Chapter 1

Introduction

1.1 The HD$^+$ molecule

This thesis concerns a test of fundamental physics through a high precision measurement on the HD$^+$ molecule. This molecule consists of a proton, a deuteron and an electron which are held together by the electromagnetic force. The proton and deuteron in turn, are composed of quarks which are bound by the strong nuclear force. Today, quarks and electrons are considered as elementary particles which by definition contain no substructure. According to quantum field theory, both elementary particles and forces can be phenomenologically described as ‘excitations of quantum fields’ and string theory considers them as multi-dimensional vibrating strings with sizes of order $10^{-33}$ m. Although these descriptions cover a faithful model of nature at the smallest scale, they serve better as mathematical concepts rather than phenomenological ideas and therefore, when depicting a particle, dots, balls or clouds are used. Figure 1.1 shows three different representations of our system of interest: HD$^+$. These figures give a qualitative picture of the phenomenon ‘HD$^+$ molecule’ and each representation depicts another intrinsic property. Figure 1.1a shows its properties of angular momentum (including the particle spins and molecular rotation), while Fig. 1.1b shows the two nuclei connected by a helical spring implying the possibility of vibration. The cloud figure of Fig. 1.1c represents the probabilistic nature of the spatial position of the constituents.

At room temperature HD$^+$ molecules will rotate but none of them will vibrate (at least in a classical picture), i.e. the molecules are in the vibrational ground state $v = 0$. If sufficient energy is added, they can undergo transitions to vibrationally excited states. For example, at a temperature of 2000°C a small fraction of the molecules will vibrate (in $v = 1$ or $v = 2$). The main topic in this thesis is an experiment in which the energy required to excite the
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HD$^+$ molecule from $v = 0$ to $v = 8$ is measured. This ‘vibrational transition’ is carried out by exciting HD$^+$ with an infrared laser of 782 nm wavelength. In this transition also the rotational state changes, and thus the name ‘ro-vibrational transition’ is actually more suitable.

1.2 Motivation

Molecular hydrogen ions like H$_2^+$ and HD$^+$ are the simplest molecular systems and therefore calculations on such systems can be performed with high accuracy. Today the precision of calculations of such three-body molecules lies at the 10$^{-11}$ level [1,2]. Owing to currently available techniques like laser cooling, ion trapping, laser frequency stabilization and frequency comb technology, measurements on molecular hydrogen ions can in principle be performed with accuracies at a similar scale as the precision of calculations. An advantageous property of HD$^+$ is its electric dipole moment, which enables the possibility to induce electric dipole transitions between vibrational states. By comparing high-precision theoretical results with high-precision experimental data, one can test the validity of a theory describing the system.

Besides testing theory, such a theory-experiment comparison can serve as a means to determine (improved) values of fundamental constants like the fine structure constant $\alpha$ or the proton-to-electron mass ratio $\mu^1$, which are independent parameters in electromagnetic theory. In case of a determination

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$^1$Strictly speaking the proton-to-electron mass ratio is not a fundamental constant, because it contains the electron and proton masses. The former is dependent on the coupling between the electron and Higgs fields. The latter depends mostly on quark and gluon interactions described by quantum chromodynamics. But for the description of atoms and molecules at the 10$^{-11}$ level this is of minor relevance.
of a fundamental constant, one *a priori* assumes that theory is correct, and *vice versa* for testing theory.

The HD$^+$ molecule is a suitable system for a new determination of $\mu$. For vibrational and rotational transitions in HD$^+$ the transition frequencies approximately scale as

$$h\nu_{\text{vibr}} \sim R_\infty \sqrt{m_e/\mu_{\text{red}}} \quad h\nu_{\text{rot}} \sim R_\infty m_e/\mu_{\text{red}}$$

where $\mu_{\text{red}}$ is the reduced mass of the two nuclei, $m_e$ is the electron mass and $R_\infty$ the Rydberg energy. The expression $m_e/\mu_{\text{red}}$ contains the proton-to-electron and proton-to-deuteron mass ratios. The determination of the proton-to-electron mass ratio from the $(v,L):(0,2)\rightarrow(8,3)$ measurement is described in Chapter 5. Besides testing existing theories, high precision measurements in HD$^+$ can provide constraints on new physical theories as well, which is introduced below.

