Computational Chemistry in Parallel

by

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Abstract

General Purpose computing with Graphics Processing Units (GPGPU) is a method of computation that allows for calculations to be performed in parallel. Graphics Processing Units (GPU) allow a single basic computer to perform as well as a super computer cluster composed of only Central Processing Units (CPU), at a fraction of the cost. As quantum computational chemistry scales very poorly with the size of systems, the use of GPGPU has been a very effective tool for quantum chemists.

This thesis presents a program called cudaDFRATOM. This program, written in CUDA Fortran, allows for the calculation and optimization of Well-Tempered Basis Sets (WTBS) at the four-component relativistic level of theory. Except for a few small initial calculations and control flow, all work is performed entirely on the GPU.

When calculating the two-electron integrals, cudaDFRATOM uses a very effective method of utilizing as much of the GPU's resources as possible and can calculate these integrals approximately 20 times faster than a similar program running on only a CPU.

Two different algorithms for forming the **P** and **Q** supermatrices are presented. The relatively small size of these matrices and the need to use double-precision floating-point operations stunts the speedup of these algorithms such that they only attain a speedup of about 2 times over the CPU program. An overall speedup of about 4 times is achieved by cudaDFRATOM.

In addition, new WTBS are calculated for non-relativistic levels of theory using the rWTBS program and at the four-component relativistic level of theory using cudaDFRATOM. In both cases, a novel algorithm for automating the optimization of these basis sets was used. The algorithm finds a basis set that is as small a possible while still retaining sufficient accuracy to numerical calculations.

Preface

This thesis is my own original work. No part of this thesis has been previously published. Computations and code were planned, performed, and written by myself with the help of Mariusz Klobukowski.

In addition, I have also worked on a project with Mariusz which is not in this thesis. The project investigated how the FHF^- molecule behaves in a confining potential. The results were published in a paper titled "Hydrogen bonding and autoionization in confined bifluoride system FHF^-" in *The Journal of Physics B: Atomic, Molecular and Optical Physics* vol. 50 pages 155101-155101 in the year 2017.

For Jessie, who puts up with more than she needs to

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Finally, I would like to thank my girlfriend Jessie Hartmann. We've been through Hell and back together, and there is no one else I would have rather had at my side than her. For some reason, she continues to love me, even as I make her watch a video on sorting algorithms for the tenth time, so for you Jessie I give my appreciation, affection, and love.

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List of Symbols

Some symbols are reused. The exact meaning will need to obtained from context.

Symbol	Description
$\hat{H}$	Hamiltonian operator
Ψ	Wavefunction
E	Energy
∇	Gradient of a function
$\hat{H}_{el}$	Electronic Hamiltonian operator
a_o	Bohr radius
ψ	Spin orbital
ϕ	Orbital
α	Spin function, four-component matrix, Gaussian nuclei exponent, well-tempered basis set parameter
β	Spin function, four-component matrix, well-tempered basis set parameter
ω	Spin coordinate
ϵ	Vector of spin orbital energies
Φ	Basis function
ζ	Basis function exponent
λ	Orbital symmetry
μ	Orbital symmetry
c	Speed of light
m_0	Mass of object at rest
$\hbar$	Reduced Planck's constant
q	Particle charge
$\hat{A}, \hat{\varphi}$	Electromagnetic field potentials
$\boldsymbol{\psi}$	Large component spinor
$\boldsymbol{\phi}$	Small component spinor
ϵ_0	Permittivity of free space
δ	Well-tempered basis set parameter
γ	Well-tempered basis set parameter

Chapter 1

Introduction

Graphics Processing Units (GPUs) have allowed quantum chemists to overcome to problem of two-electron integral scaling[1–4]. This has allowed for very large systems to be studied at a very accurate level of chemical theory [5]. There has been little advancement in the relativistic levels of chemical theory however. Therefore, this thesis presents a program called cudaDFRATOM which allows for the optimization of basis sets at the Dirac-Fock-Roothaan level of theory. In this chapter, the background of relativistic theory is discussed. In Chapter 2, the details of the code used in cudaDFRATOM are given. Chapter 3 discusses the basis sets cudaDFRATOM produces.

1.1 Solving the Schrödinger Equation

The Schrödinger equation[6] in its time-independent, non-relativistic form is given in Equation

$$\hat{H}\Psi = E\Psi \tag{1.1}$$

where $\hat{H}$ is the Hamiltonian operator, Ψ is referred to as the wavefunction, and E is the energy of the system described by the wavefunction. For a molecular system, the Hamiltonian operator in atomic units (a.u.) is given by Equation

$$\hat{H} = -\frac{1}{2}\sum_{i}^{n}\nabla_i^2 - \sum_{A}^{N}\frac{1}{2M_A}\nabla_A^2 - \sum_{i}^{n}\sum_{A}^{N}\frac{Z_A}{r_{iA}} + \sum_{i}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}} + \sum_{A}^{N}\sum_{B>A}^{N}\frac{Z_A Z_B}{r_{AB}} \tag{1.2}$$

where i and j refer to electrons, A and B refer to nuclei, and n and N refer to the maximum number of electrons and nuclei, respectively. M_A and Z_A are the mass and charge of nucleus A. r_{xy} is the distance between particles x and y, and $\nabla_n^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ where x, y, and z are the Cartesian coordinates of particle n. Each term accounts for a different kind

of energy: $-\frac{1}{2}\sum_i^n \nabla_i^2$ is the kinetic energy of the electrons, $\sum_A^N \frac{1}{2M_A}\nabla_A^2$ is the kinetic energy of the nuclei, $\sum_i^n \sum_A^N \frac{Z_A}{r_{iA}}$ is the potential energy of attraction between nuclei and electrons, $\sum_i^n \sum_{j>i}^N \frac{1}{r_{ij}}$ is the potential energy of repulsion between electrons, and $\sum_A^N \sum_{B>A}^N \frac{Z_A Z_B}{r_{AB}}$ is the potential energy of repulsion between nuclei. Together, this accounts for all of the energy of a molecular system. As this operator is quite complex, it would be helpful to simplify it if possible. Fortunately, Born and Oppenheimer[7] realized that an approximation could be made that would substantially reduce the amount of work we have to do.

Much like a satellite in orbit around the Earth, the proton and neutron vastly outweigh the electron. If we look at the second term in Equation

$$\hat{H}_{el} = -\frac{1}{2}\sum_i^n \nabla_i^2 - \sum_i^n \sum_A^N \frac{Z_A}{r_{iA}} + \sum_i^n \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{B>A}^N \frac{Z_A Z_B}{r_{AB}} \tag{1.3}$$

$\hat{H}$ can be assumed to be $\hat{H}_{el}$ for the remainder of this thesis, and with the Hamiltonian out of the way, we can now turn our attention to the wavefunction. While we were able to get away with turning nuclei into classical particles, the electrons unfortunately remain fully quantum. Therefore, we need to deal with all the complicated mathematical baggage this comes with.

Consider the hydrogen atom which, like all other one-electron atomic systems, is one of the few exactly solvable problems in quantum mechanics. The solution for its wavefunction in spherical coordinates is given in Equation

$$\Psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_l^m(\theta,\varphi) \tag{1.4}$$

where R_{nl} is called the radial function and $Y_l^m(\theta,\varphi)$ is called the angular function. The radial function has the form

$$R_{nl}(r) = \frac{1}{r}\left(\frac{r}{a_o n}\right)^{l+1} e^{-\frac{r}{a_o n}} L_{n-l-1}^{2l+1}\left(\frac{r}{a_o n}\right) \tag{1.5}$$

where a_o is the Bohr radius and $L_{n-l-1}^{2l+1}\left(\frac{r}{a_o n}\right)$ is a Laguerre polynomial of $\left(\frac{r}{a_o n}\right)$ and order $j_{\max} = n-l-1$ of $\left(\frac{r}{a_o n}\right)$. Its coefficients are given by

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)}c_j \tag{1.6}$$

where c_0 is a constant determined by normalization. The polynomial itself given by

$$L_{q-p}^p(x) = (-1)^p \left(\frac{d}{dx}\right)^q L_q(x) \tag{1.7}$$

$$L_q(x) = e^x \left(\frac{d}{dx}\right)^q \left[x^q e^{-x}\right] \tag{1.8}$$

The angular function has the form

$$Y_l^m(\theta, \varphi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos\theta) e^{im\varphi} \tag{1.9}$$

where $i = \sqrt{-1}$ and $\epsilon = (-1)^m$ for $m \geq 0$ or 1 if $m < 0$. $P_l^m(\cos\theta)$ is a polynomial of $\cos\theta$ and has the form of

$$P_l^m(x) = (1-x^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{dx^{|m|}} P_l(x) \tag{1.10}$$

$$P_l(x) = \frac{1}{2^l l!} \frac{d^j}{dx^j} (x^2-1)^l \tag{1.11}$$

Inspection of these equations reveals that n must be a positive integer greater than 0, l must be a positive integer between 0 and $n-1$, and $|m|$ can be no larger than l. The integers n, l, and m are called quantum numbers, specifically n is the principal quantum number, l is the azimuthal quantum number, and m is the magnetic quantum number. Notice that there is no limit to how large n can get, which suggests that there is not just one solution to this equation, but an infinite number of them. The hydrogen-like atom wavefunctions are given the special name of orbitals. Also, orbitals with the same value of l are referred to be of the same symmetry. Table

Table 1.1: *The first few exact solutions for the hydrogen atom wavefunction.*

n	l		
	0	1	
	$m=0$	$m=0$	$m=\pm1$
1	$\left(\frac{1}{\pi a_o^3}\right)^{\frac{1}{2}} e^{\left(-\frac{r}{a_o}\right)}$	–	–
2	$\frac{1}{\sqrt{8\pi a_o^3}}\left(1-\frac{r}{2a_o}\right)e^{\left(-\frac{r}{2a_o}\right)}$	$\frac{1}{\sqrt{32\pi a_o^3}}\frac{r}{a_o}e^{\left(-\frac{r}{2a_o}\right)}\cos\theta$	$\mp\frac{1}{\sqrt{64\pi a_o^3}}\frac{r}{a_o}e^{\left(-\frac{r}{2a_o}\right)}\sin\theta e^{\pm i\varphi}$

1.2 Hartree-Fock Method

While the wavefunction might appear complex, it is important to remember that it is still just a wave, and one of the fundamental properties of waves is that they can be added together

to produce a separate, more complex wave. Likewise, any wave, no matter how complex, can be broken down as a summation of many simpler waves[10]. Thus, any linear combination of solutions to the Schrödinger equation must therefore be a solution of a different equation. It is this property that will be exploited to solve our many electron problem. But first we must define some ground rules.

The first rule is that the overall wavefunction must describe a system of fermions. This means that the wavefunction must be antisymmetric with respect to the exchanging of electronic coordinates, i.e. $\Psi(1,2,\ldots,n,\ldots,m) = -\Psi(1,2,\ldots,m,\ldots,n)$ *and* the probability density of the wavefunction must be indistinguishable with respect to the exchanging of electronic coordinates, i.e. $|\Psi(1,2,\ldots,n,\ldots,m)|^2 = |\Psi(1,2,\ldots,m,\ldots,n)|^2$. The easiest way to meet this requirement is by using a Slater determinant[11], and by introducing the concept of spin. Spin is a fourth quantum number, which we have neglected to talk about so far. Spin is a confusing property that some quantum particles have. No one really knows what it is, other than to say it has something to do with the angular momentum of the particle, and oddly enough that it in no way refers to the direction that the particle is spinning. It has been shown to have binary values[12], which will be refered to as up spin ($\uparrow$) and down spin ($\downarrow$). A Slater determinant that obeys antisymmetry is shown in Equation

$$\Psi(1,2,3,\ldots,n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \psi_1(1) & \psi_2(1) & \psi_3(1) & \ldots & \psi_n(1) \\ \psi_1(2) & \psi_2(2) & \psi_3(2) & \ldots & \psi_n(2) \\ \psi_1(3) & \psi_2(3) & \psi_3(3) & \ldots & \psi_n(3) \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \psi_1(n) & \psi_2(n) & \psi_3(n) & \ldots & \psi_n(n) \end{vmatrix} \tag{1.12}$$

Here, n refers to the number of electrons in the system, and the numbers in parentheses refer to specific electrons. ψ_i refers to the i^{th} *spin* orbital which is equal to $\phi_{\frac{i+1}{2}}(r,\theta,\varphi)\alpha(\omega)$ if i is odd, or $\phi_{\frac{i}{2}}(r,\theta,\varphi)\beta(\omega)$ if i is even (ϕ is an orbital and ω is the spin coordinate). α and β are called spin functions. What they actually are doesn't matter, but they do have to be orthonormal to each other.

$$\begin{aligned} \langle\alpha(\omega_i)|\alpha(\omega_i)\rangle &= \langle\beta(\omega_i)|\beta(\omega_i)\rangle = 1 \\ \langle\alpha(\omega_i)|\beta(\omega_i)\rangle &= \langle\beta(\omega_i)|\alpha(\omega_i)\rangle = 0 \end{aligned} \tag{1.13}$$

Using Slater determinants has some interesting consequences. If we had a system where two electrons of the same spin were in the same spin orbital, that would mean that two of the columns would be equal to one another. Such a determinant would be equal to zero, which means that the wavefunction for such a system would not exist. This is the famous Pauli antisymmetry principle[13]. The math showing that is satisfies antisymmetry is shown below[14].

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(\omega_1) & \phi_1(1)\beta(\omega_1) \\ \phi_1(2)\alpha(\omega_2) & \phi_1(2)\beta(\omega_2) \end{vmatrix} \tag{1.14}$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \left[\phi_1(1)\alpha(\omega_1)\phi_1(2)\beta(\omega_2) - \phi_1(1)\beta(\omega_1)\phi_1(2)\alpha(\omega_2)\right] \tag{1.15}$$

$$-\Psi(1,2) = \frac{1}{\sqrt{2}} \left[\phi_1(1)\beta(\omega_1)\phi_1(2)\alpha(\omega_2) - \phi_1(1)\alpha(\omega_1)\phi_1(2)\beta(\omega_2)\right] \tag{1.16}$$

$$-\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(2)\alpha(\omega_2) & \phi_1(2)\beta(\omega_2) \\ \phi_1(1)\alpha(\omega_1) & \phi_1(1)\beta(\omega_1) \end{vmatrix} = \Psi(2,1) \tag{1.17}$$

As can be seen, changing the indexing of the electrons is equivalent to swapping the rows for those electrons, which changes the sign of the determinant. It is important to note that because observable quantities depend not the wavefunction, but the *absolute square* of the wavefunction, altering the indexing of the electrons does not change the calculation of these observables. Consider the example of the electron density probability distribution shown below (note that ϕ, α, and β are real in this example, but even if they weren't the results would not change).

$$|\Psi(1,2)|^2 = \frac{1}{2} \left[\begin{vmatrix} \phi_1(1)\alpha(\omega_1) & \phi_1(1)\beta(\omega_1) \\ \phi_1(2)\alpha(\omega_2) & \phi_1(2)\beta(\omega_2) \end{vmatrix}^2 \right] \tag{1.18}$$

$$\begin{aligned} |\Psi(1,2)|^2 = \frac{1}{2}[&(\phi_1(1)\alpha(\omega_1)\phi_1(2)\beta(\omega_2) - \phi_1(1)\beta(\omega_1)\phi_1(2)\alpha(\omega_2)) \\ &\times (\phi_1(1)\alpha(\omega_1)\phi_1(2)\beta(\omega_2) - \phi_1(1)\beta(\omega_1)\phi_1(2)\alpha(\omega_2))] \end{aligned} \tag{1.19}$$

$$\begin{aligned} |\Psi(1,2)|^2 = \frac{1}{2}\int\int\int\int [&\phi_1(1)^2\alpha(\omega_1)^2\phi_1(2)^2\beta(\omega_2)^2 + \phi_1(1)^2\beta(\omega_1)^2\phi_1(2)^2\alpha(\omega_2)^2 \\ &- 2\phi_1(1)^2\alpha(\omega_1)\beta(\omega_1)\phi_1(2)^2\beta(\omega_2)\alpha(\omega_2)] d1 d2 d\omega_1 d\omega_2 \end{aligned} \tag{1.20}$$

$$|\Psi(1,2)|^2 = \frac{1}{2}\left[|\phi_1(1)|^2|\phi_1(2)|^2 + |\phi_1(1)|^2|\phi_1(2)|^2\right] \tag{1.21}$$

1.2.1 Two-Electron Integrals

As stated before, the main difficulty of performing calculations on many electron systems is figuring out how to deal with the interactions between the electrons. We can get around this by making the assumption that these interactions can be approximated by figuring out how a single electron interacts with the *average* field generated by all the other electrons. This is called the mean-field method[15]. With this, we can replace the Hamiltonian operator with the one-electron Fock operator which is given below[14]

$$\hat{f}(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} + v^{HF}(i) \tag{1.22}$$

The first two terms are combined into an operator called the H^{core} operator ($\hat{h}(i)$) and $v^{HF}(i)$ is the potential generated by all the electrons except the i^{th} one. $v^{HF}(i)$ is composed of two different operators: the Coulomb operator and the exchange operator. The Coulomb operator is intuitive, it is simply the interaction electron 1 experiences when in a Coulomb potential generated by electron 2

$$\hat{J}_b(1)\psi_a(1) = \left[\int \psi_b^*(2)\frac{1}{r_{12}}\psi_b(2)d\mathbf{x}_2\right]\psi_a(1) \tag{1.23}$$

where $J_b(1)$ is the Coulomb operator for electron 1 when interacting with an electron in spin orbital b and $\mathbf{x}_i$ is the spatial coordinates of electron i. The exchange operator is slightly more complicated than the Coulomb operator. While the Coulomb operator can be defined without a function to operate on (simply remove $\psi_a(1)$ from both sides of Equation

$$\hat{K}_b(1)\psi_a(1) = \left[\int \psi_b^*(2)\frac{1}{r_{12}}\psi_a(2)d\mathbf{x}_2\right]\psi_b(1) \tag{1.24}$$

where $K_b(1)$ is the exchange operator for electron 1 operating on spin orbital a. At first glance, it might appear to be almost the same as Equation

Now it would be helpful to introduce some new notation. The expectation values for these operators are defined as follows

$$\left\langle \psi_a(1)|\hat{J}_b(1)|\psi_a(1)\right\rangle = \int\int \psi_a^*(1)\psi_a(1)\frac{1}{r_{12}}\psi_b^*(2)\psi_b(2)d\mathbf{x}_1 d\mathbf{x}_2 = (aa|bb) \tag{1.25}$$

$$\left\langle \psi_a(1)|\hat{K}_b(1)|\psi_a(1)\right\rangle = \int\int \psi_a^*(1)\psi_b(1)\frac{1}{r_{12}}\psi_b^*(2)\psi_a(2)d\mathbf{x}_1 d\mathbf{x}_2 = (ab|ba) \tag{1.26}$$

These are called the two-electron integrals. The Hartree-Fock equation can be written as

$$\left[\hat{h}(1) + \sum_{b\neq a}^{n}\left(J_b(1) - K_b(1)\right)\right]\psi_a(1) = \epsilon_a\psi_a(1) \tag{1.27}$$

$$\left\langle \psi_a(1)|\hat{h}(1)|\psi_a(1)\right\rangle + \sum_{b\neq a}^{n}\left[(aa|bb) - (ab|ba)\right] = \epsilon_a \tag{1.28}$$

where n is the number of spin orbitals in the system and ϵ_a is the energy of an electron in spin orbital a. If instead we are interested in the energy of an entire atom or molecule, the equation becomes

$$\sum_{a}^{n} \left\langle \psi_a(1) | \hat{h}(1) | \psi_a(1) \right\rangle + \frac{1}{2} \sum_{a}^{n} \sum_{b}^{n} \left[(aa|bb) - (ab|ba) \right] = \epsilon \tag{1.29}$$

where the factor of one half is multiplied to the two electron terms as a result of the interactions being doubly counted by the summations.

1.2.2 Basis Sets

Back in section

As mentioned, the overall wavefunction of a system (Ψ) cannot be known exactly unless we are looking only at hydrogen-like atoms. So instead we write the wavefunction as a Slater determinant composed of spin orbitals. What exactly is the mathematical form of these spin orbitals? As it turns out, unless we are talking only about atoms, we have no idea what these are either, even from a numerical stand point. However, we can make a fairly educated guess about what they *should* resemble. The general idea is this: by pre-calculating a set of functions with adjustable parameters (ζ), we can represent a wavefunction with a linear combination of $\Phi(\zeta)$ that adequately reproduces results of numerical calculations of ϕ. Mathematically, this is expressed as[14]

$$\phi_u \approx \sum_{i=1}^{K} C_{u,i} \Phi(\zeta_{u,i}) \tag{1.30}$$

where $\zeta_{u,i}$ is the i^{th} adjustable parameters of the basis function Φ which is approximating the u^{th} orbital, $C_{u,i}$ is the i^{th} coefficient of i^{th} basis function of the u^{th} ϕ, and K is the total number of basis functions that make up the basis set. $C_{u,i}^2$ can be thought of as the "weight" of ϕ that $\Phi(\zeta_{u,i})$ makes up.

When choosing the Φs, our ground rule comes into play. We must choose a function that meets the boundary conditions of the problem, which means that is must go to zero at infinity. Because an atom (or molecule) consists of electrons in the potential generated by one (or many) nuclei, it is reasonable to conclude that the wavefunction would be similar to that of the hydrogen atom. We might initially think to use the exact hydrogen atom solution, but it quickly requires lots of floating point operations to compute which makes it impractical to use for large scale calculations. A more reasonable function is the Slater-type orbital (STO)[16]. These use a different radial function, but still use the same spherical harmonics as the hydrogen-atom like wavefunctions. The radial part of the 1s orbital centered at R_A is shown below

$$\Phi_{1s}^{STO}(r - R_A) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta |r - R_A|} \tag{1.31}$$

The radial equation for any value of n is

$$\Phi^{STO}(r - R_A) = Nr^{n-1}e^{-\zeta|r-R_A|} \tag{1.32}$$

where N is a normalization constant. This is a simpler equation to work with than the exact hydrogen atom solution because it does not need to use the Laguerre polynomials. But even with these, problems arise when we try to use them in the two-electron integrals. Because we may be trying to do a two-electron integral over functions which could be located at up to four different centers, we end up with something that is very hard to compute. Therefore, Gaussian-type orbitals (GTOs) have become the preferred functions for producing basis sets. The radial part of a 1s GTO centered at R_A is shown below[17]

$$\Phi_{1s}^{GTO}(r - R_A) = \left(\frac{2\zeta}{\pi}\right)^{\frac{3}{4}} e^{-\zeta|r-R_A|^2} \tag{1.33}$$

Because the product of two different Gaussians centered at two different locations is a third Gaussian centered at a third location, this makes the two-electron integrals much easier to deal with. The trade off is that GTOs do not as accurately match the hydrogen atom solution as STOs, but this can be fixed somewhat by just using more of them.

All of this reduces our wavefunction issue to a simple optimization problem, which will be discussed more in-depth in Chapter

1.2.3 Hartree-Fock SCF

In the previous sections, we discussed the calculation of the two-electron integrals and introduced the concept of using basis sets to approximate a wavefunction. Now we will discuss how they are actually used. Inspection of the Hartree-Fock operators, Equations

SCF method begins with the formation of the density matrices. If we are looking at a single atom, we can exploit the symmetry of the problem by having a smaller density matrix for each orbital symmetry (λ), instead of one large one for the whole system. There are also two types of density matrices, one for contributions from closed shell spinors ($\mathbf{D_C}$) and one for contributions from open shelled spinors ($\mathbf{D_O}$).

Using a procedure developed independently by Roothaan and Hall[15, 18], we first need to find the matrix $\mathbf{C}$ which satisfies

$$\mathbf{FC} = \epsilon\mathbf{SC} \tag{1.34}$$

where $\mathbf{F}$ is the Fock matrix, ϵ is the vector of eigenvalues, and $\mathbf{S}$ is the overlap matrix. The matrix elements of $\mathbf{S}$ are

$$\mathbf{S}_{p_\lambda,q_\lambda} = \langle p_\lambda | q_\lambda \rangle \tag{1.35}$$

and the non-relativistic $\mathbf{F}$ for closed shells of symmetry λ is given by

$$\mathbf{F}_{p_\lambda,q_\lambda} = \langle p_\lambda | \hat{h}(1) | q_\lambda \rangle + \sum_{\mu=1}^{nsym} \sum_{r=1}^{K} \sum_{s=1}^{K} \left(2 \sum_{a=1}^{occ} \mathbf{C}_{r_\mu,a} \mathbf{C}^*_{s_\mu,a} \right) \left[(p_\lambda q_\lambda | r_\mu s_\mu) - \frac{1}{2} (p_\lambda q_\lambda | s_\lambda r_\lambda) \right] \tag{1.36}$$

where p, q, r, and s are basis functions, K is the total number of basis functions for symmetry μ, and *occ* is the number of occupied closed shells in symmetry μ. Because p and q will always be of the same symmetry, and likewise with r and s, the λ and μ subscripts will be dropped from these indices and instead will be obtained from context. As we can see, $\mathbf{F}$ is itself a function of $\mathbf{C}$ and we are left with a rather disappointing outcome, that in order to find $\mathbf{C}$, we first must know what it is. And so it would seem that all is lost and all of this hard work was for nothing. And yet, there is a glimmer of hope. $\mathbf{F}$ is made up of two terms, and as only the term corresponding to contributions from the two-electron integrals depends on $\mathbf{C}$, the term from one-electron integrals can be used independently of $\mathbf{C}$. Thus, we begin by assuming that $\mathbf{F}$ depends solely on the one-electron term, effectively assuming that $\mathbf{C} = \mathbf{0}$. Solving Equation

1.3 Special Relativity

Another field of physics that was being developed at the same time as quantum mechanics was special relativity (general relativity which involves gravity's effect on spacetime is far, *far* outside the scope of this thesis. I will therefore be referring to special relativity as just relativity from now on). Relativity traces its roots to Michelson and Morley[19] who made the startling observation that all observers, regardless of their frame of reference, will always agree on the speed of light. But it would not be until everyone's favourite Swiss patent clerk decided to examine this issue that the truly profound implications of this observation would be known.

This is perhaps a bit of an aside, but it is simply too interesting to pass up. Consider this thought experiment: you and I are in two different spaceships in space. We will define your frame of reference such that you are stationary at the origin, and that I am flying past you at a constant speed that is arbitrarily close to the speed of light, we will call this speed v. In my spaceship, there is a laser that I have pointed perfectly perpendicular to the direction I am traveling. From my frame of reference, where I am stationary, I turn the laser on and observe photons that move from the laser to the side of my spaceship, a distance equal to d_1, in time equal to t at the speed of light c. Back in your frame of reference, you are also

watching my experiment, but you make some different observations. In the time it take for the photons to move across my spaceship, I move a small distance d_2. So the total distance you see the photons move is not d_1, but d_3 which is the hypotenuse of the right angle triangle formed by d_1, d_2, and d_3. *But*, we both agree that the photons were moving at speed c! So we can not agree on the time it took to do so because $d_3 > d_1$. So you will observe the time it takes for the photons to move to be a time equal to t'. We can derive the relationship between t and t' in the following way.

$$d_1 = ct \qquad d_2 = vt' \qquad d_3 = ct' \tag{1.37}$$

$$d_3^2 = d_1^2 + d_2^2 \tag{1.38}$$

$$(ct')^2 = (vt')^2 + (ct)^2 \tag{1.39}$$

$$(ct)^2 = (ct')^2 - (vt')^2 \tag{1.40}$$

$$t = t'\sqrt{1 - \frac{v^2}{c^2}} \tag{1.41}$$

Not does this give the absolutely remarkable result that time is relative, Equation

$$m(v) = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{1.42}$$

where $m(v)$ is the mass of an object moving at speed v and m_0 is the rest mass of the object. With this we can see how it would be impossible for an object with mass to move at the speed of light. Its mass would go to infinity and would therefore need an infinite amount of energy to get there.

If we expand Equation

$$m(v) = m_0\left[1 + \frac{1}{2}\frac{v^2}{c^2} + \frac{3}{8}\frac{v^4}{c^4} + \frac{5}{16}\frac{v^6}{c^6} + \frac{35}{128}\frac{v^8}{c^8} + \ldots\right] \tag{1.43}$$

which after rearranging, and multiplying both sides by c^2 gives

$$(m(v) - m_0)c^2 = \frac{m_0 v^2}{2} + m_0\left[\frac{3}{8}\frac{v^4}{c^2} + \frac{5}{16}\frac{v^6}{c^4} + \frac{35}{128}\frac{v^8}{c^6} + \ldots\right] \tag{1.44}$$

So if we take the mass of an object at speed v and subtract the mass of the object and then multiply the result by c^2, we get the kinetic energy of the object (plus some terms that very quickly go to zero). This is what led Einstein to believe that the total kinetic energy of an object was stored in its mass. He would use this to produce the world's most famous equation

$$E_{kin} = m(v)c^2 \tag{1.45}$$

1.3.1 Relativistic Quantum Mechanics

It would seem that relativity concerns the physics of the very large and fast, while quantum mechanics is concerned with the very small. To merge the two, let us start from the beginning with the time-dependent one-dimensional Schrödinger equation which we will rewrite here in a more general and explicit form[6]

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + \hat{V}(x)\Psi(x,t) \tag{1.46}$$

where $i\hbar\frac{\partial}{\partial t}$ is the energy operator, $-\hbar^2\frac{\partial^2}{\partial x^2}$ is the momentum squared operator ($\hat{p} = -i\hbar\frac{\partial}{\partial x}$), $\hbar$ is the reduced Planck's constant ($\hbar = \frac{h}{2\pi}$) and $\hat{V}(x)$ is the potential energy operator that the particle described by $\Psi(x,t)$ experiences. The reason we can not use the Schrödinger equation directly in relativistic quantum mechanics is because it treats time and space differently (it depends on only the first derivative of time, but the second derivative of space). In order to fix this, we may express Equation

$$E_{kin}^2 = \hat{p}^2c^2 + m_0^2c^4 \tag{1.47}$$

If we want to solve for a free particle ($\hat{V}(x) = 0$), we could put the energy and momentum operator from Equation

$$-\hbar^2\frac{\partial^2\Psi(x,t)}{\partial t^2} = c^2\left(-\hbar^2\frac{\partial^2\Psi(x,t)}{\partial x^2} + m_0^2c^2\Psi(x,t)\right) \tag{1.48}$$

which is called the Klein-Gordon[21, 22] equation for a free particle. We could also solve for a particle of charge q in a electromagnetic field described by potentials $\hat{A}$ and $\hat{\varphi}$ as

$$\left(i\hbar\frac{\partial}{\partial t} - q\hat{\varphi}\right)^2\Psi(x,t) = c^2\left[\left(-i\hbar\frac{\partial}{\partial x} - \frac{q}{c}\hat{A}\right)^2 + m_0^2c^2\right]\Psi(x,t) \tag{1.49}$$

Here we are treating time and space exactly the same, but there is a problem. While this equation works perfectly well for spinless particles, we can not ad hoc add spin to this equation like we did with the original Schrödinger equation without violating its Lorentz invariance, which is also important for relativistic theories. Also, because this equation solves for the *square* of the energy, it implies that the energy could both be positive or negative. This is a puzzling result that we will return to later, but for now let us examine how Dirac fixed the issue of introducing spin.

1.3.2 Dirac Equation

Dirac[23] began with the Klein-Gordon equation which may be written in a three-dimensional form as

$$\boldsymbol{\pi}_0^2 - \left[\sum_{u=x,y,z} \boldsymbol{\pi}_u^2 + m_0^2 c^2\right] = 0 \tag{1.50}$$

$$\boldsymbol{\pi}_0 = \frac{i\hbar\frac{\partial}{\partial t} - q\hat{\varphi}}{c}, \quad \boldsymbol{\pi}_u = -i\hbar\frac{\partial}{\partial u} - \frac{q}{c}\hat{A} \tag{1.51}$$

Dirac wanted to write this equation as the product of one equation and its conjugate, which can be done as follows

$$\left(\boldsymbol{\pi}_0 + \left[\sum_{u=x,y,z} \alpha_u \boldsymbol{\pi}_u + \alpha_0 m_0 c\right]\right)\left(\boldsymbol{\pi}_0 - \left[\sum_{u=x,y,z} \alpha_u \boldsymbol{\pi}_u - \alpha_0 m_0 c\right]\right) = 0 \tag{1.52}$$

so long as we restrict α as

$$\alpha_i^2 = 1, \quad \alpha_i\alpha_j + \alpha_j\alpha_i = 0 \quad \text{for} \quad i \neq j \tag{1.53}$$

It's clear that the αs must be matrices. The simplest of these that meet the requirements of Equation

$$\alpha_i = \begin{pmatrix} \mathbf{0} & \sigma_i \\ \sigma_i & \mathbf{0} \end{pmatrix} \quad \text{for} \quad i \neq 0 \tag{1.54}$$

$$\alpha_0 \equiv \beta = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{pmatrix} \tag{1.55}$$

where σ_i are the Pauli spin matrices for $i = x, y, z$, $\mathbf{0}$ is a 2×2 matrix of zeros, and $\mathbf{I}$ is a 2×2 identity matrix[20]. We now have two different operator equations

$$\left(\boldsymbol{\pi}_0 + \sum_{u=x,y,z} \alpha_u \boldsymbol{\pi}_u + \beta m_0 c\right)\Psi(x, y, z, t) = 0 \tag{1.56}$$

$$\left(\boldsymbol{\pi}_0 - \sum_{u=x,y,z} \alpha_u \boldsymbol{\pi}_u - \beta m_0 c\right)\Psi(x, y, z, t) = 0 \tag{1.57}$$

Equation

$$\left(E - V - \beta m_0 c^2 - c\sum_{u=x,y,z} \alpha_u \boldsymbol{\pi}_u\right)\Psi(x, y, z) = 0 \tag{1.58}$$

where $V = q\hat{\varphi}$. Introducing α as a 4×4 matrix means that Ψ must also have four components. It is typically written as

$$\Psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \phi_1 \\ \phi_2 \end{pmatrix} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \phi_1 \\ \phi_2 \end{pmatrix} = \begin{pmatrix} \boldsymbol{\psi} \\ \mathbf{0} \end{pmatrix} + \begin{pmatrix} \mathbf{0} \\ \boldsymbol{\phi} \end{pmatrix} = \begin{pmatrix} \boldsymbol{\psi} \\ \boldsymbol{\phi} \end{pmatrix} \tag{1.59}$$

where $\boldsymbol{\psi}$ and $\boldsymbol{\phi}$ are called spinors. $\boldsymbol{\psi}$ is called the large component and $\boldsymbol{\phi}$ is the small component.

1.3.3 Kinetic Balancing

Recall that Equation

Using the spinors, we can write Equation

$$\begin{pmatrix} (V + \beta m_0 c^2) & c(\boldsymbol{\sigma\pi}) \\ c(\boldsymbol{\sigma\pi}) & (V + \beta m_0 c^2) \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi} \\ \boldsymbol{\phi} \end{pmatrix} = \begin{pmatrix} E & 0 \\ 0 & E \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi} \\ \boldsymbol{\phi} \end{pmatrix} \tag{1.60}$$

where $\boldsymbol{\sigma\pi} = \sum_{u=x,y,z} \alpha_u \boldsymbol{\pi}_u$. This is equivalent to adding the following two equations together

$$(E - V - m_0 c^2)\boldsymbol{\psi} - c(\boldsymbol{\sigma\pi})\boldsymbol{\phi} = 0 \tag{1.61}$$

$$(E - V + m_0 c^2)\boldsymbol{\phi} - c(\boldsymbol{\sigma\pi})\boldsymbol{\psi} = 0 \tag{1.62}$$

We can set where the energy is zero to anywhere we want, so let us make zero the energy of a free electron at rest ($\epsilon = E - m_0 c^2$). Equations

$$(\epsilon - V)\boldsymbol{\psi} - c(\boldsymbol{\sigma\pi})\boldsymbol{\phi} = 0 \tag{1.63}$$

$$(\epsilon - V + 2m_0 c^2)\boldsymbol{\phi} - c(\boldsymbol{\sigma\pi})\boldsymbol{\psi} = 0 \tag{1.64}$$

We can rewrite Equation

$$\boldsymbol{\phi} = \left(1 + \frac{(\epsilon - V)}{2m_0 c^2}\right)^{-1} \frac{1}{2m_0 c^2} \boldsymbol{\sigma\pi}\boldsymbol{\psi} \tag{1.65}$$

To a good approximation, $\epsilon - V$ will be much smaller than $2m_0 c^2$, so we can assume the term in parentheses is equal to 1. Therefore, the small component can be written in terms of just $\boldsymbol{\psi}$ and becomes

$$\boldsymbol{\phi} = \frac{\boldsymbol{\sigma\pi}}{2m_0 c^2}\boldsymbol{\psi} \tag{1.66}$$

Not only does this make solving the Dirac equation much simpler (we only need to solve for $\boldsymbol{\psi}$ instead of $\boldsymbol{\psi}$ *and* $\boldsymbol{\phi}$) it also "hides" the negative energies from numerical methods. Note, though, that it relies on the assumption that $\epsilon - V$ is much smaller than $2m_0 c^2$. If this

is not the case, such as in the electrons in the heaviest known elements, then this procedure will fail and we will get energies that are lower than they should be. When this occurs, we say that there is variational prolapse of the wavefunction.

1.3.4 The Dirac Hydrogen-Like Atom

Up until now, we have only looked at what Dirac's theory says about a free electron (well, a "free" electron in the presence of an infinite amount of positrons). In the case of hydrogen-like atom solutions, the quantum numbers are similar to the non-relativistic theory. They are: the principal quantum number ($n = 1, 2, 3, \ldots$), the azimuthal quantum number ($l = 0, 1, 2, \ldots, n-1$), the angular momentum quantum number ($j = |l \pm \frac{1}{2}|$), and the magnetic quantum number ($m = -j, -j+1, \ldots, j-1, j$). The energy in terms of the quantum numbers is given by[20]

$$E_{n,j} = -\frac{1}{2n^2}\left[1 + \frac{1}{nc^2}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right] \tag{1.67}$$

It can be seen that there is a splitting in the energy levels of spinors with the same azimuthal number, whereas in the non-relativistic theory, orbitals with the same azimuthal number would all be perfectly degenerate.

1.3.5 Relativistic Effects

The effects of relativity have a dramatic effect on chemistry. Two classic examples are gold's distinctive colour, and mercury being the only metal that is liquid at room temperature. In the case of gold, its $6s_{1/2}$ electrons are lowered in energy and its $5d_{5/2}$ electrons are raised. This shifts its absorption region into the blue end of the spectrum, making it appear yellow[25]. The $6s_{1/2}$ electrons of mercury are similarly stabilized and since its $5d_{3/2}$ and $5d_{5/2}$ orbitals are filled, it behaves quite like a noble gas, making bonding quite difficult at room temperature[26].

Relativistic effects are broken up into two categories: primary and secondary effects. Primary effects are due to the contraction of the s and p electrons. The non-relativistic Bohr radius for the 1s electron of hydrogen is[8]

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_0 e^2} \tag{1.68}$$

where ϵ_0 is the permittivity of free space, $\hbar$ is the reduced planks constant, e is the charge of an electron, and m_0 is the mass of an election at rest. Recall from Equation

$$a_v = \frac{4\pi\epsilon_0\hbar^2\sqrt{1-\frac{v^2}{c^2}}}{m_0 e^2} \tag{1.69}$$

Dividing Equation

$$\frac{a_v}{a_0} = \sqrt{1-\frac{v^2}{c^2}} \tag{1.70}$$

which is less than 1 and will get closer and closer to zero as v increases (v will increase in proportion to the nuclear charge). This contraction stabilizes the electrons, making them more inert.

Secondary effects are a direct result of the electron density contraction. The contraction of these electrons leads to greater shielding of the nucleus, reducing its effective nuclear charge. This causes the d and f electrons to feel a smaller attraction to their nucleus, which makes their orbitals enlarge. This destabilizes these electrons, making them more reactive[20].

1.3.6 Gaussian Nucleus

Up till now, we have assumed the nucleus can be represented as a point. For many applications this works just fine, but it can make it difficult to find convergence when relativity is considered. Therefore, it is helpful to use a model more grounded in reality in this case. One such model is the Gaussian nucleus. This changes the potential in Equation

$$V(\mathbf{r}) = Z\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\int\frac{e^{-\alpha(\mathbf{r}-\mathbf{R})^2}}{|\mathbf{r}-\mathbf{R}|}d\mathbf{R} \tag{1.71}$$

where $\mathbf{r}$ is the coordinates of an electron, $\mathbf{R}$ is the coordinates of the nuclei, Z is the nuclear charge, and α is an estimation of the "size" of the nucleus. This is usually approximated using the root-mean-square (RMS) radius of the nuclei[27], which can be related to the mass of the nucleus by[28]

$$\sqrt{\langle R^2\rangle} = \left(0.836A^{1/3} + 0.570\right) \tag{1.72}$$

where $\langle R^2\rangle$ is the mean-square radius in femtometers, and A is the mass of the nucleus. Converting the RMS into atomic units and substituting its value into the following equation gives the value of α[27]

$$\alpha = \frac{3}{2\langle R^2\rangle} \tag{1.73}$$

Chapter 2

cudaDFRATOM

2.1 Introduction

In this Chapter, I present a program that can optimize four-component relativistic basis sets. It was adapted from Matsuoka's and Watanabe's DFRATOM program[29]. My program was written in the CUDA Fortran programming language[30], and so I have called it cudaDFRATOM. In the following sections I give an introduction to programing with CUDA Fortran, and then I give a detailed explanation of the algorithms cudaDFRATOM uses. Finally, I show how my new program is able to outperform the original.

2.2 GPU Architecture

While general purpose computing on graphics processing units (GPGPU) (GPUs) has been adopted by the high performance computing (HPC) community for quite some time, it can seem quite complex to the uninitiated. While most quantum chemists who decide to dip their toes into computational waters can get away with having little to no understanding of what is actually going on under the hood when programming for a central processing unit (CPU), the same can not at all be said for GPUs. Therefore, in this section I will explain how a GPU works in order to help understand the terms and techniques used in the following chapter. As cudaDFRATOM was optimized for the NVIDIA Tesla C2050, I will be referring to the Tesla C2050 specifications for examples when needed. I will begin will the most granularity possible, and zoom out so that by the end of this section, the reader should come away prepared for the rest of this chapter. The bulk of this section has been adapted from [31, 30] and is based on my own experience.

2.2.1 Threads, Blocks, and Grids

The most granular element of computation on a GPU is the thread. When a CUDA function or subroutine (hereafter called a kernel) is called, it is a thread that actually executes the code. What makes GPGPU so powerful is that while a thread in a kernel is always executing the same code, the data a thread works with can be completely different between threads. This method of parallelism is called single instruction, multiple data (SIMD).

32 threads are organized into a structure called a warp. Within a warp, all threads execute code in lock-step. If a condition arises where some threads in warp must execute some code, and other threads in the same warp execute some other code (for instance in an **if else** statement), this leads to serialization of code execution, a process called warp divergence. In a worst-case scenario, this could cause all 32 threads to execute serially which could lead to a massive hit to performance.

