Non-Born-Oppenheimer calculations with Explicit Correlated Gaussians

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Master's thesis

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Abstract

Based on the semi-recent review paper by Jim Mitroy et al., on the method of Explicit Correlated Gaussians, a more classical approach to low-energy scattering calculations is tested and developed; both for Born-Oppenheimer and non-BO purposes. While the model has been successfully constructed with all theoretical calculations and aspects accounted for, the numerical verification did not bear much fruit and therefore no data has been constructed that could be compared to contemporary experiments. Although some graphs have been created that match theoretical expectations in the preliminary formula testing.

Colophon

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Master's Thesis by Nikolaj Leonhard Daugaard Peters

The project was supervised by Dmitri Fedorov

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Contents

Chapter 1

Introduction

Gauging the dynamics and shape of a system through a systematic, precise and aggressive poking with a scientific stick has been a practice for as long as humans have had hands. After many centuries of refinement of the stick in question, we finally got to see a glimpse of what this method could really do in 1911, when Rutherford introduced the world to his gold foil experiment that could pry into the structure of the atom itself[1]. This was our first step away from ideas such as Thompson's plum pudding model and it opened the world up to many new and important concepts such as the atomic nucleus, which is still being studied extensively to this day.

Nowadays scattering experiments are, despite their seemingly simple nature, one of the main tools we have at our disposal to learn about the shape and composition of microscopic structures, as well as an integral part of both detector and particle physics. For this reason, and many others, the field of scattering theory is wide and rich in methodologies that attempt to create a backbone for the calculations that underpin the experiments that are carried out at places like CERN. Unfortunately, these often have to be approximations, as there is not a systematically good way to deal with even the simplest differential equations in the realm of multi-body dynamics, which is why physicists are always eager to discover new alternatives to aid in the exploration of potential solutions.

In this thesis, we will be exploring one such alternative, and examine whether it fares well compared to previous models.

The way forward

The main goal of this thesis is to explore an avenue of scattering calculations using a more classical approach with Explicit Correlated Gaussians as the basis. This is opposed to the methods mentioned in the semi-recent review study by Jim Mitroy et al[2] that focused on more exotic methods, such as the *complex scaling method* (CSM) and *Kohn variational method* for the calculation of resonances and low-energy scattering respectively. The Gaussian method will be tested on one of the simplest non-trivial systems, that being low-energy proton-hydrogen scattering. However, the possibility for more complex calculations in the future will be also be discussed as well as its potential shortcomings.

Outline

The thesis will be split into three sections, building up to the actual scattering, with a conclusion at the end. First, we will quickly go through the relevant physics and mathematics in the form of scattering theory and the Correlated Gaussians that will be used as a basis in the numerical calculations later. We will also explore a specific scattering scenario and discuss some results to determine whether or not it behaves as expected. At the end, if successful, we will show the numerical results from the scattering, which will be compared to some experimental data.

Chapter 2

Relevant theory

To truly understand why the theory in this chapter is relevant and to create a cohesive throughline, I will dedicate the start of this chapter to give a brief overview of what the project is about and what we are doing. The scattering we are interested in studying is *low-energy* proton-hydrogen scattering using a numerical method called the Ritz method (based on the variational principle, equation (2.1)) with Explicit Correlated Gaussians (ECGs) as a basis. The numerical method is also special because we are considering a semi-classical approach where the scattering will be modelled with the use of delta functions, which will be used to keep the distance between the two protons fixed; effectively 'freezing' the incident proton. With this fixed distance, we use Born-Oppenheimer (BO) to separate the proton and hydrogen systems, allowing us to minimize the energy of the hydrogen for this given length, which creates an effective energy curve, as in figure 3.4 or 3.5, for the incident particle. This, together with some partial wave theory and the numerical grid method; a finite difference method, described in detail in appendix C, will be used to find the *phase shift*, an important quantity in scattering theory. This will be done, based on the theory of section 2.2.1, through the asymptotic fitting of a sinusoidal expression. Before getting that far, however, we first need to acquire an optimization process, which includes a method for generating positive-definite matrices.

Therefore, we are starting out this chapter by focusing on the theory of ECGs, ending with the analytical delta function matrix elements, which have been calculated in appendix B. We then move on to the scattering theory where our treatment also ends with matrix elements, but this time for scattering coefficients, that will be used in a non-BO approximation. These are calculated in appendix D. Lastly, there will also be a section on the optimization itself, specifically the available optimization methods, and the difficulties one might face using them, as well as the matrix construction which is a central part of them all.

It is also worth mentioning that we are using appendices as a way to keep messy calculations or explanations out of the main parts of the thesis, but that does not mean they are irrelevant or insignificant in their contents. So for the full comprehension and scope, they should be perused as well.

