

The effect of the Breit interaction on chiral induced spin selectivity

A derivation of the Breit equation and the implementation in a simulation of electron transport

Floris Baas, 5168325

17 August 2022

Supervisors: Jos Thijssen
Johan Dubbeldam
Committee: Yaroslav Blanter
Paul Visser



Abstract

Chiral induced spin selectivity (CISS), the phenomenon in which the interaction within chiral molecules brings about a selectivity in the spin of electrons, is an important unexplained problem within physics. Many possible theories have been proposed since its discovery in 1999, but none of them have been able to explain CISS to its full extent. Professor Luuk Visscher from the VU Amsterdam has suggested to consider the Breit interaction for this problem.

The Breit interaction describes the interaction between electrons in the weakly relativistic limit and its effect on CISS has not yet been studied.

The goal of this thesis was to investigate the Breit interaction in the context of CISS to contribute to a better understanding of the phenomenon.

First a derivation of the Breit equation is given. Starting from the non-relativistic Lagrangian that describes an electron in an electromagnetic field, the Breit interaction is derived:

$$\mathcal{B} = -\frac{q_1 q_2}{r} + \frac{q_1 q_2}{2r} \left(\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + \frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{r})(\boldsymbol{\alpha}_2 \cdot \mathbf{r})}{r^2} \right). \quad (1)$$

This operator acts on bispinors, fourvectors that describe the wave function of both an electron and its corresponding antiparticle, the positron. It is rewritten to only work on the electron part of the wave function. The following expression for the Breit equation is found:

$$\begin{aligned} \mathcal{B} = & \frac{e^2}{r} - \frac{\pi e^2}{2c^2} \delta(\mathbf{r}) \left(\frac{1}{m_1^2} + \frac{1}{m_2^2} \right) - \frac{e^2}{m_1 m_2} \frac{1}{2r} \left(\mathbf{p}_1 \cdot \mathbf{p}_2 + \frac{(\mathbf{p}_1 \cdot \mathbf{r})(\mathbf{p}_2 \cdot \mathbf{r})}{r^2} \right) \\ & - e^2 \frac{\boldsymbol{\sigma}_1 \cdot \mathbf{r} \times \mathbf{p}_1}{4m_1^2 c^2 r^3} + e^2 \frac{\boldsymbol{\sigma}_2 \cdot \mathbf{r} \times \mathbf{p}_2}{4m_2^2 c^2 r^3} + e^2 \frac{\boldsymbol{\sigma}_1 \cdot \mathbf{r} \times \mathbf{p}_2}{2m_1 m_2 c^2 r^3} - e^2 \frac{\boldsymbol{\sigma}_2 \cdot \mathbf{r} \times \mathbf{p}_1}{2m_1 m_2 c^2 r^3} \\ & + \frac{e^2}{4m_1 m_2 c^2} \left(\frac{1}{r^3} \left(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 - 3 \frac{(\boldsymbol{\sigma}_1 \cdot \mathbf{r})(\boldsymbol{\sigma}_2 \cdot \mathbf{r})}{r^2} \right) - \frac{8}{3} \pi \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \delta(\mathbf{r}) \right). \quad (2) \end{aligned}$$

In the second part of the thesis, the derived Breit equation is used to construct a simulation of the electron transport through a chiral molecule. For this, the S-shaped device is introduced. This is a simple two-dimensional chiral molecule of which both ends will be connected to leads, between which a voltage difference is applied, so that electron transport takes place within the molecule.

Abstract

A tight binding Hamiltonian is composed for this problem, which, besides the Breit interaction, also contains the eigenenergies, hopping and spin-orbit interaction. This Hamiltonian is written in matrix form and implemented in a transport code.

With the help of Green's functions and the Meir-Wingreen formula the spin-polarization of the transmission of electrons through the molecule is determined.

Additionally the spin-polarization is determined for the same Hamiltonian, but now excluding the Breit-interaction. The spin-polarizations for the two different Hamiltonians were then compared and it was concluded that they are substantially different. From that follows that the influence of the Breit interaction on the transport of an electron through a chiral molecule is significant and it should therefore not be disregarded in calculations on CISS.

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1. Introduction

Chiral molecules are molecules that can be distinguished from their mirror image, no matter how you rotate them. A simple example of a chiral molecule and its mirror image is given in figure 1.1a. In figure 1.1b it is shown that the two structures cannot be superimposed to each other.

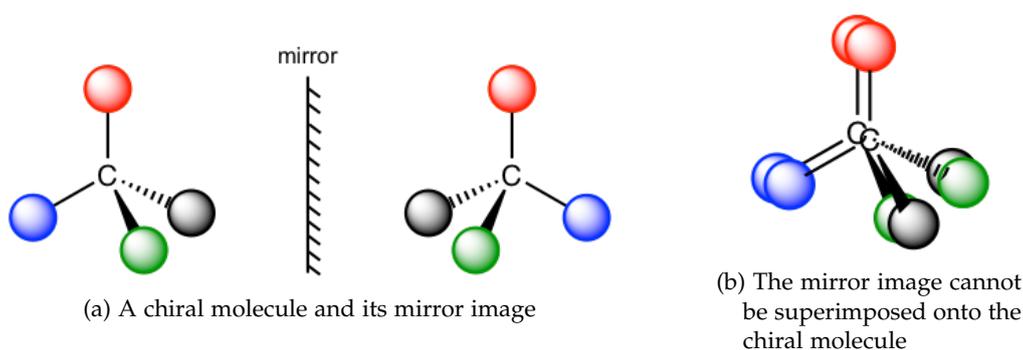


Figure 1.1.: A chiral molecule, its mirror image and the superimposing of the two [1].

Early in the nineteenth century it was discovered that chiral molecules can have a remarkable effect on the optical activity of light [2]: if linearly polarized light passes through a chiral molecule, the orientation of the polarization is rotated. The direction of the rotation is determined by the handedness of the molecule [3].

At the end of the twentieth century a similar phenomenon was discovered: the interaction of electrons within chiral molecules could lead to a spin polarization, which is also determined by the handedness [4]. This effect has been dubbed Chiral Induced Spin Selectivity, or CISS for short. In the last twenty years, the topic has been studied thoroughly and this has led to many experimental setups in which CISS occurs and to numerous possible explanations. None of these explanations has however been capable to fully explain the observations. Many of these attempts have partly explained the effect, but all lead to magnitudes of a small fraction of the observations and scientists are still in the dark as to the details of the mechanism.

In early 2020, the Weizman Institute of Science organized a workshop on the topic of CISS [5]. Numerous scientists from different fields, ranging from theoretical and computational physicists to chemists and experimentalists, were brought together to discuss the phenomenon. Ultimately this did not lead to an explanation, but it has sparked some new interest in the topic.

1. Introduction

Professor Luuk Visscher from the VU Amsterdam has suggested to look into the effect of the Breit interaction. This interaction follows from the theory on electron repulsion in the weakly relativistic limit. It was first described by and named after the American physicist Gregory Breit [6], who published a seminal paper on the topic almost a century ago [7]. This theory is not widely known or used and has not yet been applied to the CISS problem. It is not expected to fully explain the phenomenon, but research of it may lead to a better understanding of the theory, deliver new insights on CISS and perhaps function as a stepping stone towards a definitive explanation.

The goal of this thesis is to investigate the Breit interaction in the context of CISS to gain a better understanding and to examine its influence on electron transport. To that extent, a derivation of the Breit equation is given. This will then be implemented in a simulation of electron transport through a chiral atom.

This thesis is structured as follows: in chapter 2 a short background is given on the topic of CISS, where the experimental observations and the state of theoretical understanding are discussed, followed by the derivation of the Breit equation in chapter 3. In chapter 4 a short introduction of Green's functions and the Meir-Wingreen formula is given and in chapter 5 the Breit equation is used to derive the matrix form of the associated Hamiltonian, which is used to perform a simulation of the electron transport through a chiral molecule.

2. A bit on CISS

Chirality means that an object is different from its mirror image and that no matter how it is rotated, the two can be distinguished. It is applicable to a wide range of items, your own hands being a good example (you cannot turn them such that your left hand is indistinguishable from your right), but in chemistry and physics it is mainly used for molecules. The helix structure of DNA can for example be either left- or right-turning. This is illustrated by figure 2.1, where it can be seen that the handedness makes for two different molecules. The different variants are called enantiomers.

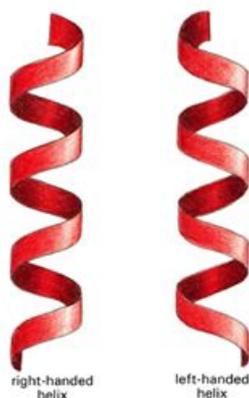


Figure 2.1.: Two different turning helix structures [8].

Chiral molecules can bring about some interesting phenomena. In 1820 optical rotation was discovered. That entails that chiral molecules can rotate the orientation of linearly polarized light that passes through it. The sign of the rotation angle is determined by the handedness of the molecule.

Nowadays another similar phenomenon is known, namely CISS. This is short for Chiral Induced Spin Selectivity and the name already describes what it represents: the collection of processes in which chiral molecules bring about a selectivity in the spin of electrons [5].

The phenomenon was first observed by Ray, Ananthavel, Waldeck and Naaman in 1999, when they noticed a significant asymmetry in the scattering probabilities of electrons that were polarized by transmission through a layer of chiral atoms [4]. At

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that time, the influence of chiral molecules in optical processes was well known, but the effect on the electronic spin led to the opening of a new field of physics.

In the following years, more research on CISS has been conducted, and it was discovered that all CISS phenomena belonged to one of either three forms; in the transmission of free, excited electrons through a chiral molecule, the transport of bound electrons from one lead to another through an enantiomeric interlayer, or in chemical reactions involving chiral molecules.

The discovery of Ray et al. concerned the transmission. For CISS of this type, usually electrons from a substrate are excited using photoemission, after which they travel through a layer of chiral atoms. It is then observed that the electrons exhibit a large asymmetry in their spin, depending on which type of circularly polarized light was used and the chirality of the enantiomeric layer. This principle is illustrated in figure 2.2.

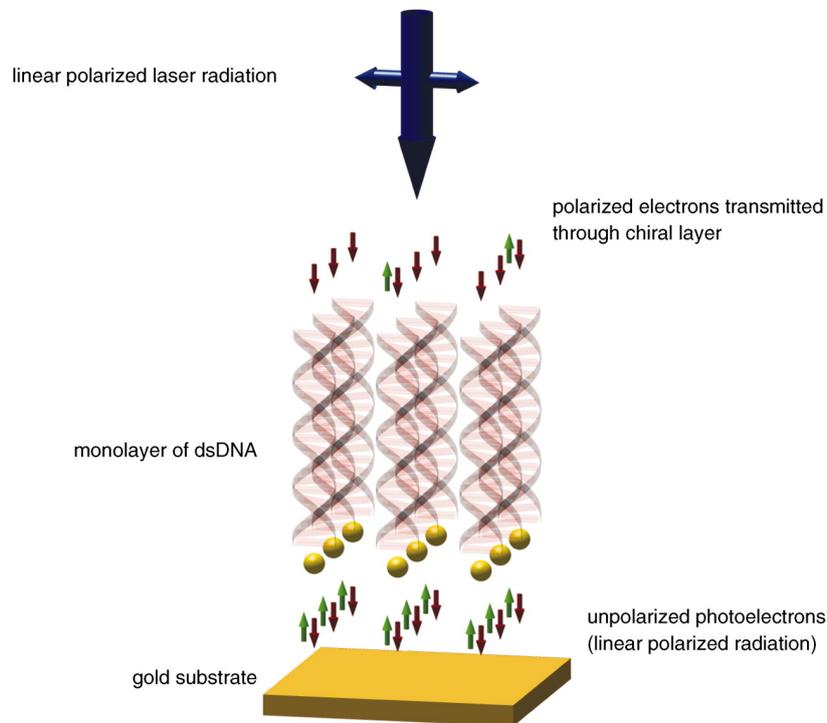


Figure 2.2.: Experimental setup for CISS in transmission. Electrons are excited from a substrate using polarized light. They travel through a chiral medium and their spin is measured [9].

It was later confirmed by Göhler et al. that it was indeed the interaction with the chiral molecules that caused the spin selectivity [9]. In their study, electrons from a gold substrate were excited by the incident light and traveled through a monolayer of

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double-stranded DNA, after which their spin was measured. This is the setup shown in figure 2.2. It was found that the spin-polarization differed for what polarization of light was used: circularly clockwise or counterclockwise or linearly. The results are shown in figure 2.3. An asymmetry between the spin-polarizations caused by the different polarizations can be noted.

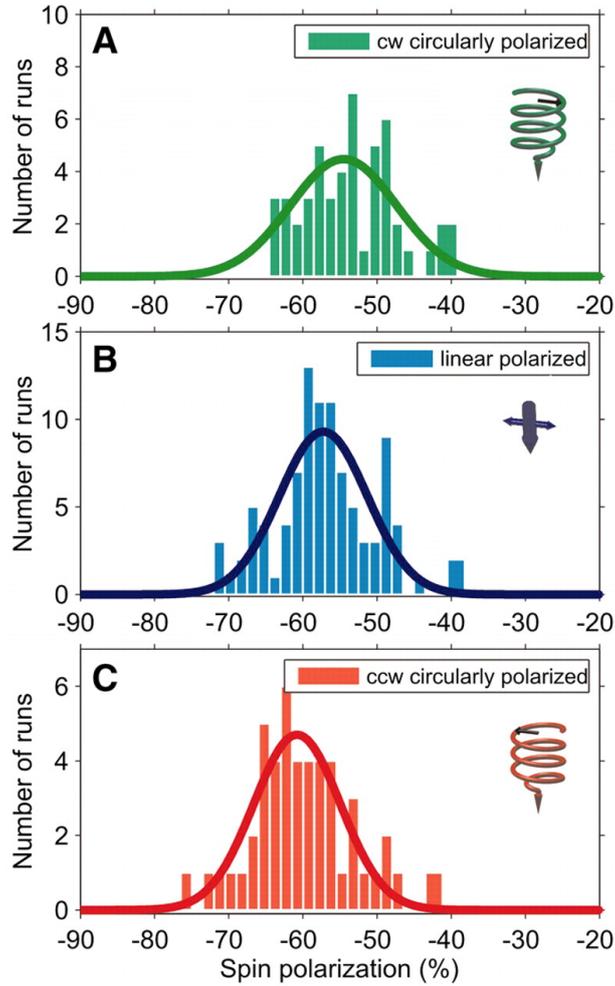


Figure 2.3.: The spin-polarization of electrons that were excited from a gold substrate by either clockwise circularly polarized light (A), linearly (B) or counterclockwise circularly (C), and traveled through a monolayer of double-stranded DNA. The found polarizations were respectively $-(54.5 \pm 7.0)\%$ (A), $-(57.2 \pm 5.9)\%$ (B) and $-(60.8 \pm 5.8)\%$ (C) [9].

