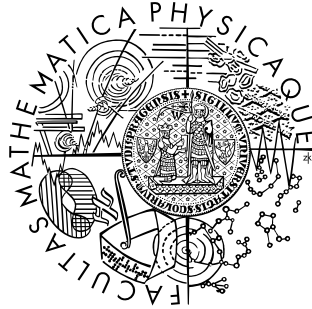


Charles University in Prague
Faculty of Mathematics and Physics

BACHELOR THESIS



Ondřej Čertík

Numerical solution of the radial Dirac equation in pseudopotential construction

Institute of Theoretical Physics

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Field of study: general physics

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I declare that I wrote the thesis by myself and listed all used sources. I agree with making the thesis publicly available.

Prague, June 3, 2006

Ondřej Čertík

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Abstract: In the present work we study numerical solution of the radial Dirac equation in a specific case — *ab-initio* pseudopotential generating process — which is needed within the electronic structure calculations using a Density Functional Theory (DFT) combined with a pseudopotential method. We give a brief introduction to DFT, derive the radial Dirac and Schrödinger equations, show how to solve them both for a given energy and as an eigenvalue problem using a known asymptotic behavior of the solution. Next we compare the non-relativistic and relativistic eigenvalues for one electron atom. Finally we state a few words about the computer implementation.

Keywords: radial Dirac equation, asymptotic behaviour, density functional theory, pseudopotential method

Název práce: Numerické řešení radiální Diracovy rovnice v konstrukci pseudopotenciálů

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Abstrakt: V předložené práci studujeme numerické řešení radiální Diracovy rovnice ve specifickém případě konstrukce *ab-initio* pseudopotenciálů, což je zapotřebí ve výpočtu elektronové struktury pomocí teorie funkcionálu hustoty (DFT) v kombinaci s metodou pseudopotenciálu. Práce obsahuje stručný úvod do DFT, odvození radiální Diracovy a Schrödingerovy rovnice, ukazuje, jak je obě vyřešit jak pro předepsanou energii, tak jako problém vlastních čísel, pomocí asymptotického chování řešení. Dále porovnáváme nerelativistické a relativistické vlastní hodnoty energie pro jednoelektronový atom. Nakonec je stručně popsána počítačová implementace.

Klíčová slova: radiální Diracova rovnice, asymptotika, metoda pseudopotenciálů, teorie funkcionálu hustoty

Chapter 1

Introduction

The outcome of this thesis is an algorithm solving the radial Dirac equation (together with the corresponding computer code) in a specific case, as a part of a particular method for electronic structure calculations in solid-state physics.

The electronic structure calculations are essential for any theoretical study of materials, which is currently an extremely active field of research and is often denoted as *computational material science*. In past few decades, electronic structure calculations made a significant contribution to our understanding of material properties, using a large variety of continuously developing methods and approaches.

This work is related to one of up-to-date *ab-initio pseudopotential* methods based on the *density-functional theory* (DFT)[15, 9], particularly to the pseudopotential generating process within the *all-electron pseudopotential* method [13, 14].

Ab-initio method means that the method do not require any empirical parameters as an input to the calculation — being based on equations derived directly from theoretical principles, with no need for experimental input data.

The standard result of the particular calculation within DFT is the total energy of the given system and the electronic charge density (or the wave function of electronic states that, integrated over the space and occupied states, form the charge density). Within DFT, the electronic charge density is a key quantity containing complete information about the system. This information allows us to answer almost any question we might ask about the solid: the structure of electronic states provides information about thermal and electrical conductivity, e.g. metallic or semiconductive behavior, optical or X-ray emission/absorption spectra and scattering properties; minimization of the total energy with respect to atomic positions provides an equilibrium geometry; derivatives of the total energy gives bulk modulus and elastic constants; spin structure of electronic states and derivatives of the total energy with respect to an external fields can provide dielectric or magnetic properties of the solid, etc.

At present, several more-or-less *ab-initio* computational methods withing DFT are widely used in solid state physics. Every method usually has it's own domain in which it excels. The success of a method is determined by many factors, including its usage in particular computer codes and their efficiency, accuracy etc. And new methods can emerge in the future. It is not the aim of this thesis to compare all the methods available. It will suffice to say that in present, the majority of calculations are based on the local-density approximation (or its extensions) to DFT, which we review very briefly now[9]. It leads to the following Kohn-Sham equations (for N electrons):

$$\left\{ -\frac{1}{2m}\nabla^2 + \sum_{n=1}^N V_n^{\text{ion}}(\mathbf{x} - \mathbf{X}_n) + V_H(\mathbf{x}) + V_{XC}(\mathbf{x}) \right\} \psi_i(\mathbf{x}) = \epsilon_i \psi_i(\mathbf{x}), \quad (1)$$

where the charge density is

$$\rho = \sum_{i=1}^N |\psi_i|^2,$$

the Hartree potential V_H is given by

$$\nabla^2 V_H = -4\pi\rho,$$

and the exchange-correlation potential V_{XC} is just a given function of the charge density ρ . The V_n^{ion} is the electrostatic potential of atomic nuclei. Within the family of up-to-date pseudopotential methods, it is constructed from nonlocal pseudopotentials. There are several ways how to do that.

These equations need to be solved self-consistently, so that the charge density, which is used for the construction of the Hartree and exchange-correlation potential is the same as the charge density calculated from the equations, see also fig. 1.

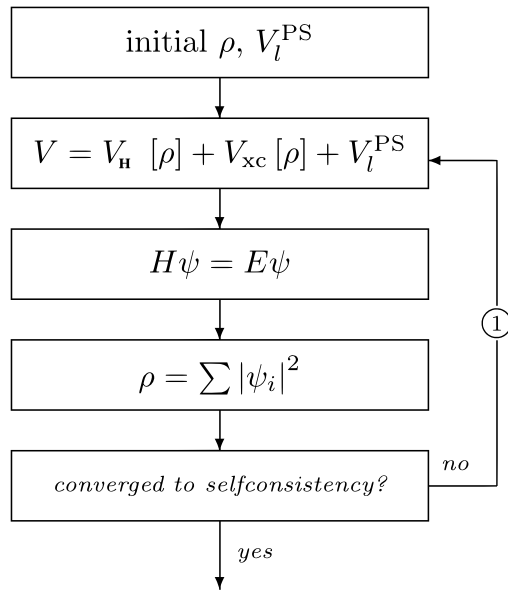


Fig. 1: Self-consistency cycle

Numerous methods have been developed to solve the resulting system of one-particle Kohn-Sham equations (1). Depending on the basis set used and other features of the particular method, some of them (in fact: almost all of them) need the radial part of the equation to be solved. For heavy atoms (approximately, starting at atomic numbers around 40-50) the equations (1) are considerably inaccurate due to the non-negligible relativistic effects, especially for the core electronic states bounded with relatively high energies. For this reason, it is desirable to use a relativistic Dirac equation instead, which is the aim of this thesis.

In the present thesis we first derive and show how to solve the radial Schrödinger equation for a given energy. Then we move to the relativistic case, Dirac equation, and do the same. Next we show how to solve the eigenproblem,

that is, how to determine the energies, for which the solution is normalizable. Then we say something about the computer implementation together with some results of the program. In the appendix we define atomic units (which is sometimes a little confusing issue) and we derive spin-angular functions including some of their properties we need in our work.

Chapter 2

Schrödinger Equation

2.1 Introduction

The Schrödinger equation describes a nonrelativistic particle in a potential field. It cannot be derived, we always have to postulate something, more or less equivalent to the equation itself:

$$\begin{aligned} H\psi &= E\psi, \\ H &= \frac{p^2}{2M} + V, \end{aligned} \tag{2}$$

where $\psi(x, y, z)$ is a (complex) function, $\mathbf{p} = -i\hbar\nabla$, M is a mass of the particle (in our case an electron), $V(x, y, z)$ the potential field (in our case we only have a spherically symmetric field $V(r)$). A physical quantity we are actually interested in is a probability density $\rho = \psi^*\psi$.

The electron has to be somewhere in the universe, thus we want

$$\int \psi d^3x = 1. \tag{3}$$

For a given energy E , we can always solve the equation, but for the energies not lying in the spectrum of H , the solution exponentially diverges to infinity and such a solution cannot be normalized so that (3) holds. To be precise - there actually exist physical solutions, which are not normalizable according to (3) (the ones lying in the continuous part of the spectrum, for example a free electron, $V = 0$), but in our case of bounded states in a potential, we always have a discrete spectrum.

The condition (3) picks up only certain energies (eigenvalues), when the solution doesn't diverge. We label the energies by an integer number n starting from the lowest one $n = 1$, second lowest $n = 2$ etc.

Besides energy, the solution also depends on quadrate of angular momentum (l) and it's z component (m). As it turns out, the radial part of the solution depends on n and l only.

So we want to solve the eigenvalue problem of finding a solution for a given n and l .

2.2 Radial Schrödinger equation

We have a spherically symmetric potential energy

$$V(\mathbf{x}) = V(r).$$

State with a given square of an angular momentum (eigenvalue $l(l+1)$) and its z component (eigenvalue m) is described by the wave function

$$\psi_{nlm}(\mathbf{x}) = R_{nl}(r) Y_{lm}\left(\frac{\mathbf{x}}{r}\right), \tag{4}$$

where $R_{nl}(r)$ obeys the equation [4] (eq. 2.400)

$$R''_{nl} + \frac{2}{r}R'_{nl} + \frac{2M}{\hbar^2}(E - V)R_{nl} - \frac{l(l+1)}{r^2}R_{nl} = 0. \quad (5)$$

This is called the radial Schrödinger equation which we want to solve numerically.

