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Electronic structure theory meets precision measurements

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Chapter 1

Introduction

The Standard Model (SM) of particle physics provides a framework of the known fundamental particles and forces (excluding gravity). It is extremely successful in describing processes on the particle, nuclear and atomic level [1]. However, especially when looking out into our universe, i.e. the subject of cosmology, the shortcomings of the SM become obvious. The SM is for example not able to explain the existence and nature of dark matter [2] and dark energy [3] which were proposed to explain the observed movement of cosmological objects and the accelerating expansion of the universe, respectively. Another example concerns the failure of the SM to explain the observed dominance of matter over anti-matter [4]. Many researchers are consequently searching for new theories which are referred to as beyond Standard Model (BSM) theories. Such theories often include a list of parameters which can be constrained by fitting to experimental observations. A very attractive group of observables consists of permanent electric dipole moments (EDMs) of elemental or composite particles [5].

A permanent EDM violates parity (P) and time-reversal (T) symmetry. Assuming the CPT theorem holds, where C stands for charge conjugation, T -violation is equivalent to CP -violation. New sources of CP -violation play an important role in the development of BSM theories since it is proposed that these theories should include more CP -violation compared to the SM in order to explain for example the observed dominance of matter over anti-matter [6]. Consequently, in the development of BSM theories, CP -violating observables are of great importance and EDMs are examples hereof.

An advantage of EDMs is that they are highly suppressed in the SM and there is consequently much room for measuring an EDM well above the SM prediction which would consequently be a direct evidence of BSM physics, sometimes denoted 'New Physics'. In addition, the measurement of any EDM would be the first direct evidence for T -violation. Most BSM theories predict EDM values much larger than the SM predictions and within reach for current or near-future experiments which makes this research field very exciting.

A measurement of an EDM is thus interesting in itself, as direct evidence of New Physics, but would also have a huge impact on the refinement and development of BSM theories which hopefully, one day, will help us understand our universe even

better [7]. This thesis is motivated by the experimental search for an EDM, and the scope will be introduced over the next few sections.

1.1 Testing fundamental physics with atoms and molecules

When being asked for an experiment to test fundamental particle physics, most people will probably think of accelerator physics such as the large hadron collider (LHC) at CERN where extremely large energies, on the order of a few TeV, can be reached [8]. However, the same energy scale, if not higher, can also be probed by high precision experiments with a considerably lower budget [9]. Such experiments take advantage of the rich internal structure of atoms and molecules as well as the rapid development in cooling and slowing of atoms and molecules, laser spectroscopy and impressive control of electric and magnetic fields, but more importantly, the relativistic enhancement which will be treated in Sec. 1.1.2. One group of such precision experiments aims to measure an EDM of an atom or molecule. An atomic or molecular EDM arises because of P, T -odd interactions between the constituents of the systems (i.e. electrons and nuclei). In the following section, a brief overview of the possible effects as well as how to disentangle them from the resulting atomic or molecular EDM will be given.

1.1.1 P, T -odd interactions in atoms and molecules

In atoms and molecules, there are several P, T -violating effects associated with either P, T -violating properties of the fundamental particles or P, T -violating interactions between them [10]. Such effects induce atomic or molecular permanent (P, T -odd) EDMs which are currently being searched for in high precision measurements [9]. A P, T -odd EDM should be distinguished from the "usual" molecular dipole moment (such as the dipole moment of water) which violates neither P nor T . Throughout this thesis a P, T -odd EDM will be denoted $d^{P, T}$ and the P, T -even molecular dipole moment will be denoted d^{mol} . The P, T -odd interactions in atoms and molecules, which contribute to $d^{P, T}$, can be divided into three groups:

Leptonic: Electron electric dipole moment (eEDM) Of all the ongoing searches for P, T -odd effects, the search for an eEDM is receiving the most attention, probably due to the more accessible nature and to the possibility of eye-catching titles such as "Improved measurement of the shape of the electron" [11] and "Is the electron round?" [12]. The SM prediction of the eEDM is extremely small, namely $< 10^{-38} e \cdot \text{cm}$, many orders of magnitude smaller than predictions from BSM theories [13]. The eEDM is one out of the two dominating contributions to a $d^{P, T}$ of paramagnetic systems. In diamagnetic systems, there are only indirect, and thus weak, contributions

of the eEDM to a $d^{P,T}$ due to the pairing of electrons [14]. The quantum mechanical description of the eEDM interaction in atoms and molecules will be introduced in Sec. 3.1.1.