The transport case is related to bound electrons in contrast to the free electrons of the transmission. For this, one or more chiral molecules are connected to metallic leads,

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one of which is magnetized, a voltage difference is applied between the two leads and the electrons travel from one lead to the other through the chiral molecule. The presence of certain enantiomers results in an imbalance in the spins of the electrons arriving at the second lead.

This is illustrated by the work of Lu et al. [10]. In panel A of figure 2.4 their setup is presented. The tip overhead of the substrate is magnetized either up or down with respect to the substrate and a voltage difference is applied between the tip and the lead at the bottom of the substrate. In this experiment has been chosen for a fluorine-doped tin oxide substrate, which is marked with FTO in the figure. The electrons will travel from the bottom lead through the layer of chiral molecules to the tip, which is detected as a current. The results are illustrated in panels B-D of the same figure. These are for layers of left-handed, achiral or right-handed chiral molecules respectively. An asymmetry between the different magnetizations for the tip can be seen.

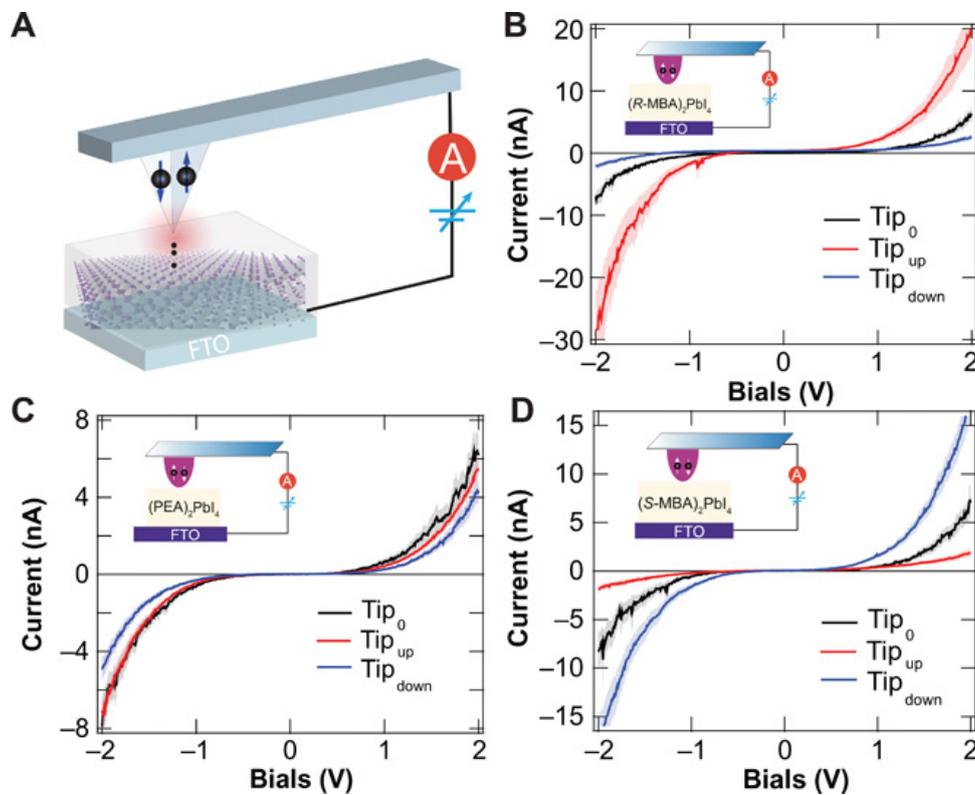


Figure 2.4.: The experimental setup in which CISS can be observed (A). A voltage difference is applied between the leads and electrons will travel through the chiral medium. The measured current as function of the voltage and the magnetization of the tip in panels B-D for respectively left-handed, achiral or right-handed chiral molecules [10]

2. A bit on CISS

The last case - CISS in chemical reactions - is the phenomenon that different enantiomers react in different rates with electrons that are either up or down polarized. This is the form that interests chemists the most.

The range of reactions it can occur in is very broad. One example is in the adsorption of enantiomers on a ferromagnetic sheet, as shown by Banerjee-Ghosh, Ben Dor and Tassinari [11]. Different adsorption densities were observed, depending on the magnetization of the sheet and the enantiomer used, which is illustrated by figure 2.5. A strong preference for the magnetization can be noted for the different enantiomers. The discrepancy was only observed for the ferromagnetic sheet.

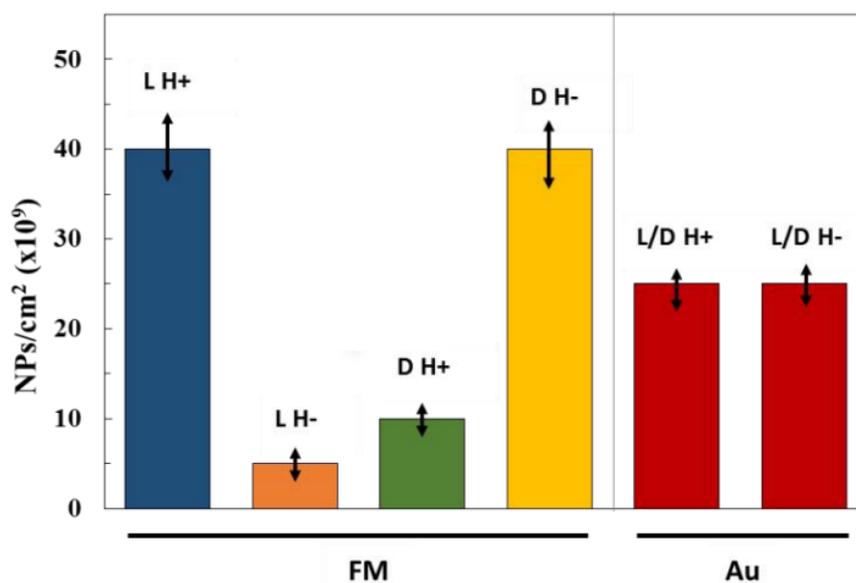


Figure 2.5.: The adsorption densities for different combinations of magnetization of the sheet (indicated by $H+$ and $H-$) and enantiomers (indicated by L and D). Shown for both a ferromagnetic sheet and a gold sheet (indicated by FM and Au) [11].

Despite all the research done into CISS, it still happens to be without a convincing explanation. Scientists have put forward many theories, but none of them has been able to describe CISS to its full extent.

It has for example been suggested that the circular motions of electrons traveling through helical enantiomers induce magnetic fields, which affect the spin of the transmitting electrons. And although that is true in principle, the magnitude of this effect happens to be only a small fraction of that measured in experiments.

2. *A bit on CISS*

Whenever there are effects that have to do with spin in physics, spin-orbit coupling is one of the first mechanisms that is considered for its explanation and CISS is no exception. And although it indeed provides some spin polarization, its magnitude is only a fraction of what is observed in experiments.

3. Derivation of the Breit equation

In this chapter the Breit equation is derived. This was first done by the American physicist Gregory Breit in 1929 and this equation describes the interaction between two electrons in the weakly relativistic limit. As a consequence of the finiteness of the speed of light, the interaction is not instantaneous and retardation effects are taken into account. These are correct up to the order $\frac{1}{c^2}$.

The derivation can be roughly split up into two parts. In the first part, a mainly classical derivation of the most general form is given. This derivation takes the Lagrangian for an electron in an electric field as its starting point and modifies it using the scalar and vector potential and the Dirac matrices, to account for the velocity-dependent interaction between two electrons. This part is largely based on the textbook by Jackson [12].

Then, bispinors are introduced, these are the wave functions the operator of the Breit equation works on and they are used to reduce the dimensionality of the equation from 4 to 2, following Berestetskii [13]. With this, a new form for the Breit equation is found, that describes the interaction of two electrons.

3.1. Maxwell equations and potentials

The Maxwell equations form the basis of electrodynamics. Usually they are written in terms of the electric and magnetic fields, but sometimes it can be useful to write them in terms of potentials.

Here we introduce the electrostatic potential or the scalar potential $\Phi(\mathbf{x}, t)$ and the magnetostatic potential or the vector potential $\mathbf{A}(\mathbf{x}, t)$. These are the potentials associated with the electric and magnetic field. Φ is a scalar field, whereas \mathbf{A} is a vector field. They are respectively defined by $\mathbf{E}(\mathbf{x}, t) = -\nabla\Phi(\mathbf{x}, t) - \frac{1}{c}\frac{\partial\mathbf{A}(\mathbf{x}, t)}{\partial t}$ and $\mathbf{B}(\mathbf{x}, t) = \nabla \times \mathbf{A}(\mathbf{x}, t)$. We assume that the electron current that induces the magnetic field is constant over time and $\mathbf{A}(\mathbf{x})$ does not depend on t . Therefore the scalar potential simplifies to $\mathbf{E}(\mathbf{x}, t) = -\nabla\Phi(\mathbf{x}, t)$.

Explicit expressions for the potentials are respectively given by

3. Derivation of the Breit equation

$$\Phi(\mathbf{x}, t) = \int \frac{\rho(\mathbf{x}', t)}{|\mathbf{x} - \mathbf{x}'|} d^3 x', \quad (3.1a)$$

$$\mathbf{A}(\mathbf{x}, t) = \frac{1}{c^2} \int \frac{\mathbf{J}(\mathbf{x}', t)}{|\mathbf{x} - \mathbf{x}'|} d^3 x'. \quad (3.1b)$$

3.1.1. Gauge transformations

From the definitions of the potentials one can see that they are invariant under so called gauge transformations, which are given by

$$\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla\Lambda \quad (3.2a)$$

$$\Phi \rightarrow \Phi' = \Phi - \frac{1}{c} \frac{\partial\Lambda}{\partial t} \quad (3.2b)$$

where $\Lambda(\mathbf{x}, t)$ is a scalar field that specifies the transformation.

For \mathbf{A} one can see that $\mathbf{B}' = \nabla \times (\mathbf{A} + \nabla\Lambda) = \nabla \times \mathbf{A} + 0 = \mathbf{B}$ and that \mathbf{B} is thus left unchanged under this transformation.

For Φ , $\mathbf{E}' = -\nabla(\Phi - \frac{1}{c} \frac{\partial\Lambda}{\partial t}) - \frac{1}{c} \frac{\partial}{\partial t}(\mathbf{A} + \nabla\Lambda) = -\nabla\Phi - \frac{1}{c} \frac{\partial\mathbf{A}}{\partial t} + 0 = \mathbf{E}$ holds. \mathbf{E} is thus also invariant under the gauge transformation.

3.2. Lagrangian

The non-relativistic Lagrangian that describes an electron in an electromagnetic field is given by [14]

$$\mathcal{L} = \frac{1}{2} m \mathbf{v}^2 - q(\Phi - \mathbf{v} \cdot \mathbf{A}). \quad (3.3)$$

This expression consists of a kinetic energy term and one of the potential.

From this expression a relativistic Lagrangian can be derived by modifying the kinetic energy term - it will take on the form of the Lagrangian of a free particle ¹ - and by using the relativistic expressions for Φ and \mathbf{A} .

Using this, we can also find an expression for the interaction between two electrons. One can observe that this is the same as the interaction of an electron with the electric

¹This term is not relevant for the derivation of the Breit interaction, but for the sake of completeness, the free particle Lagrangian is taken as $\mathcal{L}_{free} = mc^2 \sqrt{1 - (\frac{u}{c})^2}$. Using a Taylor expansion, it can easily be shown that this reduces to \mathcal{L}_{kin} in the non-relativistic limit.

3. Derivation of the Breit equation

field induced by the other electron. The free particle term can be neglected for this. We call this first electron, electron 1. We call the potentials at the position of electron 1 as a result of the electric field of electron 2 Φ_{12} and \mathbf{A}_{12} . Putting everything together we find

$$\mathcal{L}_{12} = -q_1\Phi_{12} + q_1\mathbf{v}_1 \cdot \mathbf{A}_{12}. \quad (3.4)$$

This is thus the relativistic expression for the Lagrangian of the interaction between two electrons.

3.3. Scalar potential

In order to find an explicit expression for the vector and scalar potentials it is convenient to choose the so-called Coulomb gauge. This is a transformation in which Λ is chosen such that $\nabla \cdot \mathbf{A} = 0$. As a result of this, the Maxwell equation in terms of potentials,

$$\nabla^2\Phi + \frac{\partial}{\partial t}(\nabla \cdot \mathbf{A}) = -4\pi\rho, \quad (3.5)$$

can be simplified drastically. The second term disappears and the equation now reads

$$\nabla^2\Phi = -4\pi\rho. \quad (3.6)$$

The other main advantage of using this gauge is that the scalar potential is relativistically correct for all orders of $\frac{1}{c}$.

As one can see, this is a Poisson equation and its solution as an integral involving the charge is given by

$$\Phi(\mathbf{x}, t) = -\frac{1}{4\pi} \int \frac{-4\pi\rho(\mathbf{x}', t)}{|\mathbf{x} - \mathbf{x}'|} d^3x'. \quad (3.7)$$

We notice that this is the same expression as (3.1a).

For two electrons, considered as point particles, the interaction between them can be obtained directly from this. The charge densities are given by delta functions: $\rho(\mathbf{x}', t) = q_2\delta(\mathbf{x}' - \mathbf{x}_2)$. Therefore:

$$\Phi_{12}(\mathbf{x}_1, t) = \int \frac{q_2\delta(\mathbf{x}' - \mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}'|} d^3x' = \frac{q_2}{|\mathbf{x}_1 - \mathbf{x}_2|}. \quad (3.8)$$

3.4. Vector potential

To explicitly express the vector potential, we take equation (3.1b) as the starting point and note that the current can be split up into a longitudinal and transverse part: $\mathbf{J} = \mathbf{J}_l + \mathbf{J}_t$, where the different terms are defined by $\nabla \times \mathbf{J}_l = 0$ and $\nabla \cdot \mathbf{J}_t = 0$. This is a so-called Helmholtz decomposition. As a result of the gauge we have chosen, the current is fully described by the transversal current: $\mathbf{J} = \mathbf{J}_t$.