The derivation is well-known [4, 11], so just briefly. Basically, it's just a separation of variables: we decompose the space as a tensor product $\mathbb{R}^3 = \mathbb{S}^2 \times \mathbb{R}$, where \mathbb{S}^2 is a unit sphere and \mathbb{R} is the radial part. We choose a basis in \mathbb{S}^2 , it turns out that spherical harmonics Y_{lm} are a good choice as they are eigenvectors of L^2 and L_3 . We will search for all solutions of the form (4). Substituting (4) into the equation (2) yields (5): the trick is to write ∇^2 in spherical coordinates, the angular derivatives will then act on Y_{lm} only, thus separating the equation. It turns out, that all the solutions R_{nl} form a basis of \mathbb{R} . So we have found a basis of \mathbb{R}^3 , which is also a solution of (2) and thus any other solution can be found as a (possibly infinite) linear combination of ψ_{nlm} .

2.3 Numerical integration for a given E

Equation (5) is the linear ordinary differential equation of the second order, so the general solution is a linear combination of two independent solutions. Normally, the 2 constants are determined from initial and/or boundary conditions. In our case, however, we don't have any other condition besides being interested in solutions that we can integrate on the interval $(0, \infty)$ (and which are normalizable), more exactly we want $R \in L^2$ and $\int_0^\infty r^2 R^2 dr = 1$.

It can be easily shown by a direct substitution, that there are only two asymptotic behaviors near the origin: r^l and r^{-l-1} . We are interested in quadratic integrable solutions only, so we are left with r^l and only one integration constant, which we calculate from a normalization. This determines the solution uniquely.

All the integration algorithms needs to evaluate R'' , which is a problem at the origin, where all the terms in the equation are infinite, although their sum is finite. We thus start to integrate the equation at some small r_0 (for example $r_0 = 10^{-10}$ a.u.), where all the terms in the equation are finite. If we find the initial conditions $R(r_0)$ and $R'(r_0)$, the solution is then fully determined.

If r_0 is sufficiently small, we can set $R(r_0) = r_0^l$ and $R'(r_0) = lr_0^{l-1}$. This works fine for $l > 0$. For $l = 0$, it is not strictly correct, but it works well in practice because the fourth-order Runge-Kutta method is able to quickly correct the initial derivative guess.

So when somebody gives us l and E , we are now able to compute the solution but the multiplicative constant that is later determined from a normalization. As was already mentioned, we used the fourth-order Runge-Kutta method that proved very suitable for this problem.

2.4 Asymptotic behavior

The asymptotic behavior is important for the integration routine to find the correct solution for a given E . In this section we look into more details of the asymptotic expansion and illustrate it on 2 examples.

It is well known, that the first term of the Taylor series of the solution is r^l , independent of the potential [4] (eq. 2.408). This is enough information to find the correct solution for $l > 0$ because the only thing we need to know is the value of the wave function and its derivative near the origin, which is effectively r_0^l and lr_0^{l-1} for some small r_0 . The problem is with $l = 0$, where the derivative cannot be calculated just from l and r_0 . This section shows why and in the next section we show how we solved the problem.

We start with the radial Schrödinger equation (5) and we shall search for the solution R in the form of a Taylor series:

$$R = a_0 + a_1 r + a_2 r^2 + \dots = \sum_{k=0}^{\infty} a_k r^k.$$

Substituting this into the equation we get:

$$\sum_{k=0}^{\infty} r^k a_k [k(k+1) - l(l+1)] + \frac{2M}{\hbar^2} (E - V) \sum_{k=2}^{\infty} r^k a_{k-2} = 0. \quad (6)$$

Let's assume we have a potential V of the form:

$$V = \frac{v_{-1}}{r} + v_0 + v_1 r + v_2 r^2 + \dots = \sum_{j=-1}^{\infty} v_j r^j,$$

we rearrange the double sum on the right hand side of (6)

$$\begin{aligned} V \sum_{k=2}^{\infty} r^k a_{k-2} &= \sum_{j=-1}^{\infty} \sum_{k=2}^{\infty} v_j r^j r^k a_{k-2} = \sum_{j=-1}^{\infty} \sum_{k=j+2}^{\infty} v_j r^k a_{k-j-2} = \\ &= \sum_{j=0}^{\infty} \sum_{k=j}^{\infty} v_{j-1} r^{k+1} a_{k-j} = \sum_{k=0}^{\infty} \sum_{j=0}^k v_{j-1} r^{k+1} a_{k-j} = \sum_{k=0}^{\infty} r^{k+1} \sum_{j=0}^k v_{j-1} a_{k-j} = \\ &= \sum_{k=1}^{\infty} r^k \sum_{j=0}^{k-1} v_{j-1} a_{k-j-1} \end{aligned}$$

So we get:

$$\begin{aligned} \sum_{k=0}^{\infty} r^k a_k [k(k+1) - l(l+1)] + \frac{2M}{\hbar^2} E \sum_{k=2}^{\infty} r^k a_{k-2} + \\ - \frac{2M}{\hbar^2} \sum_{k=1}^{\infty} r^k \sum_{j=0}^{k-1} v_{j-1} a_{k-j-1} = 0. \end{aligned}$$

This equation holds for every r , thus we collect the coefficients at r^k and they must vanish. We get:

$$k = 0 \quad a_0[-l(l+1)] = 0, \quad (7)$$

$$k = 1 \quad a_1[2 - l(l+1)] - \frac{2M}{\hbar^2}v_{-1}a_0 = 0, \quad (8)$$

$$k \geq 2 \quad a_k[k(k+1) - l(l+1)] - \frac{2M}{\hbar^2} \sum_{j=0}^{k-1} v_{j-1}a_{k-j-1} + \frac{2M}{\hbar^2}Ea_{k-2} = 0. \quad (9)$$

This enables us to calculate all the Taylor coefficients of the solution. To see how it works, we calculate two examples and compare them to the analytical solution. First, let

$$V = -\frac{Z}{r},$$

so $v_{-1} = -Z$, $v_0 = v_1 = \dots = 0$. For $l = 0$, we see from (7) that a_0 can be any number (including zero, but as we will see in a moment, this would imply the zero solution, which we are obviously not interested in). From (8) it follows:

$$a_1 = -\frac{MZ}{\hbar^2}a_0 = \frac{-a_0}{a},$$

where $a = \frac{\hbar^2}{ZM}$ is the Bohr radius. The first two terms of the solution are then:

$$R = a_0\left(1 - \frac{r}{a} + O(r^2)\right),$$

which is in agreement with the analytic solution [4] (eq. 2.524) (every R_{nl} for $l = 0$):

$$\begin{aligned} R_{10} &= 2\sqrt{\frac{1}{a^3}} \exp\left(-\frac{r}{a}\right), \\ R_{20} &= \sqrt{\frac{1}{2a^3}} \left[1 - \frac{r}{2a}\right] \exp\left(-\frac{r}{2a}\right), \\ R_{30} &= \frac{2}{3}\sqrt{\frac{1}{3a^3}} \left[1 - \frac{2r}{3a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right] \exp\left(-\frac{r}{3a}\right), \\ R_{40} &= \frac{1}{4a^{3/2}}\sqrt{\frac{1}{a^3}} \left[1 - \frac{3r}{4a} + \frac{1}{8}\left(\frac{r}{a}\right)^2 - \frac{1}{192}\left(\frac{r}{a}\right)^3\right] \exp\left(-\frac{r}{4a}\right). \end{aligned}$$

As the second example, we use a linear harmonic oscillator

$$V = \frac{M\omega^2 r^2}{2},$$

so $v_{-1} = v_0 = v_1 = 0$, $v_2 = \frac{M\omega^2}{2}$, $v_3 = v_4 = \dots = 0$. For $l = 0$, we see from (7) that a_0 is any number, from (8) it follows $a_1 = 0$ and from (9) we get $a_2 = -\frac{MEa_0}{3\hbar^2}$. But we know the spectrum [4] (eq. 2.484):

$$E = \hbar\omega\left(2n + l + \frac{3}{2}\right),$$

so we have $a_2 = -\frac{M\omega(2n+\frac{3}{2})a_0}{3\hbar} = -(\frac{2}{3}n + \frac{1}{2})\frac{a_0}{a^2}$, where we used the substitution $a = \sqrt{\frac{\hbar}{M\omega}}$. Finally the first two nonzero terms of the solution are:

$$R = a_0 \left(1 - \left(\frac{2}{3}n + \frac{1}{2} \right) \frac{r^2}{a^2} + O(r^3) \right),$$

which agrees with the analytic solution [4] (eq. 2.488) (again every R_{nl} for $l = 0$):

$$R_{00} = \frac{2}{\pi^{1/4}} \sqrt{\frac{1}{3a^3}} \exp\left(-\frac{r^2}{2a^2}\right),$$

$$R_{10} = \frac{1}{\pi^{1/4}} \sqrt{\frac{6}{a^3}} \left[1 - \frac{2}{3} \left(\frac{r}{a}\right)^2 \right] \exp\left(-\frac{r^2}{2a^2}\right).$$

These examples show, that for $l = 0$ the derivative R' (the second term in the R expansion) nontrivially depends on V in the first example, and on E in the second example. Which is inconvenient for a numerical computation.

