Non-relativistic three-body systems
and finite mass effects

Diplomarbeit

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Contents

1 Introduction ................................................................. 8

2 Three-body problem in non-relativistic quantum mechanics ...... 10
   2.1 Hamiltonian ......................................................... 10
   2.2 Combined spherical and cylindrical coordinate system .......... 13
   2.3 Transformation of the three-body Hamiltonian .................. 16
   2.4 Perimetric coordinates ........................................... 18

3 Wave function symmetries .............................................. 22
   3.1 Angular momentum ................................................ 22
   3.2 Wigner D-matrix .................................................... 25
   3.3 Parity .................................................................. 29
   3.4 Spin .................................................................... 31

4 Wave functions and matrix elements of the Hamiltonian .......... 32
   4.1 Wave function ansatz .............................................. 32
   4.2 S-states .............................................................. 33
   4.3 P-states .............................................................. 35
       4.3.1 Even wave functions ........................................ 35
       4.3.2 Odd wave functions ......................................... 37

5 Lagrange-mesh method ..................................................... 42
   5.1 Principle of Lagrange-mesh method ................................ 42
   5.2 Lagrange-Laguerre basis set ....................................... 43
   5.3 Wave functions and matrix elements in Lagrange-Laguerre basis set .................. 50
       5.3.1 Matrix elements for the S-states ......................... 56
       5.3.2 Matrix elements for the P-states and even parity .... 59
       5.3.3 Matrix elements for the P-states and odd parity .... 62
   5.4 Expectation values ............................................... 68
   5.5 Transition dipole matrix elements ................................ 70
   5.6 Matrix mapping of the eigenvalue equation ..................... 72

6 Variational calculation .................................................... 77
   6.1 Energy levels and accuracy of the method ....................... 77
       6.1.1 Convergence .................................................... 79
       6.1.2 Energy eigenvalues of He, dτμ, H₂⁺, and HD⁺ ............. 80
   6.2 Three-body wave functions ....................................... 90
   6.3 Expectation values for the Helium atom ......................... 93
   6.4 Transition-dipole moments ....................................... 97

7 Summary and outlook ..................................................... 102
# A Appendix

A.1 Transformation of coordinates .................................................. 103
A.2 Matrix elements of Hamiltonian .................................................. 104
   A.2.1 S-states ........................................................................ 104
   A.2.2 Even P-states ................................................................ 106
   A.2.3 Odd P-states ................................................................... 108
A.3 Matrix elements for three non-identical particles ............................. 110
List of Figures

2.2.1 The vectors $\vec{R}$ and $\vec{r}$ are represented in the usual Cartesian coordinates, i.e. $R_x$, $R_y$, $R_z$ for $\vec{R}$ and $r_x$, $r_y$, $r_z$ for $\vec{r}$. ..................................................... 14

2.2.2 The vectors $\vec{R}$ and $\vec{r}$ are described in angular coordinates, $\phi, \theta, \psi$, the two radii $R, r$ and the value $\zeta$. ..................................................... 14

5.2.1 Lagrange-Laguerre functions $\tilde{f}_i(u)$ for $N = 4$. The graph of the function $\tilde{f}_1(u)$ is red, of $\tilde{f}_2(u)$ is green, of $\tilde{f}_3(u)$ is orange, of $\tilde{f}_4(u)$ is blue. ......................... 46

5.2.2 Gridpoints for $N = 4$ ..................................................... 47

5.2.3 Gridpoints for $N = 8$ ..................................................... 47

5.2.4 Gridpoints for $N = 15$ .................................................. 48

5.2.5 Lagrange-Laguerre functions $f_i(u)$ for $N = 4$ and scale factor $h = 2$. The graph of the function $f_1(u)$ is red, of $f_2(u)$ is green, of $f_3(u)$ is orange, of $f_4(u)$ is blue. ......................... 49

5.6.2 Non-zero matrix elements of $M^u$ for two identical fermionic particles in the S singlet state with $N(M^u) = 40$ (left figure), with $N(M^u) = 126$ (center figure), and with $N(M^u) = 288$ (right figure). ..................................................... 73

5.6.3 Non-zero matrix elements of $M^t$ for two identical fermionic particles in the S triplet state with $N(M^t) = 24$ (left figure), with $N(M^t) = 90$ (center figure), and $N(M^t) = 224$ (right figure). ..................................................... 73

6.1.1 Convergence of the lowest ten bound singlet S-state energy values of Helium for different numbers $N$ of basis functions ..................................................... 80

6.1.2 Convergence of the lowest ten bound singlet S-state energy values of $H^+_2$ for different numbers $N$ of basis functions ..................................................... 81

6.1.3 Energy spectrum for $1 S^{1/2}$ for negative energy levels ..................................................... 81

6.1.4 Energy spectrum for $1 S^{1/2}$ between ground state energy and $-13.6$ eV ..................................................... 81

6.1.5 Energy level scheme of Helium with $h_{xy} = h_z = 3.5$ for bound states drawn in blue lines. The red lines mark the two-body levels with reduced mass $\mu_{12}$ of He$^+$ and $Z_1 = 2, Z_2 = -1$. 86

6.1.6 Energy level scheme of $dt\mu$ with $h_x = h_y = h_z = 3.0$ for bound states drawn in blue lines. The red lines mark the two-body levels with reduced mass $\mu_{12}$ of $t\mu^+$ and green line mark the two-body levels with reduced mass $d\mu^+$ and $Z_1 = 1, Z_2 = -1$. ..................... 86

6.1.7 Energy level scheme of $H^+_2$ for bound states drawn with blue lines. The scale factors are given by $h_{xy} = 1.28$ and $h_z = 11.2$. The red lines mark the two-body levels with reduced mass $\mu_{12}$ of Hydrogen and $Z_1 = 1, Z_2 = -1$. ..................... 86

6.1.8 Energy level scheme of $H^+_2$ for bound states drawn with blue lines. The scale factors are $h_x = h_y = 1.28$ and $h_z = 11.2$. The red lines mark the two-body levels with reduced mass $\mu_{12}$ for Hydrogen and Deuterium. ..................... 86

6.2.1 Isosurface for the square of the absolute value of the wave function for Helium without electron-electron interaction in the $1^1S$ state. The value for the isosurface is $10^{-3}$. ........ 90
6.2.2 Isosurface for the probability density of Helium without electron-electron interaction in the $1^1S$ state. The isosurface value is 0.025. .................................................. 91

6.2.3 Isosurface for the square of the absolute value of the wave function for Helium with full electron-electron interaction in the $1^1S$ state. The value for the isosurface is $10^{-3}$. .... 91

6.2.4 Isosurface for the probability density for Helium with full electron-electron interaction in the $1^1S$ state. The isosurface value is 0.025. .................................................. 91

6.2.5 Isosurface for the square of the absolute value of the wave function for H$^+$ in the $1^1S$ state.
The value for the isosurface is $5 \times 10^{-3}$. .................................................. 92

6.2.6 Isosurface for the probability density of H$^+$ in the $1^1S$ state. The value for the isosurface is 0.0012. .................................................. 92

6.3.1 Expectation values of the inter-particle distances for the Helium atom in singlet S-states.
The scale factors are given by $h_{xy} = h_z = 3.5$. The number of Lagrange-Laguerre basis functions are $N_{xy} = N_z = 40$, which leads to a total number of $N(M) = 32 800$. .... 95

6.3.2 Expectation values of the inter-particle distances for the Helium atom in triplet S-states.
The scale factors are given by $h_{xy} = h_z = 3.5$. The number of Lagrange-Laguerre basis functions are $N_{xy} = N_z = 40$, which leads to a total number of $N(M) = 31 200$. .... 95

6.3.3 Expectation values of the inter-particle distances for the Helium atom in singlet even P-states. The scale factors are given by $h_{xy} = h_z = 3.5$. The number of Lagrange-Laguerre basis functions are $N_{xy} = N_z = 40$ which leads to a total number of $N(M) = 31 200$. ........ 96

6.3.4 Expectation values of the inter-particle distances for the Helium atom in triplet even P-states. The scale factors are given by $h_{xy} = h_z = 3.5$. The number of Lagrange-Laguerre basis functions are $N_{xy} = N_z = 40$ which leads to a total number of $N(M) = 32 800$. ........ 97

6.4.1 The function $G(E)$ of H$^+$ for different mass ratios between the ions and the electron around the first excited ionization energy of Hydrogen. .................................................. 101
# List of Tables

5.1 Roots $u_i$ of Lagrange functions .............................................................. 47

6.1 Binding energies for the lowest singlet and triplet S-states of the Helium atom in atomic units using $N(M)$ Lagrange-Laguerre functions. $N_{xy}$ and $N_z$ give the number of Lagrange functions for each perimetric coordinate. The scale factors of the Lagrange-Laguerre functions are $h_{xy}$ and $h_z$. For the energy values of the column with $m_3=\text{He}$, we use $m_3 = 7.294.261\,824\,1\,m_e$. The reference values are labeled as (a) [HB01] and (b) [Dra96]. 82

6.2 Binding energies for Helium singlet and triplet P-states with even parity in atomic units. $N_{xy}$ and $N_z$ give the number of Lagrange functions for each perimetric coordinate and $N(M)$ denotes the total number of Lagrange-Laguerre basis functions. The scale factors are denoted by $h_{xy}$ and $h_z$. The masses $m_1$ and $m_2$ for the protons are given by $m_{\text{proton}} = 1\,836.142\,701\,m_e$. The reference values are labeled as (a) [HB01], (c) [GWLH91], and (d) [Bha70]. 83

6.3 Binding energies for Helium P-singlet and P-triplet states with odd parity in atomic units. $N_{xy}$ and $N_z$ give the number of Lagrange functions for each perimetric coordinate and $N(M)$ denotes the total number of Lagrange-Laguerre basis functions. The scale factors are $h_{xy}$ and $h_z$. The masses $m_1$ and $m_2$ for the protons is given by $m_{\text{proton}} = 1\,836.142\,701\,m_e$. The reference values are labeled as (a) [HB01] and (b) [Dra96]. 84

6.4 Binding energies of $d\mu$ with total number $N(M)$ of Lagrange-Laguerre functions and scale factors $h_x$, $h_y$, and $h_z$. $N_x$, $N_y$, and $N_z$ are the numbers of Lagrange-Laguerre functions for each perimetric coordinate. The reference values are labeled as (a) for Hesse and Baye [HB01] and (d) for Alexander and Monkhorst [AM88]. 85

6.5 Binding energies of $H_2^+$ with total number of Lagrange-Laguerre functions $N(M)$ and scale factors $h_{xy}$ and $h_z$. $N_{xy}$ and $N_z$ denote the number of Lagrange-Laguerre function for each perimetric coordinate. The reference values are labeled as (a) for Hesse and Baye [HB01] and (e) for Moss [Mos99]. 87

6.6 Binding energies of $HD^+$ with total number of Lagrange-Laguerre functions $N(M)$ and scale factors $h_x$, $h_y$ and $h_z$. $N_x$, $N_y$ and $N_z$ denote the number of Lagrange-Laguerre function for each perimetric coordinate. The reference values are labeled as (f) for Bubin [BPT+12]. 88

6.7 Ionization energy thresholds $E^{(n)}_{\text{ion}}$ in atomic units for $He^+$, $d\mu^+$, $t\mu^+$, Hydrogen and deuteron for the ion ground-states ($n=1$), and the four ($n = 2-4$) low lying excited states of the electron or muon. $Z_1$ denotes the charge number of the positive particle, $Z_2$ denotes the charge number of the negative particle, and $\mu_{12}$ represents the reduced mass of both particles. 88

6.8 Expectation values of inter-particle distances for S-states, even P-states. The scale factors $h_{xy}$, $h_z$, and the numbers $N_{xy}$, $N_z$, and $N_M$ are equivalent to the corresponding states in the tables (6.1), (6.2), and (6.3). 93

6.9 Expectation values of the lowest two S-states and even P-states. The scale factors $h_{xy}$ and $h_y$ are equivalent to the corresponding states in table (6.1), (6.2), and (6.3). 94
Chapter 1

Introduction

A many-body problem in general describes a large amount of interacting particles. The underlying Hamiltonian, which determines the system becomes more complex for a larger number of particles $N$. The only atomic or molecule system with more than one particle that can be solved analytically is the two-body problem. All systems with a larger particle number $N$ than two are not fully solvable by an analytical expression anymore.

However, it is possible to find approximations with a high accuracy for small particle number, e.g. $N = 3$. In the case of a three-body problem, Hylleraas introduced in 1929 functions $[\text{Hyl29}]$ which allow for an accurate description of the ground-state energy and the corresponding wave function of the Helium atom without relativistic effects and external interactions. Such accurate results compare favorably with spectroscopic results from experiment. To find an expansion of the exact non-relativistic wave function with similar accuracy for larger but still manageable particle systems is more sophisticated and impossible for a very large number of particles $N$. Nevertheless, if the system consists of heavy and lighter particles with a relatively high order ratio between the two different masses, it is in common, e.g. for calculations of the electronic structure of condensed matter, to use the Born-Oppenheimer approximation $[\text{Bor27}]$ to decouple the motion of the lighter particles from the motion of the heavier ones. The energies obtained by the Born-Oppenheimer approximation approach often the results of experiments, but in some cases the Born-Oppenheimer approximation fails. In order to identify discrepancies between the results of the Born-Oppenheimer approximation and the exact behavior, a highly accurate consideration of the exact physical problem is required.

In the present work, we introduce the Lagrange-Laguerre method and Lagrange-Laguerre functions to express the exact non-relativistic wave functions of the three-body problem which reach almost the accuracy of the Hylleraas expansion for the Helium atom. The Lagrange-Laguerre method uses the properties of the Lagrange polynomial interpolation to expand the wave function. In this approach, the scalar products of the exact wave functions are approximated by the Gauss quadrature formula. Very accurate approximations to the exact eigenvalues can be obtained by the variational principle. Without any external forces, the Coulomb potential describes the interaction of the three particles which means that the potential terms contains a singularity if the inter-particle distances approach zero. The Gauss quadrature requires function values of certain sampling points which includes mesh points near the Coulomb singularities. Since it is difficult to approximate singularities by polynomial interpolation we can improve the accuracy of the integral approximation if we transform the inter-particle distances into perimetric coordinates $[\text{Pek58}]$.

We show exemplarily the results of energies and expectation values obtained by the Lagrange-Laguerre method for the Helium atom, the $\text{d}t\mu$, the $\text{H}_2^+$ and $\text{HD}^+$ molecules. Additionally, we compare the exact non-relativistic results for the real mass value of the heavier particles with the results of an infinite-mass approximation of the heavier particles. Considering a three-body problem where one or two particles are much heavier than the remaining ones, the infinite-mass approximation is almost equivalent to the Born-Oppenheimer approximation. We compare the energies and expectation values of the Helium atom for the exact non-relativistic and the infinite-mass approximation. For low-lying states, the relative differences
between the exact non-relativistic energy eigenvalues and the finite-mass limit are in the region of a low per mille value. The situation is different if we consider instead of energies the optical absorption spectrum of the system. In this case the difference between the infinite-mass results and the exact solution with physical mass becomes sizeable in the areas close to the ionization thresholds, when one particle is ionized and the remaining two particles compose a two-body system. We demonstrate this effect by investigating the dipole transition matrix elements around the ionization threshold energy.

The thesis is organized as follows. We start with the non-relativistic Hamiltonian of the three-body system without spin-orbit interaction, separate the center of mass motion, and transform the center of mass three-body Hamiltonian into the three Euler angles and perimetric coordinates. We introduce the Wigner-D-matrices to obtain the angular eigenfunctions of three-body the wave functions. Depending on the parity, and spin, we construct a general wave function ansatz for the three-body problem and consider the matrix elements of the Hamiltonian for S-states and P-states in a Lagrange-Laguerre basis set. We employ the variational principle to obtain the eigenvalues and wave functions. After investigating the convergence behavior of the method, we calculate the energy eigenvalues of the Helium atom, the $\text{d}t\mu$, the $\text{H}_2^+$, and the $\text{HD}^+$ molecules. We perform a dense matrix diagonalization for the eigenproblem and this gives us the opportunity to plot the full energy level schemes of the four considered systems. Additionally, we plot the ground-state wave function of the Helium and the $\text{H}_2^+$ molecule. In the last part of the thesis we consider the expectation values of the inter-particle distances and the kinetic energies and we consider the mass dependency of the dipole matrix elements for transitions from the ground state to all dipole-allowed excited states in the spectrum.
Chapter 2

Three-body problem in non-relativistic quantum mechanics

2.1 Hamiltonian

In this section, we start with the Hamiltonian describing a three-body system in nine Cartesian coordinates. The Hamiltonian can be separated into one contribution for the center of mass of the system and one contribution for the internal motion of the three-body system in the center of mass frame. Due to the center of mass condition the configuration of the system in the center of mass frame is reduced to six Cartesian coordinates which describe two position vectors in the three-dimensional space of this frame. In the following, we define two linear independent vectors \( \vec{R} \) and \( \vec{r} \) and give an expression for the center of mass Hamiltonian with respect to these vectors. If the spin-orbit interaction and other relativistic effects can be neglected, the Hamiltonian of the three-body problem in terms of the particle position vectors \( \vec{r}_j \) in an arbitrary frame of reference is written as

\[
\hat{H} = -\frac{\hbar^2}{2m_1} \nabla^2 \vec{r}_1 - \frac{\hbar^2}{2m_2} \nabla^2 \vec{r}_2 - \frac{\hbar^2}{2m_3} \nabla^2 \vec{r}_3 + \hat{V}(\vec{r}_1, \vec{r}_2, \vec{r}_3),
\]

(2.1.1)

where \( m_j \) denotes the mass of particle \( j \), \( \hbar \) denotes the reduced Planck constant and \( \hat{V}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \) the potential. The interaction \( \hat{V}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \) between the particles is described by Coulomb forces. Assuming there is no external potential acting on the particles, the interaction takes the form with the elementary charge \( e \)

\[
\hat{V}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{Z_1Z_2e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{Z_1Z_3e^2}{|\vec{r}_1 - \vec{r}_3|} + \frac{Z_2Z_3e^2}{|\vec{r}_2 - \vec{r}_3|}.
\]

(2.1.2)

For the physical significance, the charge numbers \( Z_j \) and masses \( m_j \) of the respective particle define the corresponding atom or molecule. Referring to a system of particles, the center of mass vector

\[
\vec{R}_c = \frac{m_1\vec{r}_1 + m_2\vec{r}_2 + m_3\vec{r}_3}{m_1 + m_2 + m_3}
\]

(2.1.3)

is distinguished since its motion is equal to a free moving particle with mass

\[
M = m_1 + m_2 + m_3,
\]

(2.1.4)

if no external potential is acting on the system. In the next step we introduce coordinates \( \vec{r}_{cj} \) in the center of mass frame according to

\[
\vec{r}_j = \vec{R}_c + \vec{r}_{cj} \quad \text{with} \; j = \{1, 2, 3\}.
\]

(2.1.5)
The Coulomb interaction between the three particles is invariant under the previous substitution. Consequently the Hamiltonian can be separated into a kinetic operator term for the center of mass motion and into a three-body Hamiltonian in a new reference frame, i.e. the center of mass frame,

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla^2 \vec{R}_c + \hat{H}_c. \quad (2.1.6)$$

Since the Hamiltonian $\hat{H}_c$ does not depend on the center of mass coordinates $\vec{R}_c$, the total wave function $\Psi_{\text{tot}}$ in the arbitrary chosen frame of reference is a product of two functions,

$$\Psi_{\text{tot}}(\vec{R}_c, \vec{r}_{c1}, \vec{r}_{c2}, \vec{r}_{c3}, s_1, s_2, s_3) = \Psi_{\vec{R}_c}(\vec{R}_c) \Psi_c(\vec{r}_{c1}, \vec{r}_{c2}, \vec{r}_{c3}, s_1, s_2, s_3), \quad (2.1.7)$$

where $s_j$ denotes the spin coordinate of particle $j$. The wave function $\Psi_{\vec{R}_c}(\vec{R}_c)$ can be chosen as a plane wave (like a free particle with mass $M$) or as a superposition of plane waves which form a wave-packet. The second wave function has to satisfy a Schrödinger equation with the center of mass three-body Hamiltonian, which has explicitly the form

$$\hat{H}_c = -\frac{\hbar^2}{2m_{c1}} \nabla^2 \vec{r}_{c1} - \frac{\hbar^2}{2m_{c2}} \nabla^2 \vec{r}_{c2} - \frac{\hbar^2}{2m_{c3}} \nabla^2 \vec{r}_{c3} + \hat{V}(\vec{r}_{c1}, \vec{r}_{c2}, \vec{r}_{c3}) \quad (2.1.8)$$

$$\hat{V}(\vec{r}_{c1}, \vec{r}_{c2}, \vec{r}_{c3}) = Z_1 Z_2 e^2 / |\vec{r}_{c1} - \vec{r}_{c2}| + Z_1 Z_3 e^2 / |\vec{r}_{c1} - \vec{r}_{c3}| + Z_2 Z_3 e^2 / |\vec{r}_{c2} - \vec{r}_{c3}| \quad (2.1.9)$$

in position space. In the initial frame the three vectors $\vec{r}_j$ and their associated momenta describe the Hamiltonian. Since all three vectors are independent the initial Hamiltonian defines a nine dimensional problem. In the center of mass frame the three vectors have to satisfy the center of mass relation

$$m_1 \vec{r}_{c1} + m_2 \vec{r}_{c2} + m_3 \vec{r}_{c3} = 0. \quad (2.1.10)$$

Therefore, one vector is determined by the others and the problem is reduced to six dimensions. The whole three-body system can be described by two independent vectors, which have a one-to-one correspondence to the position vectors of the particles. For the following considerations it is advantageous to chose one of the relative vectors e.g. $\vec{r}_{c1} - \vec{r}_{c2}$ and the arithmetic mean vector of the two remaining relative vectors $\vec{r}_{c1} - \vec{r}_{c3}$ and $\vec{r}_{c2} - \vec{r}_{c3}$ as independent

$$\vec{R} = \vec{r}_{c1} - \vec{r}_{c2}, \quad (2.1.11)$$

$$\vec{r} = \frac{1}{2}(2\vec{r}_{c3} - \vec{r}_{c1} - \vec{r}_{c2}). \quad (2.1.12)$$

This choice is equivalent to the one used in reference [HB01]. The distance vectors are then represented as

$$\vec{r}_{c2} - \vec{r}_{c1} = \vec{R}, \quad (2.1.13)$$

$$\vec{r}_{c1} - \vec{r}_{c3} = \vec{r} + \frac{\vec{R}}{2}, \quad (2.1.14)$$

$$\vec{r}_{c2} - \vec{r}_{c3} = \vec{r} - \frac{\vec{R}}{2}. \quad (2.1.15)$$

If the vectors $\vec{R}$ and $\vec{r}$ have their origin in the center of mass, then the representation of the different position vectors of the particles $\vec{r}_{c1}$ in the center of mass frame is given by
\[ \vec{r}_{c1} = \frac{m_2 + m_3}{M} \vec{R} + \frac{m_3}{M} \vec{r}, \quad (2.1.16) \]
\[ \vec{r}_{c2} = -\frac{m_1 + m_3}{M} \vec{R} + \frac{m_3}{M} \vec{r}, \quad (2.1.17) \]
\[ \vec{r}_{c3} = \frac{m_2 - m_1}{2M} \vec{R} - \frac{m_1 + m_2}{M} \vec{r}. \quad (2.1.18) \]

\( \vec{R} \) and \( \vec{r} \) span a six-dimensional space and thus the volume element \( dV \) of this space in Cartesian coordinates is

\[ dV = d\vec{R} d\vec{r} = dR_x dR_y dR_z dr_x dr_y dr_z. \quad (2.1.19) \]

According to equations (2.1.11) and (2.1.12), the partial derivatives \( \frac{\partial R}{\partial r_j} \) and \( \frac{\partial r}{\partial r_j} \) are different for each particle. The following three equations show the \( k \)-th vector element of the transformed gradients for all three different particles

\[ \frac{\partial}{\partial r_{c1}^{(k)}} = -\frac{\partial}{\partial R_k} - \frac{1}{2} \frac{\partial}{\partial r_k}, \quad (2.1.20) \]
\[ \frac{\partial}{\partial r_{c2}^{(k)}} = \frac{\partial}{\partial R_k} - \frac{1}{2} \frac{\partial}{\partial r_k}, \quad (2.1.21) \]
\[ \frac{\partial}{\partial r_{c3}^{(k)}} = \frac{\partial}{\partial r_k}. \quad (2.1.22) \]

Using \( \nabla_{\vec{r}_{c1}}^2 = \sum_{k=3} \left( \frac{\partial}{\partial r_{c1}^{(k)}} \right)^2 \) and the expressions in equations (2.1.20) - (2.1.22), the kinetic operators of the three particles are obtained as

\[ -\frac{\hbar^2}{2m_1} \nabla_{\vec{r}_{c1}}^2 = -\frac{\hbar^2}{2m_1} \left( \frac{\partial^2}{\partial R_x^2} + \frac{\partial^2}{\partial R_y^2} + \frac{\partial^2}{\partial R_z^2} \right) - \frac{\hbar^2}{8m_1} \left( \frac{\partial^2}{\partial r_x^2} + \frac{\partial^2}{\partial r_y^2} + \frac{\partial^2}{\partial r_z^2} \right) \]
\[ -\frac{\hbar^2}{2m_1} \left( \frac{\partial}{\partial R_x} \frac{\partial}{\partial r_x} + \frac{\partial}{\partial R_y} \frac{\partial}{\partial r_y} + \frac{\partial}{\partial R_z} \frac{\partial}{\partial r_z} \right), \quad (2.1.23) \]

\[ -\frac{\hbar^2}{2m_2} \nabla_{\vec{r}_{c2}}^2 = -\frac{\hbar^2}{2m_2} \left( \frac{\partial^2}{\partial R_x^2} + \frac{\partial^2}{\partial R_y^2} + \frac{\partial^2}{\partial R_z^2} \right) - \frac{\hbar^2}{8m_2} \left( \frac{\partial^2}{\partial r_x^2} + \frac{\partial^2}{\partial r_y^2} + \frac{\partial^2}{\partial r_z^2} \right) \]
\[ + \frac{\hbar^2}{2m_2} \left( \frac{\partial}{\partial R_x} \frac{\partial}{\partial r_x} + \frac{\partial}{\partial R_y} \frac{\partial}{\partial r_y} + \frac{\partial}{\partial R_z} \frac{\partial}{\partial r_z} \right), \quad (2.1.23) \]

\[ -\frac{\hbar^2}{2m_3} \nabla_{\vec{r}_{c3}}^2 = -\frac{\hbar^2}{2m_3} \left( \frac{\partial}{\partial r_x} + \frac{\partial}{\partial r_y} + \frac{\partial}{\partial r_z} \right). \]

The whole three-body Hamiltonian can be represented in terms of \( \vec{R} \) and \( \vec{r} \), with their corresponding momentum operators \( \vec{P}, \vec{p} \), and with the reduced mass \( \mu_{12} = \frac{m_1 m_2}{m_1 + m_2} \) as

\[ \hat{H}_c = \frac{1}{8\mu_{12}} + \frac{1}{2m_3} \vec{p}^2 + \frac{\vec{P}^2}{2\mu_{21}} + \frac{1}{2} \left( \frac{1}{m_1} - \frac{1}{m_2} \right) \vec{p} \vec{P} + \frac{Z_1 Z_2}{|\vec{R}|} + \frac{Z_1 Z_3}{|\vec{r} + \vec{R}/2|} + \frac{Z_2 Z_3}{|\vec{r} - \vec{R}/2|} \quad (2.1.24) \]

with the corresponding momenta \( \vec{P} \) and \( \vec{p} \) explicitly given by
\[ \hat{P} = -i\hbar \begin{pmatrix} \partial / \partial R_x \\ \partial / \partial R_y \\ \partial / \partial R_z \end{pmatrix}, \quad \hat{p} = -i\hbar \begin{pmatrix} \partial / \partial r_x \\ \partial / \partial r_y \\ \partial / \partial r_z \end{pmatrix}. \]

Splitting the entire Hamiltonian into a kinetic operator \( \hat{T} \) and a potential operator \( \hat{V} \) results then in

\[ \hat{T}(\vec{R}, \vec{r}) = \left( \frac{1}{8\mu_{12}} + \frac{1}{2m_3} \right) \hat{p}^2 + \frac{1}{2} \left( \frac{1}{m_1} - \frac{1}{m_2} \right) \hat{p} \hat{P}, \quad (2.1.25) \]

\[ \hat{V}(\vec{R}, \vec{r}) = \frac{Z_1 Z_2}{|\vec{R}|} + \frac{Z_1 Z_3}{|\vec{r} + \vec{R}/2|} + \frac{Z_2 Z_3}{|\vec{r} - \vec{R}/2|}. \quad (2.1.26) \]

Finally, we have a new expression for the three-body Hamiltonian equivalent to the one given in (2.1.1)

\[ \hat{H} = -\frac{\hbar^2}{2M} \nabla_{\vec{R}_c}^2 + \hat{T}(\vec{R}, \vec{r}) + \hat{V}(\vec{R}, \vec{r}). \quad (2.1.27) \]

The corresponding eigenfunctions factorize in two functions, one for the center of mass position vector \( \vec{R}_c \) and the other one depending on two independent vectors \( \vec{R} \) and \( \vec{r} \). We introduced both vectors and their momenta in Cartesian coordinates. Usually, it is convenient to transform the coordinates into ones which consider directly the symmetry of the given problem and simplify the calculation. Therefore we continue in the next section with a transformation of \( \vec{R} \) and \( \vec{r} \) into combined spherical and cylindrical coordinates.

### 2.2 Combined spherical and cylindrical coordinate system

Two three-dimensional spatial vectors with the same origin describe a triangle orientated in 3D with one edge at the origin and one at the end of each vector. Since the orientation and properties of the triangle are unique for any \( \vec{R} \) and \( \vec{r} \), it is possible to find a one-to-one transformation into three Euler angles for the orientation in three-dimensional space and three independent parameters for a description of the triangle shape.

Since the three-body problem has some rotational symmetries, it is useful to transform \( \vec{R} \) into spherical coordinates \((R, \phi, \theta)\) and \( \vec{r} \) into cylindrical coordinates \((\rho, \psi, \zeta)\) with respect to \( \vec{R} \) as its distinguished Z-axis of the cylindrical coordinates. The same kind of coordinates were also used by Feagin [Fea84], but we use here \( \zeta \) instead of \( z \) and interchange the variables \( \phi \) and \( \psi \). With this choice the vector \( \vec{r} \) depends on the position of \( \vec{R} \) in space. The relation between the two sets of coordinates in the initial center of mass frame can be obtained by three rotations around two different axis, the Y- and Z-axis. The rotation matrices for such rotations are elements of the SO(3) rotation group and are given by

\[
\mathbf{R}_y(\theta) = \begin{pmatrix}
\cos(\theta) & 0 & \sin(\theta) \\
0 & 1 & 0 \\
-\sin(\theta) & 0 & \cos(\theta)
\end{pmatrix}, \quad \mathbf{R}_z(\phi) = \begin{pmatrix}
\cos(\phi) & -\sin(\phi) & 0 \\
\sin(\phi) & \cos(\phi) & 0 \\
0 & 0 & 1
\end{pmatrix}. \quad (2.2.1)
\]

For the case that \( \phi \) and \( \theta \) are zero, we define that \( \vec{R} \) is along the Z-axis of the initial center of mass frame. We label this distinguished vector with \( \vec{R}_0 \) and in Cartesian coordinates the vector is described as

\[
\vec{R}_0 = \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix}. \quad (2.2.2)
\]

In cylindrical coordinates \( \zeta \) describes the third coordinate parallel to an axis which is fixed in the reference frame of the cylindrical coordinates, in our case parallel to \( \vec{R} \). The coordinate \( \rho \) represents the radius and
\[ \psi \] the rotation angle. If \( \psi, \zeta, \phi \) and \( \theta \) are zero, we define \( \vec{r} \) being parallel to the X-axis of the initial center of mass frame. For the case that \( \vec{R} = \vec{R}_0 \), an arbitrary vector \( \vec{r}_{\vec{R}_0} \) is given in Cartesian coordinates by

\[
\vec{r}_{\vec{R}_0} = \begin{pmatrix} \rho \cos(\psi) \\ \rho \sin(\psi) \\ \zeta \end{pmatrix}.
\tag{2.2.3}
\]

The definition of spherical coordinates is equivalent to two rotations of \( \vec{R}_0 \), first around the Y-axis about the angle \( \theta \) and second around the Z-axis about the angle \( \phi \). Since \( \vec{r} \) is directly coupled to the orientation of \( \vec{R} \) in the three-dimensional space, the same rotation operation applied to \( \vec{r}_{\vec{R}_0} \) results in the vector \( \vec{r} \) in the initial center of mass frame

\[
\vec{R} = R_z(\phi) \cdot R_y(\theta) \cdot \vec{R}_0, \quad \vec{r} = R_z(\phi) \cdot R_y(\theta) \cdot \vec{r}_{\vec{R}_0}.
\tag{2.2.4}
\]

Both vectors \( \vec{R} \) and \( \vec{r} \) depend on the coordinates \( (R, \theta, \phi, \rho, \zeta, \psi) \) and are thus in Cartesian coordinates explicitly given by

\[
\vec{R} = \begin{pmatrix} R_x \\ R_y \\ R_z \end{pmatrix} = \begin{pmatrix} R \sin(\theta) \cos(\phi) \\ R \sin(\theta) \sin(\phi) \\ R \cos(\theta) \end{pmatrix},
\tag{2.2.5}
\]

\[
\vec{r} = \begin{pmatrix} r_x \\ r_y \\ r_z \end{pmatrix} = \begin{pmatrix} (\rho \cos(\theta) \cos(\psi) + \zeta \sin(\theta)) \cos(\phi) - \rho \sin(\psi) \sin(\phi) \\ (\rho \cos(\theta) \cos(\psi) + \zeta \sin(\theta)) \sin(\phi) + \rho \sin(\psi) \cos(\phi) \\ -\rho \sin(\theta) \cos(\psi) + \zeta \cos(\theta) \end{pmatrix}.
\tag{2.2.6}
\]

Figure 2.2.1: The vectors \( \vec{R} \) and \( \vec{r} \) are represented in the usual Cartesian coordinates, i.e. \( R_x, R_y, R_z \) for \( \vec{R} \) and \( r_x, r_y, r_z \) for \( \vec{r} \).

Figure 2.2.2: The vectors \( \vec{R} \) and \( \vec{r} \) are described in angular coordinates, \( \phi, \theta, \psi \), the two radii \( R, \rho \) and the value \( \zeta \).
Figure (2.2.1) shows the two vectors in Cartesian coordinates, and figure (2.2.2) visualizes the same vectors in the new combined spherical and cylindrical coordinates. The absolute value $R$ of $\vec{R}$ and the angles $\theta$ and $\phi$ represent the radial distance, the polar and the azimuth angle of the spherical coordinates. $\vec{R}$ represents the 'Z-axis' for the cylindrical coordinates, and therefore the coordinate $\zeta$ is always along $\vec{R}$. With the radial distance $\rho$ and the second azimuth angle $\psi$ it is possible to span an plane perpendicular to $\vec{R}$. Thus each configuration of $\vec{R}$ and $\vec{r}$ in the three-dimensional space can be expressed by the three angular coordinates $\phi, \theta, \psi$ and the three coordinates $R, \rho, \zeta$. The domains of the coordinates are identical with the domains of the usual spherical and cylindrical coordinates, i.e.

$$R \in [0, \infty] , \quad \rho \in [0, \infty] , \quad \zeta \in [0, \infty] , \quad (2.2.7)$$
$$\phi \in [0, 2\pi] , \quad \psi \in [0, 2\pi] , \quad \theta \in [0, \pi] . \quad (2.2.8)$$

Figure (2.2.2) illustrates the one-to-one correspondence between the triangle length $R, r, d_{Rr}$ and $R, \rho, \zeta$. The same situation can be described by a triangle orientated in space by three angular coordinates. These angles are equal to the Euler angles which are typically used for the description of the orientation of a rigid body.

For some calculations and expressions, e.g. the total angular momentum, it is advantageous to change the coordinate system from the initial center of mass laboratory frame, which is a space-fixed frame, to a body-fixed frame. In this frame $\vec{R}$ and $\vec{r}$ do not depend on the orientation angles. The transformation from the body-fixed frame to the initial center of mass is given by the operator $M_{zyz}$ with

$$M_{zyz}(\phi, \theta, \psi) = R_z(\phi) \cdot R_y(\theta) \cdot R_z(\psi). \quad (2.2.9)$$

The action of the operator on $\vec{R}_0(0,0,R)^T$ as defined in (2.2.2) and the choice $\vec{r}_0 = (\rho, 0, \zeta)^T$ with respect to the laboratory frame, leads to the same result of (2.2.5) and (2.2.6). Since the operator $M_{zyz}(\phi, \theta, \psi)$ belongs to the SO(3) group, the inverse transformation is simply

$$M_{zyz}^{-1}(\phi, \theta, \psi) = R_z(-\phi) \cdot R_y(-\theta) \cdot R_z(-\psi). \quad (2.2.10)$$

The two vectors $\vec{R}$ and $\vec{r}$ can be substituted with their Cartesian expressions (2.2.5) and (2.2.6) into equations (2.1.20) (2.1.21) and (2.1.22) for the particle position vectors. This leads to particle vectors $\vec{r}_{ci}$ in the combined spherical and cylindrical coordinates

$$\vec{r}_{c1} = \left( \begin{array}{c} \frac{m_1 + m_2}{M} R \sin(\theta) \cos(\phi) + \frac{m_3}{M} \left( \rho \cos(\theta) \cos(\psi) + \zeta \sin(\theta) \right) \cos(\phi) - \rho \sin(\psi) \sin(\phi) \\
\frac{m_1 + m_2}{M} R \sin(\theta) \sin(\phi) + \frac{m_3}{M} \left( \rho \cos(\theta) \cos(\psi) + \zeta \sin(\theta) \right) \sin(\phi) + \rho \sin(\psi) \cos(\phi) \\
\frac{m_1 + m_2}{M} R \cos(\theta) + \frac{m_3}{M} \left( -\rho \sin(\theta) \cos(\psi) + \zeta \cos(\theta) \right) \end{array} \right), \quad (2.2.11)$$

$$\vec{r}_{c2} = \left( \begin{array}{c} -\frac{m_1 + m_3}{M} R \sin(\theta) \cos(\phi) + \frac{m_2}{M} \left( \rho \cos(\theta) \cos(\psi) + \zeta \sin(\theta) \right) \cos(\phi) - \rho \sin(\psi) \sin(\phi) \\
-\frac{m_1 + m_3}{M} R \sin(\theta) \sin(\phi) + \frac{m_2}{M} \left( \rho \cos(\theta) \cos(\psi) + \zeta \sin(\theta) \right) \sin(\phi) + \rho \sin(\psi) \cos(\phi) \\
-\frac{m_1 + m_2}{M} R \cos(\theta) + \frac{m_3}{M} \left( -\rho \sin(\theta) \cos(\psi) + \zeta \cos(\theta) \right) \end{array} \right), \quad (2.2.12)$$

$$\vec{r}_{c3} = \left( \begin{array}{c} \frac{m_1 + m_3}{2M} R \sin(\theta) \cos(\phi) - \frac{m_2}{2M} \left( \rho \cos(\theta) \cos(\psi) + \zeta \sin(\theta) \right) \cos(\phi) - \rho \sin(\psi) \sin(\phi) \\
\frac{m_1 + m_3}{2M} R \sin(\theta) \sin(\phi) - \frac{m_2}{2M} \left( \rho \cos(\theta) \cos(\psi) + \zeta \sin(\theta) \right) \sin(\phi) + \rho \sin(\psi) \cos(\phi) \\
\frac{m_1 + m_2}{2M} R \cos(\theta) - \frac{m_3}{M} \left( -\rho \sin(\theta) \cos(\psi) + \zeta \cos(\theta) \right) \end{array} \right) \quad (2.2.13)$$
2.3 Transformation of the three-body Hamiltonian

In the following, we illustrate the transformation of the Hamiltonian into the coordinates introduced in section 2.1. Since the stationary Schrödinger equation is a second-order differential equation, the main task is to obtain the transformation of the differential. The Jacobian matrix $J_{s-c}$ and its determinant describe the relation between the two sets of differentials. In the following, we use the index 's-c', where 's' denotes spherical and 'c' cylindrical. The Jacobian $J_{s-c}$ and the inverse $J_{s-c}^{-1}$ are given by

$$J_{s-c} = \frac{\partial(R_x, R_y, R_z, r_x, r_y, r_z)}{\partial(R, \theta, \phi, \rho, \psi, \zeta)},$$  \hspace{1cm} (2.3.1)$$

$$J_{s-c}^{-1} = \left[\frac{\partial(R_x, R_y, R_z, r_x, r_y, r_z)}{\partial(R, \theta, \phi, \rho, \psi, \zeta)}\right]^{-1}.$$  \hspace{1cm} (2.3.2)$$

The explicit form of the Jacobi matrices are given in appendix (A.1.1) and (A.1.2). Although most matrix elements of the Jacobian $J_{s-c}$ have a relatively long expression, the determinants of both are quite short

$$\text{det}(J_{s-c}) = |J_{s-c}| = R^2 \rho \sin(\theta), \hspace{1cm} \text{det}(J_{s-c}^{-1}) = |J_{s-c}^{-1}| = \frac{\csc(\theta)}{R^2 \rho}. \hspace{1cm} (2.3.3)$$

To illustrate the transformation of the differential, we define four vectors $u$, $v$, $\partial u$, and $\partial v$. All elements of the two three-dimensional vectors $\mathbf{R}$ and $\mathbf{r}$ describe the six-dimensional vector $u$ for Cartesian coordinates and $v$ for the $(R, \theta, \phi, \rho, \psi, \zeta)$ coordinates. The differential vectors $\partial u$ and $\partial v$ are the Nabla operators of $u$ and $v$.

$$u = \begin{pmatrix} R_x \\ R_y \\ R_z \\ r_x \\ r_y \\ r_z \end{pmatrix}, \hspace{1cm} \partial u = \begin{pmatrix} \partial R_x \\ \partial R_y \\ \partial R_z \\ \partial r_x \\ \partial r_y \\ \partial r_z \end{pmatrix}, \hspace{1cm} v = \begin{pmatrix} R \\ \theta \\ \phi \\ \rho \\ \psi \\ \zeta \end{pmatrix}, \hspace{1cm} \partial v = \begin{pmatrix} \partial R \\ \partial \theta \\ \partial \phi \\ \partial \rho \\ \partial \psi \\ \partial \zeta \end{pmatrix}. \hspace{1cm} (2.3.4)$$

In this case the kinetic part of the Hamiltonian shown in equation (2.1.23) is equivalent to the following equation

$$\hat{T} = \left(\frac{\hbar^2}{8\mu_{12}} + \frac{\hbar^2}{2m_3}\right) \left(-\frac{\partial^2}{\partial u_4^2} - \frac{\partial^2}{\partial u_5^2} - \frac{\partial^2}{\partial u_6^2} + \frac{\hbar^2}{2\mu_{12}} \left(-\frac{\partial^2}{\partial u_1^2} - \frac{\partial^2}{\partial u_2^2} - \frac{\partial^2}{\partial u_3^2}\right) \right)$$

$$+ \frac{\hbar^2}{2} \left(\frac{1}{m_1} - \frac{1}{m_2}\right) \left(-\frac{\partial^2}{\partial u_1 \partial u_4} - \frac{\partial^2}{\partial u_2 \partial u_5} - \frac{\partial^2}{\partial u_3 \partial u_6}\right).$$  \hspace{1cm} (2.3.5)$$

The differentials represented by $\partial u$ are obtained simply by the matrix vector multiplication of $J_{s-c}^{-1}$ with $\partial v$

$$\frac{\partial}{\partial u_i} = \sum_{p=1}^{6} \left[J_{s-c}^{-1}\right]_{ip} \frac{\partial}{\partial v_p}. \hspace{1cm} (2.3.6)$$

\footnote{$\partial_x = \frac{\partial}{\partial x}$}
To get the transformation of the second-order partial derivative operator \( \frac{\partial^2}{\partial u_i \partial u_j} \), we substitute the \( \frac{\partial}{\partial u_i} \) with the right hand side of equation (2.3.6). This substitution and the application of the chain rule leads to

\[
\frac{\partial^2}{\partial u_i \partial u_j} = \sum_{p=1}^{6} \sum_{q=1}^{6} [J_{s-c}]^{-1}_{pq} \left\{ \left( \partial \nu_p [J_{s-c}]^{-1}_{qj} \right) + [J_{s-c}]^{-1}_{pq} \partial \nu_q \right\} \partial \nu_q
\]

(2.3.7)

\[
= \sum_{p=1}^{6} \sum_{q=1}^{6} [J_{s-c}]^{-1}_{pq} \partial \nu_p [J_{s-c}]^{-1}_{qj} \partial \nu_q + \sum_{p=1}^{6} \sum_{q=1}^{6} [J_{s-c}]^{-1}_{pq} [J_{s-c}]^{-1}_{qj} \partial \nu_p \partial \nu_q .
\]

After a rearrangement the kinetic part of the Hamiltonian can be split into two parts, denoted as \( \hat{T}_S \) and \( \hat{T}_L \). The operator \( \hat{T}_S \) does not depend on any angular coordinate \( \phi, \theta \) or \( \psi \), and is thus given by \(^2\)

\[
\hat{T}_S = \frac{\hbar^2}{2m_1} \left[ - \partial_R^2 - \frac{2}{R} \partial_R + 2 \left( \frac{\zeta}{R^2} - 1 \right) \partial_\zeta - \frac{1}{\rho} \left( \frac{\zeta^2 + 1}{4} - \frac{\rho^2}{R^2} - \frac{\zeta}{R} \right) \partial_\rho 
\]

\[
- \partial_R^2 \partial_\zeta + \left( \frac{2\rho \zeta}{R^2} - \frac{\rho}{R} \right) \partial_\rho^2 - \left( \frac{\zeta^2 + 1}{4} - \frac{\rho^2}{R^2} + \frac{\zeta}{R} \right) \partial_\rho \right]
\]

\[
+ \frac{\hbar^2}{2m_2} \left[ - \partial_R^2 - \frac{2}{R} \partial_R + 2 \left( \frac{\zeta}{R^2} + 1 \right) \partial_\zeta - \frac{1}{\rho} \left( \frac{\zeta^2 + 1}{4} - \frac{\rho^2}{R^2} + \frac{\zeta}{R} \right) \partial_\rho 
\]

\[
+ \partial_R^2 \partial_\zeta + \left( \frac{2\rho \zeta}{R^2} + \frac{\rho}{R} \right) \partial_\rho^2 - \left( \frac{\zeta^2 + 1}{4} + \frac{\rho^2}{R^2} + \frac{\zeta}{R} \right) \partial_\rho \right]
\]

(2.3.8)

\[
+ \frac{\hbar^2}{2m_3} \left[ - \frac{1}{\rho} \partial_\rho - \partial_\rho^2 - \partial_\zeta^2 \right].
\]

The remaining terms of the complete kinetic energy operator \( \hat{T} \) depend at least on one angular variable or angular derivatives. Since this part of the Hamiltonian can be described by the properties and the components of the total angular momentum \( \hat{L} \) of the three-body system, it is reasonable to denote this contribution by \( \hat{T}_L \)

\[
\hat{T}_L = \frac{\hbar^2}{2R^2} \left[ \frac{1}{m_1} + \frac{1}{m_2} \right] \left[ - \cot(\theta) \partial_\theta - \partial_\theta^2 - \csc^2(\theta) \partial_\phi^2 + 2\zeta \cos(\psi) \partial_\rho^2 - 2\rho \cos(\psi) \partial_\phi^2 
\]

\[
- 2 \frac{\zeta}{\rho} \sin(\psi) \partial_\psi^2 + 2\zeta \csc(\theta) \sin(\psi) \partial_\phi^2 - 2\rho \csc(\theta) \sin(\psi) \partial_\phi^2 
\]

\[
+ 2\rho \cot(\theta) \sin(\psi) \partial_\phi^2 + 2 \left( \frac{\zeta}{\rho} \cos(\psi) + \cot(\theta) \right) \csc(\theta) \partial_\psi^2 
\]

\[
- \left( \frac{\zeta^2}{\rho^2} - 1 + \frac{R^2}{4\rho^2} + \frac{2\zeta}{\rho} \cot(\theta) \cos(\psi) + \csc^2(\theta) \right) \partial_\psi^2 \right]
\]

(2.3.9)

\[
+ \frac{\hbar^2}{2R} \left( \frac{1}{m_1} - \frac{1}{m_2} \right) \left[ - \cos(\psi) \partial_\phi^2 + \frac{1}{\rho} \sin(\psi) \partial_\phi^2 - \csc(\theta) \sin(\psi) \partial_\rho^2 
\]

\[
- \frac{1}{\rho} \csc(\theta) \cos(\psi) \partial_\phi^2 + \cot(\theta) \sin(\psi) \partial_\phi^2 + \frac{1}{\rho^2} \left( \zeta + \rho \cos(\psi) \cot(\theta) \right) \partial_\psi^2 \right]
\]

\[
- \frac{\hbar^2}{2m_3 \rho^2} \partial_\psi^2 .
\]

If we find a valid eigenfunction \( \Psi_S \) for the whole Hamiltonian, which does not depend on any angular variable, \( \hat{T}_L \Psi_S \) accordingly vanishes. In this case the wave function is completely symmetric, invariant

\(^2\) \( \frac{\partial^2}{\partial x \partial y} = \frac{\partial^2}{\partial x^2}, \quad \frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial z^2} \)
under rotation and just depends on $R, \rho, \zeta$, and the Hamiltonian for the kinetic energy is given by $\hat{T}_S$. In this case $\Psi_S$ has the same character as the wave functions of the hydrogen atom in the S-states. Both are rotationally invariant and additionally explains the used index $S$ for the $\hat{T}_S$.

