polarization direction. For the *x*-polarization direction, there is one more harmonic that can be observed, and the intensity of the peaks is larger than for the *z*-polarization direction. There are also fairly pronounced shoulders appearing at the

lower frequency tail of the peaks for the *x*-polarization direction, indicating a mechanism of energy loss during the harmonic generation. This is attributed to excitation into electronic excited states and a resulting simultaneous increase of the internuclear distance, similar as for LiH (see Supplemental Material).

For N₂ *z*-direction, three peaks can be observed in the harmonic spectrum, appearing at the odd harmonics at first, third and fifth order. Additional peaks appear at higher orders (>6) and are attributed to electronic excitation. No nonadiabatic effects are observed for the low-order peaks. For the *x*-direction, two peaks are visible. Only the (1471) expansion length is shown; for the *z*-polarization direction, the obtained high-harmonic spectrum for the (1481) expansion length is almost identical to (1471), while for the *x*-polarization direction the (1481) expansion length exhibited numerical stability issues resulting in a 'noisy' spectrum. The peaks at higher energies result from a similar process as the high-harmonic peaks; there is no net excitation that can be observed in the position expectation values nor energies for N₂.



Figure 8.4: HHG spectra of Li₂ (651/DZ) (top) and N₂ (1471/DZ) (bottom), for each given (expansion length/basis set) and z- (along molecular axis) and x- (perpendicular to molecular axis) polarization direction of the electric field.

Summarising, in some of the high-harmonic spectra, signatures of electron-nuclear coupling are observed, either in the appearance of shoulders at the low-energy tail of the peaks due to nuclear vibration or in the destruction of resonances due to electronic excitation (overlayed features of several eigenstates that induce nuclear motion). Nuclear motion uptake as an excitation of vibrations only manifests for a polarization direction parallel to the bond (z), while further electronic excitations and the formation of a wave packet that drives the nuclei from their equilibrium position can be observed also for the x-polarization direction. The electronic excitation can affect the electron-nuclear interaction and result in a change of internuclear distance (as for BeH⁺).

8.2.5 Absorption Spectra

Using the wave functions obtained from a propagation in imaginary time as the initial state, the absorption spectrum of a molecule can be generated with MCEND by computing the autocorrelation function, $\langle \Psi(\mathbf{r}, \mathbf{R}, t = 0) | \Psi(\mathbf{r}, \mathbf{R}, t) \rangle$, and taking its inverse Fourier transform. Here, the molecule is excited using a short, non-resonant laser pulse, so that a superposition state is generated which includes components of the accessible eigenstates of the molecule. The frequency components of the autocorrelation function (and their weights) provide insight about the energies of the eigenstates and transition moments from the ground state.

An absorption spectrum was generated for BeH⁺ (DZ basis set), using the laser pulse parameters $\omega_0 = 4.08 \text{ eV} (304 \text{ nm})$, $I = 3.16 \times 10^{13} \text{ W/cm}^2$ and a pulse width of $2\sigma = 2.8 \text{ fs}$ (Fig. 8.5). The experimental transition is reproduced in the spectrum, albeit with a red shift of the peak. In concordance with the calculated bond length and dipole moment, and their deviations with respect to calculated/experimental values (bond length that is slightly too long and dipole moment that is too small), a slightly different position of the calculated peak is expected. It is noticeable that electron-nuclear coupling and vibrational excitation only seems to play a minor role in the spectrum, as no 'vibrational comb' or other, minor peaks close to the main electronic transition are observed, and also there is no nuclear motion uptake in the bond distance expectation value (not shown).



Figure 8.5: Absorption spectrum for BeH⁺ (441/DZ) with laser pulse polarized perpendicular to the bond. The experimental transition energy is overlayed as a vertical line.

To further investigate the role of electron-nuclear coupling in the electronic excitation spectra of H₂, we extend our previous treatment (¹⁵⁵) to the isotopic variants HD and D₂ (Fig. 8.6) with the ADZ-derived basis set. Note that the previous H₂ spectrum¹⁵⁵ is reproduced for a simpler comparison. The laser pulse parameters are $2\sigma = 2.8$ fs, $\omega = 0.416 \text{ E}_h$ (109.5 nm), $I = 10^{14}$ W/cm², *z*-direction (along the molecular axis); $2\sigma = 1.4$ fs, $\omega = 0.555 \text{ E}_h$ (80.9 nm), $I = 10^{14}$ W/cm², *x*-direction, for a (221) expansion length.



Figure 8.6: Absorption spectra of H_2 , HD, D_2 (ADZ/221) for *z*-polarization direction (top) and *x*-polarization direction (bottom).

A comparison of the HD and H₂ spectra shows that these are very similar. There are very slight deviations in the intensities, and all peaks are well reproduced in the HD spectrum. Some of the peaks in HD are shifted to slightly lower frequencies (i.e. at $\approx 89,000 \text{ cm}^{-1}$ for *z*-polarization direction) in comparison to H₂, signifying a slight isotope effect (a slightly lower vibrational transition frequency).

The D_2 spectrum however appears quite different from HD and H_2 , with overall lower intensities and much broader peaks than for HD and H_2 . As for these diatomics with no ground-state dipole moment, and no changing dipole moment upon vibration, a direct coupling of the nuclear part of the wavefunction to the electric field of the laser pulse is not possible. Nuclear motion can only be induced indirectly through electron-nuclear coupling¹⁵⁵ (e.g., a Raman-type process). We expect the peak intensity to be lower for the heavier nuclei, and the maxima shifted to lower energies. This is indeed the case, and exemplifies the reduced momentum transfer from electrons to nuclei (reduced intensity) and lower vibrational frequencies (shifted peak maxima) due to the higher nuclear mass of the isotopic variants.

8.3 Conclusion

The MCEND method has been applied to several closed-shell diatomics. Time-independent and time-dependent properties are obtained including correlation energy gain, equilibrium bond lengths, dipole moments, high-harmonic spectra, and excitation energies, and, overall, are in good up to excellent agreement with experimental and other theoretical values.

High-harmonic spectra of the diatomics can be generated using a laser pulse. For some of the diatomics, nonadiabatic effects could be observed (H_2 , HD, D_2 , LiH, BeH⁺, Li₂), while others exhibit pure electronic contributions to the spectra (HeH⁺, N₂). The nonadiabatic effects can occur as lower-energy shoulders in the high-harmonic spectra through excitation of nuclear motion by the laser pulse; or through the destruction of the electronic resonances by the induced nuclear motion; or through an electronic excitation into another electronic state, effectively driving the nuclei from their equilibrium position.

No nonadiabatic effects were observed in the absorption spectrum of BeH⁺, with overall good agreement with experimental data. Isotope effects in the absorption spectra of $H_2/HD/D_2$ were investigated and manifest in generally lower peak intensities, and red shifts in the peak structure (HD) and the disappearance of vibrational excitations (D₂) in the spectra.

Overall, nonadiabatic effects can be observed also for heavier nuclei such as Li and Be, depending on the driving electric field, and can manifest as different signatures in the spectra. Through carefully tailoring the strong electric fields in an experimental set-up, we expect that these effects can be enhanced or depleted, depending on the choice of the laser pulse parameters. Such studies could provide insights into the mechanism and control of nuclear motion through attosecond pulses.

CHAPTER 9

FUTURE DIRECTIONS

In terms of future investigations, for the lanthanide and actinide projects, there is further work that can be done. A greater understanding of the impact of the spin-orbit coupling (SOC) on the energies of the lanthanides is needed, especially for the more computationally difficult lanthanide species Gd-Yb. In addition to the SOC effects, an investigation of the utility of multireference methods on actinide and lanthanides is also be important These types of computations are difficult in terms of the active space selection, as many additional states may need to be included, but computationally, may not be feasible. Molecules including TbO, HoO, TmO, ErO, or DyO, using multireference methods like CASPT2, CASSCF, MRCI, and their spin–orbit variants (SO-CASPT2, SO-MRCI) would provide a natural next step. The Wilson group's *f-ccCA* composite method and MRCI are being used by the Wilson group to investigate the An66 set and lanthanide silicates and sulfides. Thus, the oxides will provide more complete insight.

To address the clear DFT deficiencies, while there are many additional functionals that can be examined, it is likely that most, if not all of the present generation of single-reference wavefunctionbased functionals will be deficient for the molecules studied herein, as well as similar molecules. However, functionals that are better able to address multireference effects may result in improved energy predictions. Recently, a multireference variant of DFT, called multiconfiguration pair-DFT (MC-PDFT),²¹⁷ was developed by the Gagliardi and Truhlar groups. The functionals include complete/restricted active space (CAS/RAS) and density matrix renormalization group (DMRG) variations. Considering these functionals for the actinide and lanthanide datasets would provide an excellent challenge for these functionals; if they are accurate for the datasets, then they may be promising for larger heavy element species (though depending upon computational cost and errors with respect to size).

For the electron-nuclear dynamics development, there are many improvements and implementations that can be made in the future. Currently, an open-shell version is being developed to allow broader applicability. As well, the code is presently applicable to diatomics, and needs to be expanded to polyatomics. Which require expanded routines to allow the positions of atoms to move in more than one dimension. To implement this a variety of coordinate system representations, such as Jacobi, curvilinear, or hyperbolic could be used. The choice of which coordinate representation depends on the problem of interest, e.g. Jacobi coordinate are good when describing molecular collisions, like H₂ and H₂. Implementing these coordinate systems will be straightforward, though time-consuming. However, an issue arises with the static basis set routine. In the current implementation, additional basis functions cause a step increase in computational time. Thus, an alternate basis set approach must be implemented to address larger systems. This approach must not rely on the static Gaussian basis sets, and instead would need to utilize a basis set that can evolve in time. This would reduce the number of basis functions needed and can alleviate issues with linear dependencies that occur at present. Implementing such an approach will be a challenge, as there is no straightforward route.

Grid type basis sets for the electrons are a possibility, though computational costs are still high and issues with numerical stability may still be problematic. There is one interesting route, based on a recently proposed method by White, that utilizes a hybrid grid/basis set.²¹⁸ Termed 'gausslets', it combines advantages of both grid and basis set approaches, by being composed of a sum of Gaussians. Diagonal approximations also introduced can reduce the computational scaling of two-electron integrals, which would need to be recalculated when the nuclei have moved. The current static set does not require the two-electron integrals to be recalculated after each update to position, which is its main advantage. But if this gausslet-type of basis set description can reduce that cost, it would be a very promising alternative. This proposed method is still new, however, and the examples presented in the White paper were restricted to one-dimensional cases, though progress for a three-dimensional case has been published in a newer paper.²¹⁹ As noted in Chapter 6, translational and rotational terms in GTO approaches for the nuclear orbitals can lead to energy contamination in a resulting spectrum. The MCEND method uses a grid-type of basis set for the nuclei, rather than a GTO-based approach, thus this contamination is likely not a concern. However, any description of the nuclei based on GTOs that may be considered, including the proposed gausslet

approoach, should be checked for contamination of the terms.

Implementation of ionization effects have not been implemented in the code and are needed for a more complete description of high-harmonic spectra. One extension to the code that could enable this would be the addition of a complex absorption potential (CAP). This would allow the absorption of the electronic wavefunction as it approaches a set distance from the nuclei, where it essentially 'ionizes' and escapes the system. The CAP allows for a better description of the continuum states, important not only for HHG but also for any process that involves electronic excitation to the continuum, such as photoionization cross sections or above-threshold ionization rates.

For applications of the MCEND method, there are many molecules that could be examined. Once polyatomic routines are implemented, there are a few reactions to look at. Already planned are a study of the reaction rates for the radical reaction $CH_4 + OH \cdot \longrightarrow CH_3 \cdot + H_2O$. This reaction is useful for methane conversion to make methanol, and is found on photocatalytic pathways. Analyzing reactions like the methane reaction requires the full functionality of an open-shell, polyatomic implementation of MCEND, and likely, with a moving basis set. APPENDICES

APPENDIX A

LANTHANIDE DATA

	LaCl3	CeCl3	PrCl3	NdCl3	GdCl3
SVWN	-184.2	-157.1	-154.1	-134.5	-153.0
BP86	-174.6	-148.1	-135.4	-113.9	-138.7
BLYP	-168.9	-141.8	-121.3	-106.0	-133.0
PW91	-178.2	-150.9	-138.8	-117.0	-141.8
PBE	-176.4	-149.7	-138.2	-116.3	-140.3
SSB-D	-172.9	-134.3	-115.2	-103.6	-205.9
B97-D	-170.9	-134.8	-124.2	-111.2	-110.7
TPSS	-183.7	-161.0	-139.4	-123.1	-148.8
M06-L	-189.3	-163.8	-151.1	-126.2	-160.3
PBE0	-174.6	-158.0	-138.6	-94.5	-137.7
B3LYP	-173.0	-153.6	-134.0	-89.4	-131.1
BHLYP	-177.1	-168.4	-142.7	-100.5	-153.9
B3P86	-180.3	-160.8	-142.4	-98.2	-136.2
B97-1	-173.1	-154.5	-132.9	-100.8	-165.0
MPW1K	-178.3	-169.1	-144.4	-101.6	-152.3
X3LYP	-168.5	-159.9	-130.1	-96.5	-128.9
TPSSH	-179.3	-160.2	-130.7	-123.4	-133.1
M06	-168.1	-154.6	-147.6	-113.9	-127.1
M06-2X	-167.3	-155.7	-136.8	-86.0	-135.0
M11	-181.6	-172.9	-144.6	-103.5	-187.0
CAM-B3LYP	-174.3	-164.9	-135.3	-88.8	-128.3
B2PLYP	-169.5	-166.6	-87.7	-46.8	-232.9
Experiment	-177.0	-171.0	-175.0	-172.0	-165.0
Error	-1.5	-1.5	-1.0	-1.2	-1.5

Table A.1: Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol⁻¹) computed with each functional for the lanthanide trichlorides (Ln54HFa subset) with experimental values shown for comparison.

	LaF3	CeF3	PrF3	NdF3	GdF3	TbF3	
SVWN	-317.8	-289.0	-286.9	-271.7	-281.2	-263.0	
BP86	-300.1	-271.6	-261.6	-254.5	-262.9	-249.5	
BLYP	-294.7	-265.5	-254.9	-249.1	-258.0	-247.4	
PW91	-304.1	-274.9	-265.1	-257.4	-266.4	-253.5	
PBE	-301.3	-272.7	-263.1	-254.9	-263.8	-252.8	
SSB-D	-302.3	-260.9	-247.5	-233.4	-331.4	-252.5	
B97-D	-300.7	-267.1	-254.4	-238.6	-268.2	-244.9	
TPSS	-305.5	-281.3	-268.9	-268.1	-270.7	-263.0	
M06-L	-314.3	-287.5	-281.6	-271.1	-284.9	-286.0	
PBE0	-304.1	-285.6	-273.4	-232.1	-281.1	-290.2	
B3LYP	-301.5	-280.0	-268.0	-226.5	-275.8	-280.0	
BHLYP	-307.9	-297.0	-285.6	-240.4	-282.9	-322.1	
B3P86	-309.6	-288.1	-276.3	-235.7	-291.6	-285.0	
B97-1	-301.7	-281.0	-271.1	-227.3	-276.9	-280.0	
MPW1K	-309.9	-298.7	-286.5	-241.8	-281.8	-316.0	
X3LYP	-300.8	-290.2	-271.2	-226.6	-255.9	-282.0	
TPSSH	-305.3	-284.6	-273.4	-247.5	-315.1	-274.8	
M06	-308.4	-292.5	-278.6	-254.8	-259.6	-301.1	
M06-2X	-301.0	-286.6	-263.8	-219.8	-266.1	-302.9	
M11	-323.5	-312.5	-296.2	-254.0	-331.6	-324.4	
CAM-B3LYP	-310.2	-298.9	-279.6	-234.6	-309.7	-289.7	
B2PLYP	-301.1	-297.8	-286.0	-225.0	-361.5	-291.7	
Experiment	-306.9	-315.1	-308.2	-315.3	-299.9	-298.7	
Error	-2.3	-1.0	-1.2	-3.2	-1.2	-3.2	

Table A.2: Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol⁻¹) computed with each functional for the lanthanide trifluorides (Ln54HFa subset) with experimental values shown for comparison.

	DyF3	HoF3	ErF3	LuF3
SVWN	-251.0	-254.3	-249.8	-292.3
BP86	-238.8	-226.8	-232.8	-274.5
BLYP	-235.6	-221.1	-229.2	-270.4
PW91	-241.9	-230.5	-236.3	-278.4
PBE	-240.4	-230.1	-234.7	-275.7
SSB-D	-232.1	-219.4	-218.0	-272.7
B97-D	-230.0	-230.4	-223.7	-275.9
TPSS	-234.4	-247.2	-250.5	-284.1
M06-L	-243.9	-243.1	-249.5	-295.9
PBE0	-221.6	-255.0	-265.5	-285.4
B3LYP	-220.6	-245.9	-257.7	-282.3
BHLYP	-203.2	-282.9	-300.1	-295.5
B3P86	-227.4	-252.7	-262.7	-288.8
B97-1	-216.4	-242.4	-256.3	-282.7
MPW1K	-212.6	-200.9	-291.5	-295.4
X3LYP	-219.0	-247.5	-259.7	-282.4
TPSSH	-228.0	-252.2	-260.9	-286.3
M06	-251.7	-228.9	-241.3	-287.3
M06-2X	-197.6	-256.5	-266.4	-285.3
M11	-209.7	-285.1	-277.8	-313.9
CAM-B3LYP	-204.9	-254.0	-266.1	-291.9
B2PLYP	-215.1	-252.2	-285.5	-288.2
Experiment	-296.6	-300.5	-301.2	-298.7
Error	-2.1	-2.5	-2.5	-3.2

Table A.3: Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol⁻¹) computed with each functional for the lanthanide trifluorides (Ln54HFa subset) with experimental values shown for comparison.

Table A.4: Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol⁻¹) computed with each functional for the lanthanide difluorides (Ln54HFb subset) with experimental values shown for comparison.

	LaF ₂	SmF ₂	EuF ₂
SVWN	-188.7	-129.1	-180.0
BP86	-174.5	-132.6	-171.0
BLYP	-171.8	-133.5	-167.3
PW91	-178.8	-134.6	-173.7
PBE	-176.7	-132.2	-171.4
SSB-D	-172.5	-152.6	-163.3
B97-D	-162.9	-162.6	-168.4
TPSS	-177.3	-141.3	-178.7
M06-L	-172.6	-122.6	-183.1
PBE0	-175.6	-140.2	-174.7
B3LYP	-173.8	-141.2	-172.2
BHLYP	-175.6	-159.4	-178.0
B3P86	-178.5	-141.4	-179.1
B97-1	-165.5	-165.6	-172.0
MPW1K	-173.4	-175.1	-181.1
X3LYP	-168.8	-165.4	-171.6
TPSSH	-171.6	-173.9	-178.5
M06	-165.5	-168.7	-175.1
M06-2X	-165.6	-165.3	-169.9
M11	-179.8	-189.6	-197.2
CAM-B3LYP	-174.2	-171.0	-177.4
B2PLYP	-167.6	-170.7	-173.7
Experiment	-147.0	-182.0	-187.0
Error	15.0	11.0	11.0

	LaCl2	CeCl ₂	PrCl ₂	NdCl ₂	SmCl ₂	EuCl ₂	GdCl2	TbCl ₂	HoCl2	ErCl ₂
SVWN	-91.4	-77.6	-83.2	-46.6	-98.4	-105.0	-105.4	-46.4	-68.3	-83.5
BP86	-83.4	-69.2	-73.1	-44.0	-48.4	-101.9	-126.2	-43.8	-62.6	-78.0
BLYP	-78.9	-64.2	-68.4	-41.3	-90.0	-97.1	-120.4	-42.5	-58.8	-72.8
PW91	-86.4	-71.9	-75.6	-45.3	-97.0	-103.9	-129.2	-45.8	-64.5	-80.2
PBE	-84.9	-70.9	-74.6	-44.2	-95.5	-102.4	-127.8	-45.8	-64.2	-79.5
SSB-D	-83.3	-60.3	-64.1	-60.1	-80.5	-93.4	-102.1	-42.6	-57.1	-69.8
B97-D	-75.2	-56.0	-65.6	-67.3	-89.9	-97.8	-126.9	-32.7	-60.4	-75.0
TPSS	-88.5	-77.4	-79.2	-55.2	-106.4	-112.3	-135.2	-54.9	-74.6	-88.8
M06-L	-87.5	-75.3	-78.2	-48.4	-110.9	-116.3	-138.2	-62.0	-50.5	-91.0
PBE0	-81.9	-72.9	-70.3	-49.4	-99.1	-104.8	-115.7	-56.2	-65.7	-82.8
B3LYP	-80.2	-69.2	-68.9	-48.2	-96.5	-102.6	-132.0	-53.1	-63.3	-80.8
BHLYP	-81.4	-79.9	-67.8	-62.5	-103.4	-108.0	-70.5	-60.8	-69.1	-87.2
B3P86	-85.9	-74.9	-74.7	-51.1	-102.9	-109.0	-130.2	-57.0	-69.8	-86.0
B97-1	-76.9	-57.6	-67.1	-68.0	-96.3	-102.6	-130.7	-55.4	-62.5	-82.1
MPW1K	-83.7	-81.7	-71.9	-75.8	-105.4	-110.3	-71.2	-64.8	-142.3	-88.9
X3LYP	-77.1	-76.6	-65.7	-65.2	-93.5	-99.5	-124.0	-51.4	-60.3	-77.8
TPSSH	-84.9	-73.4	-75.1	-79.5	-104.8	-110.3	-167.5	-55.7	-70.4	-87.8
M06	-70.6	-68.5	-64.7	-66.0	-90.4	-98.4	-99.9	-53.6	-46.4	-71.1
M06-2X	-75.6	-73.9	-61.6	-62.8	-93.0	-98.0	-58.7	-54.3	-53.4	-73.3
M11	-84.7	-82.5	-76.5	-76.9	-110.4	-118.7	-138.0	-78.7	-57.1	-102.0
CAM-B3LYP	-80.2	-79.6	-69.7	-69.6	-97.8	-104.1	-144.1	-56.2	-65.0	-82.6
B2PLYP	-76.7	-76.5	-59.1	-96.1	-97.4	-101.8	-153.7	-77.1	-25.2	-82.1
Experiment	-85.0	-70.0	-82.0	-85.0	-120.0	-109.0	-73.0	-73.0	-85.0	-84.0
Error	8.0	5.0	5.0	5.0	4.0	3.0	5.0	5.0	5.0	5.0

Table A.5: Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol⁻¹) computed with each functional for the lanthanide dichlorides (Ln54HFb subset) with experimental values shown for comparison.

	LaF	HoF	YbF	LuF
SVWN	-40.4	-19.7	-63.0	-50.9
BP86	-34.8	1.7	-58.5	-42.0
BLYP	-30.9	7.4	-57.1	-41.7
PW91	-37.6	-0.6	-60.2	-43.5
PBE	-36.3	-1.5	-58.8	-42.7
SSB-D	-39.0	-4.7	-55.0	-41.8
B97-D	-23.0	-4.7	-51.3	-40.7
TPSS	-37.1	-3.4	-63.1	-43.1
M06-L	-27.6	25.1	-62.3	-49.2
PBE0	-35.2	0.9	-59.8	-44.6
B3LYP	-31.2	6.5	-58.1	-44.5
BHLYP	-31.6	10.2	-61.2	-48.2
B3P86	-36.4	-0.4	-61.4	-45.4
B97- 1	-26.3	16.7	-53.5	-44.4
MPW1K	-36.5	-98.1	-63.5	-46.6
X3LYP	-30.6	7.2	-57.8	-44.8
TPSSH	-36.0	0.7	-62.0	-43.5
M06	-21.9	2.4	-51.5	-50.2
M06-2X	-24.2	-1.9	-56.1	-46.0
M11	-37.5	-20.3	-72.8	-53.4
CAM-B3LYP	-32.8	4.0	-60.8	-48.3
B2PLYP	-28.5	7.1	-59.0	-47.1
Experiment	-21.0	-40.0	-80.0	-14.0
Error	10.0	3.0	10.0	10.0

Table A.6: Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol⁻¹) computed with functional for the lanthanide fluorides (Ln54HFb subset) with experimental values shown for comparison.