2.1 Correlated Gaussians

One of the most fundamental tools in few-body calculations is the variational method. This tells us that the expectation value of the Hamiltonian, H, with any normalized trial wave function, Ψ, will always be greater than, or equal to, the real ground state energy, E_0 of the system[3],

$$\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0. \tag{2.1}$$

This is the foundation of the Ritz method, where one's choice of Ψ is a linear combination of N known basis functions, ψ_i, parameterized by unknown coefficients, c_i, a_i,

$$\Psi = \sum_{i=1}^{N} c_i \psi_i(\{a_i\}). \tag{2.2}$$

Inserting the ansatz of equation (2.2) into equation (2.1) leaves us with the generalized eigenvalue-problem[1]

$$\mathcal{H}\mathbf{c} = E\mathcal{N}\mathbf{c}, \tag{2.3}$$

where both $\mathcal{H}$ and $\mathcal{N}$ are $N \times N$ matrices with elements $\mathcal{H}_{ij} = \langle \psi_i | H | \psi_j \rangle$ and $\mathcal{N}_{ij} = \langle \psi_i | \psi_j \rangle$. These can be used to optimize the c_i's for a given choice of a_i parameters; giving us a nonlinear optimization problem.

All of this leads us to the discussion of the (Explicit) Correlated Gaussian (ECG) method, which is a specific choice of basis functions of the form of shifted Gaussians. It was first introduced in 1960 by Boys [5] and Singer [6] for the study of molecular systems, although the method remained widely unknown until the 1990's where it experienced a revival. In its most general form, the basis elements look like

$$G(\mathbf{s}; A, \mathbf{x}) = \exp\left(-\mathbf{x}^T A \mathbf{x} + \mathbf{s}^T \mathbf{x}\right), \qquad \mathbf{x}^T A \mathbf{x} = \sum_{i,j=1}^{N} a_{ij} \mathbf{x}_i \cdot \mathbf{x}_j, \tag{2.4}$$

where $\mathbf{x} = (\mathbf{x}_1, \cdots, \mathbf{x}_N)^T$ is an N-dimensional vector consisting of d-dimensional positional vectors, $\mathbf{x}_i$, A is an $N \times N$ symmetric[2], positive-definite ($\mathbf{x}^T A \mathbf{x} > 0$) matrix and $\mathbf{s} = (\mathbf{s}_1, \cdots, \mathbf{s}_N)^T$ is a constant shift vector analogous to $\mathbf{x}$ in its construction. The shift factor will only be used for theoretical calculations and in all numerical settings they will be disregarded, so our Gaussians will have the much simpler form

$$G(A, \mathbf{x}) = \exp\left(-\mathbf{x}^T A \mathbf{x}\right). \tag{2.6}$$

More conceptually, the $\mathbf{x}$ vector will contain all the positional vectors of the N particles in our system and since we generally work in 3-dimensional space, we will also set $d = 3$ in all our calculations.
Below we will note some of the advantages of ECGs

1: See, for example, Peter Atkin's "Molecular Quantum Mechanics" [4] for a complete derivation.

2: The reason for the symmetry requirement is that $\mathbf{x}^T A \mathbf{x}$ is a number which means $(\mathbf{x}^T A \mathbf{x})^T = \mathbf{x}^T A \mathbf{x}$ and $(\mathbf{x}^T A \mathbf{x})^T = \mathbf{x}^T A^T \mathbf{x}$, but then

$$\mathbf{x}^T (A - A^T) \mathbf{x} = 0 \tag{2.5}$$

so the **skew-symmetric** part of the matrix does not contribute.

- **Center of mass removability**

  As will be seen in a moment, it is trivial, and necessary, to remove the center of mass (COM) motion from any calculation. This procedure removes a dimension from the problem, which, in turn, reduces the computational workload

- **Analytical simplicity**

  Unlike something such as an exponential choice of basis with linear distance factors, the factor $\mathbf{x}^T A\mathbf{x}$ allows for relatively simple analytical expressions for the Hamiltonian matrix elements. More importantly, these expressions do not increase in algebraic complexity when increasing the number of particles involved either. This ensures continued tractability as the complexity of our system grows.

- **Correlated basis**

  Since our basis elements are correlated, albeit in a very simple way, it makes them better at modelling strong interparticle interactions. In general the ECG model is very flexible and is capable of accommodating most particles and interactions; as long as they are not *too* correlated or complex (like inter-nuclear interactions).

2.1.1 Jacobian coordinates

A common choice for calculations, when working in a system with no external forces, is to change to Jacobian (center-of-mass) coordinates, as demonstrated in figure 2.1. This reduces the computational workload (complexity), as the center of mass will either be stationary or move at a constant velocity, which decouples it from the system dynamics so it can be removed without any issues. In case of the scattering problem, this transformation also serves a secondary purpose, as the new variables will now indicate the relative positions, as opposed to their absolute position, of the particles. This makes it easier to include the internal distances in the calculations by use of delta functions.