Warp divergence can also cause warps to fall behind other warps and has the potential to cause race conditions to appear. A race condition appears when different threads need to use the same memory location, but there is nothing in the code to enforce the order the threads will access the memory location. If one warp needs to read data written by another warp that is several steps behind, this can cause all kinds of confusing errors to appear. Therefore, it is generally advisable to avoid warp divergence whenever possible. But, for programs of any considerable usefulness, warp divergence will be inevitable. Thankfully, NVIDIA has included the **syncthreads** command which provides a barrier that all threads within a block must meet before any can continue.

The next highest structure is the thread block, or block for short. Simply put, a block is a collection of one or more threads. When a kernel is called, the block scheduler assigns each block to a streaming multiprocessor (SM). How many blocks a SM can run at once depends on the resources each block uses (more on this in section

Finally there is the grid. The grid is the entire collection of blocks that are launched for a kernel. The grid gives a dimensionality to blocks through the $blockIdx$ variable which has similar parts to the $threadIdx$ variable. The grid also has the $gridDim$ variable which is analogous to $blockDim$.

2.2.2 Memory

To simplify the discussion of the kinds of memory available on a GPU we will limit ourselves to the three main types. They are the global memory, the shared memory, and the register memory. Because the execution time of a calculation is often not limited by the actual number of floating point operations to perform, but rather the reading and writing to memory, it is essential to be sure that the three main types of memory are managed correctly.

Global memory is both the most plentiful and the slowest available memory on a GPU. In a typical calculation, global memory will be allocated in code executed by the CPU (host). Data will be uploaded to the allocated memory and then used by the GPU (device). Global memory is distinct from the other kinds of device memory in that it can be read from and written to by all threads currently executing. This can allow threads of one block to pass messages to threads in an other block, but great care must be taken to avoid race conditions. There is an additional caveat with global memory in that if threads are reading from non-contiguous memory locations, then memory bandwidth plummets. There is also a problem when multiple threads try to read from the same location. Instead of being one transaction, the read is serialized which leads to a massive performance penalty. It is therefore to the programmers advantage to write their kernels with as little use of the global memory as possible.

Shared memory, as its name implies, is shared and private to threads in a single block. It can be accessed much faster than global memory, but this comes at the cost of a much reduced volume. The amount of it available per SM varies with hardware generation, but the maximum available on our card is 48KB. This amount is shared among all blocks that are running on the SM, so the amount available per block will typically be even less. Also, there is no guarantee that memory loaded by one thread will be available to all other threads right away, only a call to **syncthreads** ensures proper loading. But, when used properly, shared memory is indispensable for speeding up calculations. It does not suffer from threads reading from non-contiguous memory locations like global memory does, and if all threads in a warp read from the same memory location a "broadcast" occurs. This means that instead of the read being serialized, all threads are able to read the data in one transaction. Shared memory is also distinct from global memory in that instead of being declared in the host code, it is declared in the device code. This is done by giving the variable the "shared" attribute in its declaration. However, one must be careful not to overuse the shared memory. As mentioned, there is only 48KB available per SM. If a block needs more than is available, the function will fail to execute. It can also affect the occupancy of the kernel, a concept that will be explained later on.

Lastly there is the register memory. This is the fastest memory available and is also private to an individual thread. Figure

2.2.3 Occupancy and Performance

Having described the various resources, we can talk about how they can be used most effectively. The occupancy of a kernel is the number of warps that are actually able to run on a SM divided by the maximum possible warps an SM can run. Occupancy is important,

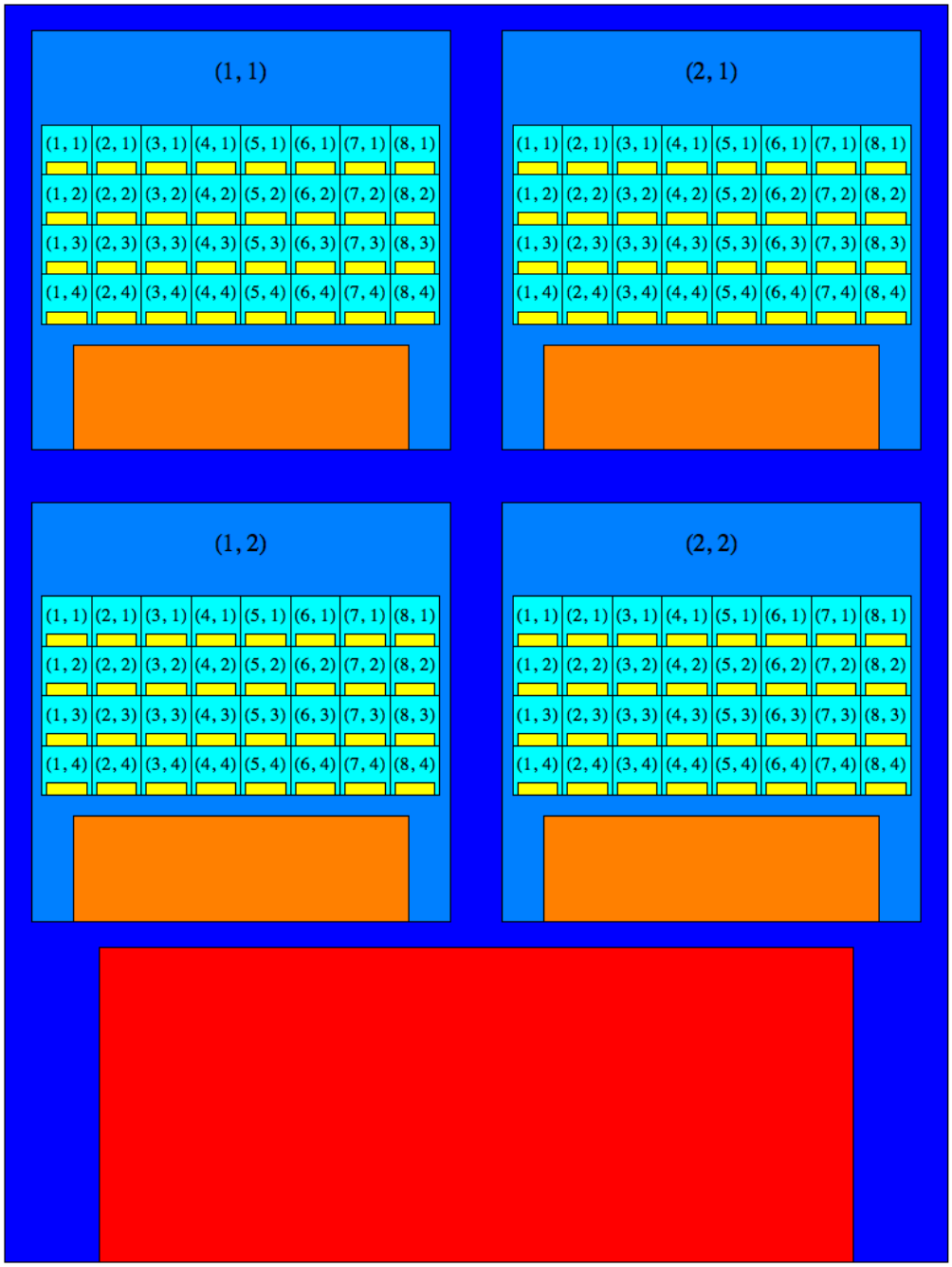


Figure 2.1: *Architecture of a GPU. Organization of threads and blocks in the grid, and the location of different memory types within them. The grid is coloured dark blue, blocks are coloured light blue, and threads are coloured cyan. The global memory is coloured red, shared memory is coloured orange, and register memory is coloured yellow. The numbers in parenthesis indicate the block or thread's $blockIdx$ or $threadIdx$ variables. In this particular case, $blockDim = (8, 4)$ and $gridDim = (2, 2)$. A thread is able to access memory that is inside its registers, but not the registers of other threads, and memory that is inside the shared memory of its block, but not the shared memory of other blocks. All threads can access all of the global memory.*

as it determines the maximum number of blocks, and thus threads that are able to run simultaneously. The occupancy of a kernel is determined by three factors: the block size, the amount of shared memory per block, and the number of registers used per thread. While block size and shared memory are explicitly set by the programmer, it is next to impossible to guess how registers will be used before compile time. Thankfully, there are compiler flags that will display this information.

Armed with the resources our kernel will need, we can now determine its occupancy. The "CUDA Occupancy Calculator" is an Excel spreadsheet provided by NVIDIA and is an indispensable tool. We can input the needed resources and the hardware generation of our card and then receive the occupancy of the current resource configuration, where the bottleneck of the current configuration is, as well as information on how the occupancy will change upon tweaking the configuration. In some sense, the best block size is determined by how the other resources are used. Therefore, in order to maximize the occupancy, we must first make sure that we are correctly using the memory provided.

Registers are the fastest memory available, but they are also the easiest to overuse. Therefore, they are best suited for small variables that need to be referenced frequently, such as accumulators. Shared memory is best used for storing large sections of non-contiguous data stored in the global memory. Finally, data that is able to be stored such that it can be accessed effectively, or is infrequently used, might best be left in the global memory.

As with everything, these rules are only guidelines. The best resource configuration will be individual not only to every kernel, but also to the GPU it is to be run on. The best way to maximize the efficiency of a calculation is to make minor alterations to where data is stored and play around with the code. Finally, it might not always be the best idea to maximize the occupancy of a kernel. If the bottleneck is not the actual calculation, but how fast the data can be read, then it might be advantageous to fill up the registers and shared memory as much as possible and have a very low occupation.

2.2.4 Matrix Multiplication Example

To complete the introduction to CUDA programming, we will go over a real example of CUDA Fortran code. For our example, we will examine code that performs matrix multiplication on matrices of arbitrary dimensions. This makes use of all the concepts we've covered so far, so it will be a good exercise to examine. The code is given below.

```
1 module mat_mul
2   implicit none
3   integer, parameter  ::  dp = kind(0.d0)
4   integer, parameter  ::  block_dim = 16
5   integer, constant ::  rowA, colA, rowB, colB
```

```
  contains
    attributes(global) subroutine mat_mul_kernel(inputA, inputB, output)
      real(dp), dimension(:,:)  ::  inputA, inputB, output
      real(dp)  ::  total
      real(dp), shared, dimension(block_dim, block_dim) ::  s_tileA, s_tileB
      integer ::  x, y, i, j

      x = threadIdx%x + blockDim%x * (blockIdx%x - 1)
      y = threadIdx%y + blockDim%y * (blockIdx%y - 1)
      total = 0.0_dp

      do i = 0, colA - 1, block_dim
        call syncthreads()
        if ((x <= rowA) .and. (threadIdx%y + i <= colA)) then
          s_tileA(threadIdx%x, threadIdx%y) = inputA(x, threadIdx%y + i)
        else
          s_tileA(threadIdx%x, threadIdx%y) = 0.0_dp
        endif

        if ((threadIdx%x + i <= rowB) .and. (y <= colB)) then
          s_tileB(threadIdx%x, threadIdx%y) = inputB(threadIdx%x + i, y)
        else
          s_tileB(threadIdx%x, threadIdx%y) = 0.0_dp
        endif

        call syncthreads()

        do j = 1, block_dim
          total = total + s_tileA(threadIdx%x, j) * s_tileB(j, threadIdx%y)
        enddo

      enddo

      if((x <= rowA) .and. (y <= colB)) then
        output(x, y) = total
      endif
    end subroutine mat_mul_kernel
end module mat_mul

program main
  use cudafor
  use mat_mul
  implicit none
  ! Host variables
  real(dp), allocatable, dimension(:, :)  ::  inputA, inputB, output
  ! Device variables
  real(dp), device, allocatable, dimension(:, :)  ::  d_inputA, d_inputB,
```

```
    d_output
! For generating random numbers
integer, allocatable, dimension(:)  ::  seed
integer ::  n
! block and grid dimensions
type(dim3)  ::  blockDim, gridDim

rowA = 1024
colA = 432
rowB = colA
colB = 1783

! Set up random number generator
call random_seed(size = n)
allocate(seed(n))
! Set seed to a constant so we always get the same matrices
seed = 150987
call random_seed(put = seed)
deallocate(seed)

! Allocate host matrices and set up matrices
allocate(inputA(rowA, colA))
allocate(inputB(rowB, colB))
allocate(output(rowA, colB))

call random_number(inputA)
call random_number(inputB)

! Allocate and upload device data
allocate(d_inputA(rowA, colA))
allocate(d_inputB(rowB, colB))
allocate(d_output(rowA, colB))
d_inputA = inputA
d_inputB = inputB

blockDim = dim3(block_dim, block_dim, 1)
gridDim = dim3((rowA - 1) / block_dim + 1, (colB - 1) / block_dim + 1, 1)

call mat_mul_kernel <<<gridDim, blockDim>>> (d_inputA, d_inputB, d_output)

! Download device data
output = d_output

! Deallocate variables
deallocate(d_inputA)
deallocate(d_inputB)
deallocate(d_output)
```

```
99    deallocate(inputA)
100   deallocate(inputB)
101   deallocate(output)
102 end program main
```

Listing 2.1: *Matrix multiplication kernel*

Lines 1 - 43 define a module which contains a matrix multiplication kernel. The kernel takes the matrices `inputA` and `inputB`, multiplies them, and stores the result in `output`. The kernel has the `attributes(global)` attribute, which means that it can be called from either device or host code. `rowA`, `colA`, `rowB`, and `colB` are the rows and columns of `inputA` and `inputB`. Because they are small and don't change over the course of the calculation, they get stored in a special memory type called constant memory. This is a small cache of read only memory that is 64KB in size and allows for constant values to be read very quickly. There are two shared variables, `s_tileA` and `s_tileB`. Each of these are square matrices with dimensions of `block_dim` and these will be used to store sections or "tiles" of `inputA` and `inputB` respectively. We want each thread to do all the calculations needed to compute a simple element of `output`. Line 13 and 14 use the `threadIdx`, `blockDim`, and `blockIdx` variables so that each thread gets a unique combination of `x` and `y` values. `x` corresponds to a row of the `output` matrix and `y` corresponds to a column, so each thread is then uniquely mapped to an element of `output`. We will see in the host code how these index values are determined, but for now it is sufficient to know that there will be at least as many threads as elements of `output`.

Lines 17 - 37 are where the actual calculation takes place. For each iteration of the loop, a different tile of `inputA` and `inputB` is fetched from the global memory and stored into the shared memory. The reason for using this tiling approach can be seen when we consider how the threads must read `inputB`. If we did not use shared memory, the loop would just be `total = total + inputA(x, i) * inputB(i, y)`. In this case, access to `inputA` is coalesced, but access to `inputB` is not. Therefore, the kernel will be stunted due this unoptimized memory usage. Instead, we load tiles in a coalesced manner into the shared memory, synchronize the threads, and then read through the shared memory in an uncoalesced fashion which carries no penalty. At the end of each loop, the tiles are moved in the `y` direction for `inputA` and in the `x` direction for `inputB`, and the process repeats. Notice how it is possible that a tile might fall on the boundary of an `input` matrix. This is why there are checks to make sure the coordinates of the tile don't exceed the boundaries of a matrix so we don't start reading garbage.

In the host code on lines 45 - 102, we have two sets of variables, those for the host and those for the device. Notice how device variables have the `device` attribute. For clarity, they are given the same name as their host variables but with a `d_` prefix. We now assign

constant variables from line 5 to arbitrary values. Next we set up the random number generator, allocate the host matrices memory, and randomly initialize the input matrices. Then the device variables are allocated memory and the host data is then uploaded to the GPU. The block and grid dimensions are set up on lines 87 and 88. `blockDim` and `gridDim` are variables of `type(dim3)` which is a tuple that is defined in the `cudafor` module. The block has two dimensions containing $\texttt{block\_dim}^2$ threads. The grid also has two dimensions, and as we need one thread per element of `output` we perform a calculation which returns the minimum number of blocks that will cover it. Finally, we launch the kernel on line 90 using the `<<< >>>` operators to provide the grid and block dimensions, download the result from the GPU, and deallocate the memory.

2.3 Program flow in cudaDFRATOM

In this section, the control flow of a typical calculation is given.

Step 1. The input file is read by the ***intin*** subroutine. If needed, the basis set and open-shell configurations are calculated by ***formbs*** and ***find_bin_configurations*** respectively. The options set in the input file are rewritten to stdout.

Step 2. The calculation of small arrays and other constants is performed by ***calc_parameters*** and ***bsnorm***. ***calc_parameters*** calls ***bcoef*** and ***setvc***.

Step 3. The mapping of threads to the unrolled one and two-electron integral matrixes are calculated by ***lmpqrsa*** on the GPU. All other data from step 1 and 2 is then uploaded to the GPU.

Step 4. The one and two electron integrals are calculated on the GPU by ***eint1gpu*** and ***eint2gpu*** respectively.

Step 5. The initial guess of the density matrix is calculated by ***guess*** on the GPU. This is done by the diagonalization of the one-electron Hamiltonian matrix.

Step 6. ***scfiter*** then performs the SCF iterations until convergence of the density matrix has been reached, or the maximum number of iterations has been reached. SCF is performed with cuSOLVER functions, as well as a few custom helper functions. The converged eigenvectors, values, and energies are downloaded from the GPU and then written to stdout.

Step 7 (optional). If jobtyp='bsopt', then an optional basis set optimization is carried out. This starts by assigning pointers to variables on the CPU and GPU through ***hookup_cpu*** and ***hookup_gpu***. Then, the four well-tempered basis set (WTBS) parameters are optimized by ***newuoa***. ***newuoa*** calls ***calc_energy*** which essentially reconstructs the basis set from new parameters from ***newuoa***, then repeats steps 2 - 6 and feeds the energy back into ***newuoa***. This repeats until optimal WTBS parameters have been found.

2.4 Alterations of DFRATOM for CUDA

While almost all of the code from the original DFRATOM[29] was modified in some way, the most extreme changes were the integral evaluation and the formation of the P and Q matrixes. Therefore, we will discuss these changes in detail in this section.

2.4.1 Two-electron Integrals

The original DFRATOM calculates the two electron integrals with a long series of nested **for** loops. Working from the outside in, the indices of the loops are L, P, Q, M, R, and S where L and M are spinor symmetries, P and Q are basis functions of symmetry L, and R and S are basis functions of symmetry M. The pseudocode for these is shown in Algorithm

Algorithm 1 The original

```
for L = 1 to nsym do
  for P = 1 to nbs(L) do
    for Q = 1 to P do
      for M = 1 to L do
        if L = M then
          maxr = P
        else
          maxr = nbs(M)
        end if
        for R = 1 to maxr do
          if (L = M) and (P = R) then
            maxs = Q
          else
            maxs = R
          end if
          for S = 1 to maxs do
            compute the J and K integrals of L, M, P, Q, R, and S
          end for
        end for
      end for
    end for
  end for
end for
```

The first problem arises due to warp divergence: as the maximum values of M, R, and S depend on L, P, and Q, different threads will have a different number of loops to complete than others. Because a streaming multiprocessor (SM) must finish the block it is currently working on before it can grab another, there is the possibility that most of the threads in

Algorithm 2 Easy code

$L = threadIdx.x + (blockIdx.x - 1) * blockDim.x$
$P = threadIdx.y + (blockIdx.y - 1) * blockDim.y$
$Q = threadIdx.z + (blockIdx.z - 1) * blockDim.z$

if $(L \leq nsym)$ **and** $(P \leq nbs(L))$ **and** $(Q \leq P)$ **then**
  for $M = 1$ to L **do**
    if $L = M$ **then**
      $maxr = P$
    else
      $maxr = nbs(M)$
    end if
    for $R = 1$ to $maxr$ **do**
      if $(L = M)$ **and** $(P = R)$ **then**
        $maxs = Q$
      else
        $maxs = R$
      end if
      for $S = 1$ to $maxs$ **do**
        compute the J and K integrals of L, M, P, Q, R, and S
      end for
    end for
  end for
end if

a block are idling while waiting for others in the same block to finish. The second problem with this method is that there will always be several blocks which have threads that remain idle throughout the block's runtime, no matter what. This can be seen more clearly in Figure

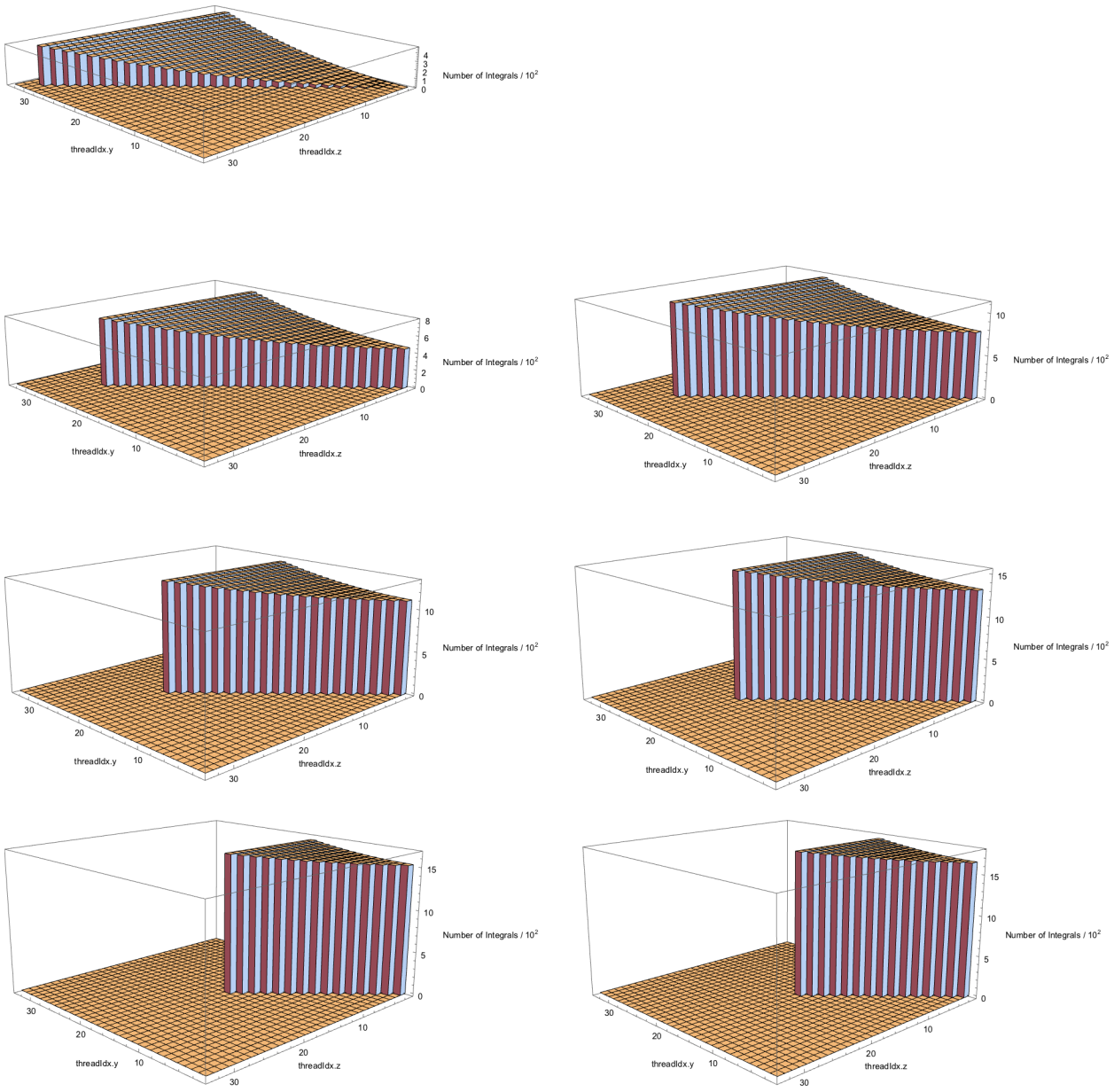


Figure 2.2: *Two-electron integral layout: naive implementation. Mapping of integrals to threads using Algorithm*

The second problem can be solved by restricting the dimensionality of the solution instead of the using the three dimensional one of Algorithm

The first and third problems can be solved by having each thread calculate one and only

one set of J and K integrals. If we start with a valid combination of L, M, P, Q, R, and S values, we can very easily figure out which thread will calculate that set of integrals by using the following equations:

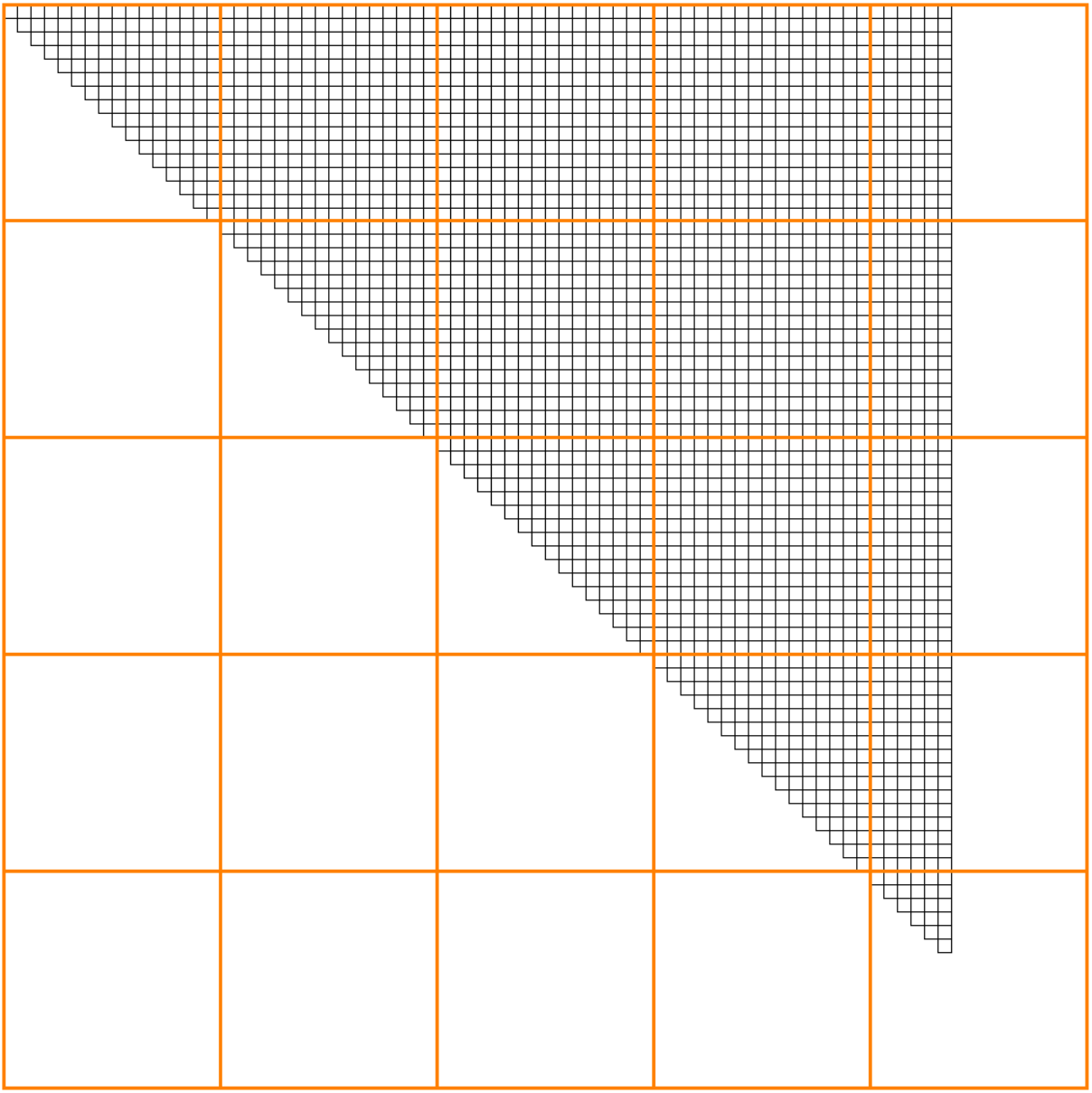


Figure 2.3: *Two-electron integral layout: 2D blocks and grid. Orange lines indicate the border of blocks. Notice that many blocks have idle threads.*

$$n'(j) = \frac{j^2 + j}{2} \tag{2.1}$$

$$y = n'(nbs(L-1)) + n'(P-1) + Q \tag{2.2}$$

$$x = n'(nbs(M-1)) + n'(R-1) + S \tag{2.3}$$

$$i = n'(x) + y \tag{2.4}$$

$$i_{max} = n'(\sum_{j=1}^{nsym} n'(nbs(j))) \tag{2.5}$$

where $nbs(0) = 0$ and $i = threadIdx.x + (blockIdx.x - 1) * blockDim.x$. Starting with a value of i and working our way back is a much more challenging task. It becomes easier if we reframe it in the following way.

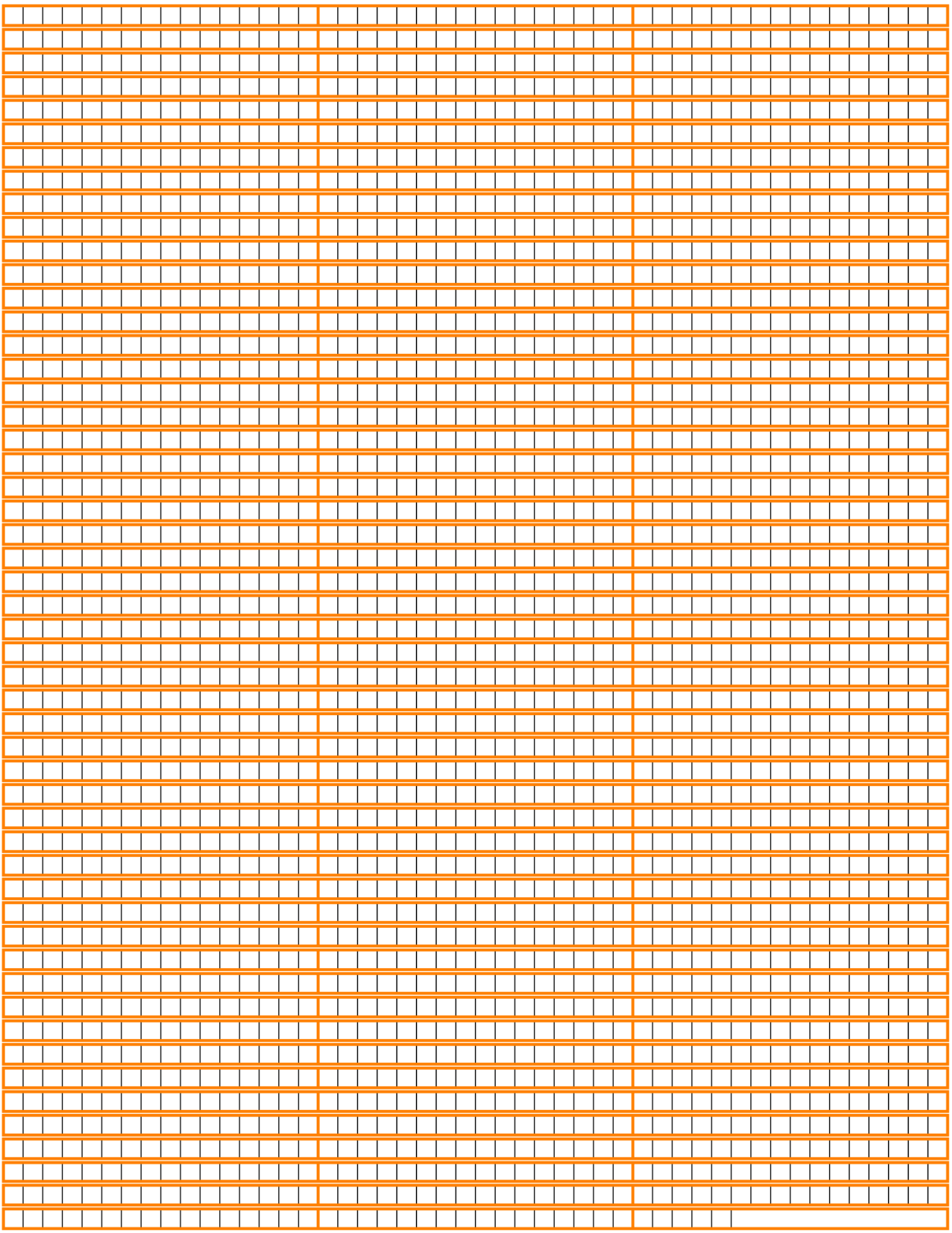


Figure 2.4: *Two-electron integral layout: 1D blocks and grid. Orange lines indicate the border of blocks. Notice that only the last block contains idle threads.*

Consider Figures

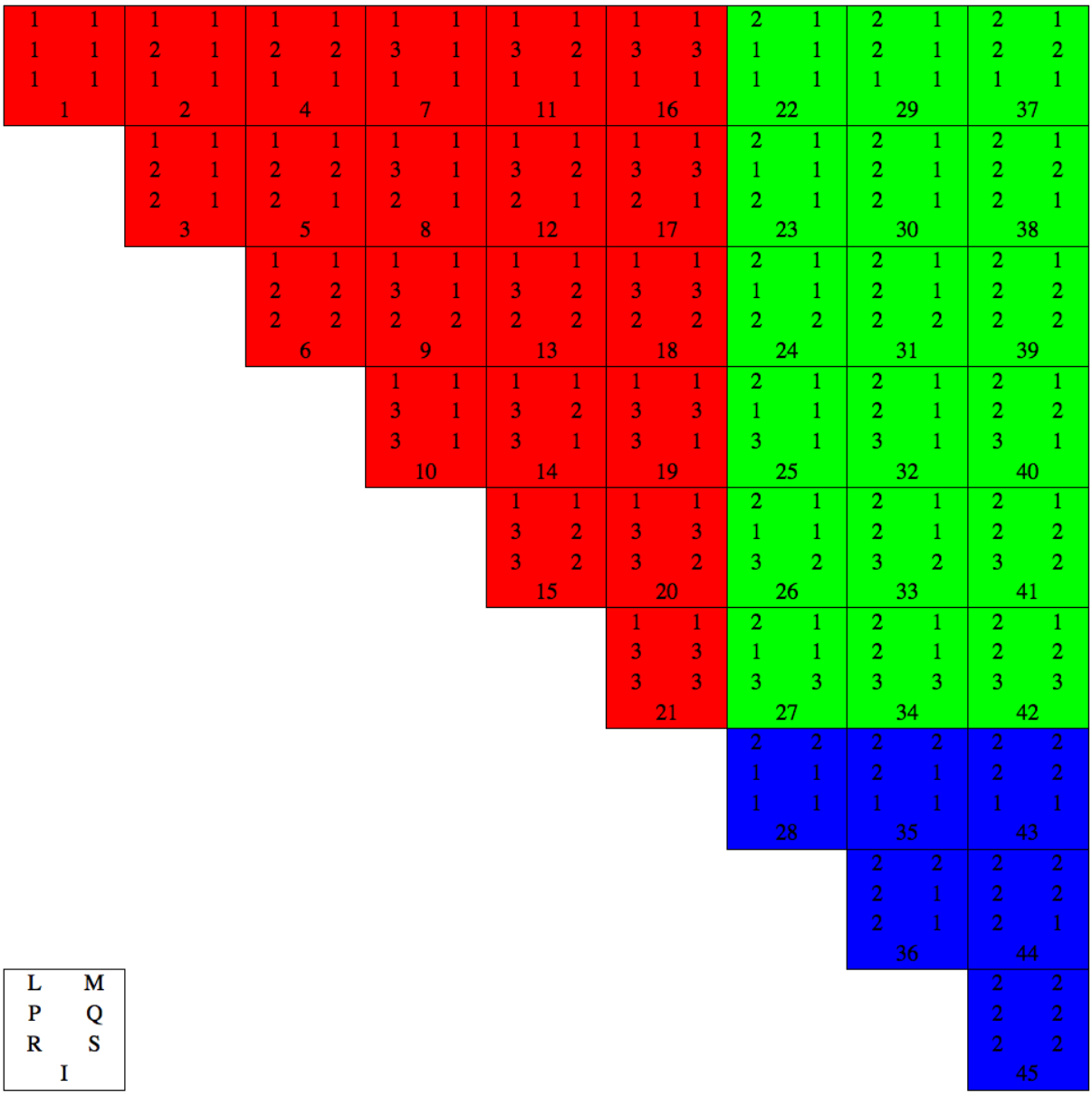


Figure 2.5: *Two-electron integral matrix as a matrix: The top triangle of the two-electron symmetric matrix in a matrix representation. In this instance, the total number of symmetries is 2, with 3 basis functions for the first symmetry and 2 basis functions for the second. The key for translating the numbers in each box into the L, M, P, Q, R, and S values is given in the bottom left. Notice how all rows have the same M, R, and S values, while all columns have the same L, P, and Q values. For clarity, the boxes have been coloured, based on the spinor symmetries that they contain.*

In this algorithm, variables with the $s\_$ prefix refer to those in the shared memory, and *lownum* and *highnum* refer to the minimum and values that i could have for the current

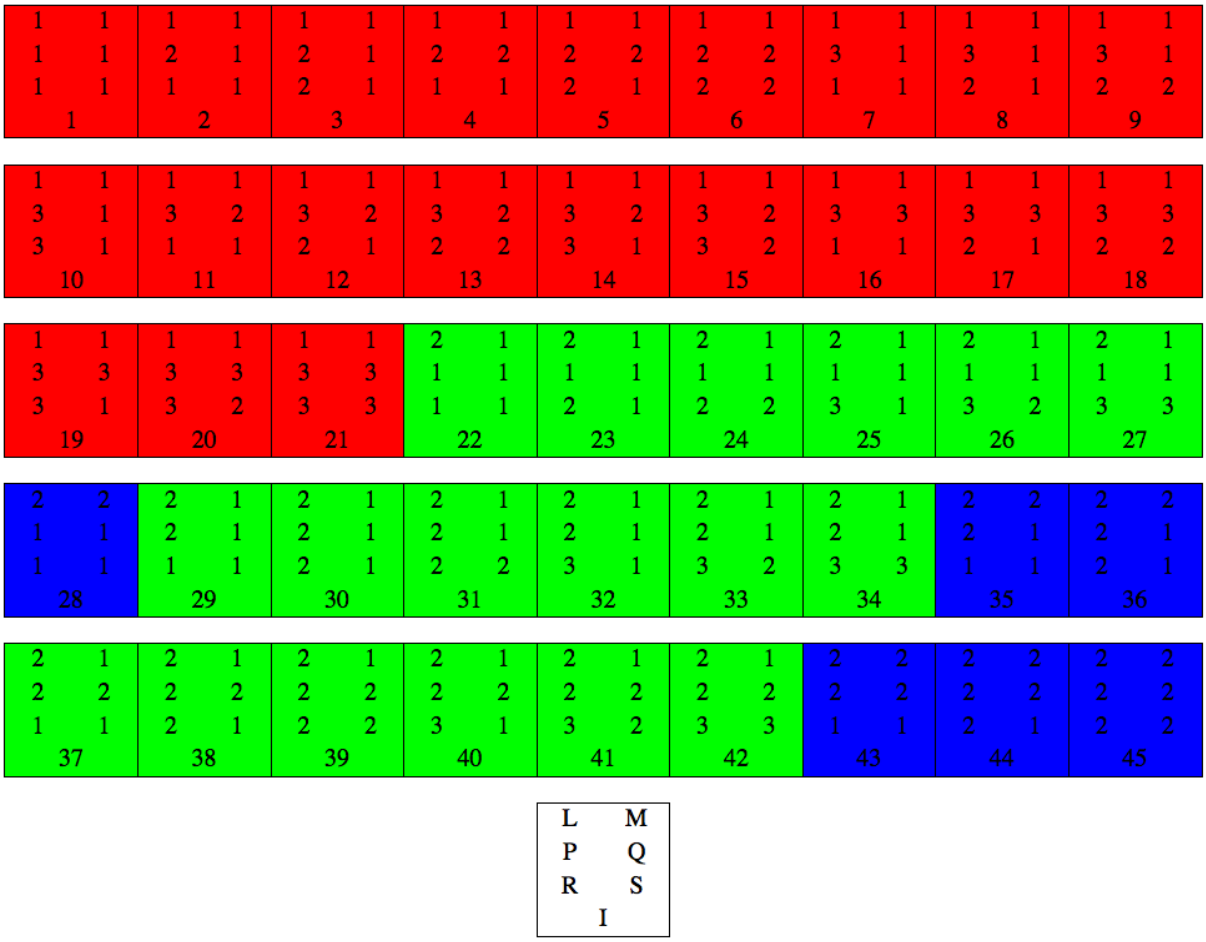


Figure 2.6: *Two-electron integral matrix as a vector: The top triangle of the two-electron symmetric matrix in a vector representation. In this instance, the total number of symmetries is 2, with 3 basis functions for the first symmetry and 2 basis functions for the second. The key for translating the numbers in each box into the L, M, P, Q, R, and S values is given in the bottom center. Notice how the L, M, P, Q, R, and S values are much harder to predict than from the matrix representation. For clarity, the boxes have been coloured based on the spinor symmetries that they contain. Gaps between rows are used to reinforce that the elements are not connected like a matrix.*

guess (mid) of y. From here, L can be found with Algorithm

From here, the new code for evaluating the integrals remains largely the same as the original, except for some minor changes to allow for more efficient global or shared memory access. We also use a process referred to as "grid-stride looping" where all these binary search algorithms have their **if** $i \leq i_{max}$ **then** removed, and then are placed within the following loop: **for** $i = threadIdx.x + (blockIdx.x - 1) * blockDim.x$ to i_{max}, i += $blockDim.x * gridDim.x$ **do**. If we know the occupancy of the algorithm on the GPU beforehand, we can launch exactly the number of blocks that will fill the GPU. This reduces the overhead of

Algorithm 3 Binary search for x and y

if $theadIdx.x \leq nsym$ **then**
  $s\_nsym = nsym$
  $s\_nbs(threadIdx.x) = nbs(threadIdx.x)$
  $s\_nprime(threadIdx.x) = n'(s\_nbs(threadIdx.x))$
end if
call **syncthreads**
$i = threadIdx.x + (blockIdx.x - 1) * blockDim.x$
if $i \leq i_{max}$ **then**
  $low = 1$
  $high =$ **sum**$(s\_nprime(1 : s\_nsym))$
  while $low \leq high$ **do**
    $mid = \frac{(low+high)}{2}$
    $lownum = \frac{(mid-1)(mid-2)}{2} + mid$
    $highnum = lownum - 1 + mid$
    if $(i \leq highnum)$ **and** $(i \geq lownum)$ **then**
      $y = mid$
      exit
    else if $i > highnum$ **then**
      $low = mid + 1$
    else if $i < lownum$ **then**
      $high = mid - 1$
    end if
  end while
  $x = i - lownum + 1$
end if

block swapping and lets us further eke out some performance.

2.4.2 Density Matrix Formation

The term in parenthesis in Equation

$$\mathbf{D_C}_{r,s} = N_\mu \sum_{a=1}^{occ} \mathbf{C}_{r,a}\mathbf{C}^*_{s,a} \tag{2.6}$$

where N_i is the number of electrons that occupy a closed shell of symmetry i. $\mathbf{D_O}$ is similar to this and is shown below.

$$\mathbf{D_O}_{r,s} = N_i \mathbf{C}_{r,(occ+1)}\mathbf{C}^*_{s,(occ+1)} \tag{2.7}$$

where N_i is equal to the number of electrons in the open shell. Note that in this program, only the most energetic shell of any symmetry can be open.