	LaO	CeO	PrO	NdO	SmO	EuO	GdO
SVWN	-47.0	-22.8	-17.3	-0.3	-3.6	-19.8	-50.1
BP86	-36.3	-12.0	-1.4	14.0	-2.4	-13.5	-63.0
BLYP	-31.7	-12.1	5.0	20.2	-0.6	-9.1	-57.0
PW91	-39.0	-14.1	-3.7	12.4	-2.6	-15.0	-65.8
PBE	-37.8	-13.6	-4.1	12.8	-0.8	-13.4	-64.4
SSB-D	-40.1	0.3	18.1	33.7	18.5	0.6	-46.8
B97-D	-24.2	19.4	24.0	41.0	35.7	-2.2	-62.8
TPSS	-36.9	-17.2	-4.0	9.1	-6.4	-19.6	-68.7
M06-L	-29.3	-10.3	0.9	26.6	3.7	-12.2	-62.3
PBE0	-31.0	-17.2	-3.7	14.2	4.7	-2.7	-48.1
B3LYP	-27.9	-11.0	2.6	19.4	3.8	-0.9	-63.2
BHLYP	-21.0	-14.3	-0.5	17.3	0.8	17.6	3.9
B3P86	-33.8	-16.8	-3.9	13.2	2.3	-7.8	-61.9
B97-1	-24.3	8.3	6.7	23.6	8.2	-0.1	-61.3
MPW1K	-25.7	-18.9	-3.8	14.6	4.1	2.0	0.2
X3LYP	-25.0	-19.0	4.7	21.6	6.2	2.6	-55.3
TPSSH	-31.8	-15.7	-1.4	12.7	-0.2	-11.9	-18.3
M06	-23.8	-16.0	4.7	26.8	34.2	4.5	-32.1
M06-2X	-20.8	-8.5	20.6	41.7	31.0	14.3	11.9
M11	-29.1	-20.2	1.8	18.8	6.7	-8.3	-64.5
CAM-B3LYP	-27.6	-20.8	2.7	20.5	7.4	2.2	-72.1
B2PLYP	-23.8	-21.2	-7.8	8.6	0.6	-0.9	7.1
Experiment	-28.4	-31.5	-34.7	-28.7	-25.1	-13.5	-16.3
Error	2.0	2.0	2.0	2.0	2.0	2.0	2.0

Table A.7: Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol⁻¹) computed with each functional for the lanthanide monoxides (Ln54HFb subset) with experimental values shown for comparison.

	ThO	DuO	H-O	ErO	TmO	VhO	LuO
	100	DyO	ПОО	EIU	Thio	100	LuO
SVWN	16.4	17.5	38.6	17.7	1.0	-4.9	-7.7
BP86	13.5	10.7	61.7	32.7	7.5	44.1	1.8
BLYP	14.4	12.8	69.6	38.7	11.2	3.7	5.2
PW91	12.9	10.8	60.4	31.3	6.2	0.3	0.5
PBE	12.7	11.6	59.5	31.3	7.9	1.9	1.9
SSB-D	18.5	21.5	64.9	25.9	18.7	16.1	10.0
B97-D	30.6	30.9	50.4	19.1	12.2	9.5	14.6
TPSS	7.6	21.4	55.1	29.1	0.3	-5.2	-1.6
M06-L	14.0	42.3	82.5	32.2	4.3	-1.2	4.2
PBE0	23.7	35.5	73.2	27.7	15.6	15.2	6.1
B3LYP	24.0	35.7	77.4	30.2	16.9	14.1	7.6
BHLYP	40.8	59.3	93.3	40.9	24.1	27.0	12.3
B3P86	20.8	30.5	68.4	23.5	10.9	9.8	3.2
B97-1	23.8	37.7	84.6	34.0	19.5	16.1	12.7
MPW1K	34.5	49.5	-75.3	34.1	19.2	22.1	9.5
X3LYP	27.4	39.6	81.7	33.6	20.2	17.5	10.2
TPSSH	16.2	30.9	65.7	17.0	7.1	3.7	3.0
M06	38.9	33.5	71.7	51.7	24.4	21.1	15.7
M06-2X	47.8	50.3	80.7	50.8	29.8	33.8	16.1
M11	9.1	22.8	56.0	17.4	-11.5	10.4	4.0
CAM-B3LYP	27.1	39.2	81.0	34.3	-32.2	18.1	9.1
B2PLYP	-45.1	-13.5	109.9	63.9	12.4	10.6	5.1
Experiment	-20.2	-17.0	-13.8	-7.9	-3.3	-3.8	-0.8
Error	2.4	5.0	2.4	2.0	2.0	2.4	2.4

Table A.8: Calculated enthalpies of formation $\Delta H_{\rm f}^{298\rm K}$ (kcal mol⁻¹) computed with each functional for the lanthanide monoxides (Ln54HFb subset) with experimental values shown for comparison.

	LaF	PrF	NdF	EuF	GdF	TbF
SVWN	181.5	154.2	152.5	149.5	158.9	193.6
BP86	163.2	130.1	125.6	131.8	169.6	184.5
BLYP	157.5	123.4	118.6	126.8	162.9	184.4
PW91	166.6	133.1	128.7	134.4	174.0	186.2
PBE	165.2	132.2	127.8	132.9	172.5	186.8
SSB-D	167.2	122.9	120.1	128.1	275.2	197.6
B97-D	150.9	117.1	117.0	117.7	167.4	183.6
TPSS	162.7	128.2	125.5	132.9	174.0	188.3
M06-L	149.6	114.5	101.5	120.8	164.1	201.8
PBE0	155.9	121.6	87.6	126.1	154.6	187.2
B3LYP	152.2	118.0	89.8	123.7	168.0	186.2
BHLYP	142.3	109.4	50.4	115.3	92.7	183.7
B3P86	159.2	125.3	97.2	129.7	167.3	187.3
B97-1	150.6	115.4	85.8	122.1	169.4	188.7
MPW1K	152.1	117.5	65.5	123.6	101.8	185.1
X3LYP	153.7	119.5	89.3	125.4	164.6	188.5
TPSSH	160.6	125.8	110.6	131.5	207.9	189.2
M06	143.5	117.8	85.0	116.3	136.7	193.9
M06-2X	144.9	114.9	39.1	118.1	92.2	185.0
M11	159.5	128.6	54.4	136.7	184.2	192.3
CAM-B3LYP	156.1	123.1	72.7	128.2	208.0	192.9
B2PLYP	149.7	120.3	76.1	123.6	219.6	228.3
Experiment	142.0	138.0	135.8	129.0	144.0	143.0
Error	10.0	11.0	3.2	4.0	7.0	10.0

Table A.9: Calculated bond dissociation energies, (D_0) (kcal mol⁻¹) computed with each functional for the lanthanide monofluorides (Ln54D0 subset) with experimental values used as a reference for the MSD/MAD calculations.

	DyF	HoF	ErF	TmF	YbF	LuF
SVWN	156.9	131.7	142.1	135.0	137.3	191.2
BP86	156.8	97.7	110.0	118.2	120.2	169.7
BLYP	155.5	90.2	103.4	113.7	117.0	167.5
PW91	162.4	100.6	112.7	120.6	122.5	171.7
PBE	161.1	101.2	124.3	119.1	120.9	170.8
SSB-D	163.1	103.8	119.6	115.6	116.5	169.2
B97-D	211.6	103.5	116.9	107.0	112.5	167.8
TPSS	139.2	99.9	107.7	120.4	122.0	167.9
M06-L	142.2	67.9	102.0	113.5	117.6	170.4
PBE0	141.9	90.8	117.1	115.0	113.8	164.5
B3LYP	141.7	85.5	114.6	112.6	112.5	164.8
BHLYP	129.2	71.4	107.6	107.3	105.2	158.0
B3P86	144.7	94.2	120.5	118.2	117.6	167.4
B97-1	142.3	78.5	113.8	110.3	111.1	167.9
MPW1K	134.3	184.6	115.3	114.5	112.3	161.3
X3LYP	143.5	86.9	116.3	114.2	114.2	167.1
TPSSH	138.6	94.8	90.6	119.9	119.9	167.3
M06	179.1	90.1	106.8	104.3	106.4	171.0
M06-2X	152.7	93.6	112.2	111.7	110.2	166.0
M11	158.8	113.2	118.0	239.1	128.1	174.6
CAM-B3LYP	147.7	90.3	119.3	228.5	117.5	170.8
B2PLYP	192.6	85.0	79.8	115.3	113.5	167.5
Experiment	129.0	130.0	138.0	135.0	135.0	135.0
Error	4.0	3.0	4.0	10.0	10.0	10.0

Table A.10: Calculated bond dissociation energies, (D_0) (kcal mol⁻¹) computed with each functional for the lanthanide monofluorides (Ln54D0 subset) with experimental values used as a reference for the MSD/MAD calculations.

	LaO	CeO	PrO	NdO	SmO	EuO	GdO
SVWN	235.9	209.8	188.2	164.4	138.8	147.4	231.0
BP86	208.7	182.5	155.7	133.6	121.1	124.6	227.3
BLYP	200.7	179.3	145.9	124.1	115.9	116.8	218.0
PW91	212.1	185.4	158.8	136.1	122.0	126.8	231.0
PBE	211.1	185.1	159.4	135.8	120.5	125.5	229.8
SSB-D	214.3	172.1	138.1	115.8	102.0	112.4	213.0
B97-D	194.1	148.7	127.9	104.1	80.5	110.8	224.7
TPSS	201.9	180.3	150.9	131.2	117.7	123.3	225.7
M06-L	193.6	172.8	145.3	113.0	107.0	115.2	218.7
PBE0	194.3	178.7	148.9	124.4	104.9	104.7	203.4
B3LYP	190.8	172.0	142.2	118.8	105.3	102.4	218.0
BHLYP	171.1	162.6	132.6	108.2	95.7	71.3	138.2
B3P86	199.9	181.1	152.0	128.2	110.1	112.6	220.0
B97-1	191.4	157.0	142.4	118.8	105.3	106.0	220.4
MPW1K	182.9	174.3	143.0	117.9	99.5	94.0	149.1
X3LYP	189.9	182.0	142.1	118.6	105.0	101.0	212.2
TPSSH	195.8	177.8	147.4	126.5	110.4	114.5	174.3
M06	187.8	178.1	141.3	112.5	76.2	98.2	188.1
M06-2X	184.0	169.8	124.5	96.7	78.5	87.5	143.2
M11	192.2	181.5	143.3	119.6	102.7	110.1	219.6
CAM-B3LYP	193.0	184.4	144.6	120.2	104.4	102.0	229.6
B2PLYP	188.0	183.6	154.1	131.0	110.0	103.9	149.2
Experiment	190.3	190.0	178.6	165.4	132.9	114.2	169.7
Error	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0

Table A.11: Calculated bond dissociation energies, (D_0) (kcal mol⁻¹) computed with each functional for the lanthanide monoxides (Ln54D0 subset) with experimental values shown for comparison.

	TbO	DyO	HoO	ErO	YbO	LuO
SVWN	162.3	137.6	121.2	123.6	127.1	195.7
BP86	148.7	127.8	81.5	92.1	61.5	169.7
BLYP	144.4	122.4	70.3	82.7	98.6	162.9
PW91	150.1	128.5	83.7	94.3	106.2	171.8
PBE	150.5	127.9	84.8	94.5	104.8	170.7
SSB-D	145.6	118.9	80.2	100.7	91.4	163.4
B97-D	129.2	105.2	90.4	103.2	93.7	154.5
TPSS	147.2	109.7	80.8	88.3	103.5	165.8
M06-L	140.2	88.2	52.7	84.6	98.8	159.3
PBE0	129.4	94.0	61.0	88.0	81.4	156.4
B3LYP	128.7	93.3	56.3	85.0	82.0	154.5
BHLYP	99.2	57.0	27.8	61.7	56.5	137.1
B3P86	135.2	101.8	68.7	95.1	89.6	162.1
B97-1	133.2	95.7	53.5	85.6	84.4	153.6
MPW1K	112.7	74.0	203.5	75.6	68.4	147.0
X3LYP	127.3	91.4	54.1	83.7	80.7	153.8
TPSSH	137.6	99.3	69.2	99.4	93.6	160.1
M06	114.9	96.7	63.2	64.7	76.2	147.5
M06-2X	105.2	79.0	53.4	64.8	62.6	146.2
M11	143.9	106.5	78.1	98.1	86.0	158.3
CAM-B3LYP	128.2	92.4	55.4	83.5	80.6	155.5
B2PLYP	199.2	144.0	25.3	52.8	87.0	158.3
Experiment	170.9	144.0	144.4	141.7	98.9	181.2
Error	-2.4	-5.0	-2.4	-2.0	2.4	-2.4

Table A.12: Calculated bond dissociation energies, (D_0) (kcal mol⁻¹) computed with each functional for the lanthanide monoxides (Ln54D0 subset) with experimental values shown for comparison.

	$\Delta H_{\rm sub} \ (\rm kcal \ mol^{-1})$
La	103.1
Ce	101.3
Pr	85.1
Nd	78.4
Sm	49.5
Eu	41.8
Gd	95.1
Tb	93.0
Dy	69.3
Но	74.0
Er	75.8
Tm	55.5
Yb	36.4
Lu	102.3

Table A.13: Experimental enthalpies of sublimation ΔH_{sub} (298 K) used in the calculation of the final enthalpies of formation for each lanthanide.


Figure A.1: The average predicted $\Delta H_{\rm f}^{298\rm K}$ (kcal mol⁻¹) for each functional class and the experimental $\Delta H_{\rm f}^{298\rm K}$ for LnCl₃ plotted across the lanthanide series.



Figure A.2: The average predicted D_0 (kcal mol⁻¹) of each functional class and experimental D_0 for LnF plotted across the lanthanide series.

Table A.14: Molecules where the ionic assumption results in higher energy solutions. The following molecules have the lanthanide in the formally +2 oxidation state with the unpaired electrons occupying orbitals localized on the lanthanide corresponding to excited electronic states of the Ln^{2+} ions.

	Ln ²⁻	+ configuration
	Ground state	Molecular environment
LaO	[Xe] 5 <i>d</i>	[Xe] 6 <i>s</i>
LaF ₂	[Xe] 5 <i>d</i>	[Xe] 6 <i>s</i>
LaCl ₂	[Xe] 5 <i>d</i>	[Xe] 6 <i>s</i>
CeO	[Xe] $4f^2$	[Xe] 6 <i>s</i> 4 <i>f</i>
CeCl ₂	[Xe] $4f^2$	[Xe] 6 <i>s</i> 4 <i>f</i>
PrO	[Xe] $4f^3$	[Xe] $6s4f^2$
NdO	[Xe] $4f^4$	[Xe] $6s4f^3$
NdCl ₂	[Xe] $4f^4$	[Xe] $6s4f^3$
SmO	[Xe] $4f^4$	[Xe] $6s4f^5$
GdO	[Xe] $5d4f^7$	[Xe] $6s4f^7$
TbO ^a	[Xe] 4 <i>f</i> ⁹	[Xe] $6s^2 4f^7$
DyO	[Xe] $4f^{10}$	[Xe] $6s^2 4f^8$

^{*a*} A sextet state was computed for TbO resulting in a doubly occupied 4f orbital



Figure A.3: The MAD/MSD weighted averages of the three Ln54 subsets: Ln54HFa, Ln54HFb, and Ln54D0.

APPENDIX B

ACTINIDE DATA

	ThO	ThO ₂	ThOF	ThF	ThF ₂	ThF3	ThF4	ThCl	ThCl ₂	ThCl3	ThCl4	ThBr
SVWN	-29.6	-137.3	-160.2	-11.3	-166.3	-303.4	-443.2	41.5	-50.5	-153.6	-247.8	90.0
BP86	-15.2	-118.1	-141.4	1.7	-145.3	-280.1	-414.6	47.7	-43.2	-141.2	-231.8	71.6
BLYP	-13.0	-111.5	-137.1	1.4	-144.6	-277.7	-412.1	48.9	-38.2	-136.3	-226.6	82.1
PW91	-16.5	-122.0	-145.2	-0.1	-149.0	-285.8	-421.7	46.5	-45.8	-144.5	-236.2	69.0
PBE	-15.6	-120.0	-143.3	1.0	-147.2	-283.2	-418.5	47.2	-44.8	-142.8	-234.3	69.7
TPSS	-12.9	-122.3	-143.0	4.6	-144.4	-283.4	-420.8	48.7	-45.8	-143.6	-236.1	63.4
M06-L	-13.9	-118.1	-137.4	3.8	-146.3	-280.9	-426.5	47.0	-40.9	-145.3	-245.5	65.9
B3P86	-12.1	-114.7	-141.1	-0.9	-146.6	-286.2	-425.1	50.1	-44.7	-143.8	-236.4	70.8
X3LYP	-9.1	-104.8	-134.9	-0.5	-145.3	-281.9	-420.0	51.6	-39.0	-138.2	-230.5	79.1
B97-1	-9.8	-109.4	-132.9	0.6	-143.4	-277.8	-419.2	50.9	-36.6	-138.9	-235.4	81.9
B3LYP	-9.3	-105.7	-135.0	-0.4	-144.6	-281.2	-419.0	51.6	-39.0	-137.8	-229.9	78.8
PBE0	-8.6	-108.6	-137.4	0.8	-144.1	-283.8	-422.1	51.4	-44.0	-142.5	-235.1	69.8
MPW1K	-4.2	-102.7	-135.1	1.8	-143.7	-287.0	-427.9	52.8	-45.4	-144.1	-237.2	68.5
BHLYP	-1.5	-92.0	-129.1	1.3	-143.9	-284.7	-426.2	54.1	-39.4	-139.0	-232.5	79.2
TPSSH	-9.6	-116.9	-139.8	0.6	-142.7	-282.8	-421.2	49.8	-46.8	-146.0	-240.0	69.6
M06	-16.2	-108.8	-132.7	-3.5	-149.9	-277.7	-422.7	49.9	-27.8	-130.0	-226.3	95.3
M06-2X	-6.8	-97.3	-131.8	-1.7	-146.2	-283.4	-422.4	50.3	-38.7	-141.2	-233.0	79.0
B2PLYP	-10.0	-103.4	-133.4	16.6	-144.6	-280.4	-419.5	52.8	-37.7	-138.3	-232.2	79.9
Experiment	-6.2	-108.8	-131.4	7.2	-141.0	-278.4	-418.3	59.0	-42.8	-136.0	-227.4	87.2
Uncertainty	1.4	3.7	2.9	3.6	4.8	3.6	2.4	4.8	4.8	6.0	1.2	4.8

Table B.1: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: ThO to ThBr.

	ThBr ₂	ThBr3	ThBr4	ThI4	UO	UO ₂	UO3	UOF4	UO ₂ F ₂	UO2Cl2	UF
SVWN	-24.7	-108.8	-194.0	-130.8	-7.6	-147.0	-243.8	-483.0	-376.8	-289.6	-12.6
BP86	-13.7	-92.2	-172.4	-107.9	-4.2	-104.4	-210.2	-438.2	-338.3	-257.0	-6.8
BLYP	-8.8	-83.3	-161.8	-96.1	2.6	-112.7	-193.6	-425.6	-323.8	-241.8	-5.1
PW91	-15.9	-95.9	-177.3	-112.8	6.2	-129.5	-213.4	-444.1	-342.7	-260.6	-8.0
PBE	-14.7	-94.4	-175.6	-111.2	2.5	-118.1	-204.6	-434.1	-333.4	-251.7	-4.5
TPSS	-12.7	-98.5	-181.9	-115.6	-4.3	-122.9	-207.2	-435.5	-335.7	-253.1	-12.3
M06-L	-8.9	-88.3	-173.4	-106.6	15.3	-102.4	-190.6	-423.7	-323.0	-242.1	-4.0
B3P86	-10.6	-96.0	-179.6	-113.2	2.0	-114.5	-191.2	-424.1	-325.5	-240.5	-9.6
X3LYP	-7.3	-87.5	-169.7	-102.1	9.0	-103.3	-173.2	-411.4	-310.6	-225.4	-9.7
B97-1	-9.1	-90.5	-176.4	-109.6	11.6	-104.4	-182.8	-414.9	-317.0	-234.4	-8.6
B3LYP	-7.0	-87.0	-168.8	-101.3	8.5	-104.6	-174.8	-411.4	-311.1	-226.2	-9.1
PBE0	-9.1	-95.7	-179.3	-113.4	4.7	-104.5	-181.6	-416.0	-317.5	-233.3	-8.5
MPW1K	-8.5	-98.3	-182.8	-116.0	9.4	-96.3	-162.8	-402.8	-304.7	-218.2	-7.4
BHLYP	-6.1	-90.5	-174.6	-105.2	18.2	-82.8	-141.3	-389.7	-288.6	-200.4	-8.1
TPSSH	-10.7	-97.8	-181.9	-115.2	-0.1	-114.5	-194.8	-424.9	-326.1	-244.8	-7.2
M06	-4.9	-76.2	-158.3	-91.2	21.4	-97.9	-171.6	-404.1	-307.6	-219.8	-7.8
M06-2X	-11.6	-95.2	-179.7	-114.9	22.2	-95.0	-167.8	-409.6	-311.9	-225.2	-11.4
B2PLYP	-9.3	-90.2	-175.3	-109.0	19.9	-124.3	-210.8	-449.3	-346.3	-263.3	2.8
Experiment	9.6	-79.8	-177.3	-110.1	8.4	-114.0	-191.0	-421.4	-323.3	-231.9	-11.2
Uncertainty	4.8	3.6	1.2	1.3	2.4	4.8	3.6	4.8	2.4	3.6	4.8

Table B.2: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: ThBr₂ to UF.

	UF ₂	UF3	UF4	UF5	UF6	UCl	UCl ₂	UCl3	UCl4	UCl5	UCl6
SVWN	-147.0	-281.3	-406.9	-511.1	-597.0	34.7	-50.9	-140.7	-215.9	-264.4	-315.4
BP86	-139.0	-265.1	-382.7	-472.6	-543.9	32.9	-51.0	-136.6	-203.3	-238.9	-277.9
BLYP	-134.0	-259.8	-376.2	-463.2	-531.8	34.7	-43.8	-130.5	-195.6	-227.2	-262.6
PW91	-142.4	-269.4	-387.6	-478.8	-551.4	32.4	-52.3	-139.0	-206.2	-243.0	-283.1
PBE	-133.3	-259.6	-377.5	-468.4	-540.8	40.3	-44.2	-129.9	-197.0	-233.4	-273.1
TPSS	-140.4	-268.5	-385.7	-473.0	-540.6	36.4	-51.0	-139.4	-202.1	-233.8	-269.7
M06-L	-130.2	-266.4	-384.6	-468.0	-530.4	36.9	-42.9	-140.8	-200.2	-231.7	-267.5
B3P86	-139.9	-268.0	-389.2	-469.6	-528.4	36.4	-49.1	-137.3	-200.9	-223.6	-248.7
X3LYP	-135.1	-262.0	-382.8	-460.6	-516.6	36.7	-44.9	-131.7	-194.8	-213.4	-234.7
B97-1	-130.4	-260.8	-382.3	-460.9	-518.0	36.3	-44.2	-135.3	-199.2	-220.3	-244.1
B3LYP	-134.6	-261.9	-381.6	-459.6	-516.2	37.1	-44.6	-131.2	-194.1	-213.3	-235.2
PBE0	-138.7	-265.2	-386.4	-464.3	-520.1	37.1	-48.9	-136.4	-199.3	-218.9	-240.4
MPW1K	-140.2	-269.0	-391.9	-461.5	-505.4	38.7	-27.5	-139.1	-199.3	-213.8	-215.5
BHLYP	-135.7	-265.1	-389.5	-455.4	-493.7	39.0	-18.3	-133.8	-194.5	-195.9	-195.8
TPSSH	-139.2	-267.3	-385.7	-467.9	-529.1	36.7	-52.7	-142.4	-204.4	-230.7	-260.7
M06	-127.6	-262.9	-381.8	-458.8	-506.8	35.2	-36.0	-129.5	-184.7	-212.0	-223.8
M06-2X	-123.5	-243.4	-382.7	-460.9	-513.3	45.4	-41.1	-131.1	-195.3	-215.9	-225.8
B2PLYP	-136.5	-264.8	-395.3	-481.6	-551.7	35.7	-46.9	-134.3	-210.0	-246.6	-289.0
Experiment	-129.1	-254.5	-383.6	-457.2	-513.5	44.7	-37.0	-125.0	-194.9	-215.1	-235.5
Uncertainty	6.0	4.8	1.6	3.6	0.5	4.8	4.8	4.8	1.1	3.6	1.2

Table B.3: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: UF₂ to UCl₆.