Another interesting application is the realization of clocks with high stability and high accuracy. Essentially a clock is a system which repeatedly sends a signal to the outside world. If this repetition rate is stable (tomorrow the same rate as today), the clock is said to be stable. Likewise, if this rate can be determined with high accuracy, the clock is said to be very accurate. The highest stabilities and accuracies are currently found in single ions clocks \[3–7\] and optical lattice clocks \[8–12\], nowadays having fractional stabilities of $\sim 10^{-16}$ at 1 s and fractional inaccuracies up to order $10^{-18}$, which is nearly two orders of magnitude more accurate than cesium fountain clocks which currently define the second \[13\]. HD$^+$ or H$^+_2$ clocks have been proposed \[14, 15\] which can be used to put new constrains on temporal variation of $\mu$ in the current epoch, i.e. variation of the proton-to-electron mass ratio in time can be measured in a laboratory setup \[14, 16\]. Using techniques like quantum logic spectroscopy \[17–19\] and ro-vibrational state preparation \[20, 21\], realization of inaccuracies in HD$^+$ or H$^+_2$ clocks at the $10^{-16}$ level should become feasible, which allow searches for a temporal $\mu$ variation with sensitivities at $10^{-16}$ per year and below.

### 1.3 Quantum Electrodynamics

The theory submitted to the high-precision test described in this thesis is called *quantum electrodynamics* (QED). In this section we summarize this theory briefly in a conceptual way. A thorough but didactic explanation of quantum electrodynamics can be found in [22].

Quantum electrodynamics is a quantum field theory (QFT) developed in the late 1940s and early 1950s by (among others) Hans Bethe, Julian Schwinger, Sin-Itiro Tomonaga, Richard Feynman and Freeman Dyson [23]. It describes the electromagnetic interaction at the quantum level and incorporates both special
relativity and quantum mechanics. In ordinary quantum mechanics, observables are treated as operators, while in quantum field theory the field itself is treated as an operator. Calculations in QFT are carried out in a framework of approximations, for example, particle interactions are treated in a perturbative way using propagators and quantized path integrals. Feynman developed a tool to write down the first few orders of perturbative approximations of a scattering matrix in a diagram, which is nowadays called the Feynman diagram [24,25].

During its initial development, QED was plagued by theoretical difficulties such as divergences and infinities appearing in integrals. Those were solved by introducing a trick called renormalization, which is intimately connected to the concept of self-energy. This means that particles can interact with virtual particles. For example, an electron may interact with a virtual photon (Fig. 1.2a) or a photon which is temporarily transformed to a virtual positron-electron pair (Fig 1.2b), which is also called vacuum polarization. These two phenomena are responsible for the famous Lamb shift, observed in 1947 by Lamb and Retherford in the hydrogen atom [26].

Despite the apparent approximative characteristic, QED has been tested with very high precision in several kinds of experiments. The group of Gabrielse determined in 2008 the electron g-factor, which relates the electron spin to its magnetic moment, with less than one part per trillion (1 ppt) precision, using a single electron in a Penning trap [27,28]. Combining this result with the state of the art calculations of Aoyama et al. [29,30] where 12672 Feynman diagrams of tenth order were evaluated, a new value of $\alpha^{-1} = 137.035999173(35)$ was obtained (0.25 ppb accuracy). In 2011, the group of Biraben in Paris obtained a similar result for $\alpha$ through the determination of the ratio of Planck’s constant and the rubidium atomic mass, $h/M_{\text{Rb}}$, by measuring Bloch oscillations in rubidium atoms [31]. Here the relation

$$\alpha^2 = \frac{2R_\infty}{c} \frac{M_{\text{Rb}}}{m_e} \frac{h}{M_{\text{Rb}}}$$  (1.2)

was used, which led together with the most up to date determinations of $M_{\text{Rb}}$ [32,33], to a new value of $\alpha^{-1} = 137.035999044(90)$ (0.66 ppb accuracy). A combination of these experimental and theoretical results led to a test of QED theory at the sub-parts per billion level, which is far more stringent than the inventors of QED ever envisioned [28,34].

1.4 Calculations of few-body molecules

For high-precision calculations on few-body molecules, a successful approach is to consider different regimes of physics and subsequently add their results: the non-relativistic part, which is solved by using the Schrödinger equation, relativistic corrections (obtained through the Breit-Pauli Hamiltonian to leading
1.4. Calculations of few-body molecules

(a) electron self-energy  
(b) vacuum polarization

Figure 1.2: Feynman diagrams of first order contributions of a) the electron self-energy and b) photon self-energy, also called vacuum polarization.

order), radiative corrections, finite nuclear size effects and hyperfine structure. The radiative corrections contain the interactions of the molecular constituents with virtual particles (most of them described by QED) and therefore this part is often called ‘QED corrections’.

In 1993, Moss et al. calculated the dissociation energies of 462 states in H$_2^+$ and 619 states in HD$^+$ with a relative accuracy of $\sim 5 \times 10^{-9}$ including leading order relativistic and leading order radiative corrections (order $\alpha^2 R_\infty$ and $\alpha^3 R_\infty$ respectively [35,36]. The recent results of Korobov et al. surpass this accuracy by two orders of magnitude. In these results, calculations of molecular hydrogen ions and antiprotonic helium are presented with precisions at the $10^{-11}$ level including corrections up to the order $\alpha^8 R_\infty$ [1,2]. In the remainder of this section, we give a brief overview of the customary calculation methods of the non-relativistic part. An introduction of the corrections can be found in [37,38].

