

Erratum

The digital version of the doctoral thesis MATTER-ANTIMATTER INTERACTIONS. The hydrogen-antihydrogen system and antiproton-matter interactions by Henrik Stegeby differs from the printed book in the following way.

- The Swedish summary is one page long in the printed version, in the digital version it has been extended to two pages.
- The table of contents and pagination differs due to the extended Swedish summary.
- In the summary of paper I a missing minus sign has been corrected in the digital version in eq. (4.2).
- In the summary of paper IV the bold face style on the coordinates R and q in eq. (4.17) has been corrected in the digital version, and the text describing the work in progress compared to the manuscript has been clarified.
- Missing minus signs in front of some of the iw terms eq. (5.74) in the appendix has been corrected in the digital version.



UPPSALA
UNIVERSITET

*Digital Comprehensive Summaries of Uppsala Dissertations
from the Faculty of Science and Technology 1674*

MATTER-ANTIMATTER INTERACTIONS

*The hydrogen-antihydrogen system and antiproton-
matter interactions*

HENRIK STEGEBY



ACTA
UNIVERSITATIS
UPSALIENSIS
UPPSALA
2018

ISSN 1651-6214
ISBN 978-91-513-0348-2
urn:nbn:se:uu:diva-348667

Dissertation presented at Uppsala University to be publicly examined in Room Å4001, Ångströmlaboratoriet, Lägerhyddsvägen 1, Uppsala, Wednesday, 13 June 2018 at 13:15 for the degree of Doctor of Philosophy. The examination will be conducted in English. Faculty examiner: Professor Dage Sundholm (University of Helsinki).

Abstract

Stegeby, H. 2018. MATTER-ANTIMATTER INTERACTIONS. *The hydrogen-antihydrogen system and antiproton-matter interactions. Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology* 1674. 103 pp. Uppsala: Acta Universitatis Upsaliensis. ISBN 978-91-513-0348-2.

Ever since antiparticles were discovered their nature has been something of a mystery. They were postulated to be identical to regular particles except for having opposite charge, but this would imply that an equal amount of antiparticles and particles should have been created at the beginning of time. However, everywhere we look the Universe seems to be constituted of regular particles, giving rise to the question whether there is something else that differentiates antiparticles from regular particles, or if there is something amiss in the Standard Model of particle physics.

This thesis focuses on a central system of study in this field, the hydrogen-antihydrogen system and the theory surrounding it, as well as an expansion into systems with an antiproton interacting with small molecules, bridging the fields of quantum physics and quantum chemistry.

Methods expanding on the Born-Oppenheimer approximation for the interaction between the two atoms are presented. The resulting 2-body interaction potential is then used for creating a part of the basis in a non-adiabatic 4-body method in order to look for resonance states whose existence could impact cross-sections of hydrogen-antihydrogen scattering. The eigenfunctions obtained from the non-adiabatic method are used by extracting the 2-body hadronic density function and comparing it to the adiabatic wave function, for measuring the adiabaticity of the hydrogen-antihydrogen system.

The antiproton-matter interaction is first investigated by a quantum dynamical approach of an antiproton scattering on molecular hydrogen, common products in high-energy collision experiments, continued by a study of the potential energy surfaces of an antiproton interacting with a range of functional groups present in the human body.

Keywords: antimatter, antiproton, matter-antimatter interactions, hydrogen-antihydrogen system

Henrik Stegeby, Department of Chemistry - Ångström, Theoretical Chemistry, Box 518, Uppsala University, SE-75120 Uppsala, Sweden.

© Henrik Stegeby 2018

ISSN 1651-6214

ISBN 978-91-513-0348-2

urn:nbn:se:uu:diva-348667 (<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-348667>)

”If we accept the view of complete symmetry between positive and negative electric charge so far as concerns the fundamental laws of Nature, we must regard it rather as an accident that the Earth (and presumably the whole solar system), contains a preponderance of negative electrons and positive protons. It is quite possible that for some of the stars it is the other way about, these stars being built up mainly of positrons and negative protons. In fact, there may be half the stars of each kind. The two kinds of stars would both show exactly the same spectra, and there would be no way of distinguishing them by present astronomical methods.”

– Paul A.M. Dirac, 1933.

List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

- I **Impact of the strong force on the Coulombic decay of a hydrogen - antihydrogen molecule**
P. Berggren, H. Stegeby, A. Voronin, and P. Froelich, *J. Phys. B: At. Mol. Opt. Phys.* **41** (2008) 155202
- II **Variational calculations for the hydrogen–antihydrogen system with a mass–scaled Born–Oppenheimer potential**
H. Stegeby, K. Piszczatowski, H. O. Karlsson, R. Lindh, P. Froelich *Cent. Eur. J. Phys.* **10(5)** (2012) 1038-1053
- III **Resonance States in the Hydrogen-Antihydrogen System from a Nonadiabatic Treatment**
H. Stegeby and K. Piszczatowski *J. Phys. B: At. Mol. Opt. Phys.* **49** (2016) 014002
- IV **Two-body hadronic densities from the four-body wave functions for the H– $\bar{\text{H}}$ system**
H. Stegeby, K. Piszczatowski and T. Yamashita, manuscript.
- V **Wave Packet Simulations of Antiproton Scattering on Molecular Hydrogen**
H. Stegeby, M. Kowalewski, K. Piszczatowski and H. O. Karlsson *J. Phys. B: At. Mol. Opt. Phys.* **48(19)** (2015) 195204
- VI **Overview of antiproton affinities for functional groups relevant in particle-beam cancer therapy**
H. Stegeby, submitted to *Cancer Reports*.

Reprints were made with permission from the publishers.

The author's contribution to the papers

Paper I: Participated in planning the study, participated in performing some of the numerical calculations and participated in analyzing the results.

Paper II: Participated in planning the study, developed the programs used (except for a polynomial fitting routine), performed most of the numerical calculations, participated in analyzing the results, participated in writing the manuscript and participated in answering the questions of the reviewers.

Paper III: Planned the study, chose numerical methods and developed the programs used, performed the numerical calculations, analyzed the results, and with guidance from the co-author wrote the manuscript and answered the questions of the reviewers.

Paper IV: Participated in planning the study, participated in developing the programs used, participated in performing the numerical calculations, participated in analyzing the results and participated in writing the manuscript.

Paper V: Participated in planning the study, participated in developing the programs used, performed the numerical calculations, participated in analyzing the results, wrote most of the manuscript and participated in answering the questions of the reviewers.

Paper VI: Sole author.

Contents

1	Introduction	1
1.1	A brief history of antimatter	1
1.2	Quantum Mechanics	10
2	Methodology	14
2.1	Ritz variational method	14
2.2	Gaussian Expansion Method	16
2.3	Perturbation theory for the interaction between two atoms	19
2.4	Born-Oppenheimer and adiabatic approximation	23
2.5	Scattering theory	31
2.6	Resonance states from real and complex scaling	34
2.7	Quantum Dynamics wave propagation	37
2.8	Molecular electronic structure theory	40
3	Hydrogen–antihydrogen system and the 4-body method	46
3.1	The $H\bar{H}$ Hamiltonian	46
3.2	The $H\bar{H}$ wave function expansion	47
3.3	$H\bar{H}$ 2-body interaction potential	49
4	Developments	53
4.1	Paper I – Including strong force interaction	53
4.2	Paper II – Mass-scaled adiabatic potential	56
4.3	Paper III – Resonance states in the $H\bar{H}$ system	59
4.4	Paper IV – Adiabaticity of the 4-body wave function	62
4.5	Paper V – Antiproton scattering on H_2	65
4.6	Paper VI – Antiproton affinities for functional groups	68
5	Summary	70
	Appendix A: Matrix elements calculations	74
	Appendix B: The Multipole expansion	84
	Appendix C: Separation of oscillations and rotations	91
	Appendix D: Derivation of the stabilization method	95
	References	99

1. Introduction

1.1 A brief history of antimatter

It all started with fire¹. Fire as a source of warmth, protection, food and light. At the end of the 19th century, fire in the shape of lanterns, candles and torches were still the main sources of light along the streets and inside homes. The convenience of electricity and Thomas Edison's energy efficient light bulb was a significant improvement of the living standard and a stepping stone in human evolution. Now, light could be emitted anywhere in a much more efficient, safe and affordable way. The road to the invention of the light bulb was founded on the collected work of many, but some of the most noteworthy contributions are the studies on magnetism and electricity by William Gilbert at the end of the 16th century, the discovery of Alessandro Volta's battery cell to which he connected a glowing copper wire at the end of the 18th century [1], and the production of vacuum first produced in a laboratory in 1643 by Evangelista Torricelli while he was inventing the mercury barometer.

The concept of vacuum or nothingness, has been debated since ancient Greek times, a concept closely related to the nature of light. Since light could obviously propagate through vacuum, the consensus after Thomas Young demonstrated the wave properties of light in his famous double-slit experiment² [3], vanquishing Newton's corpuscular (having a body, particle) theory of light and replaced by Huygen's theory that light is a wave [4], was that vacuum was not empty space, but some medium that the light wave propagated through (coined *ether* by Newton in 1730 [5]) similarly to how sound waves are propagating through air. Light was considered to be a wave of undulations (c.f. vibrations) in ether, rather than a free particle moving in empty space. In 1861 James Clerk Maxwell, summarizing and extending the work pioneered by Michael Faraday on electricity and magnetism some 30 years earlier, proposed that light was a wave caused by fluctuations between electric and magnetic fields [6]. His work was supported by papers presenting his equations on electromagnetic interaction during the years 1861 - 1873, equations that was verified by a variety of experiments (e.g. the experimental

¹Or did it all start with the invention of parents, from whom all great minds originate?

²The experimental set-up by Young to demonstrate wave properties is by producing a diffraction pattern by having a source emitting particles or waves on two slits, where the diffraction pattern is visible on a screen behind the two slits (the *double-slit experiment*). Young thought that this proved the wave theory of light, but it has been shown that particles as big as molecules with 810 atoms also display this diffraction pattern [2].

value of the speed of light was in close agreement to his electromagnetic wave equation), but the nature of the medium what the wave propagated in was not clarified. Ether was believed to be much less dense and much more elastic than air, such that it would not leave noticeable traces on the movements of galactic bodies. However, tests of the existence of this ether done by Albert A. Michelson and Edward W. Morley in 1887 showed that light seemed to move at a constant speed regardless of the direction and velocity in which the source and detector moved, defying the ideas of a surrounding ether medium in which light would propagate. The notion that vacuum could be completely empty, just nothingness, continued to befuddle the great minds, and the Michelson–Morley experiment did not completely refute the idea of ether for everyone. To explain the movement of light and the results of the experiment, new theories concerning space, time and relative motion was evolved, primarily by Hendrik Lorentz in the years 1892-1895. In his work he introduced the concepts of reference frames, local time and a rigorous description of length contraction (a moving body would contract in the direction of motion, first postulated by George Fitzgerald in 1889 [7]) to explain the null-results in the Michelson–Morley experiment and keep the idea of ether alive. Lorentz’s work attracted the interest of Jules Henri Poincaré. In 1905 Poincaré managed to make Maxwell’s equations invariant under Lorentz’s transformations, and in doing so he discovered the fully relativistic Lorentz transformations in their modern symmetrical form. Soon after this achievement, as a consequence of these transformations, he proposed the existence of gravitational waves that propagates at the speed of light.

At this time, the growing understanding of electricity from the discovery of cathode rays by Michael Faraday in 1838 [8], the discovery of the photovoltaic effect by Alexandre Edmond Becquerel in 1839 displaying the relation between light and electricity [9], and the subsequent discoveries of the electron by J. J. Thomson in 1897 when he noticed the particle nature of the cathode rays and the photoelectric effect by Heinrich Hertz in 1887 [10], led to the idea that also the energy of light could come in discrete packets (like particles) instead of in a continuous flow (like waves). The idea that energy states of a physical system can be discrete had already been used by Ludvig Boltzmann in his work on statistical thermodynamics in 1872 [11], and Boltzmann suggested to Planc in a paper in 1897 to use his statistical discrete (quantized) methods for solving a major problem of regarding light as a wave for the heat radiation of bodies (the black-body radiation described by Gustav Kirchhoff in 1860 [12]). Three years later, Boltzmann’s quantized energy level idea was used by Max Planc in 1900 to solve the *ultraviolet catastrophe* problem in black-body radiation, where the famous Planc constant h was introduced as a proportionality constant between the discretized energies and frequencies of the radiation [13]. This was the birth of the *old quantum mechanics*.

Planc's proportionality constant h was used by Einstein in 1905, where he postulated that this energy quanta was in fact the energy of one light-particle as a real physical (quantum) particle, later coined *photon*, and with this he was able to explain the experimental data in the photoelectric effect [14].

Armed with the recent understanding of the photon, the failure to detect ether, and with Poincaré's and Lorentz's work on relativity, Einstein continued his marvellous year of 1905 (*annus mirabilis*) and proposed his special theory of relativity [15], postulating that ether does not exist and that the speed of light is constant with respect to any given medium (as observed in the Michelson–Morley experiment) and that space and time are not invariant under motion (as deducted by Lorentz and Poincaré) and with these postulates aggregated together, his famous formula $E = mc^2$ for a particle at rest was derived (although Einstein denoted energy with L and wrote the equation as $m = L/c^2$). Furthermore, there followed the quantization of charge by Robert A. Millikan in 1910 when he measured the charge of the electron in his famous oil-drop experiment³ [17, 18], and in 1913 the discrete energy spectrum of atoms was explained with Niels Bohr's model of the atom, improving on Rutherford's 1911 nucleus model of the atom [19] and effectively ending J.J. Thomson's *plum-pudding* model [20], from his proposal that the energy levels of electrons are discrete [21].

In 1907, Einstein's former teacher, Hermann Minkowski showed that Einstein's special theory of relativity could be seen as a theory of four-dimensional space-time (*Minkowski space-time*), a notion that at first was seen as mathematical trickery by Einstein but later he realised that he needed this (and another technique taught by Minkowski) geometrical view for the development of his much more evolved general theory of relativity presented in 1915⁴ [24–27]. Two years later, Frank Watson Dyson conceived an experiment that would give the perceived positions of the background stars near edges of the sun their position according to Einstein's general theory of relativity (about twice as much as predicted by Newtonian physics), and during the 1919 eclipse these data was confirmed by a team led by Arthur Eddington [28]. The news of Einstein's confirmed theory of gravitation was published in New York Times, making his theory known worldwide.

The questions concerning light and electrons and their dual properties as both waves and particles was however still an unsolved issue. It seemed as if they could be seen as both waves and particles, since there were experiments and equations in good agreement with both descriptions. Maxwell's equations

³Perhaps some credit should also go to his graduate student Harvey Fletcher for his assistance in these experiments [16].

⁴Minkowski's life-long friend David Hilbert was also working on the general relativity field equations, and presented his work in the same year as Einstein [22], but Hilbert has claimed no priority for the theory of general relativity and Einstein published many articles along the way to his final equations, e.g. [23], part-results that could easily be used by his contemporaries. Thus, one can assume that credit has rightly gone to Einstein.

for the description of light as electromagnetic waves and the photon particle description where both predicting experimental outcomes, but in different contexts. In 1924, Einstein's special theory of relativity and Planck's energy quanta were used by Louis de Broglie to derive a formula relating the energy of a particle to its wavelength, stating that all matter displays a wave-particle duality [29].

Shortly after de Broglie's wave-particle duality equation, Werner Heisenberg, with help from his collaboration with Hendrik Anthony Kramers [30], was working on a way of transforming equations from the old quantum mechanics of Bohr and Einstein into what he called *theoretical quantum mechanics* [31] in which only relations between observable quantities occur. Bohr had showed how to predict the frequencies of radiation from an atom, and Heisenberg wanted to formulate a theory that could predict the intensities of the radiation. By replacing the classical remnant for calculating the intensities using Fourier amplitudes and instead introduce a set of of amplitudes that depend only on the initial and final state of the atom, and by introducing his idea of *non-commutativity* of kinematic quantities⁵, he took some important steps towards his goal.

An important equation in Heisenberg's paper was identified by Max Born as in need of an extended matrix formulation, a technique Born had learned during his study under Jakob Rosanes. Only a few months after Heisenberg had published his paper, Born and his former student Pascual Jordan published their paper, improving on Heisenberg's formulation [33]. Their paper was followed by two papers by Paul Adrien Maurice Dirac where he extended the description of non-commutativity and introduced generalizations to other systems [34, 35]. The matrix formulation of quantum mechanics ended with a three-man paper together with Heisenberg, Born and Jordan [36] in the same year as Heisenberg's first paper.

Meanwhile, building on de Broglie's work, Erwin Schrödinger developed quantum wave mechanics and the non-relativistic Schrödinger equation in a series of five papers [37–41] as an approximated generalization of de Broglie's equation.

In the same era, the *Pauli exclusion principle* was introduced by Wolfgang Pauli, helped by Edmund Clifton Stoner's findings concerning the degeneracy of energy levels of the atom [42], by introducing an additional quantum number for the electron that was later identified as the *electron spin* [43].

The formulation of matrix quantum mechanics and Schrödinger's quantum wave mechanics are viewed as the birth of *Modern quantum mechanics*.

Schrödinger and Carl Eckhart would the following year demonstrate that the two flavours of modern quantum mechanics, his own wave equation and

⁵Non-commutativity for two operators \hat{A} and \hat{B} , means that $\hat{A}\hat{B} \neq \hat{B}\hat{A}$ [32].

the matrix representation developed by Heisenberg, Born, Jordan and Dirac were equivalent⁶.

In 1927, the non-commutativity of observables, such as the position of a particle x , and its momentum p , led Heisenberg to formulate his *uncertainty principle*: $\sigma_x \sigma_p \geq \hbar/2$, which is saying that if you increase the accuracy of the position of a particle, the accuracy of the momentum of the particle decreases (and likewise for any other non-commutable observable pair, such as energy and time)⁷.

Heisenberg's uncertainty principle entails the following interesting thought experiment: if we shrink a container of vacuum, we would know that there is nothing inside, no particle that can carry a momentum, but as we decrease the volume of the container we will increase the accuracy of the position of the system that has zero momentum. The uncertainty principle implies that as we do so, the momentum will no longer be exactly zero. For momentum to be non-zero there needs to be a particle that can carry this momentum, so it seems as if particles must be created out of vacuum by this fluctuation of uncertainty. This so called *quantum fluctuation* stemming from Heisenberg's uncertainty principle is a key concept behind the big bang theory, about how the universe could be created out of nothing⁸. But can particles really be created out of vacuum, out of nothing? At this time, this seemed to be breaking the energy conservation rule, in particular the energy-momentum 4-vector conservation as formulated in Einstein's special theory of relativity. The concept of vacuum and nothingness was still a conundrum.

In the same year, 1927, the wave property of the electron was demonstrated by G. P. Thomson, the son to J. J. Thomson who demonstrated the particle property of electricity, simultaneously accidentally discovered by Clinton Davisson and Lester Germer while studying the surface of nickel, and the data from the Davisson-Germer experiment was used to confirm Louis de Broglie's relation between a particles wavelength and energy.

The unanswered nature of wave-particle dualism⁹, Heisenberg's uncertainty

⁶However, their demonstration was not foolproof [44].

⁷On a more technical note, this principle is true for all objects described by a wave function, since a function represented in two orthonormal bases in Hilbert space are Fourier transforms of each other, where a sharp localised wave in one base becomes distorted and de-localised in the other, and vice versa.

⁸On a humorous note, if Heisenberg had never formulated his principle of uncertainty, would the universe still exist?

⁹One such question is the measurement problem, a peculiar phenomenon that can be seen in Young's double slit experiment where a diffraction pattern appears for waves, and for particles on the quantum scale. When you place a detector on the two slits, detecting through which of the two slits each particle passes, the diffraction pattern disappears. It seems that if we do not measure where the particle is, it behaves like it is at both slits at the same time, thus producing a diffraction pattern. The most common explanation for this in quantum theory is that the state of the particle's position is described with a probability distribution, and if we measure

principle and the solid grounding of Einstein's relativity theories, led notable scientists such as Norbert Wiener¹⁰, Oscar Klein, Walter Gordon, Vladimir Fock, Louis de Broglie, Théophile de Donder, Fritz Reiche, Leon Rosenfeld, Pascual Jordan, Wolfgang Pauli, John Von Neumann, Gregory Breit and others [47], pioneered by Dirac's never ending desire to turn non-relativistic physics into its relativistic form [48–53], to develop relativistic quantum mechanics. In his endeavours Dirac formulated his relativistic quantum mechanical equation for the electron, to which there were two solutions¹¹, one for a negatively charged electron with positive energy (two states, one for spin up and one for spin down electrons), and one for a positively charged electron with negative energy. The consensus at the time dictated that a particle can not have negative energy, and at first Dirac ignored this second solution to his equation, but after some hesitation stood by his mathematical findings. His assertion of the physical reality of the negative energy solutions was met with harsh criticism by his colleagues¹².

Indeed, Dirac's claim had some theoretical hurdles to overcome. If an electron could occupy a negative energy state in an atom, there is nothing to stop an electron from jumping down past the ground state of the atom, thus sending out a photon with an energy higher than what is permitted and observed by experimental results. In fact, electrons would be able to emit an infinite amount of energy by repeatedly jumping down to increasingly lower energy states. Dirac's answer to this was to propose that all the negative energy states are occupied, theorizing the existence of some sort of "sea" of negative energy electrons, whereby Pauli's exclusion principle these states would be inaccessible. However, it would be possible for a negative energy electron to absorb a photon and make a jump up to a positive energy state, leaving a "hole" in the sea of negative electrons¹³, making it detectable as a particle identical to an electron, but with positive charge. Dirac's proposed infinite *Dirac sea* of particles with negative energy implies a new way of thinking about vacuum, and it was at the time more of a theoretical model than a view

where it actually is, the state collapses (the probability distribution becomes a measurement and the particle position is determined to an actual value with probability 1). Before we measure however, the position of the particle really is at both places at the same time (see Schrödinger's thought experiment with a cat that is both dead and alive at the same time [45]). Another explanation concerns the impossibility of measuring without disturbing the system.

¹⁰Norbert Wiener entered the quantum mechanical stage by introducing the quantum mechanical *operators* together with Born in a paper in 1926 [46].

¹¹just as the equation $x^2 = 4$ has the two solutions $x = 2$ and $x = -2$.

¹²Dirac's friend Heisenberg was quoted saying "The saddest chapter of modern physics is and remains the Dirac theory...I regard it as learned trash which no one can take seriously" [54].

¹³At first Dirac thought that the "hole" that was left behind in the previously completely filled sea of negative electrons after a negative energy electron jumped up to a positive energy state could be the proton, but he realised that this particle must have spin, mass and all the other quantum numbers in consideration equal to that of an electron, except for the opposite charge.

of reality. Nonetheless, Dirac interpreted his equation to mean that for every particle, there is a corresponding anti-particle.

A few years later, in 1932, Carl Anderson experimentally verified the existence of the positive electron and named it the *positron*, by studying photographs of cosmic rays¹⁴ in a cloud chamber [55]. The first anti-particle was found.

In 1929 Ernest Lawrence invented the cyclotron, a machine for accelerating and colliding particles of high energies in the hopes of unravelling the laws of quantum physics and the constituent parts of quantum particles. After the positron was found, and with Dirac's belief that all particles have a corresponding anti-particle, much of the focus was on finding the anti-particle corresponding to the proton. However, the first cyclotron built by Lawrence was not capable of accelerating protons to the optimum energy needed, so in 1954 a more powerful cyclotron was built, the *Bevatron*. With the Bevatron they discovered the anti-proton the following year [56], and the anti-neutron the year after that [57].

The consensus after the positron was found in 1932 was that Dirac was right, every particle has a corresponding anti-particle. This spurred further questions regarding the nature of the Universe. Why is it that we are surrounded by regular matter and not equally much anti-matter? It was entirely possible that other solar-systems, galaxies and entire parts of the Universe was composed almost solely of anti-matter, as formulated by Dirac in his Nobel speech in 1933:

*If we accept the view of complete symmetry between positive and negative electric charge so far as concerns the fundamental laws of Nature, we must regard it rather as an accident that the Earth (and presumably the whole solar system), contains a preponderance of negative electrons and positive protons. It is quite possible that for some of the stars it is the other way about, these stars being built up mainly of positrons and negative protons. In fact, there may be half the stars of each kind. The two kinds of stars would both show exactly the same spectra, and there would be no way of distinguishing them by present astronomical methods.*¹⁵

With the discovery of anti-matter, and Dirac's theoretical non-empty vacuum, theories of quantum fields spanning the vacuum began to gain ground. In these, vacuum is spanned by quantum fields where excitations in the fields give rise to particles, where vacuum to some degree is viewed as something extremely dense with virtual particle-antiparticle pairs that carry no mass and are otherwise non-detectable.

¹⁴The existence of cosmic rays was discovered by Victor Hess in his balloon experiments in the years 1911-1912.

¹⁵At this time, the possible existence of the neutron had just recently been published by James Chadwick [58] which explains the absence of neutrons in Dirac's speech.

Since 1955, the continued experiments in cyclotrons and large hadron colliders have revealed a sea of subatomic quantum particles, such as quarks and anti-quarks, the constituent parts of protons, neutrons and mesons, more leptons (electron, muon and tau, and their neutrino correspondent) and gauge bosons and recently, the Higgs particle [59], a scalar boson¹⁶. These findings emphasized the need for extended theories of quantum mechanics, in particular *Quantum ChromoDynamics (QCD)* or *Quantum ElectroDynamics (QED)*, a quantum field theory developed for explaining the atomic nucleus and in particular the *strong-force* holding all the protons and neutrons together in the nucleus despite their repelling charge to one another. To their aid, Richard Philip Feynman had been working on the path integral formulation in quantum mechanics, and in 1949 he had developed a diagram (the *Feynman diagram*) for representing subatomic particles and their collisions [60], which was an important tool.

For the same reason, string-theory started to be developed in 1970¹⁷, by theoretical physicists such as Leonard Susskind, Graham Frye, Claud Lovelace, Holger Bech Nielsen, Aage Kraemmer, André Neveu, Yoichiro Nambu, Joël Scherk, John Henry Schwarz and others, as they realized that theories for describing the particle spectrum also describes the quantum mechanics of oscillating strings.

While the theories for describing the sub-atomic particles were developed, the question raised by Dirac concerning the preponderance of matter over anti-matter in the visible Universe was still unanswered, but with the discovery of the new atomic-physics and improved measurements, it could be explained if differences except charge between the properties of particles and anti-particles could be detected. Properties such as mass, magnetic moment, their interaction with other subatomic particles etcetera. A small difference between matter and antimatter might make anti-atoms less stable than regular atoms, or the creation of them during the early Universe less probable.

In 1965, such a violation of the symmetry of matter and antimatter was reported by James Watson Cronin and Val Lodgson Fitch, James Christenson and René Turlay in the decay of K-mesons (a sub-atomic particle) [61]. However, the different lifetimes of the K-mesons was not enough to explain the matter-to-antimatter ratio, and the investigation of the possible differences between them was continued.

A promising test of the symmetry regarding the binding force inside the atomic nucleus, the strong-force interaction, was if a particle made up of an anti-neutron and an anti-proton, forming anti-deuteron could be stable. Would the strong-force work the same way for antimatter?

¹⁶The existence of a particle with spin 2 and no mass was predicted in 1970 from string-theory and absolutely necessary for the theory to hold.

¹⁷Perhaps one could say that string-theory originates from the discovery that electromagnetism could be derived from gravity with the help of an extra space-dimension by Theodor Kaluza and Oscar Klein in 1921, in the aftermath of Einstein's general theory of relativity.

In 1965, this atomic nucleus was created simultaneously on two fronts, one led by Antonino Zichichi at CERN using the Proton Synchrotron [62] and one led by Leon Lederman in New York using the AGS accelerator [63], revealing no differences between matter and antimatter. Improvements in the experimental tools and set-ups led to the subsequent trapping of anti-protons in 1978 at CERN and the controlled collisions of protons and anti-protons at the Super Proton Synchrotron (SPS) in 1981. Further development took place at CERN: the creation of the anti-hydrogen atom in 1995, the first cold (de-excited) antihydrogen atoms in 2002, the successful trapping of antihydrogen for more than 1000 seconds (long enough for the atom to de-excite to its ground state, enabling high precision spectroscopy) in 2011, and the same year a high precision measurement of the antiproton mass was performed that was further improved in 2015 to reveal that no difference in the mass could be found. In 2016 an optical transition state was found that was used in 2017 by exposing antihydrogen to microwaves of that particular frequency to induce hyperfine transitions and measure the hyperfine structure of antihydrogen [64, 65]. In the same year, a super precise measurement of the magnetic moment of the antiproton was carried out [66]. No difference in mass, energy levels or gravitational properties have been found between hydrogen and antihydrogen.

So far, any difference between matter and antimatter that could explain the ratio of matter over antimatter in the Universe, continues to elude us. Some differences has been found for some particular particle-antiparticle pairs however, as indicated by the decay of K-mesons in 1965 and the decay of B-mesons found at Fermilab by the D0 Collaboration in 2010 [67], but the differences are not large enough to explain the matter-antimatter ratio.

The questions of the nature of antimatter has been a key stone for the development of quantum mechanics and its derivatives, QED and string-theory, and today it rests firmly at the heart of the mystery surrounding the creation of the Universe.

1.2 Quantum Mechanics

The quantum mechanical state

In mechanics, the state defines the system in terms of a function of a set of properties. The state can be characterized by mostly anything that describes the system; a simplified view of an atom could be described by the sum of the number of protons q_1 , neutrons q_2 and electrons q_3 such that an atom with 1 proton, 1 neutron and 2 electrons would read $\psi(q_1, q_2, q_3) = 1 + 1 + 2 = 4$. Likewise, If the property we would like to know is the displacement position x of a particle with mass m hanging at the end of an oscillating spring with spring constant k , we start from the equation of motion given by Newton's second law $F = ma$ where a is the acceleration and F is the force, and apply Hooke's law¹⁸ $F = -kx$ to get

$$F = ma = m \frac{d^2x(t)}{dt^2} = -kx(t). \quad (1.1)$$

The solution to this second order differential equation is

$$x(t) = \psi(t) = A \cos(\omega t - \phi), \quad (1.2)$$

where the angular frequency $\omega = \sqrt{\frac{k}{m}}$, ϕ is the phase and A is the amplitude determined by the initial conditions. If we want to know the position of the particle, it is uniquely given by the function over time, i.e. if we know the value of t (and the starting conditions) we know the value of x . These systems are deterministic.

Now, imagine that we did not know the value of t but instead we know the magnitude of the momentum $|p|$ of the particle and we would like to know the position x . We would have two equally probable solutions from the equation of motion, one for when the particle is on the upper side of the position where the spring is at rest, and one for the lower side. Such a measurement would be indeterministic in the sense that knowing $|p|$ would not give us a unique solution in x (consider for example the case when the particle is at the lower and upper end points, in both points it would have $|p| = 0$). Without more information, the function describing x could at best be written on the form

$$x(|p|) = \psi(|p|, \alpha) = \varphi(|p|)\alpha, \quad (1.3)$$

where φ is a function returning a unique positive displacement value for each value of $|p|$ and α has the possible values of ± 1 . However, if we knew the up/down value α of the particle this previously "hidden variable" would give the equation a unique solution and the system would be deterministic¹⁹.

This thought-experiment is aimed at highlighting the inherent problems in understanding the nature of a system and the physical laws that govern it from

¹⁸We ignore other effects such as gravity and friction.

¹⁹cf. the discovery by Pauli of the quantum number for the spin of an electron [43].

measurements. Depending on which property we observe and which variables we include, our interpretation of the nature of the system and the laws of nature could be led to very different conclusions.

In the language of quantum mechanics, the quantum state is a function of the properties describing the system where the state is written as a linear superposition of all possible outcomes of a measurement of the system. A measurement of the state reveals the values of the properties (*quantum numbers*) whereas the superposition collapses. The *wave function* is a mathematical equation describing the state, formulated as a complex valued probability amplitude, such that the absolute value squared of it can be interpreted as a probability density for the system. As an example, the wave function in (1.3) would be written as a superposition on the form

$$\psi(|p\rangle, \alpha) = (A\alpha_{=1} + B\alpha_{=-1}) \varphi(|p\rangle), \quad (1.4)$$

where A and B are coefficients representing probability amplitudes for the outcome where $\alpha = 1$ and $\alpha = -1$ respectively, normalized such that the total probability is equal to 1. If the probability of a measurement on the wave function does not change over time, the state is *stationary*. Moreover, if the wave function is a function of many *observables*²⁰ they have to commute with each other, meaning that a measurement of one observable has no effect on the result of a measurement of the other. If the observables do not commute, such as position and momentum of a particle, it is impossible to simultaneously measure them²¹. With this formalism, the theory of quantum mechanics is able to predict and model a large spectrum of phenomena in nature.

The indeterministic properties of quantum states²² are peculiar and interesting, the superposition itself seems to give rise to measurable physical effects not possible if the state is in reality described by a single, but unknown state²³.

If all observables of a system can be described by an operation on the function describing the system, the question of the true nature of the system arises. For example, the probability distribution of finding a particle in a box might be described with a Gaussian wave function, but does this mean that the shape of the particle is actually given by a Gaussian wave function? Conversely, one might wonder if it is the nature of the operation on the function describing the system that projects its properties to the observer. These thoughts are a tangent to the different views in wave-particle dualism stemming from Louis de Broglie's postulate, and the ideas behind the Schrödinger wave description and Heisenberg's non-commuting observables

²⁰a variable that we can measure.

²¹The canonical commutation relation, attributed to Max Born in 1925, implies the Heisenberg uncertainty principle.

²²The (non-local) *Hidden variables interpretation* argues that quantum systems would be deterministic if we knew all the variables [68].

²³such as *entanglement* and *quantum interference* [69].

formalism. Sadly, the interpretation of quantum mechanics is out of scope for this thesis.