Additionally, we assume that the current is time-independant. The vector potential then becomes:

$$\mathbf{A}_{12}(\mathbf{x}_1) = \frac{1}{c^2} \int \frac{\mathbf{J}_t(\mathbf{x}')}{|\mathbf{x}_1 - \mathbf{x}'|} d^3x'. \quad (3.9)$$

The next step is to find an expression for \mathbf{J}_t . For this the vector identity $\nabla \times (\nabla \times \mathbf{v}) = \nabla(\nabla \cdot \mathbf{v}) - \nabla^2 \mathbf{v}$ is used:

$$\begin{aligned} \mathbf{J}_t(\mathbf{x}) &= \int \delta(\mathbf{x} - \mathbf{x}') \mathbf{J}_t(\mathbf{x}') d^3x' \\ &= -\frac{1}{4\pi} \int \nabla^2 \frac{\mathbf{J}_t(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x' \\ &= \frac{1}{4\pi} \nabla \times \nabla \times \int \frac{\mathbf{J}_t(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x' \\ &= \frac{1}{4\pi} \nabla \times \nabla \times \int \frac{\mathbf{J}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x' \\ &= \frac{1}{4\pi} \nabla(\nabla \cdot \int \frac{\mathbf{J}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x') - \frac{1}{4\pi} \nabla^2 \int \frac{\mathbf{J}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x' \\ &= -\frac{1}{4\pi} \int \nabla \left(\frac{\mathbf{J}(\mathbf{x}') \cdot (\mathbf{x} - \mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|^3} \right) d^3x' - \frac{1}{4\pi} \int -4\pi \delta(\mathbf{x} - \mathbf{x}') \mathbf{J}(\mathbf{x}') d^3x' \end{aligned} \quad (3.10)$$

Now we substitute $\mathbf{J}(\mathbf{x}') = \mathbf{v}_2 \rho(\mathbf{x}', t) = \mathbf{v}_2 q_2 \delta(\mathbf{x}' - \mathbf{x}_2)$:

$$\begin{aligned} \mathbf{J}_t(\mathbf{x}) &= \int q_2 \mathbf{v}_2 \delta(\mathbf{x} - \mathbf{x}') \delta(\mathbf{x}' - \mathbf{x}_2) d^3x' \\ &\quad - \frac{1}{4\pi} \int \nabla \left(\frac{q_2 \mathbf{v}_2 \cdot (\mathbf{x} - \mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|^3} \right) \delta(\mathbf{x}' - \mathbf{x}_2) d^3x' \\ &= q_2 \mathbf{v}_2 \delta(\mathbf{x} - \mathbf{x}_2) - \frac{q_2}{4\pi} \nabla \left(\frac{\mathbf{v}_2 \cdot (\mathbf{x} - \mathbf{x}_2)}{|\mathbf{x} - \mathbf{x}_2|^3} \right). \end{aligned} \quad (3.11)$$

We can substitute this expression in equation (3.9) and evaluate the potential:

3. Derivation of the Breit equation

$$\mathbf{A}_{12} = \frac{1}{c^2} \int \frac{q_2 \mathbf{v}_2 \delta(\mathbf{x}' - \mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}'|} - \frac{1}{|\mathbf{x}_1 - \mathbf{x}'|} \frac{q_2}{4\pi c} \nabla' \left(\frac{\mathbf{v}_2 \cdot (\mathbf{x}' - \mathbf{x}_2)}{|\mathbf{x}' - \mathbf{x}_2|^3} \right) d^3 x'. \quad (3.12)$$

The first term can be integrated directly and the second term can be found using a substitution $\mathbf{y} = \mathbf{x}' - \mathbf{x}_2$. Additionally we use $r = |\mathbf{x}_1 - \mathbf{x}_2|$. This gives:

$$\begin{aligned} \mathbf{A}_{12} &= \frac{q_2 \mathbf{v}_2}{c^2 r} - \frac{1}{c^2} \int \frac{1}{|\mathbf{y} - \mathbf{r}|} \frac{q_2}{4\pi c} \nabla_r \left(\frac{\mathbf{v}_2 \cdot \mathbf{y}}{y^3} \right) d^3 y \\ &= \frac{q_2 \mathbf{v}_2}{c^2 r} - \frac{q_2}{2c^2} \nabla_r \left(\frac{\mathbf{v}_2 \cdot \mathbf{r}}{r} \right) \\ &= \frac{q_2 \mathbf{v}_2}{c^2 r} - \frac{q_2}{2c^2} \frac{r \mathbf{v}_2 - \mathbf{v}_2 \cdot \mathbf{r}}{r^2} \\ &= \frac{q_2}{2c^2} \left(\frac{\mathbf{v}_2}{r} + \frac{\mathbf{v}_2 \cdot \mathbf{r}}{r^2} \right). \end{aligned} \quad (3.13)$$

With this, we have found an expression for the vector potential. This is correct up to the order $\frac{1}{c^2}$.

3.5. Breit interaction

Now that we have found expressions for Φ_{12} and A_{12} , we can substitute (3.8) and (3.13) into our interaction Lagrangian (3.4). We then find

$$\begin{aligned} \mathcal{L}_{12} &= -q_1 \frac{q_2}{r} + q_1 \mathbf{v}_1 \cdot \left(\frac{q_2}{2c^2 r} \left(\mathbf{v}_2 + \frac{\mathbf{r}(\mathbf{v}_2 \cdot \mathbf{r})}{r^2} \right) \right) \\ &= -\frac{q_1 q_2}{r} + \frac{q_1 q_2}{2c^2 r} \left(\mathbf{v}_1 \cdot \mathbf{v}_2 + \frac{(\mathbf{v}_1 \cdot \mathbf{r})(\mathbf{v}_2 \cdot \mathbf{r})}{r^2} \right) \end{aligned} \quad (3.14)$$

The last step on our way to the Breit interaction is to find a relativistic expression for \mathbf{v} from the Heisenberg equation of motion:

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} = -\frac{i}{\hbar} [\mathbf{r}, \mathcal{H}] = -\frac{i}{\hbar} i \hbar c \boldsymbol{\alpha} = c \boldsymbol{\alpha} \quad (3.15)$$

In this equation \mathcal{H} is the Hamiltonian in the Dirac wave equation for an electron in an electric field, as given by [15]

$$\mathcal{H} = -e\Phi + \beta E_0 + \boldsymbol{\alpha} \cdot (c\mathbf{p} + e\mathbf{A}). \quad (3.16)$$

The $\boldsymbol{\alpha}$ in equation (3.16) has the Dirac matrices α_i as its components, with $i \in \{x, y, z\}$. These operators are 4×4 matrices given by

3. Derivation of the Breit equation

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \quad (3.17)$$

where the σ_i 's are the Pauli matrices [16].

Substituting (3.15) into (3.14) gives us the Breit interaction:

$$\mathcal{B} = -\frac{q_1 q_2}{r} + \frac{q_1 q_2}{2r} \left(\alpha_1 \cdot \alpha_2 + \frac{(\alpha_1 \cdot \mathbf{r})(\alpha_2 \cdot \mathbf{r})}{r^2} \right). \quad (3.18)$$

3.6. Bispinors

Our Breit operator is an operator that works on four vectors, due to the dimensions of the α operators. It works on bispinors, four vectors that describe the wave function of both an electron and its corresponding antiparticle, the positron. Since we're only interested in the electron part, we will look for a way to reduce it such that we only have to account for this. To do this, we first compose an explicit expression for the four vectors.

The bispinor can be written as $u = \begin{pmatrix} u_L \\ u_S \end{pmatrix}$, where u_L and u_S , as we shall now see, are the large and small components of the bispinor corresponding to respectively the electron and positron. The following relation for u_L and u_S holds

$$(2m + E - V)u_S = (\boldsymbol{\sigma} \cdot \mathbf{p})u_L \quad (3.19)$$

If we assume that $m \gg E, V$ we find

$$u_S = \frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p})u_L \quad (3.20)$$

and we indeed see that u_S is small compared to u_L in the weakly relativistic limit.

We can use this expression for u_S and the identity $(\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{p}) = \mathbf{p}^2$ to calculate $\langle u_S | u_S \rangle$. This leads to

$$\langle u_S | u_S \rangle = \left\langle u_L \left| \frac{\mathbf{p}^2}{4m^2} \right| u_L \right\rangle, \quad (3.21)$$

$$\int |u_L|^2 + \frac{\mathbf{p}^2}{4m^2} |u_L|^2 d^3r \approx \int \left(1 + \frac{\mathbf{p}^2}{8m^2}\right)^2 |u_L|^2 d^3r = \int |w|^2 d^3r \quad (3.22)$$

where we have introduced a spinor w to express u_L and u_S . This is an unspecified reference spinor. Equation (3.22) allows us to find an expression for w . This can then be reformulated to give an expression for u_L :

3. Derivation of the Breit equation

$$w = \left(1 + \frac{\mathbf{p}^2}{8m^2}\right)u_L, \quad (3.23)$$

$$u_L \approx \left(1 - \frac{\mathbf{p}^2}{8m^2}\right)w. \quad (3.24)$$

Combining (3.20) and (3.24) gives us an expression for u_S and thus for u . These are given by

$$u_S = \frac{1}{2m}(\boldsymbol{\sigma} \cdot \mathbf{p})\left(1 - \frac{\mathbf{p}^2}{8m^2}\right)w \approx \frac{1}{2m}(\boldsymbol{\sigma} \cdot \mathbf{p})w, \quad (3.25)$$

$$u = \begin{pmatrix} \left(1 - \frac{\mathbf{p}^2}{8m^2}\right)w \\ \frac{1}{2m}(\boldsymbol{\sigma} \cdot \mathbf{p})w \end{pmatrix}. \quad (3.26)$$

3.7. Breit term

To investigate the Breit interaction, as described by equation (3.18), it first needs to be modified a bit more. First we substitute the elementary charge in for q_i , because that is the charge associated with the electrons. The expression is then rewritten, using $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $r = |\mathbf{r}| = \sqrt{(\mathbf{r}_1 - \mathbf{r}_2)^2}$. ∇_i is the gradient operator $\frac{\partial}{\partial \mathbf{r}_i}$ acting on \mathbf{r}_i . This gives

$$\begin{aligned} \mathcal{B} &= -\frac{ee}{r} + \frac{e\boldsymbol{\alpha}_1 \cdot e\boldsymbol{\alpha}_2}{2r} + \frac{(e\boldsymbol{\alpha}_1 \cdot \mathbf{r})(e\boldsymbol{\alpha}_2 \cdot \mathbf{r})}{2r^3} \\ &= -\frac{e^2}{r} + \frac{e\boldsymbol{\alpha}_1 \cdot e\boldsymbol{\alpha}_2}{r} + \frac{e\boldsymbol{\alpha}_1 \cdot e\boldsymbol{\alpha}_2 r + (e\boldsymbol{\alpha}_1 \cdot \mathbf{r})(e\boldsymbol{\alpha}_2 \cdot \frac{\mathbf{r}}{r})}{2r^2} \\ &= -\frac{e^2}{r} + \frac{e\boldsymbol{\alpha}_1 \cdot e\boldsymbol{\alpha}_2}{r} + \frac{1}{2}e\boldsymbol{\alpha}_1 \cdot e\boldsymbol{\alpha}_2 \nabla_1 \frac{\mathbf{r}}{r} \\ &= -\frac{e^2}{r} + \frac{e\boldsymbol{\alpha}_1 \cdot e\boldsymbol{\alpha}_2}{r} + \frac{1}{2}e\boldsymbol{\alpha}_1 \cdot e\boldsymbol{\alpha}_2 \nabla_1 \nabla_2 r \\ &= -\frac{e^2}{r} + \frac{e\boldsymbol{\alpha}_1 \cdot e\boldsymbol{\alpha}_2}{r} + \frac{1}{2}(e\boldsymbol{\alpha}_1 \cdot \nabla_1)(e\boldsymbol{\alpha}_2 \cdot \nabla_2)r. \end{aligned} \quad (3.27)$$

3.8. Fourier transform

To further express this result, (3.27) is Fourier transformed. As a result of the linearity of the Fourier transform, the transform of each individual term can be calculated.

3. Derivation of the Breit equation

3.8.1. First and second term

The Fourier transformation of $\frac{1}{r}$ is calculated by evaluating

$$\mathcal{F}\left(\frac{1}{r}\right) = \int \frac{1}{r} e^{-i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r}. \quad (3.28)$$

Here \mathbf{q} is chosen as the transformation variable. We use $\mathbf{q} = \mathbf{p}'_1 - \mathbf{p}_1 = \mathbf{p}_2 - \mathbf{p}'_2$.

This integral diverges and thus we cannot integrate it directly. To still be able to evaluate it, we introduce the Yukawa potential: $\frac{e^{-\lambda r}}{r}$ [17]. In the limit $\lambda \rightarrow 0$ it equals $\frac{1}{r}$ and the Fourier transformation of this expression does not diverge for any finite value of lambda. Its Fourier transform is given by

$$\mathcal{F}\left(\frac{e^{-\lambda r}}{r}\right) = \frac{4\pi}{\lambda^2 + q^2}. \quad (3.29)$$

Taking the limit $\lambda \rightarrow 0$, we find that $\mathcal{F}\left(\frac{1}{r}\right) = \frac{4\pi}{q^2}$. This leads to the Fourier transform of the first two terms of (3.27). Both e^2 and α_i do not depend on r and are thus invariant under the Fourier transformation.