A commonly used first step for calculations of simple molecules is the Born-Opperheimer (BO) approximation [39], in which the wavefunction of the molecule is split into a nuclear and electronic part, and in which the nuclei are considered clamped, thus ignoring their kinetic energy. Subsequently the electronic energy levels are calculated by solving the Schrödinger equation for various values of the internuclear distance. Then the motion of the nuclei subject to the electronic forces (which are a result of the determined electronic energy) is calculated. In the next step of refinement, called the adiabatic approximation (also called Born-Oppenheimer diagonal correction), the dependence of the electronic energy on the nuclear motion is included. In the ultimate step of refinement, the electronic and nuclear motions are coupled. The difference between the result of this level and the adiabatic correction is called the non-adiabatic correction. An important contribution to non-adiabatic correction methods is the derivation of an effective Hamiltonian by Bunker and Moss based on perturbative methods, and accurate up to second order in perturbation theory [40]. Today, this method is still used to calculate energies in simple molecules.

As a three-body system, the molecular hydrogen ion distinguishes itself from
more complex molecules in that it allows an analytical solution of the Born-Oppenheimer three-body Hamiltonian [41]. However, this solution does not come in a closed form, and various methods to find approximate closed-form expressions to the solution have been developed (see, for example, Refs. [41, 42], and references therein). During the late 1990s, numerical methods beyond the Born-Oppenheimer approximation were developed, giving solutions to the non-relativistic three-body problem which are essentially exact up to a certain number of digits [43, 44]. Later work by various groups improved the precision [45–47], in some cases up to 30 digits [48]. However, today’s most accurate theoretical predictions are based on the numerical method developed initially by Korobov [44].

An alternative method for high precision calculation on molecules is the use of the Dirac equation which makes the need for relativistic corrections unnecessary because this equation incorporates special relativity [49, 50]. This method seems attractive at first hand, but fundamental complications arise due to the fact that the Dirac equation is a one-particle equation and HD$^+$ consists of three bodies. This introduces a problem with the definition of time, since each body has a different inertial system. Therefore, only one constituent, for example the electron, can be described by the Dirac equation and for the nuclei customary relativistic corrections are still required. Another approach to circumvent this problem is an effective field theory called non-relativistic QED (NRQED), which has been successfully used for the molecular hydrogen ion (see for example [51]).

1.5 Spectroscopy experiments in molecular hydrogen ions

Of all molecules, neutral hydrogen, H$_2$, is the most abundant molecular species in the universe. Together with its isotopomer HD it plays an important role in astrophysics and cosmology. Molecular hydrogen serves as a main cooling agent during formation of stars and gas condensation because kinetic energy can be efficiently absorbed in their rich structure of rotational and vibrational energy levels. Due to the presence of many strong lines in their spectra, neutral hydrogen molecules are attractive objects of study and they have been extensively studied by astronomical observations and laboratory experiments.

Interstellar concentrations of ionic hydrogen molecules however, are much lower. One cause is the efficient reaction of H$_2^+$ with H$_2$ to the relatively stable species H$_3^+$ [52, 53]. Furthermore, their spectral lines are weak due to forbidden ro-vibrational and electronic transitions (due to selection rules and Franck-Condon overlap respectively). The densities of HD$^+$ are even a much lower than the H$_2^+$ densities due to the D/H ratio of $10^{-4}$–$10^{-5}$ in the universe. Thus both,
in interstellar clouds and laboratory setups, the number of ionic species stays far behind the numbers of neutrals and they are much harder to observe. For these reasons, spectroscopy on molecular hydrogen ions have remained elusive for a long period, and significant achievements were not obtained before the invention of suitable lasers, ion beam and ion trapping techniques.

The first spectroscopic measurements on H$_2^+$ were carried out by Jefferts in 1969, who measured 30 magnetic rf transitions between hyperfine levels in ro-vibrational states [54,55]. In this experiment, a linear quadrupole trap was used for ion trapping and a mercury lamp for photodissociation. Based on these results the coefficients of the spin Hamiltonian of H$_2^+$ were determined. The 1.5 kHz experimental uncertainty challenged theorist for nearly five decades, and only very recently the observations of Jefferts could be explained by theory within the experimental uncertainty [56]. Some years later in 1976, six ro-vibrational lines in HD$^+$ were measured by Wing et al. [57] with 1 part-per-million accuracy and partially resolved hyperfine structure.