The total density matrix is $\mathbf{D_T} = \mathbf{D_C} + \mathbf{D_O}$

Algorithm 4 Binary search for L

$i = threadIdx.x + (blockIdx.x - 1) * blockDim.x$
if $i \leq i_{max}$ **then**
  $low = 1$
  $high = s\_nsym$
  while $low \leq high$ **do**
    $mid = \frac{(low+high)}{2}$
    $lownum = 1 + \mathbf{sum}(s\_nprime(1 : mid - 1)$
    $highnum = lownum - 1 + s\_nprime(mid)$
    if $(i \leq highnum)$ **and** $(i \geq lownum)$ **then**
      $L = mid$
      exit
    else if $y > highnum$ **then**
      $low = mid + 1$
    else if $y < lownum$ **then**
      $high = mid - 1$
    end if
  end while
end if

Algorithm 5 Binary search for P and Q

$i = threadIdx.x + (blockIdx.x - 1) * blockDim.x$
if $i \leq i_{max}$ **then**
  $low = 1$
  $high = s\_nbs(L)$
  while $low \leq high$ **do**
    $mid = \frac{(low+high)}{2}$
    $lownum = \frac{(mid-1)(mid-2)}{2} + mid + \mathbf{sum}(s\_nprime(1 : L - 1))$
    $highnum = lownum + mid - 1$
    if $(i \leq highnum)$ **and** $(i \geq lownum)$ **then**
      $P = mid$
      exit
    else if $y > highnum$ **then**
      $low = mid + 1$
    else if $y < lownum$ **then**
      $high = mid - 1$
    end if
  end while
  $Q = y - lownum + 1$
end if

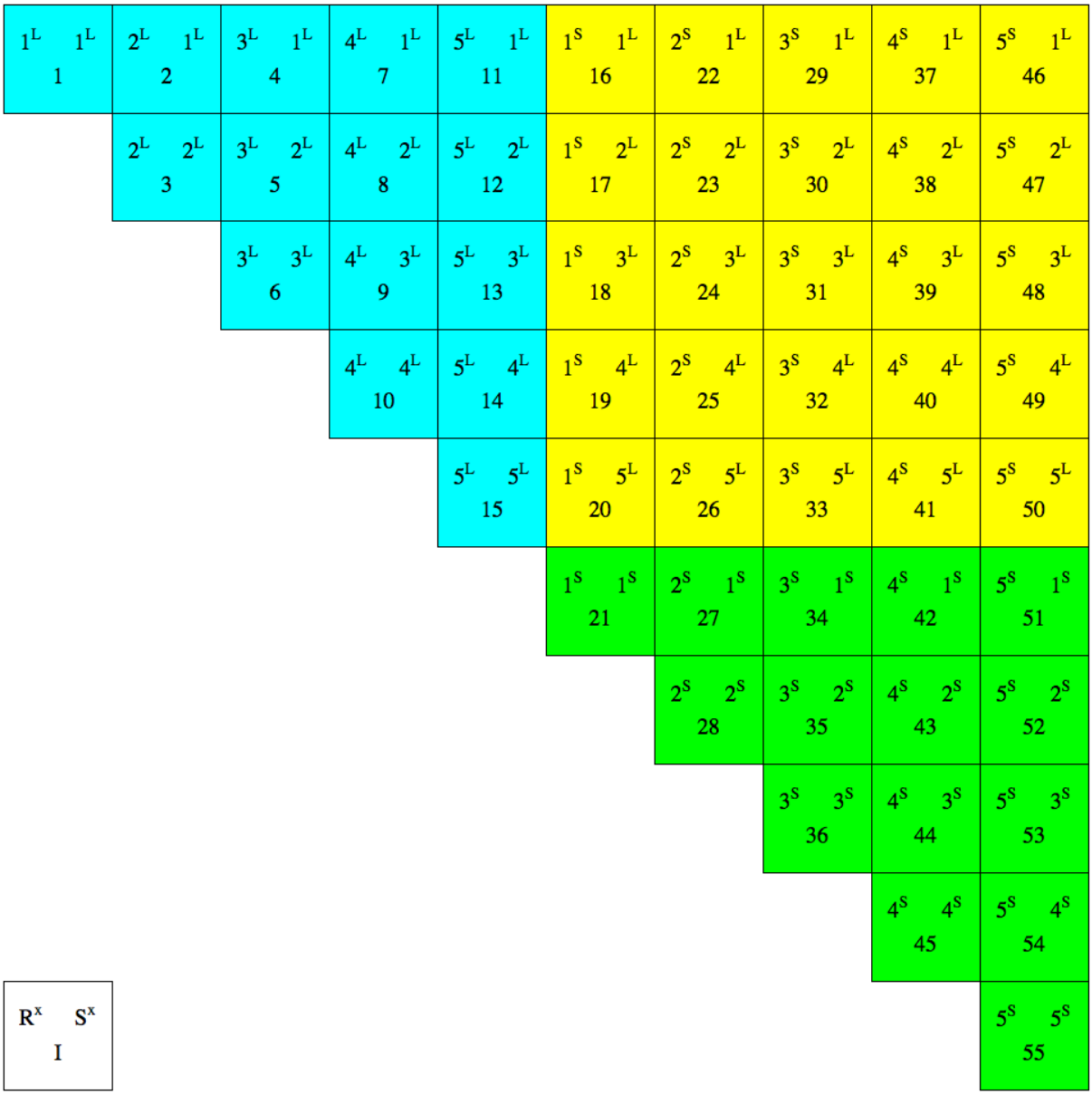


Figure 2.7: *Density matrix as a matrix. The top triangle of the symmetric density matrix in a matrix representation. The key for translating the numbers in each box into the R and S values is given in the bottom right. All active symmetries would have a similar, separate matrix. For clarity, the elements have been colorized based on the combination of large and small components they contain.*

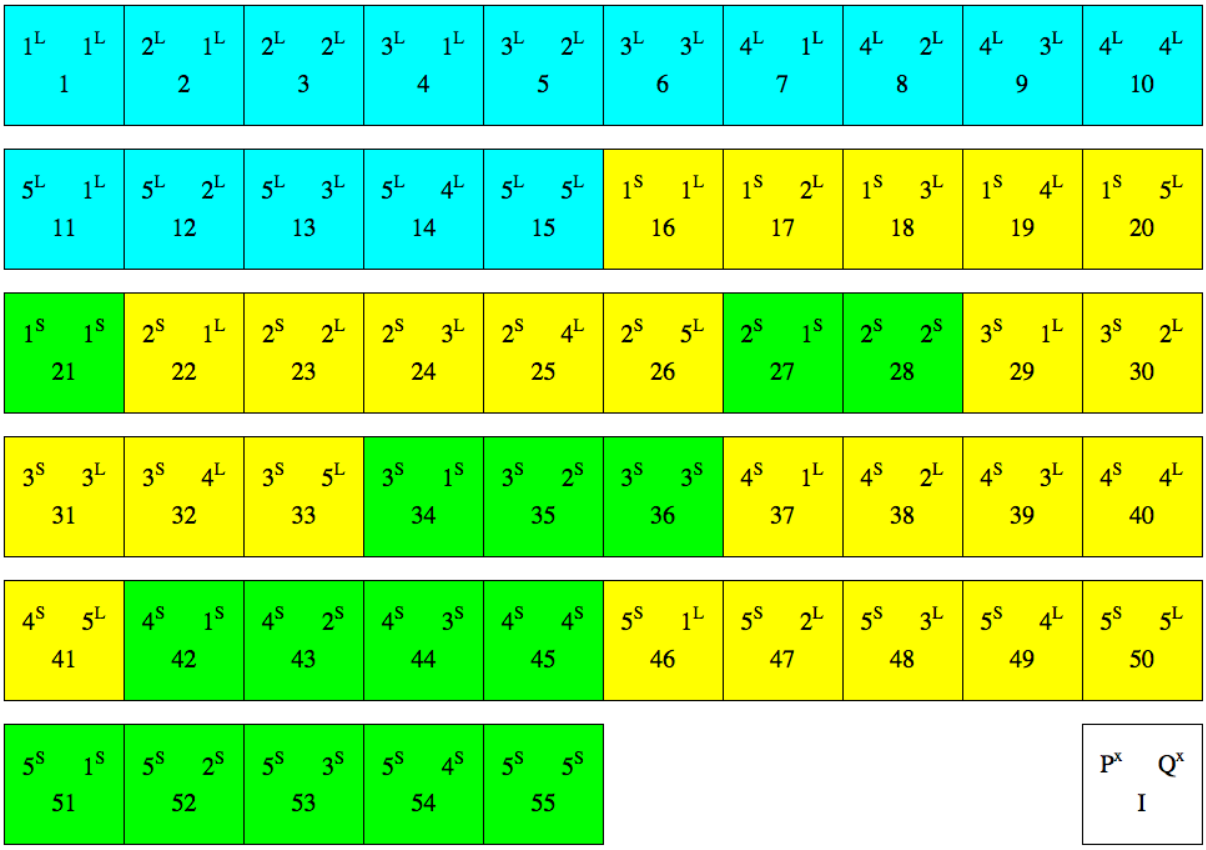


Figure 2.8: *Density matrix as a vector. The top triangle of the symmetric density matrix in a vector representation. The key for translating the numbers in each box into the R and S values is given in the bottom left. All active symmetries would have a similar, separate vector that continue one after the other. For clarity, the elements have been colorized based on the combination of large and small components they contain.*

2.4.2.1 P and Q Supermatrices

With the density matrices in hand we can begin to combine the two-electron integrals from the previous section. These integrals have the following form.[29]

$$\begin{aligned}
\mathbf{X}^1_{I(pqrs)} &= (p_L q_L | r_L s_L) - \frac{1}{2}\left[(p_L r_L | q_L s_L) + (p_L s_L | q_L r_L)\right] \\
\mathbf{X}^2_{I(pqrs)} &= (p_L q_L | r_S s_S) \\
\mathbf{X}^3_{I(pqrs)} &= (p_S q_S | r_L s_L) \\
\mathbf{X}^4_{I(pqrs)} &= -(p_L r_S | q_S s_L) \\
\mathbf{X}^5_{I(pqrs)} &= -(p_L s_S | q_S r_L) \\
\mathbf{X}^6_{I(pqrs)} &= -(p_S r_L | q_L s_S) \\
\mathbf{X}^7_{I(pqrs)} &= -(p_S s_L | q_L r_S) \\
\mathbf{X}^8_{I(pqrs)} &= (p_S q_S | r_S s_S) - \frac{1}{2}\left[(p_S r_S | q_S s_S) + (p_S s_S | q_S r_S)\right]
\end{aligned} \tag{2.8}$$

where the subscripts L and S refer to the large and small components respectively. I is a function that returns the values of x and y from Equations

The **P** and **Q** super matrices have a similar layout to the density matrices. The elements of **P** have the following form[29]

$$\begin{aligned}
\mathbf{P}^{LL}_{pq} &= \sum_{\mu=1}^{nsym} \sum_{r=1} \sum_{s=1} \left(\mathbf{D}^{LL}_{\mathbf{T}rs} \mathbf{X}^1_{pqrs} + \mathbf{D}^{SS}_{\mathbf{T}rs} \mathbf{X}^{J(pqrs)}_{pqrs} \right) \\
\mathbf{P}^{SS}_{pq} &= \sum_{\mu=1}^{nsym} \sum_{r=1} \sum_{s=1} \left(\mathbf{D}^{SS}_{\mathbf{T}rs} \mathbf{X}^8_{pqrs} + \mathbf{D}^{LL}_{\mathbf{T}rs} \mathbf{X}^{J(pqrs)}_{pqrs} \right) \\
\mathbf{P}^{LS}_{pq} &= \sum_{\mu=1}^{nsym} \sum_{r=1} \sum_{s=1} \left(\mathbf{D}^{LS}_{\mathbf{T}rs} \mathbf{X}^5_{pqrs} + \mathbf{D}^{SL}_{\mathbf{T}rs} \mathbf{X}^{J(pqrs)}_{pqrs} \right) \\
\mathbf{P}^{SL}_{pq} &= \sum_{\mu=1}^{nsym} \sum_{r=1} \sum_{s=1} \left(\mathbf{D}^{SL}_{\mathbf{T}rs} \mathbf{X}^7_{pqrs} + \mathbf{D}^{LS}_{\mathbf{T}rs} \mathbf{X}^{J(pqrs)}_{pqrs} \right)
\end{aligned} \tag{2.9}$$

where $J(pqrs)$ is an integer function that selects specific definitions of the two-electron integrals from Equation

The form of the **Q** super matrix is almost the same a **P**, but there will be and additional multiplication of the vector coupling coefficient between the open shells for each summation.

2.4.2.2 FORMPQ Algorithm

Forming the P and Q matrices proved to be the most difficult part of this program to parallelize. Its difficulty was due to the second term in the summations where each **X**

matrix used depends on how far the summation has progressed. Further, each element of **P** will have the **X** matrix change at different times. These two factors result in many **if** statements which GPUs have difficulty handling in parallel. There is also the issue where each element in the LL and SS sections need to loop over every element of the same sections of the density matrix, as do the LS and SL sections. This means that there will be lots of global memory reads unless handled properly. All together, this makes for a very ugly algorithm to parallelize.

Two different attempts were made to try and accelerate this algorithm. Each tried to exploit a different property of GPUs. One attempted to combat the amount of floating point operations to perform by distributing the amount of work to as many threads as possible. This will be referred to as the Multiple Threads Single Element (MTSE) algorithm. The second one tried to deal with the amount of global memory reads by making the most of each read. This will be referred to as Single Thread Single Element (STSE) algorithm. Each will be described in the sections below.

2.4.2.3 MTSE Algorithm

As previously stated, the purpose of the MTSE algorithm is to distribute the amount of work needed to be done to as many threads as possible. This was achieved by having multiple threads each computing two of the multiplications needed for a single element of two matrices in Equation

inttype refers to one or more if the **P** or **Q** matrices. In Algorithm

The grid will need to have $\frac{total-1}{blockDim.x} \times \frac{total-1}{blockDim.y} \times 2$ dimensions for Algorithm

2.4.2.4 STSE Algorithm

The STSE algorithm tries a different approach to this problem than the MTSE algorithm. Instead of trying to spread out the amount of work to do as much as possible, it tries to reduce the amount of global memory reads by making each thread do as much work as it can. This results in fewer blocks, but each block needs to run longer. Giving only the calculations for pmx and when $inttype = 0$, Algorithm

All variables are the same as in Algorithms

Algorithm

2.5 Discussion

In this section, the results of GPU resource usage and profiling the various algorithms discussed previously will be presented. For profiling, the radon atom was chosen. Radon was

Algorithm 6 Kernel 1 for MTSE

$i = threadIdx.x + (blockIdx.x - 1) * blockDim.x$
$j = blockIdx.y$
$inttype = blockIdx.z - 1$
if $i \leq total$ **then**
  $l = lpq\_array(i, 1)$
  $p = lpq\_array(i, 2)$
  $q = lpq\_array(i, 3)$
  $fctr = 1.0$
  if $(p \neq q)$ **and** $(inttype == 0)$ **then**
    $fctr = 2.0$
  else if $(p == q)$ **and** $(inttype == 1)$ **then**
    $fctr = 0.5$
  end if
  $loc = \mathbf{max}(i, j) + ((\mathbf{max}(i, j) - 1) * (\mathbf{max}(i, j) - 2)/2) + \mathbf{min}(i, j) - 1$
  if $(inttype == 0)$ **then**
    if $i > j$ **then**
      $k1 = 3$
      $k2 = 2$
    else
      $k1 = 2$
      $k2 = 3$
    end if
    $pos1 = locmx(l) + ((p - 1)^2 + p - 1)/2 + q$
    $pos2 = locmx(l) + ((p - 1 + nbs(l))^2 + p + nbs(l) - 1)/2 + q + nbs(l)$
    $pLL(i, j) = d(pos1) * fctr * x(1, loc) + d(pos2) * fctr * x(k1, loc)$
    $pSS(i, j) = d(pos1) * fctr * x(k2, loc) + d(pos2) * fctr * x(k8, loc)$
  else
    if $i > j$ **then**
      $k1 = 4$
      $k2 = 6$
    else
      $k1 = 6$
      $k2 = 4$
    end if
    $pos1 = locmx(l) + ((p - 1 + nbs(l))^2 + p - 1 + nbs(l))/2 + q$
    $pos2 = locmx(l) + ((q - 1 + nbs(l))^2 + q - 1 + nbs(l))/2 + p$
    $pSL(i, j) = d(pos1) * fctr * x(7, loc) + d(pos2) * fctr * x(k1, loc)$
    $pLS(i, j) = d(pos1) * fctr * x(k2, loc) + d(pos2) * fctr * x(5, loc)$
  end if
end if

Algorithm 7 Kernel 2 for MTSE

$i = threadIdx.x + (blockIdx.x - 1) * blockDim.x * 2$
$inttype = blockIdx.z - 1$
if $inttype == 0$ **then**
  if $i \leq total$ **then**
    $s\_tile(threadIdx.x) = pLL(i, blockIdx.y)$
  else
    $s\_tile(threadIdx.x) = 0.0$
  end if
  if $i + blockDim.x \leq total$ **then**
    $s\_tile(threadIdx.x + blockDim.x) = pLL(i + blockDim.x, blockIdx.y)$
  else
    $s\_tile(threadIdx.x + blockDim.x) = 0.0$
  end if
else
  Perform a similar instruction on the other pXY or qXY matrices depending on $inttype$
end if
for $j = \mathbf{log_2}(blockDim.x), j \geq 0, j = j - 1$ **do**
  call **syncthreads**
  if $threadIdx.x \leq 2^j$ **then**
    $s\_tile(threadIdx.x) = s\_tile(threadIdx.x) + s\_tile(threadIdx.x + 2^j)$
  end if
end for
if $threadIdx.x == 1$ **then**
  $l = lpq\_array(blockIdx.y, 1)$
  $p = lpq\_array(blockIdx.y, 2)$
  $q = lpq\_array(blockIdx.y, 3)$
  if $(inttype == 0)$ **then**
    $pos = locmx(l) + ((p-1)^2 + p - 1)/2 + q$
    $istat = \mathbf{atomicadd}(pmx(pos), s\_tile(threadIdx.x))$
  else
    Perform a similar instruction on the other pXY or qXY matrices depending on $inttype$
  end if
end if

Algorithm 8 STSE algorithm

$i = threadIdx.x + (blockIdx.x - 1) * blockDim.x$
$inttype = blockIdx.z - 1$
if $i \leq total$ **then**
  $l = lpq\_array(i, 1)$
  $p = lpq\_array(i, 2)$
  $q = lpq\_array(i, 3)$
  $fctr = 1.0$
  $loop = 0$
  for $j = 1, j \leq (total - 1)/blockDim.x + 1, j = j + 1$ **do**
    $mink = 1 + (j - 1) * blockDim.x$
    $maxk = \mathbf{min}(j * blockDim.x, total)$
    if $threadIdx.x + (j - 1) * blockDim.x \leq total$ **then**
      $m = lpq\_array(threadIdx.x + (j - 1) * blockDim.x, 1)$
      $r = lpq\_array(threadIdx.x + (j - 1) * blockDim.x, 2)$
      $s = lpq\_array(threadIdx.x + (j - 1) * blockDim.x, 3)$
      if $(r \neq s)$ **and** $(inttype == 0)$ **then**
        $fctr = 2.0$
      end if
      $s\_d(threadIdx.x, 1) = fctr * d(locmx(m) + ((r - 1)^2 + r - 1)/2 + s - 1)$
      $s\_d(threadIdx.x, 2) = fctr * d(locmx(m) + ((r - 1 + nbs(m))^2 + r + nbs(m) - 1)/2 + s + nbs(m))$
    end if
    $fctr = 1.0$
    call **syncthreads**
    for $k = mink, k \leq maxk, k = k + 1$ **do**
      if $(i \geq k)$ **and** $(inttype == 0)$ **then**
        $loc = ((i - 1)^2 + i - 1)/2 + k$
        $k1 = 3$
        $k2 = 2$
      else if $(i < k)$ **and** $(inttype == 0)$ **then**
        $loop = loop + k - 1$
        $loc = (i^2 + i)/2 + loop$
        $k1 = 2$
        $k2 = 3$
      end if
      $pm1 = pm1 + s\_d(1 + k - mink, 1) * x(1, loc) + s\_d(1 + k - mink, 2) * x(k1, loc)$
      $pm2 = pm2 + s\_d(1 + k - mink, 1) * x(k2, loc) + s\_d(1 + k - mink, 2) * x(k8, loc)$
    end for
    call **syncthreads**
  end for
  $pmx(locmx(l) + ((p - 1)^2 + p - 1)/2 + q) = pm1$
  $pmx(locmx(l) + ((p - 1 + nbs(l))^2 + p + nbs(l) - 1)/2 + q + nbs(l)) = pm2$
end if

selected because it contains many spinor orbitals and should be a good test of the ***formpq*** and ***eint2*** kernels on large atomic systems. Some of the smaller basis sets used do not contain a sensible number of basis functions considering the number of electrons that Radon contains. This is not an issue though, as at this stage we are only concerned with how long the calculation takes, and not with how accurate its end result is. Therefore, basis sets use the arbitrarily chosen WTBS parameters of $\alpha = 6.87 \times 10^{-2}$, $\beta = 1.83$, $\delta = 3.97$, and $\gamma = 0.78$. Additionally, due to the spherical symmetry of an atom exploited by cudaDFRATOM, the growth of a calculation differs depending on how the basis functions are distributed among the spinor symmetries. Therefore, results are reported in terms of the number of two-electron integrals instead of number of basis functions as is typically done.

2.5.1 Resource Usage

In the case of the work in this thesis, the resource bottleneck for my kernels was almost always the number of registers used per thread. 63 32-bit registers provide only 252 bytes to work with, which when using double precision 8-byte numbers is hardly anything at all. A summary of the block sizes and resource usage of all kernels is given in Table

Table 2.1: *Kernel resource usage*

Kernel	Block Size	Registers	Shared Memory (bytes)
eint1	(512, 1, 1)	63	45056
eint2	(512, 1, 1)	63	45088
vec2matrix	(512, 1, 1)	17	0
formd	(512, 1, 1)	33	28672
binary_search	(512, 1, 1)	30	60
convd	(512, 1, 1)	25	0
MTSE	(512, 1, 1)	46	32768
STSE	(512, 1, 1)	56	39388
forme	(512, 1, 1)	39	4152
formf	(512, 1, 1)	18	0
xtrpf	(512, 1, 1)	12	0
formg	(32, 16, 1)	55	12288
swapcol	(32, 16, 1)	10	0

Of these kernels, ***eint2*** and the ***formpq_alg*** kernels take up the bulk of the time needed in a typical calculation. This is in part due to the exponential growth in the number of two-electron integrals, but it is also caused by the amount of register spilling that each kernel will have. As stated in Section

2.5.2 Two-Electron Integral performance

Table

Table 2.2: ***eint2*** *kernel performance. Times are in ms. Times given are an average of five runs.*

Two-Electron Integrals[a]	CPU Time	***eint2***	***binary_search***	Total GPU time	Speedup[b]	Speedup[c]
74305	59	4.68	0.18	4.86	12.81	12.32
353220	320	18.03	0.71	18.74	17.72	17.04
1081185	980	52.50	2.21	54.71	18.66	17.90
2588950	2360	118.26	5.36	123.62	19.96	19.09
5299140	4910	237.75	11.07	248.82	20.63	19.71
9726255	8880	437.74	20.81	458.55	20.27	19.35
16476670	15140	730.56	35.96	766.52	20.73	19.75
26248635	24180	1160.82	58.00	1218.82	20.84	19.85

[a] For only the upper triangle of one of the eight **X** matrices.
[b] Speedup comparing just the time of ***eint2*** to the CPU time.
[c] Speedup comparing the time of ***eint2*** and ***binary_search*** to the CPU time.

As can be seen, the GPU calculations of the two-electron integrals outperform the CPU calculations with an average speedup factor of over 19. For calculations with fewer number of integrals to compute the speedup is not as dramatic. This is most likely due to the overhead involved in just starting a GPU kernel. Table

2.5.3 P and Q Matrix Formation Performance

As explained in section

As can be seen, the attempt at ***MTSE*** was a complete failure and it isn't even faster than the CPU calculations. ***STSE*** was much better, but only just. It achieves little more than a two-fold speedup at best.

There are several reasons this could be the case. The first due to the poor global memory access that reading x has. x is stored as a vector. This helps greatly with memory cost and integral calculation, but makes it difficult to retrieve it as if it were a matrix.There is the cost of calculating where the necessary integral is, and then the cost of the very uncoalesced reads. Calculating the integrals as a vector, and then copying them into a matrix afterwards could help with this, but the large amount of integrals needed for large calculations makes this impractical on current hardware. How much of an effect inefficient access of global

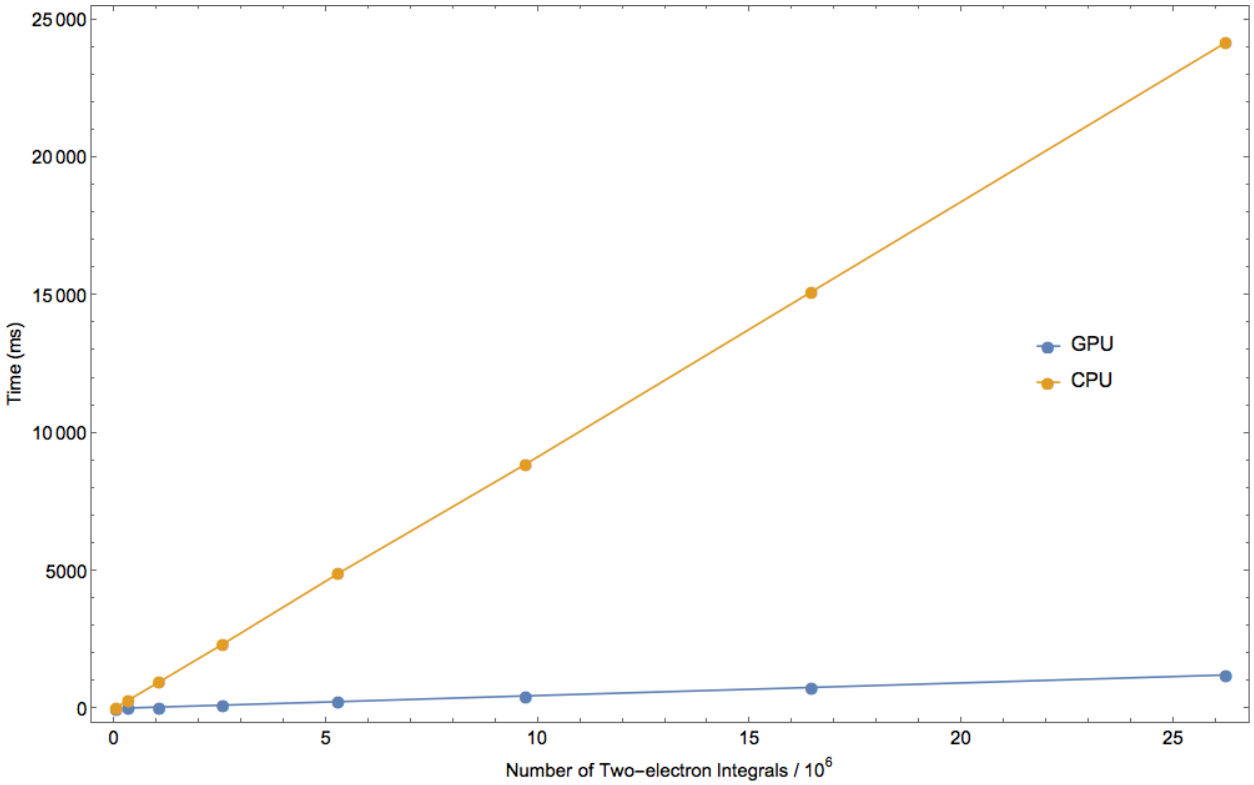


Figure 2.9: *Profiling of two-electron Integral calculations. The results of profiling the calculation of growing amounts of two-electron integrals. The blue line shows the time needed for GPU calculations and the yellow line shows time needed for CPU calculations. The time for the GPU calculations is the combined time of the* ***eint2*** *and* ***binary_search*** *kernels.*

Table 2.3: ***MTSE*** *kernel profiling results. Times are in ms. Times are given as the average time needed for a singel iteration from one calculation.*

Two-Electron Integrals	Time per Iteration CPU	Time per Iteration GPU	Speedup
74305	1.90	6.06	0.31
353220	5.78	14.25	0.40
1081185	18.42	27.81	0.66
2588950	39.47	53.95	0.73
5299140	81.05	96.13	0.84
9726255	152.50	173.64	0.87
16476670	266.53	291.79	0.91
26248635	426.25	459.38	0.92

memory has on a calculation does have a limit however which is most likely why the speedup sees an improvement as the calculations get larger. A second reason that the speedup is limited is caused by the occupancy that the kernels can achieve on the GPU. A block size

Table 2.4: ***STSE*** *kernel profiling results. Times are in ms. Times are given as the average time needed for a singel iteration from one calculation.*

Two-Electron Integrals	Time per Iteration CPU	Time per Iteration GPU	Speedup
74305	1.90	2.94	0.64
353220	5.78	7.56	0.76
1081185	18.42	15.34	1.20
2588950	39.47	26.32	1.49
5299140	81.05	39.45	2.05
9726255	152.50	88.78	1.71
16476670	266.53	135.64	1.96
26248635	426.25	193.99	2.19

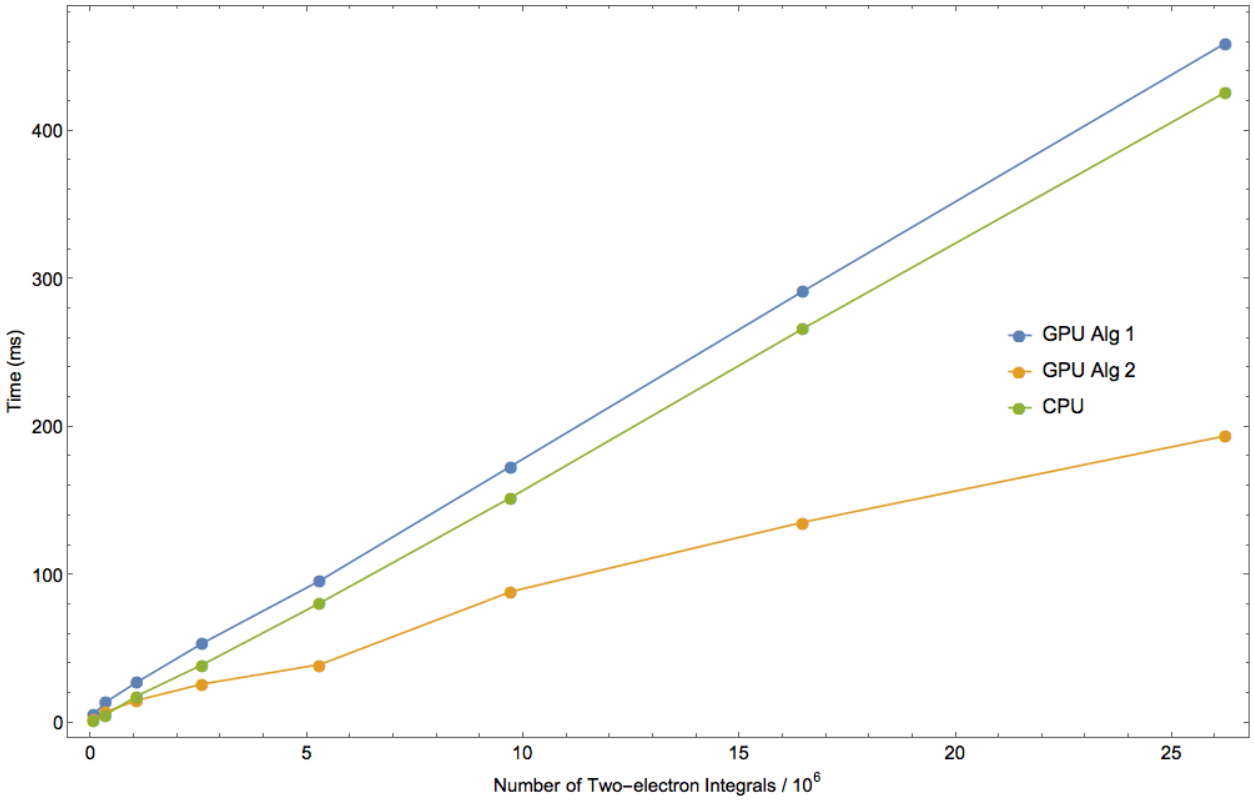


Figure 2.10: *Profiling of the* ***formpq*** *kernels. The results of profiling the formation of the* $\boldsymbol{P}$ *and* $\boldsymbol{Q}$ *matrices. The blue line shows the time needed for GPU calculations using the* ***MTSE*** *algorithm, the yellow line shows time needed for GPU calculations using* ***STSE****, and the green line shows the time needed for the CPU. Because the GPU calculations converge in fewer SCF iterations than the CPU calculations, only the average time for one iteration is shown.*

of 512 means that there is a maximum number of 3 blocks running per SM at a time. But

these kernels are both limited by the register usage to just running one block per SM at a time. This is also most likely why ***MTSE*** performs so poorly compared ***STSE***. ***MTSE*** was designed to spread out the amount of work to as many threads as possible. This results in a lot of blocks to be run. But because the amount of blocks that can run at a time is so limited there is no chance to see an improvement. But in the case of ***STSE***, there are a fewer number of blocks needing be be run, although each one needs to run for longer than those of ***MTSE***. Overall ***MTSE*** comes out on top.

At present, the limitations of these algorithms are caused by the hardware they run on, not the efficiency of the algorithms themselves. If we imagine removing these limitations, we could consider which one will be better. I propose that ***MTSE*** will eventually surpass ***STSE*** for very large systems for the following reasons: the time it takes for a single block of ***MTSE*** to run is mostly governed by how well it can read the x vector. The effect of spreading out the elements has on memory bandwidth has a limit, once the elements are spread out enough, spreading them out further has no impact. Therefore there is a maximum amount of time it takes for a single block to run. The time for a single block of ***STSE*** on the other hand is controlled by both the efficiency of reading global memory *and* the amount of two-electron integrals it must read though. So there is no limit to how long a block can take. Therefore, I predict that ***MTSE*** should be faster as the number of integrals becomes very large.

2.5.4 Total Speedup

There was some difficulty in determining the total speedup of a calculation. The reason why can be seen in Tables

Table 2.5: *Total speedup of cudaDFRATOM using* ***MTSE****. The results for a total calculation are shown. All times are in s. Times are given as the average time needed for five calculations.*

Two-Electron Integrals	SCF Iterations CPU	Total CPU Time	SCF Iteractions GPU	Total GPU Time	Speedup
74305	21	0.12	21	0.84	0.14
353220	19	0.49	19	1.19	0.41
1081185	19	1.44	19	1.75	0.82
2588950	19	3.38	19	2.58	1.30
5299140	19	6.78	19	3.80	1.78
9726255	24	13.29	19	5.77	2.30
16476670	26	23.23	19	8.60	2.69
26248635	24	35.63	19	12.5	2.82

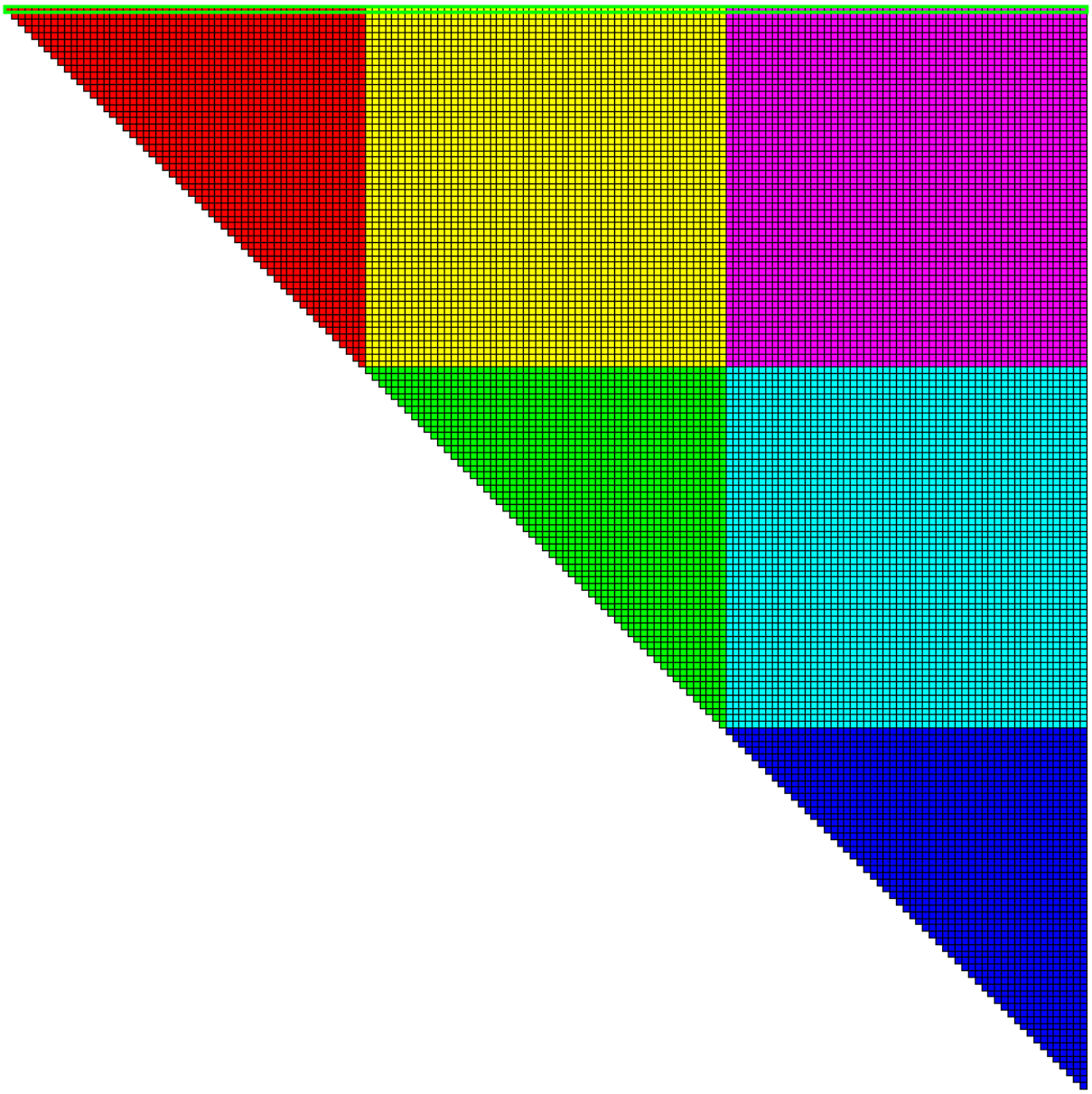


Figure 2.11: *Integrals needed for the first element of* $\boldsymbol{P}$*: The top triangle of the symmetric two-electron integral matrix in a matrix representation. The required integrals have been highlighted with a green border. The basis set used had* $nsym = 3$ *with* $nbs(i) = (10, 10, 10)$*. For clarity, the boxes have been coloured based on the spinor symmetries that they contain.*

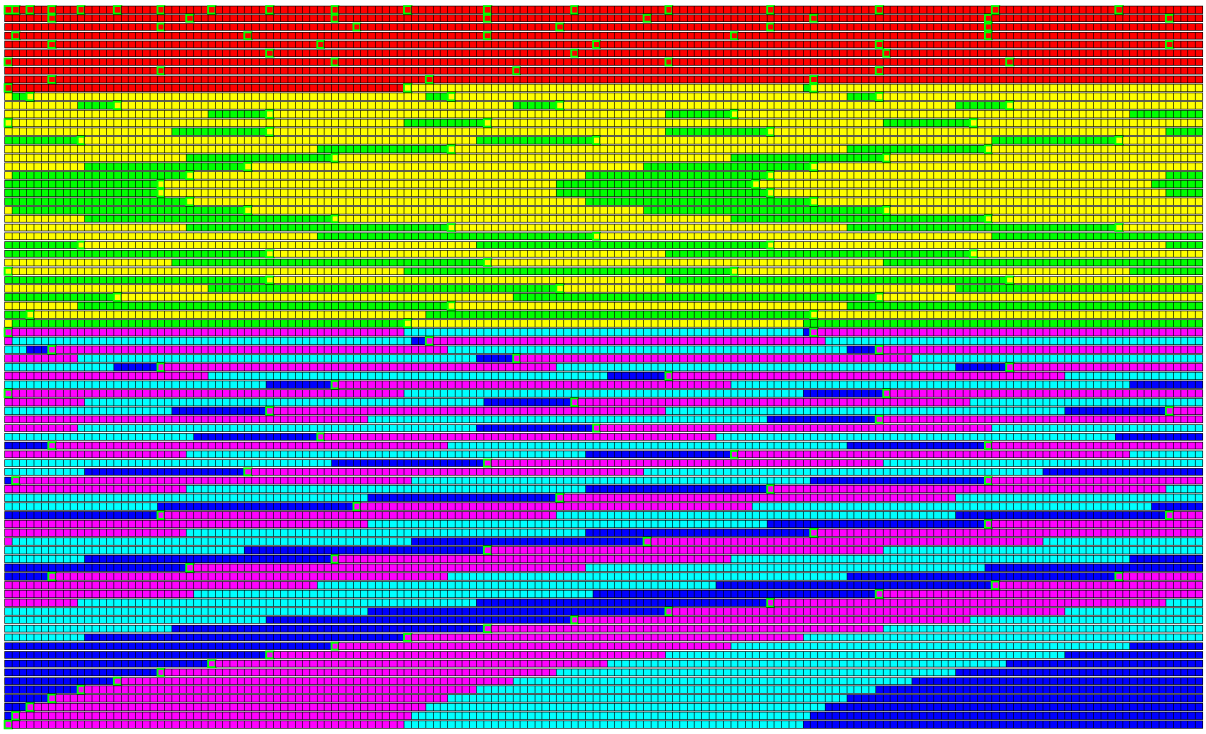


Figure 2.12: *Integrals needed for the first element of* $\boldsymbol{P}$*: The top triangle of the symmetric two-electron integral matrix in a vector representation. The required integrals have been highlighted with a green border. The spreading out of the elements means that reads to them can not be done effectively. The basis set used had* $nsym = 3$ *with* $nbs(i) = (10, 10, 10)$*. For clarity, the boxes have been coloured in the same way as Figure*

Table 2.6: *Total speedup of cudaDFRATOM using* ***STSE****. The results for a total calculation are shown. All times are in s.*

Two-Electron Integrals	SCF Iterations CPU	Total CPU Time	SCF Iteractions GPU	Total GPU Time	Speedup
74305	21	0.12	21	0.78	0.15
353220	19	0.49	19	1.07	0.46
1081185	19	1.44	19	1.51	0.95
2588950	19	3.38	19	2.08	1.62
5299140	19	6.78	19	2.72	2.49
9726255	24	13.29	19	4.14	3.20
16476670	26	23.23	19	5.57	4.16
26248635	24	35.63	19	7.47	4.76

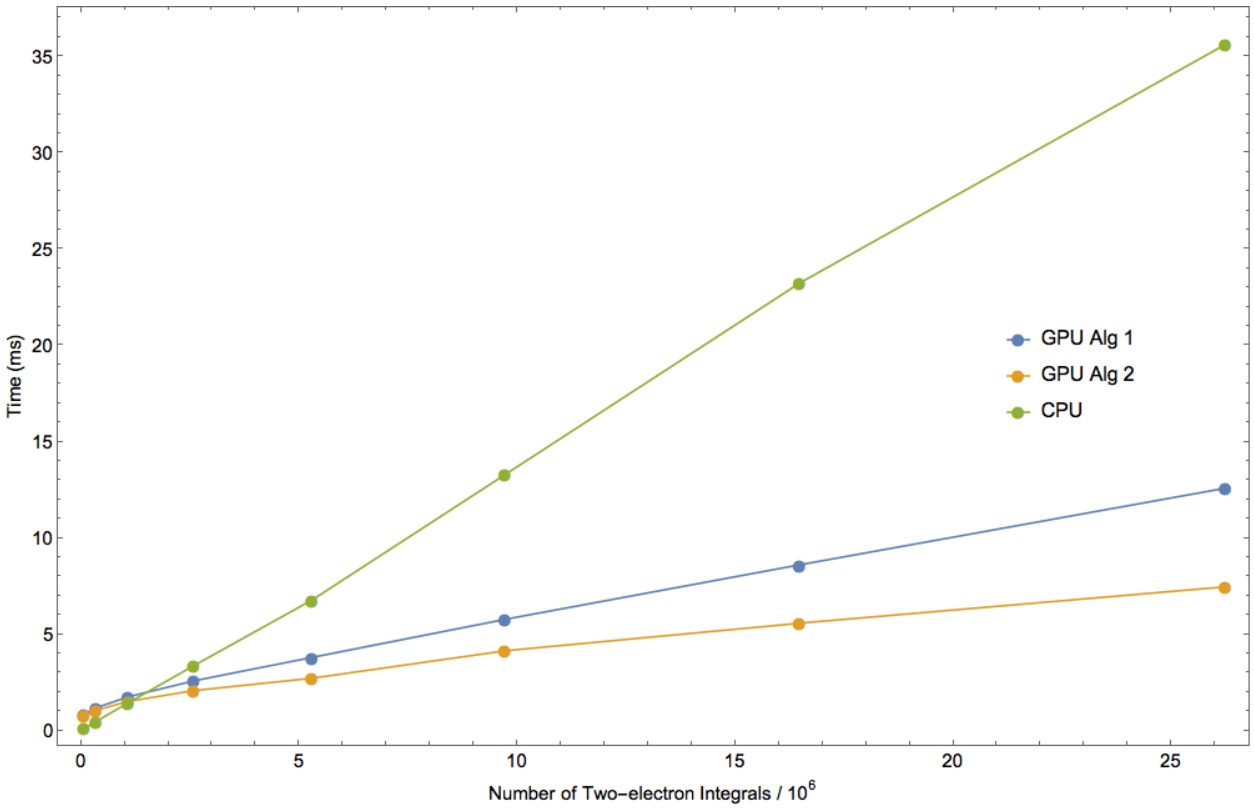


Figure 2.13: *Total time need to complete a calculation.*

As can be seen, the number of SCF iterations differs when comparing the GPU calculations to the CPU even though the convergence criteria was exactly the same. This is somewhat puzzling but I offer the following explanation. The differences do not occur in the two-electron integral calculations. We confirmed this by comparing the sum of the absolute

values of the integrals from both the GPU and non-GPU programs and found that they were the same. The problem instead occurs as a result of changing the SCF routines. First, when writing the SCF routines, it became apparent that rewriting the linear algebra into CUDA would be rather pointless when I could just use the cuSOLVER and cuBLAS libraries and achieve the same result. As such, the SCF is completed using entirely different algorithms and unfortunately, these GPU libraries do not produce exactly the same eigenvalues as the original program. Second, it is important to realize that a real number can only be *approximated* using double precision variables. This introduces numerical instability. For instance, assume that we have a computer that could only hold the first four digits of a number (leading zeros don't count). Then we take the number 1.000 and we want to add 0.0001000 to it 10000 times. The result of the first addition should be 1.0001, but because our computer can only hold four digits, the number is truncated to 1.000. The final result of this computation would not be 2.000 as expected but 1.000. During an SCF calculation, there are millions of numbers being multiplied together and added up, many of which may be close to, but not quite 0. This allows for lots of error to creep into a calculation just because of the limitations of the hardware.