The Schrödinger equation

The *time-dependent Schrödinger equation*

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t), \quad (1.5)$$

where Ψ is the state, the function over the position \mathbf{r} and time t , and \hat{H} is the Hamiltonian operator (the energy operator) defined as the sum of the kinetic and potential energy $\hat{H} = \hat{T} + \hat{V}$, describes the evolution of the state over time. The potential energy operator \hat{V} is specific to the system under study and in the following we assume that it does not depend on time²⁴, whereas the kinetic energy operator for a particle with momentum p and mass m is given as

$$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2. \quad (1.6)$$

For a time-independent Hamiltonian we can separate the wave function into a product of its spatial dependence \mathbf{r} and time dependence t , $\Psi(\mathbf{r}, t) = \varphi(\mathbf{r})\Phi(t)$, eq. (1.5) becomes

$$\varphi(\mathbf{r})i\hbar \frac{d\Phi(t)}{dt} = \Phi(t)\hat{H}\varphi(\mathbf{r}) \Leftrightarrow \frac{i\hbar}{\Phi(t)} \frac{d\Phi(t)}{dt} = \frac{1}{\varphi(\mathbf{r})}\hat{H}\varphi(\mathbf{r}). \quad (1.7)$$

Since the l.h.s. only depend on time and the r.h.s. only depend on space, both sides must equal a constant E (with dimension of energy) and we get

$$\frac{1}{\Phi(t)} \frac{d\Phi(t)}{dt} = -\frac{iE}{\hbar}, \quad (1.8)$$

$$\hat{H}\varphi(\mathbf{r}) = E\varphi(\mathbf{r}). \quad (1.9)$$

The second equation above is the regular *Schrödinger equation* (time independent Schrödinger equation) where states $\varphi(\mathbf{r})$ that satisfy (1.9) are called *stationary*, a term that should not to be confused with the movement over time of the particles described by the wave function. The first equation has the solution

$$\Phi(t) = e^{-\frac{iEt}{\hbar}}. \quad (1.10)$$

Putting the two together, we can write the time dependent wave function as

$$\Psi(\mathbf{r}, t) = \varphi(\mathbf{r})e^{-\frac{iEt}{\hbar}}, \quad (1.11)$$

or with $\Psi(0)$ understood as $\Psi(\mathbf{r}, t = 0)$, we can simplify the notation to

$$\Psi(t) = e^{-\frac{iEt}{\hbar}} \Psi(0). \quad (1.12)$$

²⁴See section 2.7 for the treatment of time-dependence in the Hamiltonian.

Dirac notation

Instead of the Schrödinger equation written in the language of functions we can write the same equation in matrix notation where functions are written as vectors and operators are written as matrices. A handy way of writing a function of \mathbf{x} , $\phi(\mathbf{x})$ and its transpose $\phi^T(\mathbf{x})$ is by using the Dirac notation

$$\phi(\mathbf{x}) = |\mathbf{x}\rangle, \quad (1.13)$$

$$\phi^T(\mathbf{x}) = \langle \mathbf{x}|. \quad (1.14)$$

In matrix notation the column vector $|\mathbf{x}\rangle$ and row vector $\langle \mathbf{x}|$ of dimension n would read

$$|\mathbf{x}\rangle = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}, \quad \langle \mathbf{x}| = (x_1, x_2, \dots, x_n)^*, \quad (1.15)$$

where the $*$ means that the values are complex conjugated. An operator \hat{A} is represented by a matrix

$$\hat{A} = \begin{pmatrix} A_{11}, A_{12}, \dots, A_{1n} \\ A_{21}, A_{22}, \dots, A_{2n} \\ \vdots & \dots & \vdots \\ A_{n1}, A_{n2}, \dots, A_{nn} \end{pmatrix}, \quad (1.16)$$

where regular matrix operations with vectors on the right and left apply, such that $\hat{A}|\mathbf{x}\rangle$ is a column vector and $\langle \mathbf{x}|\hat{A}$ is a row vector. Now, it is easy to see that an expression on the form $|\mathbf{x}\rangle\langle \mathbf{x}|$ is a matrix operator where each matrix element is given by $x(i, j) = x_i x_j$, and that the dot product $\langle \mathbf{x}|\mathbf{x}\rangle$ and expectation value $\langle \hat{A} \rangle = \langle \mathbf{x}|\hat{A}|\mathbf{x}\rangle$ are numbers.

In this notation, with $\Psi(\mathbf{r}, t) = |\mathbf{x}\rangle$, the time-dependent and time-independent Schrödinger equations are written as

$$i\hbar \frac{\partial}{\partial t} |\mathbf{x}\rangle = \hat{H}|\mathbf{x}\rangle, \quad (1.17)$$

$$\hat{H}|\mathbf{x}\rangle = E|\mathbf{x}\rangle. \quad (1.18)$$

See [70] for details on the Dirac notation.

2. Methodology

2.1 Ritz variational method

The variational method transforms the Schrödinger equation into a matrix diagonalization problem. The idea is to guess the wave function for the system and then minimize the expectation value of the energy with respect to the wave function by optimizing a set of parameters used in the expansion of the wave function. The variational theorem states that the minimum of the energy (as a functional¹ of the wave function) is the exact ground state. By reordering and multiplying the Schrödinger equation from the left with $\langle \psi |$ we get the energy functional

$$E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (2.1)$$

where \hat{H} is the Hamiltonian. In the Ritz variational method the wave function is expanded in known basis functions $\{\chi_i\}$

$$\psi = \sum_{i=1}^M c_i \chi_i, \quad (2.2)$$

where $\{\chi_i\}$ are in general non-orthogonal. By substituting (2.2) into (2.1) the energy functional becomes

$$E[\psi] = E(\{c_i\}) = \frac{\sum_{i,j=1}^M c_i^* \langle \chi_i | \hat{H} | \chi_j \rangle c_j}{\sum_{i,j=1}^M c_i^* \langle \chi_i | \chi_j \rangle c_j} = \frac{\sum_{i,j=1}^M c_i^* c_j H_{ij}}{\sum_{i,j=1}^M c_i^* c_j S_{ij}}, \quad (2.3)$$

where

$$H_{ij} = \langle \chi_i | \hat{H} | \chi_j \rangle, \quad (2.4)$$

$$S_{ij} = \langle \chi_i | \chi_j \rangle, \quad (2.5)$$

are the elements of the Hamiltonian and the overlap matrices respectively.

According to the variational theorem the energy functional is bounded from below by the ground state energy E_0 as we vary the expansion coefficients² $\{c_i\}$. Since the energy functional has a minimum we have at this minimum

$$\frac{\partial E(\{c_i\})}{\partial c_l} = 0, \quad l = 1, \dots, M. \quad (2.6)$$

¹A mapping of a set of functions from one space to another. I use square brackets instead of regular ones for the argument for functionals.

²The coefficients $\{c_i\}$ and $\{c_i^*\}$ are not independent of each other and we may select $\{c_i\}$ as the independent variables. Choosing the other set for the minimization of E gives the same result [71].

Equating this with the derivative of the energy functional with respect to a chosen c_l gives us

$$\begin{aligned}
0 &= \frac{\partial E(\{c_i\})}{\partial c_l} = \frac{\partial \sum_{i,j=1}^M c_i^* c_j H_{ij}}{\partial c_l \sum_{i,j=1}^M c_i^* c_j S_{ij}} = \\
&= \frac{\sum_{i=1}^M c_i^* H_{il} \sum_{i,j=1}^M c_i^* c_j S_{ij} - \sum_{i=1}^M c_i^* S_{il} \sum_{i,j=1}^M c_i^* c_j H_{ij}}{(\sum_{i,j=1}^M c_i^* c_j S_{ij})^2} = \\
&= \frac{\sum_{i=1}^M c_i^* H_{il}}{\sum_{i,j=1}^M c_i^* c_j S_{ij}} - \frac{\sum_{i=1}^M c_i^* S_{il}}{\sum_{i,j=1}^M c_i^* c_j S_{ij}} E(\{c_i\}) = \frac{\sum_{i=1}^M c_i^* (H_{il} - E[\psi] S_{il})}{\sum_{i,j=1}^M c_i^* c_j S_{ij}},
\end{aligned} \tag{2.7}$$

which can be written as

$$\sum_{i=1}^M c_i^* (H_{il} - E[\psi] S_{il}) = 0, \quad l = 1, \dots, M. \tag{2.8}$$

Thus, we have a set of M equations to solve in M variables (the coefficients $\{c_i^*\}$), which will result in M values for the energy $E[\psi]$. The lowest of these values is the approximation to the ground state energy E_0 and due to the *Hylleraas-Undheim-MacDonald-Löwdin* theorem the other values can be interpreted as approximations to the excited states energies. Solving (2.8) for all l corresponds to diagonalizing the Hamiltonian matrix, represented in the basis set $\{\chi_i\}$. We have arrived at the generalized matrix eigenvalue problem

$$\mathbf{Hc}_n = E_n \mathbf{Sc}_n, \tag{2.9}$$

where \mathbf{c}_n is a vector of expansion coefficients. The generalized matrix eigenvalue problem is solved numerically with a computer for large basis sets, or by hand for smaller basis sets using Gaussian elimination.

2.2 Gaussian Expansion Method

The wave function that is the solution to the Schrödinger equation with a spherically symmetrical potential can be written as

$$\chi_{klm}(\mathbf{R}) = Y_{lm}(\hat{\mathbf{R}})\phi_{kl}(R), \quad (2.10)$$

where Y_{lm} are the spherical harmonics, $\hat{\mathbf{R}}$ denotes angular coordinates of vector \mathbf{R} , and $\phi_{kl}(R)$ is the radial part of the function. In the Gaussian Expansion Method [72] the radial part $\phi_{kl}(R)$ is expanded in a basis set of Gaussian functions $g_{nl}(R)$

$$\phi_{kl}(R) = \sum_{n=1}^{n_{\max}} c_n^k g_{nl}(R), \quad (2.11)$$

where the basic form of the Gaussian functions are called the *primitive Gaussian functions*, given by

$$g_{nl}(R) = N_{nl} R^l \exp(-v_n R^2), \quad (2.12)$$

with N_{nl} a normalization coefficient and v_n related to the Gaussian gamma half-length as

$$\frac{\Gamma_n}{2} = \sqrt{\frac{\ln 2}{v_n}}. \quad (2.13)$$

The Gaussian widths v_n are chosen to be given by a geometrical progression

$$v_n = \frac{1}{r_n^2}, \quad n = 1, 2, \dots, n_{\max}, \quad (2.14)$$

with

$$r_n = r_{\min} \left(\frac{r_{\max}}{r_{\min}} \right)^{(n-1)/(n_{\max}-1)}, \quad (2.15)$$

where r_{\min} and r_{\max} are fixed parameters that we optimize depending on the physical problem we need to solve. When we increase the number of basis functions we change the shape of *all* the functions simultaneously, since all widths v_n change. The normalization constant N_{nl} is calculated in Appendix A (see (5.1) - (5.6)), to be

$$N_{nl} = \sqrt{\frac{2^{l+2} (2v_n)^{l+\frac{3}{2}}}{\sqrt{\pi} (2l+1)!!}}. \quad (2.16)$$

Advantages of using Gaussian functions

There are many advantages of using Gaussian basis functions. First of all, the integrals that one needs to solve when calculating matrix elements are on the form

$$\langle g_{il}(R) | R^a | g_{jl}(R) \rangle = \int R^{2l+a+2} \exp(-(v_i + v_j)R^2) dR, \quad (2.17)$$

which are analytically solvable, meaning that we do not need a numerical approximation when we calculate the matrix elements in the Hamiltonian and overlap matrices. Furthermore, Gaussian functions are flexible and smooth functions which can be used in an expansion to build up wave functions to a high level of accuracy. The exponentially decaying tail insures us that the expression in (2.17) is convergent as long as $a \geq -2(1+l)$.

Another advantage of using Gaussian functions is that the quadratic power of R in the exponent makes transformations between coordinate systems easy. As an example, consider the following transformation from the set Jacobi coordinates describing C_{PnPs} to the Jacobi coordinates describing $C_{\text{H}\bar{\text{H}}}$ in Figure 2.1

$$\begin{aligned}\tilde{\mathbf{r}} &= \frac{1}{2}\mathbf{r} - \frac{1}{2}\mathbf{R} + \rho, \\ \tilde{\rho} &= -\frac{1}{2}\mathbf{r} + \frac{1}{2}\mathbf{R} + \rho, \\ \tilde{\mathbf{R}} &= \frac{1}{m_{\text{H}}}\mathbf{r} + \frac{m_{\text{p}}}{m_{\text{H}}}\mathbf{R},\end{aligned}\tag{2.18}$$

where m_{p} and m_{H} is the proton and hydrogen mass respectively. This leads to the following expression for the exponent part of the transformation

$$e^{-\alpha\tilde{r}^2 - \beta\tilde{R}^2 - \gamma\tilde{\rho}^2} = e^{-a r^2 - b R^2 - c \rho^2 - 2f \mathbf{r} \mathbf{R} - 2g \mathbf{r} \rho - 2h \mathbf{R} \rho},\tag{2.19}$$

with new integrals to solve in the transformed coordinates, where

$$\begin{aligned}a &= \frac{1}{4}\alpha + \frac{1}{m_{\text{H}}^2}\beta + \frac{1}{4}\gamma, & b &= \frac{1}{4}\alpha + \frac{m_{\text{p}}^2}{m_{\text{H}}^2}\beta + \frac{1}{4}\gamma, & c &= \alpha + \gamma, \\ f &= -\frac{1}{4}\alpha + \frac{m_{\text{p}}}{m_{\text{H}}^2}\beta - \frac{1}{4}\gamma, & g &= \frac{1}{2}\alpha - \frac{1}{2}\gamma, & h &= -\frac{1}{2}\alpha + \frac{1}{2}\gamma.\end{aligned}\tag{2.20}$$

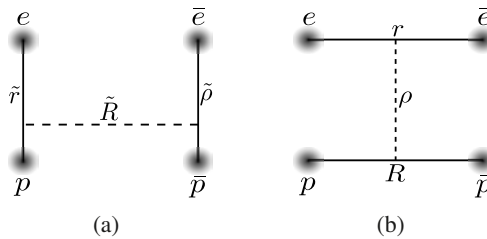


Figure 2.1. (a) $C_{\text{H}\bar{\text{H}}} = \text{H}-\bar{\text{H}}$ channel. (b) $C_{\text{PnPs}} = \text{Pn-Ps}$ channel.
(From paper III, printed with permission from ©IOP Publishing)

Oscillating Gaussian functions

For more complicated wave functions that demand a more flexible basis, we can improve on the basic form of the primitive Gaussian functions and still retain the advantages of using Gaussian functions.

For these types of wave functions we use so called *Oscillating Gaussian functions*, where we alternate between multiplying the primitive Gaussian functions with a cosine ($g_{nl}^c(R)$) or a sine part ($g_{nl}^s(R)$), i.e.

$$\sum_{n=1}^{n_{\max}} c_n^k g_{nl}^{osc}(R) = \sum_{n=1}^{n_{\max}/2} \left(c_{2n-1}^k g_{nl}^c(R) + c_{2n}^k g_{nl}^s(R) \right), \quad (2.21)$$

where

$$g_{nl}^c(R) = N_{nl}^c R^l e^{-v_n R^2} \cos(\alpha v_n R^2) = N_{nl}^c R^l \frac{1}{2} (e^{i a_n R^2} + e^{-i b_n R^2}), \quad (2.22)$$

$$g_{nl}^s(R) = N_{nl}^s R^l e^{-v_n R^2} \sin(\alpha v_n R^2) = N_{nl}^s R^l \frac{1}{2i} (e^{i a_n R^2} - e^{-i b_n R^2}), \quad (2.23)$$

and

$$\begin{aligned} a_n &= (1 + i\alpha)v_n, \\ b_n &= (1 - i\alpha)v_n. \end{aligned} \quad (2.24)$$

Here α is a parameter chosen to be $\alpha = \pi/2$, and the normalization constants N_{nl}^c and N_{nl}^s are more complicated, see Appendix A (5.24)-(5.27).

The oscillating Gaussian functions in (2.22) and (2.23) retains the advantages of using primitive Gaussian functions as they are written as a sum of primitive Gaussian functions with a complex exponent, and complex exponents do not introduce difficulties in the matrix element calculations. The advantage of using oscillating Gaussian functions is that the attached sine and cosine functions allow for a better ability to mimic wave functions with many nodes (e.g. highly excited wave functions).

2.3 Perturbation theory for the interaction between two atoms

We start by dividing the Hamiltonian into a known Hamiltonian $\hat{H}^{(0)}$ and an unknown perturbation \hat{V} as

$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \hat{V}, \quad (2.25)$$

where $\hat{H}^{(0)}$ is a sum of the Hamiltonians for isolated atoms $\hat{H}^{(0)} = \hat{H}^A + \hat{H}^B$, \hat{V} is the interatomic interaction potential and λ is the perturbation parameter. The unperturbed (zero-order) wave function is the product of the eigenfunctions of \hat{H}^A and \hat{H}^B

$$\Psi_k^{(0)} = \Psi_i^A \Psi_j^B, \quad k = (i, j), \quad (2.26)$$

where

$$\hat{H}_A \Psi_i^A = E_i^A \Psi_i^A, \quad (2.27)$$

$$\hat{H}_B \Psi_j^B = E_j^B \Psi_j^B, \quad (2.28)$$

and the zero-order energy $E^{(0)}$ corresponds to

$$\hat{H}^{(0)} \Psi_k^0 = E_k^{(0)} \Psi_k^0 = (E_i^A + E_j^B) \Psi_i^A \Psi_j^B, \quad (2.29)$$

i.e. the threshold energy, the sum of the individual atoms energies³. The interaction energy E_k^{int} is the difference between the total energy E_k and the threshold energy

$$E_k^{\text{int}} = E_k - E_k^{(0)}. \quad (2.30)$$

Now, by assuming that the wave function and eigenvalues can be written as power series of λ

$$\Psi_k = \Psi_k^{(0)} + \lambda \Psi_k^{(1)} + \lambda^2 \Psi_k^{(2)} + \dots, \quad (2.31)$$

$$E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots, \quad (2.32)$$

the Schrödinger equation becomes

$$\begin{aligned} & (\hat{H}^{(0)} + \lambda V)(\Psi_k^{(0)} + \lambda \Psi_k^{(1)} + \lambda^2 \Psi_k^{(2)} + \dots) = \\ & (E_k^{(0)} + E_k^{(1)} + E_k^{(2)} + \dots)(\Psi_k^{(0)} + \lambda \Psi_k^{(1)} + \lambda^2 \Psi_k^{(2)} + \dots). \end{aligned} \quad (2.33)$$

Equation (2.33) must be satisfied for any value of λ which means that one can separate the terms corresponding to a given order of λ . For the zeroth order we obtain the Schrödinger equation for non-interacting atoms

$$\lambda^0: \quad \hat{H}^{(0)} \Psi_k^{(0)} = E_k^{(0)} \Psi_k^{(0)} \rightarrow E_k^{(0)} = \frac{\langle \Psi_k^{(0)} | H^{(0)} | \Psi_k^{(0)} \rangle}{\langle \Psi_k^{(0)} | \Psi_k^{(0)} \rangle}. \quad (2.34)$$

³No degeneration is assumed in the following derivation.

By using the *indirect normalization* condition, i.e.

$$\langle \Psi_k^{(0)} | \Psi_k \rangle = 1, \quad \text{and} \quad \langle \Psi_k^{(i)} | \Psi_k^{(0)} \rangle = 0, \text{ for } i \neq 0, \quad (2.35)$$

we can ignore the denominator in eq. (2.34).

We do the same for terms of the first order λ and end up with

$$\begin{aligned} \lambda^1 : \quad & \hat{H}^{(0)} \Psi_k^{(1)} + V \Psi_k^{(0)} = E_k^{(0)} \Psi_k^{(1)} + E_k^{(1)} \Psi_k^{(0)} \\ & \Rightarrow (\hat{H}^{(0)} - E_k^{(0)}) \Psi_k^{(1)} = (E_k^{(1)} - \hat{V}) \Psi_k^{(0)} \end{aligned} \quad (2.36)$$

$$\begin{aligned} & \Rightarrow \langle \Psi_k^{(0)} | (\hat{H}^{(0)} - E_k^{(0)}) | \Psi_k^{(1)} \rangle = \langle \Psi_k^{(0)} | (E_k^{(1)} - \hat{V}) | \Psi_k^{(0)} \rangle \\ & \Rightarrow \left\{ \langle \Psi_k^{(0)} | (\hat{H}^{(0)} - E_k^{(0)}) \rangle = \langle \Psi_k^{(0)} | (E_k^{(0)} - E_k^{(0)}) \rangle = 0 \right\} \\ & \Rightarrow E_k^{(1)} = \langle \Psi_k^{(0)} | \hat{V} | \Psi_k^{(0)} \rangle. \end{aligned} \quad (2.37)$$

Thus, the first order energy correction is calculated as the expectation value of the interaction potential \hat{V} with respect to the unperturbed wave function.

The next order of correction to the energy is extracted by collecting the terms corresponding to λ^2 :

$$\lambda^2 : \quad (\hat{H}^{(0)} - E_k^{(0)}) \Psi_k^{(2)} = (E_k^{(1)} - \hat{V}) \Psi_k^{(1)} + E_k^{(2)} \Psi_k^{(0)}, \quad (2.38)$$

which gives us the second order correction to the energy as

$$E_k^{(2)} = \langle \Psi_k^{(0)} | \hat{V} - E_k^{(1)} | \Psi_k^{(1)} \rangle = \left\{ (2.35) \right\} = \langle \Psi_k^{(0)} | \hat{V} | \Psi_k^{(1)} \rangle. \quad (2.39)$$

Hence, to calculate the correction $E_k^{(2)}$ we need to know the function $\Psi_k^{(1)}$. To our aid we have eq. (2.36), i.e.

$$(\hat{H}^{(0)} - E_k^{(0)}) \Psi_k^{(1)} = (E_k^{(1)} - \hat{V}) \Psi_k^{(0)}. \quad (2.40)$$

We would like to get $\Psi_k^{(1)}$ alone on one side, but we cannot simply invert the operator $\hat{H}^{(0)} - E_k^{(0)}$ since that operator would not be well defined in the total Hilbert-space \mathcal{H} ($\hat{H}^{(0)} - E_k^{(0)}$ acting on $\Psi_k^{(0)}$ is zero, and dividing by zero is always a problem). However, we can define an operator \hat{Q}^0 that projects functions onto a subspace of \mathcal{H} in which the $\hat{H}^{(0)} - E_k^{(0)}$ operator can be inverted. The Hilbert-space can be divided into subspaces parallel and orthogonal to the $|\Psi_k^{(0)}\rangle$ vector as

$$\mathcal{H} = \left\{ |\Psi_k^{(0)}\rangle \right\} \cup \left\{ |\Psi_{j \neq k}^{(0)}\rangle \right\}, \quad (2.41)$$

where Q^0 projects onto the $\left\{ |\Psi_{j \neq k}^{(0)}\rangle \right\}$ subspace. This projection explicitly reads:

$$\hat{Q}^0 = 1 - |\Psi_k^{(0)}\rangle \langle \Psi_k^{(0)}| = \sum_{j \neq k} |\Psi_k^{(0)}\rangle \langle \Psi_k^{(0)}|. \quad (2.42)$$

Due to the normalization condition in (2.35) the functions $\Psi_k^{(0)}$ and $\Psi_k^{(1)}$ fulfill

$$\hat{Q}^0 \Psi_k^{(1)} = \Psi_k^{(1)}, \quad (2.43)$$

$$\hat{Q}^0 \Psi_k^{(0)} = 0, \quad (2.44)$$

and since \hat{Q}^0 is a projection operator we have

$$\hat{Q}^0 \hat{Q}^0 = \hat{Q}^0. \quad (2.45)$$

Now, let us define the *reduced resolvent* operator \mathcal{R}_0 as

$$\mathcal{R}_0 = \hat{Q}^0 \frac{1}{\hat{H}^{(0)} - E_k^{(0)}} \hat{Q}^0, \quad (2.46)$$

which is the inverse operator to $\hat{Q}^0 (\hat{H}^{(0)} - E_k^{(0)}) \hat{Q}^0$, and by operating with \mathcal{R}_0 from the left on the left-hand side of eq. (2.40) we get:

$$\begin{aligned} \mathcal{R}_0 \cdot (\hat{H}^{(0)} - E_k^{(0)}) \Psi_k^{(1)} &= \hat{Q}^0 \frac{1}{\hat{H}^{(0)} - E_k^{(0)}} \hat{Q}^0 \cdot (\hat{H}^{(0)} - E_k^{(0)}) \Psi_k^{(1)} \\ &= \left\{ \hat{Q}^0 \hat{Q}^0 = \hat{Q}^0, \text{ and } \hat{Q}^0 \Psi_k^{(1)} = \Psi_k^{(1)} \right\} = \\ &= \hat{Q}^0 \frac{1}{\hat{H}^{(0)} - E_k^{(0)}} \hat{Q}^0 \hat{Q}^0 \cdot (\hat{H}^{(0)} - E_k^{(0)}) \hat{Q}^0 \Psi_k^{(1)} = \Psi_k^{(1)}, \end{aligned} \quad (2.47)$$

thus, eq. (2.40) becomes

$$\begin{aligned} \mathcal{R}_0 (\hat{H}^{(0)} - E_k^{(0)}) |\Psi_k^{(1)}\rangle &= \mathcal{R}_0 (E_k^{(1)} - \hat{V}) |\Psi_k^{(0)}\rangle \\ \Rightarrow |\Psi_k^{(1)}\rangle &= \mathcal{R}_0 (E_k^{(1)} - \hat{V}) |\Psi_k^{(0)}\rangle = E_k^{(1)} \mathcal{R}_0 |\Psi_k^{(0)}\rangle - \mathcal{R}_0 \hat{V} |\Psi_k^{(0)}\rangle \\ \Rightarrow |\Psi_k^{(1)}\rangle &= -\mathcal{R}_0 \hat{V} |\Psi_k^{(0)}\rangle \end{aligned} \quad (2.48)$$

Now, eq. (2.39) can be written as

$$E_k^{(2)} = -\langle \Psi_k^{(0)} | \hat{V} \mathcal{R}_0 \hat{V} | \Psi_k^{(0)} \rangle. \quad (2.49)$$

This expression can be rewritten by first expanding \mathcal{R}_0 as

$$\begin{aligned}
\mathcal{R}_0 &= \sum_{j \neq k} |\Psi_j^{(0)}\rangle \langle \Psi_j^{(0)}| \frac{1}{\hat{H}^{(0)} - E_k^{(0)}} \sum_{i \neq k} |\Psi_i^{(0)}\rangle \langle \Psi_i^{(0)}| \\
&= \sum_{\substack{j \neq k \\ i \neq k}} |\Psi_j^{(0)}\rangle \langle \Psi_j^{(0)}| \frac{1}{\hat{H}^{(0)} - E_k^{(0)}} |\Psi_i^{(0)}\rangle \langle \Psi_i^{(0)}| \\
&= \sum_{\substack{j \neq k \\ i \neq k}} |\Psi_j^{(0)}\rangle \frac{\langle \Psi_j^{(0)} | \Psi_i^{(0)} \rangle}{E_i^{(0)} - E_k^{(0)}} \langle \Psi_i^{(0)}| = \sum_{\substack{j \neq k \\ i \neq k}} |\Psi_j^{(0)}\rangle \frac{\delta_{ji}}{E_i^{(0)} - E_k^{(0)}} \langle \Psi_i^{(0)}| \\
&= \sum_{j \neq k} \frac{|\Psi_j^{(0)}\rangle \langle \Psi_j^{(0)}|}{E_j^{(0)} - E_k^{(0)}},
\end{aligned} \tag{2.50}$$

and inserting this into eq. (2.49)

$$\begin{aligned}
E_k^{(2)} &= -\langle \Psi_k^{(0)} | \hat{V} \sum_{j \neq k} \frac{|\Psi_j^{(0)}\rangle \langle \Psi_j^{(0)}|}{E_j^{(0)} - E_k^{(0)}} \hat{V} | \Psi_k^{(0)} \rangle = \sum_{j \neq k} \frac{\langle \Psi_k^{(0)} | \hat{V} | \Psi_j^{(0)} \rangle \langle \Psi_j^{(0)} | \hat{V} | \Psi_k^{(0)} \rangle}{E_k^{(0)} - E_j^{(0)}} \\
\Rightarrow E^{(2)} &= \sum_{j \neq k} \frac{|\langle \Psi_k^{(0)} | \hat{V} | \Psi_j^{(0)} \rangle|^2}{E_k^{(0)} - E_j^{(0)}}.
\end{aligned} \tag{2.51}$$

Using eq. (2.26) and eq. (2.29) the second order correction becomes

$$\begin{aligned}
E_k^{(2)} &= \sum_{\substack{i' \neq i \\ j' \neq j}} \frac{|\langle \Psi_i^A \Psi_j^B | \hat{V} | \Psi_{i'}^A \Psi_{j'}^B \rangle|^2}{E_i^A + E_j^B - E_{i'}^A - E_{j'}^B} + \sum_{i' \neq i} \frac{|\langle \Psi_i^A \Psi_j^B | \hat{V} | \Psi_{i'}^A \Psi_j^B \rangle|^2}{E_i^A - E_{i'}^A} \\
&+ \sum_{j' \neq j} \frac{|\langle \Psi_i^A \Psi_j^B | \hat{V} | \Psi_i^A \Psi_{j'}^B \rangle|^2}{E_j^B - E_{j'}^B}.
\end{aligned} \tag{2.52}$$

If we look at terms two and three in (2.52), we notice that the summation is only over one of the atoms. In other words, one of the atoms is "frozen" and the electric field of the frozen atom induces a change in the charge distribution on the other atom which is described with perturbation theory. These two terms are together called the *induction energy*.

The first term in (2.52) arises from the correlation between the movement of the leptons in different monomers and this term is called the *dispersion energy*. In appendix **B** it is shown, by expanding \hat{V} according to the multipole expansion, that the dispersion energy term is the first non-vanishing term for the perturbation correction to the energy.

2.4 Born-Oppenheimer and adiabatic approximation

Following the outline in [71], we start by writing the Hamiltonian for a system of two nuclei and N leptons in a space-fixed frame as

$$\hat{H} = -\frac{\hbar^2}{2M_a}\Delta_a - \frac{\hbar^2}{2M_b}\Delta_b - \sum_{i=1}^N \frac{\hbar^2}{2m_i}\Delta_{\mathbf{r}_i} + \hat{V}. \quad (2.53)$$

With Cartesian coordinates the nuclei have the positions $\mathbf{R}_a = (X_a, Y_a, Z_a)$, $\mathbf{R}_b = (X_b, Y_b, Z_b)$ and the electron i has the position $\mathbf{r}'_i = (x'_i, y'_i, z'_i)$. The potential energy operator \hat{V} , written in these coordinates, is the Coulombic interaction potential of all the particles, nuclei-nuclei, leptons-leptons and nuclei-leptons:

$$\hat{V} = -\frac{\mathcal{L}_a \mathcal{L}_b \sum_i^N \mathcal{L}_i}{R} - \mathcal{L}_a \sum_i \frac{\mathcal{L}_i}{r_{ai}} - \mathcal{L}_b \sum_i \frac{\mathcal{L}_i}{r_{bi}} - \sum_{i < j} \frac{\mathcal{L}_i \mathcal{L}_j}{r_{ij}}, \quad (2.54)$$

where \mathcal{L} is the charge of the nucleus and \mathcal{L} is the charge of the lepton.

Separation of the center of mass motion

We can separate the center of mass motion by a change of coordinate system. The center-of-mass position is

$$\mathbf{X} = (X, Y, Z) = \frac{1}{M}(M_a \mathbf{R}_a + M_b \mathbf{R}_b + \sum_i m_i \mathbf{r}'_i), \quad (2.55)$$

where the total mass of the molecule is $M = M_a + M_b + Nm$. We also need the vector $\mathbf{R} = \mathbf{R}_a - \mathbf{R}_b = (X_a - X_b, Y_a - Y_b, Z_p - Z_b)$ which points from nucleus a to nucleus b and the lepton's position vectors are defined with respect to the geometric center of the molecule $\mathbf{r}_i = \mathbf{r}'_i - \frac{1}{2}(\mathbf{R}_a + \mathbf{R}_b)$, see Figure 2.2.

Changing the coordinate system changes the expressions for the derivative operators in the Hamiltonian. By using the chain rule for partial derivatives the *first order* derivative becomes;

$$\frac{\partial}{\partial X_a} = \frac{\partial X}{\partial X_a} \frac{\partial}{\partial X} + \frac{\partial R_x}{\partial X_a} \frac{\partial}{\partial R_x} + \sum_i \frac{\partial x_i}{\partial X_a} \frac{\partial}{\partial x_i} = \frac{M_a}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial R_x} - \frac{1}{2} \sum_i \frac{\partial}{\partial x_i}, \quad (2.56)$$

and likewise for the coordinates Y_p and Z_p . For nucleus b we have a similar expression:

$$\frac{\partial}{\partial X_b} = \frac{M_b}{M} \frac{\partial}{\partial X} - \frac{\partial}{\partial R_x} - \frac{1}{2} \sum_i \frac{\partial}{\partial x_i}. \quad (2.57)$$

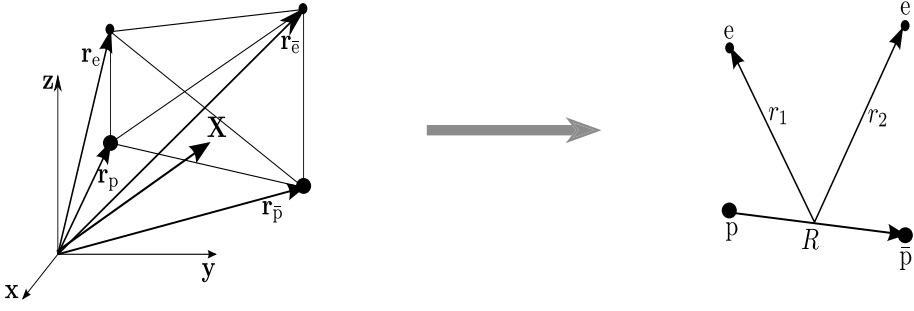


Figure 2.2. A schematic picture of the change from Cartesian coordinates to a center-of-mass coordinate system for a configuration with a proton (p), antiproton (\bar{p}), electron (e) and a positron (\bar{e}), $\mathbf{R}_p = (X_p, Y_p, Z_p)$, $\mathbf{R}_{\bar{p}} = (X_{\bar{p}}, Y_{\bar{p}}, Z_{\bar{p}})$, $\mathbf{r}_e = (x_1, y_1, z_1)$ and $\mathbf{r}_{\bar{e}} = (x_2, y_2, z_2)$. \mathbf{X} is the center-of-mass position vector, \mathbf{R} is the vector between p and \bar{p} , \mathbf{r}_1 is the vector from the center of \mathbf{R} to e and \mathbf{r}_2 is the corresponding vector to \bar{e} .