	UBr	UBr ₂	UBr3	UBr4	UBr5	UI	UI ₂	UI3	UI4	NpO	NpO2
SVWN	52.2	-23.0	-99.7	-163.4	-182.2	66.4	8.5	-54.6	-102.0	-3.2	-126.0
BP86	54.1	-20.8	-92.0	-143.6	-150.6	65.9	10.9	-47.1	-81.5	5.2	-103.5
BLYP	57.6	-12.6	-82.0	-130.2	-132.5	69.2	19.5	-36.7	-67.3	10.5	-94.2
PW91	53.7	-23.0	-95.0	-147.0	-155.5	65.4	8.8	-50.0	-84.9	6.0	-105.7
PBE	61.5	-14.5	-86.3	-138.1	-146.2	73.2	17.2	-41.4	-76.2	7.1	-104.1
TPSS	58.4	-24.0	-100.9	-146.4	-152.4	67.6	8.6	-52.5	-82.6	5.8	-107.7
M06-L	70.0	-8.8	-88.1	-126.0	-129.9	76.6	18.8	-43.9	-62.2	13.0	-99.9
B3P86	74.7	-21.6	-96.4	-125.2	-137.2	68.9	10.8	-48.1	-60.6	9.6	-93.4
X3LYP	78.0	-15.0	-88.3	-113.4	-122.3	70.4	17.9	-39.2	-47.7	16.7	-82.9
B97-1	76.2	-14.5	-93.3	-120.4	-131.3	69.2	17.8	-44.9	-55.6	19.8	-84.1
B3LYP	76.8	-14.5	-87.5	-114.0	-121.8	70.8	18.3	-40.7	-48.4	16.3	-83.8
PBE0	79.8	-21.8	-96.8	-120.0	-133.5	69.2	10.2	-48.8	-55.7	11.9	-86.9
MPW1K	97.7	-23.8	-100.9	-104.9	-123.6	70.1	8.4	-52.1	-39.3	13.7	-77.0
BHLYP	105.9	-17.0	-93.7	-89.5	-107.6	71.6	16.4	-43.2	-21.3	22.2	-66.5
TPSSH	68.4	-23.7	-101.4	-135.8	-143.7	68.9	9.1	-54.9	-71.1	-0.1	-99.9
M06	85.2	-1.2	-78.4	-93.8	-103.5	75.1	28.6	-32.7	-28.8	27.5	-71.1
M06-2X	96.8	-9.3	-83.1	-98.8	-127.2	63.7	11.7	-46.3	-35.7	31.1	-61.2
B2PLYP	103.7	-18.2	-94.2	-154.0	-157.6	68.6	14.6	-45.2	-89.4	8.1	-111.0
Experiment	58.6	-9.6	-88.7	-144.7	-154.9	81.7	24.6	-32.7	-72.9	-4.0	-109.2
Uncertainty	3.6	3.6	4.8	1.1	3.6	6.0	6.0	6.0	1.4	2.4	4.8

Table B.4: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: UBr to NpO₂.

	NpF	NpF2	NpF3	NpF4	NpF6	NpCl3	NpCl4	PuO	PuO ₂	PuO3	PuF
SVWN	-6.0	-143.3	-272.3	-379.2	-545.8	-135.8	-193.2	-10.2	-104.8	-166.4	-30.5
BP86	0.6	-129.5	-253.3	-352.1	-491.1	-128.5	-179.1	0.5	-85.4	-135.9	-24.6
BLYP	5.2	-126.5	-249.8	-348.3	-481.0	-123.3	-175.6	5.5	-77.5	-124.0	-20.5
PW91	-2.2	-132.8	-257.3	-356.6	-498.1	-130.8	-183.4	-1.0	-86.6	-137.8	-25.2
PBE	-1.1	-130.7	-254.5	-353.4	-494.4	-128.9	-181.1	0.1	-84.7	-135.2	-24.0
TPSS	12.5	-137.5	-263.3	-365.4	-496.2	-138.7	-191.1	-7.3	-89.5	-142.2	-29.6
M06-L	11.0	-129.7	-264.7	-365.4	-489.6	-140.9	-192.5	13.1	-88.0	-120.5	-17.6
B3P86	-2.2	-137.5	-265.3	-363.9	-474.9	-138.4	-184.3	21.9	-85.6	-109.4	-27.2
X3LYP	3.4	-134.2	-260.6	-359.5	-464.0	-134.3	-180.2	8.1	-72.8	-94.8	-22.1
B97-1	8.3	-128.3	-258.4	-357.2	-463.5	-136.6	-182.7	12.3	-73.6	-100.7	-17.3
B3LYP	3.2	-133.4	-259.5	-358.3	-463.8	-133.3	-177.7	7.8	-69.9	-96.9	-22.2
PBE0	-2.1	-137.2	-263.3	-361.8	-465.4	-138.9	-182.0	5.6	-78.6	-99.1	-27.2
MPW1K	-4.0	-145.1	-274.2	-373.3	-450.4	-147.6	-189.9	5.4	-71.8	-81.7	-29.6
BHLYP	3.1	-143.7	-273.3	-375.2	-439.5	-145.6	-189.0	9.8	-58.4	-67.2	-23.9
TPSSH	-3.7	-139.0	-265.6	-366.7	-483.4	-144.6	-195.2	-2.5	-92.6	-126.7	-29.4
M06	17.4	-120.1	-255.2	-353.3	-456.7	-121.5	-167.4	24.1	-70.8	-84.1	-9.2
M06-2X	14.5	-116.8	-254.8	-341.1	-419.0	-121.9	-152.8	29.6	-54.4	-50.0	-16.9
B2PLYP	2.6	-143.3	-271.2	-379.9	-505.0	-146.4	-202.0	26.2	-90.8	-118.1	-23.7
Experiment	-19.1	-137.4	-266.5	-373.1	-459.3	-140.8	-188.1	-12.4	-102.3	-135.7	-26.9
Uncertainty	6.0	7.2	6.0	5.3	4.8	2.5	1.1	3.6	4.8	3.5	2.4

Table B.5: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: NpF to PuF.

	PuF2	PuF3	PuF4	PuF6	PuCl3	PuCl4	PuBr3	PuI3	AmO	AmF3
SVWN	-151.9	-261.4	-356.1	-488.0	-131.3	-172.7	-96.3	-50.7	-5.8	-232.7
BP86	-140.5	-244.3	-331.6	-435.4	-126.8	-149.5	-85.0	-39.1	2.5	-222.6
BLYP	-137.8	-241.6	-329.6	-426.9	-122.5	-139.2	-77.1	-30.6	7.7	-223.5
PW91	-144.2	-248.5	-335.9	-442.5	-129.0	-152.7	-87.7	-41.8	1.0	-226.2
PBE	-142.2	-245.6	-332.3	-438.4	-127.0	-150.1	-85.9	-40.1	2.3	-223.6
TPSS	-147.7	-256.3	-344.2	-440.4	-134.8	-158.6	-98.5	-51.1	-2.5	-244.2
M06-L	-139.7	-255.2	-339.7	-426.4	-137.6	-154.1	-87.0	-39.5	16.0	-229.7
B3P86	-144.8	-257.7	-338.9	-409.5	-132.9	-151.0	-92.7	-46.1	7.3	-230.0
X3LYP	-141.2	-253.9	-336.7	-400.0	-129.1	-142.1	-85.8	-39.2	13.5	-229.4
B97-1	-136.7	-252.5	-332.9	-398.8	-131.4	-146.3	-89.3	-43.2	15.9	-227.1
B3LYP	-140.8	-252.8	-335.3	-400.3	-128.2	-141.1	-85.1	-38.1	12.9	-228.7
PBE0	-143.4	-256.5	-337.1	-397.9	-133.0	-149.0	-93.4	-47.5	10.6	-228.2
MPW1K	-148.2	-268.0	-345.4	-377.5	-141.3	-153.4	-103.0	-56.8	13.6	-237.2
BHLYP	-147.9	-268.6	-349.9	-367.4	-140.5	-148.2	-100.0	-52.3	19.5	-240.6
TPSSH	-147.3	-259.4	-343.8	-423.3	-139.5	-161.4	-99.4	-52.7	1.7	-232.3
M06	-130.9	-246.0	-323.8	-388.5	-116.1	-126.2	-68.8	-20.7	28.0	-222.6
M06-2X	-127.7	-244.3	-315.5	-349.5	-118.6	-112.7	-86.1	-38.5	31.3	-221.3
B2PLYP	-148.0	-265.3	-358.4	-435.9	-142.1	-165.9	-100.3	-54.4	5.7	-237.4
Experiment	-146.8	-279.1	-370.0	-433.2	-154.7	-189.3	-116.6	-72.9	-3.5	-276.4
Uncertainty	1.4	0.9	5.3	4.8	0.5	2.4	3.6	3.6	12.0	4.0

Table B.6: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated Stuttgart 1997 basis for compounds: PuF₂ to AmF₃.

	ThO	ThO ₂	ThOF	ThF	ThF ₂	ThF3	ThF4	ThCl	ThCl ₂	ThCl3	ThCl4	ThBr
SVWN	-29.8	-137.9	-161.1	-11.2	-167.6	-305.1	-445.6	42.6	-59.4	-153.5	-248.0	57.5
BP86	-14.1	-117.2	-140.8	0.1	-145.2	-280.4	-415.5	49.6	-45.9	-139.8	-230.7	65.7
BLYP	-12.4	-111.0	-136.9	0.0	-144.8	-278.2	-412.9	50.0	-44.9	-135.5	-226.3	67.4
PW91	-15.5	-121.1	-144.6	-1.9	-148.8	-286.0	-422.4	48.5	-47.7	-143.1	-235.4	64.6
PBE	-14.7	-119.2	-142.8	-0.9	-147.2	-283.5	-419.2	49.1	-46.7	-141.6	-233.6	65.1
TPSS	-11.7	-121.7	-142.4	-0.3	-144.2	-283.6	-421.5	51.0	-43.7	-141.7	-234.8	65.7
M06-L	-11.2	-115.5	-134.8	1.0	-144.2	-279.6	-426.1	49.6	-47.4	-141.8	-241.7	68.6
B3P86	-13.7	-116.8	-143.4	-0.9	-149.2	-289.6	-429.3	49.8	-47.2	-144.8	-237.8	65.3
X3LYP	-11.8	-107.9	-138.2	-0.5	-148.9	-286.1	-424.9	50.0	-46.6	-140.4	-233.2	66.6
B97-1	-12.6	-112.7	-136.4	1.0	-147.4	-282.1	-424.4	49.2	-47.9	-141.2	-238.4	65.2
B3LYP	-11.7	-108.5	-138.0	-0.2	-147.9	-285.1	-423.6	50.3	-46.0	-139.8	-232.3	66.9
PBE0	-10.8	-111.4	-140.3	0.4	-147.4	-287.8	-426.8	50.8	-45.8	-144.1	-237.3	66.1
MPW1K	-7.2	-106.6	-139.1	1.4	-147.9	-292.3	-434.1	51.8	-45.0	-146.2	-239.9	66.7
BHLYP	-6.1	-97.4	-134.5	1.7	-149.6	-291.2	-433.6	51.2	-45.7	-142.8	-236.8	67.0
TPSSH	-10.7	-118.4	-141.4	0.1	-144.7	-285.3	-424.4	50.2	-46.1	-146.2	-240.8	65.9
M06	-16.1	-109.8	-133.2	-2.9	-150.4	-279.1	-425.2	50.3	-46.2	-128.7	-225.2	68.3
M06-2X	-8.3	-99.9	-134.2	2.5	-148.8	-286.8	-427.3	50.8	-46.4	-141.7	-233.9	65.6
B2PLYP	-15.8	-111.9	-140.6	2.8	-150.3	-286.9	-427.2	50.1	-49.1	-142.6	-237.2	66.0
Experiment	-6.2	-108.8	-131.4	7.2	-141.0	-278.4	-418.3	59.0	-42.8	-136.0	-227.4	87.2
Uncertainty	1.4	3.7	2.9	3.6	4.8	3.6	2.4	4.8	4.8	6.0	1.2	4.8

Table B.7: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: ThO to ThBr.

	ThBr ₂	ThBr3	ThBr4	ThI4	UO	UO ₂	UO3	UOF4	UO ₂ F ₂	UO2Cl2	UF
SVWN	-23.9	-108.4	-193.7	-130.4	-10.6	-149.0	-247.5	-487.8	-381.0	-291.8	-18.8
BP86	-9.5	-90.5	-170.8	-106.1	0.2	-121.7	-206.1	-435.1	-334.6	-251.4	-8.8
BLYP	-6.4	-82.3	-160.9	-95.0	5.2	-112.6	-191.6	-424.5	-322.2	-238.2	-9.3
PW91	-11.4	-94.3	-175.9	-111.0	-1.6	-124.0	-209.9	-441.7	-339.7	-255.6	-10.1
PBE	-10.5	-92.9	-174.3	-109.5	-0.5	-122.6	-208.2	-438.8	-337.4	-253.8	-9.1
TPSS	-10.3	-96.3	-179.9	-113.4	12.1	-121.7	-207.7	-437.1	-336.6	-252.0	-11.3
M06-L	-5.1	-84.6	-169.2	-103.0	12.7	-103.6	-192.5	-426.1	-325.1	-242.5	-8.9
B3P86	-11.0	-96.6	-180.4	-113.8	-1.7	-117.3	-195.3	-429.1	-329.9	-242.9	-14.8
X3LYP	-8.9	-89.5	-171.9	-104.0	5.0	-106.4	-177.8	-416.8	-315.4	-228.2	-14.9
B97-1	-10.9	-92.5	-178.7	-111.7	7.9	-107.0	-187.0	-420.0	-321.5	-237.0	-13.9
B3LYP	-8.3	-88.6	-170.7	-102.8	4.5	-107.3	-179.4	-416.8	-315.9	-229.0	-14.4
PBE0	-10.0	-96.9	-180.7	-114.5	0.4	-111.7	-186.4	-421.8	-322.6	-236.4	-14.2
MPW1K	-9.8	-100.0	-184.8	-117.7	5.0	-99.9	-167.7	-408.5	-309.8	-221.0	-13.4
BHLYP	-9.1	-93.8	-178.3	-108.5	13.4	-86.4	-146.2	-395.2	-293.6	-203.2	-14.1
TPSSH	-10.3	-97.6	-182.0	-115.0	-2.7	-116.2	-197.7	-428.9	-329.4	-246.0	-12.3
M06	-3.9	-74.9	-157.0	-90.1	19.7	-99.2	-174.3	-406.7	-310.0	-220.2	-11.8
M06-2X	-11.5	-95.5	-180.0	-115.3	8.9	-99.9	-174.9	-417.6	-319.1	-230.3	-19.7
B2PLYP	-12.3	-94.0	-179.6	-112.6	2.6	-120.2	-205.0	-439.9	-338.8	-254.1	-16.1
Experiment	9.6	-79.8	-177.3	-110.1	8.4	-114.0	-191.0	-421.4	-323.3	-231.9	-11.2
Uncertainty	4.8	3.6	1.2	1.3	2.4	4.8	3.6	4.8	2.4	3.6	4.8

Table B.8: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: ThBr₂ to UF.

	UF ₂	UF3	UF4	UF5	UF6	UCl	UCl ₂	UCl3	UCl4	UCl5	UCl6
SVWN	-149.6	-285.3	-410.9	-516.0	-602.9	35.5	-51.9	-141.6	-217.0	-269.9	-316.0
BP86	-133.4	-261.3	-379.0	-469.7	-541.8	41.2	-44.5	-130.2	-196.7	-237.7	-270.8
BLYP	-130.1	-258.1	-374.5	-462.3	-531.7	41.3	-40.7	-126.0	-191.0	-227.8	-257.4
PW91	-137.0	-266.1	-384.7	-476.6	-550.0	40.7	-46.7	-133.1	-200.1	-242.3	-276.5
PBE	-135.1	-263.5	-381.6	-473.3	-546.5	41.4	-45.4	-131.3	-198.1	-239.9	-273.6
TPSS	-141.7	-269.6	-384.9	-474.8	-543.3	39.4	-49.6	-137.7	-197.3	-238.3	-266.7
M06-L	-128.2	-269.8	-387.2	-470.6	-533.3	36.8	-45.9	-145.3	-200.4	-239.9	-266.9
B3P86	-142.4	-272.1	-393.3	-474.6	-534.5	35.9	-51.3	-139.3	-202.1	-230.9	-249.4
X3LYP	-137.7	-266.9	-387.4	-466.1	-523.1	36.1	-46.8	-134.3	-196.4	-220.9	-235.6
B97-1	-133.0	-265.2	-386.7	-466.1	-524.2	35.7	-44.9	-137.5	-200.6	-227.8	-244.8
B3LYP	-137.3	-266.1	-386.2	-465.1	-522.6	36.4	-46.5	-133.7	-195.6	-220.8	-236.2
PBE0	-141.7	-270.1	-391.4	-470.2	-527.1	36.0	-51.4	-139.1	-201.2	-227.0	-241.6
MPW1K	-143.3	-273.6	-396.8	-467.3	-512.4	37.1	-52.2	-141.2	-200.9	-215.7	-216.1
BHLYP	-138.9	-269.8	-394.4	-461.0	-500.4	37.2	-47.1	-136.4	-196.2	-203.7	-196.3
TPSSH	-140.3	-270.9	-389.1	-472.0	-534.2	37.3	-52.8	-142.9	-204.6	-237.6	-259.8
M06	-125.1	-265.4	-384.1	-461.3	-509.8	36.0	-34.6	-129.1	-184.2	-212.3	-222.8
M06-2X	-137.5	-257.3	-388.4	-468.2	-522.4	35.3	-38.1	-119.1	-197.7	-218.9	-228.9
B2PLYP	-137.7	-267.5	-392.3	-474.7	-541.4	34.2	-47.8	-136.4	-202.9	-236.6	-276.5
Experiment	-129.1	-254.5	-383.6	-457.2	-513.5	44.7	-37.0	-125.0	-194.9	-215.1	-235.5
Uncertainty	6.0	4.8	1.6	3.6	0.5	4.8	4.8	4.8	1.1	3.6	1.2

Table B.9: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: UF₂ to UCl₆.

	UBr	UBr ₂	UBr3	UBr4	UBr5	UI	UI2	UI3	UI4	NpO	NpO ₂
SVWN	55.3	-24.0	-99.4	-163.5	-202.2	66.9	7.5	-52.8	-102.6	-5.6	-124.3
BP86	66.7	-14.3	-81.8	-136.1	-163.3	73.2	18.1	-37.0	-74.4	5.1	-102.6
BLYP	69.7	-7.8	-72.9	-124.5	-146.9	74.9	24.8	-29.6	-62.2	11.1	-94.0
PW91	66.1	-16.6	-89.0	-139.9	-168.4	72.6	15.8	-41.4	-78.3	3.5	-104.2
PBE	66.4	-15.3	-83.5	-138.2	-166.2	73.1	17.1	-40.0	-76.7	4.6	-102.5
TPSS	53.0	-21.8	-88.4	-143.8	-168.4	71.0	9.6	-49.8	-82.5	3.0	-110.8
M06-L	57.5	-10.2	-74.6	-130.5	-149.1	72.2	24.4	-41.0	-69.5	17.9	-101.9
B3P86	50.2	-22.6	-97.0	-145.4	-156.9	68.4	8.8	-49.4	-79.9	6.9	-101.5
X3LYP	51.5	-16.3	-88.7	-135.6	-142.1	69.9	15.5	-40.9	-68.9	13.5	-88.8
B97-1	50.6	-15.4	-93.6	-141.2	-150.9	68.8	15.9	-46.3	-75.8	17.0	-94.0
B3LYP	51.9	-15.9	-88.0	-134.6	-141.8	70.2	16.0	-40.1	-68.0	13.1	-89.6
PBE0	50.1	-23.2	-97.5	-145.2	-153.4	68.1	7.8	-50.6	-80.2	9.0	-95.9
MPW1K	51.0	-24.9	-100.8	-146.0	-142.2	68.9	5.3	-54.4	-80.7	10.1	-93.1
BHLYP	52.0	-18.5	-93.4	-138.1	-125.6	70.5	12.6	-45.9	-69.8	17.4	-80.2
TPSSH	51.9	-23.5	-99.2	-147.0	-162.7	70.0	6.2	-52.6	-82.0	5.5	-106.4
M06	53.0	-1.1	-76.6	-115.9	-122.2	71.5	31.8	-29.5	-54.2	25.6	-87.0
M06-2X	48.7	-11.2	-98.3	-144.8	-144.9	74.3	13.7	-38.7	-73.2	22.0	-74.1
B2PLYP	49.2	-18.7	-93.5	-145.4	-167.1	67.6	12.6	-46.0	-46.2	9.3	-99.2
Experiment	58.6	-9.6	-88.7	-144.7	-154.9	81.7	24.6	-32.7	-72.9	-4.0	-109.2
Uncertainty	3.6	3.6	4.8	1.1	3.6	6.0	6.0	6.0	1.4	2.4	4.8

Table B.10: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: UBr to NpO₂.

	NpF	NpF2	NpF3	NpF4	NpF6	NpCl3	NpCl4	PuO	PuO ₂	PuO3	PuF
SVWN	-7.8	-145.8	-274.4	-382.1	-549.6	-133.5	-193.9	-11.6	-105.3	-169.2	-30.9
BP86	-1.5	-134.1	-255.1	-353.8	-494.7	-126.4	-175.9	-3.6	-86.0	-139.0	-25.0
BLYP	2.8	-131.5	-252.0	-350.6	-485.0	-122.4	-171.1	1.4	-78.4	-127.4	-20.8
PW91	-4.2	-137.4	-259.5	-358.8	-502.2	-129.0	-179.1	-5.0	-87.1	-141.0	-27.7
PBE	-3.0	-135.3	-256.6	-355.4	-498.3	-127.0	-176.9	-3.7	-85.1	-138.3	-26.6
TPSS	-6.3	-141.8	-265.5	-367.6	-500.3	-135.8	-186.8	-4.4	-90.0	-130.8	-30.0
M06-L	8.8	-122.9	-260.1	-369.2	-492.2	-139.4	-185.3	7.5	-89.3	-121.2	-17.9
B3P86	-4.4	-142.6	-266.8	-365.8	-478.8	-136.7	-181.1	-1.8	-88.0	-112.4	-28.0
X3LYP	0.9	-140.0	-262.7	-362.6	-468.6	-133.0	-177.6	3.6	-75.4	-98.2	-22.9
B97-1	6.1	-133.4	-260.1	-359.2	-467.5	-134.9	-180.2	7.7	-80.5	-103.5	-18.0
B3LYP	0.8	-139.1	-261.5	-360.9	-468.3	-132.0	-176.3	3.4	-76.6	-100.3	-22.9
PBE0	-4.3	-142.7	-265.6	-364.0	-469.8	-137.5	-181.2	0.4	-80.9	-100.4	-27.9
MPW1K	-6.9	-152.0	-276.5	-376.5	-455.7	-147.2	-189.2	-0.4	-74.5	-84.7	-30.7
BHLYP	-0.8	-152.3	-276.5	-379.8	-445.7	-146.3	-189.6	4.1	-61.6	-70.8	-25.1
TPSSH	-6.1	-143.7	-267.8	-369.2	-487.7	-142.3	-191.9	-6.8	-94.8	-128.0	-29.9
M06	16.2	-124.5	-256.5	-354.4	-459.4	-114.1	-159.4	18.5	-72.8	-86.8	-9.2
M06-2X	6.7	-128.6	-250.4	-329.1	-431.6	-124.7	-156.2	20.7	-58.8	-54.4	-19.5
B2PLYP	0.6	-143.7	-267.1	-369.8	-489.6	-138.6	-186.5	-0.1	-85.2	-107.3	-22.5
Experiment	-19.1	-137.4	-266.5	-373.1	-459.3	-140.8	-188.1	-12.4	-102.3	-135.7	-26.9
Uncertainty	6.0	7.2	6.0	5.3	4.8	2.5	1.1	3.6	4.8	3.5	2.4

Table B.11: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: NpF to PuF.