Compared to the effort to get a suitable transformation for the kinetic energy operator $\hat{T}$, the adaptation of the potential $\hat{V}$ is quite simple. Equations (2.3.10) - (2.3.12) display the denominators of (2.1.9) in terms of the coordinates $R, \theta, \phi, \rho, \zeta, \psi$

\[ |\vec{R}| = R, \quad (2.3.10) \]
\[ |\vec{r} + \vec{R}/2| = \sqrt{(\zeta + R/2)^2 + \rho^2}, \quad (2.3.11) \]
\[ |\vec{r} - \vec{R}/2| = \sqrt{(\zeta - R/2)^2 + \rho^2}. \quad (2.3.12) \]

A simple substitution of the previous three equations into (2.1.26) leads to the following form of the potential term in the Hamiltonian

\[ \hat{V}(R, \rho, \zeta) = \frac{Z_1 Z_2}{R} + \frac{Z_1 Z_3}{\sqrt{(\zeta + R/2)^2 + \rho^2}} + \frac{Z_2 Z_3}{\sqrt{(\zeta - R/2)^2 + \rho^2}}. \quad (2.3.13) \]

In summary, we have transformed the Hamiltonian $\hat{H}_c$ in the center of mass frame into spherical and cylindrical coordinates. In a second step we have shown how to split the kinetic operator $\hat{T}$ into two parts, the first contribution, $\hat{T}_S$, does not carry any angular dependence and the second operator $\hat{T}_L$ includes both, angular and $R, \rho, \zeta$ dependence. The complete Hamiltonian $\hat{H}_c$, is then given by

\[ \hat{H}_c = \hat{T}_S + \hat{T}_L + \hat{V}. \quad (2.3.14) \]

Since in chapter 5 we want to calculate the energy eigenvalues of the three-body problem with a variational ansatz, we need the matrix elements of $\hat{H}_c$ which are given by $\langle \Psi_i | \hat{H}_c | \Psi_j \rangle$, where $\Psi_i$, $\Psi_j$ denote arbitrary wave functions. Referring to (2.3.14) and the right equation of (2.3.3) the matrix elements are explicitly given by

\[ \langle \Psi_i | \hat{H}_c | \Psi_j \rangle = \int_{0}^{\infty} \int_{-\infty}^{\infty} \int_{0}^{2\pi} \int_{0}^{2\pi} \int_{-\infty}^{\infty} \int_{0}^{\infty} R^2 \rho \sin(\theta) \, \Psi_i^* \hat{H}_c \Psi_j \, d\phi \, d\theta \, d\psi \, dR \, d\rho \, d\zeta. \quad (2.3.15) \]

If we use $\hat{H}_c$ in the representation of spherical and cylindrical coordinates, the integral calculations for equation (2.3.15) include some singularities, which appear because of the Coulomb potential terms. These terms rise to infinity if $R, \rho$ and $\zeta$ are equal to zero. Therefore, in the next section, we transform the three coordinates $R, \rho, \zeta$ into perimetric coordinates, since we can with these coordinates avoid singularities for the numerical integrations. Additionally, all three perimetric coordinates have the same domain, whereas the domain of $\zeta$ differs from those of $R$ and $\rho$. Therefore, when we want to expand the wave functions later, just one type of basis set functions is necessary.

### 2.4 Perimetric coordinates

The three-body Hamiltonian in spherical and cylindrical coordinates still contains the Coulomb singularity in the potential term. For an accurate numerical integration it is beneficial to regularize the singularities. In this section, we introduce the perimetric coordinates which were used for the first time by Coolidge and James [CJ37] and transform the Hamiltonian into those coordinates.

In figure (2.2.2) it can be seen that the connecting lines between all three particle positions constitute a triangle that can be described in the combined spherical and cylindrical coordinates with $R, \rho, \zeta$. The shape of this triangle can be described in many different representations obtained by a one-to-one transformation of the initial coordinates $R, \rho, \zeta$. One possible choice constitute the perimetric coordinates, which are defined by the three lengths shaping the given triangle. For the given problem the triangle lengths are directly given by the norm of $\vec{r}_{ij} \in \hat{c}_i - \hat{c}_j$ and thus the perimetric coordinates are
Three-body problem in non-relativistic quantum mechanics

\[ x = |\vec{r}_{31}| - |\vec{r}_{32}| + |\vec{r}_{12}|, \quad \text{(2.4.1)} \]
\[ y = |\vec{r}_{32}| - |\vec{r}_{31}| + |\vec{r}_{12}|, \quad \text{(2.4.2)} \]
\[ z = |\vec{r}_{31}| + |\vec{r}_{32}| - |\vec{r}_{12}|, \quad \text{(2.4.3)} \]

which is equivalent to the definition in reference [HB01]. The inverse transformation then takes the form

\[ |\vec{r}_{31}| = \frac{1}{2}(x + z), \quad \text{(2.4.4)} \]
\[ |\vec{r}_{32}| = \frac{1}{2}(y + z), \quad \text{(2.4.5)} \]
\[ |\vec{r}_{12}| = \frac{1}{2}(x + y). \quad \text{(2.4.6)} \]

Every triangle has an one-to-one correspondence between the three distances and the perimetric coordinates \( x, y, z \). Certainly the triangle inequality, \( c \leq a + b \), has to hold for all shapes of the triangle and \( x, y \) and \( z \) are always larger or equal to zero. In the limit that all three perimetric coordinates tend to zero, the whole triangle is contracted into one point.

Equations (2.1.13) - (2.1.15) and (2.3.10) - (2.3.12) connect the new perimetric coordinates with the combined spherical and cylindrical coordinates of section 2.2 and this leads with definitions (2.4.1) - (2.4.3) to

\[ x = R + \frac{1}{2}\sqrt{(R + 2\zeta)^2 + 4\rho^2} - \frac{1}{2}\sqrt{(R - 2\zeta)^2 + 4\rho^2}, \quad \text{(2.4.7)} \]
\[ y = R - \frac{1}{2}\sqrt{(R + 2\zeta)^2 + 4\rho^2} + \frac{1}{2}\sqrt{(R - 2\zeta)^2 + 4\rho^2}, \quad \text{(2.4.8)} \]
\[ z = -R + \frac{1}{2}\sqrt{(R + 2\zeta)^2 + 4\rho^2} + \frac{1}{2}\sqrt{(R - 2\zeta)^2 + 4\rho^2}, \quad \text{(2.4.9)} \]

and the corresponding inverse transformation

\[ R = \frac{x + y}{2}, \quad \text{(2.4.10)} \]
\[ \zeta = \frac{(x - y)(x + y + 2z)}{4(x + y)}, \quad \text{(2.4.11)} \]
\[ \rho = \frac{\sqrt{xyz(x + y + z)}}{x + y}. \quad \text{(2.4.12)} \]

The domain of the perimetric coordinates is given by \( x, y, z \in [0, \infty] \). Taking equations (2.4.10) - (2.4.12), \( R \) and \( \rho \) are invariant and \( \zeta \) changes its sign under permutation of \( x \) and \( y \). This circumstance is useful to construct symmetric and antisymmetric wave functions. It is another advantage of using perimetric coordinates for the Hamiltonian and the eigenfunctions in the calculations. In order to calculate integrals in perimetric coordinates, the Jacobian matrix \( \mathbf{J}_{\text{per}} \) and its inverse matrix \( [\mathbf{J}_{\text{per}}]^{-1} \) given by

\[ \mathbf{J}_{\text{per}} = \frac{\partial (R, \rho, \zeta)}{\partial (x, y, z)}, \quad [\mathbf{J}_{\text{per}}]^{-1} = \left[ \frac{\partial (R, \rho, \zeta)}{\partial (x, y, z)} \right]^{-1}, \quad \text{(2.4.13)} \]

are required. The transformed volume elements are given by

\[ \det(\mathbf{J}_{\text{per}}) = |\mathbf{J}_{\text{per}}| = \frac{(x + z)(y + z)}{8 \sqrt{xyz(x + y + z)}}, \quad \text{det}(\mathbf{J}_{\text{per}}^{-1}) = |\mathbf{J}_{\text{per}}^{-1}| = \frac{8 \sqrt{xyz(x + y + z)}}{(x + z)(y + z)}. \quad \text{(2.4.14)} \]
Together with the first transformation determinant in (2.3.3), the volume element dV shown in (2.1.19) in Cartesian coordinates can then be expressed as

\[ d\mathbf{R} \, d\mathbf{r} = |\mathbf{J}_{x-c}| \cdot |\mathbf{J}_{per}| \, dx \, dy \, dz = \frac{1}{32} \sin(\theta) (x + y) (x + z) (y + z) \, dx \, dy \, dz, \]  

(2.4.15)

and the potential terms of (2.1.26) take the form

\[ \hat{V} \, d\mathbf{R} \, d\mathbf{r} = \frac{1}{16} \sin(\theta) \left[ (x + z) (y + z) Z_1 Z_2 + (x + y) (x + z) Z_1 Z_3 + (x + y) (y + z) Z_2 Z_3 \right] \, dx \, dy \, dz. \]  

(2.4.16)

To conclude, we can say that the singularity of the Coulomb potential, which appears in the integrations over the whole space, have been regularized with the transformation into perimetric coordinates. After adapting equations (2.3.6) and (2.3.7) to the new transformation from \((R, \rho, \zeta)\) to \((x, y, z)\), they result in the following two expressions

\[ \frac{\partial}{\partial u_i} = \sum_{p=1}^{3} [J^{-1}_{per}]^{pi} \frac{\partial}{\partial \nu_p} \]  

(2.4.17)

\[ \frac{\partial^2}{\partial u_i \partial u_j} = \sum_{p=1}^{3} \sum_{q=1}^{3} [J^{-1}_{per}]^{pi} \left( \frac{\partial \nu_p}{\partial \nu_q} [J^{-1}_{per}]^{qj} \right) \frac{\partial \nu_q}{\partial \nu_p} + \sum_{p=1}^{3} \sum_{q=1}^{3} [J^{-1}_{per}]^{pi} \left( [J^{-1}_{per}]^{qj} \right) \frac{\partial \nu_p}{\partial \nu_q} \]  

(2.4.18)

where we defined \(\mathbf{u}, \mathbf{v}, \partial \mathbf{u}\) and \(\partial \mathbf{v}\) in this case as

\[ \mathbf{u} = \begin{pmatrix} R \\ \rho \\ \zeta \end{pmatrix}, \quad \partial \mathbf{u} = \begin{pmatrix} \partial R \\ \partial \rho \\ \partial \zeta \end{pmatrix}, \quad \mathbf{v} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad \partial \mathbf{v} = \begin{pmatrix} \partial x \\ \partial y \\ \partial z \end{pmatrix}. \]  

(2.4.19)

Using the five equations (2.4.10) - (2.4.12), (2.4.17) and (2.4.18) and substituting all coordinates and derivative operators in equation (2.3.8) results in the Hamiltonian part \(\hat{T}_S\) and \(\hat{V}\) in perimetric coordinates

\[ \hat{T}_S = -2\hbar^2 \left[ \frac{x(x + y + z)}{m_1(x + y)(x + z)} + \frac{xz}{m_2(x + y)(y + z)} + \frac{xy}{m_3(x + z)(y + z)} \right] \frac{\partial^2}{\partial x^2} \]  

\[ -2\hbar^2 \left[ \frac{yz}{m_1(x + y)(x + z)} + \frac{y(x + y + z)}{m_2(x + y)(y + z)} + \frac{xy}{m_3(x + z)(y + z)} \right] \frac{\partial^2}{\partial y^2} \]  

\[ -2\hbar^2 \left[ \frac{yz}{m_1(x + y)(x + z)} + \frac{z(x + y + z)}{m_2(x + y)(y + z)} + \frac{xy}{m_3(x + z)(y + z)} \right] \frac{\partial^2}{\partial z^2} \]  

\[ + 4\hbar^2 \frac{xy}{m_1(x + y)(x + z)} \frac{\partial^2}{\partial y \partial x} + 4\hbar^2 \frac{xz}{m_2(x + y)(y + z)} \frac{\partial^2}{\partial z \partial x} \]  

\[ + 4\hbar^2 \frac{xy}{m_3(y + z)(x + z)} \frac{\partial^2}{\partial y \partial x} \]  

\[ -2\hbar^2 \left[ \frac{2x + y + z}{m_1(x + y)(x + z)} + \frac{z - x}{m_2(x + y)(y + z)} + \frac{y - x}{m_3(y + z)(x + z)} \right] \frac{\partial}{\partial x} \]  

\[ -2\hbar^2 \left[ \frac{z - y}{m_1(x + y)(x + z)} + \frac{2y + x + z}{m_2(x + y)(y + z)} + \frac{2z + x + y}{m_3(y + z)(x + z)} \right] \frac{\partial}{\partial y} \]  

\[ -2\hbar^2 \left[ \frac{y - z}{m_1(x + y)(x + z)} + \frac{x - z}{m_2(x + y)(y + z)} + \frac{2z + x + y}{m_3(y + z)(x + z)} \right] \frac{\partial}{\partial z}. \]  

(2.4.20)
The kinetic operator term \( \hat{T}_L \) in perimetric coordinates is explicitly given in the next chapter, after introducing the total angular momentum operator and incorporating it into \( \hat{T}_L \). The matrix elements of the Hamiltonian \( \hat{H}_c \), which are given by equation (2.3.15) in combined spherical and cylindrical coordinates have now in perimetric coordinates the form

\[
\langle \Psi_i | \hat{H}_c | \Psi_j \rangle = \int_0^\infty \int_0^\infty \int_0^\infty \int_0^\infty \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} \int_0^{\pi} \frac{1}{32} (x + y)(y + z) \sin(\theta) \Psi_i \hat{H}_c \Psi_j \ d\phi \ d\theta \ d\psi \ dx \ dy \ dz .
\] (2.4.22)

For the previous consideration we used equation (2.4.15) for the transformed volume element \( d\vec{R} d\vec{r} \).

In the next chapter we consider the total angular momentum of the system and wave function symmetries like permutation and parity symmetry. With the properties of the rotational symmetries we construct the so called Wigner-D-matrices which are also the angular eigenfunctions for the three-body problem in the center of mass frame. Additionally, we look at the wave functions for the case of two identical fermionic particles.
Chapter 3

Wave function symmetries

3.1 Angular momentum

In addition to the Hamiltonian which determines the eigenvectors and energy eigenvalues for the three-body problem, it is useful to consider the angular momentum \( \vec{L} \) of the system. The angular momentum is a conserved quantity and this property can be used to classify the eigenvalues and eigenvectors of the system. In Cartesian coordinates the angular momentum is given in position basis by

\[
\vec{L} = \left( \begin{array}{c} \hat{L}_x \\ \hat{L}_y \\ \hat{L}_z \end{array} \right) = \frac{\hbar}{i} \left( \begin{array}{c} y \partial_z - z \partial_y \\ z \partial_x - x \partial_z \\ x \partial_y - y \partial_x \end{array} \right). \tag{3.1.1}
\]

Therefore in the center of mass frame for the three-body problem the angular momentum \( \vec{L}_{c_j} \) for particle \( j \) is

\[
\vec{L}_{c_j} = \frac{\hbar}{i} \left( \begin{array}{c} r_{c_j}^{(y)} \partial_{r_{c_j}^{(z)}} - r_{c_j}^{(z)} \partial_{r_{c_j}^{(y)}} \\ r_{c_j}^{(z)} \partial_{r_{c_j}^{(x)}} - r_{c_j}^{(x)} \partial_{r_{c_j}^{(z)}} \\ r_{c_j}^{(x)} \partial_{r_{c_j}^{(y)}} - r_{c_j}^{(y)} \partial_{r_{c_j}^{(x)}} \end{array} \right). \tag{3.1.2}
\]

The total angular momentum \( \vec{L} \) for the three-body system is obtained by summing up all three single angular momenta of each particle

\[
\vec{L} = \vec{L}_{c_1} + \vec{L}_{c_2} + \vec{L}_{c_3}. \tag{3.1.3}
\]

The elements of \( \vec{L} \) in Cartesian coordinates are explicitly given by

\[
\hat{L}_x = \frac{\hbar}{i} \left( \begin{array}{c} r_{c_1}^{(y)} \partial_{r_{c_1}^{(z)}} - r_{c_1}^{(z)} \partial_{r_{c_1}^{(y)}} + r_{c_2}^{(y)} \partial_{r_{c_2}^{(z)}} - r_{c_2}^{(z)} \partial_{r_{c_2}^{(y)}} + r_{c_3}^{(y)} \partial_{r_{c_3}^{(z)}} - r_{c_3}^{(z)} \partial_{r_{c_3}^{(y)}} \end{array} \right), \tag{3.1.4}
\]

\[
\hat{L}_y = \frac{\hbar}{i} \left( \begin{array}{c} r_{c_2}^{(y)} \partial_{r_{c_2}^{(y)}} - r_{c_2}^{(y)} \partial_{r_{c_2}^{(z)}} + r_{c_3}^{(y)} \partial_{r_{c_3}^{(y)}} - r_{c_3}^{(y)} \partial_{r_{c_3}^{(z)}} \end{array} \right), \tag{3.1.5}
\]

\[
\hat{L}_z = \frac{\hbar}{i} \left( \begin{array}{c} r_{c_3}^{(y)} \partial_{r_{c_3}^{(y)}} - r_{c_3}^{(y)} \partial_{r_{c_3}^{(z)}} + r_{c_1}^{(y)} \partial_{r_{c_1}^{(y)}} - r_{c_1}^{(y)} \partial_{r_{c_1}^{(z)}} \end{array} \right). \tag{3.1.6}
\]

Changing the representation from \( \vec{r}_{c_j} \) to \( \vec{R} \) and \( \vec{r} \) leads with equations (2.2.11) - (2.2.13) for the position vector bases and equations (2.1.20) - (2.1.22) for the derivatives to the following equation for the total angular momentum
In section 2.2 we started with a constant vector \( \hat{\vec{r}}_0 \) and obtained the \( \vec{r} \) for the center of mass frame by the rotation matrix \( M(zyz)(\phi, \theta, \psi) \) and therefore its inverse matrix is given by

\[
M^{-1}(z)(\phi, \theta, \psi) = R_z(-\psi) \cdot R_y(-\theta) \cdot R_z(-\phi). \tag{3.1.11}
\]

Applying this matrix to \( \hat{\vec{L}} \) will lead to \( \vec{L}' \) which is still the total angular momentum, but now with respect to a reference frame with invariant orientation of the triangle spanned by the three particles

\[
\vec{L}' = R_z(-\psi) \cdot R_y(-\theta) \cdot R_z(-\phi) \cdot \hat{\vec{L}}. \tag{3.1.12}
\]

The components are now given by

\[
\hat{L}_x' = i\hbar \left( \cos(\psi) \cot(\theta) \partial_\psi - \cos(\psi) \csc(\theta) \cot(\phi) \partial_\phi + \sin(\psi) \partial_\theta \right), \tag{3.1.13}
\]

\[
\hat{L}_y' = i\hbar \left( -\sin(\psi) \csc(\theta) \partial_\psi + \sin(\psi) \cot(\theta) \partial_\phi + \cos(\psi) \partial_\theta \right), \tag{3.1.14}
\]

\[
\hat{L}_z' = i\hbar \partial_\psi. \tag{3.1.15}
\]

It is generally possible to define two ladder operators, the raising operator \( \hat{L}_+ \) and the lowering operator \( \hat{L}_- \) for the angular momentum. Both operators can be expressed in combined spherical and cylindrical coordinates, as

\[
\hat{L}_+ = \hat{L}_x + i\hbar e^{i\phi} \left( \frac{1}{\sin(\theta)} \partial_\psi - \cot(\theta) \partial_\phi + i\partial_\theta \right), \tag{3.1.16}
\]

\[
\hat{L}_- = \hat{L}_y - i\hbar e^{-i\phi} \left( \frac{1}{\sin(\theta)} \partial_\psi - \cot(\theta) \partial_\phi - i\partial_\theta \right), \tag{3.1.17}
\]

and take in the body-fixed frame the form

\[
\hat{L}_+ = \hat{L}_x + i\hbar e^{i\phi} \left( \cot(\theta) \partial_\phi - \frac{1}{\sin(\theta)} \partial_\psi + i\partial_\theta \right), \tag{3.1.18}
\]

\[
\hat{L}_- = \hat{L}_y - i\hbar e^{-i\phi} \left( \cot(\theta) \partial_\phi - \frac{1}{\sin(\theta)} \partial_\psi - i\partial_\theta \right). \tag{3.1.19}
\]
The squared angular momentum operator $\hat{L}^2$ is a scalar conserved quantity, depending on the underlying eigenfunction and eigenvalue and it is equivalent to $L^2$. This is readily understood since there is no distinguished frame for the three-body problem and a scalar conserved quantity is invariant for any chosen frame. Of course the scalar product of $\hat{L}$ with itself returns the value for $\hat{L}$ but there is an equivalent operation for this in terms of the raising and lowering operators $\hat{L}_+$ and $\hat{L}_-$,

$$\hat{L}^2 = L^2 = \hat{L}_+^2 + \hat{L}_-^2 + \hat{L}_z^2 = \frac{1}{2}(\hat{L}_+ \hat{L}_- + \hat{L}_- \hat{L}_+) + \hat{L}_z^2. \quad (3.1.20)$$

The calculation of $\hat{L}^2$ in spherical coordinates $R, \theta, \phi$ and cylindrical coordinates $\rho, \zeta$ and $\psi$ leads to

$$\hat{L}^2 = \hbar^2\left(2 \cot(\theta) \csc(\theta) \partial^2_{\psi\psi} - \csc^2(\theta) \partial^2_\phi - \sin(\theta) \partial \theta - \partial^2_\theta\right). \quad (3.1.21)$$

The squared angular momentum, the ladder operators and the z-component of $\hat{L}'$ can now be substituted into the Hamiltonian part for the kinetic contribution $\hat{T}_L$ in equation (2.3.9). The following two combinations of $\hat{L}_+$ and $\hat{L}_-$ display the necessary terms for $\hat{T}_L$

$$\hat{L}'_+ - \hat{L}'_- = 2 \cos(\psi) \partial_\theta - 2 \cot(\theta) \sin(\psi) \partial_\phi + 2 \csc(\theta) \sin(\psi) \partial_\phi. \quad (3.1.22)$$

$$(\hat{L}'_+ + \hat{L}'_-)\hat{L}'_z + \hat{L}'_z(\hat{L}'_+ + \hat{L}'_-) = A_1 \partial_\psi + A_2 \partial_\phi + A_3 \partial_\theta + A_4 \partial^2_\psi + A_5 \partial^2_\phi + A_6 \partial_\phi^2. \quad (3.1.23)$$

Comparing equation (2.3.9) with $\hat{L}^2$ and equations (3.1.22), (3.1.23) leads to a new expression for $\hat{T}_L$,

$$\hat{T}_L = \frac{1}{2m_1} \left[ \frac{\hat{L}^2}{R^2} + \left( \frac{\rho}{R^2} \partial_\rho - \frac{\zeta}{R^2} \partial_\rho - \frac{\zeta}{2\rho R} + \frac{1}{4\rho R} + \frac{1}{2R} \partial_\rho \right)(\hat{L}'_+ - \hat{L}'_-) \right. \right.$$  

$$+ \left( \frac{2\rho R}{R^2} - \frac{1}{4\rho R} \right)(\hat{L}'_+ + \hat{L}'_-)(\hat{L}'_+ + \hat{L}'_-) \left. \right) \right.$$  

$$+ \left( \frac{\zeta^2}{\rho^2 R^2} - \frac{1}{R^2} + \frac{1}{4\rho^2} - \frac{\zeta}{2\rho R} \right) \hat{L}'_z^2 \right]$$  

$$+ \frac{1}{2m_2} \left[ \frac{\hat{L}^2}{R^2} + \left( \frac{\rho}{R^2} \partial_\rho - \frac{\zeta}{R^2} \partial_\rho - \frac{\zeta}{2\rho R} \right)(\hat{L}'_+ - \hat{L}'_-) \right.$$  

$$+ \left( \frac{2\rho R}{R^2} + \frac{1}{4\rho R} \right)(\hat{L}'_+ + \hat{L}'_-)(\hat{L}'_+ + \hat{L}'_-) \left. \right) \right.$$  

$$+ \left( \frac{\zeta^2}{\rho^2 R^2} - \frac{1}{R^2} + \frac{1}{4\rho^2} + \frac{\zeta}{2\rho R} \right) \hat{L}'_z^2 \right]$$  

$$+ \frac{1}{2m_3} \frac{1}{\rho^2} \hat{L}'_z^2. \quad (3.1.25)$$

With the operators $\hat{L}'_+$, $\hat{L}'_-$ and $\hat{L}'_z$ we can find the angular eigenfunctions. For this purpose we introduce the Wigner-D-matrix in the next section.
### 3.2 Wigner D-matrix

The Wigner D-matrix is from mathematical point of view a simple module or also called an irreducible representation of the $SO(3)$ group introduced by Eugene Wigner in 1927 and explicitly deduced in his book ‘Gruppentheorie und ihre Anwendungen auf die Quantenmechanik der Atomspektren’ [Wig31] from 1931. In this section we summarize the relevant aspects for the present work from chapter 15 page 153-167 of James J. Griffin’s book ‘Group Theory and its Application to the Quantum Mechanics of Atomic Spectra’ [Wig59], which is a translation of Wigner’s book into English. Wigner considered homogeneous polynomials of the $l$th degree which solve the Laplace differential equation

$$\frac{\partial^2 f(x, y, z)}{\partial x^2} + \frac{\partial^2 f(x, y, z)}{\partial y^2} + \frac{\partial^2 f(x, y, z)}{\partial z^2} = 0. \quad (3.2.1)$$

Every orthogonal transformation $R$ of the polynomial leads to one of the same degree that also satisfies (3.2.1). In this case the transformed polynomial can be obtained by a linear combination of the untransformed polynomials with coefficients denoted by $D_l^m(R)$.

Usually equation (3.2.1) is solved by transforming the Cartesian coordinates $x, y, z$ into polar coordinates $r, \theta, \phi$ and the linearly independent solutions are given by the spherical harmonics of the $l$th degree, which are for completeness given again below

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi) \quad \text{with} \quad |m| \leq l, \quad (3.2.2)$$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad (3.2.3)$$

$$\Theta_{lm}(\theta) = \sqrt{\frac{2l + 1}{2} \cdot \frac{(l - m)!}{(l + m)!}} P_l^m(\cos(\theta)). \quad (3.2.4)$$

$P_l^m(\cos(\theta))$ are the Legendre polynomials, which are defined by

$$P_l^m(x) = \frac{(-1)^m}{2^l l!} (1 - x^2)^{l-m} \frac{d^{l+m}}{dx^{l+m}}(x^2 - 1)^l. \quad (3.2.5)$$

In the next step we introduce the operator $P_R$, where $R = \{\alpha, \beta, \gamma\}$ describes the rotation about Euler angles $\alpha, \beta, \gamma$. It is defined by three consecutive rotations, first about the Z-axis through $\alpha$, second about the Y-axis through $\beta$ and finally again about the Z-axis through $\gamma$ and thus every rotation can be obtained by a two-dimensional group which is a subgroup of $D^r$. With $\beta = 0$ and $\gamma = 0$ the operator $P_{(\alpha,0,0)}$ describes only a rotation about the Z-axis which means that $\phi$ transforms to $\phi + \alpha$ and both, $r$ and $\theta$ stay invariant. $P_{(\alpha,0,0)}$ applied to $r^l Y_{lm}(\theta, \phi)$ leads to

$$P_{(\alpha,0,0)} r^l Y_{lm}(\theta, \phi) = r^l e^{i m (\phi + \alpha)} \Theta_{lm}(\theta) = e^{i m \alpha} r^l Y_{lm}(\theta, \phi). \quad (3.2.6)$$

Since there are $(2l + 1)$ spherical harmonics of degree $l$, the linear combination for the transformed polynomial is given by the sum of all allowed values for the second index of $Y_{lm}$ and this implies

$$P_{(\alpha,\beta,\gamma)} Y_{lm}(\theta, \phi) = \sum_{m' = -l}^{l} D^{(l)}((\alpha, \beta, \gamma))_{m'm} Y_{lm'}(\theta, \phi). \quad (3.2.7)$$

Comparing equation (3.2.6) with (3.2.7) gives the coefficients for a $\{\alpha, 0, 0\}$ rotation so that the following matrix elements

$$D^{(l)}((\alpha, 0, 0))_{m'm} = e^{i m \alpha} \delta_{mm'} \quad (3.2.8)$$

represent the diagonal matrix.
Using the previous considerations and the definition of the rotation operator, it is easy to see that a \(\{0,0,\gamma\}\) rotation also results in the diagonal matrix

\[
D^{(l)}(0,0,\gamma) = e^{im\gamma} \delta_{mm'}.
\]  

(3.2.10)

Finally, it is useful to consider the \(D^{(l)}(\{0,\beta,0\})\) matrix, which describes only a rotation about the Y-axis through an angle \(\beta\). In this case \(R_{(0,\beta,0)}\) acts on the coordinates \((r,\theta,0)\) and they transform to \((r,\theta+\beta,0)\).

With equation (2.5.7) the linear combination of \(r^l Y_{lm}(\theta,0)\) with coefficients \(D^{(l)}(\{0,\beta,0\})\) is equal to \(r^l Y_{lm}(\theta+\beta,0)\). For \(\theta = 0\) and \(\beta \neq 0\) all \(Y_{lm}(0,0)\) are zero, except for \(Y_{l,0}(0,0)\), but \(Y_{lm}(\beta,0)\) on the left-hand side of equation (2.5.7) is generally not zero. This means it is impossible that the \(D^{(l)}(\{0,\beta,0\})\) matrix contains no zeros.

The representation \(D^{(l)}\) is irreducible if it is not possible to find a matrix-matrix multiplication \(A \cdot B = D^{(l)}\) with the condition that neither \(A\) nor \(B\) are given by a scalar multiplication of the unity \(1\). To show this we use Schur’s lemma, and therefore we just have to show that only a constant diagonal matrix commutes with \(D^{(l)}\). The only form of a matrix that commutes with all matrices in equation (2.5.9) is a diagonal matrix. This means that a matrix commuting with all \(D^{(l)}(\{0,\beta,0\})\) has to be diagonal as well.

Considering the fact that there are no zeros in the 0-row of \(D^{(l)}(\{0,\beta,0\})\), the products in the 0-row have to satisfy the following equation

\[
D^{(l)}(\{0,\beta,0\})_m d_{ii} = d_{00} D^{(l)}(\{0,\beta,0\})_{0i},
\]  

(3.2.11)

with \(d\) being a diagonal matrix with elements \(d_{ii} \delta_{ij}\). The previous equation just holds if \(d_{00} = d_{ii}\) and \(D^{(l)}(\{0,\beta,0\})\) only commutes with constant diagonal matrices.

The whole three-dimensional rotation group is based on a combination of \(D^{(l)}\) with \(l = 0, 1, 2, 3, \ldots\), where \(D^{(0)}\) is defined as the identity representation and the numbers \(A_0, A_1, A_2 \ldots\) count each displayed \(D^{(0)}, D^{(1)}, D^{(2)} \ldots\) in this combination. The value of the \(A_i\)’s is uniquely determined. We count the number of one type of a two-dimensional rotation representation. If such a representation, e.g. \(e^{im\gamma}\), appears \(a_m\) times to get the given combined three-dimensional rotation group, the amount of \(a_m\) is given by

\[
a_m = A_m + A_{m+1} + \cdots + A_l.
\]  

(3.2.12)

It is clear, that \(A_m\) is given by \(A_m = a_m - a_{m+1}\). Generally, the rotation \(P_{\{\alpha,\beta,\gamma\}}\) can be obtained by the product \(P_{\{\alpha,0,0\}} P_{\{0,\beta,0\}} P_{\{0,0,\gamma\}}\) and this leads to

\[
D^{(l)}(\{\alpha,\beta,\gamma\}) = D^{(l)}(\{0,0,0\}) D^{(l)}(\{0,\beta,0\}) D^{(l)}(\{0,0,\gamma\}).
\]  

(3.2.13)

By expressing \(D^{(l)}(\{\alpha,0,0\})\) and \(D^{(l)}(\{0,0,\gamma\})\) with equations (3.2.8) and (3.2.10) the matrix \(D^{(l)}(\{\alpha,\beta,\gamma\})\) is complete, if the matrices \(D^{(l)}(\{0,\beta,0\})\) representing rotations about the Y-axis are also known. For the next step we will write \(D^{(l)}(\{0,\beta,0\})\)

\[
D^{(l)}(\{0,\beta,0\}) = \delta_{mm'} D^{(l)}(\beta).
\]  

(3.2.14)
which are also called the small Wigner-D-matrices. For the purpose of determining \( d^{(l)}(\beta)_{m'm} \) it is useful to look at some properties of the matrices.

(a) It is quite clear, that a real-valued matrix, multiplied by a real-valued vector results in a real-valued vector.

(b) Next, considering a matrix denoted by \( G \) which satisfies \( \langle \vec{a}|\vec{b}\rangle = \langle G\vec{a}|G\vec{b}\rangle \) for arbitrary real-valued vectors \( \vec{a} \) and \( \vec{b} \), it can be shown, that \( G \) must be complex orthogonal. Additionally, this kind of matrix applied to an arbitrary vector \( \vec{v} \) keeps its length invariant. For \( \vec{v} = \vec{a} + \vec{b} \) the condition for complex orthogonality is given by

\[ \langle \vec{v}|\vec{v}\rangle = (G\vec{v}|G\vec{v}) \quad (3.2.15) \]

Substituting \( \vec{v} = \vec{a} + \vec{b} \) and using \( \langle \vec{a}|\vec{b}\rangle = (\vec{b}|\vec{a}) \), the scalar product written in expanded form is

\[ \langle \vec{a} + \vec{b}|\vec{a} + \vec{b}\rangle = \langle \vec{a}|\vec{a}\rangle + \langle \vec{b}|\vec{b}\rangle + 2 \langle \vec{a}|\vec{b}\rangle = \langle G\vec{a}|G\vec{a}\rangle + \langle G\vec{b}|G\vec{b}\rangle + 2 \langle G\vec{a}|G\vec{b}\rangle \quad (3.2.16) \]

This means that the following three equations must be satisfied

\[ \langle \vec{a}|\vec{a}\rangle = (G\vec{a}|G\vec{a}) \quad \langle \vec{b}|\vec{b}\rangle = (G\vec{b}|G\vec{b}) \quad \langle \vec{a}|\vec{b}\rangle = (G\vec{a}|G\vec{b}) \quad (3.2.17) \]

and \( G \) is complex orthogonal and it can also be shown that \( G \) is unitary.

(c) The last property is valid for unitary two-dimensional matrices

\[ U = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \quad (3.2.18) \]

with determinant +1. The unitary condition \( UU^{\dagger} = 1 \) implies that \( aa^* + bb^* = 1 \) and \( cc^* + dd^* = 1 \) for the diagonal elements and \( ca^* + db^* = 0 \) and \( cc^* + db^* = 0 \) for the off-diagonal elements of \( UU^{\dagger} \). If we demand \( aa^* + bb^* = |a|^2 + |b|^2 = 1 \), all remaining conditions determine the general unitary matrix with determinant +1 as

\[ U = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} \quad (3.2.19) \]

All the previous properties are necessary to get an expression for the small Wigner-D-matrices. Another useful set of matrices are the three Pauli matrices

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad (3.2.20) \]

It can be shown that every two-dimensional matrix \( h \) with trace equal zero can be written as a linear combination of these three Pauli matrices with coefficients \( \alpha, \beta, \gamma \in \mathbb{R} \). For the matrix \( h \), it is easy to see that \( h_{12} + h_{21} = 2x \), \( h_{12} - h_{21} = 2iy \) and \( h_{22} = -h_{11} = z \). The matrix \( h \) is Hermitian, if the coefficients \( x, y, z \) are real.

A transformation of the matrix \( h \) with an unitary matrix \( U \) with determinant +1 has also trace zero. Since the trace remains invariant for every unitary transformation, the matrix \( h' \) can be written as a linear combination of Pauli matrices with different coefficients \( x', y', z' \)

\[ h' = UhU^{\dagger} = x'\sigma_x + y'\sigma_y + z'\sigma_z \quad (3.2.21) \]

\[ \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} \begin{pmatrix} -z & x + iy \\ x - iy & z \end{pmatrix} \begin{pmatrix} a^* & -b \\ b^* & a \end{pmatrix} = \begin{pmatrix} -z' & x' + iy' \\ x' - iy' & z' \end{pmatrix} \quad (3.2.22) \]

Solving the system of equations in (3.2.22) gives an expression for \( x', y', z' \) as linear functions of \( x, y, z \)
\[ x' = \frac{1}{2}(a^2 + a^* b^2 - b^2 - b^* a^2) x + \frac{1}{2}i(a^2 - a^* b^2 + b^2 - b^* a^2) y + (a^* b + ab) z. \]

\[ y' = \frac{1}{2}i(a^2 - a^* + b^2 - b^* a^2) x + \frac{1}{2}(a^2 + a^* + b^2 + b^* a^2) y + i(a^* b + ab) z, \quad (3.2.23) \]

\[ z' = -(a^* b + ab) x + i(a^* b - ab) y + (a a^* - b b^*) z. \]

Equation (3.2.23) can also be expressed by a matrix vector multiplication with

\[
\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \mathbf{R}_U \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \quad (3.2.24)
\]

Regarding the properties of \( U \) and (a), (b) and (c), the next step is to construct \( \mathbf{R}_U \) explicitly. Because of the multiplication rule \( \det(AB) = \det(A)\det(B) \) and \( \det(U) = 1 \) both \( h \) and the transformed \( h' \) must have the same value for their determinant and we have the condition

\[ x^2 + y^2 + z^2 = x'^2 + y'^2 + z'^2, \quad (3.2.25) \]

which means the matrix \( \mathbf{R}_U \) must be complex orthogonal according to (b). If \( h \) is Hermitian the same is true for \( h' \) and an arbitrary vector of \((x,y,z)\) transforms to a real vector \((x',y',z')\) thus \( \mathbf{R}_U \) satisfies the conditions for a rotation.

Now we assume three unitary matrices \( U_1, U_2, U_3 \), each depending on one of the variables \( \alpha, \beta, \gamma \). First we start with \( U_1(\alpha) \) with \( a = e^{\frac{1}{2}i\alpha} \) and obtain using the power series of the e-function

\[ U_1(\alpha) = e^{\frac{1}{2}i\sigma_z} = \begin{pmatrix} e^{-\frac{1}{2}i\alpha} & 0 \\ 0 & e^{\frac{1}{2}i\alpha} \end{pmatrix} \quad (3.2.26) \]

with the corresponding rotation matrix

\[ R_{U_1}(\alpha) = \begin{pmatrix} \cos(\alpha) & \sin(\alpha) & 0 \\ -\sin(\alpha) & \cos(\alpha) & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (3.2.27) \]

For the second unitary matrix we assume that

\[ U_2(\beta) = e^{\frac{1}{2}i\sigma_y} = \begin{pmatrix} \cos(\frac{1}{2}\beta) & -\sin(\frac{1}{2}\beta) \\ \sin(\frac{1}{2}\beta) & \cos(\frac{1}{2}\beta) \end{pmatrix}, \quad (3.2.28) \]

which results in the rotation matrix

\[ R_{U_2}(\beta) = \begin{pmatrix} \cos(\beta) & 0 & \sin(\beta) \\ 0 & 1 & 0 \\ -\sin(\beta) & 0 & \cos(\beta) \end{pmatrix}. \quad (3.2.29) \]

For the last unitary matrix we take \( U_1 \) and substitute \( \alpha \) with \( \gamma \), so that \( U_3(\gamma) = U_1(\gamma) \) and \( R_{U_3}(\gamma) = R_{U_1}(\gamma) \).

We continue by defining a homogeneous polynomial \( f^{(l)}_m(a) \) for the two-dimensional vector \( v = (v_1, v_2)^T \) which takes the form

\[ f^{(l)}_m(v) := \frac{(v_1)^{l+m}(v_2)^{l-m}}{\sqrt{(l+m)! (l-m)!}} \quad (3.2.30) \]

with
The previous equation (3.2.35) can be rearranged to

\[
(\mathbf{f}_m^{(l)}) U f_m^{(l)}(\mathbf{v}) = \sum_{p=0}^{l+m-l-m} (-1)^p \frac{\sqrt{(l+m)!(l-m)!}}{p!(l+m-p)!(l-m-p)!} a_p^1 a^{l+m-p} b_p b^{l-m-p} v_1^{2l-p-p'} v_2^{p+p'}.
\]  

Using the binomial theorem Equation (3.2.33) can be expressed

\[
\left( f_m^{(l)} \right)_U f_m^{(l)}(\mathbf{v}) = \sum_{m'} (-1)^p \frac{\sqrt{(l+m)!(l-m)!}}{p!(l-m')!(l-m'-p)!(l+m'-p)!} a_{m'}^1 a^{l+m-p} b_{m'} b^{l-m-p} v_1^{2l-p-p'} v_2^{p+p'}.
\]

If we substitute \(m' = l - m - p'\) and compare equation (3.2.34) with (3.2.30) we obtain

\[
\left( f_m^{(l)} \right)_U f_m^{(l)}(\mathbf{v}) = \sum_{m'} (-1)^p \frac{\sqrt{(l+m)!(l-m)!}}{p!(l-m')!(l-m'-p)!(l+m'-p)!} a_{m'}^1 a^{l+m-p} b_{m'} b^{l-m-p} v_1^{2l-p-p'} v_2^{p+p'}.
\]

The previous equation (3.2.35) can be rearranged to

\[
\left( f_m^{(l)} \right)_U f_m^{(l)}(\mathbf{v}) = \sum_{m'} \sum_p (-1)^p \frac{\sqrt{(l+m)!(l-m)!}}{p!(l-m')!(l-m'-p)!(l+m'-p)!} a_{m'}^1 a^{l+m-p} b_{m'} b^{l-m-p} v_1^{2l-p-p'} v_2^{p+p'}.
\]

Since we want to determine \(d_{m'm'}(\beta)\) in equation (3.2.14), we use the unitary matrix \(U_2(\beta)\), which corresponds to a rotation about the angle \(\beta\) around the Y-axis, the final result for \(d_{m'm'}(\beta)\) yields

\[
d_{m'm'}(\beta) = d_{m'm'}(\cos(\frac{1}{2} \beta), -\sin(\frac{1}{2} \beta)) = Q(l, m', m) \left( \cos(\sin(\beta/2))^2 \right)^{m-m-2p} (\sin(\beta/2))^{m-m+2p} \]

with

\[
Q(l, m', m) = \sum_p (-1)^p \frac{\sqrt{(l+m)!(l-m)!(l+m')!(l-m')!}}{p!(l+m-p)!(l-m'-p)!(l+m'-p)!}.
\]

Referring to equations (3.2.13), (3.2.8), (3.2.8) and (3.2.37), we obtain the final expression for the Wigner-D-matrix which is equivalent to the result of Wigner in [Wig31]

\[
D^{(l)}(\{\alpha, \beta, \gamma\}) = e^{i\alpha^1} e^{i\beta^1} e^{i\gamma^1}.
\]

Finally, for polynomials, which satisfy equation (3.2.1), we can transform those polynomials by a linear combination with the Wigner-D-matrices as coefficients. The new polynomials after this transformation still satisfy equation (3.2.1).

### 3.3 Parity

The Hamiltonian of the three-body system (2.1.8) in the center of mass frame is rotationally invariant since there is no distinguished orientation of the frame. But there is another important symmetry which the Hamiltonian satisfies: the Hamiltonian turns out to be invariant under coordinate inversion, which means
\[ \hat{H}_c(\vec{r}) = \hat{H}_c(-\vec{r}), \] (3.3.1)

with \( \vec{r} = (\vec{r}_{c1}, \vec{r}_{c2}, \vec{r}_{c3}) \) and \( -\vec{r} = (-\vec{r}_{c1}, -\vec{r}_{c2}, -\vec{r}_{c3}) \).

An operator that switches the sign of all position vectors simultaneously is called parity operator \( \hat{\Pi} \). This operator is defined as

\[ \hat{\Pi} \vec{r} = -\vec{r}. \] (3.3.2)

It is easy to see that the kinetic operator \( \hat{T} \) satisfies equation (3.3.1) because of the used Laplace operator that includes a second derivative (\( \nabla_{\vec{r}_c} = \nabla_{-\vec{r}_c} \)). Referring to the potential operator \( \hat{V} \) in the Hamiltonian in (2.1.8), the dependency on the norm of the distance vectors \( \vec{r}_{ci} - \vec{r}_{cj} \) keeps \( \hat{V} \) invariant under parity symmetry. Applying this to the Schrödinger equation leads to

\[ \hat{H}_c(\vec{r}) \Psi(\vec{r}) = E \Psi(\vec{r}) \Rightarrow \hat{\Pi} \hat{H}_c(\vec{r}) \hat{\Pi} \Psi(\vec{r}) = E \hat{\Pi} \Psi(\vec{r}) \] (3.3.3)

Hence, both, \( |\Psi(\vec{r})\rangle \) and \( |\Psi(-\vec{r})\rangle \) are eigenvectors of \( \hat{H}_c(\vec{r}) \) and if both wave functions are not identical, they differ at most by a constant \( \lambda \)

\[ |\Psi(\vec{r})\rangle = \lambda |\Psi(-\vec{r})\rangle. \] (3.3.4)

To determine \( \lambda \), we apply the parity operator \( \hat{\Pi} \) to both wave functions and obtain

\[ |\Psi(-\vec{r})\rangle = \lambda |\Psi(\vec{r})\rangle \] (3.3.5)

and thus \( \lambda^2 = 1 \) or \( \lambda = \pm 1 \). In summary, this yields the parity condition of the wave function with

(\( a \)) \[ |\Psi(\vec{r})\rangle = |\Psi(-\vec{r})\rangle \] or (\( b \)) \[ |\Psi(\vec{r})\rangle = -|\Psi(-\vec{r})\rangle. \] (3.3.6)

For the case (\( a \)) that the wave function stays invariant under parity transformation it is called even whereby (\( b \)) is denoted as odd wave function. For a given a wave function \( |\Psi(\vec{r})\rangle \) that solves the Schrödinger equation it is possible to construct explicitly the two wave functions that satisfy (3.3.5) by

\[ \Psi^{(\text{even})}(\vec{r}) = \frac{\Psi(\vec{r}) + \hat{\Pi} \Psi(\vec{r})}{\sqrt{2}}, \] (3.3.7)

\[ \Psi^{(\text{odd})}(\vec{r}) = \frac{\Psi(\vec{r}) - \hat{\Pi} \Psi(\vec{r})}{\sqrt{2}}. \] (3.3.8)

The normalization is taken into account by the factor \( \sqrt{2} \) in the denominator. Since the parity operator is defined as \( \hat{\Pi}|\vec{r}\rangle = |-\vec{r}\rangle \), it is necessary to adapt the operator to the combined spherical and cylindrical coordinates \( (R, \theta, \phi, \rho, \zeta, \psi) \). The vectors \( \vec{R} \) and \( \vec{r} \) from equations (2.1.20) - (2.1.22) have to transform according to

\[ \vec{R} \xrightarrow{\hat{\Pi}} -\vec{R}, \quad \vec{r} \xrightarrow{\hat{\Pi}} -\vec{r}. \] (3.3.9)

Referring to equations (2.2.5) and (2.2.6), each coordinate transformation for the parity is given by

\[ R \xrightarrow{\hat{\Pi}} R, \quad \theta \xrightarrow{\hat{\Pi}} \pi - \theta, \quad \phi \xrightarrow{\hat{\Pi}} \pi + \phi, \] \[ \rho \xrightarrow{\hat{\Pi}} \rho, \quad \zeta \xrightarrow{\hat{\Pi}} \zeta, \quad \psi \xrightarrow{\hat{\Pi}} \pi - \psi. \] (3.3.10)

Since the parity is defined as a point reflection with respect to the origin of the frame, it is clear that \( \hat{\Pi} \) transforms only the angular coordinates \( \phi, \theta, \psi \).
3.4 Spin

Besides the parity symmetry which all wave functions have to fulfill another symmetry arises, if we consider the spins of the particles. The complete wave function in the center of mass frame is equivalent to equation (2.1.7) denoted as \( \Psi(\vec{r}_c, \vec{r}_e, s_1, s_2, s_3) \). In the case of three equivalent Bosonic particles all three particles can be in the same state. On the other hand, due to the Pauli principle it is forbidden that any Fermionic particle occupies the same spatial and spin state as any other equal Fermionic particle. Since we consider in the present work only bound states of three-body systems, it is necessary that the charge number of one particle distinguish from the other two and therefore we just have to consider the case of two identical Fermionic particles. In this special situation the contribution of the two corresponding particle spins factorize. Additionally, since we consider no spin orbital effects, we can neglect the spin contribution of the third particle and the total wave function takes the form

\[
\Psi_{2\text{id}-F}^{(2\text{id}-F)}(\vec{r}_c, \vec{r}_e, \vec{r}_c, s_1, s_2, s_3) = \Psi_{2\text{id}-F}^{(2\text{id}-F)}(\vec{r}_c, \vec{r}_e, \vec{r}_c) \chi(s_1, s_2),
\]

and \( \Psi_{2\text{id}-F} \) describes the complete wave function for two identical Fermions, where we always use the vectors \( \vec{r}_c \) and \( \vec{r}_e \) for the two identical particles. Using the Pauli principle, we know that the total wave function \( \Psi_{2\text{id}-F} \) has to be anti-symmetric by interchanging the position vectors and spin coordinates \( \vec{r}_c, s_1, \) with and \( r_c, s_2 \). Hence, one of the functions \( \Psi_{2\text{id}-F}^{(2\text{id}-F)} \) and \( \chi(s_1, s_2) \) has to be symmetric whereas the other one in the same situation has to be anti-symmetric. A symmetric spatial wave function \( \Psi_{2\text{id}-F} \) with anti-symmetric spin function \( \chi(s_1, s_2) \) is called a singlet state. On the other hand, an anti-symmetric spatial wave function \( \Psi_{2\text{id}-F} \) and symmetric spin function \( \chi(s_1, s_2) \) is called a triplet state, if the spin function \( \chi(s_1, s_2) \) is symmetric and the spatial part of the wave function \( \Psi_{2\text{id}-F} \) is anti-symmetric. We can determine all three particle position vectors \( \vec{r}_c, \vec{r}_e \) and \( \vec{r}_c \) in the center of mass frame by \( \vec{R} \) and \( \vec{r} \). Therefore, if particles 1 and 2 are identical Fermions, the expression of the position vectors in (2.2.11) and (2.2.12) with masses \( m_1 = m_2 \) determines the permutation by transforming \( \vec{R} \) to \( (-\vec{R}) \). Thus the permutation operator \( P_{12} \) for particles 1 and 2 is defined as

\[
\vec{R} \xrightarrow{P_{12}} -\vec{R}, \quad \vec{r} \xrightarrow{P_{12}} -\vec{r}.
\]

Hence the adaption into combined spherical and cylindrical coordinates is

\[
R \xrightarrow{P_{12}} R, \quad \theta \xrightarrow{P_{12}} \pi - \theta, \quad \phi \xrightarrow{P_{12}} \pi + \phi,
\]

\[
\rho \xrightarrow{P_{12}} \rho, \quad \zeta \xrightarrow{P_{12}} -\zeta, \quad \psi \xrightarrow{P_{12}} 2\pi - \psi.
\]

Using the perimetric coordinates \( x, y, z \) instead of \( R, \rho, \zeta \), the transformation of \( x, y, \) and \( z \) by \( \hat{P}_{12} \) is given with the relation (2.4.11) for \( \zeta \) by

\[
x \xrightarrow{\hat{P}_{12}} y, \quad y \xrightarrow{\hat{P}_{12}} x, \quad z \xrightarrow{\hat{P}_{12}} z.
\]

Similarly to the case of parity, the symmetry or antisymmetry can be obtained from solutions \( \Psi(\vec{R}, \vec{r}) \) of the the Schrödinger equation according to

\[
\Psi^{(\text{sym})}(\vec{R}, \vec{r}) = \frac{\Psi(\vec{R}, \vec{r}) + P_{12} \Psi(\vec{R}, \vec{r})}{\sqrt{2}},
\]

\[
\Psi^{(\text{a-sym})}(\vec{R}, \vec{r}) = \frac{\Psi(\vec{R}, \vec{r}) - P_{12} \Psi(\vec{R}, \vec{r})}{\sqrt{2}}.
\]

As before, \( \frac{1}{\sqrt{2}} \) is a normalization factor. The wave function \( \Psi^{(\text{sym})}(\vec{R}, \vec{r}) \) is symmetric and \( \Psi^{(\text{a-sym})}(\vec{R}, \vec{r}) \) antisymmetric in space for interchanging the spatial coordinates of particle 1 and 2.
Chapter 4

Wave functions and matrix elements of the Hamiltonian

4.1 Wave function ansatz

According to section 3.2, the wave function for the three-body problem with the discussed rotation symmetries can be constructed by linear combinations as shown in equation (3.2.7). The whole ansatz of the wave function is then

$$
\Psi_{l,m}(\nu) = N_{l,m} \sum_{k=-l}^{l} D_{l,m,k}(\phi, \theta, \psi) \tilde{\Phi}_{k}(R, \rho, \zeta) \tag{4.1.1}
$$

with the Wigner-D-matrices $D_{l,m,k}(\phi, \theta, \psi)$ given in equation (3.2.39). The matrix elements $D_{l,m,k}(\phi, \theta, \psi)$ are the only part depending on the Euler angles $\phi, \theta$ and $\psi$, multiplied by a term $\tilde{\Phi}_{k}(R, \rho, \zeta)$. The function $\tilde{\Phi}_{k}(R, \rho, \zeta)$ with an internal quantum number $\nu$ will later be expressed in perimetric coordinates. The factor $N_{l,m}$ is necessary to normalize the wave function and hence its scalar product over the whole 3D space is equal to one. The scalar product of the wave function $\Psi$ with transformed volume element $R^2 \rho$ given by the left determinant in (2.3.3) and referring to the limits of each coordinate in (2.2.7) and (2.2.8) is given in terms of the following integrals

$$
\langle \Psi_{l,m}(\nu) | \Psi_{l,m}(\nu) \rangle = \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} \int_{-\infty}^{\infty} R^2 \rho \sin(\theta) \left| N_{l,m} \sum_{k=-l}^{l} D_{l,m,k}(\phi, \theta, \psi) \tilde{\Phi}_{k}(R, \rho, \zeta) \right|^2 d\phi d\theta d\psi dR d\rho d\zeta. \tag{4.1.2}
$$

The absolute value term including the sum can be written with a double sum as

$$
(\Psi_{l,m}(\nu))^2 = (N_{l,m})^2 \sum_{k=-l}^{l} \sum_{r=-l}^{l} D_{l,m,r}^{*}(\phi, \theta, \psi) D_{l,m,k}(\phi, \theta, \psi) \tilde{\Phi}_{r}(R, \rho, \zeta) \tilde{\Phi}_{k}(R, \rho, \zeta), \tag{4.1.3}
$$

where * denotes the complex conjugate of the matrix. The Wigner-D-matrices $D_{l,m,r}^{*}(\phi, \theta, \psi) D_{l,m,k}(\phi, \theta, \psi)$ are orthonormal to each other. This fact simplifies the condition for $N_{l,m}$. Since the functions $\tilde{\Phi}_{r}(R, \rho, \zeta)$ are normalized for every $k$, we arrive at

$$
\langle \tilde{\Phi}_{k}(\nu) | \tilde{\Phi}_{k}(\nu) \rangle = \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} \int_{-\infty}^{\infty} R^2 \rho \tilde{\Phi}_{r}(R, \rho, \zeta) \tilde{\Phi}_{k}(R, \rho, \zeta) dR d\rho d\zeta = 1. \tag{4.1.4}
$$
Hence, the condition for the factor \( N_{l,m} \) to normalize the whole wave function \( \Psi_{l,m}^{(v)} \) is given by

\[
(N_{l,m})^2 \sum_{k=-l}^{l} \int_0^{2\pi} \int_0^{2\pi} \sin(\theta) D_{m,k}^l(\phi, \theta, \psi) D_{m,k}^l(\phi, \theta, \psi) \, d\phi d\theta d\psi = 1. \tag{4.1.5}
\]

The angular quantum number \( l \), and the magnetic quantum number \( m \), are characterizing the wave function. The magnitude of the total angular momentum of the three-body system can be described by \( l \) through the relation \( L^2 = h^2(l + 1) \). The projection of \( \vec{L} \) onto the Z-axis of the body-fixed frame is given by \( \vec{L}_z = m\hbar \). Since we used \( \vec{L}' \) in expression (3.1.25) for \( \hat{T}_L \), \( m\hbar \) describes the projection of \( \vec{L}' \) onto the Z-axis of the body-fixed frame.

