

University of Nevada, Reno

Physics in Screening Environments

A dissertation submitted in partial fulfillment of the
requirements for the degree of Doctor of Philosophy in
Chemical Physics

by

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THE GRADUATE SCHOOL

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prepared under our supervision by

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Abstract

In the current study, we investigated atoms in screening environments like plasmas.

It is common practice to extract physical data, such as temperature and electron densities, from plasma experiments. We present results that address inherent computational difficulties that arise when the screening approach is extended to include the interaction between the atomic electrons. We show that there may arise an ambiguity in the interpretation of physical properties, such as temperature and charge density, from experimental data due to the opposing effects of electron-nucleus screening and electron-electron screening.

The focus of the work, however, is on the resolution of inherent computational challenges that appear in the computation of two-particle matrix elements. Those enter already at the Hartree-Fock level. Furthermore, as examples of post Hartree-Fock calculations, we show second-order Green's function results and many body perturbation theory results of second order.

A self-contained derivation of all necessary equations has been included. The accuracy of the implementation of the method is established by comparing standard unscreened results for various atoms and molecules against literature for Hartree-Fock as well as Green's function and many body perturbation theory.

The main results of the thesis are presented in the chapter called Screened Results, where the behavior of several atomic systems depending on electron-electron and electron-nucleus Debye screening was studied. The computer code that we have developed has been made available for anybody to use.

Finally, we present and discuss results obtained for screened interactions. We also examine thoroughly the computational details of the calculations and particular implementations of the method.

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Chapter 1

Introduction

The theory of static shielding of interacting charges, as introduced by Debye and Hückel for electrolytic solutions [26], has become an important tool in many areas of physics. Of particular interest are wide spread applications in the field of astrophysical and laboratory plasmas.

To stake out the wide area of systems to which screening is applicable, we present the Figure 1.1 where temperatures and densities of various plasmas are plotted. The Debye screening applies for example to not strongly coupled plasmas (in the graph this is above the $\Gamma_e = 1$ line, where Γ_e is the ratio of the average potential to kinetic energy [23]).

It is common practice to extract physical data, like temperature and electron densities, from plasma experiments. In the present work we study results that address inherent computational difficulties that arise when the screening approach is extended to include the interaction between the atomic electrons. The vast majority of earlier publications restricted the application of Debye screening to the electron-nucleus potential. The inclusion of screening of the electron-electron interaction in plasma studies is not completely new, however.

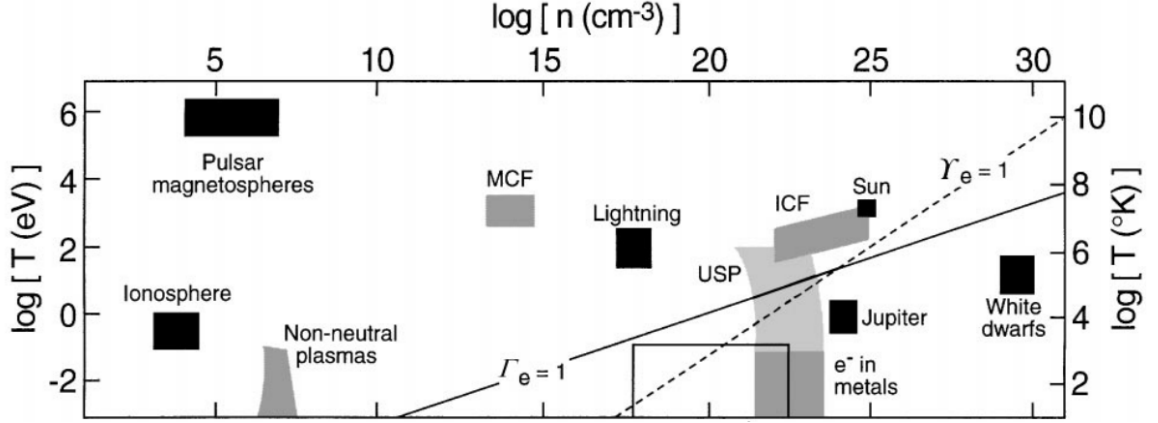


Figure 1.1: Overview of temperature and densities of several plasmas (taken from [23])

Previous work for atoms was restricted to two-electron systems. A representative list is given by references [24], [32], [18], [31], [22] and [21]. Related studies from different areas of physics, which have helped to stimulate our interest in the present problem, are from astrophysics [29] in the theory of proton scattering and an early publication from nuclear physics [25].

The motivation for not neglecting the electron-electron screening has already been addressed in [24]: if the environment offers the possibility of screening, the more mobile electron pairs will be able to take better advantage of it than the less mobile electron-ion pairs, thus lowering the overall energy of the system. It has also been shown there that in particular screening situations the bound excited states of the negative hydrogen ion are likely to exist.

While the focus of the present work has been the resolution of inherent computational challenges, we have, at the same time, established that the opposing effects of electron-nucleus screening and electron-electron screening may induce ambiguity in the physical properties (e.g. temperature and charge density) of the systems under investigation when they are deduced from experimental data. This particular feature will require more detailed

investigations in the future and is stated here only cursorily.

The particular computational difficulty dealt with here is the question of how to incorporate electron-electron screening, in an accurate and concise way, into the computation of general two-electron matrix elements. This difficulty arises already at the Hartree-Fock (HF) level of approximation, which is a common starting point for almost all many-body correlation studies. The earlier studies [24], [32], [18], [31], [22] and [21] have in common that they are computations for two-electron systems for which correlated wave functions provide a natural entry point to implement Debye screening of the interaction between electrons. The extension to larger systems is the main motivation of the current work.

In the Methods section we attempt to present a self-contained summary of the molecular and atomic Hartree-Fock (HF) equations. We present several types of basis functions: Slater Type Orbital (STO), Gaussian Type Orbital (GTO) and finite element (FE) basis functions, and show calculation of the matrix elements. We further present equations for the second order single particle many-body Green's function and Density Functional Theory to indicate how steps beyond HF might employ the present findings. To accomplish this, we present equations that deal with implementing screening into HF matrix elements and their numerical evaluation.

Chapter 3 (Unscreened Results) shows STO, GTO and FE results for atoms and simple molecules and atoms on the HF level. We also show several second order Green function calculations and second order many body perturbation theory results and compare against literature to establish our implementation. We also run several convergence studies, both for STO using even-tempered bases and FE by increasing the polynomial order.

In Chapter 4 (Screened Results) we show results of Hartree-Fock calculations in screening

environments. The method is based on article [16]. We show screened results for various Debye lengths. We also present second order Green function results as an example of going beyond Hartree-Fock to show that our method can directly be applied to post Hartree-Fock calculations.

Chapter 5 (Summary and Conclusions) presents a discussion of the screened results and an inherent ambiguity of determining the electron-electron and electron-nucleus Debye lengths from plasma data. We also discuss advantages and disadvantages of STO and FE as basis functions with regards to convergence and other numerical issues.

The Appendices contain derivations of standard, but important formulas needed for our work. In particular they contain the technical details of our accurate and fast modified Bessel function implementation in Fortran.

The main contribution of our present work is the solution of the mathematical problem of screening and its numerical implementation in computer code. We use the screened Hartree-Fock results to show the applications using some standard many body methods, it is not the implementation of new post Hartree-Fock method. When we use the screened Hartree-Fock results employing some standard many-body method, it is intended to demonstrate that the present results are applicable in the usual way.

Our particular implementation of a finite element basis in the radial Roothan-Hartree-Fock equations is a convenient technical addition to the existing literature. The usage of finite elements in Hartree-Fock equations was pioneered by [53] and [54], where p -FEM is used with Legendre polynomial shape functions. We use Lagrange interpolation polynomials basis with nodes at Lobatto points together with either Gauss-Legendre or Gauss-Lobatto quadrature. When the latter is used, then such a method is also sometimes called spectral

element method [47] or discrete variable representation [49], [48], [50], [52]. Compared to [53], we have also simplified the two-particle matrix elements calculation using a weak formulation of a second order differential equation for Hartree screening functions as suggested by [4]. Other methods to solve atomic HF equations include shooting method [2], B-spline method [3], finite differences [51] as well as Slater and Gaussian Type Orbitals [19]. A recent review of applications of finite element methods in ab-initio electronic structure calculations is [7].

Chapter 2

Methods

2.1 Derivation of the Hartree-Fock (HF) Method

In this section we derive the (unscreened) Hartree-Fock equations in terms of wavefunctions. More details can be found for example in [11].

The interacting Hamiltonian for the many body Schrödinger equation is:

$$i\hbar\partial_t |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle$$

$$\hat{H} = \hat{T} + \hat{V} = \sum_{ij} c_i^\dagger \langle i|T|j\rangle c_j + \frac{1}{2} \sum_{ijkl} c_i^\dagger c_j^\dagger \langle ij|V|kl\rangle c_l c_k$$

where $|i\rangle$ are spin orbitals that require a sum over spin indices (the integration over ω below denotes the spin sum):

$$\langle i|T|j\rangle = \int \chi_i^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{x} - \mathbf{R}_n|} \right) \chi_j(\mathbf{x}) d^3x d\omega$$

$$\langle ij|V|kl\rangle = \int \chi_i^*(\mathbf{x}) \chi_j^*(\mathbf{y}) \frac{1}{|\mathbf{x} - \mathbf{y}|} \chi_k(\mathbf{x}) \chi_l(\mathbf{y}) d^3x d\omega_x d^3y d\omega_y$$

We would like to minimize the energy $E = \langle \Psi | \hat{H} | \Psi \rangle$ using the following basis for Z electrons:

$$|\Psi\rangle = c_1^\dagger c_2^\dagger \cdots c_Z^\dagger |0\rangle$$

We express the energy E in this basis:

$$\begin{aligned} E &= \langle \Psi | \hat{H} | \Psi \rangle = \\ &= \langle 0 | c_Z \cdots c_2 c_1 \hat{H} c_1^\dagger c_2^\dagger \cdots c_Z^\dagger | 0 \rangle = \\ &= \langle 0 | c_Z \cdots c_2 c_1 \left(\sum_{i,j=1}^Z c_i^\dagger \langle i | T | j \rangle c_j + \frac{1}{2} \sum_{i,j,k,l=1}^Z c_i^\dagger c_j^\dagger \langle ij | V | kl \rangle c_l c_k \right) c_1^\dagger c_2^\dagger \cdots c_Z^\dagger | 0 \rangle = \\ &= \sum_{i=1}^Z \langle i | T | i \rangle + \frac{1}{2} \sum_{i,j=1}^Z (\langle ij | V | ij \rangle - \langle ij | V | ji \rangle) \end{aligned}$$

We minimize it with the constrain $\langle i | j \rangle = \delta_{ij}$:

$$\delta \left(E - \sum_{i,j=1}^Z \epsilon_{ij} \langle i | j \rangle \right) = 0$$

We obtain:

$$T |i\rangle + \sum_{j=1}^Z (\langle j | V | ij \rangle - \langle j | V | ji \rangle) = \epsilon_i |i\rangle \quad (2.1)$$

in the x -representation:

$$\begin{aligned} \langle \mathbf{x} | T | i \rangle + \sum_{j=1}^Z (\langle \mathbf{x} | \langle j | V | ij \rangle - \langle \mathbf{x} | \langle j | V | ji \rangle) &= \epsilon_i \langle \mathbf{x} | i \rangle \\ \langle \mathbf{x} | T | i \rangle + \sum_{j=1}^Z (\langle j \mathbf{x} | V | ij \rangle - \langle j \mathbf{x} | V | ji \rangle) &= \epsilon_i \langle \mathbf{x} | i \rangle \end{aligned}$$

And writing the individual terms explicitly (in this section, all orbitals are *spin* orbitals):

$$\begin{aligned}
\langle \mathbf{x} | i \rangle &= \psi_i(\mathbf{x}) \\
\langle \mathbf{x} | T | i \rangle &= \left(-\frac{1}{2} \nabla^2 - \sum_n \frac{Z_n}{|\mathbf{x} - \mathbf{R}_n|} \right) \psi_i(\mathbf{x}) \\
\langle j \mathbf{x} | V | i j \rangle &= \int \psi_j^*(\mathbf{y}) \frac{1}{|\mathbf{x} - \mathbf{y}|} \psi_i(\mathbf{x}) \psi_j(\mathbf{y}) d^3 y = \int \frac{|\psi_j(\mathbf{y})|^2}{|\mathbf{x} - \mathbf{y}|} d^3 y \psi_i(\mathbf{x}) \\
\langle j \mathbf{x} | V | j i \rangle &= \int \psi_j^*(\mathbf{y}) \frac{1}{|\mathbf{x} - \mathbf{y}|} \psi_j(\mathbf{x}) \psi_i(\mathbf{y}) d^3 y = \int \frac{\psi_i(\mathbf{y}) \psi_j^*(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3 y \psi_j(\mathbf{x})
\end{aligned}$$

we get the Hartree-Fock equations:

$$\left(-\frac{1}{2} \nabla^2 - \frac{Z}{|\mathbf{x}|} + \int \frac{\sum_{j=1}^Z |\psi_j(\mathbf{y})|^2}{|\mathbf{x} - \mathbf{y}|} d^3 y \right) \psi_i(\mathbf{x}) - \sum_{j=1}^Z \int \frac{\psi_i(\mathbf{y}) \psi_j^*(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3 y \psi_j(\mathbf{x}) = \epsilon_i \psi_i(\mathbf{x}) \quad (2.2)$$

Let's introduce the number density $n(\mathbf{x})$, Hartree potential $V_H(\mathbf{x})$ and nonlocal exchange potential V_x with its kernel $U(\mathbf{x}, \mathbf{y})$:

$$\begin{aligned}
n(\mathbf{x}) &= \sum_{j=1}^Z |\psi_j(\mathbf{y})|^2 \\
V_H(\mathbf{x}) &= \int \frac{\sum_{j=1}^Z |\psi_j(\mathbf{y})|^2}{|\mathbf{x} - \mathbf{y}|} d^3 y = \int \frac{n(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3 y \\
\hat{V}_x f(\mathbf{x}) &= - \sum_{j=1}^Z \int \frac{f(\mathbf{y}) \psi_j^*(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3 y \psi_j(\mathbf{x}) = \int U(\mathbf{x}, \mathbf{y}) f(\mathbf{y}) d^3 y \\
U(\mathbf{x}, \mathbf{y}) &= - \sum_{j=1}^Z \frac{\psi_j(\mathbf{x}) \psi_j^*(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|}
\end{aligned}$$

then we can write the HF equations as:

$$\begin{aligned} \left(-\frac{1}{2}\nabla^2 - \frac{Z}{|\mathbf{x}|} + V_H(\mathbf{x}) + \hat{V}_x \right) \psi_i(\mathbf{x}) &= \epsilon_i \psi_i(\mathbf{x}) \\ \left(-\frac{1}{2}\nabla^2 - \frac{Z}{|\mathbf{x}|} + V_H(\mathbf{x}) \right) \psi_i(\mathbf{x}) + \int U(\mathbf{x}, \mathbf{y}) \psi_i(\mathbf{y}) d^3y &= \epsilon_i \psi_i(\mathbf{x}) \end{aligned}$$

The Hartree potential can be calculated by solving the Poisson equation:

$$\nabla^2 V_H(\mathbf{x}) = -4\pi n(\mathbf{x})$$

where:

$$n(\mathbf{x}) = \sum_{i=1}^Z |\psi_i(\mathbf{x})|^2$$

The application of the exchange potential \hat{V}_x on any function $f(\mathbf{x})$ can be calculated by:

$$\begin{aligned} \hat{V}_x f(\mathbf{x}) &= - \sum_{j=1}^Z W_{fj}(\mathbf{x}) \psi_j(\mathbf{x}) \\ W_{fj}(\mathbf{x}) &= \int \frac{f(\mathbf{y}) \psi_j^*(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3y \\ \nabla^2 W_{fj}(\mathbf{x}) &= -4\pi f(\mathbf{x}) \psi_j^*(\mathbf{x}) \end{aligned}$$

2.2 Roothaan Equations For Closed Shell Systems

In the previous section we derived the Hartree-Fock equations in terms of wavefunctions.

In this section we write the equations in terms of basis functions, those are called Roothaan-Hartree-Fock equations.

Starting from (2.1) and integrating over spins we get (here i, k are spatial orbitals, not spin

orbitals):

$$T|i\rangle + \sum_{k=1}^{N/2} (2\langle k|V|i\rangle - \langle k|V|k\rangle) = \epsilon_i|i\rangle \quad (2.3)$$

We introduce basis functions $|\mu\rangle$ by (below the greek letters refer to basis functions, latin letters indicate spatial orbitals):

$$|i\rangle = \sum_{\nu} C_{\nu i} |\nu\rangle$$

substitute into (2.3) and multiply by $\langle\mu|$ from the left:

$$\sum_{\nu} \langle\mu|T|\nu\rangle C_{\nu i} + \sum_{\nu} \sum_{k=1}^{N/2} (2\langle\mu k|V|\nu k\rangle - \langle\mu k|V|k\rangle) C_{\nu i} = \epsilon_i \sum_{\nu} \langle\mu|\nu\rangle C_{\nu i} \quad (2.4)$$

Now we expand the orbitals $|k\rangle$ in terms of basis functions:

$$\begin{aligned} \sum_{\nu} \langle\mu|T|\nu\rangle C_{\nu i} + \sum_{\nu} \sum_{\alpha\beta} \left(2 \sum_{k=1}^{N/2} C_{\alpha k} C_{\beta k}^* \right) (\langle\mu\beta|V|\nu\alpha\rangle - \frac{1}{2} \langle\mu\beta|V|\alpha\rangle) C_{\nu i} = \\ = \epsilon_i \sum_{\nu} \langle\mu|\nu\rangle C_{\nu i} \end{aligned} \quad (2.5)$$

We introduce the density matrix:

$$\begin{aligned} \hat{\rho} = 2 \sum_{k=1}^{N/2} |k\rangle \langle k| = \sum_{\alpha\beta} |\alpha\rangle 2 \sum_{k=1}^{N/2} C_{\alpha k} C_{\beta k}^* \langle\beta| = \sum_{\alpha\beta} |\alpha\rangle P_{\alpha\beta} \langle\beta| \\ P_{\alpha\beta} = 2 \sum_{k=1}^{N/2} C_{\alpha k} C_{\beta k}^* \end{aligned}$$

and get:

$$\sum_{\nu} \left(\langle \mu | T | \nu \rangle + \sum_{\alpha\beta} P_{\alpha\beta} \left(\langle \mu\beta | V | \nu\alpha \rangle - \frac{1}{2} \langle \mu\beta | V | \alpha\nu \rangle \right) \right) C_{\nu i} = \epsilon_i \sum_{\nu} \langle \mu | \nu \rangle C_{\nu i} \quad (2.6)$$

introducing:

$$\begin{aligned} F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} + G_{\mu\nu} \\ H_{\mu\nu}^{\text{core}} &= \langle \mu | T | \nu \rangle \\ G_{\mu\nu} &= \sum_{\alpha\beta} P_{\alpha\beta} \left(\langle \mu\beta | V | \nu\alpha \rangle - \frac{1}{2} \langle \mu\beta | V | \alpha\nu \rangle \right) \\ S_{\mu\nu} &= \langle \mu | \nu \rangle \end{aligned}$$

the equations (2.6) becomes:

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} \quad (2.7)$$

These are the Roothaan equations, also called Roothaan-Hartree-Fock equations. It is a generalized eigenvalue problem.

The total energy is given below, where the a, b indices in the first equation refer to spin

orbitals, while the i, j indices in the other equations refer to spatial orbitals:

$$\begin{aligned}
E &= \sum_a \langle a|T|a \rangle + \frac{1}{2} \sum_{a,b} (\langle ab|V|ab \rangle - \langle ab|V|ba \rangle) = \\
&= \sum_i 2I(i) + \sum_{i,j} (2J(i,j) - K(i,j)) = \\
&= \sum_i 2 \langle i|T|i \rangle + \sum_{i,j} (2 \langle ij|V|ij \rangle - \langle ij|V|ji \rangle) = \\
&= \sum_i 2 \langle i|T|i \rangle + 2 \sum_{i,j} (\langle ij|V|ij \rangle - \frac{1}{2} \langle ij|V|ji \rangle) = \\
&= \sum_{\mu\nu} \sum_i 2 \langle \mu|T|\nu \rangle C_{\nu i} C_{\mu i}^* + 2 \sum_{\mu\nu} \sum_{\alpha\beta} \sum_{i,j} C_{\nu i} C_{\mu i}^* C_{\alpha j} C_{\beta j}^* (\langle \mu\beta|V|\nu\alpha \rangle - \frac{1}{2} \langle \mu\beta|V|\alpha\nu \rangle) = \\
&= \sum_{\mu\nu} \langle \mu|T|\nu \rangle P_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu} \sum_{\alpha\beta} P_{\nu\mu} P_{\alpha\beta} (\langle \mu\beta|V|\nu\alpha \rangle - \frac{1}{2} \langle \mu\beta|V|\alpha\nu \rangle) = \\
&= \sum_{\mu\nu} P_{\nu\mu} (H_{\mu\nu}^{\text{core}} + \frac{1}{2} G_{\mu\nu}) = \\
&= \sum_{\mu\nu} P_{\nu\mu} (\frac{1}{2} H_{\mu\nu}^{\text{core}} + \frac{1}{2} (H_{\mu\nu}^{\text{core}} + G_{\mu\nu})) = \\
&= \frac{1}{2} \sum_{\mu\nu} P_{\nu\mu} (H_{\mu\nu}^{\text{core}} + F_{\mu\nu})
\end{aligned}$$

The same result can be derived in x -representation starting from (2.2) and introducing spatial orbitals:

$$\left(-\frac{1}{2} \nabla^2 - \frac{Z}{|\mathbf{x}|} + \int \frac{2 \sum_{k=1}^{N/2} |\psi_k(\mathbf{y})|^2}{|\mathbf{x} - \mathbf{y}|} d^3 y \right) \psi_i(\mathbf{x}) - \sum_{k=1}^{N/2} \int \frac{\psi_i(\mathbf{y}) \psi_k^*(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3 y \psi_k(\mathbf{x}) = \epsilon_i \psi_i(\mathbf{x}) \quad (2.8)$$

The first integral in (2.8) is called the direct term and the second integral is called the exchange term, which is nonlocal (the value of the exchange operator applied to the wave-

function ψ_i at point \mathbf{x} depends on values of the wavefunction at all other points).

We introduce basis functions ϕ_μ :

$$\psi_i(\mathbf{x}) = \sum_{\nu} C_{\nu i} \phi_{\nu}(\mathbf{x})$$

substitute into (2.8) and also multiply the whole equation by ϕ_{μ}^* and integrate over \mathbf{x} :

$$\begin{aligned} & \sum_{\nu} \int \phi_{\mu}^*(\mathbf{x}) \left(-\frac{1}{2} \nabla^2 - \frac{Z}{|\mathbf{x}|} + \int \frac{2 \sum_{k=1}^{N/2} |\psi_k(\mathbf{y})|^2}{|\mathbf{x} - \mathbf{y}|} d^3 y \right) \phi_{\nu}(\mathbf{x}) d^3 x C_{\nu i} \\ & - \sum_{\nu} \int \phi_{\mu}^*(\mathbf{x}) \sum_{k=1}^{N/2} \int \frac{\phi_{\nu}(\mathbf{y}) \psi_k^*(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3 y \psi_k(\mathbf{x}) d^3 x C_{\nu i} = \epsilon_i \sum_{\nu} \int \phi_{\mu}^*(\mathbf{x}) \phi_{\nu}(\mathbf{x}) d^3 x C_{\nu i} \end{aligned} \quad (2.9)$$

This can be written as:

$$\begin{aligned} \sum_{\nu} F_{\mu\nu} C_{\nu i} &= \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} \\ F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} + G_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu} + G_{\mu\nu} \end{aligned}$$

where:

$$\begin{aligned} T_{\mu\nu} &= \int \phi_{\mu}^*(\mathbf{x}) \left(-\frac{1}{2} \nabla^2 \right) \phi_{\nu}(\mathbf{x}) d^3 x = \frac{1}{2} \int \nabla \phi_{\mu}^*(\mathbf{x}) \cdot \nabla \phi_{\nu}(\mathbf{x}) d^3 x \\ V_{\mu\nu} &= \int \phi_{\mu}^*(\mathbf{x}) \left(-\frac{Z}{|\mathbf{x}|} \right) \phi_{\nu}(\mathbf{x}) d^3 x \\ G_{\mu\nu} &= \int \phi_{\mu}^*(\mathbf{x}) \left(\int \frac{2 \sum_{k=1}^{N/2} |\psi_k(\mathbf{y})|^2}{|\mathbf{x} - \mathbf{y}|} d^3 y \right) \phi_{\nu}(\mathbf{x}) d^3 x + \\ & - \int \phi_{\mu}^*(\mathbf{x}) \sum_{k=1}^{N/2} \int \frac{\phi_{\nu}(\mathbf{y}) \psi_k^*(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3 y \psi_k(\mathbf{x}) d^3 x \\ S_{\mu\nu} &= \int \phi_{\mu}^*(\mathbf{x}) \phi_{\nu}(\mathbf{x}) d^3 x \end{aligned}$$

Introducing the density matrix and density:

$$\begin{aligned}
 \rho(\mathbf{x}, \mathbf{y}) &= \langle \mathbf{x} | \hat{\rho} | \mathbf{y} \rangle = \sum_{\alpha\beta} \langle \mathbf{x} | \alpha \rangle P_{\alpha\beta} \langle \beta | \mathbf{y} \rangle = \sum_{\alpha\beta} \phi_{\alpha}(\mathbf{x}) P_{\alpha\beta} \phi_{\beta}^*(\mathbf{y}) \\
 P_{\alpha\beta} &= 2 \sum_{k=1}^{N/2} C_{\alpha k} C_{\beta k}^* \\
 \rho(\mathbf{x}) &= 2 \sum_{k=1}^{N/2} |\psi_k(\mathbf{x})|^2 = 2 \sum_{k=1}^{N/2} |\langle \mathbf{x} | k \rangle|^2 = 2 \sum_{k=1}^{N/2} \langle \mathbf{x} | k \rangle \langle k | \mathbf{x} \rangle = \langle \mathbf{x} | \hat{\rho} | \mathbf{x} \rangle = \\
 &= \sum_{\alpha\beta} \phi_{\alpha}(\mathbf{x}) P_{\alpha\beta} \phi_{\beta}^*(\mathbf{x})
 \end{aligned}$$

Expanding the ψ_k functions and using the density matrix we get for $G_{\mu\nu}$:

$$\begin{aligned}
 G_{\mu\nu} &= \sum_{\alpha\beta} P_{\alpha\beta} \int \phi_{\mu}^*(\mathbf{x}) \left(\int \frac{\phi_{\beta}^*(\mathbf{y}) \phi_{\alpha}(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3y \right) \phi_{\nu}(\mathbf{x}) d^3x \\
 &\quad - \frac{1}{2} \sum_{\alpha\beta} P_{\alpha\beta} \int \phi_{\mu}^*(\mathbf{x}) \int \frac{\phi_{\nu}(\mathbf{y}) \phi_{\beta}^*(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3y \phi_{\alpha}(\mathbf{x}) d^3x
 \end{aligned}$$

or

$$\begin{aligned}
 G_{\mu\nu} &= \sum_{\alpha\beta} P_{\alpha\beta} \int \frac{\phi_{\mu}^*(\mathbf{x}) \phi_{\nu}(\mathbf{x}) \phi_{\beta}^*(\mathbf{y}) \phi_{\alpha}(\mathbf{y}) - \frac{1}{2} \phi_{\mu}^*(\mathbf{x}) \phi_{\alpha}(\mathbf{x}) \phi_{\beta}^*(\mathbf{y}) \phi_{\nu}(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3x d^3y \\
 &\equiv \sum_{\alpha\beta} P_{\alpha\beta} \left(\langle \mu\beta | \frac{1}{r_{12}} | \nu\alpha \rangle - \frac{1}{2} \langle \mu\beta | \frac{1}{r_{12}} | \alpha\nu \rangle \right)
 \end{aligned}$$

These two particle matrix elements are often written in two different notations:

$$G_{\mu\nu} = \sum_{\alpha\beta} P_{\alpha\beta} [\langle \mu\beta | \nu\alpha \rangle - \frac{1}{2} \langle \mu\beta | \alpha\nu \rangle] = \sum_{\alpha\beta} P_{\alpha\beta} [(\mu\nu | \beta\alpha) - \frac{1}{2} (\mu\alpha | \beta\nu)]$$

Physics notation uses the angle brackets, while the chemistry notation uses the round brackets, but the main difference is in the order of indices. Note that this notation implicitly assumes the $\frac{1}{r_{12}}$ factor, so for example $\langle \mu\beta | \nu\alpha \rangle$ actually means $\langle \mu\beta | \frac{1}{r_{12}} | \nu\alpha \rangle$ and one has to

understand this from the context.

2.3 Two-particle Matrix Element

In this section we summarize some properties of the two-particle matrix element. The two-particle matrix element is:

$$\begin{aligned} (ij|kl) &= \int \frac{\psi_i^*(\mathbf{x})\psi_j(\mathbf{x})\psi_k^*(\mathbf{x}')\psi_l(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x d^3x' = \\ &= \langle ik|jl \rangle = \int \frac{\psi_i^*(\mathbf{x})\psi_k^*(\mathbf{x}')\psi_j(\mathbf{x})\psi_l(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x d^3x' \end{aligned} \quad (2.10)$$

As said above, the $\langle ik|jl \rangle$ is called the physicists' notation because the $|jl \rangle$ and $|ik \rangle$ kets are:

$$|jl \rangle = \psi_j(\mathbf{x})\psi_l(\mathbf{x}')$$

$$|ik \rangle = \psi_i(\mathbf{x})\psi_k(\mathbf{x}')$$

The $(ij|kl)$ is called the chemists' notation. From (2.10) there are two types of symmetries — interchanging of the dummy variables:

$$\begin{aligned} (ij|kl) &= \langle ik|jl \rangle = \int \frac{\psi_i^*(\mathbf{x})\psi_j(\mathbf{x})\psi_k^*(\mathbf{x}')\psi_l(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x d^3x' = \\ &= \int \frac{\psi_i^*(\mathbf{x}')\psi_j(\mathbf{x}')\psi_k^*(\mathbf{x})\psi_l(\mathbf{x})}{|\mathbf{x}' - \mathbf{x}|} d^3x' d^3x = (kl|ij) = \langle ki|lj \rangle \end{aligned}$$

and taking the complex conjugate:

$$\begin{aligned} (ij|kl)^* &= \langle ik|jl \rangle^* = \left(\int \frac{\psi_i^*(\mathbf{x})\psi_k^*(\mathbf{x}')\psi_j(\mathbf{x})\psi_l(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x d^3x' \right)^* = \\ &= \int \frac{\psi_i(\mathbf{x})\psi_k(\mathbf{x}')\psi_j^*(\mathbf{x})\psi_l^*(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x d^3x' = \langle jl|ik \rangle = (ji|lk) \end{aligned}$$

If the matrix elements are real, then:

$$(ij|kl) = \langle ik|jl \rangle = \langle jl|ik \rangle = (ji|lk)$$

In general those are the only symmetries (4 total).

If however, the $\psi_i(\mathbf{x})$ functions are real, then there are additional symmetries: an exchange $i \leftrightarrow j$ and $k \leftrightarrow l$. The symmetries of $(ij|kl)$ are exchange of i with j or k with l or the ij and kl pairs (8 total):

$$\begin{aligned} (ij|kl) &= (ji|kl) = (ij|lk) = (ji|lk) = \\ &= (kl|ij) = (lk|ij) = (kl|ji) = (lk|ji) \end{aligned}$$

So if we view $(ij|kl)$ as two boxes $(\cdot|\cdot)$ then we can permute the labels in the given box “.”, as well as exchange the boxes (the only thing we cannot do is to take one particle from one box and exchange it with a particle from the other box — for example i cannot be exchanged with k). As such the box “.” indicates a pair of two electrons (in any order) and the two electron integral assigns a unique number to a pair of such boxes (in any order).

The symmetries of the $\langle ik|jl\rangle$ symbol are:

$$\begin{aligned}\langle ik|jl\rangle &= \langle jk|il\rangle = \langle il|jk\rangle = \langle jl|ik\rangle = \\ &= \langle ki|lj\rangle = \langle li|kj\rangle = \langle kj|li\rangle = \langle lj|ki\rangle\end{aligned}$$

Example I: the Slater integral $R^k(i, j, k, l)$ has all 8 symmetries (Slater integral uses physical notation).

Example II: In spherical symmetry, the 2-particle integrals can be written as (see below for derivation):

$$\begin{aligned}\langle \alpha\beta|\gamma\delta\rangle &= \langle n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta | n_\gamma l_\gamma m_\gamma n_\delta l_\delta m_\delta \rangle = \langle n_\alpha l_\alpha m_\alpha n_\gamma l_\gamma m_\gamma | n_\beta l_\beta m_\beta n_\delta l_\delta m_\delta \rangle = \\ &= \sum_{k=\max(|l_\alpha-l_\gamma|, |l_\beta-l_\delta|, |m_\alpha-m_\gamma|)}^{\min(l_\alpha+l_\gamma, l_\beta+l_\delta)} c^k(l_\alpha, m_\alpha, l_\gamma, m_\gamma) c^k(l_\delta, m_\delta, l_\beta, m_\beta) \\ &\quad \delta_{m_\alpha+m_\beta-m_\gamma-m_\delta, 0} \\ &\quad R^k(n_\alpha l_\alpha, n_\beta l_\beta, n_\gamma l_\gamma, n_\delta l_\delta)\end{aligned}$$

They only have 4 symmetries, because spherical harmonics are complex. In particular:

$$\begin{aligned}
\langle \beta \alpha | \delta \gamma \rangle &= \sum_{k=\max(|l_\beta-l_\delta|, |l_\alpha-l_\gamma|, |m_\beta-m_\delta|)}^{\min(l_\beta+l_\delta, l_\alpha+l_\gamma)} c^k(l_\beta, m_\beta, l_\delta, m_\delta) c^k(l_\gamma, m_\gamma, l_\alpha, m_\alpha) \\
&\quad \delta_{m_\beta+m_\alpha-m_\delta-m_\gamma, 0} \\
R^k(n_\beta l_\beta, n_\alpha l_\alpha, n_\delta l_\delta, n_\gamma l_\gamma) &= \\
= \sum_{k=\max(|l_\beta-l_\delta|, |l_\alpha-l_\gamma|, |m_\beta-m_\delta|)}^{\min(l_\beta+l_\delta, l_\alpha+l_\gamma)} c^k(l_\alpha, m_\alpha, l_\gamma, m_\gamma) c^k(l_\delta, m_\delta, l_\beta, m_\beta) (-1)^{m_\alpha-m_\gamma+m_\beta-m_\delta} \\
&\quad \delta_{m_\beta+m_\alpha-m_\delta-m_\gamma, 0} \\
R^k(n_\alpha l_\alpha, n_\beta l_\beta, n_\gamma l_\gamma, n_\delta l_\delta) &= \langle \alpha \beta | \gamma \delta \rangle
\end{aligned}$$

and

$$\begin{aligned}
\langle \gamma \delta | \alpha \beta \rangle &= \langle n_\gamma l_\gamma m_\gamma \ n_\delta l_\delta m_\delta | n_\alpha l_\alpha m_\alpha \ n_\beta l_\beta m_\beta \rangle = \langle n_\gamma l_\gamma m_\gamma \ n_\alpha l_\alpha m_\alpha | n_\delta l_\delta m_\delta \ n_\beta l_\beta m_\beta \rangle = \\
&= \sum_{k=\max(|l_\gamma-l_\alpha|, |l_\delta-l_\beta|, |m_\gamma-m_\alpha|)}^{\min(l_\gamma+l_\alpha, l_\delta+l_\beta)} c^k(l_\gamma, m_\gamma, l_\alpha, m_\alpha) c^k(l_\beta, m_\beta, l_\delta, m_\delta) \\
&\quad \delta_{m_\gamma+m_\delta-m_\alpha-m_\beta, 0} \\
R^k(n_\gamma l_\gamma, n_\delta l_\delta, n_\alpha l_\alpha, n_\beta l_\beta) &= \langle \alpha \beta | \gamma \delta \rangle
\end{aligned}$$

We used the symmetries of the Slater integrals as well as the c^k coefficients that change a sign, but thanks to the $\delta_{m_\gamma+m_\delta-m_\alpha-m_\beta, 0}$, the overall sign does not change. The other two symmetries are missing, i.e. $\langle \gamma \beta | \alpha \delta \rangle \neq \langle \alpha \beta | \gamma \delta \rangle$ and $\langle \alpha \delta | \gamma \beta \rangle \neq \langle \alpha \beta | \gamma \delta \rangle$.