For the i 'th lepton we obtain:

$$\begin{aligned} \frac{\partial}{\partial x'_i} &= \frac{\partial X}{\partial x'_i} \frac{\partial}{\partial X} + \frac{\partial Y}{\partial x'_i} \frac{\partial}{\partial Y} + \frac{\partial Z}{\partial x'_i} \frac{\partial}{\partial Z} + \frac{\partial R_x}{\partial x'_i} \frac{\partial}{\partial R_x} + \frac{\partial R_y}{\partial x'_i} \frac{\partial}{\partial R_y} + \frac{\partial R_z}{\partial x'_i} \frac{\partial}{\partial R_z} + \\ &\sum_j \frac{\partial x_j}{\partial x'_i} \frac{\partial}{\partial x_j} + \sum_j \frac{\partial y_j}{\partial x'_i} \frac{\partial}{\partial y_j} + \sum_j \frac{\partial z_j}{\partial x'_i} \frac{\partial}{\partial z_j} = \frac{m_i}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial x_i}, \end{aligned} \quad (2.58)$$

and likewise for y'_i and z'_i . The *second order* derivative operators are now easily calculated:

$$\begin{aligned} \frac{\partial^2}{\partial X_a^2} &= \left(\frac{M_a}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial R_x} - \frac{1}{2} \sum_i \frac{\partial}{\partial x_i} \right)^2 = \left(\frac{M_a}{M} \right)^2 \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial R_x^2} + \frac{1}{4} \left(\sum_i \frac{\partial}{\partial x_i} \right)^2 \\ &+ 2 \frac{M_a}{M} \frac{\partial}{\partial X} \frac{\partial}{\partial R_x} - \frac{\partial}{\partial R_x} \sum_i \frac{\partial}{\partial x_i} - \frac{M_a}{M} \frac{\partial}{\partial X} \sum_i \frac{\partial}{\partial x_i}, \end{aligned} \quad (2.59)$$

$$\begin{aligned} \frac{\partial^2}{\partial X_b^2} &= \left(\frac{M_b}{M} \frac{\partial}{\partial X} - \frac{\partial}{\partial R_x} - \frac{1}{2} \sum_i \frac{\partial}{\partial x_i} \right)^2 = \left(\frac{M_b}{M} \right)^2 \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial R_x^2} + \frac{1}{4} \left(\sum_i \frac{\partial}{\partial x_i} \right)^2 \\ &- 2 \frac{M_b}{M} \frac{\partial}{\partial X} \frac{\partial}{\partial R_x} + \frac{\partial}{\partial R_x} \sum_i \frac{\partial}{\partial x_i} - \frac{M_b}{M} \frac{\partial}{\partial X} \sum_i \frac{\partial}{\partial x_i}, \end{aligned} \quad (2.60)$$

$$\frac{\partial^2}{\partial (x'_i)^2} = \left(\frac{m_i}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial x_i} \right)^2 = \left(\frac{m_i}{M} \right)^2 \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial x_i^2} + 2 \frac{m_i}{M} \frac{\partial}{\partial X} \frac{\partial}{\partial x_i}, \quad (2.61)$$

and likewise for Y , Z , y'_i and z'_i . Inserting these transformations into the expression for the kinetic energy one obtains

$$\begin{aligned}
& -\frac{\hbar^2}{2M_a}\Delta_a - \frac{\hbar^2}{2M_b}\Delta_b - \sum_{i=1}^n \frac{\hbar^2}{2m_i}\Delta_{\mathbf{r}_i} = \\
& -\frac{\hbar^2}{2M_a} \left[\left(\frac{M_a}{M} \right)^2 \Delta_{\mathbf{X}} + \Delta_{\mathbf{R}} + \frac{1}{4} \left(\sum_i \nabla_{\mathbf{r}_i} \right)^2 + 2 \frac{M_a}{M} \nabla_{\mathbf{X}} \nabla_{\mathbf{R}} - \nabla_{\mathbf{R}} \sum_i \nabla_{\mathbf{r}_i} \right. \\
& \left. - \frac{M_a}{M} \nabla_{\mathbf{X}} \sum_i \nabla_{\mathbf{r}_i} \right] - \frac{\hbar^2}{2M_b} \left[\left(\frac{M_b}{M} \right)^2 \Delta_{\mathbf{X}} + \Delta_{\mathbf{R}} + \frac{1}{4} \left(\sum_i \nabla_{\mathbf{r}_i} \right)^2 \right. \\
& \left. - 2 \frac{M_b}{M} \nabla_{\mathbf{X}} \nabla_{\mathbf{R}} + \nabla_{\mathbf{R}} \sum_i \nabla_{\mathbf{r}_i} - \frac{M_b}{M} \nabla_{\mathbf{X}} \sum_i \nabla_{\mathbf{r}_i} \right] \\
& - \sum_i \frac{\hbar^2}{2m_i} \left[\left(\frac{m}{M} \right)^2 \Delta_{\mathbf{X}} + \Delta_{\mathbf{r}_i} + 2 \frac{m}{M} \nabla_{\mathbf{X}} \nabla_{\mathbf{r}_i} \right] \\
& = -\frac{\hbar^2}{2M} \Delta_{\mathbf{X}} - \frac{\hbar^2}{2} \left(\frac{1}{M_b} + \frac{1}{M_a} \right) \Delta_{\mathbf{R}} - \frac{\hbar^2}{8} \left(\frac{1}{M_b} + \frac{1}{M_a} \right) \left(\sum_i \nabla_{\mathbf{r}_i} \right)^2 - \\
& \frac{\hbar^2}{2} \left(\frac{1}{M_b} - \frac{1}{M_a} \right) \nabla_{\mathbf{R}} \sum_i \nabla_{\mathbf{r}_i} - \sum_i \frac{\hbar^2}{2m_i} \Delta_{\mathbf{r}_i} = \left\{ \mu = \frac{M_a M_b}{M_a + M_b} \right\} = \\
& = -\frac{\hbar^2}{2M} \Delta_{\mathbf{X}} - \sum_i \frac{\hbar^2}{2m_i} \Delta_{\mathbf{r}_i} - \frac{\hbar^2}{8\mu} \left(\sum_i \nabla_{\mathbf{r}_i} \right)^2 - \frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} - \frac{\hbar^2}{2} \left(\frac{1}{M_b} - \frac{1}{M_a} \right) \nabla_{\mathbf{R}} \sum_i \nabla_{\mathbf{r}_i},
\end{aligned} \tag{2.62}$$

where μ is the reduced mass of the nuclei. The first term is identified as the kinetic energy for the center-of-mass, the second and third is the kinetic energy of the leptons in the center-of-mass coordinates, the fourth term is the nuclear motion in center-of-mass coordinates and the last term is the coupling between the leptons and the nuclei movements. The Hamiltonian can be written in these parts as

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2M} \Delta_{\mathbf{X}} + \hat{H}_{\text{lep}} + \hat{H}', \tag{2.63}$$

where the first term is the center-of-mass kinetic energy, \hat{H}_{lep} is the *leptonic Hamiltonian*

$$\hat{H}_{\text{lep}} = -\sum_i \frac{\hbar^2}{2m_i} \Delta_{\mathbf{r}_i} + \hat{V}, \tag{2.64}$$

with $\Delta_{\mathbf{r}_i} = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$, and

$$\hat{H}' = -\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} + \hat{H}'', \tag{2.65}$$

with $\Delta_{\mathbf{R}} = \frac{\partial^2}{\partial R_x^2} + \frac{\partial^2}{\partial R_y^2} + \frac{\partial^2}{\partial R_z^2}$, and \hat{H}'' is the rest of the terms from eq. (2.62):

$$\hat{H}'' = -\frac{\hbar^2}{8\mu} \left(\sum_i \nabla_{\mathbf{r}_i} \right)^2 - \frac{\hbar^2}{2} \left(\frac{1}{M_b} - \frac{1}{M_a} \right) \nabla_{\mathbf{R}} \sum_i \nabla_{\mathbf{r}_i}.$$

An examination of the three terms in the Hamiltonian expressed in the center-of-mass coordinates indicates that the leptonic Hamiltonian is the heavily dominant term since it consists of terms of the order $1/m$, whereas the other terms is of the order $1/M$. This difference in the order of magnitude between the leptonic and the nuclear Hamiltonian is used in the approximation methods for solving the Schrödinger equation. Writing our total wave function as $\Phi(\mathbf{X}, \mathbf{r}, \mathbf{R})$, and with the Hamiltonian in (2.63), one obtains the eigenvalue problem

$$\left(-\frac{\hbar^2}{2M} \Delta_{\mathbf{X}} + \hat{H}_{\text{lep}} + \hat{H}' \right) \Phi(\mathbf{X}, \mathbf{r}, \mathbf{R}) = E^{\text{tot}} \Phi(\mathbf{X}, \mathbf{r}, \mathbf{R}), \quad (2.66)$$

where \mathbf{r} denotes a set of coordinates for N leptons

$$\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N\}. \quad (2.67)$$

Since the operator $\Delta_{\mathbf{X}}$ does not depend on the nuclei coordinate \mathbf{R} or the leptonic coordinates \mathbf{r} , and since the Hamiltonians $\hat{H}_{\text{lep}} + \hat{H}'$ does not depend on the center-of-mass coordinate \mathbf{X} , we can separate the wave function describing the leptons and the nuclei from its center-of-mass coordinate \mathbf{X} , as

$$\Phi(\mathbf{X}, \mathbf{r}, \mathbf{R}) = \xi(\mathbf{X}) \Psi(\mathbf{r}, \mathbf{R}). \quad (2.68)$$

Inserting (2.68) into (2.66) one gets

$$\left(\hat{H}_{\text{lep}} + \hat{H}' \right) \xi(\mathbf{X}) \Psi(\mathbf{r}, \mathbf{R}) = \left(E^{\text{tot}} + \frac{\hbar^2}{2M} \Delta_{\mathbf{X}} \right) \xi(\mathbf{X}) \Psi(\mathbf{r}, \mathbf{R}) \quad (2.69)$$

$$\Rightarrow \frac{1}{\Psi(\mathbf{r}, \mathbf{R})} \left(\hat{H}_{\text{lep}} + \hat{H}' \right) \Psi(\mathbf{r}, \mathbf{R}) = \frac{1}{\xi(\mathbf{X})} \left(E^{\text{tot}} + \frac{\hbar^2}{2M} \Delta_{\mathbf{X}} \right) \xi(\mathbf{X}). \quad (2.70)$$

Both sides of (2.70) must be equal to a constant E which leads to the two decoupled equations

$$-\frac{\hbar^2}{2M} \Delta_{\mathbf{X}} \xi(\mathbf{X}) = (E^{\text{tot}} - E) \xi(\mathbf{X}), \quad (2.71)$$

$$\left(\hat{H}_{\text{lep}} + \hat{H}' \right) \Psi(\mathbf{r}, \mathbf{R}) = E \Psi(\mathbf{r}, \mathbf{R}), \quad (2.72)$$

where $\xi(\mathbf{X})$ are the eigenfunctions to the Schrödinger equation for a free particle with solutions $\xi_k(\mathbf{X}) = C^{(+)} e^{i\mathbf{k}\mathbf{X}} + C^{(-)} e^{-i\mathbf{k}\mathbf{X}}$, and eigenvalues $E^{\text{tot}} - E = \hbar^2 k^2 / 2M$, i.e. the total energy $E^{\text{tot}} = \hbar^2 k^2 / 2M + E$.

Separation of the leptonic and nuclear wave functions

The wave function that describes the leptons and the nuclei can be represented as

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_k^N \psi_k(\mathbf{r}; R) f_k(\mathbf{R}), \quad (2.73)$$

where $\psi_k(\mathbf{r}; R)$ are eigenfunctions to \hat{H}_{lep} and $f_k(\mathbf{R})$ are expansion coefficients which depends on the internuclear distance R . The leptonic wave functions ψ_k depends parametrically on the internuclear distance R , i.e. for each value of R we need to calculate the eigenfunctions to the eigenvalues of interest in the equation

$$\hat{H}_{\text{lep}}(R) \psi_k(\mathbf{r}; R) = E_k^{\text{lep}}(R) \psi_k(\mathbf{r}; R). \quad (2.74)$$

Inserting (2.73) into the Schrödinger equation in (2.72) one gets

$$(\hat{H}_{\text{lep}} + \hat{H}') \sum_k^N \psi_k(\mathbf{r}; R) f_k(\mathbf{R}) = E \sum_k^N \psi_k(\mathbf{r}; R) f_k(\mathbf{R}). \quad (2.75)$$

After multiplying it by $\psi_l^*(\mathbf{r}; R)$ from the left, and integration over the leptonic coordinates \mathbf{r} (which will be denoted by the subscript " \mathcal{L} ") we obtain the following set of equations for $f_k(\mathbf{R})$

$$\sum_k^N \langle \psi_l | (\hat{H}_{\text{lep}} + \hat{H}') (\psi_k f_k) \rangle_{\mathcal{L}} = E \sum_k^N \langle \psi_l | \psi_k \rangle_{\mathcal{L}} f_k. \quad (2.76)$$

Since ψ_k are chosen to be eigenfunctions to \hat{H}_{lep} , and since the eigenfunctions are orthonormal, we can simplify this to

$$E_l^e f_l + \sum_k^N \langle \psi_l | \hat{H}' (\psi_k f_k) \rangle_{\mathcal{L}} = E f_l. \quad (2.77)$$

Turning our attention to the second term in the equation above, we expand the first term of \hat{H}' in eq. (2.65)

$$\begin{aligned} -\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} (\psi_k f_k) &= -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}} \nabla_{\mathbf{R}} (\psi_k f_k) = -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}} [(\nabla_{\mathbf{R}} \psi_k) f_k + \psi_k (\nabla_{\mathbf{R}} f_k)] = \\ &= -\frac{\hbar^2}{2\mu} \left[(\nabla_{\mathbf{R}} \psi_k) (\nabla_{\mathbf{R}} f_k) + \psi_k (\Delta_{\mathbf{R}} f_k) + (\Delta_{\mathbf{R}} \psi_k) f_k + (\nabla_{\mathbf{R}} \psi_k) (\nabla_{\mathbf{R}} f_k) \right] = \\ &= -\frac{\hbar^2}{2\mu} [2(\nabla_{\mathbf{R}} \psi_k) (\nabla_{\mathbf{R}} f_k) + \psi_k \Delta_{\mathbf{R}} f_k + (\Delta_{\mathbf{R}} \psi_k) f_k]. \end{aligned} \quad (2.78)$$

So

$$\begin{aligned}
\langle \psi_l | \hat{H}'(\psi_k f_k) \rangle_{\mathcal{L}} &= \left(-\frac{\hbar^2}{2\mu} \right) \left(2\langle \psi_l | \nabla_{\mathbf{R}} \psi_k \rangle_{\mathcal{L}} \nabla_{\mathbf{R}} f_k + \langle \psi_l | \psi_k \rangle_{\mathcal{L}} \Delta_{\mathbf{R}} f_k \right. \\
&\quad \left. + \langle \psi_l | \Delta_{\mathbf{R}} \psi_k \rangle_{\mathcal{L}} f_k \right) + \langle \psi_l | \hat{H}''(\psi_k f_k) \rangle_{\mathcal{L}} \\
&= \left\{ \langle \psi_l | \hat{H}''(\psi_k f_k) \rangle_{\mathcal{L}} = \langle \psi_l | \hat{H}'' \psi_k \rangle_{\mathcal{L}} f_k + \langle \psi_l | \psi_k \hat{H}'' f_k \rangle_{\mathcal{L}} = \langle \psi_l | \hat{H}'' \psi_k \rangle_{\mathcal{L}} f_k \right\} \\
&= -\frac{\hbar^2}{\mu} \langle \psi_l | \nabla_{\mathbf{R}} \psi_k \rangle_{\mathcal{L}} \nabla_{\mathbf{R}} f_k - \delta_{lk} \frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} f_k - \frac{\hbar^2}{2\mu} \langle \psi_l | \Delta_{\mathbf{R}} \psi_k \rangle_{\mathcal{L}} f_k + \langle \psi_l | \hat{H}'' \psi_k \rangle_{\mathcal{L}} f_k \\
&= -\frac{\hbar^2}{\mu} \langle \psi_l | \nabla_{\mathbf{R}} \psi_k \rangle_{\mathcal{L}} \nabla_{\mathbf{R}} f_k - \delta_{kl} \frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} f_k + \langle \psi_l | \left(-\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} + \hat{H}'' \right) \psi_k \rangle_{\mathcal{L}} f_k \\
&= -\frac{\hbar^2}{\mu} \langle \psi_l | \nabla_{\mathbf{R}} \psi_k \rangle_{\mathcal{L}} \nabla_{\mathbf{R}} f_k - \delta_{kl} \frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} f_k + H'_{lk} f_k. \tag{2.79}
\end{aligned}$$

The leptonic wave functions can always be written as

$$\psi_k(\mathbf{r}, R) = \varphi_k(\mathbf{r}, R) e^{i\phi(R)}, \tag{2.80}$$

where $\varphi_k(\mathbf{r}, R)$ is a real function. In the further derivation we will assume that the phase ϕ does not depend on R . By using the normalization condition:

$$\langle \psi_k | \psi_k \rangle = \langle \varphi_k e^{i\phi} | \varphi_k e^{i\phi} \rangle = \langle \varphi_k | \varphi_k \rangle \langle e^{i\phi} | e^{i\phi} \rangle = \langle \varphi_k | \varphi_k \rangle = 1, \tag{2.81}$$

we can write

$$\begin{aligned}
0 &= \nabla_{\mathbf{R}} \langle \psi_k | \psi_k \rangle = \nabla_{\mathbf{R}} \int_e \varphi_k(\mathbf{r}, R) \cdot \varphi_k(\mathbf{r}, R) d\mathbf{r} = \\
&\quad \int_e \left([\nabla_{\mathbf{R}} \varphi_k(\mathbf{r}, R)] \varphi_k(\mathbf{r}, R) + \varphi_k(\mathbf{r}, R) [\nabla_{\mathbf{R}} \varphi_k(\mathbf{r}, R)] \right) d\mathbf{r} = \\
&= 2\langle \varphi_k | \nabla_{\mathbf{R}} \varphi_k \rangle_{\mathcal{L}} \Leftrightarrow \langle \psi_k | \nabla_{\mathbf{R}} \psi_k \rangle_{\mathcal{L}} = \langle \varphi_k | \nabla_{\mathbf{R}} \varphi_k \rangle_{\mathcal{L}} = 0. \tag{2.82}
\end{aligned}$$

By using this equality, eq (2.79) becomes

$$\langle \psi_l | \hat{H}'(\psi_k f_k) \rangle_{\mathcal{L}} = (1 - \delta_{kl}) \left(-\frac{\hbar^2}{\mu} \right) \langle \psi_l | \nabla_{\mathbf{R}} \psi_k \rangle_{\mathcal{L}} \nabla_{\mathbf{R}} f_k - \delta_{kl} \frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} f_k + H'_{lk} f_k, \tag{2.83}$$

where

$$H'_{lk} = \langle \psi_l | \hat{H}' \psi_k \rangle_{\mathcal{L}}. \tag{2.84}$$

Using eq. (2.83) in eq. (2.77) gives us

$$E_l^e f_l + \sum_k^N \left[(1 - \delta_{kl}) \left(-\frac{\hbar^2}{\mu} \right) \langle \psi_l | \nabla_{\mathbf{R}} \psi_k \rangle_{\mathcal{L}} \nabla_{\mathbf{R}} f_k - \delta_{kl} \frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} f_k + \hat{H}'_{lk} f_k \right] = E f_l. \tag{2.85}$$

By writing out the $k = l$ terms from the sum and moving the terms containing f_l on the left-hand side we get a set of N equations for $l = 1, 2, 3, \dots, N$;

$$\left[-\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} + E_l^e(R) + H'_{ll}(R) - E \right] f_l(\mathbf{R}) = - \sum_{k \neq l}^N \Theta_{lk} f_k(\mathbf{R}), \quad (2.86)$$

where

$$\Theta_{lk} = - \sum_{k \neq l}^N \left[-\frac{\hbar^2}{\mu} \langle \psi_l | \nabla_{\mathbf{R}} \psi_k \rangle_{\mathcal{L}} \nabla_{\mathbf{R}} + H'_{lk} \right]. \quad (2.87)$$

The Born-Oppenheimer and the adiabatic approximation

So far we have made no approximations and equation (2.86) is equivalent to the Schrödinger equation. Now, if the differences between $E_l^e(R)$ for different quantum numbers are large, the coupling between the associated states must be small, and we can approximate Θ_{lk} for $k \neq l$ to be zero. This approximation is the *adiabatic approximation*, i.e

$$\left[-\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} + E_l^e(R) + H'_{ll}(R) \right] f_l(\mathbf{R}) = E f_l(\mathbf{R}). \quad (2.88)$$

The diagonal correction H'_{ll} is usually very small compared to $E_l^e(R)$ since the leptonic Hamiltonian is of order $\frac{1}{m}$ compared to $\frac{1}{\mu}$, so as long as the mass of the leptons are much smaller than the reduced mass of the nuclei we can approximate also this term to be zero. By doing this we arrive at the *Born-Oppenheimer approximation*, i.e.

$$\left[-\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} + E_l^e(R) \right] f_l(\mathbf{R}) = E f_l(\mathbf{R}). \quad (2.89)$$

Since the potential energy *for the motion of the nuclei* in the adiabatic approximation

$$\begin{aligned} \hat{V}^{ad} &= E_l^e(R) + H'_{ll}(R) = E_l^e(R) + \langle \psi_l | \hat{H}' \psi_l \rangle_{\mathcal{L}} \\ &= E_l^e(R) + \left\langle \psi_l \left| \frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} + \left[-\frac{\hbar^2}{8\mu} \left(\sum_i \nabla_{\mathbf{r}_i} \right)^2 - \frac{\hbar^2}{2} \left(\frac{1}{M_a} - \frac{1}{M_b} \right) \nabla_{\mathbf{R}} \sum_i \nabla_{\mathbf{r}_i} \right] \psi_l \right\rangle_{\mathcal{L}}, \end{aligned} \quad (2.90)$$

contains the masses M_a and M_b , the potential energy in the adiabatic approximation *depends on the mass of the nuclei*, whereas the potential energy in the Born-Oppenheimer approximation

$$\hat{V}^{BO} = E_l^e(R), \quad (2.91)$$

does not.

Furthermore, in molecular investigations it is often of interest to speak of rotational and oscillational energies, and for this an additional approximation in the separation of the rotational and vibrational energies is necessary, where the moment of inertia operator is approximated to be constant and equal to the equilibrium value $I_k^e = \mu (R_k^e)^2$, see appendix C for details.

2.5 Scattering theory

The collision of particles on other particles (or fields) is one of the main tools for investigating their properties, their constituent parts and for learning more about the laws of nature. This is the experimental technique that was used to discover the positron, the neutron, and all the subatomic particles found so far. In quantum mechanics, a scattering collision is mathematically viewed as a wave function colliding with a potential energy, where the incoming wave is undisturbed by the potential, and the outgoing wave has been altered because of the interaction with the potential. From knowing the incoming and outgoing wave function, one can deduce information about the potential, and conversely, from knowing either the incoming or outgoing wave function and the potential, one can calculate the unknown wave function. The wave function can be written as a linear combination of the incoming wave function Ψ_i and the perturbed (scattered) wave function Ψ_s due to the scattering potential⁴ $\Psi_f = c_i\Psi_i + c_s\Psi_s$.

In general, the wave function must be a solution to the Schrödinger equation

$$\left[-\frac{1}{2m}\nabla^2 + V(r) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r}), \quad (2.92)$$

where we usually approximate the potential to be spherically symmetric ($V(\mathbf{r}) = V(r)$) such that the spherical harmonics part of the wave function expansion for the radial dependence reduces to Legendre polynomials $P_l(\cos\theta)$, and the wave function can be written as

$$\Psi(\mathbf{r}) = \sum_l \xi_l(r) P_l(\cos\theta), \quad (2.93)$$

with l being the angular momentum. Detection of the particles occur far from the potential scattering center and at this distance the particles should behave like free particles. Therefore we write (2.93) as a plane wave by the *plane wave expansion*⁵

$$\Psi(\mathbf{r}) = e^{ikz} = \sum_{l=0}^{\infty} (2l+1) i^l j_l(kr) P_l(\cos\theta), \quad (2.94)$$

where $j_l(kr)$ are the spherical Bessel functions, which have the asymptotic form

$$j_l(kr) \rightarrow \frac{1}{2ikr} \left(e^{i(kr-l\pi/2)} - e^{-i(kr-l\pi/2)} \right), \quad (2.95)$$

which corresponds to an outgoing and an incoming wave function. Since the scattered wave function is the outgoing wave function we can write Ψ_s as

$$\Psi_s(\mathbf{r}) = f(k, \theta) \frac{e^{ikr}}{r} \quad (2.96)$$

⁴One might want to think of it as one of the particles being fixed in space and the other particle scattered on the potential of the fixed particle.

⁵Here the wave vector \mathbf{k} is aligned with the z -axis, such that $z = r \cos\theta$.

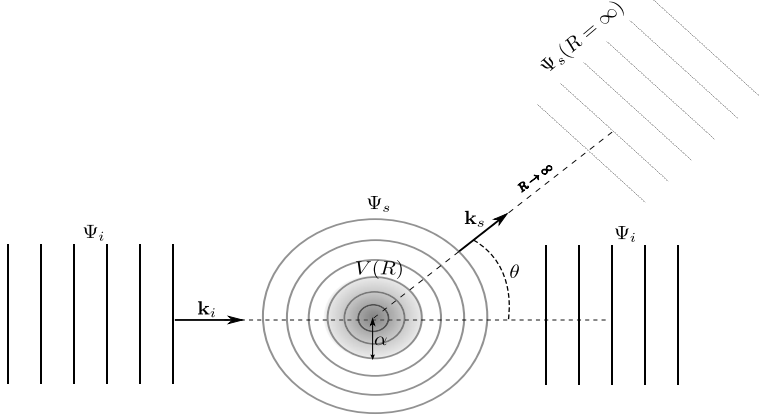


Figure 2.3. Incoming wave function Ψ_i scattered on a potential $V(R)$ with approximate scattering length α . Some of Ψ_i remains after interaction with the potential and the scattered part Ψ_s becomes a plane wave function at $R = \infty$.

and define $f(k, \theta)$ as the scattering amplitude. For conformity with (2.94) we expand $f(k, \theta)$ in Legendre functions as

$$f(k, \theta) = \sum_{l=0}^{\infty} (2l+1) f_l(k) P_l(\cos \theta), \quad (2.97)$$

where $f_l(k)$ is the partial wave amplitude related to the phase shift η_l (the distance between the scattered and the unscattered wave functions nodes) as

$$f_l(k) = \frac{1}{k \cot \eta_l - ik} = \frac{e^{i\eta_l} \sin \eta_l}{k}. \quad (2.98)$$

The differential cross section $d\sigma/d\Omega$ is defined as the ratio of the number of scattered particles $dn(\theta, \phi)$ per unit time within the solid angle $d\Omega = \sin \theta d\theta d\phi$ divided by the incident particle flux F [73]

$$\frac{d\sigma}{d\Omega} = \frac{dn(\theta, \phi)}{F d\Omega}. \quad (2.99)$$

The differential cross section is directly related to the scattering amplitude as

$$\frac{d\sigma}{d\Omega} = |f(k, \theta)|^2. \quad (2.100)$$

The total cross section is obtained by integrating the differential cross section over $d\Omega$

$$\sigma_T = \int_0^{2\pi} \phi \int_0^{\pi} \sin \theta d\theta \frac{d\sigma}{d\Omega} = 2\pi \int_0^{\pi} |f(k, \theta)|^2 \sin \theta d\theta. \quad (2.101)$$

The elastic cross section σ_e for S -wave scattering ($l = 0$), is defined as the limit of the total S -wave cross section as $k \rightarrow 0$

$$\begin{aligned}\sigma_e &= \lim_{k \rightarrow 0} \sigma_T^{l=0} = \lim_{k \rightarrow 0} 2\pi \int_0^\pi |f(k, \theta)|^2 \sin \theta d\theta = 2\pi \int_0^\pi \left| \lim_{k \rightarrow 0} f_0(k) \right|^2 \sin \theta d\theta \\ &= 2\pi \int_0^\pi \left| \frac{1}{\lim_{k \rightarrow 0} \frac{k}{\tan \eta_l}} \right|^2 \sin \theta d\theta.\end{aligned}\quad (2.102)$$

The scattering length is defined in the low-energy limit, i.e. $k \rightarrow 0$, as

$$\alpha = -\lim_{k \rightarrow 0} \frac{\tan \eta_{l=0}(k)}{k}, \quad (2.103)$$

where $\eta(k)$ is the phase shift. Inserting the expression for the scattering length, (2.102) becomes

$$\sigma_e = 4\pi |\alpha|^2 = 4\pi \alpha^2. \quad (2.104)$$

Thus, by knowing the scattering length we can calculate the phase shift, the scattering amplitude and the elastic cross section.

In appendix A in paper II it is shown that one can obtain the scattering length by a geometrical approximation as the crossing of a tangent to the last node of the wave function and the zero value of the wave function.

2.6 Resonance states from real and complex scaling

The approximation to the eigenstate energies given by the variational principle depend on how well the basis set spans the Hilbert space of the system. The spatial extension of the basis functions need to span the range of the potential and be flexible enough to describe the wave function with high accuracy. However, the use of L^2 basis functions has the effect similar to enclosing the system in a “box” whose size depends on the spatial extension of the basis set, and the continuum eigenvalues become discretized. Thus, by slightly altering the basis set the eigenvalues move, and by studying by how much they move one can identify properties of the eigenstates. For example, as long as the spatial extension is large enough to envelope the potential, the bound-state eigenvalues will not change significantly while the continuum states will change drastically. Scaling the spatial extension of the basis set can e.g. be obtained by

- (a) Enlargement of the basis set by adding functions with longer reach,
- (b) Scaling of basis-parameters that govern the spatial extension, either directly or indirectly by scaling the Hamiltonian.

One can use the *stabilization method* (also called *real scaling method*) to look for semi-bound states called *resonance states*. How bound a state is can be thought of in terms of how long lived it is. A hydrogen atom, which is Coulombically stable, has states of infinite lifetimes and these are the kind of states that we normally call *bound* states. Molecules that are temporarily bound together by attracting forces or by lack of separation energy are semi-bound, i.e. they eventually dissolve into fragments. These kinds of states are called resonance states.

Resonance states can be characterized by two different scenarios [74]. When two atoms or molecules collide, part of the kinetic energy of relative motion may be temporarily converted into vibrational or rotational energy. The additional internal energy may enable states otherwise energetically inaccessible and the decreased kinetic energy might leave the molecule with temporarily insufficient energy, for the relative motion, to separate. These kinds of states are referred to as *Feshbach* or *compound* resonance states. Eventually, the internal energy is transferred back into the relative kinetic energy of motion and the molecule breaks up. The other kind of resonance state is the *orbiting* or *shape* resonances, in which the colliding partners are temporarily held together by a centrifugal barrier, arising from forces holding the particles together.

The eigenvalues that correspond to resonant states are much more stable than eigenvalues corresponding to continuum states (see appendix **D** for a detailed derivation). As shown by Simons [75], the stabilization technique can be

used to extract the resonance width. The resonance width Γ is related to the lifetime τ of the state as

$$\tau = \frac{\hbar}{\Gamma} \quad (2.105)$$

where \hbar is the *reduced Planck constant* ($h/2\pi$) and Γ can be estimated from a stabilization plot as [75]

$$\Gamma \sim \Delta E \cdot \frac{|S_r|}{|S_c|}, \quad (2.106)$$

see Figure 2.4. Moreover, we obtain the wavelength of the state from $\lambda \approx 2\pi/k_r$ where the wave number k_r is related to the resonance energy ε_r and the particle's mass μ as $\varepsilon_r = k_r^2/2\mu$, and from the resonance energy ε_r and width Γ together with (5.102) we can calculate the phase shift which is connected to the scattering length by (2.103) and partial cross sections by (2.102).

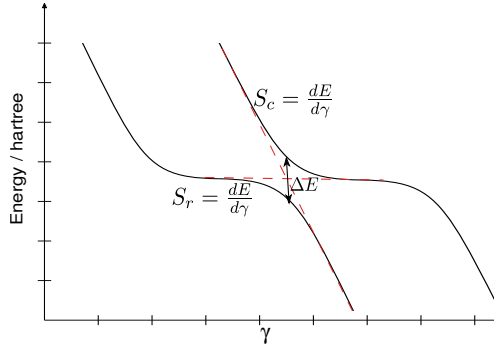


Figure 2.4. An example plot of two eigenvalues avoided crossings behaviour. We measure the energy difference at the point where the slope of the stable roots S_s , and the slope of the continuum roots S_c cross, and use it to calculate the resonance width Γ .

Complex Scaling

Similar to the stabilization method for real scaling, resonance states reveal themselves in a slightly different technique of altering the basis set in what is called *complex scaling*. This can be done in different ways, the two ways used in paper III are;

- by scaling the kinetic and potential energy matrices by a complex scaling parameter $\gamma = \cos(\theta) + i \sin(\theta)$ where we increase the angle θ by small incremental steps σ as

$$\gamma_n = \cos(\theta_n) + i \sin(\theta_n), \quad \theta_n = \theta_0 + \sigma n, \quad (2.107)$$

where $\theta_0 = 0$ and $|\theta|$ smaller than the maximum scaling angle β_{\max}

$$|\theta| < \beta_{\max} = \arcsin(2/\pi)/2, \quad (2.108)$$

- by keeping the real part of γ constant and only adding a complex part $i\zeta = i\sigma$ which we increase by small steps using an increment σ as

$$\gamma_n = \text{Re}(\gamma) + i\sigma n, \quad \frac{1}{2} \arctan\left(\frac{\sigma n}{\text{Re}(\gamma)}\right) < \beta_{max}. \quad (2.109)$$

Since roots close to resonance energies move less than continuum roots during complex scaling, we are looking for roots that travel in the complex plane by getting successively closer, or circle around a stable complex energy E_c as described in [76, 77]. From the real and imaginary part of the complex energy we can estimate the resonance energy E_{res} and the resonance width Γ from

$$E_c = E_{\text{res}} - i\Gamma/2. \quad (2.110)$$

The resonance width Γ is determined from the scaling plot at the position of the scaling path where the minimum of $dE/d\gamma$ is reached.