	PuF ₂	PuF3	PuF4	PuF6	PuCl3	PuCl4	PuBr3	PuI3	AmO	AmF3
SVWN	-152.7	-266.6	-358.6	-488.7	-134.1	-181.0	-95.7	-51.2	-5.2	-251.2
BP86	-139.1	-248.6	-333.7	-436.0	-127.4	-167.6	-85.2	-40.4	2.4	-233.2
BLYP	-135.9	-245.2	-331.5	-427.5	-123.5	-163.6	-77.5	-32.2	7.0	-230.3
PW91	-142.6	-252.6	-338.1	-442.7	-129.8	-170.1	-87.9	-43.1	1.0	-236.8
PBE	-140.6	-249.6	-334.4	-438.4	-127.7	-167.5	-86.1	-41.4	2.4	-233.8
TPSS	-148.6	-259.4	-347.1	-441.8	-136.9	-176.8	-98.7	-52.4	-2.7	-243.0
M06-L	-136.0	-255.9	-339.7	-426.9	-138.5	-174.6	-86.1	-32.8	16.6	-241.3
B3P86	-142.8	-260.3	-341.3	-411.3	-134.4	-165.2	-93.9	-47.0	7.7	-243.3
X3LYP	-138.8	-255.9	-339.0	-401.5	-130.9	-162.2	-87.9	-40.3	13.3	-239.5
B97-1	-134.5	-253.8	-335.1	-399.9	-132.9	-163.9	-91.1	-44.1	16.2	-237.5
B3LYP	-138.4	-254.8	-337.5	-401.9	-130.0	-161.4	-86.7	-39.2	12.7	-238.5
PBE0	-141.2	-258.7	-338.2	-399.5	-134.5	-162.9	-94.8	-48.3	11.0	-241.1
MPW1K	-145.6	-270.4	-348.7	-380.0	-142.9	-166.6	-104.7	-57.4	14.2	-251.3
BHLYP	-145.9	-270.9	-353.4	-370.1	-142.6	-167.9	-102.3	-53.1	19.6	-252.1
TPSSH	-145.3	-261.6	-346.5	-424.9	-141.6	-178.1	-100.7	-53.5	1.7	-244.6
M06	-128.4	-249.3	-324.1	-389.2	-118.9	-142.0	-69.4	-21.9	29.0	-234.1
M06-2X	-128.7	-245.2	-309.5	-349.1	-123.9	-134.3	-84.9	-39.1	31.6	-227.9
B2PLYP	-136.6	-258.4	-342.6	-417.1	-134.3	-166.6	-93.5	-45.7	12.1	-240.7
Experiment	-146.8	-279.1	-370.0	-433.2	-154.7	-189.3	-116.6	-72.9	-3.5	-276.4
Uncertainty	1.4	0.9	5.3	4.8	0.5	2.4	3.6	3.6	12.0	4.0

Table B.12: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated segmented basis for compounds: PuF₂ to AmF₃.

	ThO	ThO ₂	ThOF	ThF	ThF ₂	ThF3	ThF4	ThCl	ThCl ₂	ThCl3	ThCl4	ThBr
SVWN	-26.9	-133.3	-157.7	-8.2	-165.9	-303.4	-443.3	43.9	-57.5	-151.4	-245.3	74.2
BP86	-11.2	-112.6	-137.5	0.8	-143.5	-278.7	-413.2	50.8	-44.1	-137.6	-227.9	82.3
BLYP	-9.5	-106.3	-133.5	0.8	-143.1	-276.4	-410.6	51.3	-43.0	-133.2	-223.4	83.8
PW91	-12.7	-116.6	-141.4	-1.2	-147.2	-284.3	-420.1	49.8	-46.0	-141.0	-232.7	81.3
PBE	-11.9	-114.6	-139.6	-0.3	-145.5	-281.8	-417.0	50.3	-46.9	-139.4	-230.8	81.7
TPSS	-8.9	-117.2	-139.2	6.9	-142.5	-281.9	-419.3	52.2	-41.9	-139.6	-231.9	80.5
M06-L	-8.5	-110.8	-131.5	7.0	-142.6	-277.8	-423.9	50.7	-45.9	-139.8	-239.1	69.3
B3P86	-10.7	-112.0	-140.0	-0.2	-147.5	-287.9	-427.0	51.1	-45.4	-142.6	-234.9	78.7
X3LYP	-8.7	-103.0	-134.7	0.3	-147.2	-284.3	-422.5	51.4	-44.7	-138.0	-230.2	79.3
B97-1	-9.6	-107.8	-132.9	1.8	-145.6	-280.3	-422.1	50.5	-46.0	-138.9	-235.4	78.2
B3LYP	-8.6	-103.6	-134.6	0.6	-146.2	-283.3	-421.2	51.6	-44.1	-137.4	-229.3	79.9
PBE0	-7.8	-106.6	-136.9	1.2	-145.7	-286.0	-424.6	52.1	-43.9	-141.9	-234.4	78.7
MPW1K	-4.2	-101.7	-135.6	2.2	-146.1	-290.5	-431.7	53.1	-43.1	-143.9	-236.9	77.8
BHLYP	-2.9	-92.2	-130.9	2.6	-147.8	-289.4	-431.2	52.5	-43.7	-140.3	-233.7	77.5
TPSSH	-7.8	-113.8	-138.1	3.0	-143.0	-283.6	-422.1	51.4	-44.3	-144.0	-237.9	79.2
M06	-13.5	-105.3	-130.0	-2.5	-149.0	-277.5	-423.2	51.3	-44.7	-126.8	-222.8	83.5
M06-2X	-4.9	-94.6	-130.4	3.4	-146.8	-284.8	-424.7	52.1	-44.4	-139.2	-230.9	77.6
B2PLYP	-12.7	-107.0	-137.1	3.6	-148.7	-285.2	-425.1	51.3	-47.4	-140.6	-234.7	66.8
Experiment	-6.2	-108.8	-131.4	7.2	-141.0	-278.4	-418.3	59.0	-42.8	-136.0	-227.4	87.2
Uncertainty	1.4	3.7	2.9	3.6	4.8	3.6	2.4	4.8	4.8	6.0	1.2	4.8

Table B.13: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: ThO to ThBr.

	ThBr ₂	ThBr3	ThBr4	ThI4	UO	UO ₂	UO3	UOF4	UO ₂ F ₂	UO2Cl2	UF
SVWN	-22.7	-107.3	-192.6	-129.9	-0.0	-141.7	-242.1	-483.6	-376.1	-287.6	-18.0
BP86	-8.4	-89.3	-169.7	-105.5	14.1	-114.1	-200.5	-430.8	-329.4	-247.0	-8.2
BLYP	-5.3	-81.1	-159.7	-94.5	21.0	-103.9	-185.2	-419.4	-316.2	-233.0	-8.2
PW91	-10.3	-93.1	-174.7	-110.5	12.2	-117.0	-204.3	-437.3	-334.5	-251.2	-9.5
PBE	-9.4	-91.7	-173.1	-109.0	13.2	-115.6	-202.6	-434.4	-332.2	-249.4	-8.5
TPSS	-9.2	-95.1	-178.6	-112.8	15.6	-116.6	-201.8	-432.4	-331.2	-247.3	-11.2
M06-L	-4.2	-83.6	-168.2	-102.4	16.3	-101.3	-186.6	-421.6	-319.8	-237.9	-12.7
B3P86	-9.8	-95.4	-179.1	-113.2	12.7	-106.9	-191.1	-426.2	-326.3	-240.0	-16.0
X3LYP	-7.8	-88.2	-170.6	-103.3	20.9	-93.0	-173.3	-413.6	-311.3	-224.9	-16.1
B97-1	-9.7	-91.2	-177.4	-111.0	22.1	-100.7	-183.6	-417.9	-318.6	-234.8	-15.9
B3LYP	-7.2	-87.4	-169.3	-102.2	20.0	-94.1	-175.0	-413.7	-312.0	-225.8	-15.7
PBE0	-8.8	-95.7	-179.4	-113.9	16.2	-100.6	-181.2	-418.0	-318.1	-232.5	-14.7
MPW1K	-8.6	-98.7	-183.4	-117.0	22.9	-93.8	-162.9	-405.1	-305.6	-217.5	-14.5
BHLYP	-7.8	-92.5	-176.8	-107.8	33.4	-78.7	-141.6	-391.9	-289.5	-199.8	-15.9
TPSSH	-9.2	-96.4	-180.7	-114.4	15.7	-108.1	-194.0	-426.4	-326.2	-243.6	-14.7
M06	-3.0	-74.0	-156.2	-89.8	33.9	-94.7	-169.0	-402.8	-305.3	-216.2	-17.3
M06-2X	-10.2	-94.1	-178.7	-114.6	9.9	-94.2	-177.1	-421.2	-321.9	-234.0	-22.9
B2PLYP	-11.2	-93.0	-178.6	-112.2	6.0	-98.6	-199.0	-435.2	-333.3	-249.4	2.8
Experiment	9.6	-79.8	-177.3	-110.1	8.4	-114.0	-191.0	-421.4	-323.3	-231.9	-11.2
Uncertainty	4.8	3.6	1.2	1.3	2.4	4.8	3.6	4.8	2.4	3.6	4.8

Table B.14: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: ThBr₂ to UF.

	UF ₂	UF3	UF4	UF5	UF6	UCl	UCl ₂	UCl3	UCl4	UCl5	UCl6
SVWN	-148.2	-283.4	-408.3	-512.2	-597.7	42.3	-50.6	-140.0	-214.7	-267.6	-313.5
BP86	-131.9	-258.7	-375.8	-465.6	-536.3	50.1	-42.9	-128.2	-193.5	-235.1	-268.0
BLYP	-128.0	-254.8	-370.6	-457.5	-525.4	51.5	-38.2	-123.2	-186.8	-224.3	-253.7
PW91	-135.5	-263.5	-381.4	-472.5	-544.6	49.6	-45.0	-131.0	-197.1	-239.7	-273.6
PBE	-133.6	-260.9	-378.4	-469.3	-541.1	50.2	-43.7	-129.2	-195.2	-237.3	-270.8
TPSS	-139.8	-267.0	-383.3	-456.3	-537.5	51.1	-45.8	-136.5	-194.7	-235.4	-263.6
M06-L	-126.4	-265.4	-382.0	-465.7	-527.9	54.4	-41.8	-142.8	-199.0	-237.1	-263.9
B3P86	-142.3	-271.1	-391.6	-472.0	-530.5	43.9	-51.0	-138.8	-201.5	-229.7	-247.9
X3LYP	-137.4	-265.4	-385.4	-463.2	-518.8	45.1	-46.0	-133.3	-195.3	-219.3	-233.8
B97-1	-133.8	-265.2	-385.8	-464.3	-521.1	43.3	-45.5	-137.7	-201.1	-227.4	-244.2
B3LYP	-137.1	-264.9	-384.3	-462.3	-518.4	45.2	-46.0	-132.9	-194.7	-219.3	-234.5
PBE0	-140.7	-268.4	-388.7	-466.7	-522.1	45.1	-50.1	-137.3	-200.1	-224.9	-239.2
MPW1K	-142.7	-272.2	-394.4	-464.1	-507.8	47.0	-51.2	-140.0	-201.1	-213.9	-214.2
BHLYP	-138.6	-268.7	-392.2	-458.0	-496.0	48.0	-46.3	-135.3	-196.4	-202.0	-194.3
TPSSH	-140.7	-270.6	-387.8	-469.9	-530.6	46.6	-53.0	-143.4	-205.4	-236.9	-259.0
M06	-123.4	-262.4	-379.6	-457.5	-504.9	47.5	-31.0	-126.8	-183.2	-209.9	-220.4
M06-2X	-143.9	-261.6	-396.8	-472.1	-524.8	32.2	-50.2	-130.6	-207.5	-224.4	-234.2
B2PLYP	-136.0	-265.1	-388.9	-470.4	-535.8	44.5	-45.4	-133.5	-200.7	-233.6	-273.2
Experiment	-129.1	-254.5	-383.6	-457.2	-513.5	44.7	-37.0	-125.0	-194.9	-215.1	-235.5
Uncertainty	6.0	4.8	1.6	3.6	0.5	4.8	4.8	4.8	1.1	3.6	1.2

Table B.15: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: UF₂ to UCl₆.

Table B.16: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: UBr to NpO₂.

	UBr	UBr ₂	UBr3	UBr4	UBr5	UI	UI ₂	UI3	UI4	NpO	NpO ₂
SVWN	49.5	-22.6	-101.1	-163.4	-202.0	67.3	7.6	-52.2	-102.8	3.3	-92.7
BP86	56.2	-12.8	-85.6	-137.4	-162.8	73.7	17.7	-37.0	-74.1	8.1	-100.1
BLYP	58.4	-5.6	-76.6	-125.4	-145.7	75.9	25.1	-27.9	-60.9	14.2	-74.7
PW91	55.6	-15.1	-88.8	-141.2	-167.8	73.1	15.5	-40.2	-77.8	6.5	-102.5
PBE	56.1	-13.8	-87.1	-139.4	-165.6	73.7	16.7	-38.8	-76.2	7.5	-101.0
TPSS	54.1	-20.1	-95.9	-145.4	-168.6	70.3	10.4	-49.3	-82.4	5.5	-106.6
M06-L	54.8	-7.9	-84.9	-130.1	-148.1	70.2	22.6	-37.6	-68.0	20.9	-97.7
B3P86	49.5	-22.9	-97.6	-146.2	-157.9	66.7	7.8	-49.9	-81.6	9.9	-96.5
X3LYP	51.0	-16.3	-89.2	-136.2	-142.8	68.2	14.8	-41.3	-70.2	16.5	-83.8
B97-1	49.0	-16.6	-95.1	-143.2	-152.6	66.2	14.0	-47.8	-78.4	20.0	-89.0
B3LYP	51.2	-16.0	-88.5	-135.3	-142.6	68.5	15.1	-40.6	-69.2	16.1	-84.5
PBE0	50.3	-22.7	-97.1	-145.1	-153.4	67.3	7.8	-50.3	-59.7	11.9	-91.0
MPW1K	50.9	-25.0	-100.8	-146.4	-142.5	67.1	5.1	-54.4	-81.2	13.0	-88.2
BHLYP	51.6	-18.8	-93.7	-138.4	-126.2	68.0	12.1	-46.3	-70.7	19.9	-75.8
TPSSH	50.7	-24.2	-100.4	-148.2	-164.0	66.4	4.9	-54.1	-83.9	7.8	-101.9
M06	53.8	1.0	-73.9	-116.9	-121.8	70.3	32.2	-28.6	-53.3	28.9	-82.4
M06-2X	49.5	-26.2	-107.0	-153.9	-152.6	72.5	6.0	-44.8	-83.7	24.9	-68.0
B2PLYP	65.3	-17.3	-92.5	-144.9	-166.3	67.2	13.7	-44.9	-76.1	12.9	-93.5
Experiment	58.6	-9.6	-88.7	-144.7	-154.9	81.7	24.6	-32.7	-72.9	-4.0	-109.2
Uncertainty	3.6	3.6	4.8	1.1	3.6	6.0	6.0	6.0	1.4	2.4	4.8

	NpF	NpF2	NpF3	NpF4	NpF6	NpCl3	NpCl4	PuO	PuO ₂	PuO3	PuF
SVWN	-7.3	-144.8	-271.3	-380.0	-544.6	-133.0	-193.0	-8.6	-100.5	-163.3	-21.9
BP86	-0.6	-131.8	-252.5	-351.8	-489.3	-125.3	-178.0	2.3	-81.1	-133.0	-16.2
BLYP	3.7	-129.2	-250.3	-348.5	-479.6	-121.4	-173.3	7.2	-73.3	-121.2	-19.9
PW91	-3.3	-135.1	-250.0	-356.9	-496.8	-127.9	-181.0	0.8	-82.2	-135.0	-26.8
PBE	-2.2	-133.0	-247.0	-353.5	-492.9	-126.0	-178.6	2.1	-80.3	-132.5	-25.8
TPSS	-4.2	-139.9	-260.1	-366.0	-495.3	-135.9	-189.0	-4.5	-85.2	-139.1	-29.0
M06-L	8.7	-134.0	-258.7	-366.4	-488.4	-139.1	-193.1	13.1	-83.3	-114.8	-16.6
B3P86	-2.9	-140.3	-260.4	-363.9	-473.6	-134.5	-181.7	3.1	-82.4	-106.2	-27.1
X3LYP	2.7	-137.7	-256.2	-360.7	-463.3	-131.0	-178.4	8.6	-69.5	-91.7	-21.9
B97-1	7.5	-131.2	-254.5	-357.5	-462.3	-133.0	-180.5	12.7	-74.8	-97.3	-17.1
B3LYP	2.5	-136.7	-254.9	-359.0	-462.9	-129.9	-177.1	8.4	-70.8	-93.8	-22.0
PBE0	-2.7	-140.5	-259.9	-362.3	-464.6	-135.2	-181.3	4.4	-76.2	-94.8	-27.9
MPW1K	-5.0	-149.5	-272.9	-374.7	-450.6	-144.5	-188.6	4.2	-68.9	-78.1	-29.8
BHLYP	0.8	-150.2	-273.5	-378.4	-441.1	-144.0	-189.4	9.1	-55.7	-63.7	-24.2
TPSSH	-4.2	-142.0	-261.6	-368.0	-482.9	-142.0	-193.4	-2.3	-89.2	-121.9	-29.0
M06	16.9	-123.2	-248.7	-354.0	-455.1	-117.6	-164.6	21.4	-70.4	-83.9	-11.1
M06-2X	8.7	-118.4	-240.3	-338.5	-425.3	-121.9	-146.6	29.9	-51.9	-46.5	-17.2
B2PLYP	2.7	-140.4	-262.1	-366.5	-466.8	-136.1	-183.8	4.7	-79.4	-100.7	-21.6
Experiment	-19.1	-137.4	-266.5	-373.1	-459.3	-140.8	-188.1	-12.4	-102.3	-135.7	-26.9
Uncertainty	6.0	7.2	6.0	5.3	4.8	2.5	1.1	3.6	4.8	3.5	2.4

Table B.17: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: NpF to PuF.

	PuF ₂	PuF3	PuF4	PuF6	PuCl3	PuCl4	PuBr3	PuI3	AmO	AmF3
SVWN	-152.6	-264.4	-355.4	-481.9	-131.9	-178.7	-95.5	-51.2	-7.3	-278.8
BP86	-137.9	-245.9	-330.4	-429.8	-125.1	-165.2	-84.4	-39.6	2.1	-259.4
BLYP	-134.7	-241.6	-328.2	-421.1	-121.1	-161.1	-76.7	-31.5	5.5	-258.1
PW91	-141.5	-248.8	-334.8	-436.5	-127.5	-167.7	-87.0	-42.3	1.6	-261.7
PBE	-139.7	-246.0	-331.3	-432.4	-125.6	-165.3	-85.4	-40.8	3.2	-258.4
TPSS	-145.3	-255.9	-343.6	-435.4	-134.4	-174.4	-97.5	-51.9	-0.7	-268.6
M06-L	-136.3	-252.0	-336.2	-421.9	-135.8	-171.9	-84.0	-36.4	19.7	-269.6
B3P86	-141.6	-256.7	-338.0	-404.8	-132.1	-162.8	-93.1	-46.7	25.1	-270.0
X3LYP	-140.8	-252.3	-335.6	-394.8	-128.4	-159.6	-86.9	-38.4	31.3	-264.6
B97-1	-133.5	-245.1	-331.8	-393.4	-130.6	-161.5	-90.2	-41.8	35.2	-262.7
B3LYP	-137.1	-251.2	-334.1	-395.2	-127.5	-158.8	-85.8	-27.2	29.1	-264.1
PBE0	-140.8	-255.9	-335.8	-393.9	-133.0	-161.4	-94.8	-37.4	33.9	-265.8
MPW1K	-143.0	-266.5	-345.4	-373.3	-140.5	-164.2	-103.7	-57.0	53.8	-275.7
BHLYP	-135.9	-266.9	-349.9	-363.2	-139.8	-165.2	-101.2	-53.0	65.5	-275.6
TPSSH	-144.7	-258.3	-343.2	-418.4	-139.4	-175.7	-99.6	-52.9	12.2	-270.3
M06	-130.2	-248.6	-324.0	-386.3	-119.7	-142.8	-71.8	-22.7	49.4	-263.2
M06-2X	-129.3	-240.9	-305.0	-342.4	-113.0	-130.8	-78.5	-33.8	75.8	-255.1
B2PLYP	-130.8	-254.4	-339.2	-411.1	-131.9	-164.1	-92.3	-45.5	55.1	-267.9
Experiment	-146.8	-279.1	-370.0	-433.2	-154.7	-189.3	-116.6	-72.9	-3.5	-276.4
Uncertainty	1.4	0.9	5.3	4.8	0.5	2.4	3.6	3.6	12.0	4.0

Table B.18: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the Stuttgart RSC ECP and the associated atomic natural orbital (ANO) basis for compounds: PuF₂ to AmF₃.

	ThO	ThO ₂	ThOF	ThF	ThF ₂	ThF3	ThF4	ThCl	ThCl ₂	ThCl3	ThCl4	ThBr
SVWN	-28.6	-137.1	-160.5	-11.8	-167.6	-305.8	-446.6	42.0	-59.3	-153.9	-248.8	56.9
BP86	-13.6	-116.9	-140.9	0.3	-145.9	-281.8	-417.1	49.3	-46.5	-140.8	-232.0	65.4
BLYP	-12.0	-111.0	-137.2	0.1	-145.7	-279.6	-414.8	49.7	-45.5	-136.6	-227.7	67.2
PW91	-15.1	-120.9	-144.8	-1.8	-149.7	-287.4	-424.1	48.2	-48.5	-144.3	-236.9	64.3
PBE	-14.2	-118.9	-143.0	-0.8	-148.0	-284.9	-420.9	48.8	-47.4	-142.7	-235.0	64.8
TPSS	-11.7	-121.6	-142.9	-0.3	-145.4	-285.3	-423.4	50.5	-44.8	-143.2	-236.4	65.4
M06-L	-11.9	-115.9	-136.2	0.5	-146.3	-282.2	-428.8	48.8	-49.4	-144.2	-244.3	67.9
B3P86	-13.7	-116.8	-144.3	-0.9	-150.7	-291.7	-431.7	49.0	-48.6	-146.5	-239.9	64.5
X3LYP	-11.9	-108.1	-139.2	-0.4	-150.5	-288.3	-427.4	49.2	-48.0	-142.2	-235.4	65.8
B97-1	-12.6	-112.6	-137.2	1.1	-148.8	-284.1	-426.7	48.4	-49.2	-142.9	-240.4	64.5
B3LYP	-11.8	-108.7	-139.0	-0.1	-149.5	-287.2	-426.1	49.5	-47.4	-141.6	-234.5	66.1
PBE0	-10.8	-111.3	-141.1	0.4	-149.0	-289.8	-429.2	49.9	-47.2	-145.9	-239.4	65.2
MPW1K	-7.4	-106.6	-140.1	1.2	-149.6	-294.5	-436.6	50.6	-46.6	-148.1	-242.3	65.3
BHLYP	-6.3	-97.6	-135.8	1.6	-151.4	-293.6	-436.4	50.0	-47.3	-144.8	-239.3	65.8
TPSSH	-10.8	-118.4	-142.2	-0.0	-146.3	-287.3	-426.7	49.5	-47.5	-148.0	-242.8	65.2
M06	-16.7	-109.9	-134.6	-3.9	-152.6	-281.9	-428.3	48.9	-48.2	-131.1	-228.1	67.1
M06-2X	-8.0	-99.8	-135.4	2.8	-150.2	-289.1	-429.9	50.6	-47.6	-143.6	-236.1	65.4
Experiment	-6.2	-108.8	-131.4	7.2	-141.0	-278.4	-418.3	59.0	-42.8	-136.0	-227.4	87.2
Uncertainty	1.4	3.7	2.9	3.6	4.8	3.6	2.4	4.8	4.8	6.0	1.2	4.8

Table B.19: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: ThO to ThBr.