For $l > 0$, the Taylor coefficients can be calculated in the same way as for $l = 0$. From (7), (8) and (9) we see that $a_k = 0$ for all $k < l$. So indeed the first nonzero term is $a_l r^l$ as expected.

Chapter 3

Dirac Equation

3.1 Introduction

The Dirac equation for one particle is [12, 16]:

$$H\psi = W\psi, \quad (10)$$

$$H = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V(r)\mathbb{1},$$

where ψ is a four component vector:

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}, \quad \psi_A = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \quad \psi_B = \begin{pmatrix} \psi_3 \\ \psi_4 \end{pmatrix}$$

and $\boldsymbol{\alpha}$, β are 4×4 matrices:

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix},$$

$$\beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix},$$

where the Pauli matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ and $\mathbb{1}$ form a basis of all 2×2 Hermitian matrices. Substituting all of this into (10) yields:

$$c\boldsymbol{\sigma} \cdot \mathbf{p} \begin{pmatrix} \psi_B \\ \psi_A \end{pmatrix} = \begin{pmatrix} W - V - mc^2 & 0 \\ 0 & W - V + mc^2 \end{pmatrix} \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}. \quad (11)$$

To derive a continuity equation, we multiply (10) by ψ^* and subtract the conjugate transpose of (10) multiplied by ψ :

$$\frac{\partial}{\partial t}(\psi^*\psi) = -\nabla \cdot (c\psi^*\boldsymbol{\alpha}\psi),$$

so we identify the probability and current densities as

$$\rho = \psi^*\psi = \psi_1^*\psi_1 + \psi_2^*\psi_2 + \psi_3^*\psi_3 + \psi_4^*\psi_4, \quad \mathbf{j} = c\psi^*\boldsymbol{\alpha}\psi.$$

The normalization of a four-component wave function is then

$$\int \rho d^3x = \int \psi^*\psi d^3x = \int \psi_1^*\psi_1 + \psi_2^*\psi_2 + \psi_3^*\psi_3 + \psi_4^*\psi_4 d^3x = 1. \quad (12)$$

The probability density $\rho(x, y, z)$ is the physical quantity we are interested in, and all the four-component wavefunctions and other formalism is just a way of calculating it. This ρ is also the thing we should compare with the Schrödinger equation.

3.2 Derivation of the radial equation

We rewrite $\boldsymbol{\sigma} \cdot \mathbf{p}$ [2]:

$$\boldsymbol{\sigma} \cdot \mathbf{p} = \frac{1}{r} \frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \left(-i\hbar r \frac{\partial}{\partial r} + i\boldsymbol{\sigma} \cdot \mathbf{L} \right), \quad (13)$$

and search for a basis in the form

$$\psi_A = g\chi_\kappa^{j_3}, \quad (14)$$

$$\psi_B = if\chi_{-\kappa}^{j_3}. \quad (15)$$

We chose this form, because we want ψ_A and ψ_B to have the same j and j_3 , so the only thing they can differ in is l (the two allowed possibilities are $l = j \pm \frac{1}{2}$). According to (36), (37), (38) and (37), this corresponds to $\pm\kappa$ (see also [6, 12, 10, 2] and the appendix for more information about spin-angular functions).

Substituting (14), (15) and (13) into (11) we get:

$$\begin{aligned} c \frac{1}{r} \frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \left(-i\hbar r \frac{\partial}{\partial r} + i\boldsymbol{\sigma} \cdot \mathbf{L} \right) \begin{pmatrix} if\chi_{-\kappa}^{j_3} \\ g\chi_\kappa^{j_3} \end{pmatrix} &= \\ &= \begin{pmatrix} W - V - mc^2 & 0 \\ 0 & W - V + mc^2 \end{pmatrix} \begin{pmatrix} g\chi_\kappa^{j_3} \\ if\chi_{-\kappa}^{j_3} \end{pmatrix}, \end{aligned}$$

Both ψ_A and ψ_B are eigenvectors of the operator $K = \beta(\boldsymbol{\sigma} \cdot \mathbf{L} + \hbar)$:

$$K\psi_{A,B} = -\hbar\kappa\psi_{A,B},$$

so the action of the $\boldsymbol{\sigma} \cdot \mathbf{L}$ operator on the ψ_A and ψ_B can easily be determined:

$$\begin{aligned} \boldsymbol{\sigma} \cdot \mathbf{L} \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} &= (\beta K - \hbar) \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = \\ &= \begin{pmatrix} K - \hbar & 0 \\ 0 & -K - \hbar \end{pmatrix} \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = \begin{pmatrix} \hbar(-\kappa - 1)\psi_A \\ \hbar(\kappa - 1)\psi_B \end{pmatrix} \end{aligned}$$

and we can write

$$\begin{aligned} c \frac{1}{r} \frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \begin{pmatrix} (-i\hbar r \frac{\partial}{\partial r} + i(\kappa - 1)\hbar)if\chi_{-\kappa}^{j_3} \\ (-i\hbar r \frac{\partial}{\partial r} + i(-\kappa - 1)\hbar)g\chi_\kappa^{j_3} \end{pmatrix} &= \\ &= \begin{pmatrix} W - V - mc^2 & 0 \\ 0 & W - V + mc^2 \end{pmatrix} \begin{pmatrix} g\chi_\kappa^{j_3} \\ if\chi_{-\kappa}^{j_3} \end{pmatrix}. \end{aligned}$$

The operator $\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r}$ also only acts on the angular momentum parts of the state [12] (page 59). From (35):

$$\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \chi_\kappa^{j_3} = -\chi_{-\kappa}^{j_3},$$

$$\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \chi_{-\kappa}^{j_3} = -\chi_{\kappa}^{j_3},$$

so

$$\begin{aligned} c \frac{1}{r} \left((i\hbar r \frac{\partial}{\partial r} - i(\kappa - 1)\hbar) i f \chi_{\kappa}^{j_3} \right) &= \\ &= \begin{pmatrix} W - V - mc^2 & 0 \\ 0 & W - V + mc^2 \end{pmatrix} \begin{pmatrix} g \chi_{\kappa}^{j_3} \\ i f \chi_{-\kappa}^{j_3} \end{pmatrix}, \end{aligned}$$

rewriting

$$\begin{aligned} \hbar c \frac{1}{r} \begin{pmatrix} (-r \frac{\partial}{\partial r} + (\kappa - 1)) f & 0 \\ 0 & (r \frac{\partial}{\partial r} + (\kappa + 1)) g \end{pmatrix} \begin{pmatrix} \chi_{\kappa}^{j_3} \\ i \chi_{-\kappa}^{j_3} \end{pmatrix} &= \\ = \begin{pmatrix} (W - V - mc^2) g & 0 \\ 0 & (W - V + mc^2) f \end{pmatrix} \begin{pmatrix} \chi_{\kappa}^{j_3} \\ i \chi_{-\kappa}^{j_3} \end{pmatrix}, \end{aligned}$$

and canceling the same terms on both sides finally yields

$$\hbar c \begin{pmatrix} -\frac{\partial f}{\partial r} + \frac{\kappa-1}{r} f \\ \frac{\partial g}{\partial r} + \frac{\kappa+1}{r} g \end{pmatrix} = \begin{pmatrix} (W - V - mc^2) g \\ (W - V + mc^2) f \end{pmatrix}. \quad (16)$$

This is the radial Dirac equation. As we shall see in the next section, the equation for g is (with the exception of a few relativistic corrections) identical to the radial Schrödinger equation. And f vanishes in the limit $c \rightarrow \infty$. For this reason f is called the small (fein, minor) component and g the large (groß, major) component.

The probability density is

$$\rho = \psi^* \psi = \psi_A^* \psi_A + \psi_B^* \psi_B = f^2 \chi_{-\kappa}^{j_3*} \chi_{-\kappa}^{j_3} + g^2 \chi_{\kappa}^{j_3*} \chi_{\kappa}^{j_3},$$

so from the normalization condition (12) we get

$$\begin{aligned} \int \rho \, d^3x &= \int f^2 \chi_{-\kappa}^{j_3*} \chi_{-\kappa}^{j_3} + g^2 \chi_{\kappa}^{j_3*} \chi_{\kappa}^{j_3} \, d^3x = \int (f^2 \chi_{-\kappa}^{j_3*} \chi_{-\kappa}^{j_3} + g^2 \chi_{\kappa}^{j_3*} \chi_{\kappa}^{j_3}) r^2 \, dr d\Omega = \\ &= \int_0^\infty f^2 r^2 \, dr \int \chi_{-\kappa}^{j_3*} \chi_{-\kappa}^{j_3} \, d\Omega + \int_0^\infty g^2 r^2 \, dr \int \chi_{\kappa}^{j_3*} \chi_{\kappa}^{j_3} \, d\Omega = \int_0^\infty r^2 (f^2 + g^2) \, dr = 1, \end{aligned}$$

where we used the normalization of spin-angular functions (32). Also it can be seen, that the radial probability density is

$$\rho(r) = r^2 (f^2 + g^2)$$

(i.e., the probability to find the electron between r_1 and r_2 is $\int_{r_1}^{r_2} r^2 (f^2 + g^2) \, dr$). In the nonrelativistic case, the density is given by

$$\rho(r) = r^2 R^2,$$

so the correspondence between the Schrödinger and Dirac equation is $R^2 = f^2 + g^2$.