The fact that two different algorithms are being used on the GPU and CPU, and that they might not be handling numerical stability in the same way is what is most likely causing this to occur. It should also be pointed out that the final energy was not exactly the same from GPU to CPU either. Typically, the last 4 of 16 significant digits would be different. Because the rest are the same however, we still have "chemical accuracy" (the general consensus of chemical accuracy is 0.001 Hartree, which cudaDFRATOM falls well within) and I argue that cudaDFRATOMs results are therefore valid.

2.6 Input Description

cudaDFRATOM can be executed on Unix-like systems in the following way

```
$ path_to_executable input_file > output_file
```

The input file must end in ".inp" or an error will be given. Redirection of stdout to an output file is optional, but is recommended to save the results of a calculation. The input file is read using the namelist functionality of Fortran. A description of what must appear on each line of the input file is given below. Sample input files are also given in Appendix

1. A title of no more than 200 characters.

2. $contrl

jobtype			The type of calculation to be performed.
	=	'energy'	Will do a single point energy calculation.
	=	'bsopt'	Will optimize the basis set. Can only be used if bastype equals 'wtbs'.
c			The speed of light. If not given, the default is set to 137.03599976 au.

3. $nuc

znuc			The charge of the nucleus.
nucmdl			The nuclear model to use.
	=	1	Point nucleus (default).
	=	2	Finite sphere (not yet supported).
	=	3	Gaussian.
rnuc			The radius of the finite sphere nucleus.
alpha			The exponent for the gaussian nucleus. Defaults are given in litdata.f90.

4. $bas

nsym			The number of symmetries to be used.
bastype			The type of basis set given.
	=	'wtbs'	Use a WTBS basis set.
	=	'rdin'	Read in the basis set from the input file.
ngroup			The number of different groups to use in the WTBS scheme (default 1).

The next line will depend on the value of bastype. If bastype equals 'rdin' then the following lines must be the number of functions for the S+ symmetry, followed by the exponents to use, each on a new line. The pattern repeats for each new symmetry. See the sample input files for further clarification. Otherwise, if bastype equals 'WTBS' the $wtbs group is read next.

5. $wtbs has to be given if bastype='wtbs'.

wtbspara	The α, β, δ, and γ WTBS parameters. If there is more than one group, the order would be α_1, β_1, δ_1, γ_1, α_2, β_2, δ_2, γ_2 and so on.
nbs	The number of functions used in each symmetry.
start	Where in the ζ pool each symmetry starts taking exponents from (default=1,1,1,1,1,1,1).
groups	What group each symmetry belongs to (default=1,1,1,1,1,1,1).

The next line depends on what the jobtype was set to. If jobtype equals 'energy' $newuoa is skipped and $econfig will be read next. If jobtype equals 'bsopt', then the $newuoa group will be needed.

6. $newuoa has to be given if jobtype='bsopt'. Refer to the newuoa documentation [32] for detailed information if needed.

rhobeg			The initial value of the trust region used by newuoa (default=0.1).
rhoend			The final value of the trust region used by newuoa. Must be smaller than rhobeg (default=1.0×10^{-4}).
iprint			The print level for newuoa.
	=	0	No printing from newuoa (default).
	=	1	Print only when newuoa has finished.
	=	2	Print only when the trust region has decreased by an order of magnitude.
	=	3	Print every iteration of newuoa.
maxfun			The maximum number of calls to calfun newuoa will make before terminating (default=500).

7. $econfig

nclose	The number of closed spinors for each symmetry.
nopen	The number of open spinors for each symmetry. There is a limit to one open orbital per symmetry.
freeel	The number of electrons available in the open spinors.
autogen	Automatically generates all possible combinations of spinor occupancies (default=.false.).
nconf	The number of configurations to be read in (needed if autogen is false).

If autogen is false, then the next nconf lines will be the spinor occupancies. They will be given as real numbers with one configuration per line.

8. $scf

maxitr			The maximum number of SCF iterations (default=50).
ixtrp			The method of extrapolation.
	=	0	No extrapolation (default).
	=	1	Extrapolate the Fock matrix.
dfctr			Damping factor for Fock maxtrix (default=0.3).
thdll			Convergence limit for the large-large components of the density matrix (default=1.0×10^{-5})
thdsl			Convergence limit for the small-large components of the density matrix (default=1.0×10^{-7})
thdss			Convergence limit for the small-small components of the density matrix (default=1.0×10^{-9})

Chapter 3

Basis Sets

3.1 Introduction

As stated in section

For instance, we might want to find the energy of the reaction $H^+ + OH^- \rightarrow H_2O$. The calculation of H_2O will have three basis functions centers while the OH^- calculation will only have two. The OH^- fragment inside the H_2O molecule will have additional basis functions from the H^+ fragment to work with while the OH^- does not. As a result, the OH^- fragment and molecule are not being described exactly the same, and therefore errors can result from this.

There is also the possibility of approximate linear dependencies in the basis set, which may show up during the SCF process. This happens when the overlap between any two different functions is close to unity (at least as far as a double precision number is concerned) and will mean that there will be eigenvalues that are equal to zero when diagonalizing the overlap matrix. We cannot find the inverse of such a matrix, so therefore the functions leading to these eigenvalues of zero must get transformed out of the matrix. This is kind of bandaid solution though, as the resulting Fock matrix after this transformation could produce errors in the energy differences on the order of chemical accuracy. It can also lead to a very aggravating process during a geometry optimization.

For example, say we have a molecular system in geometry state A. In this state, there are no approximate linear dependencies, and the geometry optimizer determines that the system would prefer to be in geometry state B. It updates the geometry, but in state B, some atoms might be too close together and now there are eigenfunctions that need to be rejected. The energy calculated for geometry state B is inaccurate, which causes the geometry optimizer to think that it should place the atoms back into state A. But now, everything is exactly the same as it was, and the geometry optimizer, with no memory at all of what just happened, thinks that the perfect geometry is state B again. There is no way out of this loop, and we

will not be able to find a stationary state, and all because of a poor choice in basis set. It is therefore important for a computational chemist to be aware of these issues so they can identify them when they occur, but even more so for someone who wants to make a new basis set, so that these issues can be avoided in the first place.

Designing a basis set that reduces the effects of BSSE is relatively straightforward, we can simply brute force the problem by adding more and more functions until they begin to cancel each other out. Designing one that avoids the issue of approximate linear dependencies however is more tricky. It is simply not possible to test every possible combination of atoms in every possible geometry to determine if a basis set has these problems. But there are some strategies we can use to avoid this problem.

One strategy that has shown to be particularly effective is using an exponent generating function to ensure that the exponents of the basis set are sufficiently different. There are many of these generating functions. One of these give what are called even-tempered basis sets (ETBS)[33]. The generating function for an ETBS is given below

$$\zeta_{l,k} = \alpha_l \beta_l^{k-1}, \quad \alpha_l, \beta_l > 0, \quad \beta_l \neq 1, \quad k = 1, 2, \ldots \tag{3.1}$$

where $\zeta_{l,k}$ is the k^{th} exponent of basis function for orbital symmetry l, α_l is the exponent for the first, most diffuse, basis function, and β_l is a growth parameter that determines the gap between $\zeta_{l,k}$ and $\zeta_{l,k+1}$. This greatly reduces the difficulty of the problem, because instead of needing to optimize all the exponents of our basis set, we only need to optimize the α and β parameters of each symmetry. We can further reduce the number of parameters to optimize by using the same α and β parameters *for each symmetry*. This is what I did for the work in this chapter, so I will drop the l subscript. However, there is a problem with ETBS: the growth in the value of the exponents is not always sufficient. So we get diminishing returns by increasing the maximum value of k, and we have to add many more functions to improve the accuracy of the basis set by even a small amount. This is improved in the well-tempered basis set (WTBS)[34] generating function, which is shown below

$$\zeta_k = \zeta_{k-1}\beta \left[1 + \gamma \left(\frac{k}{n}\right)^{\delta}\right], \quad k = 2, 3, \ldots, n, \quad \zeta_1 = \alpha \tag{3.2}$$

where n is the maximum number of basis functions for the set, and α and β have the same restrictions on them as they did before. The parameters δ and γ have the effect of increasing the gap between ζs caused by β at high k. This means that the growth of the exponents is increased as they get larger, which allows them to make a more meaningful contribution to the total wavefunction. Thus, we get a more accurate basis set with far fewer functions. The effect that altering γ and δ has on the exponents can be seen in Figure

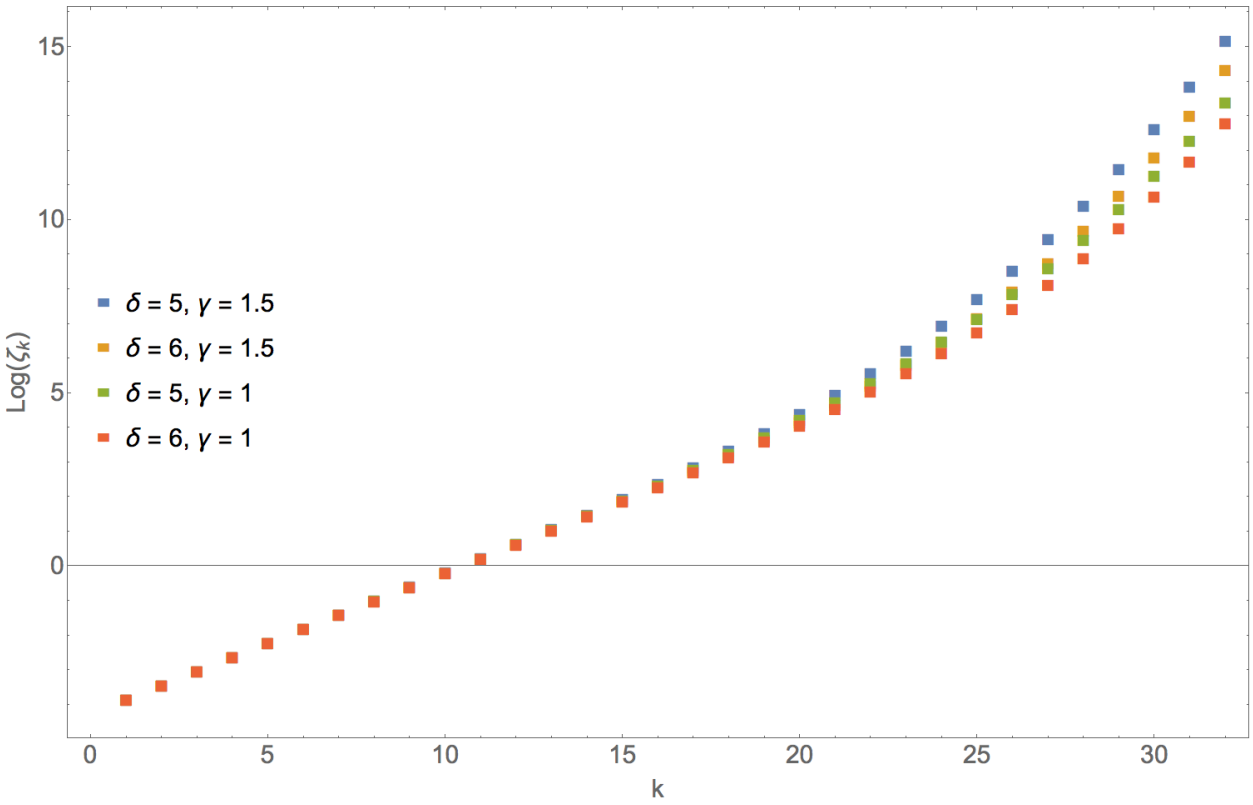


Figure 3.1: *Changes in ζ as the values of δ and γ are changed. The value of n was 36, α was 0.02, and β was 1.5*

It should be mentioned that each symmetry does not need to use the entire set of ζs that we optimize. Indeed, the most diffuse orbitals in the valence shells often don't use the most contracted functions at all, and conversely the most contracted orbitals in the core don't make much use of the most diffuse functions. Therefore, it is better to think of the set of ζs as pool, and that each symmetry is drawing a range of functions from that pool.

3.2 Methods

3.2.1 Basis set size optimization

We decided to use a somewhat novel method of generating our basis sets. We begin by choosing an arbitrarily large basis set size, such as $\mathrm{s}(1:40)\mathrm{p}(1:40)\mathrm{d}(1:40)\mathrm{f}(1:40)$ (here $i(\#:\#)$ refers to the starting and ending index of ζ's used for symmetry i). Next, we then find the optimal α, β, δ, and γ WTBS parameters for this basis set. This is done using NEWUOA[32] which finds the values α, β, δ, and γ that lead to the lowest possible energy for a given basis set size. Finally, we use the following steps to find the optimal basis set size.

Step 1. Begin by finding the fewest number of f functions necessary. This can be done by generating input files that range in size from $\mathrm{s}(1:40)\mathrm{p}(1:40)\mathrm{d}(1:40)\mathrm{f}(1:1)$ to $\mathrm{s}(1:40)\mathrm{p}(1:40)\mathrm{d}(1:40)\mathrm{f}(1:40)$.

Step 2. Optimize the basis sets and select the smallest basis set that is still below some minimum accuracy threshold. We chose a relative error to numerical calculations of no greater than 5.0×10^{-9} for non-relativistic sets and 5.0×10^{-8} for relativistic sets where relative error is defined as $\frac{|(\text{optimized energy})-(\text{numerical energy})|}{\text{numerical energy}}$. The size of this basis set is $\mathrm{s}(1:40)\mathrm{p}(1:40)\mathrm{d}(1:40)\mathrm{f}(1:x_f)$.

Step 3. Replace the WTBS parameters with those from the newly optimized set and generate a list of input files that range in size from $\mathrm{s}(1:40)\mathrm{p}(1:40)\mathrm{d}(1:x_f)\mathrm{f}(1:x_f)$ to $\mathrm{s}(1:40)\mathrm{p}(1:40)\mathrm{d}(1:40)\mathrm{f}(1:x_f)$.

Step 4. Optimize these new sets and select the smallest one that brings about an error that is still below the accuracy threshold. The size of this basis set is $\mathrm{s}(1:40)\mathrm{p}(1:40)\mathrm{d}(1:x_d)\mathrm{f}(1:x_f)$.

Step 5. Repeat steps 3 and 4 for the remaining symmetries. The size of the basis set at the end of this step will be of size $\mathrm{s}(1:x_s)\mathrm{p}(1:x_p)\mathrm{d}(1:x_d)\mathrm{f}(1:x_f)$.

Step 6. Replace the WTBS parameters with those from the newly optimized set and generate a list of input files that range in size from $\mathrm{s}(1:x_s)\mathrm{p}(1:x_p)\mathrm{d}(1:x_d)\mathrm{f}(1:x_f)$ to $\mathrm{s}(1:x_s)\mathrm{p}(1:x_p)\mathrm{d}(1:x_d)\mathrm{f}(x_f:x_f)$.

Step 7. Optimize and select from the basis sets. The new set will be of size

s$(1:x_s)$p$(1:x_p)$d$(1:x_d)$f$(y_f:x_f)$.

Step 8. Repeat steps 6 and 7 for the other symmetries except s. The final basis set will be of size s$(1:x_s)$p$(y_p:x_p)$d$(y_d:x_d)$f$(y_f:x_f)$.

This procedure is perhaps a bit clunky, so let us work through an example using Ne. Ne has both s and p type orbitals, and so will our basis set. We might initially guess that no more than 26 functions per symmetry will enough to get the accuracy we want, so we start with a basis set of size s(1:26)p(1:26). We then optimize the α, β, δ, and γ parameters for a basis set of this size. We make sure that the energy using a basis set of this size produces results that are accurate enough, and then we begin to reduce the size of the basis set for the p space. We carry over the WTBS parameters optimized in the last step, and generate input files corresponding to basis sets of size s(1:26)p(1:15) to s(1:26)p(1:26) (12 calculations in total) to determine the minimum number of tight functions we will need to accurately describe the p orbitals. After reoptimizing the WTBS parameters, we find that while s(1:26)p(1:15) is too small to be accurate enough, s(1:26)p(1:16) is still inside the threshold we want. So, we take the WTBS parameters from this calculation, and use them to generate new basis sets ranging in size from s(1:16)p(1:16) to s(1:26)p(1:16) (so we are trying to eliminate contracted functions from the s orbitals). Here we find that s(1:23)p(1:16) is the smallest basis set we can use. Now, we want to eliminate diffuse functions. Carrying over the WTBS parameter from the last acceptable basis set, we generate basis sets of size s(1:23)p(1:16) to s(1:23)p(5:16). We find that trying to remove any more functions makes the basis set unacceptable so we keep the s(1:23)p(1:16) basis set. We could try to remove diffuse functions from the s symmetry, but experience teaches that the s space needs all the functions to be accurate, so we don't bother.

This process has a major drawback in that it requires a lot of computer power to run efficiently. But this is not really a problem if access to large computer clusters is available. Additionally, considering that calculations for the chain 1-8 can be run in parallel for different atoms, this optimization process is trivially parallel. The advantages of this process are twofold: it finds a very small basis set that is still accurate and it is completely automatable. If there are no problems with individual calculations not converging, the output files never even need to be manually (and intellectually) examined! We generated non-relativistic basis sets for elements 2-86 using the rWTBS program[34–39] and relativistic basis sets for elements 55-86 using the cudaDFRATOM program which is outlined in detail in Chapter

3.2.2 Automating Optimization

Automating the optimization process was quite simple. I did this by writing two scripts: BS_sub_auto_rwtbs.sh and BS_find_best_rwtbs.sh. The code for BS_sub_auto.sh is given here

```
#!/bin/bash

sym=''
alljobs=false
bottom=false
path_to_exe='/some/path' # must be set!
wtime=01:00:00

if [[ -z $path_to_exe ]]; then
  echo "You must set the path to rwtbs.exe"
  exit
fi

while [ $# -gt 0 ]
do
  val=$1
  shift
  case $val in
    "-a")
       alljobs=true
     ;;
    "-b")
      bottom=true
    ;;
    "-S")
       sym='S'
       low=$1
       high=$2
       shift
       shift
     ;;
    "-P")
       sym='P'
       low=$1
       high=$2
       shift
       shift
     ;;
     "-D")
       sym='D'
       low=$1
       high=$2
       shift
       shift
     ;;
     "-F")
       sym='F'
```

```
       low=$1
       high=$2
       shift
       shift
     ;;
     "-t")
       wtime=$1
       shift
     ;;
     *)
       job=$val
     ;;
  esac
done


boilerplate(){
  cat << EOF
#!/bin/bash
#SBATCH --account=def-mariusz # change depending
#SBATCH --mem=2GB
#SBATCH --time=$1
#SBATCH --job-name=$2

echo ----------------------------------------
echo ----------------------------------------
echo began running on \`date\`
echo ----------------------------------------
echo ----------------------------------------
$3/rwtbs $2 >& $4
echo ----------------------------------------
echo ----------------------------------------
echo stopped running on \`date\`
echo ----------------------------------------
echo ----------------------------------------
EOF
}


if [ "$alljobs" == true ]; then
  job=`ls *inp`
elif [ -z "$job" ]; then
  echo no job given
  exit
fi

for file in $job; do
```

```
95  dir=$(echo $file | sed -e "s/-.*//")
96  if [[ -d "$dir" ]]; then
97    echo "$dir already here"
98  else
99    mkdir $dir
100 fi
101 cd $dir
102
103 # keep old out files and delete others
104 rename "out" "out-old" *.out
105 rm *inp
106 rm *GUS
107 rm *MCS
108
109 cp ../$file $file"-orig"
110 file_base=$(echo $file | sed -e 's/_.*//')
111
112 # read the number of basis functions
113 read -r -a old_bs <<< $(sed -n -e '/nbfsym/{s/.*nbfsym(1)=//; s/\$end//; p}'
      $file"-orig")
114 # get the most contracted basis function
115 IFS='+' read -r -a old_top <<< $(sed -n -e '/ +/p' $file"-orig")
116
117 # keep track of how many files are made
118 total=0
119 for i in $(seq $low $high); do
120   for j in $(seq 0 3); do
121     new_bs[j]=${old_bs[j]}
122     new_top[j]=${old_top[j]}
123   done
124
125   # make alterations based on symmetry
126   case $sym in
127     "F")
128       ((new_bs[3]-=$i))
129       # make sure that not too many functions are cut
130       if [[ "${new_bs[3]}" == "0" ]]; then
131         break
132       fi
133       ((new_top[3]+=$i))
134       ;;
135     "D")
136       ((new_bs[2]-=$i))
137       if [[ "${new_bs[2]}" == "0" ]]; then
138         break
139       fi
140       ((new_top[2]+=$i))
```

```
        ;;
      "P")
        ((new_bs[1]-=$i))
        if [[ "${new_bs[1]}" == "0" ]]; then
          break
        fi
        ((new_top[1]+=$i))
        ;;
      "S")
        ((new_bs[0]-=$i))
        if [[ "${new_bs[0]}" == "0" ]]; then
          break
        fi
        ((new_top[0]+=$i))
        ;;
    esac

    # make new calculation

    new_file=$file_base"_"${new_bs[0]}"s"${new_bs[1]}"p"${new_bs[2]}"d"${new_bs[3]}"f.inp"
    cp $file"-orig" $new_file
    sed -i "s/nalp=${old_bs[0]}/nalp=${new_bs[0]}/" $new_file
    sed -i "s/${old_bs[0]} ${old_bs[1]} ${old_bs[2]} ${old_bs[3]}/${new_bs[0]}
    ${new_bs[1]} ${new_bs[2]} ${new_bs[3]}/" $new_file
    if [ "$bottom" == false ]; then
      sed -i -e "s/${old_top[0]}+/${new_top[0]} +/" -e
    "s/${old_top[1]}+/${new_top[1]} +/" -e "s/${old_top[2]}+/${new_top[2]} +/" -e
    "s/${old_top[3]} +/${new_top[3]} +/" $new_file
    fi

    # write submission script
    boilerplate $wtime $new_file $path_to_exe ${new_file%???}out >
    ${new_file%???}.sh
    #sbatch ${new_file%???}.sh # uncomment to automatically submit job
    ((total++))
  done
  echo "$total files made"
  cd ../
done
```

Listing 3.1: *BS_sub_auto_rwtbs.sh*

The first few lines handle the arguments given to the script. The arguments are flags which tell the script what to do. The flags can be given in any order, so long as each flag is followed by the appropriate options. The default flag is a file ending in ".inp" for the calculation that you would like to run. Optionally, this flag can be omitted, which will tell the script to run over all "inp" files in the current directory. I will refer to the input file to

be used as a seed. The flags "-S", "-P", "-D", and "-F" tell the script which set of orbitals we would like to remove functions from ("-S" means s orbitals, "-P" means p orbitals, and so on). These flags *must* be followed by by two integers, with the first being smaller than the second. The first number is the minimum number for functions to cut, and the second is the maximum number to cut. By default, cutting begins with the most contracted function. For example, using "-S 0 3" would take the seed file with a basis set of size s(1:20) and produce otherwise identical files with basis sets of size s(1:20), s(1:19), s(1:18), and s(1:17). If the number are negative, this can be used to add basis functions ("-S -1 0" on the same seed would produce basis sets of size s(1:21) and s(1:20)). Using the "-B" (for bottom) flag changes the default behavior of cutting contracted functions, to cutting diffuse functions. So for example, using the flags "-S 0 3 -B" on the seed would produce s(1:20), s(2:20), s(3:20), and s(4:20).

Once the flags have been parsed, the script makes a directory with the same name as the title of the seed, moves inside this directory, and generates the needed input files. It also creates a job submission script using the boilerplate function for each of new input files and submits them. Note that this part of the script will need to be changed depending on the cluster it is being used on. If more than one seed is used, then the script will do the same thing for each seed. After the jobs are completed, the user runs BS_find_best_rwtbs.sh in the directory that contains all of the newly created directories. The code for BS_find_best_rwtbs.sh is given below

```
#!/bin/bash

tol=$1

if [ -z $tol ]; then
  tol='5*10^-9'
fi

echo The tolerance in relative error is $tol

mkdir best
for dir in `ls -d */`; do
  if [ "$dir" != 'old/' ]; then
    if [ "$dir" != 'best/' ]; then
      if [ "$dir" != 'tests/' ]; then
      cd $dir
      for file in *.out; do
        error=`grep -A 1 '[E(WT)-E(rf)]/E(rf)' $file | tail -1 | awk '{print
    $4}'`
        comperror=`echo $error | sed -e 's/D/\*10\^/'`
        testthress=$(bc -l <<< "scale=20; ($tol - $comperror)*10^10 >= 1")
        if [ $testthress -ge 1 ]; then
```

```
            cp `echo $file | sed -e 's/out/inp/'` ../best
            cp $file ../best
            echo Found best for $file
            break
          fi
        done
        fi
      fi
    fi
    cd ..
done
```

Listing 3.2: *BS_find_best_rwtbs.sh*

This script takes in one argument, the relative error we are looking for in a calculation. It enters each of the subdirectories made by BS_sub_auto.sh and scans the output files for the relative error compared to numerical calculations. It finds the file with the smallest basis set that is still under the error threshold, and copies the input and output files for that calculation into a new directory called "best". The user can then repeat this process for as many orbitals as they wish. There are also similar scripts for cudaDFRATOM which are given in Appendix

3.3 Discussion

3.3.1 Optimized Non-Relativistic Basis Sets

The optimized non-relativistic WTBS parameters and basis set sizes for elements 2-86 are shown in Table

Table 3.1: *Basis sets optimized using rWTBS. We did not have literature data for some elements. These elements are marked with a *. The size of the basis set for these elements was determined by using the size of the nearest elements.*

Element	Term Symbol	α	β	δ	γ	s	p	d	f
02 He	^1S	8.140×10^{-2}	1.953	4.504	1.515	(1:18)			
03 Li	^2S	1.596×10^{-2}	1.933	5.701	1.573	(1:22)			
04 Be	^1S	2.647×10^{-2}	1.938	5.841	1.594	(1:22)			
05 B	^2P	3.238×10^{-2}	1.948	5.573	1.523	(1:22)	(1:15)		
06 C	^3P	4.613×10^{-2}	1.941	4.717	1.317	(1:23)	(1:15)		
07 N	^4S	5.976×10^{-2}	1.923	5.183	1.442	(1:23)	(1:16)		
08 O	^3P	6.967×10^{-2}	1.936	5.170	1.426	(1:23)	(1:16)		
09 F	^2P	8.321×10^{-2}	1.942	5.084	1.408	(1:23)	(1:16)		
10 Ne	^1S	9.943×10^{-2}	1.945	4.988	1.392	(1:23)	(1:16)		

Table 3.1: *(continued)*

Element	Term Symbol	α	β	δ	γ	s	p	d	f
11 Na	^2S	1.696×10^{-2}	1.950	6.056	1.469	(1:26)	(3:19)		
12 Mg	^1S	2.375×10^{-2}	1.932	5.686	1.430	(1:26)	(3:19)		
13 Al	^2P	2.239×10^{-2}	1.898	5.555	1.413	(1:27)	(1:20)		
14 Si	^3P	3.352×10^{-2}	1.921	5.419	1.410	(1:26)	(1:19)		
15 P	^4S	4.410×10^{-2}	1.907	5.196	1.390	(1:26)	(1:19)		
16 S	^3P	5.004×10^{-2}	1.896	4.962	1.362	(1:26)	(1:19)		
17 Cl	^2P	5.831×10^{-2}	1.886	4.784	1.344	(1:26)	(1:19)		
18 Ar	^1S	6.834×10^{-2}	1.878	4.654	1.331	(1:26)	(1:19)		
19 K	^2S	1.392×10^{-2}	1.889	6.354	1.523	(1:28)	(3:22)		
20 Ca	^1S	1.837×10^{-2}	1.874	6.109	1.504	(1:28)	(3:22)		
21 Sc	^2D	2.040×10^{-2}	1.878	6.160	1.505	(1:28)	(3:22)	(2:16)	
22 Ti	^3F	2.218×10^{-2}	1.886	6.247	1.508	(1:28)	(3:22)	(2:16)	
23 V	^4F	2.361×10^{-2}	1.887	6.573	1.507	(1:29)	(3:23)	(2:16)	
24 Cr	^7S	2.345×10^{-2}	1.865	5.348	1.407	(1:29)	(3:22)	(2:17)	
25 Mn	^6S	2.572×10^{-2}	1.865	5.336	1.407	(1:29)	(3:22)	(2:17)	
26 Fe	^5D	2.621×10^{-2}	1.869	5.301	1.395	(1:29)	(3:22)	(3:17)	
27 Co	^4F	2.643×10^{-2}	1.871	5.905	1.413	(1:29)	(4:23)	(3:17)	
28 Ni	^3F	2.882×10^{-2}	1.875	5.935	1.413	(1:29)	(3:23)	(3:17)	
29 Cu	^2S	2.283×10^{-2}	1.857	5.485	1.413	(1:30)	(4:23)	(3:18)	
30 Zn	^1S	3.297×10^{-2}	1.881	5.817	1.339	(1:30)	(3:24)	(2:17)	
31 Ga	^2P	2.742×10^{-2}	1.863	5.703	1.462	(1:30)	(1:23)	(3:18)	
32 Ge	^3P	3.143×10^{-2}	1.848	5.290	1.386	(1:30)	(1:23)	(4:18)	
33 As	^4S	4.728×10^{-2}	1.869	5.325	1.340	(1:30)	(1:23)	(3:17)	
34 Se	^3P	5.087×10^{-2}	1.847	4.949	1.533	(1:30)	(1:22)	(3:18)	
35 Br	^2P	5.927×10^{-2}	1.861	5.192	1.333	(1:30)	(1:23)	(3:17)	
36 Kr	^1S	6.804×10^{-2}	1.859	5.510	1.370	(1:29)	(1:23)	(3:17)	
37 Rb	^2S	1.421×10^{-2}	1.856	7.181	1.626	(1:30)	(3:25)	(6:21)	
38 Sr	^1S	1.808×10^{-2}	1.846	6.674	1.553	(1:30)	(3:25)	(6:20)	
39 Y	^2D	1.997×10^{-2}	1.841	6.569	1.543	(1:30)	(3:25)	(2:20)	
40 Zr	^5F	2.184×10^{-2}	1.837	6.485	1.535	(1:30)	(3:25)	(2:20)	
41 Nb	^6D	2.340×10^{-2}	1.835	6.434	1.530	(1:30)	(3:25)	(2:20)	
42 Mo	^7S	2.537×10^{-2}	1.832	6.372	1.524	(1:30)	(3:25)	(2:20)	
43 Tc	^6S	2.597×10^{-2}	1.836	6.453	1.534	(1:30)	(3:25)	(2:20)	
44 Ru	^5F	2.682×10^{-2}	1.833	6.788	1.606	(1:30)	(3:25)	(2:21)	
45 Rh	^4F	2.751×10^{-2}	1.835	6.883	1.620	(1:30)	(3:25)	(2:21)	
46 Pd	^1S	5.944×10^{-2}	1.827	5.980	1.504	(1:29)	(2:24)	(1:19)	
47 Ag	^2S	2.438×10^{-2}	1.800	5.521	1.423	(1:31)	(4:25)	(3:21)	
48 Cd	^1S	2.911×10^{-2}	1.786	5.334	1.408	(1:31)	(4:25)	(3:21)	
49 In	^2P	2.714×10^{-2}	1.799	5.540	1.431	(1:31)	(1:25)	(3:21)	
50 Sn	^3P	2.884×10^{-2}	1.794	5.422	1.415	(1:31)	(1:25)	(4:21)	

Table 3.1: *(continued)*

Element	Term Symbol	α	β	δ	γ	s	p	d	f
51 Sb	^4S	4.481×10^{-2}	1.815	6.567	1.605	(1:30)	(1:25)	(3:21)	
52 Te	^3P	4.846×10^{-2}	1.817	6.247	1.528	(1:30)	(1:26)	(3:20)	
53 I	^2P	5.369×10^{-2}	1.810	6.016	1.505	(1:30)	(1:25)	(3:20)	
54 Xe	^1S	5.981×10^{-2}	1.802	5.862	1.490	(1:30)	(1:25)	(3:20)	
55 Cs	^2S	1.177×10^{-2}	1.792	6.485	1.510	(1:33)	(4:28)	(5:23)	
56 Ba	^1S	1.560×10^{-2}	1.770	6.152	1.518	(1:32)	(3:28)	(6:23)	
57 La	^2D	1.716×10^{-2}	1.764	6.067	1.513	(1:32)	(3:28)	(2:23)	(5:14)
58 Ce*	^3H	1.652×10^{-2}	1.774	6.254	1.529	(1:32)	(3:28)	(2:23)	(4:19)
59 Pr	^4I	1.696×10^{-2}	1.776	6.297	1.533	(1:32)	(3:28)	(6:23)	(4:19)
60 Nd	^5I	1.737×10^{-2}	1.778	6.563	1.579	(1:32)	(3:28)	(6:24)	(4:19)
61 Pm	^6H	1.784×10^{-2}	1.780	6.615	1.585	(1:32)	(3:28)	(6:24)	(4:19)
62 Sm	^7F	1.857×10^{-2}	1.778	5.842	1.464	(1:33)	(3:27)	(6:23)	(4:19)
63 Eu	^8S	1.876×10^{-2}	1.784	6.718	1.596	(1:32)	(3:28)	(6:24)	(4:19)
64 Gd*	^7F	1.926×10^{-2}	1.782	6.844	1.599	(1:33)	(3:28)	(6:24)	(4:19)
65 Tb*	^6H	1.971×10^{-2}	1.784	6.898	1.604	(1:33)	(3:28)	(6:24)	(4:19)
66 Dy	^5I	2.020×10^{-2}	1.788	6.543	1.540	(1:33)	(3:28)	(6:23)	(4:19)
67 Ho*	^4I	2.064×10^{-2}	1.785	7.090	1.640	(1:33)	(3:28)	(6:23)	(4:20)
68 Er	^3H	2.106×10^{-2}	1.792	7.029	1.638	(1:32)	(3:28)	(6:24)	(4:20)
69 Tm	^2F	2.152×10^{-2}	1.794	7.075	1.643	(1:32)	(3:28)	(6:24)	(4:20)
70 Yb*	^1S	2.200×10^{-2}	1.795	7.141	1.652	(1:32)	(3:28)	(2:24)	(4:20)
71 Lu	^2D	2.373×10^{-2}	1.790	7.018	1.640	(1:32)	(3:28)	(2:24)	(4:20)
72 Hf	^3F	2.511×10^{-2}	1.788	6.963	1.636	(1:32)	(3:28)	(2:24)	(5:20)
73 Ta	^4F	2.684×10^{-2}	1.784	6.907	1.633	(1:32)	(2:28)	(2:24)	(5:20)
74 W	^5D	2.814×10^{-2}	1.783	6.889	1.633	(1:32)	(3:28)	(2:24)	(5:20)
75 Re	^6S	2.931×10^{-2}	1.782	6.886	1.634	(1:32)	(3:28)	(2:24)	(5:20)
76 Os	^5D	3.075×10^{-2}	1.781	6.896	1.637	(1:32)	(2:29)	(2:24)	(4:20)
77 Ir	^4F	3.195×10^{-2}	1.780	6.867	1.635	(1:32)	(3:28)	(2:24)	(5:20)
78 Pt	^3D	3.173×10^{-2}	1.785	7.020	1.654	(1:32)	(3:28)	(2:24)	(5:20)
79 Au	^2S	3.190×10^{-2}	1.791	6.702	1.569	(1:33)	(4:28)	(2:23)	(5:19)
80 Hg	^1S	3.546×10^{-2}	1.781	6.691	1.604	(1:32)	(3:28)	(2:23)	(5:20)
81 Tl	^2P	3.241×10^{-2}	1.794	6.826	1.561	(1:34)	(1:29)	(3:23)	(6:20)
82 Pb	^3P	3.867×10^{-2}	1.778	6.948	1.656	(1:32)	(1:28)	(3:25)	(6:21)
83 Bi	^4S	4.514×10^{-2}	1.766	6.158	1.545	(1:32)	(1:27)	(2:24)	(6:19)
84 Po	^3P	4.783×10^{-2}	1.763	5.977	1.516	(1:32)	(1:27)	(3:23)	(6:19)
85 At	^2P	5.210×10^{-2}	1.757	5.846	1.502	(1:32)	(1:27)	(3:23)	(6:19)
86 Rn	^1S	5.716×10^{-2}	1.749	5.695	1.486	(1:32)	(1:27)	(3:23)	(6:19)