Semi-leptonic: Nucleon-electron interaction There are several P, T -odd interactions between electrons and nucleons [10]. The two most important interactions in the context of this thesis are the scalar-pseudoscalar nucleon-electron (S-PS) interaction, the strength of which is denoted by C_S , and the tensor nucleon-electron interaction, denoted by C_T . In paramagnetic systems, the former is expected to dominate and in diamagnetic systems only the latter contributes directly to a $d^{P,T}$. Since the main focus of this thesis lies on paramagnetic systems, the tensor interaction will not be treated further. A quantum mechanical description of the S-PS interaction can be found in Sec. 3.1.2.

Hadronic: P, T -odd nuclear moments A last class of P, T -odd interactions are entirely due to the atomic nuclei and can be probed by the interaction with electrons in atoms and molecules. In paramagnetic systems, the dominant interaction is related to the P, T -odd nuclear magnetic quadrupole moment (NMQM) which can be observed in nuclei with $I > 1/2$. For diamagnetic systems, an interesting property is the so-called nuclear Schiff moment which is generated by either nucleon EDMs or P, T -odd nucleon-nucleon interactions [10]. Neither the NMQM nor the nuclear Schiff moment will be treated further in this thesis.

To summarize, for *paramagnetic* systems, the two dominant contributions to a $d^{P,T}$ are expected to be the eEDM and S-PS interactions. Ongoing experiments to search for $d^{P,T}$ in paramagnetic systems use HfF⁺ [15], ThO [16,17], YbF [18] and BaF [19,20]. In the past, also atomic Cs [21] and Tl [22] was used and in the near future, the use of polyatomic systems is likely to take over the stage [23]. However, at present, no $d^{P,T}$ has been observed. The best upper limit of the underlying eEDM and S-PS interaction was reached by the ThO experiment resulting in $|d_e| < 1.1 \times 10^{-29} e \text{ cm}$ and $|C_S| < 7.3 \times 10^{-10}$ (90% confidence level) [17]. In order to set individual limits on these two properties from a single experiment, a "sole source" approach was used where one was considered to be zero in order to set a limit on the other. This is a very crude approximation and a better approach is to perform a so-called global analysis where all available experimental results are combined in one fit to set limits on the underlying P, T -odd interactions [5, 14, 24–26].

The result for such a global fit, performed by Kirch et al. [5], is shown in Fig. 1.1 where the experimental results using paramagnetic systems are depicted as the yellow, blue and red colored bands. The width of the band gives the obtained experimental precision and the slope is related to the sensitivity of the d_e and C_s interactions. This sensitivity will be discussed further in Sec. 1.1.2, but it is already clear that the

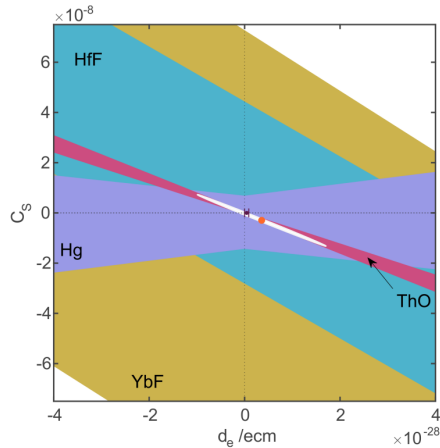


Figure 1.1 Global fit to the results of four EDM experiments using HgF^+ , ThO , YbF and Hg . Figure from Ref. 5.

three paramagnetic systems included in Fig 1.1 show similar sensitivity, i.e. similar slope. The purple band depicting the diamagnetic Hg result shows completely different sensitivity compared to the paramagnetic systems. When combining these four results, the global fit is indicated by the white area, which overlaps with $(0,0)$, meaning the fit is consistent with zero but can provide upper bounds on d_e and C_S indicated by the red dot. In the analysis of the Hg result, only the eEDM and the S-PS interaction were included, neglecting the more dominant tensor and Schiff moment contributions, which can be considered as a very crude approximation.