2.4 General Matrix Elements in Spherical Symmetry

In the case of spherical symmetry, one can evaluate all the integrals over angles analytically and one obtains the so called radial Hartree-Fock equations [33]. We derive them in this section in a step by step fashion.

In spherical symmetry the basis function can be expressed as a product of the radial function and a spherical harmonic:

$$\phi_\mu(\mathbf{x}) = \phi_{n_\mu l_\mu m_\mu}(\mathbf{x}) = \frac{\phi_{n_\mu l_\mu}(r)}{r} Y_{l_\mu m_\mu}(\Omega)$$

It can be shown that the solutions are of the form:

$$\psi_i(\mathbf{x}) = \psi_{nlm}(\mathbf{x}) = \frac{P_{nl}(r)}{r} Y_{lm}(\Omega)$$

We can now write:

$$\begin{aligned}
\psi_i(\mathbf{x}) &= \sum_{\nu} C_{\nu i} \phi_{\nu}(\mathbf{x}) \\
\int \phi_{\mu}(\mathbf{x}) \psi_i(\mathbf{x}) d^3x &= \sum_{\nu} S_{\mu\nu} C_{\nu i} \\
\sum_{\mu} S_{\mu\nu}^{-1} \int \phi_{\mu}(\mathbf{x}) \psi_i(\mathbf{x}) d^3x &= C_{\nu i} \\
\sum_{\mu} \delta_{l_{\mu} l_{\nu}} \delta_{m_{\mu} m_{\nu}} \left(S_{n_{\mu} n_{\nu}}^{l_{\mu}} \right)^{-1} \int \phi_{n_{\mu} l_{\mu} m_{\mu}}(\mathbf{x}) \psi_{n l m}(\mathbf{x}) d^3x &= C_{n_{\nu} l_{\nu} m_{\nu}; n l m} \\
\sum_{\mu} \delta_{l_{\mu} l_{\nu}} \delta_{m_{\mu} m_{\nu}} \left(S_{n_{\mu} n_{\nu}}^{l_{\mu}} \right)^{-1} \int \frac{\phi_{n_{\mu} l_{\mu}}(r)}{r} Y_{l_{\mu} m_{\mu}}(\Omega) \frac{P_{nl}(r)}{r} Y_{lm}(\Omega) r^2 dr d\Omega &= C_{n_{\nu} l_{\nu} m_{\nu}; n l m} \\
\sum_{\mu} \delta_{l_{\mu} l_{\nu}} \delta_{m_{\mu} m_{\nu}} \left(S_{n_{\mu} n_{\nu}}^{l_{\mu}} \right)^{-1} \int \phi_{n_{\mu} l_{\mu}}(r) P_{nl}(r) dr \delta_{l_{\mu} l_{\nu}} \delta_{m_{\mu} m_{\nu}} &= C_{n_{\nu} l_{\nu} m_{\nu}; n l m} \\
\delta_{l l_{\nu}} \delta_{m m_{\nu}} \sum_{n_{\mu}} \left(S_{n_{\mu} n_{\nu}}^{l_{\mu}} \right)^{-1} \int \phi_{n_{\mu} l}(r) P_{nl}(r) dr &= C_{n_{\nu} l_{\nu} m_{\nu}; n l m} \\
\delta_{l l_{\nu}} \delta_{m m_{\nu}} C_{n_{\nu} n}^l &= C_{n_{\nu} l_{\nu} m_{\nu}; n l m}
\end{aligned}$$

where

$$C_{n_{\nu} n}^l = \sum_{n_{\mu}} \left(S_{n_{\mu} n_{\nu}}^{l_{\mu}} \right)^{-1} \int \phi_{n_{\mu} l}(r) P_{nl}(r) dr$$

Also we get:

$$\begin{aligned}
\psi_{n l m}(\mathbf{x}) &= \sum_{\nu} C_{n_{\nu} l_{\nu} m_{\nu}; n l m} \phi_{n_{\nu} l_{\nu} m_{\nu}}(\mathbf{x}) \\
\frac{P_{nl}(r)}{r} Y_{lm}(\Omega) &= \sum_{\nu} C_{n_{\nu} l_{\nu} m_{\nu}; n l m} \frac{\phi_{n_{\nu} l_{\nu}}(r)}{r} Y_{l_{\nu} m_{\nu}}(\Omega) = \\
&= \sum_{\nu} \delta_{l l_{\nu}} \delta_{m m_{\nu}} C_{n_{\nu} n}^l \frac{\phi_{n_{\nu} l_{\nu}}(r)}{r} Y_{l_{\nu} m_{\nu}}(\Omega) = \\
&= \sum_{n_{\nu}} C_{n_{\nu} n}^l \frac{\phi_{n_{\nu} l}(r)}{r} Y_{lm}(\Omega)
\end{aligned}$$

From which it follows:

$$P_{nl}(r) = \sum_{n_\nu} C_{n_\nu n}^l \phi_{n_\nu l}(r)$$

The μ index runs over all combinations of nlm . In particular, here is an example of one possible way to index the basis of 12 radial functions for each l :

μ	n_μ	l_μ	m_μ
1	1	0	0
2	2	0	0
3	3	0	0
...	...		
12	12	0	0
13	1	1	-1
14	2	1	-1
15	3	1	-1
...	...		
24	12	1	-1
25	1	1	0
26	2	1	0
27	3	1	0
...	...		
36	12	1	0
37	1	1	1
38	2	1	1
39	3	1	1
...	...		
48	12	1	1
49	1	2	-2
50	2	2	-2
51	3	2	-2
...	...		

So the radial index n_μ always starts from 1 for each l_μ .

2.4.1 Overlap Matrix Element

The overlap matrix element

$$S_{\mu\nu} = \int \phi_{\mu}^*(\mathbf{x}) \phi_{\nu}(\mathbf{x}) d^3x$$

becomes

$$\begin{aligned} S_{\mu\nu} &= S_{n_{\mu}l_{\mu}m_{\mu}n_{\nu}l_{\nu}m_{\nu}} = \int \frac{\phi_{n_{\mu}l_{\mu}}(r)}{r} Y_{l_{\mu}m_{\mu}}^*(\Omega) \frac{\phi_{n_{\nu}l_{\nu}}(r)}{r} Y_{l_{\nu}m_{\nu}}(\Omega) r^2 dr d\Omega = \\ &= \delta_{l_{\mu}l_{\nu}} \delta_{m_{\mu}m_{\nu}} \int_0^{\infty} \phi_{n_{\mu}l_{\mu}}(r) \phi_{n_{\nu}l_{\nu}}(r) dr = \\ &= \delta_{l_{\mu}l_{\nu}} \delta_{m_{\mu}m_{\nu}} \int_0^{\infty} \phi_{n_{\mu}l_{\mu}}(r) \phi_{n_{\nu}l_{\mu}}(r) dr = \\ &= \delta_{l_{\mu}l_{\nu}} \delta_{m_{\mu}m_{\nu}} S_{n_{\mu}n_{\nu}}^{l_{\mu}} \end{aligned}$$

where

$$S_{n_{\mu}n_{\nu}}^l = \int_0^{\infty} \phi_{n_{\mu}l}(r) \phi_{n_{\nu}l}(r) dr$$

2.4.2 Potential Matrix Element

The potential matrix element

$$V_{\mu\nu} = \int \phi_{\mu}^*(\mathbf{x}) \left(-\frac{Z}{|\mathbf{x}|} \right) \phi_{\nu}(\mathbf{x}) d^3x$$

becomes

$$\begin{aligned}
V_{\mu\nu} &= V_{n_\mu l_\mu m_\mu n_\nu l_\nu m_\nu} = \int \frac{\phi_{n_\mu l_\mu}(r)}{r} Y_{l_\mu m_\mu}^*(\Omega) \left(-\frac{Z}{r}\right) \frac{\phi_{n_\nu l_\nu}(r)}{r} Y_{l_\nu m_\nu}(\Omega) r^2 dr d\Omega = \\
&= \delta_{l_\mu l_\nu} \delta_{m_\mu m_\nu} \int_0^\infty \phi_{n_\mu l_\mu}(r) \left(-\frac{Z}{r}\right) \phi_{n_\nu l_\nu}(r) dr = \\
&= \delta_{l_\mu l_\nu} \delta_{m_\mu m_\nu} \int_0^\infty \phi_{n_\mu l_\mu}(r) \left(-\frac{Z}{r}\right) \phi_{n_\nu l_\mu}(r) dr = \\
&= \delta_{l_\mu l_\nu} \delta_{m_\mu m_\nu} V_{n_\mu n_\nu}^{l_\mu}
\end{aligned}$$

where

$$V_{n_\mu n_\nu}^l = \int_0^\infty \phi_{n_\mu l}(r) \left(-\frac{Z}{r}\right) \phi_{n_\nu l}(r) dr$$

2.4.3 Kinetic Matrix Element

The kinetic matrix element

$$T_{\mu\nu} = \int \phi_\mu^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2\right) \phi_\nu(\mathbf{x}) d^3x$$

becomes

$$\begin{aligned}
T_{\mu\nu} &= T_{n_\mu l_\mu m_\mu n_\nu l_\nu m_\nu} = \int \frac{\phi_{n_\mu l_\mu}(r)}{r} Y_{l_\mu m_\mu}^*(\Omega) \left(\left(-\frac{1}{2}\nabla^2\right) \frac{\phi_{n_\nu l_\nu}(r)}{r} Y_{l_\nu m_\nu}(\Omega)\right) r^2 dr d\Omega = \\
&= \int \frac{\phi_{n_\mu l_\mu}(r)}{r} Y_{l_\mu m_\mu}^*(\Omega) \left(\left(-\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r} + \frac{l_\nu(l_\nu+1)}{2r^2}\right) \frac{\phi_{n_\nu l_\nu}(r)}{r} Y_{l_\nu m_\nu}(\Omega)\right) r^2 dr d\Omega = \\
&= \delta_{l_\mu l_\nu} \delta_{m_\mu m_\nu} \int_0^\infty \frac{\phi_{n_\mu l_\mu}(r)}{r} \left(\left(-\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r} + \frac{l_\mu(l_\mu+1)}{2r^2}\right) \frac{\phi_{n_\nu l_\nu}(r)}{r}\right) r^2 dr = \\
&= \delta_{l_\mu l_\nu} \delta_{m_\mu m_\nu} T_{\mu\nu}^{l_\mu}
\end{aligned}$$

where

$$\begin{aligned}
T_{n_\mu n_\nu}^l &= \int_0^\infty \frac{\phi_{n_\mu l}(r)}{r} \left(\left(-\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{1}{r} \frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} \right) \frac{\phi_{n_\nu l}(r)}{r} \right) r^2 dr = \\
&= \int_0^\infty \frac{\phi_{n_\mu l}(r)}{r} \left(\left(-\frac{1}{2r} \frac{\partial^2}{\partial r^2} r + \frac{l(l+1)}{2r^2} \right) \frac{\phi_{n_\nu l}(r)}{r} \right) r^2 dr = \\
&= \int_0^\infty \phi_{n_\mu l}(r) \left(-\frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{2r^2} \right) \phi_{n_\nu l}(r) dr = \\
&= \int_0^\infty \left(-\frac{1}{2} \phi_{n_\mu l}(r) \phi_{n_\nu l}''(r) + \phi_{n_\mu l}(r) \frac{l(l+1)}{2r^2} \phi_{n_\nu l}(r) \right) dr = \\
&= \int_0^\infty \left(\frac{1}{2} \phi_{n_\mu l}'(r) \phi_{n_\nu l}'(r) + \phi_{n_\mu l}(r) \frac{l(l+1)}{2r^2} \phi_{n_\nu l}(r) \right) dr
\end{aligned}$$

2.4.4 G Matrix Element

The G matrix is given by:

$$G_{\mu\nu} = \sum_{\alpha\beta} P_{\alpha\beta} (\langle \mu\beta | \nu\alpha \rangle - \frac{1}{2} \langle \mu\beta | \alpha\nu \rangle) = \sum_{\alpha\beta} P_{\alpha\beta} ((\mu\nu | \beta\alpha) - \frac{1}{2} (\mu\alpha | \beta\nu)) .$$

Now we use an identity that expresses the general two-particle integral $\langle \alpha\beta | \gamma\delta \rangle$ in terms of Slater integrals

$$R^k(i, j, k, l) = \int_0^\infty \int_0^\infty \frac{r_{\leq}^k}{r_{>}^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') dr dr'$$

and that is proven in the section “Two-particle Integral” below:

$$\begin{aligned}
\langle \alpha\beta | \gamma\delta \rangle &= \langle n_\alpha l_\alpha m_\alpha \ n_\beta l_\beta m_\beta | n_\gamma l_\gamma m_\gamma \ n_\delta l_\delta m_\delta \rangle = \langle n_\alpha l_\alpha m_\alpha \ n_\gamma l_\gamma m_\gamma | n_\beta l_\beta m_\beta \ n_\delta l_\delta m_\delta \rangle = \\
&= \sum_{k=\max(|l_\alpha-l_\gamma|, |l_\beta-l_\delta|, |m_\alpha-m_\gamma|)}^{\min(l_\alpha+l_\gamma, l_\beta+l_\delta)} c^k(l_\alpha, m_\alpha, l_\gamma, m_\gamma) c^k(l_\delta, m_\delta, l_\beta, m_\beta) \\
&\quad \delta_{m_\alpha+m_\beta-m_\gamma-m_\delta, 0} \\
&\quad R^k(n_\alpha l_\alpha, n_\beta l_\beta, n_\gamma l_\gamma, n_\delta l_\delta)
\end{aligned}$$

Next we need to express the density matrix:

$$\begin{aligned}
P_{\alpha\beta} &= 2 \sum_i C_{\alpha i} C_{\beta i} \\
P_{n_\alpha l_\alpha m_\alpha; n_\beta l_\beta m_\beta} &= 2 \sum_i C_{n_\alpha l_\alpha m_\alpha; n_i l_i m_i} C_{n_\beta l_\beta m_\beta; n_i l_i m_i} = \\
&= 2 \sum_i \delta_{l_i l_\alpha} \delta_{m_i m_\alpha} \delta_{l_i l_\beta} \delta_{m_i m_\beta} C_{n_\alpha n_i}^{l_i} C_{n_\beta n_i}^{l_i} = \\
&= 2 \delta_{l_\alpha l_\beta} \delta_{m_\alpha m_\beta} \sum_{n_i} C_{n_\alpha n_i}^{l_\alpha} C_{n_\beta n_i}^{l_\alpha} = \\
&= \delta_{l_\alpha l_\beta} \delta_{m_\alpha m_\beta} P_{n_\alpha n_\beta}^{l_\alpha}
\end{aligned}$$

where

$$P_{n_\alpha n_\beta}^l = 2 \sum_{n_i} C_{n_\alpha n_i}^l C_{n_\beta n_i}^l.$$

The sum over all occupied orbitals i can be written as:

$$\sum_i = \sum_{n_i l_i m_i} = \sum_{l=0}^{\infty} \sum_{m_l=-l}^l \sum_{n_l=1}^{\infty},$$

where the sum over l is the outer sum, both $m = m_l$ and $n = n_l$ depend on l . We get:

$$G_{\mu\nu} = G_{n_\mu l_\mu m_\mu n_\nu l_\nu m_\nu} = \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} P_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} (\langle \mu\beta | \nu\alpha \rangle - \frac{1}{2} \langle \mu\beta | \alpha\nu \rangle) = J_{\mu\nu} - K_{\mu\nu}$$

The first part is the direct term, the second part the exchange term. Let's treat the direct term first:

$$\begin{aligned} J_{\mu\nu} &= \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} P_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} \langle \mu\beta | \nu\alpha \rangle = \\ &= \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} P_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} \sum_{k=\max(|l_\mu-l_\nu|, |l_\beta-l_\alpha|, |m_\mu-m_\nu|)}^{\min(l_\mu+l_\nu, l_\beta+l_\alpha)} c^k(l_\mu, m_\mu, l_\nu, m_\nu) c^k(l_\alpha, m_\alpha, l_\beta, m_\beta) \\ &\quad \delta_{m_\mu+m_\beta-m_\nu-m_\alpha, 0} \\ &= \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} \delta_{l_\alpha l_\beta} \delta_{m_\alpha m_\beta} P_{n_\alpha n_\beta}^{l_\alpha} \sum_{k=\max(|l_\mu-l_\nu|, |l_\beta-l_\alpha|, |m_\mu-m_\nu|)}^{\min(l_\mu+l_\nu, l_\beta+l_\alpha)} c^k(l_\mu, m_\mu, l_\nu, m_\nu) c^k(l_\alpha, m_\alpha, l_\beta, m_\beta) \\ &\quad \delta_{m_\mu+m_\beta-m_\nu-m_\alpha, 0} \\ &= \sum_{n_\alpha n_\beta} \sum_{lm} P_{n_\alpha n_\beta}^l \sum_{k=\max(|l_\mu-l_\nu|, |m_\mu-m_\nu|)}^{\min(l_\mu+l_\nu, 2l)} c^k(l_\mu, m_\mu, l_\nu, m_\nu) c^k(l, m, l, m) \\ &\quad \delta_{m_\mu-m_\nu, 0} \\ &= R^k(n_\mu l_\mu, n_\beta l_\beta, n_\nu l_\nu, n_\alpha l_\alpha) = \\ &= \delta_{m_\mu m_\nu} \sum_{n_\alpha n_\beta} \sum_l P_{n_\alpha n_\beta}^l c^0(l_\mu, m_\mu, l_\nu, m_\nu) (2l+1) R^0(n_\mu l_\mu, n_\beta l_\beta, n_\nu l_\nu, n_\alpha l_\alpha) = \\ &= \delta_{l_\mu l_\nu} \delta_{m_\mu m_\nu} \sum_l (2l+1) \sum_{n_\alpha n_\beta} P_{n_\alpha n_\beta}^l R^0(n_\mu l_\mu, n_\beta l_\beta, n_\nu l_\nu, n_\alpha l_\alpha) \end{aligned}$$

$$\begin{aligned}
K_{\mu\nu} &= \frac{1}{2} \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} P_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} \langle \mu\beta | \alpha\nu \rangle = \\
&= \frac{1}{2} \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} P_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} \sum_{k=\max(|l_\mu-l_\alpha|, |l_\beta-l_\nu|, |m_\mu-m_\alpha|)}^{\min(l_\mu+l_\alpha, l_\beta+l_\nu)} c^k(l_\mu, m_\mu, l_\alpha, m_\alpha) c^k(l_\nu, m_\nu, l_\beta, m_\beta) \\
&\quad \delta_{m_\mu+m_\beta-m_\alpha-m_\nu, 0} \\
R^k(n_\mu l_\mu, n_\beta l_\beta, n_\alpha l_\alpha, n_\nu l_\nu) &= \\
&= \frac{1}{2} \sum_{n_\alpha l_\alpha m_\alpha n_\beta l_\beta m_\beta} \delta_{l_\alpha l_\beta} \delta_{m_\alpha m_\beta} P_{n_\alpha n_\beta}^{l_\alpha} \sum_{k=\max(|l_\mu-l_\alpha|, |l_\beta-l_\nu|, |m_\mu-m_\alpha|)}^{\min(l_\mu+l_\alpha, l_\beta+l_\nu)} c^k(l_\mu, m_\mu, l_\alpha, m_\alpha) c^k(l_\nu, m_\nu, l_\beta, m_\beta) \\
&\quad \delta_{m_\mu+m_\beta-m_\alpha-m_\nu, 0} \\
R^k(n_\mu l_\mu, n_\beta l_\beta, n_\alpha l_\alpha, n_\nu l_\nu) &= \\
&= \frac{1}{2} \delta_{m_\mu m_\nu} \sum_{n_\alpha n_\beta} \sum_{lm} P_{n_\alpha n_\beta}^l \sum_{k=\max(|l_\mu-l|, |l-l_\nu|, |m_\mu-m|)}^{\min(l_\mu+l, l+l_\nu)} c^k(l_\mu, m_\mu, l, m) c^k(l_\nu, m_\nu, l, m) \\
R^k(n_\mu l_\mu, n_\beta l, n_\alpha l, n_\nu l_\nu) &= \\
&= \frac{1}{2} \delta_{m_\mu m_\nu} \sum_{n_\alpha n_\beta} \sum_{lm} P_{n_\alpha n_\beta}^l \sum_{k=\max(|l_\mu-l|, |l-l_\nu|, |m_\mu-m|)}^{\min(l_\mu+l, l+l_\nu)} c^k(l_\mu, m_\mu, l, m) c^k(l_\nu, m_\mu, l, m) \\
R^k(n_\mu l_\mu, n_\beta l, n_\alpha l, n_\nu l_\nu) &=
\end{aligned}$$

Note: performing the sum over n_α and n_β we get:

$$\begin{aligned}
 G_{n_\mu n_\nu}^l &= \sum_{l'} 2(2l' + 1) \sum_{n'} \sum_{n_\alpha n_\beta} C_{n_\alpha n'}^{l'} C_{n_\beta n'}^{l'} \\
 &\left(R^0(n_\mu l, n_\beta l', n_\nu l, n_\alpha l') - \sum_{k=|l-l'|}^{l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^k(n_\mu l, n_\beta l', n_\alpha l', n_\nu l) \right) = \\
 &= \sum_{l'} 2(2l' + 1) \sum_{n'} \\
 &\left(R^0(n_\mu l, n' l', n_\nu l, n' l') - \sum_{k=|l-l'|}^{l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^k(n_\mu l, n' l', n' l', n_\nu l) \right)
 \end{aligned}$$

2.4.5 Two-particle Integral

We use the following functions for ψ :

$$\begin{aligned}
 \psi_i(\mathbf{x}) &= \frac{P_{n_1 l_1}(r)}{r} Y_{l_1 m_1}(\Omega) \\
 \psi_j(\mathbf{x}) &= \frac{P_{n'_1 l'_1}(r)}{r} Y_{l'_1 m'_1}(\Omega) \\
 \psi_k(\mathbf{x}) &= \frac{P_{n_2 l_2}(r)}{r} Y_{l_2 m_2}(\Omega) \\
 \psi_l(\mathbf{x}) &= \frac{P_{n'_2 l'_2}(r)}{r} Y_{l'_2 m'_2}(\Omega)
 \end{aligned}$$

And the multipole expansion:

$$\frac{1}{|\mathbf{x} - \mathbf{x}'|} = \sum_{k,q} \frac{r_{<}^k}{r_{>}^{k+1}} \frac{4\pi}{2k+1} Y_{kq}(\Omega) Y_{kq}^*(\Omega')$$

And we get:

$$\begin{aligned}
\langle ij|kl\rangle &= \langle ik|jl\rangle = \langle 11'|22'\rangle = \langle 12|1'2'\rangle = \\
&= \langle l_1 m_1 l_2 m_2 | \frac{1}{|\mathbf{x} - \mathbf{x}'|} | l'_1 m'_1 l'_2 m'_2 \rangle = \\
&= \int \frac{\psi_i^*(\mathbf{x}) \psi_j(\mathbf{x}) \psi_k^*(\mathbf{x}') \psi_l(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x d^3x' = \\
&= \int \frac{P_{n_1 l_1}(r)}{r} Y_{l_1 m_1}^*(\Omega) \frac{P_{n'_1 l'_1}(r)}{r} Y_{l'_1 m'_1}(\Omega) \frac{P_{n_2 l_2}(r')}{r'} Y_{l_2 m_2}^*(\Omega') \frac{P_{n'_2 l'_2}(r')}{r'} Y_{l'_2 m'_2}(\Omega') \\
&\quad \sum_{k,q} \frac{r_{\leq}^k}{r_{>}^{k+1}} \frac{4\pi}{2k+1} Y_{kq}(\Omega) Y_{kq}^*(\Omega') r^2 r'^2 dr dr' d\Omega d\Omega' = \\
&= \sum_{k,q} \int Y_{l_1 m_1}^*(\Omega) Y_{l'_1 m'_1}(\Omega) Y_{kq}(\Omega) d\Omega \int Y_{l_2 m_2}^*(\Omega') Y_{l'_2 m'_2}(\Omega') Y_{kq}^*(\Omega') d\Omega' \\
&\quad \int \frac{r_{\leq}^k}{r_{>}^{k+1}} \frac{4\pi}{2k+1} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' = \\
&= \sum_{k,q} (-1)^{m_1+m_2+q} \int Y_{l_1, -m_1}(\Omega) Y_{l'_1 m'_1}(\Omega) Y_{kq}(\Omega) d\Omega \int Y_{l_2, -m_2}(\Omega') Y_{l'_2 m'_2}(\Omega') Y_{k, -q}(\Omega') d\Omega' \\
&\quad \int \frac{r_{\leq}^k}{r_{>}^{k+1}} \frac{4\pi}{2k+1} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' = \\
&= \sum_{k,q} (-1)^{m_1+m_2+q} \sqrt{\frac{(2l_1+1)(2l'_1+1)(2k+1)}{4\pi}} \begin{pmatrix} l_1 & l'_1 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l'_1 & k \\ -m_1 & m'_1 & q \end{pmatrix} \\
&\quad \sqrt{\frac{(2l_2+1)(2l'_2+1)(2k+1)}{4\pi}} \begin{pmatrix} l_2 & l'_2 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ -m_2 & m'_2 & -q \end{pmatrix} \\
&\quad \int \frac{r_{\leq}^k}{r_{>}^{k+1}} \frac{4\pi}{2k+1} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' =
\end{aligned}$$

$$\begin{aligned}
&= \sum_k \sqrt{(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)} \begin{pmatrix} l_1 & l'_1 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ 0 & 0 & 0 \end{pmatrix} \\
&\quad \sum_{q=-k}^k (-1)^{m_1+m_2+q} \begin{pmatrix} l_1 & l'_1 & k \\ -m_1 & m'_1 & q \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ -m_2 & m'_2 & -q \end{pmatrix} \\
&\quad \int \frac{r_{\leq}^k}{r_{>}^{k+1}} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' = \\
&= \sum_{k=\max(|l_1-l'_1|, |l_2-l'_2|, |m_1-m'_1|)}^{\min(l_1+l'_1, l_2+l'_2)} \sqrt{(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)} \\
&\quad (-1)^{m_1+m'_2} \delta_{m_1+m_2-m'_1-m'_2, 0} \begin{pmatrix} l_1 & l'_1 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ 0 & 0 & 0 \end{pmatrix} \\
&\quad \begin{pmatrix} l_1 & l'_1 & k \\ -m_1 & m'_1 & m_1-m'_1 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ -m_2 & m'_2 & m_2-m'_2 \end{pmatrix} \\
&\quad \int \frac{r_{\leq}^k}{r_{>}^{k+1}} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr'
\end{aligned}$$

In the last step we used the fact that the $3j$ symbols are zero unless $-m_1 + m'_1 + q = 0$ and $-m_2 + m'_2 - q = 0$, from which it follows that $q = m_1 - m'_1 = -m_2 + m'_2$ and so one of the $3j$ symbols is zero unless $m_1 + m_2 - m'_1 - m'_2 = 0$, which is expressed by $\delta_{m_1+m_2-m'_1-m'_2, 0}$. Given this condition, the sum over q must be such that one q is equal to $m_1 - m'_1 = -m_2 + m'_2$, which means that $k \geq |m_1 - m'_1| = |m_2 - m'_2|$ otherwise the $3j$ symbols will be zero. Finally, k must also satisfy the conditions $|l_1 - l'_1| \leq k \leq l_1 + l'_1$ and $|l_2 - l'_2| \leq k \leq l_2 + l'_2$. The sign factor $(-1)^{m_1+m_2+q} = (-1)^{m_1+m_2+m_1-m'_1} = (-1)^{m_1+m_2-m_2+m'_2}$ is equal to both $(-1)^{m_1+m'_2}$ and $(-1)^{m_2-m'_1}$ so we just used the former.

We can write this using the c^k symbols as:

$$\begin{aligned}
(ij|kl) &= \sum_{k=\max(|l_1-l'_1|, |l_2-l'_2|, |m_1-m'_1|)}^{\min(l_1+l'_1, l_2+l'_2)} \sqrt{(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)} \\
&(-1)^{m_2-m'_2} (-1)^{-m_1} (-1)^{-m_2} \delta_{m_1+m_2-m'_1-m'_2, 0} \begin{pmatrix} l_1 & l'_1 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ 0 & 0 & 0 \end{pmatrix} \\
&\begin{pmatrix} l_1 & l'_1 & k \\ -m_1 & m'_1 & m_1-m'_1 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ -m_2 & m'_2 & m_2-m'_2 \end{pmatrix} \\
&\int \frac{r_{\leq}^k}{r_{>}^{k+1}} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' = \\
&= \sum_{k=\max(|l_1-l'_1|, |l_2-l'_2|, |m_1-m'_1|)}^{\min(l_1+l'_1, l_2+l'_2)} c^k(l_1, m_1, l'_1, m'_1) c^k(l_2, m_2, l'_2, m'_2) \\
&(-1)^{m_2-m'_2} \delta_{m_1+m_2-m'_1-m'_2, 0} \\
&\int \frac{r_{\leq}^k}{r_{>}^{k+1}} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' = \\
&= \sum_{k=\max(|l_1-l'_1|, |l_2-l'_2|, |m_1-m'_1|)}^{\min(l_1+l'_1, l_2+l'_2)} c^k(l_1, m_1, l'_1, m'_1) c^k(l'_2, m'_2, l_2, m_2) \\
&\delta_{m_1+m_2-m'_1-m'_2, 0} \\
&\int \frac{r_{\leq}^k}{r_{>}^{k+1}} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' =
\end{aligned}$$

$$\begin{aligned}
&= \sum_{k=\max(|l_1-l'_1|, |l_2-l'_2|, |m_1-m'_1|)}^{\min(l_1+l'_1, l_2+l'_2)} c^k(l_1, m_1, l'_1, m'_1) c^k(l'_2, m'_2, l_2, m_2) \\
&\quad \delta_{m_1+m_2-m'_1-m'_2, 0} \\
&\quad R^k(n_1 l_1, n_2 l_2, n'_1 l'_1, n'_2 l'_2)
\end{aligned}$$

This is the final formula, that was needed for expressing the G matrix in spherical symmetry. In this form it is also identical to the reference [43], page 175, equation (9).

In the last equation we have introduced the so called Slater integral by:

$$R^k(i, j, k, l) = \int_0^\infty \int_0^\infty \frac{r_{\leq}^k}{r_{>}^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') dr dr'$$

Another option, which was not used in this thesis, is to couple the angular momenta as follows:

$$\begin{aligned}
|l_1 l_2 LM\rangle &= \sum_{m_1 m_2} (l_1 m_1 l_2 m_2 | LM) |l_1 m_1\rangle |l_2 m_2\rangle = \\
&= \sum_{m_1 m_2} (-1)^{l_1-l_2+M} \sqrt{2L+1} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} |l_1 m_1\rangle |l_2 m_2\rangle
\end{aligned}$$

and we get for the matrix elements:

$$\begin{aligned}
&\langle l_1 l_2 LM | \frac{1}{|\mathbf{x} - \mathbf{x}'|} | l'_1 l'_2 L' M' \rangle = \\
&= \sum_{m_1 m_2} \sum_{m'_1 m'_2} (-1)^{l_1-l_2+l'_1-l'_2+M+M'} \sqrt{(2L+1)(2L'+1)} \\
&\quad \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & -M' \end{pmatrix} \\
&\quad \langle l_1 m_1 | \langle l_2 m_2 | \frac{1}{|\mathbf{x} - \mathbf{x}'|} | l'_1 m'_1 \rangle | l'_2 m'_2 \rangle =
\end{aligned}$$

$$\begin{aligned}
&= \sum_{m_1 m_2} \sum_{m'_1 m'_2} (-1)^{l_1 - l_2 + l'_1 - l'_2 + M + M'} \sqrt{(2L+1)(2L'+1)} \\
&\quad \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & -M' \end{pmatrix} \\
&\quad (ij|kl) = \\
&= \sum_{m_1 m_2} \sum_{m'_1 m'_2} (-1)^{l_1 - l_2 + l'_1 - l'_2 + M + M'} \sqrt{(2L+1)(2L'+1)} \\
&\quad \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & -M' \end{pmatrix} \\
&\quad \sum_k \sqrt{(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)} \begin{pmatrix} l_1 & l'_1 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ 0 & 0 & 0 \end{pmatrix} \\
&\quad \sum_{q=-k}^k (-1)^{m_1 + m_2 + q} \begin{pmatrix} l_1 & l'_1 & k \\ -m_1 & m'_1 & q \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ -m_2 & m'_2 & -q \end{pmatrix} \\
&\quad \int_{r_{>}^k}^{r_{\leq}^k} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' =
\end{aligned}$$

$$\begin{aligned}
&= \sum_{m_1 m_2} \sum_{m'_1 m'_2} (-1)^{l_1 - l_2 + l'_1 - l'_2} (2L + 1) \\
&\quad \delta_{MM'} \delta_{LL'} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l'_1 & l'_2 & L \\ m'_1 & m'_2 & -M \end{pmatrix} \\
&\quad \sum_k \sqrt{(2l_1 + 1)(2l'_1 + 1)(2l_2 + 1)(2l'_2 + 1)} \begin{pmatrix} l_1 & l'_1 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ 0 & 0 & 0 \end{pmatrix} \\
&\quad \sum_{q=-k}^k (-1)^{m_1 + m_2 + q} \begin{pmatrix} l_1 & l'_1 & k \\ -m_1 & m'_1 & q \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ -m_2 & m'_2 & -q \end{pmatrix} \\
&\quad \int \frac{r_{\leq}^k}{r_{>}^{k+1}} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' = \\
&= (-1)^{l_1 - l_2 + l'_1 - l'_2} (2L + 1) \\
&\quad \sum_k \sqrt{(2l_1 + 1)(2l'_1 + 1)(2l_2 + 1)(2l'_2 + 1)} \begin{pmatrix} l_1 & l'_1 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ 0 & 0 & 0 \end{pmatrix} \\
&\quad \delta_{MM'} \delta_{LL'} (-1)^{l_1 + l'_1 + L} \begin{Bmatrix} l_1 & l_2 & L \\ l'_2 & l'_1 & k \end{Bmatrix} \\
&\quad \int \frac{r_{\leq}^k}{r_{>}^{k+1}} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' = \\
&= \sum_k \int \frac{r_{\leq}^k}{r_{>}^{k+1}} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' \\
&(-1)^{L - l_2 - l'_2} (2L + 1) \delta_{MM'} \delta_{LL'} \sqrt{(2l_1 + 1)(2l'_1 + 1)(2l_2 + 1)(2l'_2 + 1)} \\
&\quad \begin{pmatrix} l_1 & l'_1 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l'_2 & l'_1 & k \end{Bmatrix} =
\end{aligned}$$

$$\begin{aligned}
&= \sum_k \int \frac{r_{\leq}^k}{r_{>}^{k+1}} P_{n_1 l_1}(r) P_{n'_1 l'_1}(r) P_{n_2 l_2}(r') P_{n'_2 l'_2}(r') dr dr' \\
&\quad (-1)^{l_1+l'_1+L}(2L+1) \\
&\quad \delta_{LL'} \delta_{MM'} \sqrt{(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)} \\
&\quad \begin{pmatrix} l_1 & k & l'_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k & l'_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l'_2 & l'_1 & k \end{Bmatrix}
\end{aligned}$$

Where we used the $6j$ symbol:

$$\begin{aligned}
&\begin{Bmatrix} l_1 & l_2 & L \\ l'_2 & l'_1 & k \end{Bmatrix} = \sum_{m_1 m_2 m'_1 m'_2 M q} (-1)^{l_1+l_2+l'_1+l'_2+L+k-m_1-m_2-m'_1-m'_2-M-q} \\
&\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l_1 & l'_1 & k \\ -m_1 & m'_1 & q \end{pmatrix} \begin{pmatrix} l'_2 & l'_1 & L \\ m'_2 & -m'_1 & M \end{pmatrix} \begin{pmatrix} l'_2 & l_2 & k \\ -m'_2 & -m_2 & -q \end{pmatrix} = \\
&= \sum_{m_1 m_2 m'_1 m'_2 M q} (-1)^{l_1+l_2+l'_1+l'_2+L+k-m_1-m_2-m'_1-m'_2-M-q} \\
&\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l_1 & l'_1 & k \\ -m_1 & m'_1 & q \end{pmatrix} \begin{pmatrix} l'_1 & l'_2 & L \\ m'_1 & -m'_2 & -M \end{pmatrix} (-1)^{l_2+l'_2+k} \times \\
&\quad \times \begin{pmatrix} l_2 & l'_2 & k \\ -m_2 & -m'_2 & -q \end{pmatrix} = \\
&= \sum_{m_1 m_2 m'_1 m'_2 q} \delta_{M, m'_1+m'_2} (-1)^{l_1+l'_1+L} (-1)^{m_1+m_2+q} \\
&\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l_1 & l'_1 & k \\ -m_1 & m'_1 & q \end{pmatrix} \begin{pmatrix} l'_1 & l'_2 & L \\ m'_1 & +m'_2 & -M \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & k \\ -m_2 & +m'_2 & -q \end{pmatrix}
\end{aligned}$$

Where we have renamed $-m'_2$ to m'_2 .