Table 3.2: *Basis sets optimized using cudaDFRATOM*

Element	Electron Configuration	α	β	δ	γ	s	p	d	f
55 Cs	[Xe] $6s^1$	1.824×10^{-2}	1.921	6.085	1.062	(1:29)	(3:28)	(5:20)	
56 Ba	[Xe] $6s^2$	2.033×10^{-2}	1.904	5.473	1.161	(1:30)	(3:28)	(6:20)	
57 La	[Ba] $4f^1$	1.540×10^{-2}	1.871	5.166	2.036	(1:33)	(4:28)	(5:22)	(4:16)
58 Ce	[Ba] $4f^2$	1.838×10^{-2}	1.857	4.969	1.450	(1:31)	(3:28)	(5:22)	(4:16)
59 Pr	[Ba] $4f^3$	1.945×10^{-2}	1.857	4.947	1.438	(1:31)	(3:28)	(5:22)	(4:16)
60 Nd	[Ba] $4f^4$	2.043×10^{-2}	1.859	4.928	1.422	(1:31)	(3:28)	(5:22)	(4:16)
61 Pm	[Ba] $4f^5$	2.142×10^{-2}	1.860	4.906	1.405	(1:31)	(2:28)	(4:22)	(4:16)
62 Sm	[Ba] $4f^6$	2.414×10^{-2}	1.856	4.854	1.379	(1:31)	(3:28)	(5:22)	(3:16)
63 Eu	[Ba] $4f^7$	1.993×10^{-2}	1.877	5.099	1.020	(1:31)	(4:29)	(5:22)	(4:16)
64 Gd	[Ba] $4f^8$	2.063×10^{-2}	1.880	5.064	0.996	(1:31)	(4:29)	(5:22)	(4:16)
65 Td	[Ba] $4f^9$	2.396×10^{-2}	1.869	4.840	0.967	(1:31)	(3:29)	(5:22)	(4:16)
66 Dy	[Ba] $4f^{10}$	2.177×10^{-2}	1.888	5.353	0.839	(1:30)	(4:29)	(5:22)	(4:16)
67 Ho	[Ba] $4f^{11}$	2.517×10^{-2}	1.878	5.126	0.816	(1:30)	(3:29)	(5:22)	(4:16)
68 Er	[Ba] $4f^{12}$	2.811×10^{-2}	1.875	5.145	1.045	(1:30)	(3:29)	(5:22)	(3:16)
69 Tm	[Ba] $4f^{13}$	2.628×10^{-2}	1.887	5.480	0.886	(1:31)	(3:30)	(5:22)	(4:16)
70 Yb	[Ba] $4f^{14}$	2.918×10^{-2}	1.883	5.490	0.873	(1:31)	(3:30)	(5:22)	(3:16)
71 Lu	[Yb] $5d^1$	3.424×10^{-2}	1.873	5.124	1.353	(1:32)	(2:29)	(1:23)	(3:16)
72 Hf	[Yb] $5d^2$	3.982×10^{-2}	1.900	6.117	1.473	(1:32)	(2:29)	(1:22)	(4:16)
73 Ta	[Yb] $5d^3$	4.271×10^{-2}	1.899	6.126	1.450	(1:32)	(3:29)	(1:22)	(4:16)
74 W	[Yb] $5d^4$	4.564×10^{-2}	1.901	5.936	1.351	(1:32)	(3:29)	(1:21)	(4:16)
75 Re	[Yb] $5d^5$	4.827×10^{-2}	1.900	5.898	1.323	(1:32)	(3:29)	(1:21)	(4:16)
76 Os	[Yb] $5d^6$	5.081×10^{-2}	1.899	5.873	1.296	(1:32)	(3:29)	(1:21)	(4:16)
77 Ir	[Yb] $5d^7$	5.333×10^{-2}	1.898	5.846	1.274	(1:32)	(3:29)	(1:21)	(4:16)
78 Pt	[Yb] $5d^8$	5.391×10^{-2}	1.892	6.058	1.365	(1:32)	(3:29)	(1:23)	(5:16)
79 Au	[Yb] $5d^9$	5.684×10^{-2}	1.893	6.111	1.354	(1:32)	(3:29)	(1:23)	(5:16)
80 Hg	[Yb] $5d^{10}$	5.965×10^{-2}	1.893	6.156	1.342	(1:32)	(3:29)	(1:23)	(5:16)
81 Tl	[Hg] $6p^1$	4.071×10^{-2}	1.875	5.161	0.944	(1:30)	(1:29)	(1:22)	(5:17)
82 Pb	[Hg] $6p^2$	4.364×10^{-2}	1.869	5.015	0.925	(1:30)	(1:29)	(3:22)	(6:17)
83 Bi	[Hg] $6p^3$	5.109×10^{-2}	1.854	3.953	0.792	(1:33)	(1:30)	(2:21)	(5:17)
84 Po	[Hg] $6p^4$	5.439×10^{-2}	1.849	4.666	0.890	(1:30)	(1:29)	(3:22)	(6:17)
85 At	[Hg] $6p^5$	6.177×10^{-2}	1.892	10.223	1.500	(1:30)	(1:31)	(3:22)	(6:16)
86 Rn	[Hg] $6p^6$	6.671×10^{-2}	1.831	3.906	0.867	(1:31)	(1:29)	(3:21)	(6:17)

Table 3.3: *Energies produced from basis sets in Tables*

Element	Calculated Energy	Literature Energy	Absolute Error	Relative Error
02 He	-2.861	-2.861	$> 1 \times 10^{-6}$	3.6×10^{-9}
03 Li	-7.432	-7.432	$> 1 \times 10^{-6}$	2.9×10^{-9}
04 Be	-14.573	-14.573	$> 1 \times 10^{-6}$	3.2×10^{-9}
05 B	-24.529	-24.529	$> 1 \times 10^{-6}$	4.8×10^{-9}

Table 3.3: *(continued)*

Element	Calculated Energy	Literature Energy	Absolute Error	Relative Error
06 C	-37.688	-37.688	$> 1 \times 10^{-6}$	4.1×10^{-9}
07 N	-54.400	-54.400	$> 1 \times 10^{-6}$	2.8×10^{-9}
08 O	-74.809	-74.809	$> 1 \times 10^{-6}$	3.4×10^{-9}
09 F	-99.409	-99.409	$> 1 \times 10^{-6}$	4.0×10^{-9}
10 Ne	-128.547	-128.547	1×10^{-6}	4.4×10^{-9}
11 Na	-161.858	-161.858	1×10^{-6}	4.4×10^{-9}
12 Mg	-199.614	-199.614	1×10^{-6}	3.9×10^{-9}
13 Al	-241.876	-241.876	1×10^{-6}	2.8×10^{-9}
14 Si	-288.854	-288.854	1×10^{-6}	4.6×10^{-9}
15 P	-340.718	-340.718	1×10^{-6}	4.3×10^{-9}
16 S	-397.504	-397.504	2×10^{-6}	4.5×10^{-9}
17 Cl	-459.482	-459.482	2×10^{-6}	4.6×10^{-9}
18 Ar	-526.817	-526.817	2×10^{-6}	4.5×10^{-9}
19 K	-599.164	-599.164	3×10^{-6}	4.6×10^{-9}
20 Ca	-676.758	-676.758	3×10^{-6}	3.8×10^{-9}
21 Sc	-759.735	-759.735	3×10^{-6}	4.3×10^{-9}
22 Ti	-848.405	-848.405	4×10^{-6}	4.9×10^{-9}
23 V	-942.884	-942.884	4×10^{-6}	4.4×10^{-9}
24 Cr	-1043.356	-1043.356	4×10^{-6}	4.1×10^{-9}
25 Mn	-1149.866	-1149.866	6×10^{-6}	4.8×10^{-9}
26 Fe	-1262.443	-1262.443	6×10^{-6}	4.5×10^{-9}
27 Co	-1381.414	-1381.414	6×10^{-6}	4.6×10^{-9}
28 Ni	-1506.870	-1506.870	7×10^{-6}	4.8×10^{-9}
29 Cu	-1638.963	-1638.963	6×10^{-6}	3.4×10^{-9}
30 Zn	-1777.848	-1777.848	9×10^{-6}	4.8×10^{-9}
31 Ga	-1923.261	-1923.261	9×10^{-6}	4.5×10^{-9}
32 Ge	-2075.359	-2075.359	7×10^{-6}	3.3×10^{-9}
33 As	-2234.238	-2234.238	1×10^{-5}	4.8×10^{-9}
34 Se	-2399.867	-2399.867	1×10^{-5}	4.4×10^{-9}
35 Br	-2572.441	-2572.441	1×10^{-5}	4.8×10^{-9}
36 Kr	-2752.054	-2752.054	1×10^{-5}	4.7×10^{-9}
37 Rb	-2938.357	-2938.357	1×10^{-5}	4.7×10^{-9}
38 Sr	-3131.545	-3131.545	1×10^{-5}	4.4×10^{-9}
39 Y	-3331.684	-3331.684	1×10^{-5}	4.4×10^{-9}
40 Zr	-3538.995	-3538.995	1×10^{-5}	4.4×10^{-9}
41 Nb	-3753.597	-3753.597	1×10^{-5}	4.3×10^{-9}
42 Mo	-3975.549	-3975.549	1×10^{-5}	4.5×10^{-9}
43 Tc	-4204.788	-4204.788	2×10^{-5}	4.7×10^{-9}
44 Ru	-4441.539	-4441.539	2×10^{-5}	4.5×10^{-9}
45 Rh	-4685.881	-4685.881	2×10^{-5}	4.8×10^{-9}
46 Pd	-4937.921	-4937.921	2×10^{-5}	4.8×10^{-9}

Table 3.3: *(continued)*

Element	Calculated Energy	Literature Energy	Absolute Error	Relative Error
47 Ag	-5197.698	-5197.698	2×10^{-5}	4.3×10^{-9}
48 Cd	-5465.133	-5465.133	2×10^{-5}	4.2×10^{-9}
49 In	-5740.169	-5740.169	2×10^{-5}	4.6×10^{-9}
50 Sn	-6022.931	-6022.931	2×10^{-5}	3.9×10^{-9}
51 Sb	-6313.485	-6313.485	2×10^{-5}	4.4×10^{-9}
52 Te	-6611.784	-6611.784	3×10^{-5}	4.8×10^{-9}
53 I	-6917.980	-6917.980	3×10^{-5}	4.6×10^{-9}
54 Xe	-7232.138	-7232.138	3×10^{-5}	4.3×10^{-9}
55 Cs	-7553.933	-7553.933	2×10^{-5}	3.6×10^{-9}
56 Ba	-7883.543	-7883.543	3×10^{-5}	4.9×10^{-9}
57 La	-8221.066	-8221.066	4×10^{-5}	4.8×10^{-9}
58 Ce	-8566.919	-	-	-
59 Pr	-8921.180	-8921.181	4×10^{-5}	4.9×10^{-9}
60 Nd	-9283.882	-9283.882	4×10^{-5}	4.8×10^{-9}
61 Pm	-9655.098	-9655.098	4×10^{-5}	4.7×10^{-9}
62 Sm	-10034.952	-10034.952	4×10^{-5}	4.4×10^{-9}
63 Eu	-10423.543	-10423.543	4×10^{-5}	4.7×10^{-9}
64 Gd	-10820.617	-	-	-
65 Tb	-11226.568	-	-	-
66 Dy	-11641.452	-11641.452	5×10^{-5}	4.4×10^{-9}
67 Ho	-12065.289	-	-	-
68 Er	-12498.152	-12498.152	6×10^{-5}	4.8×10^{-9}
69 Tm	-12940.174	-12940.174	6×10^{-5}	4.8×10^{-9}
70 Yb	-13391.456	-	-	-
71 Lu	-13851.807	-13851.808	6×10^{-5}	4.7×10^{-9}
72 Hf	-14321.249	-14321.249	6×10^{-5}	4.8×10^{-9}
73 Ta	-14799.812	-14799.812	7×10^{-5}	4.9×10^{-9}
74 W	-15287.546	-15287.546	7×10^{-5}	4.8×10^{-9}
75 Re	-15784.533	-15784.533	7×10^{-5}	4.9×10^{-9}
76 Os	-16290.648	-16290.648	8×10^{-5}	5.0×10^{-9}
77 Ir	-16806.113	-16806.113	8×10^{-5}	5.0×10^{-9}
78 Pt	-17331.069	-17331.069	8×10^{-5}	5.0×10^{-9}
79 Au	-17865.399	-17865.400	8×10^{-5}	4.9×10^{-9}
80 Hg	-18408.991	-18408.991	9×10^{-5}	5.0×10^{-9}
81 Tl	-18961.824	-18961.824	8×10^{-5}	4.6×10^{-9}
82 Pb	-19524.008	-19524.008	9×10^{-5}	4.9×10^{-9}
83 Bi	-20095.586	-20095.586	1×10^{-4}	5.0×10^{-9}
84 Po	-20676.500	-20676.500	9×10^{-5}	4.6×10^{-9}
85 At	-21266.881	-21266.881	9×10^{-5}	4.5×10^{-9}
86 Rn	-21866.772	-21866.772	9×10^{-5}	4.3×10^{-9}
55 Cs^r	-7786.771	-7786.771	3×10^{-4}	4.6×10^{-8}

Table 3.3: *(continued)*

Element	Calculated Energy	Literature Energy	Absolute Error	Relative Error
56 Ba^r	-8135.644	-8135.645	3×10^{-4}	4.7×10^{-8}
57 La^r	-8493.543	-8493.543	4×10^{-4}	4.8×10^{-8}
58 Ce^r	-8860.997	-8860.997	4×10^{-4}	4.5×10^{-8}
59 Pr^r	-9238.148	-9238.148	4×10^{-4}	4.6×10^{-8}
60 Nd^r	-9625.131	-9625.131	4×10^{-4}	4.8×10^{-8}
61 Pm^r	-10022.094	-10022.095	5×10^{-4}	4.9×10^{-8}
62 Sm^r	-10429.162	-10429.163	5×10^{-4}	4.8×10^{-8}
63 Eu^r	-10846.504	-10846.505	4×10^{-4}	4.4×10^{-8}
64 Gd^r	-11274.242	-11274.242	5×10^{-4}	4.7×10^{-8}
65 Td^r	-11712.544	-11712.545	5×10^{-4}	4.3×10^{-8}
66 Dy^r	-12161.545	-12161.545	6×10^{-4}	4.9×10^{-8}
67 Ho^r	-12621.412	-12621.413	5×10^{-4}	4.6×10^{-8}
68 Er^r	-13092.269	-13092.270	6×10^{-4}	4.9×10^{-8}
69 Tm^r	-13574.316	-13574.317	6×10^{-4}	4.8×10^{-8}
70 Yb^r	-14067.676	-14067.677	6×10^{-4}	4.6×10^{-8}
71 Lu^r	-14572.532	-14572.533	7×10^{-4}	4.9×10^{-8}
72 Hf^r	-15088.785	-15088.786	7×10^{-4}	4.9×10^{-8}
73 Ta^r	-15616.630	-15616.630	7×10^{-4}	4.7×10^{-8}
74 W^r	-16156.184	-16156.185	8×10^{-4}	4.9×10^{-8}
75 Re^r	-16707.619	-16707.620	8×10^{-4}	4.9×10^{-8}
76 Os^r	-17271.081	-17271.082	8×10^{-4}	4.9×10^{-8}
77 Ir^r	-17846.787	-17846.788	8×10^{-4}	4.9×10^{-8}
78 Pt^r	-18434.873	-18434.874	9×10^{-4}	4.9×10^{-8}
79 Au^r	-19035.525	-19035.526	9×10^{-4}	4.9×10^{-8}
80 Hg^r	-19648.895	-19648.896	9×10^{-4}	4.9×10^{-8}
81 Tl^r	-20274.849	-20274.850	9×10^{-4}	4.8×10^{-8}
82 Pb^r	-20913.713	-20913.714	9×10^{-4}	4.7×10^{-8}
83 Bi^r	-21565.705	-21565.706	1×10^{-3}	4.9×10^{-8}
84 Po^r	-22231.012	-22231.013	9×10^{-4}	4.1×10^{-8}
85 At^r	-22909.806	-22909.807	8×10^{-4}	3.7×10^{-8}
86 Rn^r	-23602.103	-23602.104	1×10^{-3}	4.8×10^{-8}

In Table

It can also be seen Table

Figures

In Figure

Finally

As for the relativistic basis sets, we can see from Figure

Table 3.4: *Comparison of basis sets produced by cudaDFRATOM and Dyall's triple-zeta basis sets. The basis sets for the 6s[41], 6p[42], and 5d[43] elements are shown. The 4f elements were calculated with a different electron configuration, so they are omitted.*

Element	Calculated Energy[a]	Calculated Energy[b]	Total basis functions[a]	Total basis functions[b]
55 Cs	-7786.771	-7786.771	113	105
56 Ba	-8135.644	-8135.644	112	104
72 Hf	-15088.785	-15088.784	158	129
73 Ta	-15616.630	-15616.628	156	129
74 W	-16156.184	-16156.183	154	129
75 Re	-16707.619	-16707.617	154	129
76 Os	-17271.081	-17271.080	154	129
77 Ir	-17846.787	-17846.786	154	129
78 Pt	-18434.873	-18434.872	156	129
79 Au	-19035.525	-19035.526	156	129
80 Hg	-19648.895	-19648.893	156	129
81 Tl	-20274.849	-20274.850	158	134
82 Pb	-20913.713	-20913.714	152	134
83 Bi	-21565.705	-21565.706	156	134
84 Po	-22231.012	-22231.013	152	134
85 At	-22909.806	-22909.807	154	134
86 Rn	-23602.103	-23602.104	151	134

[a]cudaDFRATOM basis sets
[b]Dyalls basis sets

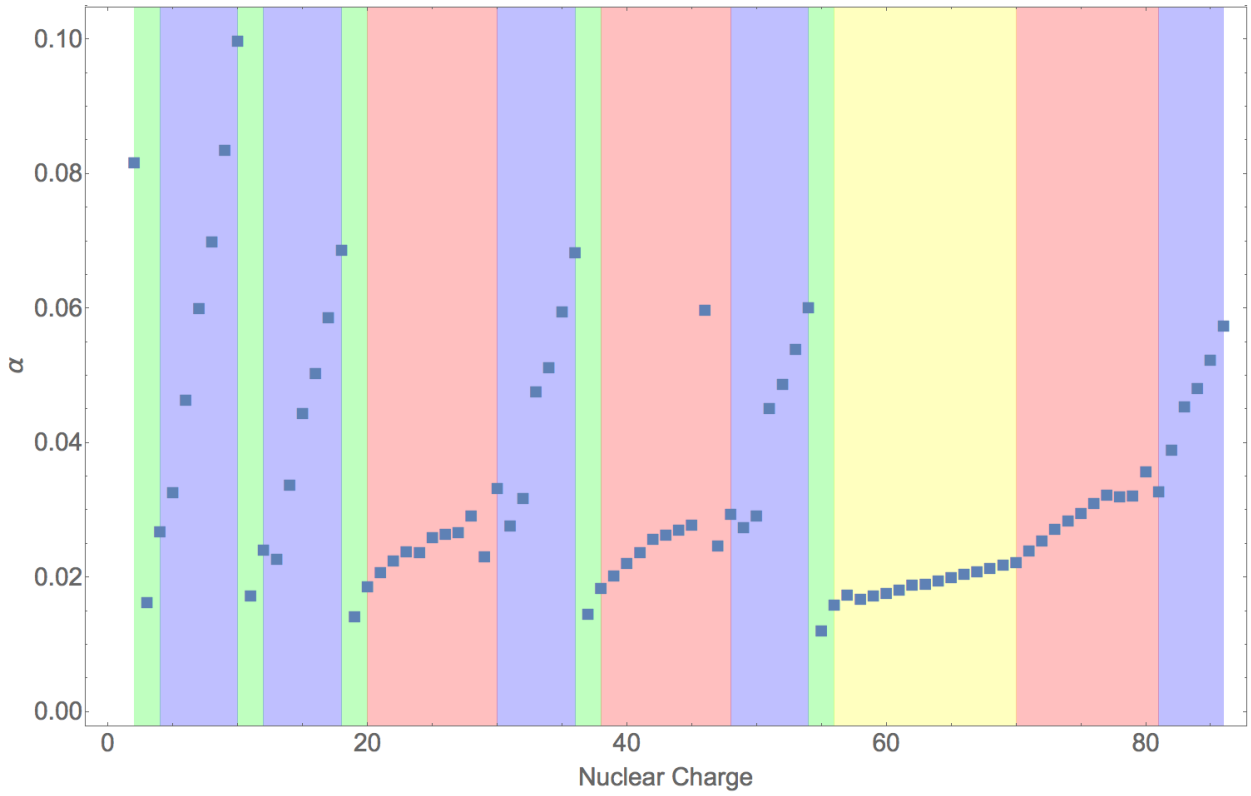


Figure 3.2: *Scatter plot of the α parameter vs. nuclear charge. Regions of the plot are shaded based on periodic table block regions. The s block is green, the p block is blue, the d block is red and the f block is yellow. There is a distinct pattern where the value of α increases along a row until a noble gas is reached. Also note how the rate of the increase changes at periodic table block boundaries.*

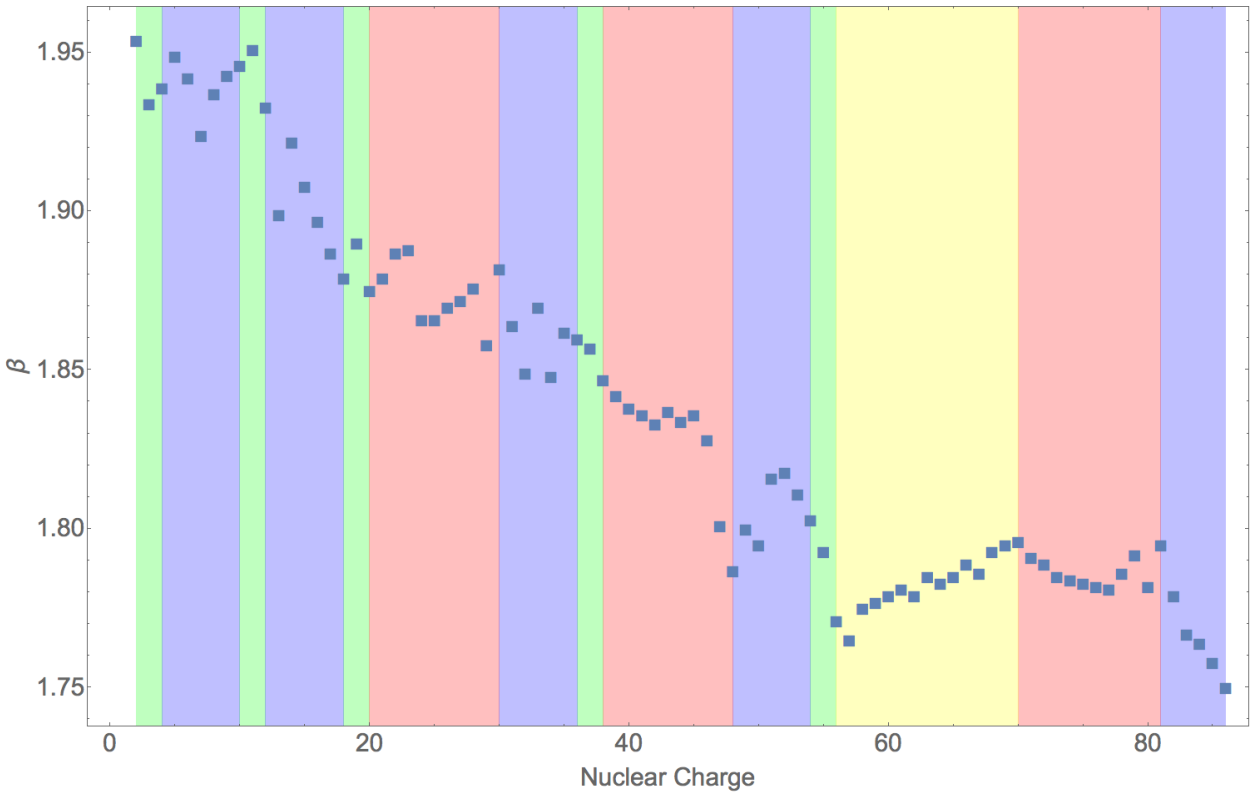
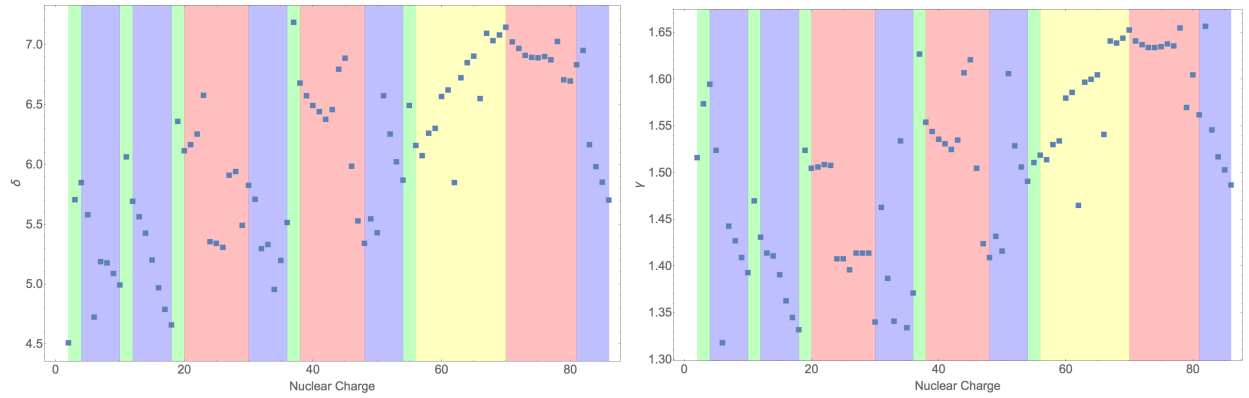


Figure 3.3: *Scatter plot of the β parameter vs. nuclear charge. Regions of the plot are shaded based on periodic table block regions. The s block is green, the p block is blue, the d block is red and the f block is yellow. There is a general trend of the value of β to decrease as the nuclear charge grows larger.*



(a) δ **(b)** γ

Figure 3.4: *Scatter plots of the δ and γ parameters. Regions of the plot are shaded based on periodic table block regions. The s block is green, the p block is blue, the d block is red and the f block is yellow. There are no clear trends with respect to the nuclear charge.*

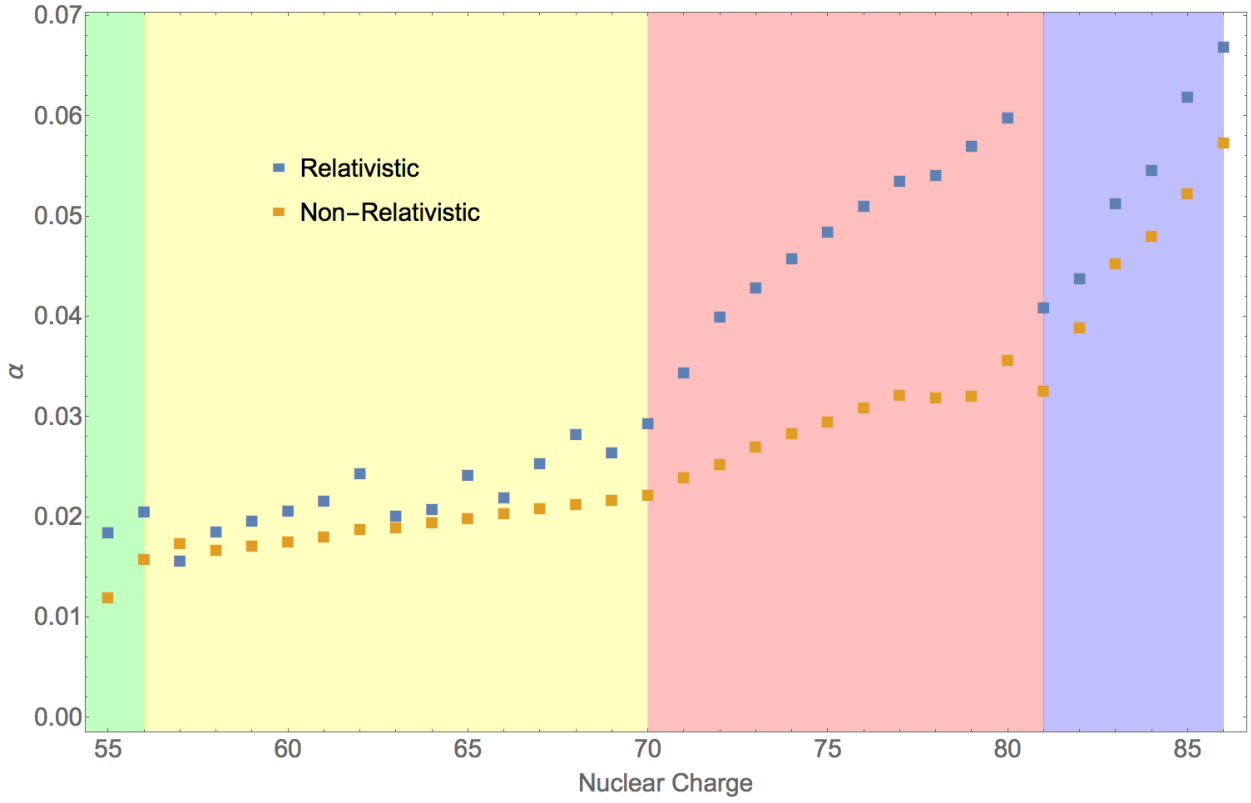


Figure 3.5: *Scatter plot of the relativistic and non-relativistic α parameters vs. nuclear charge. Regions of the plot are shaded based on periodic table block regions. The s block is green, the p block is blue, the d block is red and the f block is yellow.*

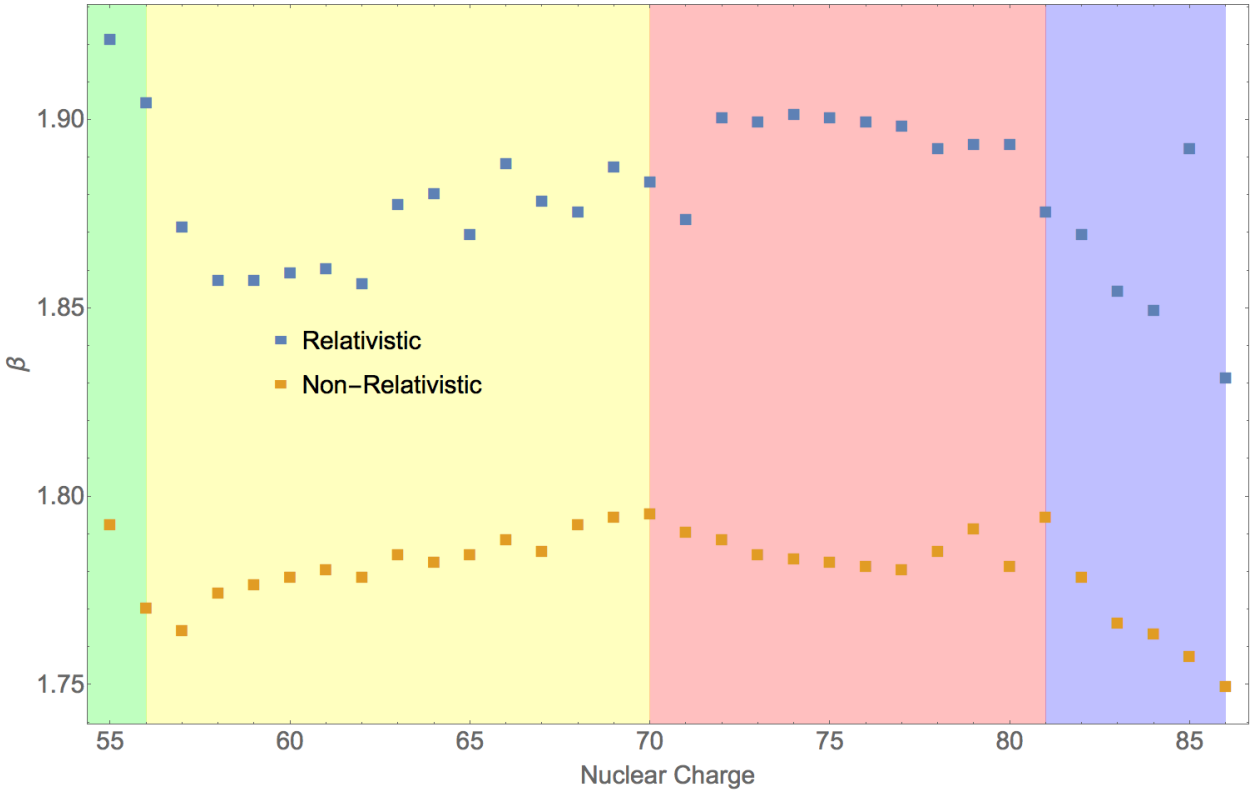
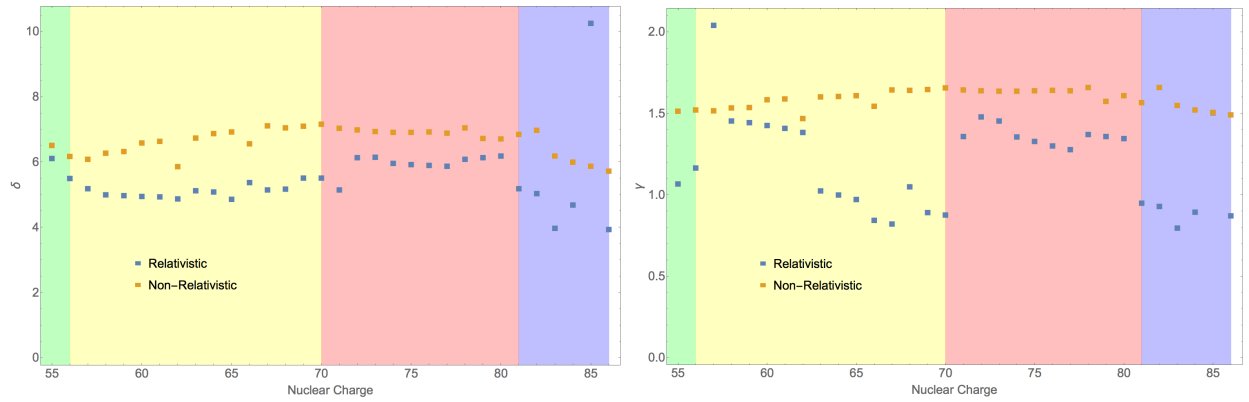


Figure 3.6: *Scatter plot of the relativistic and non-relativistic β parameters vs. nuclear charge. Regions of the plot are shaded based on periodic table block regions. The s block is green, the p block is blue, the d block is red and the f block is yellow.*



(a) δ **(b)** γ

Figure 3.7: *Scatter plot of the relativistic and non-relativistic δ and γ parameters. Regions of the plot are shaded based on periodic table block regions. The s block is green, the p block is blue, the d block is red and the f block is yellow.*

Chapter 4

Conclusions and Future Work

In this thesis I have illustrated how even small problems in computational quantum chemistry can benefit from parallel computation. I have done this both in the internal sense, where I rewrote the DFRATOM program to calculate the electronic structure of atoms on GPUs, and in the external sense, where I designed an algorithm that very effectively optimizes basis sets. This chapter will be broken up into two sections: the first which covers the rewriting of DFRATOM into cudaDFRATOM, and the second one which summarizes the results of basis set optimization using cudaDFRATOM and rwtbs.

4.1 cudaDFRATOM

By harnessing the power of GPUs, I was able get the cudaDFRATOM program to accelerate the biggest bottleneck of these calculations, the evaluation of the two-electron integrals, by almost a factor of 20. This changes the bottleneck to be the matrix operations required in SCF. As a result, the total speedup is only about 2-4 times faster than the original DFRATOM program. While this is not as much of an increase as we originally hoped, it is still a very big improvement on the original program.

It is also worth pointing out that as the problems get larger, the speedup gets larger as well. This indicates that the algorithms written for this program could potentially work even better on even larger problems such as molecules. Modifications required to make the algorithms work on molecules are as follows.

One could implement direct SCF. As the amount of two-electron integrals grows, it becomes impractical to try and store them all in memory. Instead, in the direct SCF algorithm, the integrals are calculated and consumed as needed. The current program has the following flow: the threads are mapped to all the integrals, all the integrals are calculated and stored in memory, and then all the integrals are used to form the $\mathbf{P}$ and $\mathbf{Q}$ matrices. If we wish to reuse as much of the code I've written as possible, the direct SCF implementation would

work as follows. First we would map the threads to a chunk of the integrals, then we could calculate only that chunk, and then we would build up only the elements of the **P** and **Q** that use those integrals. Now, we no longer need these integrals, so we can throw them away and start the calculation of a new chunk. We would then loop over these steps until the the **P** and **Q** matrices have been completely calculated. The mapping takes very little time to calculate, so the fact that we are calling it so many times would have relatively little impact on performance.

One could also add some prescreening of the integrals to determine a rough estimate of their order of magnitude. If a particular integral is very close to zero, the effect it has on the calculation is relatively negligible. Therefore we could skip the calculation of this integral, and there would be almost no impact on the accuracy of the calculation. Due to how GPUs perform the calculations in warps, we would need to presort the integrals so that the ones that are likely to be close to zero are grouped together in order to maximize the returns of this procedure.

One would also need to alter the mapping algorithm so that it can handle calculations of different point groups. Atoms have spherical symmetry, meaning we can eliminate the need to calculate a lot of the integrals because many of them will be symmetrically the same. But this would not be the case in systems that have no symmetry, so we would need to change the mapping accordingly. This would actually be very simple to change, as we would just need to write nearly identical code for each symmetry that we would want to support.

One final comment regarding cudaDFRATOM is the algorithm to form the **P** and **Q** matrices. I am still not completely satisfied with the current state of this part of the code. It is quite complicated and inelegant. It would seem to me that there should be a better way of performing this calculation, but so far I have been unable to improve upon the version that appears in this thesis. One possible approach would be to break up the calculation of the matrices into two different subroutines: one that calculates **P** and one that calculates **Q**. The calculation of **P** can be reformed into a simple matrix multiplication problem, but **Q** requires many conditional statements as a result of having to deal with the math of open shells. I did not try this as I believed the main bottleneck was reading the two-electron integrals. Therefore, I only wanted to have to read them once to reduce the amount of global memory reads as possible. But it might be the case that specialized code for each matrix could outperform generalized code for both.

4.2 Basis Set Optimization

This thesis also covered the optimization of new basis sets. I used a novel algorithm that almost entirely eliminates the need for human involvement in the optimization process. It

produces useful accurate basis sets, that are practically guarantied to be as small as possible. I have optimized non-relativistic basis sets for the elements helium through radon. I have also optimized relativistic basis sets for the elements caesium through radon. Future work in the area would be the optimization of relativistic basis sets for the rest of the periodic table. Care must be taken when optimizing sets for the seventh row elements, because the assumption made for kinetic balancing begins to break down there. As a result, early attempts to optimize basis sets for these elements have proven to be prone to prolapsing. As a result, the method of automating the optimization process should be used with caution in this range, as the results it produces may erroneously appear to be successful.

Further work that could be done includes modifications to the cudaDFRATOM program to support basis sets other than WTBS, and also to include other optimization algorithms than ***newuoa***, which might be less prone to generating prolapsing basis sets. cudaDFRATOM also includes the option to optimize a different set of ζs for different groups of spinor symmetries. Therefore, it might be best to try and optimize basis sets that have grouped the s and p type spinors into one group and the d and f type spinors in another. The logic of this is that relativity has different effects on these two groups, so it might be best to try and separate the two so that each gets its own set of specialized basis functions.

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Appendix A

cudaDFRATOM Input and Output files

This appendix shows cudaDFRATOM input files for a few common calculations. The output files are also given.