The different behavior of the Hg result in Fig 1.1 underlines the importance of diamagnetic systems in order to disentangle the underlying P, T -violating effects. There are several ongoing experiments which are using diamagnetic atoms and molecules; Hg [27], Xe [28], Ra [29] and TlF [30,31] with the Hg experiment setting the most stringent limit on an atomic EDM, $d^{P,T}$, to date.

1.1.2 Enhancement in atoms and molecules

When reading the previous section one could ask: Why should we bother with these relatively complicated heavy atoms and even more complicated molecules when one could simply study the bare electron or nucleon? The answer is that the mentioned P, T -odd moments and interactions, be it leptonic, semi-leptonic or hadronic, are enhanced in atoms and molecules containing heavy elements.

This atomic and molecular enhancement is related to relativistic effects due to the heavy element and to polarization effects in the case of molecules. As an example let us

consider the eEDM enhancement. By evaluating matrix elements of the eEDM operator, which will be introduced in Sec. 3.1.1, over an appropriate atomic or molecular wave function one can derive approximate expressions for the enhancement [32]:

$$\langle \hat{H}^{\text{eEDM}} \rangle_{\text{atom}} \approx 8Z(Z\alpha)^2 d_e E_{\text{ext}} \Omega \quad (1.1)$$

$$\langle \hat{H}^{\text{eEDM}} \rangle_{\text{mol}} \approx 0.8Z(Z\alpha)^2 d_e \Omega \quad (1.2)$$

where α is the fine structure constant and Ω is the projection of electronic angular momentum onto the axis defined by the external electric field in the case of atoms and the molecular axis in the case of molecules. It can be seen that in both cases, the enhancement scales as $\alpha^2 Z^3$.

The big difference between the atomic and molecular cases is the linear dependence on E_{ext} in the expression for the atomic enhancement. In order for the atomic and molecular enhancements to be of the same order of magnitude, an external electric field of 0.1 a.u. = 0.5 GV/cm should be used. This is around five orders of magnitude larger than the largest laboratory accessible electric fields (~ 10 kV/cm) which means that molecular systems are to be preferred. The much larger molecular enhancement is due to the fact that the molecular valence orbital is strongly polarized due to the existence of the ligand atom.

In Eq. (1.2), full polarization was assumed which implies that the electronic angular momentum is aligned with the internuclear axis. The degree of polarization depends on the employed electronic state, or more precisely, on the separation between states of opposite parity. In the case of ThO and HfF⁺ the employed electronic state exhibits a so-called Ω -doubling structure in which two states of opposite parity are nearly degenerate which means that these systems can be fully polarized in a moderate electric field [15, 17]. The experiments using BaF and YbF cannot take advantage of this type of structure and the closest levels of opposite parity are higher rotational states which have much larger splittings. Consequently these systems can be only partly polarized even when large electric fields (~ 10 kV/cm) are used [18, 19, 33].

The enhancement of the additional P, T -odd interactions will not be discussed here but it is worth to mention the relation between the eEDM and S-PS enhancement factors. Even though the eEDM and S-PS enhancement factors both scale as Z^3 , the ratio between the two for paramagnetic species has been shown to depend mainly on Z [34]. Consequently, in order to disentangle the eEDM and S-PS contributions, systems with a large difference in Z are to be preferred.

1.2 Other tests with atoms and molecules

The previous sections introduced P, T -odd properties which all contribute to atomic or molecular EDMs that are being searched for by current experiments. There are however many more possibilities to test fundamental physics with atoms and molecules.