	ThBr ₂	ThBr3	ThBr4	ThI4	UO	UO ₂	UO3	UOF4	UO ₂ F ₂	UO2Cl2	UF
SVWN	-23.8	-108.8	-194.6	-129.5	-16.5	-152.2	-250.8	-494.1	-385.4	-295.5	-22.1
BP86	-10.0	-91.3	-172.0	-105.8	-3.1	-127.0	-212.6	-444.7	-342.2	-258.3	-12.0
BLYP	-7.1	-83.5	-162.6	-94.6	0.6	-117.6	-198.1	-433.9	-329.7	-245.0	-11.9
PW91	-12.0	-95.2	-177.1	-110.8	-5.0	-129.5	-216.5	-451.5	-347.4	-262.7	-13.4
PBE	-11.0	-93.8	-175.5	-109.3	-3.9	-128.1	-214.7	-448.5	-345.1	-260.8	-12.5
TPSS	-11.2	-97.5	-181.3	-113.4	9.6	-126.6	-214.4	-447.1	-344.5	-259.2	-13.2
M06-L	-6.9	-86.6	-171.7	-104.1	10.6	-108.8	-199.3	-436.9	-333.5	-250.2	-11.0
B3P86	-12.2	-98.3	-182.5	-114.9	-2.1	-118.2	-198.3	-436.4	-334.5	-247.1	-14.8
X3LYP	-10.2	-91.2	-173.9	-105.1	4.4	-108.1	-181.9	-424.9	-320.9	-233.4	-15.1
B97-1	-12.1	-94.1	-180.7	-112.7	6.3	-109.4	-191.4	-428.6	-327.5	-242.6	-15.1
B3LYP	-9.5	-90.3	-172.7	-103.9	3.7	-109.3	-183.8	-425.2	-321.8	-234.4	-14.9
PBE0	-11.4	-98.8	-183.1	-115.8	1.1	-111.0	-187.8	-427.6	-325.7	-239.1	-13.2
MPW1K	-11.7	-102.4	-187.8	-119.3	6.7	-95.0	-165.1	-410.9	-309.0	-220.0	-10.9
BHLYP	-10.7	-95.9	-180.9	-110.1	15.6	-81.5	-143.8	-397.8	-292.9	-202.3	-11.0
TPSSH	-11.6	-99.3	-184.0	-115.8	-3.9	-120.2	-203.8	-439.0	-337.0	-253.2	-13.4
M06	-5.6	-76.9	-159.8	-92.3	18.6	-95.0	-171.9	-409.5	-309.6	-219.5	-12.5
M06-2X	-12.7	-97.5	-182.5	-116.9	6.1	-109.1	-187.8	-435.7	-333.9	-244.8	-22.1
Experiment	9.6	-79.8	-177.3	-110.1	8.4	-114.0	-191.0	-421.4	-323.3	-231.9	-11.2
Uncertainty	4.8	3.6	1.2	1.3	2.4	4.8	3.6	4.8	2.4	3.6	4.8

Table B.20: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: ThBr₂ to UF.

	UF ₂	UF3	UF4	UF5	UF6	UCl	UCl ₂	UCl3	UCl4	UCl5	UCl6
SVWN	-151.3	-289.4	-417.1	-522.9	-611.0	32.1	-54.8	-145.9	-222.4	-275.7	-321.6
BP86	-136.8	-266.5	-386.6	-479.2	-553.3	38.0	-47.7	-134.8	-203.9	-245.9	-279.7
BLYP	-133.1	-262.9	-381.7	-471.5	-542.9	38.7	-43.3	-130.0	-197.6	-235.5	-266.0
PW91	-140.5	-271.4	-392.4	-486.2	-561.6	37.4	-50.0	-137.8	-207.4	-250.7	-285.6
PBE	-138.6	-268.9	-389.4	-482.9	-558.1	38.0	-48.7	-136.1	-205.5	-248.4	-282.8
TPSS	-144.5	-273.9	-392.1	-484.3	-555.2	37.3	-52.0	-140.8	-207.2	-246.3	-276.2
M06-L	-131.0	-273.4	-394.3	-480.8	-546.3	34.7	-48.5	-148.2	-207.9	-248.6	-277.3
B3P86	-141.3	-272.9	-397.2	-480.9	-543.7	35.6	-51.6	-140.3	-205.5	-235.8	-256.0
X3LYP	-137.2	-268.3	-391.9	-473.2	-533.2	35.7	-47.2	-135.4	-200.4	-226.6	-243.0
B97-1	-133.2	-267.2	-391.9	-473.8	-534.8	34.2	-46.5	-139.7	-205.4	-234.2	-253.0
B3LYP	-137.1	-267.9	-391.0	-472.5	-532.9	35.9	-47.2	-135.2	-199.9	-226.7	-243.8
PBE0	-139.1	-269.4	-393.7	-475.1	-534.9	36.7	-50.8	-138.6	-203.2	-230.6	-247.1
MPW1K	-136.6	-269.0	-395.7	-468.6	-517.0	39.7	-49.7	-138.0	-199.4	-215.9	-218.5
BHLYP	-131.7	-264.8	-393.1	-462.3	-505.2	40.1	-44.4	-132.8	-194.3	-203.8	-198.7
TPSSH	-141.8	-273.9	-395.3	-481.1	-546.2	36.1	-54.4	-145.0	-210.4	-245.3	-269.4
M06	-121.3	-262.1	-384.0	-463.4	-514.9	38.5	-31.5	-126.4	-183.7	-212.9	-225.2
M06-2X	-140.6	-263.4	-398.5	-482.6	-542.7	30.2	-42.5	-124.6	-209.7	-231.8	-246.5
Experiment	-129.1	-254.5	-383.6	-457.2	-513.5	44.7	-37.0	-125.0	-194.9	-215.1	-235.5
Uncertainty	6.0	4.8	1.6	3.6	0.5	4.8	4.8	4.8	1.1	3.6	1.2

Table B.21: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: UF₂ to UCl₆.

	UBr	UBr ₂	UBr3	UBr4	UBr5	UI	UI2	UI3	UI4	NpO	NpO ₂
SVWN	45.9	-27.4	-104.4	-170.3	-209.3	64.4	5.2	-55.5	-107.4	-11.0	-127.7
BP86	52.8	-17.6	-90.5	-145.2	-171.9	70.9	15.2	-41.0	-80.2	0.1	-108.3
BLYP	54.8	-10.7	-81.1	-133.8	-155.6	73.3	22.7	-31.6	-67.2	6.3	-100.0
PW91	52.1	-20.0	-94.0	-149.1	-177.2	70.2	12.8	-44.4	-84.4	-1.5	-110.1
PBE	52.6	-18.8	-92.2	-147.4	-175.0	70.7	14.0	-43.0	-82.8	-0.5	-108.3
TPSS	51.4	-24.0	-99.9	-153.1	-177.8	69.8	6.7	-52.8	-87.9	-0.6	-116.7
M06-L	55.5	-12.5	-90.1	-137.1	-160.0	70.9	20.5	-44.7	-74.6	6.9	-106.1
B3P86	50.7	-23.8	-105.3	-150.0	-163.1	69.2	9.3	-49.1	-91.1	0.5	-104.0
X3LYP	51.8	-17.3	-97.6	-140.5	-148.6	70.5	15.8	-40.8	-81.7	7.3	-91.8
B97-1	49.8	-17.6	-103.3	-146.7	-158.2	68.3	15.1	-47.2	-88.4	10.6	-96.9
B3LYP	51.9	-17.0	-96.7	-139.7	-148.6	70.5	16.0	-40.4	-79.6	6.9	-92.8
PBE0	51.8	-23.5	-106.2	-148.9	-158.5	70.1	9.4	-49.2	-91.9	2.5	-98.1
MPW1K	54.3	-23.9	-112.5	-148.7	-145.0	72.7	9.5	-50.4	-96.0	3.3	-93.6
BHLYP	56.1	-16.9	-106.0	-139.6	-127.6	75.0	17.4	-41.2	-86.3	10.4	-81.1
TPSSH	51.0	-24.9	-105.1	-152.9	-170.8	69.4	5.5	-53.5	-87.0	1.3	-110.4
M06	56.0	1.4	-85.1	-118.5	-123.8	74.8	34.8	-26.0	-63.7	19.4	-88.8
M06-2X	44.9	-15.2	-125.1	-154.3	-158.5	71.3	10.6	-42.8	-93.5	17.6	-83.9
Experiment	58.6	-9.6	-88.7	-144.7	-154.9	81.7	24.6	-32.7	-72.9	-4.0	-109.2
Uncertainty	3.6	3.6	4.8	1.1	3.6	6.0	6.0	6.0	1.4	2.4	4.8

Table B.22: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: UBr to NpO₂.

	NpF	NpF2	NpF3	NpF4	NpF6	NpCl3	NpCl4	PuO	PuO ₂	PuO3	PuF
SVWN	-22.4	-152.4	-280.5	-390.9	-560.7	-141.0	-204.7	-16.9	-123.8	-180.8	-35.4
BP86	-15.1	-139.3	-261.3	-363.7	-507.9	-131.8	-184.8	-8.3	-103.6	-151.0	-23.9
BLYP	-15.5	-136.6	-258.3	-360.5	-498.5	-127.7	-179.9	-3.5	-87.9	-139.7	-29.1
PW91	-16.4	-142.7	-265.8	-368.8	-515.5	-134.5	-188.1	-9.7	-105.8	-153.0	-26.7
PBE	-15.5	-140.6	-262.9	-365.3	-511.5	-132.5	-185.7	-8.4	-103.9	-150.3	-25.4
TPSS	-17.0	-146.2	-270.9	-377.1	-514.0	-140.4	-195.1	-14.2	-99.7	-157.8	-29.8
M06-L	-18.1	-134.9	-266.1	-378.6	-507.1	-146.6	-198.3	2.6	-94.3	-133.9	-17.9
B3P86	-3.3	-148.3	-272.7	-375.5	-492.2	-141.3	-190.4	-6.7	-91.5	-123.5	-26.2
X3LYP	-22.1	-145.2	-268.4	-372.4	-482.3	-137.4	-186.6	-1.3	-79.7	-109.8	-21.6
B97-1	7.2	-139.0	-266.2	-369.0	-481.2	-140.0	-189.6	3.1	-84.3	-114.9	-16.4
B3LYP	1.3	-144.3	-267.3	-370.7	-482.1	-136.6	-185.4	-1.6	-80.8	-111.9	-21.7
PBE0	-2.9	-148.6	-271.5	-373.9	-483.2	-142.2	-190.8	-4.5	-84.5	-111.3	-26.0
MPW1K	-4.2	-158.4	-283.0	-386.5	-468.5	-151.9	-199.9	-3.6	-77.2	-94.7	-27.7
BHLYP	2.6	-158.2	-282.9	-389.5	-458.9	-150.7	-199.6	1.1	-64.6	-81.1	-22.4
TPSSH	-6.6	-148.5	-273.3	-378.3	-502.2	-147.0	-200.4	-11.6	-99.8	-140.4	-29.6
M06	17.4	-134.3	-264.2	-365.3	-472.1	-127.3	-163.3	13.5	-75.3	-97.0	-6.1
M06-2X	5.4	-133.5	-256.7	-340.5	-451.5	-129.1	-166.1	16.0	-66.2	-68.1	-20.7
Experiment	-19.1	-137.4	-266.5	-373.1	-459.3	-140.8	-188.1	-12.4	-102.3	-135.7	-26.9
Uncertainty	6.0	7.2	6.0	5.3	4.8	2.5	1.1	3.6	4.8	3.5	2.4

Table B.23: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: NpF to PuF.

	PuF ₂	PuF3	PuF4	PuF6	PuCl3	PuCl4	PuBr3	PuI3	AmO	AmF3
SVWN	-156.0	-274.5	-373.8	-508.9	-141.0	-193.6	-106.0	-56.2	-10.0	-266.7
BP86	-143.1	-257.5	-347.5	-455.4	-135.3	-179.4	-92.8	-46.6	-2.3	-246.5
BLYP	-140.2	-254.2	-345.1	-447.0	-131.3	-175.3	-85.4	-38.2	2.2	-243.3
PW91	-146.5	-261.6	-351.9	-462.3	-137.6	-182.0	-95.5	-49.3	-3.7	-250.2
PBE	-144.4	-258.6	-348.2	-458.1	-135.6	-179.4	-93.7	-47.7	-2.3	-247.3
TPSS	-150.2	-268.2	-360.6	-461.8	-144.7	-188.7	-106.1	-58.6	-7.4	-255.1
M06-L	-139.9	-265.8	-353.6	-448.4	-146.3	-186.9	-93.9	-44.7	11.6	-252.2
B3P86	-147.1	-269.5	-357.1	-432.0	-143.2	-179.2	-103.8	-54.8	2.8	-258.0
X3LYP	-143.8	-265.1	-354.5	-422.4	-139.7	-176.1	-97.5	-48.0	8.2	-253.6
B97-1	-138.6	-262.9	-350.7	-420.6	-141.7	-177.9	-100.8	-51.8	11.6	-251.9
B3LYP	-143.3	-263.9	-352.8	-422.6	-138.7	-175.0	-96.2	-46.8	7.6	-252.6
PBE0	-145.7	-268.0	-354.8	-420.5	-143.5	-177.8	-105.5	-56.4	6.0	-256.2
MPW1K	-151.3	-279.4	-367.5	-401.9	-152.4	-184.3	-117.8	-66.3	8.8	-267.2
BHLYP	-151.8	-279.6	-372.2	-392.4	-151.8	-185.7	-114.7	-62.0	13.9	-267.6
TPSSH	-149.9	-270.3	-360.4	-445.5	-149.8	-190.6	-108.5	-60.3	-3.2	-256.9
M06	-132.6	-260.5	-345.1	-411.0	-129.7	-160.2	-81.7	-31.7	24.3	-250.6
M06-2X	-133.0	-252.8	-321.5	-374.9	-131.3	-145.0	-90.8	-44.4	26.3	-236.8
Experiment	-146.8	-279.1	-370.0	-433.2	-154.7	-189.3	-116.6	-72.9	-3.5	-276.4
Uncertainty	1.4	0.9	5.3	4.8	0.5	2.4	3.6	3.6	12.0	4.0

Table B.24: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the SODFT routine using the segmented Stuttgart Basis and ECP for compounds: PuF₂ to AmF₃.

	ThO	ThO ₂	ThOF	ThF	ThF ₂	ThF3	ThF4	ThCl	ThCl ₂	ThCl3	ThCl4	ThBr
SVWN	-24.8	-132.5	-156.2	-8.3	-163.9	-301.6	-441.6	44.2	-55.5	-149.6	-243.7	74.2
BP86	-10.6	-113.1	-137.4	1.2	-143.0	-278.3	-412.9	50.9	-43.5	-137.2	-227.6	82.0
BLYP	-8.8	-107.0	-133.4	1.1	-142.5	-276.0	-410.3	51.5	-42.2	-132.8	-223.0	83.5
PW91	-12.1	-117.2	-141.3	-0.8	-146.7	-284.0	-419.8	49.8	-45.4	-140.7	-232.5	81.0
PBE	-11.3	-115.2	-139.5	0.1	-145.1	-281.5	-416.7	50.3	-46.5	-139.2	-230.6	81.4
TPSS	-8.8	-118.1	-139.6	0.5	-142.6	-282.1	-419.3	52.1	-41.8	-139.7	-232.1	64.4
M06-L	-8.9	-112.0	-132.4	1.5	-143.2	-278.5	-424.4	50.5	-46.2	-140.4	-239.8	69.2
B3P86	-9.8	-112.2	-139.6	0.4	-146.7	-287.2	-426.2	51.2	-44.5	-141.8	-234.3	82.0
X3LYP	-7.8	-103.3	-134.3	0.6	-146.3	-283.6	-421.8	51.6	-43.7	-137.2	-229.5	83.1
B97-1	-8.8	-108.1	-132.6	1.9	-144.9	-279.7	-421.4	50.7	-45.1	-138.3	-234.8	81.7
B3LYP	-7.7	-104.0	-134.2	0.6	-145.4	-282.6	-420.5	51.8	-43.1	-136.7	-228.7	83.3
PBE0	-7.2	-107.2	-136.9	1.5	-145.3	-285.7	-424.1	52.0	-43.4	-141.5	-234.1	82.4
MPW1K	-3.3	-102.0	-135.3	2.8	-145.4	-289.7	-430.9	53.1	-42.2	-143.2	-236.2	83.9
BHLYP	-0.2	-90.8	-128.7	5.2	-145.2	-286.8	-428.6	54.2	-40.9	-137.7	-231.0	86.4
TPSSH	-7.7	-114.7	-138.5	4.2	-143.1	-283.7	-422.1	51.3	-44.2	-144.1	-238.1	80.6
M06	-10.3	-103.0	-127.3	-0.9	-145.9	-274.6	-420.1	52.9	-41.4	-123.8	-219.9	89.7
M06-2X	-15.7	-107.2	-142.1	-6.2	-157.8	-296.1	-435.9	42.2	-55.1	-150.4	-242.1	75.7
Experiment	-6.2	-108.8	-131.4	7.2	-141.0	-278.4	-418.3	59.0	-42.8	-136.0	-227.4	87.2
Uncertainty	1.4	3.7	2.9	3.6	4.8	3.6	2.4	4.8	4.8	6.0	1.2	4.8

Table B.25: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: ThO to ThBr.

	ThBr ₂	ThBr3	ThBr4	ThI4	UO	UO ₂	UO3	UOF4	UO ₂ F ₂	UO2Cl2	UF
SVWN	-20.9	-105.8	-191.3	-127.0	-0.8	-144.7	-241.6	-482.4	-375.0	-286.9	-19.5
BP86	-8.1	-89.0	-169.4	-104.1	12.3	-119.5	-203.4	-433.1	-331.8	-249.8	-9.7
BLYP	-4.8	-81.0	-159.7	-92.8	16.2	-109.6	-188.6	-422.1	-319.0	-236.2	-9.5
PW91	-9.9	-92.9	-174.5	-109.1	10.4	-121.9	-207.3	-439.8	-337.0	-254.1	-11.0
PBE	-9.0	-91.5	-172.9	-107.7	11.4	-120.5	-205.5	-436.8	-334.7	-252.3	-10.1
TPSS	-9.2	-95.3	-178.8	-111.8	14.0	-119.3	-205.4	-435.5	-334.4	-250.8	-12.0
M06-L	-4.6	-84.2	-168.8	-102.1	14.8	-103.5	-190.3	-425.1	-323.2	-241.7	-13.4
B3P86	-9.3	-95.2	-178.9	-113.1	14.4	-103.3	-189.6	-424.6	-324.6	-238.9	-13.8
X3LYP	-7.0	-87.8	-170.2	-103.2	22.1	-90.3	-172.6	-412.6	-310.4	-224.6	-13.9
B97-1	-9.1	-91.0	-177.1	-110.9	23.6	-97.5	-182.4	-416.6	-317.3	-234.1	-13.8
B3LYP	-6.5	-87.0	-169.0	-102.0	20.9	-91.8	-174.7	-413.2	-311.5	-225.9	-13.8
PBE0	-8.7	-96.0	-179.8	-114.4	18.6	-96.0	-178.8	-415.4	-315.4	-230.6	-11.9
MPW1K	-8.5	-99.1	-184.0	-117.8	27.6	-83.9	-155.3	-397.6	-298.0	-210.7	-9.0
BHLYP	-5.5	-90.7	-175.0	-106.8	38.4	-68.2	-133.4	-383.8	-281.3	-192.3	-9.1
TPSSH	-9.3	-96.8	-181.1	-114.3	14.5	-109.6	-197.3	-429.4	-329.2	-247.1	-14.9
M06	-0.1	-71.4	-153.6	-87.9	37.6	-86.9	-163.2	-397.3	-299.5	-211.1	-12.8
M06-2X	-21.6	-106.8	-190.9	-127.9	17.8	-89.5	-174.4	-418.4	-319.1	-232.0	-14.3
Experiment	9.6	-79.8	-177.3	-110.1	8.4	-114.0	-191.0	-421.4	-323.3	-231.9	-11.2
Uncertainty	4.8	3.6	1.2	1.3	2.4	4.8	3.6	4.8	2.4	3.6	4.8

Table B.26: Density Functional computed enthalpies of formation $\Delta H^{\circ}_{f,298}$ (kcal mol⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: ThBr₂ to UF.

	LIES	LIES	LIEA	LIE-	LIEC	UCI	UCIa	UCla	UCL	UCL	
	UF2	0F3	0г4	015	06	UCI	0012	0013	UCI4	0015	0016
SVWN	-147.6	-284.1	-409.7	-512.1	-597.1	44.6	-51.7	-142.1	-218.2	-270.5	-317.2
BP86	-133.2	-261.1	-378.6	-468.4	-539.4	49.5	-44.7	-131.1	-197.1	-240.5	-275.1
BLYP	-129.4	-257.3	-373.4	-460.5	-528.8	50.9	-40.0	-126.1	-190.4	-229.9	-261.0
PW91	-136.9	-265.9	-384.3	-475.4	-547.7	49.1	-46.9	-134.1	-200.7	-245.3	-281.0
PBE	-135.0	-263.4	-381.3	-472.1	-544.2	49.7	-45.6	-132.3	-198.8	-242.9	-278.1
TPSS	-141.1	-268.8	-385.8	-473.6	-541.4	45.5	-47.6	-138.9	-201.1	-241.1	-271.6
M06-L	-127.7	-267.6	-384.4	-469.8	-532.3	34.8	-43.4	-144.8	-202.5	-242.9	-272.3
B3P86	-138.8	-268.9	-389.9	-470.2	-529.7	50.0	-49.5	-137.7	-199.7	-230.6	-251.3
X3LYP	-134.3	-263.8	-384.1	-462.1	-518.7	50.6	-44.7	-132.3	-194.0	-220.7	-237.7
B97-1	-130.4	-263.0	-384.4	-462.9	-520.6	49.0	-44.2	-136.8	-199.6	-228.5	-247.8
B3LYP	-134.4	-263.6	-383.4	-461.6	-518.7	50.2	-44.8	-132.3	-193.8	-221.1	-238.8
PBE0	-136.2	-265.1	-392.1	-464.0	-520.5	52.3	-48.3	-135.7	-197.4	-224.9	-241.8
MPW1K	-133.5	-264.7	-387.9	-456.6	-501.4	59.3	-47.0	-134.9	-193.4	-209.1	-212.0
BHLYP	-128.5	-260.2	-384.8	-449.8	-488.9	61.1	-41.4	-129.3	-187.7	-196.3	-191.3
TPSSH	-141.1	-271.8	-389.6	-472.6	-534.5	47.6	-54.1	-145.2	-207.9	-242.2	-266.9
M06	-118.3	-257.1	-375.5	-452.0	-500.4	57.4	-28.9	-123.5	-178.2	-207.1	-220.2
M06-2X	-134.4	-253.6	-389.9	-466.9	-523.1	40.6	-42.4	-123.0	-202.5	-221.8	-236.8
Experiment	-129.1	-254.5	-383.6	-457.2	-513.5	44.7	-37.0	-125.0	-194.9	-215.1	-235.5
Uncertainty	6.0	4.8	1.6	3.6	0.5	4.8	4.8	4.8	1.1	3.6	1.2

Table B.27: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: UF₂ to UCl₆.

	UBr	UBr ₂	UBr3	UBr4	UBr5	UI	UI ₂	UI3	UI4	NpO	NpO ₂
SVWN	47.8	-25.1	-103.5	-166.9	-206.6	66.0	6.9	-54.9	-105.1	-3.6	-125.3
BP86	54.7	-15.0	-88.5	-141.8	-169.1	72.4	16.2	-39.3	-79.5	4.7	-104.6
BLYP	57.0	-8.0	-79.8	-130.2	-152.7	74.8	23.8	-29.8	-66.5	10.9	-95.9
PW91	54.1	-17.3	-91.8	-145.7	-174.3	71.8	14.0	-42.6	-83.3	3.0	-107.0
PBE	54.6	-16.1	-90.2	-144.0	-172.1	72.3	15.1	-41.3	-81.7	4.1	-105.5
TPSS	53.2	-21.8	-98.2	-149.6	-175.0	69.7	8.2	-50.5	-85.6	-4.6	-110.8
M06-L	54.2	-9.6	-90.7	-134.0	-154.6	69.7	21.6	-39.0	-71.1	19.2	-100.1
B3P86	46.5	-21.4	-102.6	-152.6	-160.4	63.6	10.0	-48.6	-88.8	0.5	-97.1
X3LYP	47.7	-14.8	-94.3	-142.8	-145.5	64.9	16.9	-40.0	-78.0	12.1	-84.8
B97-1	46.0	-15.2	-100.1	-149.7	-155.2	63.0	15.9	-46.5	-85.7	15.1	-90.3
B3LYP	48.0	-14.8	-93.6	-141.9	-145.6	65.2	16.8	-39.6	-76.7	7.3	-85.8
PBE0	47.1	-20.6	-103.0	-152.0	-155.3	64.0	10.4	-48.4	-80.2	7.5	-91.1
MPW1K	47.2	-21.1	-107.3	-154.0	-140.8	64.1	10.7	-49.3	-89.3	7.5	-87.2
BHLYP	48.1	-13.6	-100.0	-145.6	-122.8	65.1	18.8	-40.0	-78.9	14.0	-75.1
TPSSH	47.6	-25.4	-105.0	-154.4	-170.1	63.5	4.4	-55.0	-90.0	4.9	-104.8
M06	50.9	4.2	-79.3	-121.9	-120.4	67.2	36.0	-24.2	-58.3	24.4	-81.8
M06-2X	61.4	-20.1	-116.8	-150.1	-151.0	74.4	14.9	-36.9	-83.4	22.3	-75.9
Experiment	58.6	-9.6	-88.7	-144.7	-154.9	81.7	24.6	-32.7	-72.9	-4.0	-109.2
Uncertainty	3.6	3.6	4.8	1.1	3.6	6.0	6.0	6.0	1.4	2.4	4.8

Table B.28: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: UBr to NpO₂.