3.3 Numerical integration for a given E

We rewrite (16) to a form found in [12] (eq. 8.10 and 8.12):

$$g'_\kappa = -\frac{\kappa+1}{r}g_\kappa + \frac{1}{c\hbar}(W-V+mc^2)f_\kappa, \quad (17)$$

$$f'_\kappa = +\frac{\kappa-1}{r}f_\kappa - \frac{1}{c\hbar}(W-V-mc^2)g_\kappa. \quad (18)$$

Let $\hbar = 1$ and define $E = W - mc^2$, so that E doesn't contain the electron rest mass energy. Next we define a relativistic mass

$$M = m + \frac{1}{2c^2}(E - V) \quad (19)$$

and we get

$$g'_\kappa = -\frac{\kappa+1}{r}g_\kappa + 2Mc f_\kappa, \quad (20)$$

$$f'_\kappa = +\frac{\kappa-1}{r}f_\kappa + \frac{1}{c}(V-E)g_\kappa, \quad (21)$$

which are the same equations as in [7] (eq. 2a and 2b).

From (20) we express f_κ and substitute it into (21). At the same time we introduce a new variable

$$\phi_\kappa = \frac{1}{2M}g'_\kappa, \quad (22)$$

(beware, [7] introduce $\phi_\kappa = \frac{1}{2Mc}g'_\kappa$) to simplify our equations:

$$f_\kappa = \frac{g'_\kappa}{2Mc} + \frac{\kappa+1}{r} \frac{g_\kappa}{2Mc} = \frac{\phi_\kappa}{c} + \frac{\kappa+1}{c} \frac{g_\kappa}{2Mr}, \quad (23)$$

differentiate

$$f'_\kappa = \frac{\phi'_\kappa}{c} + \frac{\kappa+1}{c} \left(\frac{g_\kappa}{2Mr} \right)' = \frac{\phi'_\kappa}{c} + \frac{\kappa+1}{cr} \phi_\kappa + \frac{\kappa+1}{2M^2cr} g_\kappa \frac{V'}{2c^2} - \frac{\kappa+1}{2Mcr^2} g_\kappa$$

and substitute f_κ and f'_κ back to (21):

$$\begin{aligned} & \frac{\phi'_\kappa}{c} + \frac{\kappa+1}{cr} \phi_\kappa + \frac{\kappa+1}{2M^2cr} g_\kappa \frac{V'}{2c^2} - \frac{\kappa+1}{2Mcr^2} g_\kappa = \\ & = \frac{\kappa-1}{r} \left(\frac{\phi_\kappa}{c} + \frac{\kappa+1}{c} \frac{g_\kappa}{2Mr} \right) + \frac{1}{c}(V-E)g_\kappa, \end{aligned}$$

by a simplification we finally get

$$\phi'_\kappa(r) = -\frac{2}{r}\phi_\kappa(r) + \left[(V(r) - E) + \frac{\kappa(\kappa+1)}{2M(r)r^2} - \frac{\kappa+1}{4M^2(r)c^2r} V'(r) \right] g_\kappa(r). \quad (24)$$

Equations (24), (22) and (19) are the equations we are solving. It is instructive to write equation for g_κ directly. For this, we need to calculate

$$\phi'_\kappa = \frac{g''}{2M} - \frac{g'M'}{2M^2}$$

and substituting for ϕ_κ and ϕ'_κ into (24) gives

$$\frac{g''_\kappa}{2M} - \frac{g'_\kappa M'}{2M^2} = -\frac{2}{r} \frac{g'_\kappa}{2M} + \left[(V - E) + \frac{\kappa(\kappa + 1)}{2Mr^2} - \frac{\kappa + 1}{4M^2 c^2 r} V' \right] g_\kappa,$$

multiplying by $2M$ and rewriting

$$g''_\kappa = -\left(\frac{2}{r} - \frac{M'}{M}\right) g'_\kappa + \left[(V - E) + \frac{\kappa(\kappa + 1)}{2Mr^2} - \frac{\kappa + 1}{4M^2 c^2 r} V' \right] 2M g_\kappa.$$

From (19) it follows

$$\frac{M'}{M} = -\frac{V'}{2Mc^2},$$

so we finally get

$$g''_\kappa = -\left(\frac{2}{r} + \frac{V'}{2Mc^2}\right) g'_\kappa + \left[(V - E) + \frac{\kappa(\kappa + 1)}{2Mr^2} - \frac{\kappa + 1}{4M^2 c^2 r} V' \right] 2M g_\kappa. \quad (25)$$

Comparing (25) with (5) we clearly see the two relativistic corrections, both depending on V' and both vanishing for $c \rightarrow \infty$ as expected. Also it should be noted that there is another difference, that (25) contains the relativistic mass (19), but (5) contains the rest mass m .

All the terms in the (25) are the same for both possibilities $j = l \pm \frac{1}{2}$ (i.e. $\kappa(\kappa + 1) = l(l + 1)$ for both $\kappa = -l - 1$ and $\kappa = l$), except for the spin-orbit coupling term $\frac{\kappa+1}{4M^2 c^2 r} V'(r)$, see for example [12] (eq. 2.64). Sometimes it makes sense to consider a semirelativistic case, where we neglect the spin-orbit coupling term, in which case we are left with the Schrödinger equation with the relativistic mass M and only one correction $\frac{V'}{2Mc^2}$.

In practice, the potential V is given on a discrete grid, so we need to compute it's derivative V' numerically. This is the reason we solve (24) instead of (25), because we need to evaluate V' only once for the spin-orbit term (for the semirelativistic case we don't even need the V' at all). But besides this minor technical thing, there is no other reason we chose (24) and not (25), which looks more familiar.

Once we have calculated g_κ and ϕ_κ , we calculate f_κ from (23). So the result of the radial Dirac equation are two functions f_κ and g_κ . The physically relevant quantity is the radial probability density

$$\rho(r) = r^2(f_\kappa^2 + g_\kappa^2).$$

We calculate the functions f_κ and g_κ in a similar way as we calculated R for the Schrödinger equation, thus we need the asymptotic behavior at the origin.

The potential can always be treated as $V = 1/r + \dots$ and in this case it can be shown [16], that the asymptotic is

$$g_\kappa = r^{\beta-1},$$

$$\phi_\kappa = \frac{(\beta-1)r^{\beta-2}}{2M},$$

where

$$\beta = \sqrt{\kappa^2 - \left(\frac{Z}{c}\right)^2}, \quad (26)$$

or, if we write it explicitly, for $j = l + \frac{1}{2}$

$$\beta^+ = \sqrt{(-l-1)^2 - \left(\frac{Z}{c}\right)^2}$$

and $j = l - \frac{1}{2}$

$$\beta^- = \sqrt{l^2 - \left(\frac{Z}{c}\right)^2}.$$

In the semirelativistic case (which is an approximation — we neglect the spin-orbit coupling term) we choose

$$\beta = \sqrt{\frac{1}{2}(|\beta^+|^2 + |\beta^-|^2)} = \sqrt{l^2 + l + \frac{1}{2} - \left(\frac{Z}{c}\right)^2}.$$

It should be noted that in the literature we can find other types of asymptotic behaviour for the semirelativistic case, it's just a question of the used approximation. One can hardly say that some of them are correct and another is not since the semirelativistic (sometimes denoted as scalar-relativistic) approximation itself is not correct, it's just an approximation.

It follows from (26) that for $j = l + \frac{1}{2}$ the radial Dirac equation completely becomes the radial Schrödinger equation in the limit $c \rightarrow \infty$ (and gives exactly the same solutions). For $j = l - \frac{1}{2}$ however, we get a wrong asymptotic: we get a radial Schrödinger equation for l , but the asymptotic for $l - 1$.

3.4 Other forms of the equations

Unfortunately, there are a lot of different forms the radial Dirac equation can be found in the literature. Many authors use different symbols, different units, I even found a mistake in [8]. For the reader's comfort, this section is devoted to deriving and presenting the most common forms of the equations.