2.7 Quantum Dynamics wave propagation

Quantum dynamics involves describing the time evolution of the system by solving the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(R, t) = \hat{H} \Psi(R, t). \quad (2.111)$$

Since the Hamiltonian operator and the time derivative are both linear operators, eq. (2.111) is linear and the evolution of the state $\Psi(R, t)$ from time t_0 to t can be described as the action of a linear time evolution operator (or *propagator*) $\hat{U}(t, t_0)$ on the state

$$\Psi(t) = \hat{U}(t, t_0) \Psi(t_0). \quad (2.112)$$

The propagator needs to fulfil a number of physical properties. To conserve the total probability $\hat{U}(t, t_0)$ must be unitary, i.e. $\hat{U}^\dagger(t, t_0) \hat{U}(t, t_0) = \mathbf{1}$, and from the continuity condition we have

$$\lim_{dt \rightarrow 0} \hat{U}(t_0 + dt, t_0) = \mathbf{1}, \quad (2.113)$$

which is satisfied if the propagator differs from the identity operator by an order of dt . These two conditions are satisfied by writing it as

$$\hat{U}(t_0 + dt, t_0) = \mathbf{1} - i\hat{A}dt. \quad (2.114)$$

If \hat{A} is a Hermitian operator the propagator also fulfils the composition condition

$$\hat{U}(t_2, t_0) = \hat{U}(t_2, t_1) \hat{U}(t_1, t_0), \quad t_2 > t_1 > t_0. \quad (2.115)$$

From classical mechanics we know that the Hamiltonian is the generator of infinitesimal time translation, so we set $\hat{A} = \hat{H}$ and divide by \hbar to get the dimension and classical limit correct, and define the infinitesimal propagator as

$$\hat{U}(t_0 + dt, t_0) = \mathbf{1} - \frac{i}{\hbar} \hat{H} dt. \quad (2.116)$$

Using (2.115) in (2.116) we get

$$\begin{aligned} \hat{U}(t + dt, t_0) &= \hat{U}(t + dt, t) \hat{U}(t, t_0) = \left(\mathbf{1} - \frac{i}{\hbar} \hat{H} dt \right) \hat{U}(t, t_0) \\ \frac{\hat{U}(t + dt, t_0) - \hat{U}(t, t_0)}{dt} &= -\frac{i}{\hbar} \hat{H} \hat{U}(t, t_0), \end{aligned} \quad (2.117)$$

which in the limit as $dt \rightarrow 0$ gives us the time-dependent Schrödinger equation for the propagator

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H} \hat{U}(t, t_0), \quad (2.118)$$

or, written in integral form and selecting $\mathbf{1}$ as the constant in order for it to correspond with (2.116)

$$\hat{U}(t, t_0) = \mathbf{1} - \frac{i}{\hbar} \int_{t_0}^t \hat{H} \hat{U}(t', t_0) dt'. \quad (2.119)$$

If the Hamiltonian does not depend explicitly on time the solution to (2.118) is simply

$$\hat{U}(t, t_0) = e^{-\frac{i}{\hbar} \hat{H} \Delta t} \quad (2.120)$$

with $\Delta t = t - t_0$. If the Hamiltonian depends on time but each time-specific Hamiltonian commute with the others, then the solution is

$$\hat{U}(t, t_0) = e^{-\frac{i}{\hbar} \int_{t_0}^t \hat{H}(t') dt'}, \quad (2.121)$$

but in the most general case⁶ the integral form is used and solved by recursive insertion of (2.119) to get

$$\hat{U}(t, t_0) = \mathbf{1} + \sum_n \left(\frac{i}{\hbar}\right)^n \int_{t_0}^t dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1 \hat{H}(t_n) \hat{H}(t_{n-1}) \cdots \hat{H}(t_1). \quad (2.122)$$

The order of the integrals are important and it is common to introduce the *time-ordering* operator $\hat{\mathcal{T}}$ to get a simpler notation of the r.h.s of (2.122)

$$\hat{U}(t, t_0) = \hat{\mathcal{T}} e^{-\frac{i}{\hbar} \int_{t_0}^t dt \hat{H}(t)}. \quad (2.123)$$

By selecting equidistant time steps $\Delta t = t/N$ and using (2.115) we can write (2.122) as

$$\hat{U}(t, t_0) = \prod_{n=0}^{N-1} \hat{U}((n+1)\Delta t, n\Delta t), \quad (2.124)$$

where in a numerical solution the change in the Hamiltonian during Δt is approximated to be negligible, such that we can use (2.120) and write the propagation for each term in (2.124) as

$$\hat{U}((n+1)\Delta t, n\Delta t) = e^{-\frac{i}{\hbar} \hat{H}(n\Delta t) \Delta t}. \quad (2.125)$$

A propagator written in exponential form as in 2.125 can be approximated numerically by a number of methods. In paper **V** we used the *Chebyshev* polynomial method where $e^{-i\hat{H}t}$ is expanded in Chebyshev polynomials⁷ $T_k(\hat{H})$ as

$$e^{-i\hat{H}t} = \sum_k (2 - \delta_{k0}) (-i)^k J_k(t) T_k(\hat{H}), \quad (2.126)$$

⁶e.g. a charged particle in a magnetic field that changes orientation over time.

⁷Chebyshev polynomials can be defined as the polynomials satisfying $T_k(\cos \theta) = \cos(k\theta)$, for $k = 0, 1, 2, \dots$

where J_k are Bessel functions of the first kind and \hat{H} is scaled to $[-1, 1]$ by transforming the Hamiltonian into an angle operator $\hat{\Theta}$ as

$$\hat{\Theta} = \arccos(\hat{H}). \quad (2.127)$$

Chebyshev polynomials have the numerical advantage of satisfying the recursion formula

$$T_{k+1}(\hat{\Theta}) = 2T_k(\hat{\Theta}) - T_{k-1}(\hat{\Theta}) \quad k \geq 1, \quad (2.128)$$

with

$$T_0(\hat{\Theta}) = 1, \quad T_1(\hat{\Theta}) = \hat{\Theta}. \quad (2.129)$$

The recursion formula in (2.128) is an analogy to the trigonometric cosine addition identity

$$\cos[(k+1)\hat{\Theta}] + \cos[(k-1)\hat{\Theta}] = 2\cos(\hat{\Theta})\cos(k\hat{\Theta}). \quad (2.130)$$

For more details on the Chebyshev propagator scheme, see [78].

In paper V we used the *Fast Fourier Transform*⁸ method to calculate $\hat{H}\Psi(R, t)$ on a grid of points, where we take advantage of the close relation between cosine functions and Chebyshev polynomials since the Fourier transform of cosine functions are trivial.

The idea of the FFT method is to separate the operation $\hat{H}\Psi(R, t) = (\hat{T} + \hat{V})\Psi(R, t)$ into two parts for each time step. One operation by the potential part of the Hamiltonian in local coordinate space and one operation by the kinetic part. For the kinetic part, the wave function is transformed to momentum space by a *backward discrete Fourier transform*, where the kinetic operation is a simple discrete momentum multiplication, and the result returned to coordinate space by its inverse, the *forward discrete Fourier transform*.

⁸See [79] for details on Fourier transform.

2.8 Molecular electronic structure theory

Hartree-Fock Theory

In quantum chemistry we need to solve the Schrödinger equation for molecular systems with many electrons and nuclei. Starting from the Born-Oppenheimer approximation with the leptonic Hamiltonian in (2.64) and with \hat{V} in (2.54) where we only consider leptons being electrons e , written in atomic units as

$$\hat{V} = -\sum_{a,i} \frac{1}{r_{ai}} + \sum_{a>b} \frac{1}{R_{ab}} + \sum_{i>j} \frac{1}{r_{ij}} = \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}), \quad (2.131)$$

we arrive at the Schrödinger equation for the electronic motion

$$(\hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})) \Psi(\mathbf{r}; \mathbf{R}) = E_{el} \Psi(\mathbf{r}; \mathbf{R}), \quad (2.132)$$

where the kinetic operator $\hat{T}_e(\mathbf{r}) = \frac{1}{2} \sum_i \nabla_{\mathbf{r}_i}^2$. Douglas Hartree noticed that if the interaction between the electrons are negligible, $\hat{V}_{ee}(\mathbf{r}) = 0$, the individual electron coordinates are separable which led him to approximate the electronic wave function as the product of spin orbital wave functions⁹ $\{\chi_i(\mathbf{x}_i)\}$ describing individual electronic systems as

$$\begin{aligned} \Psi_{HP}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) &= \psi_1(\mathbf{r}_1) \sigma(\omega_1) \psi_2(\mathbf{r}_2) \sigma(\omega_2) \dots \psi_N(\mathbf{r}_N) \sigma(\omega_N) \\ \Rightarrow \Psi_{HP}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) &= \chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2) \dots \chi_N(\mathbf{x}_N). \end{aligned} \quad (2.133)$$

The *Hartree-Product* expansion above is not antisymmetric with respect to exchange of indistinguishable fermions (electrons), but this is fixed by writing the expansion as a (*Slater*) determinant¹⁰

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \dots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \dots & \chi_N(\mathbf{x}_2) \\ \dots & \dots & \dots & \dots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \dots & \chi_N(\mathbf{x}_N) \end{vmatrix}. \quad (2.134)$$

This symmetrized approximation is used for the expansion of the wave function, and now we go back and write (2.132) as an eigenvalue problem $\hat{H}_{el} \Psi = E_{el} \Psi$ with

$$\hat{H}_{el} = \hat{h} + \hat{g} + h_{nuc} = \sum_i \hat{h}(i) + \sum_{i<j} \hat{v}(i, j) + h_{nuc}, \quad (2.135)$$

where the nuclear-nuclear repulsion term h_{nuc} acts as a constant that shifts the eigenvalues, and $h(i)$ is the one-electron operator representing the kinetic

⁹The spin orbital wave functions $\chi(\mathbf{x})$ are the product of the spatial and spin components, where the spin can be either α (up) or β (down).

¹⁰Since the expression $\Psi(x_1, x_2) = \chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1)$ is clearly antisymmetric, i.e. interchanging x_1 for x_2 , which corresponds to shifting two rows in the determinant, results in $\Psi(x_1, x_2) = -\Psi(x_2, x_1)$.

energy of the electron and its attractive interaction with the nuclei (terms $\hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R})$ in (2.132))

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_a \frac{1}{r_{ia}}, \quad (2.136)$$

and $\hat{v}(i, j)$ is the two-electron operator representing the repulsive Coulomb interaction between two electrons (the term $\hat{V}_{ee}(\mathbf{r})$ in (2.132))

$$\hat{v}(i, j) = \frac{1}{r_{ij}}. \quad (2.137)$$

With the simplified expression for the leptonic Hamiltonian and with the wave function expanded by the determinant in (2.134), the eigenvalue problem can be solved by the variational method by minimizing the energy functional

$$E_{el}[\Psi] = \frac{\langle \Psi | \hat{H}_{el} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (2.138)$$

through varying the parameters describing the spin orbital set $\{\chi_j\}$. In order to keep the spin orbital set orthonormal we vary the parameters by Lagrange's method of undetermined multipliers, where the altered functional is given by

$$\mathcal{L}[\{\chi_i\}] = E[\{\chi_i\}] - \sum_{i,j} \varepsilon_{ij} \left(\int \chi_i^*(\mathbf{x}) \chi_j(\mathbf{x}) d\mathbf{x} - \delta_{ij} \right), \quad (2.139)$$

where the integral describes the overlap between spin orbitals i and j . Considering a two electron molecule with electrons at coordinates \mathbf{x}_1 and \mathbf{x}_2 , the minimum for the energy functional using the Lagrange method results in a set of equations known as the Hartree-Fock equations

$$\left(\hat{h}(\mathbf{x}_1) + \sum_j \hat{\mathcal{J}}_j(\mathbf{x}_1) - \sum_j \hat{\mathcal{K}}_j(\mathbf{x}_1) \right) \chi_i(\mathbf{x}_1) = \varepsilon_i \chi_i(\mathbf{x}_1), \quad (2.140)$$

where the *Coulomb* operator $\hat{\mathcal{J}}_i(\mathbf{x}_1)$ represent the average potential¹¹ affecting the electron at \mathbf{x}_1 due to the charge distribution from the electron in spin orbital χ_i , defined as

$$\hat{\mathcal{J}}_i(\mathbf{x}_1) = \int \frac{|\chi_i(\mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_2, \quad (2.141)$$

and the *exchange* operator (arising from the anti-symmetrization of the wave function) is defined by its action on a spin orbital as

$$\hat{\mathcal{K}}_i(\mathbf{x}_1) \chi_j(\mathbf{x}_1) = \left(\int \frac{\chi_i^*(\mathbf{x}_2) \chi_j(\mathbf{x}_2)}{r_{ij}} d\mathbf{x}_2 \right) \chi_i(\mathbf{x}_1). \quad (2.142)$$

¹¹The potential is summed over all the electrons where each electron is interacting with the average distribution of the other electrons, making it easy to see the mean-field character of the Hartree-Fock method. In other words, the true two-electron contribution \hat{g} in (2.135) is replaced by an effective one-electron *Fock potential* \hat{V} .

By introducing the *Fock operator* \hat{f} as

$$\hat{f}(\mathbf{x}_1) = \hat{h}(\mathbf{x}_1) + \sum_j \hat{\mathcal{J}}_j(\mathbf{x}_1) - \sum_i \hat{\mathcal{K}}_i(\mathbf{x}_1), \quad (2.143)$$

the Hartree-Fock equations are written as an eigenvalue problem

$$\hat{f}(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \varepsilon_i\chi_i(\mathbf{x}_1), \quad (2.144)$$

with the spin orbital functions $\{\chi_i(\mathbf{x}_1)\}$ and associated eigenenergy ε_i being the eigenfunctions to the Fock operator, where from (2.141) and (2.142) it is evident that f depends on the spin orbital set $\{\chi_i\}$ and \mathbf{x} . Commonly, the spin orbitals are themselves expanded in atomic orbital basis functions $\tilde{\chi}$ using Gaussian functions for simplified integral expressions as

$$\chi_i = \sum_k c_k^i \tilde{\chi}_k, \quad (2.145)$$

which turns (2.144) into the *Hartree-Fock-Roothaan* equations, a generalized matrix diagonalization problem.

The Hartree-Fock (and thus also the Hartree-Fock-Roothaan) equations are solved numerically in an iterative manner since the set of equations depend on the spin orbital set $\{\chi_j\}$, which is updated between each energy minimization to get closer to the true energy minimum. This self-dependent solution procedure is why this method is referred to as a *Self-Consistent-Field* (SCF) procedure.

The general SCF procedure makes some assumptions on the wave function, such as the inherent Born-Oppenheimer approximation since the electronic wave function does not depend on the coordinates of the nuclei, ignoring relativistic effects, using a finite basis set and the fact that we write the wave function as an anti-symmetrized product of 1-electron functions which ignores the effects of electron correlation. The last assumption is improved upon by post-Hartree Fock methods such as MCSCF, CASSCF and FCI in terms of including mainly the static electron correlation, and to include more of the dynamical electron correlation effects perturbation methods can be used. In the CASPT2 method both static and dynamic correlations are included, as the CASSCF wave function is used as a starting point for the perturbation method.

MCSCF, FCI and CASSCF

When solving the Hartree-Fock equations, we calculate and minimize the energies for one particular configuration of electrons, as we calculate the specific form of one Slater determinant. Furthermore, each Hartree-Fock equation is written in terms of one electron reacting with the rest of the electrons as a mean-field approximation, which fails to capture the finer details

of electron-electron interactions needed for describing many chemically interesting systems. In the *Multi-Configurational Self Consistent Field* (MCSCF) method, the wave function ansatz is improved upon by expanding the wave function as a linear combination of Slater determinants

$$\Psi^{(0)} = \sum_i c_i \det|\chi_1^{(i)}, \chi_2^{(i)}, \dots, \chi_N^{(i)}| = \sum_i c_i \phi_i, \quad (2.146)$$

where each determinant ϕ_i corresponds to a particular configuration of electrons in specific orbitals. The number of ways one can place the electrons depends on the number of electrons and the number of orbitals available, which determines the number of possible determinants that can be formed in the wave function expansion. In paper V we included all possible determinants in the wave function expansion which is called a *Full Configuration Interaction* (FCI) expansion. If the determinants to include are selected by hand the expansion is a general MCSCF wave function. In the *Complete Active Space Self Consistent Field* (CASSCF¹²) method the idea is to include all possible determinants ϕ_i that can be formed within a selected set (the CAS set) of active orbitals

$$\Psi_{CAS}^{(0)} = \sum_i^{CAS} c_i \phi_i, \quad (2.147)$$

where the expansion coefficients c_i in front of the Slater determinants ϕ_i are called the configuration interaction coefficients. This method leaves the user to select the active orbitals to include instead of hand picking a specific set of configurations. The process of finding the optimal orbitals for the active space is generally done in an iterative process similar to the one described in the Hartree-Fock Theory section with the added complexity of not only optimizing the molecular orbital set but also which ones to include in the CAS space, making the CAS method a self-consistent field method (CASSCF).

Multi-configurational perturbation theory

In the Hartree-Fock method, a single determinant is used to expand the wave function, which lets us arrange the spin orbital functions in canonical order such that the Fock operator can be brought to diagonal form where the spin orbital functions are eigenfunctions to the Fock operator, i.e.

$$\hat{f} = \sum_{pq} f_{pq} E_{pq} = \sum_p \varepsilon_p E_{pp}, \quad (2.148)$$

where ε_p is the eigenenergy of spin orbital p and E_{pq} is the excitation operator from orbital q to p , usually expressed in the formulation of the *second*

¹²Sometimes referred to as *Full-Optimized Reaction Space* (FORS).

quantization with the creation and annihilation operators¹³ as

$$E_{pq} = a_p^\dagger a_q. \quad (2.149)$$

The Fock operator is for this special canonical configuration the sum of the spin orbital eigenenergies, allowing for using it as the zero-order Hamiltonian in perturbation expansion as in the Møller-Plesset Perturbation Theory (MPPT) [80]. For a multi-configuration wave function, the wave function is no longer an eigenfunction to the Fock operator so the Fock operator cannot be used as the zero-order Hamiltonian. However, by writing $\hat{H}^{(0)}$ as

$$\hat{H}^{(0)} = E^{(0)}|0\rangle\langle 0| + \hat{P}\hat{f}\hat{P}, \quad (2.150)$$

with

$$\hat{P} = (1 - |0\rangle\langle 0|)\hat{f}(1 - |0\rangle\langle 0|), \quad (2.151)$$

where $E^{(0)} = \langle 0|\hat{f}|0\rangle$, and $|0\rangle$ the multi-configurational wave function (the reference wave function), $|0\rangle$ becomes an eigenfunction to $\hat{H}^{(0)}$

$$\begin{aligned} \hat{H}^{(0)}|0\rangle &= E^{(0)}|0\rangle\langle 0|0\rangle + (1 - |0\rangle\langle 0|)\hat{f}(1 - |0\rangle\langle 0|)|0\rangle \\ &= E^{(0)}|0\rangle + (1 - |0\rangle\langle 0|)\hat{f}(|0\rangle - |0\rangle) = E^{(0)}|0\rangle. \end{aligned} \quad (2.152)$$

In the CASPT (*Complete Active Space Perturbation Theory*) method a clever partitioning scheme for the zero-order Hamiltonian is employed (described more in detail in [81]) to ensure that the operator is suitable for perturbation expansion in the sense that corrections truncated at finite levels of excitations and energy corrections do not contain much higher excitations of the CAS reference wave function $|0\rangle$. The resulting zero-order Hamiltonian is brought to block matrix form via projection operators onto different subspaces of the spin orbitals as

$$\hat{H}^{(0)} = E^{(0)}|0\rangle\langle 0| + \hat{P}_K\hat{f}\hat{P}_K + \hat{P}_{SD}\hat{f}\hat{P}_{SD} + \hat{P}_{TQ}\hat{f}\hat{P}_{TQ}, \quad (2.153)$$

where the projection operators fulfil

$$1 = |0\rangle\langle 0| + \hat{P}_K + \hat{P}_{SD} + \hat{P}_{TQ} + \dots. \quad (2.154)$$

The subscript K refers to the part of the CAS space that is orthogonal to $|0\rangle$, SD is the space spanned by single and double excitations from $|0\rangle$ which are not included in the CAS space, TQ is the space orthogonal to the CAS space and spanned by triple and quadruple excitations of $|0\rangle$. The process can

¹³ $a_p^\dagger a_q$ acting on a state written as a determinant of spin orbitals annihilates an electron from orbital q and creates one in orbital p , in essence it excites an electron from orbital q to p , and returns 0 if there is no electron in orbital q . This means that $\sum_p E_{pp}$ acting on such a state counts the number of electrons in the orbitals, and $\sum_p \varepsilon_p E_{pp}$ becomes the operator that sums the occupied spin orbital eigenenergies.

be extended onto more subspaces by using more projection operators onto spaces not included in the CAS space. The idea of this partitioning also makes sense from a physical point of view since the physics describing the electronic orbitals are vastly different for occupied interior orbitals where the electrons are not actively involved in the chemical interaction, compared to valence electrons in the exterior orbitals.

In the CASPT2 method perturbation expansions up to second-order are included, where the reference state $|0\rangle$ is the wave function obtained from the CASSCF step. We used the CASPT2 method in paper **VI** by an implementation in the program package MOLCAS [82]. For further reading on the CASPT2 method, see [83–85].

3. Hydrogen–antihydrogen system and the 4-body method

3.1 The $H\bar{H}$ Hamiltonian

For the 4-body calculations the $H\bar{H}$ system is described by electromagnetic interactions at the non relativistic level. For this purpose we write down the Hamiltonian consisting of Coulomb interactions between the particles and the kinetic energy of every particle in a chosen coordinate system, and solve the Schrödinger equation.

The interaction potential in the 4-body system in a non-relativistic treatment are the Coulomb interactions¹

$$\hat{V} = -\frac{1}{r_{p\bar{p}}} + \frac{1}{r_{p\bar{e}}} + \frac{1}{r_{e\bar{p}}} - \frac{1}{r_{e\bar{e}}} - \frac{1}{r_{pe}} - \frac{1}{r_{e\bar{e}}}. \quad (3.1)$$

where p stands for proton, \bar{p} antiproton, e electron and \bar{e} is the anti electron, i.e. the positron.

The classical kinetic energy is the squared momentum of the particle divided by two times its mass, and in quantum physics it is handled by the kinetic energy operator $\hat{T} = -\frac{\hbar^2}{2m}\Delta_{\mathbf{r}}$, where the Greek delta symbol is the Laplacian operator. The total kinetic energy becomes

$$\hat{T} = -\frac{1}{2m_p}\Delta_{\mathbf{r}_p} - \frac{1}{2m_{\bar{p}}}\Delta_{\mathbf{r}_{\bar{p}}} - \frac{1}{2}\Delta_{\mathbf{r}_e} - \frac{1}{2}\Delta_{\mathbf{r}_{\bar{e}}}. \quad (3.2)$$

The total Hamiltonian is the sum of the kinetic and potential energy

$$\hat{H} = \hat{T} + \hat{V}. \quad (3.3)$$

The r -coordinates in (3.3) are written in a space fixed system where \mathbf{r}_e denotes the vector from the origin to the electron and $r_{pe} = |\mathbf{r}_p - \mathbf{r}_e|$ (i.e. the distance between the electron and the proton) and so on for the other particles. Bold letters denote vectors while regular letters denotes distances (see Figure 3.1).

Now when we have defined the Hamiltonian we are set with the task to solve the Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}_p, \mathbf{r}_e, \mathbf{r}_{\bar{p}}, \mathbf{r}_{\bar{e}}) = E_n\Psi(\mathbf{r}_p, \mathbf{r}_e, \mathbf{r}_{\bar{p}}, \mathbf{r}_{\bar{e}}). \quad (3.4)$$

¹Atomic units have been used here, where $\hbar = 1$, the electron mass $m_e = 1$, the elementary charge $e = 1$ and the Coulomb constant $(4\pi\epsilon_0)^{-1} = 1$.

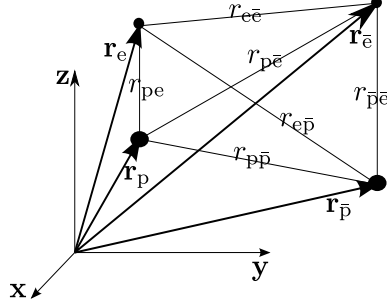


Figure 3.1. Space fixed Cartesian coordinate system for our 4-body molecule with a proton (p), antiproton (\bar{p}), electron (e) and a positron (\bar{e}), $\mathbf{r}_p = (x_p, y_p, z_p)$, $\mathbf{r}_{\bar{p}} = (x_{\bar{p}}, y_{\bar{p}}, z_{\bar{p}})$, $\mathbf{r}_e = (x_e, y_e, z_e)$ and $\mathbf{r}_{\bar{e}} = (x_{\bar{e}}, y_{\bar{e}}, z_{\bar{e}})$.

This equation can be rewritten into a form depending on only three \mathbf{r} vectors by a coordinate transformation into body fixed Jacobi coordinates and separating the center-of-mass motion (as described in section 2.4). Part from having one less variable in our equation, since we use a variational method to solve the Schrödinger equation above, this coordinate transformation is also very practical as we can give the 4-body system a basis consisting of products of the individual 2-body fragments eigenfunctions. These product bases helps us interpret the 4-body wave function by inspection of its composition, i.e. we can look at which principal quantum numbers are being used in the dominating product contributions.

3.2 The $\text{H}\bar{\text{H}}$ wave function expansion

The wave function is written as a linear combination of its basis-functions. In the 4-body method we use Jacobi coordinates with three variables to describe the relative motion of 2-body fragments. The total 4-body wave function is written as a sum of the product of the Jacobi coordinates for each channel (c) as

$$\begin{aligned} \Psi_{J=0} &= \sum_{\substack{c=1 \\ k, \kappa, K}}^{18} A_{k, \kappa, K}^{(c)} \left[\Phi_{kl}^{(c)}(\mathbf{r}_c) \vartheta_{\kappa\lambda}^{(c)}(\rho_c) \xi_{KL}^{(c)}(\mathbf{R}_c) \right]_{J=0} \quad (3.5) \\ &= \sum_{\substack{c=1 \\ k, \kappa, K}}^{18} A_{k, \kappa, K}^{(c)} \phi_k^{(c)}(r_c) \varphi_{\kappa}^{(c)}(\rho_c) \chi_K^{(c)}(R_c) \left[Y_{lm}(\hat{r}_c) Y_{\lambda\mu}(\hat{\rho}_c) Y_{LM}(\hat{R}_c) \right]_{J=0}. \end{aligned}$$

The angular part is coupled to a total angular momentum $J = 0$ as

$$\left[Y_{lm}(\hat{r}) Y_{\lambda\mu}(\hat{\rho}) Y_{LM}(\hat{R}) \right]_{J=0} = \left[[Y_{lm}(\hat{r}), Y_{LM}(\hat{R})]_{I, M_I}, Y_{\lambda\mu}(\hat{\rho}) \right]_{J=0}, \quad (3.6)$$

and

$$[Y_{lm}(\hat{r}), Y_{LM}(\hat{R})]_{I, M_I} = \sum_m \sum_M \langle lm, LM | IM_I \rangle Y_{lm}(\hat{r}) Y_{LM}(\hat{R}), \quad (3.7)$$

where the coefficients, written as $\langle lm, LM | IM_I \rangle$, to the spherical harmonics wave function products, are the Clebsch-Gordan coefficients.

By coupling the H- \bar{H} and Pn-Ps channels (C=13 and C=17 in Figure 3.2), using angular momentum configurations with a total angular momentum of $J = 0$ we take into account the most probable excitations in the rearrangement reaction for the energy region of interest. For these two

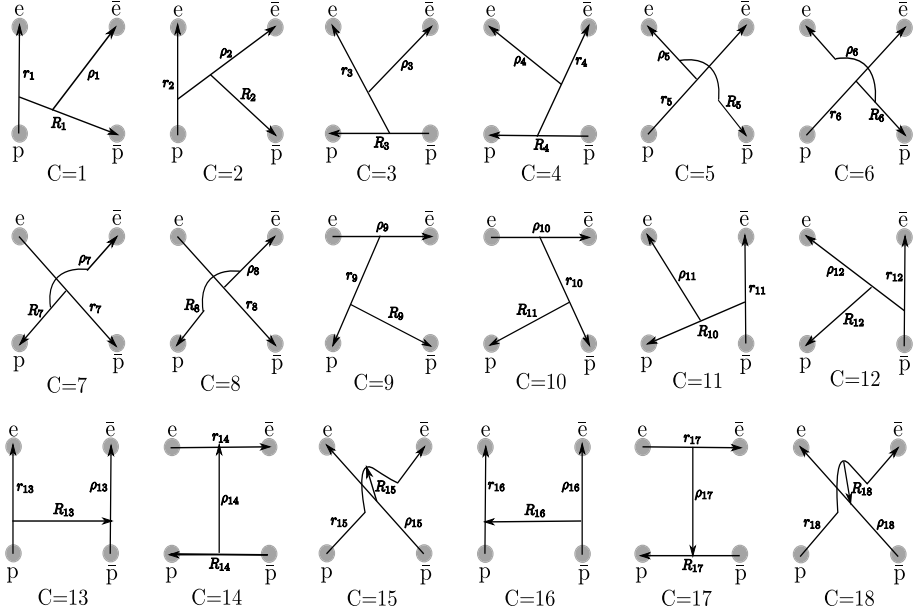


Figure 3.2. All the Jacobi configuration channels for the 4-body system [72]. The hydrogen-antihydrogen channel is labelled C=13, and the protonium-positronium is labelled C=17.

channels, the eigenfunctions to the 2-body fragments corresponding to the Jacobi coordinates r_c and ρ_c are expanded in primitive Gaussian functions (see eq. (2.12))

$$\phi_k(r_c) = \sum_{n,l} c_{nl}^k g_{nl}(r_c), \quad (3.8)$$

$$\varphi_\kappa(\rho_c) = \sum_{n,\lambda} c_{n\lambda}^\kappa g_{n\lambda}(\rho_c), \quad (3.9)$$

and the eigenfunctions for the 2-body fragments corresponding to R_c are expanded in oscillating Gaussian functions (*vide* (2.21)–(2.23)) as

$$\chi_K(R_c) = \sum_n c_n^K g_n^{osc}(R_c). \quad (3.10)$$

The coefficients c_n^K in eq. (3.10) are obtained by *pre-diagonalization*, i.e. solving the Schrödinger equation for the 2-body atoms for each Jacobi coordinate (the numerical procedure are described in detail in Appendix A).

The total expansion of the 4-body wave function becomes

$$\begin{aligned}
\Psi_{J=0} = & \sum_{k,\kappa,K} A_{k,\kappa,K}^{(13)} \sum_{n,l} c_{nl}^k g_{nl}(r_{13}) \sum_{n,\lambda} c_{n\lambda}^\kappa g_{n\lambda}(\rho_{13}) \sum_{n,L} c_{nL}^K g_{nL}^{osc}(R_{13}) \\
& \times \left[Y_{lm}(\hat{r}_{13}) Y_{\lambda\mu}(\hat{\rho}_{13}) Y_{LM}(\hat{R}_{13}) \right]_{J=0} \\
& + \sum_{k,\kappa,K} A_{k,\kappa,K}^{(17)} \sum_{n,l} c_{nl}^k g_{nl}(r_{17}) \sum_{n,\lambda} c_{n\lambda}^\kappa g_{n\lambda}(\rho_{17}) \sum_{n,L} c_{nL}^K g_{nL}^{osc}(R_{17}) \cdot \\
& \times \left[Y_{lm}(\hat{r}_{17}) Y_{\lambda\mu}(\hat{\rho}_{17}) Y_{LM}(\hat{R}_{17}) \right]_{J=0}. \tag{3.11}
\end{aligned}$$

For the hydrogen-antihydrogen channel (C=13) we have labelled the Jacobi coordinates as $r_{13} = \tilde{r}$ (hydrogen fragment), $\rho_{13} = \tilde{\rho}$ (antihydrogen fragment) and $R_{13} = \tilde{R}$ (relative motion of hydrogen and antihydrogen), and for the protonium-positronium channel (C=17) we use the notation $r_{17} = r$ (positronium fragment), $\rho_{17} = \rho$ (relative motion of protonium and positronium) and $R_{17} = R$ (protonium fragment).

Since we are using two sets of Jacobi coordinates in the wave function expansion (3.11), it is necessary to know the transformation from one coordinate system to another (*vide* (2.18)–(2.20)) in order to calculate the matrix elements.

3.3 $\text{H}\bar{\text{H}}$ 2-body interaction potential

For the purpose of creating a basis set for the 2-body Jacobi fragment describing the relative motion of the hydrogen atom and the antihydrogen atom (the Jacobi coordinate $R_{13} = \tilde{R}$), the interaction potential between them must be calculated.

This interaction potential has been modeled in many different ways, e.g. by the coupled channel method [86, 87], the close-coupling method [88] and the adiabatic distorted wave approximation [89–91].

The method we have used for approximating this potential in paper **I** and **II** is based on building it up by parts, calculated by different approximations at different ranges and fit together, where the eigenfunctions obtained from the mass-scaled Born-Oppenheimer potential in paper **II** is the basis we use in the 4-body method.

Long range interaction

Seen from a distance, at an internuclear separation of $R > 15$ a.u. hydrogen and antihydrogen are both neutral atoms. However, unlike two electrically neutral and structureless spheres, they interact with each other. The interatomic forces comes from the correlation of the movements of particles constituting both monomers. Using perturbation theory for the interaction between hydrogen and antihydrogen (see section 2.3) the interaction can be seen as an interaction between multipoles created by instantaneous fluctuations of leptonic densities on both atoms. From the multipole expansion (see appendix B)

$$\hat{V} = \sum_{i \in A} \sum_{j \in B} \frac{q_i q_j}{r_{ij}}, \quad (3.12)$$

the first non-vanishing terms correspond to $1/R^6$ terms which comes from the dipole-dipole interaction, collected in the *van der Waals* coefficient C_6 between interacting atoms in their ground state (see the subsection in appendix B). Including higher order terms gives a more exact description and in paper **I** and **II** we describe the long range interaction between instantaneous dipoles as

$$V^{lep}(R) = \frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}}, \quad (3.13)$$

where $C_6 = -6.4990267$, $C_8 = -124.39908$ and $C_{10} = -3285.8284$ [92].