	NpF	NpF2	NpF3	NpF4	NpF6	NpCl3	NpCl4	PuO	PuO ₂	PuO3	PuF
SVWN	-20.3	-149.1	-275.3	-382.6	-546.8	-138.2	-197.3	-11.7	-115.9	-170.2	-31.4
BP86	-12.5	-134.4	-255.8	-355.4	-493.6	-128.7	-182.6	-0.4	-95.7	-140.4	-23.8
BLYP	-12.8	-131.7	-253.0	-352.1	-484.1	-124.6	-177.7	4.4	-87.1	-128.9	-26.7
PW91	-13.9	-137.8	-257.7	-360.5	-501.2	-131.4	-185.7	-1.8	-98.0	-142.5	-25.4
PBE	-12.9	-135.8	-254.8	-357.1	-497.2	-129.5	-183.3	-0.4	-96.0	-139.8	-24.2
TPSS	-15.2	-142.1	-263.2	-369.2	-500.5	-138.9	-193.2	-7.2	-101.7	-147.0	-28.5
M06-L	-11.8	-135.6	-260.9	-368.8	-493.2	-141.5	-198.1	10.1	-86.5	-122.7	-23.2
B3P86	-1.6	-143.0	-264.8	-366.4	-476.6	-138.2	-185.8	0.8	-83.8	-112.3	-25.0
X3LYP	4.0	-139.9	-260.9	-363.0	-466.6	-134.1	-182.1	6.2	-71.4	-98.1	-20.2
B97-1	8.4	-134.2	-258.9	-360.4	-465.9	-136.9	-185.1	10.3	-76.5	-103.7	-15.3
B3LYP	3.7	-139.0	-259.6	-361.4	-466.4	-133.0	-180.9	6.0	-72.7	-100.3	-20.3
PBE0	-1.1	-143.2	-263.9	-364.5	-467.2	-138.9	-185.6	-1.2	-80.8	-104.2	-29.0
MPW1K	-2.3	-154.2	-276.9	-377.4	-452.4	-149.4	-194.0	2.6	-69.0	-83.0	-26.4
BHLYP	2.6	-155.3	-277.5	-381.0	-443.1	-148.9	-194.4	7.8	-55.8	-68.7	-21.0
TPSSH	-16.2	-144.2	-264.5	-370.9	-488.1	-144.7	-197.5	-4.9	-92.7	-129.3	-28.3
M06	18.9	-129.1	-256.3	-355.5	-456.3	-123.2	-168.6	19.0	-74.6	-92.9	-11.8
M06-2X	7.3	-121.7	-241.6	-343.4	-433.0	-124.4	-150.4	28.5	-56.5	-54.9	-18.3
Experiment	-19.1	-137.4	-266.5	-373.1	-459.3	-140.8	-188.1	-12.4	-102.3	-135.7	-26.9
Uncertainty	6.0	7.2	6.0	5.3	4.8	2.5	1.1	3.6	4.8	3.5	2.4

Table B.29: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: NpF to PuF.

	PuF ₂	PuF3	PuF4	PuF6	PuCl3	PuCl4	PuBr3	PuI3	AmO	AmF3
SVWN	-155.9	-271.3	-364.0	-493.7	-136.8	-187.6	-103.0	-58.0	-14.4	-290.1
BP86	-141.3	-251.1	-337.5	-440.6	-130.9	-173.2	-90.2	-43.8	-4.8	-270.2
BLYP	-138.1	-247.5	-334.9	-431.7	-126.7	-168.8	-82.7	-35.4	-1.6	-267.1
PW91	-144.8	-252.4	-341.9	-447.4	-133.3	-175.8	-92.9	-46.6	-5.4	-272.6
PBE	-142.8	-249.5	-338.3	-443.1	-131.3	-173.2	-91.2	-44.9	-3.8	-269.3
TPSS	-148.2	-259.5	-350.0	-445.9	-139.3	-182.1	-103.1	-56.2	-7.8	-277.1
M06-L	-138.8	-255.8	-342.6	-432.5	-141.2	-179.7	-90.2	-41.4	12.0	-277.1
B3P86	-145.7	-259.6	-346.4	-415.3	-138.5	-171.9	-99.9	-51.5	-1.1	-280.3
X3LYP	-144.4	-255.3	-343.4	-405.1	-134.6	-168.4	-93.5	-44.2	3.2	-275.1
B97-1	-137.4	-256.5	-340.0	-403.7	-136.9	-170.6	-97.0	-48.0	8.1	-272.7
B3LYP	-141.3	-254.1	-341.8	-405.4	-133.6	-167.5	-92.2	-27.4	2.8	-274.4
PBE0	-148.6	-262.1	-348.1	-407.8	-142.9	-174.5	-106.3	-40.7	2.9	-276.4
MPW1K	-151.0	-268.3	-356.1	-383.9	-147.3	-176.1	-114.2	-63.8	4.8	-286.8
BHLYP	-151.3	-268.5	-360.3	-373.8	-146.3	-176.9	-110.9	-59.3	8.6	-286.7
TPSSH	-147.8	-261.6	-349.6	-428.9	-144.9	-183.4	-105.1	-57.2	-4.3	-278.6
M06	-134.6	-254.9	-341.0	-401.2	-131.9	-159.7	-85.3	-34.8	22.1	-274.9
M06-2X	-131.7	-243.6	-307.3	-355.1	-116.6	-135.2	-82.2	-37.3	25.9	-259.0
Experiment	-146.8	-279.1	-370.0	-433.2	-154.7	-189.3	-116.6	-72.9	-3.5	-276.4
Uncertainty	1.4	0.9	5.3	4.8	0.5	2.4	3.6	3.6	12.0	4.0

Table B.30: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) with the SODFT routine using the atomic natural orbital (ANO) Stuttgart Basis and ECP for compounds: PuF₂ to AmF₃.

	ThO	ThO ₂	ThOF	ThF	ThF ₂	ThF3	ThF4	ThCl	ThCl ₂	ThCl3	ThCl4	ThBr
SVWN	-28.7	-138.1	-160.8	-11.2	-149.9	-305.6	-446.4	42.4	-58.5	-154.1	-248.8	56.8
BP86	9.6	-116.6	-140.2	-1.1	-135.6	-280.9	-416.4	49.5	-45.6	-140.3	-231.3	65.2
BLYP	-11.0	-110.2	-136.2	-1.9	-133.2	-278.7	-413.9	50.1	-44.4	-135.6	-226.4	67.0
PW91	-14.0	-120.4	-143.9	10.7	-139.6	-286.5	-423.3	48.6	-49.7	-143.5	-235.8	64.3
PBE	-13.3	-118.7	-142.3	8.1	-138.0	-284.0	-420.3	49.1	-46.1	-141.9	-234.0	64.7
TPSS	-10.2	-121.5	-141.9	0.2	-146.2	-283.9	-422.3	49.8	-45.9	-146.1	-240.6	65.3
M06-L	-9.7	-116.4	-135.2	-0.1	-140.3	-280.3	-427.6	49.7	-46.5	-142.8	-243.9	68.5
B3P86	-12.7	-116.4	-143.1	6.7	-141.3	-290.3	-430.3	49.7	-47.3	-145.6	-238.9	64.8
X3LYP	-10.7	-107.3	-137.8	12.4	-138.0	-286.8	-426.0	50.0	-46.8	-140.8	-233.8	66.2
B97-1	-11.8	-112.9	-136.5	-2.0	-132.2	-283.0	-425.7	49.0	-48.1	-141.9	-239.2	64.7
B3LYP	-10.6	-107.9	-137.6	-2.4	-137.5	-285.8	-424.7	50.2	-46.2	-140.2	-232.9	66.5
PBE0	-9.7	-111.1	-140.1	5.9	-140.5	-288.6	-428.1	50.8	-45.7	-144.9	-238.2	65.7
MPW1K	-6.1	-106.2	-138.8	4.2	-143.1	-293.1	-435.2	51.7	-47.7	-147.3	-241.2	66.1
BHLYP	-5.1	-96.9	-134.2	-2.5	-140.7	-292.0	-434.8	51.1	-46.2	-143.5	-237.7	66.6
TPSSH	-9.4	-118.3	-141.1	8.2	-138.7	-285.8	-425.3	50.1	-46.7	-147.0	-241.8	65.4
M06	-15.1	-112.2	-134.8	-3.1	-147.4	-282.5	-429.9	50.5	-46.6	-131.9	-229.7	68.5
M06-2X	-5.5	-96.3	-132.1	17.9	-145.1	-286.8	-427.4	51.2	-52.8	-141.6	-234.2	65.5
B2PLYP	-16.0	-114.7	-142.5	12.0	-139.1	-290.1	-431.8	61.2	-43.9	-146.4	-242.3	64.3
Experiment	-6.2	-108.8	-131.4	7.2	-141.0	-278.4	-418.3	59.0	-42.8	-136.0	-227.4	87.2
Uncertainty	1.4	3.7	2.9	3.6	4.8	3.6	2.4	4.8	4.8	6.0	1.2	4.8

Table B.31: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: ThO to ThBr.

	ThBr ₂	ThBr3	ThBr4	ThI4	UO	UO ₂	UO3	UOF4	UO ₂ F ₂	UO2Cl2	UF
SVWN	-25.3	-110.6	-196.6	-132.0	-10.3	-134.0	-247.4	-488.2	-382.1	-292.3	-18.3
BP86	-12.8	-92.1	-173.1	-107.4	-0.4	-110.4	-211.2	-438.5	-338.0	-254.0	-9.3
BLYP	-8.6	-83.8	-163.1	-96.0	5.2	-99.4	-198.8	-428.2	-325.6	-240.6	-9.5
PW91	-14.8	-95.6	-177.8	-112.0	-2.6	-114.0	-215.1	-445.9	-343.8	-258.6	-10.9
PBE	-13.8	-94.3	-176.3	-110.7	-1.3	-112.0	-212.9	-442.4	-341.0	-256.4	-9.7
TPSS	-15.4	-97.8	-182.2	-114.5	-10.6	-122.8	-218.1	-445.7	-345.7	-263.0	-16.6
M06-L	-6.0	-85.9	-171.7	-105.9	-0.7	-115.9	-195.7	-429.8	-329.4	-246.2	-23.2
B3P86	-15.1	-98.5	-182.9	-115.1	5.2	-114.8	-199.5	-436.1	-336.9	-249.2	-17.8
X3LYP	-11.1	-90.8	-173.8	-104.9	2.3	-101.1	-184.0	-424.3	-322.7	-234.5	-17.7
B97-1	-13.1	-94.0	-180.9	-112.9	3.9	-109.0	-192.4	-426.9	-328.6	-243.2	-17.6
B3LYP	-10.6	-90.0	-172.7	-103.9	1.6	-102.2	-186.0	-424.3	-323.2	-235.3	-17.4
PBE0	-14.7	-98.7	-183.2	-115.7	-2.5	-109.4	-189.7	-429.0	-329.8	-242.7	-16.9
MPW1K	-16.4	-102.2	-187.7	-118.8	12.9	-103.0	-169.7	-417.7	-318.7	-229.3	-16.4
BHLYP	-12.7	-95.3	-180.3	-109.4	10.5	-87.5	-149.8	-405.0	-303.0	-211.7	-16.9
TPSSH	-15.8	-99.4	-184.5	-116.2	-6.8	-117.4	-204.5	-436.1	-336.9	-253.0	-15.7
M06	-4.8	-77.9	-161.8	-95.3	7.7	-107.0	-176.7	-416.0	-318.1	-227.0	-23.8
M06-2X	-16.4	-96.7	-182.4	-116.3	25.3	-85.5	-172.0	-422.3	-321.6	-231.9	-1.2
B2PLYP	1.9	-99.5	-187.0	-120.2	6.8	-110.5	-215.9	-448.9	-347.5	-262.5	-18.7
Experiment	9.6	-79.8	-177.3	-110.1	8.4	-114.0	-191.0	-421.4	-323.3	-231.9	-11.2
Uncertainty	4.8	3.6	1.2	1.3	2.4	4.8	3.6	4.8	2.4	3.6	4.8

Table B.32: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: ThBr₂ to UF.
	UF ₂	UF3	UF4	UF5	UF6	UCl	UCl ₂	UCl3	UCl4	UCl5	UCl6
SVWN	-146.5	-285.5	-408.1	-516.5	-603.5	34.6	-49.9	-140.8	-215.6	-269.5	-316.1
BP86	-131.5	-262.4	-378.1	-472.5	-545.7	40.1	-42.7	-130.1	-195.2	-239.1	-273.3
BLYP	-127.8	-259.1	-374.2	-465.3	-535.9	40.8	-38.1	-125.1	-188.5	-228.7	-259.5
PW91	-135.6	-267.8	-384.3	-480.2	-554.7	39.3	-45.3	-133.2	-198.8	-244.1	-279.3
PBE	-133.4	-264.8	-380.9	-476.4	-550.6	40.2	-43.6	-131.2	-196.4	-241.2	-275.9
TPSS	-142.7	-276.6	-392.9	-482.8	-551.9	31.4	-56.2	-147.1	-206.3	-251.7	-282.3
M06-L	-139.2	-280.1	-388.3	-475.4	-537.0	30.7	-54.6	-152.0	-198.2	-237.4	-268.7
B3P86	-143.3	-276.0	-394.5	-480.7	-542.1	32.9	-52.5	-141.8	-206.6	-228.9	-255.4
X3LYP	-134.9	-270.8	-389.3	-472.6	-531.3	33.5	-47.4	-136.1	-200.2	-219.9	-241.5
B97-1	-131.5	-269.8	-388.6	-472.4	-531.4	32.0	-46.9	-140.5	-205.2	-225.7	-250.4
B3LYP	-138.1	-270.1	-388.2	-471.6	-530.7	33.7	-47.3	-135.7	-199.6	-219.8	-242.2
PBE0	-137.7	-273.9	-392.3	-476.4	-534.9	33.6	-52.4	-141.1	-205.8	-225.0	-247.3
MPW1K	-135.0	-277.6	-398.2	-475.0	-522.3	34.5	-53.8	-143.2	-206.7	-216.3	-223.9
BHLYP	-125.2	-273.8	-396.2	-469.1	-511.0	34.9	-48.2	-137.7	-201.8	-204.1	-204.3
TPSSH	-142.3	-276.0	-391.2	-478.4	-541.4	32.7	-55.3	-146.0	-195.0	-236.7	-266.2
M06	-122.0	-275.9	-387.9	-470.0	-520.4	34.5	-41.8	-135.7	-196.5	-211.3	-228.4
M06-2X	-132.3	-252.6	-390.1	-471.9	-530.0	38.4	-35.3	-121.2	-196.9	-216.1	-232.0
B2PLYP	-128.0	-273.2	-394.9	-482.8	-551.6	31.7	-49.8	-139.9	-209.1	-238.6	-287.0
Experiment	-129.1	-254.5	-383.6	-457.2	-513.5	44.7	-37.0	-125.0	-194.9	-215.1	-235.5
Uncertainty	6.0	4.8	1.6	3.6	0.5	4.8	4.8	4.8	1.1	3.6	1.2

Table B.33: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: UF₂ to UCl₆.

	UBr	UBr ₂	UBr3	UBr4	UBr5	UI	UI ₂	UI3	UI4	NpO	NpO ₂
SVWN	48.8	-23.5	-100.4	-164.7	-204.5	67.1	9.6	-53.0	-102.3	-7.9	-121.4
BP86	55.5	-12.4	-82.9	-138.1	-166.7	73.5	20.5	-39.5	-74.8	3.4	-105.8
BLYP	57.4	-5.1	-73.7	-126.3	-150.5	75.7	28.4	-27.6	-62.0	8.7	-97.5
PW91	54.6	-15.1	-86.4	-142.0	-172.0	72.7	17.9	-40.5	-78.9	1.7	-107.9
PBE	55.5	-13.7	-84.6	-139.9	-169.3	73.5	19.1	-38.9	-77.1	3.0	-106.0
TPSS	46.7	-24.2	-97.0	-151.3	-178.5	65.0	9.3	-53.5	-87.9	0.4	-91.7
M06-L	49.3	-7.8	-84.3	-132.9	-154.0	67.3	24.4	-47.5	-76.0	11.3	-95.2
B3P86	47.6	-21.1	-100.4	-150.2	-163.4	66.1	12.7	-50.4	-83.0	19.6	-96.9
X3LYP	49.2	-13.5	-91.5	-139.7	-148.2	67.9	20.7	-41.2	-71.6	26.8	-85.0
B97-1	47.3	-14.7	-97.3	-145.7	-156.9	65.8	18.8	-47.9	-79.2	31.6	-88.6
B3LYP	49.4	-13.5	-91.0	-138.9	-148.0	68.0	20.7	-40.7	-70.9	25.2	-85.5
PBE0	48.1	-20.8	-100.6	-149.5	-159.6	66.5	12.8	-51.2	-77.8	25.3	-92.1
MPW1K	48.4	-21.6	-104.5	-152.6	-150.2	66.8	12.4	-54.8	-84.3	38.7	-90.1
BHLYP	49.7	-13.3	-96.1	-143.3	-132.9	68.5	21.5	-45.4	-73.0	50.1	-78.4
TPSSH	47.6	-22.5	-88.3	-152.3	-169.8	66.1	11.4	-53.8	-85.7	8.5	-102.6
M06	52.0	1.9	-84.1	-127.8	-129.1	70.3	35.2	-33.4	-60.9	36.3	-87.0
M06-2X	52.1	-11.2	-89.7	-140.9	-151.6	69.8	20.8	-39.8	-75.5	68.7	-79.5
B2PLYP	46.4	-17.1	-99.6	-153.5	-178.3	64.9	16.7	-50.1	-87.9	46.5	-95.2
Experiment	58.6	-9.6	-88.7	-144.7	-154.9	81.7	24.6	-32.7	-72.9	-4.0	-109.2
Uncertainty	3.6	3.6	4.8	1.1	3.6	6.0	6.0	6.0	1.4	2.4	4.8

Table B.34: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: UBr to NpO₂.

	NpF	NpF ₂	NpF3	NpF4	NpF6	NpCl3	NpCl4	PuO	PuO ₂	PuO3	PuF
SVWN	-12.2	-149.4	-277.9	-384.3	-555.8	-137.2	-191.5	-12.9	-110.2	-174.0	-33.1
BP86	-0.2	-135.1	-257.0	-356.4	-501.2	-128.1	-174.0	-3.1	-91.6	-144.4	-27.3
BLYP	19.6	-132.4	-254.2	-352.9	-492.5	-123.8	-168.6	2.3	-84.4	-133.3	-20.2
PW91	-5.9	-138.8	-261.9	-362.0	-509.4	-130.8	-177.1	-4.7	-93.2	-146.9	-30.1
PBE	-4.8	-136.7	-258.9	-359.2	-504.9	-128.7	-174.7	-3.4	-90.9	-143.8	-29.0
TPSS	-4.8	-141.9	-267.5	-367.6	-505.9	-141.8	-195.8	-5.9	-85.6	-152.1	-29.1
M06-L	2.8	-140.4	-272.0	-378.1	-495.4	-149.2	-183.6	13.3	-94.4	-130.5	-18.4
B3P86	-5.9	-143.1	-269.3	-369.6	-487.8	-137.6	-160.7	16.7	-95.5	-120.7	-28.2
X3LYP	-0.8	-140.5	-265.6	-366.3	-478.5	-133.8	-155.0	24.4	-83.3	-106.9	-23.1
B97-1	4.8	-132.4	-261.1	-360.6	-473.5	-134.0	-155.9	28.2	-87.0	-108.8	-17.8
B3LYP	-0.8	-139.5	-264.3	-364.4	-477.9	-132.7	-155.3	22.3	-84.4	-108.8	-23.2
PBE0	-6.1	-143.5	-268.6	-368.8	-479.7	-138.4	-156.2	23.9	-88.9	-109.0	-28.0
MPW1K	-8.8	-152.6	-280.1	-383.0	-468.6	-148.3	-147.8	42.0	-82.8	-94.0	-29.8
BHLYP	-3.1	-153.1	-280.7	-386.5	-460.2	-147.4	-140.4	55.2	-69.9	-62.7	-23.7
TPSSH	-8.0	-144.5	-270.3	-370.9	-494.8	-144.2	-176.1	5.2	-102.0	-134.9	-29.9
M06	8.9	-138.0	-271.8	-376.5	-477.8	-135.9	-147.7	39.4	-86.3	-109.6	-15.6
M06-2X	8.0	-128.6	-258.2	-367.1	-455.3	-126.3	-118.9	57.9	-65.1	-64.2	-9.8
B2PLYP	-0.4	-142.0	-268.8	-371.5	-499.0	-138.9	-190.1	48.0	-93.1	-132.6	-22.2
Experiment	-19.1	-137.4	-266.5	-373.1	-459.3	-140.8	-188.1	-12.4	-102.3	-135.7	-26.9
Uncertainty	6.0	7.2	6.0	5.3	4.8	2.5	1.1	3.6	4.8	3.5	2.4

Table B.35: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: NpF to PuF.

	PuF ₂	PuF3	PuF4	PuF6	PuCl3	PuCl4	PuBr3	PuI3	AmO	AmF3
SVWN	-156.4	-270.8	-361.5	-498.1	-134.5	-182.1	-98.1	-52.8	-6.9	-254.7
BP86	-142.3	-252.1	-337.4	-447.7	-128.1	-169.9	-87.5	-41.7	0.5	-237.1
BLYP	-139.2	-249.1	-335.4	-440.3	-124.0	-165.8	-80.1	-33.4	5.1	-234.7
PW91	-146.2	-256.6	-342.6	-455.2	-130.6	-172.6	-90.3	-44.8	-1.1	-241.5
PBE	-144.1	-253.5	-338.7	-450.3	-128.4	-169.8	-88.4	-42.9	0.3	-238.3
TPSS	-149.3	-261.2	-349.2	-451.1	-140.3	-181.8	-100.2	-52.6	-4.2	-246.6
M06-L	-142.5	-265.6	-353.6	-438.8	-144.2	-180.0	-94.2	-46.1	14.0	-247.9
B3P86	-147.5	-264.6	-347.4	-426.9	-136.9	-165.4	-98.2	-49.1	5.1	-249.0
X3LYP	-143.6	-260.7	-345.2	-418.2	-133.2	-167.1	-91.8	-42.3	10.7	-245.3
B97-1	-138.8	-256.3	-338.0	-412.0	-133.4	-165.1	-93.0	-44.2	14.7	-241.8
B3LYP	-142.6	-259.4	-343.4	-418.3	-132.3	-161.6	-90.7	-41.5	10.1	-244.2
PBE0	-146.1	-263.4	-345.5	-415.9	-137.1	-165.3	-99.2	-50.6	8.2	-247.6
MPW1K	-146.9	-274.6	-357.5	-398.6	-145.7	-172.0	-109.3	-59.8	10.6	-258.6
BHLYP	-145.0	-275.0	-361.7	-389.7	-145.0	-173.4	-106.1	-55.2	15.8	-259.1
TPSSH	-150.0	-265.1	-349.4	-437.3	-143.4	-180.7	-103.7	-55.6	-0.2	-249.2
M06	-140.3	-267.3	-355.9	-418.0	-133.3	-165.1	-87.6	-37.9	20.2	-250.7
M06-2X	-133.9	-248.9	-318.6	-373.5	-119.8	-143.3	-79.4	-38.5	27.4	-235.9
B2PLYP	-135.3	-262.4	-347.4	-434.5	-136.4	-168.2	-97.6	-49.1	10.6	-245.3
Experiment	-146.8	-279.1	-370.0	-433.2	-154.7	-189.3	-116.6	-72.9	-3.5	-276.4
Uncertainty	1.4	0.9	5.3	4.8	0.5	2.4	3.6	3.6	12.0	4.0

Table B.36: Density Functional computed enthalpies of formation $\Delta H_{f,298}^{\circ}$ (kcal mol⁻¹) at the third-order Douglas-Kroll-Hess level with the all-electron cc-pVTZ-DK basis for compounds: PuF₂ to AmF₃.