The function \( \Phi_k^{(v)}(R, \rho, \zeta) \) will be calculated later numerically by expanding it in a polynomial basis set. These polynomials have to satisfy the boundary conditions for the given physical problem. The purpose of our calculations is to find bound states for the three-body problem and hence it is necessary to make the assumption that the wave function value vanishes if \( R, \rho \) and \( |\zeta| \) go to infinity. If we substitute

\[
\Phi_k^{(v)}(R, \rho, \zeta) = \Phi_k^{(v)}(x, y, z),
\]

the same condition is given by

\[
\lim_{x,y,z \to \infty} \Phi_k^{(v)}(x, y, z) = 0, \forall k. \tag{4.1.7}
\]

In the next two sections we construct the wave functions for S-states and P-states with \( m \) equal to zero.

We also consider the matrix elements \( \langle \Psi_{l,m}^{(v)} | \hat{H}_e | \Psi_{l',m'}^{(v)} \rangle \) by integrating first over all angular coordinates. The matrix elements in combined spherical and cylindrical coordinates are defined in equation (2.3.15).

The angular dependence of the \( \Psi_{l,m} \) stays invariant if we apply the operators \( \hat{T} \) and \( \hat{V} \) to them, but some operations of \( \hat{T}_L \) transform the angular functions of \( |\Psi_{l,m}^{(v)}\rangle \) to a form, which is orthogonal to those of \( \langle \Psi_{l,m}^{(v)} | \). Therefore we can reduce \( \hat{T}_L \) by dropping all terms that lead to an orthogonal state of \( \langle \Psi_{l,m}^{(v)} | \). Consequently, we introduce a reduced operator \( \hat{H} \) of the entire \( \hat{H}_e \) satisfying the following condition

\[
\langle \Psi_{l,m}^{(v)} | \hat{H} | \Psi_{l',m'}^{(v)} \rangle = \langle \Psi_{l,m}^{(v)} | \hat{H}_e | \Psi_{l,m}^{(v)} \rangle. \tag{4.1.8}
\]

As a final step, we transform the remaining expression into perimetric coordinates.

### 4.2 S-states

The total angular momentum in the S-state is by definition zero. Consequently, \( l \) is equal to zero and the Wigner-D-matrix becomes \( D_{0,0}^0 = 1 \). Together with equation (4.1.1) the ansatz of the wave function becomes relatively simple

\[
\Psi_{0,0}^{(v)} = N_{0,0} \Phi^{(v)}(R, \rho, \zeta), \tag{4.2.1}
\]

with the norm factor \( N_{0,0} \), which we get by equation (4.1.5)

\[
N_{0,0} = \frac{1}{\sqrt{8\pi}}. \tag{4.2.2}
\]

The constant angular factor means, that the wave function is rotationally invariant. Automatically all properties of the wave function, i.e. symmetric or antisymmetric for two identical particles, are embedded in the function \( \Phi^{(v)}(R, \rho, \zeta) \). The function \( \Phi^{(v)}(R, \rho, \zeta) \) becomes \( \Phi^{(v)}(x, y, z) \) in the perimetric coordinates and the wave function is given by

\[
\Psi_{0,0}^{(v)} = N_{0,0} \Phi^{(v)}(x, y, z). \tag{4.2.3}
\]
To symmetrize or anti-symmetrize the wave function, we have to symmetrize or anti-symmetrize \( \Phi^{(\nu)}(x, y, z) \) which leads with equations (3.4.5) and (3.4.6) to

\[
\Phi^{(\nu)(\text{sym})}(x, y, z) = \frac{\Phi^{(\nu)}(x, y, z) + \Phi^{(\nu)}(y, x, z)}{\sqrt{2}},
\]

\[
\Phi^{(\nu)(\text{a-sym})}(x, y, z) = \frac{\Phi^{(\nu)}(x, y, z) - \Phi^{(\nu)}(y, x, z)}{\sqrt{2}}.
\]

Since the wave function does not depend on any angular coordinate, the \( \hat{T}_L \) part of the kinetic Hamiltonian vanishes and according to (4.1.8) only \( \hat{H}_S = \hat{T}_S + \hat{V} \) remains. Our goal is to find an expression for the matrix elements \( \langle \Psi^{(\nu)}_{\Omega,0} \rangle | \hat{H}_S | \Psi^{(\eta)}_{\Omega,0} \rangle \) and to this end we first consider the angular integration. Referring to equations (2.3.15) and (4.1.5), the integration over the angular coordinates is equal to one due to the normalization factor \( N_{0,0} \), and \( \langle \Psi^{(\nu)}_{\Omega,0} | \hat{H}_S | \Psi^{(\eta)}_{\Omega,0} \rangle \) reduces to \( \langle \Phi^{(\nu)} | \hat{H}_S | \Phi^{(\eta)} \rangle \), which only comprises a triple integration over \( x, y, z \). The operators \( \hat{T} \) and \( \hat{V} \) are given in perimetric coordinates in equations (2.4.20) and (2.4.21). Since the Hamiltonian \( \hat{H}_S \) includes second derivatives of the wave function, the matrix elements can be simplified as shown in the appendix (A.2.1) by using partial integration and in this case only first-order derivative operators remain. In summary, the two matrix elements \( \langle \Phi^{(\nu)} | \hat{T}_S | \Phi^{(\eta)} \rangle \) and \( \langle \Phi^{(\nu)} | \hat{V} | \Phi^{(\eta)} \rangle \) are obtained as

\[
\langle \Phi^{(\nu)} | \hat{H}_S | \Phi^{(\eta)} \rangle = \int_0^\infty \int_0^\infty \int_0^\infty \left[ T_S(\Phi^{(\nu)*}, \Phi^{(\eta)}) + V(\Phi^{(\nu)*}, \Phi^{(\eta)}) \right] \, dx \, dy \, dz,
\]

with

\[
T_S(\Phi^{(\nu)*}, \Phi^{(\eta)}) = 2\hbar^2 \left[ A_{x,y,z}^m + B_{x,z}^m + B_{y,z}^m \right] \partial_x \Phi^{(\nu)*}(x, y, z) \partial_x \Phi^{(\eta)}(x, y, z) + 2\hbar^2 \left[ A_{x,y,z}^m + B_{y,z}^m + B_{x,z}^m \right] \partial_y \Phi^{(\nu)*}(x, y, z) \partial_y \Phi^{(\eta)}(x, y, z) + 2\hbar^2 \left[ A_{x,y,z}^m + B_{y,z}^m + B_{x,z}^m \right] \partial_z \Phi^{(\nu)*}(x, y, z) \partial_z \Phi^{(\eta)}(x, y, z) - 2\hbar^2 B_{x,y,z}^m \left[ \partial_y \Phi^{(\nu)*}(x, y, z) \partial_y \Phi^{(\eta)}(x, y, z) + \partial_z \Phi^{(\nu)*}(x, y, z) \partial_z \Phi^{(\eta)}(x, y, z) \right] - 2\hbar^2 B_{y,x,z}^m \left[ \partial_x \Phi^{(\nu)*}(x, y, z) \partial_x \Phi^{(\eta)}(x, y, z) + \partial_y \Phi^{(\nu)*}(x, y, z) \partial_y \Phi^{(\eta)}(x, y, z) \right] - 2\hbar^2 B_{z,x,y}^m \left[ \partial_x \Phi^{(\nu)*}(x, y, z) \partial_x \Phi^{(\eta)}(x, y, z) + \partial_y \Phi^{(\nu)*}(x, y, z) \partial_y \Phi^{(\eta)}(x, y, z) \right],
\]

\[
A_{x,y,z}^m = \frac{x(y+z)(x+y+z)}{m},
\]

\[
B_{x,y}^m = \frac{xy(x+y)}{m},
\]

and

\[
V(\Phi^{(\nu)*}, \Phi^{(\eta)}) = 2\varepsilon^2 \left[ (x+z)(y+z)Z_1Z_2 + (x+y)(x+z)Z_1Z_3 + (x+y)(y+z)Z_2Z_3 \right] \Phi^{(\nu)*} \Phi^{(\eta)}.
\]

The matrix elements which we obtain in this way are equal to the results of [HB01] and [HB99]. In Hesse’s and Baye’s paper from 1999 they just considered two identical Fermions for the spin singlet \( s \)-states. Thus, the spatial part of the wave function has to be symmetric. For this case \( \Phi^{(\nu)} \) is substituted by \( \Phi^{(\nu)(\text{sym})} \) from equation (4.2.4). If we use \( \Phi^{(\nu)(\text{a-sym})} \) in equation (4.2.5), we obtain the spin triplet \( S \)-states for two identical Fermions. In chapter 5, we show how to expand the functions \( \Phi^{(\nu)}(x, y, z) \), \( \Phi^{(\nu)(\text{sym})}(x, y, z) \) and \( \Phi^{(\nu)(\text{a-sym})}(x, y, z) \) by the Lagrange mesh method and continue to consider the matrix elements of the Hamiltonian. In the next section we adapt the previous steps to arrive at the wave functions and matrix elements for the \( P \)-states.
4.3 P-states

The P-state is defined by the eigenvalue of the total angular momentum \( l(l + 1) \) with \( l = 1 \). The sum over all possible magnetic numbers \( m = \{-1, 0, 1\} \) gives the wave function ansatz (4.1.1) in terms of the Wigner-D-matrices

\[
\Psi_{1,0}^{(\nu)} = N_{1,0} \left[ \frac{1}{\sqrt{2}} \sin(\theta) e^{i\psi} \tilde{\Phi}_{-1}^{(\nu)}(R, \rho, \zeta) + \cos(\theta) \tilde{\Phi}_{0}^{(\nu)}(R, \rho, \zeta) - \frac{1}{\sqrt{2}} \sin(\theta) e^{-i\psi} \tilde{\Phi}_{1}^{(\nu)}(R, \rho, \zeta) \right]. \tag{4.3.1}
\]

According to equation (4.1.4) each of the appearing integrals returns \( \frac{\pi}{2} \), since we sum over \( k = \{-1, 0, 1\} \) and the norm factor is identical to the case of the S-state

\[
N_{1,0} = \frac{1}{\sqrt{8\pi}}. \tag{4.3.2}
\]

The previous ansatz of the wave function is neither even nor odd under parity transformation, therefore we use equation (3.3.7) and (3.3.7) to construct even and odd wave functions and afterwards look at each case separately.

4.3.1 Even wave functions

The result for the even wave function with (3.3.7) and ansatz (4.3.1) is given by

\[
\Psi_{1,0}^{(\nu)(\text{even})} = -i N_{1,0} \sin(\theta) \sin(\psi) \left( \tilde{\Phi}_{-1}^{(\nu)}(R, \rho, \zeta) + \tilde{\Phi}_{1}^{(\nu)}(R, \rho, \zeta) \right). \tag{4.3.3}
\]

This expression is complex-valued. But since the factor \( i \) is just a constant phase factor of the wave function, the following equation holds

\[
\langle i\varphi | \hat{O} | i\varphi \rangle = \langle \varphi | \hat{O} | \varphi \rangle. \tag{4.3.4}
\]

The operator \( \hat{O} \) is an arbitrary observable and \( \varphi \) is a real-valued wave function. Consequently the wave function in equation (4.3.3) can also be chosen as

\[
\Psi_{1,0}^{(\nu)(\text{even})} = N_{1,0} \sin(\theta) \sin(\psi) \left( \tilde{\Phi}_{-1}^{(\nu)}(R, \rho, \zeta) + \tilde{\Phi}_{1}^{(\nu)}(R, \rho, \zeta) \right). \tag{4.3.5}
\]

In all following considerations, we consider the real-valued wave function \( \Psi_{1,0}^{(\nu)(\text{even})} \) in equation (4.3.5). In \( \Psi_{1,0}^{(\nu)(\text{even})} \), the addition of the two \( \Phi \) terms which depend on the coordinates \( R, \rho, \zeta \) can be combined to a single function with \( \tilde{\Phi}^{(\nu)(\text{even})} = \tilde{\Phi}_{-1}^{(\nu)} + \tilde{\Phi}_{1}^{(\nu)} \) to

\[
\Psi_{1,0}^{(\nu)(\text{even})} = N_{1,0} \sin(\theta) \sin(\psi) \tilde{\Phi}^{(\nu)(\text{even})}(R, \rho, \zeta). \tag{4.3.6}
\]

With equation (3.3.7) and (3.3.8) applied to \( \Psi_{1,0}^{(\nu)(\text{even})} \), the permutation operator \( \hat{P}_{12} \) transforms \( \sin(\psi) \) to \( (-\sin(\psi)) \) and \( \tilde{\Phi}^{(\nu)}(R, \rho, \zeta) \) to \( \tilde{\Phi}^{(\nu)}(R, \rho, -\zeta) \) and keeps \( \sin(\theta) \) invariant. The symmetric wave function \( \Psi_{1,0}^{(\nu)(\text{even})(\text{sym})} \) and the antisymmetric wave function \( \Psi_{1,0}^{(\nu)(\text{even})(\text{a-sym})} \) for two identical particles 1 and 2 are now

\[
\Psi_{1,0}^{(\nu)(\text{even})(\text{sym})} = N_{1,0} \sin(\theta) \sin(\psi) \tilde{\Phi}^{(\nu)(\text{even})(\text{a-sym})}(R, \rho, \zeta), \tag{4.3.7}
\]

\[
\Psi_{1,0}^{(\nu)(\text{even})(\text{a-sym})} = N_{1,0} \sin(\theta) \sin(\psi) \tilde{\Phi}^{(\nu)(\text{even})(\text{sym})}(R, \rho, \zeta), \tag{4.3.8}
\]

with

\[
\tilde{\Phi}^{(\nu)(\text{even})(\text{sym})}(R, \rho, \zeta) = \frac{1}{\sqrt{2}} \left( \tilde{\Phi}^{(\nu)(\text{even})}(R, \rho, \zeta) + \tilde{\Phi}^{(\nu)(\text{even})}(R, \rho, -\zeta) \right). \tag{4.3.9}
\]
and

\[ \vec{\Phi}^{(\nu)(\text{even})(a-sym)}(R, \rho, \zeta) = \frac{1}{\sqrt{2}} \left( \vec{\Phi}^{(\nu)(\text{even})}(R, \rho, \zeta) - \vec{\Phi}^{(\nu)(\text{even})}(R, \rho, -\zeta) \right), \quad (4.3.10) \]

Referring to (3.4.3), (3.4.4) and (2.4.11), the two functions \( \vec{\Phi}^{(\nu)(\text{even})}(R, \rho, \zeta) \) and \( \vec{\Phi}^{(\nu)(\text{even})}(R, \rho, -\zeta) \) in perimetric coordinates are given by

\[ \vec{\Phi}^{(\nu)(\text{even})}(R, \rho, \zeta) = \Phi^{(\nu)(\text{even})}(x, y, z), \quad (4.3.11) \]

\[ \vec{\Phi}^{(\nu)(\text{even})}(R, \rho, -\zeta) = \Phi^{(\nu)(\text{even})}(y, x, z). \quad (4.3.12) \]

If we use equations (4.2.4) and (4.2.5) and replace \( \Phi^{(\nu)}(x, y, z) \) with \( \Phi^{(\nu)(\text{even})}(x, y, z) \), the complete symmetric and anti-symmetric wave functions for even parity can be written as

\[ \Psi^{(\nu)(\text{even})(\text{sym})}_{1,0} = N_{1,0} \sin(\theta) \sin(\psi) \Phi^{(\nu)(\text{even})(a-sym)}(x, y, z), \quad (4.3.13) \]

\[ \Psi^{(\nu)(\text{even})(\text{a-sym})}_{1,0} = N_{1,0} \sin(\theta) \sin(\psi) \Phi^{(\nu)(\text{even})(\text{sym})}(x, y, z). \quad (4.3.14) \]

In contrast to the S-state these wave functions depend on the orientation in space and the angular part of the Hamiltonian \( \hat{H}_L \) does not vanish any more. When we apply the operators in (3.1.15), (3.1.18) and (3.1.19) to the wave function, all terms of \( \hat{T}_L \) including \( \hat{L}_z^2 \) and \( \hat{L}^2 \) have a non-zero contribution and we find

\[ \hat{L}_z^2 \Psi^{(\nu)(\text{even})}_{1,0} = \hbar^2 N_{1,0} \sin(\theta) \sin(\psi) \tilde{\Phi}^{(\nu)(\text{even})}(R, \rho, \zeta), \quad (4.3.15) \]

\[ (\hat{L}_+ - \hat{L}_- ) \Psi^{(\nu)(\text{even})}_{1,0} = 0, \quad (4.3.16) \]

\[ (\hat{L}_+ + \hat{L}_- ) \hat{L}_+ + \hat{L}_- ) \Psi^{(\nu)(\text{even})}_{1,0} = 0. \quad (4.3.17) \]

The value of the squared angular momentum in the P-state with \( l = 1 \) is given by its eigenvalues with \( \hat{L}^2 = \hbar^2 l(l+1) = 2\hbar^2 \). Then, the \( \hat{T}_L \) operator for the even P-state with magnetic quantum number \( m = 0 \) is explicitly

\[ \hat{T}_L \Psi^{(\nu)(\text{even})}_{1,0} = \hbar^2 \left[ \frac{1}{\mu_{12} R^2} + \frac{1}{2 \mu_{12} R^2} \left( \frac{\zeta^2}{\rho^2} - 1 + \frac{R^2}{4 \rho^2} \right) - \frac{1}{2} \left( \frac{1}{m_1} - \frac{1}{m_2} \right) \frac{\zeta}{ho^2 R} + \frac{1}{2m_3 \rho^2} \right] \Psi^{(\nu)(\text{even})}_{1,0}(R, \rho, \zeta). \quad (4.3.18) \]

The previous equation is an additional contribution to the \( \hat{T}_S \) operator, so we define

\[ \hat{T}_L^{(\text{even})} = \frac{\hbar^2}{\mu_{21} R^2} + \frac{\hbar^2}{2 \mu_{21} R^2} \left( \frac{\zeta^2}{\rho^2} - 1 + \frac{R^2}{4 \rho^2} \right) - \frac{\hbar^2}{2} \left( \frac{1}{m_1} - \frac{1}{m_2} \right) \frac{\zeta}{\rho^2 R} + \frac{\hbar^2}{2m_3 \rho^2} \hat{T}_L^{(\text{even})} = \hat{T}_S + \hat{T}_L^{(\text{even})} + \hat{\Psi}. \quad (4.3.19) \]

and the reduced operator \( \hat{\mathcal{H}}_P^{(\text{even})} \) of the Hamiltonian for the even P-state which satisfies the equation (4.1.8) is

\[ \hat{\mathcal{H}}_P^{(\text{even})} = \hat{T}_S + \hat{T}_L^{(\text{even})} + \hat{\Psi}. \quad (4.3.20) \]

If we look at the denominators of the previous equation of \( \hat{T}_L \), the terms containing \( \rho R \) and \( \rho^2 R^2 \) has a singularity for the case that \( x, y, z \) are all equal to zero. Even if we take the transformed volume element in (2.4.15) into account, the integral which we calculate for the matrix elements will have a singularity. To avoid numerical problems which are caused by these singularities, a regularization is necessary and this can be obtained by a substitution of \( \Phi^{(\nu)(\text{even})}_{1,0} \) with
Consequently the regularized symmetric and anti-symmetric wave functions are given by
\[
\Phi^{(\nu)\text{even}}(R, \rho, \zeta) = \rho \mathcal{R} \Phi^{(\nu)\text{even}}(R, \rho, \zeta),
\]
(4.3.21)
Consequently the regularized symmetric and anti-symmetric wave functions are given by
\[
\Phi^{(\nu)\text{even}}(R, \rho, \zeta) = \rho \mathcal{R} \Phi^{(\nu)\text{even}}(R, \rho, \zeta),
\]
(4.3.22)
\[
\Phi^{(\nu)\text{a-sym}}(R, \rho, \zeta) = \rho \mathcal{R} \Phi^{(\nu)\text{a-sym}}(R, \rho, \zeta).
\]
(4.3.23)
After this it is necessary to express the matrix elements in perimetric coordinates for the regularized Hamiltonian with regularization factor
\[
\mathcal{R} = \rho \mathcal{R} = \frac{1}{2} \sqrt{x y z (x + y + z)}.
\]
(4.3.24)
According to the S-state matrix elements the equation
\[
\langle \Psi^{(\nu)\text{even}}_{1,0} | \mathcal{H}^{(\text{even})} | \Psi^{(\eta)\text{even}}_{1,0} \rangle = \langle \Phi^{(\nu)\text{even}} | \mathcal{H}^{(\text{even})} | \Phi^{(\eta)\text{even}} \rangle
\]
(4.3.25)
is also valid for the same reason, that the integration over the angular coordinates yields one because of the choice of \(N_{1,0}\). With \(\Phi^{(\nu)\text{even}}(R, \rho, \zeta) = \mathcal{R}(x, y, z) \Phi^{(\nu)\text{even}}(x, y, z)\), a similar calculation as for the S-states which is explicitly given in the appendix (A.2.2), leads to the matrix elements for the even wave functions in the P-states
\[
\langle \mathcal{R} \Phi^{(\nu)\text{even}}_{1,0} | \mathcal{H}^{(\text{even})}_{P} | \mathcal{R} \Phi^{(\eta)\text{even}}_{1,0} \rangle = \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} \left[ T_{S}(\Phi^{(\nu)\text{even}}^{*}, \Phi^{(\eta)\text{even}}) + V(\Phi^{(\nu)\text{even}}^{*}, \Phi^{(\eta)\text{even}}) \right] d\zeta d\eta d\zeta.
\]
(4.3.26)
So far, the only difference between the matrix elements for the S-state in (4.2.6) and those for the P-state with even wave function and \(m = 0\) is the regularization factor \(\mathcal{R}(x, y, z)\) which is multiplied by \(T(\Phi^{(\nu)*}, \Phi^{(\eta)})\) and \(V(\Phi^{(\nu)*}, \Phi^{(\eta)})\). Hesse and Baye obtained the same expression in their article from 2001 [HB01]. Similar to the case of the spin singlet and triplet S-states, we just have to substitute \(\Phi^{(\nu)\text{even}}_{1,0}\) by \(\Phi^{(\nu)\text{even}\text{a-sym}}_{1,0}\) for the singlet and by \(\Phi^{(\nu)\text{even}\text{a-sym}}_{1,0}\) for the triplet P-states and even wave functions. Consequently, we continue to apply all previous considerations to the odd wave function for P-states with magnetic number \(m\) equal to zero.

### 4.3.2 Odd wave functions
The formula (3.3.8) for constructing an odd wave function leads with the P-state ansatz (4.3.1) to
\[
\Psi^{(\nu)\text{odd}}_{1,0} = \sqrt{2} N_{1,0} \cos(\theta) \Phi^{(\nu)}_{0}(R, \rho, \zeta) - N_{1,0} \sin(\theta) \cos(\psi) \left( \Phi^{(\nu)}_{-1}(R, \rho, \zeta) - \Phi^{(\nu)}_{1}(R, \rho, \zeta) \right)
\]
(4.3.27)
and once again we can combine the two \(\Phi^{(\nu)}_{-1}\) and \(\Phi^{(\nu)}_{1}\) functions, hence \(\Phi^{(\nu)\text{odd}}_{1,0} = \Phi^{(\nu)}_{1} - \Phi^{(\nu)}_{-1}\). Additionally we also substitute \(\sqrt{2} \Phi^{(\nu)}_{0}\) with \(\Phi^{(\nu)\text{odd}}_{0}\). After that the wave function transforms to
\[
\Psi^{(\nu)\text{odd}}_{1,0} = N_{1,0} \cos(\theta) \Phi^{(\nu)\text{odd}}_{0}(R, \rho, \zeta) - N_{1,0} \sin(\theta) \cos(\psi) \Phi^{(\nu)\text{odd}}_{1}(R, \rho, \zeta).
\]
(4.3.28)
Now the angular part of the wave function does not factorize with any combination of \(\Phi^{(\nu)}_{1,0}\), \(\Phi^{(\nu)}_{0}\) or \(\Phi^{(\nu)}_{1}\). Consequently, it is necessary to introduce two \(R, \rho, \zeta\) dependent functions, namely \(\Phi^{(\nu)\text{odd}}_{0}\) and \(\Phi^{(\nu)\text{odd}}_{1}\). Symmetric and antisymmetric wave functions for two identical particles are in this case again with (3.4.5) and (3.4.6) obtained by
\[ \Psi_{1,0}^{(\nu)\text{(odd)(sym)}} = N_{1,0} \cos(\theta) \frac{1}{\sqrt{2}} \Phi_{0}^{(\nu)\text{(odd)(a-sym)}}(R, \rho, \zeta) - N_{1,0} \sin(\theta) \cos(\psi) \frac{1}{\sqrt{2}} \tilde{\Phi}_{1}^{(\nu)\text{(odd)(sym)}}(R, \rho, \zeta), \]  
(4.3.29)

\[ \Psi_{1,0}^{(\text{odd)(a-sym)}} = N_{1,0} \cos(\theta) \frac{1}{\sqrt{2}} \Phi_{0}^{(\nu)\text{(odd)(sym)}}(R, \rho, \zeta) - N_{1,0} \sin(\theta) \cos(\psi) \frac{1}{\sqrt{2}} \tilde{\Phi}_{1}^{(\nu)\text{(odd)(a-sym)}}(R, \rho, \zeta), \]  
(4.3.30)

with

\[ \Phi_{k}^{(\nu)\text{(odd)(sym)}}(R, \rho, \zeta) = \left( \Phi_{k}^{(\nu)\text{(odd)}}(R, \rho, \zeta) + \tilde{\Phi}_{k}^{(\nu)\text{(odd)}}(R, \rho, -\zeta) \right) \quad k = \{0,1\}, \]  
(4.3.31)

\[ \tilde{\Phi}_{k}^{(\nu)\text{(odd)(a-sym)}}(R, \rho, \zeta) = \left( \tilde{\Phi}_{k}^{(\nu)\text{(odd)}}(R, \rho, \zeta) - \tilde{\Phi}_{k}^{(\nu)\text{(odd)}}(R, \rho, -\zeta) \right) \quad k = \{0,1\}. \]  
(4.3.32)

Since the odd wave functions are a combination of two terms, the matrix elements of the corresponding Hamiltonian can be split into four different scalar products with

\[ \langle \Psi_{1,0}^{(\nu)\text{(odd)}} | \hat{H}_c | \Psi_{1,0}^{(\nu)\text{(odd)}} \rangle = \langle \varphi_0 | \hat{H}_c | \varphi_0 \rangle + \langle \varphi_1 | \hat{H}_c | \varphi_0 \rangle + \langle \varphi_0 | \hat{H}_c | \varphi_1 \rangle + \langle \varphi_1 | \hat{H}_c | \varphi_1 \rangle \]  
(4.3.33)

and

\[ \varphi_0 = N_{1,0} \cos(\theta) \tilde{\Phi}_{0}^{(\nu)\text{(odd)}}, \quad \varphi_1 = -N_{1,0} \sin(\theta) \cos(\psi) \tilde{\Phi}_{1}^{(\nu)\text{(odd)}}. \]  
(4.3.34)

Next, we consider each term on the right-hand side of (4.3.33) separately. The complete Hamiltonian \( \hat{H}_c \) in the center of mass frame can be written as a sum of three operators, \( \hat{H}_c = \hat{T}_S + \hat{T}_L + \hat{V} \), which we introduced in equation (2.3.8), (3.1.25) and (2.3.13). In this section we want to simplify the matrix elements of the Hamiltonian which are defined in equation (2.3.15) in combined spherical and cylindrical coordinates. Therefore we integrate over all angular coordinates \( \phi, \theta, \psi \). The only operator that has an influence on the angular functions \( \cos(\theta) \) of \( \varphi_0 \) and \( \sin(\theta) \), \( \cos(\psi) \) of \( \varphi_1 \) is \( \hat{T}_L \). The three involved operators, which are expressed in (3.1.22), (3.1.23) and (3.1.15), applied to \( \varphi_0 \) and \( \varphi_1 \) yield

\[ \hat{L}_z^2 \varphi_0 = 0, \]  
(4.3.35)

\[ (\hat{L}_+ - \hat{L}_-) \varphi_0 = 2N_{1,0} \sin(\theta) \cos(\psi) \tilde{\Phi}_{0}^{(\nu)\text{(odd)}}, \]  
(4.3.36)

\[ (\hat{L}_+ + \hat{L}_-) \hat{L}_z + \hat{L}_z (\hat{L}_+ + \hat{L}_-) \varphi_0 = 2N_{1,0} \sin(\theta) \cos(\psi) \tilde{\Phi}_{0}^{(\nu)\text{(odd)}}, \]  
(4.3.37)

and

\[ \hat{L}_z^2 \varphi_1 = -N_{1,0} \sin(\theta) \cos(\psi) \tilde{\Phi}_{1}^{(\nu)\text{(odd)}}, \]  
(4.3.38)

\[ (\hat{L}_+ - \hat{L}_-) \varphi_1 = 2N_{1,0} \cos(\theta) \tilde{\Phi}_{1}^{(\nu)\text{(odd)}}, \]  
(4.3.39)

\[ (\hat{L}_+ + \hat{L}_-) \hat{L}_z + \hat{L}_z (\hat{L}_+ + \hat{L}_-) \varphi_1 = -2N_{1,0} \cos(\theta) \tilde{\Phi}_{1}^{(\nu)\text{(odd)}}, \]  
(4.3.40)

The two functions, i.e. \( \sin(\theta) \) and \( \cos(\theta) \sin(\psi) \) are orthogonal to each other with respect to the angular volume element \( \sin(\theta) \). With these considerations we can find for each scalar product of the right-hand side of equation (4.3.33) a suitable operator \( \hat{H} \) which is satisfying equation (4.1.8) and gives an explicit and simplified expression for the matrix elements in perimetric coordinates.

If we take equations (4.3.35) - (4.3.37) and (3.1.25) into account, the first scalar product \( \langle \varphi_0 | \hat{H}_c | \varphi_0 \rangle \) is equal to \( \langle \varphi_0 | \hat{H}_{(P(0,0))}^{(\text{odd})} | \varphi_0 \rangle \) where \( \hat{H}_{(P(0,0))}^{(\text{odd})} \) can easily be written as

\[ \hat{H}_{(P(0,0))}^{(\text{odd})} = \hat{T}_S + \hat{T}_L^{(0,0)} + \hat{V}, \]  
(4.3.41)
with
\[ \hat{T}^{(0,0)}_L = \frac{\hbar^2}{\mu_{12} R^2}. \] (4.3.42)

Compared to the matrix elements for the S-states given in (4.2.6), the transformation of (4.3.41) to perimetric coordinates with \( \tilde{\Phi}_0^{(\nu)(\text{odd})} \) \( (R, \rho, \zeta) = \Phi_0^{(\nu)(\text{odd})} (x, y, z) \) leads almost to the same result as for the S-states, but with the additional \( \hat{T}^{(0,0)}_L \)-term in perimetric coordinates. Finally, we get with equations (4.2.7) and (4.2.10)
\[ \langle \Phi_0^{(\nu)(\text{odd})} | \hat{H}_P^{(0,0)} | \Phi_0^{(\eta)(\text{odd})} \rangle = \int_0^\infty \int_0^\infty \int_0^\infty \left[ T_S(\Phi_0^{(\nu)(\text{odd})}, \Phi_0^{(\eta)(\text{odd})}) + V(\Phi_0^{(\nu)(\text{odd})}, \Phi_0^{(\eta)(\text{odd})}) + \frac{4\hbar^2(y+z)(x+z)}{\mu_{12}(x+y)} \right] dx dy dz. \] (4.3.43)

In the next step we consider the last scalar product on the right-hand side, i.e. \( \langle \varphi_1 | \hat{H}_c | \varphi_1 \rangle \). The orthonormality condition implies that the scalar product stays invariant, if we simplify the operator \( \hat{T}_L \) by \( \hat{T}^{(1,1)}_L \) with
\[ \hat{T}^{(1,1)}_L = \frac{\hbar^2}{2\mu_{12} R^2} \left( \frac{\zeta^2}{\rho^2} + \frac{R^2}{4\rho^2} + 1 \right) - \frac{\hbar^2}{2} \left( \frac{1}{m_1} - \frac{1}{m_2} \right) \frac{\zeta^2}{\rho^2 R} + \frac{\hbar^2}{2m_3 \rho^2}. \] (4.3.44)

In this case \( \hat{H}_c \) in \( \langle \varphi_1 | \hat{H}_c | \varphi_1 \rangle \) can be reduced to \( \hat{H}_P^{(0,1)} = \hat{T}^{(1,1)}_L + \hat{V} \). The operator \( \hat{T}^{(1,1)}_L \) is equal to \( \hat{T}^{(\text{even})}_L \) given in equation (4.3.19) which implies that \( \hat{H}_P^{(0,1)} = \hat{H}^{(\text{even})}_P \) is also equal to equation (4.3.20). Therefore the scalar product can be written as
\[ \langle \varphi_1 | \hat{H}_c | \varphi_1 \rangle = \langle \tilde{\Phi}_1^{(\nu)(\text{odd})} | \hat{H}_P^{(0,1)} | \tilde{\Phi}_1^{(\eta)(\text{odd})} \rangle = \langle \tilde{\Phi}_1^{(\nu)(\text{odd})} | \hat{H}^{(\text{even})}_P | \tilde{\Phi}_1^{(\eta)(\text{odd})} \rangle \] (4.3.45)
and we have to use the same regularization like for the P-states and even wave functions, as explained in equation 4.3.1. We substitute \( \tilde{\Phi}_1^{(\nu)(\text{odd})} \) with
\[ \tilde{\Phi}_1^{(\nu)(\text{odd})} = \rho R \tilde{\Phi}_1^{(\nu)(\text{odd})} \] (4.3.46)
and get the same matrix elements like for the P-even states, when we express \( \rho R \tilde{\Phi}_1^{(\nu)(\text{odd})} \) in perimetric coordinates. Referring to (4.3.24) the regularization factor is \( \rho R = R(x, y, z) \) and \( \tilde{\Phi}_1^{(\nu)(\text{even})} \) \( (R, \rho, \zeta) \) becomes \( \Phi_1^{(\nu)(\text{odd})} \) \( (x, y, z) \). Compared with the matrix elements (4.3.26) for the even wave function, we obtain
\[ \langle \mathcal{R} \Phi_1^{(\nu)(\text{odd})} | \hat{T}^{(0,1)}_P | \mathcal{R} \Phi_1^{(\eta)(\text{odd})} \rangle = \int_0^\infty \int_0^\infty \int_0^\infty \left[ T_S(\Phi_1^{(\nu)(\text{odd})}, \Phi_1^{(\eta)(\text{odd})}) + V(\Phi_1^{(\nu)(\text{odd})}, \Phi_1^{(\eta)(\text{odd})}) \right] dx dy dz, \] (4.3.47)
where \( T_S(\Phi_1^{(\nu)(\text{odd})}, \Phi_1^{(\eta)(\text{odd})}) \) and \( V(\Phi_1^{(\nu)(\text{odd})}, \Phi_1^{(\eta)(\text{odd})}) \) is explicitly expressed in equations (4.2.7) and (4.2.10).

Finally, we consider the last two scalar products, i.e. \( \langle \varphi_0 | \hat{H}_c | \varphi_0 \rangle \) and \( \langle \varphi_1 | \hat{H}_c | \varphi_0 \rangle \), together in one step. According to the two previous matrix elements we obtain again two reduced operators \( \hat{H}_P^{(0,1)} \) and \( \hat{H}_P^{(0,0)} \) with
\[ \hat{H}^{\text{odd}}_P^{(0,1)} = \hat{T}^{(0,1)}_L, \] (4.3.48)
and
\[ \hat{H}^{\text{odd}}_P^{(0,0)} = \hat{T}^{(1,0)}_L. \] (4.3.49)

The right-hand side of equation (4.3.38) is orthogonal to \( \varphi_0 \) and \( \hat{T}^{(0,1)}_L \) and is given by
Taking equations \(4.3.35\) - \(4.3.37\) into account, leads to the following expression for \(\hat{T}_L^{(1,0)}\)

\[
\hat{T}_L^{(1,0)} = c_1 \left(\rho \partial_\rho - \zeta \partial_\zeta - \frac{\zeta}{\rho} + \frac{1}{2} \left(\frac{1}{m_1} - \frac{1}{m_2}\right) \frac{1}{\rho R} \left(1 + \rho \partial_\rho\right)\right).
\] (4.3.50)

The integration over all angular coordinates in equation (2.3.15) leads to

\[
\hat{T}_L^{(1,0)} = \int_0^{\pi/2} \int_0^{\pi/2} \int_0^{2\pi} \left(\zeta \partial_\zeta - \rho \partial_\rho\right) - \frac{1}{2} \left(\frac{1}{m_1} - \frac{1}{m_2}\right) \frac{1}{\rho R} \partial_\rho. \tag{4.3.51}
\]

The integration over all angular coordinates in equation (2.3.15) leads to

\[
\langle \hat{\varphi}_0 | \hat{\mathcal{H}}_{P(0,1)}^{(odd)} | \hat{\varphi}_1 \rangle = \langle \hat{\Phi}_0^{(\nu)(odd)} | \hat{\mathcal{H}}_{P(0,1)}^{(odd)} | \hat{\Phi}_1^{(\nu)(odd)} \rangle \tag{4.3.52}
\]

and

\[
\langle \hat{\varphi}_1 | \hat{\mathcal{H}}_{P(0,1)}^{(odd)} | \hat{\varphi}_0 \rangle = \langle \hat{\Phi}_1^{(\nu)(odd)} | \hat{\mathcal{H}}_{P(0,1)}^{(odd)} | \hat{\Phi}_0^{(\nu)(odd)} \rangle, \tag{4.3.53}
\]

where we substituted \(\hat{T}_c\) with \(\hat{\mathcal{H}}_{P(0,1)}^{(odd)}\) respectively \(\hat{\mathcal{H}}_{P(0,1)}^{(odd)}\) and taking into account that relation (4.1.4) is satisfied. The \(\hat{\Phi}_1^{(\nu)(odd)}\) function is again substituted by \(\rho \hat{R} \hat{\Phi}_1^{(\nu)(odd)}\) as in equation (4.3.46) and afterwards we use \(\Phi_0^{(\nu)(odd)}(x, y, z)\) and \(\Phi_1^{(\nu)(odd)}(x, y, z)\) for the representation of \(\Phi_0^{(\nu)(odd)}(R, \rho, \zeta)\) and \(\Phi_1^{(\nu)(odd)}(R, \rho, \zeta)\) in perimetric coordinates. If we split the differential operator terms which occur in the matrix elements of

\[
\langle \Phi_0^{(\nu)(odd)} | \hat{\mathcal{H}}_{P(0,1)}^{(odd)} | \Phi_1^{(\nu)(odd)} \rangle \tag{4.3.54}
\]

and

\[
\langle \hat{\mathcal{R}} \Phi_1^{(\nu)(odd)} | \hat{\mathcal{H}}_{P(0,1)}^{(odd)} | \Phi_0^{(\nu)(odd)} \rangle \tag{4.3.55}
\]

into two equal parts and integrate one of them by parts, we see that

\[
\langle \hat{\mathcal{R}} \Phi_1^{(\nu)(odd)} | \hat{\mathcal{H}}_{P(0,1)}^{(odd)} | \Phi_0^{(\nu)(odd)} \rangle = \langle \hat{\mathcal{R}} \Phi_1^{(\nu)(odd)} | \hat{\mathcal{H}}_{P(0,1)}^{(odd)} | \Phi_0^{(\nu)(odd)} \rangle. \tag{4.3.56}
\]

This calculation is given explicitly in the appendix (A.2.3). The final result for \(\langle \Phi_0^{(\nu)(odd)} | \hat{\mathcal{H}}_{P(0,1)}^{(odd)} | \Phi_1^{(\nu)(odd)} \rangle\) in perimetric coordinates is then given by

\[
\langle \Phi_0^{(\nu)(odd)} | \hat{\mathcal{H}}_{P(0,1)}^{(odd)} | \Phi_1^{(\nu)(odd)} \rangle = \int_0^\infty \int_0^\infty \int_0^\infty \left[\mathcal{D}(\Phi_0^{(\nu)(odd)}, \Phi_1^{(\nu)(odd)}) + \mathcal{E}(\Phi_0^{(\nu)(odd)}, \Phi_1^{(\nu)(odd)})\right] dx dy dz, \tag{4.3.57}
\]

\[
\mathcal{D}(\Phi_0^{(\nu)(odd)}, \Phi_1^{(\nu)(odd)}) = \left[\frac{x + z}{m_2} - \frac{y + z}{m_1}\right] \Phi_0^{(\nu)(odd)}(x, y, z) \left(\partial_x \Phi_1^{(\nu)(odd)}(x, y, z)\right) + \left[\frac{y + z}{m_2} - \frac{x + z}{m_1}\right] \Phi_1^{(\nu)(odd)}(x, y, z) \left(\partial_y \Phi_1^{(\nu)(odd)}(x, y, z)\right) \tag{4.3.58}
\]

\[
\mathcal{E}(\Phi_0^{(\nu)(odd)}, \Phi_1^{(\nu)(odd)}) = \left[\frac{y + z}{x + y} \left(\frac{xz - yz - x^2 + xy}{m_1} + \frac{y^2 - yz + x^2 + xy}{m_2}\right)\right] \Phi_0^{(\nu)(odd)}(x, y, z) \Phi_1^{(\nu)(odd)}(x, y, z) \tag{4.3.59}
\]
To conclude the consideration of the P-states and odd wave functions we summarize our results for the complete matrix elements of $\langle \Psi^{(\nu)(\text{odd})}_{1,0} | \hat{H}_c | \Psi^{(\eta)(\text{odd})}_{1,0} \rangle$. Together with the equations (4.3.33), (4.3.43), (4.3.47), and (5.3.115) we obtain

$$
\langle \Psi^{(\nu)(\text{odd})}_{1,0} | \hat{H}_c | \Psi^{(\eta)(\text{odd})}_{1,0} \rangle = \langle \Phi^{(\nu)(\text{odd})}_{0} | \hat{H}^{(\text{odd})}_{P(0,0)} | \Phi^{(\eta)(\text{odd})}_{0} \rangle + \langle \Phi^{(\nu)(\text{odd})}_{0} | \hat{H}^{(\text{odd})}_{P(0,1)} | \Phi^{(\eta)(\text{odd})}_{1} \rangle + \langle \Phi^{(\nu)(\text{odd})}_{0} | \hat{H}^{(\text{odd})}_{P(1,0)} | \Phi^{(\eta)(\text{odd})}_{0} \rangle + \langle \Phi^{(\nu)(\text{odd})}_{0} | \hat{H}^{(\text{odd})}_{P(1,1)} | \Phi^{(\eta)(\text{odd})}_{1} \rangle.
$$

(4.3.60)

The first and last terms on the right-hand side of the previous equation coincide with the result of Hesse and Baye [HB01], but the result of $\langle \Phi^{(\nu)(\text{odd})}_{0} | \hat{H}^{(\text{odd})}_{P(0,1)} | \Phi^{(\eta)(\text{odd})}_{1} \rangle$ and $\langle \Phi^{(\nu)(\text{odd})}_{0} | \hat{H}^{(\text{odd})}_{P(1,0)} | \Phi^{(\eta)(\text{odd})}_{0} \rangle$ differ by a factor 2. We have to take into account that Hesse and Baye used the regularization factor $xyz\sqrt{x+y+z}$ where they dropped the factor $\frac{1}{2}$. This factor arises from the transformation from $\rho R$ into perimetric coordinates referring to equation (4.3.24). But we obtain the same results like Hesse and Baye since the factor will be reduced in our considerations in the next chapter.
Chapter 5

Lagrange-mesh method

5.1 Principle of Lagrange-mesh method

Since it is not possible to find an analytical expression for the three-body wave function, it is worthwhile to find a quite accurate numerical approximation. In this section we introduce the Lagrange-mesh method, according to Baye’s and Heenen’s article [BH86]. The basic idea of the Lagrange-mesh method is based on an expansion of the wave function in terms of a linear combination of \( N \) continuous functions \( g_i(u) \) called Lagrange functions

\[
\Psi(u) \approx \sum_{i=1}^{N} \Psi(u_i) g_i(u),
\]

which assumes that we know the wave function values \( \Psi(u_i) \) for \( N \) certain sampling points \( u_i \). The Lagrange functions satisfy the following two conditions

\[
g_i(u_j) = \delta_{ij},
\]

\[
\int_{a}^{b} g_i^*(u) g_j(u) \, du = \lambda_i \delta_{ij},
\]

i.e. the function value vanishes at all sampling points except one and the Lagrange functions are orthogonal to each other. The orthogonality condition (5.1.3) becomes very important to get a simple form for the scalar product of the required wave function. Calculating the scalar product of the wave function as accurately as possible is significant for the accuracy of the variational calculations, where the coefficients for the linear combination of \( g_i(u) \) are obtained. With the approximate wave function of equation (5.1.1) and the orthogonality condition in equation (5.1.3) the scalar product is given by

\[
\int_{a}^{b} \Phi^*(u) \Psi(u) \, du \approx \sum_{i=1}^{N} \lambda_i \Phi^*(u_i) \Psi(u_i).
\]

By defining \( G(u) = \Phi^*(u) \Psi(u) \), equation (5.1.4) turns into a special formula of the generalized Gauss quadrature method

\[
\int_{a}^{b} G(u) \, du \approx \sum_{i=1}^{N} \lambda_i G(u_i),
\]

and the previous approximation is exact if \( G(u) \) represents a polynomial of degree \( 2N - 1 \) or less. The \( \lambda_i \) coefficients represent the weights for the respective point \( u_i \) of the quadrature formula also known as Christoffel numbers. They are determined by the used mesh type and especially by the boundary conditions at the integration limits \( a \) and \( b \). Based on the given physical problem, fixed values for the
wave function or their derivatives at point $a$ and $b$ are required. Therefore it is helpful to construct Lagrange functions $g_i(u)$ which satisfy in addition to equations (5.1.2) and (5.1.3) also the boundary conditions. In the following, we construct a set of $N$ basis functions $\varphi_k(u)$ which satisfy the requested boundary conditions and are orthonormal on the interval $[a, b]$

\[
\langle \varphi_k | \varphi_l \rangle = \int_a^b \varphi_k^*(u) \varphi_l(u) du = \delta_{kl} .
\]

(5.1.6)

An ansatz for the Lagrange function $g_i(u)$ is now given by a linear combination of $\varphi_k(u)$ with $\varphi_k(u_i)$ at the local mesh point $u_i$ multiplied with $\lambda_i$ as associated coefficients

\[
g_i(u) = \lambda_i \sum_{k=1}^{N} \varphi_k^*(u_i) \varphi_k(u) .
\]

(5.1.7)

The scalar product of $g_i(u)$ and $g_j(u)$ substituted with expression (5.1.7) results with (5.1.6) in

\[
\int_a^b g_i^*(u) g_j(u) du = \lambda_i \lambda_j \sum_{k=1}^{N} \sum_{l=1}^{N} \varphi_k^*(u_i) \varphi_l(u_j) \int_a^b \varphi_k^*(u) \varphi_l(u) du = \lambda_i \delta_{ij} .
\]

(5.1.8)

The last equal sign with exclamation mark refers to (5.1.3) and thus we get once more a condition for $\varphi_k(u)$ given by

\[
\sum_{k=1}^{N} \varphi_k^*(u_i) \varphi_k(u_j) = \lambda_i^{-1} \delta_{ij} .
\]

(5.1.9)

Due to the fact that the left term in the previous equation has to be zero for different $i$ and $j$, the mesh points $u_i$ must satisfy $\frac{1}{2}N(N - 1)$ conditions, but equation (5.1.9) is automatically fulfilled if the matrix $A_{ik} = \lambda_i^{1/2} \varphi_k(u_i)$ is unitary. For $i$ equal $j$, the left term determines the Christoffel numbers $\lambda_i$

\[
\lambda_i = \left( \sum_{k=1}^{N} |\varphi_k(u_i)|^2 \right)^{-1} .
\]

(5.1.10)

Equation (5.1.7) can be inverted for the case that the Lagrange function and the sampling point values of the orthonormal set $\varphi_k(u)$ are already known. This inverse equation is given by

\[
\varphi_k(u) = \sum_{i=1}^{N} \varphi_k(u_i) f_i(u) .
\]

(5.1.11)

In summary, an arbitrary continuous function can be expanded, if an orthogonal basis set $\varphi_k(u)$ can be found that satisfies the boundary conditions of the original function. In the next subsection we illustrate how to expand the wave function for our three-body problem in terms of Lagrange functions.