The recent review by Safronova et al [9] gives a comprehensive overview including the search for variation of fundamental constants, Dark Matter, Lorentz invariance, etc.

Another field of research is the study of parity violation which is predicted by the Standard Model and which has been observed in many atoms with the most accurate one being the measurement on Cs [35]. However, to date, P -violation has not been observed in molecules and several groups are working towards such a measurement using different approaches. One approach is to look for the nuclear anapole moment, a P -violating spin-dependent nuclear moment, which is also enhanced in heavy systems and where experimental techniques similar to the EDM experiments can be used [36]. In another very interesting proposal, a clever but seemingly simple nuclear magnetic resonance (NMR) experiment is proposed to measure molecular P -violation in chiral molecules [37].

As a last example, another approach to measure P -violation in chiral molecules will be briefly introduced. I have been happy to contribute to the collaborative work between theoretical groups in Groningen and experimental researchers at the the Laboratoire de Physique des Lasers (LPL) in Paris. The majority of this work was performed by Marit Fiechter who worked on her bachelor's thesis in our group and it is summarized in the following manuscript:

Paper 10: *"Large parity violating shifts in chiral Ru(acac)₃ and Os(acac)₃ and implications for measurements", Marit R. Fiechter, Pi A.B. Haase, Nidal Saleh, Pascale Soulard, Benoît Tremblay, Remco W.A. Havenith, Rob G.E. Timmermans, Jeanne Crassous, Benoît Darquié, Lukáš F. Pašteska, and Anastasia Borschevsky, in preparation*

Contribution: *Solving technical challenges of the calculations, interpretation of the results in terms of theoretical uncertainty as well as the preparations for the manuscript.*

In this work, P -violating shifts of vibrational transitions in chiral molecules were studied. The purpose of these theoretical investigations was to identify the most suitable transitions to use in precision experiments at the LPL. The idea behind the planned measurements is that vibrational levels in the two enantiomers are shifted in opposite directions due to P -violating effects. By performing ultra-precise vibrational spectroscopy on the isolated enantiomers this energy shift can be measured. Due to the smallness of this shift, it is necessary to choose a system and vibrational transition which is particularly sensitive to the P -violating effects. Since the sensitivity is proposed to scale as Z^5 , with Z being the nuclear charge, systems containing heavy elements should be preferred. Consequently, in this work Ru- and Os-containing compounds were considered. The calculations were performed on the DFT level with various treatments of relativistic effects, to both optimize the molecular structures and to study the dependency of vibrational modes on the P -violating interaction. The

study resulted in the identification of a few transitions with good spectral properties and, more importantly, with a sensitivity which lies within the range of the proposed experimental sensitivity.

1.3 NL-*e*EDM collaboration: Search for *P, T*-odd effects with BaF

In this section an example will be shown of how an experimental search for *P, T*-odd effects in molecules works. This PhD thesis has been conducted within the framework of the NL-*e*EDM collaboration which is mainly an experimental collaboration between researchers from the University of Groningen, Nikhef and Vrije Universiteit in Amsterdam. The goal of this collaboration is to measure a *P, T*-odd EDM in BaF using sophisticated cooling and slowing techniques and excellent control of electric and magnetic fields. Even though any measurement of a *P, T*-odd molecular EDM is exciting in itself, one would also like to relate such a measurement to the underlying *P, T*-odd interactions which, in the case of the paramagnetic BaF system, would be dominated by the *e*EDM and the S-PS interactions, as was discussed in Sec. 1.1.1. For this, molecule specific coupling parameters, often referred to as molecular enhancement factors, are needed. As long as the *e*EDM and the S-PS interaction are not known, such enhancement factors must be predicted by theory and that is where this thesis comes into play.