2.5 Radial Roothaan Equations

The Roothaan equations are:

$$\begin{aligned}
 \sum_{\nu} (T + V + G)_{\mu\nu} C_{\nu i} &= \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} \\
 \sum_{\nu} (T + V + G)_{n_{\mu} l_{\mu} m_{\mu} n_{\nu} l_{\nu} m_{\nu}} C_{n_{\nu} l_{\nu} m_{\nu} n_i l_i m_i} &= \epsilon_{n_i l_i m_i} \sum_{\nu} S_{n_{\mu} l_{\mu} m_{\mu} n_{\nu} l_{\nu} m_{\nu}} C_{n_{\nu} l_{\nu} m_{\nu} n_i l_i m_i} \\
 \sum_{\nu} (T + V + G)_{n_{\mu} l_{\mu} m_{\mu} n_{\nu} l_{\nu} m_{\nu}} \delta_{l_i l_{\nu}} \delta_{m_i m_{\nu}} C_{n_{\nu} n_i}^{l_i} &= \epsilon_{n_i l_i m_i} \sum_{\nu} S_{n_{\mu} l_{\mu} m_{\mu} n_{\nu} l_{\nu} m_{\nu}} \delta_{l_i l_{\nu}} \delta_{m_i m_{\nu}} C_{n_{\nu} n_i}^{l_i} \\
 \sum_{n_{\nu}} (T + V + G)_{n_{\mu} l_{\mu} m_{\mu} n_{\nu} l_i m_i} C_{n_{\nu} n_i}^{l_i} &= \epsilon_{n_i l_i m_i} \sum_{n_{\nu}} S_{n_{\mu} l_{\mu} m_{\mu} n_{\nu} l_i m_i} C_{n_{\nu} n_i}^{l_i} \\
 \delta_{l_{\mu} l_i} \delta_{m_{\mu} m_i} \sum_{n_{\nu}} (T + V + G)_{n_{\mu} n_{\nu}}^{l_i} C_{n_{\nu} n_i}^{l_i} &= \delta_{l_{\mu} l_i} \delta_{m_{\mu} m_i} \epsilon_{n_i l_i m_i} \sum_{n_{\nu}} S_{n_{\mu} n_{\nu}}^{l_i} C_{n_{\nu} n_i}^{l_i}
 \end{aligned}$$

The eigenvalues will be degenerate with respect to m_i and so the radial Roothaan equations are to be solved for each l :

$$\sum_{n_{\nu}} (T + V + G)_{n_{\mu} n_{\nu}}^l C_{n_{\nu} n_i}^l = \epsilon_{n_i l} \sum_{n_{\nu}} S_{n_{\mu} n_{\nu}}^l C_{n_{\nu} n_i}^l \quad (2.11)$$

These equations are also sometimes called the radial Roothaan-Hartree-Fock equations.

The matrices S^l , T^l , V^l and G^l were given in the previous section.

The total energy as given by various references can be expressed in several equivalent

forms:

$$\begin{aligned}
E &= \frac{1}{2} \sum_{\mu\nu} P_{\nu\mu} (H_{\mu\nu}^{\text{core}} + F_{\mu\nu}) = \\
&= \sum_{\mu\nu} P_{\nu\mu} (F_{\mu\nu} - \frac{1}{2} G_{\mu\nu}) = \\
&= \sum_{\mu\nu} \delta_{l_\mu l_\nu} \delta_{m_\mu m_\nu} P_{n_\mu n_\nu}^{l_\mu} \delta_{l_\mu l_\nu} \delta_{m_\mu m_\nu} (F - \frac{1}{2} G)_{n_\mu n_\nu}^{l_\mu} = \\
&= \sum_{l_\mu} \sum_{m_\mu} \sum_{n_\mu n_\nu} P_{n_\mu n_\nu}^{l_\mu} (F - \frac{1}{2} G)_{n_\mu n_\nu}^{l_\mu} = \\
&= \sum_{l_\mu} \sum_{n_\mu n_\nu} (2l_\mu + 1) P_{n_\mu n_\nu}^{l_\mu} (F - \frac{1}{2} G)_{n_\mu n_\nu}^{l_\mu} = \\
&= \sum_l \sum_{n_\mu n_\nu} (2l + 1) P_{n_\mu n_\nu}^l (F - \frac{1}{2} G)_{n_\mu n_\nu}^l = \\
&= \sum_l \sum_{n_\mu n_\nu} (2l + 1) \sum_n 2C_{n_\mu n}^l C_{n_\nu n}^l (F_{n_\mu n_\nu}^l - \frac{1}{2} G_{n_\mu n_\nu}^l) = \\
&= \sum_l \sum_{n_\mu n_\nu} (2l + 1) \sum_n 2C_{n_\mu n}^l C_{n_\nu n}^l \left(\epsilon_{nl} S_{n_\mu n_\nu}^l - \frac{1}{2} \sum_{l'} 2(2l' + 1) \sum_{n'} \right. \\
&\quad \left. \left(R^0(n_\mu l, n' l', n_\nu l, n' l') - \sum_{k=|l-l'|}^{l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^k(n_\mu l, n' l', n' l', n_\nu l) \right) \right) = \\
&= \sum_l \sum_n 2(2l + 1) \left(\epsilon_{nl} - \sum_{l'} \sum_{n'} (2l' + 1) (R^0(nl, n' l', nl, n' l') + \right. \\
&\quad \left. - \frac{1}{2} \sum_{k=|l-l'|}^{k=l+l'} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^k(nl, n' l', n' l', nl) \right)
\end{aligned}
\tag{2.12}$$

Any of these formulas can be used in a computer program.

2.6 Slater Type Orbitals (STO)

In this section we express the matrix elements in the STO basis. It turns out that all integrals that we need can be expressed in terms of the following two simple integrals (where $n, \zeta \geq 0$):

$$\int_0^\infty r^n e^{-\zeta r} dr = \int_0^\infty \left(\frac{x}{\zeta}\right)^n e^{-x} \frac{dx}{\zeta} = \frac{1}{\zeta^{n+1}} \int_0^\infty x^n e^{-x} dx = \frac{\Gamma(n+1)}{\zeta^{n+1}} = \frac{n!}{\zeta^{n+1}} \quad (2.13)$$

and

$$\int_u^\infty r^n e^{-\zeta r} dr = \frac{1}{\zeta^{n+1}} \int_{\zeta u}^\infty x^n e^{-x} dx = \frac{\Gamma(n+1, \zeta u)}{\zeta^{n+1}} = \frac{n!}{\zeta^{n+1}} e^{-\zeta u} \sum_{\nu=0}^n \frac{u^\nu \zeta^\nu}{\nu!}$$

where

$$\Gamma(n, x) = \int_x^\infty t^{n-1} e^{-t} dt = (n-1)! e^{-x} \sum_{\nu=0}^{n-1} \frac{x^\nu}{\nu!}$$

is the incomplete gamma function.

The STO basis function for the radial Schrödinger equation for $P(r)$ is:

$$P_{n\zeta}(r) = N_{n\zeta} r^n e^{-\zeta r} \quad (2.14)$$

Where the normalization constant $N_{n\zeta}$ is such that the STO orbital is normalized as the radial wavefunction $P(r)$:

$$1 = \int_0^\infty P_{n\zeta}^2(r) dr = N_{n\zeta}^2 \int_0^\infty r^{2n} e^{-2\zeta r} dr = N_{n\zeta}^2 \frac{(2n)!}{(2\zeta)^{2n+1}}$$

from which we get:

$$N_{n\zeta} = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}}$$

Note that for $R(r) = \frac{P(r)}{r}$ we get the following STO basis function:

$$R_{n\zeta}(r) = \frac{P_{n\zeta}(r)}{r} = N_{n\zeta} r^{n-1} e^{-\zeta r} \quad (2.15)$$

One uses either (2.14) or (2.15) depending on whether one solves the radial Schrödinger equation for P or for $R = \frac{P}{r}$.

2.6.1 Overlap Matrix Element

$$\begin{aligned} S_{ij} &= \int P_{n_i\zeta_i}(r) P_{n_j\zeta_j}(r) dr = \\ &= \int N_{n_i\zeta_i} r^{n_i} e^{-\zeta_i r} N_{n_j\zeta_j} r^{n_j} e^{-\zeta_j r} dr = \\ &= N_{n_i\zeta_i} N_{n_j\zeta_j} \int r^{n_i+n_j} e^{-(\zeta_i+\zeta_j)r} dr = \\ &= N_{n_i\zeta_i} N_{n_j\zeta_j} \frac{(n_i + n_j)!}{(\zeta_i + \zeta_j)^{n_i+n_j+1}} \end{aligned}$$

2.6.2 Potential Matrix Element

$$\begin{aligned}
 V_{ij} &= \int P_{n_i\zeta_i}(r) \left(-\frac{Z}{r}\right) P_{n_j\zeta_j}(r) dr = \\
 &= \int N_{n_i\zeta_i} r^{n_i} e^{-\zeta_i r} \left(-\frac{Z}{r}\right) N_{n_j\zeta_j} r^{n_j} e^{-\zeta_j r} dr = \\
 &= -Z N_{n_i\zeta_i} N_{n_j\zeta_j} \int r^{n_i+n_j-1} e^{-(\zeta_i+\zeta_j)r} dr = \\
 &= -Z N_{n_i\zeta_i} N_{n_j\zeta_j} \frac{(n_i+n_j-1)!}{(\zeta_i+\zeta_j)^{n_i+n_j}}
 \end{aligned}$$

2.6.3 Kinetic Matrix Element

$$\begin{aligned}
 T_{ij} &= \int \left(\frac{1}{2} P'_{n_i\zeta_i}(r) P'_{n_j\zeta_j}(r) + P_{n_i\zeta_i}(r) \frac{l(l+1)}{2r^2} P_{n_j\zeta_j}(r) \right) dr = \\
 &= \frac{1}{2} N_{n_i\zeta_i} N_{n_j\zeta_j} \int \left(\frac{d}{dr} (r^{n_i} e^{-\zeta_i r}) \frac{d}{dr} (r^{n_j} e^{-\zeta_j r}) + r^{n_i} e^{-\zeta_i r} \frac{l(l+1)}{r^2} r^{n_j} e^{-\zeta_j r} \right) dr = \\
 &= \frac{1}{2} N_{n_i\zeta_i} N_{n_j\zeta_j} \int \left((n_i r^{n_i-1} e^{-\zeta_i r} - \zeta_i r^{n_i} e^{-\zeta_i r}) (n_j r^{n_j-1} e^{-\zeta_j r} - \zeta_j r^{n_j} e^{-\zeta_j r}) + \right. \\
 &\quad \left. + l(l+1) r^{n_i+n_j-2} e^{-(\zeta_i+\zeta_j)r} \right) dr = \\
 &= \frac{1}{2} N_{n_i\zeta_i} N_{n_j\zeta_j} \int \left(\left(\frac{n_i n_j}{r^2} - \frac{n_i \zeta_j + n_j \zeta_i}{r} + \zeta_i \zeta_j \right) r^{n_i+n_j} e^{-(\zeta_i+\zeta_j)r} + \right. \\
 &\quad \left. + l(l+1) r^{n_i+n_j-2} e^{-(\zeta_i+\zeta_j)r} \right) dr = \\
 &= \frac{1}{2} N_{n_i\zeta_i} N_{n_j\zeta_j} \int \left((n_i n_j + l(l+1)) r^{n_i+n_j-2} e^{-(\zeta_i+\zeta_j)r} - (n_i \zeta_j + n_j \zeta_i) r^{n_i+n_j-1} e^{-(\zeta_i+\zeta_j)r} + \right. \\
 &\quad \left. + \zeta_i \zeta_j r^{n_i+n_j} e^{-(\zeta_i+\zeta_j)r} \right) dr = \\
 &= \frac{1}{2} N_{n_i\zeta_i} N_{n_j\zeta_j} \left((n_i n_j + l(l+1)) \frac{(n_i+n_j-2)!}{(\zeta_i+\zeta_j)^{n_i+n_j-1}} - (n_i \zeta_j + n_j \zeta_i) \frac{(n_i+n_j-1)!}{(\zeta_i+\zeta_j)^{n_i+n_j}} + \right. \\
 &\quad \left. + \zeta_i \zeta_j \frac{(n_i+n_j)!}{(\zeta_i+\zeta_j)^{n_i+n_j+1}} \right)
 \end{aligned}$$

2.6.4 Slater Integral

The Slater integral is

$$\begin{aligned}
 R^k(i, j, k, l) &= \int_0^\infty \int_0^\infty \frac{r_{\leq}^k}{r_{>}^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') dr dr' = \\
 &= \int_0^\infty dr \int_0^r dr' \frac{r'^k}{r^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') + \\
 &+ \int_0^\infty dr \int_r^\infty dr' \frac{r^k}{r'^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') = \\
 &= \int_0^\infty dr \int_0^r dr' \frac{r'^k}{r^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') + \\
 &+ \int_0^\infty dr' \int_0^{r'} dr \frac{r^k}{r'^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') = \\
 &= \int_0^\infty dr \int_0^r dr' \frac{r'^k}{r^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') + \\
 &+ \int_0^\infty dr \int_0^r dr' \frac{r'^k}{r^{k+1}} P_i(r') P_k(r') P_j(r) P_l(r) = \\
 &= R_{\triangle}^k(i, j, k, l) + R_{\triangle}^k(j, i, l, k)
 \end{aligned}$$

where $R_{\Delta}^k(i, j, k, l)$ is the integral over the lower triangle (assuming r is the x -axis and r' is the y -axis), that is $r > r'$:

$$\begin{aligned}
R_{\Delta}^k(i, j, k, l) &= \int_0^{\infty} dr \int_0^r dr' \frac{r'^k}{r^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') = \\
&= \int_0^{\infty} dr' \int_{r'}^{\infty} dr \frac{r'^k}{r^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') = \\
&= N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \int_0^{\infty} dr' \int_{r'}^{\infty} dr \frac{r'^k}{r^{k+1}} r^{n_i+n_k} r'^{n_j+n_l} e^{-(\zeta_i+\zeta_k)r} e^{-(\zeta_j+\zeta_l)r'} = \\
&= N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \int_0^{\infty} dr' r'^k r'^{n_j+n_l} e^{-(\zeta_j+\zeta_l)r'} \frac{(n_i+n_k-k-1)!}{(\zeta_i+\zeta_k)^{n_i+n_k-k}} e^{-(\zeta_i+\zeta_k)r'} \times \\
&\quad \times \sum_{\nu=0}^{n_i+n_k-k-1} \frac{r'^{\nu} (\zeta_i+\zeta_k)^{\nu}}{\nu!} = \\
&= N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \frac{(n_i+n_k-k-1)!}{(\zeta_i+\zeta_k)^{n_i+n_k-k}} \sum_{\nu=0}^{n_i+n_k-k-1} \frac{(n_j+n_l+k+\nu)! (\zeta_i+\zeta_k)^{\nu}}{\nu! (\zeta_i+\zeta_j+\zeta_k+\zeta_l)^{n_j+n_l+k+\nu+1}} = \\
&= N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \frac{(n_i+n_k-k-1)!}{(\zeta_i+\zeta_k)^{n_i+n_k-k}} H_{ijkl}^k
\end{aligned}$$

where:

$$H_{ijkl}^k = \sum_{\nu=0}^{n_i+n_k-k-1} \frac{(n_j+n_l+k+\nu)! (\zeta_i+\zeta_k)^{\nu}}{\nu! (\zeta_i+\zeta_j+\zeta_k+\zeta_l)^{n_j+n_l+k+\nu+1}}$$

The final formula for the Slater integral then is:

$$R^k(i, j, k, l) = N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \left(\frac{(n_i+n_k-k-1)!}{(\zeta_i+\zeta_k)^{n_i+n_k-k}} H_{ijkl}^k + \frac{(n_j+n_l-k-1)!}{(\zeta_j+\zeta_l)^{n_j+n_l-k}} H_{jilk}^k \right)$$

2.7 Gaussian Type Orbitals (GTO)

In this section we express the matrix elements in the GTO basis [19]. It turns out that all integrals that we need can be expressed in terms of the following simple integral (where

$n, \zeta \geq 0$):

$$\int_0^\infty r^n e^{-\zeta r^2} dr = \frac{1}{\sqrt{\zeta^{n+1}}} \int_0^\infty x^n e^{-x^2} dx = \frac{1}{2\sqrt{\zeta^{n+1}}} \int_0^\infty t^{\frac{n-1}{2}} e^{-t} dt = \frac{\Gamma(\frac{n+1}{2})}{2\zeta^{\frac{n+1}{2}}} = \quad (2.16)$$

$$= \begin{cases} (n-1)!! \sqrt{\frac{\pi}{2(2\zeta)^{n+1}}} & \text{for even } n \\ \frac{(\frac{n-1}{2})!}{2\sqrt{\zeta^{n+1}}} & \text{for odd } n \end{cases}$$

The GTO basis function for the radial Schrödinger equation for $P(r)$ is:

$$P_{n\zeta}(r) = N_{n\zeta} r^n e^{-\zeta r^2} \quad (2.17)$$

However, unlike STO, the GTO functions must satisfy the condition $n = l + 2i + 1$ where $i = 0, 1, 2, \dots$ (this condition is later used in (2.16) to determine whether n is even or odd).

The normalization constant $N_{n\zeta}$ is such that the GTO orbital is normalized as the radial wavefunction $P(r)$:

$$1 = \int_0^\infty P_{n\zeta}^2(r) dr = N_{n\zeta}^2 \int_0^\infty r^{2n} e^{-2\zeta r^2} dr = N_{n\zeta}^2 (2n-1)!! \sqrt{\frac{\pi}{2(4\zeta)^{2n+1}}}$$

from which we get:

$$N_{n\zeta} = \sqrt{\frac{1}{(2n-1)!!} \sqrt{\frac{2(4\zeta)^{2n+1}}{\pi}}}$$

Note that for $R(r) = \frac{P(r)}{r}$ we get the following GTO basis function:

$$R_{n\zeta}(r) = \frac{P_{n\zeta}(r)}{r} = N_{n\zeta} r^{n-1} e^{-\zeta r^2} \quad (2.18)$$

One uses either (2.14) or (2.15) depending on whether one solves the radial Schrödinger equation for P or for $R = \frac{P}{r}$.

2.7.1 Overlap Matrix Element

$$\begin{aligned}
 S_{ij} &= \int P_{n_i\zeta_i}(r)P_{n_j\zeta_j}(r)dr = \\
 &= \int N_{n_i\zeta_i}r^{n_i}e^{-\zeta_i r^2}N_{n_j\zeta_j}r^{n_j}e^{-\zeta_j r^2}dr = \\
 &= N_{n_i\zeta_i}N_{n_j\zeta_j} \int r^{n_i+n_j}e^{-(\zeta_i+\zeta_j)r^2}dr = \\
 &= N_{n_i\zeta_i}N_{n_j\zeta_j} \frac{\Gamma(\frac{n_i+n_j+1}{2})}{2(\zeta_i+\zeta_j)^{\frac{n_i+n_j+1}{2}}} = \\
 &= N_{n_i\zeta_i}N_{n_j\zeta_j}(n_i+n_j-1)!! \sqrt{\frac{\pi}{2(2\zeta_i+2\zeta_j)^{n_i+n_j+1}}}
 \end{aligned}$$

2.7.2 Potential Matrix Element

$$\begin{aligned}
 V_{ij} &= \int P_{n_i\zeta_i}(r) \left(-\frac{Z}{r}\right) P_{n_j\zeta_j}(r)dr = \\
 &= \int N_{n_i\zeta_i}r^{n_i}e^{-\zeta_i r^2} \left(-\frac{Z}{r}\right) N_{n_j\zeta_j}r^{n_j}e^{-\zeta_j r^2}dr = \\
 &= -ZN_{n_i\zeta_i}N_{n_j\zeta_j} \int r^{n_i+n_j-1}e^{-(\zeta_i+\zeta_j)r^2}dr = \\
 &= -ZN_{n_i\zeta_i}N_{n_j\zeta_j} \frac{\Gamma(\frac{n_i+n_j}{2})}{2(\zeta_i+\zeta_j)^{\frac{n_i+n_j}{2}}} = \\
 &= -ZN_{n_i\zeta_i}N_{n_j\zeta_j} \frac{\left(\frac{n_i+n_j-2}{2}\right)!}{2\sqrt{(\zeta_i+\zeta_j)^{n_i+n_j}}}
 \end{aligned}$$

2.7.3 Kinetic Matrix Element

$$\begin{aligned}
T_{ij} &= \int \left(\frac{1}{2} P'_{n_i \zeta_i}(r) P'_{n_j \zeta_j}(r) + P_{n_i \zeta_i}(r) \frac{l(l+1)}{2r^2} P_{n_j \zeta_j}(r) \right) dr = \\
&= \frac{1}{2} N_{n_i \zeta_i} N_{n_j \zeta_j} \int \left(\frac{d}{dr} (r^{n_i} e^{-\zeta_i r^2}) \frac{d}{dr} (r^{n_j} e^{-\zeta_j r^2}) + r^{n_i} e^{-\zeta_i r^2} \frac{l(l+1)}{r^2} r^{n_j} e^{-\zeta_j r^2} \right) dr = \\
&= \frac{1}{2} N_{n_i \zeta_i} N_{n_j \zeta_j} \int \left((n_i r^{n_i-1} e^{-\zeta_i r^2} - 2\zeta_i r^{n_i+1} e^{-\zeta_i r^2}) (n_j r^{n_j-1} e^{-\zeta_j r^2} - 2\zeta_j r^{n_j+1} e^{-\zeta_j r^2}) + \right. \\
&\quad \left. + l(l+1) r^{n_i+n_j-2} e^{-(\zeta_i+\zeta_j)r^2} \right) dr = \\
&= \frac{1}{2} N_{n_i \zeta_i} N_{n_j \zeta_j} \int \left(\left(\frac{n_i n_j}{r^2} - 2(n_i \zeta_j + n_j \zeta_i) + 4\zeta_i \zeta_j r^2 \right) r^{n_i+n_j} e^{-(\zeta_i+\zeta_j)r^2} + \right. \\
&\quad \left. + l(l+1) r^{n_i+n_j-2} e^{-(\zeta_i+\zeta_j)r^2} \right) dr = \\
&= \frac{1}{2} N_{n_i \zeta_i} N_{n_j \zeta_j} \int \left((n_i n_j + l(l+1)) r^{n_i+n_j-2} e^{-(\zeta_i+\zeta_j)r^2} - 2(n_i \zeta_j + n_j \zeta_i) r^{n_i+n_j} e^{-(\zeta_i+\zeta_j)r^2} + \right. \\
&\quad \left. + 4\zeta_i \zeta_j r^{n_i+n_j+2} e^{-(\zeta_i+\zeta_j)r^2} \right) dr = \\
&= \frac{1}{2} N_{n_i \zeta_i} N_{n_j \zeta_j} \left((n_i n_j + l(l+1)) \frac{\Gamma(\frac{n_i+n_j-1}{2})}{2(\zeta_i + \zeta_j)^{\frac{n_i+n_j-1}{2}}} - 2(n_i \zeta_j + n_j \zeta_i) \frac{\Gamma(\frac{n_i+n_j+1}{2})}{2(\zeta_i + \zeta_j)^{\frac{n_i+n_j+1}{2}}} + \right. \\
&\quad \left. + 4\zeta_i \zeta_j \frac{\Gamma(\frac{n_i+n_j+3}{2})}{2(\zeta_i + \zeta_j)^{\frac{n_i+n_j+3}{2}}} \right) dr = \\
&= \frac{1}{2} N_{n_i \zeta_i} N_{n_j \zeta_j} \left((n_i n_j + l(l+1)) (n_i + n_j - 3)!! \sqrt{\frac{\pi}{2(2\zeta_i + 2\zeta_j)^{n_i+n_j-1}}} + \right. \\
&\quad - 2(n_i \zeta_j + n_j \zeta_i) (n_i + n_j - 1)!! \sqrt{\frac{\pi}{2(2\zeta_i + 2\zeta_j)^{n_i+n_j+1}}} + \\
&\quad \left. + 4\zeta_i \zeta_j (n_i + n_j + 1)!! \sqrt{\frac{\pi}{2(2\zeta_i + 2\zeta_j)^{n_i+n_j+3}}} \right)
\end{aligned}$$

2.7.4 Slater Integral

We will need the following integral:

$$\int_u^\infty r^n e^{-\zeta r^2} dr = \frac{1}{2\zeta^{\frac{n+1}{2}}} \int_{\zeta u^2}^\infty x^{\frac{n-1}{2}} e^{-x} dx = \frac{\Gamma(\frac{n+1}{2}, \zeta u^2)}{2\zeta^{\frac{n+1}{2}}}$$

Just like for STO, we get:

$$R^k(i, j, k, l) = R_\Delta^k(i, j, k, l) + R_\Delta^k(j, i, l, k)$$

where $R_\Delta^k(i, j, k, l)$ is the integral over the lower triangle (assuming r is the x -axis and r' is the y -axis), that is $r > r'$:

$$\begin{aligned} R_\Delta^k(i, j, k, l) &= \int_0^\infty dr \int_0^r dr' \frac{r'^k}{r^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') = \\ &= \int_0^\infty dr' \int_{r'}^\infty dr \frac{r'^k}{r^{k+1}} P_i(r) P_k(r) P_j(r') P_l(r') = \\ &= N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \int_0^\infty dr' \int_{r'}^\infty dr \frac{r'^k}{r^{k+1}} r^{n_i+n_k} r'^{n_j+n_l} e^{-(\zeta_i+\zeta_k)r^2} e^{-(\zeta_j+\zeta_l)r'^2} = \\ &= N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \int_0^\infty dr' r'^k r'^{n_j+n_l} e^{-(\zeta_j+\zeta_l)r'^2} \frac{\Gamma(\frac{n_i+n_k-k}{2}, (\zeta_i+\zeta_k)r'^2)}{2(\zeta_i+\zeta_k)^{\frac{n_i+n_k-k}{2}}} = \\ &= N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \int_0^\infty dr' r'^k r'^{n_j+n_l} e^{-(\zeta_i+\zeta_j+\zeta_k+\zeta_l)r'^2} \frac{(\frac{n_i+n_k-k}{2} - 1)!}{2(\zeta_i+\zeta_k)^{\frac{n_i+n_k-k}{2}}} \times \\ &\quad \times \sum_{\nu=0}^{\frac{n_i+n_k-k-2}{2}} \frac{(\zeta_i+\zeta_k)^\nu r'^{2\nu}}{\nu!} = \end{aligned}$$

$$\begin{aligned}
&= N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \frac{\left(\frac{n_i+n_k-k}{2} - 1\right)!}{2(\zeta_i + \zeta_k)^{\frac{n_i+n_k-k}{2}}} \times \\
&\times \sum_{\nu=0}^{\frac{n_i+n_k-k-2}{2}} \frac{(\zeta_i + \zeta_k)^\nu}{\nu!} \frac{\Gamma\left(\frac{n_j+n_l+k+2\nu+1}{2}\right)}{2(\zeta_i + \zeta_j + \zeta_k + \zeta_l)^{\frac{n_j+n_l+k+2\nu+1}{2}}} = \\
&= N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \frac{\left(\frac{n_i+n_k-k}{2} - 1\right)!}{2(\zeta_i + \zeta_k)^{\frac{n_i+n_k-k}{2}}} \times \\
&\times \sum_{\nu=0}^{\frac{n_i+n_k-k-2}{2}} \frac{(\zeta_i + \zeta_k)^\nu}{\nu!} \frac{(n_j + n_l + k + 2\nu - 1)!! \sqrt{\pi}}{2^{\frac{n_j+n_l+k+2\nu+2}{2}} (\zeta_i + \zeta_j + \zeta_k + \zeta_l)^{\frac{n_j+n_l+k+2\nu+1}{2}}} = \\
&= N_{n_i \zeta_i} N_{n_j \zeta_j} N_{n_k \zeta_k} N_{n_l \zeta_l} \frac{\sqrt{\pi}}{2^{p+2} \sqrt{(\zeta_i + \zeta_j + \zeta_k + \zeta_l)^{2p+1}}} H_{ijkl}^k
\end{aligned}$$

where $p = \frac{n_i+n_j+n_k+n_l-2}{2}$ and:

$$H_{ijkl}^k = \sum_{\nu=0}^{\frac{n_i+n_k-k}{2}} \frac{(2p - 2\nu - 1)!! \left(\frac{n_i+n_k-k}{2}\right)! 2^\nu (\zeta_i + \zeta_j + \zeta_k + \zeta_l)^\nu}{(n_i + n_k - \nu)! (\lambda_i + \lambda_k)^{1+\nu}}$$

2.8 Occupation Numbers

This section elucidates the occupation numbers in spherical symmetry. We have a sum over N electron states like this:

$$\sum_{i=1}^N A_i(\mathbf{x}) = \sum_{nlms} A_{nlms}(\mathbf{x})$$

where $A_{nlms}(\mathbf{x})$ are some functions that depend on the state numbers (for example squares of the wavefunctions). Then there are two options — either there is a way to sum over the m and s degrees of freedom, so that the sum can be written exactly as:

$$\sum_{nlms} A_{nlms}(\mathbf{x}) = \sum_{nl(ms)} B_{nl}(\mathbf{x})$$

where B_{nl} (that don't depend on m and s) will in general be different to A_{nlms} , but the sum will be the same. Or we have to approximate the sum (for example by averaging over the angles, or in some other way) as:

$$\sum_{nlms} A_{nlms}(\mathbf{x}) \rightarrow \sum_{nl(ms)} B_{nl}(\mathbf{x})$$

In either case, the occupation numbers f_{nl} are simply the number of times the functions $B_{nl}(\mathbf{x})$ appear in the sum for the given n and l :

$$\sum_{nl(ms)} B_{nl}(\mathbf{x}) = \sum_{nl} f_{nl} B_{nl}(\mathbf{x})$$

So for closed shells atoms, it is always:

$$f_{nl} = 2(2l + 1)$$

because there are two spins, and $2l + 1$ possibilities for m , for open shell atoms, f_{nl} is anything between 0 and $2l + 1$.

2.8.1 Example I

As an example, let's say that after some calculation for closed shell systems we get exactly:

$$\sum_{nlms} A_{nlms}(\mathbf{x}) = \sum_{nl} 2(2l + 1) B_{nl}(\mathbf{x})$$

Then because there are exactly $2(2l + 1)$ states in the nl shell, we write the above as:

$$\sum_{nlms} A_{nlms}(\mathbf{x}) = \sum_{nl} 2(2l + 1) B_{nl}(\mathbf{x}) = \sum_{nl} f_{nl} B_{nl}(\mathbf{x})$$

Then we do similar calculation for the open shell system, and we have to use some approximations to get the following formula, where the $B_{nl}(\mathbf{x})$ happen to be exactly the same as for the closed shell system:

$$\sum_{nlms} A_{nlms}(\mathbf{x}) \rightarrow \sum_{nl(m)} 2B_{nl}(\mathbf{x})$$

Then we denote by f_{nl} the number of electrons in the shell nl (at least one of them will be open, for which nl we have $f_{nl} < 2(2l + 1)$), and we can write the above as:

$$\sum_{nlms} A_{nlms}(\mathbf{x}) \rightarrow \sum_{nl(m)} 2B_{nl}(\mathbf{x}) = \sum_{nl} f_{nl} B_{nl}(\mathbf{x})$$

2.8.2 Example II

The usual chemical occupation numbers for the uranium atom are:

$$f_{1l} = 2(2l + 1)$$

$$f_{2l} = 2(2l + 1)$$

$$f_{3l} = 2(2l + 1)$$

$$f_{4l} = 2(2l + 1)$$

$$f_{5l} = 2(2l + 1) \quad \text{for } l \leq 2$$

$$f_{53} = 3$$

$$f_{60} = 2$$

$$f_{61} = 6$$

$$f_{62} = 1$$

$$f_{70} = 2$$

So the $n = 5, l = 3$ and $n = 6, l = 2$ shells are open, all others are closed. By summing all these f_{nl} , we get 92 states as expected:

$$\sum_{nl} f_{nl} = 2 + (2 + 6) + (2 + 6 + 10) + (2 + 6 + 10 + 14) + (2 + 6 + 10) + \\ + 3 + 2 + 6 + 1 + 2 = 92$$

Code:

```
def f_nl(n, l):
    if n < 5 or (n == 5 and l <= 2):
        return 2*(2*l+1)
    else:
        d = {
            (5, 3): 3,
            (6, 0): 2,
            (6, 1): 6,
            (6, 2): 1,
            (7, 0): 2,
        }
        if (n, l) in d:
            return d[n, l]
        else:
            return 0

print "Sum f_nl =", sum([f_nl(n, l) for n in range(8) for l in range(n)])
```

prints:

Sum f_nl = 92

2.9 Radial Hartree-Fock Equations in Terms of Wavefunctions

The Roothaan-Hartree-Fock equations (2.11) are expressed in terms of basis functions. Another approach to express radial Hartree-Fock equations is in terms of radial wavefunctions. This can then be used to solve the radial Hartree-Fock equations numerically for example by finite difference method, shooting method, or formulate a continuous weak formulation to be solved by a finite element method.

We first introduce the Hartree screening functions that simplify many formulas in this section, then calculate the direct and exchange terms in spherical symmetry and finally express the radial Hartree-Fock equations in terms of radial wavefunctions.

2.9.1 Hartree Screening Functions

Hartree screening function $Y^k(f, r)$ is defined as:

$$Y^k(f, r) = r \int_0^\infty \frac{r'^k}{r'^{k+1}} f(r') dr'$$

and it occurs in many formulas in the Hartree-Fock theory, so this section shows how to calculate it. It depends on k and a function $f(r)$.

We first do the integral:

$$\begin{aligned} Y^k(f, r) &= r \int_0^\infty \frac{r'^k}{r'^{k+1}} f(r') dr' = r \int_0^r \frac{r'^k}{r'^{k+1}} f(r') dr' + r \int_r^\infty \frac{r'^k}{r'^{k+1}} f(r') dr' = \\ &= \frac{1}{r^k} \int_0^r x^k f(x) dx + r^{k+1} \int_r^\infty \frac{1}{x^{k+1}} f(x) dx = Z^k(r) + r^{k+1} \int_r^\infty \frac{1}{x^{k+1}} f(x) dx \end{aligned}$$

where:

$$\begin{aligned} Z^k(r) &= \frac{1}{r^k} \int_0^r x^k f(x) dx \\ \frac{dZ^k(r)}{dr} &= -\frac{k}{r} Z^k(r) + f(r) \\ Z^k(0) &= 0 \end{aligned}$$

Now we differentiate $Y^k(r)$:

$$\begin{aligned} \frac{dY^k(r)}{dr} &= \frac{dZ^k(r)}{dr} + \frac{k+1}{r} r^{k+1} \int_r^\infty \frac{1}{x^{k+1}} f(x) dx - f(r) = \\ &= -\frac{k}{r} Z^k(r) + f(r) + \frac{k+1}{r} r^{k+1} \int_r^\infty \frac{1}{x^{k+1}} f(x) dx - f(r) = \\ &= -\frac{k}{r} Z^k(r) + \frac{k+1}{r} r^{k+1} \int_r^\infty \frac{1}{x^{k+1}} f(x) dx = \\ &= -\frac{k}{r} Z^k(r) + \frac{k+1}{r} (Y^k(r) - Z^k(r)) = \\ &= -\frac{2k+1}{r} Z^k(r) + \frac{k+1}{r} Y^k(r) \end{aligned}$$

Also $Y^k(\infty) = Z^k(\infty)$, so we get the following set of first order differential equations with boundary conditions:

$$\begin{aligned} \left(\frac{d}{dr} - \frac{k+1}{r} \right) Y^k(r) &= -\frac{2k+1}{r} Z^k(r) \\ \left(\frac{d}{dr} + \frac{k}{r} \right) Z^k(r) &= f(r) \\ Y^k(\infty) &= Z^k(\infty) \\ Z^k(0) &= 0 \end{aligned}$$

One way to calculate the Hartree screening function is to integrate the second equation from the left using the boundary condition $Z^k(0) = 0$ and then integrate the first equation from the right, using the boundary condition $Y^k(\infty) = Z^k(\infty)$.