Medium range interaction

For long range interaction we considered leptonic motion while the nuclear positions were fixed. As the atoms come closer to each other, in the region of internuclear separation $0.74 < R < 15$ this approach is no longer valid and instead it is necessary to solve the Schrödinger equation with the full Hamiltonian H . It can be done by means of the variational method. However, since the leptons are about 1836 times lighter than the hadrons, they move much faster than the hadrons which motivates us to treat the motion of the leptons and hadrons separately. The separation of the motion of the fast moving leptons and the slowly moving hadrons, by calculating the leptonic potential at parametrized values of the hadronic internuclear separation, is one of the pillar stones in molecular physics, summed up as the *Born-Oppenheimer approximation* and the more accurate *Adiabatic approximation* (see section 2.4).

For medium internuclear distances, the Hamiltonian in the BO approximation is given by

$$\left[-\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} + E_l^e(R) \right] f_l(\mathbf{R}) = E f_l(\mathbf{R}), \quad (3.14)$$

where $f_l(\mathbf{R})$ is the hadronic part of the potential (for a specific hadronic internuclear distance \mathbf{R}) and $E_l^e(R)$ is calculated numerically for each parametrized value of the hadronic internuclear distance \mathbf{R} . In paper II we expand $E_l^e(R)$ in a Gaussian basis (see section 2.2) and fit the expansion to the mass-scaled version of the potential calculated in [93].

Short range interaction

For an internuclear separation of $R < 0.74$ the BO potential for the H- $\bar{\text{H}}$ system has a significantly different character than a BO potential for an "ordinary" molecule (e.g. H_2). The H- $\bar{\text{H}}$ potential has no repulsive wall for small internuclear distances R . For some distance $R_c \approx 0.74$ (the *critical distance*) the leptonic part of the potential ($V^{\text{lep}}(R) = V^{\text{BO}}(R) + 1/R$) reaches the value of the positronium ground state energy. An intuitive picture of what can happen at this range is that the leptons are no longer bound to the hadrons and instead they form positronium that dissociates from the two hadrons, whom in turn can form protonium.

The value of the BO potential ($V^{\text{BO}}(R)$) in this region is assumed to be the sum of the positronium ground state energy ($E_{\text{Ps}(1)} = 0.25$ a.u.) and the proton-antiproton Coulombic repulsion for $R < R_c$ (see Figure 3.3), i.e.

$$V^{\text{BO}}(R) = E_{\text{Ps}(1)} - \frac{1}{R}. \quad (3.15)$$

The range of the short-range potential can be estimated by calculating the C_6 coefficients. The two Pn(N)-Ps(n) combinations of states with energy closest to the threshold energy of H- $\bar{\text{H}} = -1$ is $(N, n) = (24, 1)$ and $(22, 2)$. The C_6 coefficient for the interaction between Pn(22) and Ps(2) calculated by (5.74) is

$$C_6^{\text{Pn}(22)\text{Ps}(2)} = \frac{3}{\pi} \int_0^\infty \alpha_1^{\text{Pn}(22)}(iw) \alpha_1^{\text{Ps}(2)}(iw) dw = 5.8526 \dots, \quad (3.16)$$

which is of the same order of magnitude as the C_6 coefficient for the hydrogen-antihydrogen interaction, and the range of potential is approximated by β_6 from the formula

$$\beta_6 = (2\mu C_6)^{1/4}, \quad (3.17)$$

which gives $\beta_6^{\text{Pn}(22)\text{Ps}(2)} \approx 2.2$.

For Pn(24) and Ps(1) the value of C_6 is much smaller

$$C_6^{\text{Pn}(24)\text{Ps}(1)} = 0.6142 \dots, \quad (3.18)$$

which by (3.17) gives the range of the dispersion forces to be $\beta_6^{\text{Pn}(24)\text{Ps}(1)} \approx 1.25$. Due to the reduced mass difference between H- $\bar{\text{H}}$ and Pn-Ps, both these values are significantly smaller than the range of the

dispersion forces for H- $\bar{\text{H}}$ interaction $\beta_6^{\text{H}(1)\bar{\text{H}}(1)} \approx 10.5$, which justifies the approximation to set the dispersion forces between Pn-Ps to zero between these atoms for the purpose of creating the basis functions for this Jacobi fragment.

The composition of the adiabatic BO-potential is summarized in Figure 3.3.

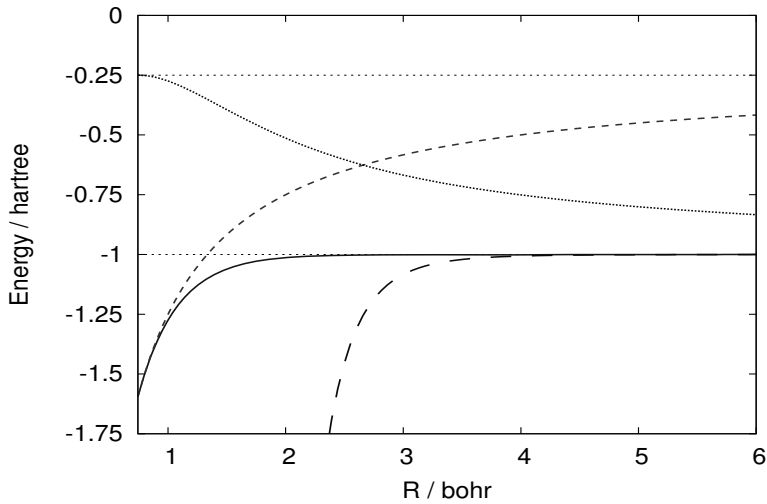


Figure 3.3. The different parts of the interaction potential for small R . The positronium potential (dotted), the shifted (with the ground state positronium energy $E = -0.25$) protonium potential (short dashed), the long range interaction (long dashed) and the mass-scaled BO potential (solid).

(From paper II, printed with permission from Open Physics)

4. Developments

4.1 Paper I – Including strong force interaction

Motivation

The annihilation of a particle and its antiparticle, the inverse of the creation process of energy into a particle–antiparticle pair, has a central role in the topic of antimatter and can only be described by including the strong force interaction, stemming from sub-atomic relativistic effects described by QCD theory which is outside the scope of this thesis. However, it is possible to include the effect of the strong force interaction in the Coulombic description of electromagnetic forces by approximate means, thus extending on the Born-Oppenheimer approximation.

Since the decay lifetime of a state is related to the imaginary part of the eigenvalues, a complex valued Schrödinger equation would be able to model the decay of the states. Previous methods, focused on scattering of hydrogen and antihydrogen, had achieved this by using a complex potential or by imposing short ranged complex boundary conditions in terms of the scattering length.

In this paper we impose complex boundary conditions for the wave function at very small internuclear distances, utilizing experimental values for Pn annihilation life times. From the eigenvalues and eigenfunctions obtained we may calculate decay rates of the meta stable $\text{H}\bar{\text{H}}$ molecule.

By this method, we intended to calculate lifetimes of the adiabatic states and probabilities of decay via annihilation and rearrangement.

Questions

- How will including the effect of the strong force by complex boundary conditions affect the adiabatic energy spectrum?
- How will including the effect of the strong force affect the probabilities of decay via annihilation and rearrangement?
- How will including the effect of the strong force affect the life times of the adiabatic states due to rearrangement and annihilation?

Method

The strong force interaction needed for describing the annihilation of particles is not defined in the non-relativistic Schrödinger equation, but the effect of

the strong force can be modelled by using complex boundary conditions. The reduced radial part of the initial adiabatic wave function Ψ_i at internuclear distances larger than the nuclear scale but much smaller than the atomic scale $10^{-5} < R \ll 1$ bohr, are matched to the Coulomb solution distorted by an irregular Coulomb function due to the nuclear forces. Thus, for this region we write the reduced radial part as a linear combination of regular (first kind) F_0 and irregular (second kind) G_0 complex valued Coulomb wave functions

$$u_0(R) = \mathcal{N}[\cot(\vartheta_{si})F_0(k, R) + G_0(k, R)] \quad (4.1)$$

and fit $\Psi_i(R)$ to $u_0(R)$ in the limit $R \rightarrow 0$. The initial wave function Ψ_i is calculated from the Schrödinger equation by numerical integration using an interpolation of the Born-Oppenheimer approximated interaction potential from previous work [93].

Since the imaginary part of eigenvalues is connected to the mean life time of the state by the time dependence of the Schrödinger wave function

$$\Psi(r, t) = e^{-\frac{iE_I t}{\hbar}} \Psi(r) = e^{-\frac{i(E_0 + \varepsilon_{Re} - i\varepsilon_{Im})t}{\hbar}} \Psi(r) = e^{-\frac{i(E_0 + \varepsilon_{Re})t}{\hbar}} e^{-\frac{\varepsilon_{Im} t}{\hbar}} \Psi(r), \quad (4.2)$$

and since complex boundary conditions have the effect of shifting the eigenvalues by a complex number $\varepsilon_{Re} - i\varepsilon_{Im}$, we can use experimental values for Pn annihilation as described in the paper¹ to determine the phase shift ϑ_{si} .

Once we have the proper form of (4.1) we use the boundary condition to numerically solve the Schrödinger equation within the Born-Oppenheimer approximation. The complex valued wave function results in a real and imaginary shift of the adiabatic eigenvalues for the $\text{H}\bar{\text{H}}$ molecule, where the imaginary part of the eigenvalue ε_{Im} gives the decay probability $\rho(r, t)$

$$\rho(r, t) = |\langle r, t \rangle|^2 = e^{-2\varepsilon_{Im} t} |\Psi(r)|^2, \quad (4.3)$$

and the decay width (resonance width) $\Gamma = 2\varepsilon_{Im}$ is related to the lifetime due to annihilation as

$$\tau = \frac{1}{\Gamma} = \frac{1}{2\varepsilon_{Im}}. \quad (4.4)$$

With the improved initial wave function we use the transition matrix element \mathcal{T}_{fi} describing the transition from the initial state Ψ_i to the final state Ψ_f

$$\mathcal{T}_{fi} = \langle \Psi_f | V_f | \Psi_i \rangle, \quad (4.5)$$

to calculate transition probabilities per unit time which are related to the life times of states resulting from the transition of specific vibrational states of

¹The experimental values for the scattering length of proton-antiproton scattering, the ground state energy for protonium, and Bohr radius for protonium are related to the phase shift ϑ_{si} , and using only protonium is motivated by the results that the annihilation of protonium $\text{H}\bar{\text{H}} \rightarrow e^+ + e^- + \text{decay products}$ is three orders of magnitude more likely, due to three order of magnitude larger reduced mass of protonium, compared to positronium annihilation.

the hydrogen-antihydrogen molecule into different final state wave functions Ψ_f . In this manner we present annihilation life times for initial states with the inclusion of the effect of the strong force, and tables of life times for transitions between specific initial and final states, such as the probability for decay of the adiabatic $H\bar{H}$ molecule in a particular state to the rearrangement into P_n and P_s , with and without inclusion of the effect of the strong force in order to compare the effect it has on the decay rates.

Results and discussion

The change of the lifetimes of the adiabatic meta stable states due to inclusion of the effect of the strong force² was found to be surprisingly relevant, on average a 30% change. For the uppermost states the effect of the strong force increases the lifetime with respect to rearrangement, which is somewhat counter intuitive since these are the forces responsible for annihilation, but might be understood by the fact that the range of the strong force is very short and opening up the annihilation channel destabilizes the molecule.

Tables were presented showing how the adiabatic energy spectrum shifts due to the effect of the strong force, which had not been studied before. Furthermore, the annihilation lifetimes was shown to agree with a previous result, and the annihilation and rearrangement lifetimes were shown to be comparable.

²compared to the value using a discretization technique in conjunction with the complex coordinate method, as described in the paper and [94].

4.2 Paper II – Mass-scaled adiabatic potential

Motivation

The interaction potential between hydrogen and antihydrogen had previously been calculated with methods based on the Born-Oppenheimer approximation where including the adiabatic correction had been shown to be impossible since the adiabatic correction does not converge. However, in this paper we show that it is possible to include a part of the adiabatic correction by a mass-scaling procedure.

The significance of this correction is investigated carefully since a shift of the eigenvalues is likely to affect the expected number of bound states for in adiabatic hydrogen-antihydrogen description, as the distance between the eigenenergies becomes successively smaller the closer we get to the dissociation energy.

A proper description of the adiabatic states just below the dissociation energy of the $H\bar{H}$ molecule has a significant impact on the 4-body expansion since 4-body solutions in this region are difficult to describe using a linear combination of pre-diagonalized protonium, positronium and hydrogen eigenfunctions³.

Furthermore, a more accurate description of the adiabatic interaction potential between hydrogen and antihydrogen is important as the bound states for this potential are precursors to where we should look for resonance states.

Questions

- Will including a part of the adiabatic correction have a significant impact on the adiabatic energy spectrum?
- Will including a part of the adiabatic correction change the estimated number of bound states?
- Are the continuum states obtained from the mass-scaled potential of sufficient quality for estimating the scattering length?
- For internuclear distances where the adiabatic correction converges, how much of it do we incorporate by the mass-scaling procedure?

Method

We improve on the Born-Oppenheimer 2-body interaction potential by taking into account the effect of mass-scaling the leptonic Hamiltonian⁴

$$H_{lep} = -\frac{1}{2}\nabla_{\mathbf{R}_{ep}} - \frac{1}{2}\nabla_{\mathbf{R}_{\bar{e}\bar{p}}} + V(\mathbf{R}_{ep}, \mathbf{R}_{\bar{e}\bar{p}}, \mathbf{R}_{p\bar{p}}), \quad (4.6)$$

³together with the discretized energy of relative motion of these fragments.

⁴written in body-fixed coordinates after separation of the center of mass motion as described in section 2.4.

by replacing the electron mass with the reduced mass of the electron-proton (and likewise for the positron-antiproton) $\mu = m_p/(m_p + 1)$ such that we get

$$\tilde{H}_{lep} = H_{lep} - \frac{1}{2m_p} \nabla_{\mathbf{R}_{ep}} - \frac{1}{2m_p} \nabla_{\mathbf{R}_{\bar{e}\bar{p}}} = -\frac{1}{2\mu} \nabla_{\mathbf{R}_{ep}} - \frac{1}{2\mu} \nabla_{\mathbf{R}_{\bar{e}\bar{p}}} + V(\mathbf{R}_{ep}, \mathbf{R}_{\bar{e}\bar{p}}, \mathbf{R}_{p\bar{p}}), \quad (4.7)$$

as described in the appendix to the paper. Incorporation of the reduced mass amounts to including a part of the adiabatic correction to the BO-approximation, and for internuclear distances large enough for the adiabatic correction to converge we compared the adiabatic correction obtained from mass-scaling to the values obtained in [95], presented in the appendix to the paper. Solving the Schrödinger equation with the mass-scaled Hamiltonian in (4.7) gives a leptonic energy curve $\tilde{E}_{lep}(R)$ which includes the converging part of the adiabatic correction and is shown to be related to the Born-Oppenheimer energy E_{BO} as

$$\tilde{E}_{lep}(R) = \mu E_{BO}(\mu R). \quad (4.8)$$

The Born-Oppenheimer energy E_{BO} is assumed to be the sum of the ground state energy of positronium and the Coulomb attraction between the nuclei for the region $R < R_C \approx 0.744$ bohr, and between R_C and the asymptotic region starting at $R \approx 20$ bohr it is computed by an interpolation of the potential energy calculated in [93], and in the asymptotic region it is set to be given by the threshold energy of separated hydrogen atoms ($E_{BO}^\infty = -1$) subtracted by the Van der Waals potential as

$$E_{BO}(R) = E_{BO}^\infty - \sum_{n=6}^{26} \frac{C_n}{R^n}, \quad (4.9)$$

where C_n are the Van der Waals constants.

Since we use the Gaussian expansion method as outlined in section 2.2, both $E_{BO}(R)$ and the mass-scaled version of it $\tilde{E}_{lep}(R)$ are fitted to an expansion of Gaussian polynomial functions to enable us to calculate the matrix elements analytically as described in appendix A. The analytical expressions for the matrix elements are scaled and inserted into a numerical routine that diagonalizes the Hamiltonian as outlined in section 2.1 whereby we obtain the energy spectrum of the mass-scaled adiabatic potential together with the eigenfunctions that we examined in order to estimate the scattering length⁵. The scattering length was estimated as the crossing of the R-axis and the tangent line to the last node of the first continuum state.

Lastly, we compared the number of bound states obtained to the result using the WKB approach by applying the quantization function given in [96].

⁵and for use as part of the 4-body basis expansion in subsequent papers.

Results and discussion

Including a part of the adiabatic correction results in a significant shift of the eigenvalues compared to previous methods, in particular for states close to the dissociation threshold energy. The effect of the shift resulted in, after careful examination and in good agreement with the WKB approach, the number of bound states to be 29, an extra bound state compared to previous results.

The mass-scaling procedure was shown to incorporate 95% of the total adiabatic correction, for internuclear distances $R > 2$ bohr.

By the mass-scaling procedure the dissociation energy is shifted, which strongly impacts the description of states in the near-dissociation region. Possible resonances in this region could act as intermediate states, temporarily capturing the hydrogen and antihydrogen atoms before the molecule breaks down into other fragments. The states obtained from this method are used in the 4-body expansion in paper **III** and **IV**.

The scattering length of the adiabatic potential was estimated in good agreement with previous methods, which is a quality insurance for the continuum states obtained.

Furthermore, we gave a description of the fitting procedure for fitting to the mass-scaled and regular Born-Oppenheimer potentials, and demonstrated the convergence of the adiabatic energies with respect to the number of Gaussian basis functions used in the expansion of the wave function, which is used in filtering out continuum states in paper **III**.

4.3 Paper III – Resonance states in the $\text{H}\bar{\text{H}}$ system

Motivation

A number of bound states have been found in previous work using adiabatic approaches. However, since the adiabatic approximation breaks down for small internuclear distances and since methods based on the Born-Oppenheimer approximation are approximative descriptions of the $\text{H}\bar{\text{H}}$ system, a more exact description is expected in the 4-body non-adiabatic method. Findings of resonance states using a non-adiabatic method would therefore be a measure of the accuracy of the adiabatic methods. If the previous adiabatic methods are accurate, the resulting energy spectrum of the 4-body method should contain semi-bound states near the bound states calculated using the adiabatic methods. However, the energy spectrum obtained by the 4-body method also contains all kinds of continuum states from Pn–Ps fragments, and sorting out resonance states from a sea of continuum states is a major task, but might be possible by using a combination of different kinds of scaling techniques coupled with inspection of the composition of the resulting 4-body states.

Moreover, the existence of resonance states near the threshold energies of Pn–Ps fragments could act as intermediate states for Pn–Ps formation from $\text{H}\bar{\text{H}}$ scattering, and as such would affect the previously calculated cross sections.

Due to the amount of states resulting from the 4-body method, we need to limit the energy region in which we search for resonance states. In this paper we search for these states near the adiabatic $\text{H}\bar{\text{H}}$ eigenenergies that are close to the dissociation energy of $\text{H}\bar{\text{H}}$ calculated in paper II, as the existence of such a resonance state is relevant for low energy scattering of hydrogen and antihydrogen.

Questions

- Will we find resonances close to the predicted energies from the adiabatic treatment?
- Is the 4-body method suitable for detecting resonances?
- How can we filter out resonance states from a sea of continuum states?
- Can we use real scaling as a starting point for where to focus the attention using complex scaling?
- How should we vary the parameters in complex scaling?
- Will the composition of a candidate resonance state give us useful information?
- Is the width of any possible resonance large enough to bridge the energy difference of the $\text{H}\bar{\text{H}}$ dissociation energy and the energy of a Pn–Ps fragment?

Method

The 4-body method as described in section 3.1 and 3.2 is used iteratively in a numerical procedure for calculating the 4-body energy spectrum, where the 2-body basis calculated in paper **II** is utilized for the Jacobi coordinate of the relative motion of the hydrogen-antihydrogen fragment. For each iteration of diagonalizing the 4-body Hamiltonian matrix, the matrix elements are scaled by a non-complex scaling parameter γ in the stabilization method as

$$\hat{V}(\gamma\mathbf{r}, \gamma\rho, \gamma\mathbf{R}) = \frac{1}{\gamma} \hat{V}(\mathbf{r}, \rho, \mathbf{R}), \quad (4.10)$$

$$\hat{T}(\gamma\mathbf{r}, \gamma\rho, \gamma\mathbf{R}) = \frac{1}{\gamma^2} \hat{T}(\mathbf{r}, \rho, \mathbf{R}), \quad (4.11)$$

and in complex scaling by two variants

- by the scaling parameter $\gamma = \cos(\theta) + i\sin(\theta)$ where we increase the angle θ by small incremental steps σ as

$$\gamma_n = \cos(\theta_n) + i\sin(\theta_n), \quad \theta_n = \theta_0 + \sigma n, \quad (4.12)$$

where $\theta_0 = 0$ and $|\theta|$ smaller than the maximum scaling angle β_{\max}

$$|\theta| < \beta_{\max} = \arcsin(2/\pi)/2, \quad (4.13)$$

- by keeping the real part of γ constant and only adding a complex part $i\zeta = i\sigma$ which we increase by small steps using an increment σ as

$$\gamma_n = \text{Re}(\gamma) + i\sigma n, \quad \frac{1}{2} \arctan\left(\frac{\sigma n}{\text{Re}(\gamma)}\right) < \beta_{\max}. \quad (4.14)$$

The resulting eigenvalues are difficult to connect to a specific physical state, since for energies below the dissociation threshold of $\text{H}\bar{\text{H}}$ we obtain solutions corresponding to unbound $\text{Pn} - \text{Ps}$ fragments moving with a discretized kinetic energy as well as possible semi-stable $\text{H}\bar{\text{H}}$ states. For this reason, we filter out the movement of $\text{Pn}\text{--}\text{Ps}$ roots by identifying the roots obtained in a corresponding scaling of the 4-body Hamiltonian with only the $\text{Pn}\text{--}\text{Ps}$ channel open, and by altering the discretized eigenfunctions used in the 4-body basis for the relative motion of the $\text{Pn}\text{--}\text{Ps}$ fragment. We also filter out continuum roots with respect to the dimensionality of Hamiltonian matrix, since non-continuum states are less sensitive to truncation of the pre-diagonalized basis supplied.

After filtering out $\text{Pn}\text{--}\text{Ps}$ continuum states we focus our attention to energy regions of interest – energies near the adiabatic bound states calculated in paper **II** close to the mass-scaled dissociation energy \tilde{E}_{BO}^{∞} of $\text{H}\bar{\text{H}}$. Resonances in this region might bridge the energy of slowly moving $\text{H}\bar{\text{H}}$ atoms and $\text{Pn}\text{--}\text{Ps}$ fragments and thus affect the scattering cross sections. After we find a potential resonance state we again filter out $\text{Pn}\text{--}\text{Ps}$ continuum states by looking

at the composition of it in terms of which pre-diagonalized eigenfunctions are used to describe it. If the composition is dominated by a mixture of eigenfunctions from the H- $\bar{\text{H}}$ and Pn-Ps channel, it is a candidate for further study where we apply both real scaling and complex scaling as described in section 2.6 and appendix **D**.

In this manner, possible resonance states are detected for which we calculate the resonance decay width Γ and the lifetime τ of the state using

$$\tau = \frac{\hbar}{\Gamma}, \quad (4.15)$$

where Γ is estimated from a stabilization plot from the slopes of an avoided crossing as described in section 2.6 as

$$\Gamma \sim \Delta E \cdot \frac{|S_r|}{|S_c|}. \quad (4.16)$$

Results and discussion

After much optimization and trial and error when it comes to the granularity of the scaling method, applying real and complex scaling in the 4-body method for detecting possible resonance states was successful.

Two roots, α_1 and α_2 , were found with energies close to the adiabatic energy levels calculated in paper **II** that satisfy the criteria for resonance states in terms of both real and complex scaling. Out of these two, the one closest to the H- $\bar{\text{H}}$ threshold energy (α_2) has a width comparable to the energy difference between the H- $\bar{\text{H}}$ threshold energy and the resonance energy $E^{H\bar{\text{H}}}(\nu)$ as well as the energy difference between the resonance energy $E^{H\bar{\text{H}}}(\nu)$ and the closest Pn-Ps fragment $E_{PnPs}^{thres}(22, 2)$, making it interesting for further investigation in terms of its effect on the scattering cross sections.

4.4 Paper IV – Adiabaticity of the 4-body wave function

Motivation

The interaction between hydrogen and antihydrogen has been approximated by methods based on the Born-Oppenheimer approximation, where different improvements such as including the effect of strong interaction in paper **I** and parts of the adiabatic correction in paper **II** have been made. However, for internuclear distances smaller than a critical value $R_C \approx 0.7$ bohr, the Born-Oppenheimer approximation is no longer valid as the leptons are no longer bound in the dipole field formed by the proton and the antiproton. In this region we have approximated the interaction potential to be the sum of ground state Ps and the internuclear Coulomb interaction, resulting from formation of Pn and Ps, but for a proper description of this region a fully non-adiabatic method must be used. The 4-body method is such a method, where the limitations of this method lie in the completeness of the expansion of the 4-body wave function and in interpreting the results.

In this paper, we investigated to what extent the resulting wave function from the adiabatic treatment employed in paper **II** matches the 2-body wave function resulting from an out-integration of the leptonic coordinates in the 4-body wave function. This is a way of measuring the “adiabaticity” of the 2-body function. More precisely, we compare the hadronic 2-body density function resulting from 4-body calculations to the mass-scaled Born-Oppenheimer wave function for the hydrogen-antihydrogen system. By knowing the difference of the two, we know more about how accurate the methods based on the Born-Oppenheimer approximation are in describing the hydrogen-antihydrogen system.

Questions

- How accurate is an adiabatic description of the hydrogen-antihydrogen system?
- Is the 4-body wave function expansion flexible enough to describe the wave function for small internuclear distances?
- Is the 4-body wave function expansion flexible enough to describe the asymptotic region?

Method

The hadronic *pseudo wave function* $\varepsilon(R)$ is defined as the root of the 2-body nuclear density obtained from a full 4-body calculation as

$$\xi(R) = \sqrt{\rho(R)} = \sqrt{\int |\Psi(\mathbf{r}, \mathbf{q}, \mathbf{R})|^2 d\mathbf{r} d\mathbf{q} d\hat{R}}, \quad (4.17)$$

where $\mathbf{r}, \mathbf{q}, \mathbf{R}$ denote the Jacobi coordinates for the Pn-Ps arrangement channel and R is the proton-antiproton distance. The region of interest for this comparison is formed by the states just above the hydrogen-antihydrogen dissociation threshold, since these states describe the low energy collisions of hydrogen and antihydrogen, which is what the adiabatic wave function for the hadronic motion is approximating. The expansion of the 4-body wave function Ψ in (4.17) has been further improved compared to the manuscript by explicitly including the 1s-hydrogen and 1s-antihydrogen wave functions by writing the total wave function as a sum of the 1s-functions with a correlating nuclear function $\chi(R)$ and a linear combination of the 4-body wave functions as

$$\Psi = 1s(r_1)1s(r_2) \frac{\chi(R)}{\sqrt{4\pi R}} + \sum_{\nu} b_{\nu} \Phi_{\nu}, \quad (4.18)$$

where r_1, r_2, R denote electron-proton, positron-antiproton and H- $\bar{\text{H}}$ distances respectively. A symmetrization scheme for the basis set is used to decrease the dimensionality of the numerical diagonalization procedure. We investigate the non-adiabaticity of the adiabatic wave function by inspecting the rate of change of the logarithmic derivative of the total wave function with respect to the internuclear coordinate R , and by comparing the difference of the position of the nodes of the nuclear pseudo wave function compared to the adiabatic 2-body wave function. From knowing the hadronic pseudo wave function $\rho(\mathbf{R})$, and the p- $\bar{\text{p}}$ annihilation potential defined as

$$V_{\text{an}}^{\text{p}\bar{\text{p}}} = A^{\text{p}\bar{\text{p}}} \delta(R_{Pn}), \quad (4.19)$$

where $A^{\text{p}\bar{\text{p}}}$ is the proton-antiproton annihilation constant and R_{Pn} the protonium Bohr radius, we can calculate the cross section for the hadronic annihilation as

$$\sigma_{\text{an}}^{\text{p}\bar{\text{p}}} = \frac{(2\pi)^3}{k^2} \langle \rho_{\mathbf{k}}(\mathbf{R}) | V_{\text{an}}^{\text{p}\bar{\text{p}}} | \rho_{\mathbf{k}}(\mathbf{R}) \rangle = \frac{(2\pi)^3}{k^2} A^{\text{p}\bar{\text{p}}} |\rho_{\mathbf{k}}(0)|^2. \quad (4.20)$$

By using an experimental value for $A^{\text{p}\bar{\text{p}}}$ the cross section is calculated and compared to the value obtained from the adiabatic wave function.

Results and discussion

This article is a work-in-progress manuscript at the time of writing, where we work on improving the manuscript by including a linear combination of 4-body eigenfunctions for the hadronic wave function expansion together with a term with hydrogen 1s functions as written in (4.18).

Thus far, by only including 4-body eigenfunctions the non-adiabaticity is significant for very small values of the interatomic distances, but already for $R = 0.1$ bohr, which is well inside the critical rearrangement distance $R_c \approx$

0.7 bohr, the adiabatic description seems accurate. However, the dramatic difference of the adiabatic and non-adiabatic wave function near $R = 0$ seems to have a strong impact on the cross-section for in flight annihilation as this was calculated to be about 7 times smaller than the value obtained from the adiabatic wave function.

4.5 Paper V – Antiproton scattering on H₂

Motivation

The system of an antiproton and molecular hydrogen is interesting because of its relative simplicity in theoretical calculations targeted at understanding the interaction between matter and antimatter, but also because of the experimental accessibility since both antiprotons and molecular hydrogen are created as side products in many high-energy reactions in particle accelerators. Furthermore, learning more of the scattering process of these might help in analysing experimental results, since it is often of importance to filter out background noise stemming from residual products.

Questions

- What is the minimum kinetic energy needed for an antiproton to dissociate a molecular hydrogen molecule in its electronic ground state?
- What are the probabilities for exciting the molecular hydrogen molecule into different vibrational states from its electronic ground state by collision with an antiproton?
- How do these probabilities for vibrational excitation depend on the kinetic energy of the antiproton?
- How different is the H₂ – \bar{p} system compared to molecular hydrogen?
- Can an avoided crossing between the PES of excited states in molecular hydrogen become a conical intersection (energy degeneracy) in the H₂ – \bar{p} system?

Method

To simulate the collision between the hydrogen molecule and the antiproton we solve the time-dependent Schrödinger equation for the nuclei

$$i\hbar \frac{\partial}{\partial t} \Psi(R_{HH}, R_{\bar{p}}, t) = \hat{H} \Psi(R_{HH}, R_{\bar{p}}, t), \quad (4.21)$$

with the Hamiltonian in Jacobi coordinates:

$$\hat{H} = \hat{T}_{R_{\bar{p}}} + \hat{T}_{R_{HH}} + \hat{V}(R_{HH}, R_{\bar{p}}) = -\frac{1}{2\mu_{HH}} \frac{\partial^2}{\partial R_{HH}^2} - \frac{1}{2\mu_{\bar{p}}} \frac{\partial^2}{\partial R_{\bar{p}}^2} + \hat{V}(R_{HH}, R_{\bar{p}}), \quad (4.22)$$

where R_{HH} , $R_{\bar{p}}$ and the geometry of the system are defined in Figure 4.1.

The reduced masses and $\mu_{\bar{p}}$ and μ_{HH} are given by

$$\mu_{HH} = \frac{m_p}{2}, \quad \mu_{\bar{p}} = \frac{2m_p^2}{(m_p + 2m_p)} = \frac{2}{3}m_p, \quad (4.23)$$

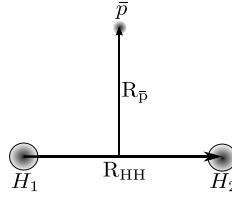


Figure 4.1. Jacobi coordinates for the $H_2 - \bar{p}$ system. We investigated the case of perpendicular scattering of an antiproton on the mass-centre of molecular hydrogen in order to focus on the specifics of the vibrational and dissociation dynamics of $H_2 - \bar{p}$ scattering.

(From paper V, printed with permission from ©IOP Publishing)

where m_p is the rest mass of the proton.

Eq. 4.21 is solved numerically as outlined in section 2.7 by a Chebyshev time propagation scheme [97] on a grid where we used a perfectly matched layer (PML) [98] at the edges of the grid to absorb the wave function and to avoid spurious reflections.

The initial wave function is written as a product state of the H_2 vibrational ground state wave function ϕ_0 and a Gaussian wave packet representing the antiproton where the collision energy $\rho_0 = p^2/2\mu_{\bar{p}}$ enters through the momentum $p = \hbar k$:

$$\Psi(R_{HH}, R_{\bar{p}}, t = 0) = \sqrt{\frac{2}{\sigma\sqrt{2\pi}}} e^{-(R_{\bar{p}} - R_{\bar{p}0})^2/2\sigma^2} e^{ikR_{\bar{p}}} \phi_0(R_{HH}), \quad (4.24)$$

where σ is the width of the Gaussian wave packet.

We calculated the probabilities for finding the H_2 molecule at a certain time t in the vibrational state ϕ_v , for different initial antiproton kinetic energies, as the projection of the state on the total wave function

$$|c_v(t)|^2 = \int |\phi_v(R_{HH}) \Psi(R_{HH}, R_{\bar{p}0}, t)|^2 dR_{HH}, \quad (4.25)$$

where the total probability is obtained by integrating (4.25) over time from $t = 0$ to the time end point $t = T$ as

$$P_v = N^T \int_0^T |c_v(t)|^2 dt. \quad (4.26)$$

We divide $c_v(t)$ into a reflected and a transmitted part and analyse them. Furthermore, we analyse the dissociation probabilities of the H_2 molecule via the continuity equation⁶ for the probability flux [99]:

$$\frac{\partial \Psi^* \Psi}{\partial t} + \nabla \cdot \vec{j} = 0, \quad (4.27)$$

⁶Continuity equations are a stronger form of conservation laws, since it limits the system to continuous transport of quantities, i.e., a quantity can not disappear at one location and appear at another, it is locally conserved.

where \vec{j} is the probability flux. We define the probability flux as

$$F(t) = -\frac{2}{\hbar} \int_V \Im (\Psi(R_{HH}, R_{\bar{p}}, t)^* \hat{T} \Psi(R_{HH}, R_{\bar{p}}, t)) dV, \quad (4.28)$$

where V is the volume corresponding to a bound H_2 molecule in the coordinate system $R_{HH}, R_{\bar{p}}$ and \hat{T} is the kinetic operator in (4.22), and we define H_2 as dissociated if $R_{HH} > 15 \text{ \AA}$. We solve (4.28) numerically for different initial kinetic energy for the antiproton.