### 5.2 Lagrange-Laguerre basis set

In equation (5.1.6) the function $\Phi(x, y, z)$ was introduced which represents the part of the wave function just depending on the perimetric coordinates. It is not possible to find analytically a function $\Phi(x, y, z)$ which solves the Schrödinger equation for the three-body Hamiltonian. Accordingly, we have to resort to a numerical expansion of the the wave function. The functions which we will construct in this section are additionally a valid basis set for the Lagrange-mesh method. The whole deduction that follows refers to [BH86]. We assume that this basis set is given by polynomials $P_k(u)$ of degree $N$ with norm factor $n_k$. These polynomials satisfy our boundary conditions and they are equal to zero for $u \to \infty$. They also have to be orthogonal on the domain $[0, \infty]$ of $u$. 
The Lagrange functions $g$ and (5.2.4), which results in consideration for the right-hand side of (5.2.2)

$$
\sum_{k=0}^{N-1} \frac{P_k(u)P_k(v)}{n_k} = \frac{k_{N-1}}{n_{N-1}k_N} \frac{P_N(u)P_{N-1}(v) - P_{N-1}(u)P_N(v)}{u - v},
$$

where $k_n$ is the coefficient of $u^n$ in $P_n(u)$. For the case that $u$ approaches $v$, we get the following limit consideration for the right-hand side of (5.2.2)

$$
\lim_{u \to v} \frac{P_N(u)P_{N-1}(v) - P_{N-1}(u)P_N(v)}{u - v} = P_{N-1}(v)P_N'(v) - P_N(v)P_{N-1}'(v).
$$

Referring to both equations, (5.2.2) and (5.2.3), the mesh condition in (5.1.9) is satisfied for the $N$ roots $(u_1, ..., u_i, ..., u_N)$ of the polynomials, with

$$
P_k(u_i) = 0.
$$

Finally, we divide $P_k(u)$ by $n_k^{1/2}$ to define $\varphi_k(u)$ which satisfies equations (5.1.6) and (5.1.9)

$$
\varphi_k(u) = n_k^{-1/2}P_k(u).
$$

With equations (5.1.10), (5.2.2), (5.2.4), and (5.2.3), the Christoffel numbers $\lambda_i$ are given by

$$
\lambda_i = \frac{k_N}{k_{N-1}} \left( \frac{n_N}{n_{N-1}} \right)^{1/2} \left( \varphi'_N(u_i)\varphi_{N-1}(u_i) \right)^{-1}.
$$

We can now construct the Lagrange functions $g_i(u)$ by using equations (5.1.7), (5.2.5), (5.2.2), (5.2.6), and (5.2.4), which results in

$$
g_i(u) = \frac{1}{u - u_i} \frac{\varphi_N(u)}{\varphi'_N(u_i)}.
$$

The Lagrange functions $g_i(u)$, which we obtain by the previous construction, are polynomials of degree $N - 1$, and therefore have $N - 1$ roots.

After the general considerations for an arbitrary polynomial $P_k(u)$, we now return to our three body problem. As mentioned before, in our case the value of the polynomials at $u = 0$ have to be equal to zero and $P_k(u)$ for $u \to \infty$ has to vanish. A valid kind of polynomials which fulfill these requirements are the Laguerre polynomials $L_k(u)$. The Laguerre polynomials are orthogonal considering a weight function $w(u) = e^{-u}$ and the norm factor $n_k$

$$
\int_{0}^{\infty} e^{-u} L_k(u)L_l(u)du = n_k \delta_{kl}.
$$

If we compare equation (5.2.8) with (5.2.1) and use the definition of $\varphi_k(u)$ we find $\tilde{\varphi}_k(u)$ which is given by

$$
\tilde{\varphi}_k(u) = n^{-1/2}e^{-u/2}L_k(u).
$$

The Laguerre polynomials and their first derivatives can be obtained by two recursion formulae [AS65]

$$
(N + 1)L_{N+1}(u) = (2N + 1 - u)L_N(u) - NL_{N-1}(u),
$$

$$
\int_{0}^{\infty} e^{-u} L_k(u)L_l(u)du = n_k \delta_{kl}.
$$
\[ uL'_{N}(u) = NL_{N}(u) - NL_{N-1}(u) \, , \]
with the initial term \( L_{1}(u) = 1 \). We substitute \( \varphi_k(u) \) in (5.2.6) and (5.2.7) with equation (5.2.9) and use the previous equations (5.2.10) and (5.2.11) for the Laguerre polynomials to find the expression for \( \lambda_i \) and \( g_i(u) \),

\[ \tilde{\lambda}_i = u_i e^{u_i} \left[ (N + 1)L_{N+1}(u_i) \right]^{-2} \, , \]

(5.2.12)

\[ \tilde{g}_i(u) = \frac{u_i}{e^{-u_i/2}(N+1)L_{N+1}(u_i)} \frac{e^{-u/2}L_{N}(u)}{u - u_i} \, . \]

(5.2.13)

Without loss of generality it is possible to orthonormalize the Lagrange functions \( g_i(u) \) and to adapt all equations in section 5.1 to the new orthonormal functions which we denote as \( f_i(u) \). It can be seen readily by equation (5.1.3) that \( f_i(u) \) is given by

\[ f_i(u) = \lambda_i^{-1/2} g_i(u) \, , \]

(5.2.14)

with the condition of orthonormalization

\[ \int_0^\infty f_i(u)f_j(u)du = \delta_{ij} \, . \]

(5.2.15)

Hence, the wave function ansatz from equation (5.1.1) expressed by the functions \( f_i(u) \) takes the form

\[ \Psi(u) \approx \sum_{i=1}^{N} \Psi(u_i) \lambda_i^{1/2} f_i(u) \, . \]

(5.2.16)

Since we calculate the wave functions values \( \Psi(u_i) \) in chapter 6 numerically, it is possible to combine \( \Psi(u_i) \) and \( \lambda_i^{1/2} \) into one sampling value \( \Psi(u_i) \) with

\[ \Psi(u_i) = \Psi(u_i) \lambda_i^{1/2} \]

(5.2.17)

and we obtain

\[ \Psi(u) \approx \sum_{i=1}^{N} \Psi(u_i) f_i(u) \, . \]

(5.2.18)

If we use the definition of \( f_i(u) \) in equation (5.2.14) and substitute \( \lambda_i \) and \( g_i(u) \) by \( \tilde{\lambda}_i \), \( \tilde{g}_i(u) \) in equations (5.2.12) and (5.2.13), we obtain the orthonormalized functions \( \tilde{f}_i(u) \) for the corresponding Laguerre polynomials. But we have to take into account, referring to equation (5.2.10), that \( \sqrt{\lambda}_i \) is always positive definite and that \( L_{N+1}(u_i) \) has an alternating sign for \( i \rightarrow i+1 \). Therefore the so called Lagrange-Laguerre functions \( \tilde{f}_i(u) \) are given by

\[ \tilde{f}_i(u) = (-1)^i u_i^{1/2} \frac{L_{N}(u)}{u - u_i} e^{-u/2} \, , \]

(5.2.19)

for the Laguerre polynomial \( L_{N}(u) \) and a weight factor \( e^{u} \). Two further properties of \( f_i(u) \) which we will use in the next section are

\[ \int_0^\infty \tilde{f}_i(u)\tilde{f}_j(u)du = \delta_{ij} \, , \]

(5.2.20)

\[ \tilde{f}_i(u_j) = \tilde{\lambda}_i^{-1/2} \delta_{ij} \, . \]

(5.2.21)
In addition to the values of $f_i(u)$ at the sampling points $u_i$ we also need the derivatives $f'_i(u_j)$ at the sampling points $u_j$. Referring to equation (5.2.11) and (5.2.19), we obtain the following two expressions

$$
\tilde{f}'_i(u_j) = (-1)^{i+j} \lambda_j^{-1/2} \frac{1}{u_j - u_i} \sqrt{\frac{u_i}{u_j}}, \quad i \neq j,
$$

(5.2.22)

$$
\tilde{f}'_i(u_i) = -\lambda_i^{-1/2} \frac{1}{2u_i}, \quad i = j.
$$

(5.2.23)

Both previous equations are equivalent to the expressions given in reference of [HB01].

As an example, we show in figure (5.2.1) all functions $\tilde{f}_i(u)$ with $N = 4$. For $u \to \infty$ all graphs $f_i(u)$ approach zero. Additionally, it can be seen directly, that three of the four graphs cross the X-axis in only one point, and just one graph has a non-zero value at this point. Referring to equations (5.1.1) and (5.1.9) these points are the sampling points of the Gauss quadrature and therefore we have to determine the $N$ roots $u_i$ of the Laguerre polynomials $L_N(u)$. To achieve a numerical high accuracy we use the method which is described in [SW97]. The eigenvalues of the following $N \times N$ tri-diagonal matrix are equal to the roots $u_i$ of $L_N$. The tri-diagonal matrix $A_{Lg}$ referred to [SW97] is given by

$$
A_{Lg} = \begin{pmatrix}
1 & 1 & & & & \\
1 & 3 & 2 & & & \\
2 & 5 & 3 & & & \\
3 & 7 & \ddots & b & & \\
\vdots & \ddots & b & a & \ddots & \\
\vdots & & b & a & \ddots & d \\
& & & d & c &
\end{pmatrix},
$$

(5.2.24)
where \( j \) denotes the \( j^{th} \) row of the matrix \( A_{L_g} \). In our numerical considerations, we calculate the eigenvalues with the linear algebra package, ‘LAPACK’. This package relies on the QR method which was introduced by John G. F. Francis in 1961 [Fra61]. Table (5.1) shows the values for the sampling points which result from the eigenvalue calculation for the four Lagrange-Laguerre functions \( \tilde{f}_i(u) \) in figure (5.2.1).

<table>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
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<tbody>
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<td>4.53662</td>
<td>9.39507</td>
</tr>
</tbody>
</table>

Table 5.1: Roots \( u_i \) of Lagrange functions

With the values of \( u_i \) we can span a multi-dimensional grid. In the next section, we consider a three-dimensional box where we span a three-dimensional grid of sampling points \( u_i \) to express the wave functions with the Gauss approximation. To illustrate the properties of such grids, we show in figures (5.2.2), (5.2.3), and (5.2.3) two-dimensional grids of Lagrange-Laguerre sampling points. We chose in both directions the same size of the basis set \( N \), which yields a square grid. The previous example of Lagrange-Laguerre polynomials \( f_i(u) \) of figure (5.2.1) with \( N = 4 \) and their calculated roots, which are explicitly given in table (5.1) is illustrated in figure (5.2.2). For the two other examples shown in figures (5.2.3), and (5.2.3) we chose a grid size of \( N = 8 \) and \( N = 15 \) in each dimension. We can see directly, that the interval between two different zero points \( u_i \) and \( u_j \) of the polynomial \( L_N(u) \) of degree \( N \) is not equidistant. The grid is much denser near the origin and the gridpoints thin out for larger \( u \). Obviously the grid size is determined by the number of sampling points \( N \). Comparing figure (5.2.2) with (5.2.3) the grid limit for \( N = 8 \) becomes more than twice as big for \( N = 15 \).
As mentioned before, all graphs in figure (5.2.1) converge to zero for increasing values of $u$ due to the factor $e^{-u/2}$ which is included in the Laguerre functions $f_i(u)$, and they have $N - 1$ roots. According to equation (5.1.1), we approximate the exact wave function by a linear combination of Laguerre polynomials. Consequently, we already know that the wave function always approach zero for large values of $u$. It is known from mathematical analysis, that a continuous polynomial that converges to zero must have a certain value $u_d$; where the absolute function values $f_i(u)$ of all polynomials are strictly monotonically decreasing. The value $u_d$ depends on the degree $N$ of the Lagrange functions and it raises monotonically for greater $N$. Now, if we consider a wave function that has a certain value, denoted as $\Psi(u_b)$, whose absolute value is much greater than zero at an arbitrary point $u_b$, far beyond $u_d$ for a given $N$. But we also consider, that this wave function converges monotonically to zero for $u > u_b$. For this case, it is not possible to describe this wave function in a linear combination of the $N$ Lagrange functions $f_i(u)$ in a good approximation. Since $u_d$ increases if $N$ grows, we can certainly choose a greater $N$, where we obtain $u_d > u_b$ and the approximation of the wave function becomes more accurate. Therefore, for the limit $N \to \infty$ every wave function can be expressed exactly by equation (5.1.1). Unfortunately it is not possible to reach this limit for numerical calculations in practice. However, there is a alternative way to achieve a better approximation for wave functions which do not approach zero at the point $u_b$, but converge to zero monotonically for $u > u_b$. We can shift $u_d$ for a fixed chosen $N$ by rescaling the function $f_i(u)$. Therefore we define $\tilde{u}$, with

$$\tilde{u} = hu , \quad (5.2.27)$$

where $h$ denotes a real-valued linear scaling factor. We substitute $u$ in equation (5.2.14) with

$$u = \frac{\tilde{u}}{h} , \quad (5.2.28)$$

and obtain

$$f_i(\tilde{u}/h) = \lambda_i^{-1/2} g_i(\tilde{u}/h) . \quad (5.2.29)$$

With the substitution in equation (5.2.28), the Lagrange-Laguerre functions $\tilde{f}_i(u)$ are explicitly given by

$$\tilde{f}_i(\tilde{u}/h) = (-1)^i u_i^{1/2} L_N(\tilde{u}/h) e^{-\tilde{u}/(2h)} , \quad (5.2.30)$$

and their first derivative at the sampling points $\tilde{u}_j$ take the form
\[
\tilde{f}_i'(\tilde{u}_j) = (-1)^{i+j+1} \frac{1}{h} \lambda_j^{-1/2} \frac{1}{u_j - u_i} \sqrt{\frac{u_i}{u_j}} \quad i \neq j ,
\]
(5.2.31)

\[
\tilde{f}_i'(\tilde{u}_i) = -\frac{1}{h} \lambda_i^{-1/2} \frac{1}{2u_i} \quad i = j .
\]
(5.2.32)

The first derivative of the substituted functions \(\tilde{f}_i(\tilde{u}/h)\) at the sampling points \(\tilde{u}_j\) are equal to those of the original functions \(f_i(u)\) at the roots \(u_j\) of the Laguerre polynomials multiplied by the factor \(1/h\).

Figure 5.2.5: Lagrange-Laguerre functions \(\tilde{f}_i(\tilde{u}/h)\) for \(N = 4\) and scale factor \(h = 2\). The graph of the function \(\tilde{f}_1(\tilde{u})\) is red, of \(\tilde{f}_2(\tilde{u})\) is green, of \(\tilde{f}_3(\tilde{u})\) is orange, of \(\tilde{f}_4(\tilde{u})\) is blue.

Figure (5.2.5) shows the rescaled Lagrange-Laguerre functions \(\tilde{f}_i(\tilde{u}/h)\) for the factor \(h = 2\). Compared to figure (5.2.1) all four polynomials have a new scale and they are distorted by the factor 2. The positions of their local minima and maxima stay invariant for \(\tilde{f}_i(\tilde{u}/h)\), and since they are obviously broadened compared to the normalized functions \(\tilde{f}_i(\tilde{u})\) it is quite clear, that \(\tilde{f}_i(\tilde{u}/h)\) is not normalized. Since the orthonormality of equation (5.2.15) still has to hold, we have to transform the integral concerning the substitution in equation (5.2.28) which leads to

\[
\int_0^\infty \frac{1}{h} f_i(\tilde{u}/h)f_j(\tilde{u}/h) \, d\tilde{u} = \delta_{ij} .
\]
(5.2.33)

Additionally, the sampling points for the substituted function in equation (5.2.29) have to obey

\[
f_i(\tilde{u}_j/h) = \lambda_i^{-1/2} \delta_{ij} .
\]
(5.2.34)

Hence, the points \(\tilde{u}_j\) represent the corresponding scaled sampling points \(u_j\) and they are obviously given by

\[
\tilde{u}_j = hu_j .
\]
(5.2.35)

Finally, we show how to express the new scaled wave function \(\Psi^{(h)}\). Referring to equation (5.2.18), we substitute \(u\) by equation (5.2.28). The new wave function implies the normalization factor \(1/h\) which appears in equation (5.2.33) and therefore \(\Psi^{(h)}\) takes the form
\[
\Psi^{(h)}(\tilde{u}) \approx \frac{1}{N} \sum_{i=1}^{N} \frac{1}{\sqrt{h}} \Psi(\tilde{u}_i) f_i(\tilde{u}/h),
\]
(5.2.36)

with
\[
\Psi(\tilde{u}) = \Psi(\tilde{u}) \lambda^{1/2}_i.
\]
(5.2.37)

Additionally, we adapt the scalar product of equation (5.1.4) to the rescaled wave functions \(\Psi^{(h)}(\tilde{u})\) and obtain
\[
\int_{\tilde{a}}^{\tilde{b}} \Phi^{(h)}(\tilde{u}) \Psi^{(h)}(\tilde{u}) d\tilde{u} \approx \sum_{i=1}^{N} \lambda_i h \Phi^{(h)*}(\tilde{u}_i) \Psi^{(h)}(\tilde{u}_i).
\]
(5.2.38)

Hence, for the general Gauss quadrature approximation, referring to equation (5.1.5), we have to substitute \(\tilde{u}\) by equation (5.2.27) which leads to
\[
\int_{\tilde{a}}^{\tilde{b}} G(\tilde{u}) d\tilde{u} = \int_{a}^{b} hG(hu) du \approx \sum_{i=1}^{N} h\lambda_i G(hu_i).
\]
(5.2.39)

In the following section we span a three-dimensional grid for each of the three scaled perimetric coordinates \(\tilde{x}, \tilde{y}\) and \(\tilde{z}\) according to equation (5.2.27) in order to expand the wave function. Additionally, we determine the matrix elements by using the Gauss quadrature to approximate the necessary integrations with the roots \(u_j\) of the Laguerre polynomial \(L_N(u)\) as sampling points.

### 5.3 Wave functions and matrix elements in Lagrange-Laguerre basis set

The basis set which we introduced in the previous section gives the opportunity to make an expansion for the required wave functions \(\Psi_\nu\) where \(\nu\) denotes the principle quantum number. These wave functions have to solve the stationary Schrödinger equation
\[
\hat{H} |\Psi_\nu\rangle = E_\nu |\Psi_\nu\rangle
\]
with \(E_\nu\) being the energy eigenvalues to the corresponding wave function \(\Psi_\nu\). In the next few steps we want to summarize in a simple way the general formalism of finding the energy eigenvalues. After that, we adapt this considerations to the three-body problem by using the Hamiltonian \(\hat{H}_c\) which is given in equation (2.1.24) and the wave functions ansatz of equation (4.1.1). Generally it is possible to make a linear combination ansatz with an orthonormal basis set \(\phi_n\), which span the whole space. With coefficients \(a_n\) the wave function ansatz is explicitly given by
\[
|\Psi_\nu\rangle = \sum_{n}^{N} a^{(\nu)}_n |\phi_n\rangle,
\]
(5.3.2)

with \(N\) different elements of the basis set which all fulfill the following orthonormality condition
\[
\langle \phi_m |\phi_n\rangle = \delta_{nm}.
\]
(5.3.3)

All wave functions \(\Psi_\nu\) are normalized which means that
\[
\langle \Psi_\nu |\Psi_\nu\rangle = \sum_{m}^{N} \sum_{n}^{N} a^{(\nu)}_m a^{(\nu)}_n \langle \phi_m |\phi_n\rangle = 1.
\]
(5.3.4)

With equation (5.3.4) the linear coefficients \(a^{(\nu)}_n\) have to obey the condition
\[
\sum_n^{N} (a_n^{(\nu)})^2 = 1 .
\]

(5.3.5)

For the next steps, we introduce the closure relation
\[
1 = \sum_m |\varphi_m\rangle \langle \varphi_m | ,
\]
and we substitute \(\Psi_\nu\) with the wave function expansion in equation (5.3.2) in the Schrödinger equation (5.3.1). Therefore, we get after some rearrangements
\[
0 = \hat{H} |\Psi_\nu\rangle - E_\nu |\Psi_\nu\rangle
\]
\[
= \sum_m \left( |\varphi_m\rangle \langle \varphi_m | \hat{H} |\Psi_\nu\rangle - E_\nu |\varphi_m\rangle \langle \varphi_m | \Psi_\nu\rangle \right)
\]
\[
= \sum_m \sum_n \left( a_n^{(\nu)} |\varphi_m\rangle \langle \varphi_m | \hat{H} |\varphi_n\rangle - a_n^{(\nu)} |\varphi_m\rangle \langle \varphi_n | \varphi_m\rangle \right) |\varphi_m\rangle
\]
\[
= \sum_m \sum_n a_n^{(\nu)} \left( |\varphi_m\rangle \langle \varphi_m | \hat{H} |\varphi_n\rangle - E_\nu \delta_{mn} \right) |\varphi_m\rangle .
\]

(5.3.7)

The last term on the right-hand side in equation (5.3.7) is equal to zero when the following equation is satisfied
\[
\sum_n \left( \langle \varphi_m | \hat{H} |\varphi_n\rangle - E_\nu \delta_{mn} \right) a_n^{(\nu)} = 0 .
\]

(5.3.8)

This equation can also be written in matrix vector form with
\[
\vec{a}_\nu = (a_1^{(\nu)}, ..., a_n^{(\nu)}, ..., a_N^{(\nu)})
\]

and matrix
\[
[H_{m,n}] = \langle \varphi_m | \hat{H} |\varphi_n\rangle
\]

(5.3.10)

as a standard eigenvalue problem
\[
\left( [H_{m,n}] - E_\nu \delta_{mn} \right) \vec{a}_\nu = 0 .
\]

(5.3.11)

The solution of the eigenvalue equation returns the energies \(E_\nu\) as eigenvalues and the coefficients \((a_1^{(\nu)}, ..., a_N^{(\nu)})\) as eigenvectors. This principle can be adapted to the given three-body problem to calculate numerically the eigenvalues and eigenfunctions. In chapter 4 we have chosen an ansatz given in equation (4.1.1) for the wave functions in the S-states and P-states with magnetic quantum number \(m = 0\) which was a product of the Wigner-D-matrices and a function \(\tilde{\Phi}(R, \rho, \zeta)\). It is not possible to express \(\tilde{\Phi}(R, \rho, \zeta)\) analytically, hence, we have to expand it. As mentioned in 2.4 we can regularize the singularities of the Coulomb potential terms if we use perimetric coordinates and substitute
\[
\tilde{\Phi}(R, \rho, \zeta) = \Phi(\tilde{x}, \tilde{y}, \tilde{z}) .
\]

(5.3.12)

Similar to section 5.3, we already scaled the perimetric coordinates \(x, y,\) and \(z\) in the previous equation (5.3.12) with
\[
\tilde{x} = h_x x , \quad \tilde{y} = h_y y , \quad \tilde{z} = h_z z .
\]

(5.3.13)

Referring to equation (5.3.2) we can chose an ansatz for the wave functions for three distinguished particles which takes the form of a triple sum
\[ \Phi^{(\nu)}(\bar{x}, \bar{y}, \bar{z}) = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} C_{ijk}^{(\nu)} F_{ijk}(\bar{x}, \bar{y}, \bar{z}) . \] (5.3.14)

The linear coefficients \( C_{ijk}^{(\nu)} \) are real-valued and vary for each different principle quantum number \( \nu \). On the other hand the functions \( F_{ijk}(\bar{x}, \bar{y}, \bar{z}) \) stay invariant for each \( \nu \). According to condition (5.3.5) the coefficients \( C_{ijk}^{(\nu)} \) have to obey

\[ \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} (C_{ijk}^{(\nu)})^2 = 1 . \] (5.3.15)

The limits of each sum, i.e. \( N_x, N_y \) and \( N_z \), determine the degree of the corresponding Lagrange function in \( F_{ijk}(\bar{x}, \bar{y}, \bar{z}) \) and \( F_{ijk'}(\bar{x}, \bar{y}, \bar{z}) \). Therefore the polynomials are of degree \( N_x - 1, N_y - 1, \) and \( N_z - 1 \). The wave function ansatz for \( \Psi_\nu \) depending on combined spherical and cylindrical coordinates is given in equation (4.1.1). In the following we show how to express the wave functions \( \Psi_\nu(x, y, z) \) in perimetric coordinates. The two linear coefficients \( C_{ijk}^{(\nu)(\text{even})} \) and \( C_{ijk}^{(\nu)(\text{odd})} \), which we need to expand the odd wave functions are independent of each other. Now, we want to link this ansatz with the Lagrange mesh method. Therefore we assume that \( F_{ijk}(x, y, z) \) is a product of three Laguerre Lagrange functions \( f_i(u) \) in equation (5.2.19), where each of the perimetric coordinates is substituted with \( u \) and we obtain

\[ F_{ijk}(\bar{x}, \bar{y}, \bar{z}) = N_{ijk}^{-1/2} h_x^{-1/2} h_y^{-1/2} h_z^{-1/2} f_i(\bar{x}/h_x) f_j(\bar{y}/h_y) f_k(\bar{z}/h_z) . \] (5.3.19)

where \( N_{ijk} \) denotes the normalization factor and \( N_x, N_y, N_z \) represent the degree \( N \) of the used Laguerre polynomials. The factors \( h_x^{-1/2}, h_y^{-1/2}, h_z^{-1/2} \) have been introduced because of the scaled ansatz of the wave function according to equation (5.2.36). The total number \( N_b \) of basis functions \( f_i(u) \) is therefore given by

\[ N_b = N_x N_y N_z . \] (5.3.20)

To determine \( N_{ijk} \) we take the wave functions \( \Psi(\phi, \theta, \psi, R, \rho, \zeta) \) given in equation (4.1.1) and consider the scalar product which is explicitly expressed in equation (4.1.2). The wave functions \( \Psi_\nu \) are normalized if the scalar product is equal to 1. Therefore, we integrate over all three angular coordinates \( \phi, \theta, \psi \), first. According to (4.1.5) we know that this three-fold integral is equal to one for all considered wave functions in the S-states and P-states which we made in chapter 4. The remaining integrals lead to the condition in equation (4.1.4), which is in scaled perimetric coordinates given by
\begin{align}
\langle \Phi_{\nu} | \Phi_{\nu} \rangle &= \int_0^\infty \int_0^\infty (\bar{x} + \bar{y})(\bar{x} + \bar{z})(\bar{y} + \bar{z}) \Phi_{\nu}^*(\bar{x}, \bar{y}, \bar{z}) \Phi_{\nu}(\bar{x}, \bar{y}, \bar{z}) \text{d}\bar{x}\text{d}\bar{y}\text{d}\bar{z} = 1 . 
\end{align}

If we use the ansatz (5.3.14) for \( \Phi_{\nu}(\bar{x}, \bar{y}, \bar{z}) \), the equation (5.3.21) takes the form

\begin{align}
\sum_{i,v} \sum_{j,j'} \sum_{k,k'} C_{ijk}^{(\nu)} C_{ijk'}^{(\nu)} \int_0^\infty \int_0^\infty (\bar{x} + \bar{y})(\bar{x} + \bar{z})(\bar{y} + \bar{z}) F_{ijk'}(\bar{x}, \bar{y}, \bar{z}) F_{ijk}(\bar{x}, \bar{y}, \bar{z}) \text{d}\bar{x}\text{d}\bar{y}\text{d}\bar{z} = 1 , 
\end{align}

where the sum indices \( i, i', j, j', k, k' \) start at 1. Taking into account that condition (5.3.15) is fulfilled for the linear coefficient \( C_{ijk}^{(\nu)} \), the function \( \Phi(x, y, z) \) is normalized if the triple integral in equation (5.3.22) is equal to the triple Kronecker delta function \( \delta_{ii'} \delta_{jj'} \delta_{kk'} \). We define this triple integral as the scalar product of \( F_{ijk'} \) and \( F_{ijk} \)

\begin{align}
\langle F_{ijk'} | F_{ijk} \rangle = \int_0^\infty \int_0^\infty (\bar{x} + \bar{y})(\bar{x} + \bar{z})(\bar{y} + \bar{z}) F_{ijk'}(\bar{x}, \bar{y}, \bar{z}) F_{ijk}(\bar{x}, \bar{y}, \bar{z}) \text{d}\bar{x}\text{d}\bar{y}\text{d}\bar{z} = \delta_{ii'} \delta_{jj'} \delta_{kk'} . 
\end{align}

We consider the integral in equation (5.3.23) with the Gauss quadrature approximation. The general Gauss approximation for the scaled Lagrange-Laguerre functions \( \bar{f}_i(x/h_x) \), \( \bar{f}_j(y/h_y) \), and \( \bar{f}_k(z/h_z) \) is given in (5.2.39). We substitute the three integrals in equation (5.3.23) by three sums and multiply weight factors \( \lambda \)'s, which depend on the sum indices \( p, q, r \). Additionally, we need the function values of \( F_{ijk}(x_h, y_h, z_h) \) and \( F_{ijk'}(x_h, y_h, z_h) \) at the sampling points \( x_p, y_q, z_r \), which are in this case equal to the roots of the Laguerre polynomials. As mentioned in section 5.2, the degree of the used polynomials \( N_x, N_y, N_z \) determines the number and values of the sampling points and also the size of the mesh. Finally, the equation (5.3.23) represented in Gauss quadrature approximation is given by

\begin{align}
\langle F_{ijk'} | F_{ijk} \rangle \approx \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \bar{\lambda}_p \bar{\lambda}_q \bar{\lambda}_r h_x h_y h_z (\bar{x}_p + \bar{y}_q) (\bar{x}_p + \bar{z}_r) (\bar{y}_q + \bar{z}_r) F_{ijk'}(\bar{x}_p, \bar{y}_q, \bar{z}_r) F_{ijk}(\bar{x}_p, \bar{y}_q, \bar{z}_r) = \delta_{ii'} \delta_{jj'} \delta_{kk'} ,
\end{align}

with

\begin{align}
\bar{x}_p &= h_x x_p , \quad \bar{y}_q = h_y y_q , \quad \bar{z}_r = h_z z_r .
\end{align}

The weights \( \bar{\lambda}_p, \bar{\lambda}_q \) and \( \bar{\lambda}_r \) are given by the equation (5.2.12). The sampling points \( x_p, y_q \) and \( z_r \) are in this case equal to the roots of the Laguerre polynomials of the corresponding degree \( N_x, N_y, N_z \). The substitution of \( F_{ijk'}(\bar{x}, \bar{y}, \bar{z}) \) and \( F_{ijk}(\bar{x}, \bar{y}, \bar{z}) \) with the right-hand expression of equation (5.3.19) leads with equation (5.2.21) after summing up all three sums to the following condition for \( N_{ijk} \)

\begin{align}
(h_x x_i + h_y y_j)(h_x x_i + h_z z_k)(h_y y_j + h_z z_k) \left( N_{ijk'} N_{ijk} \right)^{-1/2} \delta_{ii'} \delta_{jj'} \delta_{kk'} = 1 .
\end{align}

Comparing the equation (5.3.24) with equation (5.3.26) gives the norm factor \( N_{ijk} \)

\begin{align}
N_{ijk} = (h_x x_i + h_y y_j)(h_x x_i + h_z z_k)(h_y y_j + h_z z_k) .
\end{align}

The ansatz in equation (5.3.14) together with (5.3.19) is almost equivalent to the ansatz of [HB01]. Hesse and Baye also scaled their perimetric coordinates for their calculations by the factors \( h_x, h_y, h_z \), but they used the notation \( x, y, z \) and \( z \) of the non-scaled perimetric coordinates also for the scaled ones. But their wave function ansatz is not normalized. Our \( F_{ijk}(\bar{x}, \bar{y}, \bar{z}) \) implies the factor \( h_x^{-1/2} h_y^{-1/2} h_z^{-1/2} \), which according to the previous section 5.2, is necessary to normalize the wave function with respect to the scaled scalar product in equation (5.3.21). However, Hesse and Baye get the correct eigenvalues and
for the anti-symmetric function \( \Phi \).

Since the ansatz in equation (5.3.14) holds just for three non-identical particles, we want to expand the wave function ansatz for two identical Fermionic particles referring to section 3.4. We have seen there, that for two identical particles 1 and 2, the wave functions \( \Psi_\nu(x, y, z) \) have to be symmetric or antisymmetric. Therefore, depending on the states which we consider, the wave functions \( \Phi_\nu(x, y, z) \) must be symmetric or anti-symmetric for interchanging \( x \) and \( y \). To reach this, we apply equation (4.2.4) and (4.2.5) to the function \( F_{ijk}(x, y, z) \) and obtain the symmetric function \( F_{ijk}^{(\text{sym})}(x, y, z) \) and the anti-symmetric one \( F_{ijk}^{(\text{a-sym})}(x, y, z) \)

\[
F_{ijk}^{(\text{sym})}(x, y, z) = \frac{1}{\sqrt{2}} \left( F_{ijk}(x, y, z) + F_{ijk}(y, x, z) \right), \quad (5.3.28)
\]

\[
F_{ijk}^{(\text{a-sym})}(x, y, z) = \frac{1}{\sqrt{2}} \left( F_{ijk}(x, y, z) - F_{ijk}(y, x, z) \right). \quad (5.3.29)
\]

We substitute \( F_{ijk}(x, y, z) \) in equation (5.3.14) with the previous functions \( F_{ijk}^{(\text{sym})}(x, y, z) \) and \( F_{ijk}^{(\text{a-sym})}(x, y, z) \). The circumstance that the expansion of the wave function in the \( x \)-dimension and \( y \)-dimension are now related to each other, due to the their symmetry properties, has also an effect to the limits of their sums in equation (5.3.14). Both limits have to be equal now, and we denote for that case

\[
N_{xy} = N_x = N_y. \quad (5.3.30)
\]

The newly obtained functions, the symmetric ones, \( \Phi_\nu^{(\text{sym})}(x, y, z) \), and the anti-symmetric ones, \( \Phi_\nu^{(\text{a-sym})}(x, y, z) \), still have to fulfill the normalization condition of equation (5.3.21). Therefore, \( \Phi_\nu^{(\text{sym})}(x, y, z) \) and \( \Phi_\nu^{(\text{a-sym})}(x, y, z) \) are now given by

\[
\Phi_\nu^{(\text{sym})}(x, y, z) = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} C_{ijk}^{(\nu)} d_{ij}^{-1/2} F_{ijk}^{(\text{sym})}(x, y, z), \quad (5.3.31)
\]

\[
\Phi_\nu^{(\text{a-sym})}(x, y, z) = \sum_{i=0}^{N_x} \sum_{j=0}^{N_y} \sum_{k=0}^{N_z} C_{ijk}^{(\nu)} F_{ijk}^{(\text{a-sym})}(x, y, z), \quad (5.3.32)
\]

with

\[
d_{ij} = 1 + \delta_{ij}. \quad (5.3.33)
\]

The same condition for the linear coefficients \( C_{ijk}^{(\nu)} \), like in equation (5.3.15), has to hold for the symmetric and anti-symmetric case. Hence, the following equations

\[
\sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} (C_{ijk}^{(\nu)})^2 = 1 \quad (5.3.34)
\]

for the symmetric ansatz of \( \Phi_\nu^{(\text{sym})}(x, y, z) \), and

\[
\sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} (C_{ijk}^{(\nu)})^2 = 1 \quad (5.3.35)
\]

for the anti-symmetric function \( \Phi_\nu^{(\text{a-sym})}(x, y, z) \) have to be satisfied.

Due to the symmetry and anti-symmetry of \( F_{ijk}^{(\text{sym})}(x, y, z) \) and \( F_{ijk}^{(\text{a-sym})}(x, y, z) \) respectively, the sum over \( j \) is reduced and related to the sum index \( i \). Obviously, the number of basis functions has a lower value...
than for the case of three non-identical particles in equation (5.3.20). The number of basis functions for 
\( \Phi_\nu^{(\text{sym})}(x, y, z) \) and \( \Phi_\nu^{(\text{a-sym})}(x, y, z) \) are

\[
N_\nu^s = \frac{1}{2} (N_{xy} (N_{xy} + 1) N_z), \quad (5.3.36)
\]
\[
N_\nu^a = \frac{1}{2} (N_{xy} (N_{xy} - 1) N_z). \quad (5.3.37)
\]

According to the wave functions equations (5.3.16), (5.3.17), (5.3.18), we can readily express the symmetric
or anti-symmetric wave functions of the corresponding wave functions by substituting \( \Phi_\nu^{(\nu)}(x, y, z) \) with
\( \Phi_\nu^{(\nu)(\text{sym})}(x, y, z) \) in equation (5.3.31) and \( \Phi_\nu^{(\nu)(\text{a-sym})}(x, y, z) \) in equation (5.3.32). Therefore, we obtain
for the S-states

\[
\Psi_0^{(\nu)(\text{sym})}(\phi, \theta, \psi) = \frac{1}{\sqrt{8\pi}} \Phi_\nu^{(\nu)(\text{sym})}(x, y, z), \quad (5.3.38)
\]
\[
\Psi_0^{(\nu)(\text{a-sym})}(\phi, \theta, \psi) = \frac{1}{\sqrt{8\pi}} \Phi_\nu^{(\nu)(\text{a-sym})}(x, y, z). \quad (5.3.39)
\]

The P-states are now completely given by four different wave function, ansaetze two for each parity
symmetry. The even parity is represented by

\[
\Psi_1^{(\nu)(\text{even})(\text{sym})}(\phi, \theta, \psi) = \frac{1}{\sqrt{8\pi}} \sin(\theta) \cos(\psi) \Phi_\nu^{(\nu)(\text{a-sym})}(x, y, z), \quad (5.3.40)
\]
\[
\Psi_1^{(\nu)(\text{even})(\text{a-sym})}(\phi, \theta, \psi) = \frac{1}{\sqrt{8\pi}} \sin(\theta) \cos(\psi) \Phi_\nu^{(\nu)(\text{sym})}(x, y, z). \quad (5.3.41)
\]

Finally, the remaining P-states with odd parity take the form

\[
\Psi_1^{(\nu)(\text{odd})(\text{sym})}(\phi, \theta, \psi) = \frac{1}{\sqrt{8\pi}} \cos(\theta) \Phi_\nu^{(\nu)(\text{sym})}(x, y, z) + \sin(\theta) \cos(\psi) \Phi_\nu^{(\nu)(\text{a-sym})}(x, y, z), \quad (5.3.42)
\]
\[
\Psi_1^{(\nu)(\text{odd})(\text{a-sym})}(\phi, \theta, \psi) = \frac{1}{\sqrt{8\pi}} \cos(\theta) \Phi_\nu^{(\nu)(\text{a-sym})}(x, y, z) + \sin(\theta) \cos(\psi) \Phi_\nu^{(\nu)(\text{sym})}(x, y, z). \quad (5.3.43)
\]

After the introduction of the wave function ansatz we return to equation (5.3.8) which we want to solve for
the three-body problem. Referring to the wave function ansatz for \( \Psi_{0,0} \) in equation (5.3.16), we substitute
\( \langle \varphi_m \rangle \) and \( |\varphi_n\rangle \) in equation (5.3.8) with of the following expression

\[
\varphi_{i,j,k}^{(0,0)} = A_{0,0}(\phi, \theta, \psi) F_{ijk}(x, y, z). \quad (5.3.44)
\]

where \( A_{0,0}(\phi, \theta, \psi) \) includes the normalization factor and the angular dependence of the wave function,
which is in this case simply given by

\[
A_{0,0}(\phi, \theta, \psi) = \frac{1}{\sqrt{8\pi}}. \quad (5.3.45)
\]

We compare the ansaetze of the wave functions equations (5.3.16)with the eigenvalue condition in equation
(5.3.7). This leads finally to the following eigenvalue equation for three non-identical particles in the S-
states with the three-body Hamiltonian \( \hat{H}_c \)

\[
\sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left[ \langle A_{0,0} F_{ij,k} | \hat{H}_c | A_{0,0} F_{ijk} \rangle - E_\nu \delta_{ii'} \delta_{jj'} \delta_{kk'} \right] C_{ijk}^{(\nu)} = 0. \quad (5.3.46)
\]
Similar to the case of the S-states we want obtain the corresponding eigenvalue equation for the P-states and even wave functions. Hence, we substitute once again \( |\varphi_m\rangle \) and \( |\varphi_n\rangle \) in equation (5.3.8) with

\[
\varphi_{i,j,k}^{(1,0)(\text{even})} = A_{i,0}^{(\text{even})}(\phi, \theta, \psi) F_{ijk}(\bar{x}, \bar{y}, \bar{z}),
\]

(5.3.47)

with the angular factor \( A_{i,0}^{(\text{even})}(\phi, \theta, \psi) \) given by

\[
A_{i,0}^{(\text{even})}(\phi, \theta, \psi) = \frac{1}{\sqrt{8\pi}} \sin(\theta) \cos(\psi).
\]

(5.3.48)

Consequently, referring to equation (5.3.46), the eigenvalue equation for the P-states with even parity becomes

\[
\sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left[ \langle A_{i,0}^{(\text{even})} F_{i'j'k'} | \hat{H}_c | A_{i,0}^{(\text{even})} F_{ijk} \rangle - E_\nu \delta_{i'i'} \delta_{j'j} \delta_{kk'} \right] C_{ijk}^{(\nu)} = 0.
\]

(5.3.49)

For the last considered case, the P-states with odd parity, we use the same principle as before to get the eigenvalue equation, but we have to expand it, since we have two distinguished angular terms, denoted as

\[
A_{i,0}^{(0)(\text{odd})}(\phi, \theta, \psi) = \frac{1}{\sqrt{8\pi}} \cos(\theta),
\]

(5.3.50)

\[
A_{i,0}^{(1)(\text{odd})}(\phi, \theta, \psi) = -\frac{1}{\sqrt{8\pi}} \sin(\theta) \cos(\psi).
\]

(5.3.51)

Taking this into account leads to the following eigenvalue expression for the P-states with odd parity

\[
\sum_{p=0}^{1} \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left[ \langle A_{i,0}^{(p)(\text{odd})} F_{i'j'k'} | \hat{H}_c | A_{i,0}^{(p)(\text{odd})} F_{ijk} \rangle - E_\nu \delta_{pp'} \delta_{i'i'} \delta_{j'j} \delta_{kk'} \right] C_{ijk}^{(p)(\nu)} = 0.
\]

(5.3.52)

The fact, that we need twice as many linear coefficients, i.e. \( C_{ijk}^{(0)(\nu)} \) and \( C_{ijk}^{(1)(\nu)} \) to expand the wave functions with odd parity leads consequently to a four times greater matrix. Therefore, it is more elaborate to calculate the odd wave functions compared to the case of the even wave functions. The scalar products \( \langle A F_{i'j'k'} | \hat{H}_c | A F_{ijk} \rangle \) are explicitly given by a six-fold integral of the form

\[
\langle A F_{i'j'k'} | \hat{H}_c | A F_{ijk} \rangle = \int_0^\infty \int_0^\infty \int_0^\infty \int_0^{2\pi} \int_0^{2\pi} \int_0^\infty (\bar{x} + \bar{y})(\bar{x} + \bar{z})(\bar{y} + \bar{z}) \sin(\theta) AF_{i'j'k'} \hat{H}_c AF_{ijk} d\bar{x} d\bar{y} d\bar{z} d\theta d\psi.
\]

(5.3.53)

In the next step we have to find the expressions in Gauss approximation for the matrix elements in the previous eigenvalue equations. For this reason, we revert to the results in chapter 4, where we already made some considerations about the matrix elements of the Hamiltonian \( \hat{H}_c \). Additionally, we give for each state and parity symmetry separately the eigenvalue functions for the corresponding triplet and singlet states, for the case that two particles are Fermions.

### 5.3.1 Matrix elements for the S-states

Since we want to obtain the matrix elements in Gauss approximation, we consider the six-fold integral given in equation (5.3.53) in two steps. First, we integrate over all angular coordinates, which can be performed analytically, and afterwards we use the Gauss approximations for the remaining triple integral for the perimetric coordinates. In the section 4.2 we have seen, that the integral \( \langle \Psi_{\nu,0}^{(n)} | \hat{H}_S | \Phi_{\nu,0}^{(n)} \rangle \) is equivalent to \( \langle \Phi_{\nu,0}^{(n)} | \hat{H}_S | \Phi_{\nu,0}^{(n)} \rangle \) after integrating over all angular coordinates concerning two arbitrary wave functions \( \Psi_{\nu,0}^{(n)} \) and \( \Psi_{\nu,0}^{(n)} \) in the S-state. The functions \( \Psi_{\nu,0}^{(n)} \) and \( \Psi_{\nu,0}^{(n)} \) are explicitly given in equation
(4.2.3). The other functions, i.e. $\Phi_{0,0}^{(\nu)}$ and $\Phi_{0,0}^{(\eta)}$, depend only on the perimetric coordinates and are now expressed exactly in equation (5.3.14). We substitute both functions, $\Phi_{0,0}^{(\nu)}$ by $F_{\nu'k'}$ and $\Phi_{0,0}^{(\eta)}$ by $F_{ijk}$. The operator $\hat{H}_S = \hat{T} + \hat{V}$ with $\hat{T}$ and $\hat{V}$ is explicitly given in equations (2.4.20) and (2.4.21). With this considerations it is obvious that the eigenvalue equation (5.3.46) for three non-identical particles in the S-states is equivalent to

$$\sum_{i=1}^{N_z} \sum_{j=1}^{N_y} \sum_{k=1}^{N_x} \left[ \langle F_{\nu'k'} | \hat{H}_S | F_{ijk} \rangle - E_{\nu'} \delta_{\nu'\nu} \delta_{j'j} \delta_{k'k} \right] C_{ijk}^{(\nu)} = 0.$$  \hspace{1cm} (5.3.54)

According to section 4.2 and equation (4.2.6), we can obtain the matrix elements $\langle F_{\nu'k'} | \hat{H}_S | F_{ijk} \rangle$ by the following triple integral

$$\langle F_{\nu'k'} | \hat{H}_S | F_{ijk} \rangle = \int_0^\infty \int_0^\infty \int_0^\infty \left[ T_S \left( F_{\nu'k'}^{*}(\bar{x}, \bar{y}, \bar{z}), F_{ijk}(\bar{x}, \bar{y}, \bar{z}) \right) + V \left( F_{\nu'k'}^{*}(\bar{x}, \bar{y}, \bar{z}), F_{ijk}(\bar{x}, \bar{y}, \bar{z}) \right) \right] \frac{d\bar{x} d\bar{y} d\bar{z}}{h_x h_y h_z},$$  \hspace{1cm} (5.3.55)

and the explicit expressions for $T_S \left( F_{\nu'k'}^{*}(\bar{x}, \bar{y}, \bar{z}), F_{ijk}(\bar{x}, \bar{y}, \bar{z}) \right)$, $V \left( F_{\nu'k'}^{*}(\bar{x}, \bar{y}, \bar{z}), F_{ijk}(\bar{x}, \bar{y}, \bar{z}) \right)$ are given in equation (4.2.7), (4.2.10). Since we can not solve the integrals in equation (5.3.55) analytically, we use the Gauss approximation to approach the correct matrix elements with a high accuracy. Referring to equation (5.3.24), we obtain for the matrix elements $\langle F_{\nu'k'} | \hat{H}_S | F_{ijk} \rangle$

$$\langle F_{\nu'k'} | \hat{H}_S | F_{ijk} \rangle \approx \sum_{p=1}^{N_x} \sum_{q=1}^{N_y} \sum_{r=1}^{N_z} \bar{x}_p \bar{y}_q \bar{z}_r h_x h_y h_z \left[ T_S^G + V^G \right],$$  \hspace{1cm} (5.3.56)

where $T_S^G$ and $V^G$ denotes the functions $T$ and $V$ which are evaluated at the scaled sampling points $\bar{x}_p$, $\bar{y}_q$, $\bar{z}_r$ of the Gauss quadrature. These points are equivalent to those in equation (5.3.25). $T_S^G$ and $V^G$ are given by

$$T_S^G = T_S \left( F_{\nu'k'}^{*}(\bar{x}_p, \bar{y}_q, \bar{z}_r), F_{ijk}(\bar{x}_p, \bar{y}_q, \bar{z}_r) \right),$$  \hspace{1cm} (5.3.57)

$$V^G = V \left( F_{\nu'k'}^{*}(\bar{x}_p, \bar{y}_q, \bar{z}_r), F_{ijk}(\bar{x}_p, \bar{y}_q, \bar{z}_r) \right).$$  \hspace{1cm} (5.3.58)

Due to the Lagrange condition in equation (5.2.21), we can simplify the previous triple sum. All steps are explicitly shown in the appendix (A.3.1), and the result is given by
\[ \langle F'_{j'k'} | \hat{H}_S | F_{ijk} \rangle = \frac{2\hbar^2}{N^2} \sum_{p=1}^{N_0} \sum_{q=1}^{N_1} \left[ A^{m_1}(x_p, y_j, z_k) + B^{m_2}(x_p, z_k) + B^{m_3}(x_p, y_j) \right] f'_{j'}(x_p) f'_{k'}(x_p) + 2\hbar^2 \sum_{p=1}^{N_0} \sum_{q=1}^{N_1} \left[ A^{m_2}(y_q, x_i, z_k) + B^{m_1}(y_q, z_r) + B^{m_3}(x_i, z_r) \right] f'_{j'}(y_q) f'_{k'}(y_q) + 2\hbar^2 \sum_{p=1}^{N_0} \sum_{q=1}^{N_1} \left[ A^{m_3}(z_r, x_i, y_j) + B^{m_1}(y_j, z_r) + B^{m_3}(x_i, z_r) \right] f'_{j'}(x_i) f'_{k'}(z_r) + \ldots \]

\[ C_N = (N_{ij}N_{j'k'})^{-1/2} \]  

\[ A^m_{x_i, y_j, z_k} = \frac{h_x x_i (h_y y_j + h_z z_k)(h_x x_i + h_y y_j + h_z z_k)}{m} \]  

\[ B^m_{x_i, y_j} = \frac{h_x x_i (h_y y_j + h_y y_j)}{m} \]

The eigenvalue equation (5.3.54) is valid for three non-identical particles and in the next steps we express the eigenvalue equations for the singlet and triplet states of two identical Fermionic particles. For the singlet states we have to use the symmetric function \( \Phi^{(\text{sym})}_\nu(x, y, z) \) in perimetric coordinates. According to section 4.2, with the ansatz (5.3.31) and equation (5.3.8), we obtain the following eigenvalue equation after integrating over all angular coordinates

\[ \sum_{i=1}^{N_{xy}} \sum_{j=1}^{N_x} \sum_{k=1}^{N_z} \left( d^{1/2}_{ij} d^{1/2}_{ij} \langle F^{(\text{sym})}_{i'j'k'} | \hat{H}_S | F^{(\text{sym})}_{ijk} \rangle - E_{ij} \delta_{ij} \delta_{jk} \right) C^{(\nu)}_{ijk} = 0, \]  

with \( F^{(\text{sym})}_{ijk} \) given in equation (5.3.28), and

\[ d_{ij} = 1 + \delta_{ij}. \]

To conclude our considerations for the S-states, the eigenvalue equation for the triplet S-states, after the integration over all angular coordinates, is given with the anti-symmetric function \( \Phi^{(a-sym)}_\nu(x, y, z) \) in equation (5.3.32) by

\[ \sum_{i=1}^{N_{xy}} \sum_{j=1}^{N_x} \sum_{k=1}^{N_z} \left( F^{(a-sym)}_{i'j'k'} | \hat{H}_S | F^{(a-sym)}_{ijk} \rangle - E_{ij} \delta_{ij} \delta_{jk} \right) C^{(\nu)}_{ijk} = 0, \]
with $F_{ijk}^{(a-sym)}$ represented in equation (5.3.29). Referring to equations (5.3.28) and (5.3.29), the two scalar products $\langle F_{i'j'k'}^{(sym)} | \hat{H}_S | F_{ijk}^{(e-nm)} \rangle$ and $\langle F_{i'j'k'}^{(a-sym)} | \hat{H}_S | F_{ijk}^{(a-sym)} \rangle$ are equivalent to the following expressions

$$\langle F_{i'j'k'}^{(sym)} | \hat{H}_S | F_{ijk}^{(sym)} \rangle = \frac{1}{2} \left( \langle F_{i'j'k'} | \hat{H}_S | F_{ijk} \rangle + \langle F_{i'j'k'} | \hat{H}_S | F_{ijk} \rangle + \langle F_{i'j'k'} | \hat{H}_S | F_{ijk} \rangle + \langle F_{i'j'k'} | \hat{H}_S | F_{ijk} \rangle \right),$$  

(5.3.66)

$$\langle F_{i'j'k'}^{(a-sym)} | \hat{H}_S | F_{ijk}^{(a-sym)} \rangle = \frac{1}{2} \left( \langle F_{i'j'k'} | \hat{H}_S | F_{ijk} \rangle - \langle F_{i'j'k'} | \hat{H}_S | F_{ijk} \rangle - \langle F_{i'j'k'} | \hat{H}_S | F_{ijk} \rangle + \langle F_{i'j'k'} | \hat{H}_S | F_{ijk} \rangle \right).$$  

(5.3.67)

Hence, we need only the representation of the matrix elements $\langle F_{i'j'k'} | \hat{H}_S | F_{ijk} \rangle$, which is given in equation (5.3.59), to obtain also the other two matrix elements in equations (5.3.66) and (5.3.67). It is just necessary to adapt the corresponding indices. In the next section, we continue with the P-states considerations, and for the case of even parity, the results are similar to those of the S-states.