3.8.2. Last term

For the last term, we can directly evaluate the integral of the Fourier transform:

$$\mathcal{F}(\nabla_1 \nabla_2 r) = \int \nabla_1 \nabla_2 r e^{-i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r}. \quad (3.30)$$

Writing out the derivatives results in:

$$\begin{aligned} \mathcal{F}(\nabla_1 \nabla_2 r) &= \int \frac{\partial}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{r}_2} r e^{-i\mathbf{q}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} d^3\mathbf{r} \\ &= \int -i\mathbf{q} \cdot i\mathbf{q} r e^{-i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r} \\ &= -\frac{8\pi\mathbf{q} \cdot \mathbf{q}}{q^4}. \end{aligned} \quad (3.31)$$

3. Derivation of the Breit equation

3.8.3. Total Fourier transform

Combining the results of (3.29) and (3.31) with (3.27), we find

$$\mathcal{F}[\mathcal{B}] = -\frac{4\pi e^2}{q^2} + \frac{4\pi e^2}{q^2} \boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 - \frac{4\pi (e\boldsymbol{\alpha}_1 \cdot \mathbf{q})(e\boldsymbol{\alpha}_2 \cdot \mathbf{q})}{q^4} \quad (3.32)$$

as an expression for the Fourier transform of the Breit interaction.

3.9. Interaction

To investigate how this operator describes the interaction between the two electrons, the expectation value of it is calculated using the joint wave function of the electrons. This wave function is the product $u_1 u_2$, where u_i is as given by (3.26). This is done for each term individually and afterwards the results are combined.

3.9.1. First term

For the first term it is important to first work out $u_1'^* u_1$ in terms of w_1 . This is done by using the definition of u_1 as given by (3.26):

$$\begin{aligned} u_1'^* u_1 &= \sqrt{2m_1} \left(1 - \frac{\mathbf{p}_1'^2}{8m_1^2 c^2}\right) w_1'^* \sqrt{2m_1} \left(1 - \frac{\mathbf{p}_1^2}{8m_1^2 c^2}\right) w_1 \\ &\quad + \sqrt{2m_1} \frac{1}{2m_1 c^2} w_1'^* (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1') \sqrt{2m_1} \frac{1}{2m_1 c^2} (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1) w_1 \\ &= 2m_1 \left(1 - \frac{\mathbf{p}_1'^2}{8m_1^2 c^2}\right) \left(1 - \frac{\mathbf{p}_1^2}{8m_1^2 c^2}\right) w_1'^* w_1 + \frac{1}{2m_1 c^2} w_1'^* (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1') (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1) w_1 \\ &= 2m_1 w_1'^* \left(1 - \frac{\mathbf{p}_1'^2 + \mathbf{p}_1^2}{8m_1^2 c^2}\right) w_1 + \frac{1}{2m_1 c^2} w_1'^* (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1') (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1) w_1 \\ &= 2m_1 w_1'^* \left(1 - \frac{(\mathbf{p}_1' - \mathbf{p}_1)^2}{8m_1^2 c^2}\right) + \frac{1}{4m_1^2 c^2} (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1') (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1) \Big) w_1 \\ &= 2m_1 w_1'^* \left(1 - \frac{(\mathbf{p}_1' - \mathbf{p}_1)^2}{8m_1^2 c^2} + \frac{i}{4m_1^2 c^2} (\mathbf{p}_1' \times \mathbf{p}_1) \cdot \boldsymbol{\sigma}_1\right) w_1 \\ &= 2m_1 w_1'^* \left(1 - \frac{(\mathbf{p}_1' - \mathbf{p}_1)^2}{8m_1^2 c^2} + \frac{i}{4m_1^2 c^2} (\mathbf{q} \times \mathbf{p}_1) \cdot \boldsymbol{\sigma}_1\right) w_1. \end{aligned} \quad (3.33)$$

3. Derivation of the Breit equation

The derivation of an expression for $u_2'^* u_2$ is completely analogous to the foregoing. The only difference in the end result is that the subscripts 1 are replaced by 2 and that \mathbf{q} is substituted by $-\mathbf{q}$.

Using (3.33) and its equivalent for $u_2'^* u_2$ the first term of equation (3.32) can be evaluated. This leads to

$$\begin{aligned}
& \langle u_1' u_2' | -\frac{4\pi e^2}{q^2} | u_1 u_2 \rangle \\
&= (u_1'^* u_2'^*) - \frac{4\pi e^2}{q^2} (u_1 u_2) = -\frac{4\pi e^2}{q^2} (u_1'^* u_1) (u_2'^* u_2) \\
&= -\frac{4\pi e^2}{q^2} 2m_1 w_1'^* \left(1 - \frac{(\mathbf{p}_1' - \mathbf{p}_1)^2}{8m_1^2 c^2} + \frac{i}{4m_1^2 c^2} (\mathbf{q} \times \mathbf{p}_1) \cdot \boldsymbol{\sigma}_1 \right) w_1 \\
&\quad 2m_2 w_2'^* \left(1 - \frac{(\mathbf{p}_2' - \mathbf{p}_2)^2}{8m_2^2 c^2} - \frac{i}{4m_2^2 c^2} (\mathbf{q} \times \mathbf{p}_2) \cdot \boldsymbol{\sigma}_2 \right) w_2 \\
&= -\frac{4\pi e^2}{q^2} 4m_1 m_2 w_1'^* w_2'^* \left(1 - \frac{(\mathbf{p}_1' - \mathbf{p}_1)^2}{8m_1^2 c^2} + \frac{i}{4m_1^2 c^2} (\mathbf{q} \times \mathbf{p}_1) \cdot \boldsymbol{\sigma}_1 \right) \\
&\quad \left(1 - \frac{(\mathbf{p}_2' - \mathbf{p}_2)^2}{8m_2^2 c^2} - \frac{i}{4m_2^2 c^2} (\mathbf{q} \times \mathbf{p}_2) \cdot \boldsymbol{\sigma}_2 \right) w_1 w_2 \\
&= -\frac{4\pi e^2}{q^2} 4m_1 m_2 w_1'^* w_2'^* \left(1 - \frac{(\mathbf{p}_1' - \mathbf{p}_1)^2}{8m_1^2 c^2} - \frac{(\mathbf{p}_2' - \mathbf{p}_2)^2}{8m_2^2 c^2} \right. \\
&\quad \left. + \frac{i}{4m_1^2 c^2} (\mathbf{q} \times \mathbf{p}_1) \cdot \boldsymbol{\sigma}_1 - \frac{i}{4m_2^2 c^2} (\mathbf{q} \times \mathbf{p}_2) \cdot \boldsymbol{\sigma}_2 \right) w_1 w_2. \tag{3.34}
\end{aligned}$$

3.9.2. Second and third term

To evaluate the second and third term, we need to work out $u_1'^* \alpha u_1$. This is again evaluated using the definitions of the different terms as in equations (3.17) and (3.26), resulting into:

3. Derivation of the Breit equation

$$\begin{aligned}
u_1'^* \boldsymbol{\alpha}_1 u_1 &= \sqrt{2m_1} \left(\left(1 - \frac{\mathbf{p}_1'^2}{8m_1^2 c^2}\right) w_1'^* \quad \frac{1}{2m_1 c} (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1') w_1'^* \right) \\
&\quad \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_1 \\ \boldsymbol{\sigma}_1 & \mathbf{0} \end{pmatrix} \sqrt{2m_1} \begin{pmatrix} \left(1 - \frac{\mathbf{p}_1^2}{8m_1^2 c^2}\right) w_1 \\ \frac{1}{2m_1 c} (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1) w_1 \end{pmatrix} \\
&= 2m_1 \left(\frac{1}{2m_1 c} (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1') w_1'^* \boldsymbol{\sigma}_1 \left(1 - \frac{\mathbf{p}_1^2}{8m_1^2 c^2}\right) w_1 \right. \\
&\quad \left. + \left(1 - \frac{\mathbf{p}_1'^2}{8m_1^2 c^2}\right) w_1'^* \boldsymbol{\sigma}_1 \frac{1}{2m_1 c} (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1) w_1 \right) \\
&= \frac{1}{c} \left((\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1') w_1'^* \boldsymbol{\sigma}_1 w_1 + w_1'^* \boldsymbol{\sigma}_1 (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1) w_1 \right) + \mathcal{O}\left(\frac{1}{c^3}\right) \\
&= \frac{1}{c} w_1'^* \left((\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1') \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_1 (\boldsymbol{\sigma}_1 \cdot \mathbf{p}_1) \right) w_1 \\
&= \frac{1}{c} w_1'^* (\sigma_{1i} (\sigma_{1j} p_{1j}) + (\sigma_{1k} p'_{1k}) \sigma_{1i}) w_1 \\
&= \frac{1}{c} w_1'^* (i\epsilon_{ijl} \sigma_{1l} p_{1j} + p_{1i} + i\epsilon_{kil} p'_{1k} \sigma_{1l} + p'_{1i}) w_1 \\
&= \frac{1}{c} w_1'^* (p_{1i} + p'_{1i} + i(\mathbf{p}_1 \times \boldsymbol{\sigma})_i - i(\mathbf{p}'_1 \times \boldsymbol{\sigma})_i) w_1 \\
&= \frac{1}{c} w_1'^* (2p_{1i} + q_i - i\mathbf{q} \times \boldsymbol{\sigma}_1) w_1 \\
&= \frac{1}{c} w_1'^* (2\mathbf{p}_1 + \mathbf{q} + i\boldsymbol{\sigma}_1 \times \mathbf{q}) w_1. \tag{3.35}
\end{aligned}$$

The expression for $u_2'^* \boldsymbol{\alpha}_2 u_2$ can again be found by changing the subscripts in (3.35) and by substituting $-\mathbf{q}$ for \mathbf{q} . Using this, the second term of (3.32) can be evaluated. That gives

$$\begin{aligned}
&\langle u_1' u_2' | \frac{4\pi e^2}{q^2} \boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 | u_1 u_2 \rangle \\
&= (u_1'^* u_2'^*) - \frac{4\pi e^2}{q^2} \boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 (u_1 u_2) \\
&= \frac{4\pi e^2}{q^2} (u_1'^* \boldsymbol{\alpha}_1 u_1) (u_2'^* \boldsymbol{\alpha}_2 u_2) \\
&= \frac{4\pi e^2}{q^2} \frac{1}{c} w_1'^* (2\mathbf{p}_1 + \mathbf{q} + i\boldsymbol{\sigma}_1 \times \mathbf{q}) w_1 \frac{1}{c} w_2'^* (2\mathbf{p}_2 - \mathbf{q} - i\boldsymbol{\sigma}_2 \times \mathbf{q}) w_2 \\
&= \frac{4\pi e^2}{q^2 c^2} w_1'^* w_2'^* (4\mathbf{p}_1 \mathbf{p}_2 - q^2 + 2\mathbf{q}(\mathbf{p}_2 - \mathbf{p}_1) + q^2 (\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2) - 2i\mathbf{p}_1 (\boldsymbol{\sigma}_2 \times \mathbf{q}) \\
&\quad + 2i\mathbf{p}_2 (\boldsymbol{\sigma}_1 \times \mathbf{q}) - i\mathbf{q} (\boldsymbol{\sigma}_1 \times \mathbf{q}) - i\mathbf{q} (\boldsymbol{\sigma}_2 \times \mathbf{q})) w_1 w_2. \tag{3.36}
\end{aligned}$$

3. Derivation of the Breit equation

Ultimately we only have the third term of (3.32) left. For this we again use the result (3.35). This way we find the third term to be

$$\begin{aligned}
& \langle u'_1 u'_2 | -4\pi e^2 \frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{q})(\boldsymbol{\alpha}_2 \cdot \mathbf{q})}{q^4} | u_1 u_2 \rangle \\
&= (u_1'^* u_2'^*) - 4\pi e^2 \frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{q})(\boldsymbol{\alpha}_2 \cdot \mathbf{q})}{q^4} (u_1 u_2) \\
&= -\frac{4\pi e^2}{q^4} (u_1'^* (\boldsymbol{\alpha}_1 \cdot \mathbf{q}) u_1) (u_2'^* (\boldsymbol{\alpha}_2 \cdot \mathbf{q}) u_2) \\
&= -\frac{4\pi e^2}{q^4} \frac{1}{c} w_1'^* (\mathbf{q} \cdot (2\mathbf{p}_1 + \mathbf{q} + i\boldsymbol{\sigma}_1 \times \mathbf{q})) w_1 \frac{1}{c} w_2'^* (\mathbf{q} \cdot (2\mathbf{p}_2 - \mathbf{q} - i\boldsymbol{\sigma}_2 \times \mathbf{q})) w_2 \\
&= -\frac{4\pi e^2}{q^4 c^2} w_1'^* w_2'^* (q^2 (4\mathbf{p}_1 \mathbf{p}_2 - q^2 + 2\mathbf{q}(\mathbf{p}_2 - \mathbf{p}_1) + q^2(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2) - 2i\mathbf{p}_1(\boldsymbol{\sigma}_2 \times \mathbf{q}) \\
&\quad + 2i\mathbf{p}_2(\boldsymbol{\sigma}_1 \times \mathbf{q}) - i\mathbf{q}(\boldsymbol{\sigma}_1 \times \mathbf{q}) - i\mathbf{q}(\boldsymbol{\sigma}_2 \times \mathbf{q}))) w_1 w_2 \\
&= -\frac{4\pi e^2}{q^4 c^2} w_1'^* w_2'^* (4(\mathbf{p}_1 \cdot \mathbf{q})(\mathbf{p}_2 \cdot \mathbf{q}) - q^4 + 2q^3(\mathbf{p}_2 - \mathbf{p}_1)) w_1 w_2. \tag{3.37}
\end{aligned}$$

3.9.3. Total interaction

Now that we have expressions for all the terms of (3.32), in the forms of (3.34), (3.36) and (3.37), they can be substituted back into the original expression, giving:

3. Derivation of the Breit equation

$$\begin{aligned}
\mathcal{F}(\mathcal{B}) &= -\frac{4\pi e^2}{q^2} 4m_1 m_2 w_1'^* w_2'^* \left(1 - \frac{(\mathbf{p}'_1 - \mathbf{p}_1)^2}{8m_1^2 c^2} - \frac{(\mathbf{p}'_2 - \mathbf{p}_2)^2}{8m_2^2 c^2} + \frac{i(\mathbf{q} \times \mathbf{p}_1) \cdot \boldsymbol{\sigma}_1}{4m_1^2 c^2} \right. \\
&\quad \left. - \frac{i(\mathbf{q} \times \mathbf{p}_2) \cdot \boldsymbol{\sigma}_2}{4m_2^2 c^2} \right) w_1 w_2 + \frac{4\pi e^2}{q^2 c^2} w_1'^* w_2'^* (4\mathbf{p}_1 \mathbf{p}_2 - q^2 + 2\mathbf{q}(\mathbf{p}_2 - \mathbf{p}_1) \\
&\quad + q^2(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2) - 2i\mathbf{p}_1(\boldsymbol{\sigma}_2 \times \mathbf{q}) + 2i\mathbf{p}_2(\boldsymbol{\sigma}_1 \times \mathbf{q}) - i\mathbf{q}(\boldsymbol{\sigma}_1 \times \mathbf{q}) \\
&\quad - i\mathbf{q}(\boldsymbol{\sigma}_2 \times \mathbf{q})) w_1 w_2 - \frac{4\pi e^2}{q^4 c^2} w_1'^* w_2'^* (4(\mathbf{p}_1 \cdot \mathbf{q})(\mathbf{p}_2 \cdot \mathbf{q}) - q^4 \\
&\quad + 2q^3(\mathbf{p}_2 - \mathbf{p}_1)) w_1 w_2 \\
&= -4\pi e^2 4m_1 m_2 w_1'^* w_2'^* \left(\frac{1}{q^2} - \frac{1}{8m_1^2 c^2} - \frac{1}{8m_2^2 c^2} + \frac{i(\mathbf{q} \times \mathbf{p}_1) \boldsymbol{\sigma}_1}{4m_1^2 c^2 q^2} - \frac{i(\mathbf{q} \times \mathbf{p}_2) \boldsymbol{\sigma}_2}{4m_2^2 c^2 q^2} \right. \\
&\quad - \frac{\mathbf{p}_1 \mathbf{p}_2}{m_1 m_2 c^2 q^2} + \frac{1}{4m_1 m_2 c^2} - \frac{\mathbf{p}_2 - \mathbf{p}_1}{2m_1 m_2 c^2 \mathbf{q}} - \frac{\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2}{4m_1 m_2 c^2} + \frac{2i(\boldsymbol{\sigma}_2 \times \mathbf{q}) \mathbf{p}_1}{4m_1 m_2 c^2 q^2} \\
&\quad - \frac{2i(\boldsymbol{\sigma}_1 \times \mathbf{q}) \mathbf{p}_2}{4m_1 m_2 c^2 q^2} + \frac{(\mathbf{q} \cdot \boldsymbol{\sigma}_1)(\mathbf{q} \cdot \boldsymbol{\sigma}_2)}{4m_1 m_2 c^2 q^2} + \frac{(\mathbf{p}_1 \cdot \mathbf{q})(\mathbf{p}_2 \cdot \mathbf{q})}{m_1 m_2 c^2 q^4} - \frac{1}{4m_1 m_2 c^2} \\
&\quad \left. + \frac{\mathbf{p}_2 - \mathbf{p}_1}{2m_1 m_2 c^2 \mathbf{q}} \right) w_1 w_2 \\
&= -4\pi e^2 4m_1 m_2 w_1'^* w_2'^* \left(\frac{1}{q^2} - \frac{1}{8m_1^2 c^2} - \frac{1}{8m_2^2 c^2} + \frac{(\mathbf{p}_1 \cdot \mathbf{q})(\mathbf{p}_2 \cdot \mathbf{q})}{m_1 m_2 c^2 q^4} \right. \\
&\quad - \frac{\mathbf{p}_1 \mathbf{p}_2}{m_1 m_2 c^2 q^2} + \frac{i(\mathbf{q} \times \mathbf{p}_1) \boldsymbol{\sigma}_1}{4m_1^2 c^2 q^2} - \frac{i(\mathbf{q} \times \mathbf{p}_2) \boldsymbol{\sigma}_2}{4m_2^2 c^2 q^2} + \frac{i(\boldsymbol{\sigma}_2 \times \mathbf{q}) \mathbf{p}_1}{2m_1 m_2 c^2 q^2} - \frac{i(\boldsymbol{\sigma}_1 \times \mathbf{q}) \mathbf{p}_2}{2m_1 m_2 c^2 q^2} \\
&\quad + \frac{(\mathbf{q} \cdot \boldsymbol{\sigma}_1)(\mathbf{q} \cdot \boldsymbol{\sigma}_2)}{4m_1 m_2 c^2 q^2} - \frac{\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2}{4m_1 m_2 c^2} + \frac{1}{4m_1 m_2 c^2} - \frac{1}{4m_1 m_2 c^2} - \frac{\mathbf{p}_2 - \mathbf{p}_1}{2m_1 m_2 c^2 \mathbf{q}} \\
&\quad \left. + \frac{\mathbf{p}_2 - \mathbf{p}_1}{2m_1 m_2 c^2 \mathbf{q}} \right) w_1 w_2. \tag{3.38}
\end{aligned}$$

As one can see, the last four terms cancel each other out and they leave us with the Fourier transformed result of the Breit interaction. The last step is to transform this back.

3.10. Inverse Fourier transform

The different terms of (3.38) can be split up into a couple of different groups, according to their dependence on \mathbf{q} . This is important to note for the inverse Fourier transform. It can be of the form $\frac{4\pi}{q^2}$, such as terms 1 and 5, of the form $\frac{4\pi \mathbf{q}}{q^2}$, which are terms 6 up until 9, of the form $\frac{4\pi(\mathbf{a} \cdot \mathbf{q})(\mathbf{b} \cdot \mathbf{q})}{q^4}$, as is term 4, of the form $\frac{4\pi(\mathbf{a} \cdot \mathbf{q})(\mathbf{b} \cdot \mathbf{q})}{q^2}$, such as term 10, or it can be independent of \mathbf{q} , which are terms 2, 3 and 11.

3. Derivation of the Breit equation

For each of these forms in general the inverse Fourier transform can be determined using

$$f(\mathbf{r}) = \frac{1}{(2\pi)^3} \int \mathcal{F}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{q}. \quad (3.39)$$

And using these results the inverse Fourier transform of (3.38) can be determined as a linear combination of these with the correct prefactors from (3.38).

From (3.28) we know that for the inverse Fourier transform of $\frac{4\pi}{q^2}$ the following holds:

$$\mathcal{F}^{-1}\left(\frac{4\pi}{q^2}\right) = \frac{1}{(2\pi)^3} \int \frac{4\pi}{q^2} e^{i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{q} = \frac{1}{r}. \quad (3.40)$$

Solving integral (3.39) for the other forms can be quite tedious. To avoid this, (3.40) is taken as a starting point and modified using the appropriate derivatives, so that the forms we want to evaluate start to appear within the integral. If we then also take the same derivative on the right hand side, we have an outcome for the integral of the inverse Fourier transform.

3.10.1. Second form

For $\frac{4\pi\mathbf{q}}{q^2}$, we differentiate both sides with respect to \mathbf{r} . That results in

$$\begin{aligned} \frac{\partial}{\partial \mathbf{r}} \frac{1}{(2\pi)^3} \int \frac{4\pi}{q^2} e^{i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{q} &= \frac{\partial}{\partial \mathbf{r}} \frac{1}{r} \\ \frac{1}{(2\pi)^3} \int \frac{4\pi}{q^2} i\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{q} &= \frac{\partial}{\partial \mathbf{r}} \frac{1}{\sqrt{r^2}} \\ \frac{1}{(2\pi)^3} \int \frac{4\pi\mathbf{q}}{q^2} e^{i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{q} &= \frac{1}{i} \frac{-1}{2} \frac{2\mathbf{r}}{r^2\sqrt{r^2}} = \frac{i\mathbf{r}}{r^3}. \end{aligned} \quad (3.41)$$

3.10.2. Third form

For the term $\frac{4\pi(\mathbf{a}\cdot\mathbf{q})(\mathbf{b}\cdot\mathbf{q})}{q^4}$, we multiply both sides of (3.40) by $\frac{1}{2}(\mathbf{a}\cdot\frac{\partial}{\partial \mathbf{r}})(\mathbf{b}\cdot\mathbf{r})$ and we use the variable substitution $\mathbf{q} = -\mathbf{u}$:

3. Derivation of the Breit equation

$$\begin{aligned}
\frac{1}{2}(\mathbf{a} \cdot \frac{\partial}{\partial \mathbf{r}})(\mathbf{b} \cdot \mathbf{r}) \frac{1}{(2\pi)^3} \int \frac{4\pi}{q^2} e^{i\mathbf{q} \cdot \mathbf{r}} d^3 \mathbf{q} &= \frac{1}{2}(\mathbf{a} \cdot \frac{\partial}{\partial \mathbf{r}})(\mathbf{b} \cdot \mathbf{r}) \frac{1}{r} \\
-\frac{1}{2} \mathbf{a} \cdot \mathbf{b} \frac{1}{(2\pi)^3} \int \frac{4\pi}{u^2} \frac{\partial}{\partial \mathbf{r}} \mathbf{r} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} &= \frac{1}{2}(\mathbf{a} \cdot \frac{\partial}{\partial \mathbf{r}}) \mathbf{b} \cdot \frac{\mathbf{r}}{r} \\
-\frac{1}{2} \mathbf{a} \cdot \mathbf{b} \frac{1}{(2\pi)^3} \int \frac{4\pi}{u^2} \frac{\partial}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{u}} \frac{-1}{i} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} &= \frac{1}{2} \mathbf{a} \cdot \mathbf{b} \cdot \frac{r - \mathbf{r} \cdot \frac{\mathbf{r}}{r}}{r^2} \\
\frac{1}{2} \mathbf{a} \cdot \mathbf{b} \frac{1}{(2\pi)^3} \int \frac{4\pi}{u^2} \frac{\partial}{\partial \mathbf{u}} -\mathbf{u} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} &= \frac{1}{2} \mathbf{a} \cdot \mathbf{b} \frac{1}{r} - \frac{1}{2} \mathbf{a} \cdot \mathbf{b} \cdot \frac{\mathbf{r} \mathbf{r}}{r^3}. \tag{3.42}
\end{aligned}$$

The left hand side of the equality is evaluated using integration by parts. To keep the calculation clear, the prefactors are omitted for now. Later on they will be added back:

$$\begin{aligned}
\int \frac{1}{u^2} \frac{\partial}{\partial \mathbf{u}} -\mathbf{u} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} &= \left[\frac{1}{u^2} -\mathbf{u} e^{-i\mathbf{u} \cdot \mathbf{r}} \right] - \int \frac{-2}{u^3} -\mathbf{u} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} \\
&\quad - \int \frac{1}{u^2} (-1 + i\mathbf{u} \mathbf{r}) e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} \\
&= - \left[\frac{1}{u} e^{-i\mathbf{u} \cdot \mathbf{r}} \right] - \int \frac{2}{u^3} \mathbf{u} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} \\
&\quad + \int \frac{1}{u^2} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} - \int \frac{1}{u} i\mathbf{r} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} \\
&= - \left[\frac{1}{u} e^{-i\mathbf{u} \cdot \mathbf{r}} \right] - \int \frac{2}{u^3} \mathbf{u} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} \\
&\quad + \left[\frac{-1}{\mathbf{u}} e^{-i\mathbf{u} \cdot \mathbf{r}} \right] - \int \frac{1}{u} -i\mathbf{r} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} \\
&= - \int \frac{2}{u^3} \mathbf{u} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u}. \tag{3.43}
\end{aligned}$$

If we now combine the results of (3.42) and (3.43), we find

$$\begin{aligned}
\frac{1}{2} \mathbf{a} \cdot \mathbf{b} \frac{1}{(2\pi)^3} 4\pi \int -\frac{2}{u^3} \mathbf{u} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} &= \frac{1}{2} \mathbf{a} \cdot \mathbf{b} \frac{1}{r} - \frac{1}{2} \mathbf{a} \cdot \mathbf{b} \cdot \frac{\mathbf{r} \mathbf{r}}{r^3} \\
-\mathbf{a} \cdot \mathbf{b} \frac{1}{(2\pi)^3} \int \frac{4\pi}{u^3} \mathbf{u} \frac{\mathbf{u}}{\mathbf{u}} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} &= \frac{1}{2r} \mathbf{a} \cdot \mathbf{b} - \frac{1}{2r^3} (\mathbf{a} \cdot \mathbf{r})(\mathbf{b} \cdot \mathbf{r}) \\
-\frac{1}{(2\pi)^3} \int \frac{4\pi (\mathbf{a} \cdot \mathbf{u})(\mathbf{b} \cdot \mathbf{u})}{u^4} e^{-i\mathbf{u} \cdot \mathbf{r}} d^3 \mathbf{u} &= \frac{1}{2r} \left(\mathbf{a} \cdot \mathbf{b} - \frac{1}{r^2} (\mathbf{a} \cdot \mathbf{r})(\mathbf{b} \cdot \mathbf{r}) \right) \\
\frac{1}{(2\pi)^3} \int \frac{4\pi (\mathbf{a} \cdot \mathbf{q})(\mathbf{b} \cdot \mathbf{q})}{q^4} e^{i\mathbf{q} \cdot \mathbf{r}} d^3 \mathbf{q} &= \frac{1}{2r} \left(\mathbf{a} \cdot \mathbf{b} - \frac{1}{r^2} (\mathbf{a} \cdot \mathbf{r})(\mathbf{b} \cdot \mathbf{r}) \right) \tag{3.44}
\end{aligned}$$

and this is the expression for the inverse Fourier transform of $\frac{4\pi(\mathbf{a} \cdot \mathbf{q})(\mathbf{b} \cdot \mathbf{q})}{q^4}$.