We realize the fact

$$f'_\kappa - \frac{\kappa-1}{r}f_\kappa = \frac{1}{r}\left(\frac{d}{dr} - \frac{\kappa}{r}\right)(rf_\kappa),$$

$$g'_\kappa + \frac{\kappa+1}{r}g_\kappa = \frac{1}{r}\left(\frac{d}{dr} + \frac{\kappa}{r}\right)(rg_\kappa),$$

and rewrite equations (17) and (18):

$$\begin{aligned}\frac{1}{r} \left(\frac{d}{dr} + \frac{\kappa}{r} \right) (r g_\kappa) - \frac{1}{c} (W - V + mc^2) f_k &= 0, \\ \frac{1}{r} \left(\frac{d}{dr} - \frac{\kappa}{r} \right) (r f_\kappa) + \frac{1}{c} (W - V - mc^2) g_k &= 0.\end{aligned}$$

These equations could be found in [16] (eq. 8.10 and 8.9). Let's make the substitution [8]

$$\begin{aligned}P_\kappa &= r g_\kappa, \\ Q_\kappa &= r f_\kappa\end{aligned}$$

and write

$$\begin{aligned}\left(\frac{d}{dr} + \frac{\kappa}{r} \right) P_\kappa - \frac{1}{c} (W - V + mc^2) Q_\kappa &= 0, \\ \left(\frac{d}{dr} - \frac{\kappa}{r} \right) Q_\kappa + \frac{1}{c} (W - V - mc^2) P_\kappa &= 0,\end{aligned}$$

which can be found in [3] (eq. 3 and 4: they write $a_{nlj}(r) \equiv P_\kappa$ and $b_{nlj}(r) \equiv Q_\kappa$) and also in [12] (eq. 8.13: he uses $u_\kappa \equiv P_\kappa$ and $v_\kappa \equiv Q_\kappa$).

Now we use (19) and these relations become

$$\begin{aligned}W - V + mc^2 &= E - V + 2mc^2 = 2Mc^2, \\ W - V - mc^2 &= E - V,\end{aligned}$$

to write

$$\begin{aligned}\frac{dP_\kappa}{dr} &= -\frac{\kappa}{r} P_\kappa + 2McQ_\kappa, \\ \frac{dQ_\kappa}{dr} &= \frac{\kappa}{r} Q_\kappa - \frac{1}{c} (E - V) P_\kappa,\end{aligned}$$

which can be found in [8] (eq. 2a and 2b) (there is a mistake there, they forgot to divide by r). $2M$ can be written explicitly as

$$2M = \left[\frac{E - V}{c^2} + 2m \right] = \left[\frac{E - V}{c^2} + 2 \right] \text{ a.u.},$$

so we get

$$\begin{aligned}\frac{dP_\kappa}{dr} &= -\frac{\kappa}{r} P_\kappa + \left[\frac{E - V}{c^2} + 2 \right] cQ_\kappa, \\ \frac{dQ_\kappa}{dr} &= \frac{\kappa}{r} Q_\kappa - \frac{1}{c} (E - V) P_\kappa,\end{aligned}$$

which can be found in [16] (eq. 8.12 and 8.13), where they have one c hidden in $Q_\kappa = cr f_\kappa$ and use Rydberg atomic units, so they have 1 instead of 2 in the square bracket. It can be found in [1] as well, they use Hartree atomic units, but have a different notation $G_\kappa \equiv P_\kappa$ and $F_\kappa \equiv Q_\kappa$, also they made a substitution $c = \frac{1}{\alpha}$.

Some authors also use $\epsilon \equiv E$.

Chapter 4

Eigenproblem

4.1 Introduction

In the previous two chapters, we learned how to calculate the solution of both radial Schrödinger and Dirac equations for a given E . For most of the energies, however, the solution for $r \rightarrow \infty$ exponentially diverges to $\pm\infty$. Only for the energies equal to eigenvalues, the solution tends exponentially to zero for $r \rightarrow \infty$. The spectrum for bounded states is discrete, so we label the energies by n , starting from 1.

We want to find the eigenvalue and eigenfunction for a given n and l (and a spin in the relativistic case). The algorithm is the same for both nonrelativistic and relativistic case and is based on two facts, first that the number of nodes (ie. the number of intersections with the x axis, not counting the one at the origin and in the infinity) of R_{nl} and g_κ is $n - l - 1$ and second that the solution must tend to zero at infinity.

4.2 Algorithm for solving the eigenproblem

We calculate the solution for some (random) energy E_0 , using the procedure described above. Then we count the number of nodes (for diverging solutions, we don't count the last one) and check, if the solution is approaching the zero from top or bottom in the infinity. From the number of nodes and the direction it is approaching the zero it can be determined whether the energy E_0 is below or above the eigenvalue E belonging to a given n and l . The rest is simple, we find two energies, one below E , one above E and by halving the interval we calculate E with any precision we want.

There are a few technical numerical problems that are unimportant from the theoretical point of view, but that need to be solved if one attempts to actually implement this algorithm. One of them is that when we end the algorithm, because the energy interval is sufficiently small, it doesn't mean the solution is near zero for the biggest r we are integrating the equation. Remember, the solution goes exponentially to $\pm\infty$ for every E except the eigenvalues and because we never find the exact eigenvalue, the solution will (at some point) diverge from zero.

Possible solution that we have employed is as follows: when the algorithm ends we find the last minimum (which is always near zero) and trim the solution behind it (set it to zero).

Another solution of this problem is to end the algorithm not only when the energy interval is small enough, but also when the solution is sufficiently near zero for the biggest r we integrate. One would thought (including me at first :) that in this case we don't need to trim the solution. Mistake. If the biggest r is big enough, then even the variation of the initial E by 10^{-15} is not enough to push the tail of the solution to zero. It can actually be above zero by even 50% of the maximum of the wave function or more, so we would have to trim

the solution anyway (not mentioning that the algorithm never ends, because the solution will never be close enough to zero to pass the ending condition — that actually cannot even be formulated...).

The second rather technical problem is how to choose the initial interval of energies so that the eigenvalue lies inside the interval.

Chapter 5

Implementation

5.1 Fortran routine

The original Fortran 77 routine solves the equation (5) on a hyperbolic grid (27) using a simple polynomial approximation at each step. The input is the energy E , grid parameters a_P , k_0 and j_M , plus an array with values of the potential $V(r)$ at the grid points. The output is an array with values of $R_{El}(r)$ at the grid points. Our task was to replace this routine (with minimum changes in other parts of the code) with the new routine that solves the equations (24), (22) and (19) on the hyperbolic grid using the fourth-order Runge-Kutta method. The input is the same as for the original routine, plus Z . The output are the two functions f and g .

This means that in the limit $c \rightarrow \infty$ the g component of the new routine gives the same results as the original one.

This new routine can switch between the fully relativistic (Dirac) case, a semirelativistic case (we neglect the spin-orbit coupling term) and a nonrelativistic case (we neglect the spin-orbit coupling term and use a nonrelativistic mass, which effectively restores the Schrödinger equation).

5.2 Eigenvalue problem

This routine uses the algorithm described in the preceding chapter. It can use either the new or the old routine for the integration.

5.3 Hyperbolic grid

The routines solve the equations on a hyperbolic grid, which is defined as

$$r = a_P \frac{\xi}{1 - \xi}, \quad (27)$$

where $0 \leq \xi < 1$ is a dimensionless parameter and a_P is a scaling (in the same units as r), it is the value of r for $\xi = 0.5$. We take equidistant values for ξ

$$\xi = \frac{1}{j_M}, \frac{2}{j_M}, \dots, \frac{k_0}{j_M}, \quad k_0 < j_M, \quad (28)$$

by substituting (28) into (27) we get

$$r(j) = a_P \frac{j}{j_M - j}, \quad j = 1, 2, \dots, k_0. \quad (29)$$

The following values of the grid parameters has proven successful: $a_P = 1$, $k_0 = 500$ and $j_M = 525$.

Routines accepts the parameters a_P , k_0 and j_M , then the array $r(j)$ of a dimension k_0 , which gives the values of r in the points $j = 1, 2, \dots, k_0$ calculated

using the relation (29). The routine can easily calculate all the values of $r(j)$ from (29), or use the values directly from the array $r(j)$. We use the way that is more readable.

A formula for the inverse transformation can be derived from (29):

$$j = j_M \frac{r(j)}{a_P + r(j)}.$$

Chapter 6

Results

6.1 One electron atom calculation

To check that our program works, we have computed a spectrum of a one electron atom with these parameters: $Z = 92$, $k_0 = 2920$, $j_M = 3000$, $a_P = 1.0$. The result can be compared to fig. 8.3 in [12].

In the following table, E_1 represents eigenvalues calculated from the non-relativistic formula

$$E_n = -\frac{Z^2}{2n^2},$$

E_2 represents eigenvalues in the nonrelativistic case (so it should not depend on l) and E_3 eigenvalues computed from the radial Dirac equation, so it depends on l . The energies are given in eV.

Case $j = l + \frac{1}{2}$:

n=1, l=0, E1=-115156.9520	E2=-114712.4604	E3=-131994.5289
n=2, l=0, E1= -28789.2380	E2= -28733.2317	E3= -34151.9041
n=2, l=1, E1= -28789.2380	E2= -28789.2246	E3= -29649.2912
n=3, l=0, E1= -12795.2168	E2= -12778.5942	E3= -14649.7703
n=3, l=1, E1= -12795.2168	E2= -12795.2121	E3= -13307.1396
n=3, l=2, E1= -12795.2168	E2= -12795.2167	E3= -12959.5541
n=4, l=0, E1= -7197.3095	E2= -7190.2921	E3= -8026.0999
n=4, l=1, E1= -7197.3095	E2= -7197.3073	E3= -7466.8873
n=4, l=2, E1= -7197.3095	E2= -7197.3094	E3= -7318.8303
n=4, l=3, E1= -7197.3095	E2= -7197.3094	E3= -7248.7232

Case $j = l - \frac{1}{2}$ (for $l = 0$ we take $j = \frac{1}{2}$):

n=1, l=0, E1=-115156.9520	E2=-114712.4604	E3=-131994.5289
n=2, l=0, E1= -28789.2380	E2= -28733.2317	E3= -34151.9041
n=2, l=1, E1= -28789.2380	E2= -28789.2246	E3= -34226.2202
n=3, l=0, E1= -12795.2168	E2= -12778.5942	E3= -14649.7703
n=3, l=1, E1= -12795.2168	E2= -12795.2121	E3= -14673.2066
n=3, l=2, E1= -12795.2168	E2= -12795.2167	E3= -13307.1884
n=4, l=0, E1= -7197.3095	E2= -7190.2921	E3= -8026.0999
n=4, l=1, E1= -7197.3095	E2= -7197.3073	E3= -8035.9706
n=4, l=2, E1= -7197.3095	E2= -7197.3094	E3= -7466.9097
n=4, l=3, E1= -7197.3095	E2= -7197.3094	E3= -7318.8305

It should be noted that the eigenvalues don't depend on l in the nonrelativistic case only for exactly the Coulomb potential. In practice, for potentials screened by other electrons in real atoms, this is not the case.