Before discussing the basic principles of the NL-*e*EDM experiment and the role of electronic structure theory (Sec. 1.4), the benefits of using BaF should be mentioned. A very practical reason for choosing BaF was the relatively easy transition from SrF, which was already used in the lab in Groningen, to its heavier homologue, BaF. Another important reason is the fact that BaF is laser-coolable and that it can be decelerated in a Stark decelerator and of course that the radical lives long enough to survive the course of the experiment. However, in my opinion, the most important reason for using BaF ($Z = 56$) is how it complements the ongoing EDM experiments in terms of *e*EDM and S-PS enhancements. The remaining EDM experiments use considerably heavier systems, i.e. YbF ($Z = 70$), HfF⁺ ($Z = 72$) and ThO ($Z = 90$), which means that the ratio between the *e*EDM and S-PS enhancements in BaF differs more from ThO than those of YbF and HfF⁺ which I will come back to at the end of **Chapter 5**. Provided the BaF experiment can reach competitive sensitivity, the expected result will be able to constrain the global fit shown in Fig 1.1 further. The enhancement factors are of course smaller for BaF but one could imagine that the sensitivity of the BaF experiment could exceed that of the heavier systems due to the easier cooling and slowing and the possibility for trapping due to the long-lived ground state. For comparison, the ThO experiment will at some point be limited by the short lifetime of the employed meta-stable state [17].

The details on the experimental setup can be found in the following proposal paper (as well as in the theses of Artem Zapara [38], Kevin Esajas [39] and Parul Aggarwal [40]):

Paper 2 *"Measuring the electric dipole moment of the electron in BaF"*, P. Aggarwal, H. L. Bethlem, A. Borschevsky, M. Denis, K. Esajas, P. A. B. Haase, Y. Hao, S. Hoekstra, K. Jungmann, T. B. Meijknecht, M. C. Mooij, R. G. E. Timmermans, W. Ubachs, L. Willmann, and A. Zapara, *Eur. Phys. J. D72*, 197 (2018)

Contributions: *Preparation of the section on the role of ab initio theory.*

The setup of the NL-eEDM experiment is sketched in Fig. 1.2. BaF radicals are produced on the far left in a cryogenic source where a Ba target is ablated in the presence of SF₆ gas to form (among many other products) BaF. The BaF radicals are transported out of the cryogenic source by means of a cold buffer gas and through an electrostatic guide before entering the 4.5 m long Stark decelerator. Here the molecules are slowed down (in the forward direction) from ~ 200 m/s to ~ 30 m/s. In order to prevent rapid spreading of this cold and slow beam, transverse laser cooling will be used and the beam is ready to enter the interaction zone.

The interaction zone is shielded by several layers of a magnetic shielding material in order to have good control of the magnetic field inside. At the beginning of the interaction zone, a superposition state is being created in the $F = 1$, $m_F = \pm 1$ hyperfine levels of the lowest electronic, vibrational and rotational state. This coherent beam then passes through a region with constant and well controlled electric and magnetic fields. Due to the existence of P, T -violating interactions in the system, the $m_F = \pm 1$ levels will slightly shift in opposite directions in the presence of the external electric field. During the coherent interaction time this energy difference will result in an accumulated P, T -odd phase which can then be read out using optical detection. By using different configurations of the electric and magnetic fields, the P, T -odd EDM of BaF, or an upper limit, can be extracted.

Provided the systematic uncertainties can be well controlled, which is not at all straightforward, the probably most important experimental quantity is the statistical uncertainty. If we for now assume the eEDM to be the only P, T -violating source, it is given as:

$$\sigma_{d_e} \propto \frac{1}{2|P|W_d\Omega\tau\sqrt{N}} \quad (1.3)$$

In order to get the best sensitivity, the denominator should be maximized. To understand the challenges of an EDM experiment the different quantities will be briefly introduced. P is the previously mentioned polarization factor. W_d is the enhancement factor for the eEDM interaction. This quantity should be provided by theory as will be discussed further in the next section. Ω is the projection of the electronic angular