Another way is to obtain one second order equation. Expressing Z^k from the first equation:

$$\begin{aligned} Z^k(r) &= -\frac{r}{2k+1} \left(\frac{d}{dr} - \frac{k+1}{r} \right) Y^k(r) = \\ &= -\frac{r}{2k+1} \frac{dY^k(r)}{dr} + \frac{k+1}{2k+1} Y^k(r) \end{aligned}$$

and substituting into the second equation we get:

$$\begin{aligned} -\left(\frac{d}{dr} + \frac{k}{r} \right) \left(-\frac{r}{2k+1} \frac{dY^k(r)}{dr} + \frac{k+1}{2k+1} Y^k \right) &= f(r) \\ -\frac{r}{2k+1} \left(\frac{d^2}{dr^2} - \frac{k(k+1)}{r^2} \right) Y^k(r) &= f(r) \\ \left(-\frac{d^2}{dr^2} + \frac{k(k+1)}{r^2} \right) Y^k(r) &= \frac{2k+1}{r} f(r) \end{aligned}$$

With boundary condition on the left:

$$\begin{aligned} Z^k(0) &= \frac{k+1}{2k+1} Y^k(0) = 0 \\ Y^k(0) &= 0 \end{aligned}$$

and on the right:

$$\begin{aligned} Z^k(r) &= -\frac{r}{2k+1} \frac{dY^k(r)}{dr} + \frac{k+1}{2k+1} Y^k(r) = Y^k(r) \\ -\frac{r}{2k+1} \frac{dY^k(r)}{dr} - \frac{k}{2k+1} Y^k(r) &= 0 \\ \frac{dY^k(r)}{dr} + \frac{k}{r} Y^k(r) &= 0 \end{aligned}$$

which for $r \rightarrow \infty$ becomes:

$$\left. \frac{dY^k(r)}{dr} \right|_{r=\infty} = 0$$

but in practise, it's better to use the former Newton (Robin) boundary condition. We have obtained one second order equation for $Y^k(r)$

$$\left(-\frac{d^2}{dr^2} + \frac{k(k+1)}{r^2}\right) Y^k(r) = \frac{2k+1}{r} f(r)$$

with boundary conditions:

$$\begin{aligned} Y^k(0) &= 0 \\ \frac{dY^k(r)}{dr} + \frac{k}{r} Y^k(r) &= 0 \end{aligned}$$

The weak formulation is:

$$\int_0^{r_{max}} Y^{k'}(r) v'(r) + \frac{k(k+1)}{r^2} Y^k(r) v(r) dr - [Y^{k'}(r) v(r)]_0^{r_{max}} = \int_0^{r_{max}} \frac{2k+1}{r} f(r) v(r) dr$$

The boundary term can be simplified using the boundary conditions as:

$$\begin{aligned} -[Y^{k'}(r) v(r)]_0^{r_{max}} &= -Y^{k'}(r_{max}) v(r_{max}) + Y^{k'}(0) v(0) = -Y^{k'}(r_{max}) v(r_{max}) = \\ &= \frac{k}{r_{max}} Y^k(r_{max}) v(r_{max}) \end{aligned}$$

so we get

$$\begin{aligned} \int_0^{r_{max}} Y^{k'}(r) v'(r) + \frac{k(k+1)}{r^2} Y^k(r) v(r) dr + \frac{k}{r_{max}} Y^k(r_{max}) v(r_{max}) &= \\ &= \int_0^{r_{max}} \frac{2k+1}{r} f(r) v(r) dr \end{aligned}$$

where the test functions $v(r)$ have the constrain $v(0) = 0$ on the left boundary and no constrain on the right.

2.9.2 Hartree Potential in Spherical Symmetry

For both open and closed shell atoms we get exactly:

$$\begin{aligned}
 V_H(\mathbf{x}) &= \int \frac{n(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3y = \int \frac{\sum_{j=1}^Z |\psi_j(\mathbf{y})|^2}{|\mathbf{x} - \mathbf{y}|} d^3y = \\
 &= 2 \sum_{nlm} \int \frac{|Y_{lm}(\Omega')|^2 P_{nl}^2(r')}{|\mathbf{x} - \mathbf{y}|} d\Omega' dr' = \\
 &= 2 \sum_{nlm} \sum_{l'm'} \int \frac{r_{<}^{l'}}{r_{>}^{l'+1}} \frac{4\pi}{2l'+1} Y_{lm}^*(\Omega') Y_{lm}(\Omega') Y_{l'm'}^*(\Omega') Y_{l'm'}(\Omega') P_{nl}^2(r') d\Omega' dr' = \\
 &= 2 \sum_{nlm} \sum_{l'} \int \frac{r_{<}^{l'}}{r_{>}^{l'+1}} \frac{4\pi}{2l'+1} Y_{l'0}^*(\Omega) \sqrt{\frac{2l'+1}{4\pi}} c^{l'}(l, m, l, m) P_{nl}^2(r') dr' = \\
 &= 2 \sum_{nl} \sum_{l'=0}^{2l} \int \frac{r_{<}^{l'}}{r_{>}^{l'+1}} \sqrt{\frac{4\pi}{2l'+1}} Y_{l'0}^*(\Omega) \sum_m c^{l'}(l, m, l, m) P_{nl}^2(r') dr' = \\
 &= 2 \sum_{nl} \int \frac{1}{r_{>}} \sqrt{4\pi} Y_{00}^*(\Omega) \sum_m c^0(l, m, l, m) P_{nl}^2(r') dr' + \\
 &+ 2 \sum_{nl} \sum_{l'=1}^{2l} \int \frac{r_{<}^{l'}}{r_{>}^{l'+1}} \sqrt{\frac{4\pi}{2l'+1}} Y_{l'0}^*(\Omega) \sum_m c^{l'}(l, m, l, m) P_{nl}^2(r') dr' = \\
 &= \sum_{nl} 2 \sum_m c^0(l, m, l, m) \int \frac{1}{r_{>}} P_{nl}^2(r') dr' + \\
 &+ 2 \sum_{nl} \sum_{l'=1}^{2l} \int \frac{r_{<}^{l'}}{r_{>}^{l'+1}} \sqrt{\frac{4\pi}{2l'+1}} Y_{l'0}^*(\Omega) \sum_m c^{l'}(l, m, l, m) P_{nl}^2(r') dr' = \\
 &= \sum_{nl} 2 \sum_m \int \frac{1}{r_{>}} P_{nl}^2(r') dr' + \\
 &+ 2 \sum_{nl} \sum_{l'=1}^{2l} \int \frac{r_{<}^{l'}}{r_{>}^{l'+1}} \sqrt{\frac{4\pi}{2l'+1}} Y_{l'0}^*(\Omega) \sum_m c^{l'}(l, m, l, m) P_{nl}^2(r') dr' = \\
 &= \sum_{nl} f_{nl} \int \frac{1}{r_{>}} P_{nl}^2(r') dr' + \\
 &+ 2 \sum_{nl} \sum_{l'=1}^{2l} \sqrt{\frac{4\pi}{2l'+1}} Y_{l'0}^*(\Omega) \sum_m c^{l'}(l, m, l, m) \int \frac{r_{<}^{l'}}{r_{>}^{l'+1}} P_{nl}^2(r') dr'
 \end{aligned}$$

For closed shell atoms we use the fact, that

$$\sum_{m=-l}^l c''(l, m, l, m) = (2l + 1)\delta_{l'0}$$

and the second term disappears, and for open shell atoms we have to use the central field approximation: we average the integral for V_H over the angles:

$$V_H(\mathbf{x}) \rightarrow V_H(r) = \frac{1}{4\pi} \int V_H(\mathbf{x}) d\Omega$$

and using the fact, that

$$\int Y_{l'0}^*(\Omega) d\Omega = \sqrt{4\pi}\delta_{l'0}$$

the second term disappears as well. We got the same expression for both open shell (with central field approximation) and closed shell (no approximation) atoms. The radial charge density is:

$$n(r) = \frac{1}{4\pi} \sum_{nl} f_{nl} \left(\frac{P_{nl}(r)}{r} \right)^2$$

So we got:

$$V_H(r) = \sum_{nl} f_{nl} \int \frac{1}{r_{>}} P_{nl}^2(r') dr' = \int \frac{4\pi n(r') r'^2}{r_{>}} dr' = \frac{Y^0(4\pi n(r) r^2, r)}{r}$$

The Hartree screening function $Y^0(4\pi n(r) r^2, r)$ is given by the equation:

$$-\frac{d^2}{dr^2} Y^0(r) = \frac{1}{r} 4\pi n(r) r^2$$

So $V_H(r)$ satisfies the radial Poisson equation:

$$(V_H(r)r)'' = -\frac{1}{r}4\pi n(r)r^2$$

$$V_H''(r)r + 2V_H'(r) = -4\pi n(r)r$$

$$V_H''(r) + \frac{2}{r}V_H'(r) = -4\pi n(r)$$

2.9.3 Nonlocal Exchange Potential in Spherical Symmetry

Similarly, we calculate:

$$\begin{aligned}
& \sum_{j=1}^Z \int \frac{\psi_i(\mathbf{x}')\psi_j^*(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x' \psi_j(\mathbf{x}) = \\
& = \sum_{n'l'm'} \sum_{k,q} \int \frac{P_{nl}(r')}{r'} Y_{lm}(\Omega') \frac{P_{n'l'}(r')}{r'} Y_{l'm'}^*(\Omega') \frac{P_{n'l'}(r)}{r} Y_{l'm'}(\Omega) \times \\
& \quad \times \frac{r_{<}^k}{r_{>}^{k+1}} \frac{4\pi}{2k+1} Y_{kq}(\Omega) Y_{kq}^*(\Omega') r'^2 dr' d\Omega' = \\
& = \sum_{n'l'm'} \sum_{k,q} \frac{P_{n'l'}(r)}{r} \frac{4\pi}{2k+1} \int Y_{lm}(\Omega') Y_{l'm'}^*(\Omega') Y_{kq}^*(\Omega') Y_{l'm'}(\Omega) Y_{kq}(\Omega) d\Omega' \times \\
& \quad \times \int \frac{r_{<}^k}{r_{>}^{k+1}} P_{nl}(r') P_{n'l'}(r') dr' = \\
& = \sum_{n'l'} \sum_k \frac{P_{n'l'}(r)}{r} \frac{4\pi}{2k+1} \frac{2k+1}{4\pi} \sqrt{\frac{2l'+1}{2l+1}} c^k(l', 0, l, 0) Y_{lm}(\Omega) \int \frac{r_{<}^k}{r_{>}^{k+1}} P_{nl}(r') P_{n'l'}(r') dr' = \\
& = \frac{Y_{lm}(\Omega)}{r} \sum_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \sqrt{\frac{2l'+1}{2l+1}} c^k(l', 0, l, 0) \int \frac{r_{<}^k}{r_{>}^{k+1}} P_{nl}(r') P_{n'l'}(r') dr' P_{n'l'}(r) = \\
& = \frac{Y_{lm}(\Omega)}{r} \sum_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} (2l'+1) \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \int \frac{r_{<}^k}{r_{>}^{k+1}} P_{nl}(r') P_{n'l'}(r') dr' P_{n'l'}(r) = \\
& = \frac{Y_{lm}(\Omega)}{r} \sum_{n'l'} f_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \int \frac{r_{<}^k}{r_{>}^{k+1}} P_{nl}(r') P_{n'l'}(r') dr' P_{n'l'}(r)
\end{aligned}$$

Functions with different spins don't contribute to the sum, so there is no multiplication by 2. We assumed closed shells atoms (we summed over all m' in the above). We used the result of the integral of Example VI in the section Gaunt Coefficients from Appendix. We also used:

$$\sqrt{\frac{2l'+1}{2l+1}} c^k(l', 0, l, 0) = \sqrt{\frac{2l'+1}{2l+1}} \sqrt{(2l'+1)(2l+1)} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 = (2l'+1) \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \quad (2.19)$$

2.9.4 Radial Hartree-Fock Equations

Using the above integrals, the HF equations become:

$$-\frac{1}{2}P_{nl}''(r) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_H(r) \right) P_{nl}(r) +$$

$$- \sum_{n'l'} f_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \int \frac{r_{<}^k}{r_{>}^{k+1}} P_{nl}(r') P_{n'l'}(r') dr' P_{n'l'}(r) = \epsilon_{nl} P_{nl}(r)$$

with:

$$V_H(r) = \sum_{nl} f_{nl} \int \frac{1}{r_{>}} P_{nl}^2(r') dr'$$

Using the Hartree screening functions, the HF equations are:

$$-\frac{1}{2}P_{nl}''(r) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_H(r) \right) P_{nl}(r) +$$

$$- \sum_{n'l'} f_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{Y^k(P_{nl}(r) P_{n'l'}(r), r)}{r} P_{n'l'}(r) = \epsilon_{nl} P_{nl}(r)$$

with:

$$V_H(r) = \sum_{nl} f_{nl} \frac{Y^0(P_{nl}^2(r), r)}{r} = \frac{Y^0(4\pi n(r)r^2, r)}{r}$$

2.9.5 Total Energy

We start with the formula (2.12) and express it using Hartree screening functions:

$$\begin{aligned} E &= \sum_a 2(2l_a + 1) \times \\ &\times \left(\epsilon_a - \sum_b (2l_b + 1) \left(R_0(a, b, a, b) - \sum_l \frac{1}{2} \begin{pmatrix} l_a & l & l_b \\ 0 & 0 & 0 \end{pmatrix}^2 R_l(a, b, b, a) \right) \right) = \\ &= \sum_{nl} f_{nl} \times \\ &\times \left(\epsilon_{nl} - \sum_{n'l'} \frac{1}{2} f_{n'l'} \left(R_0(nl, n'l', nl, n'l') - \sum_k \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R_l(nl, n'l', n'l', nl) \right) \right) = \\ &= \sum_{nl} f_{nl} \epsilon_{nl} - \sum_{nl} \sum_{n'l'} \frac{1}{2} f_{nl} f_{n'l'} \left(\int_0^\infty P_{nl}^2(r) \frac{Y^0(P_{n'l'}^2(r), r)}{r} dr + \right. \\ &\left. - \sum_k \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \int_0^\infty P_{nl}(r) P_{n'l'}(r) \frac{Y^l(P_{nl}(r) P_{n'l'}(r), r)}{r} dr \right) = \end{aligned}$$

$$\begin{aligned}
&= \sum_{nl} f_{nl} \epsilon_{nl} - \frac{1}{2} \int_0^\infty 4\pi n(r) r^2 \frac{Y^0(4\pi n(r) r^2, r)}{r} dr + \\
&+ \sum_{nl} \sum_{n'l'} \frac{1}{2} f_{nl} f_{n'l'} \sum_k \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \int_0^\infty P_{nl}(r) P_{n'l'}(r) \frac{Y^l(P_{nl}(r) P_{n'l'}(r), r)}{r} dr = \\
&= \sum_{nl} f_{nl} \epsilon_{nl} - 2\pi \int_0^\infty V_H(r) n(r) r^2 dr + \\
&+ \sum_{nl} \sum_{n'l'} \frac{1}{2} f_{nl} f_{n'l'} \sum_k \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \int_0^\infty P_{nl}(r) P_{n'l'}(r) \frac{Y^l(P_{nl}(r) P_{n'l'}(r), r)}{r} dr .
\end{aligned}$$

Any of these equations can be used to calculate the total energy.

2.9.6 Example: Helium

For the helium atom, the only nonzero occupation numbers are:

$$f_{10} = 2$$

and the sum over $n'l'$ simplifies to:

$$\sum_{n'l'} f_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 = f_{10} \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}^2 = f_{10} \frac{1}{2} = 1$$

so we only need to solve for the $1s$ state and we get:

$$-\frac{1}{2} P_{10}''(r) + \left(-\frac{Z}{r} + V_H(r) \right) P_{10}(r) - \frac{Y^0(P_{10}(r) P_{10}(r), r)}{r} P_{10}(r) = \epsilon_{10} P_{10}(r)$$

with:

$$V_H(r) = 2 \frac{Y^0(P_{10}^2(r), r)}{r} = \frac{Y^0(4\pi n(r)r^2, r)}{r}$$

We can combine the equations:

$$-\frac{1}{2}P_{10}''(r) + \left(-\frac{Z}{r} + 2\frac{Y^0(P_{10}^2(r), r)}{r}\right) P_{10}(r) - \frac{Y^0(P_{10}^2(r), r)}{r} P_{10}(r) = \epsilon_{10} P_{10}(r)$$

and we obtain:

$$-\frac{1}{2}P_{10}''(r) + \left(-\frac{Z}{r} + \frac{Y^0(P_{10}^2(r), r)}{r}\right) P_{10}(r) = \epsilon_{10} P_{10}(r)$$

2.10 Finite Element Method (FEM)

This section derives the finite element weak formulation and describes how the Hartree-Fock equations can be solved using FEM.

The weak formulation is ($u(r) = P_{nl}(r)$):

$$\begin{aligned} & \int_0^\infty \left(\frac{1}{2} u'(r) v'(r) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_H(r) \right) u(r) v(r) \right) dr + \\ & - \sum_{n'l'} f_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \int_0^\infty v(r) P_{n'l'}(r) \frac{Y^k(u(r) P_{n'l'}(r), r)}{r} dr = \epsilon \int_0^\infty u(r) v(r) dr \end{aligned}$$

for closed shell atoms:

$$\begin{aligned}
& \int_0^\infty \left(\frac{1}{2} u'(r) v'(r) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_H(r) \right) u(r) v(r) \right) dr + \\
& - \sum_{n'l'} 2(2l'+1) \sum_{k=|l-l'|}^{k=l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \int_0^\infty v(r) P_{n'l'}(r) \frac{Y^k(u(r) P_{n'l'}(r), r)}{r} dr = \\
& = \epsilon \int_0^\infty u(r) v(r) dr
\end{aligned}$$

or (here we use the il index to label all functions u_i for the given l)

$$\begin{aligned}
& \int_0^\infty \left(\frac{1}{2} u'_{il}(r) v'(r) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_H(r) \right) u_{il}(r) v(r) \right) dr + \\
& - \sum_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \sqrt{\frac{2l'+1}{2l+1}} c^k(l, 0, l', 0) \int_0^\infty v(r) P_{n'l'}(r) \frac{Y^k(u_{il}(r) P_{n'l'}(r), r)}{r} dr = \\
& = \epsilon \int_0^\infty u_{il}(r) v(r) dr
\end{aligned}$$

Introducing radial basis $\phi_{\mu l}(r)$ (where μ, ν labels all basis functions for the given l):

$$\begin{aligned}
u_{il}(r) &= \sum_{\nu} C_{\nu il} \phi_{\nu l}(r) \\
v(r) &= \phi_{\mu l}(r)
\end{aligned}$$

we get (here i is again restricted for the subset corresponding to the given l):

$$\begin{aligned}
& \sum_{\nu} \int_0^\infty \left(\frac{1}{2} \phi'_{\mu l}(r) \phi'_{\nu l}(r) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_H(r) \right) \phi_{\mu l}(r) \phi_{\nu l}(r) \right) dr C_{\nu il} + \\
& - \sum_{\nu} \sum_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \sqrt{\frac{2l'+1}{2l+1}} c^k(l, 0, l', 0) \int_0^\infty \phi_{\mu l}(r) P_{n'l'}(r) \frac{Y^k(\phi_{\nu l}(r) P_{n'l'}(r), r)}{r} dr C_{\nu il} = \\
& = \epsilon \sum_{\nu} \int_0^\infty \phi_{\mu l}(r) \phi_{\nu l}(r) dr C_{\nu il}
\end{aligned}$$

This is the discrete weak formulation of the radial Hartree-Fock equations. Let us now show that this form is equivalent to Roothaan-Hartree-Fock equations. We write the above as:

$$\sum_{\nu} F_{\mu\nu}^l C_{\nu il} = \epsilon_i \sum_{\nu} S_{\mu\nu}^l C_{\nu il}$$

$$F_{\mu\nu}^l = H_{\mu\nu}^{\text{core}} + G_{\mu\nu}^l = T_{\mu\nu}^l + V_{\mu\nu}^l + G_{\mu\nu}^l$$

where

$$T_{\mu\nu}^l = \int_0^{\infty} \frac{1}{2} \phi'_{\mu l}(r) \phi'_{\nu l}(r) + \phi_{\mu l}(r) \frac{l(l+1)}{2r^2} \phi_{\nu l}(r) dr$$

$$V_{\mu\nu}^l = \int_0^{\infty} \phi_{\mu l}(r) \left(-\frac{Z}{r} \right) \phi_{\nu l}(r) dr$$

$$G_{\mu\nu}^l = \int_0^{\infty} \phi_{\mu l}(r) V_H(r) \phi_{\nu l}(r) dr +$$

$$- \sum_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \sqrt{\frac{2l'+1}{2l+1}} c^k(l, 0, l', 0) \int_0^{\infty} \phi_{\mu l}(r) P_{n'l'}(r) \frac{Y^k(\phi_{\nu l}(r) P_{n'l'}(r), r)}{r} dr$$

$$S_{\mu\nu}^l = \int_0^{\infty} \phi_{\mu l}(r) \phi_{\nu l}(r) dr$$

$$V_H(r) = \sum_{n'l'} 2(2l'+1) \frac{Y^0(P_{n'l'}^2(r), r)}{r}.$$

The indices $n'l'$ go over all occupied orbitals $P_{n'l'}$. We introduce the charge density:

$$n(\mathbf{x}) = 2 \sum_{k=1}^{N/2} |\psi_k(\mathbf{x})|^2 = 2 \sum_{nlm} |\psi_{nlm}(\mathbf{x})|^2 = 2 \sum_{nlm} \frac{P_{nl}^2(r)}{r^2} |Y_{lm}(\Omega)|^2 =$$

$$= 2 \sum_{nl} \frac{P_{nl}^2(r)}{r^2} \frac{2l+1}{4\pi} = \frac{1}{4\pi} \sum_{nl} 2(2l+1) \frac{P_{nl}^2(r)}{r^2} = n(r)$$

We also introduce the density matrix $P_{\alpha\beta}^l$ (where as before α, β run over basis functions

for the given l only):

$$P_{\alpha\beta}^l = 2 \sum_{nm} C_{\alpha n l m} C_{\beta n l m} = \sum_n 2(2l+1) C_{\alpha n l} C_{\beta n l}$$

where the $C_{\alpha n l}$ coefficients are the same for all m corresponding to the given l . The index n runs over all occupied states for the given l . We can write $n(r)$ as

$$\begin{aligned} P_{nl}(r) &= \sum_{\alpha} C_{\alpha n l} \phi_{\alpha l}(r) \\ n(r) &= \frac{1}{4\pi} \sum_{nl} 2(2l+1) \frac{P_{nl}^2(r)}{r^2} = \frac{1}{4\pi} \sum_{nl} 2(2l+1) \sum_{\alpha\beta} C_{\alpha n l} C_{\beta n l} \frac{\phi_{\alpha l}(r) \phi_{\beta l}(r)}{r^2} = \\ &= \frac{1}{4\pi} \sum_l \sum_{\alpha\beta} \frac{\phi_{\alpha l}(r) P_{\alpha\beta}^l \phi_{\beta l}(r)}{r^2} \end{aligned}$$

Finally we get:

$$V_H(r) = \sum_{nl} 2(2l+1) \frac{Y^0(P_{nl}^2(r), r)}{r} = \frac{Y^0(4\pi n(r) r^2, r)}{r} = \sum_l \sum_{\alpha\beta} P_{\alpha\beta}^l \frac{Y^0(\phi_{\alpha l}(r) \phi_{\beta l}(r), r)}{r}$$

and

$$\begin{aligned} \int_0^\infty \phi_{\mu l}(r) V_H(r) \phi_{\nu l}(r) dr &= \sum_{l'} \sum_{\alpha\beta} P_{\alpha\beta}^{l'} \int_0^\infty \phi_{\mu l}(r) \phi_{\nu l}(r) \frac{Y^0(\phi_{\alpha l'}(r) \phi_{\beta l'}(r), r)}{r} dr = \\ &= \sum_{l'} \sum_{\alpha\beta} P_{\alpha\beta}^{l'} R^0(\mu l, \beta l', \nu l, \alpha l') \end{aligned}$$

and

$$\begin{aligned}
& - \sum_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} \sqrt{\frac{2l'+1}{2l+1}} c^k(l, 0, l', 0) \int_0^\infty \phi_{\mu l}(r) P_{n'l'}(r) \frac{Y^k(\phi_{\nu l}(r) P_{n'l'}(r), r)}{r} dr = \\
& = - \sum_{n'l'} \sum_{k=|l-l'|}^{k=l+l'} 2(2l'+1)^{\frac{1}{2}} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{\alpha\beta} C_{\alpha n'l'} C_{\beta n'l'} \times \\
& \quad \times \int_0^\infty \phi_{\mu l}(r) \phi_{\alpha l'}(r) \frac{Y^k(\phi_{\nu l}(r) \phi_{\beta l'}(r), r)}{r} dr = \\
& = -\frac{1}{2} \sum_{l'} \sum_{\alpha\beta} P_{\alpha\beta}^{l'} \sum_{k=|l-l'|}^{k=l+l'} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^k(\mu l, \beta l', \alpha l', \nu l)
\end{aligned}$$

So we get our final equation for $G_{\mu\nu}^l$:

$$\begin{aligned}
G_{\mu\nu}^l &= \sum_{l'} \sum_{\alpha\beta} P_{\alpha\beta}^{l'} R^0(\mu l, \beta l', \nu l, \alpha l') + \\
& - \frac{1}{2} \sum_{l'} \sum_{\alpha\beta} P_{\alpha\beta}^{l'} \sum_{k=|l-l'|}^{k=l+l'} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^k(\mu l, \beta l', \alpha l', \nu l) = \\
& = \sum_{l'=0}^{\infty} \sum_{\alpha\beta} P_{\alpha\beta}^{l'} \left(R^0(\mu l, \beta l', \nu l, \alpha l') - \frac{1}{2} \sum_{k=|l-l'|}^{k=l+l'} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^k(\mu l, \beta l', \alpha l', \nu l) \right)
\end{aligned}$$

The density matrix is zero if there are no occupied orbitals for the given l' . As we can see, all the matrices T , V , S and G are identical to the Roothaan-Hartree-Fock results.

We use the spectral element method, which uses Lagrange interpolation polynomials and Gauss-Lobatto integration [47]. This method is also sometimes called discrete variable representation [49], [48], [50]. We can also use Gauss-Legendre integration points.

2.11 4-Index Transformation

The 4-index transformation is a way to convert the two-particle integrals over basis functions $(\alpha\beta|\gamma\delta)$ into two-particle integrals over atomic (or molecular) orbitals $(ij|kl)$:

$$(ij|kl) = \sum_{\alpha\beta\gamma\delta} C_{\alpha i} C_{\beta j} C_{\gamma k} C_{\delta l} (\alpha\beta|\gamma\delta)$$

See for example [11] for more details.

2.12 Many Body Single-Particle Green's Function

In this section we present all equations that are needed to perform Green function calculations in the second order.

The self energy up to a second order is given by:

$$\Sigma_{ij}(E) = \sum_{ars} \frac{(ir|as)(2(jr|as) - (js|ar))}{E + \epsilon_a - \epsilon_r - \epsilon_s} + \sum_{abr} \frac{(ia|br)(2(ja|br) - (jb|ar))}{E + \epsilon_r - \epsilon_a - \epsilon_b}$$

The a, b are occupied orbitals, r, s are virtual orbitals. The Dyson equation is:

$$\mathbf{G}(E) = \mathbf{G}_0(E) + \mathbf{G}_0(E)\Sigma(E)\mathbf{G}(E) \quad (2.20)$$

where

$$\mathbf{G}_0(E) = \frac{1}{E - \boldsymbol{\epsilon}} = \sum_k \frac{|k\rangle \langle k|}{E - \epsilon_k}$$

$$\mathbf{G}(E) = \frac{1}{E - \mathbf{E}} = \sum_k \frac{|k_{int}\rangle \langle k_{int}|}{E - E_k}$$

The ϵ_k and $|k\rangle$ are HF energies and eigenvectors, E_k and $|k_{int}\rangle$ are interacting energies and eigenvectors. The matrix ϵ is a diagonal matrix of the ϵ_k eigenvalues, \mathbf{E} is a diagonal matrix of the E_k eigenvalues. Any Green's function $\mathbf{G}(E)$ (interacting or not) can be written using the spectral density function $\mathbf{A}(z)$ as follows:

$$\begin{aligned}\mathbf{G}(E) &= \frac{1}{E - \epsilon} = \sum_k \frac{|k\rangle \langle k|}{E - \epsilon_k} = \\ &= \sum_k \int_{-\infty}^{\infty} \frac{|k\rangle \langle k|}{E - z} \delta(z - \epsilon_k) dz = \\ &= \int_{-\infty}^{\infty} \frac{\mathbf{A}(z)}{E - z} dz\end{aligned}$$

where

$$\begin{aligned}\mathbf{A}(z) &= \sum_k |k\rangle \langle k| \delta(z - \epsilon_k) = \\ &= \sum_k |k\rangle \langle k| \lim_{\eta \rightarrow 0} \frac{\eta}{\pi} \frac{1}{(z - \epsilon_k)^2 + \eta^2} = \\ &= \sum_k |k\rangle \langle k| \lim_{\eta \rightarrow 0} \frac{i}{2\pi} \left(\frac{1}{z - \epsilon_k + i\eta} - \frac{1}{z - \epsilon_k - i\eta} \right) = \\ &= \lim_{\eta \rightarrow 0} \frac{i}{2\pi} (\mathbf{G}(z + i\eta) - \mathbf{G}(z - i\eta))\end{aligned}$$

From (2.20) we get:

$$\begin{aligned}\frac{1}{\mathbf{G}_0(E)} \mathbf{G}(E) &= 1 + \Sigma(E) \mathbf{G}(E) \\ \frac{1}{\mathbf{G}_0(E)} &= \frac{1}{\mathbf{G}(E)} + \Sigma(E) \\ \mathbf{G}(E) &= \frac{1}{\frac{1}{\mathbf{G}_0(E)} - \Sigma(E)} = \frac{1}{E - \epsilon - \Sigma(E)}\end{aligned}$$

The poles E_k of the Green's function $\mathbf{G}(E)$ are then given by:

$$D(E) = \det(E - \epsilon - \Sigma(E)) = 0$$

or equivalently:

$$(\Sigma(E_k) + \epsilon) |v\rangle = E_k |v\rangle$$

and from the theory of matrices:

$$\begin{aligned} \text{Tr} \frac{1}{E - \mathbf{h}} &= \text{Tr} \frac{\frac{\partial}{\partial E}(E - \mathbf{h})}{E - \mathbf{h}} = \text{Tr} \frac{\partial}{\partial E} \log(E - \mathbf{h}) = \frac{\partial}{\partial E} \text{Tr} \log(E - \mathbf{h}) = \\ &= \frac{\partial}{\partial E} \log |\det(E - \mathbf{h})| = \frac{1}{\det(E - \mathbf{h})} \frac{\partial \det(E - \mathbf{h})}{\partial E} \end{aligned}$$

one obtains that

$$G_{ij}(E) = (-1)^{i+j+1} \frac{\partial \log D(E)}{\partial (\Sigma(E_k) + \epsilon)_{ji}}$$

and

$$\text{Tr} \mathbf{G}(E) = \sum_k G_{kk}(E) = \frac{\partial \log |D(E)|}{\partial E}$$

The number of particles N can be calculated as follows (a are occupied orbitals, k are all

orbitals):

$$\begin{aligned}
 N &= \sum_a |\langle \mathbf{r}|a\rangle|^2 = \\
 &= \sum_a \langle \mathbf{r}|a\rangle \langle a|\mathbf{r}\rangle = \\
 &= \text{Tr} \sum_a |a\rangle \langle a| = \\
 &= \frac{1}{2\pi i} \text{Tr} \int_C \sum_k \frac{|k\rangle \langle k|}{E - E_k} dE = \\
 &= \frac{1}{2\pi i} \int_C \text{Tr} \mathbf{G}(E) dE = \\
 &= \frac{1}{2\pi i} \int_C \frac{\partial \log |D(E)|}{\partial E} dE
 \end{aligned}$$

The contour C only encloses poles E_a corresponding to occupied orbitals a . Similarly for the total energy E_{tot} :

$$\begin{aligned}
 E_{tot} &= \sum_a E_a |\langle \mathbf{r}|a\rangle|^2 = \\
 &= \sum_a \langle \mathbf{r}|a\rangle E_a \langle a|\mathbf{r}\rangle = \\
 &= \text{Tr} \sum_a |a\rangle E_a \langle a| = \\
 &= \frac{1}{2\pi i} \text{Tr} \int_C \sum_k \frac{|k\rangle \langle k|}{E - E_k} E dE = \\
 &= \frac{1}{2\pi i} \int_C \text{Tr} \mathbf{G}(E) E dE = \\
 &= \frac{1}{2\pi i} \int_C \frac{\partial \log |D(E)|}{\partial E} E dE
 \end{aligned}$$

For doubly filled orbitals we multiply the expressions by 2.

2.13 Radial Density Functional Theory (DFT)

Since we give results obtained with DFT in the Unscreened Results section, we present here the standard formulas for atomic (radial) DFT. A general overview of DFT is given for example in [10] and [9]. In this section we only state the radial Kohn-Sham equations, that are needed to solve atomic problems using DFT.

2.13.1 Kohn-Sham Equations

For spherically symmetric potentials, we write all eigenfunctions as:

$$\psi_{nlm} = R_{nl}Y_{lm}$$

and we need to solve the following Kohn-Sham equations:

$$-\frac{1}{2}R_{nl}'' - \frac{1}{r}R_{nl}' + \left(V + \frac{l(l+1)R}{2r^2}\right)R_{nl} = \epsilon_{nl}R_{nl}$$

With normalization:

$$\int R_{nl}^2 r^2 dr = 1$$

For Schroedinger equation, the charge density is calculated by adding all “(n, l, m)” states together, counting each one twice (for spin up and spin down):

$$n(\mathbf{r}) = \sum_{nlm} 2|\psi_{nlm}|^2 = \sum_{nlm} R_{nl}^2 2|Y_{lm}|^2 = \sum_{nl} R_{nl}^2 2 \sum_m |Y_{lm}|^2 = \frac{1}{4\pi} \sum_{nl} f_{nl} R_{nl}^2$$

where we have introduced the occupation numbers f_{nl} by

$$f_{nl} = 4\pi \sum_m |Y_{lm}|^2$$

Normalization of the charge density is:

$$\begin{aligned} Z &= \int n(\mathbf{r}) d^3x = \int n(r) r^2 d\Omega dr = 4\pi \int n(r) r^2 dr = \\ &= 4\pi \int \frac{1}{4\pi} \sum_{nl} f_{nl} R_{nl}^2 r^2 d\Omega dr = \\ &= \sum_{nl} f_{nl} \int R_{nl}^2 r^2 dr = \\ &= \sum_{nl} f_{nl} \end{aligned}$$

So we can see, that it must hold:

$$\sum_{nl} f_{nl} = Z$$

where Z is the atomic number (number of electrons), and as such, f_{nl} are indeed the occupation numbers (integers). The factor 4π is explicitly factored out, as it cancels with the spherical harmonics: assuming all m states are occupied, this can be simplified to:

$$f_{nl} = 4\pi \sum_m |Y_{lm}|^2 = 4\pi \frac{2l+1}{4\pi} = 2(2l+1)$$

We can also use this machinery to prescribe “chemical occupation numbers”, that don’t necessarily correspond to the DFT ground state. For example for the uranium atom we get:

$$f_{1l} = 2(2l + 1)$$

$$f_{2l} = 2(2l + 1)$$

$$f_{3l} = 2(2l + 1)$$

$$f_{4l} = 2(2l + 1)$$

$$f_{5l} = 2(2l + 1) \quad l \leq 2$$

$$f_{53} = 3$$

$$f_{60} = 2$$

$$f_{61} = 6$$

$$f_{62} = 1$$

$$f_{70} = 2$$

By summing all these f_{nl} , we get 92 as expected:

$$\begin{aligned} \sum_{nl} f_{nl} &= 2 + (2 + 6) + (2 + 6 + 10) + (2 + 6 + 10 + 14) + (2 + 6 + 10) + \\ &\quad + 3 + 2 + 6 + 1 + 2 = 92 \end{aligned}$$

But this isn’t the DFT ground state, because some KS energies are skipped, for example there is only one state for $n = 6, l = 2$, but there are nine more states with the same energy — instead two more states are occupied in $n = 7, l = 0$, but those have higher energy. So this corresponds to an excited DFT state, which is strictly speaking not physically valid in the DFT formalism. But in practice this approach is often used. One can also prescribe

fractional occupation numbers (in the Dirac case).