An important contribution in the development of molecular hydrogen ion spectroscopy and theory is the work of Carrington et al. [58–62], which has been carried out in the 1980s and early 1990s but is still considered as a benchmark in the field. This work includes measurements as well as calculations of microwave and infrared spectra belonging to high $v$ and high $L$ ro-vibrational or electronic transitions in HD$^+$ and D$_2^+$. Also the nuclear hyperfine structure in the electronic transition $2p\sigma_u(v, L) = (0, 2) \rightarrow 1s\sigma_g(v, L) = (18, 3)$ in H$_2^+$ has been measured. With theoretical and experimental accuracies in the order of 0.0001 cm$^{-1}$ these results provided the most stringent tests of theory of 3-body molecules at that time.

More than a decade later, in 2007, Koelemeij et al. performed laser spectroscopy of the $(v,L):(0,2)\rightarrow(4,3)$ transition in HD$^+$ at 1395 nm with 2 ppb accuracy [63]. In 2012, the Düsseldorf group published the first detection of a purely rotational transition [21]. In the same year results on HD$^+$ were presented in which the individual hyperfine states of the $(v,L):(0,0)\rightarrow(1,1)$ transition were addressed. This led to a 1.1 ppb precision in the determination of the line center$^2$ [64].

Another approach to determine energy intervals in molecular hydrogen ions is via spectroscopy of Rydberg states of neutral molecules. This was recently demonstrated by Haase et al. [65]. By using multichannel quantum-defect theory (MQDT) [66,67] spectroscopic results could be extrapolated to a pure rotational energy splitting in para-H$_2^+$.

$^2$This result differs by 2.4σ from the theoretical prediction [2] of this line.
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1.6 New physics

The physics describing electronic, vibrational and rotational transitions in light molecules is fully described by effects of electromagnetism, i.e. by QED theory. The effects of the other forces, strong, weak and gravity, are many orders of magnitude smaller than the uncertainties of both experiment and QED theory and are therefore negligible. This means that any presence of new physics in a molecule could be measured as a deviation from QED theory. Analogous to the Cavendish torsion experiment detecting gravitation between lead spheres [68], hypothetical ‘fifth forces’ at the Ångström scale could be measured in diatomic molecules like $\text{H}_2$, $\text{D}_2$, $\text{H}_2^+$ and $\text{HD}^+$. In [69] and [70] Salumbides et al. explain that one can put new constraints on the existence of fifth forces between hadrons by measuring the ro-vibrational transitions in diatomic molecules, while searching for deviations between experiment and (QED) theory.

In quantum field theory, each fundamental interaction is mediated through gauge bosons, which means that any force can be phenomenologically parameterized by a Yukawa-type potential,

$$ V_5(r) = \alpha_5 \frac{\exp(-r/\lambda)}{r} \hbar c \equiv \alpha_5 Y(r), $$

where $\alpha_5$ is the coupling strength and $\lambda$ the effective range of the force related to the mass $m_\gamma$ of the gauge boson by $\lambda = \hbar/m_\gamma c$. Considering ro-vibrational transitions in diatomic molecules, energy contributions $\langle V_5 \rangle$ originating from a fifth-force potential can be calculated from perturbation theory. Combining this with experimental measurement uncertainties, new limits can be set on the strength of the coupling constant $\alpha_5$. Although the $\langle V_5 \rangle$ sensitivity in transitions in neutral hydrogen molecules is higher, the current precision of both theory and experiment in the ionic species $\text{HD}^+$ is an order of magnitude better, and the latter give the tightest constraints on $\alpha_5$ and $\lambda$.

Not only hypothetical fifth forces can be probed with molecular hydrogen. String theory predicts the presence of compactified dimensions in addition to the (3+1) observable ones. According to the framework of Arkani-Hamed, Dimopoulos, and Dvali [71] (ADD model) molecular hydrogen molecules can be used to set constraints on the compactification radii of extra dimensions [72]. In addition, another theory called the Randal-Sundrum models [73, 74] (RS scenarios) can be used in combination with molecular spectroscopy data to derive limits on the curvature of space due to branes which may be hiding in higher dimensions, and on the separation between ‘our’ brane and the hidden brane.
In Chapter 2 the setup of the HD$^+$ experiment is described. First, the concept of ion traps is introduced, followed by the derivation (and solution) of the equations of motion of a single trapped ion. Chapter 3 describes a novel widely tunable offset lock used in the 626 nm laser system, which is an essential part of the laser cooling system. The content of this chapter has been published in Optics Express [75]. Chapter 4 forms the core of this thesis and presents the high precision spectroscopy measurement on HD$^+$ in detail. Here the spectroscopic data and the model which constructs the fit function of the (0,2)$\rightarrow$(8,3) spectrum is explained, and various systematic effects that play a role in the spectroscopy are discussed. In Chapter 5, where this measurement is discussed in concise form, the determination of a new value for $\mu$ and new constraints of hypothetical fifth forces based on the spectroscopic results are presented. This chapter has been published in journal Nature Communications [76].