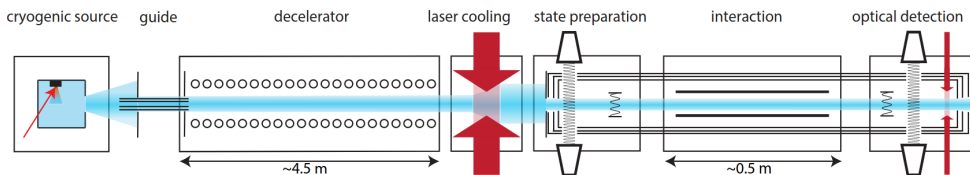


Figure 1.2 Overview of the NL-*e*EDM experiment from Ref. 19

momentum on the internuclear axis. τ is the coherent interaction time, i.e. the time in which the beam of molecules travels through the external electric and magnetic fields while staying in the desired superposition state, and N is the number of molecules. When a specific molecule has been chosen, the magnitudes of P , W_d and Ω can hardly be increased. However, by optimizing the production of molecules as well as slowing, cooling, state preparation and detection techniques, τ and N can be increased and this requires a tremendous amount of preparation by a large group of people.

1.4 The role of reliable electronic structure methods

Having introduced the motivation for searching for a molecular EDM, the possible P, T -odd effects that can contribute to it and an experimental setup which aims to measure it, it is now time to narrow down the actual scope of this thesis. The interpretation of a molecular EDM experiment, as well as the design of new ones, depends strongly on the input from electronic structure theory. In this section, the importance of reliable electronic structure theory methods will be discussed.

The easiest way to describe an EDM experiment with paramagnetic systems, such as the NL-*e*EDM experiment, is by the effective Hamiltonian [41]:

$$\hat{H}^{P,T} = (W_d d_e + W_s k_s) \vec{S} \cdot \hat{n} \quad (1.4)$$

The concept of an effective Hamiltonian will be introduced in Sec. 3.3.2. The projection of electron spin, \vec{S} , onto the internuclear axis, \hat{n} , can be related to the polarization factor, P , and Ω and the measurable P, T -violating phase is given as [33]:

$$\phi^{P,T} \propto (W_d d_e + W_s k_s) \Omega |P| \tau \quad (1.5)$$

where d_e and k_s are the magnitudes of the *e*EDM and S-PS interaction and W_d and W_s are the corresponding molecular enhancement factors.

As long as d_e and k_s are not known, W_d and W_s should be provided by theoretical methods. There are several ways of approaching this. A simple order of magnitude estimate for W_d was already given in Eq. (1.2). However, this expression was obtained

with a very crude approximation of the electronic structure. To improve this description, a large range of molecular electronic structure methods, also referred to as *ab initio* methods, have been used to calculate such enhancement factors for several molecules, from semi-empirical methods [41], over quasi-relativistic density functional theory methods [42] to state-of-the-art 4-component coupled-cluster methods [33, 43, 44] (see also **Chapter 5**).

In the context of EDM experiments, *ab initio* methods are not only used to calculate molecular enhancement factors, but have also applications related to the planning and optimization of experimental techniques. In preparation for an EDM experiment, a careful investigation of the chosen system is performed including a series of spectroscopy measurements. In this context, it can be helpful to have predictions from *ab initio* theory of the electronic spectra. For example, when designing an efficient laser cooling scheme, transition dipole moments and Frack-Condon factors, which describe the coupling between electronic and vibrational levels, respectively, can be useful [45]. For simulating electronic spectra also hyperfine structure constants can be of relevance, as will be demonstrated in **Chapter 6**. Another interesting property which can be calculated with *ab initio* methods is the static and dynamic polarizability which can be helpful when studying optical trapping [46]. Also the calculation of spectroscopic constants and electron affinities can be very useful when searching for new and better systems in the search for P, T -violating effects in molecules [47].