3. Derivation of the Breit equation

3.10.3. Fourth form

To transform $\frac{4\pi(\mathbf{a}\cdot\mathbf{q})(\mathbf{b}\cdot\mathbf{q})}{q^2}$ back, we multiply both sides of (3.40) with $-(\mathbf{a}\cdot\frac{\partial}{\partial\mathbf{r}})(\mathbf{b}\cdot\frac{\partial}{\partial\mathbf{r}})$:

$$\begin{aligned}
 & -(\mathbf{a}\cdot\frac{\partial}{\partial\mathbf{r}})(\mathbf{b}\cdot\frac{\partial}{\partial\mathbf{r}})\frac{1}{(2\pi)^3}\int\frac{4\pi}{q^2}e^{i\mathbf{q}\cdot\mathbf{r}}d^3\mathbf{q} = -(\mathbf{a}\cdot\frac{\partial}{\partial\mathbf{r}})(\mathbf{b}\cdot\frac{\partial}{\partial\mathbf{r}})\frac{1}{r} \\
 & -\frac{1}{(2\pi)^3}\int\frac{4\pi}{q^2}(i\mathbf{a}\cdot\mathbf{q})(i\mathbf{b}\cdot\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}d^3\mathbf{q} = -(\mathbf{a}\cdot\frac{\partial}{\partial\mathbf{r}})\mathbf{b}\cdot-\frac{\mathbf{r}}{r^3} \\
 & \frac{1}{(2\pi)^3}\int\frac{4\pi(\mathbf{a}\cdot\mathbf{q})(\mathbf{b}\cdot\mathbf{q})}{q^2}e^{i\mathbf{q}\cdot\mathbf{r}}d^3\mathbf{q} = \mathbf{a}\cdot\mathbf{b}\frac{r^3-3\mathbf{r}r}{r^6} \\
 & \frac{1}{(2\pi)^3}\int\frac{4\pi(\mathbf{a}\cdot\mathbf{q})(\mathbf{b}\cdot\mathbf{q})}{q^2}e^{i\mathbf{q}\cdot\mathbf{r}}d^3\mathbf{q} = \frac{1}{r^3}\left((\mathbf{a}\cdot\mathbf{b})-3\frac{(\mathbf{a}\cdot\mathbf{r})(\mathbf{b}\cdot\mathbf{r})}{r^2}\right). \tag{3.45}
 \end{aligned}$$

The second derivative at the right hand side of this expression, however, diverges at $\mathbf{r} = 0$. To prevent this problem, the term $\frac{4\pi}{3}\mathbf{a}\cdot\mathbf{b}\delta(\mathbf{r})$ is added onto the expression.

3.10.4. Fifth form

And lastly, for the constant term, we know that [18]

$$\mathcal{F}^{-1}(1) = \delta(r). \tag{3.46}$$

3.10.5. Total inverse Fourier transform

To calculate the inverse Fourier transform of (3.38), all that is left to do, is combining the results of (3.40), (3.41), (3.44), (3.45) and (3.46) with the corresponding prefactors from (3.38). This leads to

3. Derivation of the Breit equation

$$\begin{aligned}
\mathcal{B} &= \frac{e^2}{r} - \frac{\pi e^2}{2m_1^2 c^2} \delta(\mathbf{r}) - \frac{\pi e^2}{2m_2^2 c^2} \delta(\mathbf{r}) + \frac{e^2}{m_1 m_2} \frac{1}{2r} \left(\mathbf{p}_1 \cdot \mathbf{p}_2 - \frac{(\mathbf{p}_1 \cdot \mathbf{r})(\mathbf{p}_2 \cdot \mathbf{r})}{r^2} \right) \\
&\quad - \frac{e^2 \mathbf{p}_1 \cdot \mathbf{p}_2}{m_1 m_2 r} - e^2 \frac{\boldsymbol{\sigma}_1 \cdot \mathbf{r} \times \mathbf{p}_1}{4m_1^2 c^2 r^3} + e^2 \frac{\boldsymbol{\sigma}_2 \cdot \mathbf{r} \times \mathbf{p}_2}{4m_2^2 c^2 r^3} + e^2 \frac{\boldsymbol{\sigma}_1 \cdot \mathbf{r} \times \mathbf{p}_2}{2m_1 m_2 c^2 r^3} \\
&\quad - e^2 \frac{\boldsymbol{\sigma}_2 \cdot \mathbf{r} \times \mathbf{p}_1}{2m_1 m_2 c^2 r^3} + \frac{e^2}{4m_1 m_2 c^2} \left(\frac{1}{r^3} \left(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 - 3 \frac{(\boldsymbol{\sigma}_1 \cdot \mathbf{r})(\boldsymbol{\sigma}_2 \cdot \mathbf{r})}{r^2} \right) \right) \\
&\quad + \frac{4}{3} \pi \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \delta(\mathbf{r}) \Big) - \pi e^2 \frac{\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2}{m_1 m_2 c^2} \delta(\mathbf{r}) \\
&= \frac{e^2}{r} - \frac{\pi e^2}{2c^2} \delta(\mathbf{r}) \left(\frac{1}{m_1^2} + \frac{1}{m_2^2} \right) - \frac{e^2}{m_1 m_2} \frac{1}{2r} \left(\mathbf{p}_1 \cdot \mathbf{p}_2 + \frac{(\mathbf{p}_1 \cdot \mathbf{r})(\mathbf{p}_2 \cdot \mathbf{r})}{r^2} \right) \\
&\quad - e^2 \frac{\boldsymbol{\sigma}_1 \cdot \mathbf{r} \times \mathbf{p}_1}{4m_1^2 c^2 r^3} + e^2 \frac{\boldsymbol{\sigma}_2 \cdot \mathbf{r} \times \mathbf{p}_2}{4m_2^2 c^2 r^3} + e^2 \frac{\boldsymbol{\sigma}_1 \cdot \mathbf{r} \times \mathbf{p}_2}{2m_1 m_2 c^2 r^3} - e^2 \frac{\boldsymbol{\sigma}_2 \cdot \mathbf{r} \times \mathbf{p}_1}{2m_1 m_2 c^2 r^3} \\
&\quad + \frac{e^2}{4m_1 m_2 c^2} \left(\frac{1}{r^3} \left(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 - 3 \frac{(\boldsymbol{\sigma}_1 \cdot \mathbf{r})(\boldsymbol{\sigma}_2 \cdot \mathbf{r})}{r^2} \right) \right) - \frac{8}{3} \pi \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \delta(\mathbf{r}) \Big) \tag{3.47}
\end{aligned}$$

which is our final expression for the Breit interaction.

4. Green's functions and the Meir-Wingreen formula

A way to calculate the transport of electrons through a material is through so-called nonequilibrium Green's function theory [19]. This is a way to find the current in a quantum device [20]. The theory is based around the Green's function. For a closed system that is the operator

$$G(z) = (zI - \mathcal{H})^{-1} \quad (4.1)$$

that is defined in terms of the Hamiltonian \mathcal{H} . Using the eigenfunctions $|\phi_j\rangle$ of the Hamiltonian with corresponding eigenvalues ϵ_j , this can be written as

$$G(z) = \sum_j |\phi_j\rangle \frac{1}{z - \epsilon_j} \langle \phi_j|. \quad (4.2)$$

This expression however, diverges for $z \rightarrow \epsilon_j$. To prevent this, the retarded and advanced Green's function are introduced:

$$G^R(\epsilon) = (\epsilon I - \mathcal{H} + i\eta)^{-1} \quad (4.3a)$$

$$G^A(\epsilon) = (\epsilon I - \mathcal{H} - i\eta)^{-1} \quad (4.3b)$$

where η is a small positive number. We see that $G^A = (G^R)^*$.

Ultimately, using the retarded and advanced Green's function, an equation for the transmission of electrons through a material can be determined. That is the Meir-Wingreen formula, given by:

$$\mathcal{T}(\epsilon) = \text{Tr}(G^R \Gamma_D G^A \Gamma_S). \quad (4.4)$$

Here Γ_D and Γ_S are the couplings with respectively the drain and the source of the system. These are matrices that determine the in- and outflow of the system. They are defined by the following set of equations:

4. Green's functions and the Meir-Wingreen formula

$$\Gamma_{D,S} = i(\Sigma_{D,S} - \Sigma_{D,S}^*) \quad (4.5a)$$

$$\Sigma_{D,S} = \tau_{D,S}^* g_{D,S} \tau_{D,S} \quad (4.5b)$$

where τ is the coupling parameter, a constant that determines the flowrate, and $g_{D,S}$ is the Green's function of either the drain or the source subsystem.

5. Simulation of electron transport through a chiral molecule

To look into the effect of the Breit interaction on the transport of an electron through a chiral molecule, a transport code is used. Such a code is composed following a couple of steps. Firstly the chiral molecule which is used in the simulation is introduced and a tight binding Hamiltonian is constructed for this problem. This is written as a matrix and its elements are determined and implemented in the simulation. In this way the electron transport is investigated.

5.1. Chiral molecule

As chiral medium, an S-shaped device is chosen, as depicted in figure 5.1. It is easily seen that this molecule is different from its mirror image and hence chiral. The simplicity of the molecule ensures that it lends itself well for the analysis of problems in which chirality plays a role.

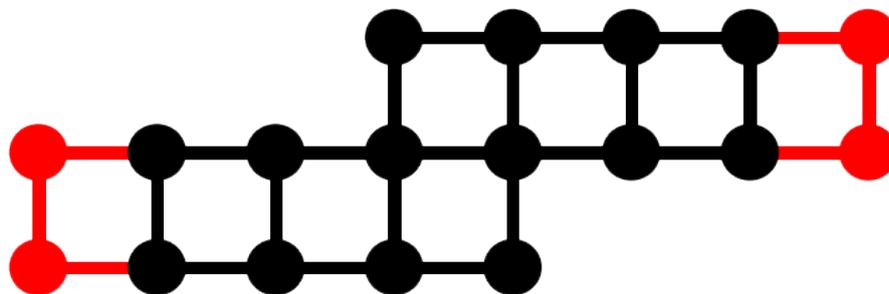


Figure 5.1.: An S-shaped device, where each dot indicates a different site with the given connections inbetween. The colored ends are the connections to the leads [21].

Each dot is an atom or a site of the molecule and the the lines between are the connections between different sites. The colored ends are where the molecule is connected

5. Simulation of electron transport through a chiral molecule

a spin-up electron at the same site. The elements in the off-diagonal blocks are the energies associated with the interactions between different sites of the molecule. For clarity, only the nearest-neighbour interactions are included in (5.2), but it can easily be expanded to further neighbour interactions, at the expense of losing particle-hole symmetry.

5.4. Determining the matrix elements

The matrix elements of (5.2) can be determined by evaluating $\mathcal{H}_{is,i's'} = \langle is | \mathcal{B} | i's' \rangle$ for the different combinations of is and $i's'$. This can be done for all terms of (5.1) individually due to linearity, after which they will all be added up to find the total Hamiltonian in matrix form.

5.4.1. Kinetic and potential energies

The terms K and V together lead to the eigenenergies and hopping [22]. The eigenenergies are elements such that $\mathcal{H}_{i,i} = \epsilon_0$. The hopping is given by the hopping parameter t . This represents the energy associated with the electron moving between two orbitals. We assume that this can only happen for near-neighbours. This leads to off-diagonal elements $\mathcal{H}_{i,i'} = -t$, where i and i' are chosen such that they correspond to neighbouring sites.

5.4.2. Spin-orbit interaction

The Hamiltonian associated with the spin-orbit interaction is given by

$$\mathcal{H}_{SOI} = C \mathbf{S} \cdot \mathbf{B} = C \mathbf{S} \cdot (\mathbf{E} \times \hat{\mathbf{p}}) \quad (5.3)$$

where C is an unspecified constant and \mathbf{E} is an imaginary electric field. This can be rewritten such that it leads to matrix elements

$$\mathcal{H}_{i,i'} = -i\alpha \boldsymbol{\sigma} \cdot (e_{i,i'} \times d_{i,i'}). \quad (5.4)$$

Here a new constant $\alpha = \frac{eC\hbar}{2a} \mathbf{E}(\frac{i+i'}{2})$ and vectors $e_{i,i'}$ and $d_{i,i'}$ are introduced, which respectively are the unit vectors in the direction of the electric field at the middle point between the two sites and the vector connecting the two sites: $d_{i,i'} = i - i'$ [21].

5.4.3. Breit terms

The \mathcal{B} term of (5.1) can be implemented directly into the Hamiltonian matrix, following the expression of (3.47). The terms of that equation become elements of the matrix and it is assumed that the Breit interaction only works for near-neighbours.

As one can see, we have the momentum \mathbf{p} in this expression. This term is represented by the average motion through a location. That is the average of all the possible paths that have that location in the middle and two neighbouring locations as begin and end points. This is illustrated by an example in figure 5.2.

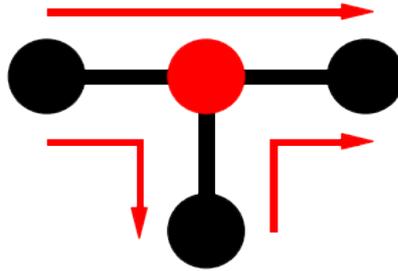


Figure 5.2.: The momentum at the location of the red dot is calculated as the average of the possible paths through that location, represented by the arrows.

Here the red dot represents the location we want to determine the momentum for and the black dots are all neighbouring locations. The paths through this point are represented by the arrows. The momentum is calculated as the average of these paths:

$$\mathbf{p}_i = \frac{1}{N} \sum_{n,m} \mathbf{r}_n - \mathbf{r}_m \quad (5.5)$$

where we sum over the begin and end points n, m of all possible paths through location i and N is the amount of paths.

5.5. Simulation

Based on the theory of the previous sections an implementation of the Breit interaction for the transport of an electron through a chiral medium has been constructed. For this, the Hamiltonian (5.2), with elements as described by section 5.4, is applied to the chiral molecule of 5.1.

5. Simulation of electron transport through a chiral molecule

For this, the locations of all sites are stored in an three-dimensional array. These are chosen such that the molecule lays in the x - y plane. The z coordinate is therefore zero. In another array the indices of all connected sites are stored. Using these, the distances between the connected sites are calculated and an expression for the momentum at each site is determined as described in section 5.4.3.

These arrays are three-dimensional, so that they can seamlessly be used in the determining of the matrix elements; the spin-orbit terms and the Breit terms are all given by three-dimensional expressions. Since the molecule is two-dimensional and lays in the x - y plane, the electron transport also is exclusively in this plane.

The constants that are present in the Hamiltonian are estimated: the onsite energy and the hopping as $\epsilon_0 = 1$ and $t = 4$ and the α from the spin-orbit interaction as $\alpha = 1.6$. The electric field of the spin-orbit interaction is chosen in the x -direction along the molecule. These estimates are based on an earlier thesis on a similar topic [21].

These estimates are not exact and have as main purpose to provide an indication for the effect of the Breit interaction in CISS. Since the S-shaped device we have chosen is not a real physical molecule, there is no way to make experimental observations from which more accurate values for all constants can be determined. This is an issue that could be considered in a follow-up research.

Using this all, the total Hamiltonian in its matrix form is constructed and implemented in the coding software. The total Hamiltonian for this problem looks like figure 5.3.