2.13.2 Poisson Equation

Poisson equation becomes:

$$V_H''(r) + \frac{2}{r}V_H'(r) = -4\pi n(r)$$

2.13.3 Total Energy

The total energy is given by:

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + V[n]$$

where

$$\begin{aligned} T_s[n] &= \sum_{nl} f_{nl} \epsilon_{nl} - \int (V_H(r) + V_{xc}(r) + v(r))_{in} n(r) d^3r = \\ &= \sum_{nl} f_{nl} \epsilon_{nl} - \int \left(V_H(r) + V_{xc}(r) - \frac{Z}{r} \right)_{in} n(r) d^3r \\ E_H[n] &= \frac{1}{2} \int V_H(r) n(r) d^3r \\ E_{xc}[n] &= \int \epsilon_{xc}(r; n) n(r) d^3r \\ V[n] &= \int v(r) n(r) d^3r = - \int \frac{Z}{r} n(r) d^3r \end{aligned}$$

performing the angular integrations we obtain:

$$\begin{aligned}
 T_s[n] &= \sum_{nl} f_{nl} \epsilon_{nl} - 4\pi \int \left(V_H(r) + V_{xc}(r) - \frac{Z}{r} \right)_{in} n(r) r^2 dr \\
 E_H[n] &= 2\pi \int V_H(r) n(r) r^2 dr \\
 E_{xc}[n] &= 4\pi \int \epsilon_{xc}(r; n) n(r) r^2 dr \\
 V[n] &= -4\pi \int \frac{Z}{r} n(r) r^2 dr = -4\pi Z \int n(r) r dr
 \end{aligned}$$

We can also express everything using the charge density $\rho(r) = -n(r)$:

$$\begin{aligned}
 T_s[n] &= \sum_{nl} f_{nl} \epsilon_{nl} + 4\pi \int \left(V_H(r) + V_{xc}(r) - \frac{Z}{r} \right)_{in} \rho(r) r^2 dr \\
 E_H[n] &= -2\pi \int V_H(r) \rho(r) r^2 dr \\
 E_{xc}[n] &= -4\pi \int \epsilon_{xc}(r; n) \rho(r) r^2 dr \\
 V[n] &= 4\pi \int \frac{Z}{r} \rho(r) r^2 dr = 4\pi Z \int \rho(r) r dr
 \end{aligned}$$

2.13.4 Asymptotic of Radial Schrödinger and Dirac Equations

In solving the atomic Kohn-Sham equations, one possible numerical method is a shooting method, which needs to start with a proper asymptotic at the origin. Below we describe the correct asymptotic for both Schrödinger and Dirac equations. The present approach is directly applicable to the Dirac equation, so we also show the asymptotic for the radial Dirac equation.

Schrödinger

The radial Schrödinger equation is:

$$P''(r) + 2 \left(E - V(r) - \frac{l(l+1)}{2r^2} \right) P(r) = 0$$

$$Q(r) = P'(r)$$

For $r \rightarrow \infty$, assuming $V(r) \rightarrow 0$ we get:

$$P''(r) + 2EP(r) = 0$$

And the asymptotic is:

$$P(r) = e^{-\sqrt{-2E}r}$$

$$Q(r) = P'(r) = -\sqrt{-2E}e^{-\sqrt{-2E}r}$$

For $r \rightarrow 0$ and assuming that $V(r)$ can be neglected compared to the $\frac{l(l+1)}{2r^2}$ term (for example $V(r) = -Z/r + O(1)$ is acceptable) we get:

$$P''(r) - \frac{l(l+1)}{r^2}P(r) = 0$$

And the asymptotic is:

$$P(r) = r^{l+1}$$

$$Q(r) = (l+1)r^l$$

Dirac

The Dirac equation is:

$$H = \begin{pmatrix} V(r) + c^2 & c \left(-\frac{d}{dr} + \frac{\kappa}{r} \right) \\ c \left(\frac{d}{dr} + \frac{\kappa}{r} \right) & V(r) - c^2 \end{pmatrix}$$

$$H \begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = W \begin{pmatrix} P(r) \\ Q(r) \end{pmatrix}$$

Where the relativistic energy $W = E + c^2$. In terms of the nonrelativistic energy it becomes:

$$H_{nonrel} = \begin{pmatrix} V(r) & c \left(-\frac{d}{dr} + \frac{\kappa}{r} \right) \\ c \left(\frac{d}{dr} + \frac{\kappa}{r} \right) & V(r) - 2c^2 \end{pmatrix}$$

$$H_{nonrel} \begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = E \begin{pmatrix} P(r) \\ Q(r) \end{pmatrix}$$

For $r \rightarrow \infty$, assuming $V(r) \rightarrow 0$ we get:

$$H = \begin{pmatrix} c^2 & -c \frac{d}{dr} \\ c \frac{d}{dr} & -c^2 \end{pmatrix}$$

and in terms of $P(r)$ and $Q(r)$:

$$c^2 P - c Q' = W P$$

$$c P' - c^2 Q = W Q$$

let's put the derivatives on the left hand side:

$$cP' = (W + c^2)Q$$

$$cQ' = -(W - c^2)P$$

write a second order equation:

$$c^2 P'' = (W + c^2)cQ' = -(W + c^2)(W - c^2)P = -(W^2 - c^4)P$$

and finally we get:

$$P'' + \frac{W^2 - c^4}{c^2}P = 0$$

$$Q = \frac{c}{W + c^2}P'$$

The asymptotic is:

$$P(r) = e^{-\sqrt{\frac{c^4 - W^2}{c^2}}r}$$

$$Q(r) = \frac{c}{W + c^2} \left(-\sqrt{\frac{c^4 - W^2}{c^2}} \right) e^{-\sqrt{\frac{c^4 - W^2}{c^2}}r} = -\sqrt{\frac{c^2 - W}{c^2 + W}} e^{-\sqrt{\frac{c^4 - W^2}{c^2}}r}$$

We can also write it in terms of E :

$$P(r) = e^{-\sqrt{-2E - \left(\frac{E}{c}\right)^2}r}$$

$$Q(r) = -\sqrt{-\frac{E}{E + 2c^2}}P(r)$$

For $r \rightarrow 0$ we write the full equations:

$$(V + c^2)P - cQ' + c\frac{\kappa}{r}Q = WP$$

$$cP' + c\frac{\kappa}{r}P + (V - c^2)Q = WQ$$

The we assume $P(r) = r^\beta$ and use the second equation to express $Q(r)$:

$$Q(r) = \frac{cP' + c\frac{\kappa}{r}P}{W - V + c^2} = \frac{c\beta r^{\beta-1} + c\frac{\kappa}{r}r^\beta}{W - V + c^2} = r^{\beta-1} \frac{c(\beta + \kappa)}{W - V + c^2}$$

We can always write any potential as $V(r) = -\frac{Z(r)}{r}$ and we get:

$$Q(r) = r^{\beta-1} \frac{c(\beta + \kappa)}{W + \frac{Z(r)}{r} + c^2} = r^\beta \frac{c(\beta + \kappa)}{Z(r) + (W + c^2)r}$$

If $Z(r) \rightarrow Z$ as $r \rightarrow 0$ then the term $(W + c^2)r$ goes to zero and we get:

$$Q(r) = r^\beta \frac{c(\beta + \kappa)}{Z}$$

If $Z(r) \rightarrow Z_1 r$, then we get:

$$Q(r) = r^\beta \frac{c(\beta + \kappa)}{Z_1 r + (W + c^2)r} = r^{\beta-1} \frac{c(\beta + \kappa)}{Z_1 + W + c^2}$$

If $Z(r) \sim r^3$ (harmonic oscillator) or $Z(r) \sim r^2$, then the $Z(r)$ term goes to zero and we get:

$$Q(r) = r^{\beta-1} \frac{c(\beta + \kappa)}{W + c^2}$$

2.14 Systematic Convergence of STO and GTO Bases

A perhaps not so well known feature of STO and GTO bases is the fact that they can be made systematically convergent towards the exact answer for the ground state Hartree-Fock calculation. This section gives an overview of the convergence algorithm.

2.14.1 GTO and STO Completeness

The mathematical framework was given by Klahn in 1985 in papers [36] and [35]. It is shown there (see [36], eq. (29) and (30)) that the following set of N GTO basis functions:

$$\sqrt{r} e^{-\zeta_n^N r^2}$$

for $n = 1, 2, 3, \dots, N$ and $\zeta_n^N > 0$ is asymptotically complete in $L^2(0, \infty)$ if and only if the following condition holds for the exponents as we increase the number of basis functions $N \rightarrow \infty$:

$$\lim_{N \rightarrow \infty} \sum_{n=1}^N \frac{\zeta_n^N}{1 + (\zeta_n^N)^2} = \infty \quad (2.21)$$

It is furthermore shown that the following set of N STO basis functions:

$$e^{-\zeta_n^N r}$$

for $n = 1, 2, 3, \dots, N$ and $\zeta_n^N > 0$ is asymptotically complete in $L^2(0, \infty)$ if and only if the condition (2.21) holds.

The condition (2.21) can also be reformulated in various other ways, see the papers for more details. The task is now to provide a systematic construction of GTO and STO bases to satisfy this condition and thus provide systematic convergence. One way to do that is using a so called even-tempered basis.

2.14.2 Even-tempered Bases

An even-tempered (ET) basis is defined by making a special choice for the exponents ζ_n^N :

$$\zeta_n^N = \alpha_N (\beta_N)^n$$

where $\alpha_N > 0$ and $\beta_N > 0$. The whole basis for a given N then only depends on two parameters α_N and β_N (as opposed to a general basis which depends on N usually distinct parameters ζ_n^N). The paper [36] shows that a necessary condition for this basis to satisfy (2.21) (and thus being asymptotically complete) is:

$$\lim_{N \rightarrow \infty} \beta_N = 1$$

and also shows that this condition is sufficient if furthermore one of the following additional conditions is fulfilled for all $N = 1, 2, 3, \dots$:

1. $\beta_N > 1$ and $\alpha_N < \alpha' < \infty$

or

2. $\beta_N < 1$ and $\alpha_N > \alpha'' > 0$

or

3. $0 < \alpha'' < \alpha_N < \alpha' < \infty$

One of the first widely cited publications on even-tempered bases is [37] from 1979, which uses the choice 1. The article provides a good motivation why that should work using Gaussian integral transforms, as well as gives empirical evidence from numerical studies. The Klahn papers [36] and [35] put this onto a firm mathematical ground.

In order to systematically converge the even-tempered basis, we need to find a formula (preferably) for updating the coefficients α_N and β_N as we increase the basis from N to $N + 1$ such that the necessary and sufficient condition is asymptotically satisfied. There are obviously many ways to do that, but one particular construction has worked well [38], [44]: by imposing even more restrictions on α_N and β_N while still satisfying the convergence criterion stated above, we can require:

$$\alpha \rightarrow 0; \beta \rightarrow 1; \beta^N \rightarrow \infty$$

from which it follows

$$\log \alpha \rightarrow -\infty; \log \beta \rightarrow 0; N \log \beta \rightarrow \infty$$

Which is satisfied for example by:

$$\alpha \sim (\beta - 1)^a$$

$$\log \beta \sim N^b$$

where $a > 0$ and $-1 < b < 0$. By taking the log of both sides we get:

$$\log \alpha_N = a \log(\beta_N - 1) + a'$$

$$\log \log \beta_N = b \log N + b'$$

The constants a , b , a' and b' are independent of N . Writing these equations for $N - 1$ we get:

$$\log \alpha_{N-1} = a \log(\beta_{N-1} - 1) + a'$$

$$\log \log \beta_{N-1} = b \log(N - 1) + b'$$

and subtracting from the above, we obtain:

$$\begin{aligned} \beta_N &= (\beta_{N-1})^{\left(\frac{N}{N-1}\right)^b} \\ \alpha_N &= \alpha_{N-1} \left(\frac{\beta_N - 1}{\beta_{N-1} - 1} \right)^a \end{aligned} \tag{2.22}$$

This construction provides a systematic choice of the exponents. Reference [38] recommends $a = 0.5$ and $b = -0.5$ for s -states and $a = 0.6$ and $b = -0.45$ for p -states based on the numerical results of [37], but any values satisfying $a > 0$ and $-1 < b < 0$ must eventually converge, because they satisfy the convergence condition (but they might not converge as fast). Note that due to its construction, the equation (2.22) is not the only possible way to update the coefficients α_N and β_N , indeed a more general way has been proposed in [39], but even the simplest update formula (2.22) seems to work well in most cases as suggested by [37].

In practice, one starts from some preoptimized even-tempered basis for the given N and then one updates α and β in each iteration using the equation (2.22). The basis must converge towards the complete basis (exact Hartree-Fock limit). The update works for both STO and GTO.

For molecular calculations, the reference [40] shows by numerical examples that one can reuse the even-tempered bases that were optimized for the individual atoms.

2.14.3 Rate of Convergence

Now when completeness is established, the next question is to ask about the rate of convergence. All empirical evidence in [37], [40], [38] as well as our own results in this thesis seem to suggest that the convergence is exponential with increasing N . A theoretical study [41] shows that Laguerre polynomials converge exponentially (using L^2 projections) towards any function that has power series expansion about the origin, and has also an exponential decay at ∞ (citing: “This is the exponential convergence which we believe is typical of all problems wherein the trial functions are similar in kind to the function to be fitted, but are different only in details of the shape.”). As shown in [41], the situation is more complicated for the variational approximations to solutions of Schrödinger’s equation, because one has to study the solutions of the complete Hamiltonian. The article shows that for explicitly correlated Hylleraas-type wavefunctions the convergence is not always exponential, neither it is for the s -wave electron-hydrogen scattering at zero energy and other problems. However, all these examples are two electron systems with a two-particle Hamiltonian and the convergence rate is then determined by cusps and singularities of the wavefunction (citing: “the slower power rate of convergence results when the trial functions do not have the same analytical behavior as the function being represented.”).

On the other hand, for a ground state radial Hartree-Fock calculation, where the exact radial wavefunction has a simple power expansion at origin and exponential decay at infinity, the article seems to suggest that the STO basis should converge exponentially, as indeed seems to be the case given our numerical results.

For GTO basis, several theoretical studies have been made as well. For example the papers [42] and [46] seem to establish that the convergence of even-tempered GTO bases is also exponential. A recent review article [45] is comparing STO and GTO.

2.15 Screened Hartree-Fock

In this section we derive equations that implement screening in the Hartree-Fock matrix elements. The idea is that the results presented here can then be used in the usual way in any post Hartree-Fock calculation that is based on the HF matrix elements.

For convenience, let us repeat the radial Roothaan-Hartree-Fock equations for closed shell atoms [33], [34]:

$$\sum_{n_\nu} (T + V + G)_{n_\mu n_\nu}^l C_{n_\nu n_i}^l = \epsilon_{n_i l} \sum_{n_\nu} S_{n_\mu n_\nu}^l C_{n_\nu n_i}^l ,$$

where the orbitals $P_{n_i l}(r)$ are given in terms of judiciously selected basis functions $\phi_{n_\nu l}(r)$:

$$P_{n_i l}(r) = \sum_{n_\nu} C_{n_\nu n_i}^l \phi_{n_\nu l}(r) .$$

Here the $\epsilon_{n_i l}$ are the orbital eigenenergies; the $C_{n_\nu n_i}^l$ are the coefficients of the eigenvector corresponding to the $(n_i l)$ orbital. The matrix $T_{n_\mu n_\nu}^l$ is the kinetic term given by:

$$T_{n_\mu n_\nu}^l = \int_0^\infty \left(\frac{1}{2} \phi'_{n_\mu l}(r) \phi'_{n_\nu l}(r) + \phi_{n_\mu l}(r) \frac{l(l+1)}{2r^2} \phi_{n_\nu l}(r) \right) dr ,$$

the matrix $V_{n_\mu n_\nu}^l$ is the electron-nuclei potential term given by:

$$V_{n_\mu n_\nu}^l = \int_0^\infty \phi_{n_\mu l}(r) V_{en}(r) \phi_{n_\nu l}(r) dr , \quad (2.23)$$

which for the Coulomb potential is the well-known potential

$$V_{en}(r) = -\frac{Z}{r} . \quad (2.24)$$

The matrix $S_{n_\mu n_\nu}^l$ contains all the overlap matrix elements of the type:

$$S_{n_\mu n_\nu}^l = \int_0^\infty \phi_{n_\mu l}(r) \phi_{n_\nu l}(r) dr.$$

Finally the matrix $G_{n_\mu n_\nu}^l$ is the electron-electron interaction term:

$$G_{n_\mu n_\nu}^l = \sum_{l'} 2(2l' + 1) \sum_{n'} \sum_{n_\alpha n_\beta} C_{n_\alpha n'}^{l'} C_{n_\beta n'}^{l'} \left(R^0(n_\mu l, n_\beta l', n_\nu l, n_\alpha l') \right. \\ \left. - \sum_{k=|l-l'|}^{l+l'} \frac{1}{2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^k(n_\mu l, n_\beta l', n_\alpha l', n_\nu l) \right).$$

The index l' runs over the orbitals in occupied shells. $R^k(a, b, c, d)$ is the Slater integral over the real basis functions $\phi_{nl}(r)$

$$R^k(a, b, c, d) = \int_0^\infty \int_0^\infty \phi_a(r_1) \phi_b(r_2) V_k(r_1, r_2) \phi_c(r_1) \phi_d(r_2) dr_1 dr_2, \quad (2.25)$$

the indices a, b, c and d extend over all combinations of (nl) and for the Coulomb potential the function $V_k(r_1, r_2)$ is given by:

$$V_k(r_1, r_2) = \frac{r_{<}^k}{r_{>}^{k+1}}, \quad (2.26)$$

where $r_{<} = \min(r_1, r_2)$, $r_{>} = \max(r_1, r_2)$.

The screening in plasma is a correlated many-body effect given in the lowest order by the Debye-Hückel potential between an ion and an electron [20], [23], [22]:

$$V(r) = -\frac{Ze^2}{r} e^{-\frac{r}{D}}.$$

Here $D = \sqrt{k_B T_e / 4\pi e^2 n_e}$ is the Debye screening length. T_e and n_e are the plasma electron

temperature and density, k_B is the Boltzmann constant and Z is the ion charge. The Debye theory is limited to static screening.

In the presence of Debye screening, the two modifications to the Roothaan equations which make this a challenging problem is that the electron-nuclei potential in (2.23) is now given by:

$$V_{en}(r) = -\frac{Ze^{-\frac{r}{D_{en}}}}{r} \quad (2.27)$$

and the electron-electron interaction potential is given by:

$$V_{ee}(|\mathbf{r}_1 - \mathbf{r}_2|) = +\frac{e^{-\frac{|\mathbf{r}_1 - \mathbf{r}_2|}{D_{ee}}}}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (2.28)$$

which changes the $V_k(r_1, r_2)$ function in the Slater integral (2.25), that now becomes [16]:

$$\begin{aligned} V_k(r_1, r_2) &= \frac{2k+1}{2} \int_{-1}^1 \frac{e^{-\frac{|\mathbf{r}_1 - \mathbf{r}_2|}{D_{ee}}}}{|\mathbf{r}_1 - \mathbf{r}_2|} P_k(\cos \theta) d \cos \theta = \\ &= \frac{2k+1}{2r_1 r_2} \int_{|r_1 - r_2|}^{r_1 + r_2} e^{-\frac{r}{D_{ee}}} P_k\left(\frac{r_1^2 - r^2 + r_2^2}{2r_1 r_2}\right) dr. \end{aligned} \quad (2.29)$$

Here the $P_k(x)$ are Legendre polynomials. The integral (2.29) can be evaluated analytically as [25]:

$$V_k(r_1, r_2) = (2k+1) \frac{I_{k+\frac{1}{2}}\left(\frac{r_{<}}{D_{ee}}\right)}{\sqrt{r_{<}}} \frac{K_{k+\frac{1}{2}}\left(\frac{r_{>}}{D_{ee}}\right)}{\sqrt{r_{>}}} \quad (2.30)$$

where $I_{k+\frac{1}{2}}(r)$ and $K_{k+\frac{1}{2}}(r)$ are the modified Bessel functions of the first and second kind.

In the limit $D_{en} \rightarrow \infty$ and $D_{ee} \rightarrow \infty$ (pure Coulomb interaction) we obtain the Coulomb

case $V_k(r_1, r_2) \rightarrow \frac{r^k}{r^{k+1}}$ (using asymptotic forms of the modified Bessel functions around $r = 0$) regaining equations (2.26) from (2.30) and (2.24) from (2.27).

Now we need to accurately evaluate the function $V_k(r_1, r_2)$ using either the equation (2.29) or (2.30). The method proposed in [16] is to use Legendre expansion for (2.29). That method suffers from numerical cancellations for high D_{ee} so we simply evaluate $V_k(r_1, r_2)$ using (2.30). This method depends on fast and accurate evaluation of the modified Bessel functions of half integer order for all arguments from zero to infinity. For half integer order the functions are given by an analytic formula involving hyperbolic trigonometric functions and a polynomial [30]. This formula also suffers from numerical cancellation for small arguments of the function $I_{k+\frac{1}{2}}$, so one has to use its hypergeometric series representation for arguments smaller than a certain threshold [30]. However, the problem is that summing a series is quite slow, so we have chosen a different route and implemented the modified Bessel functions in terms of a rational approximation, which provides very accurate results and it is also efficient at the same time. See the Appendix for more details and a provided Fortran code.

Another problem is that for large $r_1 = r_2$, the function $I_{k+\frac{1}{2}}(r)$ exponentially grows while the function $K_{k+\frac{1}{2}}(r)$ exponentially decays, so the product of the two eventually becomes numerically unstable. To remedy this issue, we factor the exponentials out and calculate them separately.

Once we can accurately evaluate the function $V_k(r_1, r_2)$, we need to calculate the Slater integral (2.25). The method proposed in [16] is exploiting the analytic structure of $V_k(r_1, r_2)$ and then for the special case of the Slater Type Orbitals basis functions it gives a final formula that uses Gauss-Laguerre quadrature for the lower and upper triangular part of (2.25). It works well for small D_{ee} .

In the modified Bessel functions method we only know $V_k(r_1, r_2)$ numerically and as such

we show here a general method that is independent of the particular form of the basis functions or $V_k(r_1, r_2)$ and which is a generalization of the method proposed in [16]. The function $V_k(r_1, r_2)$ has a cusp at $r_1 = r_2$, so in order to accurately evaluate the integral (2.25) using Gaussian quadrature, we use the approach by [17] that splits the integral into integration over lower and upper triangles as follows:

$$\begin{aligned}
R^k(a, b, c, d) &= \int_0^\infty \int_0^\infty V_k(r_1, r_2) \phi_a(r_1) \phi_c(r_1) \phi_b(r_2) \phi_d(r_2) dr_1 dr_2 = \\
&= \int_0^\infty \int_0^{r_1} V_k(r_1, r_2) \phi_a(r_1) \phi_c(r_1) \phi_b(r_2) \phi_d(r_2) dr_1 dr_2 + \\
&+ \int_0^\infty \int_{r_1}^\infty V_k(r_1, r_2) \phi_a(r_1) \phi_c(r_1) \phi_b(r_2) \phi_d(r_2) dr_1 dr_2 = \\
&= \int_0^\infty \int_0^{r_1} V_k(r_1, r_2) \phi_a(r_1) \phi_c(r_1) \phi_b(r_2) \phi_d(r_2) dr_1 dr_2 + \\
&+ \int_0^\infty \int_0^{r_2} V_k(r_1, r_2) \phi_a(r_1) \phi_c(r_1) \phi_b(r_2) \phi_d(r_2) dr_1 dr_2 = \\
&= \int_0^\infty \int_0^{r_1} V_k(r_1, r_2) \phi_a(r_1) \phi_c(r_1) \phi_b(r_2) \phi_d(r_2) dr_1 dr_2 + \\
&+ \int_0^\infty \int_0^{r_1} V_k(r_1, r_2) \phi_b(r_1) \phi_d(r_1) \phi_a(r_2) \phi_c(r_2) dr_1 dr_2 = \\
&= R_\Delta^k(a, b, c, d) + R_\Delta^k(b, a, d, c)
\end{aligned}$$

where

$$R_\Delta^k(a, b, c, d) = \int_0^\infty dr_1 \int_0^{r_1} dr_2 V_k(r_1, r_2) \phi_a(r_1) \phi_c(r_1) \phi_b(r_2) \phi_d(r_2) \quad (2.31)$$

In (2.31) we first evaluate the integral over r_2 :

$$f_{bd}^k(r_1) = \int_0^{r_1} V_k(r_1, r_2) \phi_b(r_2) \phi_d(r_2) dr_2$$

using Gauss-Legendre quadrature of order N_q . Then we can calculate the integral over r_1 :

$$R_{\Delta}^k(a, b, c, d) = \int_0^{\infty} f_{bd}^k(r_1) \phi_a(r_1) \phi_c(r_1) dr_1$$

by dividing the interval $(0, \infty)$ into elements $(0, a_1)$, (a_1, a_2) , dots, (a_n, ∞) . We use Gauss-Laguerre quadrature rule on the infinite element (a_n, ∞) and Gauss-Legendre quadrature rule with the same number of points on all the other finite elements.

This method works for any types of basis functions.

2.15.1 Slater Type Orbitals Basis

In the STO basis, the above integrals can be evaluated analytically for the Coulomb case [19]. In the presence of screening, the potential term (2.27) can still be evaluated analytically as:

$$V_{ij}^l = -ZN_{n_i\zeta_i}N_{n_j\zeta_j} \frac{(n_i + n_j - 1)!}{(\zeta_i + \zeta_j + \frac{1}{D_{en}})^{n_i+n_j}}$$

The Slater integral (2.25) can either be evaluated by Legendre expansion and Gauss-Laguerre quadrature as described in [16], or by first evaluating $V_k(r_1, r_2)$ numerically by using modified Bessel functions as described above and then evaluating the integral (2.31) by the combination of Gauss-Legendre and Gauss-Laguerre quadrature as described in the previous section.

In all calculations below, when evaluating the integral (2.31) we use a 52 points quadrature approach and two elements $(0, 0.1)$, $(0.1, \infty)$ in atomic units. We found these settings to be sufficient to obtain converged results to all printed digits.

Chapter 3

Unscreened Results

The purpose of this section is to provide evidence that our program works and is able to reproduce known results from the literature. We perform convergence tests for the Hartree-Fock total energy, we check the energies for a particular STO basis, we check second order perturbation theory as well as second order Green function results against literature.

Historically, the standard reference for accurate STO orbitals used to be [28]. Lately, the new state of the art reference seems to be given in the references [14] and [8], that provides very accurate and small STO bases for any atom from He to Lr.

3.1 Hartree-Fock

3.1.1 Ra

Radium is a closed shell atom with $Z = 88$ and the configuration:

$$f_{n,0} = [2, 2, 2, 2, 2, 2, 2]$$

$$f_{n,1} = [6, 6, 6, 6, 6]$$

$$f_{n,2} = [10, 10, 10]$$

$$f_{n,3} = [14]$$

We used the STO basis from [8]. Then the self-consistent SCF Hartree-Fock energies are (we used `tolE=1e-10` and `tolP=1e-4`):

Orbital energies:

n	l	E [a.u.]	E [eV]
1	0	-3388.94104039	-92217.77956191
2	0	-587.74420729	-15993.33393552
3	0	-147.87172991	-4023.79458059
4	0	-37.34157119	-1016.11587210
5	0	-8.25316973	-224.58017937
6	0	-1.37067573	-37.29798516
7	0	-0.14876040	-4.04797645
8	0	0.08165397	2.22191763
9	0	0.72340804	19.68493462
10	0	4.66147311	126.84513981
11	0	25.24608995	686.98107455
12	0	120.95628254	3291.38797843
13	0	535.76303483	14578.85423631
14	0	2517.93096422	68516.38899682
15	0	17467.06888395	475303.13709612
1	1	-566.94278080	-15427.29830980
2	1	-137.79866067	-3749.69241475
3	1	-32.72200096	-890.41096784
4	1	-6.44987601	-175.51005952
5	1	-0.81981163	-22.30820982

6	1	0.30903607	8.40929961
7	1	3.55206062	96.65648921
8	1	18.98639327	516.64605785
9	1	72.27839685	1966.79528758
10	1	251.72462436	6849.77568014
11	1	976.90370346	26582.90283152
12	1	5274.79312909	143534.42689472
1	2	-119.22873420	-3244.37899532
2	2	-24.19779669	-658.45556300
3	2	-3.29686823	-89.71235093
4	2	0.70184142	19.09807715
5	2	6.25455310	170.19505280
6	2	24.88623637	677.18896040
7	2	82.85779377	2254.67533067
8	2	299.22996892	8142.46190290
9	2	1466.26202858	39899.02064377
1	3	-12.43050199	-338.25117611
2	3	0.82042589	22.32492479
3	3	7.01801677	190.96995658
4	3	24.88560409	677.17175514
5	3	78.31351681	2131.01926041
6	3	314.75842103	8565.01259240

E_{KIN}+E_{HF} (a.u.): 1.33E-04
 KINETIC ENERGY (a.u.): 23094.3036253898
 HF ATOMIC ENERGY (a.u.): -23094.3034926210

Which agrees with [8] to every single printed digit. There are a total of 42 DOFs. We print 8 decimal digits after the floating point in order to show the numerical accuracy of our results.

In the FE basis, with $p = 20$ we get:

```

tolE: 1.00000000000000006E-009
tolP: 1.00000000000000005E-004
dP: 1.23226187438905178E-006
Emax-Emin: 6.00266503170132637E-010
Orbital energies:

```

n	l	E [a.u.]	E [eV]
1	0	-3388.94108567	-92217.78079401
2	0	-587.74424129	-15993.33486066
3	0	-147.87175129	-4023.79516241
4	0	-37.34161387	-1016.11703329

Method	E_{tot} [a.u.]
STO	-23094.303492621
[8]	-23094.303492621
FE	-23094.30366642
[6]	-23094.30367

Table 3.1: Ra energies summary

5	0	-8.25320196	-224.58105652
6	0	-1.37070249	-37.29871325
7	0	-0.14877117	-4.04826955
1	1	-566.94280420	-15427.29894631
2	1	-137.79868421	-3749.69305533
3	1	-32.72204108	-890.41205938
4	1	-6.44990553	-175.51086305
5	1	-0.81983794	-22.30892576
1	2	-119.22876709	-3244.37989034
2	2	-24.19783041	-658.45648063
3	2	-3.29689595	-89.71310530
1	3	-12.43052485	-338.25179817
EKIN+EHF (a.u.): 7.46E-08			
KINETIC ENERGY (a.u.): 23094.30366649			
HF ATOMIC ENERGY (a.u.): -23094.30366642			

There is total of 316 DOFs (79 DOFs for each $l = 0, 1, 2, 3$). In order to determine the accuracy of the total energy, we did a p-study, see Figure 3.1. Instead of plotting the accuracy depending on p , we can also plot the corresponding DOFs on the x -axis, see the Figure 3.2 (this graph also contains the accuracy of the STO calculation above, as a black dot).

The figure above shows that the total energy is converged to 10^{-8} a.u. accuracy. This total energy agrees with the converged HF energy $E_{tot} = -23094.30367$ from [6]. Compared to our converged energy, we can see that the STO energy is 1.74×10^{-4} a.u. accurate.

The total energies are summarized in Table 3.1.

Note that using the same STO basis for Ne we get.

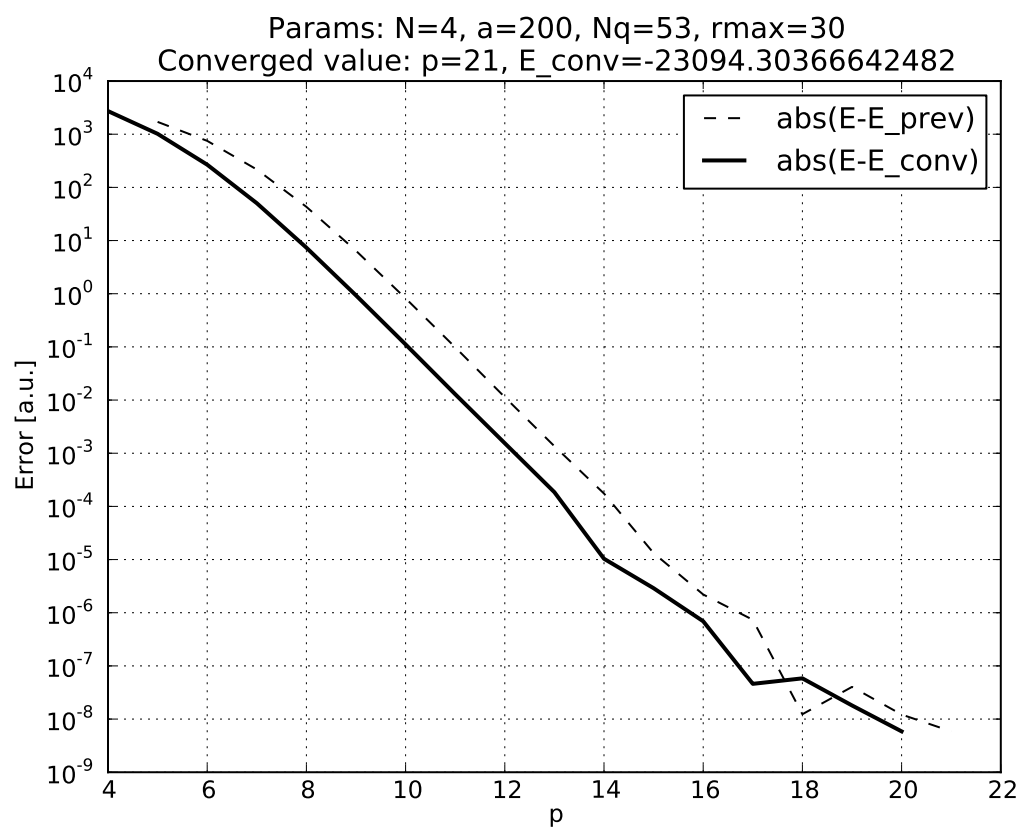


Figure 3.1: The FE p-study for radium.

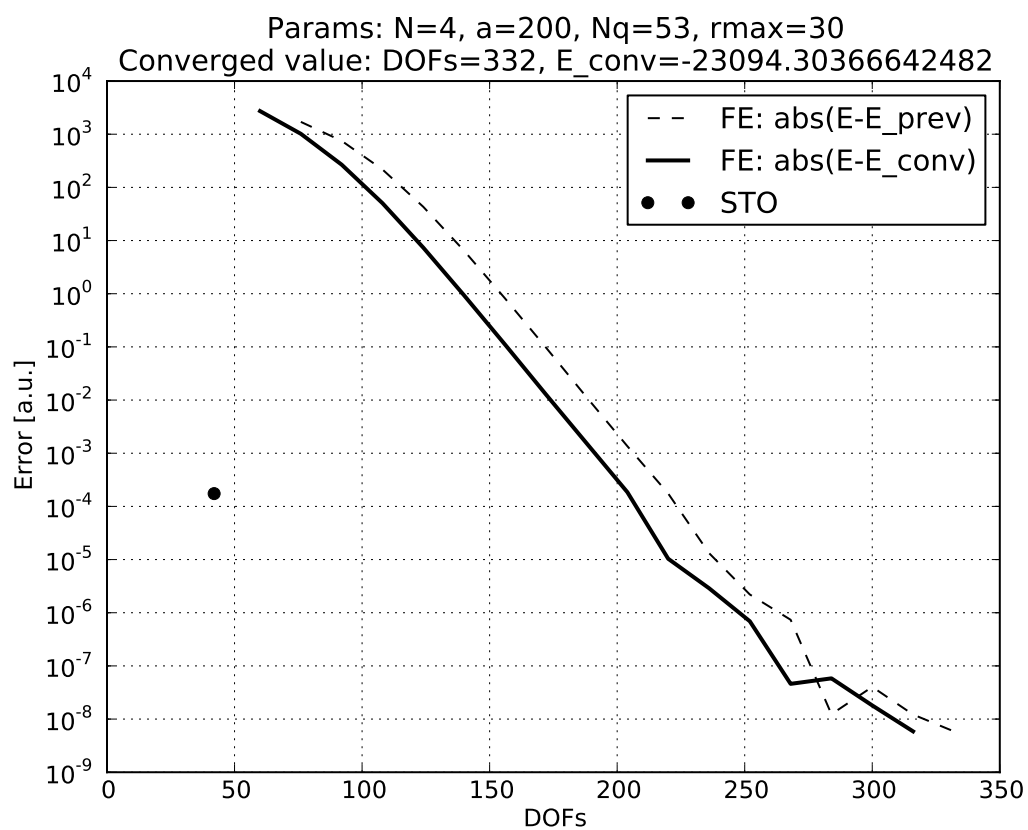


Figure 3.2: The FE and STO convergence study for radium.

```

Orbital energies:
  n  l          E [a.u.]          E [eV]
  1  0      -32.77356052      -891.81397481
  2  0      -1.93123658      -52.55162211
  1  1      -0.85098345      -23.15643837
      EKIN+EHF (a.u.):  2.21E-03
      KINETIC ENERGY (a.u.):  128.54698875
      HF ATOMIC ENERGY (a.u.): -128.54478045

```

Which seems less accurate than the results for Ra as can be seen from the virial theorem.