Results and discussion

The dissociation probability was plotted as a function of the initial antiproton kinetic energy, displaying a rapid increase for antiproton kinetic energies larger than 6 eV, where we have accounted for the increased dissociation energy of the $H_2 - \bar{p}$ system compared to molecular hydrogen. The dissociation energy of the $H_2 - \bar{p}$ system was estimated to be about 1.5 eV above the dissociation energy of molecular hydrogen.

Furthermore, the $H_2 - \bar{p}$ system shows clear signs of possible conical intersections between the excited states $2^1\Pi_g$ and $2^1\Sigma_u$, which are not present in molecular hydrogen.

A complete map of the probability distribution for excitation into different vibrational states of molecular hydrogen was presented, for both the reflected (\bar{p} reflected by the H_2 molecule) and transmitted (\bar{p} passing through the H_2 molecule) wave functions, as a function of different initial kinetic energies of the antiproton.

4.6 Paper VI – Antiproton affinities for functional groups

Motivation

One of the latest cancer treatment ideas is to harness the energy release in antiproton-proton annihilation by using antiproton beams instead of proton beams for radiation therapy. The point being that antiproton beams cause more damage to nearby cells in a more localized area, which increases the survival rate for the patient as it results in less damage to neighbouring healthy cells and fewer treatments. We investigate the antiproton interaction with common chemical functional groups that exists in the human body, where the dominating key atoms in the chemical compounds in the human body are those containing carbon, nitrogen and oxygen atoms. This is done by comparing the impact on the antiproton affinity atomic and molecular properties have, such as the atomic number, type of interatomic bond, bond polarization due to electronegativity and charge.

The presented overview study is aimed at understanding the effects involved in antiproton particle-beam cancer therapy, primarily in the ultra-low energy collision regime, but also as a starting point for quantum dynamical treatments.

The data presented is meant to aid and inspire further research in this important topic.

Questions

- Can we extract interesting information about the reaction site of a molecule interacting with a slowly moving antiproton from the potential energy surface?
- What is the relative importance of molecular and atomic properties – such as charge, electronegativity, number of lone pairs, type of bond and atomic number – in terms of antiproton affinity?

Method

We considered scattering of antiprotons on different functional groups (see figure 4.2) which are treated at the CASPT2 level implemented by the MOLCAS program package [82] to calculate the electronic ground states. The antiproton is simulated by adding a negative point charge to the geometry definition and the valence electrons are placed in the active space.

More specifically, we investigated the functional groups by comparing the impact of atomic characteristics such as the atomic number, electronegativity and type of bond between the atoms (single, double, triple bonds and number of lone pairs), on the chemical affinity of \bar{p} .

Apart from the more common functional groups containing carbon, nitrogen and oxygen, we also investigated how hydrogen together with an electro-positive element interacts with an antiproton (LiH).

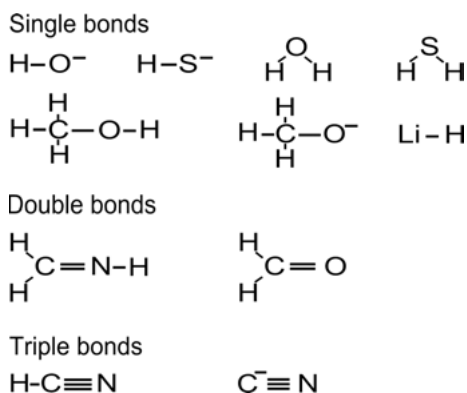


Figure 4.2. The molecules investigated in terms of their antiproton interaction.

Results and discussion

The potential energy surfaces could be compared relative to each other and by varying a set of parameters and comparing the results, a relative ordering of the effect of the atomic and molecular properties was suggested.

Charge is of course a dominant factor regulating the antiproton attraction, but since the electronic density is polarized by the charge it is not obvious toward which atom the antiproton falls. For neutral molecules with atoms that are not particularly electropositive, the effect of the atomic number was shown to be dominating due to the antiproton passing the repulsive electronic energy barrier sooner, but for larger distances the antiproton is more attracted to atoms with a lower atomic number, due to the weaker electronic repulsion at a distance.

In general, the strength of the impact of the compared parameters depend on the details of the molecular electronic distribution. For the molecules investigated a rule of thumb for the relative order was found to be: *charge* > *bond polarization due to electronegativity* > *lone pair* > *atomic number*, for antiproton distances outside the electronic barrier, for shorter distances the spatial extension of the electronic density, closely related to the atomic number, becomes a dominating factor. However, such an ordering can never be precise since the effects are not independent, e.g. the lone pair effect increases the effect of electronegativity and bond polarization. For a more precise description of the effects of the parameters, more experimental data is needed.

5. Summary

This thesis is devoted to the study of the interaction between matter and antimatter. Special attention has been given to the model system of a hydrogen atom interacting with an antihydrogen atom, in particular to extensions of the Born-Oppenheimer approximation of the interaction between the two atoms, and to the non-adiabatic method of the 4-body description developed by the Kamimura group [72]. This is followed by a quantum dynamical description of the interaction of an antiproton with molecular hydrogen and an overview study of antiproton interaction with common functional groups (small molecules) in the human body.

The thesis starts with a historical summary of the scientific findings and thoughts that led to the discovery of antimatter, followed by an introduction to the field of quantum mechanics and a methodology chapter describing in an explanatory way the body of methods used in the subsequent papers. A full chapter is devoted to the numerical 4-body method, followed by a summary of each article included in the thesis.

A selection of key points where this work has contributed to the field of matter–antimatter interaction:

- Measuring the accuracy of the adiabatic approximation by comparing the findings from adiabatic methods to the non-adiabatic 4-body method, by calculation of a 2-body hadronic density wave function and by exploring the existence of resonance states.
- Calculating probabilities of decay of the $H\bar{H}$ molecule through rearrangement into protonium and positronium as well as by direct annihilation.
- Investigating how the adiabatic $H\bar{H}$ states are affected by including the effect of the strong force, and by including a part of the adiabatic correction through a mass-scaling procedure.
- Developing a method of finding resonance states by combining different scaling methods and inspection of the composition of the states.
- Investigating possible conical intersections in molecular hydrogen due to the interaction with an antiproton.
- Exploring the dynamics of an antiproton scattering on molecular hydrogen, two common products in high collision experiments.
- Giving an overview of an antiproton interacting with key molecular groups in the human body, aimed to aid research concerned with using an antiproton beam in cancer treatment.

Sammanfattning

Denna avhandling behandlar interaktionen mellan materia och antimateria. Särskild fokus har tillägnats modell-systemet där väte interagerar med antiväte genom att använda 4-kropparsmetoden utvecklad av Kamimura et. al. [72], kompletterad med förbättringar av Born-Oppenheimer approximationen. Förbättringar av Born-Oppenheimer approximationen görs med två olika metoder; först genom att inkludera effekten av stark växelverkan genom att använda komplexa randvillkor för vågfunktionen, och sedan genom att inkludera en del av den adiabatiska korrektionen i en masskalningsprocedur.

Genom att använda vågfunktionerna från den förbättrade Born-Oppenheimer approximationen via masskalningsproceduren i expansionen av vågfunktionen i 4-kropparsmetoden beräknades hur korrekt den adiabatiska behandlingen av väte-antiväte systemet är för olika internukleära avstånd, via jämförelse av vågfunktionen erhållen från den förbättrade Born-Oppenheimer approximationen med en hadronisk täthetsfunktion beräknad från 4-kropparsvågfunktionerna.

Vidare användes den förbättrade vågfunktionsexpansionen i 4-kropparsmetoden för att leta efter resonanstillstånd nära de adiabatiskt beräknade bundna tillstånden, genom att tillämpa reell och komplex skalning i kombination med inspektion av sammansättningen av egentillstånden hörande till de intressanta rötterna.

För interaktionen mellan en antiproton och materia har en kvantdynamisk beskrivning av interaktionen mellan en antiproton och en vätemolekyl genomförts, där sannolikhetsfördelningar för excitation till olika egentillstånd och dissociation av vätemolekylen beräknades. Detta följs av en överblicksstudie av den relativa effekten av olika atomära och molekylära egenskaper för interaktionen mellan en antiproton och molekylgrupper som är vanliga i människokroppen, av intresse för vidare studier av de processer som rör behandling av tumörer med antiprotonstrålning.

Avhandlingen börjar med en historisk sammanfattning över de framsteg och tankar som ledde till upptäckten av antipartiklar, vilket följs av en introduktion till kvantmekanik och ett kapitel som på ett förklarande sätt beskriver teorin bakom metoderna som används i de efterföljande artiklarna, såsom Ritz variationsmetod, Gaussian Expansion Method, störningsteori för interaktionen mellan två atomer, Born-Oppenheimer och den adiabatiska approximationen, spridningsteori, reell och komplex skalning för att leta efter resonanstillstånd samt vad som kännetecknar ett resonanstillstånd,

kvantdynamikteori och slutligen ett avsnitt som beskriver molekylär elektronstrukturteori.

Ett särskilt kapitel tillägnas 4-kropparsmetoden, vilket efterföljs av en sammanfattning av varje artikel inkluderad i avhandlingen.

Slutligen ingår fyra abstracts som i detalj visar matematiska härledningar som utelämnats från kapitlet som beskriver metodiken.

Nedan följer några sammanfattande punkter angående hur detta arbete har bidragit till förståelsen kring interaktionen mellan materia och antimateria:

- Estimering av hur korrekt den adiabatiska approximationen är genom att jämföra resultaten med en icke-adiabatisk metod, via beräkning av en hadronisk täthetsvägfunktion och via beräkning av resonanstillstånd.
- Beräkning av sannolikheter för sönderfall av väte-antiväte molekylen via omformation till protonium och positronium samt via direkt annihilation.
- Beräkning av hur de adiabatiska väte-antiväte tillstånden påverkas av inkludering av effekten av stark växelverkan.
- Beräkning av hur de adiabatiska väte-antiväte tillstånden påverkas av inkludering av en del av den adiabatiska korrektionen.
- Utveckling av en masskalningsprocedur som kan användas för att inkludera en stor del av den adiabatiska korrektionen för väte-antiväte systemet.
- Utveckling av en metod för att finna resonanstillstånd genom kombinerad av olika skalningsmetoder samt inspektion av sammansättningen för tillstånden.
- Utforskning av möjliga koniska intersektioner i vätemolekylen inducerad av interaktionen med en antiproton.
- Utforskning av kvantdynamiska egenskaper hos en antiproton som kolliderar med en vätemolekyl, två vanliga produkter i hög-energi experiment.
- Överblick över hur atomiska och molekylära egenskaper påverkar interaktionen med en antiproton, riktad till att inspirera och underlätta forskning kring att använda antiprotonstrålning inom tumörbehandling.

Acknowledgments

First of all, I would like to thank the following three people:

- **Konrad Piszczatowski** for all the time and effort he spent on teaching me quantum chemistry,
- **Roland Lindh** for his genuine support making this thesis possible and for his excellent help with Fortran programming,
- **Ignacio Fernández Galván** for his time and effort in helping me get the hang of the MOLCAS program package and various quantum chemistry methods.

I would also like to thank **Piotr Froelich** for constantly pushing me towards learning more about this field of physics and **Hans O. Karlsson** for helping me with all kinds of obstacles I had to overcome as a starting out Ph.D student.

I am grateful for the extended hospitality that **Masao Kamimura** and **Emiko Hiyama** showed me during my visit to Japan, and for the lessons given to me about the 4-body program they had written.

My warmest thanks go to my parents **Per Stegeby** and **Ann-Cathrin Stegeby** for always supporting and believing in me, my brother **Daniel Stegeby** and his family for everything that you might want from a brother and his family, my grandmother **Britt-Marie Stegeby** for inspiring me to continue my scientific endeavors, my grandparents **Bert Grannas** and **Inga Grannas** whom ever since I was a child encouraged my interest in physics and math, and to my very special someone **Greta Brydolf** for being part of my life.

Last, but definitely not least, I would like to direct a very special thanks to my friend **Tobias Carlsson**, for being who he is, elevating my self esteem.

Appendix A.

Matrix elements calculations

Primitive Gaussian functions

Overlap matrix

The matrix elements for the overlap matrix in the subspace of (l, m) are given from the basis functions as

$$S_{ij} = \langle \phi_{ilm} | \phi_{jlm} \rangle, \quad (5.1)$$

where ϕ_{ilm} and ϕ_{jlm} are the primitive Gaussian functions multiplied by the spherical harmonics functions Y_{lm}

$$g_{nl}(R) = N_{nl} R^l \exp(-v_n R^2) Y_{lm}(\Omega). \quad (5.2)$$

The matrix elements for a fixed angular momenta l are easy to calculate:

$$\begin{aligned} S_{ij} &= \langle \phi_{ilm}^G | \phi_{jlm}^G \rangle = \int g_{il}^* Y_{lm}^*(R) g_{jl} Y_{lm}(R) dV = \\ &= N_{il} N_{jl} \int R^{2l} e^{-R^2(v_i+v_j)} Y_{lm}^*(R) Y_{lm}(R) dV = \\ &= N_i N_j \int_0^\infty R^{2(l+1)} e^{-R^2(v_i+v_j)} dR. \end{aligned} \quad (5.3)$$

The known solution to those kinds of integrals is

$$\int_0^\infty R^n e^{-aR^2} dR = \begin{cases} \frac{(2k-1)!!}{2^{k+1} a^k} \sqrt{\frac{\pi}{a}} & (n = 2k, k \text{ integer}, a > 0) \\ \frac{k!}{2a^{k+1}} & (n = 2k+1, k \text{ integer}, a > 0). \end{cases} \quad (5.4)$$

Using this formula in (5.3) gives us the result

$$S_{ij} = N_{il} N_{jl} \frac{(2l+1)!!}{2^{l+2} (v_i + v_j)^{l+1}} \sqrt{\frac{\pi}{v_i + v_j}} = N_{il} N_{jl} \frac{(2l+1)!! \sqrt{\pi}}{2^{l+2} (v_i + v_j)^{l+3/2}}. \quad (5.5)$$

The primitive Gaussian functions are normalized so that $S_{ii} = 1$, which gives us the normalization coefficients

$$N_{il} = \sqrt{\frac{2^{l+2} (2v_i)^{l+3/2}}{(2l+1)!! \sqrt{\pi}}}. \quad (5.6)$$

Potential energy matrix

The interaction potential between the two particles for which we use primitive Gaussian functions is the Coulomb potential

$$\hat{U} = -\frac{1}{R}, \quad (5.7)$$

where R is the distance between the particles. Since the potential operator does not depend on the angular coordinates, the matrix elements for a fixed angular momenta l are given by

$$U_{ij} = \langle g_i(R) | -\frac{1}{R} | g_j(R) \rangle, \quad (5.8)$$

which is an integral that is easy to calculate:

$$U_{ij} = -\int_0^\infty g_i^*(R) \frac{1}{R} g_j(R) R^2 dR = -N_i N_j \int_0^\infty R^{2l+1} e^{-R^2(v_i+v_j)} dR \quad (5.9)$$

The solution to this integral is given by (5.4) and the matrix element i, j becomes

$$U_{ij} = -N_i N_j \frac{l!}{2(v_i+v_j)^{l+1}} = \frac{2^{l+1}}{\sqrt{\pi}} \frac{l!}{(2l+1)!!} \sqrt{v_i+v_j} \left(\frac{2\sqrt{v_i v_j}}{v_i+v_j} \right)^{l+3/2}. \quad (5.10)$$

Kinetic energy matrix

The kinetic energy operator depends on both the distance R and the angular coordinates

$$\hat{T} = -\frac{1}{2\mu} \nabla_{\mathbf{R}}^2. \quad (5.11)$$

The total wave function is separated into a radial part (primitive Gaussian functions) and a part which contains the angular coordinates

$$\phi_{nlm}(\mathbf{R}) = g_{nl}(R) Y_{lm}(\Omega). \quad (5.12)$$

This operator operating on the angular part of the wave function gives

$$\hat{T} Y_{lm}(\Omega) = -\frac{1}{2\mu} \nabla_{\mathbf{R}}^2 Y_{lm}(\Omega) = -\frac{l(l+1)}{2\mu R^2} Y_{lm}(\Omega). \quad (5.13)$$

Armed with this we calculate the matrix element i, j for a fixed angular momentum l

$$\begin{aligned}
T_{i,j} &= \langle \phi_i^G | -\frac{1}{2\mu} \nabla_{\mathbf{R}}^2 | \phi_j^G \rangle = -\frac{1}{2\mu} N_i N_j \int R^l e^{-v_i R^2} Y_{l,m}^* \nabla_{\mathbf{R}}^2 (R^l e^{-v_j R^2} Y_{l,m}) dV \\
&= -\frac{1}{2\mu} N_i N_j \int R^l e^{-v_i R^2} Y_{l,m}^* \left(\frac{1}{R} \frac{\partial^2}{\partial R^2} (R^{l+1} e^{-v_j R^2}) Y_{l,m} \right. \\
&\quad \left. - \frac{l(l+1)}{R^2} (R^l e^{-v_j R^2} Y_{l,m}) \right) dV \\
&= -\frac{1}{2\mu} N_i N_j \int R^l e^{-v_i R^2} Y_{l,m}^* \left(\frac{1}{R} \frac{\partial}{\partial R} ((l+1)R^l - 2v_j R^{l+2}) e^{-v_j R^2} Y_{l,m} \right. \\
&\quad \left. - \frac{l(l+1)}{R^2} (R^l e^{-v_i R^2} Y_{l,m}) \right) dV \\
&= -\frac{1}{2\mu} N_i N_j \int R^l e^{-v_i R^2} Y_{l,m}^* \left(\frac{1}{R} (l(l+1)R^{l-1} - 2v_i(l+2)R^{l+1} \right. \\
&\quad \left. - 2v_i(l+1)R^{l+1} + 4v_i^2 R^{l+3}) e^{-v_i R^2} Y_{l,m} - \frac{l(l+1)}{R^2} (R^l e^{-v_i R^2} Y_{l,m}) \right) dV \\
&= -\frac{1}{2\mu} N_i N_j \int Y_{l,m}^* Y_{l,m} \int_0^\infty R^l e^{-v_i R^2} \left(l(l+1)R^l - 2v_i(2l+3)R^{l+2} \right. \\
&\quad \left. + 4v_i^2 R^{l+4} - (l(l+1)R^l) e^{-v_i R^2} \right) dR \\
&= -\frac{1}{2\mu} N_i N_j \int_0^\infty \left(-2v_i(2l+3)R^{l+2} + 4v_i^2 R^{l+4} \right) e^{-(v_i+v_i)R^2} dR \\
&= -\frac{1}{2\mu} N_i N_j \left(4v_i^2 \frac{(2(l+2)-1)!! \sqrt{\pi}}{2^{l+3} (v_n + v_i)^{l+5/2}} - 2v_i(2l+3) \frac{(2(l+1)-1)!! \sqrt{\pi}}{2^{l+2} (v_n + v_i)^{l+3}} \right) \\
&\quad - \frac{1}{2\mu} N_i N_j \frac{\sqrt{\pi}}{2^{l+1} (v_n + v_i)^{l+3/2}} \left(v_i^2 \frac{(2l+3)!!}{v_n + v_i} - v_i(2l+3)(2l+1)!! \right)
\end{aligned} \tag{5.14}$$

With the simplification

$$-\frac{1}{2\mu} N_i N_j = \frac{-1}{\mu} \frac{2^{l+2} (2\sqrt{v_n v_i})^{l+3/2}}{\sqrt{\pi} (2l+1)!!} \tag{5.15}$$

5.14 becomes

$$\begin{aligned}
T_{i,j} &= \frac{-1}{\mu} \left(\frac{2\sqrt{v_n v_i}}{v_n + v_i} \right)^{l+3/2} (2l+3) \left(\frac{v_i^2}{v_n + v_i} - v_i \right) \\
&= \left\{ \frac{v_i^2}{v_n + v_i} - v_i = \frac{v_i^2 - v_i(v_n + v_i)}{v_n + v_i} = \frac{v_i^2 - v_i v_n - v_i^2}{v_n + v_i} = \frac{-v_n v_i}{v_n + v_i} \right\} \\
&= \frac{1}{\mu} \frac{(2l+3)v_n v_i}{v_n + v_i} \left(\frac{2\sqrt{v_n v_i}}{v_n + v_i} \right)^{l+3/2}
\end{aligned} \tag{5.16}$$

Thus, the matrix element i, j is given by

$$T_{i,j} = \frac{1}{\mu} \frac{(2l+3)v_n v_i}{v_n + v_i} \left(\frac{2\sqrt{v_n v_i}}{v_n + v_i} \right)^{l+3/2} \tag{5.17}$$

Oscillating Gaussian functions

Overlap matrix

For oscillating Gaussian functions we have sine and cosine functions multiplied to our primitive Gaussian functions as described in 2.2, where the primitive Gaussian functions are

$$g_{nl}(R) = N_{nl} R^l \exp(-v_n R^2), \tag{5.18}$$

where the norm N_{nl} is real. We use Euler's formula

$$\sin(\alpha v_n R^2) = \frac{1}{2i} (e^{i\alpha v_n R^2} - e^{-i\alpha v_n R^2}), \tag{5.19}$$

to write our sine oscillating Gaussian functions as

$$\begin{aligned}
g_{nl}^S(R) &= N_{nl} R^l e^{-v_n R^2} \sin(\alpha v_n R^2) = N_{nl} R^l e^{-v_n R^2} \frac{1}{2i} (e^{i\alpha v_n R^2} - e^{-i\alpha v_n R^2}) \\
&= N_{nl} R^l \frac{1}{2i} (e^{-a_n R^2} - e^{-b_n R^2}),
\end{aligned} \tag{5.20}$$

where

$$\begin{aligned}
a_n &= (1 + i\alpha) v_n \\
b_n &= (1 - i\alpha) v_n.
\end{aligned} \tag{5.21}$$

The matrix element for a sine oscillating Gaussian times another sine oscillating Gaussian at row i and column j with a fixed angular momenta l , can now be written as

$$\begin{aligned}
S_{ij}^{SS} &= \langle g_{il}^S | g_{jl}^S \rangle = N_i N_j \int_0^\infty R^{2l} \frac{1}{4} (e^{-b_i R^2} - e^{-a_i R^2}) (e^{-b_j R^2} - e^{-a_j R^2}) R^2 dR \\
&= \frac{N_i N_j}{4} \int_0^\infty R^{2(l+1)} \left(e^{-R^2(b_i+a_j)} - e^{-R^2(b_i+b_j)} - e^{-R^2(a_i+a_j)} + e^{-R^2(a_i+b_j)} \right) dR.
\end{aligned} \tag{5.22}$$

Although the constants a_i , a_j , b_i and b_j are complex numbers, the known analytical solution to this integral are the same as for the case where all the constants are real, i.e.

$$\int_0^{\infty} R^n e^{-aR^2} dR = \begin{cases} \frac{(2k-1)!!}{2^{k+1}a^k} \sqrt{\frac{\pi}{a}} & (n = 2k, k \text{ integer}, a > 0) \\ \frac{k!}{2a^{k+1}} & (n = 2k + 1, k \text{ integer}, a > 0) \end{cases} \quad (5.23)$$

Using this in (5.22) gives

$$S_{ij}^{SS} = \frac{N_i N_j (2l+1)!! \sqrt{\pi}}{4 \cdot 2^{l+2}} \left(\frac{1}{(b_i + a_j)^{l+3/2}} - \frac{1}{(b_i + b_j)^{l+3/2}} - \frac{1}{(a_i + a_j)^{l+3/2}} + \frac{1}{(a_i + b_j)^{l+3/2}} \right). \quad (5.24)$$

Similarly we have for the other sine–cosine combinations

$$S_{ij}^{CS} = \frac{N_i N_j (2l+1)!! \sqrt{\pi}}{4 \cdot 2^{l+2}} \left(\frac{1}{(b_i + a_j)^{l+3/2}} - \frac{1}{(b_i + b_j)^{l+3/2}} + \frac{1}{(a_i + a_j)^{l+3/2}} - \frac{1}{(a_i + b_j)^{l+3/2}} \right), \quad (5.25)$$

$$S_{ij}^{SC} = \frac{N_i N_j (2l+1)!! \sqrt{\pi}}{4 \cdot 2^{l+2}} \left(-\frac{1}{(b_i + a_j)^{l+3/2}} - \frac{1}{(b_i + b_j)^{l+3/2}} + \frac{1}{(a_i + a_j)^{l+3/2}} + \frac{1}{(a_i + b_j)^{l+3/2}} \right), \quad (5.26)$$

and

$$S_{ij}^{CC} = \frac{N_i N_j (2l+1)!! \sqrt{\pi}}{4 \cdot 2^{l+2}} \left(\frac{1}{(b_i + a_j)^{l+3/2}} + \frac{1}{(b_i + b_j)^{l+3/2}} + \frac{1}{(a_i + a_j)^{l+3/2}} + \frac{1}{(a_i + b_j)^{l+3/2}} \right). \quad (5.27)$$

Potential energy matrix for a Coulomb potential

Similarly to the calculation of the overlap matrix, but here with the term $1/R$ inside the integral which decreases the power of R by one, we get

$$\begin{aligned} U_{ij}^{SS} &= \langle g_{il}^S | \hat{U} | g_{jl}^S \rangle = N_i N_j \int_0^{\infty} R^{2l} \frac{1}{4R} (e^{-b_i R^2} - e^{-a_i R^2}) (e^{-b_j R^2} - e^{-a_j R^2}) R^2 dR \\ &= \frac{N_i N_j}{4} \int_0^{\infty} R^{2l+1} \left(e^{-R^2(b_i+a_j)} - e^{-R^2(b_i+b_j)} - e^{-R^2(a_i+a_j)} + e^{-R^2(a_i+b_j)} \right) dR \\ &= \frac{N_i N_j l!}{4 \cdot 2} \left(\frac{1}{(b_i + a_j)^{l+1}} - \frac{1}{(b_i + b_j)^{l+1}} - \frac{1}{(a_i + a_j)^{l+1}} + \frac{1}{(a_i + b_j)^{l+1}} \right). \end{aligned} \quad (5.28)$$

Similarly, we have for the other sine–cosine combinations

$$U_{ij}^{CS} = \frac{N_i N_j l!}{4 \cdot 2} \left(\frac{1}{(b_i + a_j)^{l+1}} - \frac{1}{(b_i + b_j)^{l+1}} + \frac{1}{(a_i + a_j)^{l+1}} - \frac{1}{(a_i + b_j)^{l+1}} \right), \quad (5.29)$$

$$U_{ij}^{SC} = \frac{N_i N_j l!}{4 \cdot 2} \left(-\frac{1}{(b_i + a_j)^{l+1}} - \frac{1}{(b_i + b_j)^{l+1}} + \frac{1}{(a_i + a_j)^{l+1}} + \frac{1}{(a_i + b_j)^{l+1}} \right), \quad (5.30)$$

and

$$U_{ij}^{CC} = \frac{N_i N_j l!}{4 \cdot 2} \left(\frac{1}{(b_i + a_j)^{l+1}} + \frac{1}{(b_i + b_j)^{l+1}} + \frac{1}{(a_i + a_j)^{l+1}} + \frac{1}{(a_i + b_j)^{l+1}} \right). \quad (5.31)$$

Potential energy matrix for the mass-scaled BO potential

The mass-scaled BO potential V_{ad} is expanded in a series of primitive Gaussian functions

$$\phi_{nk}(R) = N_{nk} R^k e^{-\xi_n R^2}, \quad (5.32)$$

such that

$$U_{ij}^{CC} = \langle g_{il}^C(R) | \hat{V}_{ad} | g_{jl}^C(R) \rangle = \langle g_{il}^C(R) | \sum_{nk} c_{nk} \phi_{nk}(R) | g_{jl}^C(R) \rangle. \quad (5.33)$$

Straightforward calculation gives us

$$\begin{aligned} U_{ij}^{CC} &= \frac{N_i N_j}{4} \sum_{nk} c_{nk} N_{nk} \int_0^\infty R^{2l+k+2} (e^{-b_i R^2} - e^{-a_i R^2}) (e^{-b_j R^2} - e^{-a_j R^2}) e^{-\xi_n R^2} dR \\ &= \frac{N_i N_j}{4} \sum_{nk} c_{nk} N_{nk} \int_0^\infty R^{2l+k+2} \left(e^{-R^2(b_i+a_j+\xi_n)} + e^{-R^2(b_i+b_j+\xi_n)} \right. \\ &\quad \left. + e^{-R^2(a_i+a_j+\xi_n)} + e^{-R^2(a_i+b_j+\xi_n)} \right) dR. \end{aligned} \quad (5.34)$$

Here the solutions to the integral depends on the parity of k , and in our fitted expansion to the mass-scaled BO potential we use both even and odd values

of k . After defining

$$p_1 = \frac{1}{(b_i + a_j + \xi_n)^{l+k+3/2}} \quad (5.35)$$

$$p_2 = \frac{1}{(b_i + b_j + \xi_n)^{l+k+3/2}} \quad (5.36)$$

$$p_3 = \frac{1}{(a_i + a_j + \xi_n)^{l+k+3/2}} \quad (5.37)$$

$$p_4 = \frac{1}{(a_i + b_j + \xi_n)^{l+k+3/2}} \quad (5.38)$$

$$p_5 = \frac{1}{(b_i + a_j + \xi_n)^{l+\frac{k+1}{2}+1}} \quad (5.39)$$

$$p_6 = \frac{1}{(b_i + b_j + \xi_n)^{l+\frac{k+1}{2}+1}} \quad (5.40)$$

$$p_7 = \frac{1}{(a_i + a_j + \xi_n)^{l+\frac{k+1}{2}+1}} \quad (5.41)$$

$$p_8 = \frac{1}{(a_i + b_j + \xi_n)^{l+\frac{k+1}{2}+1}}, \quad (5.42)$$

we can write

$$U_{ij}^{CC} = \frac{N_i N_j}{4} \sum_{nk} c_{nk} N_{nk} \times \begin{cases} \frac{(2l+k+1)!!\sqrt{\pi}}{2^{l+2+k/2}} (p_1 + p_2 + p_3 + p_4) \\ \frac{(l+\frac{k+1}{2})!}{2} (p_5 + p_6 + p_7 + p_8), \end{cases} \quad (5.43)$$

where the first alternative is for even values of k and the one below is for odd values of k . We have for the other sine–cosine combinations the matrix elements

$$U_{ij}^{CS} = \frac{N_i N_j}{4} \sum_{nk} c_{nk} N_{nk} \times \begin{cases} \frac{(2l+k+1)!!\sqrt{\pi}}{2^{l+2+k/2}} (p_1 - p_2 + p_3 - p_4) \\ \frac{(l+\frac{k+1}{2})!}{2} (p_5 - p_6 + p_7 - p_8), \end{cases} \quad (5.44)$$

$$U_{ij}^{SC} = \frac{N_i N_j}{4} \sum_{nk} c_{nk} N_{nk} \times \begin{cases} \frac{(2l+k+1)!!\sqrt{\pi}}{2^{l+2+k/2}} (-p_1 - p_2 + p_3 + p_4) \\ \frac{(l+\frac{k+1}{2})!}{2} (-p_5 - p_6 + p_7 + p_8), \end{cases} \quad (5.45)$$

and

$$U_{ij}^{SS} = \frac{N_i N_j}{4} \sum_{nk} c_{nk} N_{nk} \times \begin{cases} \frac{(2l+k+1)!!\sqrt{\pi}}{2^{l+2+k/2}} (p_1 - p_2 - p_3 + p_4) \\ \frac{(l+\frac{k+1}{2})!}{2} (p_5 - p_6 - p_7 + p_8). \end{cases} \quad (5.46)$$

Kinetic energy matrix

Now we get to calculations which are a bit more cumbersome since the kinetic energy operator contains the angular dependence and second order derivatives. However, it is still fairly straightforward so buckle up. The integral for matrix element at row i , column j is

$$\begin{aligned} T_{ij}^{SS} &= -\frac{1}{2\mu} \frac{N_i N_j}{4} \int R^l (e^{-b_i R^2} - e^{-a_i R^2}) Y_l^* \nabla_{\mathbf{R}}^2 (R^l (e^{-a_j R^2} - e^{-b_j R^2}) Y_l) R^2 dR d\Omega \\ &= -\frac{1}{2\mu} \frac{N_i N_j}{4} \int R^l (e^{-b_i R^2} - e^{-a_i R^2}) Y_l^* \left[\frac{1}{R} \frac{\partial^2}{\partial R^2} (R^{l+1} (e^{-b_i R^2} - e^{-a_i R^2})) Y_l \right. \\ &\quad \left. - \frac{l(l+1)}{R^2} (R^l (e^{-a_j R^2} - e^{-b_j R^2}) Y_l) \right] R^2 dR d\Omega \\ &= -\frac{1}{2\mu} \frac{N_i N_j}{4} \int_0^\infty R^{l-1} (e^{-b_i R^2} - e^{-a_i R^2}) \left[\frac{\partial^2}{\partial R^2} (R^{l+1} (e^{-a_j R^2} - e^{-b_j R^2})) \right. \\ &\quad \left. - \frac{l(l+1)}{R^2} (R^{l-1} (e^{-a_j R^2} - e^{-b_j R^2})) \right] R^2 dR. \end{aligned} \quad (5.47)$$