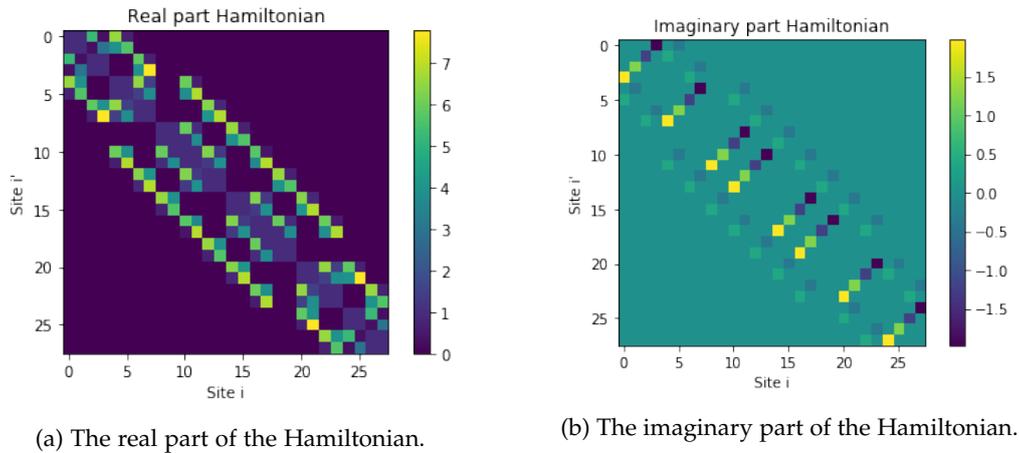


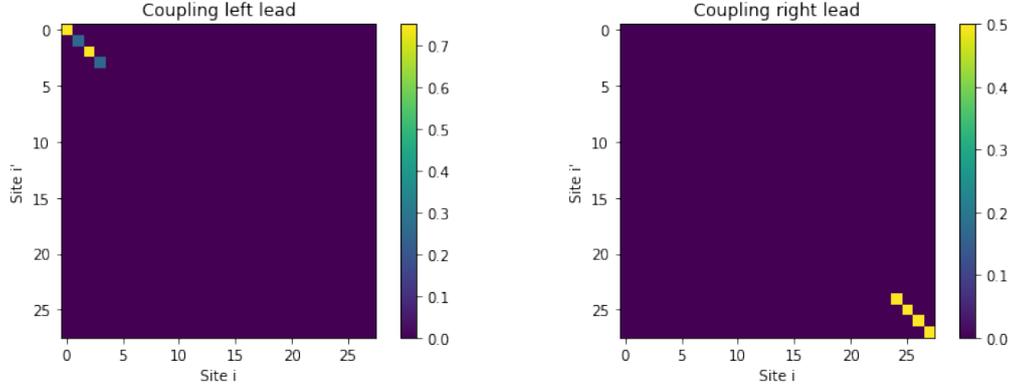
Figure 5.3.: Visualization of the total Hamiltonian in matrix form.

5.5.1. Transmission

This Hamiltonian is used to construct the advanced and retarded Green's functions, as described by equations (4.3a) and (4.3b). For η a small value is chosen, namely $\eta = 0.001$ and the value of ϵ is varied over.

5. Simulation of electron transport through a chiral molecule

The coupling matrices Γ_D and Γ_S are taken independently of the energy. This is the wide band limit. It are 28×28 matrices and they are non-zero for spin-up and down on the red sites in figure 5.1 only. The left lead is magnetized. These matrices are depicted in figures 5.4a and 5.4b.



(a) The coupling of the S-shaped molecule to the left lead.

(b) The coupling of the S-shaped molecule to the right lead.

Figure 5.4.: The matrices for the coupling of the S-shaped molecule to the leads visualised. The color difference between the two spin-directions in the first four diagonal elements of the left lead arises as a result of the fact that the left lead is magnetized.

These coupling matrices are then multiplied with the spin occupations of the electron. The left lead with the spin occupation of the electron that enters the molecule and the right lead with that of the leaving electron. We do this for all possible combinations (down-down, up-up, down-up and up-down). This way we can calculate the transmission for the different spin-combinations.

This is all combined in the Meir-Wingreen formula, which was given by (4.4). This way the transmission of an electron through the S-shaped molecule is obtained for the different spins: $\mathcal{T}_{\downarrow\downarrow}$, $\mathcal{T}_{\uparrow\uparrow}$, $\mathcal{T}_{\downarrow\uparrow}$ and $\mathcal{T}_{\uparrow\downarrow}$, with the subscripts representing the states of the ingoing and outgoing electron.

This is done for a whole range of values of ϵ . In figure 5.5 the total transmission is plotted. That is the sum of the different transmissions of all spin-combinations: $\mathcal{T} = \mathcal{T}_{\downarrow\downarrow} + \mathcal{T}_{\uparrow\uparrow} + \mathcal{T}_{\downarrow\uparrow} + \mathcal{T}_{\uparrow\downarrow}$. In appendix A, the plots for the different transmissions can be found. The plots have been cut off at $\mathcal{T} = 100$ for clarity.

5. Simulation of electron transport through a chiral molecule

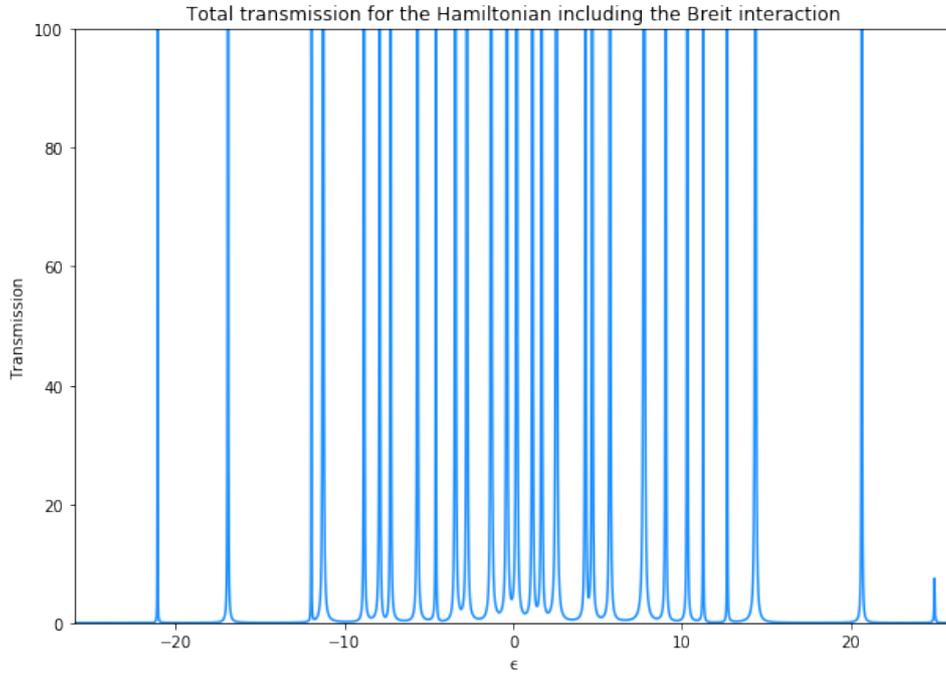


Figure 5.5.: Plot of the total electron transmission as a function of ϵ .

In total 28 distinct peaks can be seen in the figure. This makes sense, because the Hamiltonian is a 28×28 matrix with 28 distinct eigenvalues ϵ . And because we chose η to be small, the transmission will assume high values for these ϵ 's and relatively low values away from these resonances.

Using the transmissions found the spin-polarization is determined. That is done as

$$P = \frac{\mathcal{T}_{\uparrow\uparrow} + \mathcal{T}_{\uparrow\downarrow} - \mathcal{T}_{\downarrow\downarrow} - \mathcal{T}_{\downarrow\uparrow}}{\mathcal{T}_{\uparrow\uparrow} + \mathcal{T}_{\uparrow\downarrow} + \mathcal{T}_{\downarrow\downarrow} + \mathcal{T}_{\downarrow\uparrow}}. \quad (5.6)$$

This is also done for the range of ϵ values and this is plotted in figure 5.6.

5. Simulation of electron transport through a chiral molecule

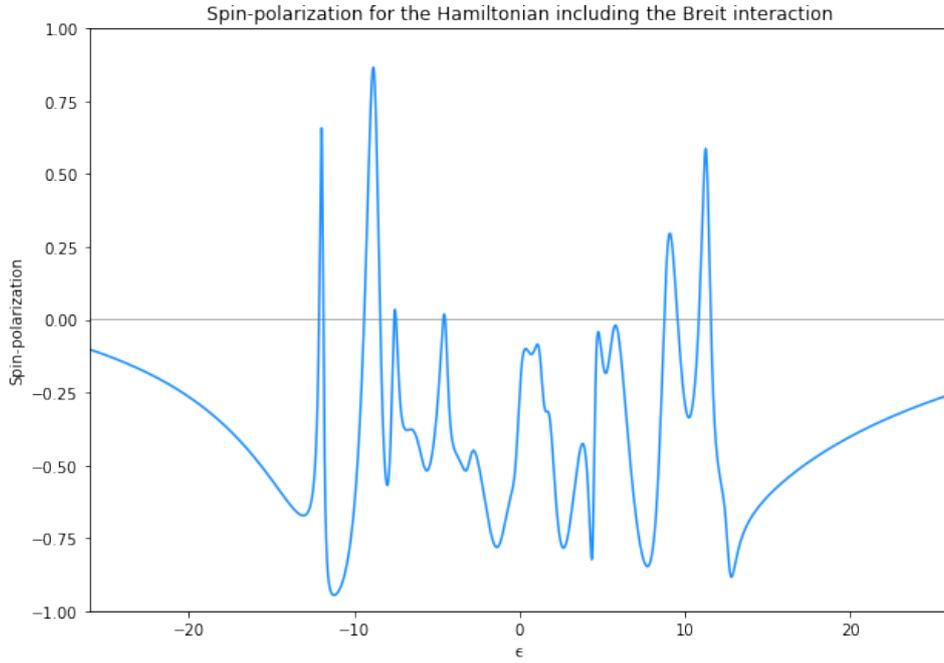


Figure 5.6.: The spin-polarization of the electron transport through the chiral molecule as a function of ϵ .

5.5.2. Non-Breit Hamiltonian

This process is repeated for the Hamiltonian $\mathcal{H} = K + V + \mathcal{H}_{SOI}$. That is thus the same Hamiltonian as in the foregoing sections minus the Breit interaction. The constructing of the matrix Hamiltonian and the calculating of the transmission is done the same as before.

For this Hamiltonian we find figures 5.7 and 5.8 for the total transmission and the spin-polarization respectively.

5. Simulation of electron transport through a chiral molecule

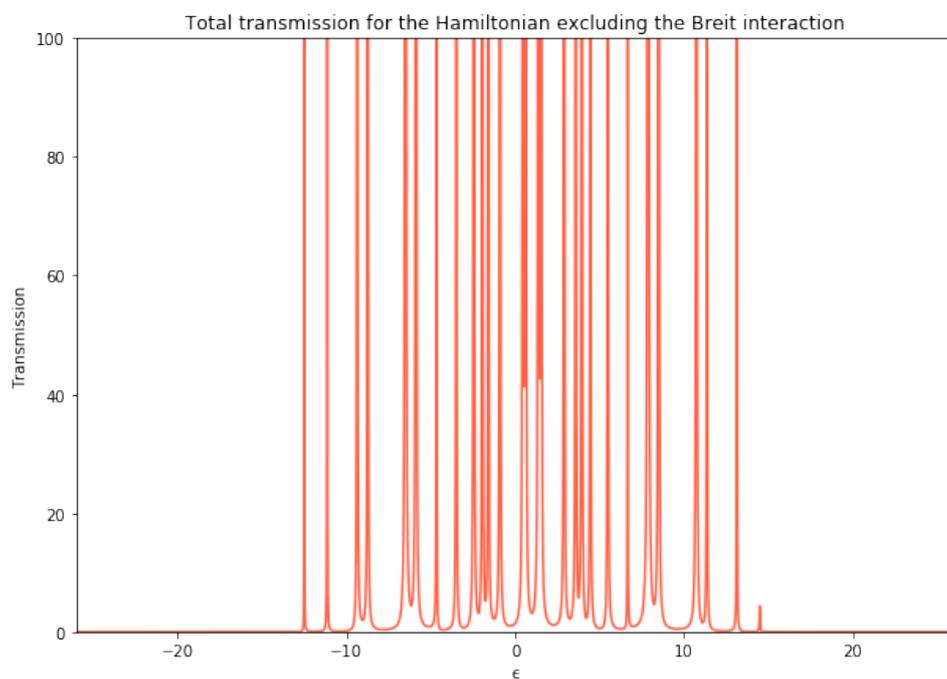


Figure 5.7.: The electron transmission for the Hamiltonian excluding the Breit interaction as a function of ϵ .

Again 28 peaks can be distinguished in this plot. This is because of the same reason as before: The Hamiltonian has 28 eigenvalues, for which a high transmission value is obtained.

5. Simulation of electron transport through a chiral molecule

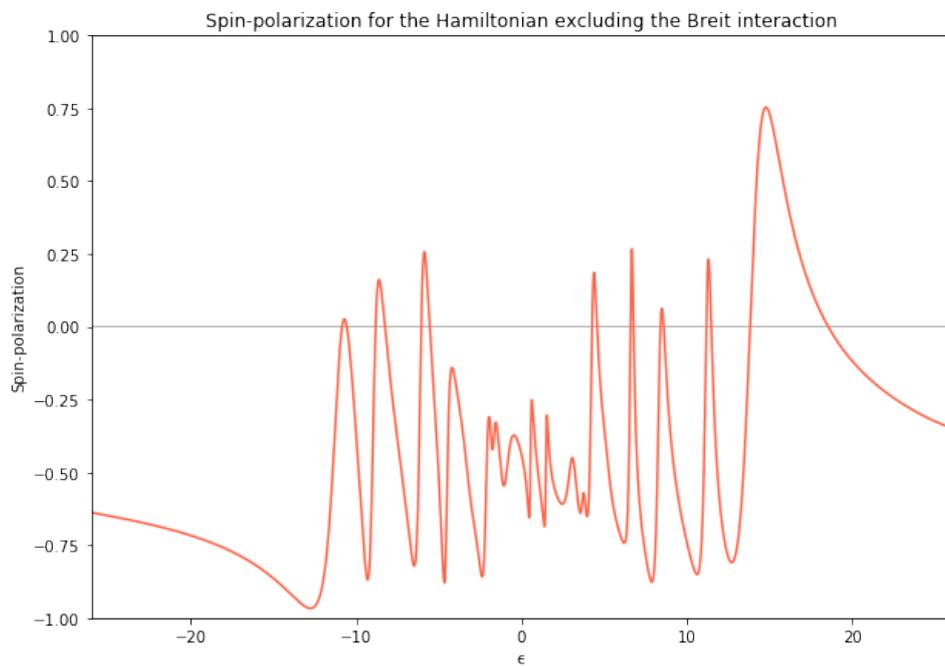


Figure 5.8.: The spin-polarization of the Hamiltonian excluding the Breit interaction, plotted as a function of ϵ .