### 5.3.2 Matrix elements for the P-states and even parity

The following considerations are close to those for the S-states in section (5.3.1). Referring to section 4.3.1, we can find again an equivalent scalar product of equation (5.3.53) after integrating over all angular coordinates, with a reduced Hamiltonian $\hat{H}_P^{(even)}$. According to equation (4.3.26) this scalar product is given by

$$\langle \mathcal{R} \Phi_R^{(\nu)(even)} | \hat{H}_P^{(even)} | \mathcal{R} \Phi_R^{(\eta)(even)} \rangle = \int_0^\infty \int_0^\infty \int_0^\infty \mathcal{R} \left[ T_2(\Phi_R^{(\nu)(even)}, \Phi_R^{(\eta)(even)}) + V(\Phi_R^{(\nu)(even)}, \Phi_R^{(\eta)(even)}) \right] dx dy dz.$$  

(5.3.68)

As mentioned in section 4.3.1, this scalar product contains a regularization function $\mathcal{R} = \mathcal{R}(x, y, z)$ to avoid singularities. This regularization function is defined in equation (4.3.24) by

$$\mathcal{R} = \frac{1}{2} \sqrt{x + y + z}.$$  

(5.3.69)

Next, we assume that the same ansatz for $\Phi_R^{(\nu)}(x, y, z)$ is equal to the one we used in the S-states, i.e. $\Phi_R^{(\nu)}(x, y, z)$

$$\Phi_R^{(\nu)}(x, y, z) = \Phi^{(\nu)}(x, y, z).$$  

(5.3.70)

Taking this regularization into account and using equation (5.3.14) for $\Phi_R^{(\nu)}(x, y, z)$, we substitute $\mathcal{R} \Phi_R$ in the matrix elements on the right hand side of equation (5.3.68) by $\mathcal{R} F_{i'j'k'}$ respectively $\mathcal{R} F_{ijk}$. This leads, referring to equation (5.3.49), with the reduced Hamiltonian operator $\hat{H}_P^{(even)}$ to the following regularized eigenvalue problem

$$\sum_{i=1}^{N_\nu} \sum_{j=1}^{N_\nu} \sum_{k=1}^{N_\nu} \left[ \langle \mathcal{R} F_{i'j'k'} | \hat{H}_P^{(even)} | \mathcal{R} F_{ijk} \rangle - \mathcal{R}^2 E_\nu \delta_{i'i'} \delta_{j'j'} \delta_{k'k'} \right] C^{(\nu)}_{ijk} = 0,$$  

(5.3.71)

with a real valued factor $\mathcal{R}$. The term that includes the energy eigenvalues $E_\nu$ is, referring to the considerations in equation (5.3.7), equivalent to

$$\mathcal{R}^2 E_\nu \delta_{i'i'} \delta_{j'j'} \delta_{k'k'} = E_\nu \langle \mathcal{R} F_{i'j'k'} | \mathcal{R} F_{ijk} \rangle$$  

(5.3.72)

with the following condition for $\langle \mathcal{R} F_{i'j'k'} | \mathcal{R} F_{ijk} \rangle$
\[
\langle R F_{i'j'k'} | R F_{ijk} \rangle = \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} R^2(\tilde{x}, \tilde{y}, \tilde{z}) R_{i'j'k'}(\tilde{x}, \tilde{y}, \tilde{z}) F_{ijk}(\tilde{x}, \tilde{y}, \tilde{z}) d\tilde{x} d\tilde{y} d\tilde{z} = \tilde{R}^2 \delta_{ii'} \delta_{jj'} \delta_{kk'}. \quad (5.3.73)
\]

It is not necessary to calculate the previous integral analytically, since we use the Gauss approximation for the matrix elements in equation (5.3.78). Hence, we will also apply the Gauss quadrature to the integrals in equation (5.3.73), which finally leads with equation (5.2.39) to

\[
\langle R F_{i'j'k'} | R F_{ijk} \rangle \approx R(\tilde{x}_i, \tilde{y}_j, \tilde{z}_k)^2 h_x h_y h_z \delta_{ii'} \delta_{jj'} \delta_{kk'}. \quad (5.3.74)
\]

The three factors \(h_x, h_y, h_z\) also appear if we use the Gauss quadrature for the matrix elements in equation (5.3.68), and we can reduce them, since they factorize in the eigenvalue equation and are never equal to zero. Taking all of the previous considerations into account, it is not necessary to solve the regularized eigenvalue problem of equation (5.3.78), since we modify the wave function ansatz of equation (5.3.70). Hence, we choose the following ansatz for \(\Phi^{(\nu)}(x, y, z)\) which is equivalent to Hesse and Baye [HB01]

\[
\Phi^{(\nu)}(\tilde{x}, \tilde{y}, \tilde{z}) = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} C^{(\nu)}_{ijk} F^{(R)}(\tilde{x}, \tilde{y}, \tilde{z}), \quad (5.3.75)
\]

with

\[
F^{(R)}_{ijk}(\tilde{x}, \tilde{y}, \tilde{z}) = R^{-1}_{ijk} F_{ijk}(\tilde{x}, \tilde{y}, \tilde{z}), \quad (5.3.76)
\]

and

\[
R_{ijk} = \frac{1}{2} \sqrt{\tilde{x}_i \tilde{y}_j \tilde{z}_k (\tilde{x}_i + \tilde{y}_j + \tilde{z}_k)}. \quad (5.3.77)
\]

With the new wave function ansatz in equation (5.3.75), we can now give an eigenvalue equation that eliminates the factor \(\tilde{R}\) and the energy values are simply obtained by the eigenvalues of the matrix elements in the following equation

\[
\sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left[ \langle F^{(R)}_{i'j'k'} | \hat{H}_P^{(even)} | F^{(R)}_{ijk} \rangle - E_\nu \delta_{ii'} \delta_{jj'} \delta_{kk'} \right] C^{(\nu)}_{ijk} = 0, \quad (5.3.78)
\]

where we substituted \(\tilde{R}^{-1}_{ijk} F_{ijk}\) by

\[
F^{(R)}_{ijk} = \tilde{R}^{-1}_{ijk} F_{ijk}. \quad (5.3.79)
\]

The Gauss quadrature for the matrix elements in equation (5.3.78) leads to
\[
(\bar{F}^{(\overline{R})}_{i'j'k'}|R_{\text{even}})\bar{F}^{(\text{even})}_{ijk}) \approx 2\hbar^2 \delta_{i'j'} \delta_{kk'} C_N \sum_{q=1}^{N_y} \frac{1}{\hbar_q^2} \left[ \bar{A}(m_1, x_p, y_q, z_k) + \bar{B}(m_2, x_p, z_k) + \bar{B}(m_3, x_p, y_q) \right] R^{-1}_{ij'k'} f_{ij'}(x_p) R^{-1}_{kk'} f_{kk'}(x_p) \\
+ 2\hbar^2 \delta_{i'j'} \delta_{kk'} C_N \sum_{r=1}^{N_y} \frac{1}{\hbar_r^2} \left[ \bar{A}(m_2, y_q, x_r, z_k) + \bar{B}(m_1, y_q, z_r) + \bar{B}(m_3, x_r, y_q) \right] R^{-1}_{ij'k'} f_{ij'}(y_q) R^{-1}_{kk'} f_{kk'}(y_q) \\
+ 2\hbar^2 \delta_{i'j'} \delta_{kk'} C_N \sum_{r=1}^{N_y} \frac{1}{\hbar_r^2} \left[ \bar{A}(m_3, x_r, x_r, y_q) + \bar{B}(m_1, x_r, z_r) + \bar{B}(m_2, x_r, y_q) \right] R^{-1}_{ij'k'} f_{ij'}(z_r) R^{-1}_{kk'} f_{kk'}(z_r) \\
- 2\hbar^2 \delta_{i'j'} \delta_{kk'} C_N \frac{1}{\hbar_y} (\lambda_j \lambda_k) \bar{B}(m_1, y_q, z_k) R^{-1}_{ij'k'} f_{ij'}(y_q) R^{-1}_{kk'} f_{kk'}(z_k) \\
- 2\hbar^2 \delta_{i'j'} \delta_{kk'} C_N \frac{1}{\hbar_y} (\lambda_j \lambda_k) \bar{B}(m_2, x_r, z_k) R^{-1}_{ij'k'} f_{ij'}(x_r) R^{-1}_{kk'} f_{kk'}(z_k) \\
- 2\hbar^2 \delta_{i'j'} \delta_{kk'} C_N \frac{1}{\hbar_y} (\lambda_j \lambda_k) \bar{B}(m_3, x_r, y_q) R^{-1}_{ij'k'} f_{ij'}(x_r) R^{-1}_{kk'} f_{kk'}(y_q) \\
- 2\hbar^2 \delta_{i'j'} \delta_{kk'} C_N \frac{1}{\hbar_y} (\lambda_j \lambda_k) \bar{B}(m_3, x_r, y_q) R^{-1}_{ij'k'} f_{ij'}(x_r) R^{-1}_{kk'} f_{kk'}(y_q) \\
+ 2\hbar^2 \delta_{i'j'} \delta_{kk'} \bar{R}^2(ijk)[\frac{z_1 z_2}{h_x h_y + h_x h_z} + \frac{z_2 z_3}{h_y h_z + h_x h_z} + \frac{z_1 z_3}{h_x h_y + h_x h_z}], \\
(5.3.80)
\]

\[
C_N = (N_{ijk} N_{ij'k'})^{-1/2} \quad (5.3.81)
\]

\[
\tilde{A}(m, x_i, y_j, z_k) = \tilde{R}_{ijk}\frac{h_x x_i (h_y y_j + h_z z_k) (h_x x_i + h_y y_j + h_z z_k)}{m}, \quad (5.3.82)
\]

\[
\tilde{B}(m, x_i, y_j) = \tilde{R}_{ijk}\frac{h_x x_i h_y y_j (h_x x_i + h_y y_j)}{m}, \quad (5.3.83)
\]

\[
\tilde{R}_{ijk} = \frac{1}{2}\sqrt{h_x x_i h_y y_j h_z z_k (h_x x_i + h_y y_j + h_z z_k)}. \quad (5.3.84)
\]

The eigenvalues and matrix elements for the symmetric and anti-symmetric wave functions are obtained in the same way as for the S-states. With \(F^{(\overline{R})}_{ijk}(\bar{x}, \bar{y}, \bar{z})\) we obtain similar to the construction of the symmetric function \(F^{(\text{sym})}_{ijk}(\bar{x}, \bar{y}, \bar{z})\) and the anti-symmetric function \(F^{(\text{a-sym})}_{ijk}(\bar{x}, \bar{y}, \bar{z})\) in the equations (5.3.28) and (5.3.29) two functions, the symmetric one \(F^{(\text{sym})}_{ijk}(\bar{x}, \bar{y}, \bar{z})\), and the anti-symmetric one \(F^{(\text{a-sym})}_{ijk}(\bar{x}, \bar{y}, \bar{z})\)

\[
F^{(\overline{R})}_{ijk}(\bar{x}, \bar{y}, \bar{z}) = \frac{1}{\sqrt{2}} \left( \tilde{R}^{-1}_{ijk} F_{ijk}(\bar{x}, \bar{y}, \bar{z}) + \tilde{R}^{-1}_{ijk} F_{ijk}(\bar{y}, \bar{x}, \bar{z}) \right), \quad (5.3.85)
\]

\[
F^{(\overline{R})}_{ijk}(\bar{x}, \bar{y}, \bar{z}) = \frac{1}{\sqrt{2}} \left( \tilde{R}^{-1}_{ijk} F_{ijk}(\bar{x}, \bar{y}, \bar{z}) - \tilde{R}^{-1}_{ijk} F_{ijk}(\bar{y}, \bar{x}, \bar{z}) \right). \quad (5.3.86)
\]

Hence, we can define the symmetric function \(\bar{F}^{(\overline{R})}_{ijk}(\text{sym})\) and the anti-symmetric one \(\bar{F}^{(\overline{R})}_{ijk}(\text{a-sym})\) corresponding to equation (5.3.79) with

\[
\bar{F}^{(\overline{R})}_{ijk}(\text{sym}) = \overline{\mathcal{R}} \tilde{R}^{-1}_{ijk} F^{(\text{sym})}_{ijk}, \quad (5.3.87)
\]

\[
\bar{F}^{(\overline{R})}_{ijk}(\text{a-sym}) = \overline{\mathcal{R}} \tilde{R}^{-1}_{ijk} F^{(\text{a-sym})}_{ijk}. \quad (5.3.88)
\]

In summary, the symmetric regularized wave function ansatz \(\Phi^{(\nu)(\text{sym})}_R\) and the anti-symmetric one \(\Phi^{(\nu)(\text{a-sym})}_R\) referring to equation (5.3.31) and (5.3.32) are given by
\[
\Phi^{(\nu)(\text{sym})}_{\mathcal{R}}(\vec{x}, \vec{y}, \vec{z}) = \sum_{i=1}^{N_{\nu}} \sum_{j=1}^{N_{\nu}} \sum_{k=1}^{N_{\nu}} C^{(\nu)}_{ijk} d_{ij}^{-1/2} \widetilde{F}_{ijk}^{(\text{sym})}(\vec{x}, \vec{y}, \vec{z}) ,
\]
\[
\Phi^{(\nu)(\text{a-sym})}_{\mathcal{R}}(\vec{x}, \vec{y}, \vec{z}) = \sum_{i=1}^{N_{\nu}} \sum_{j=1}^{N_{\nu}} \sum_{k=1}^{N_{\nu}} C^{(\nu)}_{ijk} \widetilde{F}_{ijk}^{(\text{a-sym})}(\vec{x}, \vec{y}, \vec{z}) ,
\]

with \(d_{ij}\) given in equation (5.3.33). To obtain the correct eigenvalue equations for the P-states with even parity we have to consider the complete wave functions which are given in equations (5.3.40) and (5.3.40). In contrast to the S-states, we need the anti-symmetric functions \(\Phi^{(\nu)(\text{a-sym})}_{\mathcal{R}}(\vec{x}, \vec{y}, \vec{z})\) for the singlet states and the symmetric functions \(\Phi^{(\nu)(\text{sym})}_{\mathcal{R}}(\vec{x}, \vec{y}, \vec{z})\) for the triplet states. Taking this into account, we can express the corresponding eigenvalue equation referring to section (4.3.1) and after integrating over the angular coordinates by

\[
\sum_{i=1}^{N_{\nu}} \sum_{j=1}^{N_{\nu}} \sum_{k=1}^{N_{\nu}} \left[ \langle \widetilde{F}_{ij'k'}^{(\text{a-sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{a-sym})} \rangle - E_{\nu} \delta_{ii'} \delta_{jj'} \delta_{kk'} \right] C^{(\nu)}_{ijk} = 0 ,
\]

for the singlet even P-states and

\[
\sum_{i=1}^{N_{\nu}} \sum_{j=1}^{N_{\nu}} \sum_{k=1}^{N_{\nu}} \left[ \left( d_{ij}^{-1/2} d_{ij}^{-1/2} \langle \widetilde{F}_{ij'k'}^{(\text{sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{sym})} \rangle \right) - E_{\nu} \delta_{ii'} \delta_{jj'} \delta_{kk'} \right] C^{(\nu)}_{ijk} = 0
\]

for the triplet even P-states. Additionally, we can once again express the two matrix elements in the equations (5.3.92) and (5.3.92) alternatively, using equations (5.3.85) and (5.3.86). Thus the scalar products \(\langle \widetilde{F}_{ij'k'}^{(\text{sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{sym})} \rangle\) and \(\langle \widetilde{F}_{ij'k'}^{(\text{a-sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{a-sym})} \rangle\) are equivalent to

\[
\langle \widetilde{F}_{ij'k'}^{(\text{sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{sym})} \rangle = \frac{1}{2} \left( \langle \widetilde{F}_{ij'k'}^{(\text{sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{sym})} \rangle + \langle \widetilde{F}_{ij'k'}^{(\text{sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{sym})} \rangle \right)
\]

\[
\langle \widetilde{F}_{ij'k'}^{(\text{a-sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{a-sym})} \rangle = \frac{1}{2} \left( \langle \widetilde{F}_{ij'k'}^{(\text{a-sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{a-sym})} \rangle - \langle \widetilde{F}_{ij'k'}^{(\text{a-sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{a-sym})} \rangle \right) - \langle \widetilde{F}_{ij'k'}^{(\text{a-sym})} | \hat{\mathcal{H}}_{\nu}^{\text{even}} | \widetilde{F}_{ijk}^{(\text{a-sym})} \rangle
\]

Next, we consider the odd parity of the P-states and we use again the method to avoid a calculation of a regularized eigenvalue equation like we have done in this section.

### 5.3.3 Matrix elements for the P-states and odd parity

In this section we consider the eigenvalue equation (5.3.125). Compared to the other two equations (5.3.46) and (5.3.49) there is an additional sum over \(p\) which can have the two values \(\{0, 1\}\). This means we have to consider in this case four different matrix elements. We use the results from section 4.3.2 where we already obtained the equivalent scalar products after integrating over all angular coordinates with a reduced Hamiltonian operator \(\hat{\mathcal{H}}_{\nu}^{(\text{odd})}(p,p')\) for each of the matrix elements. The operator \(\hat{\mathcal{H}}_{\nu}^{(\text{odd})}(p,p')\) differs for each of the scalar products which are given in equation (4.3.60)

\[
\Phi^{(\nu)(\text{sym})}_{\mathcal{R}}(\vec{x}, \vec{y}, \vec{z}) = \sum_{i=1}^{N_{\nu}} \sum_{j=1}^{N_{\nu}} \sum_{k=1}^{N_{\nu}} C^{(\nu)}_{ijk} d_{ij}^{-1/2} \widetilde{F}_{ijk}^{(\text{sym})}(\vec{x}, \vec{y}, \vec{z}) ,
\]

\[
\Phi^{(\nu)(\text{a-sym})}_{\mathcal{R}}(\vec{x}, \vec{y}, \vec{z}) = \sum_{i=1}^{N_{\nu}} \sum_{j=1}^{N_{\nu}} \sum_{k=1}^{N_{\nu}} C^{(\nu)}_{ijk} \widetilde{F}_{ijk}^{(\text{a-sym})}(\vec{x}, \vec{y}, \vec{z}) ,
\]
If we substitute the function $\Phi_0^{(odd)}$ by $F_{i'j'k'}(\bar{x}, \bar{y}, \bar{z})$ for the bra vector and $F_{ijk}(\bar{x}, \bar{y}, \bar{z})$ for the ket vector for the first scalar product with $p = p' = 0$, we obtain with equation (4.3.43)

$$
\langle F_{i'j'k'} | H_{(0,0)} | F_{ijk} \rangle = \int_{0}^{\infty} \int_{0}^{\infty} \left[ T_S(F_{i'j'k'}, F_{ijk}) + V(F_{i'j'k'}, F_{ijk}) + \frac{4\hbar^2}{\mu_2(x+y)^2} \right] d\bar{x} d\bar{y} d\bar{z} .
$$

(5.3.99)

The functions $T_S(\Phi^*, \Phi)$ and $V(\Phi^*, \Phi)$ for an arbitrary function $\Phi$ are given in equation (4.2.7) and (4.2.10). We consider the remaining three matrix elements in one step, since we have to regularize the matrix elements again. If we take the same ansatz for $\Phi_{iR}^{(odd)(\nu)}(\bar{x}, \bar{y}, \bar{z})$ as for the P-even states considerations, i.e. $\Phi_{iR}^{(odd)(\nu)}(\bar{x}, \bar{y}, \bar{z}) = \Phi^{(\nu)}(x, y, z)$, we can make the following substitutions for the matrix elements in equations (5.3.95) - (5.3.98)

$$
\langle \Phi_0^{(odd)} | = \langle F_{i'j'k'} | , \quad \langle \Phi_{iR}^{(odd)} | = \langle \Phi_{iR} | , \quad | \Phi_0^{(odd)} \rangle = | F_{ijk} \rangle , \quad | \Phi_{iR}^{(odd)} \rangle = | \Phi_{iR}(\nu) \rangle .
$$

(5.3.100)

According to this substitution the eigenvalue equation (5.3.125) can be expressed as

$$
\begin{pmatrix}
M_{(0,0)}^{(odd)} & M_{(0,1)}^{(odd)} \\
M_{(1,0)}^{(odd)} & M_{(1,1)}^{(odd)}
\end{pmatrix}
\begin{pmatrix}
\bar{C}^{(0)(\nu)} \\
\bar{C}^{(1)(\nu)}
\end{pmatrix} = E_{\nu}
\begin{pmatrix}
1 & 0 \\
0 & \bar{R}^2
\end{pmatrix}
\begin{pmatrix}
\bar{C}^{(0)(\nu)} \\
\bar{C}^{(1)(\nu)}
\end{pmatrix} ,
$$

(5.3.101)

where $\bar{M}_{(p,p')}^{(odd)}$ represents $N_p \times N_p$ matrices and $\bar{R}$ denotes again the regularization factor. We assume a mapping, which we express explicitly in the next chapter that maps the three indices $(i, j, k)$ to an integer $a_p$ and the other indices $(i', j', k')$ to $a_{p'}$. Then, the matrix elements of $\bar{M}_{(p,p')}^{(odd)}$ are given by

$$
[M_{(0,0)}]_{a_0b_0} = \langle F_{i'j'k'} | H_{(0,0)}^{(odd)} | F_{ijk} \rangle
$$

(5.3.102)

$$
[M_{(0,1)}]_{a_0b_1} = \langle F_{i'j'k'} | H_{(0,1)}^{(odd)} | F_{ijk} \rangle
$$

(5.3.103)

$$
[M_{(1,0)}]_{a_1b_0} = \langle \Phi_{iR}^{(odd)} | H_{(1,0)} | F_{ijk} \rangle
$$

(5.3.104)

$$
[M_{(1,1)}]_{a_1b_1} = \langle \Phi_{iR}^{(odd)} | H_{(1,1)} | F_{ijk} \rangle
$$

(5.3.105)

and the vector components of the two vectors $\bar{C}^{(0)(\nu)}$ and $\bar{C}^{(1)(\nu)}$ take the form

$$
[\bar{C}^{(0)(\nu)}]_{b_0} = C^{(0)(\nu)}_{ijk} , \quad [\bar{C}^{(1)(\nu)}]_{b_1} = C^{(1)(\nu)}_{ijk} .
$$

(5.3.106)

In the same way as for the P-states with even parity we can avoid to solve the regularized eigenvalue problem. We can take the same ansatz for the regularized wave function as for the P-even states in equation (5.3.75). Adapting this to the odd wave function $\Phi_{iR}^{(odd)(\nu)}(\bar{x}, \bar{y}, \bar{z})$ we obtain

$$
\Phi_{iR}^{(odd)(\nu)}(\bar{x}, \bar{y}, \bar{z}) = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} C^{(\nu)(\nu)}_{ijk} F^{(R)}_{ijk}(\bar{x}, \bar{y}, \bar{z}) ,
$$

(5.3.107)
with $F_{ijk}^{(R)}(\tilde{x}, \tilde{y}, \tilde{z})$ given in equation (5.3.76). According to this ansatz and the substitutions in (5.3.108) we transform them to

$$
\langle \Phi_0^{\text{odd}} | = \langle F_{i'j'k'} |, \quad \langle \mathcal{R} \Phi_0^{\text{odd}} | = \langle \mathcal{R} F_{i'j'k'} |, \quad | \Phi_0^{\text{odd}} \rangle = | F_{ijk} \rangle, \quad | \mathcal{R} \Phi_0^{\text{odd}} \rangle = | \mathcal{R} F_{i'j'k'} \rangle.
$$

(5.3.108)

Therefore with the previous bra and kets, its is not necessary to calculate the regularization factor $\mathcal{R}$, since it is eliminated, if we consider the eigenvalue equation in the Gauss approximation in the same way we have shown in section 5.3.2. Finally, the eigenvalue equation is now given by

$$
\begin{pmatrix}
M_{P(0,0)}^{(\text{odd})} & M_{P(0,1)}^{(\text{odd})} \\
M_{P(1,0)}^{(\text{odd})} & M_{P(1,1)}^{(\text{odd})}
\end{pmatrix}
\begin{pmatrix}
\tilde{C}^{(0)}(\nu) \\
\tilde{C}^{(1)}(\nu)
\end{pmatrix} = E_{\nu} \begin{pmatrix}
\tilde{C}^{(0)}(\nu) \\
\tilde{C}^{(1)}(\nu)
\end{pmatrix}.
$$

(5.3.109)

Equation (5.3.106) holds for the vectors $\tilde{C}^{(0)}(\nu)$ and $\tilde{C}^{(1)}(\nu)$, and the matrices are now given by

$$
[M_{P(0,0)}^{(\text{odd})}]_{a_0,b_0} = \langle F_{i'j'k'} | \tilde{\mathcal{H}}_{(0,0)}^{(\text{odd})} | F_{ijk} \rangle
$$

(5.3.110)

$$
[M_{P(0,1)}^{(\text{odd})}]_{a_0,b_1} = \langle F_{i'j'k'} | \tilde{\mathcal{H}}_{(0,1)}^{(\text{odd})} | F_{ijk} \rangle
$$

(5.3.111)

$$
[M_{P(1,0)}^{(\text{odd})}]_{a_1,b_0} = \langle F_{i'j'k'}^{(R)} | \tilde{\mathcal{H}}_{(1,0)}^{(\text{odd})} | F_{ijk} \rangle
$$

(5.3.112)

$$
[M_{P(1,1)}^{(\text{odd})}]_{a_1,b_1} = \langle F_{i'j'k'}^{(R)} | \tilde{\mathcal{H}}_{(1,1)}^{(\text{odd})} | F_{ijk} \rangle
$$

(5.3.113)

and we used $\tilde{F}_{ijk}^{(R)} = \mathcal{R} F_{ijk}^{(R)}$ which is equivalent to equation (5.3.79).

In the next steps, we express the matrix elements in terms of the Gauss quadrature. The first matrix element, is given exactly in terms of the triple integral in equation (5.3.99). Since the triple integral of $\mathcal{T}_S(F_{i'j'k'}, F_{ijk}) + \mathcal{V}(F_{i'j'k'}, F_{ijk})$ is equal to equation (5.3.55), we can use its Gauss approximation which is given by the matrix elements $\langle F_{i'j'k'} | \mathcal{H}_S | F_{ijk} \rangle$ of the S-states in equation (5.3.59). Therefore we obtain readily

$$
\langle F_{i'j'k'} | \tilde{\mathcal{H}}_{P(0,0)}^{(\text{odd})} | F_{ijk} \rangle = \langle F_{i'j'k'} | \mathcal{H}_S | F_{ijk} \rangle + \delta_{i'i} \delta_{j'j} \delta_{k'k} \frac{4\hbar^2}{\mu_{12}(h_x x_i + h_y y_j)^2}.
$$

(5.3.114)

According to equation (5.3.115) the matrix elements $\langle F_{i'j'k'} | \tilde{\mathcal{H}}_{P(0,1)}^{(\text{odd})} | \tilde{F}_{ijk}^{(R)} \rangle$ of $M_{P(0,1)}^{(\text{odd})}$ are given exactly by the two following integrals

$$
\langle F_{i'j'k'} | \tilde{\mathcal{H}}_{P(0,1)}^{(\text{odd})} | \tilde{F}_{ijk}^{(R)} \rangle = \int_0^\infty \int_0^\infty \int_0^\infty \int_0^\infty \int_0^\infty \int_0^\infty \mathcal{D}(F_{i'j'k'}, \tilde{F}_{ijk}^{(R)}) + \mathcal{E}(F_{i'j'k'}, \tilde{F}_{ijk}^{(R)}) \, d\tilde{x} d\tilde{y} d\tilde{z},
$$

(5.3.115)

where $\mathcal{D}(F_{i'j'k'}, \tilde{F}_{ijk}^{(R)})$ and $\mathcal{E}(F_{i'j'k'}, \tilde{F}_{ijk}^{(R)})$ are expressed in equation (4.3.58) and (4.3.58), with the substitution of $\Phi_0^{(\text{odd})}$ by $F_{i'j'k'}$ and $\Phi_{1R}^{(\text{odd})}$ by $\tilde{F}_{ijk}^{(R)}$. Referring to equation (4.3.56), the matrix elements $\langle \tilde{F}_{i'j'k'}^{(R)} | \mathcal{H}_{(0,1)} | F_{ijk} \rangle$ of $M_{(1,0)}^{(\text{odd})}$ are given by

$$
\langle \tilde{F}_{i'j'k'}^{(R)} | \mathcal{H}_{(0,1)} | F_{ijk} \rangle = \langle \tilde{F}_{i'j'k'}^{(R)} | \mathcal{H}_{(0,1)} | F_{ijk} \rangle.
$$

(5.3.116)

Using the Gauss quadrature approximation in equation (5.2.39) for the triple integral in equation (5.3.115) leads to the final result.
\langle F_{i'j'k'} | \hat{\mathcal{H}}^{(\text{odd})}_{P(0,1)} | \vec{F}^{(R)}_{ijk} \rangle \approx 2 \hbar^2 \delta_{ii'} \delta_{jj'} C_N \frac{1}{\pi R} K^{1/2}_N \langle \tilde{A}(x_i', y_j', z_k') - \tilde{B}(m_2, x_i', z_k') - \tilde{B}(m_1, y_j', z_k') \rangle \mathcal{R}^{-1}_{ijk} f'_{i'}(z_k') \\
+ 2 \hbar^2 \delta_{ii'} \delta_{jj'} C_N \frac{1}{\pi R} K^{1/2}_N \langle \tilde{A}(x_i, y_j, z_k) - \tilde{B}(m_1, y_j, z_k) - \tilde{B}(m_2, x_i, z_k) \rangle \mathcal{R}^{-1}_{ijk} f'_{i'}(z_k) \\
- 2 \hbar^2 \delta_{ii'} \delta_{kk'} C_N \frac{1}{\pi R} K^{1/2}_N \langle \tilde{A}(x_i, y_j', z_k') - \tilde{A}(x_i, y_j, z_k) \rangle \mathcal{R}^{-1}_{ijk} f'_{i'}(z_k) \\
- 2 \hbar^2 \delta_{ii'} \delta_{kk'} C_N \frac{1}{\pi R} K^{1/2}_N \langle \tilde{A}(x_i, y_j, z_k) - \tilde{B}(m_1, y_j, z_k) - \tilde{B}(m_2, x_i, z_k) \rangle \mathcal{R}^{-1}_{ijk} f'_{i'}(z_k) \\
+ 2 \hbar^2 \delta_{ii'} \delta_{kk'} C_N \frac{1}{\pi R} K^{1/2}_N \langle \tilde{A}(x_i, y_j, z_k) - \tilde{B}(m_1, y_j, z_k) - \tilde{B}(m_2, x_i, z_k) \rangle \mathcal{R}^{-1}_{ijk} f'_{i'}(z_k) \\
- 2 \hbar^2 \delta_{ii'} \delta_{kk'} C_N \frac{1}{\pi R} K^{1/2}_N \langle \tilde{A}(x_i, y_j, z_k) - \tilde{B}(m_1, y_j, z_k) - \tilde{B}(m_2, x_i, z_k) \rangle \mathcal{R}^{-1}_{ijk} f'_{i'}(z_k) \\
+ 2 \hbar^2 \delta_{ii'} \delta_{kk'} C_N \frac{1}{\pi R} K^{1/2}_N \langle \tilde{A}(x_i, y_j, z_k) - \tilde{B}(m_1, y_j, z_k) - \tilde{B}(m_2, x_i, z_k) \rangle \mathcal{R}^{-1}_{ijk} f'_{i'}(z_k) \\
+ 2 \hbar^2 \delta_{ii'} \delta_{kk'} C_N \mathcal{R}^{-1}_{ijk} \left[ D_1 + D_2 \right] (h_x x_i + h_y y_j)^{-2}, \hspace{1cm} (5.3.117)

\mathcal{C}_N = (N_{ijk} N_{i'j'k'})^{-1/2}, \hspace{1cm} (5.3.118)

\tilde{A}(x_i, y_j, z_k) = \frac{h_x x_i \ h_y y_j \ h_z z_k (h_x x_i + h_y y_j + h_z z_k)}{h_x x_i + h_y y_j}, \hspace{1cm} (5.3.119)

\tilde{B}(m, x_i, y_j) = \frac{h_x x_i + h_y y_j}{m}, \hspace{1cm} (5.3.120)

D_1 = \frac{h_x h_z x_i z_k - h_y h_z y_j z_k - h_y^2 y_j^2 - h_x h_x x_i y_j}{m_1}, \hspace{1cm} (5.3.121)

D_2 = \frac{h_x h_z x_i z_k - h_y h_z y_j z_k - h_x^2 x_i^2 + h_x h_x x_i y_j}{m_2}. \hspace{1cm} (5.3.122)

The remaining matrix elements of \( \mathbf{M}^{(\text{odd})}_{P(1,1)} \) are easy to obtain in terms of equation (4.3.45). Since the reduced Hamiltonian \( \hat{\mathcal{H}}^{(\text{odd})}_{P(1,1)} \) is equivalent to \( \hat{\mathcal{H}}^{(\text{even})}_{P} \), the reduced Hamiltonian which we used in section 5.3.2 for even parity becomes

\[ \hat{\mathcal{H}}^{(\text{odd})}_{P(1,1)} = \hat{\mathcal{H}}^{(\text{even})}_{P}. \hspace{1cm} (5.3.123) \]

Hence, the matrix elements for \( \langle \vec{F}^{(R)}_{ijk} | \hat{\mathcal{H}}^{(\text{odd})}_{P(1,1)} | \vec{F}^{(R)}_{ijk} \rangle \) are exactly equal to the matrix elements which are given in equation (5.3.80) and we can reduce it to

\[ \langle \vec{F}^{(R)}_{ijk} | \hat{\mathcal{H}}^{(\text{odd})}_{P(1,1)} | \vec{F}^{(R)}_{ijk} \rangle = \langle \vec{F}^{(R)}_{ijk} | \hat{\mathcal{H}}^{(\text{even})}_{P} | \vec{F}^{(R)}_{ijk} \rangle. \hspace{1cm} (5.3.124) \]

To conclude our considerations for the P-odd-states for three non-identical particles we express the complete eigenvalue equation in the same notation as in equation (5.3.125)

\[ 0 = \sum_{i_1=1}^{N_x} \sum_{j_1=1}^{N_y} \sum_{k_1=1}^{N_z} \left[ \langle F_{i'j'k'} | \hat{\mathcal{H}}^{(\text{odd})}_{P(0,0)} | F_{ijk} \rangle - E_\nu \delta_{ii'} \delta_{jj'} \delta_{kk'} \right] C^{(0)(\nu)}_{ijk} \hspace{1cm} (5.3.125) \]
In the remaining part of this section we consider the triplet and singlet states of the P-states with even parity and two identical Fermions. In this case the eigenvalue equation (5.3.125) is not valid. We have to take into account that, referring to the wave functions ansaetze (5.3.42) and (5.3.43) and the definitions of $\Phi^{(\nu)(sym)}$ and $\Phi^{(\nu)(a-sym)}$ in equations (5.3.31) and (5.3.32), the sum limits of $j$ differ for $p \neq p'$. Hence, referring to section 4.3.2 and after integrating over all angular coordinates, the eigenvalue equation for the singlet states is given by

\[
0 = \sum_{i=1}^{N_{sy}} \sum_{j<j'}^{N_{sy}} \sum_{k=1}^{N_{sy}} \left[ \langle F_{i'j'}^{(a-sym)} | \hat{H}^{(\nu)(sym)}_{P(0,0)} | F_{ij}^{(a-sym)} \rangle - E_{\nu} \delta_{ii'} \delta_{jj'} \delta_{kk'} \right] C_{ijk}^{(\nu)} + \sum_{i=1}^{N_{sy}} \sum_{j<j'}^{N_{sy}} \sum_{k=1}^{N_{sy}} \left[ \langle F_{i'j'}^{(a-sym)} | \hat{H}^{(\nu)(sym)}_{P(0,1)} | F_{ij}^{(a-sym)} \rangle - E_{\nu} \delta_{ii'} \delta_{jj'} \delta_{kk'} \right] C_{ijk}^{(\nu)} \tag{5.3.126}
\]

Additionally, we obtain the corresponding eigenvalue equation for triplet states

\[
0 = \sum_{i=1}^{N_{sy}} \sum_{j<j'}^{N_{sy}} \sum_{k=1}^{N_{sy}} \left[ \langle F_{i'j'}^{(a-sym)} | \hat{H}^{(\nu)(sym)}_{P(0,0)} | F_{ij}^{(a-sym)} \rangle - E_{\nu} \delta_{ii'} \delta_{jj'} \delta_{kk'} \right] C_{ijk}^{(\nu)} + \sum_{i=1}^{N_{sy}} \sum_{j<j'}^{N_{sy}} \sum_{k=1}^{N_{sy}} \left[ \langle F_{i'j'}^{(a-sym)} | \hat{H}^{(\nu)(sym)}_{P(0,1)} | F_{ij}^{(a-sym)} \rangle - E_{\nu} \delta_{ii'} \delta_{jj'} \delta_{kk'} \right] C_{ijk}^{(\nu)} \tag{5.3.127}
\]

Similar to equation (5.3.109) the two equations (5.3.127) and (5.3.126) can be expressed in matrix form. Again, we map the indices $i', j'$, and $k'$ to an integer $\nu'$ and $i$, $j$, and $k$ to $b$, but this map differs from the one, we used in equation (5.3.109). Additionally, the mapping for the singlet matrices $M^{(s)(odd)}_{P(0,0)}$ and the triplet matrices $M^{(t)(odd)}_{P(1,0)}$ differs, too. Both mappings are explained in the next chapter. Now, the eigenvalue equation takes the form

\[
\begin{pmatrix}
M^{(s)(odd)}_{P(0,0)} & M^{(s)(odd)}_{P(1,0)} \\
M^{(s)(odd)}_{P(1,0)} & M^{(s)(odd)}_{P(1,1)}
\end{pmatrix}
\begin{pmatrix}
\tilde{C}^{(0)(\nu)} \\
\tilde{C}^{(1)(\nu)}
\end{pmatrix}
= E_{\nu}
\begin{pmatrix}
\tilde{C}^{(0)(\nu)} \\
\tilde{C}^{(1)(\nu)}
\end{pmatrix},
\tag{5.3.128}
\]

and the matrices $M^{(t)(odd)}_{P(p,p')}$ are given by

\[
\begin{align*}
[M^{(s)(odd)}_{P(0,0)}]_{a_{0}b_{0}}^{(s)} &= \langle F_{i'j'k'}^{(a-sym)} | \hat{H}^{(\nu)(sym)}_{P(0,0)} | F_{ij}^{(a-sym)} \rangle, \\
[M^{(s)(odd)}_{P(0,1)}]_{a_{0}b_{1}}^{(t)} &= d_{ij}^{-1/2} \langle F_{i'j'k'}^{(a-sym)} | \hat{H}^{(\nu)(sym)}_{P(0,1)} | F_{ij}^{(a-sym)} \rangle, \\
[M^{(s)(odd)}_{P(1,0)}]_{a_{1}b_{0}}^{(t)} &= \langle F_{i'j'k'}^{(a-sym)} | \hat{H}^{(\nu)(sym)}_{P(1,0)} | F_{ij}^{(a-sym)} \rangle, \\
[M^{(s)(odd)}_{P(1,1)}]_{a_{1}b_{1}}^{(t)} &= d_{ij}^{-1/2} d_{i'j'}^{-1/2} \langle F_{i'j'k'}^{(a-sym)} | \hat{H}^{(\nu)(sym)}_{P(1,1)} | F_{ij}^{(a-sym)} \rangle.
\end{align*}
\tag{5.3.129}
\]

Thus, the the eigenvalue equation for the triplet states takes the form

\[
\begin{pmatrix}
M^{(t)(odd)}_{P(0,0)} & M^{(t)(odd)}_{P(1,0)} \\
M^{(t)(odd)}_{P(1,0)} & M^{(t)(odd)}_{P(1,1)}
\end{pmatrix}
\begin{pmatrix}
\tilde{C}^{(0)(\nu)} \\
\tilde{C}^{(1)(\nu)}
\end{pmatrix}
= E_{\nu}
\begin{pmatrix}
\tilde{C}^{(0)(\nu)} \\
\tilde{C}^{(1)(\nu)}
\end{pmatrix},
\tag{5.3.133}
\]

with the matrices
In chapter 6 we solve the eigenvalue equations which we have considered in this section for a variety of

\[ M_{P(0,1)}^{(\ell)}(i,j,k) = \mathfrak{d}^{1/2} \mathfrak{d}^{1/2} \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle, \]

(5.3.134)

\[ M_{P(0,1)}^{(\ell)}(i,j,k) = \mathfrak{d}^{1/2} \mathfrak{d}^{1/2} \langle F^{(sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(sym)} \rangle, \]

(5.3.135)

\[ M_{P(0,1)}^{(\ell)}(i,j,k) = \mathfrak{d}^{1/2} \mathfrak{d}^{1/2} \langle F^{(sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(sym)} \rangle, \]

(5.3.136)

\[ M_{P(0,1)}^{(\ell)}(i,j,k) = \mathfrak{d}^{1/2} \mathfrak{d}^{1/2} \langle F^{(sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(sym)} \rangle. \]

(5.3.137)

According to the S-states and P-states with even parity considerations we can express all scalar products in equations (5.3.129) - (5.3.132) and (5.3.134) - (5.3.137) in terms of the four scalar products for three non-identical particles which are given in equations (5.3.114), (5.3.117), (5.3.116), and (5.3.124). Hence, it is not necessary to make further considerations of scalar products, since we can use for the singlet and triplet states of two Fermionic particles the four scalar products corresponding to the three non-identical particles. To conclude this section we list all corresponding eight relations, starting with the singlet states

\[ \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle = \frac{1}{2} \left( \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle - \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle \right), \]

(5.3.138)

\[ \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle = \frac{1}{2} \left( \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle - \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle \right), \]

(5.3.139)

\[ \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle = \frac{1}{2} \left( \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle - \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle \right), \]

(5.3.140)

And consequently, the four relations for the triplet states

\[ \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle = \frac{1}{2} \left( \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle + \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle \right), \]

(5.3.142)

\[ \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle = \frac{1}{2} \left( \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle - \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle \right), \]

(5.3.143)

\[ \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle = \frac{1}{2} \left( \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle - \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle \right), \]

(5.3.144)

\[ \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle = \frac{1}{2} \left( \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle - \langle F^{(a-sym)} | \hat{H}_{P(0,1)}^{(odd)} | F^{(a-sym)} \rangle \right). \]

(5.3.145)

In chapter 6 we solve the eigenvalue equations which we have considered in this section for a variety of physical systems. In addition to the eigenvalues, the solutions give us the corresponding eigenvectors \( C_{i,j,k}^{(\ell)} \),
For an arbitrary observable \( \hat{O} \) quantum number \( \nu \) operators. The expectation value of an arbitrary observable operator for a state \( \Psi_\nu \) is given by

\[
\langle \Psi_\nu | \hat{O} | \Psi_\nu \rangle = \int_0^\infty \int_0^{2\pi} \int_0^\pi \sin(\theta) (\vec{x} + \vec{y})(\vec{x} + \vec{z})(\vec{y} + \vec{z}) \Psi_\nu \hat{O} \Psi_\nu d\phi d\theta d\psi d\vec{x} d\vec{y} d\vec{z}
\]

The previous equation (5.5.3) is also valid if we substitute \( \Phi_\nu \) with one of the ansätze which we made in the previous section and this results in the expectation value of \( \hat{O} \) for the corresponding wave function and state \( \nu \). Since we know the angular dependence of the wave functions analytically due to the Wigner-D-matrices, we can integrate the three integrals over the angular coordinates analytically. The remaining three integrals over the perimetric coordinates are considered in terms of Gauss quadrature.