A.1 Single Point Energy with predefined WTBS parameters

This input file will perform a calculation on lead using predefined well-tempered basis set (WTBS) parameters. It uses the "autogen" option to automatically generate electron configurations.

```
Pb
  $contrl jobtype='energy' $end
  $nuc znuc=82 nucmdl=3 $end
  $bas nsym=7 bastype='wtbs' $end
  $wtbs wtbspara= 3.5433483E-02  1.8399050E+00  4.4867042E+00  2.0048353E+00
        nbs=35 30 30 25 25 20 20 $end
  $econfig nclose=6 4 4 3 3 1 1 nopen=0 1 1 0 0 0 0 freeel=2 autogen=.t. $end
  $scf maxitr=50 ixtrp=1 dfctr=0.3 $end
```

Listing A.1: *Input file for calculating the single point energy of Pb.*

```
 &CONTRL
 JOBTYPE = energy,
 C =    137.0359997600000
 /
 &NUC
 ZNUC =    82.00000000000000     ,
 NUCMDL =            3,
 RNUC =    0.000000000000000     ,
 ALPHA =    137688400.8100000
 /
 &BAS
 NSYM =            7,
 BASTYPE = wtbs ,
 NGROUP =            1
 /
 &WTBS
 WTBSPARA =   3.5433483000000002E-002,
               1.839905000000000     ,
               4.486704200000000     ,
               2.004835300000000     ,
 NBS =          35,
                30,
                30,
                25,
                25,
                20,
                20,
 START =           1,
                   1,
```

```
                    1,
                    1,
                    1,
                    1,
                    1,
 GROUPS =            1,
                     1,
                     1,
                     1,
                     1,
                     1,
                     1
 /
 &ECONFIG
 NCLOSE =            6,
                     4,
                     4,
                     3,
                     3,
                     1,
                     1,
 NOPEN =            0,
                    1,
                    1,
                    0,
                    0,
                    0,
                    0,
 FREEEL =            2,
 AUTOGEN =  T,
 NCONF =            3
 /
 nconf = 3
  1  0.00  0.00  2.00  0.00  0.00  0.00  0.00
  2  0.00  1.00  1.00  0.00  0.00  0.00  0.00
  3  0.00  2.00  0.00  0.00  0.00  0.00  0.00
 &SCF
 MAXITR =          50,
 IXTRP =           1,
 DFCTR =   0.3000000000000000     ,
 THDLL =   1.0000000000000001E-005,
 THDSL =   9.9999999999999995E-008,
 THDSS =   1.0000000000000001E-009
 /
       31560
    166068720
        82680
        82680
    221424960
 Calculating one electron integrals
 Calculating two electron integrals
 Calculating guess
 Starting SCF
 SCF converged at iteration 21 Final energy =    -20913.71321671859

                          1S+            2S+            3S+            4S+            5S+            6S+
               -3.2558910E+03 -5.8788484E+02 -1.4375419E+02 -3.3985791E+01 -6.1449434E+00 -5.6643943E-01


  3.5433483E-02 -1.9140257E-07 -9.7159398E-06  8.4857239E-05  2.1986574E-04  5.1415800E-04  2.0636937E-02
  6.5194589E-02  8.2570189E-07  4.1921119E-05 -3.6562370E-04 -9.4709963E-04 -2.1895500E-03  1.7096292E-01
  1.1995578E-01 -1.9767881E-06 -1.0027465E-04  8.7018398E-04  2.2414603E-03  4.9281942E-03  4.6563303E-01
  2.2073350E-01  3.5996723E-06  1.8260591E-04 -1.5762467E-03 -4.0630949E-03 -9.8724076E-03  4.9206077E-01
  4.0626020E-01 -5.6936298E-06 -2.8865907E-04  2.4671919E-03  6.4082992E-03 -1.1737844E-02  1.8824719E-01
  7.4802875E-01  8.3491287E-06  4.2257668E-04 -3.5241493E-03 -8.9348378E-03 -2.9905373E-01 -3.0010508E-01
  1.3783189E+00 -1.1366730E-05 -5.8146938E-04  4.8783856E-03  1.5097459E-02 -7.8158376E-01 -5.1043840E-01
  2.5427420E+00  1.5670362E-05  7.9374845E-04 -6.0504748E-03  2.7343372E-02 -5.2239957E-01 -2.8601945E-01
  4.6995778E+00 -1.9958101E-05 -1.0286165E-03  6.5909755E-03  5.2434329E-01  7.2696910E-01  3.0687539E-01
  8.7095624E+00  1.9050301E-05  1.1054521E-03 -2.3451833E-02  9.3510165E-01  8.5987922E-01  3.3842577E-01
  1.6203217E+01 -2.6144911E-05 -1.4336986E-03 -2.3995069E-01 -1.1495177E-01 -5.6246536E-02 -2.2090975E-02
  3.0302910E+01  2.8420699E-05  3.7197373E-03 -8.1531809E-01 -1.0354558E+00 -5.7885493E-01 -2.0220940E-01
  5.7068236E+01  7.7841668E-05  8.1191015E-02 -3.4478787E-01 -3.3138799E-01 -1.7960886E-01 -6.2968065E-02
  1.0845021E+02 -1.7007069E-04  4.1109997E-01  4.9103230E-01  3.2296539E-01  1.5765479E-01  5.4052594E-02
  2.0847323E+02 -2.9589527E-03  5.0903323E-01  4.6725787E-01  2.7638266E-01  1.2821564E-01  4.3348064E-02
  4.0651542E+02 -5.8530537E-02  1.5500969E-01  1.2163377E-01  6.9594624E-02  3.2609524E-02  1.1089595E-02
  8.0667635E+02 -2.0848170E-01 -1.1977939E-01 -6.2191906E-02 -3.2239372E-02 -1.4726348E-02 -4.9831695E-03
  1.6348107E+03 -2.9189696E-01 -1.6951366E-01 -8.7418119E-02 -4.4770915E-02 -2.0115505E-02 -6.7655030E-03
  3.3969005E+03 -2.4399646E-01 -1.2374164E-01 -6.2334097E-02 -3.1843346E-02 -1.4364272E-02 -4.8398193E-03
  7.2674336E+03 -1.5514532E-01 -7.1929749E-02 -3.5560267E-02 -1.8046013E-02 -8.1052706E-03 -2.7270821E-03
  1.6080864E+04 -8.5723247E-02 -3.7776777E-02 -1.8531501E-02 -9.3982955E-03 -4.2280724E-03 -1.4235773E-03
  3.6974132E+04 -4.4254206E-02 -1.8890041E-02 -9.2074939E-03 -4.6580915E-03 -2.0916796E-03 -7.0381814E-04
  8.8762050E+04 -2.2211543E-02 -9.2756569E-03 -4.5077689E-03 -2.2802569E-03 -1.0247971E-03 -3.4495102E-04
  2.2355921E+05 -1.1030466E-02 -4.5272219E-03 -2.1929860E-03 -1.1079619E-03 -4.9748954E-04 -1.6740559E-04
  5.9356339E+05 -5.4653284E-03 -2.2126683E-03 -1.0697906E-03 -5.4040349E-04 -2.4274024E-04 -8.1695794E-05
  1.6690414E+06 -2.6711743E-03 -1.0700322E-03 -5.1634550E-04 -2.6065392E-04 -1.1702741E-04 -3.9380312E-05
  4.9925105E+06 -1.2803414E-03 -5.0897019E-04 -2.4533622E-04 -1.2383272E-04 -5.5608079E-05 -1.8713930E-05
  1.5952595E+07 -5.6814462E-04 -2.2469528E-04 -1.0820468E-04 -5.4596862E-05 -2.4511059E-05 -8.2480821E-06
  5.4660323E+07 -2.1789453E-04 -8.5878190E-05 -4.1336406E-05 -2.0856799E-05 -9.3648388E-06 -3.1514882E-06
  2.0153596E+08 -2.1829984E-05 -8.5856049E-06 -4.1303396E-06 -2.0833500E-06 -9.3511877E-07 -3.1465061E-07
  8.0207663E+08  1.5047170E-06  5.9151312E-07  2.8444110E-07  1.4340856E-07  6.4331467E-08  2.1641631E-08
  3.4548830E+09 -2.3058546E-07 -9.0633416E-08 -4.3576601E-08 -2.1966863E-08 -9.8520247E-09 -3.3140430E-09
```

```
  1.6143750E+10  3.5734594E-08  1.4045396E-08  6.7527666E-09  3.4039038E-09  1.5265427E-09  5.1348999E-10
  8.1990099E+10 -5.0569076E-09 -1.9875952E-09 -9.5559025E-10 -4.8168458E-10 -2.1601720E-10 -7.2662291E-11
  4.5329140E+11  5.7727825E-10  2.2689646E-10  1.0908642E-10  5.4987096E-11  2.4659548E-11  8.2947901E-12


  3.5433483E-02  1.6954819E-09 -1.9755659E-08  1.0517252E-07  2.5786097E-07  6.0705258E-07  2.4548192E-05
  6.5194589E-02 -6.1192070E-09  9.9944811E-08 -6.0718398E-07 -1.5143279E-06 -3.5153647E-06  2.7587966E-04
  1.1995578E-01  1.2288718E-08 -2.9311326E-07  1.9454770E-06  4.8761399E-06  1.0747339E-05  1.0191707E-03
  2.2073350E-01 -1.8377497E-08  6.7468779E-07 -4.7570165E-06 -1.2013960E-05 -2.9243701E-05  1.4610285E-03
  4.0626020E-01  2.2094317E-08 -1.3755421E-06  1.0067995E-05  2.5740826E-05 -4.7401652E-05  7.5820245E-04
  7.4802875E-01 -1.9732962E-08  2.6328827E-06 -1.9470061E-05 -4.8740114E-05 -1.6346171E-03 -1.6403132E-03
  1.3783189E+00  7.0802976E-09 -4.7913481E-06  3.6517250E-05  1.1190759E-04 -5.7997109E-03 -3.7872066E-03
  2.5427420E+00  3.3353393E-08  8.6948262E-06 -6.1451021E-05  2.7604343E-04 -5.2632551E-03 -2.8813285E-03
  4.6995778E+00 -1.0558631E-07 -1.5093361E-05  9.0963356E-05  7.1885186E-03  9.9617188E-03  4.2051363E-03
  8.7095624E+00  1.2906609E-07  2.2027770E-05 -4.3912334E-04  1.7443639E-02  1.6029779E-02  6.3081111E-03
  1.6203217E+01 -3.6214254E-07 -3.8443478E-05 -6.1234284E-03 -2.9533854E-03 -1.4537621E-03 -5.7043669E-04
  3.0302910E+01  5.2836853E-07  1.3285756E-04 -2.8417938E-02 -3.6003287E-02 -2.0119705E-02 -7.0279292E-03
  5.7068236E+01  4.6114972E-06  3.9263140E-03 -1.6339710E-02 -1.5654581E-02 -8.4797945E-03 -2.9727261E-03
  1.0845021E+02 -1.2950972E-05  2.7337032E-02  3.2407503E-02  2.1295257E-02  1.0391632E-02  3.5625331E-03
  2.0847323E+02 -2.9073865E-04  4.6496978E-02  4.2189645E-02  2.4898158E-02  1.1543726E-02  3.9023181E-03
  4.0651542E+02 -8.0613553E-03  1.9021333E-02  1.4724956E-02  8.4033363E-03  3.9370652E-03  1.3390133E-03
  8.0667635E+02 -3.9844448E-02 -2.1952178E-02 -1.1434990E-02 -5.9321659E-03 -2.7091031E-03 -9.1660186E-04
  1.6348107E+03 -7.7242278E-02 -4.2059759E-02 -2.1528276E-02 -1.1006504E-02 -4.9428729E-03 -1.6622820E-03
  3.3969005E+03 -8.8701783E-02 -4.2001749E-02 -2.0959345E-02 -1.0683736E-02 -4.8172258E-03 -1.6229926E-03
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  7.4802875E-01 -2.1738056E-04 -8.3176454E-04 -3.2770786E-01
  1.3783189E+00  3.0219815E-04  6.3470740E-03 -3.8344665E-01
  2.5427420E+00 -4.4994548E-04  5.7171355E-02 -2.4878259E-01
  4.6995778E+00  3.9049198E-05  2.6346697E-01  4.0375292E-02
  8.7095624E+00 -8.0122761E-03  4.5805697E-01  2.0149629E-01
  1.6203217E+01 -7.4226625E-02  3.3001447E-01  1.4691305E-01
  3.0302910E+01 -2.5949707E-01 -6.3462926E-03  1.1012835E-02
  5.7068236E+01 -3.7266615E-01 -1.8898131E-01 -6.5016978E-02
  1.0845021E+02 -2.8171189E-01 -1.5480799E-01 -5.4074551E-02
  2.0847323E+02 -1.4190235E-01 -7.8386764E-02 -2.7469477E-02
  4.0651542E+02 -5.4081638E-02 -2.9251770E-02 -1.0187547E-02
  8.0667635E+02 -1.7643813E-02 -9.4798446E-03 -3.3057717E-03
  1.6348107E+03 -5.2335178E-03 -2.7774063E-03 -9.6304002E-04
  3.3969005E+03 -1.5325460E-03 -8.1584319E-04 -2.8426295E-04
  7.2674336E+03 -4.6095060E-04 -2.4259466E-04 -8.3902621E-05
  1.6080864E+04 -1.4789734E-04 -7.8497956E-05 -2.7352488E-05
  3.6974132E+04 -4.7671984E-05 -2.5017391E-05 -8.6454048E-06
  8.8762050E+04 -1.6984983E-05 -8.9980573E-06 -3.1333861E-06
  2.2355921E+05 -4.5486942E-06 -2.3853540E-06 -8.2421615E-07
  5.9356339E+05 -2.4306190E-06 -1.2844651E-06 -4.4653051E-07


  3.5433483E-02  6.6378334E-08  5.0504761E-08  1.5844785E-07
  6.5194589E-02 -5.5134818E-08 -3.8586568E-07 -2.6097866E-06
  1.1995578E-01  3.3208145E-07  9.7973562E-07 -2.4484243E-05
  2.2073350E-01 -2.5675922E-07 -2.5626833E-06 -2.5057139E-04
  4.0626020E-01  1.4400230E-06  4.5493849E-06 -1.0610208E-03
  7.4802875E-01 -8.2919598E-07 -7.4959695E-06 -2.7357957E-03
  1.3783189E+00  5.6902067E-06  7.0748212E-05 -4.3450043E-03
  2.5427420E+00 -2.2419726E-06  8.7781103E-04 -3.8281416E-03
  4.6995778E+00  1.1210953E-05  5.5097183E-03  8.4595301E-04
  8.7095624E+00 -2.0650628E-04  1.3039108E-02  5.7362336E-03
  1.6203217E+01 -2.8411004E-03  1.2798368E-02  5.6966163E-03
  3.0302910E+01 -1.3701878E-02 -3.4945280E-04  5.7576690E-04
  5.7068236E+01 -2.6948928E-02 -1.3689346E-02 -4.7117273E-03
  1.0845021E+02 -2.7850497E-02 -1.5316871E-02 -5.3508675E-03
  2.0847323E+02 -1.9120857E-02 -1.0566583E-02 -3.7033238E-03
  4.0651542E+02 -9.8424297E-03 -5.3236691E-03 -1.8539306E-03
  8.0667635E+02 -4.2476636E-03 -2.2836292E-03 -7.9658186E-04
  1.6348107E+03 -1.6035530E-03 -8.5066614E-04 -2.9479257E-04
  3.3969005E+03 -5.6267228E-04 -3.0040086E-04 -1.0484829E-04
  7.2674336E+03 -1.8688183E-04 -9.8013826E-05 -3.3782723E-05
  1.6080864E+04 -6.0891217E-05 -3.2665057E-05 -1.1464903E-05
  3.6974132E+04 -1.8933714E-05 -9.7813981E-06 -3.3354802E-06
  8.8762050E+04 -6.0219396E-06 -3.2810341E-06 -1.1659544E-06
  2.2355921E+05 -1.6877326E-06 -8.4801421E-07 -2.8284055E-07
  5.9356339E+05 -6.4693359E-07 -3.5510080E-07 -1.2693531E-07


                          3D+            4D+            5D+
                -9.2970175E+01 -1.6065511E+01 -1.0359352E+00


  3.5433483E-02  7.7221792E-06  4.6214141E-05  2.1952461E-05
  6.5194589E-02 -2.7509786E-05 -1.6424473E-04 -1.4251127E-03
  1.1995578E-01  5.8345961E-05  3.3612523E-04 -1.0625745E-02
  2.2073350E-01 -9.9974735E-05 -5.7481199E-04 -6.7684219E-02
  4.0626020E-01  1.5324515E-04  8.4486783E-04 -1.9241282E-01
  7.4802875E-01 -2.2082310E-04 -8.0559176E-04 -3.3969689E-01
  1.3783189E+00  3.0703567E-04  7.6648169E-03 -3.7325459E-01
  2.5427420E+00 -4.7377597E-04  6.6624936E-02 -2.2119312E-01
  4.6995778E+00 -4.9467905E-05  2.8397802E-01  6.0585886E-02
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  1.6203217E+01 -8.3937657E-02  3.0682572E-01  1.3437091E-01
  3.0302910E+01 -2.7503581E-01 -2.9655066E-02  1.3186423E-03
  5.7068236E+01 -3.7518565E-01 -1.9434691E-01 -6.5989400E-02
  1.0845021E+02 -2.7089678E-01 -1.4943064E-01 -5.1260616E-02
  2.0847323E+02 -1.3041137E-01 -7.2047242E-02 -2.4782130E-02
  4.0651542E+02 -4.6786023E-02 -2.5268754E-02 -8.6328259E-03
  8.0667635E+02 -1.3903256E-02 -7.4694054E-03 -2.5574685E-03
  1.6348107E+03 -3.5609354E-03 -1.8857418E-03 -6.4088663E-04
  3.3969005E+03 -8.3665106E-04 -4.4694872E-04 -1.5325926E-04
  7.2674336E+03 -1.8163087E-04 -9.4900642E-05 -3.2022507E-05
  1.6080864E+04 -3.7997791E-05 -2.0491370E-05 -7.0895064E-06
  3.6974132E+04 -7.3043431E-06 -3.7234375E-06 -1.2330269E-06
  8.8762050E+04 -1.4317186E-06 -7.9759591E-07 -2.8274095E-07
  2.2355921E+05 -2.3262340E-07 -1.1047266E-07 -3.4394045E-08
  5.9356339E+05 -5.4159164E-08 -3.1421800E-08 -1.1456088E-08


  3.5433483E-02  1.7888758E-08  8.7508825E-08  4.1293182E-08
  6.5194589E-02 -8.0684778E-08 -4.1663370E-07 -3.5173993E-06
  1.1995578E-01  2.2176303E-07  1.1482697E-06 -3.5517803E-05
  2.2073350E-01 -4.9930096E-07 -2.6490778E-06 -3.0699962E-04
  4.0626020E-01  1.0155200E-06  5.2650364E-06 -1.1839084E-03
  7.4802875E-01 -1.9543164E-06 -6.8268672E-06 -2.8362358E-03
  1.3783189E+00  3.6453134E-06  8.7043689E-05 -4.2300188E-03
  2.5427420E+00 -7.5384829E-06  1.0257309E-03 -3.4043702E-03
  4.6995778E+00 -6.8517101E-07  5.9447614E-03  1.2688310E-03
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  1.6203217E+01 -3.2669877E-03  1.1909188E-02  5.2142294E-03
  3.0302910E+01 -1.4631652E-02 -1.5947712E-03  6.1298599E-05
  5.7068236E+01 -2.7323725E-02 -1.4142790E-02 -4.8018676E-03
  1.0845021E+02 -2.7076282E-02 -1.4913646E-02 -5.1146126E-03
  2.0847323E+02 -1.7926708E-02 -9.8861261E-03 -3.3994994E-03
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  8.0667635E+02 -3.6213113E-03 -1.9414600E-03 -6.6454224E-04
  1.6348107E+03 -1.2728527E-03 -6.7217021E-04 -2.2827054E-04
  3.3969005E+03 -4.0840295E-04 -2.1786340E-04 -7.4727838E-05
  7.2674336E+03 -1.1946568E-04 -6.2106636E-05 -2.0903646E-05
  1.6080864E+04 -3.3287385E-05 -1.8026340E-05 -6.2634465E-06
  3.6974132E+04 -8.1967293E-06 -4.0946848E-06 -1.3349317E-06
  8.8762050E+04 -2.0517720E-06 -1.1841925E-06 -4.3034993E-07
  2.2355921E+05 -3.8529477E-07 -1.5977439E-07 -4.3020909E-08
  5.9356339E+05 -1.0740559E-07 -7.0576947E-08 -2.7714538E-08


                        4F-
                -5.9331805E+00


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  6.5194589E-02  4.9086264E-05
  1.1995578E-01 -9.8691162E-05
  2.2073350E-01  1.2122985E-04
  4.0626020E-01 -5.7573123E-04
  7.4802875E-01 -3.7129185E-03
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  8.7095624E+00 -3.2184810E-01
  1.6203217E+01 -2.9865700E-01
  3.0302910E+01 -1.9561991E-01
  5.7068236E+01 -8.8370628E-02
  1.0845021E+02 -3.0872542E-02
  2.0847323E+02 -8.4857068E-03
  4.0651542E+02 -1.9423015E-03
  8.0667635E+02 -4.1900690E-04
  1.6348107E+03 -8.3141076E-05
  3.3969005E+03 -1.5517453E-05
  7.2674336E+03 -4.6868130E-06


  3.5433483E-02 -3.0184033E-08
  6.5194589E-02  1.4123331E-07
  1.1995578E-01 -3.6812892E-07
  2.2073350E-01  6.5493014E-07
  4.0626020E-01 -3.9507151E-06
  7.4802875E-01 -3.4920504E-05
  1.3783189E+00 -3.8022076E-04
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  2.0847323E+02 -1.2821405E-03
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  8.0667635E+02 -1.1098769E-04
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  3.3969005E+03 -6.3265217E-06
  7.2674336E+03 -1.6293580E-06


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                -5.7413469E+00


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  6.5194589E-02  4.9990333E-05
  1.1995578E-01 -1.0088117E-04
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  1.6203217E+01 -2.9517418E-01
  3.0302910E+01 -1.9089221E-01
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  1.0845021E+02 -2.9037579E-02
  2.0847323E+02 -7.7172949E-03
  4.0651542E+02 -1.6767727E-03
  8.0667635E+02 -3.3097325E-04
  1.6348107E+03 -5.4957097E-05
  3.3969005E+03 -8.8754940E-06
  7.2674336E+03 -1.4989268E-06
```

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  3.5433483E-02 -3.2617168E-08
  6.5194589E-02  1.4149420E-07
  1.1995578E-01 -3.8604183E-07
  2.2073350E-01  5.9849482E-07
  4.0626020E-01 -4.5010270E-06
  7.4802875E-01 -4.0093122E-05
  1.3783189E+00 -4.0951459E-04
  2.5427420E+00 -1.9678245E-03
  4.6995778E+00 -5.7167356E-03
  8.7095624E+00 -1.0444036E-02
  1.6203217E+01 -1.2993386E-02
  3.0302910E+01 -1.1476039E-02
  5.7068236E+01 -7.0050481E-03
  1.0845021E+02 -3.2756335E-03
  2.0847323E+02 -1.1959300E-03
  4.0651542E+02 -3.5705524E-04
  8.0667635E+02 -9.7043968E-05
  1.6348107E+03 -2.1994873E-05
  3.3969005E+03 -4.9229745E-06
  7.2674336E+03 -1.0697561E-06


 Calculated energy =   -2.0913713216718592E+04
 Literature energy =   -2.0913714331849998E+04
 Difference (cal - lit) = 1.12E-03
 Relative error (abs((cal - lit)/lit)) = 5.33E-08
 Basis set for original program
35 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.5433483000000002E-02 1.0d0 1.0d0
   6.5194588593144476E-02 1.0d0 1.0d0
   1.1995577607433897E-01 1.0d0 1.0d0
   2.2073349756341545E-01 1.0d0 1.0d0
   4.0626019965028504E-01 1.0d0 1.0d0
   7.4802874797813979E-01 1.0d0 1.0d0
   1.3783189024559244E+00 1.0d0 1.0d0
   2.5427420408376111E+00 1.0d0 1.0d0
   4.6995778331749465E+00 1.0d0 1.0d0
   8.7095624280738555E+00 1.0d0 1.0d0
   1.6203216735620309E+01 1.0d0 1.0d0
   3.0302909733749487E+01 1.0d0 1.0d0
   5.7068235542655763E+01 1.0d0 1.0d0
   1.0845021407222320E+02 1.0d0 1.0d0
   2.0847323449769911E+02 1.0d0 1.0d0
   4.0651541537167549E+02 1.0d0 1.0d0
   8.0667634870078655E+02 1.0d0 1.0d0
   1.6348107232313521E+03 1.0d0 1.0d0
   3.3969004983391187E+03 1.0d0 1.0d0
   7.2674336199173958E+03 1.0d0 1.0d0
   1.6080864381912534E+04 1.0d0 1.0d0
   3.6974131657844009E+04 1.0d0 1.0d0
   8.8762049980994911E+04 1.0d0 1.0d0
   2.2355921269411492E+05 1.0d0 1.0d0
   5.9356338843429903E+05 1.0d0 1.0d0
   1.6690413606262361E+06 1.0d0 1.0d0
   4.9925104726352403E+06 1.0d0 1.0d0
   1.5952594555420512E+07 1.0d0 1.0d0
   5.4660322670399554E+07 1.0d0 1.0d0
   2.0153596325467077E+08 1.0d0 1.0d0
   8.0207663178819859E+08 1.0d0 1.0d0
   3.4548829687578516E+09 1.0d0 1.0d0
   1.6143749848481022E+10 1.0d0 1.0d0
   8.1990099053523590E+10 1.0d0 1.0d0
   4.5329140391053540E+11 1.0d0 1.0d0
30 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.5433483000000002E-02 1.0d0 1.0d0
   6.5194588593144476E-02 1.0d0 1.0d0
   1.1995577607433897E-01 1.0d0 1.0d0
   2.2073349756341545E-01 1.0d0 1.0d0
   4.0626019965028504E-01 1.0d0 1.0d0
   7.4802874797813979E-01 1.0d0 1.0d0
   1.3783189024559244E+00 1.0d0 1.0d0
   2.5427420408376111E+00 1.0d0 1.0d0
   4.6995778331749465E+00 1.0d0 1.0d0
   8.7095624280738555E+00 1.0d0 1.0d0
   1.6203216735620309E+01 1.0d0 1.0d0
   3.0302909733749487E+01 1.0d0 1.0d0
   5.7068235542655763E+01 1.0d0 1.0d0
   1.0845021407222320E+02 1.0d0 1.0d0
   2.0847323449769911E+02 1.0d0 1.0d0
   4.0651541537167549E+02 1.0d0 1.0d0
   8.0667634870078655E+02 1.0d0 1.0d0
   1.6348107232313521E+03 1.0d0 1.0d0
   3.3969004983391187E+03 1.0d0 1.0d0
   7.2674336199173958E+03 1.0d0 1.0d0
   1.6080864381912534E+04 1.0d0 1.0d0
   3.6974131657844009E+04 1.0d0 1.0d0
   8.8762049980994911E+04 1.0d0 1.0d0
   2.2355921269411492E+05 1.0d0 1.0d0
   5.9356338843429903E+05 1.0d0 1.0d0
   1.6690413606262361E+06 1.0d0 1.0d0
   4.9925104726352403E+06 1.0d0 1.0d0
   1.5952594555420512E+07 1.0d0 1.0d0
```

```
   5.4660322670399554E+07 1.0d0 1.0d0
   2.0153596325467077E+08 1.0d0 1.0d0
30 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.5433483000000002E-02 1.0d0 1.0d0
   6.5194588593144476E-02 1.0d0 1.0d0
   1.1995577607433897E-01 1.0d0 1.0d0
   2.2073349756341545E-01 1.0d0 1.0d0
   4.0626019965028504E-01 1.0d0 1.0d0
   7.4802874797813979E-01 1.0d0 1.0d0
   1.3783189024559244E+00 1.0d0 1.0d0
   2.5427420408376111E+00 1.0d0 1.0d0
   4.6995778331749465E+00 1.0d0 1.0d0
   8.7095624280738555E+00 1.0d0 1.0d0
   1.6203216735620309E+01 1.0d0 1.0d0
   3.0302909733749487E+01 1.0d0 1.0d0
   5.7068235542655763E+01 1.0d0 1.0d0
   1.0845021407222320E+02 1.0d0 1.0d0
   2.0847323449769911E+02 1.0d0 1.0d0
   4.0651541537167549E+02 1.0d0 1.0d0
   8.0667634870078655E+02 1.0d0 1.0d0
   1.6348107232313521E+03 1.0d0 1.0d0
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   7.2674336199173958E+03 1.0d0 1.0d0
   1.6080864381912534E+04 1.0d0 1.0d0
   3.6974131657844009E+04 1.0d0 1.0d0
   8.8762049980994911E+04 1.0d0 1.0d0
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   1.6690413606262361E+06 1.0d0 1.0d0
   4.9925104726352403E+06 1.0d0 1.0d0
   1.5952594555420512E+07 1.0d0 1.0d0
   5.4660322670399554E+07 1.0d0 1.0d0
   2.0153596325467077E+08 1.0d0 1.0d0
25 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
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   6.5194588593144476E-02 1.0d0 1.0d0
   1.1995577607433897E-01 1.0d0 1.0d0
   2.2073349756341545E-01 1.0d0 1.0d0
   4.0626019965028504E-01 1.0d0 1.0d0
   7.4802874797813979E-01 1.0d0 1.0d0
   1.3783189024559244E+00 1.0d0 1.0d0
   2.5427420408376111E+00 1.0d0 1.0d0
   4.6995778331749465E+00 1.0d0 1.0d0
   8.7095624280738555E+00 1.0d0 1.0d0
   1.6203216735620309E+01 1.0d0 1.0d0
   3.0302909733749487E+01 1.0d0 1.0d0
   5.7068235542655763E+01 1.0d0 1.0d0
   1.0845021407222320E+02 1.0d0 1.0d0
   2.0847323449769911E+02 1.0d0 1.0d0
   4.0651541537167549E+02 1.0d0 1.0d0
   8.0667634870078655E+02 1.0d0 1.0d0
   1.6348107232313521E+03 1.0d0 1.0d0
   3.3969004983391187E+03 1.0d0 1.0d0
   7.2674336199173958E+03 1.0d0 1.0d0
   1.6080864381912534E+04 1.0d0 1.0d0
   3.6974131657844009E+04 1.0d0 1.0d0
   8.8762049980994911E+04 1.0d0 1.0d0
   2.2355921269411492E+05 1.0d0 1.0d0
   5.9356338843429903E+05 1.0d0 1.0d0
25 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.5433483000000002E-02 1.0d0 1.0d0
   6.5194588593144476E-02 1.0d0 1.0d0
   1.1995577607433897E-01 1.0d0 1.0d0
   2.2073349756341545E-01 1.0d0 1.0d0
   4.0626019965028504E-01 1.0d0 1.0d0
   7.4802874797813979E-01 1.0d0 1.0d0
   1.3783189024559244E+00 1.0d0 1.0d0
   2.5427420408376111E+00 1.0d0 1.0d0
   4.6995778331749465E+00 1.0d0 1.0d0
   8.7095624280738555E+00 1.0d0 1.0d0
   1.6203216735620309E+01 1.0d0 1.0d0
   3.0302909733749487E+01 1.0d0 1.0d0
   5.7068235542655763E+01 1.0d0 1.0d0
   1.0845021407222320E+02 1.0d0 1.0d0
   2.0847323449769911E+02 1.0d0 1.0d0
   4.0651541537167549E+02 1.0d0 1.0d0
   8.0667634870078655E+02 1.0d0 1.0d0
   1.6348107232313521E+03 1.0d0 1.0d0
   3.3969004983391187E+03 1.0d0 1.0d0
   7.2674336199173958E+03 1.0d0 1.0d0
   1.6080864381912534E+04 1.0d0 1.0d0
   3.6974131657844009E+04 1.0d0 1.0d0
   8.8762049980994911E+04 1.0d0 1.0d0
   2.2355921269411492E+05 1.0d0 1.0d0
   5.9356338843429903E+05 1.0d0 1.0d0
20 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.5433483000000002E-02 1.0d0 1.0d0
   6.5194588593144476E-02 1.0d0 1.0d0
   1.1995577607433897E-01 1.0d0 1.0d0
   2.2073349756341545E-01 1.0d0 1.0d0
   4.0626019965028504E-01 1.0d0 1.0d0
   7.4802874797813979E-01 1.0d0 1.0d0
```

```
   1.3783189024559244E+00 1.0d0 1.0d0
   2.5427420408376111E+00 1.0d0 1.0d0
   4.6995778331749465E+00 1.0d0 1.0d0
   8.7095624280738555E+00 1.0d0 1.0d0
   1.6203216735620309E+01 1.0d0 1.0d0
   3.0302909733749487E+01 1.0d0 1.0d0
   5.7068235542655763E+01 1.0d0 1.0d0
   1.0845021407222320E+02 1.0d0 1.0d0
   2.0847323449769911E+02 1.0d0 1.0d0
   4.0651541537167549E+02 1.0d0 1.0d0
   8.0667634870078655E+02 1.0d0 1.0d0
   1.6348107232313521E+03 1.0d0 1.0d0
   3.3969004983391187E+03 1.0d0 1.0d0
   7.2674336199173958E+03 1.0d0 1.0d0
20 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.5433483000000002E-02 1.0d0 1.0d0
   6.5194588593144476E-02 1.0d0 1.0d0
   1.1995577607433897E-01 1.0d0 1.0d0
   2.2073349756341545E-01 1.0d0 1.0d0
   4.0626019965028504E-01 1.0d0 1.0d0
   7.4802874797813979E-01 1.0d0 1.0d0
   1.3783189024559244E+00 1.0d0 1.0d0
   2.5427420408376111E+00 1.0d0 1.0d0
   4.6995778331749465E+00 1.0d0 1.0d0
   8.7095624280738555E+00 1.0d0 1.0d0
   1.6203216735620309E+01 1.0d0 1.0d0
   3.0302909733749487E+01 1.0d0 1.0d0
   5.7068235542655763E+01 1.0d0 1.0d0
   1.0845021407222320E+02 1.0d0 1.0d0
   2.0847323449769911E+02 1.0d0 1.0d0
   4.0651541537167549E+02 1.0d0 1.0d0
   8.0667634870078655E+02 1.0d0 1.0d0
   1.6348107232313521E+03 1.0d0 1.0d0
   3.3969004983391187E+03 1.0d0 1.0d0
   7.2674336199173958E+03 1.0d0 1.0d0
```

Listing A.2: *Output file for calculating the single point energy of Pb.*

A.2 Optimizing a Basis Set for a Specific Electron Configuration

This input file will optimize a WTBS basis set for protactinium with a specific electron configuration. Note that in the output file, the "freeel" variable is set to 1. "freeel" only matters if "autogen" is set to true, the actual number of electrons in open shells is determined from the electron configurations that are read in.

```
91Pa
 $contrl jobtype='bsopt' $end
 $nuc znuc=91 nucmdl=3 $end
 $bas nsym=7  bastype='wtbs' $end
 $wtbs wtbspara=1.9453737E-02 1.8578241E+00 4.9471334E+00 1.4389341E+00
       nbs=35 30 30 25 25 20 20
       start=1 1 1 1 1 1 1 $end
 $newuoa rhobeg=1.0e-1 rhoend=1.0e-5 iprint=2 maxfun=2000 $end
 $econfig nclose=7 5 5 3 3 1 1 nopen=0 0 0 1 1 1 1 nconf=6 $end
 0.0 0.0 0.0 1.0 0.0 0.0 2.0
 0.0 0.0 0.0 1.0 0.0 1.0 1.0
 0.0 0.0 0.0 1.0 0.0 2.0 0.0
 0.0 0.0 0.0 0.0 1.0 0.0 2.0
 0.0 0.0 0.0 0.0 1.0 1.0 1.0
 0.0 0.0 0.0 0.0 1.0 2.0 0.0
 $scf maxitr=100 ixtrp=1 dfctr=0.5 $end
```

Listing A.3: *Input file for Pa basis set optimization calculation.*

```
 &CONTRL
 JOBTYPE = bsopt ,
 C =    137.0359997600000
 /
 &NUC
 ZNUC =    91.00000000000000     ,
 NUCMDL =            3,
 RNUC =    0.000000000000000     ,
 ALPHA =    129305395.1200000
 /
 &BAS
 NSYM =            7,
 BASTYPE = wtbs ,
```

```
 NGROUP =            1
 /
 &WTBS
 WTBSPARA =   1.9453736999999999E-002,
               1.857824100000000     ,
               4.947133400000000     ,
               1.438934100000000     ,
 NBS =          35,
                30,
                30,
                25,
                25,
                20,
                20,
 START =           1,
                   1,
                   1,
                   1,
                   1,
                   1,
                   1,
 GROUPS =           1,
                    1,
                    1,
                    1,
                    1,
                    1,
                    1
 /
 &NEWUOA
 RHOBEG =   0.1000000000000000     ,
 RHOEND =   1.0000000000000001E-005,
 IPRINT =           2,
 MAXFUN =        2000
 /
 &ECONFIG
 NCLOSE =           7,
                    5,
                    5,
                    3,
                    3,
                    1,
                    1,
 NOPEN =           0,
                   0,
                   0,
                   1,
                   1,
                   1,
                   1,
 FREEEL =           1,
 AUTOGEN =  F,
 NCONF =           6
 /
 nconf = 6
  1  0.00  0.00  0.00  1.00  0.00  0.00  2.00
  2  0.00  0.00  0.00  1.00  0.00  1.00  1.00
  3  0.00  0.00  0.00  1.00  0.00  2.00  0.00
  4  0.00  0.00  0.00  0.00  1.00  0.00  2.00
  5  0.00  0.00  0.00  0.00  1.00  1.00  1.00
  6  0.00  0.00  0.00  0.00  1.00  2.00  0.00
 &SCF
 MAXITR =         100,
 IXTRP =           1,
 DFCTR =   0.5000000000000000     ,
 THDLL =   1.0000000000000001E-005,
 THDSL =   9.9999999999999995E-008,
 THDSS =   1.0000000000000001E-009
 /
        31560
    166068720
        82680
        82680
    221424960
 Calculating one electron integrals
 Calculating two electron integrals
 Calculating guess
 Starting SCF
 SCF converged at iteration 38 Final energy =    -27274.37615333940


                          1S+           2S+           3S+           4S+           5S+           6S+           7S+
                -4.1678558E+03 -7.8202807E+02 -1.9970550E+02 -5.2156121E+01 -1.1997891E+01 -2.0501109E+00 -1.9881466E-01


  1.9453737E-02  4.5526064E-07  6.1600046E-06 -6.1423490E-05  4.8451991E-05 -1.0511245E-04  1.3158903E-04 -1.8724908E-01
  3.6141658E-02 -1.9479713E-06 -2.6351782E-05  2.6251028E-04 -2.0608864E-04  4.3702976E-04 -4.8933088E-04 -5.0769082E-01
  6.7145353E-02  4.6364451E-06  6.2698403E-05 -6.2360865E-04  4.8527658E-04 -9.8904771E-04  2.4811733E-03 -4.9371359E-01
  1.2474818E-01 -8.4540743E-06 -1.1426442E-04  1.1332041E-03 -8.7060948E-04  1.6324965E-03  1.8661239E-02 -1.0195880E-01
  2.3178217E-01  1.3450491E-05  1.8159861E-04 -1.7957389E-03  1.3273407E-03 -2.3445935E-03  2.7533799E-01  2.9432366E-01
  4.3071120E-01 -1.9941795E-05 -2.6910486E-04  2.6311082E-03 -1.9276497E-03  1.1089307E-03  7.8850453E-01  4.5209924E-01
  8.0058681E-01  2.8321063E-05  3.8110568E-04 -3.7093835E-03  2.3287542E-03 -3.6107270E-02  5.0398773E-01  2.2648026E-01
```

```
 1.4887931E+00 -3.9289907E-05 -5.2704055E-04  5.0770781E-03 -1.9095251E-03 -4.6247606E-01 -6.1984690E-01 -2.3106351E-01
 2.7707233E+00  5.4127358E-05  7.3096927E-04 -6.5063021E-03  1.0470406E-02 -1.0705943E+00 -9.6963877E-01 -3.4091033E-01
 5.1625848E+00 -7.1730547E-05 -9.5665668E-04  8.5020340E-03  2.3278340E-01  1.2248776E-01  4.3766720E-02  1.5356681E-02
 9.6361639E+00  9.2150385E-05  1.1905804E-03 -1.4907331E-02  9.8537025E-01  1.2755242E+00  7.2196144E-01  2.2937092E-01
 1.8031447E+01 -1.2623899E-04 -1.7792297E-03 -1.1538348E-01  3.8510740E-01  3.3727265E-01  1.7145582E-01  5.4245805E-02
 3.3858337E+01  1.5373486E-04  2.6018880E-03 -6.9733818E-01 -9.8256369E-01 -6.2697726E-01 -2.9682747E-01 -9.2176854E-02
 6.3875692E+01 -1.1535749E-04  3.8093540E-02 -6.0473604E-01 -6.4464917E-01 -3.9125068E-01 -1.8064621E-01 -5.5605763E-02
 1.2125177E+02  1.2587653E-04  3.1220205E-01  3.3102664E-01  2.2711991E-01  1.2336342E-01  5.5360335E-02  1.6941375E-02
 2.3200920E+02 -1.4331244E-03  5.2657623E-01  5.2989905E-01  3.2983813E-01  1.6974036E-01  7.5889627E-02  2.3305591E-02
 4.4845175E+02 -3.5900271E-02  2.6241533E-01  2.1315943E-01  1.2658256E-01  6.4910423E-02  2.8848768E-02  8.8309114E-03
 8.7781809E+02 -1.6237035E-01 -5.4377180E-02 -2.1340131E-02 -1.0567654E-02 -5.2701286E-03 -2.2994560E-03 -6.9793578E-04
 1.7450942E+03 -2.6616678E-01 -1.5722966E-01 -8.1885030E-02 -4.2968044E-02 -2.1145552E-02 -9.3451415E-03 -2.8633384E-03
 3.5348455E+03 -2.5104786E-01 -1.3570153E-01 -6.9567552E-02 -3.6553325E-02 -1.8070096E-02 -7.9768505E-03 -2.4411779E-03
 7.3220404E+03 -1.7657870E-01 -8.7651162E-02 -4.4131448E-02 -2.3016579E-02 -1.1330730E-02 -5.0026903E-03 -1.5318434E-03
 1.5571453E+04 -1.0699572E-01 -5.0377636E-02 -2.5130416E-02 -1.3098900E-02 -6.4564612E-03 -2.8493119E-03 -8.7210360E-04
 3.4144729E+04 -6.0291269E-02 -2.7398442E-02 -1.3574384E-02 -7.0546649E-03 -3.4711606E-03 -1.5320152E-03 -4.6902952E-04
 7.7552073E+04 -3.2990939E-02 -1.4620144E-02 -7.2147644E-03 -3.7489374E-03 -1.8457668E-03 -8.1446829E-04 -2.4930193E-04
 1.8331766E+05 -1.7803523E-02 -7.7317238E-03 -3.8017386E-03 -1.9725466E-03 -9.7034370E-04 -4.2819453E-04 -1.3108227E-04
 4.5318823E+05 -9.5990017E-03 -4.1018510E-03 -2.0118317E-03 -1.0435985E-03 -5.1349929E-04 -2.2657310E-04 -6.9353811E-05
 1.1774969E+06 -5.0914462E-03 -2.1481685E-03 -1.0512710E-03 -5.4487705E-04 -2.6798839E-04 -1.1824674E-04 -3.6197166E-05
 3.2312890E+06 -2.6779367E-03 -1.1191252E-03 -5.4684284E-04 -2.8337545E-04 -1.3938706E-04 -6.1499403E-05 -1.8825057E-05
 9.4102964E+06 -1.3140471E-03 -5.4552441E-04 -2.6624977E-04 -1.3791178E-04 -6.7820854E-05 -2.9923603E-05 -9.1599121E-06
 2.9216892E+07 -6.0990887E-04 -2.5203190E-04 -1.2291586E-04 -6.3662896E-05 -3.1309573E-05 -1.3813841E-05 -4.2284427E-06
 9.7128202E+07 -1.6932067E-04 -6.9765935E-05 -3.4006601E-05 -1.7609042E-05 -8.6588446E-06 -3.8203370E-06 -1.1694392E-06
 3.4711732E+08  1.0855661E-06  4.4974166E-07  2.1919545E-07  1.1319830E-07  5.5504153E-08  2.4499931E-08  7.5040942E-09
 1.3384720E+09 -4.9489131E-07 -2.0408921E-07 -9.9444185E-08 -5.1421172E-08 -2.5249045E-08 -1.1142486E-08 -3.4118104E-09
 5.5867382E+09  9.2667492E-08  3.8202503E-08  1.8613396E-08  9.6245329E-09  4.7258361E-09  2.0855266E-09  6.3858531E-10
 2.5314129E+10 -1.2866632E-08 -5.3038951E-09 -2.5841696E-09 -1.3361905E-09 -6.5608747E-10 -2.8953396E-10 -8.8655105E-11


 1.9453737E-02 -5.0363706E-09  4.1816344E-09 -7.1130274E-08  3.2626997E-08 -1.0191264E-07  1.1005684E-07 -1.6505317E-04
 3.6141658E-02  1.8534158E-08 -2.7073422E-08  3.8148473E-07 -2.0882476E-07  5.6083489E-07 -5.6502652E-07 -6.0995107E-04
 6.7145353E-02 -3.8743877E-08  9.3105993E-08 -1.1705575E-06  7.0835292E-07 -1.6996928E-06  4.0121203E-06 -8.0851446E-04
 1.2474818E-01  6.2211854E-08 -2.3973054E-07  2.7968485E-06 -1.7915559E-06  3.7853494E-06  4.1745601E-05 -2.2754793E-04
 2.3178217E-01 -8.5290474E-08  5.3161181E-07 -5.8924309E-06  3.8006383E-06 -7.3563981E-06  8.3761902E-04  8.9545248E-04
 4.3071120E-01  1.0208035E-07 -1.0912541E-06  1.1564757E-05 -7.6428230E-06  4.9288760E-06  3.2706490E-03  1.8751516E-03
 8.0058681E-01 -1.0113876E-07  2.1306620E-06 -2.1943188E-05  1.2659057E-05 -2.0469811E-04  2.8494050E-03  1.2804352E-03
 1.4887931E+00  5.7963374E-08 -4.0508702E-06  4.0571690E-05 -1.3989995E-05 -3.5664257E-03 -4.7796997E-03 -1.7817799E-03
 2.7707233E+00  8.0268709E-08  7.7097835E-06 -7.0519182E-05  1.0916315E-04 -1.1264127E-02 -1.0199493E-02 -3.5858463E-03
 5.1625848E+00 -3.7857508E-07 -1.3828225E-05  1.2511857E-04  3.3482341E-03  1.7666122E-03  6.3456555E-04  2.2254868E-04
 9.6361639E+00  9.5854938E-07  2.3593188E-05 -2.9713533E-04  1.9342317E-02  2.5017145E-02  1.4157942E-02  4.4979590E-03
 1.8031447E+01 -2.3080850E-06 -4.8277108E-05 -3.1055434E-03  1.0304204E-02  9.0112601E-03  4.5792045E-03  1.4487425E-03
 3.3858337E+01  4.2624324E-06  9.6726112E-05 -2.5736242E-02 -3.6158839E-02 -2.3065390E-02 -1.0918611E-02 -3.3905903E-03
 6.3875692E+01 -3.9222807E-06  1.9604252E-03 -3.0450329E-02 -3.2337647E-02 -1.9610198E-02 -9.0525363E-03 -2.7863962E-03
 1.2125177E+02  6.0105809E-06  2.2053270E-02  2.3275860E-02  1.5984258E-02  8.6821874E-03  3.8967421E-03  1.1925690E-03
 2.3200920E+02 -1.4693522E-04  5.0989297E-02  5.0595306E-02  3.1409317E-02  1.6152076E-02  7.2202503E-03  2.2172770E-03
 4.4845175E+02 -5.3310399E-03  3.4317940E-02  2.7410756E-02  1.6222173E-02  8.3130239E-03  3.6937536E-03  1.1306051E-03
 8.7781809E+02 -3.3138881E-02 -1.1199777E-02 -4.7571173E-03 -2.4170697E-03 -1.2082964E-03 -5.2904485E-04 -1.6088394E-04
 1.7450942E+03 -7.4346622E-02 -4.0725194E-02 -2.1062736E-02 -1.1035434E-02 -5.4284824E-03 -2.3988415E-03 -7.3499143E-04
 3.5348455E+03 -9.4791276E-02 -4.7154793E-02 -2.3907837E-02 -1.2529869E-02 -6.1904548E-03 -2.7322183E-03 -8.3610751E-04
 7.3220404E+03 -8.8657364E-02 -4.0506359E-02 -2.0147306E-02 -1.0475076E-02 -5.1518739E-03 -2.2742441E-03 -6.9638073E-04
 1.5571453E+04 -6.9734773E-02 -3.0375011E-02 -1.4973564E-02 -7.7832300E-03 -3.8340378E-03 -1.6916478E-03 -5.1773708E-04
 3.4144729E+04 -4.9557458E-02 -2.1009571E-02 -1.0294910E-02 -5.3347585E-03 -2.6224758E-03 -1.1572758E-03 -3.5430612E-04
 7.7552073E+04 -3.2965670E-02 -1.3787754E-02 -6.7413567E-03 -3.4955699E-03 -1.7203202E-03 -7.5897747E-04 -2.3230106E-04
 1.8331766E+05 -2.0881919E-02 -8.6643540E-03 -4.2282845E-03 -2.1893129E-03 -1.0762097E-03 -4.7486954E-04 -1.4537414E-04
 4.5318823E+05 -1.2669461E-02 -5.2369602E-03 -2.5546250E-03 -1.3236088E-03 -6.5117130E-04 -2.8728442E-04 -8.7932535E-05
 1.1774969E+06 -7.3479864E-03 -3.0292815E-03 -1.4766257E-03 -7.6444915E-04 -3.7581084E-04 -1.6581658E-04 -5.0760481E-05
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  3.3858337E+01  2.0918124E-01 -9.0538223E-02  6.8020582E-02  1.8184440E-02
  6.3875692E+01  3.6808534E-01  1.7719762E-01 -7.2767881E-02 -1.8121532E-02
  1.2125177E+02  3.1529005E-01  1.8203443E-01 -8.0174035E-02 -2.0259119E-02
  2.3200920E+02  1.7091567E-01  9.9398001E-02 -4.3637462E-02 -1.1003657E-02
  4.4845175E+02  6.9494681E-02  3.9939466E-02 -1.7558094E-02 -4.4348522E-03
  8.7781809E+02  2.3873371E-02  1.3493698E-02 -5.8836773E-03 -1.4818314E-03
  1.7450942E+03  7.6257647E-03  4.2969254E-03 -1.8824352E-03 -4.7542439E-04
  3.5348455E+03  2.3509435E-03  1.3111106E-03 -5.6913149E-04 -1.4316013E-04
  7.3220404E+03  7.7673255E-04  4.3465144E-04 -1.9037934E-04 -4.8106375E-05
  1.5571453E+04  2.4819454E-04  1.3762045E-04 -5.9590324E-05 -1.4976820E-05
  3.4144729E+04  1.0097160E-04  5.6322678E-05 -2.4649097E-05 -6.2274833E-06
  7.7552073E+04  2.3593046E-05  1.3051841E-05 -5.6438896E-06 -1.4177230E-06
  1.8331766E+05  1.9141952E-05  1.0646356E-05 -4.6448722E-06 -1.1718580E-06