	ZPVE (au)	Multiplicity
ThO	0.005397	1
ThO ₂	0.007575	1
ThOF	0.007233	2
ThF	0.003798	2
ThF_2	0.006639	1
ThF ₃	0.010026	2
ThF ₄	0.013386	1
ThCl	0.003493	2
ThCl ₂	0.005076	1
ThCl ₃	0.009078	2
ThCl ₄	0.012137	1
ThBr	0.003387	2
ThBr ₂	0.005827	1
ThBr ₃	0.008756	2
ThBr ₄	0.011692	1
ThI ₄	0.011549	1
UO	0.004365	5
UO_2	0.008075	3
UO ₃	0.011678	1
UOF ₄	0.01774	1
UO_2F_2	0.014947	1
UO_2Cl_2	0.014272	1
UF	0.003902	4
UF ₂	0.006714	5

Table B.37: Zero-point energies from TPSS geometry optimization and determined multiplicity. Compounds ThO–UF $_2$

	ZPVE (au)	Multiplicity
UF ₃	0.010089	4
UF ₄	0.013708	3
UF ₅	0.01713	2
UF ₆	0.020738	1
UCl	0.003499	4
UCl ₂	0.006028	5
UCl ₃	0.009049	4
UCl ₄	0.012157	3
UCl ₅	0.015253	2
UCl ₆	0.018345	1
UBr	0.003388	4
UBr ₂	0.005823	5
UBr ₃	0.008745	4
UBr ₄	0.0117	3
UBr ₅	0.014631	2
UI	0.003352	4
UI_2	0.005758	5
UI ₃	0.008643	4
UI ₄	0.009658	3

Table B.38: Zero-point energies from TPSS geometry optimization and determined multiplicity. Compounds $\rm UF_3-\rm UI_4$

	ZPVE (au)	Multiplicity
NpO	0.004391	6
NpO ₂	0.008041	4
NpF	0.003772	7
NpF ₂	0.006701	6
NpF ₃	0.010095	5
NpF ₄	0.012591	4
NpF ₆	0.020816	2
NpCl ₃	0.009055	5
NpCl ₄	0.012148	4
PuO	0.004036	7
PuO ₂	0.00779	5
PuO ₃	0.011523	3
PuF	0.003777	8
PuF ₂	0.006683	7
PuF ₃	0.009978	6
PuF ₄	0.013476	5
PuF ₆	0.020487	3
PuCl ₃	0.009102	6
PuCl ₄	0.012108	5
PuBr ₃	0.008735	6
PuI ₃	0.008661	6
AmO	0.004278	8
AmF ₃	0.009892	7

Table B.39: Zero-point vibrational energies (ZPVE) from TPSS geometry optimization and determined multiplicity. Compounds $NpO-AmF_3$

	$\Delta_{\rm f} H^{\circ}_{\rm m}$ (kcal/mol)
Th	143.9
U	127.4
Np	111.2
Pu	83.4
Am	67.8
Br ₂	7.388
I ₂	14.919

Table B.40: Experimental sublimation (vaporization for Br₂) values for atoms and diatomics used (Data from NIST and NEA).

BIBLIOGRAPHY

BIBLIOGRAPHY

- [1] Löble, M. W. et al. Covalency in Lanthanides. An X-ray Absorption Spectroscopy and Density Functional Theory Study of $LnCl_6^{x-}$ (x = 3, 2). J. Am. Chem. Soc. **2015**, 137, 2506–2523.
- [2] Gelis, A. V.; Lumetta, G. J. Actinide lanthanide separation process ALSEP. *Ind. Eng. Chem. Res.* **2014**, *53*, 1624–1631.
- [3] Hohenberg, P.; Kohn, W. Inhomogenous Electron Gas. *Phys. Rev.* **1964**, *136*, 864–871.
- [4] Becke, A. D. Perspective: Fifty years of density-functional theory in chemical physics. *J. Chem. Phys.* **2014**, *140*.
- [5] Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, 1133–1138.
- [6] Becke, A. D. Density-functional thermochemistry. I. The effect of the exchange-only gradient correction. *J. Chem. Phys.* **1992**, *96*, 2155–2160.
- [7] Rappoport, D.; Crawford, N. R. M.; Furche, F.; Burke, K. Approximate Density Functionals: Which Should I Choose? *Encycl. Inorg. Chem.* **2009**, 159–172.
- [8] Jensen, K. P.; Cirera, J. Accurate computed enthalpies of spin crossover in iron and cobalt complexes. *J. Phys. Chem. A* **2009**, *113*, 10033–10039.
- [9] Schultz, N. E.; Zhao, Y.; Truhlar, D. G. Density Functionals for Inorganometallic and Organometallic Chemistry. J. Phys. Chem. A 2005, 109, 11127–11143.
- [10] Burke, K.; Cancio, A.; Gould, T.; Pittalis, S. Locality of correlation in density functional theory. *J. Chem. Phys.* **2016**, *145*.
- [11] Pyykkö, P. Relativistic effects in structural chemistry. *Chem. Rev.* **1988**, 88, 563–594.
- [12] Götz, D. A.; Schäfer, R.; Schwerdtfeger, P. The performance of density functional and wavefunction-based methods for 2D and 3D structures of Au₁₀. J. Comput. Chem. 2013, 34, 1975–1981.
- [13] Cao, X.; Dolg, M. Relativistic energy-consistent ab initio pseudopotentials as tools for quantum chemical investigations of actinide systems. *Coord. Chem. Rev.* **2006**, *250*, 900–910.
- [14] Dolg, M.; Mooßen, O. Cerium oxidation state and covalent 4f-orbital contributions in the ground state of bis(η8-pentalene)cerium. J. Organomet. Chem. 2015, 794, 17–22.
- [15] Cotton, S. Lanthanide and Actinide Chemistry; John Wiley & Sons, Inc., 2006.
- [16] Mai, S.; Müller, T.; Plasser, F.; Marquetand, P.; Lischka, H.; González, L. Perturbational treatment of spin-orbit coupling for generally applicable high-level multi-reference methods. *J. Chem. Phys.* 2014, 141, 074105.

- [17] Saue, T. Relativistic Hamiltonians for chemistry. AIP Conf. Proc. 2012, 1504, 219–227.
- [18] Douglas, M.; Kroll, N. M. Quantum electrodynamical corrections to the fine structure of helium. *Ann. Phys.* (*N. Y*). **1974**, *82*, 89–155.
- [19] Visscher, L.; Saue, T. In Comput. Methods Lanthanides Actinides, 1st ed.; Dolg, M., Ed.; Wiley, 2015; Chapter 3, pp 55–87.
- [20] Kovács, A.; Konings, R. J. M.; Gibson, J. K.; Infante, I.; Gagliardi, L. Quantum chemical calculations and experimental investigations of molecular actinide oxides. *Chem. Rev.* 2015, 115, 1725–1759.
- [21] Hess, B. A. Relativistic electronic-structure calculations employing a two-component no-pair formalism with external-field projection operators. *Phys. Rev. A* **1986**, *33*, 3742–3748.
- [22] Nakajima, T.; Hirao, K. The higher-order Douglas–Kroll transformation. 2000, 7786.
- [23] Dolg, M.; Stoll, H.; Preuss, H.; Pitzer, R. M. Relativistic and correlation effects for element 105 (hahnium, Ha): a comparative study of M and MO (M = Nb, Ta, Ha) using energy-adjusted ab initio pseudopotentials. J. Phys. Chem. 1993, 97, 5852–5859.
- [24] Cao, X.; Dolg, M.; Stoll, H. Valence basis sets for relativistic energy-consistent small-core actinide pseudopotentials. *J. Chem. Phys.* **2003**, *118*, 487–496.
- [25] Dolg, M.; Cao, X. Accurate relativistic small-core pseudopotentials for actinides. Energy adjustment for uranium and first applications to uranium hydride. *J. Phys. Chem. A* **2009**, *113*, 12573–12581.
- [26] Aebersold, L. E.; Yuwono, S. H.; Schoendorff, G.; Wilson, A. K. Efficacy of Density Functionals and Relativistic Effective Core Potentials for Lanthanide-Containing Species: The Ln54 Molecule Set. J. Chem. Theory Comput. 2017, 13, 2831–2839.
- [27] Tekarli, S. M.; Drummond, M. L.; Williams, T. G.; Cundari, T. R.; Wilson, A. K. Performance of Density Functional Theory for 3d Transition Metal-Containing Complexes: Utilization of the Correlation Consistent Basis Sets. J. Phys. Chem. A 2009, 113, 8607–8614.
- [28] Jiang, W.; DeYonker, N. J.; Determan, J. J.; Wilson, A. K. Toward Accurate Thermochemistry of First Row Transition Metal Complexes. J. Phys. Chem. A. 2012, 116, 870.
- [29] Laury, M. L.; Wilson, A. K. Performance of Density Functional Theory for Second Row (4d) Transition Metal Thermochemistry. J. Chem. Theory Comput. 2013, 9, 3939–3946.
- [30] Hunt, P. A. Organolanthanide mediated catalytic cycles: a computational perspective. *Dalt. Trans.* **2007**, 1743–1754.
- [31] Roca-Sabio, A.; Regueiro-Figueroa, M.; Esteban-Gómez, D.; de Blas, A.; Rodríguez-Blas, T.; Platas-Iglesias, C. Density functional dependence of molecular geometries in lanthanide(III) complexes relevant to bioanalytical and biomedical applications. *Comput. Theor. Chem.* 2012, 999, 93–104.

- [32] Edelmann, F. T. Lanthanides and actinides: Annual survey of their organometallic chemistry covering the year 2015. *Coord. Chem. Rev.* **2016**, *318*, 29–130.
- [33] Schoendorff, G.; Wilson, A. K. Low valency in lanthanides: A theoretical study of NdF and LuF. J. Chem. Phys. 2014, 140, 224314.
- [34] Schoendorff, G.; South, C.; Wilson, A. K. A Neoteric Neodymium Model: Ground and Excited Electronic State Analysis of NdF 2+. *J. Phys. Chem. A* **2013**, *117*, 10881–10888.
- [35] Siegbahn, P.; Heiberg, A.; Roos, B.; Levy, B. A Comparison of the Super-CI and the Newton-Raphson Scheme in the Complete Active Space SCF Method. *Phys. Scr.* **1980**, *21*, 323–327.
- [36] Hess, B. A. Applicability of the no-pair equation with free-particle projection operators to atomic and molecular structure calculations. *Phys. Rev. A* **1985**, *32*, 756–763.
- [37] Chang, C.; Pelissier, M.; Durand, P. Regular Two-Component Pauli-Like Effective Hamiltonians in Dirac Theory. *Phys. Scr.* **2006**, *34*, 394–404.
- [38] Molnár, J.; Hargittai, M. Prediction of the Molecular Shape of Lanthanide Trihalides. J. Phys. Chem. **1995**, 99, 10780–10784.
- [39] Barysz, M.; Sadlej, A. J. Infinite-order two-component theory for relativistic quantum chemistry. J. Chem. Phys. 2002, 116, 2696.
- [40] Barysz, M.; Mentel, Ł.; Leszczyński, J. Recovering four-component solutions by the inverse transformation of the infinite-order two-component wave functions. *J. Chem. Phys.* **2009**, *130*, 164114.
- [41] Cao, X.; Dolg, M. Pseudopotentials and modelpotentials. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1*, 200–210.
- [42] Cundari, T. R.; Arturo Ruiz Leza, H.; Grimes, T.; Steyl, G.; Waters, A.; Wilson, A. K. Calculation of the enthalpies of formation for transition metal complexes. *Chem. Phys. Lett.* 2005, *401*, 58–61.
- [43] Souza, B. S.; Brandão, T. A. S.; Orth, E. S.; Roma, A. C.; Longo, R. L.; Bunton, C. A.; Nome, F. Hydrolysis of 8-quinolyl phosphate monoester: Kinetic and theoretical studies of the effect of lanthanide ions. *J. Org. Chem.* 2009, 74, 1042–1053.
- [44] Ali, S. M.; Pahan, S.; Bhattacharyya, A.; Mohapatra, P. K. Complexation thermodynamics of diglycolamide with f-elements: solvent extraction and density functional theory analysis. *Phys. Chem. Chem. Phys.* 2016, 18, 9816–9828.
- [45] Wang, C.-Z.; Lan, J.-H.; Wu, Q.-Y.; Zhao, Y.-L.; Wang, X.-K.; Chai, Z.-F.; Shi, W.-Q. Density functional theory investigations of the trivalent lanthanide and actinide extraction complexes with diglycolamides. *Dalton Trans.* 2014, 43, 8713–20.
- [46] Jones, M. B.; Gaunt, A. J.; Gordon, J. C.; Kaltsoyannis, N.; Neu, M. P.; Scott, B. L. Uncovering f-element bonding differences and electronic structure in a series of 1 : 3 and 1 : 4 complexes with a diselenophosphinate ligand. *Chem. Sci.* 2013, 4, 1189–1203.

- [47] Fang, Z.; Thanthiriwatte, K. S.; Dixon, D. A.; Andrews, L.; Wang, X. Properties of Cerium Hydroxides from Matrix Infrared Spectra and Electronic Structure Calculations. *Inorg. Chem.* 2016, 55, 1702–1714.
- [48] Vent-Schmidt, T.; Fang, Z.; Lee, Z.; Dixon, D.; Riedel, S. Extending the Row of Lanthanide Tetrafluorides: A Combined Matrix-Isolation and Quantum-Chemical Study. *Chem. - A Eur. J.* 2016, 22, 2406–2416.
- [49] Yungman, V.; Glushko, V. P.; Medvedev, V. A.; Gurvich, L. V. *Thermal Constants of Substances*; 1999.
- [50] Zmbov, K. F. Mass-Spectrometric Studies at High Temperatures. XI. The Sublimation Pressure of NdF₃ and the Stabilities of Gaseous NdF₂ and NdF. *J. Chem. Phys.* **1966**, *45*, 3167.
- [51] Zmbov, K. F.; Margrave, J. L. Mass spectrometric studies at high temperatures. XIII. Stabilities of samarium, europium and gadoliniummono- and difluorides. *J. Inorg. Nucl. Chem.* **1967**, *29*, 59–63.
- [52] Ames, L. L.; Walsh, P. N.; White, D. Rare earths. IV. Dissociation energies of the gaseous monoxides of the rare earths. *J. Phys. Chem.* **1967**, *71*, 2707–2718.
- [53] Konings, R. J.; Beneš, O.; Kovács, A.; Manara, D.; Sedmidubský, D.; Gorokhov, L.; Iorish, V. S.; Yungman, V.; Shenyavskaya, E.; Osina, E. The Thermodynamic Properties of the *f*-Elements and their Compounds: Part 2. The Lanthanide and Actinide Oxides. *J. Phys. Chem. Ref. Data* 2014, 43, 013101.
- [54] Hastie, J. W.; Hauge, R. H.; Margrave, J. L. Geometries and entropies of metal trifluorides from infrared spectra: ScF₃, YF₃, LaF₃, CeF₃, NdF₃, EuF₃ and GdF₃. *J. Less-Common Met.* **1975**, *39*, 309–334.
- [55] Grimmel, S.; Schoendorff, G.; Wilson, A. K. Gauging the Performance of Density Functionals for Lanthanide-Containing Molecules. *J. Chem. Theory Comput.* **2016**, *12*, 1259–1266.
- [56] Valiev, M.; Bylaska, E. J.; Govind, N.; Kowalski, K.; Straatsma, T. P.; Van Dam, H. J.; Wang, D.; Nieplocha, J.; Apra, E.; Windus, T. L.; De Jong, W. A. NWChem: A comprehensive and scalable open-source solution for large scale molecular simulations. *Comput. Phys. Commun.* 2010, 181, 1477–1489.
- [57] Cao, X.; Dolg, M. Segmented contraction scheme for small-core actinide pseudopotential basis sets. *J. Mol. Struct. THEOCHEM* **2004**, *673*, 203–209.
- [58] Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. **1989**, *90*, 1007.
- [59] Woon, D. E.; Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon. *J. Chem. Phys.* **1993**, *98*, 1358.
- [60] Dunning, T. H.; Peterson, K. A.; Wilson, A. K. Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited. *J. Chem. Phys.* **2001**, *114*, 9244.

- [61] de Jong, W. A.; Harrison, R. J.; Dixon, D. A. Parallel Douglas–Kroll energy and gradients in NWChem: Estimating scalar relativistic effects using Douglas–Kroll contracted basis sets. *J. Chem. Phys.* **2001**, *114*, 48.
- [62] Feller, D. The role of databases in support of computational chemistry calculations. *J. Comput. Chem.* **1996**, *17*, 1571–1586.
- [63] Weber, R.; Yuwono, S.; Jeffrey, C.; Ouyang, J.; Schoendorff, G.; Wilson, A. K. Structure and Energetics of LnX₃ (Ln = La-Lu, X = F, Cl, Br). 70th Southwest Reg. Meet. Am. Chem. Soc. 2014.
- [64] Slater, J. C.; Johnson, K. H. Self-Consistent-Field X α Cluster Method for Polyatomic Molecules and Solids. *Phys. Rev. B* 1972, 5, 844–853.
- [65] Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.* **1980**, *58*, 1200–1211.
- [66] Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A At., Mol., Opt. Phys.* **1988**, *38*, 3098.
- [67] Perdew, J. P. No Title. Phys. Rev. B Condens. Matter Mater. Phys. 1986, 33, 8822.
- [68] Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785–789.
- [69] Perdew, J. P. In *Electron. Struct. solids '91*; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991; p 11.
- [70] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [71] Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- [72] Swart, M.; Solà, M.; Bickelhaupt, F. M. Switching between OPTX and PBE exchange functionals. J. Comput. Methods Sci. Eng. 2009, 9, 69–77.
- [73] Swart, M.; Solà, M.; Bickelhaupt, F. M. A new all-round density functional based on spin states and S(N)2 barriers. J. Chem. Phys. 2009, 131, 094103.
- [74] Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the density functional ladder: nonempirical meta-generalized gradient approximation designed for molecules and solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.
- [75] Zhao, Y.; Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **2006**, *125*, 194101.
- [76] Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158.

- [77] Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. *Phys.* **1993**, *98*, 5648.
- [78] Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372.
- [79] Becke, A. D. Density-functional thermochemistry. V. Systematic optimization of exchangecorrelation functionals. J. Chem. Phys. **1997**, 107, 8554.
- [80] Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. Development and assessment of new exchange-correlation functionals. *J. Chem. Phys.* **1998**, *109*, 6264.
- [81] Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. Adiabatic Connection for Kinetics. J. Phys. Chem. A 2000, 104, 4811–4815.
- [82] Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. *J. Chem. Phys.* 2003, 119, 12129.
- [83] Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other function. *Theor. Chem. Acc.* 2008, 120, 215–241.
- [84] Yanai, T.; Tew, D. P.; Handy, N. C. A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.
- [85] Peverati, R.; Truhlar, D. G. Improving the accuracy of hybrid meta-GGA density functionals by range separation. *J. Phys. Chem. Lett.* **2011**, *2*, 2810–2817.
- [86] Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618–622.
- [87] Schall, H.; Dulick, M.; Field, R. W. The electronic structure of LaF: A multiconfiguration ligand field calculation. *J. Chem. Phys.* **1987**, *87*, 2898.
- [88] Schamps, J.; Bencheikh, M.; Barthelat, J.-C.; Field, R. W. The electronic structure of LaO: Ligand field versus ab initio calculations. *J. Chem. Phys.* **1995**, *103*, 8004.
- [89] Becke, A. D. Density functionals for static, dynamical, and strong correlation. *J. Chem. Phys.* **2013**, *138*, 074109.
- [90] Becke, A. D. Density-functional thermochemistry. I. The effect of the exchange-only gradient correction. *J. Chem. Phys.* **1992**, *96*, 2155.
- [91] Pahan, S.; Boda, A.; Ali, S. M. Density functional theoretical analysis of structure, bonding, interaction and thermodynamic selectivity of hexavalent uranium (UO_2^{2+}) and tetravalent plutonium (Pu^{4+}) ion complexes of tetramethyl diglycolamide (TM). *Theor. Chem. Acc.* **2015**, *134*, 1–16.

- [92] Eliav, E.; Kaldor, U. In *Comput. Methods Lanthan. Actin. Chem.*, 1st ed.; Dolg, M., Ed.; 2015; Chapter 2, pp 23–54.
- [93] Cao, Z.; Dolg, M. Relativistic Methods for Chemists; Springer: Berlin, 2009; p 37.
- [94] Karton, A.; Daon, S.; Martin, J. M. L. W4-11: A high-confidence benchmark dataset for computational thermochemistry derived from first-principles W4 data. *Chem. Phys. Lett.* 2011, *510*, 165–178.
- [95] DeYonker, N. J.; Cundari, T. R.; Wilson, A. K. The correlation consistent composite approach (ccCA): An alternative to the Gaussian-n methods. *J. Chem. Phys.* **2006**, *124*.
- [96] Grimmel, S.; Schoendorff, G.; Wilson, A. K. Gauging the Performance of Density Functionals for Lanthanide-Containing Molecules. *J. Chem. Theory Comput.* **2016**, *12*, 1259–1266.
- [97] Becke, A. D. Density-Functional Exchange-Energy Approximation with Corrects Asymptotic-Behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [98] Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B* **1986**, *33*, 8822–8824.
- [99] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865–3868.
- [100] Becke, A. D. Density-functional thermochemistry. V. Systematic optimization of exchangecorrelation functionals. J. Chem. Phys. 1997, 107, 8554.
- [101] Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158.
- [102] Staroverov, V. N.; Scuseria, G. E.; Tao, J. M.; Perdew, J. P. Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. J. Chem. Phys. 2004, 121, 11507.
- [103] Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. Energy-adjusted pseudopotentials for the actinides. Parameter sets and test calculations for thorium and thorium monoxide. J. Chem. Phys. 1994, 100, 7535–7542.
- [104] Cao, X.; Dolg, M.; Stoll, H. Valence basis sets for relativistic energy-consistent small-core actinide pseudopotentials. J. Chem. Phys. 2003, 118, 487–496.
- [105] Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuß, H. Ab initio energy-adjusted pseudopotentials for elements of groups 13–17. *Mol. Phys.* **1993**, *80*, 1431–1441.
- [106] Cao, X.; Dolg, M. Segmented contraction scheme for small-core actinide pseudopotential basis sets. J. Mol. Struct. THEOCHEM 2004, 673, 203–209.
- [107] Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. **1989**, 90, 1007–1023.

- [108] Dunning T.H., J.; Peterson, K. A.; Wilson, A. K. Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited. J. Chem. Phys. 2001, 114, 9244–9253.
- [109] Peterson, K. A. Systematically convergent basis sets with relativistic pseudopotentials. I. Correlation consistent basis sets for the post-d group 13-15 elements. J. Chem. Phys. 2003, 119, 11099–11112.
- [110] De Jong, W. A.; Harrison, R. J.; Dixon, D. A. Parallel Douglas-Kroll energy and gradients in NWChem: Estimating scalar relativistic effects using Douglas-Kroll contracted basis sets. J. Chem. Phys. 2001, 114, 48–53.
- [111] Peterson, K. A. Correlation consistent basis sets for actinides. I. the Th and U atoms. *J. Chem. Phys.* **2015**, *142*.
- [112] Feng, R.; Peterson, K. A. Correlation consistent basis sets for actinides. II. the atoms Ac and Np-Lr. J. Chem. Phys. 2017, 147, 084108.
- [113] Nakajima, T.; Hirao, K. Extended Douglas–Kroll transformations applied to the relativistic many-electron Hamiltonian. J. Chem. Phys. 2003, 119, 4105–4111.
- [114] Bross, D. H.; Peterson, K. A. Correlation consistent, douglas-kroll-hess relativistic basis sets for the 5p and 6p elements. *Theor. Chem. Acc.* **2014**, *133*, 1–12.
- [115] Hong, G.; Dolg, M.; Li, L. A comparison of scalar-relativistic ZORA and DKH density functional schemes: Monohydrides, monooxides and monofluorides of La, Lu, Ac and Lr. *Chem. Phys. Lett.* 2001, 334, 396–402.
- [116] Guillaumont, R.; Fanghänel, T.; Fuger, J.; Palmer, D. A.; Grenthe, I.; Rand, M.; Mompean, F. J.; Illemassene, M.; Domenech-Orti, C.; Said, K. B. Update on the Chemical Thermodynamics of Uranium, Neptiunium, Plutonium, Americium, and Technitium; OECD Publications: Paris, 2003; Vol. 5.
- [117] Rand, M. H.; Fuger, J.; Grenthe, I.; Neck, V.; Rai, D. Chemical Thermodynamics of Thorium. OECD Nuclear Energy Agency Data Bank - Chemical Thermodynamics; OECD Publications: Paris, 2008; Vol. 11.
- [118] Boguslawski, K.; Réal, F.; Tecmer, P.; Duperrouzel, C.; Gomes, A. S. P.; Legeza, Ö.; Ayers, P. W.; Vallet, V. On the multireference nature of plutonium oxides: PuO₂²⁺, PuO₂, PuO₃ and PuO₂(OH)₂ . *Phys. Chem. Chem. Phys.* **2017**, *19*, 4317–4329.
- [119] Pereira Gomes, A. S.; Réal, F.; Galland, N.; Angeli, C.; Cimiraglia, R.; Vallet, V. Electronic structure investigation of the evanescent AtO+ ion. *Phys. Chem. Chem. Phys.* 2014, 16, 9238–9248.
- [120] Gomes, A. S.; Dyall, K. G.; Visscher, L. Relativistic double-zeta, triple-zeta, and quadruplezeta basis sets for the lanthanides La-Lu. *Theor. Chem. Acc.* **2010**, *127*, 369–381.