The obvious advantage of *ab initio* methods is that they are usually much cheaper, both in terms of time and equipment, compared to experimental methods. It should however be emphasized that even though an *ab initio* calculation is much faster to conduct, it does not mean that one simply needs to press a button, go have coffee and wait for the result. First of all, one needs to understand the employed methods, the strengths and weaknesses and the approximations which are made in order to choose the best suitable method for a given purpose. Second of all, especially when calculations become very demanding in terms of memory, disk space and computer time usage, one needs to figure out how to best fit the calculation with the given hardware. However, for a fair comparison of time consumption between experiment and *ab initio* methods, one should compare the time used to build up an experiment with implementing a new method, either from scratch or in an existing program. In this case it is not obvious which of the two would be fastest as *ab initio* method development is often not straightforward. With that said, if we assume that a desired *ab initio* method has already been implemented, it becomes a great tool to study large numbers of systems which can ultimately lead to a better understanding of for example the enhancement of P, T -violating effects in molecules, as was demonstrated nicely in Ref. 34. Another advantage of *ab initio* methods is that one can conduct "experiments" which are not possible in the lab. An obvious example is that of the mentioned molecular P, T -violating enhancement factors, which simply cannot be measured in the lab currently. A similar example is the calculation of hyperfine coupling constants

which are used to extract nuclear magnetic dipole and electric quadrupole moments of exotic nuclei [48, 49]. Another additional possibility with *ab initio* methods is that not only the magnitude of a given property can be determined but the result can also be analyzed for example in terms of orbital contributions [50] or bond lengths [47]. Such analyses can often contribute to a better qualitative understanding of the underlying mechanisms. The development of *ab initio* methods, on the other hand, benefits greatly from high precision measurements which can be used to benchmark new methods. To summarize, in my opinion there are only mutual benefits from a close collaboration between theoretical and experimental groups.

I hope by now that I have convinced the reader of the importance of *ab initio* methods in the context of searching for P, T -violation in molecular systems and of a good collaboration between experimental and theoretical groups. However, in order for such a collaboration to be most successful, an important aspect is the reliability of the theoretical predictions. In most experimental sciences any result comes with an error bar. This is however not customary within the field of *ab initio* theory, partly because there is no straightforward way to do so which is applicable to all possible methods. There are two overall strategies that one can follow. Probably the most common strategy involves comparison of calculated *ab initio* values with experimental values. However, especially when there are no measurements of a given property, a purely theoretical uncertainty estimate can be established, provided the employed method is systematically improvable. This issue will be discussed thoroughly throughout this thesis, with the background presented in Sec. 3.2 and practical applications and discussions in **Chapters 4, 5 and 6**.

1.5 Thesis outline

The body of this thesis will be concerned with the application of state-of-the-art *ab initio* methods to properties of atoms and diatomic molecules relevant for the experimental search for P, T -violating effects in molecules. The emphasis will lie on the reliability of such methods as well as the connection between the predicted values and the experimental situation. Some parts of the following two chapters might be obvious for readers within the field of *ab initio* theory, but since this thesis has come to life in the void between *ab initio* theory and experimental molecular physics, it seems appropriate to treat the basic principles on an introductory level, limited, however, to the aspects which are relevant for following the discussions in the last three chapters.

In **Chapter 2**, the relativistic coupled-cluster method will be briefly introduced, focusing on the aspects which are relevant for the remaining chapters and with illustrative examples from published studies. In **Chapter 3**, details on the studied P, T -violating properties will be given along with a discussion on the uncertainty of the employed method and the connection between theory and experiment via the effective

Hamiltonian. In the remaining chapters, different studies on the relativistic coupled cluster level will be presented; **Chapter 4** deals with the magnetic hyperfine coupling constants in ^{133}Cs and ^{137}BaF , **Chapter 5** includes the calculation of P, T -violating molecular enhancement factors in BaF and **Chapter 6** presents the magnetic hyperfine coupling constants in the ground and excited state of Ba^{19}F along with a thorough discussion of the connection between the *ab initio* parameters and the measured energy splittings via effective Hamiltonians. Lastly, in **Chapter 7**, a general conclusion based on the findings in this thesis will be presented together with an outlook within the field.