  1.9453737E-02 -2.3494679E-08  2.6208878E-09  4.6634915E-08  2.0101141E-05
  3.6141658E-02 -1.9322798E-08  6.5634513E-08 -1.9694197E-07  1.6643639E-04
  6.7145353E-02 -3.7623054E-08 -1.3504919E-07  4.5212975E-07  5.4281184E-04
  1.2474818E-01 -1.7982510E-07  4.7295761E-07 -1.6027518E-06  1.0454788E-03
  2.3178217E-01 -1.0906279E-07 -6.8682944E-07 -3.8029510E-06  1.4830538E-03
  4.3071120E-01 -8.6077940E-07  2.1426726E-06 -1.2615206E-04  1.4546706E-03
  8.0058681E-01 -6.0012341E-07 -1.6582379E-06 -1.1417297E-03  5.5549240E-04
  1.4887931E+00 -3.7513449E-06  2.5787163E-06 -4.5032764E-03 -1.3286172E-03
  2.7707233E+00 -3.9610437E-06 -2.7331159E-04 -7.7561746E-03 -2.5348380E-03
  5.1625848E+00 -1.2698453E-05 -3.3672176E-03 -3.7359314E-03 -1.2732659E-03
  9.6361639E+00  5.8900205E-05 -1.3005742E-02  6.7252198E-03  1.7056459E-03
  1.8031447E+01  1.7787270E-03 -1.7785899E-02  1.0400561E-02  2.7403220E-03
  3.3858337E+01  1.1643180E-02 -5.0457069E-03  3.7911647E-03  1.0135104E-03
  6.3875692E+01  2.8130069E-02  1.3583480E-02 -5.5843513E-03 -1.3909320E-03
  1.2125177E+02  3.2908758E-02  1.9024063E-02 -8.3813030E-03 -2.1179794E-03
  2.3200920E+02  2.4220728E-02  1.4094371E-02 -6.1882584E-03 -1.5604250E-03
  4.4845175E+02  1.3211997E-02  7.5954655E-03 -3.3396728E-03 -8.4360128E-04
  8.7781809E+02  5.9478115E-03  3.3626162E-03 -1.4658614E-03 -3.6912643E-04
  1.7450942E+03  2.3895830E-03  1.3480030E-03 -5.9112469E-04 -1.4935917E-04
  3.5348455E+03  8.7767933E-04  4.8937629E-04 -2.1203365E-04 -5.3281030E-05
  7.3220404E+03  3.1659229E-04  1.7794360E-04 -7.8319996E-05 -1.9834947E-05
  1.5571453E+04  1.0762715E-04  5.9443293E-05 -2.5514972E-05 -6.3839772E-06
  3.4144729E+04  3.8715731E-05  2.1846633E-05 -9.7070014E-06 -2.4699387E-06
  7.7552073E+04  1.1319909E-05  6.1760611E-06 -2.6064317E-06 -6.4670721E-07
  1.8331766E+05  5.6586060E-06  3.1874249E-06 -1.4152137E-06 -3.6001496E-07


                         3D+            4D+            5D+            6D+
                -1.2828009E+02 -2.6929354E+01 -3.8109062E+00 -1.8232759E-01


  1.9453737E-02 -1.7210672E-06  7.3132785E-06 -2.7776140E-05 -1.9530883E-02
  3.6141658E-02  6.0569545E-06 -2.6038313E-05  1.1990627E-04 -1.0438260E-01
  6.7145353E-02 -1.2879308E-05  5.3836184E-05 -1.6720252E-04 -2.3373561E-01
  1.2474818E-01  2.2080100E-05 -9.2557207E-05  5.8753465E-04 -3.1566074E-01
  2.3178217E-01 -3.4204831E-05  1.3382386E-04  1.4429520E-03 -3.1354910E-01
  4.3071120E-01  5.0047368E-05 -2.2717258E-04  2.5351517E-02 -2.0760139E-01
  8.0058681E-01 -7.0646065E-05  2.1103922E-04  1.5247930E-01 -3.9034285E-02
  1.4887931E+00  9.8359381E-05  2.7872922E-04  4.0535099E-01  1.2157603E-01
  2.7707233E+00 -1.0556997E-04  2.1603697E-02  4.6918787E-01  1.4784763E-01
  5.1625848E+00 -4.9550393E-05  1.7560741E-01  1.2765354E-01  4.3641198E-02
  9.6361639E+00 -3.7085325E-03  4.5397419E-01 -2.4344193E-01 -6.0722751E-02
```

```
  1.8031447E+01 -5.3425366E-02  4.1453450E-01 -2.4127529E-01 -6.1822179E-02
  3.3858337E+01 -2.2898645E-01  5.5727504E-02 -4.9313322E-02 -1.2973639E-02
  6.3875692E+01 -3.7665564E-01 -1.9087229E-01  7.9486784E-02  1.9348904E-02
  1.2125177E+02 -3.0417809E-01 -1.7732290E-01  7.7728580E-02  1.9124179E-02
  2.3200920E+02 -1.5582420E-01 -9.0941139E-02  3.9705444E-02  9.7488921E-03
  4.4845175E+02 -5.9172363E-02 -3.4051989E-02  1.4873841E-02  3.6575156E-03
  8.7781809E+02 -1.8361206E-02 -1.0392119E-02  4.5029277E-03  1.1039906E-03
  1.7450942E+03 -5.0293490E-03 -2.8410282E-03  1.2378659E-03  3.0452018E-04
  3.5348455E+03 -1.2433202E-03 -6.9394483E-04  2.9877826E-04  7.3078820E-05
  7.3220404E+03 -2.9812421E-04 -1.6799494E-04  7.3538561E-05  1.8143947E-05
  1.5571453E+04 -6.5763503E-05 -3.6294888E-05  1.5444178E-05  3.7554984E-06
  3.4144729E+04 -1.5152583E-05 -8.6075592E-06  3.8213515E-06  9.4970447E-07
  7.7552073E+04 -2.7567414E-06 -1.4902716E-06  6.1579429E-07  1.4740009E-07
  1.8331766E+05 -8.5925459E-07 -4.8980789E-07  2.1885493E-07  5.4570737E-08


  1.9453737E-02 -4.7665861E-09  8.1805294E-09 -3.6249172E-08 -2.6296851E-05
  3.6141658E-02  1.9195897E-08 -4.2306839E-08  2.1627369E-07 -1.9156671E-04
  6.7145353E-02 -4.8849001E-08  1.2343567E-07 -4.1049585E-07 -5.8467694E-04
  1.2474818E-01  1.0380432E-07 -2.9641068E-07  1.9900451E-06 -1.0762744E-03
  2.3178217E-01 -2.0414601E-07  5.9173652E-07  6.7275140E-06 -1.4572199E-03
  4.3071120E-01  3.8613103E-07 -1.3933250E-06  1.6059381E-04 -1.3152239E-03
  8.0058681E-01 -7.1410391E-07  1.7536461E-06  1.3171861E-03 -3.3708597E-04
  1.4887931E+00  1.3136455E-06  3.3901664E-06  4.7746749E-03  1.4319939E-03
  2.7707233E+00 -1.9267861E-06  3.4719011E-04  7.5386331E-03  2.3753685E-03
  5.1625848E+00 -7.4723028E-07  3.8540012E-03  2.7970369E-03  9.5627200E-04
  9.6361639E+00 -1.1191286E-04  1.3605693E-02 -7.2944336E-03 -1.8194942E-03
  1.8031447E+01 -2.1949542E-03  1.6976115E-02 -9.8769744E-03 -2.5306567E-03
  3.3858337E+01 -1.2885923E-02  3.0958817E-03 -2.7485193E-03 -7.2321262E-04
  6.3875692E+01 -2.9036735E-02 -1.4706197E-02  6.1253089E-03  1.4911026E-03
  1.2125177E+02 -3.2140078E-02 -1.8703353E-02  8.1956820E-03  2.0163590E-03
  2.3200920E+02 -2.2569729E-02 -1.3141606E-02  5.7348291E-03  1.4079636E-03
  4.4845175E+02 -1.1722481E-02 -6.7283794E-03  2.9373860E-03  7.2227047E-04
  8.7781809E+02 -4.9597391E-03 -2.7988715E-03  1.2118459E-03  2.9706335E-04
  1.7450942E+03 -1.8420135E-03 -1.0375926E-03  4.5193033E-04  1.1118511E-04
  3.5348455E+03 -6.1075133E-04 -3.3963629E-04  1.4600229E-04  3.5690622E-05
  7.3220404E+03 -1.9417130E-04 -1.0924950E-04  4.7892364E-05  1.1828134E-05
  1.5571453E+04 -5.5414419E-05 -3.0380139E-05  1.2843419E-05  3.1128767E-06
  3.4144729E+04 -1.6218355E-05 -9.2679551E-06  4.1602860E-06  1.0398485E-06
  7.7552073E+04 -3.6486776E-06 -1.9252975E-06  7.6724542E-07  1.7990722E-07
  1.8331766E+05 -1.2882697E-06 -7.5080026E-07  3.4612983E-07  8.7631389E-08


                          4F-             5F-
                -1.4283914E+01 -2.9213544E-01


  1.9453737E-02  6.6519343E-06 -7.5234628E-05
  3.6141658E-02 -2.1360454E-05 -2.6536652E-03
  6.7145353E-02  4.6289376E-05 -1.8069774E-02
  1.2474818E-01 -6.6350273E-05 -5.9145321E-02
  2.3178217E-01  1.2967025E-04 -1.2997399E-01
  4.3071120E-01 -1.3368066E-04 -2.2013932E-01
  8.0058681E-01  4.0938667E-04 -2.9387764E-01
  1.4887931E+00  3.0219209E-03 -3.0617901E-01
  2.7707233E+00  3.7821876E-02 -2.2297888E-01
  5.1625848E+00  1.5394501E-01 -7.7968302E-02
  9.6361639E+00  3.0647180E-01  5.1295935E-02
  1.8031447E+01  3.4548477E-01  9.1788477E-02
  3.3858337E+01  2.5411508E-01  7.2862946E-02
  6.3875692E+01  1.2634752E-01  3.7217372E-02
  1.2125177E+02  4.5722954E-02  1.3327572E-02
  2.3200920E+02  1.3450450E-02  3.9475329E-03
  4.4845175E+02  3.1290776E-03  9.0396660E-04
  8.7781809E+02  7.5391295E-04  2.2220654E-04
  1.7450942E+03  1.2847135E-04  3.6367372E-05
  3.5348455E+03  4.9214287E-05  1.4522570E-05


  1.9453737E-02  9.7802298E-09 -1.1425213E-07
  3.6141658E-02 -4.5904641E-08 -5.5196843E-06
  6.7145353E-02  1.2937723E-07 -5.1249869E-05
  1.2474818E-01 -2.6772194E-07 -2.2864402E-04
  2.3178217E-01  6.6021547E-07 -6.8490365E-04
  4.3071120E-01 -1.0452365E-06 -1.5812801E-03
  8.0058681E-01  3.7845584E-06 -2.8778807E-03
  1.4887931E+00  3.9665323E-05 -4.0883228E-03
  2.7707233E+00  6.8727947E-04 -4.0609157E-03
  5.1625848E+00  3.8233705E-03 -1.9368644E-03
  9.6361639E+00  1.0396309E-02  1.7415482E-03
  1.8031447E+01  1.6009999E-02  4.2547758E-03
  3.3858337E+01  1.6086541E-02  4.6134703E-03
  6.3875692E+01  1.0916987E-02  3.2160372E-03
  1.2125177E+02  5.3763349E-03  1.5670944E-03
  2.3200920E+02  2.1331360E-03  6.2619880E-04
  4.4845175E+02  6.6181052E-04  1.9105941E-04
  8.7781809E+02  2.0336879E-04  6.0086793E-05
  1.7450942E+03  4.5163176E-05  1.2694798E-05
  3.5348455E+03  1.7481944E-05  5.2199366E-06


                          4F+             5F+
```

```
                -1.3899400E+01 -2.7004390E-01


  1.9453737E-02 -7.5710755E-06  1.4358729E-04
  3.6141658E-02  2.4162114E-05  3.7346339E-03
  6.7145353E-02 -5.2886361E-05  2.2106892E-02
  1.2474818E-01  7.4984490E-05  6.6652471E-02
  2.3178217E-01 -1.4619715E-04  1.3906611E-01
  4.3071120E-01  1.5321002E-04  2.2654866E-01
  8.0058681E-01 -4.5908422E-04  2.9384540E-01
  1.4887931E+00 -3.4599894E-03  3.0112350E-01
  2.7707233E+00 -4.0854397E-02  2.1487666E-01
  5.1625848E+00 -1.6027303E-01  6.9670258E-02
  9.6361639E+00 -3.1187985E-01 -5.4403079E-02
  1.8031447E+01 -3.4421117E-01 -9.0715310E-02
  3.3858337E+01 -2.4827600E-01 -7.0373982E-02
  6.3875692E+01 -1.2151771E-01 -3.5284216E-02
  1.2125177E+02 -4.2830578E-02 -1.2308746E-02
  2.3200920E+02 -1.2088313E-02 -3.4969605E-03
  4.4845175E+02 -2.6662822E-03 -7.5896215E-04
  8.7781809E+02 -5.7540121E-04 -1.6751694E-04
  1.7450942E+03 -8.8544591E-05 -2.4524420E-05
  3.5348455E+03 -2.3576924E-05 -6.9470986E-06


  1.9453737E-02 -1.2101571E-08  2.1907964E-07
  3.6141658E-02  5.1973800E-08  7.7720385E-06
  6.7145353E-02 -1.5341845E-07  6.2702951E-05
  1.2474818E-01  2.9575690E-07  2.5768755E-04
  2.3178217E-01 -7.7984903E-07  7.3285185E-04
  4.3071120E-01  1.1153267E-06  1.6274525E-03
  8.0058681E-01 -4.5192354E-06  2.8778425E-03
  1.4887931E+00 -4.6192042E-05  4.0215028E-03
  2.7707233E+00 -7.4463276E-04  3.9142810E-03
  5.1625848E+00 -3.9866749E-03  1.7314970E-03
  9.6361639E+00 -1.0595697E-02 -1.8487122E-03
  1.8031447E+01 -1.5983972E-02 -4.2120077E-03
  3.3858337E+01 -1.5775294E-02 -4.4706439E-03
  6.3875692E+01 -1.0569570E-02 -3.0682566E-03
  1.2125177E+02 -5.1013080E-03 -1.4655355E-03
  2.3200920E+02 -1.9715140E-03 -5.7017825E-04
  4.4845175E+02 -5.9357692E-04 -1.6884944E-04
  8.7781809E+02 -1.7454005E-04 -5.0836243E-05
  1.7450942E+03 -3.6449349E-05 -1.0060536E-05
  3.5348455E+03 -1.2858668E-05 -3.8037142E-06


 Calculated energy =   -2.7274376153339403E+04
 Literature energy =   -2.7274378906250000E+04
 Difference (cal - lit) = 2.75E-03
 Relative error (abs((cal - lit)/lit)) = 1.01E-07
 SCF converged at iteration 38 Final energy =    -27274.37615333940
 SCF converged at iteration 40 Final energy =    -27274.37652373574
 SCF converged at iteration 39 Final energy =    -27274.36557271042
 SCF converged at iteration 38 Final energy =    -27274.37328631207
 SCF converged at iteration 38 Final energy =    -27274.37681712200
 SCF converged at iteration 36 Final energy =    -27274.37555675471
 SCF converged at iteration 38 Final energy =    -27274.02325483119
 SCF converged at iteration 38 Final energy =    -27274.37703303956
 SCF converged at iteration 38 Final energy =    -27274.37463387263
 SCF converged at iteration 40 Final energy =    -27274.36624593227
 SCF converged at iteration 39 Final energy =    -27274.36325682023
 SCF converged at iteration 38 Final energy =    -27274.37675780536
 SCF converged at iteration 40 Final energy =    -27274.37705991919
 SCF converged at iteration 40 Final energy =    -27274.37711582447
 SCF converged at iteration 39 Final energy =    -27274.36526340017
 SCF converged at iteration 40 Final energy =    -27274.37525627186
 SCF converged at iteration 40 Final energy =    -27274.37554430689
 SCF converged at iteration 39 Final energy =    -27274.37525819958
 SCF converged at iteration 40 Final energy =    -27274.37618439044
 SCF converged at iteration 40 Final energy =    -27274.37569386304
       interm  rho nf F del 0.010000000    20   -27274.377 115 824 5   -27274.377 115 824 5
  :::>   1.1000000       1.0000000      0.90000000       1.0000000
 SCF converged at iteration 40 Final energy =    -27274.37624394280
 SCF converged at iteration 40 Final energy =    -27274.37681479764
 SCF converged at iteration 40 Final energy =    -27274.37660684840
 SCF converged at iteration 40 Final energy =    -27274.37710938528
 SCF converged at iteration 40 Final energy =    -27274.37709990601
 SCF converged at iteration 40 Final energy =    -27274.37712130963
 SCF converged at iteration 40 Final energy =    -27274.37716226352
 SCF converged at iteration 40 Final energy =    -27274.37717442678
 SCF converged at iteration 40 Final energy =    -27274.37716723333
 SCF converged at iteration 40 Final energy =    -27274.37709635337
 SCF converged at iteration 40 Final energy =    -27274.37717330824
 SCF converged at iteration 40 Final energy =    -27274.37700224991
 SCF converged at iteration 40 Final energy =    -27274.37717427240
 SCF converged at iteration 40 Final energy =    -27274.37679601249
 SCF converged at iteration 40 Final energy =    -27274.37717971213
 SCF converged at iteration 40 Final energy =    -27274.37716637889
 SCF converged at iteration 40 Final energy =    -27274.37680382172
 SCF converged at iteration 40 Final energy =    -27274.37718793943
 SCF converged at iteration 40 Final energy =    -27274.37718724257
```

```
 SCF converged at iteration 40 Final energy =    -27274.37697998060
 SCF converged at iteration 40 Final energy =    -27274.37719820330
 SCF converged at iteration 40 Final energy =    -27274.37720555374
 SCF converged at iteration 40 Final energy =    -27274.37721015110
 SCF converged at iteration 40 Final energy =    -27274.37721989711
 SCF converged at iteration 40 Final energy =    -27274.37723141619
 SCF converged at iteration 40 Final energy =    -27274.37724506508
 SCF converged at iteration 40 Final energy =    -27274.37727356602
 SCF converged at iteration 40 Final energy =    -27274.37726115421
 SCF converged at iteration 40 Final energy =    -27274.37679573947
 SCF converged at iteration 40 Final energy =    -27274.37729431578
 SCF converged at iteration 40 Final energy =    -27274.37731317497
 SCF converged at iteration 40 Final energy =    -27274.37732184126
 SCF converged at iteration 40 Final energy =    -27274.37734102829
 SCF converged at iteration 40 Final energy =    -27274.37737425937
 SCF converged at iteration 41 Final energy =    -27274.37741422374
 SCF converged at iteration 40 Final energy =    -27274.37747058523
 SCF converged at iteration 41 Final energy =    -27274.37143110862
 SCF converged at iteration 41 Final energy =    -27274.37751839181
 SCF converged at iteration 41 Final energy =    -27274.37753025332
 SCF converged at iteration 40 Final energy =    -27274.37668602075
 SCF converged at iteration 41 Final energy =    -27274.37739254861
 SCF converged at iteration 41 Final energy =    -27274.37729343396
 SCF converged at iteration 41 Final energy =    -27274.37753046981
 SCF converged at iteration 41 Final energy =    -27274.37738289865
 SCF converged at iteration 41 Final energy =    -27274.37745108623
 SCF converged at iteration 41 Final energy =    -27274.37745035628
 SCF converged at iteration 41 Final energy =    -27274.37752038428
 SCF converged at iteration 41 Final energy =    -27274.37747841063
 SCF converged at iteration 41 Final energy =    -27274.37753539678
 SCF converged at iteration 41 Final energy =    -27274.37753189082
 SCF converged at iteration 41 Final energy =    -27274.37753338237
 SCF converged at iteration 41 Final energy =    -27274.37739192332
 SCF converged at iteration 41 Final energy =    -27274.37753340209
 SCF converged at iteration 41 Final energy =    -27274.37753764559
 SCF converged at iteration 41 Final energy =    -27274.37753647355
 SCF converged at iteration 41 Final energy =    -27274.37743857712
 SCF converged at iteration 41 Final energy =    -27274.37753417706
 SCF converged at iteration 41 Final energy =    -27274.37746150104
 SCF converged at iteration 41 Final energy =    -27274.37753562298
 SCF converged at iteration 41 Final energy =    -27274.37727249676
 SCF converged at iteration 41 Final energy =    -27274.37753843775
 SCF converged at iteration 41 Final energy =    -27274.37743420742
 SCF converged at iteration 41 Final energy =    -27274.37744247752
 SCF converged at iteration 41 Final energy =    -27274.37753800378
 SCF converged at iteration 41 Final energy =    -27274.37752144962
 SCF converged at iteration 41 Final energy =    -27274.37753749272
       interm  rho nf F del 0.001000000    86   -27274.377 538 437 7       -0.000 422 613 3
  :::>   1.6627416       1.0021141       1.0254277       1.0623435
 SCF converged at iteration 41 Final energy =    -27274.37753764903
 SCF converged at iteration 41 Final energy =    -27274.37753839733
 SCF converged at iteration 41 Final energy =    -27274.37753881774
 SCF converged at iteration 41 Final energy =    -27274.37753908531
 SCF converged at iteration 41 Final energy =    -27274.37753966563
 SCF converged at iteration 41 Final energy =    -27274.37754040643
 SCF converged at iteration 41 Final energy =    -27274.37754022898
 SCF converged at iteration 41 Final energy =    -27274.37751653413
 SCF converged at iteration 41 Final energy =    -27274.37754015865
 SCF converged at iteration 41 Final energy =    -27274.37753751040
 SCF converged at iteration 41 Final energy =    -27274.37754101662
 SCF converged at iteration 41 Final energy =    -27274.37754084213
 SCF converged at iteration 41 Final energy =    -27274.37753869069
 SCF converged at iteration 41 Final energy =    -27274.37754104751
 SCF converged at iteration 41 Final energy =    -27274.37753933119
 SCF converged at iteration 41 Final energy =    -27274.37754116962
 SCF converged at iteration 41 Final energy =    -27274.37754138718
 SCF converged at iteration 41 Final energy =    -27274.37754179706
 SCF converged at iteration 41 Final energy =    -27274.37754246896
 SCF converged at iteration 41 Final energy =    -27274.37754335791
 SCF converged at iteration 41 Final energy =    -27274.37754042695
 SCF converged at iteration 41 Final energy =    -27274.37748754261
 SCF converged at iteration 41 Final energy =    -27274.37754395899
 SCF converged at iteration 41 Final energy =    -27274.37749778102
 SCF converged at iteration 41 Final energy =    -27274.37754367125
 SCF converged at iteration 41 Final energy =    -27274.37753077486
 SCF converged at iteration 41 Final energy =    -27274.37754428152
 SCF converged at iteration 41 Final energy =    -27274.37754418491
 SCF converged at iteration 41 Final energy =    -27274.37754109361
 SCF converged at iteration 41 Final energy =    -27274.37754440276
 SCF converged at iteration 41 Final energy =    -27274.37754461948
 SCF converged at iteration 41 Final energy =    -27274.37754500144
 SCF converged at iteration 41 Final energy =    -27274.37754557010
 SCF converged at iteration 41 Final energy =    -27274.37754603123
 SCF converged at iteration 41 Final energy =    -27274.37754609415
 SCF converged at iteration 41 Final energy =    -27274.37754610645
 SCF converged at iteration 41 Final energy =    -27274.37754254067
 SCF converged at iteration 41 Final energy =    -27274.37754561090
 SCF converged at iteration 41 Final energy =    -27274.37754609332
 SCF converged at iteration 41 Final energy =    -27274.37754602444
 SCF converged at iteration 41 Final energy =    -27274.37754608405
 SCF converged at iteration 41 Final energy =    -27274.37754392067
 SCF converged at iteration 41 Final energy =    -27274.37754610813
```

```
 SCF converged at iteration 41 Final energy =    -27274.37754439248
 SCF converged at iteration 41 Final energy =    -27274.37754610794
 SCF converged at iteration 41 Final energy =    -27274.37754526297
 SCF converged at iteration 41 Final energy =    -27274.37754610373
 SCF converged at iteration 41 Final energy =    -27274.37754374482
 SCF converged at iteration 41 Final energy =    -27274.37754610522
 SCF converged at iteration 41 Final energy =    -27274.37754610387
 SCF converged at iteration 41 Final energy =    -27274.37754610267
       interm  rho nf F del 0.000100000   137   -27274.377 546 108 1       -0.000 007 670 4
  :::>   1.6853380       1.0025643       1.0865944       1.1572454
 SCF converged at iteration 41 Final energy =    -27274.37754610732
 SCF converged at iteration 41 Final energy =    -27274.37754605688
 SCF converged at iteration 41 Final energy =    -27274.37754610859
 SCF converged at iteration 41 Final energy =    -27274.37754610906
 SCF converged at iteration 41 Final energy =    -27274.37754610936
 SCF converged at iteration 41 Final energy =    -27274.37754610938
 SCF converged at iteration 41 Final energy =    -27274.37754610937
 SCF converged at iteration 41 Final energy =    -27274.37754609040
 SCF converged at iteration 41 Final energy =    -27274.37754610926
 SCF converged at iteration 41 Final energy =    -27274.37754608270
 SCF converged at iteration 41 Final energy =    -27274.37754610941
 SCF converged at iteration 41 Final energy =    -27274.37754610939
 SCF converged at iteration 41 Final energy =    -27274.37754608488
 SCF converged at iteration 41 Final energy =    -27274.37754610936
 SCF converged at iteration 41 Final energy =    -27274.37754608941
 SCF converged at iteration 41 Final energy =    -27274.37754610772
 SCF converged at iteration 41 Final energy =    -27274.37754610937
 SCF converged at iteration 41 Final energy =    -27274.37754608604
 SCF converged at iteration 41 Final energy =    -27274.37754610927
       interm  rho nf F del 0.000010000   156   -27274.377 546 109 4       -0.000 000 001 3
  :::>   1.6849066       1.0025845       1.0874081       1.1585546
 SCF converged at iteration 41 Final energy =    -27274.37754610938
 SCF converged at iteration 41 Final energy =    -27274.37754610940
 SCF converged at iteration 41 Final energy =    -27274.37754610942
 SCF converged at iteration 41 Final energy =    -27274.37754610938
 SCF converged at iteration 41 Final energy =    -27274.37754610911
 SCF converged at iteration 41 Final energy =    -27274.37754610940
 SCF converged at iteration 41 Final energy =    -27274.37754610917
 SCF converged at iteration 41 Final energy =    -27274.37754610942
 SCF converged at iteration 41 Final energy =    -27274.37754610939
 SCF converged at iteration 41 Final energy =    -27274.37754610940
 SCF converged at iteration 41 Final energy =    -27274.37754610939
 SCF converged at iteration 41 Final energy =    -27274.37754610930
 SCF converged at iteration 41 Final energy =    -27274.37754610940
 SCF converged at iteration 41 Final energy =    -27274.37754610910
 SCF converged at iteration 41 Final energy =    -27274.37754610940
 SCF converged at iteration 41 Final energy =    -27274.37754610916
 SCF converged at iteration 41 Final energy =    -27274.37754610941

     At the return from NEWUOA     number of function values =   173
     F=  -27274.37754610942
        1.6848935       1.0025849       1.0874118       1.1585570
 New parameters are
  3.2777475E-02  1.8626263E+00  5.3795715E+00  1.6670872E+00
 SCF converged at iteration 41 Final energy =    -27274.37754610942


                         1S+            2S+            3S+            4S+            5S+            6S+            7S+
               -4.1678552E+03 -7.8202739E+02 -1.9970482E+02 -5.2155429E+01 -1.1997194E+01 -2.0494257E+00 -1.9849676E-01


  3.2777475E-02  6.3766410E-07  5.7309076E-06 -6.1014939E-05  1.3503449E-04 -8.9549947E-05  2.0217706E-04  7.7763953E-01
  6.1052208E-02 -2.7212503E-06 -2.4451140E-05  2.5997072E-04 -5.7257873E-04  3.6084676E-04 -1.8505829E-03  1.9084131E-01
  1.1371780E-01  6.4661788E-06  5.8087512E-05 -6.1594002E-04  1.3479564E-03 -7.5938581E-04 -1.0442761E-02  4.3509449E-01
  2.1181678E-01 -1.1776869E-05 -1.0570257E-04  1.1185370E-03 -2.4045368E-03  1.2148510E-03 -2.1151300E-01 -4.1956006E-01
  3.9455421E-01  1.8769658E-05  1.6866127E-04 -1.7636196E-03  3.7907496E-03 -1.2618495E-04 -7.3718664E-01 -3.5322441E-01
  7.3499994E-01 -2.7775219E-05 -2.4890013E-04  2.6020802E-03 -5.2448412E-03  2.1094051E-02 -6.2243418E-01 -3.3766148E-01
  1.3694267E+00  3.9581146E-05  3.5469575E-04 -3.6690519E-03  6.5256712E-03  3.6524111E-01  4.7977497E-01  2.0741439E-01
  2.5522453E+00 -5.5531012E-05 -5.0644472E-04  4.8195743E-03 -1.3768212E-02  1.0628665E+00  1.0136423E+00  3.4555769E-01
  4.7592004E+00  7.5042533E-05  6.7454424E-04 -6.6562007E-03 -1.5840398E-01  1.2336517E-01  1.2190063E-01  4.7160748E-02
  8.8821010E+00 -9.9650704E-05 -8.8184744E-04  1.1265810E-02 -9.1814825E-01 -1.2574109E+00 -7.1892239E-01 -2.3332330E-01
  1.6598538E+01  1.3971887E-04  1.4607049E-03  7.8898658E-02 -5.7101352E-01 -5.1418558E-01 -2.6643838E-01 -8.2270513E-02
  3.1079528E+01 -1.7602025E-04 -2.0695834E-03  6.1053018E-01  8.6852650E-01  5.6179744E-01  2.6866146E-01  8.2644473E-02
  5.8358006E+01  1.6963083E-04 -2.3283094E-02  7.0220007E-01  7.7741233E-01  4.7333116E-01  2.1834120E-01  6.7834903E-02
  1.1000966E+02 -2.3821652E-04 -2.5386103E-01 -2.1304165E-01 -1.4183476E-01 -7.6052348E-02 -3.3602641E-02 -1.0499887E-02
  2.0848751E+02  8.5338160E-04 -5.1752274E-01 -5.4684268E-01 -3.4531663E-01 -1.7912344E-01 -8.0359590E-02 -2.4606349E-02
  3.9793692E+02  2.2723041E-02 -3.2469759E-01 -2.6916770E-01 -1.6072880E-01 -8.2191235E-02 -3.6464966E-02 -1.1231440E-02
  7.6660359E+02  1.2996824E-01  7.6465413E-03 -8.8975780E-03 -6.2835928E-03 -3.2962445E-03 -1.5389625E-03 -4.5630116E-04
  1.4944323E+03  2.4681387E-01  1.4585997E-01  7.6029536E-02  3.9881367E-02  1.9666704E-02  8.7101348E-03  2.6628490E-03
  2.9570622E+03  2.5643870E-01  1.4221656E-01  7.3229143E-02  3.8524236E-02  1.9030766E-02  8.3940292E-03  2.5765332E-03
  5.9602824E+03  1.9274715E-01  9.7608608E-02  4.9362514E-02  2.5773385E-02  1.2700084E-02  5.6108718E-03  1.7187114E-03
  1.2287274E+04  1.2229619E-01  5.8398368E-02  2.9197147E-02  1.5227645E-02  7.5035816E-03  3.3103362E-03  1.0152861E-03
  2.6025475E+04  7.1426092E-02  3.2800158E-02  1.6284612E-02  8.4675426E-03  4.1682198E-03  1.8402301E-03  5.6389575E-04
  5.6920168E+04  4.0099771E-02  1.7926580E-02  8.8580193E-03  4.6043650E-03  2.2666591E-03  1.0000444E-03  3.0662309E-04
  1.2924147E+05  2.2205546E-02  9.7155189E-03  4.7836464E-03  2.4828387E-03  1.2216568E-03  5.3917832E-04  1.6524649E-04
  3.0640048E+05  1.2181181E-02  5.2395866E-03  2.5724532E-03  1.3347501E-03  6.5674013E-04  2.8975990E-04  8.8829643E-05
  7.6297421E+05  6.6597693E-03  2.8244368E-03  1.3834892E-03  7.1723201E-04  3.5280484E-04  1.5568362E-04  4.7717415E-05
  2.0076699E+06  3.5575042E-03  1.4928906E-03  7.2995848E-04  3.7832779E-04  1.8609143E-04  8.2104714E-05  2.5168451E-05
  5.6164426E+06  1.8566153E-03  7.7288988E-04  3.7740417E-04  1.9551278E-04  9.6154484E-05  4.2426773E-05  1.3004305E-05
  1.6802886E+07  8.8408903E-04  3.6609607E-04  1.7860420E-04  9.2513170E-05  4.5497769E-05  2.0073628E-05  6.1532077E-06
  5.4065393E+07  3.6372280E-04  1.5003603E-04  7.3149434E-05  3.7880674E-05  1.8628161E-05  8.2191072E-06  2.5192723E-06
  1.8809445E+08  3.9084666E-05  1.6088047E-05  7.8407006E-06  4.0605376E-06  1.9968838E-06  8.8097218E-07  2.7005784E-07
```

```
 7.1100931E+08 -2.6913120E-06 -1.1074607E-06 -5.3969183E-07 -2.7956824E-07 -1.3750197E-07 -6.0650654E-08 -1.8595851E-08
 2.9330971E+09  4.2284342E-07  1.7399041E-07  8.4788201E-08  4.3925941E-08  2.1605380E-08  9.5292259E-09  2.9219333E-09
 1.3255936E+10 -6.6036810E-08 -2.7172566E-08 -1.3241564E-08 -6.8602231E-09 -3.3743106E-09 -1.4882350E-09 -4.5634558E-10
 6.5852665E+10  8.2684455E-09  3.4022696E-09  1.6579716E-09  8.5897268E-10  4.2250091E-10  1.8634247E-10  5.7139514E-11


 3.2777475E-02  6.6583018E-09  5.1997131E-09 -9.0280402E-08  1.4001238E-07 -1.1702732E-07  2.2257972E-07  8.8973711E-04
 6.1052208E-02 -2.7234862E-08 -3.3234803E-08  4.8543240E-07 -8.3875912E-07  6.1956519E-07 -2.8561455E-06  2.9801286E-04
 1.1371780E-01  6.5584587E-08  1.1357878E-07 -1.4921476E-06  2.7503848E-06 -1.7436024E-06 -2.2330833E-05  9.2721339E-04
 2.1181678E-01 -1.2687135E-07 -2.9131507E-07  3.5750657E-06 -6.7804012E-06  3.7545795E-06 -6.1508893E-04 -1.2202708E-03
 3.9455421E-01  2.2292090E-07  6.4801348E-07 -7.5181259E-06  1.4716319E-05 -8.4814951E-07 -2.9266569E-03 -1.4022390E-03
 7.3499994E-01 -3.7623323E-07 -1.3240078E-06  1.4888317E-05 -2.7928998E-05  1.1483385E-04 -3.3719703E-03 -1.8292450E-03
 1.3694267E+00  6.2820434E-07  2.6019932E-06 -2.8314609E-05  4.7559797E-05  2.7010967E-03  3.5481729E-03  1.5339608E-03
 2.5522453E+00 -1.0548532E-06 -5.1099838E-06  5.0406770E-05 -1.3805043E-04  1.0733461E-02  1.0233838E-02  3.4886688E-03
 4.7592004E+00  1.7607038E-06  9.3408006E-06 -9.4370031E-05 -2.1881955E-03  1.6938343E-03  1.6747161E-03  6.4816516E-04
 8.8821010E+00 -2.9467977E-06 -1.6757433E-05  2.1620569E-04 -1.7304956E-02 -2.3680505E-02 -1.3537694E-02 -4.3935092E-03
 1.6598538E+01  5.1797725E-06  3.8010920E-05 -2.0360874E-03 -1.4680955E-02 -1.3203591E-02 -6.8396882E-03 -2.1117539E-03
 3.1079528E+01 -8.5036007E-06 -7.3720904E-05  2.1595179E-02  3.0642804E-02  1.9816957E-02  9.4758500E-03  2.9149436E-03
 5.8358006E+01  1.1461839E-05 -1.1455299E-03  3.3856539E-02  3.7345896E-02  2.2720121E-02  1.0478503E-02  3.2554645E-03
 1.1000966E+02 -2.0387677E-05 -1.7093763E-02 -1.4384488E-02 -9.6242069E-03 -5.1671769E-03 -2.2851648E-03 -7.1377344E-04
 2.0848751E+02  8.9042294E-05 -4.7607546E-02 -4.9636309E-02 -3.1268197E-02 -1.6208787E-02 -7.2705507E-03 -2.2261834E-03
 3.9793692E+02  3.1750790E-03 -4.0355126E-02 -3.2905184E-02 -1.9582457E-02 -1.0005800E-02 -4.4379426E-03 -1.3669924E-03
 7.6660359E+02  2.4905109E-02  2.4571143E-03 -6.4702145E-04 -5.6630997E-04 -3.0559609E-04 -1.4848940E-04 -4.2804830E-05
 1.4944323E+03  6.4312504E-02  3.5404032E-02  1.8368843E-02  9.6269446E-03  4.7461617E-03  2.1018145E-03  6.4257151E-04
 2.9570622E+03  8.9937328E-02  4.5939928E-02  2.3407135E-02  1.2284219E-02  6.0646469E-03  2.6744338E-03  8.2093827E-04
 5.9602824E+03  8.9537818E-02  4.1711583E-02  2.0842689E-02  1.0849360E-02  5.3416257E-03  2.3596508E-03  7.2272164E-04
 1.2287274E+04  7.3753937E-02  3.2516176E-02  1.6061406E-02  8.3530855E-03  4.1130977E-03  1.8140569E-03  5.5641213E-04
 2.6025475E+04  5.4420421E-02  2.3238701E-02  1.1407274E-02  5.9138670E-03  2.9087461E-03  1.2840890E-03  3.9342287E-04
 5.6920168E+04  3.7450532E-02  1.5729658E-02  7.6951575E-03  3.9906895E-03  1.9634095E-03  8.6601592E-04  2.6555365E-04
 1.2924147E+05  2.4513497E-02  1.0196669E-02  4.9794708E-03  2.5787438E-03  1.2680510E-03  5.5964584E-04  1.7149460E-04
 3.0640048E+05  1.5383160E-02  6.3679065E-03  3.1066330E-03  1.6096318E-03  7.9171441E-04  3.4923746E-04  1.0707400E-04
 7.6297421E+05  9.2503621E-03  3.8170961E-03  1.8612148E-03  9.6364657E-04  4.7383792E-04  2.0909878E-04  6.4081524E-05
 2.0076699E+06  5.2989334E-03  2.1831696E-03  1.0641632E-03  5.5118940E-04  2.7107876E-04  1.1958448E-04  3.6660831E-05
 5.6164426E+06  2.8243198E-03  1.1621686E-03  5.6638269E-04  2.9323102E-04  1.4418577E-04  6.3623385E-05  1.9499446E-05
 1.6802886E+07  1.3403351E-03  5.5119574E-04  2.6858785E-04  1.3909881E-04  6.8406847E-05  3.0177984E-05  9.2513068E-06
 5.4065393E+07  4.2517766E-04  1.7477765E-04  8.5163139E-05  4.4087413E-05  2.1677739E-05  9.5657566E-06  2.9316483E-06
 1.8809445E+08  9.8714923E-06  4.0808855E-06  1.9896300E-06  1.0343690E-06  5.0954248E-07  2.2422999E-07  6.8918938E-08
 7.1100931E+08  1.1624993E-06  4.7251887E-07  2.3006947E-07  1.1756714E-07  5.7473477E-08  2.5582624E-08  7.7693109E-09
 2.9330971E+09 -5.6493630E-07 -2.3038071E-07 -1.1220197E-07 -5.7527294E-08 -2.8164677E-08 -1.2508763E-08 -3.8077421E-09
 1.3255936E+10  2.0123625E-07  8.2100500E-08  3.9986755E-08  2.0510704E-08  1.0043772E-08  4.4594273E-09  1.3578940E-09
 6.5852665E+10 -5.6896317E-08 -2.3214553E-08 -1.1306646E-08 -5.8000751E-09 -2.8403099E-09 -1.2610270E-09 -3.8400415E-10