Chapter 7

Conclusion

Radial numeric solution of the Dirac equation has been implemented under specific conditions for *all-electron pseudopotential* generating process and the corresponding computer code has been debugged.

Chapter 8

Appendix

8.1 Atomic units (au)

There are two types of atomic units — Hartree units and Rydberg units. The term "atomic units" usually means Hartree atomic units and we use it in this meaning as well. Some authors however [16] mean Rydberg units when they write "atomic units"...

All (Hartree) atomic units can be derived from this relation:

$$\hbar = m = e = 4\pi\epsilon_0 = 1,$$

where m is the mass of the electron, e a charge of the electron, ϵ_0 the permittivity of vacuum.

Examples: dimension of length is a Bohr radius

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = \frac{\hbar}{mc\alpha} = 1 \text{ a.u.} = 0.529 \text{ \AA} = 0.529 \cdot 10^{-10} \text{ m},$$

where α is the dimensionless fine-structure constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137.036},$$

so the speed of light is

$$c = \frac{1}{\alpha} \text{ a.u.} = 137.036 \text{ a.u.}$$

Energy is measured in Hartrees, one Hartree is

$$E_H = \frac{\hbar^2}{ma_0^2} = mc^2\alpha^2 = 1 \text{ a.u.} = 27.211 \text{ eV}.$$

Hydrogen atom Hamiltonian in SI units:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$

and au units:

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r}.$$

The energy spectrum for hydrogen is

$$E_n = -\frac{\hbar^2}{ma_0^2}\frac{1}{2n^2} = -\frac{1}{2n^2}.$$

The Rydberg atomic units are defined as

$$\hbar = 4\pi\epsilon_0 = 1, \quad m = \frac{1}{2}, \quad e^2 = 2,$$

in these units

$$\begin{aligned} a_0 &= 1, \\ E_H &= \frac{\hbar^2}{ma_0^2} = mc^2\alpha^2 = \frac{1}{2}, \\ E_{Ry} &= \frac{\hbar^2}{2ma_0^2} = 1 = 13.606 \text{ eV}, \\ H &= -\nabla^2 - \frac{2}{r}, \\ E_n &= -\frac{\hbar^2}{ma_0^2} \frac{1}{2n^2} = -\frac{1}{n^2}, \\ c &= \frac{2}{\alpha} = 274.072. \end{aligned}$$

This is why the asymptotic term $Z\alpha$ is mostly written as $\frac{Z}{c}$ (Hartree units), but sometimes as $\frac{2Z}{c}$ (Rydberg units).

8.2 Spin-angular functions

The operators L^2 (quadrade of angular momentum), L_3 (z component of angular momentum) and S_3 (z component of a spin, $\pm\frac{1}{2}$) mutually commute, so let's denote the corresponding normalized eigenvectors by $|lms_3\rangle$. We can however also use commuting operators J^2 (quadrade of total momentum), L^2 and J_3 (z component of total momentum) and denote their normalized eigenvectors by $|jlj_3\rangle$.

First we want to find a relation between these two bases. A standard procedure is to use Clebsch-Gordan coefficients [5]:

$$|jlj_3\rangle = \sum_{m=-l}^l \sum_{s_3=-\frac{1}{2}}^{\frac{1}{2}} (l, \frac{1}{2}, m, s_3 | j, j_3) |lms_3\rangle = \quad (30)$$

$$= (l, \frac{1}{2}, j_3 - \frac{1}{2}, \frac{1}{2} | j, j_3) |l; j_3 - \frac{1}{2}; \frac{1}{2}\rangle + (l, \frac{1}{2}, j_3 + \frac{1}{2}, -\frac{1}{2} | j, j_3) |l; j_3 + \frac{1}{2}; -\frac{1}{2}\rangle,$$

where $(j_1, j_2, m_1, m_2 | j, m)$ are Clebsch-Gordan coefficients and we used the fact that they are nonzero only for $m_1 + m_2 = m$. Because we are adding angular momenta l and $\frac{1}{2}$, the only possible values of j are $j = l \pm \frac{1}{2}$. $j = l + \frac{1}{2}$ means, that the spin has the same orientation as the angular momentum, $j = l - \frac{1}{2}$ corresponds to the opposite orientation. So we will only need these 4 coefficients

(see eq. K58 in [4] or table 2.2 in [12]):

$$\begin{aligned}
(l, \frac{1}{2}, j_3 - \frac{1}{2}, \frac{1}{2} | l + \frac{1}{2}, j_3) &= \sqrt{\frac{l + j_3 + \frac{1}{2}}{2l + 1}}, \\
(l, \frac{1}{2}, j_3 + \frac{1}{2}, -\frac{1}{2} | l + \frac{1}{2}, j_3) &= \sqrt{\frac{l - j_3 + \frac{1}{2}}{2l + 1}}, \\
(l, \frac{1}{2}, j_3 - \frac{1}{2}, \frac{1}{2} | l - \frac{1}{2}, j_3) &= -\sqrt{\frac{l - j_3 + \frac{1}{2}}{2l + 1}}, \\
(l, \frac{1}{2}, j_3 + \frac{1}{2}, -\frac{1}{2} | l - \frac{1}{2}, j_3) &= \sqrt{\frac{l + j_3 + \frac{1}{2}}{2l + 1}}.
\end{aligned}$$

Substituting into (30) yields the desired relation between the two basis:

$$\begin{aligned}
|j = l + \frac{1}{2}; l; j_3\rangle &= \sqrt{\frac{l + j_3 + \frac{1}{2}}{2l + 1}} |l; m = j_3 - \frac{1}{2}; \frac{1}{2}\rangle + \\
&\quad + \sqrt{\frac{l - j_3 + \frac{1}{2}}{2l + 1}} |l; m = j_3 + \frac{1}{2}; -\frac{1}{2}\rangle, \\
|j = l - \frac{1}{2}; l; j_3\rangle &= -\sqrt{\frac{l - j_3 + \frac{1}{2}}{2l + 1}} |l; m = j_3 - \frac{1}{2}; \frac{1}{2}\rangle + \\
&\quad + \sqrt{\frac{l + j_3 + \frac{1}{2}}{2l + 1}} |l; m = j_3 + \frac{1}{2}; -\frac{1}{2}\rangle.
\end{aligned}$$

Now we want to find representations of these "kets". Our Hilbert space can be decomposed as

$$H = \mathbb{S}^2 \otimes \mathbb{C}^2,$$

where \mathbb{S}^2 is a vector space of quadratic integrable functions on a unit sphere (the angular momentum operator L acts here) and \mathbb{C}^2 is a two dimensional complex vector space (the spin operator S acts here).

The eigenvectors of the S_3 operator form a basis of the space \mathbb{C}^2 , let's denote them Φ_s , where $s = \pm\frac{1}{2}$:

$$\Phi_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \Phi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The eigenvectors of L^2 and L_3 form a basis of \mathbb{S}^2 , they are called spherical harmonics Y_{lm} .