Now I expand the second derivative term in the integral

$$\begin{aligned} \frac{\partial^2}{\partial R^2} (R^{l+1} (e^{-a_j R^2} - e^{-b_j R^2})) &= \\ &= \frac{\partial}{\partial R} \left((l+1) R^l (e^{-a_j R^2} - e^{-b_j R^2}) + R^{l+1} (-2R a_j e^{-a_j R^2} + 2R b_j e^{-b_j R^2}) \right) \\ &= l(l+1) R^{l-1} (e^{-a_j R^2} - e^{-b_j R^2}) + 2(l+1) R^l (-2R a_j e^{-a_j R^2} + 2R b_j e^{-b_j R^2}) \\ &\quad + R^{l+1} (-2a_j e^{-a_j R^2} + 4R^2 a_j^2 e^{-a_j R^2} + 2R b_j e^{-b_j R^2} + 4R^2 b_j^2 e^{-b_j R^2}) \\ &= 4R^{l+3} (a_j^2 e^{-a_j R^2} - b_j^2 e^{-b_j R^2}) - 2R^{l+1} \left(2(l+1) (a_j e^{-a_j R^2} - b_j e^{-b_j R^2}) \right. \\ &\quad \left. + a_j e^{-a_j R^2} - b_j e^{-b_j R^2} \right) + l(l+1) R^{l-1} (e^{-a_j R^2} - e^{-b_j R^2}). \end{aligned} \quad (5.48)$$

Inserting the above expression back into (5.47) gives us

$$\begin{aligned}
T_{ij}^{SS} &= -\frac{1}{2\mu} \frac{N_i N_j}{4} \int_0^\infty R^{l-1} (e^{-b_i R^2} - e^{-a_i R^2}) 4R^{l+3} (a_j^2 e^{-a_j R^2} - b_j^2 e^{-b_j R^2}) R^2 dR \\
&+ \frac{1}{2\mu} \frac{N_i N_j}{4} \int_0^\infty R^{l-1} (e^{-b_i R^2} - e^{-a_i R^2}) 2R^{l+1} \left(2(l+1)(a_j e^{-a_j R^2} - b_j e^{-b_j R^2}) \right. \\
&\quad \left. + a_j e^{-a_j R^2} - b_j e^{-b_j R^2} \right) R^2 dR \\
&- \frac{1}{2\mu} \frac{N_i N_j}{4} l(l+1) \int_0^\infty R^{l-1} (e^{-b_i R^2} - e^{-a_i R^2}) \left(R^{l-1} (e^{-a_j R^2} - e^{-b_j R^2}) \right) R^2 dR \\
&+ \frac{1}{2\mu} \frac{N_i N_j}{4} l(l+1) \int_0^\infty R^{l-1} (e^{-b_i R^2} - e^{-a_i R^2}) \left(R^{l-1} (e^{-a_j R^2} - e^{-b_j R^2}) \right) R^2 dR.
\end{aligned} \tag{5.49}$$

The last two terms cancel each other out and we have

$$\begin{aligned}
T_{ij}^{SS} &= -\frac{1}{2\mu} \frac{N_i N_j}{4} \int_0^\infty R^{l-1} (e^{-b_i R^2} - e^{-a_i R^2}) 4R^{l+3} (a_j^2 e^{-a_j R^2} - b_j^2 e^{-b_j R^2}) R^2 dR \\
&+ \frac{1}{2\mu} \frac{N_i N_j}{4} \int_0^\infty R^{l-1} (e^{-b_i R^2} - e^{-a_i R^2}) 2R^{l+1} \left(2(l+1)(a_j e^{-a_j R^2} - b_j e^{-b_j R^2}) \right. \\
&\quad \left. + a_j e^{-a_j R^2} - b_j e^{-b_j R^2} \right) R^2 dR \\
&= -\frac{4}{2\mu} \frac{N_i N_j}{4} \int_0^\infty R^{2(l+2)} \left(a_j^2 e^{-R^2(b_i+a_j)} - b_j^2 e^{-R^2(b_i+b_j)} \right. \\
&\quad \left. - a_j^2 e^{-R^2(a_i+a_j)} + b_j^2 e^{-R^2(a_i+b_j)} \right) dR \\
&+ \frac{2}{2\mu} \frac{N_i N_j}{4} \int_0^\infty R^{2(l+2)} \left((2(l+1)+1)(a_j e^{-R^2(b_i+a_j)} - b_j e^{-R^2(b_i+b_j)}) \right. \\
&\quad \left. - a_j e^{-R^2(a_i+a_j)} + b_j e^{-R^2(a_i+b_j)} \right) dR.
\end{aligned} \tag{5.50}$$

We now have the integrals on the form where we can use the known solution in (5.23)

$$\begin{aligned}
T_{ij}^{SS} &= -\frac{4}{2\mu} \frac{N_i N_j}{4} \frac{(2l+3)!!\sqrt{\pi}}{2^{l+3}} \left(\frac{a_j^2}{(b_i+a_j)^{l+5/2}} - \frac{b_j^2}{(b_i+b_j)^{l+5/2}} \right. \\
&\quad \left. - \frac{a_j^2}{(a_i+a_j)^{l+5/2}} + \frac{b_j^2}{(a_i+b_j)^{l+5/2}} \right) \\
&+ \frac{2}{2\mu} \frac{N_i N_j}{4} (2(l+1)+1) \frac{(2l+1)!!\sqrt{\pi}}{2^{l+2}} \left(\frac{a_j}{(b_i+a_j)^{l+3/2}} - \frac{b_j}{(b_i+b_j)^{l+3/2}} \right. \\
&\quad \left. - \frac{a_j}{(a_i+a_j)^{l+3/2}} + \frac{b_j}{(a_i+b_j)^{l+3/2}} \right).
\end{aligned} \tag{5.51}$$

After a quick inspection of the fraction in front of the big parenthesis we see that they are identical for the two terms, and after the simplification

$$\frac{a_j^2}{(b_i + a_j)^{l+5/2}} - \frac{a_j}{(b_i + a_j)^{l+3/2}} = \frac{a_j^2 - a_j(b_i + a_j)}{(b_i + a_j)^{l+5/2}} = -\frac{a_j b_i}{(b_i + a_j)^{l+5/2}}, \quad (5.52)$$

we can write the expression for the kinetic energy matrix element as

$$T_{ij}^{SS} = -\frac{N_i N_j (2l+3)!! \sqrt{\pi}}{8\mu} \frac{1}{2^{l+1}} \left(\frac{a_j b_i}{(b_i + a_j)^{l+5/2}} - \frac{b_j b_i}{(b_i + b_j)^{l+5/2}} - \frac{a_j a_i}{(a_i + a_j)^{l+5/2}} + \frac{b_j a_i}{(a_i + b_j)^{l+5/2}} \right). \quad (5.53)$$

Similarly we get for the other sine–cosine combinations

$$T_{ij}^{CS} = -\frac{N_i N_j (2l+3)!! \sqrt{\pi}}{8\mu} \frac{1}{2^{l+1}} \left(\frac{a_j b_i}{(b_i + a_j)^{l+5/2}} - \frac{b_j b_i}{(b_i + b_j)^{l+5/2}} + \frac{a_j a_i}{(a_i + a_j)^{l+5/2}} - \frac{b_j a_i}{(a_i + b_j)^{l+5/2}} \right), \quad (5.54)$$

$$T_{ij}^{SC} = -\frac{N_i N_j (2l+3)!! \sqrt{\pi}}{8\mu} \frac{1}{2^{l+1}} \left(-\frac{a_j b_i}{(b_i + a_j)^{l+5/2}} - \frac{b_j b_i}{(b_i + b_j)^{l+5/2}} + \frac{a_j a_i}{(a_i + a_j)^{l+5/2}} + \frac{b_j a_i}{(a_i + b_j)^{l+5/2}} \right), \quad (5.55)$$

and

$$T_{ij}^{CC} = -\frac{N_i N_j (2l+3)!! \sqrt{\pi}}{8\mu} \frac{1}{2^{l+1}} \left(\frac{a_j b_i}{(b_i + a_j)^{l+5/2}} + \frac{b_j b_i}{(b_i + b_j)^{l+5/2}} + \frac{a_j a_i}{(a_i + a_j)^{l+5/2}} + \frac{b_j a_i}{(a_i + b_j)^{l+5/2}} \right). \quad (5.56)$$

The values of the Gaussian parameters r_{\min} and r_{\max} are optimized to give a good description of the 29 bound states and a few continuum states. The first bound states wave functions have a very small range where the bulk of the wave function lives in $0 < R < 0.01$, so it is clear that we need a very small value for r_{\min} . The wave function to the weakest bound state stretches out to $R \approx 15$. In Paper II we optimized r_{\max} and r_{\min} to be $r_{\max} = 15$ and $r_{\min} = 7 \cdot 10^{-5}$.

Appendix B.

The Multipole expansion

The total interaction potential¹ \hat{V}_I between the two atoms is

$$\hat{V}_I = \sum_{i \in A} \sum_{j \in B} \frac{q_i q_j}{r_{ij}}. \quad (5.57)$$

Using the full form of the interaction potential leads in general to tedious calculations, since it contains 2-lepton operators. However, when the internuclear separation is large enough the overlap between the leptonic clouds of both monomers is negligible and the interaction potential V_I can be represented by the multipole expansion, which only contains 1-lepton operators.

Following the description in [71], the multipole expansion of V_I is

$$\begin{aligned} \hat{V} &= \sum_{i \in A} \sum_{j \in B} \frac{q_i q_j}{r_{ij}} = \sum_{i \in A} \sum_{j \in B} \sum_{p=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-s}^{m=+s} \frac{A_{pl|m|}}{R^{p+l+1}} \hat{M}_A^{(p,m)}(i) \hat{M}_B^{(l,m)}(j) = \\ &= \sum_{p=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-s}^{m=+s} \frac{A_{pl|m|}}{R^{p+l+1}} \sum_{i \in A} \hat{M}_A^{(p,m)}(i) \sum_{j \in B} \hat{M}_B^{(l,m)}(j) \\ &= \sum_{p=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-s}^{m=+s} \frac{A_{pl|m|}}{R^{p+l+1}} \hat{M}_A^{(p,m)} \hat{M}_B^{(l,m)}, \end{aligned} \quad (5.58)$$

where R is the distance between atom A and B , and the expansion coefficient

$$A_{pl|m|} = (-1)^{l+m} \frac{(p+l)!}{(p+|m|)!(l+|m|)!}, \quad (5.59)$$

and the multipole moment operator

$$\hat{M}_X^{(p,m)}(i) = q_i r_{Xi}^p P_p^{|m|}(\cos \theta_{Xi}) \exp(im\phi_{Xi}), \quad X = A, B, \quad (5.60)$$

where r , θ and ϕ are the spherical coordinates of the particles in their individual coordinate systems in atom A and B .

¹Includes the internuclear interaction $1/R_{AB}$.

The associated Legendre polynomials $P_p^{|m|}$, with $|m| \leq k$, are defined as

$$P_p^{|m|}(x) = \frac{1}{2^p p!} (1-x^2)^{|m|/2} \frac{d^{p+|m|}}{dx^{p+|m|}} (x^2-1)^p, \quad (5.61)$$

where $s = \min\{p, l\}$. The coefficients for the multipole expansion up to octupole order are presented in Table 5.1.

The physical interpretation of this formula is that at a distance much larger than the average inter-monomer distance, the electric field generated by the particles in the monomer can be seen as generated by a set of multipoles. Hence, the interaction between two such monomers takes the form of the interaction between two sets of multipoles, see Figure 5.1.

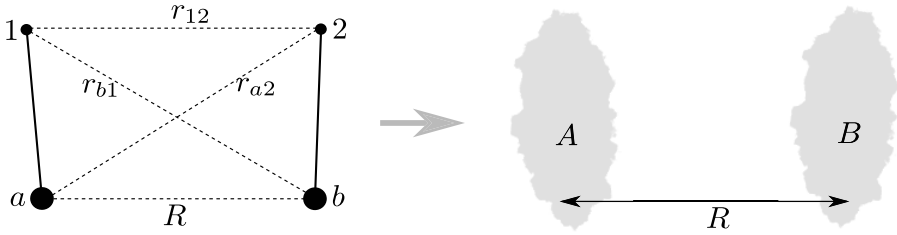


Figure 5.1. Two atoms with nucleus A and B and leptons 1 and 2 are rewritten as interacting multipoles.

Perturbation theory of the H- \bar{H} interaction with multipole expansion

From (2.30) and (2.32) the first order approximation to the interaction energy is given by $E^{(1)}$ and by inserting the multipole expansion for \hat{V} in eq (2.37) we get

$$\begin{aligned} E_k^{(1)}(R) &= \langle \Psi_k^0 | \hat{V} | \Psi_k^0 \rangle = \langle \Psi_i^A \Psi_j^B | \hat{V} | \Psi_i^A \Psi_j^B \rangle \\ &= \langle \Psi_i^A \Psi_j^B | \sum_{p=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-s}^{m=+s} \frac{A_{pl|m|}}{R^{p+l+1}} \hat{M}_A^{(p,m)} \hat{M}_B^{(l,m)} | \Psi_i^A \Psi_j^B \rangle \\ &= \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-s}^{m=+s} \frac{A_{pl|m|}}{R^{p+l+1}} \langle \Psi_i^A | \hat{M}_A^{(p,m)} | \Psi_i^A \rangle \langle \Psi_j^B | \hat{M}_B^{(l,m)} | \Psi_j^B \rangle \\ &= \left\{ \langle \Psi_i^A | \hat{M}_A^{(p,m)} | \Psi_i^A \rangle = \langle \Psi_j^B | \hat{M}_B^{(l,m)} | \Psi_j^B \rangle = 0 \right\} = 0, \quad (5.62) \end{aligned}$$

where $\langle \dots | \dots \rangle$ denotes integration over the leptonic coordinates. The last expression is zero since all the multipole operators except for the monopole belongs to different symmetry group representations than unperturbed

Table 5.1. The coefficients for the multipole expansion up to octupole order. The multipole expansion term is the product of column 4,5,6 and 7.

p	l	m	$A_{p l m}$	$M(p, m)$	$M(l, m)$	$\frac{1}{R^{p+l+1}}$
0	0	0	1	q_a	q_b	$1/R$
1	0	0	1	$q_a Z_a$	q_b	$1/R^2$
1	1	-1	1/2	$q_a(X_a - iY_a)$	$q_b(X_b - iY_b)$	$1/R^3$
1	1	0	-2	$q_a Z_a$	$q_b Z_b$	$1/R^3$
1	1	1	1/2	$q_a(X_a + iY_a)$	$q_b(X_b + iY_b)$	$1/R^3$
2	0	0	1	$q_a \frac{1}{2}(3Z_a^2 - r_a^2)$	q_b	$1/R^3$
2	1	-1	1/2	$q_a 3Z_a(X_a - iY_a)$	$q_b(X_b - iY_b)$	$1/R^4$
2	1	0	-3	$q_a \frac{1}{2}(3Z_a^2 - r_a^2)$	q_b	$1/R^4$
2	1	1	1/2	$q_a 3Z_a(X_a + iY_a)$	$q_b(X_b + iY_b)$	$1/R^4$
2	2	-2	1/24	$q_a 3(X_a - iY_a)^2$	$q_b 3(X_b - iY_b)^2$	$1/R^5$
2	2	-1	-2/3	$q_a 3Z_a(X_a - iY_a)$	$q_b 3Z_b(X_b - iY_b)$	$1/R^5$
2	2	0	6	$q_a \frac{1}{2}(3Z_a^2 - r_a^2)$	$q_b \frac{1}{2}(3Z_b^2 - r_b^2)$	$1/R^5$
2	2	1	-2/3	$q_a 3Z_a(X_a + iY_a)$	$q_b 3Z_b(X_b + iY_b)$	$1/R^5$
2	2	2	1/24	$q_a 3(X_a + iY_a)^2$	$q_b 3(X_b + iY_b)^2$	$1/R^5$
3	0	0	1	$q_a \frac{1}{2}(5Z_a^3 - 3Z_a r_a^2)$	q_b	$1/R^4$
3	1	-1	1/2	$q_a \frac{3}{2}(X_a - iY_a)(5Z_a^2 - r_a^2)$	$q_b(X_b - iY_b)$	$1/R^5$
3	1	0	-4	$q_a \frac{1}{2}(5Z_a^3 - 3Z_a r_a^2)$	$q_b Z_b$	$1/R^5$
3	1	1	1/2	$q_a \frac{3}{2}(X_a + iY_a)(5Z_a^2 + r_a^2)$	$q_b(X_b + iY_b)$	$1/R^5$
3	2	-2	1/120	$q_a 15Z_a(X_a - iY_a)^2$	$q_b 3(X_b - iY_b)^2$	$1/R^6$
3	2	-1	-5/6	$q_a \frac{3}{2}(X_a - iY_a)(5Z_a^2 - r_a^2)$	$q_b 3Z_b(X_b - iY_b)$	$1/R^6$
3	2	0	10	$q_a \frac{1}{2}(5Z_a^3 - 3Z_a r_a^2)$	$q_b \frac{1}{2}(3Z_b^2 - r_b^2)$	$1/R^6$
3	2	1	-5/6	$q_a \frac{3}{2}(X_a + iY_a)(5Z_a^2 + r_a^2)$	$q_b 3Z_b(X_b + iY_b)$	$1/R^6$
3	2	2	1/120	$q_a 15Z_a(X_a + iY_a)^2$	$q_b 3(X_b + iY_b)^2$	$1/R^6$
3	3	-3	1/720	$q_a 15Z_a(X_a - iY_a)^3$	$q_b 15Z_b(X_b - iY_b)^3$	$1/R^7$
3	3	-2	-1/20	$q_a 15Z_a(X_a - iY_a)^2$	$q_b 15Z_b(X_b - iY_b)^2$	$1/R^7$
3	3	-1	30/24	$q_a \frac{3}{2}(X_a - iY_a)(5Z_a^2 - r_a^2)$	$q_b \frac{3}{2}(X_b - iY_b)(5Z_b^2 - r_b^2)$	$1/R^7$
3	3	0	-20	$q_a \frac{1}{2}(5Z_a^3 - 3Z_a r_a^2)$	$q_b \frac{1}{2}(5Z_b^3 - 3Z_b r_b^2)$	$1/R^7$
3	3	1	30/24	$q_a \frac{3}{2}(X_a + iY_a)(5Z_a^2 + r_a^2)$	$q_b \frac{3}{2}(X_b + iY_b)(5Z_b^2 + r_b^2)$	$1/R^7$
3	3	2	-1/20	$q_a 15Z_a(X_a + iY_a)^2$	$q_b 15Z_b(X_b + iY_b)^2$	$1/R^7$
3	3	3	1/720	$q_a 15Z_a(X_a + iY_a)^3$	$q_b 15Z_b(X_b + iY_b)^3$	$1/R^7$

hydrogen and antihydrogen in their 1s states. In other words, the integrals contain an odd function multiplied by even wave functions, integrated over the leptonic coordinates, which is zero. The terms containing monopole (charge) operators also vanishes, since the total charge of the monomers is zero. In the same manner one can show that the induction part of the second order correction is zero. What is left of the second order correction for the hydrogen and antihydrogen interaction for the two atoms being in state $k = (i, j)$ is

$$E_k^{(2)} = \sum_{\substack{i \neq i \\ j' \neq j}} \frac{|\langle \Psi_i^A \Psi_j^B | \hat{V} | \Psi_{i'}^A \Psi_{j'}^B \rangle|^2}{E_i^A + E_j^B - E_{i'}^A - E_{j'}^B}. \quad (5.63)$$

Now we expand the interaction potential in (5.63) with the sum of multipoles (5.58) which are calculated in Table 5.1. The first term in (5.58), i.e. $(p, l, m) = (0, 0, 0)$, correspond to charge-charge interaction \hat{V}^{c-c} with the R dependence $1/R$:

$$\begin{aligned} E_{disp}^{(2)c-c} &= \sum_{\substack{i' \neq i \\ j' \neq j}} \frac{|\langle \Psi_i^A \Psi_j^B | \hat{V}^{c-c} | \Psi_{i'}^A \Psi_{j'}^B \rangle|^2}{E_i^A + E_j^B - E_{i'}^A - E_{j'}^B} = \\ &= \sum_{\substack{i' \neq i \\ j' \neq j}} \frac{|\langle \Psi_i^A | q_a | \Psi_{i'}^A \rangle \langle \Psi_j^B | q_b | \Psi_{j'}^B \rangle|^2}{E_i^A + E_j^B - E_{i'}^A - E_{j'}^B} = 0, \end{aligned} \quad (5.64)$$

where we have used the normalization condition (2.35) in the last step. Similarly, the dipole-charge interaction \hat{V}^{d-c} (from indexes $(p, m, l) = (1, 0, 0)$) corresponding to the R dependence $1/R^2$ is equal zero:

$$E_{disp}^{(2)d-c} = \sum_{\substack{i' \neq i \\ j' \neq j}} \frac{|\langle \Psi_i^A | Z_a q_a | \Psi_{i'}^A \rangle \langle \Psi_j^B | q_b | \Psi_{j'}^B \rangle|^2}{E_i^A + E_j^B - E_{i'}^A - E_{j'}^B} = 0. \quad (5.65)$$

For the next terms in Table 5.1 we see that we have four contributions to the $1/R^3$ term, namely the dipole-dipole interactions \hat{V}^{d-d} for $(p, l, m) = (1, 1, -1), (1, 1, 0), (1, 1, 1)$ and the quadrupole-charge interaction \hat{V}^{q-c} , for $(p, l, m) = (2, 0, 0)$. As before, the quadrupole-charge interaction vanishes since

$$\begin{aligned} E_{disp}^{(2)q-c} &= \sum_{\substack{i' \neq i \\ j' \neq j}} \frac{|\langle \Psi_i^A \Psi_j^B | \hat{V}^{q-c} | \Psi_{i'}^A \Psi_{j'}^B \rangle|^2}{E_i^A + E_j^B - E_{i'}^A - E_{j'}^B} \\ &= \sum_{\substack{i' \neq i \\ j' \neq j}} \frac{|\langle \Psi_i^A | q_a \frac{1}{2} (3Z_a^2 - r_a^2) | \Psi_{i'}^A \rangle \langle \Psi_j^B | q_b | \Psi_{j'}^B \rangle|^2}{E_i^A + E_j^B - E_{i'}^A - E_{j'}^B} = \\ &= \left\{ \langle \Psi_j^B | q_b | \Psi_{j'}^B \rangle = q_b \langle \Psi_j^B | \Psi_{j'}^B \rangle = \delta_{j,j'} \right\} = 0. \end{aligned} \quad (5.66)$$

What is left for the $1/R^3$ dependent terms is the dipole-dipole interactions. First we simplify the expression

$$\begin{aligned} \hat{V}^{d-d} &= \frac{q_a(X_a - iY_a)q_b(X_b - iY_b)}{2R^3} - \frac{2q_a Z_a q_b Z_b}{R^3} + \frac{q_a(X_a + iY_a)q_b(X_b + iY_b)}{2R^3} \\ &= \frac{q_a q_b}{2R^3} (X_a X_b - Y_a Y_b - 2Z_a Z_b) = \frac{1}{R^3} (\mu_x^A \mu_x^B - \mu_y^A \mu_y^B - 2\mu_z^A \mu_z^B). \end{aligned} \quad (5.67)$$

where μ_A denotes the dipole operator

$$\mu_x^A = q_a X_a, \quad (5.68)$$

and similarly for the other coordinates. The dipole-dipole part of the dispersion energy can be written as

$$\begin{aligned}
E_{disp}^{(2)d-d} &= \sum_{\substack{i' \neq i \\ j' \neq j}} \frac{|\langle \Psi_i^A \Psi_j^B | \hat{V}^{d-d} | \Psi_{i'}^A \Psi_{j'}^B \rangle|^2}{E_i^A + E_j^B - E_{i'}^A - E_{j'}^B} = \\
&= \sum_{\substack{i' \neq i \\ j' \neq j}} \frac{|\langle \Psi_i^A \Psi_j^B | \frac{1}{2R^3} (\mu_x^A \mu_x^B - \mu_y^A \mu_y^B - 2\mu_z^A \mu_z^B) | \Psi_{i'}^A \Psi_{j'}^B \rangle|^2}{E_i^A + E_j^B - E_{i'}^A - E_{j'}^B} = \\
&= \frac{1}{R^6} \sum_{\substack{i' \neq i \\ j' \neq j}} \frac{|\langle \Psi_i^A \Psi_j^B | (\mu_x^A \mu_x^B - \mu_y^A \mu_y^B - 2\mu_z^A \mu_z^B) | \Psi_{i'}^A \Psi_{j'}^B \rangle|^2}{E_i^A + E_j^B - E_{i'}^A - E_{j'}^B}.
\end{aligned} \tag{5.69}$$

In the system where hydrogen and antihydrogen are in their ground states, we have states of $1S$ -symmetry in the *bras*, which belongs to the fully symmetric representation of the symmetry group. The dipole operator belongs to the same symmetric representation as P -states so the only non-zero contributions in (5.69) are for states of P -symmetry in the *kets*. Setting the symmetry in the bras to $1S$ simplifies (5.69) to

$$\begin{aligned}
E_{disp}^{(2)d-d} &= \frac{1}{R^6} \sum_{i',j'} \frac{\left| \langle \Psi_{1S}(A) \Psi_{1S}(B) | (\mu_x^A \mu_x^B - \mu_y^A \mu_y^B - 2\mu_z^A \mu_z^B) | \Psi_{i'P}(A) \Psi_{j'P}(B) \rangle \right|^2}{E_1^A + E_1^B - E_{i'}^A - E_{j'}^B} \\
&= \frac{1}{R^6} \sum_{i',j'} \frac{1}{E_1^A + E_1^B - E_{i'}^A - E_{j'}^B} \times \\
&\quad \times \left(\left| \langle \Psi_{1S}(A) \Psi_{1S}(B) | (\mu_x^A \mu_x^B - \mu_y^A \mu_y^B - 2\mu_z^A \mu_z^B) | \Psi_{i'P_x}(A) \Psi_{j'P_x}(B) \rangle \right|^2 \right. \\
&\quad + \left| \langle \Psi_{1S}(A) \Psi_{1S}(B) | (\mu_x^A \mu_x^B - \mu_y^A \mu_y^B - 2\mu_z^A \mu_z^B) | \Psi_{i'P_y}(A) \Psi_{j'P_y}(B) \rangle \right|^2 \\
&\quad \left. + \left| \langle \Psi_{1S}(A) \Psi_{1S}(B) | (\mu_x^A \mu_x^B - \mu_y^A \mu_y^B - 2\mu_z^A \mu_z^B) | \Psi_{i'P_z}(A) \Psi_{j'P_z}(B) \rangle \right|^2 \right).
\end{aligned} \tag{5.70}$$

By collecting the x , y and z terms one gets

$$\begin{aligned}
E_{disp}^{(2)d-d} &= \frac{1}{R^6} \sum_{i',j'} \frac{1}{E_1^A + E_1^B - E_{i'}^A - E_{j'}^B} \times \\
&\times \left(\left| \langle \Psi_{1S}(A) | \mu_x^A | \Psi_{i'P_x}(A) \rangle \langle \Psi_{1S}(B) | \mu_x^B | \Psi_{j'P_x}(B) \rangle \right|^2 \right. \\
&+ \left| \langle \Psi_{1S}(A) | \mu_y^A | \Psi_{i'P_y}(A) \rangle \langle \Psi_{1S}(B) | \mu_y^B | \Psi_{j'P_y}(B) \rangle \right|^2 \\
&+ 4 \left| \langle \Psi_{1S}(A) | \mu_z^A | \Psi_{i'P_z}(A) \rangle \langle \Psi_{1S}(B) | \mu_z^B | \Psi_{j'P_z}(B) \rangle \right|^2 \Big). \quad (5.71)
\end{aligned}$$

Since $\langle \Psi_{1S} | \mu_x | \Psi_{i'P_x} \rangle = \langle \Psi_{1S} | \mu_y | \Psi_{i'P_y} \rangle = \langle \Psi_{1S} | \mu_z | \Psi_{i'P_z} \rangle$, (5.71) becomes

$$E_{disp}^{(2)d-d} = \frac{6}{R^6} \sum_{i',j'} \frac{\left| \langle \Psi_{1S}(A) | \mu_z^A | \Psi_{i'P_z}(A) \rangle \langle \Psi_{1S}(B) | \mu_z^B | \Psi_{j'P_z}(B) \rangle \right|^2}{E_1^A + E_1^B - E_{i'}^A - E_{j'}^B}. \quad (5.72)$$

At this point it is useful to introduce the following mathematical trick

$$\frac{ab}{a+b} = \frac{1}{2\pi} \int_0^\infty \left(\frac{a}{a+iw} + \frac{a}{a-iw} \right) \left(\frac{b}{b+iw} + \frac{b}{b-iw} \right) dw. \quad (5.73)$$

Using (5.73) in (5.72) one obtains

$$\begin{aligned}
E_{disp}^{(2)d-d} &= \frac{6}{R^6} \sum_{i',j'} \frac{1}{2\pi} \int_0^\infty \left(\frac{|\langle \Psi_{1S}(A) | \mu_z^A | \Psi_{i'P_z}(A) \rangle|^2}{E_1^A - E_{i'}^A + iw} + \frac{|\langle \Psi_{1S}(A) | \mu_z^A | \Psi_{i'P_z}(A) \rangle|^2}{E_1^A - E_{i'}^A - iw} \right) \\
&\times \left(\frac{|\langle \Psi_{1S}(B) | \mu_z^B | \Psi_{j'P_z}(B) \rangle|^2}{E_1^B - E_{j'}^B + iw} + \frac{|\langle \Psi_{1S}(B) | \mu_z^B | \Psi_{j'P_z}(B) \rangle|^2}{E_1^B - E_{j'}^B - iw} \right) dw = \\
&= \frac{1}{R^6} \frac{3}{\pi} \int_0^\infty \alpha_1^A(iw) \alpha_1^B(iw) dw = \frac{C_6}{R^6}, \quad (5.74)
\end{aligned}$$

where

$$\alpha_1^A(iw) = \sum_{i' \neq 1} \left(\frac{|\langle \Psi_{1S}(A) | \mu_z^A | \Psi_{i'P_z}(A) \rangle|^2}{E_1^A - E_{i'}^A + iw} + \frac{|\langle \Psi_{1S}(A) | \mu_z^A | \Psi_{i'P_z}(A) \rangle|^2}{E_1^A - E_{i'}^A - iw} \right), \quad (5.75)$$

is called the *dynamic dipole polarizability*. Hence, the first non-vanishing terms in the multipole expansion correspond to $1/R^6$ terms which comes from the dipole-dipole interaction, where C_6 is the van der Waals coefficient between interacting atoms in their ground state defined by

$$C_6 = \frac{3}{\pi} \int_0^\infty \alpha_1^A(iw) \alpha_1^B(iw) dw. \quad (5.76)$$

The other van der Waals coefficients are given by including higher terms in the multipole expansion and higher orders of the perturbation theory.

Approximation of the C_6 constant

To get a grasp of the magnitude of the C_6 coefficient for the interaction between atoms in their ground states, we approximate the denominator in (5.70) to be $2E_1$, by ignoring all energy eigenvalues except the ground state energies for the two atoms. For bound states the eigenvalues decrease with n as

$$|E_n| = \frac{E_1}{n^2}, \quad (5.77)$$

so the largest error in the denominator in (5.70) introduced by this approximation is 25%. This approximation enables us to ignore the denominator indexes and use the resolution of identity to simplify (5.69)

$$\begin{aligned} E_{disp}^{(2)d-d} &= \frac{6}{R^6 2E_1} \sum_{\substack{i \neq 1 \\ j \neq 1}} \left| \langle \Psi_{1S}(A) \Psi_{1S}(B) | (\mu_x^A \mu_x^B - \mu_y^A \mu_y^B \right. \\ &\quad \left. - 2\mu_z^A \mu_z^B) | \Psi_i(A) \Psi_j(B) \rangle \right|^2 = \left\{ \mu_x^A \mu_x^B - \mu_y^A \mu_y^B - 2\mu_z^A \mu_z^B = \hat{V}^{dd} \right\} = \\ &= \frac{6}{R^6 2E_1} \sum_{\substack{i \neq 1 \\ j \neq 1}} \left\langle \Psi_{1S}(A) \Psi_{1S}(B) \right| \hat{V}^{d-d} \times \\ &\quad \times \left| \Psi_i(A) \Psi_j(B) \right\rangle \left\langle \Psi_i(A) \Psi_j(B) \right| \hat{V}^{d-d} \left| \Psi_{1S}(A) \Psi_{1S}(B) \right\rangle \\ &= \frac{6}{R^6 2E_1} \left\langle \Psi_{1S}(A) \Psi_{1S}(B) \right| \hat{V}^{d-d} \times \\ &\quad \times \left(\mathbf{1} - \left| \Psi_{1S}(A) \Psi_{1S}(B) \right\rangle \left\langle \Psi_{1S}(A) \Psi_{1S}(B) \right| \right) \hat{V}^{d-d} \left| \Psi_{1S}(A) \Psi_{1S}(B) \right\rangle \\ &= \frac{6}{R^6 2E_1} \left(\left\langle \Psi_{1S}(A) \Psi_{1S}(B) \right| (\hat{V}^{d-d})^2 \left| \Psi_{1S}(A) \Psi_{1S}(B) \right\rangle \right. \\ &\quad \left. + \left\langle \Psi_{1S}(A) \right| \hat{V}^{d-d} \left| \Psi_{1S}(A) \right\rangle \left\langle \Psi_{1S}(B) \right| \hat{V}^{dd} \left| \Psi_{1S}(B) \right\rangle \right), \quad (5.78) \end{aligned}$$

where the last term is zero because of the symmetry of the 1S state and the dipole-dipole operator. Furthermore, due to the spherical symmetry of the 1s states all the cross terms (of the type $\mu_x^A \mu_y^A$) after squaring the operator \hat{V}^{dd} are zero and

$$\langle \Psi_{1S}(A) | (\mu_x^A)^2 | \Psi_{1S}(A) \rangle = \langle \Psi_{1S}(A) | (\mu_y^A)^2 | \Psi_{1S}(A) \rangle = \langle \Psi_{1S}(A) | (\mu_z^A)^2 | \Psi_{1S}(A) \rangle. \quad (5.79)$$

Since all these terms are equal to one third of the mean value of the operator \hat{r}^2 we can write the expression for C_6 as

$$C_6 = \frac{2}{E_1} \left| \langle \Psi_{1S}(A) | r_A^2 | \Psi_{1S}(A) \rangle \right|^2. \quad (5.80)$$

Appendix C.