For all observables \( \hat{O}^{(\text{per})} \) which have no angular dependence, the equation (5.5.3) can be reduced, which is presented in the following for all wave function ansätze from section 5.3. For the S-states wave functions and the P-states wave function with even parity which are given in equation (5.3.16) and (5.3.17) the expectation value equation in (5.5.3) is also valid if we substitute \( \Phi_\nu \) by \( \Phi_\nu^{(\text{sym})} \) or \( \Phi_\nu^{(a-\text{sym})} \) which are expressed in equations (5.3.31) and (5.3.32). Using the Gauss approximation in equation (5.2.39) and the ansätz of \( \Phi_\nu^{(\text{sym})} \) and \( \Phi_\nu^{(a-\text{sym})} \) in equations (5.3.14), (5.3.31), and (5.3.32) leads to three different expressions for the expectation values \( \hat{O}^{(\text{per})} \). Therefore, we obtain for three non-identical particles in the S-states and P-states with even parity

\[
\langle \Psi_\nu | \hat{O}^{(\text{per})} | \Psi_\nu \rangle = \int_0^\infty \int_0^{2\pi} \int_0^\pi (\vec{x} + \vec{y})(\vec{x} + \vec{z})(\vec{y} + \vec{z}) \Phi_\nu \hat{O}^{(\text{per})} \Phi_\nu d\phi d\theta d\psi d\vec{x} d\vec{y} d\vec{z}.
\]

The previous equation (5.5.3) is also valid if we substitute \( \Phi_\nu \) by \( \Phi_\nu^{(\text{sym})} \) or \( \Phi_\nu^{(a-\text{sym})} \) which are expressed in equations (5.3.31) and (5.3.32). Using the Gauss approximation in equation (5.2.39) and the ansätz of \( \Phi_\nu^{(\text{sym})} \) and \( \Phi_\nu^{(a-\text{sym})} \) in equations (5.3.14), (5.3.31), and (5.3.32) leads to three different expressions for the expectation values \( \hat{O}^{(\text{per})} \). Therefore, we obtain for three non-identical particles in the S-states and P-states with even parity

\[
\langle \Phi_\nu^{(\text{sym})} | \hat{O}^{(\text{per})} | \Phi_\nu^{(\text{sym})} \rangle = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} (C_{i,j,k}^{(\nu)})^2 \hat{O} (h_x x_i, h_y y_j, h_z z_k).
\]

Referring to the wave functions in equations (5.3.38) and (5.3.40), the expectation values for the singlet S-states and triplet P-even-states are given by

\[
\langle \Psi_\nu | \hat{O}^{(\text{per})} | \Psi_\nu \rangle = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} (C_{i,j,k}^{(\nu)})^2 \hat{O} (h_x x_i, h_y y_j, h_z z_k).
\]

Consequently, the expectation values for the triplet S-states and singlet P-even-states takes the form

\[
\langle \Phi_\nu^{(a-\text{sym})} | \hat{O}^{(\text{per})} | \Phi_\nu^{(a-\text{sym})} \rangle = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} (C_{i,j,k}^{(\nu)})^2 \hat{O} (h_x x_i, h_y y_j, h_z z_k).
\]

\[\text{Lagrange-mesh method}\]

\[C_{ij}^{(0)(\nu)}, C_{ij}^{(1)(\nu)}.\] Together with the wave functions ansatze we can consider arbitrary expectation values and we discuss this subject in the next section.
\[ \langle \Psi_\nu | \hat{O}^{(\text{per})} | \Psi_\nu \rangle = \langle \Phi_\nu | \hat{O}^{(\text{per})} | \Phi_\nu \rangle = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left( C_{ijk}^{(\nu)} \right)^2 \hat{O}(x_{ixi}, y_{iyj}, z_{izk}) . \]  

Finally, we consider the expectation values for the P-states with odd parity. The corresponding wave functions are given in equation (5.3.18), (5.3.42), and (5.3.43) which we use together with \( \hat{O}^{(\text{per})} \) for equation (5.5.3). The integration over all angular coordinates leads to

\[ \langle \Psi_\nu | \hat{O}^{(\text{per})} | \Psi_\nu \rangle = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left[ \left( C_{ijk}^{(0)(\nu)} \right)^2 \hat{O}(x_{ixi}, y_{iyj}, z_{izk}) + \left( C_{ijk}^{(1)(\nu)} \right)^2 \hat{O}(x_{ixi}, y_{iyj}, z_{izk}) \right] \]

for three non-identical particles. Similarly we obtain the following expressions for the singlet P-odd-states

\[ \langle \Psi_\nu | \hat{O}^{(\text{per})} | \Psi_\nu \rangle = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left( C_{ijk}^{(0)(\nu)} \right)^2 \hat{O}(x_{ixi}, y_{iyj}, z_{izk}) + \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left( C_{ijk}^{(1)(\nu)} \right)^2 \hat{O}(x_{ixi}, y_{iyj}, z_{izk}) . \]

and the triplet states

\[ \langle \Psi_\nu | \hat{O}^{(\text{per})} | \Psi_\nu \rangle = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left( C_{ijk}^{(0)(\nu)} \right)^2 \hat{O}(x_{ixi}, y_{iyj}, z_{izk}) + \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left( C_{ijk}^{(1)(\nu)} \right)^2 \hat{O}(x_{ixi}, y_{iyj}, z_{izk}) . \]

In chapter 6 we calculate the expectation values for the inter-particle distances and their variances. Since the distances between the particles are described by a triangle as mentioned in chapter 6, the distance observable operators do not depend on any angular coordinate. The corresponding inter-particle distance observables \( \hat{O}_{rij} \) between particle \( i \) and \( j \) respectively, the squared inter-particle distance observables which we can substitute for \( \hat{O}(x_{ixi}, y_{iyj}, z_{izk}) \) are given by

\[ \hat{O}_{r_{12}}(x_{ixi}, y_{iyj}) = \frac{x_{ixi} + y_{iyj}}{2} , \quad \hat{O}_{r_{13}}(x_{ixi}, y_{iyj}) = \frac{(x_{ixi} + y_{iyj})^2}{4} , \]

\[ \hat{O}_{r_{23}}(y_{iyj}, z_{izk}) = \frac{y_{iyj} + z_{izk}}{2} , \quad \hat{O}_{r_{23}}(y_{iyj}, z_{izk}) = \frac{(y_{iyj} + z_{izk})^2}{4} , \]

\[ \hat{O}_{r_{32}}(x_{ixi}, z_{izk}) = \frac{x_{ixi} + z_{izk}}{2} , \quad \hat{O}_{r_{32}}(x_{ixi}, z_{izk}) = \frac{(x_{ixi} + z_{izk})^2}{4} . \]

In addition to the distance observables we consider the kinetic energies of the three particles. These expectation values do not lead to a short expression as in the case of the inter-particle distance expectation values, since we have to take the derivative operators into account. In general, the kinetic expectation values for particle \( i \) are given by

\[ \langle \Psi_\nu | \hat{T}_i | \Psi_\nu \rangle = \int \int \int \int \int \int \sin(\theta)(\bar{x} + \bar{y})(\bar{x} + \bar{z})(\bar{y} + \bar{z})\Psi_\nu \hat{T}_i \Psi_\nu d\phi d\theta d\psi d\bar{x} d\bar{y} d\bar{z} . \]

The kinetic operator \( \hat{T}_i \) is given by \( \hat{T}_S + \hat{T}_L \) if we eliminate all contributions which do depend on \( m_i \), the mass of particle \( i \). The operators \( \hat{T}_S \) and \( \hat{T}_L \) are explicitly given in equation (2.4.20) and (3.1.25). Depending on the states which we consider in section 5.3, we can substitute \( \Psi_\nu \) by \( \Psi_\nu^{(\nu)} \) for the S-states or \( \Psi_\nu^{(0)} \) for the P-states. Together with the linear coefficients \( C_{ijk} \), we have the exact wave function expansion and therefore we can use the Gauss approximation of the previous equation (5.4.13) to obtain the kinetic expectation value for the corresponding particle \( i \).
5.5 Transition dipole matrix elements

In section 5.3 we considered the three-body wave functions in the S-states and the P-states with the magnetic quantum number equal to zero. Additionally, the wave functions split in a singlet and triplet wave function for each of the states if two particles are identical Fermionic particles. For those wave functions, we express in this section the dipole matrix elements which is necessary for the electronic dipole approximation. The dipole matrix elements $\bar{D}_{\nu\eta}$ are defined as

$$\bar{D}_{\nu\eta} = \langle \Psi_{LM}^{(\nu)} | e\vec{r} | \Psi_{LM}^{(\eta)} \rangle ,$$  

(5.5.1)

with the elementary charge $e$ and the position vector $\vec{r}$ of a particle. In the present work we consider the transition from and arbitrary state $\nu$ from the the S-states which is given by $\Psi_{0,0}^{(\nu)}$ for three non identical particles or $\Psi_{0,0}^{(\text{sym})}$ for two identical particles to one of the excited states. The elementary charge $e$ is just a scalar factor which factorizes with the whole expression. Hence the transition matrix elements referring to a transition from the ground state to an excited state is given by

$$\bar{D}_{\nu\eta}^{(i)} = e\langle \Psi_{0,0}^{(\nu)} | \vec{r}_c | \Psi_{LM}^{(\eta)} \rangle .$$

(5.5.2)

Referring to equation (2.3.15) where we consider the expectation values, the previous equation (5.5.2) is also a six-fold integral

$$\bar{D}_{\nu\eta}^{(i)} = \int \int \int \int \int \int \sin(\theta) R^2 \rho d \gamma_{\nu\eta}^{(i)}(\phi, \theta, \psi, R, \rho, \zeta) d\phi d\theta d\psi dR d\rho d\zeta ,$$

(5.5.3)

with

$$d \gamma_{\nu\eta}^{(i)}(\phi, \theta, \psi, R, \rho, \zeta) = \Psi_{0,0}^{(\nu)}(\phi, \theta, \psi, R, \rho, \zeta) e \vec{r}_c(\psi, \theta, \phi, x, y, z) \Psi_{LM}^{(\eta)}(\phi, \theta, \psi, R, \rho, \zeta) .$$

(5.5.4)

The position vectors $\vec{r}_c(\psi, \theta, \phi, x, y, z)$ are all given in equations (2.2.11) - (2.2.13). If we substitute $\Psi_{LM}^{(\eta)}$ by a wave function and integrate over all angular coordinates $\psi, \theta, \phi$ the transitions from $\Psi_{LM}^{(0)} \rightarrow \Psi_{LM}^{(\eta)}$ with $\eta > 0$, and $\Psi_{LM}^{(0)} \rightarrow \Psi_{LM}^{(\text{even})}$ are equal to zero. This fact represents the selection rules which imply that $\Delta l \pm 1$ , which means that the total angular momentum must raise or descend by one. Therefore all transitions from a S-state to another one are forbidden. The second transition from the ground state to the $\Psi_{LM}^{(\text{even})}$ states are zero, because the term $\vec{w}^{(i)}(\phi, \theta, \psi, R, \rho, \zeta)$ has the following odd property

$$\vec{d}^{(i)}_{\nu\eta}(\phi, \theta, \psi, R, \rho, \zeta) = -\vec{d}^{(i)}_{\nu\eta}(\pi + \phi, \pi - \theta, \pi + \psi, R, \rho, \zeta) ,$$

(5.5.5)

under parity transformation which is given in equation (3.3.10). Whereas, the transitions $\Psi_{LM}^{(\nu)} \rightarrow \Psi_{LM}^{(\text{odd})}$ are not dipole forbidden, since the term $\vec{w}^{(i)}_{\nu\eta}(\phi, \theta, \psi, R, \rho, \zeta)$ has even parity, cf. equation (3.3.10).

With equation (5.3.14), (5.3.18) and (5.3.12), we use the following two wave function ansaetze for the integration

$$\Psi_{0,0}^{(\nu)}(\phi, \theta, \psi, R, \rho, \zeta) = \frac{1}{\sqrt{8\pi}} \tilde{\Phi}_{\nu}^{(\nu)}(R, \rho, \zeta)$$

(5.5.6)

and

$$\Psi_{1,0}^{(\nu)}(\phi, \theta, \psi, R, \rho, \zeta) = \frac{1}{\sqrt{8\pi}} \cos(\theta) \tilde{\Phi}_{0}^{(\nu)}(R, \rho, \zeta) + \frac{1}{\sqrt{8\pi}} \sin(\theta) \cos(\psi) \tilde{\Phi}_{1}^{(\nu)}(R, \rho, \zeta)$$

(5.5.7)

The integration over all angular coordinates for each of the particles leads to

$$\vec{d}^{(i)}_{\nu\eta}(R, \rho, \zeta) = \begin{pmatrix} 0 \\ 0 \\ e^{4\pi^2(2m_2R \Phi^a+m_3(R+2\zeta) \Phi^a+2m_3 \Phi^a)} \end{pmatrix} \frac{1}{3(m_1+m_2+m_3)}$$

(5.5.8)
for particle 1,

\[ d^{(2)}_{\nu \eta}(R, \rho, \zeta) = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} 4 \pi \exp \left( 2m_1 R \Phi^a + m_3 (R-2\zeta) \Phi^a - 2m_3 \rho \Phi^b \right) \\ 3(m_1 + m_2 + m_3) \end{pmatrix} \] (5.5.9)

for particle 2, and

\[ d^{(3)}_{\nu \eta}(R, \rho, \zeta) = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} 4 \pi \exp \left( (m_2 - m_1) R \Phi^a - 2(m_1 + m_2) \zeta \Phi^a - 2(m_1 + m_2) \rho \Phi^b \right) \\ 3(m_1 + m_2 + m_3) \end{pmatrix} \] (5.5.10)

for the third particle. Therefore, the components in X-direction and Y-direction in Cartesian coordinates referring to the center of mass frame are equal to zero and only in the Z-direction we obtain the whole contribution of the transition matrix elements. Finally, we consider the remaining integral over the coordinates \( R, \rho, \) and \( \zeta. \) We transform this integral into perimetric coordinates and apply Gauss quadrature for the three-fold integral. The transformed expressions of the \( Z \)-components for each particle yields

\[ d^{(i)}_{\nu \eta}(x, y, z) = e \begin{pmatrix} 0, 0, q_a^{(i)}(x, y, z) \Phi_0(x, y, z) + q_b^{(i)}(x, y, z) \Phi_1(x, y, z) \end{pmatrix}^T \] (5.5.11)

with

\[ q_a^{(1)}(\bar{x}, \bar{y}, \bar{z}) = \frac{8 \pi^2 m_3 \sqrt{\bar{x} \bar{y} \bar{z}}} {3(m_1 + m_2 + m_3)(\bar{x} + \bar{y})} \] (5.5.12)

\[ q_a^{(2)}(\bar{x}, \bar{y}, \bar{z}) = \frac{4 \pi^2 (m_2(\bar{x} + \bar{y})^2 + m_3 \bar{z}(\bar{x} + \bar{y}) + m_3 \bar{z}(\bar{x} - \bar{y}))} {3(m_1 + m_2 + m_3)(\bar{x} + \bar{y})} \] (5.5.13)

\[ q_a^{(3)}(\bar{x}, \bar{y}, \bar{z}) = \frac{8 \pi^2 m_3 \sqrt{\bar{x} \bar{y} \bar{z}}} {3(m_1 + m_2 + m_3)(\bar{x} + \bar{y})} \] (5.5.14)

\[ q_b^{(2)}(\bar{x}, \bar{y}, \bar{z}) = \frac{4 \pi^2 (m_2(\bar{x} + \bar{y})^2 + m_3 \bar{y}(\bar{x} + \bar{y}) + m_3 \bar{y}(\bar{x} - \bar{y}))} {3(m_1 + m_2 + m_3)(\bar{x} + \bar{y})} \] (5.5.15)

\[ q_b^{(3)}(\bar{x}, \bar{y}, \bar{z}) = \frac{8 \pi^2 (m_1 + m_2) \sqrt{\bar{x} \bar{y} \bar{z}}(\bar{x} + \bar{y})} {3(m_1 + m_2 + m_3)(\bar{x} + \bar{y})} \] (5.5.16)

\[ q_b^{(3)}(\bar{x}, \bar{y}, \bar{z}) = \frac{4 \pi^2 ((m_2 \bar{y} - m_1 \bar{x})(\bar{x} + \bar{y}) - (m_1 + m_2)(\bar{x} - \bar{y}) \bar{z})} {3(m_1 + m_2 + m_3)(\bar{x} + \bar{y})} \] (5.5.17)

Since the integrals in equation (5.4.3) are very similar to those we need for the transition values, we obtain the right expression, if we compare equation (5.5.2) with (5.4.7). Hence, the transition dipole matrices after Gauss quadrature are given by

\[ \langle \Psi_{0,0}^{(\nu)} | B_{\nu \eta}^{(i)} | \Psi_{1,0}^{(\eta)} \rangle = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} \left[ C_{ijk}^{(\nu)} B_{ijk}^{(\eta)}(q_a^{(i)}(h_x x_i, h_y y_j, h_z z_k) + C_{ijk}^{(\nu)} B_{ijk}^{(j)}(q_b^{(i)}(h_x x_i, h_y y_j, h_z z_k) \right], \] (5.5.18)

where \( C_{ijk} \) represents the linear coefficients of the wave function initial state \( \Psi_{0,0}^{(\nu)} \) with its ansatz in equation (5.3.14). \( B_{ijk}^{(\eta)} \) and \( B_{ijk}^{(j)} \) denote the linear coefficients of \( \Psi_{1,0}^{(\eta)} \) referring to the wave function
The matrix elements of $M$ and for the triplet $S$-states according to equation (5.3.37) by

\[
\langle \Psi_{0,0}^{(s)} | B_{ijk}^{(s)} | \Psi_{1,0}^{(s)} \rangle = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} C_{ijk}^{(s)} B_{ijk}^{(s)}(\eta) \ e^{i(q_{a}^{(i)}(h_{x}x_{i}, h_{y}y_{j}, h_{z}z_{k}) + \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} C_{ijk}^{(s)} B_{ijk}^{(s)}(\eta) \ e^{i(q_{b}^{(i)}(h_{x}x_{i}, h_{y}y_{j}, h_{z}z_{k}))},
\]

(5.5.19)

\[
\langle \Psi_{0,0}^{(t)} | B_{ijk}^{(t)} | \Psi_{1,0}^{(t)} \rangle = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} C_{ijk}^{(t)} B_{ijk}^{(t)}(\eta) \ e^{i(q_{a}^{(i)}(h_{x}x_{i}, h_{y}y_{j}, h_{z}z_{k}) + \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} C_{ijk}^{(t)} B_{ijk}^{(t)}(\eta) \ e^{i(q_{b}^{(i)}(h_{x}x_{i}, h_{y}y_{j}, h_{z}z_{k}))}).
\]

(5.5.20)

5.6 Matrix mapping of the eigenvalue equation

In this section we map the matrix elements which depend on six indices into a two dimensional matrix. Hence, the three-tuple $\{i, j, k\}$ has to be mapped by an one-to-one correspondence into an integer. For the $S$-states of three non-identical particles we map the matrix $M$ with elements $\langle F_{i}^{s} | H_{S} | F_{ijk} \rangle$ which are explicitly given in equation (5.3.59) to a $N(M_{S}) \times N(M_{S})$ matrix, with

\[
N(M_{S}) = N_{y}N_{z}N_{x},
\]

(5.6.1)

which is equal to the number of basis functions $N_{b}$ in equation (5.3.20). If $[M_{S}]_{a,b}$ denotes the matrix element of row $a$ and column $b$, a prescription for the index mapping is given by

\[
a = N_{y}N_{z}(i' - 1) + N_{z}(j' - 1) + k',
\]

(5.6.2)

\[
b = N_{y}N_{z}(i - 1) + N_{z}(j - 1) + k.
\]

(5.6.3)

In terms of this mapping, the matrix $M_{S}$ is given by

\[
[M_{S}]_{a,b} = \langle F_{i}^{s} | H_{S} | F_{ijk} \rangle.
\]

(5.6.4)

Since equation (5.3.59) includes some Kronecker delta functions we obtain a matrix $M_{S}$ with a large fraction of zero-valued components. In figure (5.6.1) we illustrate in matrix sparsity plots with small blue squares all matrix elements of $M_{S}$ which are not equal to zero.

The matrices $M_{S}^{(s)}$ for the $S$-singlet states and $M_{S}^{(t)}$ for $S$-triplet states differ, since we have to consider symmetric and anti-symmetric wave functions and we obtain two different eigenvalue equations (5.3.92) and (5.3.65). The number $N_{b}^{(s)}$ and $N_{b}^{(t)}$ of basis functions, which we need for the singlet and triplet states are reduced compared to the case of three non-identical particles. Consequently, the matrix sizes of $M_{S}^{(s)}$ and $M_{S}^{(t)}$ are both smaller than the size of $M_{S}$. The number $N(M_{S}^{(s)})$ for the singlet $S$-states is given by

\[
N(M_{S}^{(s)}) = N_{x}N_{y}/2,
\]

(5.6.5)

and for the triplet $S$-states according to equation (5.3.37) by

\[
N(M_{S}^{(t)}) = N_{x}N_{y}/2.
\]

(5.6.6)

The matrix elements of $M_{S}^{(s)}$ and $M_{S}^{(t)}$ are denoted as $[M_{S}^{(s)}]_{a,b}$. The index mapping for the singlet matrix is given by

\[\text{ansatz in equation (5.3.18). The dipole transition matrix elements in equation (5.5.18) for three non-identical particles can be extended to the case of two identical Fermionic particles. We do not consider the effect of a spin flip, which means, that we have just transitions from singlet to singlet state or from triplet to triplet state.} \]
Figure 5.6.1: Non-zero matrix elements of $M_S$ for three non identical particles in the S-state with $N(M_S) = 64$ (left figure), with $N(M_S) = 216$ (center figure), and with $N(M_S) = 512$ (right figure).

Figure 5.6.2: Non-zero matrix elements of $M_S^{(s)}$ for two identical fermionic particles in the S singlet state with $N(M_S^{(s)}) = 40$ (left figure), with $N(M_S^{(s)}) = 126$ (center figure), and $N(M_S^{(s)}) = 288$ (right figure).

Figure 5.6.3: Non-zero matrix elements of $M_S^{(t)}$ for two identical fermionic particles in the S triplet state with $N(M_S^{(t)}) = 24$ (left figure), with $N(M_S^{(t)}) = 90$ (center figure), and $N(M_S^{(t)}) = 224$ (right figure).
\[ a^{(s)} = N_z(i'(i' + 1) + 1) + N_z(j' - 1) + k' , \quad (5.6.7) \]
\[ b^{(s)} = N_z(i + 1)(i - 1)/2 + N_z(j - 1) + k . \quad (5.6.8) \]

The index mapping for the triplet S-states is very similar to the one of the singlet S-states. We have just to take into account, that the maximum of index \( j \) or \( j' \) is \( i - 1 \) respectively \( i' - 1 \) instead of \( i \) or \( j \) like for the S-singlet. Therefore we use the following mapping rules

\[ a^{(t)} = N_z(i' - 1)(i' - 2)/2 + N_z(j' - 1) + k' , \quad (5.6.9) \]
\[ b^{(t)} = N_z(i - 1)(i - 2)/2 + N_z(j - 1) + k . \quad (5.6.10) \]

Referring to the eigenvalue equation (5.3.92), the exact matrix elements for \( M_{s}^{(s)} \) take the form

\[ [M_{s}^{(s)}]_{a^{(s)}, b^{(s)}} = d_{ij}^{-1/2} d_{i'j'}^{-1/2} \langle \hat{H}_{S} | F_{ijkl}^{(s)} \rangle , \quad (5.6.11) \]

with \( d_{ij} = 1 + \delta_{ij} \), and \( \langle F_{ijkl}^{(s)} | \hat{H}_{S} | F_{ijkl}^{(s)} \rangle \) from equation (5.3.65). Equation (5.3.65) determines the matrix \( M_{s}^{(s)} \), with

\[ [M_{s}^{(t)}]_{a^{(t)}, b^{(t)}} = \langle F_{ijkl}^{(t)} | \hat{H}_{S} | F_{ijkl}^{(t)} \rangle , \quad (5.6.12) \]

and its elements \( \langle F_{ijkl}^{(a-sym)} | \hat{H}_{S} | F_{ijkl}^{(a-sym)} \rangle \) are given in equation (5.3.67).

The same index mapping rules of the S-states in equation (5.6.2) for \( a \) and (5.6.2) for \( b \) can be used for the P-states with even parity, since the structure of their eigenvalue equations are equal to the S-states structure. The mapping for the \( M_{P}^{(even)} \) which describes three non-identical particles is completely equivalent to \( M_{S} \). According to the eigenvalue equation (5.3.78), the matrix elements \( [M_{P}^{(even)}]_{a,b} \) are given by

\[ N(M_{P}^{(even)}) = N_x N_y N_z , \quad (5.6.14) \]

\[ M_{p}^{(even)} \] is a \( N(M_{p}^{(even)}) \times N(M_{p}^{(even)}) \) matrix and the number \( N(M_{p}^{(even)}) \) is equivalent to the matrix \( M_{S} \) for the S-states matrix

For the singlet and triplet P-states with even parity, where the matrices are denoted as \( M_{p}^{(s)(even)} \) for singlet states and \( M_{p}^{(t)(even)} \) for triplet states, we have to take into account, that the sum limits of the eigenvalue equations are interchanged with respect to the singlet and triplet S-states. This means, that the index mapping for the P-singlet state is equal to the one of the S-triplet state, and vice versa. Hence, the indices for the \( M_{P}^{(s)} \) are mapped by \( a^{(t)} \) and \( b^{(t)} \) and the matrix elements are expressed by

\[ [M_{p}^{(s)(even)}]_{a^{(t)}, b^{(t)}} = \langle F_{ijkl}^{(R)(a-sym)} | \hat{H}_{P}^{(even)} | F_{ijkl}^{(R)(a-sym)} \rangle , \quad (5.6.15) \]

where we can use equation (5.3.94) for \( \langle F_{ijkl}^{(R)(a-sym)} | \hat{H}_{P}^{(even)} | F_{ijkl}^{(R)(a-sym)} \rangle \). Consequently, the indices for \( M_{p}^{(t)} \) are mapped by \( a^{(s)} \) and \( b^{(s)} \) with its matrix elements

\[ [M_{p}^{(t)(even)}]_{a^{(s)}, b^{(s)}} = d_{ij}^{-1/2} d_{i'j'}^{-1/2} \langle \hat{H}_{P}^{(even)} | F_{ijkl}^{(R)(sym)} \rangle , \quad (5.6.16) \]

again with \( d_{ij} = 1 + \delta_{ij} \), and \( \langle \hat{H}_{P}^{(even)} | F_{ijkl}^{(R)(sym)} \rangle \) from equation (5.3.93). Both matrices, \( M_{p}^{(s)(even)} \), and \( M_{p}^{(t)(even)} \) are quadratic and their size is given by
\begin{equation}
N(M_P^{(s)(even)}) = N_{xy}(N_{xy} - 1)/2N_z,
\end{equation}
\begin{equation}
N(M_P^{(t)(even)}) = N_{xy}(N_{xy} + 1)/2N_z.
\end{equation}

The sparsity plot of \( M_P^{(even)} \) is equivalent to \( M_S \) due to the same Kronecker delta relations for both matrices. Additionally, we obtain a similar result for the matrices \( M_P^{(s)(even)} \) and \( M_P^{(t)(even)} \). The Kronecker delta functions, which appear at certain matrix elements are equal to those of the \( M_S^{(s)} \), and \( M_S^{(t)} \) matrix. Therefore, the matrix plot of \( M_S^{(s)} \) is equal to \( M_P^{(t)(even)} \), and the remaining pair \( M_S^{(t)} \) and \( M_P^{(s)(even)} \) have also exactly the same sparsity pattern.

The last matrices which we have to consider are the ones for P-states with odd parity. These matrices are denoted as \( M_P^{(odd)} \) for three non-identical particles and \( M_P^{(s)(odd)} \) for the calculations of singlet states and \( M_P^{(t)(odd)} \) for triplet states. We have seen in section 5.3.3 that these matrices can be divided into four partitions. The matrix \( M_P^{(odd)} \) is given by
\begin{equation}
M_P^{(odd)} = \begin{pmatrix}
M_{(0,0)P}^{(odd)} & M_{(0,1)P}^{(odd)} \\
M_{(1,0)P}^{(odd)} & M_{(1,1)P}^{(odd)}
\end{pmatrix},
\end{equation}
and the matrix elements of the four submatrices are explicitly given in equation (5.3.102) - (5.3.105).

Similarly, we obtain the matrix for odd singlet P-states and the odd triplet P-states
\begin{equation}
M_P^{(s)(odd)} = \begin{pmatrix}
M_{(0,0)P}^{(s)(odd)} & M_{(0,1)P}^{(s)(odd)} \\
M_{(1,0)P}^{(s)(odd)} & M_{(1,1)P}^{(s)(odd)}
\end{pmatrix},
\end{equation}
\begin{equation}
M_P^{(t)(odd)} = \begin{pmatrix}
M_{(0,0)P}^{(t)(odd)} & M_{(0,1)P}^{(t)(odd)} \\
M_{(1,0)P}^{(t)(odd)} & M_{(1,1)P}^{(t)(odd)}
\end{pmatrix},
\end{equation}
and all matrix elements of the \( M_P^{(s)(odd)} \) submatrices are expressed in equations (5.3.129) - (5.3.132). The remaining four matrix elements for \( M_P^{(t)(odd)} \) can be taken from equation (5.3.134) - (5.3.137). All matrices \( M_P^{(odd)} \), \( M_P^{(s)(odd)} \), and \( M_P^{(t)(odd)} \) are quadratic and have sizes \( N(M_P^{(odd)}) \), \( N(M_P^{(s)(odd)}) \), and \( N(M_P^{(t)(odd)}) \), respectively which is directly given by the sizes of the submatrices. Referring to the eigenvalue equation (5.3.125) for \( M_P^{(odd)} \), all four submatrices have the same size which is equal to the size of the \( M_S \) matrix. Therefore \( N(M_P^{(odd)}) \) is given by
\begin{equation}
N(M_P^{(odd)}) = 2N_xN_yN_z.
\end{equation}

According to the remaining two eigenvalue equations (5.3.127) and (5.3.126) the matrix sizes of the corresponding submatrices are not equal, since we have different limits for the sum. Additionally, the submatrices are not square matrices. Hence, the matrix sizes of the submatrices of \( M_P^{(s)(odd)} \) are given by
\begin{align}
M_{P(0,0)}^{(s)(odd)} &= N(M_S^{(s)}) \times N(M_S^{(s)}) \\
M_{P(0,1)}^{(s)(odd)} &= N(M_S^{(s)}) \times N(M_S^{(t)}) \\
M_{P(1,0)}^{(s)(odd)} &= N(M_S^{(t)}) \times N(M_S^{(s)}) \\
M_{P(1,1)}^{(s)(odd)} &= N(M_S^{(t)}) \times N(M_S^{(t)}).
\end{align}
The sizes of the submatrices of $M_{P}^{(t)(\text{odd})}$ are

\[
M_{P(0,0)}^{(t)(\text{odd})} = N(M_{S}^{(t)}) \times N(M_{S}^{(t)}) \quad (5.6.27)
\]

\[
M_{P(0,1)}^{(t)(\text{odd})} = N(M_{S}^{(s)}) \times N(M_{S}^{(t)}) \quad (5.6.28)
\]

\[
M_{P(1,0)}^{(s)(\text{odd})} = N(M_{S}^{(s)}) \times N(M_{S}^{(s)}) \quad (5.6.29)
\]

\[
M_{P(1,1)}^{(t)(\text{odd})} = N(M_{S}^{(s)}) \times N(M_{S}^{(s)}) . \quad (5.6.30)
\]

Therefore, the matrix $N(M_{P}^{(s)(\text{odd})})$ in equation (5.6.20) and \( N(M_{P}^{(t)(\text{odd})}) \) (5.6.21) have both the same size which is given by

\[
N(M_{P}^{(s)(\text{odd})}) = N(M_{P}^{(t)(\text{odd})}) = N_{xy}(N_{xy} + 1)/2N_{z} + N_{xy}(N_{xy} - 1)/2N_{z} = N_{xy}^{2}N_{z}/2 . \quad (5.6.31)
\]

After introducing all necessary matrices, we analyze their eigenvalues and eigenvectors for some physical three-body systems in the next chapter.
Chapter 6

Variational calculation

6.1 Energy levels and accuracy of the method

In chapter 2 we transformed the Hamiltonian $\hat{H}_c$ from the usual Cartesian coordinates into angular coordinates $\phi, \theta, \psi$, the Euler angles, and the perimetric coordinates $x, y, z$. In chapter 3 and 4 we considered the symmetries of the wave functions and introduced a linear combination of the Wigner-D-matrix elements with $\Phi(x, y, z)$. The function $\Phi(x, y, z)$ depends only on the perimetric coordinates and can be expanded by a linear combination of Lagrange-Laguerre $\tilde{f}_i(u)$ polynomials as we have seen in chapter 5. Using the Lagrange-Laguerre ansatz, we have introduced eigenvalue equations depending on the symmetry of the wave functions. The eigenvalues and eigenfunctions of those equations are solutions of the three-body Schrödinger equation. In this chapter we show explicit applications of the Lagrange-Laguerre variational method. To compute accurate energy values $E_\nu$ and expansion coefficients, we wrote a Fortran 90 code, which implements the Lagrange-Laguerre variational method. The eigenvalues and eigenvectors are calculated by the software package 'ScaLAPACK' [BCC+96]. The matrices which result from the Lagrange-Laguerre approach are rather sparse. Nevertheless, we perform a dense matrix diagonalization with the advantage of an access to all eigenvalues and eigenfunctions. This allows us to compute e.g. transition matrix elements for all states which are represented within the basis set. Solving the matrices in section 5.6 with the physical parameters $m_i$ for the particle mass $i$ and $Z_i$ the charge number of the particle $i$, yields the binding energy of the considered system. If a system is bound we obtain negative energy values. The lowest eigenvalue, i.e. the ground-state energy corresponds to the lowest energy of the S-states. In the case of three identical particles or three particles with identical charges, the Coulomb interaction in equation (2.1.9) leads to a repulsion of all three particles. Obviously, particles with identical charged sign are never bound and the energy eigenvalues are always above zero. In the present work, we consider three-body systems where one particle has charge of opposite sign. The Lagrange-Laguerre variational method leads to highly accurate results of binding energies which we demonstrate with explicit calculations of the energy eigenvalues for the S-states and P-states for the Helium atom, the $\text{dt}_\mu$, $\text{H}_2^+$ and the $\text{HD}^+$ molecules. Since we do not rely on the Born-Oppenheimer approximation in our approach, these results can serve as benchmark to study finite-mass effects. All results are calculated and given in atomic units (a.u.)

$$e = \hbar = m_e = \frac{1}{4\pi\varepsilon_0} = 1.$$ (6.1.1)

The $\text{dt}_\mu$ and $\text{HD}^+$ molecules describe two systems of three non-identical particles, whereas the Helium atom consists of two electrons and one $\alpha$-particle and $\text{H}_2^+$ of two protons and one electron.

- Helium atom

The Helium nucleus is equal to an alpha particle, composed of two protons and two neutrons. It has total spin of zero and the mass ratio between an electron and an alpha particle, referring to [HB01], is given by
\begin{align}
    m_{\text{nucleus}}^{(\text{He})} &= 7.294.261.824.1 \, m_e . 
\end{align}

Since each electron or proton has spin 1/2, the total wave function \( \Psi_{\text{tot}} \) has to be anti-symmetric. Referring to the product of a spatial function \( \Psi \) and a spin function \( \Xi \) of the total wave function ansatz in equation (2.1.7), one of the two functions has to be symmetric and the other one anti-symmetric when we interchange coordinates of identical particles. According to section 3.4, all states with anti-symmetric spin function are singlet states, and all states with symmetric spin function are triplet states. As mentioned in section 3.4, our considerations for symmetric and anti-symmetric wave functions in chapter 4 and chapter 5 are only valid, if particles 1 and 2 describe Fermionic particles. The complete set of used Helium parameters is given by

\begin{align}
    m_1 &= m_e = 1 , \quad m_2 = m_e = 1 , \quad m_3 = m_{\text{nucleus}}^{(\text{He})} , \quad Z_1 = -1 , \quad Z_2 = -1 , \quad Z_3 = 2 , \quad (6.1.3)
\end{align}

where \( m_j \) denotes the mass \( m_j \) and \( Z_j \) the charge number of particle \( j \) referring to the section 2.1.

- **H\(_2^+\)** molecule

  The second system which has two identical Fermionic particles is the charged H\(_2^+\) molecule. It consists of one electron and two protons, which have, similar to the electron, spin 1/2. Hence, we have the same considerations as for Helium. In this case, the total wave function \( \Psi_{\text{tot}} \) in equation (2.1.7) is anti-symmetric in the proton coordinates. Similar to the electrons in Helium, two protons in H\(_2^+\) arise in singlet or triplet states. The mass ratio of the H\(_2^+\) proton mass and the electron mass is chosen for the present considerations equal to the value used by Hesse and Baye [HB01]

\begin{align}
    m_{\text{proton}} &= 1.836.142.701 \, m_e . 
\end{align}

The corresponding parameters for the H\(_2^+\) molecule are then given as

\begin{align}
    m_1 &= m_{\text{proton}} , \quad m_2 = m_{\text{proton}} , \quad m_3 = m_e = 1 , \quad Z_1 = 1 , \quad Z_2 = 1 , \quad Z_3 = -1 . \quad (6.1.5)
\end{align}

- **HD\(^+\)** molecule

  To clarify the effects of two identical Fermionic particles, we compare the H\(_2^+\) with the HD\(^+\) molecule. In contrast to H\(_2^+\), the HD\(^+\) molecule consists of three non-identical particles. One proton is replaced by a deuteron which has spin and charge number of one. We use the same mass for the deuteron as Alexander and Monkhorst [AM88]

\begin{align}
    m_{\text{deuteron}} &= 3670.581 \, m_e , 
\end{align}

and the complete set of parameters is given by

\begin{align}
    m_1 &= m_{\text{proton}} , \quad m_2 = m_{\text{deuteron}} , \quad m_3 = m_e = 1 , \quad Z_1 = 1 , \quad Z_2 = 1 , \quad Z_3 = -1 . \quad (6.1.7)
\end{align}

- **dt\(\mu\)** molecule

  The last system, which we consider is also composed of three non-identical particles. The dt\(\mu\) molecule has two positive charged particles, one deuteron and one triton, and a single negative charged particle, the muon. The deuteron and the triton have the same charge number, which is one, but different masses. The muon has the charge number one like the electron, but it has a larger mass. The masses which we use for our calculations are all adopted from Alexander and Monkhorst [AM88] with
\[ m_{\text{triton}} = 5496.918 \, m_e, \quad (6.1.8) \]

and

\[ m_{\text{muon}} = 206.7686 \, m_e. \quad (6.1.9) \]

In summary, all necessary parameters are given by

\[ m_1 = m_{\text{deuteron}}, \quad m_2 = m_{\text{triton}}, \quad m_3 = m_{\text{muon}}, \quad (6.1.10) \]

\[ Z_1 = 1, \quad Z_2 = 1, \quad Z_3 = -1. \quad (6.1.11) \]

### 6.1.1 Convergence

Based on variational calculations of Helium and H\textsuperscript{2+}, we exemplify the convergence of the energy eigenvalues for increasing system sizes \( N_x, N_y, \text{ and } N_z \). Additionally, we demonstrate the quantitative accuracy of our Lagrange-Laguerre variational method by comparing the results with the literature. In section 5.2 we have seen that it is necessary to scale the Lagrange-Laguerre functions \( f_i(u) \) which appear in the wave function ansatz in section 5.3 to get the optimal results for e.g. the ground-state energy. Although, we use the variational principle to obtain the lowest energy values, the Lagrange-Laguerre method is not strictly variational, since we calculate the integrals of the corresponding matrix elements by the Gauss quadrature. The difference between the integral approximation and the exact values can result in lower eigenvalues than the exact ones. However, such eigenvalues turn out to be not stable for a increasing amount of Lagrange-Laguerre basis functions. Therefore, we vary the three scaling factors \( h_x, h_y, \text{ and } h_z \) within a certain interval by small steps and calculate the lowest energy eigenvalue for all combinations of the scaling factors. Taking the errors of the Gauss quadrature into account, the optimal scale factors are those, which give us the lowest energy and stable eigenvalues for increasing number of Lagrange-Laguerre functions \( N_x, N_y, \text{ and } N_z \). After determining the scale factors \( h_x, h_y \text{ and } h_z \), we start to analyze the convergence behavior for increasing \( N_x, N_y, \text{ and } N_z \). Afterwards we calculate for the Helium atom, the dt\textsubscript{µ}, the H\textsuperscript{+}\textsubscript{2}, and the HD\textsuperscript{+}\textsubscript{m} molecules the four lowest energy values for the different states which we have considered in chapter 5.3. The convergence behavior gives us the possibility to determine the necessary system size, which we need in order to reach in order a stable lowest energy. First, we take a look at the system size \( N \). Since we consider the convergence exemplarily for the singlet S-states of Helium and H\textsuperscript{2+}, we know from the wave function ansatz in equation (5.3.31) that two numbers, i.e \( N_{xy} \text{ and } N_z \), determine the number of matrix elements by equation (5.6.5). We use the same number of basis functions for all three dimensions of the perimetric coordinates and therefore we define

\[ N = N_{xy} = N_z. \quad (6.1.12) \]

Next, we perform a series of eigenvalue calculations where we start with the lowest system size \( N = 2 \) and end at \( N = 40 \) for the Helium atom and \( N = 30 \) for the H\textsuperscript{2+} molecule. With the two sets of parameters, in equation (6.1.3) for the Helium atom and in equation (6.1.5) for the H\textsuperscript{2+} molecule, we determine first the optimal scale factors \( h_{xy} \text{ and } h_z \) for the lowest energy level. For the Helium atom, we obtain \( h_{xy} = 0.5 \text{ and } h_z = 0.4 \), and for the H\textsuperscript{2+} it turns out that \( h_{xy} = 0.16 \text{ and } h_z = 1.4 \) lead to the lowest value. In figures (6.1.1) and (6.1.2) we plot the lowest ten eigenvalues of Helium and H\textsuperscript{2+} as function of the system size \( N \). In both plots it can be seen clearly that the values decrease monotonically for each eigenvalue and consecutively starting with the lowest energy level they stabilize around a certain value. Especially the ground-state energy of Helium, which is the black line in figure (6.1.1), reaches a stable value already for the lowest system size of 2, while the first excited \(^1S\)-state can be regard as converged for \( N \geq 8 \). The system size \( N \) for high-lying excited S-states has to be larger in order to obtain convergence. In the plot on the right-hand side of figure (6.1.1), we see that for \( N = 40 \) only the first four excited S-states have reached a quantitative converge. In contrast, the
Variational calculation

Figure 6.1.1: Convergence of the lowest ten bound singlet S-state energy values of Helium for different numbers $N$ of basis functions

convergence behavior for $H^+_2$ differs. The ground state energy value for $N = 2$ is even positive and far away from its stable value which is approximately reached for $N = 8$. On the other hand, the convergence of the excited S-states are distinctly better than for Helium. For $N \geq 30$ the ground state and the six lowest-lying excited states can be regarded as converged.

As further example, we show the convergence of the energy level scheme for the $H^+_2 \ ^1S$-states. In figure (6.1.3) we plot all energy levels which are below zero for $N = 20$, $N = 30$, $N = 40$, and $N = 50$. Obviously, with greater system size, the amount of negative eigenvalues and therefore the number of bound eigenstates increases. Additionally, the distribution of the eigenvalues stabilizes. The plot reveals an accumulation point around an energy value of $-0.5$ a.u. Above this level the density of energy levels is getting lower. The density of energy levels increases again at around $-0.17$ a.u. and getting denser and denser for higher energies. We analyze this property more in detail in the next section. Figure (6.1.4) shows for the same system sizes $N$ as in figure (6.1.3) the energy level scheme starting from the ground-state energy to the accumulation point. The four lowest energy levels vary all just in small steps if we compare the schemes from left to right. According to figure (6.1.2) they reach stable values for $N \geq 40$. The number of energy values which is between the energy interval of the third excited S-state and $-0.5$ a.u. grows for a larger system size and the energy level difference between two states decrease more and more if we approach $-0.5$ a.u. Close to this energy value it seems that the difference converges to zero and this value should have a special meaning, which we consider more in detail in section 6.1.2.

6.1.2 Energy eigenvalues of He, dt$\mu$, $H^+_2$, and HD$^+$

In this section we calculate the eigenvalues of the S-states and P-states with magnetic quantum number equal to zero for the case of Helium, the dt$\mu$ molecule, $H^+_2$ and HD$^+$. For each of these three-body systems, we tabulate some of the lowest eigenvalues. Due to the Gauss-quadrature and the variational nature, the Lagrange-Laguerre method can reach a high accuracy. To demonstrate this, we compare our results with values from the literature, which have a similar accuracy. Additionally, we calculate the infinite-mass limit for the nucleus of Helium and the two protons of $H^+_2$ to obtain the quantitative difference of the infinite-mass approximation. Further, since we obtain all eigenvalues and states, we additionally illustrate the energy level schemes for different symmetry classes.

For Helium, we use the parameters from equation (6.1.3). The results of the eigenvalue calculations are shown in table 6.1 for the S-states, in table 6.2 for the P-states with even parity and in table 6.3 for the P-states with odd parity. Each of the tables includes both electronic spin combinations, the singlet states
Variational calculation

Figure 6.1.2: Convergence of the lowest ten bound singlet S-state energy values of $H_2^+$ for different numbers $N$ of basis functions

Figure 6.1.3: Energy spectrum for $1S_{1/2}$ for negative energy levels

Figure 6.1.4: Energy spectrum for $1S_{1/2}$ between ground state energy and $-13.6$ eV

and the triplet states.

All of the lower energy eigenvalues, which we calculate correspond to a state in the standard atomic notation. For the S-states this notation is given by $(1s \, n \, L)^{(2S+1)}/L^{(II)}$ with parity $\Pi$. According to this consideration, one of the electrons is in the 1s state and the other one is in the excited state. The capital letter $L$ determines the total angular momentum, and $S$ is the total spin of the two electrons. The table 6.1 is divided into two columns, the left one gives the eigenvalues with the real physical mass of $m_3 = m(\text{He})$ of the Helium nucleus. In the right column we consider the infinite-mass limit ($m_3 \rightarrow \infty$). We compare our eigenvalues for the real physical Helium nucleus mass with those of Hesse and Baye [HB01] which are labeled by (a). Their results are almost equivalent to ours, since they used the same method. They used 24 600 basis functions for the $^1S^0$ calculations, while we increase the number up to 32 800 basis functions. Additionally to the results of Hesse and Baye, we give in table 6.1 the eigenvalues of Drake (1996) [Dra96] which we labeled with (b). Drake used a different method and employed about 1000 Hylleraas basis functions. His values have an accuracy, which is better than $10^{-14}$ for the S and P states of the Helium atom. The Lagrange-Laguerre variational method can almost reach this accuracy. Compared to the results of Drake our accuracy in the present case reaches a level of $10^{-13}$. Although our basis set was larger than Hesse’s and Baye’s, we have not achieved much more accuracy. For the lowest energy
level of Helium about 24 600 Lagrange Laguerre basis functions are sufficient to obtain an accuracy of 10\(^{-12}\). The comparison between our infinite-mass results and the real non-relativistic three-body system with physical mass agree up to an order of 10\(^{-3}\). We obtain a relative deviation of 0.014 % to the exact non-relativistic value. The relative deviation between the infinite-mass limit and the exact non-relativistic three-body problem stays approximately constant for the higher-lying excited states. Increasing the mass \(m_3\) to infinity is equivalent to neglecting all terms which contain \(\hat{h}_3\). In table 6.2 we consider the (2p 2p)\(^\text{P}\)(even) states which corresponds to our 2\(^2\text{P}\)(even) and 2\(^3\text{P}\)(even) singlet states and 2\(^4\text{P}\)(even) and 2\(^5\text{P}\)(even) triplet states. Obviously the binding energy of the P-even-states is lower than the S-states. Similar to the case of the S-state our results agree with those of Hesse, Baye and Drake quantitatively up to the order of 10\(^{-12}\).

Table 6.2 gives the results of the four lowest energy values for the P-states and wave functions with even parity. The even P-states are labeled with \((2p \, n\, p)^{2S+1}\, P\text{(even)}\) in the standard atomic notation with the principal quantum number \(n\). In table 6.2 we consider the \((2p \, 2p)^{2S+1}\, P\text{(even)}, \,(2p \, 3p)^{2S+1}\, P\text{(even)}, \,(2p \, 4p)^{2S+1}\, P\text{(even)}, \,(2p \, 5p)^{2S+1}\, P\text{(even)}\) states which corresponds to our 2\(^2\text{P}\text{(even)}, \,3\(^2\text{P}\text{(even)}, \,4\(^2\text{P}\text{(even)}, \,5\(^2\text{P}\text{(even)}\) singlet states and 2\(^3\text{P}\text{(even)}, \,3\(^3\text{P}\text{(even)}, \,4\(^3\text{P}\text{(even)}, \,5\(^3\text{P}\text{(even)}\) triplet states. Obviously the binding energy of the P-even-states is lower than the S-states. Similar to the case of the S-state our results agree with those of Hesse and Baye. For the case of infinite-mass we compare our results with Goodson et al. [GWLH91] which agree to an order of 10\(^{-12}\). They consider excited \(P\text{(even)}\) states by interdimensional degeneracies based on calculations of singly excited S-states energies. Our reference for the finite physical mass calculation for the 2\(^2\text{P}\text{(even)}\) state is taken from Bhatia [Bha70]. Again, the difference between the physical mass and the infinite-mass calculations is of the order of 10\(^{-3}\). The relative deviation is also about 0.015% for all considered even P-states.

Additionally we consider the P-states states with odd parity. The binding energies are equivalent to the eigenvalues of the matrices \(M^{(a)\text{(odd)}}_P\) in equation (5.6.20) for the singlet states and \(M^{(b)\text{(odd)}}_P\) in equation (5.6.21) for the triplet states. According to section 5.3.3, more linear coefficients are required to expand the odd

<table>
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<th>state</th>
<th>(N_{xy})</th>
<th>(N_z)</th>
<th>(N(M))</th>
<th>(h_{xy})</th>
<th>(h_z)</th>
<th>(\langle E \rangle) (a.u.) ((m_3=\text{He}))</th>
<th>(\langle E \rangle) (a.u.) ((m_3=\infty))</th>
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<tbody>
<tr>
<td>(1^1\text{S}\text{(even)})</td>
<td>40</td>
<td>40</td>
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<td>30</td>
<td>24 600</td>
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<td>0.5</td>
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<td>-2.903 724 377 034 3 (^{(a)})</td>
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<tr>
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<td>40</td>
<td>32 800</td>
<td>0.8</td>
<td>0.5</td>
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<td>-2.145 974 046 050 0 (^{(a)})</td>
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<tr>
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<td>16 400</td>
<td>0.8</td>
<td>0.5</td>
<td>-2.145 678 586 051 (^{(a)})</td>
<td>-2.145 974 046 044 (^{(a)})</td>
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<tr>
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<td>0.5</td>
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<td>16 400</td>
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<td>0.5</td>
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<tr>
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<td>40</td>
<td>32 800</td>
<td>1.4</td>
<td>0.6</td>
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<td>40</td>
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<td>8700</td>
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<tr>
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<td>40</td>
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<td>31 200</td>
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<td>0.5</td>
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<td>-2.068 689 067 472 0 (^{(a)})</td>
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<td>-2.068 689 067 472 4 (^{(a)})</td>
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<tr>
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<td>40</td>
<td>31 200</td>
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<td>-2.022 341 571 737 5 (^{(a)})</td>
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In summary, for the infinite-mass limit of the Helium three-body system we find approximately a relative agreement with the results of Hesse and Baye and Drake. For the lowest even P-state we obtain an error of 10^{-14} for the singlet states and 10^{-12} for the triplet states referring to Drake. For the first higher excited even singlet and triplet P-states, the error increases to 10^{-10}. The results of Hesse and Baye differ a little more to those of Drake since they used a smaller number of Lagrange-Laguerre functions. The binding energies for the even P-states are obviously much lower than for even parity and distinctly closer to energies of the S-states than to the energies of P-even states. Therefore, the two matrices for the odd P-states are distinctly larger than the corresponding matrices of the even states for the same number $N_{xy}$ and $N_z$ of Lagrange-Laguerre functions. Both row and column sizes, $N(M^{(x)(odd)}_P)$ for the singlet states and $N(M^{(t)(odd)}_P)$ for the triplet states, are given by equation (5.6.31). Despite of the smaller size of the basis set, we obtain almost the same accuracy of the energy values compared to the S-states and even P-states. They are in good agreement with the results of Hesse and Baye and Drake. The reference values are labeled as (a) [HB01], (c) [GWLH91], and (d) [Bha70].

Table 6.2: Binding energies for Helium singlet and triplet P-states with even parity in atomic units. $N_{xy}$ and $N_z$ give the number of Lagrange functions for each perimetric coordinate and $N(M)$ denotes the total number of Lagrange-Laguerre basis functions. The scale factors are denoted by $h_{xy}$ and $h_z$. The masses $m_1$ and $m_2$ for the protons are given by $m_{proton} = 1.836.142.701 m_e$. The reference values are labeled as (a) [HB01], (c) [GWLH91], and (d) [Bha70].

<table>
<thead>
<tr>
<th>state</th>
<th>$N_{xy}$</th>
<th>$N_z$</th>
<th>$N(M)$</th>
<th>$h_{xy}$</th>
<th>$h_z$</th>
<th>$\langle E \rangle$ (a.u.) $(m_3 \approx \text{He})$</th>
<th>$\langle E \rangle$ (a.u.) $(m_3 \approx \infty)$</th>
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<td>12 600</td>
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<td>-0.567 733 869 714 03 (a)</td>
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<td>40</td>
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<td>32 800</td>
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<td>-0.519 549 181 840 335</td>
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</table>

As second example we consider the $dt\mu$ molecule. The notation of the states is chosen as $(\eta, L)$, where $\eta$ denotes a vibrational quantum number and $L$ the rotational level which is equivalent to the total angular momentum. All states with angular momentum $L = 0$, which corresponds to $S^{(even)}$ can be calculated by $M_S$. Whereas the eigenvalues of the $(\eta, 1)$ states are eigenvalues of the two matrices $M_P^{(even)}$, and $M_P^{(odd)}$, since both describe an angular momentum of $L = 1$. The $(0, 0)$ and $(0, 1)$ correspond to the $1S^{(even)}$ and $2S^{(even)}$ states, the $(1, 0)$ represents the $2P^{(odd)}$ and $(1, 1)$ the $3P^{(odd)}$ states. The scale parameters are given by $h_x = h_y = 0.6$ and $h_z = 0.7$ for the S-states, $h_x = h_y = 0.6, h_z = 0.8$ for the $2P^{(odd)}$ and $h_x = h_y = 1.4, h_z = 0.8$ for the $3P^{(odd)}$ states. The comparison with the reference values of Alexander and Monkhorst [AM88] shows a consistence of our results with an absolute error of about $10^{-8}$ for the
Finally we consider the two similar systems, the $\text{H}_2^+$ and HD$^+$ molecule and compare their energy values. The matrices which give us the eigenvalues for $\text{H}_2^+$ are the same as for Helium, we have just to change in equation (6.1.5) the parameters to those of $\text{H}_2^+$. The HD$^+$ eigenvalues are calculated in the same fashion as for the $\text{d}t\mu$ matrices, but with the parameters in equation (6.1.7). Similar to our considerations for the $\text{d}t\mu$ molecule, we can compare our states with vibrational and rotational levels and use the same notation. The 1$^1S$ and 2$^1S$ states are represented by (0, 0) and (1, 0) states, whereas (1, 0) and (1, 1) correspond to the 2$^3P$ and 2$^3P$ states. The results for $\text{H}_2^+$ are shown in table (6.5). The scale parameters are $h_{xy} = 0.16$, $h_z = 1.4$ for the (0, 0) and (1, 0) S-states, $h_{xy} = 0.11$, $h_z = 0.8$ for the (0, 1) and (1, 1) S-states. The absolute error of our results compared to Moss [Mos99] is about $10^{-12}$. In contrast to the Helium atom and the $\text{d}t\mu$ molecule, the difference between the ground-state energy of (0, 0) and the first excited rotational state energy of (0, 1) is very small, about $3 \times 10^{-3}$, 0.5% of the ground-state energy. The gap between the Helium 1$^1S$ and the following lowest energy of the 2$^3S$ is about 0.75 a.u., which is 25.8% of the ground-state energy.