Then

$$|lm; s_3 = \frac{1}{2}\rangle = Y_{lm} \Phi_{\frac{1}{2}} = \begin{pmatrix} Y_{lm} \\ 0 \end{pmatrix}$$

$$\begin{aligned}
|lm; s_3 = -\frac{1}{2}\rangle &= Y_{lm}\Phi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ Y_{lm} \end{pmatrix} \\
|j = l + \frac{1}{2}; lj_3\rangle &= \frac{1}{\sqrt{2l+1}} \left(\sqrt{l+j_3+\frac{1}{2}} Y_{l,m=j_3-\frac{1}{2}} \Phi_{\frac{1}{2}} + \right. \\
&\quad \left. + \sqrt{l-j_3+\frac{1}{2}} Y_{l,m=j_3+\frac{1}{2}} \Phi_{-\frac{1}{2}} \right) = \\
&= \frac{1}{\sqrt{2l+1}} \begin{pmatrix} \sqrt{l+j_3+\frac{1}{2}} Y_{l,m=j_3-\frac{1}{2}} \\ \sqrt{l-j_3+\frac{1}{2}} Y_{l,m=j_3+\frac{1}{2}} \end{pmatrix} = y_{jl}^{j_3} \\
|j = l - \frac{1}{2}; lj_3\rangle &= \frac{1}{\sqrt{2l+1}} \left(-\sqrt{l-j_3+\frac{1}{2}} Y_{l,m=j_3-\frac{1}{2}} \Phi_{\frac{1}{2}} + \right. \\
&\quad \left. + \sqrt{l+j_3+\frac{1}{2}} Y_{l,m=j_3+\frac{1}{2}} \Phi_{-\frac{1}{2}} \right) = \\
&= \frac{1}{\sqrt{2l+1}} \begin{pmatrix} -\sqrt{l-j_3+\frac{1}{2}} Y_{l,m=j_3-\frac{1}{2}} \\ \sqrt{l+j_3+\frac{1}{2}} Y_{l,m=j_3+\frac{1}{2}} \end{pmatrix} = y_{jl}^{j_3}
\end{aligned}$$

The $y_{jl}^{j_3}$ are called "spin-angular functions"[11], or "spin spherical harmonics"[16]. For the two possibilities $j = l \pm \frac{1}{2}$ we introduce a new quantity κ :

$$\kappa = \begin{cases} -l-1, & \text{for } j = l + \frac{1}{2}; \\ l, & \text{for } j = l - \frac{1}{2}, \end{cases}$$

so that we can deduce from κ both l and the spin orientation and thus we can label all the spin-angular functions by just two parameters κ and j_3 and write:

$$\chi_{\kappa}^{j_3} \equiv y_{jl}^{j_3} = \begin{pmatrix} (l, \frac{1}{2}, j_3 - \frac{1}{2}, +\frac{1}{2} | j, j_3) Y_{l,m=j_3-\frac{1}{2}} \\ (l, \frac{1}{2}, j_3 + \frac{1}{2}, -\frac{1}{2} | j, j_3) Y_{l,m=j_3+\frac{1}{2}} \end{pmatrix}. \quad (31)$$

Any integer value of κ is permissible except $\kappa = 0$. Some authors also use a different notation $j_3 \equiv m_j \equiv \mu$ for the eigenvalue of J_3 .

It can be easily shown, that because of the normalization of spherical harmonics Y_{lm} :

$$\int Y_{lm}^*(\mathbf{n}) Y_{l'm'}(\mathbf{n}) d\Omega = \delta_{ll'} \delta_{mm'},$$

the spin-angular functions have the following normalization:

$$\int \chi_{\kappa}^{j_3*}(\mathbf{n}) \chi_{\kappa'}^{j_3'}(\mathbf{n}) d\Omega = \delta_{\kappa\kappa'} \delta_{j_3j_3'}. \quad (32)$$

To be more precise, $-\hbar\kappa$ is actually defined as the eigenvalue of the operator [12] (eq. 2.85 and 2.86)

$$K = \boldsymbol{\sigma} \cdot \mathbf{L} + \hbar = \left(\frac{2}{\hbar^2} \mathbf{S} \cdot \mathbf{L} + 1 \right) \hbar = \left(\frac{1}{\hbar^2} (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) + 1 \right) \hbar,$$

$$\begin{aligned}
K\psi &= \left(\frac{1}{\hbar^2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) + 1 \right) \hbar\psi = \\
&= (j(j+1) - l(l+1) - s(s+1) + 1) \hbar\psi = \\
&= \left(j(j+1) - l(l+1) + \frac{1}{4} \right) \hbar\psi = \\
&= -\hbar\kappa\psi,
\end{aligned}$$

so we have $\kappa = -j(j+1) + l(l+1) - \frac{1}{4}$. For $j = l + \frac{1}{2}$:

$$\kappa = -(l + \frac{1}{2})(l + \frac{1}{2} + 1) + l(l+1) - \frac{1}{4} = -l - 1$$

and for the other case $j = l - \frac{1}{2}$:

$$\kappa = -(l - \frac{1}{2})(l - \frac{1}{2} + 1) + l(l+1) - \frac{1}{4} = l.$$

Another way of looking at κ follows from

$$\kappa = \begin{cases} -l - 1 = -(j + \frac{1}{2}), & \text{for } j = l + \frac{1}{2}; \\ l = +(j + \frac{1}{2}), & \text{for } j = l - \frac{1}{2}, \end{cases}$$

which means that $|\kappa|$ is actually the value of the total angular momentum (plus $\frac{1}{2}$ so that we only have integer values) and the sign depends on whether the spin and the orbital angular momentum have the same or opposite orientation ($j = l \pm \frac{1}{2}$).

In the text, we need to find how the operator

$$\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r}$$

acts on the spin-angular functions. It commutes with \mathbf{J} , as is easy to prove, which means it also commutes with J_3 and \mathbf{J}^2 and so $\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \chi_{\kappa}^{j_3}$ must have the same values of j and j_3 as $\chi_{\kappa}^{j_3}$. Furthermore, it anticommutes with K [12], so

$$K \frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \chi_{\kappa}^{j_3} = -\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} K \chi_{\kappa}^{j_3} = -\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} (-\hbar\kappa) \chi_{\kappa}^{j_3} = \hbar\kappa \frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \chi_{\kappa}^{j_3},$$

but also

$$K \chi_{-\kappa}^{j_3} = \hbar\kappa \chi_{-\kappa}^{j_3},$$

which shows that

$$\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \chi_{\kappa}^{j_3} = C \chi_{-\kappa}^{j_3} \tag{33}$$

for some (complex) constant C . From now on, there are mistakes in the literature. For example [12] implicitly concludes at this point that $C = -1$, which is obviously incorrect. It can easily be shown that $(\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r})^2 = \mathbb{1}$, so $C^2 = 1$, or $C = \pm 1$. The sign of C can generally depend on κ and j_3 , but doesn't depend on \mathbf{x} . To determine it, one option is to find it explicitly for all values of κ and j_3 . [10] chooses $\mathbf{x} = \hat{\mathbf{e}}_z$, the unit vector along the z -axis, and writes

$$Y_{lm}(\hat{\mathbf{e}}_z) = \sqrt{\frac{2l+1}{4\pi}} \delta_{m0}, \tag{34}$$

$$\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} = \sigma_z,$$

so using (33)

$$\sigma_z \chi_\kappa^{j_3} = \sigma_z y_{j, j \pm \frac{1}{2}}^{j_3} = C \chi_{-\kappa}^{j_3} = C y_{j, j \mp \frac{1}{2}}^{j_3},$$

where the + sign corresponds to $\kappa > 0$ and the - sign to $\kappa < 0$. Using (31)

$$\begin{aligned} & \left(\begin{array}{c} (j \pm \frac{1}{2}, \frac{1}{2}, j_3 - \frac{1}{2}, +\frac{1}{2} | j, j_3) Y_{j \pm \frac{1}{2}, j_3 - \frac{1}{2}} \\ -(j \pm \frac{1}{2}, \frac{1}{2}, j_3 + \frac{1}{2}, -\frac{1}{2} | j, j_3) Y_{j \pm \frac{1}{2}, j_3 + \frac{1}{2}} \end{array} \right) = \\ & = C \left(\begin{array}{c} (j \mp \frac{1}{2}, \frac{1}{2}, j_3 - \frac{1}{2}, +\frac{1}{2} | j, j_3) Y_{j \mp \frac{1}{2}, j_3 - \frac{1}{2}} \\ (j \mp \frac{1}{2}, \frac{1}{2}, j_3 + \frac{1}{2}, -\frac{1}{2} | j, j_3) Y_{j \mp \frac{1}{2}, j_3 + \frac{1}{2}} \end{array} \right), \end{aligned}$$

evaluating the Clebsch-Gordan coefficients

$$\begin{aligned} & \frac{1}{\sqrt{2j+1 \pm 1}} \left(\begin{array}{c} \mp \sqrt{j \mp j_3 + \frac{1}{2} \pm \frac{1}{2}} Y_{j \pm \frac{1}{2}, j_3 - \frac{1}{2}} \\ -\sqrt{j \pm j_3 + \frac{1}{2} \pm \frac{1}{2}} Y_{j \pm \frac{1}{2}, j_3 + \frac{1}{2}} \end{array} \right) = \\ & = \frac{1}{\sqrt{2j+1 \mp 1}} C \left(\begin{array}{c} \pm \sqrt{j \pm j_3 + \frac{1}{2} \mp \frac{1}{2}} Y_{j \mp \frac{1}{2}, j_3 - \frac{1}{2}} \\ \sqrt{j \mp j_3 + \frac{1}{2} \mp \frac{1}{2}} Y_{j \mp \frac{1}{2}, j_3 + \frac{1}{2}} \end{array} \right). \end{aligned}$$

Using (34) it follows that $C = -1$ for $j > 0$ and $j_3 = \pm \frac{1}{2}$ (and both \pm). For other values of j_3 however, the spherical harmonic $Y_{lm}(\hat{\mathbf{e}}_z) = 0$ (because $m \neq 0$), so we can say nothing. Unfortunately, j_3 can be any number from $-j, -j+1, \dots, j$, so proving that $C = -1$ only for $j_3 = \pm \frac{1}{2}$ is insufficient and [10] is wrong as well. We'll give a correct proof using a Wigner-Eckart theorem that $C = -1$ indeed in a moment. So we finally get

$$\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \chi_\kappa^{j_3} = -\chi_{-\kappa}^{j_3}. \quad (35)$$

Let's look at the relation between $\chi_\kappa^{j_3}$ and $\chi_{-\kappa}^{j_3}$ more closely. For $\kappa \geq 0$:

$$\chi_\kappa^{j_3} = y_{\kappa - \frac{1}{2}, \kappa}^{j_3}, \quad (36)$$

$$\chi_{-\kappa}^{j_3} = y_{\kappa - \frac{1}{2}, (\kappa-1)}^{j_3} = y_{(\kappa-1) + \frac{1}{2}, (\kappa-1)}^{j_3}, \quad (37)$$

for $\kappa < 0$:

$$\chi_\kappa^{j_3} = y_{-\kappa - \frac{1}{2}, (-\kappa-1)}^{j_3} = y_{(-\kappa-1) + \frac{1}{2}, (-\kappa-1)}^{j_3}, \quad (38)$$

$$\chi_{-\kappa}^{j_3} = y_{-\kappa - \frac{1}{2}, -\kappa}^{j_3}. \quad (39)$$

Basically, $\chi_\kappa^{j_3}$ and $\chi_{-\kappa}^{j_3}$ have the same j and j_3 , and differ in l . There are only two possibilities $l = j \pm \frac{1}{2}$, so $\chi_\kappa^{j_3}$ picks one and $\chi_{-\kappa}^{j_3}$ has the other one (which one depends on the sign of κ). So the operator $\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r}$ preserves j and j_3 and flips the l to the other possibility.