Separation of oscillations and rotations

The nuclear wave function can be written as a product of a radial and an angular part as

$$f_k(\mathbf{R}) = f_k(R, \theta, \phi) = Y(\theta, \phi)\xi_k(R), \quad (5.81)$$

By writing the Hamiltonian in the following form

$$\hat{H}_N = \hat{T} + \hat{V} = -\frac{\hbar^2}{2\mu}\nabla_{\mathbf{R}}^2 + \hat{V}_k(R) = -\frac{\hbar^2}{2\mu R^2}\left[\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} - \hat{L}^2\right] + \hat{V}_k(R) \quad (5.82)$$

and using (5.81) one obtains

$$\begin{aligned} & \left[-\frac{\hbar^2}{2\mu R^2}\left(\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} - \hat{L}^2\right) + \hat{V}_k(R)\right]Y(\Omega)\xi_k(R) = EY(\Omega)\xi_k(R) \\ \Rightarrow & \left[-\frac{\hbar^2}{2\mu R^2}\left(\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} - \hat{L}^2\right)Y(\Omega)\xi_k(R) + \hat{V}_k(R)Y(\Omega)\xi_k(R)\right] = EY(\Omega)\xi_k(R) \\ \Rightarrow & -\frac{\hbar^2}{2\mu R^2}Y(\Omega)\left(\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}\right)\xi_k(R) + \xi_k(R)\frac{\hbar^2}{2\mu R^2}\hat{L}^2Y(\Omega) \\ & + \hat{V}_k(R)Y(\Omega)\xi_k(R) = EY(\Omega)\xi_k(R), \end{aligned} \quad (5.83)$$

where $Y(\Omega) = Y(\theta, \phi)$. Multiplying (5.83) by $1/Y(\Omega)\xi_k(R)$ from left one gets

$$-\frac{\hbar^2}{2\mu R^2}\frac{1}{\xi_k(R)}\left(\frac{d}{dR}R^2\frac{d}{dR}\right)\xi_k(R) + \frac{1}{Y(\Omega)}\frac{\hbar^2}{2\mu R^2}\hat{L}^2Y(\Omega) + \hat{V}_k(R) = E. \quad (5.84)$$

Now we make the substitution $\chi_k(R) = \xi_k(R)/R$ to get a simplified expression for the first term in the equation above

$$\begin{aligned} \frac{1}{\xi_k(R)}\left(\frac{d}{dR}R^2\frac{d}{dR}\right)\xi_k(R) &= \frac{R}{\chi_k(R)}\left(\frac{d}{dR}R^2\frac{d}{dR}\right)\frac{\chi_k(R)}{R} \\ &= \frac{R}{\chi_k(R)}\frac{d}{dR}R^2\left(\frac{1}{R}\frac{d\chi_k(R)}{dR} - \frac{\chi_k(R)}{R^2}\right) \\ &= \frac{R}{\chi_k(R)}\frac{d}{dR}\left(R\frac{d\chi_k(R)}{dR} - \chi_k(R)\right) \\ &= \frac{R^2}{\chi_k(R)}\frac{d^2\chi_k(R)}{dR^2}, \end{aligned} \quad (5.85)$$

and with $\hat{L}^2 Y(\Omega) = J(J+1)Y(\Omega)$ and moving the angular dependent term over to the right hand side we have

$$-\frac{\hbar^2}{2\mu} \frac{1}{\chi_k(R)} \frac{d^2 \chi_k(R)}{dR^2} + \hat{V}_k(R) - E = -\frac{1}{Y(\Omega)} \frac{\hbar^2}{2\mu R^2} J(J+1)Y(\Omega). \quad (5.86)$$

If we multiply this equation by R^2 from left we get an equation where the left-hand side only depends on R and the right-hand side only depends on the angular coordinates, thus each side must be equal to a constant λ

$$\lambda = -\frac{\hbar^2}{2\mu} \frac{R^2}{\chi_k(R)} \frac{d^2 \chi_k(R)}{dR^2} + R^2 \hat{V}_k(R) - R^2 E \quad (5.87)$$

$$\lambda = -\frac{1}{Y(\Omega)} \frac{\hbar^2}{2\mu} J(J+1)Y(\Omega). \quad (5.88)$$

We write (5.88) as

$$\frac{\lambda}{R^2} Y(\Omega) = -\frac{\hbar^2}{2\mu R^2} J(J+1)Y(\Omega), \quad (5.89)$$

and identify the r.h.s. of (5.89) as the right-hand side of the Schrödinger equation for a rigid rotor, i.e.

$$-\frac{1}{2\mu} \nabla^2 Y(\Omega) = -\frac{\hbar^2}{2I} J(J+1)Y(\Omega), \quad (5.90)$$

where I is the moment of inertia and the permitted values for J are $J = 0, 1, 2, \dots$

This gives

$$\lambda = -\frac{\hbar^2}{2\mu} J(J+1), \quad J = 0, 1, 2, \dots \quad (5.91)$$

Inserting the permitted values for λ in (5.87) leads to the equation for vibrational motion for a given J

$$-\frac{\hbar^2}{2\mu} \left(\frac{d^2 \chi_{kJ}(R)}{dR^2} \right) + \hat{V}_k(R) \chi_{kJ}(R) - E \chi_{kJ}(R) = -\frac{\hbar^2}{2\mu R^2} J(J+1) \chi_{kJ}(R). \quad (5.92)$$

We can write this equation as

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \hat{V}_{kJ}(R) \right) \chi_{kJ}(R) = E_{kJ} \chi_{kJ}(R), \quad (5.93)$$

where

$$\hat{V}_{kJ}(R) = \hat{V}_k(R) + \frac{\hbar^2}{2\mu R^2} J(J+1). \quad (5.94)$$

The solutions χ_{kvJ} to eq. (5.93) describe the vibrations of the nuclei where we now have three quantum numbers; the rotational quantum number J , since the potential $V_{kJ}(R)$ in (5.93) depends on J parametrically, ν (the numbering of the solutions $\nu = 0, 1, 2, \dots$), and k identifies the leptonic energy (i.e. the BO leptonic state of the molecule). The energy E_{kvJ} depends on the leptonic quantum number k as well as both the vibrational and the rotational quantum numbers for the motion of the nuclei, and we will now try to separate rotations from vibrations.

It should be noted that we are forced to make an approximation here, because vibrations cannot be exactly separated from rotations since if the length R of the molecule changes during vibration, the momentum of inertia $I = \mu R^2$ changes, which in turn influences the rotation of the molecule. The approximation we do is to use the equilibrium value R_k^e , i.e. the position of the minimum of the BO potential V_k , of the distance R for the last term on the right hand side in (5.94), which correspond to the solutions to the rigid rotor problem. We use the equilibrium value of the momentum of inertia instead of the exact value

$$I = \mu R^2 \rightarrow I_k^e = \mu (R_k^e)^2, \quad (5.95)$$

which turns (5.94) into

$$\hat{V}_{kJ}(R) = \hat{V}_k(R) + \frac{\hbar^2}{2\mu(R_k^e)^2} J(J+1) = \hat{V}_k(R) + E^{\text{rot}}(J), \quad (5.96)$$

where we identify E^{rot} as the rotational contribution to the energy. The approximation for the moment of inertia can be motivated by the fact that the mean value of the momentum of inertia is supposed to be close to I_k^e .

Since E^{rot} is a constant for each value of J , we can move this term over to the r.h.s. of (5.93). Such actions can always be taken since it only affects the energy scale and not the solutions, thus, with (5.96), equation (5.93) becomes

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \hat{V}_k(R) \right) \chi_{kv}(R) = (E_{kv} - E_J^{\text{rot}}) \chi_{kv}(R), \quad (5.97)$$

where we have dropped the index J since the operator on the l.h.s. does not depend on it. Further more, we can rewrite the leptonic potential $\hat{V}_k(R)$ into a part corresponding to the leptonic energy of the molecule at the equilibrium distance R_k^e for each solution k and one part which depends on R as

$$\hat{V}_k(R) = V_k(R_k^e) + \hat{V}_k^{\text{osc}}(R) = E_k^{\text{lep}} + \hat{V}_k^{\text{osc}}(R), \quad (5.98)$$

and we have

$$\begin{aligned} \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \hat{V}_k^{\text{osc}}(R) \right) \chi_{kv}(R) &= (E_{kvJ} - E_k^{\text{rot}}(J) - E_k^{\text{lep}}) \chi_{kv}(R) \\ &= E_{kv}^{\text{osc}} \chi_{kv}(R). \end{aligned} \quad (5.99)$$

If one wants to add the translational energy of the center of mass motion we can treat this energy as a constant in the same manner and write the total energy $E_{k\nu J}^{\text{tot}}$ as

$$E_{k\nu J}^{\text{tot}} = E^{\text{trans}} + E_k^{\text{lep}} + E_{k\nu}^{\text{osc}} + E_{kJ}^{\text{rot}}, \quad (5.100)$$

and we have the simplified expression for the decoupled eigenvalue problem

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \hat{V}_k^{\text{osc}}(R) \right) \chi_{k\nu}(R) = \left(E^{\text{trans}} + E_k^{\text{lep}} + E_{k\nu}^{\text{osc}} + E_{kJ}^{\text{rot}} \right) \chi_{k\nu}(R). \quad (5.101)$$

Appendix D.

Derivation of the stabilization method

Following [100], we will show that resonance energies are much more stable than other energy eigenvalues with respect to scaling of the basis functions. For energies near the resonance energy the phase shift of the wave function is assumed to be on the form

$$\eta(E) = \eta_{\text{pot}}(E) + \arctan\left(\frac{\Gamma/2}{\varepsilon_r - E}\right), \quad (5.102)$$

where ε_r is the resonance energy, E is the energy of the state, Γ is called the resonance width, and $\eta_{\text{pot}}(E)$ is the contribution of the potential scattering to the phase shift. The continuum solutions behaves as

$$\Psi(R) \sim \sin[kR + \eta(k)]. \quad (5.103)$$

Since we use basis functions that decay as e^{-R^2} we have a "semi-box" where the wall of the box R_N is where our basis functions have died out, giving us the boundary condition for (5.103)

$$\sin[kR_N + \eta(k)] = 0. \quad (5.104)$$

With (5.104) we get a set of j equations relating the wave number k_j and the extension of the basis set R_N

$$k_j R_N + \eta(k_j) = j\pi, \quad j = 1, 2, \dots, N, \quad (5.105)$$

and k_j is related to the energy as $\varepsilon_j = k_j^2/2\mu$.

Now we investigate the change of the discretized energy as a function of the size of the box, i.e. we evaluate $\partial\varepsilon_j/\partial R_N$. By using the chain rule

$$\frac{\partial k}{\partial R_N} = \frac{\partial k}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial R_N} = \frac{\sqrt{\mu}}{\sqrt{2\varepsilon}} \frac{\partial \varepsilon}{\partial R_N} = \frac{\mu}{k} \frac{\partial \varepsilon}{\partial R_N}, \quad (5.106)$$

we differentiate (5.105) with respect to R_N

$$\frac{\partial}{\partial R_N} (k_j R_N + \eta(k_j)) = 0 \Rightarrow \frac{\mu}{k_j} \frac{\partial \varepsilon_j}{\partial R_N} R_N + k_j + \frac{\partial}{\partial R_N} \eta(\varepsilon_j) = 0. \quad (5.107)$$

For the last term with $\eta(\varepsilon_j)$ given by (5.102) we assume that η_{pot} is a slowly varying function of ε_j , and we approximate

$$\frac{\partial \eta_{\text{pot}}}{\partial R_N} = \frac{\partial \eta_{\text{pot}}}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial R_N} \approx 0, \quad (5.108)$$

and (5.107) becomes

$$\begin{aligned}
0 &= \frac{\mu}{k} \frac{\partial \varepsilon_j^N}{\partial R_N} R_N + k_j + \frac{\partial \varepsilon}{\partial R_N} \frac{\partial}{\partial \varepsilon_j^N} \arctan \left(\frac{\Gamma/2}{\varepsilon_r - \varepsilon_j^N} \right) \\
&\approx \frac{\mu}{k_j} \frac{\partial \varepsilon_j^N}{\partial R_N} R_N + k_j + \frac{\partial \varepsilon_j^N}{\partial R_N} \frac{1}{1 + \left(\frac{\Gamma/2}{\varepsilon_r - \varepsilon_j^N} \right)^2} \left(\frac{\Gamma/2}{(\varepsilon_r - \varepsilon_j^N)^2} \right) \\
&= \frac{\mu}{k_j} \frac{\partial \varepsilon_j^N}{\partial R_N} R_N + k_j + \frac{\partial \varepsilon_j^N}{\partial R_N} \left(\frac{2\Gamma}{4(\varepsilon_r - \varepsilon_j^N)^2 + \Gamma^2} \right) \\
\Rightarrow \frac{\partial \varepsilon_j^N}{\partial R_N} \left(R_N + \frac{2\Gamma k_j}{4\mu(\varepsilon_r - \varepsilon_j^N)^2 + \mu\Gamma^2} \right) &= -\frac{k_j^2}{\mu} = -2\varepsilon_j^N, \quad (5.109)
\end{aligned}$$

thus

$$\frac{\partial \varepsilon_j^N}{\partial R_N} = -2\varepsilon_j^N \left(R_N + \frac{2\Gamma k_j}{4\mu(\varepsilon_r - \varepsilon_j^N)^2 + \mu\Gamma^2} \right)^{-1}. \quad (5.110)$$

Now the trick is to realise that for narrow resonances and states with ε_j^N not close to ε_r we have

$$\varepsilon_r - \varepsilon_j^N \gg \Gamma \Rightarrow R_N > \frac{\Gamma k_j}{2\mu(\varepsilon_r - \varepsilon_j^N)^2}, \quad (5.111)$$

and (5.110) becomes

$$\frac{\partial \varepsilon_j^N}{\partial R_N} \approx -\frac{2\varepsilon_j^N}{R_N}, \quad (5.112)$$

which describes the slope of the roots for non-resonant states.

Likewise, for an eigenvalue at the resonance energy, $\varepsilon_i^N = \varepsilon_r$ (5.110) reduces to

$$\frac{\partial \varepsilon_i^N}{\partial R_N} = \frac{-2\varepsilon_r}{R_N + 2k_r/\mu\Gamma}. \quad (5.113)$$

For Γ small enough, where

$$\frac{2k_r}{\mu\Gamma} \gg R_N, \quad (5.114)$$

eq. (5.113) becomes

$$\frac{\partial \varepsilon_i^N}{\partial R_N} \approx -\frac{\varepsilon_r \mu \Gamma}{k_r} = \left\{ \varepsilon_r = \frac{k_r^2}{2\mu} \right\} = -\frac{k_r \Gamma}{2} = \sqrt{\frac{\mu \varepsilon_r}{2}} \Gamma. \quad (5.115)$$

Thus, for a small enough Γ the fraction between the slope of roots corresponding to a resonance eigenvalue ε_i to the slope of roots corresponding

to a non-resonant eigenvalue ε_j is

$$\frac{\partial \varepsilon_i^N}{\partial R_N} / \frac{\partial \varepsilon_j^N}{\partial R_N} \approx \frac{\sqrt{\frac{\mu \varepsilon_r}{2}} \Gamma}{-\frac{2\varepsilon_j}{R_N}} = \frac{R_N \sqrt{\mu \varepsilon_r} \Gamma}{2\sqrt{2}\varepsilon_j} \approx \frac{R_N \mu \varepsilon_r}{2k_r \varepsilon_j} \Gamma \ll 1, \quad (5.116)$$

i.e. the slope of a root corresponding to a resonance state is much more stable than other eigenvalues.

Scaling procedure used in the 4-body system

The scaling procedure that we use for the 4-body system is a scaling of the Hamiltonian. This is done by scaling the Jacobi coordinates between the fragments by a parameter γ

$$\tilde{R} = \gamma \cdot R. \quad (5.117)$$

The kinetic energy operator is a homogeneous function of order -2 so scaling the coordinate results in a scaling of the operator as

$$-2\hat{T}(\tilde{R}) = \frac{d^2}{d\tilde{R}^2} - \frac{l(l+1)}{\tilde{R}^2} = \left\{ \frac{dR}{d\tilde{R}} = \frac{1}{\gamma} \right\} = \frac{1}{\gamma^2} \frac{d^2}{dR^2} - \frac{l(l+1)}{\gamma^2 R^2} = -2 \frac{1}{\gamma^2} \hat{T}(R), \quad (5.118)$$

and the Coulomb potential energy operator is a homogeneous function of order -1 , so scaling the coordinate results in scaling the operator as

$$-\hat{V}(\tilde{R}) = \frac{1}{\tilde{R}} = \frac{1}{\gamma R} = -\frac{1}{\gamma} \hat{V}(R). \quad (5.119)$$

The total Hamiltonian given by (3.3), is a sum of such kinetic and potential energy terms given above, so we have

$$\hat{V}(\gamma\mathbf{r}, \gamma\rho, \gamma\mathbf{R}) = \frac{1}{\gamma} \hat{V}(\mathbf{r}, \rho, \mathbf{R}), \quad (5.120)$$

$$\hat{T}(\gamma\mathbf{r}, \gamma\rho, \gamma\mathbf{R}) = \frac{1}{\gamma^2} \hat{T}(\mathbf{r}, \rho, \mathbf{R}), \quad (5.121)$$

which means that by scaling the kinetic and potential energy matrices, we scale *all* the coordinates simultaneously.

For each 2-body fragment, the size of the box R_γ changes with γ as

$$R_\gamma = \gamma \cdot R_1, \quad (5.122)$$

where R_1 is the size of the box for $\gamma = 1$, not to be confused with the size of the box R_N with $N = 1$ in (5.105) in the previous section where method (a) was used. By using the chain rule we get the relation

$$\frac{\partial \varepsilon}{\partial R_\gamma} = \frac{\partial \gamma}{\partial R_\gamma} \frac{\partial \varepsilon}{\partial \gamma} = \frac{1}{R_1} \frac{\partial \varepsilon}{\partial \gamma}, \quad (5.123)$$

and use it in (5.112) to get

$$\frac{\partial \varepsilon_j^\gamma}{\partial R_\gamma} \approx -\frac{2\varepsilon_j^\gamma}{R_\gamma} \Leftrightarrow \frac{1}{R_1} \frac{\partial \varepsilon_j^\gamma}{\partial \gamma} \approx -\frac{1}{R_1} \frac{2\varepsilon_j^\gamma}{\gamma} \Leftrightarrow \frac{\partial \varepsilon_j^\gamma}{\partial \gamma} \approx -\frac{2\varepsilon_j^\gamma}{\gamma}, \quad (5.124)$$

i.e. the slope of a root corresponding to non-resonant states. The slope of roots corresponding to resonance states in (5.115) becomes

$$\frac{\partial \varepsilon_i^\gamma}{\partial R_\gamma} \approx -\frac{k_r \Gamma}{2} \Leftrightarrow \frac{\partial \varepsilon_i^\gamma}{\partial \gamma} \approx -\frac{R_\gamma k_r \Gamma}{2\gamma} = -\frac{R_1 k_r \Gamma}{2}. \quad (5.125)$$

References

- [1] J. Munro. *Pioneers of Electricity*. William Clowes and sons, Limited, London, Stanford street and caring cross., 1890.
- [2] S. Eibenberger et al. Matter-wave interference with particles selected from a molecular library with masses exceeding 10000 amu. *Physical Chemistry Chemical Physics*, 15:14696, 2013.
- [3] T. Young. The bakerian lecture: On the theory of light and colours. *Phil. Trans. R. Soc. Lond.*, 92:12–48, 1802.
- [4] C. Huygens. *Traité de la lumiere (Treatise of the Light)*. Pieter van der Aa, Leiden, Netherlands, 1690.
- [5] I. Newton. *Qu. 22 in Opticks, 4th edition (A Treatise of the Reflexions, Refractions, Inflections and Colours of Light)*. Printed for William Innys at the West End of St. Paul's, London, Printer to the Royal Society, at the Prince's Arms in St. Paul's Church-yard., 1730.
- [6] J. C. Maxwell. A dynamical theory of the electromagnetic field. *Phil. Trans. R. Soc. Lond.*, 155:459–512, 1865.
- [7] George F. Fitzgerald. The ether and the earth's atmosphere. *Science*, 13:390, 1889.
- [8] M. Faraday. Experimental researches in electricity -thirteenth series. *Phil. Trans. R. Soc. Lond.*, 128:125–168, 1838.
- [9] E. Becquerel. Mémoire sur les effets électriques produits sous l'influence des rayons solaires. *Comptes Rendus*, 9:561–567, 1839.
- [10] H. Hertz. On an effect of ultra-violet light upon the electrical discharge. *Annalen der Physik*, 267:8, 1887.
- [11] L. Boltzmann. Weitere studien über das wärmeleichgewicht unter gasmolekülen. *Wiener Berichte, in WA I, paper 23*, 66:275–370, 1872.
- [12] T. Young. The bakerian lecture: On the theory of light and colours. *Phil. Trans. R. Soc. Lond.*, 92:12–48, 1802.
- [13] M. Planc. The ether and the earth's atmosphere. *Science*, 13:390, 1889.
- [14] A. Einstein. On a heuristic viewpoint concerning the production and transformation of light. *Annalen der Physik*, 17:132–148, 1905.
- [15] A. Einstein. On the electrodynamics of moving bodies. *Annalen der Physik*, 17:891–921, 1905.
- [16] H. Fletcher. *Physics Today*, 35:6–43, 1982.
- [17] R.A. Millikan. A new modification of the cloud method of determining the elementary electrical charge and the most probable value of that charge. *Phys. Mag. XIX*, 6:209, 1910.
- [18] R.A. Millikan. On the elementary electric charge and the avogadro constant. *Physical Review II*, 2:109–143, 1913.
- [19] E. Rutherford. The scattering of α and β particles by matter and the structure of the atom. *Philosophical Magazine, Series 6*, 21, 1911.

- [20] J.J. Thomson. On the structure of the atom: an investigation of the stability and periods of oscillation of a number of corpuscles arranged at equal intervals around the circumference of a circle; with application of the results to the theory of atomic structure. *Philosophical Magazine, Series 6*, 39:237–265, 1904.
- [21] N. Bohr. On the constitution of atoms and molecules. *Physikalische Zeitschrift*, 10-9:323–324, 1913.
- [22] D. Hilbert. *Nac. Ges. Wiss. Goettingen*, 395, 1901.
- [23] A. Einstein. Covariance properties of the field equations of the theory of gravitation based on the generalized theory of relativity. *Zeitschrift für Mathematik und Physik*, 63:215–225, 1914.
- [24] A. Einstein. Fundamental ideas of the general theory of relativity and the application of this theory in astronomy. *Preussische Akademie der Wissenschaften, Sitzungsberichte*, 1:315, 1915.
- [25] A. Einstein. On the general theory of relativity. *Preussische Akademie der Wissenschaften, Sitzungsberichte*, 2:778–786, 1915.
- [26] A. Einstein. Explanation of the perihelion motion of mercury from the general theory of relativity. *Preussische Akademie der Wissenschaften, Sitzungsberichte*, 3:831–839, 1915.
- [27] A. Einstein. The field equations of gravitation. *Preussische Akademie der Wissenschaften, Sitzungsberichte*, 4:844–847, 1915.
- [28] A. Eddington, F. W. Dyson, and C. Davidson. A determination of the deflection of light by the sun's gravitational field, from observations made at the total eclipse of 29 may 1919. *Phil. Tran. R. Soc.*, 220A:291–333, 1920.
- [29] L. de Broglie. A tentative theory of light quanta. *Phil. Mag.*, 47:446, 1924.
- [30] H. A. Kramers and W. Heisenberg. Über die streuung von strahlung durch atome. *Zeitschrift für Physik*, 31:681–708, 1925.
- [31] Ian J.R. Aitchison, David A. MacManus, and Thomas K. Snyder. *American Journal of Physics*, 72:1370, 2006.
- [32] W. Heisenberg. Über quantentheoretische umdeutung kinematischer und mechanischer beziehungen. *Zeitschrift für Physik*, 33:879–893, 1925.
- [33] M. Born. Zur quantenmechanik. *Zeitschrift für Physik*, 34:858–888, 1925.
- [34] P. A. M. Dirac. The fundamental equations of quantum mechanics. *Proc. R. Soc. London*, 109:642–653, 1926.
- [35] P. A. M. Dirac. Quantum mechanics and a preliminary investigation of the hydrogen atom. *Proc. R. Soc. London*, 110:561–579, 1926.
- [36] M. Born, P. Jordan, and W. Heisenberg. Zur quantenmechanik ii. *Zeitschrift für Physik*, 35:8–9, 1925.
- [37] E. Schrödinger. über das verhältnis der heisenberg-born-jordanschen quantenmechanik zu der meinen. *Annalen der Physik*, 4, 79:734–756, 1926.
- [38] E. Schrödinger. Quantisierung als eigenwertproblem (dritte mitteilung: Störungstheorie, mit anwendung auf den starkeffekt der balmerlinien). *Annalen der Physik*, 4, 80:437–490, 1926.
- [39] E. Schrödinger. Quantisierung als eigenwertproblem (vierte mitteilung). *Annalen der Physik*, 4, 81:109–139, 1926.
- [40] E. Schrödinger. Der stetige Übergang von der mikro- zur makromechanik. *Die Naturwissenschaften*, 14:664–666, 1926.

- [41] E. Schrödinger. An undulatory theory of the mechanics of atoms and molecules. *Physical Review*, 28:1049–1070, 1926.
- [42] C. S Stoner. The distribution of electrons among atomic levels. *Phil. Mag., Series 6*, 48:719–736, 1924.
- [43] W. Pauli. Über den zusammenhang des abschlusses der elektronengruppen im atom mit der komplexstruktur der spektren. *Zeitschrift für Physik*, 31(1):765–783, Feb 1925.
- [44] F. A. Muller. The equivalence myth of quantum mechanics-part i. *Stud. Hist. Phil. Mod. Phys.*, 28, No. 1:35–61, 1907.
- [45] E. Schrödinger. The present situation in quantum mechanics. *Naturwissenschaften*, 23:807–812, 1935.
- [46] M. Born and N. Wiener. A new formulation of the laws of quantization of periodic and aperiodic phenomena. *Journal of Mathematics and Physics (M.I.T.)*, 5:84–98, 1926.
- [47] H. Kragh. *Genesis of Dirac's Relativistic Theory chapter in Science and Society, Quantum Histories*. Routledge, Taylor & Francis Group, 711 Third Avenue, New York, NY 10017, 2001.
- [48] P. A. M. Dirac. On the theory of quantum mechanics. *Proc. Roy. Soc. London*, A112:661–677, 1926.
- [49] P. A. M. Dirac. The elimination of the nodes in quantum mechanics. *Proc. Roy. Soc. London*, A111:281–305, 1926.
- [50] P. A. M. Dirac. The quantum theory of the emission and absorption of radiation. *Proc. Roy. Soc. London*, A114:243–265, 1927.
- [51] P. A. M. Dirac. The quantum theory of dispersion. *Proc. Roy. Soc. London*, A114:710–728, 1927.
- [52] P. A. M. Dirac. The quantum theory of the electron, i. *Proc. Roy. Soc. London*, A117:610–624, 1928.
- [53] P. A. M. Dirac. The quantum theory of the electron, ii. *Proc. Roy. Soc. London*, A118:351–361, 1928.
- [54] G. Farmelo. *The Strangest Man: the Hidden Life of Paul Dirac, Mystic of the Atom*. Faber and Faber, 2009.
- [55] C. D. Anderson. The positive electron. *Phys. Rev*, 43:491, 1933.
- [56] O. Chamberlain, E. Segré, C. Wiegand, and T. Ypsilantis. Observation of antiprotons. *Phys. Rev*, 100:947–950, 1955.
- [57] B. Cork, G. R. Lambertson, O. Piccioni, and W. A. Wenzel. Antineutrons produced from antiprotons in charge-exchange collisions. *Phys. Rev*, 104:1193–1197, 1956.
- [58] J. Chadwick. Possible existence of a neutron. *Nature*, 129:3252, 1932.
- [59] ATLAS Collaboration et al. Observation of a new particle in the search for the standard model higgs boson with the atlas detector at the lhc. *Phys. Lett. B*, 716:1–29, 2012.
- [60] R. P. Feynman. Space-time approach to quantum electrodynamics. *Phys. Rev.*, 76:769, 1949.
- [61] J. H. Christenson, J. W. Cronin, V. L. Fitch, and R. Turlay. Evidence for the 2-pion decay of the k meson. *Phys. Rev. Lett.*, 13:138–140, 2012.
- [62] T. Massam, Th. Muller, B. Righini, M. Schneegans, and A. Zichichi. Experimental observation of antideuteron production. *Il Nuovo Cimento A*,

- 63(1):10–14, Sep 1965.
- [63] D. E. Dorfan, J. Eades, L. M. Lederman, W. Lee, and C. C. Ting. Observation of antideuterons. *Phys. Rev. Lett.*, 14:1003–1006, Jun 1965.
- [64] S. Ulmer et al. Optical transition seen in antihydrogen. *Nature*, 541:467, 2017.
- [65] M. Ahmadi et al. Observation of the 1s–2s transition in trapped antihydrogen. *Nature*, 541:506, 2017.
- [66] C. Smorra et al. A parts-per-billion measurement of the antiproton magnetic moment. *Nature*, 550:371, 2017.
- [67] M.R.J. Williams. Evidence for an anomalous like-sign dimuon charge asymmetry. *Nuclear Physics B - Proceedings Supplements*, 210:141 – 146, 2011. Proceedings of the 9th International Conference on Beauty, Charm and Hyperons in Hadronic Interactions.
- [68] David Bohm. A suggested interpretation of the quantum theory in terms of "hidden" variables. i. *Phys. Rev.*, 85:166–179, Jan 1952.
- [69] Jonathan G. Richens, John H. Selby, and Sabri W. Al-Safi. Entanglement is necessary for emergent classicality in all physical theories. *Phys. Rev. Lett.*, 119:080503, Aug 2017.
- [70] J. J. Sakurai. *Modern Quantum Mechanics*. Addison-Wesley Publishing Company, University of Hawaii, Manoa, 1994.
- [71] Lucjan Piela. *Ideas of quantum chemistry, first edition*. Elsevier, Amsterdam, The Netherlands, 2007.
- [72] E. Hiyama, Y. Kino, and M. Kamimura. *Prog. Part. Nucl. Phys.*, 51:233, 2003.
- [73] Yolav Peleg, Reuven Pnini, Elyahu Zaarur, and Eugene Hecht. *Schaum's Outline of Quantum Mechanics, second edition*. The McGraw-Hill Companies, United States of America, 2010.
- [74] Zlatko Bacic and Jack. Simons. *J. Chem. Phys.*, 86:1192–1200, 1982.
- [75] Jack. Simons. *J. Chem. Phys.*, 75:2465–2467, 1981.
- [76] S. Aoyama, T. Myo, and K. Ikeda. *Prog. Theoretical Phys.*, 116, 2006.
- [77] William. P Reinhardt. *Ann. Rev. Phys. Chem.*, 33:223–255, 1982.
- [78] Rongqing Chen and Hua Guo. *The Chebyshev Propagator for Quantum Systems*. University of New Mexico, Albuquerque, New Mexico, 87131, USA, 1998.
- [79] B. Gerald Folland. *Fourier analysis and its applications*. Brooks/Cole Publishing Company, a division of International Thomson Publishing Inc., Pacific Grove, California 93950, 1992.
- [80] Chr. Møller and M. S. Plesset. Note on an approximation treatment for many-electron systems. *Phys. Rev.*, 46:618–622, Oct 1934.
- [81] Trygve Helgaker, Poul Jørgensen, and Jeppe Olsen. *Molecular Electronic-Structure Theory*. John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England, 2004.
- [82] K. Andersson et al. *J. Comp. Chem.*, 31:224, 2014.
- [83] Peter Pulay. A perspective on the caspt2 method. *International Journal of Quantum Chemistry*, 111(13):3273–3279, 2011.
- [84] Daniel Roca-Sanjuán, Francesco Aquilante, and Roland Lindh. Multiconfiguration second-order perturbation theory approach to strong electron correlation in chemistry and photochemistry. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2(4):585–603, 2012.

- [85] O. B. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, and P.-O. Widmark. *Multiconfigurational Quantum Chemistry*. Wiley, Lund, 2016.
- [86] A. Y. Voronin and J. Carbonell. *Hyperfine Interactions*, 115:146–158, 1998.
- [87] A. Y. Voronin and J. Carbonell. *Nucl. Instrum. Methods Phys. Res. Sect B*, 214:139, 2004.
- [88] P. K. Sinha and A. S. Ghosh. *Europhys. Lett.*, 49:558–563, 2000.
- [89] P. Froelich, S. Jonsell, A. Saenz, S. Eriksson, B. Zygelman, and A. Dalgarno. *Phys. Rev. A*, 70:022509, 2004.
- [90] S. Jonsell, A. Saenz, P. Froelich, B. Zygelman, and A. Dalgarno. *Phys. Rev. A*, 64:052712, 2001.
- [91] P. Froelich, S. Jonsell, A. Saenz, B. Zygelman, and A. Dalgarno. *Phys. Rev. Lett.*, 84:4577, 2000.
- [92] J. Mitroy and V. D. Ovsiannikov. *Chem. Phys. Lett.*, 412:76, 2005.
- [93] K. Strasburger. *J. Phys. B: At. Mol. Opt. Phys.*, 35:L435, 2002.
- [94] Svante Jonsell, Alejandro Saenz, Piotr Froelich, Bernard Zygelman, and Alexander Dalgarno. Stability of hydrogen-antihydrogen mixtures at low energies. *Phys. Rev. A*, 64:052712, Oct 2001.
- [95] Krzysztof Strasburger. Hydrogen–antihydrogen interaction: spectacular breakdown of the adiabatic approximation. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 37(22):4483, 2004.
- [96] Harald Friedrich and Patrick Raab. Near-threshold quantization and scattering lengths. *Phys. Rev. A*, 77:012703, Jan 2008.
- [97] H. Tal Ezer and R. Kosloff. *J. Chem. Phys.*, 81:3967–3971, 1984.
- [98] Anna Nissen, Hans O. Karlsson, and Gunilla Kreiss. *J. Chem. Phys.*, 133:054306, 2010.
- [99] Claude Cohen-Tannoudji, Bernard Diu, and Frank Laloe. *Quantum Mechanics, Volume I*. Wiley-Interscience, volume 1 edition, 1977.
- [100] A. Hazi, U and S. Taylor, Howard. *Phys. Rev. A*, 1:1109–1119, 1970.

Acta Universitatis Upsaliensis

*Digital Comprehensive Summaries of Uppsala Dissertations
from the Faculty of Science and Technology 1674*

Editor: The Dean of the Faculty of Science and Technology

A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)

Distribution: publications.uu.se
urn:nbn:se:uu:diva-348667



ACTA
UNIVERSITATIS
UPSALIENSIS
UPPSALA
2018