- [121] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC19 (2019), written by A. S. P. Gomes, T. Saue, L. Visscher, H. J. Aa. Jensen, and R. Bast, with contributions from I. A. Aucar, V. Bakken, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, E. Faßhauer, T. Fleig, O. Fossgaard, L. Halbert, E. D. Hedegård, B. Heimlich-Paris, T. Helgaker, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, S. Komorovský, O. Kullie, J. K. Lærdahl, C. V. Larsen, Y. S. Lee, H. S. Nataraj, M. K. Nayak, P. Norman, G. Olejniczak, J. Olsen, J. M. H. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, R. di Remigio, K. Ruud, P. Sałek, B. Schimmelpfennig, B. Senjean, A. Shee, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, M. L. Vidal, S. Villaume, O. Visser, T. Winther, and S. Yamamoto (available at http://dx.doi.org/10.5281/zenodo.3572669, see also http://www.diracprogram.org).
- [122] Lu, Q.; Peterson, K. A. Correlation consistent basis sets for lanthanides: The atoms La-Lu. J. *Chem. Phys.* **2016**, *145*.
- [123] Solomonik, V. G.; Smirnov, A. N. Toward Chemical Accuracy in ab Initio Thermochemistry and Spectroscopy of Lanthanide Compounds: Assessing Core-Valence Correlation, Second-Order Spin-Orbit Coupling, and Higher Order Effects in Lanthanide Diatomics. J. Chem. Theory Comput. 2017, 13, 5240–5254.
- [124] Palacios, A.; Martín, F. The quantum chemistry of attosecond molecular science. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2019**, 1–28.
- [125] Pandey, G.; Dey, D.; Tiwari, A. K. Controlling the Ultrafast Dynamics of HD⁺ by the Carrier-Envelope Phases of an Ultrashort Laser Pulse: A Quasi-Classical Dynamics Study. *Journal* of Physical Chemistry A 2020, 124, 9710–9720.
- [126] Palacios, A.; Martín, F. The quantum chemistry of attosecond molecular science. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2020**, *10*, e1430.
- [127] Cabrera-Trujillo, R.; Vendrell, O.; Cederbaum, L. S. Interatomic coulombic decay of a li dimer in a coupled electron and nuclear dynamics approach. *Physical Review A* 2020, *102*, 1–7.
- [128] Weinkauf, R.; Schanen, P.; Metsala, A.; Schlag, E. W.; Bürgle, M.; Kessler, H. Highly Efficient Charge Transfer in Peptide Cations in the Gas Phase: Threshold Effects and Mechanism. J. Phys. Chem. 1996, 100, 18567–18585.
- [129] Weinkauf, R.; Schlag, E. W.; Martinez, T. J.; Levine, R. D. Nonstationary Electronic States and Site-Selective Reactivity. J. Phys. Chem. A 1997, 101, 7702–7710.
- [130] Remacle, F.; Levine, R. D.; Schlag, E. W.; Weinkauf, R. Electronic Control of Site Selective Reactivity : A Model Combining Charge Migration and Dissociation. J. Phys. Chem. 1999, 103, 10149–10158.
- [131] Meyer, H.-D.; Manthe, U.; Cederbaum, L. The multi-configurational time-dependent Hartree approach. *Chem. Phys. Lett.* **1990**, *165*, 73–78.

- [132] Beck, M. H.; Jäckle, A.; Worth, G.; Meyer, H.-D. The multiconfiguration time-dependent Hartree (MCTDH) method: a highly efficient algorithm for propagating wavepackets. *Phys. Rep.* 2000, 324, 1–105.
- [133] Chelkowski, S.; Zuo, T.; Atabek, O.; Bandrauk, A. D. Dissociation, ionization, and Coulomb explosion of H⁺₂ in an intense laser field by numerical integration of the time-dependent Schrödinger equation. *Phys. Rev. A* **1995**, *52*, 2977–2983.
- [134] Bandrauk, A. D.; Chelkowski, S.; Nguyen, H. S. Attosecond localization of electrons in molecules. *Int. J. Quantum Chem.* 2004, 100, 834–844.
- [135] Yuan, K. J.; Lu, H.; Bandrauk, A. D. Linear- and circular-polarization photoionization angular distributions in H2 and H2+ by attosecond xuv laser pulses. *Phys. Rev. A At. Mol. Opt. Phys.* 2011, *83*, 043418.
- [136] Deumens, E.; Öhrn, Y. Electron-nuclear dynamics with diabatic and adiabatic wave packets. J. Phys. Chem. 1988, 92, 3181–3189.
- [137] Cabrera-Trujillo, R.; Deumens, E.; Öhrn, Y.; Quinet, O.; Sabin, J. R.; Stolterfoht, N. Watermolecule fragmentation induced by charge exchange in slow collisions with He⁺ and He²⁺ ions in the keV-energy region. *Phys. Rev. A - At. Mol. Opt. Phys.* **2007**, *75*, 1–13.
- [138] Deumens, E.; Öhrn, Y. Complete Electron Nuclear Dynamics. J. Phys. Chem. A 2001, 105, 2660–2667.
- [139] Deumens, E.; Öhrn, Y. Dynamics of electrons and nuclei. Mol. Phys. 2010, 108, 3195–3198.
- [140] Curchod, B. F. E.; Rothlisberger, U.; Tavernelli, I. Trajectory-Based Nonadiabatic Dynamics with Time-Dependent Density Functional Theory. *Chem. Phys. Chem.* **2013**, *14*, 1314–1340.
- [141] Lisinetskaya, P. G.; Mitri, R. Simulation of laser-induced coupled electron-nuclear dynamics and time-resolved harmonic spectra in complex systems. *Phys. Rev. A* **2011**, *83*, 033408.
- [142] Nakatsukasa, T.; Matsuyanagi, K.; Matsuo, M.; Yabana, K. Time-dependent density-functional description of nuclear dynamics. *Rev. Mod. Phys.* 2016, 88, 1–53.
- [143] Webb, S. P.; Iordanov, T.; Hammes-Schiffer, S. Multiconfigurational nuclear-electronic orbital approach: Incorporation of nuclear quantum effects in electronic structure calculations. J. Chem. Phys. 2002, 117, 4106–4118.
- [144] Tachikawa, M.; Mori, K.; Nakai, H.; Iguchi, K. An extension of ab initio molecular orbital theory to nuclear motion. *Chem. Phys. Lett.* **1998**, *290*, 437–442.
- [145] Tachikawa, M.; Mori, K.; Suzuki, K.; Iguchi, K. Full variational molecular orbital method: Application to the positron-molecule complexes. *Int. J. Quantum Chem.* **1998**, *70*, 491–501.
- [146] Kinghorn, D. B.; Adamowicz, L. Improved nonadiabatic ground-state energy upper bound for dihydrogen. *Phys. Rev. Lett.* **1999**, *83*, 2541–2543.

- [147] Cafiero, M.; Adamowicz, L. Non-Born-Oppenheimer Isotope Effects on the Polarizabilities of [Formula presented]. *Phys. Rev. Lett.* 2002, 89, 1–4.
- [148] Cafiero, M.; Adamowicz, L. Nonadiabatic Calculations of the Dipole Moments of LiH and LiD. Phys. Rev. Lett. 2002, 88, 4.
- [149] Nakai, H.; Hoshino, M.; Miyamoto, K.; Hyodo, S. Elimination of translational and rotational motions in nuclear orbital plus molecular orbital theory. J. Chem. Phys. 2005, 122.
- [150] Bochevarov, A. D.; Valeev, E. F.; Sherrill, C. D. The electron and nuclear orbitals model: Current challenges and future prospects. *Mol. Phys.* 2004, 102, 111–123.
- [151] Nest, M. Can Electron Equilibration in Excited Na₈ Clusters be Interpreted as Thermalization? *Int. J. Quantum Chem.* 2011, 111, 505–509.
- [152] Nest, M. The multi-configuration electron-nuclear dynamics method. *Chem. Phys. Lett.* **2009**, 472, 171–174.
- [153] Akima, H. A New Method of Interpolation and Smooth Curve Fitting Based on Local Procedures. J. ACM 1970, 17, 589–602.
- [154] Parrish, R. M. et al. Psi4 1.1: An Open-Source Electronic Structure Program Emphasizing Automation, Advanced Libraries, and Interoperability. J. Chem. Theory Comput. 2017, 13, 3185–3197.
- [155] Aebersold, L. E.; Ulusoy, I. S.; Wilson, A. K. Coupled electron and nuclear motion in strong laser fields. *Phys. Rev. A* 2019, 100, 1–9.
- [156] Paul, P. M.; Toma, E. S.; Breger, P.; Mullot, G.; Auge, F.; Balcou, P.; Muller, H. G.; Agostini, P. Observation of a Train of Attosecond Pulses from High Harmonic Generation. *Science* 2001, 292, 1689–1692.
- [157] Hentschel, M.; Kienberger, R.; Spielmann, C.; Reider, G. A.; Milosevic, N.; Brabec, T.; Corkum, P.; Heinzmann, U.; Drescher, M.; Krausz, F. Attosecond metrology. *Nature* 2001, 414, 509–513.
- [158] Itatani, J.; Levesque, J.; Zeidler, D.; Niikura, H.; Pépin, H.; Kieffer, J. C.; Corkum, P. B.; Villeneuve, D. M. Tomographic imaging of molecular orbitals. *Nature* 2004, 432, 867–871.
- [159] Zhao, K.; Zhang, Q.; Chini, M.; Wu, Y.; Wang, X.; Chang, Z. Tailoring a 67 attosecond pulse through advantageous phase-mismatch. *Opt. Lett.* 2012, *37*, 3891–3893.
- [160] Kraus, P. M.; Mignolet, B.; Baykusheva, D.; Rupenyan, A.; Horný, L.; Penka, E. F.; Grassi, G.; Tolstikhin, O. I.; Schneider, J.; Jensen, F.; Madsen, L. B.; Bandrauk, A. D.; Remacle, F.; Wörner, H. J. Measurement and laser control of attosecond charge migration in ionized iodoacetylene. *Science* 2015, *350*, 790–795.
- [161] Stensitzki, T.; Yang, Y.; Kozich, V.; Ahmed, A. A.; Kössl, F.; Kühn, O.; Heyne, K. Acceleration of a ground-state reaction by selective femtosecond-infrared-laser-pulse excitation. *Nat. Chem.* 2018, *10*, 126–131.

- [162] Cederbaum, L. S.; Zobeley, J. Ultrafast charge migration by electron correlation. *Chem. Phys. Lett.* **1999**, 307, 205–210.
- [163] Kuleff, A. I.; Lünnemann, S.; Cederbaum, L. S. Electron-correlation-driven charge migration in oligopeptides. *Chem. Phys.* 2013, 414, 100–105.
- [164] Kuleff, A. I.; Cederbaum, L. S. Ultrafast correlation-driven electron dynamics. J. Phys. B: At. Mol. Opt. Phys. 2014, 47, 124002.
- [165] Znakovskaya, I.; von den Hoff, P.; Zherebtsov, S.; Wirth, A.; Herrwerth, O.; Vrakking, M. J. J.; de Vivie-Riedle, R.; Kling, M. F. Attosecond control of electron dynamics in carbon monoxide. *Phys. Rev. Lett.* **2009**, *103*, 103002.
- [166] Siu, W.; Kelkensberg, F.; Gademann, G.; Rouzée, A.; Johnsson, P.; Dowek, D.; Lucchini, M.; Calegari, F.; Giovannini, U. D.; Rubio, A.; Lucchese, R. R.; Kono, H.; Lépine, F.; Vrakking, M. J. J. Attosecond control of dissociative ionization of O₂ molecules. *Phys. Rev. A* 2011, 84, 063412.
- [167] Bocharova, I.; Karimi, R.; Penka, E. F.; Brichta, J. P.; Lassonde, P.; Fu, X.; Kieffer, J. C.; Bandrauk, A. D.; Litvinyuk, I.; Sanderson, J.; Légaré, F. Charge resonance enhanced ionization of CO₂ probed by laser coulomb explosion imaging. *Phys. Rev. Lett.* **2011**, *107*, 063201.
- [168] Siu, W.; Kelkensberg, F.; Gademann, G.; Rouzée, A.; Johnsson, P.; Dowek, D.; Lucchini, M.; Calegari, F.; De Giovannini, U.; Rubio, A.; Lucchese, R. R.; Kono, H.; Lépine, F.; Vrakking, M. J. J. Attosecond control of dissociative ionization of O₂ molecules. *Phys. Rev. A* 2011, 84, 4–7.
- [169] Kreibich, T.; Lein, M.; Engel, V.; Gross, E. K. U. Even-Harmonic Generation due to Beyond-Born-Oppenheimer Dynamics. *Phys. Rev. Lett.* 2001, 87, 103901.
- [170] Cheng, Y.; Chini, M.; Wang, X.; Gonz, A.; Palacios, A.; Argenti, L.; Mart, F. Reconstruction of an excited-state molecular wave packet with attosecond transient absorption spectroscopy. *Phys. Rev. A* 2016, 023403, 1–10.
- [171] Cattaneo, L.; Vos, J.; Bello, R. Y.; Palacios, A.; Heuser, S.; Pedrelli, L.; Lucchini, M.; Cirelli, C.; Martín, F.; Keller, U. Attosecond coupled electron and nuclear dynamics in dissociative ionization of H₂. *Nat. Phys.* **2018**, *14*, 733–738.
- [172] Ulusoy, I. S.; Nest, M. The multi-configuration electron-nuclear dynamics method applied to LiH. J. Chem. Phys. 2012, 136, 054112.
- [173] Ulusoy, I. S.; Nest, M. Remarks on the validity of the fixed nuclei approximation in quantum electron dynamics. *J. Phys. Chem. A* **2012**, *116*, 11107–11110.
- [174] Kato, T.; Kono, H. Time-dependent multiconfiguration theory for electronic dynamics of molecules in an intense laser field. *Chem. Phys. Lett.* 2004, 392, 533–540.
- [175] Caillat, J.; Zanghellini, J.; Kitzler, M.; Koch, O.; Kreuzer, W.; Scrinzi, A. Correlated multielectron systems in strong laser fields: A multiconfiguration time-dependent Hartree-Fock approach. *Phys. Rev. A* 2005, *71*, 012712.

- [176] Nest, M.; Klamroth, T.; Saalfrank, P. The multiconfiguration time-dependent Hartree–Fock method for quantum chemical calculations. *J. Chem. Phys.* **2005**, *122*, 124102.
- [177] Abedi, A.; Maitra, N. T.; Gross, E. K. U. Exact Factorization of the Time-Dependent Electron-Nuclear Wave Function. *Phys. Rev. Lett.* **2010**, *105*, 123002.
- [178] Cederbaum, L. S. The exact molecular wavefunction as a product of an electronic and a nuclear wavefunction. *J. Chem. Phys.* **2013**, *138*, 224110.
- [179] Khosravi, E.; Abedi, A.; Maitra, N. T. Exact Potential Driving the Electron Dynamics in Enhanced Ionization of H2+. *Phys. Rev. Lett.* 2015, *115*, 263002.
- [180] Skouteris, D.; Gervasi, O.; Lagan, A. Non-Born-Oppenheimer MCTDH calculations on the confined H⁺₂ molecular ion. *Chem. Phys. Lett.* **2010**, *500*, 144–148.
- [181] Haxton, D. J.; Lawler, K. V.; McCurdy, C. W. Multiconfiguration time-dependent Hartree-Fock treatment of electronic and nuclear dynamics in diatomic molecules. *Phys. Rev. A* 2011, 83, 1–16.
- [182] Cassam-Chenaï, P.; Suo, B.; Liu, W. Decoupling electrons and nuclei without the Born-Oppenheimer approximation: The electron-nucleus mean-field configuration-interaction method. *Phys. Rev. A* 2015, *92*, 1–15.
- [183] Huber, K. P.; Herzberg, G. Molecular Spectra and Molecular Structure— IV. Constants of Diatomic Molecules; Van Nostrand Reinhold: New York, 1979.
- [184] Herzberg, G.; Howe, L. L. The Lyman bands of molecular hydrogen. *Can. J. Phys.* **1959**, *37*, 636–659.
- [185] Stwalley, W. C.; Zemke, W. T. Spectroscopy and Structure of the Lithium Hydride Diatomic Molecules and Ions. J. Phys. Chem. Ref. Data 1993, 22, 87–112.
- [186] Vacher, M.; Bearpark, M. J.; Robb, M. A.; Malhado, J. P. Electron Dynamics upon Ionization of Polyatomic Molecules: Coupling to Quantum Nuclear Motion and Decoherence. *Phys. Rev. Lett.* 2017, *118*, 083001.
- [187] Arnold, C.; Vendrell, O.; Santra, R. Electronic decoherence following photoionization: Full quantum-dynamical treatment of the influence of nuclear motion. *Phys. Rev. A* 2017, 95, 33425.
- [188] Tiwari, V.; Peters, W. K.; Jonas, D. M. Electronic resonance with anticorrelated pigment vibrations drives photosynthetic energy transfer outside the adiabatic framework. *Proc. Natl. Acad. Sci.* 2013, 110, 1203–1208.
- [189] Hoffman, D. P.; Mathies, R. A. Femtosecond Stimulated Raman Exposes the Role of Vibrational Coherence in Condensed-Phase Photoreactivity. Acc. Chem. Res 2016, 49, 616–625.
- [190] Holzmeier, F. et al. Control of H₂ Dissociative Ionization in the Nonlinear Regime Using Vacuum Ultraviolet Free-Electron Laser Pulses. *Phys. Rev. Lett.* 2018, 121, 103002.

- [191] Jelovina, D.; Feist, J.; Martín, F.; Palacios, A. A pump–probe scheme with a single chirped pulse to image electron and nuclear dynamics in molecules. *New J. Phys.* **2018**, *20*, 123004.
- [192] Baykusheva, D.; Kraus, P. M.; Zhang, S. B.; Rohringer, N.; Wörner, H. J. The sensitivities of high-harmonic generation and strong-field ionization to coupled electronic and nuclear dynamics. *Faraday Discuss.* **2014**, *171*, 113.
- [193] Born, M.; Oppenheimer, R. Zur Quantentheorie der Molekeln. Ann. Phys. 1927, 389, 457–484.
- [194] Agostini, F.; Curchod, B. F. Different flavors of nonadiabatic molecular dynamics. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2019**, 1–21.
- [195] Tully, J. C.; Preston, R. K. Trajectory Surface Hopping Approach to Nonadiabatic Molecular Collisions: The Reaction of H⁺ with D₂. J. Chem. Phys. **1971**, 55, 562–572.
- [196] Yonehara, T.; Takahashi, S.; Takatsuka, K. Non-Born–Oppenheimer electronic and nuclear wavepacket dynamics. J. Chem. Phys. 2009, 130, 214113.
- [197] Janeček, I.; Janča, T.; Naar, P.; Kalus, R.; Gadea, F. X. Multiscale approach combining nonadiabatic dynamics with long-time radiative and non-radiative decay: Dissociative ionization of heavy rare-gas tetramers revisited. J. Chem. Phys. 2013, 138, 044303.
- [198] Mendive-Tapia, D.; Vacher, M.; Bearpark, M. J.; Robb, M. A. Coupled electron-nuclear dynamics: Charge migration and charge transfer initiated near a conical intersection. J. Chem. Phys. 2013, 139, 044110.
- [199] Min, S. K.; Agostini, F.; Gross, E. K. Coupled-Trajectory Quantum-Classical Approach to Electronic Decoherence in Nonadiabatic Processes. *Phys. Rev. Lett.* 2015, 115, 1–5.
- [200] Walters, P. L.; Makri, N. Iterative quantum-classical path integral with dynamically consistent state hopping. *J. Chem. Phys.* **2016**, *144*, 044108.
- [201] Agostini, F.; Min, S. K.; Abedi, A.; Gross, E. K. U. Quantum-Classical Nonadiabatic Dynamics: Coupled- vs Independent-Trajectory Methods. J. Chem. Theory Comput. 2016, 12, 2127–2143.
- [202] Geppert, D.; von den Hoff, P.; de Vivie-Riedle, R. Electron dynamics in molecules: a new combination of nuclear quantum dynamics and electronic structure theory. J. Phys. B At. Mol. Opt. Phys. 2008, 41, 074006.
- [203] Seki, Y.; Takayanagi, T.; Shiga, M. Photoexcited Ag ejection from a low-temperature He cluster: a simulation study by nonadiabatic Ehrenfest ring-polymer molecular dynamics. *Phys. Chem. Chem. Phys.* 2017, 19, 13798–13806.
- [204] Shakib, F. A.; Huo, P. Ring Polymer Surface Hopping: Incorporating Nuclear Quantum Effects into Nonadiabatic Molecular Dynamics Simulations. J. Phys. Chem. Lett. 2017, 8, 3073–3080.
- [205] Ben-Nun, M.; Martínez, T. J. Semiclassical Tunneling Rates from Ab Initio Molecular Dynamics. J. Phys. Chem. A 1999, 103, 6055–6059.

- [206] Levine, B. G.; Martínez, T. J. Isomerization Through Conical Intersections. *Annu. Rev. Phys. Chem.* **2007**, *58*, 613–634.
- [207] Worth, G. A.; Meyer, H.-D.; Köppel, H.; Cederbaum, L. S.; Burghardt, I. Using the MCTDH wavepacket propagation method to describe multimode non-adiabatic dynamics. *Int. Rev. Phys. Chem.* 2008, 27, 569–606.
- [208] Hochstuhl, D.; Hinz, C. M.; Bonitz, M. Time-dependent multiconfiguration methods for the numerical simulation of photoionization processes of many-electron atoms. *Eur. Phys. J. Special Topics* 2014, 223, 177–336.
- [209] Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. J. Chem. Phys. 1989, 90, 1007–1023.
- [210] Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. Electron Affinities of the First-Row Atoms Revisited. Systematic Basis Sets and Wave Functions. J. Chem. Phys. 1992, 96, 6796–6806.
- [211] Prascher, B. P.; Woon, D. E.; Peterson, K. A.; Dunning, T. H., Jr.; Wilson, A. K. Gaussian basis sets for use in correlated molecular calculations. VII. Valence and core-valence basis sets for Li, Na, Be, and Mg. *Theor. Chem. Acc.* 2011, *128*, 69.
- [212] Linstrom, P. J.; Mallard, W. *NIST Chem. Web.*; National Institute of Standards and Technology: Gaithersburg MD.
- [213] Nelson, R. D.; Lide, D. R.; Maryott, A. A. Selected Values of Electric Dipole Moments for Molecules in the Gas Phase; NSRDS-NBS10, 1967.
- [214] Engel, E. A.; Doss, N.; Harris, G. J.; Tennyson, J. Calculated spectra for HeH + and its effect on the opacity of cool metal-poor stars. *Mon. Not. R. Astron. Soc.* **2005**, *357*, 471–477.
- [215] White, A. F.; Heide, C. J.; Saalfrank, P.; Head-Gordon, M.; Luppi, E. Computation of highharmonic generation spectra of the hydrogen molecule using time-dependent configurationinteraction. *Mol. Phys.* 2016, 114, 947–956.
- [216] Bian, X. B.; Bandrauk, A. D. Probing nuclear motion by frequency modulation of molecular high-order harmonic generation. *Phys. Rev. Lett.* **2014**, *113*, 1–5.
- [217] Li Manni, G.; Carlson, R. K.; Luo, S.; Ma, D.; Olsen, J.; Truhlar, D. G.; Gagliardi, L. Multiconfiguration Pair-Density Functional Theory. J. Chem. Theory Comput. 2014, 10, 3669–3680.
- [218] White, S. R. Hybrid grid/basis set discretizations of the Schrödinger equation. J. Chem. Phys. 2017, 147.
- [219] White, S. R.; Stoudenmire, E. M. Multisliced gausslet basis sets for electronic structure. *Phys. Rev. B* 2019, 99, 1–5.