Let's get back to determining the constant C . We denote the eigenvector of J_1^2 , J_2^2 , J^2 and J_z by a ket

$$|j_1 j_2 j m\rangle ,$$

where $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. In this notation,

$$\chi_\kappa^m = \langle \mathbf{x} | j \pm \frac{1}{2}; \frac{1}{2} j m \rangle ,$$

where \mathbf{J}_1 is the orbital angular momentum, \mathbf{J}_2 is the spin, $j = |\kappa| - \frac{1}{2}$ and the plus sign is taken for $\kappa > 0$, negative sign is for $\kappa < 0$. We want to determine the constant C in

$$\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} \chi_\kappa^{j_3} = C \chi_{-\kappa}^{j_3} ,$$

that is

$$\frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} |j \pm \frac{1}{2}; \frac{1}{2} j m\rangle = C |j \mp \frac{1}{2}; \frac{1}{2} j m\rangle .$$

The kets $|j_1 j_2 j m\rangle$ are orthogonal, so

$$C = \langle j \mp \frac{1}{2}; \frac{1}{2} j m | \frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} |j \pm \frac{1}{2}; \frac{1}{2} j m\rangle .$$

We introduce two vector operators

$$\mathbf{T} = \frac{\mathbf{x}}{r} ,$$

$$\mathbf{V} = \boldsymbol{\sigma} ,$$

and form tensor operators $T(1, q)$ and $V(1, q)$ ($q = -1, 0, 1$) in the standard way:

$$T(1, 0) = \frac{x_3}{r}, \quad T(1, \pm 1) = \mp \frac{x_1 \pm ix_2}{r\sqrt{2}} ,$$

$$V(1, 0) = \sigma_3, \quad V(1, \pm 1) = \mp \frac{\sigma_1 \pm i\sigma_2}{\sqrt{2}} ,$$

they obey the following commutation relations

$$[T(1, q), \mathbf{J}_2] = 0 ,$$

$$[V(1, q), \mathbf{J}_1] = 0 ,$$

so we can use the Wigner-Eckart (W-E) theorem for the scalar product of two tensor operators (note that $\mathbf{T}(1) \cdot \mathbf{V}(1) \equiv \sum_q (-1)^q T(1, q) V(1, -q) = T_1 V_1 + T_2 V_2 + T_3 V_3$):

$$C = \langle j \mp \frac{1}{2}; \frac{1}{2} j m | \frac{\boldsymbol{\sigma} \cdot \mathbf{x}}{r} |j \pm \frac{1}{2}; \frac{1}{2} j m\rangle = \langle j \mp \frac{1}{2}; \frac{1}{2} j m | \mathbf{T}(1) \cdot \mathbf{V}(1) |j \pm \frac{1}{2}; \frac{1}{2} j m\rangle =$$

$$= (-1)^{j+j\pm\frac{1}{2}+\frac{1}{2}} \left\{ \begin{matrix} j & j \mp \frac{1}{2} & \frac{1}{2} \\ 1 & \frac{1}{2} & j \pm \frac{1}{2} \end{matrix} \right\} (j \mp \frac{1}{2} \parallel \mathbb{T}(1) \parallel j \pm \frac{1}{2}) (\frac{1}{2} \parallel \mathbb{V}(1) \parallel \frac{1}{2}).$$

Now (remember j can be either integer or half integer)

$$(-1)^{j+j\pm\frac{1}{2}+\frac{1}{2}} = \mp(-1)^{2j},$$

$$\left\{ \begin{matrix} j & j \mp \frac{1}{2} & \frac{1}{2} \\ 1 & \frac{1}{2} & j \pm \frac{1}{2} \end{matrix} \right\} = \left\{ \begin{matrix} j & \frac{1}{2} & j + \frac{1}{2} \\ 1 & j - \frac{1}{2} & \frac{1}{2} \end{matrix} \right\} = -\frac{(-1)^{2j}}{\sqrt{6(j+\frac{1}{2})}},$$

$$(j \mp \frac{1}{2} \parallel \mathbb{T}(1) \parallel j \pm \frac{1}{2}) = \mp\sqrt{j+\frac{1}{2}},$$

$$(\frac{1}{2} \parallel \mathbb{V}(1) \parallel \frac{1}{2}) = \sqrt{6},$$

so

$$C = \mp(-1)^{2j} \left(-\frac{(-1)^{2j}}{\sqrt{6(j+\frac{1}{2})}} \right) \left(\mp\sqrt{j+\frac{1}{2}} \right) \sqrt{6} = -1.$$

The $6j$ symbol was determined from the formula [4] (K.108)

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b \end{matrix} \right\} = (-1)^{a+b+c} \sqrt{\frac{(a+b+c+1)(-a+b+c)(a-b+c)}{b(2b+1)(2b+2)(2c-1)2c(2c+1)}} \cdot \sqrt{a+b-c+1},$$

The reduced matrix element $(\frac{1}{2} \parallel \mathbb{V}(1) \parallel \frac{1}{2})$ was determined from another application of the W-E theorem:

$$\begin{aligned} \langle \frac{1}{2} \frac{1}{2} | V(1,0) | \frac{1}{2} \frac{1}{2} \rangle &= (-1)^{\frac{1}{2}+1-\frac{1}{2}} \frac{(1, \frac{1}{2}, 0, \frac{1}{2} | \frac{1}{2}, \frac{1}{2})}{\sqrt{2 \cdot \frac{1}{2} + 1}} (\frac{1}{2} \parallel \mathbb{V}(1) \parallel \frac{1}{2}) = \\ &= \frac{1}{\sqrt{6}} (\frac{1}{2} \parallel \mathbb{V}(1) \parallel \frac{1}{2}), \end{aligned}$$

but also

$$\langle \frac{1}{2} \frac{1}{2} | V(1,0) | \frac{1}{2} \frac{1}{2} \rangle = \langle \frac{1}{2} \frac{1}{2} | \sigma_3 | \frac{1}{2} \frac{1}{2} \rangle = (1 \ 0) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1,$$

so

$$(\frac{1}{2} \parallel \mathbb{V}(1) \parallel \frac{1}{2}) = \sqrt{6}.$$

Similarly for the reduced matrix element $(j \mp \frac{1}{2} \parallel \mathbb{T}(1) \parallel j \pm \frac{1}{2})$:

$$\langle j \mp \frac{1}{2}; m | T(1,0) | j \pm \frac{1}{2}; m \rangle = (-1)^{j \mp \frac{1}{2} + 1 - j \mp \frac{1}{2}} \frac{(1, j \pm \frac{1}{2}, 0, m | j \mp \frac{1}{2}, m)}{\sqrt{2j \mp 1 + 1}} \times$$

$$\times (j \mp \frac{1}{2} \parallel \mathbb{T}(1) \parallel j \pm \frac{1}{2}) = \mp \frac{1}{2} \sqrt{\frac{(j + \frac{1}{2})^2 - m^2}{j(j+1)(j + \frac{1}{2})}} (j \mp \frac{1}{2} \parallel \mathbb{T}(1) \parallel j \pm \frac{1}{2}),$$

but also

$$\begin{aligned} \langle j \mp \frac{1}{2}; m | T(1, 0) | j \pm \frac{1}{2}; m \rangle &= \langle j \mp \frac{1}{2}; m | \frac{x_3}{r} | j \pm \frac{1}{2}; m \rangle = \\ &= \int Y_{j \mp \frac{1}{2}; m}^*(\vartheta, \varphi) \cos \vartheta Y_{j \pm \frac{1}{2}; m}(\vartheta, \varphi) d\Omega = \frac{1}{2} \sqrt{\frac{(j + \frac{1}{2})^2 - m^2}{j(j+1)}}, \end{aligned}$$

so

$$(j \mp \frac{1}{2} \parallel \mathbb{T}(1) \parallel j \pm \frac{1}{2}) = \mp \sqrt{j + \frac{1}{2}}.$$

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