3.1.2 Mg

Using the basis from [14] we obtain the following energies:

```

Orbital energies:
  n  l          E [a.u.]          E [eV]
  1  0      -49.03173628      -1334.22145568
  2  0      -3.76772161      -102.52492359
  3  0      -0.25305242       -6.88590681
  4  0       0.19036542        5.18010663
  5  0       1.31843427       35.87642254
  6  0       6.21612265      169.14930695
  7  0      23.31152940      634.33900255
  8  0      82.63946152     2248.73420784
  9  0     354.50455399     9646.55992069
 10  0    2672.27000174    72716.16797485
  1  1      -2.28222603      -62.10253134
  2  1       0.06757963       1.83893544
  3  1       0.89720617      24.41422262
  4  1       4.69875505     127.85963292
  5  1      18.45916821     502.29953397
  6  1      72.19528066    1964.53358083
  7  1     291.83482629    7941.22982924
      EKIN+EHF (a.u.):  2.73E-08
      KINETIC ENERGY (a.u.):  199.61463630
      HF ATOMIC ENERGY (a.u.): -199.61463627

```

The total energy from this STO result is plotted (circle) with FE convergence study in Figure 3.3. We also plotted a so called even-tempered STO basis from [15] and plotted

Nb	DOFS	Etot	virial theorem
3	9	-1.9564661093751155E+02	2.3306633268013258E+01
4	12	-1.9961452117971305E+02	8.6578325391428734E-04
5	15	-1.9961458931754072E+02	8.5459817000810290E-08
6	18	-1.9961459732988519E+02	1.9453174084560487E-04
7	21	-1.9961460026776570E+02	2.8981480468814880E-04
8	24	-1.9961460111276716E+02	3.2856031558026189E-04
9	27	-1.9961460141633930E+02	3.4488235490925945E-04
10	30	-1.9961460153923431E+02	3.5201552296371119E-04
11	33	-1.9961460159216077E+02	3.5519382603865779E-04
12	36	-1.9961460161569153E+02	3.5646990903615006E-04
13	39	-1.9961460162633020E+02	3.5544459390735028E-04
14	42	-1.9961460163116988E+02	3.7544886237128594E-04

Table 3.2: Even-tempered STO basis Etot and virial theorem values for Mg

convergence (triangles) as well as the virial theorem (crosses) into the same graph. The values are in the Table 3.2. Notice that for DOF=15 the virial theorem says 8.5×10^{-8} a.u., but from the graph, the accuracy of the solution is only around 10^{-4} a.u.. With increasing the size of the basis (the N_b column), the virial theorem error gets worse to almost 10^{-4} a.u.. This is caused by the fact, that the virial theorem only provides a lower bound of the error. By properly updating the α and β parameters of the even-tempered STO basis we can converge the total energy to 10^{-9} a.u., see Figure 3.4.

3.1.3 Xe

We did even-tempered STO convergence study for Xe, see Figure 3.5.

And we get the total energy -7232.138362 with accuracy 2×10^{-6} a.u..

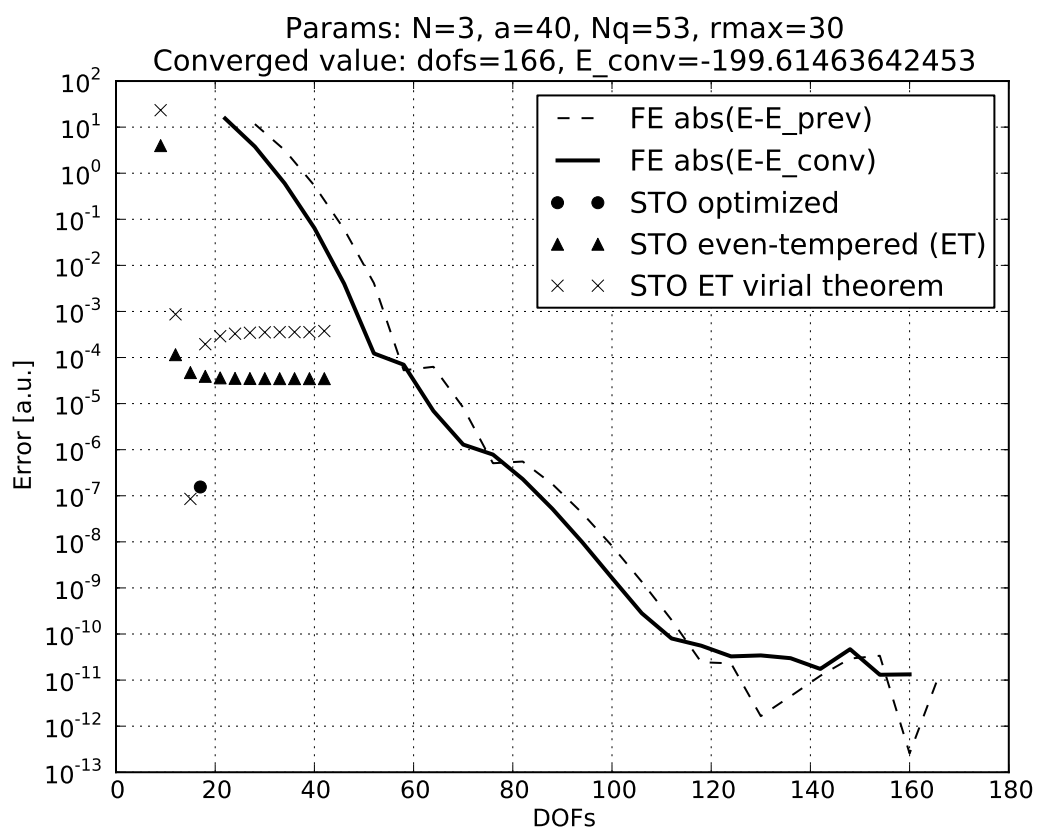


Figure 3.3: The FE and STO convergence study for Mg

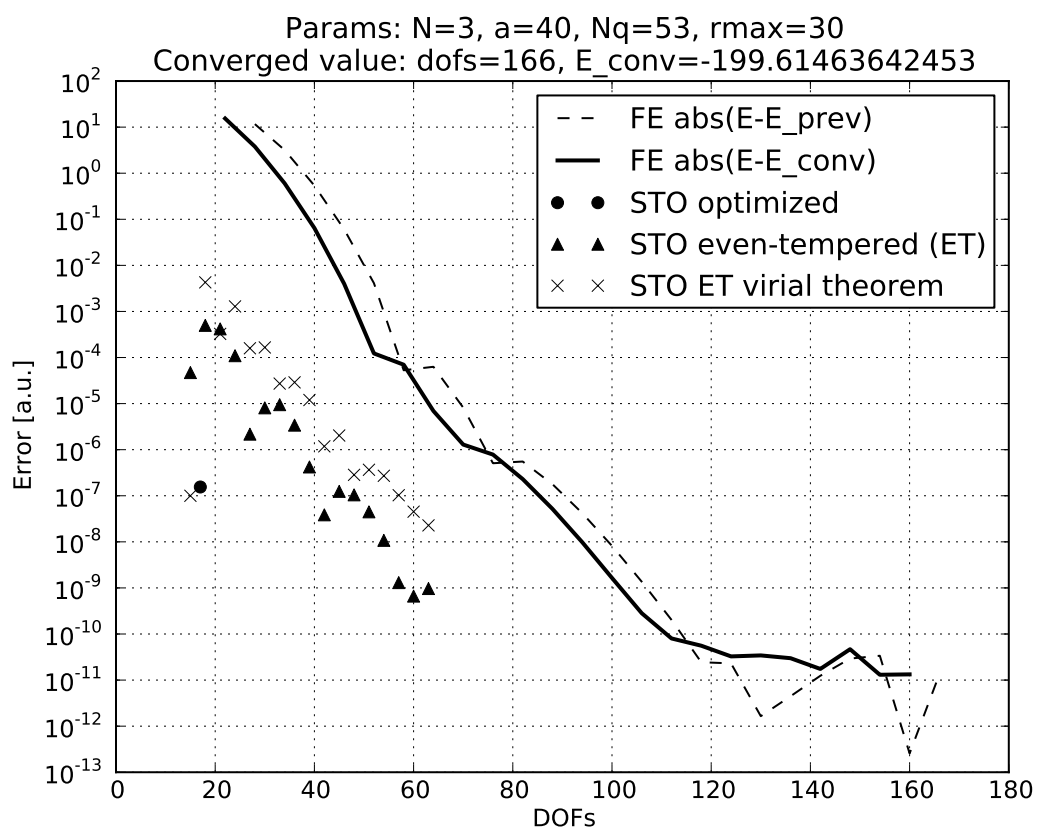


Figure 3.4: The FE and even-tempered STO convergence study for Mg

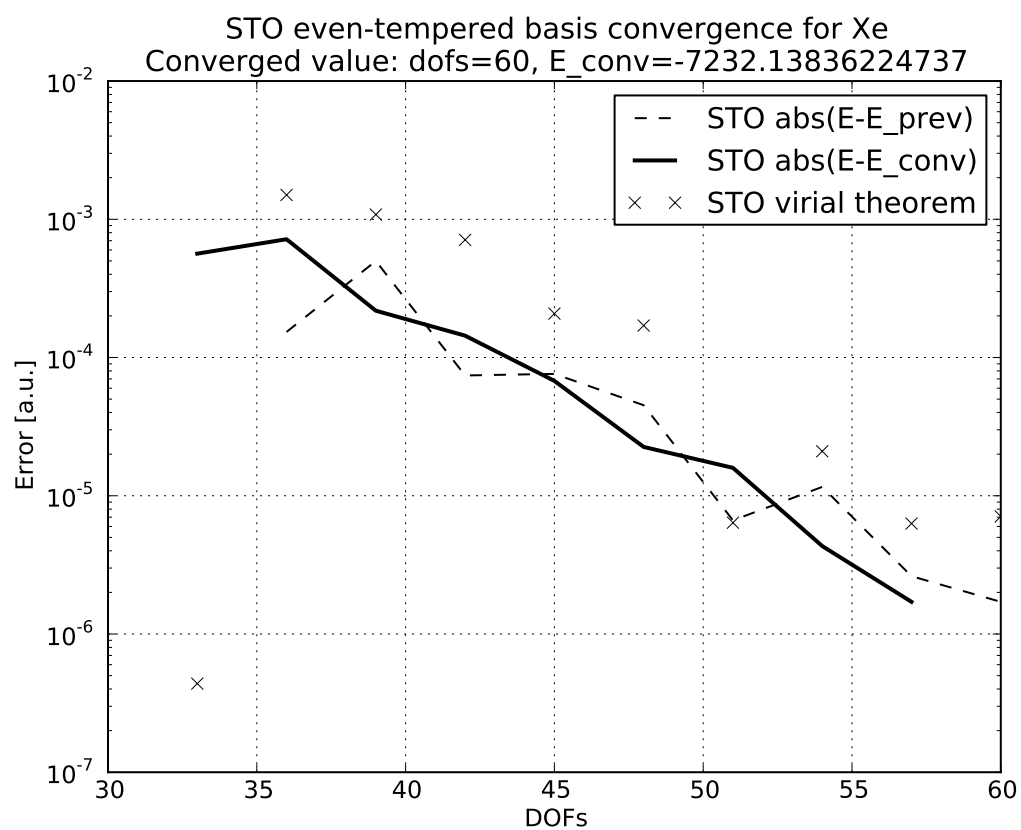


Figure 3.5: Even-tempered STO convergence study for Mg

3.2 Green's Function

3.2.1 Be

We use the basis from [27]:

```

nbfl(0) = 5
nl(:5, 0) = [1, 1, 3, 2, 2]
zl(:5, 0) = [5.4297_dp, 2.9954_dp, 3.5810_dp, 1.1977_dp, 0.8923_dp]
nbfl(1) = 5
nl(:5, 1) = [2, 2, 4, 3, 3]
zl(:5, 1) = [5.6998_dp, 2.7850_dp, 4.1500_dp, 1.4387_dp, 0.9819_dp]
nbfl(2) = 2
nl(:2, 2) = [3, 3]
zl(:2, 2) = [1.2662_dp, 7.8314_dp]

```

and obtain for Hartree-Fock:

```

Orbital energies:
  n   l           E [a.u.]           E [eV]
  ---
  1   0       -4.73091975       -128.73487906
  2   0       -0.30838296        -8.39152746
  3   0        0.28793901         7.83521917
  4   0        2.86050169        77.83821285
  5   0       24.42017728       664.50684701
  1   1        0.06564083         1.78617784
  2   1        0.36350961         9.89160007
  3   1        1.84075556        50.08950845
  4   1        8.60671953       234.20075914
  5   1       39.89676518      1085.64623955
  1   2        0.58990240        16.05206144
  2   2       25.29557149       688.32753589
      EKIN+EHF (a.u.):    9.87E-04
      KINETIC ENERGY (a.u.):    14.57377528
      HF ATOMIC ENERGY (a.u.):   -14.57278856

```

The MBPT2 gives:

Method	E_{tot} [a.u.]
HF	-14.57278856
HF [27]	-14.572789
GF	-14.647063
GF [27]	-14.641639

Table 3.3: Green's function total energies for Be

Method	E_1 [a.u.]	E_2 [a.u.]
HF	-4.73091975	-0.30838296
HF [27]	-4.731	-0.308
GF	-4.61175302	-0.32724971
GF [27]	-4.612	-0.327

Table 3.4: Green's function IP energies for Be

```

MBPT results:
E0+E1 (HF)      =      -14.57278856

```

The Green's function calculation gives:

```

Green's function calculation:
  E =      -4.61175302    dE =    7.65E-11
  E =      -0.32724971    dE =    6.27E-12
Ntot =    4.0052366660634702
Etot =   -14.666238504287731

```

The total energy was calculated using a rectangular contour from 0 to -60 a.u.. Extending the integration contour further than -60 a.u. does not change the total energy. We partition the domain into 0.1×0.1 rectangles and integrate using Gaussian integration of order $N_q = 20$ over the top and bottom parts of each rectangle (as well as the left resp. right side of the very left resp. very right rectangle), see the Figure 3.6. Following the approach from [27], we have corrected the Green's function total energy for lack of trace conservation by dividing it by the ratio of the true trace to that actually produced. In the case of Be we did $E_{tot} / N_{tot} * 4$. The total energies are summarized in Table 3.3. The ionization potentials are summarized in the Table 3.2.2.

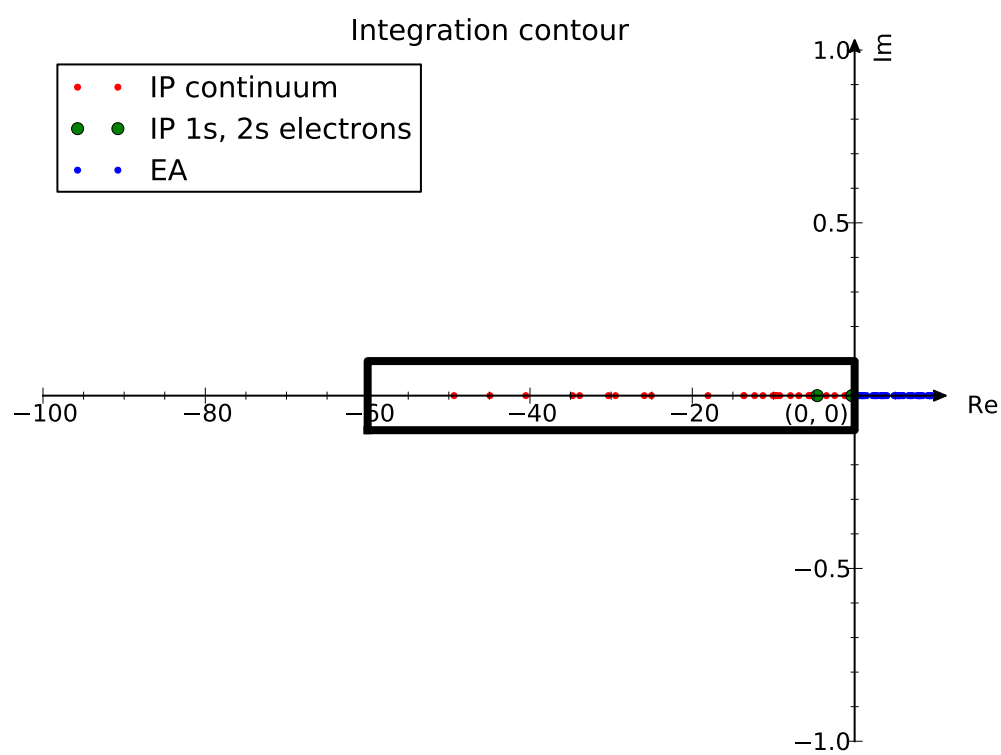


Figure 3.6: The contour for total energy integration of Be.

3.2.2 He

For He we use again the basis from [27]:

```

nbfl(0) = 5
nl(:5, 0) = [1, 1, 2, 3, 3]
zl(:5, 0) = [1.4191_dp, 2.5722_dp, 4.2625_dp, 3.9979_dp, 5.4864_dp]
nbfl(1) = 4
nl(:4, 1) = [2, 2, 3, 4]
zl(:4, 1) = [2.5834_dp, 3.6413_dp, 5.5308_dp, 5.7217_dp]
nbfl(2) = 3
nl(:3, 2) = [3, 3, 4]
zl(:3, 2) = [3.6365_dp, 4.8353_dp, 6.9694_dp]

```

and we get for HF:

```

Orbital energies:
  n   l           E [a.u.]           E [eV]
  1   0       -0.91804537       -24.98128597
  2   0         0.88239287        24.01113203
  3   0         5.07439794       138.08139625
  4   0        19.66534934       535.12139290
  5   0       119.00491186      3238.28847938
  1   1         1.16674233        31.74867471
  2   1         5.07923156       138.21292570
  3   1        17.00970593       462.85765772
  4   1        55.12789316      1500.10632781
  1   2         3.79051952       103.14528608
  2   2        16.77713044       456.52895653
  3   2        60.33563243      1641.81612641
      Ekin+EHF (a.u.): -4.08E-04
      KINETIC ENERGY (a.u.): 2.86127076
      HF ATOMIC ENERGY (a.u.): -2.86167868

```

for MBPT2:

```

MBPT results:
E0+E1 (HF) = -2.86167868

```

and Green's function:

Method	E_{tot} [a.u.]
HF	-2.86167868
HF [27]	-2.86168
GF	-2.9010108
GF [27]	-2.90090

Table 3.5: Green's function total energies for He

Method	E_1 [a.u.]
HF	-0.91804537
HF [27]	-0.918
GF	-0.90587321
GF [27]	-0.906

Table 3.6: Green's function IP energies for He

```

Green's function calculation:
  E =      -0.90587321    dE =    9.02E-12
Ntot =    2.0001613956929334
Etot =   -2.9012448886081441

```

We correct the total energy for lack of trace conservation. We used the same contour as for Be (Figure 3.6) and the same integration order $N_q = 20$. The total energies are summarized in Table 3.5. The ionization potentials are summarized in the Table 3.2.3.

3.2.3 Hydrogen Molecule

For the H_2 we use the interatomic distance 1.4 a.u. and the 6-31G** Gaussian basis, the same configuration as in [11] (see also this reference for a detailed description of the basis). Total energy comparison is in the Table 3.7. The ionization potentials are in the Table 3.8.

3.2.4 Ammonia

For NH_3 we use the atomic configuration from [11] and the 6-31G** Gaussian basis. Total energy comparison is in the Table 3.9. The ionization potentials are in the Table 3.10. Note:

Method	E_{tot} [a.u.]
HF	-1.13128434
HF [11]	-1.131
MBPT2	-0.026341791
MBPT2 [11]	-0.0263
MBPT2 [12]	-0.02634179
MBPT3	-0.005515979
MBPT3 [12]	-0.00551598

Table 3.7: HF and MBPT2 total energies for the hydrogen molecule

Method	E_1 [a.u.]
HF	-0.59465997
HF [11]	-0.595
GF	-0.59832340
GF [11]	-0.598

Table 3.8: Green's function IP energies for the hydrogen molecule

the HF energy -0.421 from [11] is probably wrong, because the total energy as well as the Green's function ionization potential agrees.

3.2.5 Methane

For the CH_4 molecule we use the CH bond length of 2.05 a.u. and the 6-31G** Gaussian basis, the same configuration as in [11]. Total energy comparison is in the Table 3.11. The ionization potentials are in the Table 4.

Method	E_{tot} [a.u.]
HF	-56.19457246
HF [11]	-56.195

Table 3.9: HF total energies for ammonia

Method	E_1 [a.u.]
HF	-0.41491598
HF [11]	-0.421
GF	-0.35357570
GF [11]	-0.353

Table 3.10: Green's function IP energies for ammonia

Method	E_{tot} [a.u.]
HF	-40.20170036
HF [11]	-40.202
MBPT2	-0.16815509
MBPT2 [12]	-0.16815509
MBPT3	-0.01819243
MBPT3 [12]	-0.01819243

Table 3.11: HF and MBPT2 total energies for the methane molecule

Method	E_1 [a.u.]
HF	-0.54451008
HF [11]	-0.543
HF [12]	-0.54451009
GF	-0.51384473
GF [11]	-0.510

Table 3.12: Green's function IP energies for the methane molecule

Chapter 4

Screened Results

After having presented plenty of evidence for the trustworthiness of our computational tools, we present in this section the results for screened electron-nucleus as well as electron-electron interaction.

In particular, we show that if we only screen electron-nucleus as opposed to both electron-nucleus and electron-electron screening, we can produce the same total energy. This means that the experimental results can be interpreted in different ways.

4.1 Be

In Figure 4.1 we plot the Hartree-Fock eigenvalues together with second order Green's function results for Be. Both exhibit similar trend.

We have also performed a calculation with $D_{en} = 100$ and $D_{ee} = \infty$ (i.e. without $e - e$ screening):

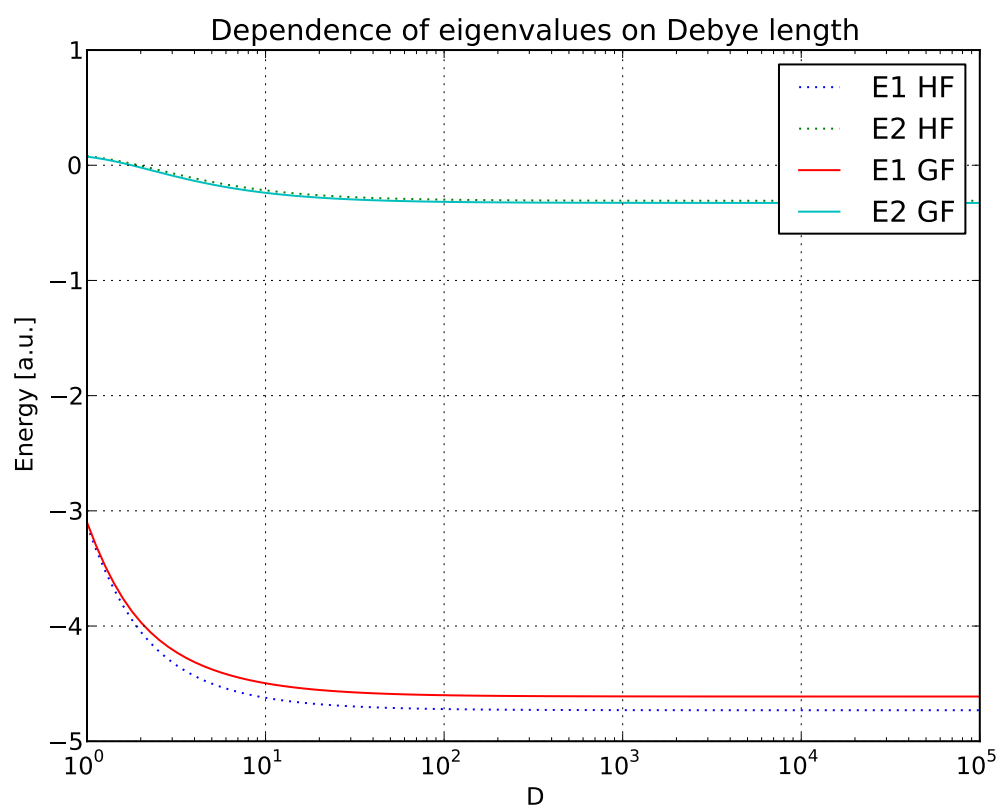


Figure 4.1: HF and GF eigenvalues for beryllium.

Orbital energies:

n	l	E [a.u.]	E [eV]
1	0	-4.69136904	-127.65864930
2	0	-0.26897735	-7.31924625
3	0	0.32713617	8.90182828
4	0	2.89995575	78.91181265
5	0	24.45968140	665.58180867
1	1	0.10485005	2.85311497
2	1	0.40275502	10.95952181
3	1	1.88017673	51.16221303
4	1	8.64622701	235.27581235
5	1	39.93628578	1086.72164972
1	2	0.62923171	17.12226644
2	2	25.33510034	689.40317060
E _{KIN} +E _{HF} (a.u.): 1.59E-01			
KINETIC ENERGY (a.u.): 14.57263329			
HF ATOMIC ENERGY (a.u.): -14.41399656			

The total energy -14.41399656 a.u. can be reproduced alternatively with $D_{en} = 80$ and $D_{ee} = 151.32235$ to accuracy 10^{-8} a.u.:

Orbital energies:

n	l	E [a.u.]	E [eV]
1	0	-4.70120880	-127.92640299
2	0	-0.27891615	-7.58969477
3	0	0.31064466	8.45307135
4	0	2.88349893	78.46399957
5	0	24.44323726	665.13434093
1	1	0.08836110	2.40442782
2	1	0.38626422	10.51078439
3	1	1.86371042	50.71414173
4	1	8.62977885	234.82823507
5	1	39.91984324	1086.27422554
1	2	0.61274761	16.67371109
2	2	25.31865776	688.95574533
E _{KIN} +E _{HF} (a.u.): 1.58E-01			
KINETIC ENERGY (a.u.): 14.57230512			
HF ATOMIC ENERGY (a.u.): -14.41399656			

as well as with $D_{en} = 50$ and $D_{ee} = 37.102069$ to accuracy 10^{-8} a.u.:

Orbital energies:

n	l	E [a.u.]	E [eV]
1	0	-4.72975509	-128.70318697
2	0	-0.30806010	-8.38274204
3	0	0.26320819	7.16225946
4	0	2.83506986	77.14617762
5	0	24.39469170	663.81334896
1	1	0.04090382	1.11304972
2	1	0.33855496	9.21254935
3	1	1.81533650	49.39782038
4	1	8.58115980	233.50524356
5	1	39.87122358	1084.95121734
1	2	0.56467167	15.36549832
2	2	25.26998935	687.63141044
		EKIN+EHF (a.u.):	1.60E-01
		KINETIC ENERGY (a.u.):	14.57416124
		HF ATOMIC ENERGY (a.u.):	-14.41399656

or with $D_{en} = D_{ee} = 62.50862$ to accuracy 10^{-8} a.u.:

Orbital energies:

n	l	E [a.u.]	E [eV]
1	0	-4.71470166	-128.29356232
2	0	-0.29263351	-7.96296299
3	0	0.28814455	7.84081227
4	0	2.86073937	77.84468044
5	0	24.42045295	664.51434834
1	1	0.06585616	1.79203731
2	1	0.36368780	9.89644875
3	1	1.84096083	50.09509399
4	1	8.60697118	234.20760691
5	1	39.89703911	1085.65369363
1	2	0.59006984	16.05661757
2	2	25.29583992	688.33484027
		EKIN+EHF (a.u.):	1.59E-01
		KINETIC ENERGY (a.u.):	14.57264209
		HF ATOMIC ENERGY (a.u.):	-14.41399656

For $D_{en} = 100$, $D_{ee} = \infty$ we calculate DFT results using the LDA exchange and correlation potential:

```

Z=          4 N=          5500
E_tot=      -14.288416
state      E              occupancy
1s         -3.816913      2.000
2s         -0.166421      2.000

```

and with $D_{en} = D_{ee} = \infty$:

```

Z=          4 N=          5500
E_tot=      -14.447209
state      E              occupancy
1s         -3.856411      2.000
2s         -0.205744      2.000

```

4.2 Mg

In the Figure 4.2 we plot Hartree-Fock eigenvalues together with second order Green's function results for Mg.

For $D_{en} = 100$, $D_{ee} = \infty$ we calculate DFT results using the LDA exchange and correlation potential:

```

Z=          12 N=          5500
E_tot=      -197.706607
state      E              occupancy
1s         -45.854891      2.000
2s         -2.785497      2.000
2p         -1.600722      6.000
3s         -0.057813      2.000

```

and with $D_{en} = D_{ee} = \infty$:

```

Z=          12 N=          5500
E_tot=      -199.139406
state      E              occupancy
1s         -45.973167      2.000
2s         -2.903746      2.000

```

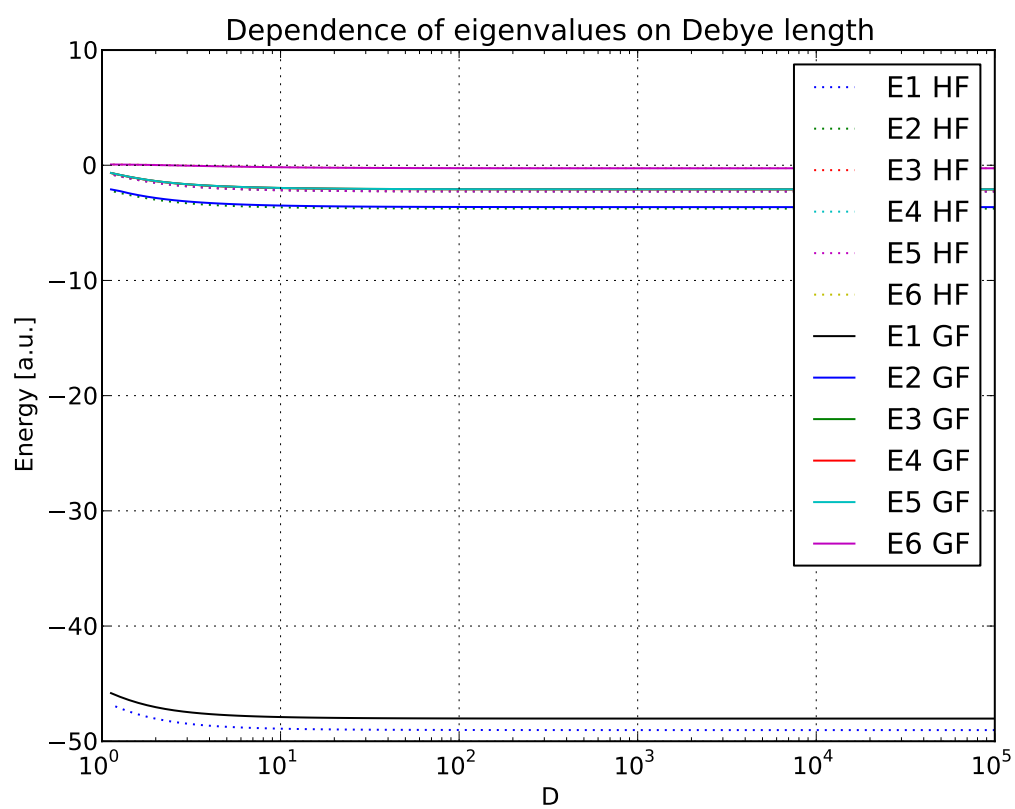


Figure 4.2: HF and GF eigenvalues for magnesium.

2p	-1.718970	6.000
3s	-0.175427	2.000

4.3 H Minus Ion

For H^- we did a Coulomb calculation:

```
Orbital energies:
  n  l          E [a.u.]          E [eV]
  1  0      -0.04622233      -1.25777362
      Ekin+EHF (a.u.):  1.05E-07
      KINETIC ENERGY (a.u.):  0.48792984
      HF ATOMIC ENERGY (a.u.): -0.48792973
```

then $D_{ee} = D_{en} = 20$:

```
Orbital energies:
  n  l          E [a.u.]          E [eV]
  1  0      -0.04533145      -1.23353158
      Ekin+EHF (a.u.):  4.68E-02
      KINETIC ENERGY (a.u.):  0.48635786
      HF ATOMIC ENERGY (a.u.): -0.43951187
```

The accuracy of this calculation is roughly 10^{-5} a.u. in total energy, from a convergence study. We also did $D_{ee} = 40$, $D_{en} = 20$:

```
Orbital energies:
  n  l          E [a.u.]          E [eV]
  1  0      -0.02467076      -0.67132558
      Ekin+EHF (a.u.):  6.58E-02
      KINETIC ENERGY (a.u.):  0.48350408
      HF ATOMIC ENERGY (a.u.): -0.41771724
```

The accuracy of this calculation is roughly 10^{-5} a.u. in total energy.

Finally we did $D_{ee} = 10$, $D_{en} = 20$:

Den	Dee	HF total energy	Correlated wf.
oo	oo	-0.48793	-0.5277
20	20	-0.43951	-0.47904
20	10	-0.47794	-0.51590

Table 4.1: H minus screened total energies summary

```

Orbital energies:
  n  l          E [a.u.]          E [eV]
  1  0      -0.08019560      -2.18223338
      Ekin+EHF (a.u.):  1.79E-02
      KINETIC ENERGY (a.u.):  0.49583783
      HF ATOMIC ENERGY (a.u.): -0.47793727

```

The accuracy of this calculation is roughly 10^{-6} a.u. in total energy.

This can be compared with correlated wave function results [24], see the Table 4.1.

Chapter 5

Summary and Conclusions

We chose radium as a benchmark for our Hartree-Fock (HF) code, because it requires Slater integrals up to $k = 6$ and has non zero occupation numbers up to $l = 3$. By comparing the total energy with [8] for the same Slater Type Orbital (STO) basis, and agreeing to 14 significant digits (all digits given in [8]), means that our Hartree-Fock and STO code works well. By using the finite element (FE) basis, we get the converged value which agrees exactly with [6] (10 significant digits), and from the p -convergence graph it suggests that our FE total energy is actually correct to 10^{-8} , a.u. (13 significant digits). This establishes that our FE basis works correctly as well.

The STO basis is highly efficient, for example for Ra one can get 10^{-4} accuracy with only 42 degrees of freedom. One has to optimize the basis for each atom separately, one cannot reuse the basis directly, for example the basis for radium is less accurate if used for Ne as established in the section Unscreened Results. However, when an optimized basis is used for Ne, it provides better accuracy with fewer basis functions.

The very same basis is less accurate for Ne. The disadvantage of the STO basis is that it is not straightforward to improve the accuracy – one has to add more functions to the basis

and optimize the exponents.

The efficiency of the FE basis, on the other hand, is determined by the choice of a mesh. Once the mesh is fixed, then the systematic, robust and variational way to improve the accuracy is just to increase the polynomial order. An exponential mesh with the mesh parameter $a = 200$ and polynomial order $p = 20$ allows to get accuracy 10^{-6} for all atoms up to radium.

The traditional FE approach is to solve the Poisson problem by solving the differential equation and the exchange term by calculating the integrals on the fly. As shown above, this approach is equivalent to first calculating all two particle integrals, and then solving the Roothaan equations.

The even-tempered STO basis for Mg shows nicely that the virial theorem cannot always be trusted as an error indicator, because it only provides the lower bound on the actual error of the total energy. In that example for DOF=15, the virial theorem gives almost 10^{-8} accuracy, while the actual error is 10^{-4} . As such, the only reliable way to assess the accuracy is to do a convergence study. Other possible error indicators that may provide information about the quality of the wavefunctions (and ultimately the basis) include the cusp condition and various sum rules like the Thomas-Reiche-Kuhn sum rule.

By properly updating the α and β coefficients as increasing the number (N) of basis functions, one can converge to the exact HF solution. The convergence rate is exponential. The only practical disadvantage is that the overlap matrix eventually becomes ill-conditioned for high N , preventing the self-consistency cycle to converge. The FE approach does not suffer from ill-conditioning.

We use STO basis that is optimized for unscreened (Coulomb) potential. More thorough study would be needed to reoptimize the basis for the given Debye screening. The virial theorem in the presence of screening takes a more complicated form than just a simple sum

of kinetic and total energy. The best way to judge the accuracy of results is to perform a convergence with respect to the STO basis, for example using the even-tempered basis set.

As a few examples of post-HF calculations, we show results for Green's function and many body perturbation theory in second order. Other common post Hartree-Fock methods include configuration interaction and coupled cluster. The unscreened results can be directly compared to literature and the energies are in good agreement, thus establishing that our implementation is correct.

In the screened results, we concentrate on the HF level of theory. We ran various calculations for He and Mg as well as H^- . As an example of a post-HF calculation, we show screened second order Green's function calculations for He and Mg. We also compare our Hartree-Fock H^- results with a correlated wave function approach and as seen from the behavior of energies as we decrease the Debye length, both set of energies follow the same trend.

The computational methods we have presented in this thesis are developed to the point where one can include essentially any screening potential and are accurate enough to distinguish between results and help resolve possible ambiguities in the interpretation of plasma data.