Table (6.5) lists the energy values for the 1$^1S$, 2$^1S$, 2$^3P$, and 3$^3P$ states for the HD$^+$ molecule. The corresponding notation of these states in vibrational and rotational levels is (0, 0), (0, 1), (1, 0), (1, 1). We used the same scale factors as for the $\text{H}_2^+$ molecule. Referring to the values of Bubin [BPT+12], our calculations lead to a difference of about $10^{-10}$ for a basis set of 42 875 Lagrange-Laguerre functions. All results are close to those of $\text{H}_2^+$. Since the mass of a deuteron is larger than the mass of a proton and taking into account that the wave functions are not symmetric in the X- and Y-direction of the perimetric coordi-

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<th>state</th>
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<th>$N(M)$</th>
<th>$h_{xy}$</th>
<th>$h_z$</th>
<th>$\langle E \rangle$ (a.u.) ($m_3 = \text{He}$)</th>
<th>$\langle E \rangle$ (a.u.) ($m_3 = \infty$)</th>
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<td>0.4</td>
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<td>-2.020 685 096 285 44</td>
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Table 6.3: Binding energies for Helium P-singlet and P-triplet states with odd parity in atomic units. $N_{xy}$ and $N_z$ give the number of Lagrange functions for each perimetric coordinate and $N(M)$ denotes the total number of Lagrange-Laguerre basis functions. The scale factors are $h_{xy}$ and $h_z$. The masses $m_1$ and $m_2$ for the protons is given by $m_{\text{proton}} = 1 836.142 701 m_e$. The reference values are labeled as (a) [HB01] and (b) [Dra96].

(0, 0) and (1, 0) states and about $10^{-7}$ for the remaining states calculated by the larger $\mathbf{M}_P^{(\text{odd})}$ states. The three lowest energy values of the even P-states can not be represented by variational and rotational levels. We denote them as $2P^{(\text{even})}$, $3P^{(\text{even})}$ and $4P^{(\text{even})}$. If we compare the three P-states with even parity, the energy of $2P^{(\text{even})}$ and $3P^{(\text{even})}$ are relatively close together with an absolute difference of 0.09 a.u., whereas a large gap of 14.08 a.u. arises between the energies of $3P^{(\text{even})}$ and $4P^{(\text{even})}$. We list all considered states in table (6.4).
The lowest accumulation point above the ground state is equivalent to the ionization energy for all µ above the ground-state is about −

All plots reveal several accumulation points at certain values. For Helium, the first accumulation point even P-states energy levels of H shows six columns, two for each parity state. If we compare the singlet and triplet states with even parity h scale factors the optimal stable eigenvalues. The optimal scale factors h eigenvectors. Therefore, we can plot energy level schemes which contain eigenvalues for all states which As mentioned in section 5.6, we perform a dense matrix diagonalization to obtain our eigenvalues and eigenvectors. Therefore, we can plot energy level schemes which contain eigenvalues for all states which are supported by the Lagrange-Laguerre basis set. In section (5.2) we introduced the scale factor h to get the optimal stable eigenvalues. The optimal scale factors h, h, and h vary for each state. If we choose factors which have a large difference to the optimal values e.g. for the ground-state energy, the absolute error compared to the references in literature increases. Nevertheless, to get stable energy values above the ground-state energy, we have to select larger scale factors. In the case of a large number of basis functions the ground-state energy, and the first few excited states are still accurate enough to plot the complete energy level scheme. Figure (6.1.5) and (6.1.6) show the energy level schemes for the Helium atom and the dt molecule. The scale factors are h = h = 3.5 for Helium, and h = h = h = 3.0 for dt. Since the Helium atom can be in a singlet or a triplet state, the S(even), P(even), and P(odd) split into two columns. Additionally, we plot the level schemes of the two similar molecules H and HD with the scale factors h = 1.28 and h = 11.2. Similar to the Helium atom, the plot for H in equation (6.1.7) shows six columns, two for each parity state. If we compare the singlet and triplet states with even parity of Helium and H, the lowest energy for the singlet states are lower than the triplet states. In the case of odd parity, the lowest binding energy of the triplet is larger than for the singlet states. The corresponding wave functions of HD are neither symmetric nor anti-symmetric. Therefore the energy level scheme of HD in figure (6.1.8) is illustrated in three columns. Considering the states with even parity, the energy level scheme of HD is rather similar to the singlet states of H with even parity. In contrast, the triplet even P-states energy levels of H have a higher similarity to the levels of HD with odd parity. All plots reveal several accumulation points at certain values. For Helium, the first accumulation point above the ground-state is about −2.0 a.u., the second one about −0.5 a.u. The location of the first two accumulation points above the ground states for the dt, H, and HD are about −0.5 a.u. and −0.125 a.u. The lowest accumulation point above the ground state is equivalent to the ionization energy for all

<table>
<thead>
<tr>
<th>state</th>
<th>N_x</th>
<th>N_y</th>
<th>N_z</th>
<th>N(M)</th>
<th>h_x</th>
<th>h_y</th>
<th>h_z</th>
<th>⟨E⟩ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1S(\text{even}) \doteq (0, 0)</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>42 875</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>-111.364 511 513 887</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>8 000</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>-111.364 511 513 92\text{ (a)}</td>
</tr>
<tr>
<td>2S(\text{even}) \doteq (1, 0)</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>42 875</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>-100.916 572 087</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>8 000</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>-100.916 572 05\text{ (a)}</td>
</tr>
<tr>
<td>2P(\text{odd}) \doteq (0, 1)</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>54 000</td>
<td>0.6</td>
<td>0.6</td>
<td>0.8</td>
<td>-108.179 542 471 876</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>6 750</td>
<td>0.6</td>
<td>0.6</td>
<td>0.8</td>
<td>-108.179 542 49\text{ (a)}</td>
</tr>
<tr>
<td>3P(\text{odd}) \doteq (1, 1)</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>54 000</td>
<td>1.4</td>
<td>1.4</td>
<td>0.8</td>
<td>- 99.660 699 367 173</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>30</td>
<td>20</td>
<td>36 000</td>
<td>1.4</td>
<td>1.4</td>
<td>0.8</td>
<td>- 99.660 694 \text{ (a)}</td>
</tr>
<tr>
<td>2P(\text{even})</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>54 000</td>
<td>0.5</td>
<td>0.5</td>
<td>0.8</td>
<td>- 40.382 572 313 040</td>
</tr>
<tr>
<td>3P(\text{even})</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>54 000</td>
<td>0.5</td>
<td>0.5</td>
<td>0.8</td>
<td>- 39.690 139 402 670</td>
</tr>
<tr>
<td>4P(\text{even})</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>54 000</td>
<td>0.5</td>
<td>0.5</td>
<td>0.8</td>
<td>- 25.611 970 997 000</td>
</tr>
</tbody>
</table>

Table 6.4: Binding energies of dt with total number N(M) of Lagrange-Laguerre functions and scale factors h, h, and h. N, N, and N are the numbers of Lagrange-Laguerre functions for each perimetric coordinate. The reference values are labeled as (a) for Hesse and Baye [HB01] and (d) for Alexander and Monkhorst [AM88].

nates, the energy values of the HD+ molecule are lower than the energies of H2+. The difference between the ground-state energies of the H2+ and HD+ molecule is rather small with an absolute value of 7.5 × 10⁻⁴.
Figure 6.1.5: Energy level scheme of Helium with $h_{xy} = h_z = 3.5$ for bound states drawn in blue lines. The red lines mark the two-body levels with reduced mass $\mu_{12}$ of He$^+$ and $Z_1 = 2, Z_2 = -1$.

Figure 6.1.6: Energy level scheme of dt$^+$ with $h_x = h_y = h_z = 3.0$ for bound states drawn in blue lines. The red lines mark the two-body levels with reduced mass $\mu_{12}$ of t$^+$ and green line mark the two-body levels with reduced mass d$t^+$ and $Z_1 = 1, Z_2 = -1$.

Figure 6.1.7: Energy level scheme of H$_2^+$ for bound states drawn with blue lines. The scale factors are given by $h_{xy} = 1.28$ and $h_z = 11.2$. The red lines mark the two-body levels with reduced mass $\mu_{12}$ of Hydrogen and $Z_1 = 1, Z_2 = -1$.

Figure 6.1.8: Energy level scheme of HD$^+$ for bound states drawn with blue lines. The scale factors are $h_x = h_y = 1.28$ and $h_z = 11.2$. The red lines mark the two-body levels with reduced mass $\mu_{12}$ for Hydrogen and deuteron.
Table 6.5: Binding energies of H$_2^+$ with total number of Lagrange-Laguerre functions $N(M)$ and scale factors $h_{xy}$ and $h_z$. $N_{xy}$, and $N_z$ denote the number of Lagrange-Laguerre function for each perimetric coordinate. The reference values are labeled as (a) for Hesse and Baye [HB01] and (e) for Moss [Mos99].

<table>
<thead>
<tr>
<th>state</th>
<th>$N_{xy}$</th>
<th>$N_z$</th>
<th>$N(M)$</th>
<th>$h_{xy}$</th>
<th>$h_z$</th>
<th>$\langle E \rangle$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1S^{(even)}(\Omega = (0, 0))$</td>
<td>40</td>
<td>40</td>
<td>32 800</td>
<td>0.16</td>
<td>1.4</td>
<td>-0.597 139 063 121</td>
</tr>
<tr>
<td>$1^1S^{(even)}(\Omega = (0, 0))$</td>
<td>40</td>
<td>25</td>
<td>20 500</td>
<td>0.16</td>
<td>1.4</td>
<td>-0.597 139 063 121 (a)</td>
</tr>
<tr>
<td>$2^1S^{(even)}(\Omega = (1, 0))$</td>
<td>40</td>
<td>40</td>
<td>32 800</td>
<td>0.16</td>
<td>1.4</td>
<td>-0.587 155 679 14</td>
</tr>
<tr>
<td>$2^1S^{(even)}(\Omega = (1, 0))$</td>
<td>40</td>
<td>25</td>
<td>20 500</td>
<td>0.16</td>
<td>1.4</td>
<td>-0.587 155 679 14 (a)</td>
</tr>
<tr>
<td>$2^3S^{(even)}$</td>
<td>40</td>
<td>40</td>
<td>31 200</td>
<td>0.2</td>
<td>1.4</td>
<td>-0.597 743 211 346 2</td>
</tr>
<tr>
<td>$2^3S^{(even)}$</td>
<td>40</td>
<td>25</td>
<td>20 500</td>
<td>0.2</td>
<td>1.4</td>
<td>-0.597 743 211 346 2 (a)</td>
</tr>
<tr>
<td>$2^1P^{(odd)}$</td>
<td>35</td>
<td>35</td>
<td>42 875</td>
<td>0.15</td>
<td>1.2</td>
<td>-0.499 006 565 292 8</td>
</tr>
<tr>
<td>$3^1P^{(odd)}$</td>
<td>35</td>
<td>35</td>
<td>42 875</td>
<td>0.15</td>
<td>1.2</td>
<td>-0.497 599 336 718 4</td>
</tr>
<tr>
<td>$2^3P^{(odd)}(\Omega = (0, 1))$</td>
<td>35</td>
<td>35</td>
<td>42 875</td>
<td>0.11</td>
<td>0.8</td>
<td>-0.596 873 738 832 7</td>
</tr>
<tr>
<td>$2^3P^{(odd)}(\Omega = (0, 1))$</td>
<td>35</td>
<td>35</td>
<td>42 875</td>
<td>0.11</td>
<td>0.8</td>
<td>-0.596 873 738 832 7 (a)</td>
</tr>
<tr>
<td>$3^3P^{(odd)}(\Omega = (1, 1))$</td>
<td>35</td>
<td>35</td>
<td>42 875</td>
<td>0.11</td>
<td>0.8</td>
<td>-0.586 904 321 039 7</td>
</tr>
<tr>
<td>$3^3P^{(odd)}(\Omega = (1, 1))$</td>
<td>35</td>
<td>35</td>
<td>42 875</td>
<td>0.11</td>
<td>0.8</td>
<td>-0.586 904 321 039 7 (a)</td>
</tr>
</tbody>
</table>

The negative charged particle, i.e. the electron or the muon, can bind with one of the two positive particles, and the other particle is separated from the system. Consequentely, we obtain two thresholds for the ionization of d$\mu$ and HD$^+$. The d$\mu$ molecule can be ionized into d$\mu^+$ and triton or into t$\mu^+$ and a deuteron. Similarly the HD$^+$ can ionize into a Hydrogen atom and a deuteron or into a deuteron and H$^+$. Since all remaining ions are two-body systems with reduced mass $\mu$ and opposite sign for the charge, the energy levels for the ions are given in atomic units by [BJ03]

$$E^{(n)}_{\text{ion}}(\mu_{12}) = \frac{\mu_{12}Z_1Z_2}{2n^2},$$ (6.1.13)

where $Z_1$ and $Z_2$ denotes the charge number of the particles and $n \in \mathbb{N}$ labels the principal quantum number. For $n = 1$ the ion is in the ground-state and all values for $n > 1$ describe the higher excited states of the negative charged particle, i.e. electron or muon. In table (6.7) we list the first five thresholds of He$^+$, d$\mu^+$, t$\mu^+$, Hydrogen and deuteron.

All thresholds of the corresponding ions which the three-body systems Helium, d$\mu$, H$_2^+$ and HD$^+$ can occupy, are drawn in figures (6.1.5), (6.1.6), (6.1.7), and (6.1.8) by red lines. Due to the small difference between the two reduced masses $\mu_{12}$ for the different ionization channels of HD$^+$ we plot the mean values. A comparison of the location of the accumulation points in figures (6.1.5), (6.1.6), (6.1.7), and (6.1.8) shows an agreement with the values of the ionization thresholds. For all four three-body systems we obtain the same situation if the system has exactly the energy of an ionization threshold. In this case, the negative charged particle is bound to one of the heavier positive particles. The remaining particle ionizes...
The function \( Y \) have an arbitrary positive energy value. For a higher threshold, \( n > n^0 \) with wave vectors \( \vec{r} \) of the positive and negative particle of the two-body system and \( n = 1 \) in equation (6.1.13) are the only states which the system can occupy. Between the first (of a wave packet can be prepared in a continuous range. This fact has an important consequence for the complete wave function for non-identical particles without spin function is given in atomic units by
\[
\phi = \sum_{\mu_1 \mu_2} \Phi_{\text{Lag-Lag}}(\vec{r}_c^{\text{pos}}, \vec{r}_c^{\text{neg}}) \Phi_{\text{Lag-Lag}}(\vec{r}_c^{\text{free}}) \cdot \Psi_{\text{wp}}(\vec{r}_c^{\text{free}}).
\]

The function \( Y_{1,0}(\theta, \phi) \) determine the orientation of the vector \( \vec{r}_c^{\text{pos}} - \vec{r}_c^{\text{neg}} \) in the three-dimensional space. \( \Phi_{\text{Lag-Lag}}^{(L)}(r) \) describes the radial part of the Hydrogen wave function. The last function in equation (6.1.14) \( \Psi_{\text{wp}}(\vec{r}_c^{\text{free}}) \) is a superposition of plane waves of the form [CTDL99]

\[
\Psi_{\text{wp}}(\vec{r}_c^{\text{free}}) = \int_{-\infty}^{\infty} c(\vec{k}) \exp(-i\vec{k} \cdot \vec{r}_c^{\text{free}}) d\vec{k},
\]

with wave vectors \( \vec{k} \) and coefficients \( c(\vec{k}) \) which describe a wave packet for the free particle. The energies of a wave packet can be prepared in a continuous range. This fact has an important consequence for the three-body system. All discrete energy levels below the first threshold of the ionization energy, i.e. \( n = 1 \) in equation (6.1.13) are the only states which the system can occupy. Between the first (\( n = 1 \)) and the second (\( n = 2 \)) threshold the ion has the discrete energy of \( E^{(1)}(\mu_{12}) \), but the wave packet can have an arbitrary positive energy value. For a higher threshold, \( n > 1 \), the two-body system is in the

Table 6.6: Binding energies of HD* with total number of Lagrange-Laguerre functions \( N(\text{M}) \) and scale factors \( h_x, h_y \) and \( h_z \). \( N_z, N_y \) and \( N_x \) denote the number of Lagrange-Laguerre function for each perimetric coordinate. The reference values are labeled as (f) for Bubin [BPT+12].

<table>
<thead>
<tr>
<th>ion/atom</th>
<th>( \mu_{12} )</th>
<th>( Z_1 )</th>
<th>( Z_2 )</th>
<th>( E^{(1)}(\mu_{12}) )</th>
<th>( E^{(2)}(\mu_{12}) )</th>
<th>( E^{(3)}(\mu_{12}) )</th>
<th>( E^{(4)}(\mu_{12}) )</th>
<th>( E^{(5)}(\mu_{12}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He*</td>
<td>0.999863</td>
<td>2</td>
<td>-1</td>
<td>-1.999730</td>
<td>-0.499931</td>
<td>-0.222192</td>
<td>-0.124983</td>
<td>-0.079989</td>
</tr>
<tr>
<td>d( \mu^* )</td>
<td>0.946671</td>
<td>1</td>
<td>-1</td>
<td>-97.8711</td>
<td>-24.4678</td>
<td>-10.8746</td>
<td>-6.1169</td>
<td>-3.9148</td>
</tr>
<tr>
<td>t( \mu^* )</td>
<td>0.963748</td>
<td>1</td>
<td>-1</td>
<td>-99.6364</td>
<td>-24.9091</td>
<td>-11.0707</td>
<td>-6.2273</td>
<td>-3.9856</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.999456</td>
<td>1</td>
<td>-1</td>
<td>-0.499728</td>
<td>-0.124932</td>
<td>-0.0555253</td>
<td>-0.031233</td>
<td>-0.019989</td>
</tr>
<tr>
<td>Deuteron</td>
<td>0.999728</td>
<td>1</td>
<td>-1</td>
<td>-0.499864</td>
<td>-0.124966</td>
<td>-0.055540</td>
<td>-0.031242</td>
<td>-0.019995</td>
</tr>
</tbody>
</table>

Table 6.7: Ionization energy thresholds \( E_{\text{ion}}^{(n)} \) in atomic units for He*, d\( \mu^* \), t\( \mu^* \), Hydrogen and deuteron for the ion ground-states (\( n=1 \)), and the four (\( n=2-4 \)) low lying excited states of the electron or muon. \( Z_1 \) denotes the charge number of the positive particle, \( Z_2 \) denotes the charge number of the negative particle, and \( \mu_{12} \) represents the reduced mass of both particles.
corresponding excited state and the remaining free particle can again have an arbitrary kinetic energy. Returning to the four level schemes in figures (6.1.5) - (6.1.8), one would therefore expect a continuum starting at the first threshold. However, it seems that a continuum starts in a small interval above the threshold energy, but the density of energy levels is reduced very fast for larger energies. This effect can be seen best in the level scheme of Helium in figure (6.1.5). In the area around the second threshold energy, the density rises again and reaches a maximum at the first excited ionization energy. Then the density decreases until the energy levels approach the third ionization threshold. Close to the third threshold the density of the levels increases again. Above the third ionization threshold the level schemes in figures (6.1.5) - (6.1.8) suggest a continuum. The reason, why the levels do not form a full continuum at the first ionization threshold is due to the fact that our three-dimensional space is limited. Referring to section 5.2, the sampling points of our Lagrange-Laguerre functions determine the size of a box. Therefore the wave function of the ionized particle is not completely free, but it behaves like a particle in a box. The general wave function for a particle in a three-dimensional box is given by [BJ00]

\[ \Psi_{\text{box}}(\vec{r}_{\text{free}}) = \frac{\hbar^2 \pi^2}{2m_{\text{free}}} \sin(n_x \frac{\pi}{K_x} x) \sin(n_y \frac{\pi}{K_y} y) \sin(n_z \frac{\pi}{K_z} z), \]  

(6.1.16)

where \( K_x, K_y, \) and \( K_z \) denote the size of the box for the corresponding \( x, y, \) or \( z \) direction in perimetric coordinates. The integers \( n_x, n_y, \) and \( n_z \) determine discrete energy values which take the form [BJ00]

\[ E_{\text{box}}(n_x, n_y, n_z) = \frac{\hbar^2 \pi^2}{2m_{\text{free}}} \left( \frac{n_x^2}{K_x^2} + \frac{n_y^2}{K_y^2} + \frac{n_z^2}{K_z^2} \right). \]  

(6.1.17)

This relation can be seen in the energy spectrum of Helium above the first ionization threshold in figure (6.1.5). The difference between two discrete energy values in this region is small near the threshold and rises for higher energies. This effect is almost unnoticeable for the remaining energy levels of \( \text{dt} \mu, \ H_2^+ \) and \( \text{HD}^+ \), since the mass of the free particle appears in the denominator of the energy equation. The free particles for \( \text{dt} \mu, \ H_2^+ \) and \( \text{HD}^+ \) are much heavier than the free electron of Helium. Nevertheless, there are some infrequent energy levels in the area between the two first ionization thresholds for \( \text{dt} \mu, \ H_2^+ \) and \( \text{HD}^+ \). It is possible that there are bound states for the corresponding eigenvalue. If we choose larger numbers for \( N_x, N_y, \) and \( N_z, \) the box sizes \( K_x, K_y, K_z \) grow, and we obtain more energy levels from the discretization of the continuum. The levels become denser, since the box sizes appear in the denominator of the energy equation in (6.1.17). Therefore, we can assume that we reach a true continuum if \( N_x, N_y, \) and \( N_z \) reach infinity.

Finally, we consider the convergence of the ionization thresholds. According to equation (6.1.13) the limit is reached at the energy equal to zero for large \( n \). In this case, the electron, or muon is in a very high excited state and the binding energy becomes very small, since the positive particle of the two-body system has a lower attraction in those states. The third particle is still ionized as mentioned above. If the energy of the three-body system is above zero, the former two-body system does also ionize and we can describe the complete system as three free particles in space.

To summarize this section, we have seen, that the Lagrange-Laguerre variational method can reach a high accuracy for the low-lying energy eigenvalues of about \( 10^{-14} \) compared to literature. The infinite mass limit is in the case of Helium a good approximation with a relative error of about 0.015% for the energy values. Further, in the level schemes of the three-body systems appear some accumulation points which we identified as ionization energies. At these energies, one of the particles with the same charged sign ionizes and the remaining two can be treated as a two-body system. This system can be in the ground-state or in any excited state. This excited states explain the further accumulation points above the first ionization energy. If the energy crosses zero, all three particles are ionized. Since we have highly accurate energy values for the ground state and therefore the corresponding linear coefficients to expand the complete wave function, we consider the ground-state wave function for Helium and \( H_2^+ \) in the next section.
6.2 Three-body wave functions

In chapter 4 we have seen that the S-states do not depend on the angular coordinates \( \phi, \theta, \psi \), which means they are a function of the three dimensional perimetric coordinates \( x, y, z \). Therefore, it is possible to plot the wave functions of the S-states in a three-dimensional plot. In this section we plot exemplarily the ground states of the Helium atom and the \( \text{H}_2^+ \) molecule. However, first we consider the wave function of Helium without electron-electron interaction. For this case the Schrödinger equation can be solved analytically. Referring to equation (2.1.8), the three-body Hamiltonian \( \hat{H}_{c}^{(\text{no-e-e})} \) is given by

\[
\hat{H}_{c}^{(\text{no-e-e})} = -\frac{\hbar^2}{2m_1} \nabla_{\vec{r}_{c1}}^2 - \frac{\hbar^2}{2m_2} \nabla_{\vec{r}_{c2}}^2 - \frac{\hbar^2}{2m_3} \nabla_{\vec{r}_{c3}}^2 + \frac{Z_1 Z_3 e^2}{|\vec{r}_{c1} - \vec{r}_{c3}|} + \frac{Z_2 Z_3 e^2}{|\vec{r}_{c2} - \vec{r}_{c3}|}.
\] (6.2.1)

The solution of the Schrödinger equation with the Hamiltonian in equation (6.2.1) can be written as a product of two hydrogen-like wave functions

\[
\Psi^{(\text{no-e-e})}(r_{31}, r_{32}) = \Psi^{(H)}(r_{31})\Psi^{(H)}(r_{32}),
\] (6.2.2)

where \( r_{3i} \) denotes the distance between particle 3 and \( i \) and \( \Psi^{(H)}(r_{3i}) \) are the Hydrogen wave functions, but with the corresponding parameters of Helium. The ground state of \( \Psi^{(H)}(r_{3i}) \) is given by

\[
\Psi^{(H)}(r_{3i}) = 2(\mu_3 r_{3i})^{3/2} \exp(-\mu r_{3i})
\] (6.2.3)

with the reduced masses \( \mu_3 = m_3 m_i / (m_3 + m_i) \). Since we consider Helium in atomic units, we obtain \( m_1 = m_2 = m_e = 1 \), \( Z_1 = Z_2 = 1 \) and the two reduced masses are equal with \( m_3 = m_{\text{He}}^{(\text{nucleus})} \) and we define \( \mu = \mu_3 = \mu_3 \). Hence, the eigenvalue for the ground-state wave function (6.2.2) is \( 4\mu \). Finally, we transform the wave function in equation (6.2.2) into perimetric coordinates. Using equations (2.4.4) and (2.4.5) this leads to

\[
\Psi^{(\text{no-e-e})}(x, y, z) = 4(\mu)^3 \exp(-\mu \frac{y + z}{2}) \exp(-\mu \frac{x + z}{2}).
\] (6.2.4)

Figure 6.2.1: Isosurface for the square of the absolute value of the wave function for Helium without electron-electron interaction in the \( 1^1S \) state. The value for the isosurface is \( 10^{-3} \).

The squared values \( |\Psi^{(\text{no-e-e})}(x, y, z)|^2 \) with the mass of Helium \( m_{\text{He}}^{(\text{nucleus})} \) equivalent to (6.1.3) are plotted in figure (6.2.1). For the Helium atom without any electron-electron interaction we obtain parallel plane surfaces as isosurfaces. Additionally, we show the probability amplitude of the wave function in a three-dimensional plot in perimetric coordinates in figure (6.2.2). According to the transformed volume element \( dV = (x + y)(x + z)(y + z) \) from Cartesian to perimetric Coordinates, the probability density in the space in terms of the perimetric coordinates is generally given by

\[
p(x, y, z) = (x + y)(x + z)(y + z) |\Psi(x, y, z)|^2.
\] (6.2.5)
The probability density $p(x_0, y_0, z_0)$ determines the probability to find the three particles at the point $x_0, y_0, z_0$ by $p(x_0, y_0, z_0) \, dx \, dy \, dz$.

Referring to section 6.1.2, we calculate the ground state $^1S^e$ energy values with an error of $10^{-12}$. Therefore, we can assume that the expansion of the corresponding wave function $\Psi_{0,0}^{(0)(\text{sym})(\text{He})}$ with the ansatz
Variational calculation

given in equation (5.3.16) is also a very good approximation to the exact wave function. For the expansion we use the eigenvectors $C_{ijk}$ of the lowest S-state singlet eigenvalue. Similar to the case of no electron-electron interaction we plot both functions, the squared wave function $|\psi^{(0)(evm)}_{0,0}(\text{He})|^2$ and the probability density in figure (6.2.3) and (6.2.4).

In comparison to the plot without electron-electron interaction in figure (6.2.1), the wave function iso-surfaces are not given by planes any more. Instead they exhibit a slight curvature. Additionally, the maximum $z$-value is reduced by a small factor. The Helium state with full electron-electron interaction is more localized around the origin of the $x$, $y$, $z$ frame than without electron-electron interaction.

Figure 6.2.5: Isosurface for the square of the absolute value of the wave function for $\text{H}^+_2$ in the $1^1S$ state. The value for the isosurface is $5 \times 10^{-3}$.

In contrast to the Helium atom with one heavy positive charged nucleus and two electrons, we consider in the second part of this section the $\text{H}^+_2$ molecule with two heavy positive charged protons and one electron. Referring to our calculations we adapt the parameters to those of the $\text{H}^+_2$ molecule in equation (6.1.5). The ground-state wave function of the $\text{H}^+_2$ molecule shows a completely different form. The isosurface of the wave function is significantly bent and does not cross the $z$-axis. The symmetric character of the wave function in $x$- and $y$-direction is obvious. The whole shape of the isosurface is similar to a tunnel with a bent ceiling. Figure (6.2.5) shows the isosurface of the $(0,0)$ ground-state wave function for a isosurface value of $5 \times 10^{-3}$ and figure (6.2.6) illustrates the corresponding probability density $p(x,y,z)$ isosurface for a value of $0.0012$. The probability density is located at the same area as the wave function and is more extended in the $z$-direction than the case of Helium which rises just about a small value into the

Figure 6.2.6: Isosurface for the probability density of $\text{H}^+_2$ in the $1^1S$ state. The value for the isosurface is 0.0012.
the infinite mass limit ([85x258]m

consider two identical Fermions, which can not be distinguished. Additionally we give the results for infinite-mass limit expectation values are rather small. They differ by an absolute value of about 5 ×

those of Frolov [Fro98] for the infinite-mass limit. The difference between the exact non-relativistic and the
tances and the square of the distances agree with those of Hesse and Baye [HB99] and additionally with
p
matrix elements from section 5.6. In general the kinetic energy expectation value for particle
appear in the kinetic energy operators the calculations are more sophisticated but we can utilize the
analyze the kinetic energies of the two electrons and the Helium nucleus. Due to the derivatives which
work in the literature and extend our considerations of the Lagrange-Laguerre variational method and
Hesse and Baye calculated only expectation values without derivative operators. Here we go beyond the
ground-state converges for a smaller set of Lagrange-Laguerre basis functions than for the H
located closer to the origin. Taking this into account it becomes clear, that the eigenvalues of the Helium
arround the origin of the axis. Hence, the approximation of a wave function should be more accurate if it is
located closer to the origin. Taking this into account it becomes clear, that the eigenvalues of the Helium
ground-state converges for a smaller set of Lagrange-Laguerre basis functions than for the H
+ molecule as we have seen in section 6.1.1.

6.3 Expectation values for the Helium atom

The high accuracy of the Lagrange-Laguerre variational method gives us the opportunity to obtain some
other expectation values beside the highly accurate energy values of the three-body systems in section
6.1.2. Exemplarily, we give the accurate expectation values of Helium for the inter-particle distances, the
square values of those distances, the expectation values of the kinetic and potential energies. Each observ-
able which depends on position coordinates only can be calculated with Gauss quadrature by equation
(5.4.5) for the singlet S-states and even triplet P-states and by equation (5.4.6) for the triplet S-states
and even singlet P-states. In the case of odd P-states we use equation (5.4.8) for the singlet states and
(5.4.9) for the triplet states. The corresponding contributions for the Gauss quadrature of the inter-particle distances observables and their square values are given in equations (5.4.10) - (5.4.12). The exact non-relativistic expectation values of the electron-electron distance is represented by ⟨
⟩ and the electron-nucleus distance represented by ⟨
⟩ are shown in table (6.8) for the lowest singlet and triplet S-states and P-states with wave function of even parity. We denote ⟨
⟩ = ⟨
⟩ = ⟨
⟩, since we consider two identical Fermions, which can not be distinguished. Additionally we give the results for the infinite mass limit (m∞). Our results of the ground state expectation values of inter-particle distances and the square of the distances agree with those of Hesse and Baye [HB99] and additionally with those of Frolov [Fvo98] for the infinite-mass limit. The difference between the exact non-relativistic and the infinite-mass limit expectation values are rather small. They differ by an absolute value of about 5 × 10⁻⁴.

Hesse and Baye calculated only expectation values without derivative operators. Here we go beyond the
work in the literature and extend our considerations of the Lagrange-Laguerre variational method and
analyze the kinetic energies of the two electrons and the Helium nucleus. Due to the derivatives which appear in the kinetic energy operators the calculations are more sophisticated but we can utilize the matrix elements from section 5.6. In general the kinetic energy expectation value for particle p in state Ψ is given by

\[ \langle T_p \rangle = \langle \Psi | \hat{T}_p | \Psi \rangle . \] (6.3.1)

We substitute Ψ by one of our considered wave function in chapter 4. Afterwards, we drop all contributions of the operators \( \hat{T}_S \) and \( \hat{T}_L \) in equations (2.3.8) and (2.3.9) which do not depend on the mass \( m_p \) of particle

<table>
<thead>
<tr>
<th>state</th>
<th>mass of ( m_3 )</th>
<th>( \langle r_{12} \rangle )</th>
<th>( \langle r_{31/32} \rangle )</th>
<th>( \langle T_1^2 \rangle )</th>
<th>( \langle r_{31/32}^2 \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^3S(\text{even}) ) ( m_3 = \text{He} )</td>
<td>4.447 545 520 520 4</td>
<td>5.550 668 066 411 8</td>
<td>23.046 295 004 320 9</td>
<td>11.464 403 690 467 1</td>
<td></td>
</tr>
<tr>
<td>( ^3S(\text{even}) ) ( m_3 = \infty )</td>
<td>4.447 545 520 520 4</td>
<td>5.550 668 066 411 8</td>
<td>23.046 295 004 320 9</td>
<td>11.464 403 690 467 1</td>
<td></td>
</tr>
<tr>
<td>( ^3P(\text{even}) ) ( m_3 = \text{He} )</td>
<td>17.850 620 991 716 4</td>
<td>10.045 468 284 899 2</td>
<td>76.371 372 695 343 9</td>
<td>176.371 372 695 343 9</td>
<td></td>
</tr>
<tr>
<td>( ^3P(\text{even}) ) ( m_3 = \infty )</td>
<td>17.850 620 991 716 4</td>
<td>10.045 468 284 899 2</td>
<td>76.371 372 695 343 9</td>
<td>176.371 372 695 343 9</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.8: Expectation values of inter-particle distances for S-states, even P-states. The scale factors \( h_{xy}, h_z \), and the numbers \( N_{xy}, N_z \) and \( N_M \) are equivalent to the corresponding states in the tables (6.1), (6.2), and (6.3).
Table 6.9: Expectation values of the lowest two S-states and even P-states. The scale factors $h_{xy}$ and $h_y$ are equivalent to the corresponding states in table (6.1), (6.2), and (6.3).

<table>
<thead>
<tr>
<th>state</th>
<th>mass of $m_3$</th>
<th>$\langle \hat{T}_{1/2} \rangle$</th>
<th>$\langle \hat{T}_3 \rangle$</th>
<th>$\langle \hat{V} \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1S^{(even)}$</td>
<td>$m_3 = \text{He}$</td>
<td>1.451 442 401 726 2</td>
<td>0.000 419 752 104 5</td>
<td>-5.806 609 111 117 9</td>
</tr>
<tr>
<td>$^3S^{(even)}$</td>
<td>$m_3 = \infty$</td>
<td>1.451 794 414 654 4</td>
<td>0.000 000 000 000 0</td>
<td>-5.807 169 658 624 2</td>
</tr>
<tr>
<td>$^2S^{(even)}$</td>
<td>$m_3 = \text{He}$</td>
<td>1.087 270 244 546 2</td>
<td>0.000 000 000 000 0</td>
<td>-4.349 786 637 336 6</td>
</tr>
<tr>
<td>$^2P^{(even)}$</td>
<td>$m_3 = \infty$</td>
<td>1.087 693 723 446 2</td>
<td>0.000 000 000 000 0</td>
<td>-4.350 774 893 462 3</td>
</tr>
</tbody>
</table>

$p$ and denote the new operator $\hat{T}_p$. If we consider all steps in chapter 4 and 5 to obtain the matrix elements with operator $\hat{T}_p$, we obtain the same matrix elements of section 5.6 where all contributions of terms which do not depend on $m_p$ are equal to zero. Therefore we used such matrices denoted as $M^{(t)(T_p)}$ for the singlet S-state, $M^{(t)(T_p)}$ for the triplet S-state, $M^{(t)(T_p)(s)(even)}$ for the singlet even P-states, $M^{(t)(T_p)(even)}$ for the triplet even P-states, $M^{(T_p)(s)(odd)}$ and $M^{(T_p)(P)(odd)}$. For all fowllowing considerations we simply use the notation $M^{(T_p)}$ for one of those matrices. Further, we use the eigenvectors $\vec{C}$ of the corresponding eigenvalue equations whose components are defined equivalent to equation (5.3.106) by the expansion coefficients $C_{ijk}$ of the wave function.

$$ [\vec{C}]_a = C_{ijk} \quad (6.3.2) $$

The index mapping $a$ of $i, j, k$ is explicitly given in section 5.6 for the corresponding matrix $M$. Finally, we obtain the expectation values of the kinetic operator $\hat{T}_p$ using the Gauss quadrature for equation (5.4.13). The result is equivalent to the following scalar product of a matrix vector product

$$ \langle \hat{T}_p \rangle = \vec{C} \cdot (M^{(T_p)} \vec{C}) \quad (6.3.3) $$

Similar to the inter-particle distance expectation values we list the kinetic energy $\langle \hat{T}_3 \rangle$ of the nucleus and the kinetic energy of the electron $\langle \hat{T}_{1/2} \rangle$ of the Helium atom in table (6.9) for the lowest singlet and triplet S-states and P-states with wave function of even parity. Additionally, we list the expectation values of the potential $\hat{V}$. Based on this expectation values we validate the virial theorem which is given by [BJ03]

$$ 2\langle \hat{T} \rangle = -\langle \hat{V} \rangle \quad (6.3.4) $$

with total kinetic energy $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$. Hence, the absolute value of the quotient of $\langle \hat{V} \rangle$ and $\langle \hat{T} \rangle$ should be exactly two. Using the values in table (6.9), the quotient $-\langle \hat{V} \rangle / \langle \hat{T} \rangle$ differs only in the order of $10^{-13}$ from the exact value of two. This fact implies that our expectation values and therefore our expansion of the wave functions has a very high accuracy.

Since we have all eigenvectors of the matrices, we can analyze the expectation values of the inter-particle distances for all eigenstates. In this case, the accuracy of the expectation values of each state does not reach the quality of the expectation values in table (6.8) and (6.9) but it is sufficient to plot all distance expectation values $\langle r_{12} \rangle$ and $\langle r_{31/32} \rangle$ and to interprete the course of the graphs.

Figures (6.3.1) and (6.3.2) show the expectation values of the inter-particle distances of $\langle r_{12} \rangle$ and $\langle r_{31/32} \rangle$ for each state for scale factors $h_{xy} = h_z = 3.5$. Both shapes of the graphs are rather similar up to the ground-state of Helium which is given by the lowest energy of the singlet S-state. The ground-state of Helium has distinctly the lowest expectation value for the inter-particle distances. Again, the two plots illustrate the relatively large energy gap between the ground-state and the first excited state energy. The
Figure 6.3.1: Expectation values of the inter-particle distances for the Helium atom in singlet S-states. The scale factors are given by $h_{xy} = h_z = 3.5$. The number of Lagrange-Laguerre basis functions are $N_{xy} = N_z = 40$, which leads to a total number of $N(M) = 32,800$.

Figure 6.3.2: Expectation values of the inter-particle distances for the Helium atom in triplet S-states. The scale factors are given by $h_{xy} = h_z = 3.5$. The number of Lagrange-Laguerre basis functions are $N_{xy} = N_z = 40$, which leads to a total number of $N(M) = 31,200$. 
green vertical lines in both figures mark the He\(^+\) energy levels according to equation (6.1.13) and table (6.7) for the Helium atom. At the locations of the He\(^+\) energy levels we can see large peaks of the inter-particle distances. The rising peaks at the ionization thresholds correspond to our explanations in section 6.1.2, where one electron ionizes and is moving freely in space and the remaining Helium core and electron constitute a two-body system. For an increasing number of basis functions \(N_{xy}\) and \(N_z\) the maximum of the peaks always increases, so that we assume that in the limit of infinite basis functions the expectation values of the inter-particle distances diverge. Although we still have a bound two-body system with an analytical expectation value for the inter-particle distance, we find that the expectation value of \(\langle r_{31/32}\rangle\) reaches infinity. Due to the Fermionic nature of the electrons, it is not possible to distinguish the electron which bound to the Helium core to the one which ionizes. Hence, the expectation value of the inter-particle distances of a free particle and a second bound particle reaches infinity for an infinite system size, since the free particle can be located at any position in space. Considering a three-body system of three distinguished particles, e.g. the dt\(\mu\) molecule, we obtain two different thresholds which can be seen in figure (6.1.6). In this case the expectation values \(\langle r_{31}\rangle\) and \(\langle r_{32}\rangle\) are not equal and we obtain two different graphs with peaks for \(\langle r_{31}\rangle\) at the ionization energies of t\(\mu^+\), since particle 1, the deuteron is ionized, and peaks for \(\langle r_{32}\rangle\) at the ionization energies of d\(\mu^+\) for the ionized particle 2, the Triton. Referring to section 6.1.2, the energy levels should reach a continuum with the lowest ionization energy. Therefore, the expectation values of the inter-particle distances between the ionized particle and the two body particles should always diverge. Due to the fact that we have a finite size of our system, it is not possible to get all continuous energy levels of the free particle. As mentioned in section 6.1.2 the free particle is represented as a particle in a box. In this case, the wave functions are given by equation (6.1.16) and the excited states of this wave functions in combination with the bound two body-system lead to increasing expectation values of inter-particle distances instead of a divergence. The peaks of both plots in figures (6.3.1) and (6.3.2) show clearly the series of the excited ionization energies of He\(^+\) which get closer to the energy level equal to zero. Above this energy, none of the particles is bound and the expectation value of the inter-particle distances reach a value which approach the finite box size of the system.

Figure 6.3.3: Expectation values of the inter-particle distances for the Helium atom in singlet even P-states. The scale factors are given by \(h_{xy} = h_z = 3.5\). The number of Lagrange-Laguerre basis functions are \(N_{xy} = N_z = 40\) which leads to a total number of \(N(M) = 31\ 200\).
Variational calculation

Figure 6.3.4: Expectation values of the inter-particle distances for the Helium atom in triplet even P-states. The scale factors are given by \( h_{xy} = h_z = 3.5 \). The number of Lagrange-Laguerre basis functions are \( N_{xy} = N_z = 40 \) which leads to a total number of \( N(M) = 32\,800 \).

The figures (6.3.3) and (6.3.4) of the even P-states for the Helium atom show a few different features. Similar peaks appear around the ionization energy levels, but they are not located at the exact energy thresholds. The peaks are shifted to a lower energy value. Since the peaks are shifted further to lower energies for smaller system sizes, we assume that this is again an effect of our finite size box. The explanation for the peaks is the same as for the S-states. Besides the peaks at the ionization thresholds, there is a second class of peaks which appear at the first lower excited state of the singlet P-states (\( 3^1 P^{(even)} \)) in figure (6.3.3) and at the second lower excited states of the triplet P-states (\( 4^3 P^{(even)} \)) in figure (6.3.4). Such a peak appears along the complete three-body ionization energy series, always below the two-body energy levels, and always around an energy value equal to 10% of those energy levels below. All peaks are above the absolute lowest energy ionization threshold, the first ionization energy of the singlet S-state, which means all of those states are autoionizing. It seems as if at least one electron is dissociated but we have not found an explanation for those peaks yet. Therefore, we have to examine the wave functions corresponding to the peaks more in detail. Since the even P-states depend on the three perimetric coordinates and two Euler angles, it is not possible to illustrate them similar to section 6.2. Maybe it is necessary to obtain different expectation values, e.g. the expectation values of the angular momentum, to find a sufficient explanation for the effect. Taking the reference values of Goodson et al. [GWLH91] for the \( 3^1 P^{(even)} \) state into account, our energy values agree to an order of \( 10^{-12} \). Hence, the approximation for this wave function with the Lagrange-Laguerre method should be very close to the exact physical non-relativistic wave function without spin-orbit interaction.