5.5.3. Comparison

The spin-polarization of the two different Hamiltonians can be plotted in one figure. That is done in figure 5.9. Here the blue graph is the spin-polarization of the Hamiltonian including the Breit interaction and the red is for the Hamiltonian excluding it.

5. Simulation of electron transport through a chiral molecule

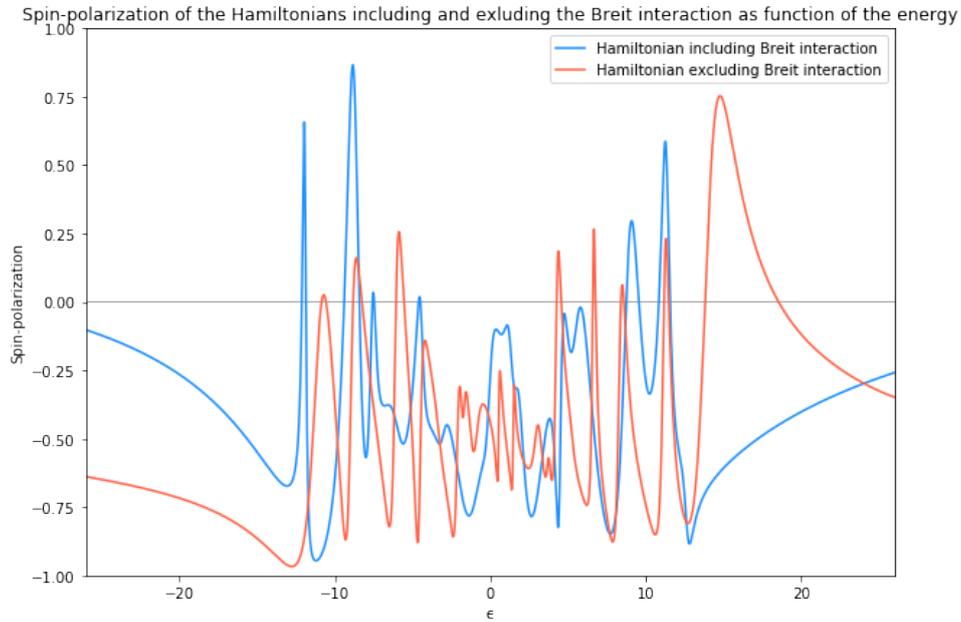


Figure 5.9.: The spin-polarization of the Hamiltonians including and excluding the Breit interaction plotted in one figure, in respectively blue and red. Both as a function of ϵ .

One can clearly see that these different Hamiltonians result in a different spin-polarization. From this we can conclude that the influence of the Breit interaction on the transport of an electron through a chiral molecule is significant and of the same order of magnitude as the hopping and the spin-orbit interaction. It is therefore not sensible to disregard the Breit interaction in further calculations on CISS.

It should however be noted that this simulation is not physical and its conclusion is therefore only a directive. The chosen chiral molecule is an artificial enantiomer and can therefore not directly be compared to experimental observations on CISS and the estimates for all constants are most certainly not exact. In further research it could for example be expanded to cover set-ups in which chiral induced spin selectivity can be observed in experiments, so that better physical results can be obtained and a more well-advised conclusion can be made, which can also be compared to experimental observations.

6. Conclusion

The goal of this thesis was to investigate the Breit interaction in the context of CISS and to examine its influence on electron transport. To do so, a simulation of the transport of an electron through an S-shaped device, a simple chiral molecule, was made. This was performed for a Hamiltonian that includes eigenenergies, hopping, spin-orbit interaction and the Breit interaction, as well as that same Hamiltonian excluding the Breit interaction. For both simulations the transmission and the spin-polarization were determined, which were compared to each other.

It was found that the spin-polarizations associated with the two Hamiltonians formed substantially different patterns when determined as function of the energy.

From this it was concluded that the Breit interaction has a significant influence on the transport of an electron through a chiral molecule and that it is of the same order of magnitude as the hopping and spin-orbit interaction.

Additionally the conclusion has been drawn that because of its significant influence, it is not sensible to neglect the Breit interaction in any future calculations of chiral induced spin selectivity.

This study has not found a definitive explanation for the phenomenon of CISS. Therefore there is one main suggestion that follows from this thesis to further help in the search. In future research the simulation can be improved upon by enhancing its physical correctness. The S-shaped device is simple chiral molecule that was chosen to ease the calculations, but in future research it can be replaced by a chiral molecule that is used in experimental research of CISS, such as DNA. This way the simulation results can be compared to the experimental observations. Furthermore, the accuracy of the estimates of the constants in the Hamiltonian can be improved upon, possibly on the basis of experimental observations of a more physical model. Since the current estimates have as main purpose to provide an indication for the effect of the Breit interaction and are not exact.

A. Appendix

In this appendix, the plots of all the individual spin-combination transmissions, $\mathcal{T}_{\downarrow\downarrow}$, $\mathcal{T}_{\uparrow\uparrow}$, $\mathcal{T}_{\downarrow\uparrow}$ and $\mathcal{T}_{\uparrow\downarrow}$, are presented.

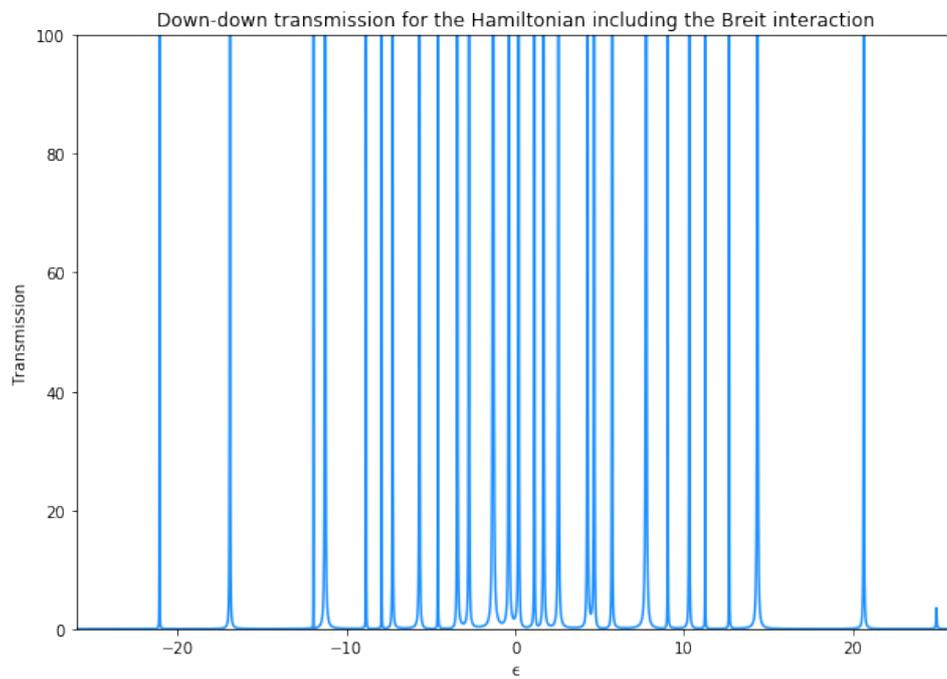


Figure A.1.: Plot of the down-down electron transmission as a function of ϵ .

A. Appendix

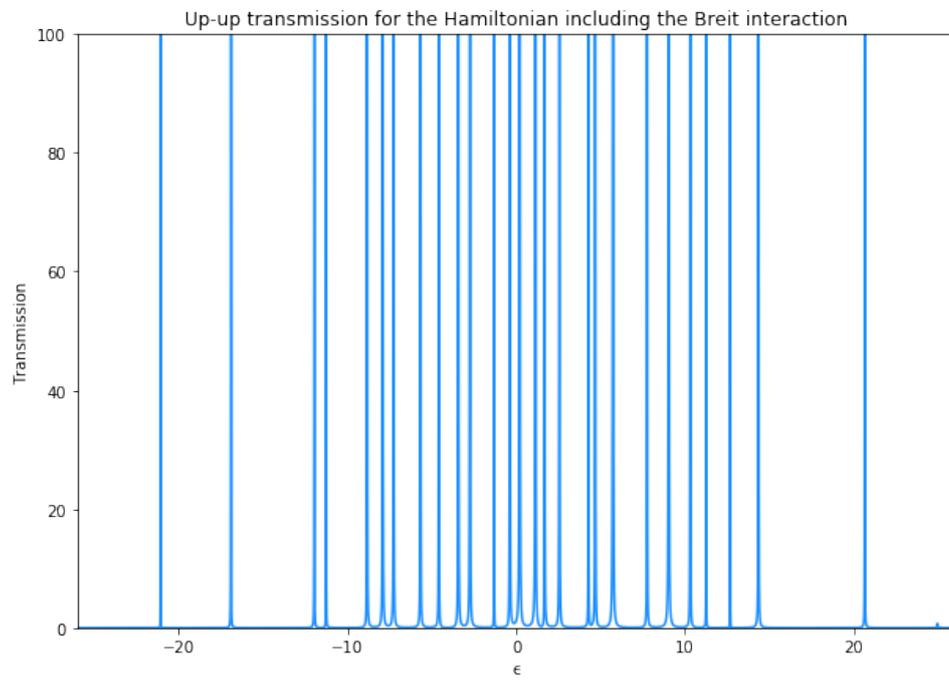


Figure A.2.: Plot of the up-up electron transmission as a function of ϵ .

A. Appendix

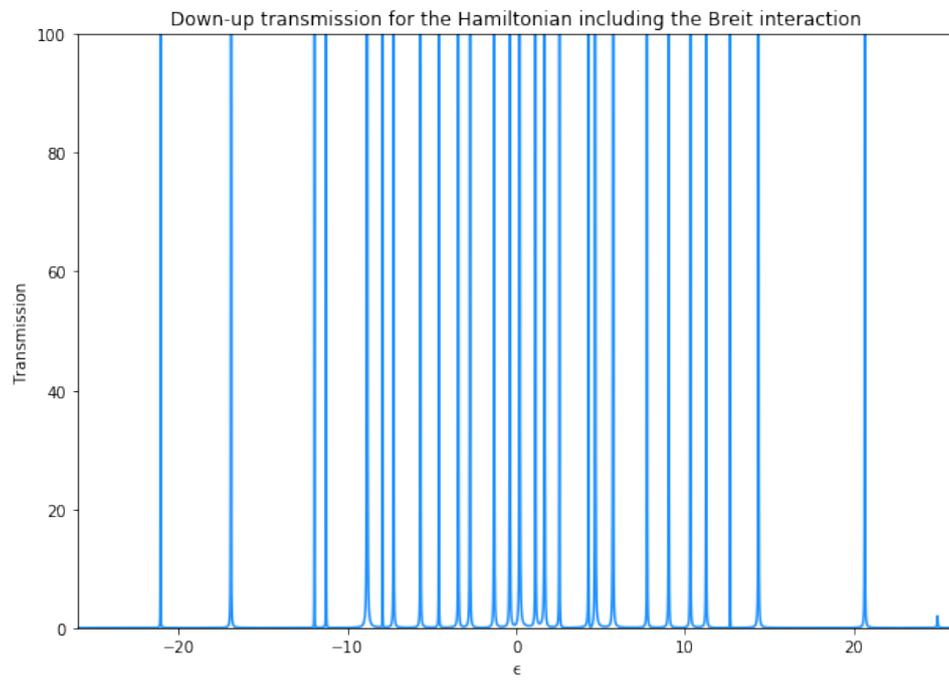


Figure A.3.: Plot of the down-up electron transmission as a function of ϵ .

A. Appendix

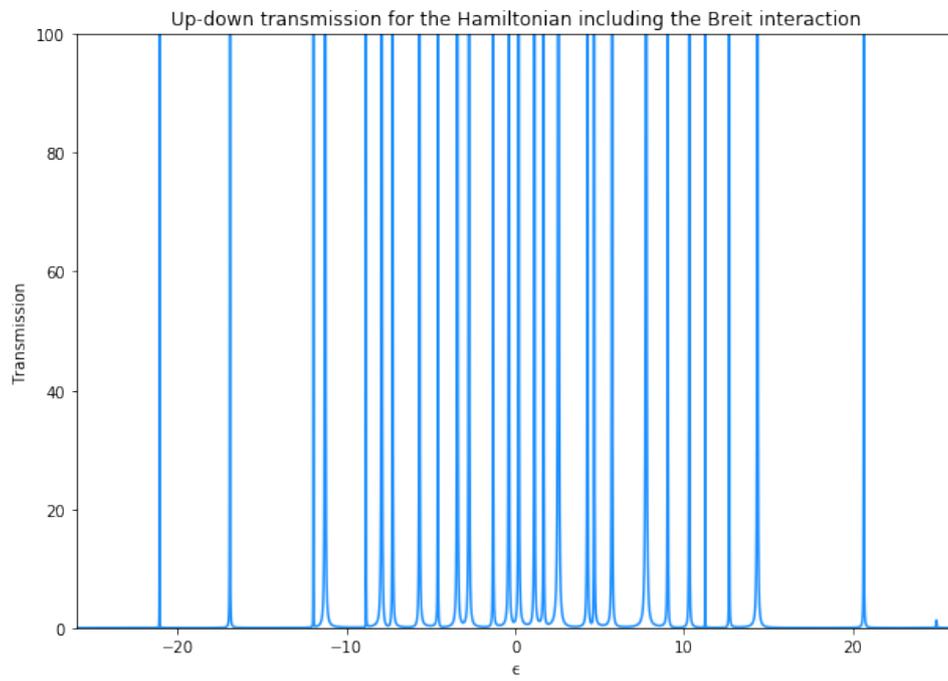


Figure A.4.: Plot of the up-down electron transmission as a function of ϵ .

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