Chapter 6

Appendices

6.1 Legendre Polynomials

Legendre polynomials $P_l(x)$ defined by the Rodrigues formula

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} [(x^2 - 1)^l]$$

they also obey the completeness relation

$$\sum_{l=0}^{\infty} \frac{2l+1}{2} P_l(x') P_l(x) = \delta(x - x') \quad (6.1)$$

and orthogonality relation:

$$\int_{-1}^1 P_k(x) P_l(x) dx = \frac{2\delta_{kl}}{2k+1}$$

Two Legendre polynomials can be expanded in a series:

$$P_k(x)P_l(x) = \sum_{m=|k-l|}^{k+l} \begin{pmatrix} k & l & m \\ 0 & 0 & 0 \end{pmatrix}^2 (2m+1)P_m(x)$$

This was first proven by [1], where he shows:

$$P_k(x)P_l(x) = \sum_{m=|k-l|}^{k+l} \frac{A(s-k)A(s-l)A(s-m)}{A(s)} \frac{2m+1}{2s+1} P_m(x)$$

where $s = \frac{k+l+m}{2}$ and

$$A(n) = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{1 \cdot 2 \cdot 3 \cdots n} = \frac{(2n)!}{2^n (n!)^2} = \frac{1}{2^n} \binom{2n}{n}$$

The coefficient in the expansion can then be written using a $3j$ symbol as:

$$\begin{aligned} & \frac{A(s-k)A(s-l)A(s-m)}{A(s)} \frac{1}{2s+1} = \\ &= \frac{\frac{1}{2^{s-k}} \binom{2s-2k}{s-k} \frac{1}{2^{s-l}} \binom{2s-2l}{s-l} \frac{1}{2^{s-m}} \binom{2s-2m}{s-m}}{\frac{1}{2^s} \binom{2s}{s}} \frac{1}{2s+1} = \\ &= \frac{2^s}{2^{s-k+s-l+s-m}} \frac{\binom{2s-2k}{s-k} \binom{2s-2l}{s-l} \binom{2s-2m}{s-m}}{\binom{2s}{s}} \frac{1}{2s+1} = \\ &= \frac{\binom{2s-2k}{s-k} \binom{2s-2l}{s-l} \binom{2s-2m}{s-m}}{\binom{2s}{s}} \frac{1}{2s+1} = \\ &= \frac{(2s-2k)! (2s-2l)! (2s-2m)! (s!)^2}{((s-k)!)^2 ((s-l)!)^2 ((s-m)!)^2 (2s)!} \frac{1}{2s+1} = \\ &= \frac{(2s-2k)!(2s-2l)!(2s-2m)!}{(2s+1)!} \left[\frac{s!}{(s-k)!(s-l)!(s-m)!} \right]^2 = \\ &= \begin{pmatrix} k & l & m \\ 0 & 0 & 0 \end{pmatrix}^2 \end{aligned}$$

So we will just use the $3j$ symbol form from now on. We can now calculate the integral of three Legendre polynomials:

$$\begin{aligned}
 & \int_{-1}^1 P_k(x)P_l(x)P_m(x)dx = \\
 &= \int_{-1}^1 \sum_{n=|k-l|}^{k+l} \begin{pmatrix} k & l & n \\ 0 & 0 & 0 \end{pmatrix}^2 (2n+1)P_n(x)P_m(x)dx = \\
 &= \sum_{n=|k-l|}^{k+l} \begin{pmatrix} k & l & n \\ 0 & 0 & 0 \end{pmatrix}^2 (2n+1) \frac{2\delta_{nm}}{2n+1} = \\
 &= 2 \begin{pmatrix} k & l & m \\ 0 & 0 & 0 \end{pmatrix}^2
 \end{aligned} \tag{6.2}$$

This is consistent with the series expansion:

$$\begin{aligned}
 P_k(x)P_l(x) &= \sum_{m=|k-l|}^{k+l} \frac{2m+1}{2} \int_{-1}^1 P_k(x)P_l(x)P_m(x)dx P_m(x) = \\
 &= \sum_{m=|k-l|}^{k+l} \begin{pmatrix} k & l & m \\ 0 & 0 & 0 \end{pmatrix}^2 (2m+1)P_m(x)
 \end{aligned}$$

Any function $f(x)$ (where $-1 \leq x \leq 1$) can be expanded as:

$$\begin{aligned}
 f(x) &= \sum_{l=0}^{\infty} f_l P_l(x) \\
 f_l &= \frac{(2l+1)}{2} \int_{-1}^1 f(x)P_l(x)dx
 \end{aligned}$$

For the following choice of $f(x)$ we get (for $|t| \leq 1$):

$$\begin{aligned}
 f(x) &= \frac{1}{\sqrt{1-2xt+t^2}} \\
 f_l &= \frac{(2l+1)}{2} \int_{-1}^1 \frac{P_l(x)}{\sqrt{1-2xt+t^2}} dx = \frac{(2l+1)}{2} \int_{|1-t|}^{|1+t|} \frac{P_l\left(\frac{1-R^2+t^2}{2t}\right)}{R} \left(-\frac{R}{t}\right) dR = \\
 &= \frac{(2l+1)}{2t} \int_{|1-t|}^{|1+t|} P_l\left(\frac{1-R^2+t^2}{2t}\right) dR = \frac{(2l+1)}{2t} \int_{1-t}^{1+t} P_l\left(\frac{1-R^2+t^2}{2t}\right) dR = \\
 &= t^l
 \end{aligned}$$

Code:

```

>>> from sympy import var, legendre, integrate
>>> var("l R t")
(l, R, t)
>>> f = (2*l+1) / (2*t) * integrate(legendre(l, (1-R**2+t**2) / (2*t)),
...                               (R, 1-t, 1+t))
>>> for _l in range(20): print _l, f.subs(l, _l).doit().simplify()
...
0 1
1 t
2 t**2
3 t**3
4 t**4
5 t**5
6 t**6
7 t**7
8 t**8
9 t**9
10 t**10
11 t**11
12 t**12
13 t**13
14 t**14
15 t**15
16 t**16
17 t**17
18 t**18
19 t**19

```

So the Legendre polynomials are the coefficients of the following expansion for $|t| \leq 1$:

$$\frac{1}{\sqrt{1-2xt+t^2}} = \sum_{l=0}^{\infty} P_l(x)t^l$$

Note that for $|t| > 1$ we get:

$$\frac{1}{\sqrt{1-2xt+t^2}} = \frac{1}{|t|} \frac{1}{\sqrt{1-2x\frac{1}{t}+(\frac{1}{t})^2}} = \frac{1}{|t|} \sum_{l=0}^{\infty} P_l(x) \left(\frac{1}{t}\right)^l = \text{sign } t \sum_{l=0}^{\infty} P_l(x)t^{-l-1}$$

6.1.1 Example I

Very important is the following multipole expansion:

$$\begin{aligned} \frac{1}{|\mathbf{r}-\mathbf{r}'|} &= \frac{1}{\sqrt{(\mathbf{r}-\mathbf{r}')^2}} = \frac{1}{\sqrt{r^2-2\mathbf{r}\cdot\mathbf{r}'+r'^2}} = \frac{1}{r_{>}\sqrt{1-2\left(\frac{r_{\leq}}{r_{>}}\right)\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}'+\left(\frac{r_{\leq}}{r_{>}}\right)^2}} = \\ &= \frac{1}{r_{>}} \sum_{l=0}^{\infty} \left(\frac{r_{\leq}}{r_{>}}\right)^l P_l(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}') = \sum_{l=0}^{\infty} \frac{r_{\leq}^l}{r_{>}^{l+1}} P_l(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}') \end{aligned} \quad (6.3)$$

Where $r_{>} = \max(r, r')$ and $r_{<} = \min(r, r')$. Assuming $r > r'$, we get for the first few terms:

$$\begin{aligned} \frac{1}{|\mathbf{r}-\mathbf{r}'|} &= \frac{1}{r} \left(P_0(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}') + P_1(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}')\frac{r'}{r} + P_2(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}')\left(\frac{r'}{r}\right)^2 + O\left(\frac{r'^3}{r^3}\right) \right) = \\ &= \frac{1}{r} \left(1 + \hat{\mathbf{r}}\cdot\hat{\mathbf{r}}'\frac{r'}{r} + \frac{1}{2}(3(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}')^2 - 1)\left(\frac{r'}{r}\right)^2 + O\left(\frac{r'^3}{r^3}\right) \right) = \\ &= \frac{1}{r} + \frac{\mathbf{r}\cdot\mathbf{r}'}{r^3} + \frac{3(\mathbf{r}\cdot\mathbf{r}')^2 - r^2r'^2}{2r^5} + O\left(\frac{r'^3}{r^4}\right) \end{aligned}$$

6.1.2 Example II

Let's find the expansion of

$$f(x) = \frac{e^{-\alpha\sqrt{1-2xt+t^2}}}{\sqrt{1-2xt+t^2}}$$

for $|t| \leq 1$. We get:

$$\begin{aligned} f_l &= \frac{(2l+1)}{2} \int_{-1}^1 \frac{P_l(x) e^{-\alpha\sqrt{1-2xt+t^2}}}{\sqrt{1-2xt+t^2}} dx = \\ &= \frac{(2l+1)}{2} \int_{|1-t|}^{|1+t|} \frac{P_l\left(\frac{1-R^2+t^2}{2t}\right) e^{-\alpha R}}{R} \left(-\frac{R}{t}\right) dR = \\ &= \frac{(2l+1)}{2t} \int_{|1-t|}^{|1+t|} P_l\left(\frac{1-R^2+t^2}{2t}\right) e^{-\alpha R} dR = \\ &= \frac{(2l+1)}{2t} \int_{1-t}^{1+t} P_l\left(\frac{1-R^2+t^2}{2t}\right) e^{-\alpha R} dR \end{aligned}$$

Here is the result for the first few l :

$$\begin{aligned} f_0 &= \frac{(e^{2\alpha t} - 1) e^{-\alpha t - \alpha}}{2\alpha t} \\ f_1 &= \frac{3(\alpha^2 t e^{2\alpha t} + \alpha^2 t + \alpha t e^{2\alpha t} + \alpha t - \alpha e^{2\alpha t} + \alpha - e^{2\alpha t} + 1) e^{-\alpha t - \alpha}}{2\alpha^3 t^2} \\ f_2 &= \frac{5(\alpha^4 t^2 e^{2\alpha t} - \alpha^4 t^2 + 3\alpha^3 t^2 e^{2\alpha t} - 3\alpha^3 t^2 - 3\alpha^3 t e^{2\alpha t} - 3\alpha^3 t + 3\alpha^2 t^2 e^{2\alpha t} + X) e^{-\alpha t - \alpha}}{2\alpha^5 t^3} \\ X &= -3\alpha^2 t^2 - 9\alpha^2 t e^{2\alpha t} - 9\alpha^2 t 3\alpha^2 e^{2\alpha t} - 3\alpha^2 - 9\alpha t e^{2\alpha t} - 9\alpha t + 9\alpha e^{2\alpha t} - 9\alpha + 9e^{2\alpha t} - 9 \end{aligned}$$

Expanding in t up to $\mathcal{O}(t^7)$ we get:

$$\begin{aligned}
 f_l &= e^{-\alpha} g_l \\
 g_0 &= 1 + \frac{1}{6}\alpha^2 t^2 + \frac{1}{120}\alpha^4 t^4 + \frac{1}{5040}\alpha^6 t^6 + \mathcal{O}(t^7) \\
 g_1 &= t + \alpha t + \frac{1}{10}\alpha^2 t^3 + \frac{1}{10}\alpha^3 t^3 + \frac{1}{280}\alpha^4 t^5 + \frac{1}{280}\alpha^5 t^5 + \mathcal{O}(t^7) \\
 g_2 &= t^2 + \alpha t^2 + \frac{1}{3}\alpha^2 t^2 + \frac{1}{14}\alpha^2 t^4 + \frac{1}{14}\alpha^3 t^4 + \frac{1}{42}\alpha^4 t^4 + \frac{1}{504}\alpha^4 t^6 + \frac{1}{504}\alpha^5 t^6 + \\
 &\quad + \frac{1}{1512}\alpha^6 t^6 + \mathcal{O}(t^7) \\
 g_3 &= t^3 + \alpha t^3 + \frac{2}{5}\alpha^2 t^3 + \frac{1}{18}\alpha^2 t^5 + \frac{1}{15}\alpha^3 t^3 + \frac{1}{18}\alpha^3 t^5 + \frac{1}{45}\alpha^4 t^5 + \frac{1}{270}\alpha^5 t^5 + \mathcal{O}(t^7) \\
 g_4 &= t^4 + \alpha t^4 + \frac{3}{7}\alpha^2 t^4 + \frac{1}{22}\alpha^2 t^6 + \frac{2}{21}\alpha^3 t^4 + \frac{1}{22}\alpha^3 t^6 + \frac{1}{105}\alpha^4 t^4 + \frac{3}{154}\alpha^4 t^6 + \frac{1}{231}\alpha^5 t^6 + \\
 &\quad + \frac{1}{2310}\alpha^6 t^6 + \mathcal{O}(t^7)
 \end{aligned}$$

Code:

```

>>> from sympy import var, legendre, integrate, exp, latex, cse
>>> var("l R t alpha")
(l, R, t, alpha)
>>>
>>> f = (2*l+1) / (2*t) * integrate(legendre(l, (1-R**2+t**2) \
...      / (2*t)) * exp(-alpha*R), (R, 1-t, 1+t))
>>>
>>> for _l in range(3):
...     print "f_%d & =" %_l, latex(f.subs(l, _l).doit() \
...     .simplify()), "\\\\"
...
f_0 & = \frac{\left(e^{2 \alpha t} - 1\right) e^{-\dots} \\\
f_1 & = \frac{3}{2} \frac{\left(\alpha^2 t e^{2 \dots} \\\
f_2 & = \frac{5}{2} \frac{\left(\alpha^4 t^2 \dots \\\
>>> for _l in range(5):
...     result = f.subs(l, _l).doit().simplify() / exp(-alpha)
...     print "g_%d & =" %_l, latex(result.series(t, 0, 7)), "\\\\"
...
g_0 & = 1 + \frac{1}{6} \alpha^2 t^2 + \frac{1}{120} \dots \\\
g_1 & = t + \alpha t + \frac{1}{10} \alpha^2 t^3 + \dots \\\
g_2 & = t^2 + \alpha t^2 + \frac{1}{3} \alpha^2 \dots \\\
g_3 & = t^3 + \alpha t^3 + \frac{2}{5} \alpha^2 \dots \\\
g_4 & = t^4 + \alpha t^4 + \frac{3}{7} \alpha^2 \dots \\\

```

The long output of the script has been truncated by the dots ”...”.

6.1.3 Example III

$$\frac{e^{-\frac{|\mathbf{r}-\mathbf{r}'|}{D}}}{|\mathbf{r}-\mathbf{r}'|} = \frac{e^{-\frac{r_{>}\sqrt{1-2\left(\frac{r_{\leq}}{r_{>}}\right)\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}'+\left(\frac{r_{\leq}}{r_{>}}\right)^2}}}{r_{>}\sqrt{1-2\left(\frac{r_{\leq}}{r_{>}}\right)\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}'+\left(\frac{r_{\leq}}{r_{>}}\right)^2}} = \frac{1}{r_{>}} \frac{e^{-\alpha\sqrt{1-2xt+t^2}}}{\sqrt{1-2xt+t^2}}$$

where:

$$\alpha = \frac{r_{>}}{D}$$

$$x = \hat{\mathbf{r}} \cdot \hat{\mathbf{r}}'$$

$$t = \frac{r_{\leq}}{r_{>}}$$

6.1.4 Example IV

$$V(|\mathbf{r}_1 - \mathbf{r}_2|) = \frac{e^{-\frac{|\mathbf{r}_1 - \mathbf{r}_2|}{D}}}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

The potential V is a function of r_1 , r_2 and $\cos \theta$ only:

$$\begin{aligned} V(|\mathbf{r}_1 - \mathbf{r}_2|) &= V\left(\sqrt{r_1^2 - 2\mathbf{r}_1 \cdot \mathbf{r}_2 + r_2^2}\right) = V\left(\sqrt{r_1^2 - 2r_1r_2\cos\theta + r_2^2}\right) = \\ &= V(r_1, r_2, \cos\theta) \end{aligned}$$

So we expand in the $\cos \theta$ variable using the Legendre expansion:

$$V(|\mathbf{r}_1 - \mathbf{r}_2|) = V(r_1, r_2, \cos \theta) = \sum_{l=0}^{\infty} V_l(r_1, r_2) P_l(\cos \theta)$$

where $V_l(r_1, r_2)$ only depends on r_1 and r_2 :

$$\begin{aligned} V_l(r_1, r_2) &= \frac{2l+1}{2} \int_{-1}^1 V(|\mathbf{r}_1 - \mathbf{r}_2|) P_l(\cos \theta) d(\cos \theta) = \\ &= \frac{2l+1}{2} \int_{-1}^1 \frac{e^{-\frac{|\mathbf{r}_1 - \mathbf{r}_2|}{D}}}{|\mathbf{r}_1 - \mathbf{r}_2|} P_l(\cos \theta) d(\cos \theta) = \\ &= \frac{2l+1}{2r_1 r_2} \int_{|r_1 - r_2|}^{r_1 + r_2} e^{-\frac{r}{D}} P_l\left(\frac{r_1^2 - r^2 + r_2^2}{2r_1 r_2}\right) dr \end{aligned}$$

In the limit $D \rightarrow \infty$ we get:

$$V_l(r_1, r_2) \rightarrow \frac{r_{<}^l}{r_{>}^{l+1}}$$

In general, the $V_l(r_1, r_2)$ expressions are complicated. For the first two lowest l we get:

$$\begin{aligned} V_0(r_1, r_2) &= \frac{D}{2r_1 r_2} \left(e^{-\frac{|r_1 - r_2|}{D}} - e^{-\frac{r_1 + r_2}{D}} \right) \\ V_1(r_1, r_2) &= \frac{3}{2} \frac{D \left(-D^2 e^{2\frac{r_2}{D}} + D^2 - Dr_1 e^{2\frac{r_2}{D}} + Dr_1 + Dr_2 e^{2\frac{r_2}{D}} + X \right) e^{-\frac{r_1}{D} - \frac{r_2}{D}}}{r_1^2 r_2^2} \\ X &= Dr_2 + r_1 r_2 e^{2\frac{r_2}{D}} + r_1 r_2 \end{aligned}$$

In $V_1(r_1, r_2)$ we assume $r_1 \geq r_2$.

Another option is to use the Gegenbauer's addition theorem, which gives directly:

$$V_k(r_1, r_2) = (2k+1) \frac{K_{k+\frac{1}{2}}\left(\frac{r_{>}}{D}\right) I_{k+\frac{1}{2}}\left(\frac{r_{<}}{D}\right)}{\sqrt{r_{>}} \sqrt{r_{<}}}$$

Using:

$$I_\nu(z) = \frac{1}{\Gamma(\nu+1)} \left(\frac{z}{2}\right)^\nu {}_0F_1\left(\nu+1; \frac{z^2}{4}\right)$$

$$K_\nu(z) = \frac{\Gamma(\nu)}{2} \left(\frac{2}{z}\right)^\nu {}_0F_1\left(1-\nu; \frac{z^2}{4}\right) + \frac{\Gamma(-\nu)}{2} \left(\frac{z}{2}\right)^\nu {}_0F_1\left(\nu+1; \frac{z^2}{4}\right)$$

and

$$I_\nu(x)K_\nu(y) = \frac{1}{2\nu} \left(\frac{x}{y}\right)^\nu {}_0F_1\left(\nu+1; \frac{x^2}{4}\right) {}_0F_1\left(1-\nu; \frac{y^2}{4}\right) +$$

$$+ \frac{\Gamma(-\nu)}{2\Gamma(\nu+1)} \left(\frac{xy}{4}\right)^\nu {}_0F_1\left(\nu+1; \frac{x^2}{4}\right) {}_0F_1\left(\nu+1; \frac{y^2}{4}\right)$$

we get

$$V_k(r_1, r_2) = \frac{2k+1}{(r_{>}r_{<})^{\frac{1}{2}}} \left(\frac{1}{2k+1} \left(\frac{r_{<}}{r_{>}}\right)^{k+\frac{1}{2}} {}_0F_1\left(k+\frac{3}{2}; \frac{r_{<}^2}{4D^2}\right) {}_0F_1\left(\frac{1}{2}-k; \frac{r_{>}^2}{4D^2}\right) + \right.$$

$$+ \frac{\pi}{2} \frac{1}{\Gamma^2(k+\frac{3}{2}) \sin(\pi(k+\frac{3}{2}))} \left(\frac{r_{<}r_{>}}{4D^2}\right)^{k+\frac{1}{2}} {}_0F_1\left(k+\frac{3}{2}; \frac{r_{<}^2}{4D^2}\right) {}_0F_1\left(k+\frac{3}{2}; \frac{r_{>}^2}{4D^2}\right) \Bigg) =$$

$$= \frac{r_{<}^k}{r_{>}^{k+1}} {}_0F_1\left(k+\frac{3}{2}; \frac{r_{<}^2}{4D^2}\right) {}_0F_1\left(\frac{1}{2}-k; \frac{r_{>}^2}{4D^2}\right) +$$

$$+ \frac{\pi}{(2D)^{2k+1}} (r_{<}r_{>})^k \frac{(-1)^{k+1}}{\Gamma(k+\frac{1}{2})\Gamma(k+\frac{3}{2})} {}_0F_1\left(k+\frac{3}{2}; \frac{r_{<}^2}{4D^2}\right) {}_0F_1\left(k+\frac{3}{2}; \frac{r_{>}^2}{4D^2}\right)$$

where we used:

$$\Gamma(-\nu) = \frac{\pi}{\sin(\pi(\nu+1))} \frac{1}{\Gamma(\nu+1)}$$

Since ${}_0F_1(a; 0) = 1$, we get for $D \rightarrow \infty$:

$$V_k(r_1, r_2) \rightarrow \frac{r_{<}^k}{r_{>}^{k+1}}$$

as we should.

6.2 Spherical Harmonics

Are defined for $m \geq 0$ by

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) e^{im\phi}$$

where P_l^m are associated Legendre polynomials defined by

$$P_l^m(x) = (-1)^m (1-x^2)^{m/2} \frac{d^m}{dx^m} P_l(x)$$

and P_l are Legendre polynomials. For $m < 0$ they are defined by:

$$Y_{lm}(\Omega) = (-1)^m Y_{l,-m}^*(\Omega)$$

Sometimes the spherical harmonics are written as:

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta) \Phi_m(\phi)$$

where:

$$\begin{aligned} \Phi_m(\phi) &= \frac{1}{\sqrt{2\pi}} e^{im\phi} \\ \Theta_{lm}(\theta) &= \begin{cases} \sqrt{\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) & \text{for } m \geq 0 \\ (-1)^m \Theta_{l,-m}(\theta) & \text{for } m < 0 \end{cases} \end{aligned}$$

The spherical harmonics are orthonormal:

$$\int Y_{lm} Y_{l'm'}^* d\Omega = \int_0^{2\pi} \int_0^\pi Y_{lm}(\theta, \phi) Y_{l'm'}^*(\theta, \phi) \sin \theta d\theta d\phi = \delta_{mm'} \delta_{ll'} \quad (6.4)$$

and complete (both in the l -subspace and the whole space):

$$\sum_{m=-l}^l |Y_{lm}(\theta, \phi)|^2 = \frac{2l+1}{4\pi} \quad (6.5)$$

$$\sum_{l=0}^{\infty} \sum_{m=-l}^l Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi') = \frac{1}{\sin \theta} \delta(\theta - \theta') \delta(\phi - \phi') = \delta(\hat{\mathbf{r}} - \hat{\mathbf{r}}') \quad (6.6)$$

The relation (6.5) is a special case of an addition theorem for spherical harmonics

$$\sum_{m=-l}^l Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi') = \frac{2l+1}{4\pi} P_l(\cos \gamma) \quad (6.7)$$

where γ is the angle between the unit vectors given by $\hat{\mathbf{r}} = (\theta, \phi)$ and $\hat{\mathbf{r}}' = (\theta', \phi')$:

$$\cos \gamma = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi') = \hat{\mathbf{r}} \cdot \hat{\mathbf{r}}'$$

Relations between complex conjugates is:

$$Y_{lm}^*(\Omega) = (-1)^m Y_{l,-m}(\Omega)$$

$$(-1)^m Y_{l,-m}^*(\Omega) = Y_{lm}(\Omega)$$

6.2.1 Examples

$$\int_{-1}^1 P_k(x) dx = \int_{-1}^1 P_k(x) P_0(x) dx = 2\delta_{k0}$$

$$\int Y_{k0}(\Omega) d\Omega = \int Y_{k0}(\Omega) \sqrt{4\pi} Y_{00}(\Omega) d\Omega = \sqrt{4\pi} \delta_{k0}$$

6.3 Gaunt Coefficients

We use the Wigner-Eckart theorem:

$$\langle jm | T_q^k | j' m' \rangle = (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} (j || T^k || j')$$

Where:

$$T_q^k = Y_{kq}$$

In order to calculate the reduced matrix element $(j || T^k || j')$, we evaluate the W-E theorem for $m = q = m' = 0$:

$$\langle j0 | T_0^k | j'0 \rangle = (-1)^j \begin{pmatrix} j & k & j' \\ 0 & 0 & 0 \end{pmatrix} (j || T^k || j')$$

and also evaluate the left hand side explicitly:

$$\begin{aligned}
\langle j0|T_0^k|j'0\rangle &= \langle j0|Y_{k0}|j'0\rangle = \int Y_{j0}^*(\Omega)Y_{k0}(\Omega)Y_{j'0}(\Omega)d\Omega = \\
&= \sqrt{\frac{(2j+1)(2k+1)(2j'+1)}{4\pi}} \frac{1}{4\pi} \int P_j(\cos\theta)P_k(\cos\theta)P_{j'}(\cos\theta)\sin\theta d\theta d\phi = \\
&= \sqrt{\frac{(2j+1)(2k+1)(2j'+1)}{4\pi}} \frac{1}{2} \int_{-1}^1 P_j(x)P_k(x)P_{j'}(x)dx = \\
&= \sqrt{\frac{(2j+1)(2k+1)(2j'+1)}{4\pi}} \begin{pmatrix} j & k & j' \\ 0 & 0 & 0 \end{pmatrix}^2
\end{aligned}$$

where we used (6.2). Comparing these two results, we get:

$$(j||T^k||j') = (-1)^{-j} \sqrt{\frac{(2j+1)(2k+1)(2j'+1)}{4\pi}} \begin{pmatrix} j & k & j' \\ 0 & 0 & 0 \end{pmatrix}$$

and finally:

$$\begin{aligned}
&\int Y_{jm}^*(\Omega)Y_{kq}(\Omega)Y_{j'm'}(\Omega)d\Omega = \\
&= \langle jm|T_q^k|j'm'\rangle = (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} (j||T^k||j') = \\
&= (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} (-1)^{-j} \sqrt{\frac{(2j+1)(2k+1)(2j'+1)}{4\pi}} \begin{pmatrix} j & k & j' \\ 0 & 0 & 0 \end{pmatrix} = \\
&= (-1)^{-m} \sqrt{\frac{(2j+1)(2k+1)(2j'+1)}{4\pi}} \begin{pmatrix} j & k & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix}
\end{aligned}$$

In order to evaluate other integrals of spherical harmonics, we just use the above result, for example:

$$\begin{aligned}
& \int Y_{l_1 m_1}(\Omega) Y_{l_2 m_2}(\Omega) Y_{l_3 m_3}(\Omega) d\Omega = \\
& = (-1)^{m_1} \int Y_{l_1 -m_1}^*(\Omega) Y_{l_2 m_2}(\Omega) Y_{l_3 m_3}(\Omega) d\Omega = \\
& = (-1)^{m_1} (-1)^{-(-m_1)} \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ -(-m_1) & m_2 & m_3 \end{pmatrix} = \\
& = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}
\end{aligned}$$

This is the most symmetric relation. It was first obtained by [5] (equation (9), p. 194, where the author expanded the $3j$ symbols, so his formula is more complex but equivalent to the above).

It is useful to incorporate the selection rule $m_1 + m_2 + m_3 = 0$ of the $3j$ symbols into the formula and we get:

$$\begin{aligned}
c^k(l, m, l', m') &= \sqrt{\frac{4\pi}{4k+1}} \int Y_{lm}^*(\Omega) Y_{k, m-m'}(\Omega) Y_{l'm'}(\Omega) d\Omega = \\
&= (-1)^{-m} \sqrt{\frac{4\pi}{4k+1}} \sqrt{\frac{(2l+1)(2k+1)(2l'+1)}{4\pi}} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ -m & m-m' & m' \end{pmatrix} = \\
&= (-1)^{-m} \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ -m & m-m' & m' \end{pmatrix}
\end{aligned}$$

In this form the c^k symbols are the same as in [43]. From the other selection rules of the $3j$

symbols it follows, that the $c^k(l, m, l', m')$ coefficients are nonzero only when:

$$|l - l'| \leq k \leq l + l'$$

$$l + l' + k = \text{even integer}$$

6.3.1 Example I

$$c^0(l, m, l', m') = \sqrt{4\pi} \int Y_{lm}^*(\Omega) Y_{00}(\Omega) Y_{l'm'}(\Omega) d\Omega = \delta_{ll'} \delta_{mm'}$$

6.3.2 Example II

$$\begin{aligned} \sum_{m=-l}^l c^k(l, m, l, m) &= \sum_m \sqrt{\frac{4\pi}{4k+1}} \int Y_{lm}^*(\Omega) Y_{k0}(\Omega) Y_{lm}(\Omega) d\Omega = \\ &= \sqrt{\frac{4\pi}{4k+1}} \int \sum_m |Y_{lm}(\Omega)|^2 Y_{k0}(\Omega) d\Omega = \\ &= \sqrt{\frac{4\pi}{4k+1}} \frac{2l+1}{4\pi} \int Y_{k0}(\Omega) d\Omega = \\ &= \sqrt{\frac{4\pi}{4k+1}} \frac{2l+1}{4\pi} \sqrt{4\pi} \delta_{k0} = \\ &= (2l+1) \delta_{k0} \end{aligned}$$

6.3.3 Example III

$$\begin{aligned}
c^k(l, m, l', m') &= \sqrt{\frac{4\pi}{4k+1}} \int Y_{lm}^*(\Omega) Y_{k,m-m'}(\Omega) Y_{l'm'}(\Omega) d\Omega = \\
&= \sqrt{\frac{4\pi}{4k+1}} \int \Theta_{lm} \Phi_m^* \Theta_{k,m-m'} \Phi_{m-m'} \Theta_{l'm'} \Phi_{m'} \sin \theta d\theta d\phi = \\
&= \sqrt{\frac{4\pi}{4k+1}} \int_0^\pi \Theta_{lm} \Theta_{k,m-m'} \Theta_{l'm'} \sin \theta d\theta \int_0^{2\pi} \Phi_m^* \Phi_{m-m'} \Phi_{m'} d\phi = \\
&= \sqrt{\frac{4\pi}{4k+1}} \int_0^\pi \Theta_{lm} \Theta_{k,m-m'} \Theta_{l'm'} \sin \theta d\theta \left(\frac{1}{\sqrt{2\pi}} \right)^3 \int_0^{2\pi} e^{-im\phi} e^{i(m-m')\phi} e^{im'\phi} d\phi = \\
&= \sqrt{\frac{4\pi}{4k+1}} \int_0^\pi \Theta_{lm} \Theta_{k,m-m'} \Theta_{l'm'} \sin \theta d\theta \left(\frac{1}{\sqrt{2\pi}} \right)^3 \int_0^{2\pi} d\phi = \\
&= \sqrt{\frac{2}{4k+1}} \int_0^\pi \Theta_{lm} \Theta_{k,m-m'} \Theta_{l'm'} \sin \theta d\theta
\end{aligned}$$

6.3.4 Example IV

$$\begin{aligned}
c^k(l, -m, l', -m') &= \\
&= (-1)^m \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ m & -m+m' & -m' \end{pmatrix} = \\
&= (-1)^m (-1)^{l+k+l'} \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ -m & m-m' & m' \end{pmatrix} = \\
&= (-1)^{-m} \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ -m & m-m' & m' \end{pmatrix} = \\
&= c^k(l, m, l', m')
\end{aligned}$$

Where we used the fact, that $l + k + l'$ is an even integer and $(-1)^m = (-1)^{-m}$. c^k is not

symmetric in lm and $l'm'$:

$$\begin{aligned}
& c^k(l', m', l, m) \\
&= (-1)^{-m'} \sqrt{(2l' + 1)(2l + 1)} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & k & l \\ -m' & m' - m & m \end{pmatrix} = \\
&= (-1)^{-m'} \sqrt{(2l + 1)(2l' + 1)} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ m & m' - m & -m' \end{pmatrix} = \\
&= (-1)^{-m'} \sqrt{(2l + 1)(2l' + 1)} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ -m & m - m' & m' \end{pmatrix} = \\
&= (-1)^{m-m'} (-1)^{-m} \sqrt{(2l + 1)(2l' + 1)} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ -m & m - m' & m' \end{pmatrix} = \\
&= (-1)^{m-m'} c^k(l, m, l', m')
\end{aligned}$$

Few other identities:

$$\begin{aligned}
c^k(l, 0, l', 0) &= \sqrt{(2l + 1)(2l' + 1)} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \\
\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 &= \frac{c^k(l, 0, l', 0)}{\sqrt{(2l + 1)(2l' + 1)}} = \frac{c^{l'}(l, 0, k, 0)}{\sqrt{(2l + 1)(2k + 1)}} = \frac{c^l(l', 0, k, 0)}{\sqrt{(2l' + 1)(2k + 1)}} \\
c^k(l, 0, l', 0) &= c^k(l', 0, l, 0)
\end{aligned}$$

6.3.5 Example V

$$\begin{aligned}
& \sum_{m'} (c^k(l, m, l', m'))^2 = \\
&= \sum_{m'} (2l+1)(2l'+1) \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l & k & l' \\ -m & m-m' & m' \end{pmatrix}^2 = \\
&= (2l+1)(2l'+1) \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{m'} \begin{pmatrix} l & k & l' \\ -m & m-m' & m' \end{pmatrix}^2 = \\
&= (2l+1)(2l'+1) \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{1}{2l+1} = \\
&= (2l'+1) \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 = \\
&= \sqrt{\frac{2l'+1}{2l+1}} c^k(l', 0, l, 0)
\end{aligned}$$

6.3.6 Example VI

$$\begin{aligned}
& \sum_{m'} \sum_q \int Y_{l'm'}(\Omega) Y_{l'm'}^*(\Omega') Y_{kq}(\Omega) Y_{kq}^*(\Omega') Y_{lm}(\Omega') d\Omega' = \quad (6.8) \\
&= \int \frac{2l'+1}{4\pi} P_{l'}(\hat{\mathbf{x}} \cdot \hat{\mathbf{x}}') \frac{2k+1}{4\pi} P_k(\hat{\mathbf{x}} \cdot \hat{\mathbf{x}}') Y_{lm}(\Omega') d\Omega' = \\
&= \int \frac{2l'+1}{4\pi} \frac{2k+1}{4\pi} \sum_{\lambda=|l'-k|}^{\lambda=l'+k} \sqrt{\frac{2\lambda+1}{2l'+1}} c^k(l', 0, \lambda, 0) \frac{4\pi}{2\lambda+1} \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}^*(\Omega') Y_{\lambda\mu}(\Omega) Y_{lm}(\Omega') d\Omega' = \\
&= \frac{2l'+1}{4\pi} \frac{2k+1}{4\pi} \sum_{\lambda=|l'-k|}^{\lambda=l'+k} \sqrt{\frac{2\lambda+1}{2l'+1}} c^k(l', 0, \lambda, 0) \frac{4\pi}{2\lambda+1} \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}(\Omega) \delta_{\lambda l} \delta_{\mu m} = \\
&= \frac{2k+1}{4\pi} \sqrt{\frac{2l'+1}{2l+1}} c^k(l', 0, l, 0) Y_{lm}(\Omega)
\end{aligned}$$

Where we used the following identities:

$$\begin{aligned}
\sum_{m'} Y_{l'm'}(\Omega) Y_{l'm'}^*(\Omega') &= \frac{2l'+1}{4\pi} P_{l'}(\hat{\mathbf{x}} \cdot \hat{\mathbf{x}}') \\
\sum_q Y_{kq}(\Omega) Y_{kq}^*(\Omega') &= \frac{2k+1}{4\pi} P_k(\hat{\mathbf{x}} \cdot \hat{\mathbf{x}}') \\
P_k(\hat{\mathbf{x}} \cdot \hat{\mathbf{x}}') P_{l'}(\hat{\mathbf{x}} \cdot \hat{\mathbf{x}}') &= \sum_{\lambda=|l'-k|}^{l'+k} \begin{pmatrix} k & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 (2\lambda+1) P_\lambda(\hat{\mathbf{x}} \cdot \hat{\mathbf{x}}') = \\
&= \sum_{\lambda=|l'-k|}^{\lambda=l'+k} \sqrt{\frac{2\lambda+1}{2l'+1}} c^k(l', 0, \lambda, 0) P_\lambda(\hat{\mathbf{x}} \cdot \hat{\mathbf{x}}') = \\
&= \sum_{\lambda=|l'-k|}^{\lambda=l'+k} \sqrt{\frac{2\lambda+1}{2l'+1}} c^k(l', 0, \lambda, 0) \frac{4\pi}{2\lambda+1} \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}^*(\Omega') Y_{\lambda\mu}(\Omega)
\end{aligned}$$

Note: using the integral of 3 spherical harmonics directly in (6.8):

$$\begin{aligned}
\sum_{m'} \sum_q \int Y_{l'm'}(\Omega) Y_{l'm'}^*(\Omega') Y_{kq}(\Omega) Y_{kq}^*(\Omega') Y_{lm}(\Omega') d\Omega' &= \\
&= \sum_{m'} Y_{l'm'}(\Omega) Y_{k,m-m'}(\Omega) \sqrt{\frac{4\pi}{2k+1}} c^k(l, m, l', m')
\end{aligned}$$

doesn't straightforwardly lead to the final result, as it is not obvious how to simplify things further.