                         2P-           3P-           4P-           5P-           6P-
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  1.1371780E-01  1.5149148E-07 -6.8163196E-07 -1.6165852E-06  9.9782587E-04
  2.1181678E-01  1.7093311E-07  1.2680016E-06 -1.1699505E-06  1.4231482E-03
  3.9455421E-01  5.8354045E-07 -3.3044203E-06 -8.8017777E-05  1.5196087E-03
  7.3499994E-01  9.5286576E-07  4.2711904E-06 -8.8497625E-04  7.4213549E-04
  1.3694267E+00  2.5613533E-06 -9.4734702E-06 -3.9447915E-03 -1.0579134E-03
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  1.6598538E+01 -1.2668094E-03  1.8043647E-02  1.0560150E-02  2.7838624E-03
  3.1079528E+01 -9.5791864E-03  7.5931119E-03  5.0588871E-03  1.3376943E-03
  5.8358006E+01 -2.5906001E-02 -1.1405232E-02 -4.4834319E-03 -1.1062167E-03
  1.1000966E+02 -3.2939316E-02 -1.8940614E-02 -8.3445574E-03 -2.1081864E-03
  2.0848751E+02 -2.5687730E-02 -1.4944831E-02 -6.5558307E-03 -1.6518885E-03
  3.9793692E+02 -1.4730133E-02 -8.5051338E-03 -3.7462797E-03 -9.4625040E-04
  7.6660359E+02 -6.8893687E-03 -3.8966271E-03 -1.6970918E-03 -4.2702250E-04
  1.4944323E+03 -2.8874401E-03 -1.6343513E-03 -7.1820842E-04 -1.8148297E-04
  2.9570622E+03 -1.0971088E-03 -6.1041945E-04 -2.6378718E-04 -6.6204885E-05
  5.9602824E+03 -4.1131546E-04 -2.3233303E-04 -1.0267240E-04 -2.6017839E-05
  1.2287274E+04 -1.4526502E-04 -7.9726162E-05 -3.4004690E-05 -8.4885749E-06
  2.6025475E+04 -5.3097540E-05 -3.0262169E-05 -1.3565060E-05 -3.4583031E-06
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  1.2924147E+05 -6.0357247E-06 -3.5020021E-06 -1.6064965E-06 -4.1341700E-07
  3.0640048E+05 -2.7989375E-06 -1.5096828E-06 -6.3118668E-07 -1.5620812E-07


                         3D+           4D+           5D+           6D+
                -1.2827939E+02 -2.6928655E+01 -3.8101969E+00 -1.8169381E-01


  3.2777475E-02 -4.4802587E-07  2.4275314E-05 -7.5317133E-05 -1.0707794E-01
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  1.1371780E-01 -3.3669023E-06  1.7587412E-04 -5.8806415E-04 -3.1991976E-01
  2.1181678E-01  5.6351388E-06 -2.9003014E-04 -7.3087509E-04 -3.1570572E-01
  3.9455421E-01 -8.3286912E-06  4.6510025E-04 -1.8676569E-02 -2.3125690E-01
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  2.5522453E+00 -6.0920422E-06 -1.5488351E-02 -4.8552690E-01  1.5427095E-01
  4.7592004E+00  1.3841937E-04 -1.4245950E-01 -1.8761814E-01  6.0618295E-02
  8.8821010E+00  2.2622365E-03 -4.2633114E-01  2.1406810E-01 -5.2331763E-02
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  3.1079528E+01  1.9887657E-01 -1.0644157E-01  7.5275550E-02 -1.9454885E-02
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  2.0848751E+02  1.7529852E-01  1.0234078E-01 -4.4647524E-02  1.0953251E-02
  3.9793692E+02  7.0461699E-02  4.0733158E-02 -1.7825555E-02  4.3835269E-03
  7.6660359E+02  2.2927985E-02  1.2979953E-02 -5.6181141E-03  1.3760728E-03
  1.4944323E+03  6.6296509E-03  3.7587050E-03 -1.6416421E-03  4.0398079E-04
  2.9570622E+03  1.7162680E-03  9.5520955E-04 -4.0992766E-04  1.0009302E-04
  5.9602824E+03  4.3584798E-04  2.4710517E-04 -1.0871783E-04  2.6857714E-05
  1.2287274E+04  1.0119312E-04  5.5350430E-05 -2.3344938E-05  5.6550027E-06
  2.6025475E+04  2.4512440E-05  1.4120973E-05 -6.3442033E-06  1.5822968E-06
  5.6920168E+04  5.1949414E-06  2.7463397E-06 -1.1095423E-06  2.6310949E-07
  1.2924147E+05  1.1521615E-06  6.8995617E-07 -3.2368921E-07  8.2241922E-08
  3.0640048E+05  3.0400933E-07  1.5808078E-07 -6.2498362E-08  1.4655020E-08


  3.2777475E-02 -2.5112890E-09  4.1934348E-08 -1.3098950E-07 -1.8714305E-04
  6.1052208E-02  9.5532465E-09 -1.9775127E-07  3.9426617E-07 -4.7556643E-04
  1.1371780E-01 -2.2638410E-08  5.6940672E-07 -1.9101004E-06 -1.0414533E-03
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  7.3499994E-01  1.4317164E-07 -4.5883166E-06 -1.0349402E-03 -5.2172390E-04
  1.3694267E+00 -2.4505475E-07  5.2366233E-06 -4.2269885E-03  1.1873505E-03
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  8.8821010E+00  6.5489371E-05 -1.2268290E-02  6.1592757E-03 -1.5057738E-03
  1.6598538E+01  1.5963932E-03 -1.7471504E-02  1.0170578E-02 -2.6079155E-03
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  5.8358006E+01  2.6975934E-02  1.2723409E-02 -5.1328540E-03  1.2409059E-03
  1.1000966E+02  3.2419769E-02  1.8801788E-02 -8.2428979E-03  2.0278041E-03
  2.0848751E+02  2.4114276E-02  1.4046415E-02 -6.1248998E-03  1.5024841E-03
  3.9793692E+02  1.3197018E-02  7.6097968E-03 -3.3285423E-03  8.1849208E-04
  7.6660359E+02  5.8221774E-03  3.2862557E-03 -1.4212514E-03  3.4805303E-04
  1.4944323E+03  2.2707250E-03  1.2839997E-03 -5.6067292E-04  1.3798793E-04
  2.9570622E+03  7.8370384E-04  4.3440158E-04 -1.8606588E-04  4.5400882E-05
  5.9602824E+03  2.6332078E-04  1.4918807E-04 -6.5774960E-05  1.6268067E-05
  1.2287274E+04  7.8488463E-05  4.2535433E-05 -1.7781357E-05  4.2895664E-06
  2.6025475E+04  2.4632134E-05  1.4332594E-05 -6.5269824E-06  1.6378398E-06
  5.6920168E+04  6.0733526E-06  3.0796907E-06 -1.1747621E-06  2.7012610E-07
  1.2924147E+05  1.8431209E-06  1.1573922E-06 -5.7003982E-07  1.4770355E-07
  3.0640048E+05  4.3591834E-07  2.0024127E-07 -6.4421032E-08  1.3266370E-08


                            4F-            5F-
                -1.4283216E+01 -2.9142420E-01


  3.2777475E-02 -1.0725471E-05  1.8335167E-03
  6.1052208E-02  3.7371756E-05  1.4299458E-02
  1.1371780E-01 -6.5117205E-05  5.1474113E-02
  2.1181678E-01  1.3410944E-04  1.1826153E-01
  3.9455421E-01 -1.5304599E-04  2.0834794E-01
  7.3499994E-01  3.9034287E-04  2.8704100E-01
  1.3694267E+00  1.8711942E-03  3.1098500E-01
  2.5522453E+00  2.9485902E-02  2.3916164E-01
  4.7592004E+00  1.3401088E-01  9.8299863E-02
  8.8821010E+00  2.9018994E-01 -3.8916120E-02
  1.6598538E+01  3.4836741E-01 -9.0866778E-02
  3.1079528E+01  2.6972459E-01 -7.6747815E-02
  5.8358006E+01  1.4163449E-01 -4.1716302E-02
  1.1000966E+02  5.3462215E-02 -1.5589750E-02
  2.0848751E+02  1.6463172E-02 -4.8330990E-03
  3.9793692E+02  4.0383670E-03 -1.1670891E-03
  7.6660359E+02  9.6404242E-04 -2.8455384E-04
  1.4944323E+03  2.0990334E-04 -5.9438911E-05
  2.9570622E+03  4.2739189E-05 -1.2950119E-05
  5.9602824E+03  1.5565905E-05 -4.3943503E-06


  3.2777475E-02 -2.0783188E-08  3.6300411E-06
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  1.1371780E-01 -2.3659580E-07  1.8998293E-04
  2.1181678E-01  6.3262257E-07  5.9574736E-04
  3.9455421E-01 -1.0880802E-06  1.4323838E-03
  7.3499994E-01  3.4104055E-06  2.6933700E-03
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  8.8821010E+00  9.4515168E-03 -1.2688828E-03
  1.6598538E+01  1.5493324E-02 -4.0424851E-03
  3.1079528E+01  1.6367583E-02 -4.6582595E-03
  5.8358006E+01  1.1712012E-02 -3.4499746E-03
  1.1000966E+02  6.0012126E-03 -1.7499308E-03
  2.0848751E+02  2.4902691E-03 -7.3123932E-04
  3.9793692E+02  8.0917742E-04 -2.3369431E-04
  7.6660359E+02  2.5236369E-04 -7.4645254E-05
  1.4944323E+03  6.5321088E-05 -1.8336818E-05
  2.9570622E+03  1.7865583E-05 -5.4973542E-06
  5.9602824E+03  5.2672434E-06 -1.4302192E-06


                            4F+            5F+
                -1.3898700E+01 -2.6933365E-01


  3.2777475E-02  1.1675980E-05 -2.6792931E-03
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  1.1371780E-01  7.0857124E-05 -5.8567071E-02
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  1.3694267E+00 -2.1767351E-03 -3.0639932E-01
  2.5522453E+00 -3.2039098E-02 -2.3140727E-01
  4.7592004E+00 -1.4005668E-01 -8.9645492E-02
  8.8821010E+00 -2.9608946E-01  4.2772328E-02
  1.6598538E+01 -3.4809129E-01  9.0168542E-02
  3.1079528E+01 -2.6411894E-01  7.4324210E-02
  5.8358006E+01 -1.3656877E-01  3.9659289E-02
  1.1000966E+02 -5.0325596E-02  1.4467214E-02
  2.0848751E+02 -1.4919582E-02  4.3176435E-03
  3.9793692E+02 -3.4681534E-03  9.8742386E-04
  7.6660359E+02 -7.6780228E-04  2.2383383E-04
  1.4944323E+03 -1.3866054E-04  3.8326704E-05
  2.9570622E+03 -2.6734026E-05  8.1305216E-06
  5.9602824E+03 -5.2648888E-06  1.3970692E-06
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  3.2777475E-02  2.4030104E-08 -5.3099163E-06
  6.1052208E-02 -1.1468771E-07 -4.8102747E-05
  1.1371780E-01  2.6715090E-07 -2.1618653E-04
  2.1181678E-01 -7.5061919E-07 -6.4167480E-04
  3.9455421E-01  1.1736847E-06 -1.4814308E-03
  7.3499994E-01 -4.0316229E-06 -2.7020456E-03
  1.3694267E+00 -2.7854269E-05 -3.9245322E-03
  2.5522453E+00 -5.6048759E-04 -4.0459078E-03
  4.7592004E+00 -3.3449889E-03 -2.1394404E-03
  8.8821010E+00 -9.6582637E-03  1.3958154E-03
  1.6598538E+01 -1.5510672E-02  4.0174278E-03
  3.1079528E+01 -1.6082860E-02  4.5249404E-03
  5.8358006E+01 -1.1361507E-02  3.2985776E-03
  1.1000966E+02 -5.7154982E-03  1.6425083E-03
  2.0848751E+02 -2.3118320E-03  6.6885753E-04
  3.9793692E+02 -7.2978324E-04  2.0764163E-04
  7.6660359E+02 -2.1946679E-04  6.4005928E-05
  1.4944323E+03 -5.2827097E-05  1.4546466E-05
  2.9570622E+03 -1.4013535E-05  4.2861177E-06
  5.9602824E+03 -3.3747959E-06  8.7670867E-07


 Calculated energy =   -2.7274377546109416E+04
 Literature energy =   -2.7274378906250000E+04
 Difference (cal - lit) = 1.36E-03
 Relative error (abs((cal - lit)/lit)) = 4.99E-08
 Basis set for original program
35 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
   1.2287273922270530E+04 1.0d0 1.0d0
   2.6025474503929181E+04 1.0d0 1.0d0
   5.6920167949008617E+04 1.0d0 1.0d0
   1.2924146561822579E+05 1.0d0 1.0d0
   3.0640047899595002E+05 1.0d0 1.0d0
   7.6297421342751326E+05 1.0d0 1.0d0
   2.0076698631188064E+06 1.0d0 1.0d0
   5.6164425941082174E+06 1.0d0 1.0d0
   1.6802885560418982E+07 1.0d0 1.0d0
   5.4065392869313173E+07 1.0d0 1.0d0
   1.8809445122304142E+08 1.0d0 1.0d0
   7.1100930633447683E+08 1.0d0 1.0d0
   2.9330970963636436E+09 1.0d0 1.0d0
   1.3255935848588299E+10 1.0d0 1.0d0
   6.5852664686153687E+10 1.0d0 1.0d0
30 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
   1.2287273922270530E+04 1.0d0 1.0d0
   2.6025474503929181E+04 1.0d0 1.0d0
   5.6920167949008617E+04 1.0d0 1.0d0
   1.2924146561822579E+05 1.0d0 1.0d0
   3.0640047899595002E+05 1.0d0 1.0d0
   7.6297421342751326E+05 1.0d0 1.0d0
   2.0076698631188064E+06 1.0d0 1.0d0
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   5.6164425941082174E+06 1.0d0 1.0d0
   1.6802885560418982E+07 1.0d0 1.0d0
   5.4065392869313173E+07 1.0d0 1.0d0
30 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
   1.2287273922270530E+04 1.0d0 1.0d0
   2.6025474503929181E+04 1.0d0 1.0d0
   5.6920167949008617E+04 1.0d0 1.0d0
   1.2924146561822579E+05 1.0d0 1.0d0
   3.0640047899595002E+05 1.0d0 1.0d0
   7.6297421342751326E+05 1.0d0 1.0d0
   2.0076698631188064E+06 1.0d0 1.0d0
   5.6164425941082174E+06 1.0d0 1.0d0
   1.6802885560418982E+07 1.0d0 1.0d0
   5.4065392869313173E+07 1.0d0 1.0d0
25 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
   1.2287273922270530E+04 1.0d0 1.0d0
   2.6025474503929181E+04 1.0d0 1.0d0
   5.6920167949008617E+04 1.0d0 1.0d0
   1.2924146561822579E+05 1.0d0 1.0d0
   3.0640047899595002E+05 1.0d0 1.0d0
25 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
   1.2287273922270530E+04 1.0d0 1.0d0
   2.6025474503929181E+04 1.0d0 1.0d0
   5.6920167949008617E+04 1.0d0 1.0d0
   1.2924146561822579E+05 1.0d0 1.0d0
   3.0640047899595002E+05 1.0d0 1.0d0
20 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
```

```
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
20 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
```

Listing A.4: *Output file for Pa basis set optimization calculation.*

A.3 Single Point Energy using a predefined Basis Set

This input file will perform a single point energy calculation on protactinium using the basis optimized in Section

```
91Pa
 $contrl jobtype='energy' $end
 $nuc znuc=91 nucmdl=3 $end
 $bas nsym=7  bastype='rdin' $end
35
   3.2777474514072306E-02
   6.1052208024089318E-02
   1.1371779544172864E-01
   2.1181678224305334E-01
   3.9455421330447510E-01
   7.3499993917294237E-01
   1.3694267119018748E+00
   2.5522453323068639E+00
   4.7592004160127050E+00
   8.8821010163462422E+00
   1.6598538397889143E+01
   3.1079527707765703E+01
   5.8358006063602978E+01
   1.1000966104096939E+02
   2.0848750508658674E+02
   3.9793692474094433E+02
   7.6660358942891128E+02
   1.4944323346681333E+03
   2.9570621576747585E+03
   5.9602824302208819E+03
   1.2287273922270530E+04
   2.6025474503929181E+04
   5.6920167949008617E+04
   1.2924146561822579E+05
   3.0640047899595002E+05
   7.6297421342751326E+05
   2.0076698631188064E+06
   5.6164425941082174E+06
   1.6802885560418982E+07
   5.4065392869313173E+07
   1.8809445122304142E+08
   7.1100930633447683E+08
   2.9330970963636436E+09
   1.3255935848588299E+10
   6.5852664686153687E+10
```

```
30
   3.2777474514072306E-02
   6.1052208024089318E-02
   1.1371779544172864E-01
   2.1181678224305334E-01
   3.9455421330447510E-01
   7.3499993917294237E-01
   1.3694267119018748E+00
   2.5522453323068639E+00
   4.7592004160127050E+00
   8.8821010163462422E+00
   1.6598538397889143E+01
   3.1079527707765703E+01
   5.8358006063602978E+01
   1.1000966104096939E+02
   2.0848750508658674E+02
   3.9793692474094433E+02
   7.6660358942891128E+02
   1.4944323346681333E+03
   2.9570621576747585E+03
   5.9602824302208819E+03
   1.2287273922270530E+04
   2.6025474503929181E+04
   5.6920167949008617E+04
   1.2924146561822579E+05
   3.0640047899595002E+05
   7.6297421342751326E+05
   2.0076698631188064E+06
   5.6164425941082174E+06
   1.6802885560418982E+07
   5.4065392869313173E+07
30
   3.2777474514072306E-02
   6.1052208024089318E-02
   1.1371779544172864E-01
   2.1181678224305334E-01
   3.9455421330447510E-01
   7.3499993917294237E-01
   1.3694267119018748E+00
   2.5522453323068639E+00
   4.7592004160127050E+00
   8.8821010163462422E+00
   1.6598538397889143E+01
   3.1079527707765703E+01
   5.8358006063602978E+01
   1.1000966104096939E+02
   2.0848750508658674E+02
   3.9793692474094433E+02
   7.6660358942891128E+02
   1.4944323346681333E+03
   2.9570621576747585E+03
   5.9602824302208819E+03
   1.2287273922270530E+04
   2.6025474503929181E+04
   5.6920167949008617E+04
   1.2924146561822579E+05
   3.0640047899595002E+05
   7.6297421342751326E+05
   2.0076698631188064E+06
   5.6164425941082174E+06
   1.6802885560418982E+07
   5.4065392869313173E+07
25
   3.2777474514072306E-02
   6.1052208024089318E-02
   1.1371779544172864E-01
   2.1181678224305334E-01
   3.9455421330447510E-01
   7.3499993917294237E-01
   1.3694267119018748E+00
   2.5522453323068639E+00
   4.7592004160127050E+00
   8.8821010163462422E+00
   1.6598538397889143E+01
   3.1079527707765703E+01
   5.8358006063602978E+01
   1.1000966104096939E+02
   2.0848750508658674E+02
   3.9793692474094433E+02
   7.6660358942891128E+02
   1.4944323346681333E+03
   2.9570621576747585E+03
   5.9602824302208819E+03
   1.2287273922270530E+04
   2.6025474503929181E+04
   5.6920167949008617E+04
   1.2924146561822579E+05
   3.0640047899595002E+05
25
   3.2777474514072306E-02
   6.1052208024089318E-02
   1.1371779544172864E-01
```

```
   2.1181678224305334E-01
   3.9455421330447510E-01
   7.3499993917294237E-01
   1.3694267119018748E+00
   2.5522453323068639E+00
   4.7592004160127050E+00
   8.8821010163462422E+00
   1.6598538397889143E+01
   3.1079527707765703E+01
   5.8358006063602978E+01
   1.1000966104096939E+02
   2.0848750508658674E+02
   3.9793692474094433E+02
   7.6660358942891128E+02
   1.4944323346681333E+03
   2.9570621576747585E+03
   5.9602824302208819E+03
   1.2287273922270530E+04
   2.6025474503929181E+04
   5.6920167949008617E+04
   1.2924146561822579E+05
   3.0640047899595002E+05
20
   3.2777474514072306E-02
   6.1052208024089318E-02
   1.1371779544172864E-01
   2.1181678224305334E-01
   3.9455421330447510E-01
   7.3499993917294237E-01
   1.3694267119018748E+00
   2.5522453323068639E+00
   4.7592004160127050E+00
   8.8821010163462422E+00
   1.6598538397889143E+01
   3.1079527707765703E+01
   5.8358006063602978E+01
   1.1000966104096939E+02
   2.0848750508658674E+02
   3.9793692474094433E+02
   7.6660358942891128E+02
   1.4944323346681333E+03
   2.9570621576747585E+03
   5.9602824302208819E+03
20
   3.2777474514072306E-02
   6.1052208024089318E-02
   1.1371779544172864E-01
   2.1181678224305334E-01
   3.9455421330447510E-01
   7.3499993917294237E-01
   1.3694267119018748E+00
   2.5522453323068639E+00
   4.7592004160127050E+00
   8.8821010163462422E+00
   1.6598538397889143E+01
   3.1079527707765703E+01
   5.8358006063602978E+01
   1.1000966104096939E+02
   2.0848750508658674E+02
   3.9793692474094433E+02
   7.6660358942891128E+02
   1.4944323346681333E+03
   2.9570621576747585E+03
   5.9602824302208819E+03
 $econfig nclose=7 5 5 3 3 1 1 nopen=0 0 0 1 1 1 1 nconf=6 $end
 0.0 0.0 0.0 1.0 0.0 0.0 2.0
 0.0 0.0 0.0 1.0 0.0 1.0 1.0
 0.0 0.0 0.0 1.0 0.0 2.0 0.0
 0.0 0.0 0.0 0.0 1.0 0.0 2.0
 0.0 0.0 0.0 0.0 1.0 1.0 1.0
 0.0 0.0 0.0 0.0 1.0 2.0 0.0
 $scf maxitr=100 ixtrp=1 dfctr=0.5 $end
```

Listing A.5: *Input file for calculating the single point energy of Pa using a predefined basis set.*

```
 &CONTRL
 JOBTYPE = energy,
 C =    137.0359997600000
 /
 &NUC
 ZNUC =    91.00000000000000     ,
 NUCMDL =            3,
 RNUC =    0.000000000000000     ,
 ALPHA =    129305395.1200000
 /
 &BAS
 NSYM =            7,
 BASTYPE = rdin ,
```

```
 NGROUP =            1
 /
 &ECONFIG
 NCLOSE =            7,
                     5,
                     5,
                     3,
                     3,
                     1,
                     1,
 NOPEN =            0,
                    0,
                    0,
                    1,
                    1,
                    1,
                    1,
 FREEEL =            1,
 AUTOGEN =  F,
 NCONF =            6
 /
 nconf = 6
  1  0.00  0.00  0.00  1.00  0.00  0.00  2.00
  2  0.00  0.00  0.00  1.00  0.00  1.00  1.00
  3  0.00  0.00  0.00  1.00  0.00  2.00  0.00
  4  0.00  0.00  0.00  0.00  1.00  0.00  2.00
  5  0.00  0.00  0.00  0.00  1.00  1.00  1.00
  6  0.00  0.00  0.00  0.00  1.00  2.00  0.00
 &SCF
 MAXITR =         100,
 IXTRP =           1,
 DFCTR =   0.5000000000000000     ,
 THDLL =   1.0000000000000001E-005,
 THDSL =   9.9999999999999995E-008,
 THDSS =   1.0000000000000001E-009
 /
        31560
    166068720
        82680
        82680
    221424960
 Calculating one electron integrals
 Calculating two electron integrals
 Calculating guess
 Starting SCF
 SCF converged at iteration 41 Final energy =    -27274.37754610942


                         1S+           2S+           3S+           4S+           5S+           6S+           7S+
               -4.1678552E+03 -7.8202739E+02 -1.9970482E+02 -5.2155429E+01 -1.1997194E+01 -2.0494257E+00 -1.9849676E-01


  3.2777475E-02  6.3766410E-07  5.7309076E-06 -6.1014939E-05  1.3503449E-04 -8.9549947E-05  2.0217706E-04  7.7763953E-01
  6.1052208E-02 -2.7212503E-06 -2.4451140E-05  2.5997072E-04 -5.7257873E-04  3.6084676E-04 -1.8505829E-03  1.9084131E-01
  1.1371780E-01  6.4661788E-06  5.8087512E-05 -6.1594002E-04  1.3479564E-03 -7.5938581E-04 -1.0442761E-02  4.3509449E-01
  2.1181678E-01 -1.1776869E-05 -1.0570257E-04  1.1185370E-03 -2.4045368E-03  1.2148510E-03 -2.1151300E-01 -4.1956006E-01
  3.9455421E-01  1.8769658E-05  1.6866127E-04 -1.7636196E-03  3.7907496E-03 -1.2618495E-04 -7.3718664E-01 -3.5322441E-01
  7.3499994E-01 -2.7775219E-05 -2.4890013E-04  2.6020802E-03 -5.2448412E-03  2.1094051E-02 -6.2243418E-01 -3.3766148E-01
  1.3694267E+00  3.9581146E-05  3.5469575E-04 -3.6690519E-03  6.5256712E-03  3.6524111E-01  4.7977497E-01  2.0741439E-01
  2.5522453E+00 -5.5531012E-05 -5.0644472E-04  4.8195743E-03 -1.3768212E-02  1.0628665E+00  1.0136423E+00  3.4555769E-01
  4.7592004E+00  7.5042533E-05  6.7454424E-04 -6.6562007E-03 -1.5840398E-01  1.2336517E-01  1.2190063E-01  4.7160748E-02
  8.8821010E+00 -9.9650704E-05 -8.8184744E-04  1.1265810E-02 -9.1814825E-01 -1.2574109E+00 -7.1892239E-01 -2.3332330E-01
  1.6598538E+01  1.3971887E-04  1.4607049E-03  7.8898658E-02 -5.7101352E-01 -5.1418558E-01 -2.6643838E-01 -8.2270513E-02
  3.1079528E+01 -1.7602025E-04 -2.0695834E-03  6.1053018E-01  8.6852650E-01  5.6179744E-01  2.6866146E-01  8.2644473E-02
  5.8358006E+01  1.6963083E-04 -2.3283094E-02  7.0220007E-01  7.7741233E-01  4.7333116E-01  2.1834120E-01  6.7834903E-02
  1.1000966E+02 -2.3821652E-04 -2.5386103E-01 -2.1304165E-01 -1.4183476E-01 -7.6052348E-02 -3.3602641E-02 -1.0499887E-02
  2.0848751E+02  8.5338160E-04 -5.1752274E-01 -5.4684268E-01 -3.4531663E-01 -1.7912344E-01 -8.0359590E-02 -2.4606349E-02
  3.9793692E+02  2.2723041E-02 -3.2469759E-01 -2.6916770E-01 -1.6072880E-01 -8.2191235E-02 -3.6464966E-02 -1.1231440E-02
  7.6660359E+02  1.2996824E-01  7.6465413E-03 -8.8975780E-03 -6.2835928E-03 -3.2962445E-03 -1.5389625E-03 -4.5630116E-04
  1.4944323E+03  2.4681387E-01  1.4585997E-01  7.6029536E-02  3.9881367E-02  1.9666704E-02  8.7101348E-03  2.6628490E-03
  2.9570622E+03  2.5643870E-01  1.4221656E-01  7.3229143E-02  3.8524236E-02  1.9030766E-02  8.3940292E-03  2.5765332E-03
  5.9602824E+03  1.9274715E-01  9.7608608E-02  4.9362514E-02  2.5773385E-02  1.2700084E-02  5.6108718E-03  1.7187114E-03
  1.2287274E+04  1.2229619E-01  5.8398368E-02  2.9197147E-02  1.5227645E-02  7.5035816E-03  3.3103362E-03  1.0152861E-03
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  6.1052208E-02  9.3085995E-08  3.8674853E-05
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  2.1181678E-01  6.3262257E-07  5.9574736E-04
  3.9455421E-01 -1.0880802E-06  1.4323838E-03
  7.3499994E-01  3.4104055E-06  2.6933700E-03
  1.3694267E+00  2.3452890E-05  3.9826033E-03
  2.5522453E+00  5.1386501E-04  4.1805895E-03
  4.7592004E+00  3.1956728E-03  2.3449523E-03
  8.8821010E+00  9.4515168E-03 -1.2688828E-03
  1.6598538E+01  1.5493324E-02 -4.0424851E-03
  3.1079528E+01  1.6367583E-02 -4.6582595E-03
  5.8358006E+01  1.1712012E-02 -3.4499746E-03
  1.1000966E+02  6.0012126E-03 -1.7499308E-03
  2.0848751E+02  2.4902691E-03 -7.3123932E-04
  3.9793692E+02  8.0917742E-04 -2.3369431E-04
  7.6660359E+02  2.5236369E-04 -7.4645254E-05
  1.4944323E+03  6.5321088E-05 -1.8336818E-05
  2.9570622E+03  1.7865583E-05 -5.4973542E-06
  5.9602824E+03  5.2672434E-06 -1.4302192E-06


                            4F+            5F+
                -1.3898700E+01 -2.6933365E-01


  3.2777475E-02  1.1675980E-05 -2.6792931E-03
  6.1052208E-02 -4.1377000E-05 -1.7785577E-02
  1.1371780E-01  7.0857124E-05 -5.8567071E-02
  2.1181678E-01 -1.4708650E-04 -1.2737380E-01
  3.9455421E-01  1.6844262E-04 -2.1546329E-01
  7.3499994E-01 -4.2699706E-04 -2.8794124E-01
  1.3694267E+00 -2.1767351E-03 -3.0639932E-01
  2.5522453E+00 -3.2039098E-02 -2.3140727E-01
  4.7592004E+00 -1.4005668E-01 -8.9645492E-02
  8.8821010E+00 -2.9608946E-01  4.2772328E-02
  1.6598538E+01 -3.4809129E-01  9.0168542E-02
  3.1079528E+01 -2.6411894E-01  7.4324210E-02
  5.8358006E+01 -1.3656877E-01  3.9659289E-02
  1.1000966E+02 -5.0325596E-02  1.4467214E-02
  2.0848751E+02 -1.4919582E-02  4.3176435E-03
  3.9793692E+02 -3.4681534E-03  9.8742386E-04
  7.6660359E+02 -7.6780228E-04  2.2383383E-04
  1.4944323E+03 -1.3866054E-04  3.8326704E-05
  2.9570622E+03 -2.6734026E-05  8.1305216E-06
  5.9602824E+03 -5.2648888E-06  1.3970692E-06


  3.2777475E-02  2.4030104E-08 -5.3099163E-06
  6.1052208E-02 -1.1468771E-07 -4.8102747E-05
  1.1371780E-01  2.6715090E-07 -2.1618653E-04
  2.1181678E-01 -7.5061919E-07 -6.4167480E-04
  3.9455421E-01  1.1736847E-06 -1.4814308E-03
  7.3499994E-01 -4.0316229E-06 -2.7020456E-03
  1.3694267E+00 -2.7854269E-05 -3.9245322E-03
  2.5522453E+00 -5.6048759E-04 -4.0459078E-03
```

```
  4.7592004E+00 -3.3449889E-03 -2.1394404E-03
  8.8821010E+00 -9.6582637E-03  1.3958154E-03
  1.6598538E+01 -1.5510672E-02  4.0174278E-03
  3.1079528E+01 -1.6082860E-02  4.5249404E-03
  5.8358006E+01 -1.1361507E-02  3.2985776E-03
  1.1000966E+02 -5.7154982E-03  1.6425083E-03
  2.0848751E+02 -2.3118320E-03  6.6885753E-04
  3.9793692E+02 -7.2978324E-04  2.0764163E-04
  7.6660359E+02 -2.1946679E-04  6.4005928E-05
  1.4944323E+03 -5.2827097E-05  1.4546466E-05
  2.9570622E+03 -1.4013535E-05  4.2861177E-06
  5.9602824E+03 -3.3747959E-06  8.7670867E-07


 Calculated energy =   -2.7274377546109416E+04
 Literature energy =   -2.7274378906250000E+04
 Difference (cal - lit) = 1.36E-03
 Relative error (abs((cal - lit)/lit)) = 4.99E-08
 Basis set for original program
35 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
   1.2287273922270530E+04 1.0d0 1.0d0
   2.6025474503929181E+04 1.0d0 1.0d0
   5.6920167949008617E+04 1.0d0 1.0d0
   1.2924146561822579E+05 1.0d0 1.0d0
   3.0640047899595002E+05 1.0d0 1.0d0
   7.6297421342751326E+05 1.0d0 1.0d0
   2.0076698631188064E+06 1.0d0 1.0d0
   5.6164425941082174E+06 1.0d0 1.0d0
   1.6802885560418982E+07 1.0d0 1.0d0
   5.4065392869313173E+07 1.0d0 1.0d0
   1.8809445122304142E+08 1.0d0 1.0d0
   7.1100930633447683E+08 1.0d0 1.0d0
   2.9330970963636436E+09 1.0d0 1.0d0
   1.3255935848588299E+10 1.0d0 1.0d0
   6.5852664686153687E+10 1.0d0 1.0d0
30 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
   1.2287273922270530E+04 1.0d0 1.0d0
   2.6025474503929181E+04 1.0d0 1.0d0
   5.6920167949008617E+04 1.0d0 1.0d0
   1.2924146561822579E+05 1.0d0 1.0d0
   3.0640047899595002E+05 1.0d0 1.0d0
   7.6297421342751326E+05 1.0d0 1.0d0
   2.0076698631188064E+06 1.0d0 1.0d0
   5.6164425941082174E+06 1.0d0 1.0d0
   1.6802885560418982E+07 1.0d0 1.0d0
   5.4065392869313173E+07 1.0d0 1.0d0
30 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
```

```
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
   1.2287273922270530E+04 1.0d0 1.0d0
   2.6025474503929181E+04 1.0d0 1.0d0
   5.6920167949008617E+04 1.0d0 1.0d0
   1.2924146561822579E+05 1.0d0 1.0d0
   3.0640047899595002E+05 1.0d0 1.0d0
   7.6297421342751326E+05 1.0d0 1.0d0
   2.0076698631188064E+06 1.0d0 1.0d0
   5.6164425941082174E+06 1.0d0 1.0d0
   1.6802885560418982E+07 1.0d0 1.0d0
   5.4065392869313173E+07 1.0d0 1.0d0
25 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
   1.2287273922270530E+04 1.0d0 1.0d0
   2.6025474503929181E+04 1.0d0 1.0d0
   5.6920167949008617E+04 1.0d0 1.0d0
   1.2924146561822579E+05 1.0d0 1.0d0
   3.0640047899595002E+05 1.0d0 1.0d0
25 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
   1.2287273922270530E+04 1.0d0 1.0d0
   2.6025474503929181E+04 1.0d0 1.0d0
   5.6920167949008617E+04 1.0d0 1.0d0
   1.2924146561822579E+05 1.0d0 1.0d0
   3.0640047899595002E+05 1.0d0 1.0d0
20 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
```

```
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
20 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
   3.2777474514072306E-02 1.0d0 1.0d0
   6.1052208024089318E-02 1.0d0 1.0d0
   1.1371779544172864E-01 1.0d0 1.0d0
   2.1181678224305334E-01 1.0d0 1.0d0
   3.9455421330447510E-01 1.0d0 1.0d0
   7.3499993917294237E-01 1.0d0 1.0d0
   1.3694267119018748E+00 1.0d0 1.0d0
   2.5522453323068639E+00 1.0d0 1.0d0
   4.7592004160127050E+00 1.0d0 1.0d0
   8.8821010163462422E+00 1.0d0 1.0d0
   1.6598538397889143E+01 1.0d0 1.0d0
   3.1079527707765703E+01 1.0d0 1.0d0
   5.8358006063602978E+01 1.0d0 1.0d0
   1.1000966104096939E+02 1.0d0 1.0d0
   2.0848750508658674E+02 1.0d0 1.0d0
   3.9793692474094433E+02 1.0d0 1.0d0
   7.6660358942891128E+02 1.0d0 1.0d0
   1.4944323346681333E+03 1.0d0 1.0d0
   2.9570621576747585E+03 1.0d0 1.0d0
   5.9602824302208819E+03 1.0d0 1.0d0
```

Listing A.6: *Output file for calculating the single point energy of Pa using a predefined basis set.*

Appendix B

Scripts for cudaDFRATOM

These are the scripts for automating the optimization of basis sets using cudaDFRATOM.

```
#!/bin/bash

sym=''
nuc=''
exepath=/home/dhenness/prophet/exe  # path to the executable
ver=dfratomgpu_binarysearch2.x      # the cudaDFRATOM executable file
alljobs=false
bottom=false
wtime=01:00:00

if [[ -z $exepath ]]; then
  echo "You must set the path to the executable"
  exit
fi

while [ $# -gt 0 ]
do
  val=$1
  shift
  case $val in
    "-a")
       alljobs=true
     ;;
    "-b")
      bottom=true
    ;;
    "-gauss")
       nuc='gauss_'
     ;;
    "-point")
       nuc='point_'
     ;;
    "-S")
       sym='S'
       low=$1
       high=$2
       shift
       shift
     ;;
    "-P")
       sym='P'
       low=$1
       high=$2
       shift
       shift
     ;;
     "-D")
       sym='D'
       low=$1
       high=$2
       shift
       shift
     ;;
     "-F")
       sym='F'
       low=$1
       high=$2
       shift
       shift
     ;;
     "-t")
       wtime=$1
       shift
```

```
    ;;
    *)
      job=$val
    ;;
  esac
done

boilerplate(){
  cat << EOF
#!/bin/bash
#SBATCH --account=def-mariusz
#SBATCH --gres=gpu:1
#SBATCH --mem=4GB
#SBATCH --time=$1
#SBATCH --job-name=$2
#SBATCH --output=%x-%j.out

echo ----------------------------------------
echo ----------------------------------------
echo began running on \`date\`
echo ----------------------------------------
echo ----------------------------------------
$3 $4 > $5
echo ----------------------------------------
echo ----------------------------------------
echo stopped running on \`date\`
echo ----------------------------------------
echo ----------------------------------------
EOF
}

if [[ -z $nuc ]]; then
  echo No nuc entered
  exit
fi

if [ "$alljobs" = true ]; then
  job=`ls *inp`
elif [ -z "$job" ]; then
  echo no job given
  exit
fi

for file in $job; do
  dir=`echo $file | sed 's/_.*$//'`
  mkdir $dir
  cp $file $dir/$file-orig
  cd $dir

  # keep old out files and delete others
  rename "out" "out-old" *.out
  rm *inp
  rm *sh

  file_base=$(echo $file | sed -e "s/$nuc.*/$nuc/")
  read -r -a old_bs <<< $(sed -n -e "/nbs/{s/nbs=//; p}" $file-orig)
  read -r -a old_start <<< $(sed -n -e "/start/{s/start=//; s/\$end//; p}" $file-orig)

  # keep track of how many files are made
  total=0
  for i in $(seq $low $high); do
    for j in $(seq 0 6); do
      new_bs[j]=${old_bs[j]}
      new_start[j]=${old_start[j]}
    done

    # make alterations based on symmetry

    case $sym in
      "F")
        ((new_bs[5]-=$i))
        ((new_bs[6]-=$i))
        # make sure that the number of basis functions is not zero
        if [[ "${new_bs[5]}" == "0" ]]; then
          break
        fi
        ((new_start[5]+=$i))
        ((new_start[6]+=$i))
        ;;
      "D")
        ((new_bs[3]-=$i))
        ((new_bs[4]-=$i))
        if [[ "${new_bs[3]}" == "0" ]]; then
          break
        fi
        ((new_start[3]+=$i))
        ((new_start[4]+=$i))
        ;;
      "P")
        ((new_bs[1]-=$i))
        ((new_bs[2]-=$i))
        if [[ "${new_bs[1]}" == "0" ]]; then
```

```
          break
        fi
        ((new_start[1]+=$i))
        ((new_start[2]+=$i))
        ;;
      "S")
        ((new_bs[0]-=$i))
        if [[ "${new_bs[0]}" == "0" ]]; then
          break
        fi
        ((new_start[0]+=$i))
        ;;
    esac
    new_file=$file_base${new_bs[0]}"s"${new_bs[1]}"p-"${new_bs[2]}"p+"${new_bs[3]}"d-"${new_bs[4]}"d+"${new_bs[5]}"f-"${new_bs[6]}"f+.inp"
    cp $file-orig $new_file
    sed -i -e "s/${old_bs[0]} ${old_bs[1]} ${old_bs[2]} ${old_bs[3]} ${old_bs[4]} ${old_bs[5]} ${old_bs[6]}/\
${new_bs[0]} ${new_bs[1]} ${new_bs[2]} ${new_bs[3]} ${new_bs[4]} ${new_bs[5]} ${new_bs[6]}/" $new_file # continuing from last line
    if [ "$bottom" == true ]; then
      sed -i -e "s/${old_start[0]} ${old_start[1]} ${old_start[2]} ${old_start[3]} ${old_start[4]} ${old_start[5]} ${old_start[6]}/\
${new_start[0]} ${new_start[1]} ${new_start[2]} ${new_start[3]} ${new_start[4]} ${new_start[5]} ${new_start[6]}/" $new_file # continuing from last
       line
    fi

    boilerplate $wtime ${new_file%????} $exepath/$ver $new_file ${new_file%???}log > ${new_file%???}sh
    ((total++))
  done


  echo "Submitting $total input files"
  for sub in *sh; do
    sbatch $sub
  done
done
```

Listing B.1: *BS_sub_auto.sh: Generate and submit input files.*

```
#!/bin/bash

tol=$1

if [ -z $tol ]; then
  tol='5*10^-8'
fi

echo The tolerance in relative error is $tol

mkdir best
for dir in `ls -d */`; do
  if [ "$dir" != 'old/' ]; then
    if [ "$dir" != 'best/' ]; then
      if [ "$dir" != 'tests/' ]; then
      echo entering $dir
      cd $dir
      for file in *.inp; do
        error=`grep -i 'rela' ${file%????}*log | tail -1 | awk '{print $7}'`
        comperror=`echo $error | sed -e 's/E/\*10\^/'`
        testthress=`echo "scale=20; ($tol - $comperror)*10^10 >= 1" | bc -l`
        if [ $testthress -ge 1 ]; then
          cp $file ../best
          cp ${file%????}*out ../best
          echo Found best for $file
          break
        fi
      done
      fi
    fi
  fi
  cd ..
done
```

Listing B.2: *BS_get_best.sh: Find the best basis set.*