6.4 Transition-dipole moments

All our results in the previous sections describe an isolated three-body system. In this section we consider the coupling of the three-body system to electromagnetic radiation. As a result we find that the dipole absorption spectrum has a strong mass dependency close to the second ionization threshold. The Hamiltonian for a three-body system without any perturbation is given in equation (2.1.8). The Hamiltonian \( \hat{H}^{(em-field)} \) for a single particle with mass \( m \), momentum \( \vec{p} \), position vector \( \vec{r} \), charge number \( Z \) and ele-
mentary charge $e$ in an electromagnetic field with the vector potential $\vec{A}^{(\text{em-field})}$ of the electromagnetic field is given by [BJ03]

$$
\hat{H}^{(\text{em-field})} = \frac{1}{2m} \left( -\frac{i\hbar}{m} \vec{\nabla} + Z e \vec{A}^{(\text{em-field})} \right)^2 + Z \Phi_{\text{el}}(\vec{r}) + V^{(\text{ex})}(\vec{r}) ,
$$

(6.4.1)

where $V^{(\text{ex})}(\vec{r})$ denotes an external scalar potential that acts on the particle and $\Phi_{\text{el}}(\vec{r})$ describes the electrostatic potential. If we use Coulomb gauge with $\vec{\nabla} \cdot \vec{A} = 0$, the Hamiltonian in equation (6.4.2) yields

$$
\hat{H}^{(\text{em-field})} = \frac{\hbar^2}{2m} \nabla^2 + \frac{i\hbar}{m} Z e \vec{A}^{(\text{em-field})} \nabla + \frac{Z^2 e^2}{2m} \left( \vec{A}^{(\text{em-field})} \right)^2 + Z \Phi_{\text{el}}(\vec{r}) + V^{(\text{ex})}(\vec{r}) .
$$

(6.4.2)

Since we are limiting our selves to weak radiation fields, we neglect the contribution with $\vec{A}^2$ of the Hamiltonian in equation (6.4.2). With the consideration from above for a single particle the Hamiltonian $\hat{H}_c^{(\text{em-field})}$ of a three-body system in the center of mass frame, which is exposed to an electromagnetic field takes the form

$$
\hat{H}_c^{(\text{em-field})} = -\sum_{j=1}^3 \frac{\hbar^2}{2m} \nabla_{\vec{r}_c}^2 - \sum_{j=1}^3 \frac{i\hbar}{m} Z_j e \vec{A}^{(\text{em-field})} \nabla_{\vec{r}_c} + \frac{Z_1 Z_2}{|\vec{r}_c_1 - \vec{r}_c_2|} + \frac{Z_1 Z_3}{|\vec{r}_c_1 - \vec{r}_c_3|} + \frac{Z_2 Z_3}{|\vec{r}_c_2 - \vec{r}_c_3|} ,
$$

(6.4.3)

The time-dependent Schrödinger equation for this three-body Hamiltonian with electromagnetic field is given by

$$
i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}_{c_1}, \vec{r}_{c_2}, \vec{r}_{c_3}, t) = \hat{H}_c^{(\text{em-field})} \Psi(\vec{r}_{c_1}, \vec{r}_{c_2}, \vec{r}_{c_3}, t)
$$

(6.4.4)

Compared to the Hamiltonian in equation (2.1.8) we can express the three-body Hamiltonian with electromagnetic field by

$$
\hat{H}_c^{(\text{em-field})} = \hat{H}_c + \hat{H}' ,
$$

(6.4.5)

with

$$
\hat{H}' = \sum_{j=1}^3 \frac{i\hbar}{m_j} Z_j e \vec{A}^{(\text{em-field})} \nabla_{\vec{r}_c} .
$$

(6.4.6)

The energy eigenvalues $E_\nu$ of the three-body Hamiltonian $\hat{H}_c$ for the S-states and P-states with magnetic quantum number $m = 0$ are the results of the eigenvalue equations in chapter 6. The wave functions corresponding to the energy eigenvalues can be obtained by the wave function ansaetze in this chapter. Hence, referring to Brandson and Joachain [BJ03] the general solution of the time-dependent Schrödinger equation can be expressed as

$$
\Psi(\vec{r}_{c_1}, \vec{r}_{c_2}, \vec{r}_{c_3}, t) = \sum_\nu c_\nu(t) \Psi_\nu(\vec{r}_{c_1}, \vec{r}_{c_2}, \vec{r}_{c_3}) e^{iE_\nu t/\hbar} ,
$$

(6.4.7)

where $c_\nu(t)$ denotes linear coefficients and the sum has to be over both, the discrete values of $\nu$ and the continuous eigenfunctions $\Psi_\nu(\vec{r}_{c_1}, \vec{r}_{c_2}, \vec{r}_{c_3})$ which appear referring to section (6.1.2), above the first ionization threshold. Using the time-dependent Schrödinger equation in equation (6.4.4) leads to the following condition for the linear coefficients $c_\nu(t)$

$$
\frac{\partial c_\nu(t)}{\partial t} = \frac{1}{i\hbar} \sum_\nu \hat{H}'_{\nu\nu}(t)c_\nu(t)e^{i\omega_{\nu\nu}t} ,
$$

(6.4.8)

with
\[
\hat{H}'_{\nu} = \langle \Psi_\eta | \hat{H}' | \Psi_\nu \rangle ,
\]

and

\[
\omega_{\eta\nu} = \frac{E_\eta - E_\nu}{\hbar} .
\]

In the next step, we use perturbation theory and the coefficients \(c_\eta(t)\) are determined in first order (reference [BJ03]) with \(\hat{H}'_{\nu}\) given in equation (6.4.9) and \(\hat{H}'\) in equation (6.4.6) by

\[
c_\eta^{(1)}(t) = \frac{1}{i\hbar} \int_0^t \hat{H}'_{\nu} e^{i\omega_{\eta\nu} t'} dt' = \sum_{j=1}^3 \frac{Z_j e}{m_j} \int_0^t \langle \Psi_\eta | \hat{A}^{(\text{em-field})} \cdot \nabla_{\vec{r}_c_j} | \Psi_\nu \rangle e^{i\omega_{\eta\nu} t'} dt' .
\]

In the case that the electromagnetic field is described by a superposition of plane waves, the vector potential \(\hat{A}^{(\text{em-field})}\) takes the form [BJ03]

\[
\hat{A}^{(\text{em-field})}(\vec{r}_c, t) = \int_{\Delta \omega} A_0(\omega) \tilde{c} e^{i(\vec{k} \cdot \vec{r}_c - \omega t)} d\omega
\]

with position vector \(\vec{r}_c\) in the center of mass frame, the wave vector \(\vec{k}\), frequency of the wave \(\omega\), amplitude \(A_0(\omega)\), and polarization vector \(\tilde{c}\). Hence, \(\hat{H}'_{\nu}\) is equivalent to

\[
\hat{H}'_{\nu} = \sum_{j=1}^3 \frac{i\hbar}{m_j} Z_j e \langle \Psi_\eta | \hat{c} e^{i\vec{k} \cdot \vec{r}_c} \cdot \nabla_{\vec{r}_c_j} | \Psi_\nu \rangle .
\]

If we assume that the wave length of the electromagnetic wave is much longer in relation to the extension of the bound three-body system, the corresponding scalar product \(\hat{\vec{k}} \cdot \vec{r}\) becomes very small and we can truncate the Taylor series of the exponential function \(e^{i\vec{k} \cdot \vec{r}} = 1 + i\vec{k} \cdot \vec{r} + 1/2!(i\vec{k} \cdot \vec{r})^2 + \cdots\) after the first term. \(\hat{H}'_{\nu}\) then takes the following form

\[
\hat{H}'_{\nu} = \sum_{j=1}^3 \frac{i\hbar}{m_j} Z_j e \cdot \langle \Psi_\eta | \nabla_{\vec{r}_c_j} | \Psi_\nu \rangle .
\]

Transforming \(\langle \Psi_\eta | \nabla_{\vec{r}_c_j} | \Psi_\nu \rangle\) into momentum space gives us the relation

\[
\nabla_{\vec{r}} = \frac{i}{\hbar} \frac{d}{dt} \vec{r} = \frac{im}{\hbar} \frac{d}{dt} \vec{r}
\]

The Heisenberg equation of motion for \(\vec{r}\) is given by

\[
\frac{d}{dt} \vec{r} = \frac{1}{\hbar} [\vec{r}, \hat{H}]
\]

with an arbitrary Hamiltonian \(\hat{H}\). Applying this relation to our considerations, we can substitute \(\vec{r}\) by \(\vec{r}_{c_j}\), \(m\) by \(m_j\) and \(\hat{H}\) by \(\hat{H}_c\). Hence, using equations (6.4.14) - (6.4.16) and (6.4.10) we obtain with the Hermitian Hamiltonian \(\hat{H}_c\) and \(\hat{H}_c \Psi_\nu = E_\nu \Psi_\nu\)

\[
\langle \Psi_\eta | \nabla_{\vec{r}_c_j} | \Psi_\nu \rangle = \frac{m_j}{\hbar^2} \langle \Psi_\eta | \vec{r}_{c_j} \hat{H}_c | \Psi_\nu \rangle = \frac{m_j}{\hbar^2} (E_\nu - E_\eta) \langle \Psi_\eta | \vec{r}_{c_j} | \Psi_\nu \rangle = -\frac{m_j}{\hbar} \omega_{\eta\nu} \langle \Psi_\eta | \vec{r}_{c_j} | \Psi_\nu \rangle .
\]

Using this result for equation (6.4.14) yields

\[
\hat{H}'_{\nu} = -\sum_{j=1}^3 \frac{i}{\hbar} Z_j e \omega_{\eta\nu} \cdot \langle \Psi_\eta | \vec{r}_{c_j} | \Psi_\nu \rangle .
\]
The dipole approximation is useful to describe a lot of effects in spectroscopy, in particular especially to consider absorption spectra. Decisive for the absorption are the transition probability rates which are given in first order of perturbation theory by [BJ03]

\[ W_{\eta \nu} = \frac{2\pi}{\hbar} |\hat{H}_{\eta \nu}|^2 \rho(E_\nu), \]  

(6.4.19)

where \( \rho(E_\nu) \) denotes the density of states. Hence, if we take equation (6.4.18) into account, the transition probability rate depends on the dipole matrix elements which are given by

\[ D_{\eta \nu} = \epsilon \langle \Psi_\eta | \vec{r} | \Psi_\nu \rangle \]  

(6.4.20)

with initial state \( \Psi_\nu \), final state \( \Psi_\eta \) and position vector \( r \). The transition dipole matrix elements \( D_{\eta \nu}^{(i)} \) for each particle \( i \) of the three-body problem from the singlet S-states to the triplet odd P-states are completely described in section 5.5. Without loss of generality we assume that the direction of the polarization of the electromagnetic wave is along the Z-axis of the three-body center-of-momentum frame with \( \bar{e} = \epsilon_z \). Hence, equation (6.4.18) is equivalent to expression

\[ \hat{H}_{\eta \nu} = -i \epsilon_\nu \epsilon_z \sum_{j=1}^{3} Z_j \langle \Psi_\eta | \vec{r}_{cz_j} | \Psi_\nu \rangle. \]  

(6.4.21)

We define the sum in equation (6.4.21) as \( \tilde{G}_{\eta \nu} \)

\[ \tilde{G}_{\eta \nu} = e \sum_{j=1}^{3} Z_j \langle \Psi_\eta | \vec{r}_{cz_j} | \Psi_\nu \rangle. \]  

(6.4.22)

In this section we analyze the mass dependency of the transition dipole matrix elements from the \(^1S_0\) ground-state as initial state to the odd \(^1P\)-states for \( H_2^+ \). We denote the initial state \( \Psi_\nu \) in equation (6.4.22) as \( \nu = 0 \) and the odd P-states as \( \Psi_\eta \). Referring to section 5.5 these transitions are not dipole forbidden. To visualize a strong mass dependence on the dipole matrix elements, we focus on the region around the first excited ionization energy. Referring to equation (6.1.13) and table (6.6), the first excited ionization energy \( E^{(2)(\mu_{12})}_{\text{ion}} \) for Hydrogen is given by

\[ E^{(2)(\mu_{12})}_{\text{ion}} = -0.124 \, 932. \]  

(6.4.23)

In the region around the first excited ionization energy \( E^{(2)(\mu_{12})}_{\text{ion}} \) of the Hydrogen atom we can see in figure (6.1.7) that the density of the energy levels is rather high. In the limit of infinite system size, when the number of Lagrange-Laguerre basis functions \( N_{xy} \) and \( N_z \) approach infinity, the discrete energies would become continuous above the lowest ionization energy \( E^{(1)(\mu_{12})}_{\text{ion}} \) threshold. In this limit, the dipole matrix elements become also continuous. Since we only have a discretized continuum available, we broaden each dipole matrix element by a Lorentz-distribution, which is given by [AS65]

\[ f^{(\text{Lorentz})}(u) = \frac{1}{\pi} \frac{\sigma}{\sigma^2 + (u - v)^2}. \]  

(6.4.24)

The parameter \( \sigma \) determines the width of the Lorentz-distribution and the median is \( v \). Using this distribution we broaden \( \tilde{G}_{\eta \nu} \) in equation (6.4.22) and obtain a continuous function \( G(E) \) which takes the form

\[ G(E) = \sum_{j=1}^{3} \sum_{\eta=1}^{\nu} Z_j \tilde{D}_{\eta \nu}^{(j)} \frac{1}{\pi} \frac{\sigma}{\sigma^2 + (E - E_\eta_j)^2}. \]  

(6.4.25)

where we sum over all singlet odd P-states denoted by \( \eta \), which we obtain by solving the eigenvalue equation (5.3.126) for \( H_2^+ \) and \( D_{\eta \nu}^{(j)} \) are the dipole matrix elements for the corresponding particle \( j \). The results for those dipole moments can be obtained by equation (5.5.19). In figure (6.4.1) we show the
Variational calculation

non-normalized function $G(E)$ with a broadening parameter $\sigma = 8 \cdot 10^{-3}$ for the $H_2^+$ molecule for two different proton masses, the exact physical mass for the proton in equation (6.1.4) ($m_1 = m_2 = m_{\text{proton}}$) and the infinite mass-limit ($m_1 = m_2 \to \infty$). In both cases, we can see a large peak around the first excited ionization energy $E_{\text{ion}}^{(2)(\mu_{12})}$ of Hydrogen. The small difference between the exact threshold energy, which is marked by a vertical blue line, can have the same reasons as the small shift of the peaks in the even $P$-states for the case of inter-particle expectation values. This means the difference would be caused by finite size effects due to the limited box size and the peaks in figure (6.4.1) would move directly to the second ionization energy of Hydrogen for an infinite numbers of Lagrange-Laguerre functions. Although the center of the peaks can be influenced by the box size, the peak amplitude turns out to be insensitive to this and is quite different between the infinite mass and physical mass cases.

The mechanism behind this mass effect is at this point not fully understood. We therefore plan to investigate the wave functions at the second ionization energy in more detail in a future study.

Figure 6.4.1: The function $G(E)$ of $H_2^+$ for different mass ratios between the ions and the electron around the first excited ionization energy of Hydrogen.
Chapter 7

Summary and outlook

In the present work, we have introduced a variational Lagrange-Laguerre method for the description of non-relativistic three-body systems. Our approach does not rely on the Born-Oppenheimer approximation and allows to compute the exact energy eigenvalues and wave functions of a general non-relativistic three-body system with a rather high relative accuracy of about $10^{-12}$ for the lowest bound states. We have applied the approach to the Helium atom, the $\text{d}t\mu$, $\text{H}_2^+$, and $\text{HD}^+$ molecules. For all systems we report accurate energies, expectation values of inter-particle distances, dipole matrix elements, as well as kinetic and potential energy contributions. Our results of the lowest energy eigenvalues reach the high accuracy of current references in literature which are usually used as benchmarks, e.g. the Hylleraas method for the Helium atom. In contrast to the standard sparse matrix diagonalization that is usually employed in the literature, we perform here a dense matrix diagonalization of the discretized eigenproblem. This gives us access to the full spectrum of eigenvalues and eigenvectors and allows to investigate matrix elements also for high-lying states. Since we have a qualitatively good approximation of the exact non-relativistic three-body energy eigenvalues and wave functions, we have investigated the difference between the infinite-mass approximation for the heavier particles in the considered three-body systems and the solutions obtained for the proper physical mass. For the case of Helium we found a deviation of about 0.015% for the infinite-mass approximation from the exact non-relativistic energies for low-lying bound states. For low-lying energies, the infinite-mass limit can therefore be regarded as an accurate approximation. However, the situation is different for the case of dipole matrix elements. There we found for the case of $\text{H}_2^+$ a sizeable mass dependence close to the second ionization threshold of the system. Considering different isotopes of $\text{H}_2^+$, this effect should also be accessible in experiments.

In future work we plan to extend our approach to also include relativistic effects such as spin-orbit coupling, the Darwin term or quantum electrodynamic corrections like the Lamb shift. Since our Lagrange-Laguerre approach is based on a numerical grid, the method is also suited to solve the time-dependent Schrödinger equation for situations that require non-perturbative treatments. This allows for example to study three-body systems exposed to femtosecond laser pulses. For the case of the molecular systems that we considered in this work, the accurate wave functions can also serve as benchmark input for electron-phonon matrix elements. Here effects beyond the usual bilinear electron-phonon coupling are accessible within our approach.
Appendix A

Appendix

A.1 Transformation of coordinates

In section 2.2 we introduced the combined spherical and cylindrical coordinates $R$, $\rho$, $\zeta$, $\phi$, $\theta$, $\psi$ to describe the two vectors $\vec{R}$ and $\vec{r}$. The transformation for $\vec{R}$ and $\vec{r}$ for combined spherical and cylindrical coordinates into Cartesian coordinates is given by equation (2.2.5) and (2.2.6). The Jacobian matrix $J_{s-c}$ of this transformation takes the form

\[
J_{s-c} = \begin{pmatrix}
a_{11} & a_{12} & a_{13} & 0 & 0 & 0 \\
a_{21} & a_{22} & a_{23} & 0 & 0 & 0 \\
a_{31} & a_{32} & 0 & 0 & 0 & 0 \\
0 & a_{42} & a_{43} & a_{44} & a_{45} & a_{46} \\
0 & a_{52} & a_{53} & a_{54} & a_{55} & a_{56} \\
0 & a_{62} & 0 & a_{64} & a_{65} & a_{66}
\end{pmatrix}
\]  

(A.1.1)

with

\[
\begin{align*}
a_{11} &= \sin(\theta) \cos(\phi), \\
a_{12} &= R \cos(\theta) \cos(\phi), \\
a_{13} &= -R \sin(\theta) \sin(\phi), \\
a_{21} &= \sin(\theta) \sin(\phi), \\
a_{22} &= R \cos(\theta) \sin(\phi), \\
a_{23} &= R \sin(\theta) \cos(\phi), \\
a_{31} &= \cos(\theta), \\
a_{32} &= -R \sin(\theta), \\
a_{42} &= \cos(\phi) \{ \zeta \cos(\theta) - \rho \sin(\theta) \cos(\psi) \}, \\
a_{43} &= -(\rho \cos(\theta) \cos(\phi) + \zeta \sin(\theta)) \sin(\phi) - \rho \cos(\phi) \sin(\psi), \\
a_{44} &= \cos(\theta) \cos(\phi) \cos(\psi) - \sin(\phi) \sin(\psi), \\
a_{45} &= -\rho(\sin(\phi) \cos(\psi) + \cos(\theta) \cos(\psi) \sin(\psi)), \\
a_{46} &= \sin(\theta) \cos(\phi), \\
a_{52} &= (\zeta \cos(\theta) - \rho \sin(\theta) \cos(\psi)) \sin(\phi), \\
a_{53} &= \rho \cos(\theta) \cos(\phi) \cos(\psi) + \zeta \cos(\phi) \sin(\theta) - \rho \sin(\phi) \sin(\psi), \\
a_{54} &= \cos(\theta) \sin(\phi) \cos(\psi) + \cos(\phi) \sin(\psi), \\
a_{55} &= \rho \{ \cos(\phi) \cos(\psi) - \cos(\theta) \sin(\phi) \sin(\psi) \}, \\
a_{56} &= \sin(\theta) \sin(\phi), \\
a_{62} &= -\rho \cos(\theta) \cos(\psi) - \zeta \sin(\theta), \\
a_{64} &= -\sin(\theta) \cos(\psi), \\
a_{65} &= \rho \sin(\theta) \sin(\psi), \\
a_{66} &= \cos(\theta).
\end{align*}
\]

To transform the derivatives of the Hamiltonian in equation (2.1.24) from Cartesian coordinates into
combined spherical and cylindrical coordinates, we need the inverse Jacobian matrix $J_{s-c}^{-1}$ which is given by

\[
J_{s-c}^{-1} = \begin{pmatrix}
    b_{11} & b_{12} & b_{13} & 0 & 0 & 0 \\
    b_{21} & b_{22} & b_{23} & 0 & 0 & 0 \\
    b_{31} & b_{32} & b_{33} & 0 & 0 & 0 \\
    b_{41} & b_{42} & b_{43} & b_{44} & b_{45} & b_{46} \\
    b_{51} & b_{52} & b_{53} & b_{54} & b_{55} & b_{56} \\
    b_{61} & b_{62} & b_{63} & b_{64} & b_{65} & b_{66}
\end{pmatrix}
\] (A.1.2)

with

\[
\begin{align*}
    b_{11} &= \sin(\theta) \cos(\phi), \\
    b_{12} &= \sin(\theta) \sin(\phi), \\
    b_{13} &= \cos(\theta), \\
    b_{21} &= \cos(\theta) \cos(\phi)/R, \\
    b_{22} &= \cos(\theta) \sin(\phi)/R, \\
    b_{23} &= -\sin(\theta)/R, \\
    b_{31} &= -\csc(\theta) \sin(\phi)/R, \\
    b_{32} &= \csc(\theta) \cos(\phi)/R, \\
    b_{41} &= \zeta \left( -\cos(\theta) \cos(\phi) \cos(\psi) + \sin(\phi) \sin(\psi) \right)/R, \\
    b_{42} &= -\zeta \left( \cos(\theta) \sin(\phi) \cos(\psi) + \cos(\phi) \sin(\psi) \right)/R, \\
    b_{43} &= \zeta \sin(\theta) \cos(\psi)/R, \\
    b_{44} &= \cos(\theta) \cos(\phi) \cos(\psi) - \sin(\phi) \sin(\psi), \\
    b_{45} &= \cos(\theta) \sin(\phi) \cos(\psi) + \cos(\phi) \sin(\psi), \\
    b_{46} &= -\sin(\theta) \cos(\psi), \\
    b_{51} &= \left[ \zeta \sin(\phi) \cos(\psi) + \rho \cot(\theta) \sin(\phi) + \zeta \cos(\theta) \cos(\phi) \sin(\psi) \right]/(R\rho), \\
    b_{52} &= \left[ -\cos(\theta) \left( \zeta \sin(\phi) + \rho \cot(\theta) \right) + \zeta \cos(\theta) \sin(\phi) \sin(\psi) \right]/(R\rho), \\
    b_{53} &= \left[ \rho \sin(\theta) \sin(\psi) \right]/(R\rho), \\
    b_{54} &= \left[ \sin(\phi) \cos(\psi) + \cos(\theta) \cos(\phi) \sin(\psi) \right]/\rho, \\
    b_{55} &= \left[ \cos(\phi) \cos(\psi) - \cos(\theta) \sin(\phi) \sin(\psi) \right]/\rho, \\
    b_{56} &= \sin(\theta) \sin(\psi)/\rho, \\
    b_{61} &= \left[ \rho \cos(\theta) \cos(\phi) \cos(\psi) - \sin(\phi) \sin(\psi) \right]/R, \\
    b_{62} &= \left[ \rho \cos(\theta) \cos(\psi) \sin(\phi) + \cos(\phi) \sin(\psi) \right]/R, \\
    b_{63} &= -\rho \sin(\theta) \cos(\psi)/R, \\
    b_{64} &= \sin(\theta) \cos(\phi), \\
    b_{65} &= \sin(\theta) \sin(\phi), \\
    b_{66} &= \cos(\theta).
\end{align*}
\]

A.2 Matrix elements of Hamiltonian

In chapter 4 we consider the scalar product $\langle \Psi^{(\nu)} | \hat{H}_c | \Psi^{(\eta)} \rangle$ of two arbitrary wave functions $\Psi^{(\nu)}$ and $\Psi^{(\eta)}$ and the Hamiltonian $\hat{H}_c$. These scalar products depend on the states of the wave function $\Psi^{(\nu)}$ and $\Psi^{(\eta)}$ and we simplified them in chapter 4 by integrating over all angular coordinates $\phi, \theta, \psi$. The remaining three-fold integral over all perimetric coordinates $x, y, z$ can be simplified by using integration by parts. Therefore, in this section of the appendix we show the rearrangement of the scalar products for the corresponding S-states, even and odd P-states.

A.2.1 S-states

Referring to the Hamiltonian in equation (2.4.20) in section 2.4 the scalar product of $\langle \Phi^{(\nu)} | \hat{T}_S | \Phi^{(\eta)} \rangle$ is given by
\begin{align*}
\langle \Phi^{(\nu)} | \hat{T}_S | \Phi^{(\eta)} \rangle &= \int_0^\infty \int_0^\infty \int_0^\infty (x+y)(x+z)(y+z) \Phi(x,y,z) \hat{T}_S \Phi(x,y,z) \, dx \, dy \, dz \\
&= 2\hbar^2 \int_0^\infty \int_0^\infty \int_0^\infty \Phi^{(\nu)}(x,y,z) \left[ B_{x,z}^{m_2} \partial_x + B_{x,y}^{m_3} \partial_y - \left[ A_{x,y,z}^{m_1} + B_{x,z}^{m_2} + B_{x,y}^{m_3} \right] \partial_x \right] \Phi^{(\eta)}(x,y,z) \, dx \, dy \, dz \\
&\quad + 2\hbar^2 \int_0^\infty \int_0^\infty \int_0^\infty \Phi^{(\nu)}(x,y,z) \left[ B_{y,z}^{m_2} \partial_y + B_{x,z}^{m_3} \partial_x - \left[ A_{y,x,z}^{m_1} + B_{y,z}^{m_2} + B_{x,z}^{m_3} \right] \partial_y \right] \Phi^{(\eta)}(x,y,z) \, dx \, dy \, dz \\
&\quad + 2\hbar^2 \int_0^\infty \int_0^\infty \int_0^\infty \Phi^{(\nu)}(x,y,z) \left[ B_{y,z}^{m_2} \partial_x + B_{x,y}^{m_3} \partial_y - \left[ A_{y,x,z}^{m_1} + B_{y,z}^{m_2} + B_{x,y}^{m_3} \right] \partial_x \right] \Phi^{(\eta)}(x,y,z) \, dx \, dy \, dz \\
&\quad - 2\hbar^2 \int_0^\infty \int_0^\infty \int_0^\infty \Phi^{(\nu)}(x,y,z) \left[ \frac{(y+z)(2x+y+z)}{m_1} + \frac{z^2 - x^2}{m_2} + \frac{y^2 - x^2}{m_3} \right] \partial_y \Phi^{(\eta)}(x,y,z) \, dx \, dy \, dz \\
&\quad - 2\hbar^2 \int_0^\infty \int_0^\infty \int_0^\infty \Phi^{(\nu)}(x,y,z) \left[ \frac{z^2 - y^2}{m_1} + \frac{(x+z)(2y+x+z)}{m_2} + \frac{x^2 - y^2}{m_3} \right] \partial_x \Phi^{(\eta)}(x,y,z) \, dx \, dy \, dz \\
&\quad - 2\hbar^2 \int_0^\infty \int_0^\infty \int_0^\infty \Phi^{(\nu)}(x,y,z) \left[ \frac{y^2 - z^2}{m_1} + \frac{x^2 - z^2}{m_2} + \frac{(x+y)(2z+x+y)}{m_3} \right] \partial_z \Phi^{(\eta)}(x,y,z) \, dx \, dy \, dz
\end{align*}

with
\begin{align*}
A_x^{m} &= \frac{x(y+z)(x+y+z)}{m} , \\
B_x^{m} &= \frac{y(x+y)}{m} .
\end{align*}

The expression in equation (A.2.1) can be rearranged by using
\begin{align*}
\int_0^\infty \Phi^{(\nu)}(u) K_u \partial_u \Phi^{(\eta)}(u) \, du = \left[ \Phi^{(\nu)}(u) K_u \Phi^{(\eta)}(u) \right]_0^\infty - \int_0^\infty \left( \Phi^{(\nu)}(u) (\partial_u K_u) \Phi^{(\eta)}(u) + (\partial_u \Phi^{(\nu)}(u)) K_u \Phi^{(\eta)}(u) \right) \, du .
\end{align*}

Therefore we substitute the variable \( u \) by one element of the perimetric coordinates \( \{x, y, z\} \) and substitute \( K_u \) by the corresponding expression which are given by
\begin{align*}
K_x &= B_x^{m_2} \partial_x + B_x^{m_3} \partial_y - \left[ A_x^{m_1} + B_x^{m_2} + B_x^{m_3} \right] \partial_x , \\
K_y &= B_y^{m_1} \partial_y + B_y^{m_3} \partial_x - \left[ A_y^{m_2} + B_y^{m_1} + B_y^{m_3} \right] \partial_y , \\
K_z &= B_z^{m_1} \partial_y + B_z^{m_2} \partial_x - \left[ A_z^{m_2} + B_z^{m_1} + B_z^{m_2} \right] \partial_z .
\end{align*}

For \( u \in \{x, y, z\} \) equal to zero we obtain \( K_u = 0 \) and according to section 4.1 the two functions \( \Phi^{(\nu)}(u) \), and \( \Phi^{(\eta)}(u) \) approach zero for the limit \( u \to \infty \). Therefore, the equation (A.2.4) is equivalent to
\begin{align*}
\int_0^\infty \Phi^{(\nu)}(u) K_u \partial_u \Phi^{(\eta)}(u) \, du = - \int_0^\infty \left( \Phi^{(\nu)}(u) (\partial_u K_u) \Phi^{(\eta)}(u) + (\partial_u \Phi^{(\nu)}(u)) K_u \Phi^{(\eta)}(u) \right) \, du .
\end{align*}

Finally, the scalar product \( \langle \Phi^{(\nu)} | \hat{T}_S | \Phi^{(\eta)} \rangle \) can be simplified in this way to
\begin{align*}
\langle \Phi^{(\nu)} | \hat{T}_S | \Phi^{(\eta)} \rangle &= \int_0^\infty \int_0^\infty \int_0^\infty \hat{T}_S \Phi^{(\nu)} \Phi^{(\eta)} \, dx \, dy \, dz ,
\end{align*}
\[ \mathcal{T}_S(\Phi^{(\nu)}, \Phi^{(n)}) = 2 \hbar^2 [A_{x,y,z}^1 + B_{x,y}^1 + B_{x,y}^2] \partial_x \Phi^{(\nu)}(x, y, z) \partial_z \Phi^{(n)}(x, y, z) \\
+ 2 \hbar^2 [A_{y,z}^2 + B_{y,z}^2] \partial_y \Phi^{(\nu)}(x, y, z) \partial_y \Phi^{(n)}(x, y, z) \\
+ 2 \hbar^2 [A_{z,x}^2 + B_{z,x}^2] \partial_z \Phi^{(\nu)}(x, y, z) \partial_z \Phi^{(n)}(x, y, z) \\
- 2 \hbar^2 B_{m} \left[ \partial_y \Phi^{(\nu)}(x, y, z) \partial_y \Phi^{(n)}(x, y, z) + \partial_x \Phi^{(\nu)}(x, y, z) \partial_y \Phi^{(n)}(x, y, z) \right] \\
- 2 \hbar^2 B_{m} \left[ \partial_x \Phi^{(\nu)}(x, y, z) \partial_y \Phi^{(n)}(x, y, z) + \partial_y \Phi^{(\nu)}(x, y, z) \partial_x \Phi^{(n)}(x, y, z) \right] \\
- 2 \hbar^2 B_{m} \left[ \partial_z \Phi^{(\nu)}(x, y, z) \partial_y \Phi^{(n)}(x, y, z) + \partial_y \Phi^{(\nu)}(x, y, z) \partial_z \Phi^{(n)}(x, y, z) \right] , \tag{A.2.10} \]

with
\[ A_{m}^n = \frac{x(y+z)(x+y+z)}{m} , \tag{A.2.11} \]
\[ B_{m}^n = \frac{xy(x+y)}{m} . \tag{A.2.12} \]

Using the potential operator \( \hat{V} \) from equation (2.4.21), we obtain the scalar product \( \langle \Phi^{(\nu)} | \hat{V} | \Phi^{(n)} \rangle \). This scalar product can be expressed as
\[ \langle \Phi^{(\nu)} | \hat{V} | \Phi^{(n)} \rangle = \int_0^\infty \int_0^\infty \int_0^\infty (x+y)(y+z) \Phi^{(\nu)} \Phi^{(n)} dx dy dz = \int_0^\infty \int_0^\infty \int_0^\infty \mathcal{V}(\Phi^{(\nu)}, \Phi^{(n)}) dx dy dz \tag{A.2.13} \]

with
\[ \mathcal{V}(\Phi^{(\nu)}, \Phi^{(n)}) = 2e^2 [x+z](y+z)Z_1Z_2 + (x+y)(x+z)Z_1Z_3 + (x+y)(y+z)Z_2Z_3] \Phi^{(\nu)} \Phi^{(n)} . \tag{A.2.14} \]

### A.2.2 Even P-states

In the case of the P-states of wave functions with even parity, we have to consider the scalar product \( \langle \mathcal{R} \Phi^{(\nu)} | \hat{T}_S + \hat{T}_L^{(\text{even})} + \hat{V} | \mathcal{R} \Phi^{(n)} \rangle \) of section 4.3.1. According to equation (4.3.24) the regularization factor \( \mathcal{R} \) is given by
\[ \mathcal{R} = \frac{1}{2} \sqrt{xyz(x+y+z)} . \tag{A.2.15} \]

Using equation (2.4.20) for \( \hat{T}_S \), equation (4.3.19) for \( \hat{T}_L^{(\text{even})} \) in perimetric coordinates, and \( \mathcal{T}_S \) from equation (A.2.10) the scalar product takes the form
\[ \langle \mathcal{R} \Phi^{(\nu)} | \hat{T}_S + \hat{T}_L^{(\text{even})} | \mathcal{R} \Phi^{(n)} \rangle = \int_0^\infty \int_0^\infty \int_0^\infty \mathcal{R}^2 \mathcal{T}_S(\Phi^{(\nu)}, \Phi^{(n)}) dx dy dz + \int_0^\infty \int_0^\infty \int_0^\infty \mathcal{R}^2 \mathcal{T}_L^{(\text{even})}(\Phi^{(\nu)}, \Phi^{(n)}) dx dy dz \\
+ \int_0^\infty \int_0^\infty \int_0^\infty \mathcal{T}_S^{(1)}(\Phi^{(\nu)}, \Phi^{(n)}) dx dy dz + \int_0^\infty \int_0^\infty \int_0^\infty \mathcal{T}_S^{(2)}(\Phi^{(\nu)}, \Phi^{(n)}) dx dy dz \tag{A.2.16} \]

with
\[ T^{(\text{even})}_{L} = \frac{m_1 m_2 (x + y)^2 + m_1 m_3 (x + z)^2 + m_2 m_3 (y + z)^2}{2m_1 m_2 m_3 x y z (x + y + z)} , \]  
(A.2.17)

\[ T^{(1)}_{S} (\Phi^{(v)}, \Phi^{(u)}) = 2 h^2 \left[ A^m_{x,y,z} + B^m_{x,y} + B^m_{x,z} \right] (\partial_x R) \Phi^{(v)}_x (x, y, z) \Phi^{(u)}_x (x, y, z) + (\partial_y R) \Phi^{(v)}_y (x, y, z) \Phi^{(u)}_y (x, y, z) + (\partial_z R) \Phi^{(v)}_z (x, y, z) \Phi^{(u)}_z (x, y, z) \]  
\[ \quad + 2 h^2 \left[ A^m_{x,y,z} + B^m_{y,z} + B^m_{y,x} \right] (\partial_y R) \Phi^{(v)}_y (x, y, z) \Phi^{(u)}_y (x, y, z) + (\partial_z R) \Phi^{(v)}_z (x, y, z) \Phi^{(u)}_z (x, y, z) \]  
\[ \quad + 2 h^2 \left[ A^m_{x,y,z} + B^m_{z,x} + B^m_{z,y} \right] (\partial_z R) \Phi^{(v)}_z (x, y, z) \Phi^{(u)}_z (x, y, z) \]  
\[ \quad - 2 h^2 B^m_{y,x} (\partial_x R) \Phi^{(v)}_x (x, y, z) (\partial_y R) \Phi^{(u)}_x (x, y, z) + (\partial_z R) \Phi^{(v)}_x (x, y, z) \Phi^{(u)}_z (x, y, z) \]  
\[ \quad - 2 h^2 B^m_{x,y} (\partial_x R) \Phi^{(v)}_y (x, y, z) (\partial_y R) \Phi^{(u)}_y (x, y, z) + (\partial_z R) \Phi^{(v)}_y (x, y, z) \Phi^{(u)}_z (x, y, z) \]  
\[ \quad - 2 h^2 B^m_{x,z} (\partial_x R) \Phi^{(v)}_z (x, y, z) (\partial_y R) \Phi^{(u)}_z (x, y, z) + (\partial_z R) \Phi^{(v)}_z (x, y, z) \Phi^{(u)}_z (x, y, z) \]  
\[ \quad - 2 h^2 B^m_{x,y} (\partial_x R) \Phi^{(v)}_y (x, y, z) (\partial_z R) \Phi^{(u)}_y (x, y, z) + (\partial_y R) \Phi^{(v)}_y (x, y, z) \Phi^{(u)}_z (x, y, z) \]  
\[ \quad - 2 h^2 B^m_{x,z} (\partial_x R) \Phi^{(v)}_z (x, y, z) (\partial_z R) \Phi^{(u)}_z (x, y, z) + (\partial_z R) \Phi^{(v)}_z (x, y, z) \Phi^{(u)}_z (x, y, z) \]  
\[ , \]  
(A.2.18)

\[ T^{(2)}_{S} (\Phi^{(v)}, \Phi^{(u)}) = 2 h^2 \left[ A^m_{x,y,z} + B^m_{y,z} + B^m_{y,x} \right] (\partial_x R) \Phi^{(v)}_x (x, y, z) \Phi^{(u)}_x (x, y, z) \]  
\[ \quad + 2 h^2 \left[ A^m_{y,z} + B^m_{y,z} + B^m_{y,x} \right] (\partial_y R) \Phi^{(v)}_y (x, y, z) \Phi^{(u)}_y (x, y, z) \]  
\[ \quad + 2 h^2 \left[ A^m_{x,y,z} + B^m_{z,x} + B^m_{z,y} \right] (\partial_z R) \Phi^{(v)}_z (x, y, z) \Phi^{(u)}_z (x, y, z) \]  
\[ \quad - 4 h^2 B^m_{y,x} (\partial_x R) (\partial_y R) \Phi^{(v)}_x (x, y, z) \Phi^{(u)}_y (x, y, z) \]  
\[ \quad - 4 h^2 B^m_{x,y} (\partial_x R) (\partial_y R) \Phi^{(v)}_x (x, y, z) \Phi^{(u)}_y (x, y, z) \]  
\[ \quad - 4 h^2 B^m_{x,z} (\partial_x R) (\partial_y R) \Phi^{(v)}_x (x, y, z) \Phi^{(u)}_y (x, y, z) \]  
\[ \quad - 4 h^2 B^m_{x,z} (\partial_x R) (\partial_z R) \Phi^{(v)}_x (x, y, z) \Phi^{(u)}_z (x, y, z) \]  
\[ = A^m_{x,y,z} \frac{x (y + z) + (x + y + z)}{m} \]  
\[ , \]  
(A.2.20)

\[ B^m_{x,y} = \frac{xy (x + y)}{m} . \]  
(A.2.21)

The three-fold integral of \( T^{(1)}_{S} \) can be simplified again by using integration by parts. Therefore we employ the two equations

\[ \int_{0}^{\infty} K^{(1)}_{x} (\partial_x R) \Phi^{(u)} (u) (\partial_x \Phi^{(v)} (u)) = \left[ K^{(1)}_{x} (\partial_x R) \Phi^{(u)} (u) \Phi^{(v)} (u) \right]_{0}^{\infty} - \int_{0}^{\infty} (\partial_u) \left[ K^{(1)}_{x} (\partial_x R) \Phi^{(u)} (u) \right] \Phi^{(v)} (u) , \]  
(A.2.22)

\[ \int_{0}^{\infty} K^{(2)}_{y} (\partial_x R) \Phi^{(u)} (u) (\partial_u \Phi^{(v)} (u)) = \left[ K^{(2)}_{y} (\partial_x R) \Phi^{(u)} (u) \Phi^{(v)} (u) \right]_{0}^{\infty} - \int_{0}^{\infty} (\partial_u) \left[ K^{(2)}_{y} (\partial_x R) \Phi^{(u)} (u) \right] \Phi^{(v)} (u) . \]  
(A.2.23)

The variables \( u \) and \( v \) represent one element of the perimetric coordinates \( \{ x, y, z \} \) with \( u \neq v \). The functions \( K^{(1)}_{x} \) and \( K^{(2)}_{y} \) are explicitly given by

\[ K^{(1)}_{x} = A^{m}_{x,y,z} + B^{m}_{x,z} + B^{m}_{x,y} , \]
\[ K^{(1)}_{y} = A^{m}_{y,x,z} + B^{m}_{y,z} + B^{m}_{x,y} , \]
\[ K^{(1)}_{z} = A^{m}_{x,y,z} + B^{m}_{y,z} + B^{m}_{x,z} , \]
Appendix

As seen in section 4.3.2, the scalar product of \( \langle R \Phi_r | R \Phi_s \rangle \) is equal to zero for \( u = 0 \) and \( v = 0 \). Referring to section 4.1 the two functions \( \Phi(u) \) and \( \Psi(u) \) are zero for the limit \( u \to \infty \). Consequently, we obtain

\[
\int_0^\infty \int_0^\infty \int_0^\infty \mathcal{T}_S^{(1)}(\Phi^{(v)}, \Phi^{(q)})dx dy dz = 0
\]

where \( \mathcal{T}_S^{(1)}(\Phi^{(v)}, \Phi^{(q)}) \) represents the scalar product of the wave functions \( \Phi^{(v)} \) and \( \Phi^{(q)} \). According to equation (A.2.26) the scalar product \( \langle R \Phi^{(v)} | R \Phi^{(q)} \rangle \) is equal to zero.

Comparing this result with equation (A.2.16), the scalar product \( \langle R \Phi^{(v)} | \tilde{T}_S + \tilde{T}_L^{(even)} \rangle \) is equal to zero.

If we consider all derivatives and add \( \mathcal{T}_S^{(1)} \) to \( \mathcal{T}_L^{(2)} \), we can reduce the complete expression to the following relation

\[
\mathcal{T}_S^{(1)} + \mathcal{T}_L^{(2)} = -\mathcal{R}^2 \mathcal{T}_L^{(even)} \quad \text{(A.2.26)}
\]

The function \( V(\Phi^{(v)}, \Phi^{(q)}) \) is equal to the one in the S-state consideration which is expressed in equation (A.2.14).

A.2.3 Odd P-states

As seen in section 4.3.2, the scalar product of \( \langle \Psi^{(v)} | H_L | \Psi^{(q)} \rangle \) can be separated into four scalar products. The wave functions \( \Psi^{(v)} \) and \( \Phi^{(q)} \) represent two arbitrary P-states with odd parity. We have also shown
in section 4.3.2 that two of the four scalar products can be obtained by the results of section A.2.1 and A.2.2. The last two scalar products which we consider in this section are in section 4.3.2 that two of the four scalar products can be obtained by the results of section A.2.1

Using the following equation

with

and

Then, we can express the two integrals in equations (A.2.31) and (A.2.33) by

Using the following equation

where we can \( k \) substitute by any of the perimetric coordinates \( x, y, z \), and \( K \) can be substituted by the factors in front of the derivative operator in equations (A.2.32) and (A.2.34) which also depend on the perimetric coordinates. If we use additionally that \( \left[ K \Phi \Psi \right]_0^\infty \) is equal to zero since \( K \) is always equal to zero if one of the perimetric coordinates is equal to zero, and since the wave functions \( \Phi \) and \( \Psi \) approach zero for the limit \( x, y, z \to \infty \), we can express the two integrals in equations (A.2.31) and (A.2.33) by


\[
\langle \Phi_0^{(\nu)}(\text{odd}) | \hat{H}_{P(0,1)} | \Phi_1^{(\nu)}(\text{odd}) \rangle = \int_0^\infty \int_0^\infty \left[ \begin{array}{c}
xyz(x+y+z) \\
x+y
\end{array} \right] \mathcal{D}(\Phi_0^{(\nu)}(\text{odd}), \Phi_1^{(\nu)}(\text{odd})) + \mathcal{E}(\Phi_0^{(\nu)}(\text{odd}), \Phi_1^{(\nu)}(\text{odd})) \] \\
\cdot dz \, dy \, dx ,
\]

(A.2.36)

\[
\mathcal{D}(\Phi_0^{(\nu)}(\text{odd}), \Phi_1^{(\nu)}(\text{odd})) = \left[ \begin{array}{c}
\left[ \frac{x+z}{m_2} - \frac{y+z}{m_1} \right] \Phi_0^{(\nu)}(\text{odd})(x, y, z) (\partial_z \Phi_1^{(\nu)}(\text{odd})(x, y, z)) \\
\left[ \frac{x+z}{m_2} - \frac{y+z}{m_1} \right] (\partial_x \Phi_0^{(\nu)}(\text{odd})(x, y, z)) \Phi_1^{(\nu)}(\text{odd})(x, y, z) \\
\left[ \frac{y+z}{m_2} + \frac{x+z}{m_1} \right] \Phi_0^{(\nu)}(\text{odd})(x, y, z) (\partial_y \Phi_1^{(\nu)}(\text{odd})(x, y, z)) \\
\left[ \frac{y+z}{m_2} + \frac{x+z}{m_1} \right] (\partial_y \Phi_0^{(\nu)}(\text{odd})(x, y, z)) \Phi_1^{(\nu)}(\text{odd})(x, y, z) \\
\left[ \frac{y+z}{m_2} + \frac{x+z}{m_1} \right] (\partial_y \Phi_0^{(\nu)}(\text{odd})(x, y, z)) \Phi_1^{(\nu)}(\text{odd})(x, y, z)
\end{array} \right]
\]

(A.2.37)

\[
\mathcal{E}(\Phi_0^{(\nu)}(\text{odd}), \Phi_1^{(\nu)}(\text{odd})) = \frac{(x+z)(y+z)}{x+y} \left[ \begin{array}{c}
\frac{xyz(y^2 + x^2)}{m_1} + \frac{xyz^2 + xz(y^2 + x^2)}{m_2} \end{array} \right] \Phi_0^{(\nu)}(\text{odd})(x, y, z) \Phi_1^{(\nu)}(\text{odd})(x, y, z) .
\]

(A.2.38)

### A.3 Matrix elements for three non-identical particles

Matrix elements:

\[
\langle F_{ijk} | H(x, y, z) | F'_{i'j'k'} \rangle = 2\hbar^2 \int \int \int dx \, dy \, dz \, N^{-1/2}_{ijk} \cdot N^{-1/2}_{i'j'k'} \left[ \begin{array}{c}
A(x, y, z, m, M) \frac{1}{h^2} f_i \left( \frac{x}{h_x} \right) f_i' \left( \frac{x}{h_x} \right) f_j \left( \frac{y}{h_y} \right) f_j' \left( \frac{y}{h_y} \right) f_k \left( \frac{z}{h_z} \right) f_k' \left( \frac{z}{h_z} \right) \\
+ B(x, y, z, m, M) \frac{1}{h^2} f_i \left( \frac{x}{h_x} \right) f_i' \left( \frac{x}{h_x} \right) f_j \left( \frac{y}{h_y} \right) f_j' \left( \frac{y}{h_y} \right) f_k \left( \frac{z}{h_z} \right) f_k' \left( \frac{z}{h_z} \right) \\
+ C(x, y, z, m, M) \frac{1}{h^2} f_i \left( \frac{x}{h_x} \right) f_i' \left( \frac{x}{h_x} \right) f_j \left( \frac{y}{h_y} \right) f_j' \left( \frac{y}{h_y} \right) f_k \left( \frac{z}{h_z} \right) f_k' \left( \frac{z}{h_z} \right) \\
- D(x, z, m) \frac{1}{h^2} f_i \left( \frac{x}{h_x} \right) f_i' \left( \frac{x}{h_x} \right) f_j \left( \frac{y}{h_y} \right) f_j' \left( \frac{y}{h_y} \right) f_k \left( \frac{z}{h_z} \right) f_k' \left( \frac{z}{h_z} \right) \\
- E(x, y, z, M) \frac{1}{h^2} f_i \left( \frac{x}{h_x} \right) f_i' \left( \frac{x}{h_x} \right) f_j \left( \frac{y}{h_y} \right) f_j' \left( \frac{y}{h_y} \right) f_k \left( \frac{z}{h_z} \right) f_k' \left( \frac{z}{h_z} \right) \\
- E(x, y, z, M) \frac{1}{h^2} f_i \left( \frac{x}{h_x} \right) f_i' \left( \frac{x}{h_x} \right) f_j \left( \frac{y}{h_y} \right) f_j' \left( \frac{y}{h_y} \right) f_k \left( \frac{z}{h_z} \right) f_k' \left( \frac{z}{h_z} \right) \\
- F(x, y, M) \frac{1}{h^2} f_i \left( \frac{x}{h_x} \right) f_i' \left( \frac{x}{h_x} \right) f_j \left( \frac{y}{h_y} \right) f_j' \left( \frac{y}{h_y} \right) f_k \left( \frac{z}{h_z} \right) f_k' \left( \frac{z}{h_z} \right) \\
- F(x, y, M) \frac{1}{h^2} f_i \left( \frac{x}{h_x} \right) f_i' \left( \frac{x}{h_x} \right) f_j \left( \frac{y}{h_y} \right) f_j' \left( \frac{y}{h_y} \right) f_k \left( \frac{z}{h_z} \right) f_k' \left( \frac{z}{h_z} \right)
\end{array} \right] \\
+ 2\hbar^2 \int \int \int dx \, dy \, dz \, N^{-1/2}_{ijk} \cdot N^{-1/2}_{i'j'k'} \left[ \begin{array}{c}
G(x, y, z) f_i \left( \frac{x}{h_x} \right) f_i' \left( \frac{x}{h_x} \right) f_j \left( \frac{y}{h_y} \right) f_j' \left( \frac{y}{h_y} \right) f_k \left( \frac{z}{h_z} \right) f_k' \left( \frac{z}{h_z} \right)
\end{array} \right]
\]

(A.3.1)
with

\[ A(x, y, z, m_1, m_2, m_3) = \frac{x(y + z)(x + y + z)}{m_1} + \frac{xz(x + z)}{m_2} + \frac{xy(x + y)}{m_3} \]

\[ B(x, y, z, m_1, m_2, m_3) = \frac{yz(y + z)}{m_1} + \frac{y(x + z)(x + y + z)}{m_2} + \frac{xy(x + y)}{m_3} \]

\[ C(x, y, z, m_1, m_2, m_3) = \frac{yz(y + z)}{m_1} + \frac{xz(x + z)}{m_2} + \frac{z(x + y)(x + y + z)}{m_3} \]

\[ D(x, z, m_1) = \frac{yz(y + z)}{m_1} \]

\[ E(y, z, m_2) = \frac{xz(x + z)}{m_2} \]

\[ F(x, y, m_3) = \frac{xy(x + y)}{m_3} \]

\[ G(x, y, z) = (x + z)(y + z)Z_1Z_2 + (x + y)(x + z)Z_1Z_3 + (x + y)(y + z)Z_2Z_3 \]

\[
\langle F_{ijk} \mid H(x, y, z) \mid F_{i'j'k'} \rangle \\
\approx 2\hbar^2 \sum_{p=1}^{N_x} \sum_{q=1}^{N_y} \sum_{r=1}^{N_z} \lambda_p \lambda_q \lambda_r \cdot N_{ijk}^{-1/2} N_{i'j'k'}^{-1/2} \\
\cdot \left[ A(h_x p_x, h_y q_y, h_z r_z, m_1, m_2, m_3) \frac{1}{h^2} f'_i(x_p) f'_j(x_p) \lambda_j^{-1/2} \lambda_{j'}^{-1/2} \lambda_k^{-1/2} \delta_{ij} \delta_{j'k} \delta_{k'} \right. \\
+ B(h_x p_x, h_y q_y, h_z r_z, m_1, m_2, m_3) \frac{1}{h^2} f'_i(x_p) f'_j(x_p) \lambda_k^{-1/2} \lambda_{j'}^{-1/2} \lambda_{k'}^{-1/2} \delta_{ij} \delta_{j'k'} \delta_{k'} \right. \\
+ C(h_x p_x, h_y q_y, h_z r_z, m_1, m_2, m_3) \frac{1}{h^2} f'_i(x_p) f'_j(x_p) \lambda_k^{-1/2} \lambda_{j'}^{-1/2} \lambda_{k'}^{-1/2} \delta_{ij} \delta_{j'k} \delta_{k'} \right. \\
- D(h_y q_y, h_z r_z, m_1) \frac{1}{h^2} f'_i(y_q) f'_j(y_q) \lambda_k^{-1/2} \lambda_{j'}^{-1/2} \lambda_{k'}^{-1/2} \delta_{ij} \delta_{j'k} \delta_{k'} \right. \\
- D(h_y q_y, h_z r_z, m_1) \frac{1}{h^2} f'_i(y_q) f'_j(y_q) \lambda_k^{-1/2} \lambda_{j'}^{-1/2} \lambda_{k'}^{-1/2} \delta_{ij} \delta_{j'k} \delta_{k'} \right. \\
- E(h_x p_x, h_z r_z, m_2) \frac{1}{h^2} f'_i(x_p) f'_j(x_p) \lambda_k^{-1/2} \lambda_{j'}^{-1/2} \lambda_{k'}^{-1/2} \delta_{ij} \delta_{j'k} \delta_{k'} \\
- E(h_x p_x, h_z r_z, m_2) \frac{1}{h^2} f'_i(x_p) f'_j(x_p) \lambda_k^{-1/2} \lambda_{j'}^{-1/2} \lambda_{k'}^{-1/2} \delta_{ij} \delta_{j'k} \delta_{k'} \\
- F(h_x p_x, h_y q_y, m_3) \frac{1}{h^2} f'_i(x_p) f'_j(x_p) \lambda_k^{-1/2} \lambda_{j'}^{-1/2} \lambda_{k'}^{-1/2} \delta_{ij} \delta_{j'k} \delta_{k'} \\
- F(h_x p_x, h_y q_y, m_3) \frac{1}{h^2} f'_i(x_p) f'_j(x_p) \lambda_k^{-1/2} \lambda_{j'}^{-1/2} \lambda_{k'}^{-1/2} \delta_{ij} \delta_{j'k} \delta_{k'} \\
\left. + 2\epsilon^2 \sum_{p=1}^{N_x} \sum_{q=1}^{N_y} \sum_{r=1}^{N_z} \lambda_p \lambda_q \lambda_r \cdot N_{ijk}^{-1/2} N_{i'j'k'}^{-1/2} \right] \\
\cdot G(h_x p_x, h_y q_y, h_z r_z) \lambda_i^{-1/2} \lambda_{i'}^{-1/2} \lambda_j^{-1/2} \lambda_{j'}^{-1/2} \lambda_k^{-1/2} \lambda_{k'}^{-1/2}
\[
\langle F_{ijk} | H(x, y, z) | F'_{i'j'k'} \rangle \\
\approx 2\hbar^2 \frac{N_{i'j'k'}}{N_{i'j'k'}^{1/2}} \sum_{p=1}^{N_z} A(h, x_p, h, y_p, h, z_p, m_1, m_2, m_3) f'_i (x_p) f'_{i'} (x_p) \lambda_p \\
+ \frac{1}{h_z} \sum_{p=1}^{N_z} B(h, x_i, h, y_p, h, z_k, m_1, m_2, m_3) f_j (y_p) f'_{j'} (y_p) \lambda_p \\
+ \frac{1}{h_z} \sum_{p=1}^{N_z} C(h, x_i, h, y_p, h, z_p, m_1, m_2, m_3) f'_{k'} (z_p) \lambda_p \\
- \frac{1}{h_z} D(h, y_p, h, z, m_1) f'_i (x_i) f'_{i'} (x_k) \lambda^{1/2}_{i'} \lambda^{1/2}_k \\
- \frac{1}{h_z} D(h, y_p, h, z, m_1) f'_{i'} (x_i) \lambda^{1/2}_{i'} \lambda^{1/2}_k \\
- \frac{1}{h_z} E(h, x_i, h, z, m_2) f_j (y_j) f'_{j'} (y_k) \lambda^{1/2}_{j'} \lambda^{1/2}_k \\
- \frac{1}{h_z} E(h, x_i, h, z, m_2) f'_{j'} (y_j) \lambda^{1/2}_{j'} \lambda^{1/2}_k \\
- \frac{1}{h_z} F(h, x_i, h, z, m_3) f'_i (x_i) f'_{j'} (y_k) \lambda^{1/2}_{i'} \lambda^{1/2}_{j'} \\
- \frac{1}{h_z} F(h, x_i, h, z, m_3) f'_{j'} (y_j) \lambda^{1/2}_{j'} \lambda^{1/2}_{i'} \\
+ \frac{1}{h_z} 2\hbar^2 N_{i'j'k'}^{-1/2} \sum_{p=1}^{N_z} \left[ (x_p + z_p) (y_q + z_r) Z_1 Z_2 + (x_p + y_q) (x_p + z_r) Z_1 Z_3 + (x_p + y_q) (y_q + z_r) Z_2 Z_3 \right]
\]
Bibliography