6.4 Wigner 3j Symbols

Relation between the Wigner 3j symbols and Clebsch-Gordan coefficients:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}} (j_1 m_1 j_2 m_2 | j_3 -m_3)$$

$$(j_1 m_1 j_2 m_2 | j_3 m_3) = (-1)^{j_1-j_2+m_3} \sqrt{2j_3+1} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}$$

They are nonzero only when:

$$m_1 + m_2 + m_3 = 0$$

$$j_1 + j_2 + j_3 = \text{integer (or even integer if } m_1 = m_2 = m_3 = 0)$$

$$|m_i| \leq j_i$$

$$|j_1 - j_2| \leq j_3 \leq j_1 + j_2$$

They have lots of symmetries. The 3j symbol is invariant for an even permutation of columns:

$$\begin{aligned} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} &= \\ &= \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \\ &= \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} \end{aligned}$$

For an odd permutation of columns it changes sign if $j_1 + j_2 + j + 3$ is an odd integer:

$$\begin{aligned}
 & \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \\
 & = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = \\
 & = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} = \\
 & = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix}
 \end{aligned}$$

and the same if you change the sign of the second row:

$$\begin{aligned}
 & \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \\
 & = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix}
 \end{aligned}$$

Orthogonality relations:

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j' \\ m_1 & m_2 & m' \end{pmatrix} = \frac{\delta_{jj'} \delta_{mm'}}{2j+1}$$

As a special case, we get:

$$\sum_{m'} \begin{pmatrix} l & k & l' \\ -m & m-m' & m' \end{pmatrix}^2 = \frac{1}{2l+1} \tag{6.9}$$

Here is a script to check that the equation (6.9) works:

```

from sympy import S
from sympy.physics.wigner import wigner_3j

def doit(l, k, lp, m):
    s = 0
    for mp in range(-lp, lp+1):
        s += wigner_3j(l, k, lp, -m, m-mp, mp)**2
    print "%2d %2d %2d %2d " % (l, k, lp, m), s, " ", S(1)/(2*l+1)

k = 4
lp = 3
print " l  k  lp m:  lhs   rhs"
for l in range(1, 6):
    for m in range(-l, l+1):
        doit(l, k, lp, m)

```

it prints:

l	k	lp	m:	lhs	rhs
1	4	3	-1	1/3	1/3
1	4	3	0	1/3	1/3
1	4	3	1	1/3	1/3
2	4	3	-2	1/5	1/5
2	4	3	-1	1/5	1/5
2	4	3	0	1/5	1/5
2	4	3	1	1/5	1/5
2	4	3	2	1/5	1/5
3	4	3	-3	1/7	1/7
3	4	3	-2	1/7	1/7
3	4	3	-1	1/7	1/7
3	4	3	0	1/7	1/7
3	4	3	1	1/7	1/7
3	4	3	2	1/7	1/7
3	4	3	3	1/7	1/7
4	4	3	-4	1/9	1/9
4	4	3	-3	1/9	1/9
4	4	3	-2	1/9	1/9
4	4	3	-1	1/9	1/9
4	4	3	0	1/9	1/9
4	4	3	1	1/9	1/9
4	4	3	2	1/9	1/9
4	4	3	3	1/9	1/9

4	4	3	4	1/9	1/9
5	4	3	-5	1/11	1/11
5	4	3	-4	1/11	1/11
5	4	3	-3	1/11	1/11
5	4	3	-2	1/11	1/11
5	4	3	-1	1/11	1/11
5	4	3	0	1/11	1/11
5	4	3	1	1/11	1/11
5	4	3	2	1/11	1/11
5	4	3	3	1/11	1/11
5	4	3	4	1/11	1/11
5	4	3	5	1/11	1/11

Values of the $3j$ coefficients for a few special cases (use the symmetries above to obtain values for permuted symbols):

$$\begin{aligned}
\begin{pmatrix} k & l & m \\ 0 & 0 & 0 \end{pmatrix} &= (-1)^s \sqrt{\frac{(2s-2k)!(2s-2l)!(2s-2m)!}{(2s+1)!}} \times \\
&\times \frac{s!}{(s-k)!(s-l)!(s-m)!} \quad \text{for } 2s = k + l + m \text{ even} \\
\begin{pmatrix} k & l & m \\ 0 & 0 & 0 \end{pmatrix} &= 0 \quad \text{for } 2s = k + l + m \text{ odd} \\
\begin{pmatrix} j + \frac{1}{2} & j & \frac{1}{2} \\ m & -m - \frac{1}{2} & \frac{1}{2} \end{pmatrix} &= (-1)^{j-m-\frac{1}{2}} \sqrt{\frac{j-m+\frac{1}{2}}{(2j+1)(2j+2)}} \\
\begin{pmatrix} j+1 & j & 1 \\ m & -m-1 & 1 \end{pmatrix} &= (-1)^{j-m-1} \sqrt{\frac{(j-m)(j-m+1)}{(2j+1)(2j+2)(2j+3)}} \\
\begin{pmatrix} j+1 & j & 1 \\ m & -m & 0 \end{pmatrix} &= (-1)^{j-m-1} \sqrt{\frac{2(j+m+1)(j-m+1)}{(2j+1)(2j+2)(2j+3)}}
\end{aligned}$$

6.4.1 Examples

$$\begin{aligned}
& \begin{pmatrix} j_3 - \frac{1}{2} & \frac{1}{2} & j_3 \\ m_3 - \frac{1}{2} & \frac{1}{2} & -m_3 \end{pmatrix} = \begin{pmatrix} j_3 & j_3 - \frac{1}{2} & \frac{1}{2} \\ -m_3 & m_3 - \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \\
& = \begin{pmatrix} j + \frac{1}{2} & j & \frac{1}{2} \\ m & -m - \frac{1}{2} & \frac{1}{2} \end{pmatrix} \Big|_{j=j_3-\frac{1}{2}; m=-m_3} = \\
& = (-1)^{j_3-\frac{1}{2}+m_3-\frac{1}{2}} \sqrt{\frac{j_3 - \frac{1}{2} + m_3 + \frac{1}{2}}{(2j_3 - 1 + 1)(2j_3 - 1 + 2)}} = (-1)^{j_3+m_3-1} \sqrt{\frac{j_3 + m_3}{2j_3(2j_3 + 1)}}
\end{aligned}$$

$$\begin{aligned}
& \begin{pmatrix} j_3 - \frac{1}{2} & \frac{1}{2} & j_3 \\ m_3 + \frac{1}{2} & -\frac{1}{2} & -m_3 \end{pmatrix} = (-1)^{j_3-\frac{1}{2}+\frac{1}{2}+j_3} \begin{pmatrix} j_3 & j_3 - \frac{1}{2} & \frac{1}{2} \\ m_3 & -m_3 - \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \\
& = (-1)^{2j_3} \begin{pmatrix} j + \frac{1}{2} & j & \frac{1}{2} \\ m & -m - \frac{1}{2} & \frac{1}{2} \end{pmatrix} \Big|_{j=j_3-\frac{1}{2}; m=m_3} = \\
& = (-1)^{2j_3} (-1)^{j_3-\frac{1}{2}-m_3-\frac{1}{2}} \sqrt{\frac{j_3 - \frac{1}{2} - m_3 + \frac{1}{2}}{(2j_3 - 1 + 1)(2j_3 - 1 + 2)}} = \\
& = (-1)^{2j_3} (-1)^{j_3-m_3-1} \sqrt{\frac{j_3 - m_3}{2j_3(2j_3 + 1)}}
\end{aligned}$$

$$\begin{aligned}
\begin{pmatrix} j_3 + \frac{1}{2} & \frac{1}{2} & j_3 \\ m_3 - \frac{1}{2} & \frac{1}{2} & -m_3 \end{pmatrix} &= (-1)^{j_3 + \frac{1}{2} + \frac{1}{2} + j_3} \begin{pmatrix} j_3 + \frac{1}{2} & j_3 & \frac{1}{2} \\ m_3 - \frac{1}{2} & -m_3 & \frac{1}{2} \end{pmatrix} = \\
&= (-1)^{2j_3+1} \begin{pmatrix} j + \frac{1}{2} & j & \frac{1}{2} \\ m & -m - \frac{1}{2} & \frac{1}{2} \end{pmatrix} \Big|_{j=j_3; m=m_3-\frac{1}{2}} = \\
&= (-1)^{2j_3+1} (-1)^{j_3-m_3+\frac{1}{2}-\frac{1}{2}} \sqrt{\frac{j_3 - m_3 + \frac{1}{2} + \frac{1}{2}}{(2j_3+1)(2j_3+2)}} = \\
&= (-1)^{2j_3+1} (-1)^{j_3-m_3} \sqrt{\frac{j_3 - m_3 + 1}{(2j_3+1)(2j_3+2)}} \\
\\
\begin{pmatrix} j_3 + \frac{1}{2} & \frac{1}{2} & j_3 \\ m_3 + \frac{1}{2} & -\frac{1}{2} & -m_3 \end{pmatrix} &= \begin{pmatrix} j_3 + \frac{1}{2} & j_3 & \frac{1}{2} \\ -m_3 - \frac{1}{2} & m_3 & \frac{1}{2} \end{pmatrix} = \\
&= \begin{pmatrix} j + \frac{1}{2} & j & \frac{1}{2} \\ m & -m - \frac{1}{2} & \frac{1}{2} \end{pmatrix} \Big|_{j=j_3; m=-m_3-\frac{1}{2}} = \\
&= (-1)^{j_3+m_3+\frac{1}{2}-\frac{1}{2}} \sqrt{\frac{j_3 + m_3 + \frac{1}{2} + \frac{1}{2}}{(2j_3+1)(2j_3+2)}} = (-1)^{j_3+m_3} \sqrt{\frac{j_3 + m_3 + 1}{(2j_3+1)(2j_3+2)}}
\end{aligned}$$

6.5 Multipole Expansion

Using (6.3) we get:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{r}}') = \sum_{l,m} \frac{r_{<}^l}{r_{>}^{l+1}} \frac{4\pi}{2l+1} Y_{lm}(\hat{\mathbf{r}}) Y_{lm}^*(\hat{\mathbf{r}}')$$

where we used the formula:

$$\sum_m \langle \hat{\mathbf{r}} | lm \rangle \langle lm | \hat{\mathbf{r}}' \rangle = \frac{2l+1}{4\pi} \langle \hat{\mathbf{r}} \cdot \hat{\mathbf{r}}' | P_l \rangle$$

6.6 Robust, Accurate and Fast Evaluation of Modified Bessel Functions

For the screened Hartree-Fock calculations we need Fortran routines for a fast and robust evaluation of the modified Bessel functions. The following implementation using rational approximation has proven to work well:

```

real(dp) function Inu(k, x) result(r)
integer, intent(in) :: k
real(dp), intent(in) :: x
select case (k)
case (0)
! r = sinh(x) / exp(x)
if (x < 20) then
r = sinh(x) / exp(x)
else
r = 1._dp / 2
end if
case (1)
! r = -sinh(x)/x + cosh(x)
! r = r * sqrt(2/(pi*x)) / exp(x)
if (x < 0.55_dp) then
r = x**2/3 + x**4/30 + x**6/840 + x**8/45360 + &
x**10/3991680 + &
x**12/518918400 + x**14/93405312e3_dp
r = r / exp(x)
else if (x < 2) then
r = (-1.0118340437504393201742626606e-13_dp + &
x*(1.816670640113517482116741309e-12_dp + &
x*(0.333333333318047257036705475493_dp + &
x*(0.0283477684328350973136495456416_dp + &
x*(0.0236972901524850660936691284628_dp + &
x*(0.0018095002919993302530473889535_dp + &
x*(0.000376379638016770111327098946609_dp + &
(0.0000200246480593843172713997406232_dp + &
1.01338637272678665804111511983e-6_dp*x)*x)))))/ &
(1 + x*(1.08504330505794283765963608202_dp + &
x*(0.556135176398351735247605123725_dp + &
x*(0.177204358493610809522295217793_dp + &
x*(0.0387591827785532218461461492913_dp + &

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        x*(0.00603331772767809320892209353842_dp + &
        x*(0.000663930390602843320578606798458_dp + &
        (0.0000484437498700383824299885362686_dp + &
        1.88315077527785406856560709781e-6_dp*x)*x))))))
else if (x < 20) then
    r = (-sinh(x)/x + cosh(x)) / exp(x)
else
    r = (-1/x + 1) / 2
end if
case (2)
    ! r = (3/x**2 + 1)*sinh(x) - 3/x*cosh(x)
    ! r = r * sqrt(2/(pi*x)) / exp(x)
    if (x < 0.4_dp) then
        r = x**3/15 + x**5/210 + x**7/7560 + x**9/498960 + &
            x**11/51891840 + x**13/7783776e3_dp
        r = r / exp(x)
    else if (x < 3.5_dp) then
        r = (2.53492679940778614368716713944e-12_dp + &
            x*(-4.54239143359406142775391525584e-11_dp + &
            x*(3.74155600551604503226833667911e-10_dp + &
            x*(0.0666666647818812413079530441494_dp + &
            x*(0.00828258168209346350068333077357_dp + &
            x*(0.00316314651226673854191486006661_dp + &
            x*(0.000312916425508586674670599989463_dp + &
            (0.0000347881775004914918533122949261_dp + &
            1.78379773794153349607916665442e-6_dp*x)*x)))))))/ &
            (1. + x*(1.12423862743404991052489502731_dp + &
            x*(0.600257501089318988530867089925_dp + &
            x*(0.20062393658095786500607161529_dp + &
            x*(0.0464529738128345227818430451247_dp + &
            x*(0.00775200781581904134897323422714_dp + &
            x*(0.000932283869002308809130049094732_dp + &
            (0.0000765450448110628850893821308195_dp + &
            3.64978189893775492541031628736e-6_dp*x)*x))))))
    else if (x < 8) then
        r = (-0.0500329770733375148059871692299_dp + &
            x*(0.225443974816227263854027844348_dp + &
            x*(-0.490706738714676572173733908052_dp + &
            x*(0.754739228306267786750520915722_dp + &
            x*(-0.0229222956512753039643375612586_dp + &
            x*(0.0417199171935382735527783646423_dp + &
            x*(0.00129242688582393560040014185308_dp + &
            (0.000436655909016956929989211236885_dp + &
            0.0000544588062620298286123134699247_dp*x)*x)))))))/ &
            (1 + x*(11.1481461018360358000411784178_dp + &
            x*(2.95111664564331863128521306942_dp + &

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x*(2.07069035717497213861002964422_dp + &
x*(0.212130624675779325122087859297_dp + &
x*(0.0985267048591193186479900210954_dp + &
x*(0.00581026870781213052737501655128_dp + &
(0.00120128946303470807826705767304_dp + &
0.000108903528444754760503502120599_dp*x)*x))))))
else if (x < 20) then
  r = ((3/x**2 + 1)*sinh(x) - 3/x*cosh(x)) / exp(x)
else
  r = (3/x**2 - 3/x + 1) / 2
end if
case (3)
! r = -(15/x**3 + 6/x)*sinh(x) + (15/x**2 + 1)*cosh(x)
! r = r / exp(x)
if (x < 0.4_dp) then
  r = x**4/105 + x**6/1890 + x**8/83160 + x**10/6486480 +&
x**12/778377600 + x**14/132324192e3_dp
  r = r / exp(x)
else if (x < 3) then
  r = (-3.70655078828583097759525479916e-13_dp + &
x*(7.15112302218910770115285755762e-12_dp + &
x*(-6.36681926888695741582309642988e-11_dp + &
x*(3.47928680854080370346525732791e-10_dp + &
x*(0.00952380821395522376879618243177_dp + &
x*(0.00113757240229334056047517957181_dp + &
x*(0.000297467643525496580117283299361_dp + &
(0.0000243340659637433371695954961197_dp + &
1.81721245776908511864649367981e-6_dp*x)*x)))))))/ &
(1 + x*(1.11944472257087316750869453522_dp + &
x*(0.595124068593635706143579962619_dp + &
x*(0.197986316667328417652509149837_dp + &
x*(0.0456127952595471262482188760838_dp + &
x*(0.00757090880409778905789353557549_dp + &
x*(0.000905726554901565254770825575224_dp + &
(0.0000739095656995355486962496918923_dp + &
3.54519707102049776194411547746e-6_dp*x)*x))))))
else if (x < 8.5_dp) then
  r = (0.00117649571172537032041386386937_dp + &
x*(-0.00530534669296740084953876529485_dp + &
x*(0.0113989437968364216304855248904_dp + &
x*(-0.0155143209720413375494757271933_dp + &
x*(0.0245092943569822333734792982989_dp + &
x*(-0.00194266321525633715561142461716_dp + &
x*(0.00125839658564675731614612557048_dp + &
(-0.0000560593512807954817946224257333_dp + &
0.0000154307073445195296381347198964_dp*x)*x)))))))/ &

```



```

(1 + x*(1.93920721196223643040357762209_dp + &
  x*(0.871960706430017695531414950855_dp + &
  x*(0.294335907964445235622348955601_dp + &
  x*(0.076510324944994462960832902772_dp + &
  x*(0.0103358291871056058873144950985_dp + &
  x*(0.00249717323564249173430366673788_dp + &
  (0.0000729070672630135675918235119142_dp + &
  0.0000308632011694791287440146822781_dp*x)*x))))))
else if (x < 20) then
  r = (- (15/x**3 + 6/x)*sinh(x) + &
    (15/x**2 + 1)*cosh(x)) / exp(x)
else
  r = (-15/x**3 + 15/x**2 - 6/x + 1)/2
end if
case (4)
! r = (105/x**4 + 45/x**2 + 1)*sinh(x) &
  - (105/x**3 + 10/x)*cosh(x)
! r = r / exp(x)
if (x < 0.2_dp) then
  r = x**5/945 + x**7/20790 + x**9/1081080 + &
    x**11/97297200 + x**13/132324192e2_dp
  r = r / exp(x)
else if (x < 1.7_dp) then
  r = (8.24833340467311342180121686171e-18_dp + &
    x*(-2.9977388208095462038421382427e-16_dp + &
    x*(4.98591599598783667120520966419e-15_dp + &
    x*(-5.04172127797261339201651796769e-14_dp + &
    x*(3.47424275623446932695212209666e-13_dp + &
    x*(0.00105820105646713443251629043736_dp + &
    x*(0.0000979757728258499019673125884795_dp + &
    (0.0000182024072642408317859820498652_dp + &
    1.0631472458547091790087783848e-6_dp*x)*x)))))) / &
(1 + x*(1.09258709917337245791086210753_dp + &
  x*(0.564333846348740813775052159905_dp + &
  x*(0.181503092836557003863165983269_dp + &
  x*(0.040177538019272720474585552471_dp + &
  x*(0.00635509731709913059075978583153_dp + &
  x*(0.000715397138065847382814527384553_dp + &
  (0.0000540407967369787069953788458276_dp + &
  2.26320060646140077482435126776e-6_dp*x)*x))))))
else if (x < 4) then
  r = (-1.79380868029518008655845945341e-7_dp + &
    x*(1.42021959889593932447404701528e-6_dp + &
    x*(-5.3621673060507414018999203431e-6_dp + &
    x*(0.0000128612071905009120973461141937_dp + &
    x*(-0.0000220283666472339963720124703845_dp + &

```

```

x*(0.00108692026226442881323459546524_dp + &
x*(-0.000108914780493366312610770062505_dp + &
(0.0000213026860907556990203197490202_dp - &
2.40044294668610963152692356425e-6_dp*x)*x)))))) /&
(1 + x*(0.92511576565864173804826819565_dp + &
x*(0.376185570863101848786874779376_dp + &
x*(0.0979599622990753625780606726782_dp + &
x*(0.0139543384283183184757129378369_dp + &
x*(0.00167710554949622675142353677903_dp + &
x*(-0.0000841270733243543647065400772874_dp + &
(-4.04735930419963375054951672688e-6_dp - &
4.82907242383463140296057166244e-6_dp*x)*x))))))
else if (x < 10) then
r = (0.000395502959013236968661582656143_dp + &
x*(-0.001434648369704841686633794071_dp + &
x*(0.00248783474583503473135143644434_dp + &
x*(-0.00274477921388295929464613063609_dp + &
x*(0.00216275018107657273725589740499_dp + &
x*(-0.000236779926184242197820134964535_dp + &
x*(0.0000882030507076791807159699814428_dp + &
(-4.62078105288798755556136693122e-6_dp + &
8.23671374777791529292655504214e-7_dp*x)*x)))))) /&
(1 + x*(0.504839286873735708062045336271_dp + &
x*(0.176683950009401712892997268723_dp + &
x*(0.0438594911840609324095487447279_dp + &
x*(0.00829753062428409331123592322788_dp + &
x*(0.00111693697900468156881720995034_dp + &
x*(0.000174719963536517752971223459247_dp + &
(7.22885338737473776714257581233e-6_dp + &
1.64737453771748367647332279826e-6_dp*x)*x))))))
else if (x < 20) then
r = (1.49435717183021678294278540018_dp + &
x*(-1.9954827594990599398954087063_dp + &
x*(1.19185825369343226912112655137_dp + &
x*(-0.40866680980235804096143699423_dp + &
x*(0.0852839860059780325406440673318_dp + &
(-0.00980617919194154929317057489645_dp + &
0.000550291361244287676343295379476_dp*x)*x)))) /&
(1 + x*(0.420439518058743727857466136746_dp + &
x*(0.144024726914933127664739439568_dp + &
x*(0.035261250406130055921113600336_dp + &
x*(0.0349770458351085078647522073879_dp + &
(-0.00860653991097136433951965579037_dp + &
0.00110058277850687516223459976889_dp*x)*x))))
else
r = (105/x**4 - 105/x**3 + 45/x**2 - 10/x + 1)/2

```

```

        end if
    case default
        r = -1 ! For compiler warning "fix"
        call stop_error("k = " // str(k) // " not implemented.")
end select
r = r * sqrt(2/(pi*x))
end function

real(dp) function Knu(k, x) result(r)
integer, intent(in) :: k
real(dp), intent(in) :: x
select case (k)
    case (0)
        r = 1
    case (1)
        r = 1/x + 1
    case (2)
        r = 3/x**2 + 3/x + 1
    case (3)
        r = 15/x**3 + 15/x**2 + 6/x + 1
    case (4)
        r = 105/x**4 + 105/x**3 + 45/x**2 + 10/x + 1
    case default
        call stop_error("k = " // str(k) // " not implemented.")
end select
r = r * sqrt(pi/(2*x))
end function

```

These routines were tested against arbitrary precision implementation in SymPy [13], the results are in Figures 6.1, 6.2, 6.3, 6.4, 6.5.

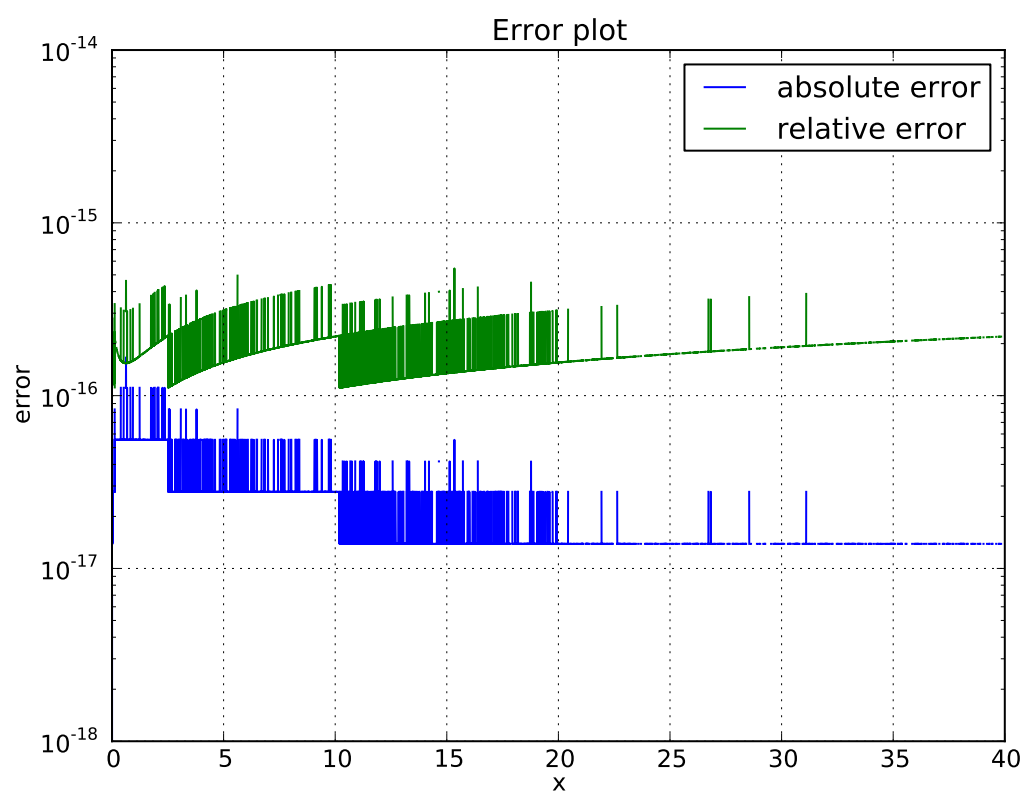


Figure 6.1: The convergence of modified Bessel function for $k=0$

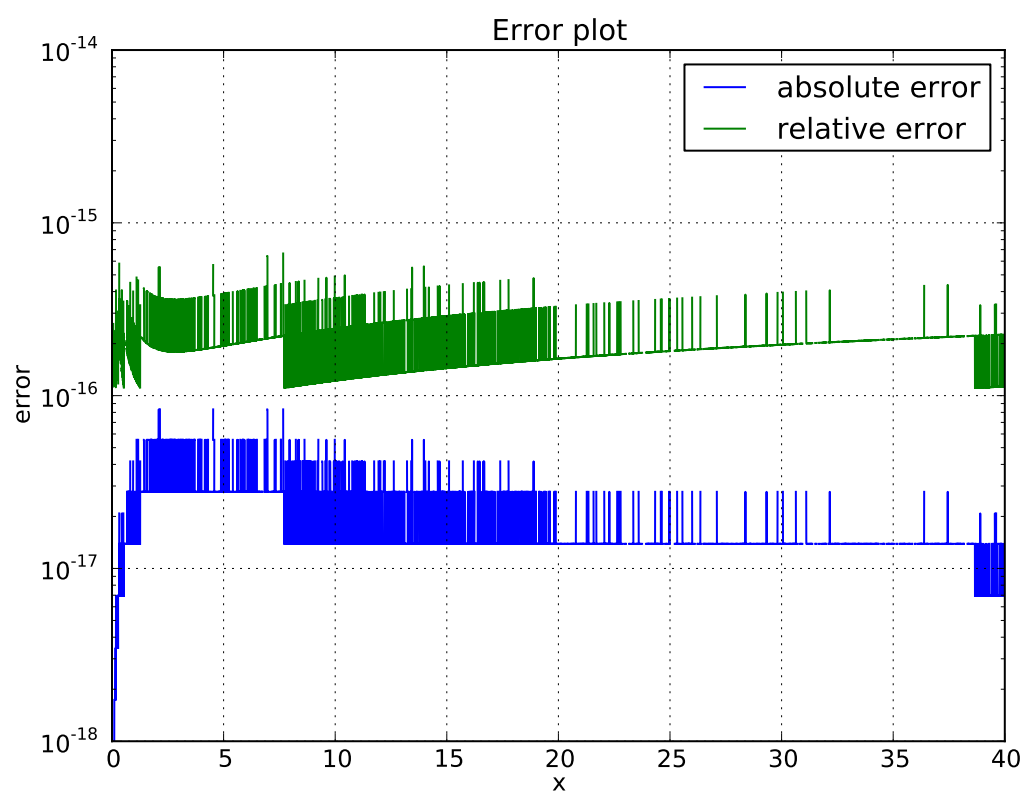


Figure 6.2: The convergence of modified Bessel function for $k=1$

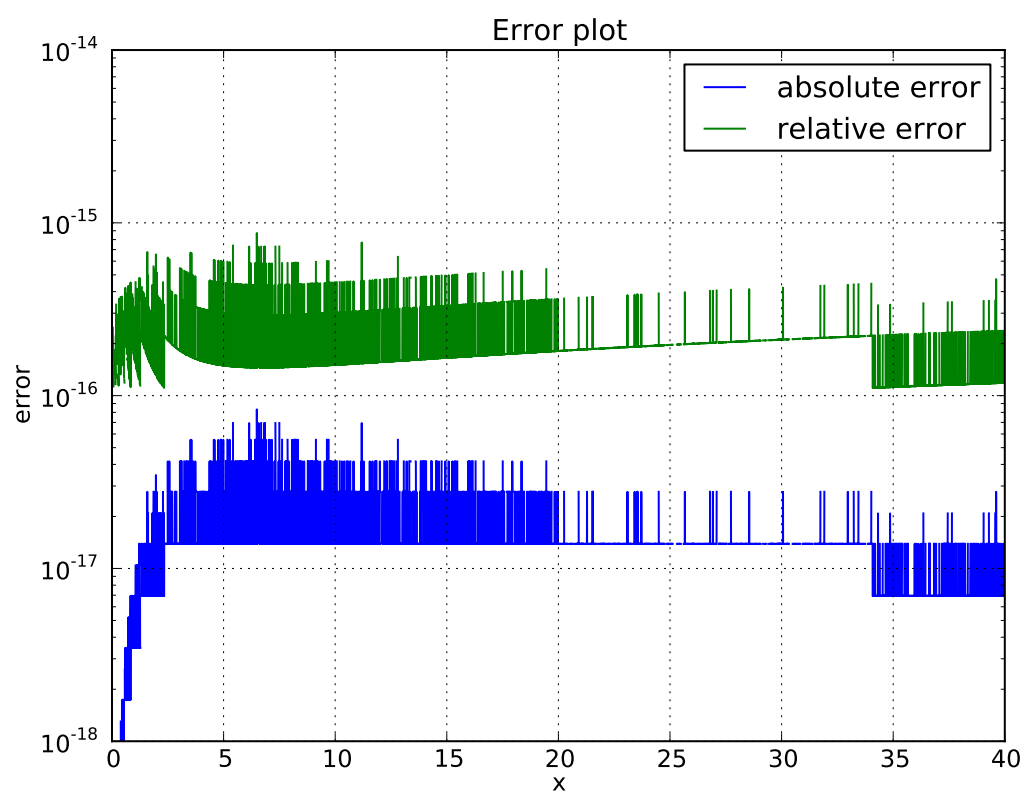


Figure 6.3: The convergence of modified Bessel function for $k=2$

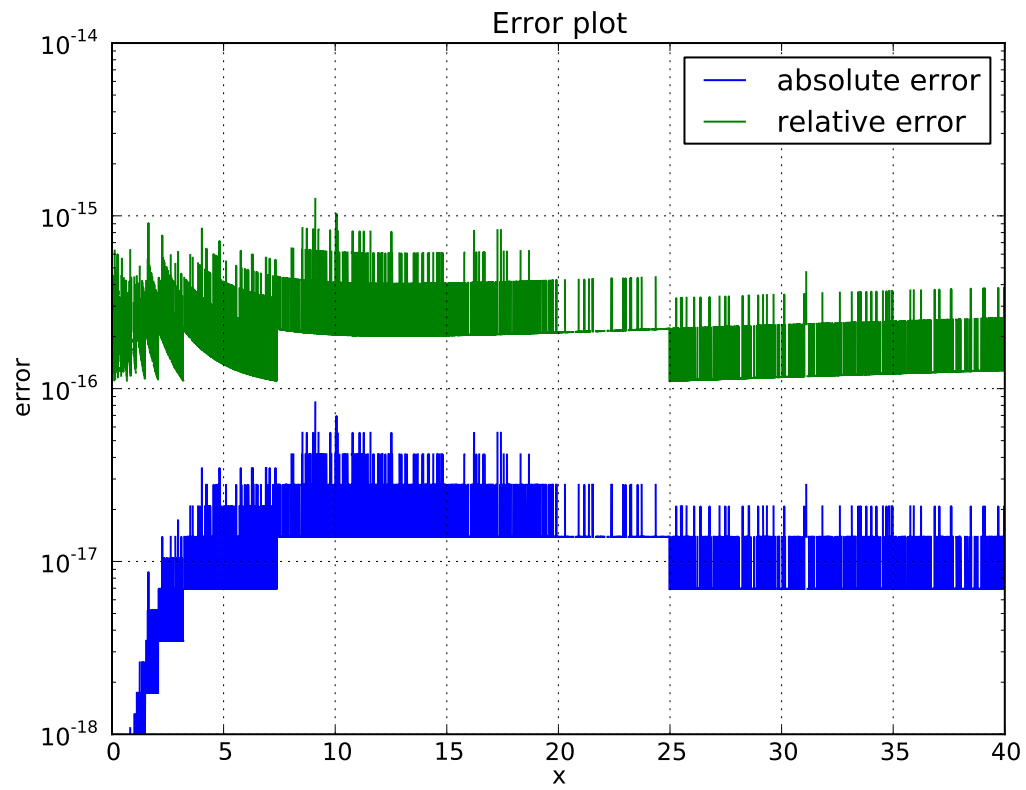


Figure 6.4: The convergence of modified Bessel function for $k=3$

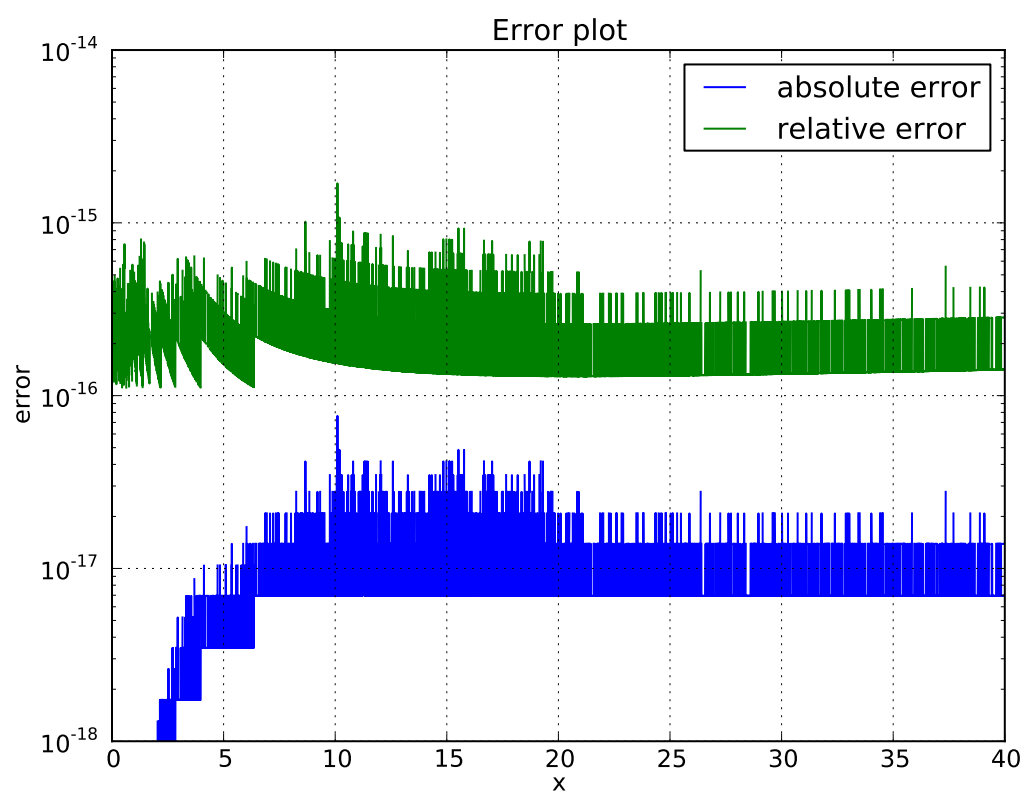


Figure 6.5: The convergence of modified Bessel function for $k=4$

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