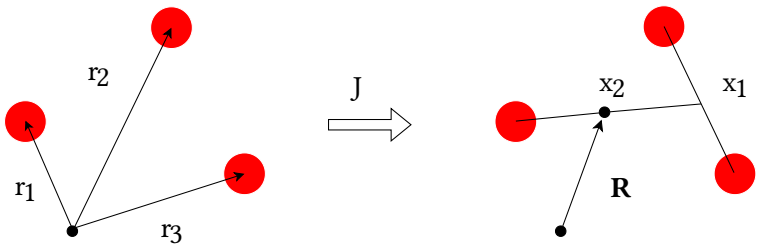

FIGURE 2.1: A picture depicting the transformation from absolute to Jacobi coordinates for a three particle system. As can be seen, the system on the left shows absolute coordinates measured in accordance with some origin, while the one on the right has two relative coordinates, $\mathbf{x}_1$, $\mathbf{x}_2$, and a third, R, measured relative to the COM (from origo) which gets removed. This means the origin in the new system is essentially arbitrary. The credit for the image goes to its creator Martin C. Østerlund[7].

It is well known that the Jacobian coordinate transformation is linear and given by the matrix

$$J = \begin{bmatrix} 1 & -1 & 0 & \cdots & 0 \\ \frac{m_1}{M_2} & \frac{m_2}{M_2} & -1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{m_1}{M_{N-1}} & \frac{m_2}{M_{N-1}} & \frac{m_3}{M_{N-1}} & \cdots & -1 \\ \frac{m_1}{M_N} & \frac{m_2}{M_N} & \frac{m_3}{M_N} & \cdots & \frac{m_n}{M_N} \end{bmatrix}, \qquad M_k = \sum_{i=1}^{k} m_i, \tag{2.7}$$

where m_i is the mass of the i'th particle. As seen in appendix A, it can be easily shown that the transformation of a general kinetic matrix, K, which will be introduced in section 2.1.2, and general vector, ω, will have the form

$$K \to JKJ^T, \tag{A.4}$$

$$\omega \to \left(J^{-1}\right)^T \omega. \tag{A.6}$$

In order to ignore the COM term we simply remove the last row of J, which means ignoring the center of mass term is done by discarding the last row of J and last column of $\left(J^{-1}\right)^T$; effectively reducing the dimensional complexity of the computation by 1.

2.1.2 Matrix elements

As noted, one of the advantages of the ECGs is that the matrix elements are relatively simple and analytic. Therefore, when working with a new system, one of the first courses of action is to determine, which of them are needed present in the Hamiltonian for the generalized eigenvalue problem. Below, all the elements that will be used are noted and most of them have been explicitly calculated in appendix B with the exception of the standard overlap, which we decided to take from other sources [8]. As we are concerned with low-energy scattering, we will only be dealing with s-waves and as such only the lowest order matrix elements have been used. However, extending the calculations to p-waves, and even d-waves, is not too difficult once one has these general expressions, as one can simply perform a Taylor expansion of the terms relating to the total shift vector, $\mathbf{v}$; see equation (2.9), and then match up the elements on both sides[3], which is a well-recognized trick when working with generating functions and Taylor series.

In order to avoid unnecessary clutter in the following equations, a shorthand notation for the Gaussian basis elements is introduced as

$$G' = G(\mathbf{s}'; A', \mathbf{x}), \quad G = G(\mathbf{s}; A, \mathbf{x}). \tag{2.8}$$

The Overlap Matrix Element

The most important element is the standard overlap between two basis elements as it shows up in every calculation at some point. The idea of the calculation is that when

3: For an explicit example of this, see "Dressing of Proton with Virtual Pions in a Nuclear Model with Explicit Mesons" by Martin Østerlund [7].

the inner product is written in the integral form, we can combine the exponentials

$$\begin{aligned}\langle G' \,|\, G \rangle &= \int d\mathbf{x} \exp\Big(-\mathbf{x}^T \left(A' + A\right) \mathbf{x} + \left(\mathbf{s}' + \mathbf{s}\right)^T \mathbf{x}\Big) \\ &= \int d\mathbf{x} \exp\big(-\mathbf{x}^T B \mathbf{x} + \mathbf{v}^T \mathbf{x}\big),\end{aligned} \tag{2.9}$$

where $B = A' + A$ and $\mathbf{v} = \mathbf{s}' + \mathbf{s}$. One can then diagonalize B so we end up with a product of N shifted Gaussians, which we can calculate individually and then combine again. Once that has been done, one will end up with something of the form[8]

$$\begin{aligned}\langle G' \,|\, G \rangle = M_0(B, \mathbf{v}) &= \exp\left(\frac{1}{4}\mathbf{v}^T R \mathbf{v}\right) \left(\frac{\pi^N}{\det(B)}\right)^{3/2} \\ &\xrightarrow{\mathbf{v}=0} M_0(B, \mathbf{0}) = \left(\frac{\pi^N}{\det(B)}\right)^{3/2},\end{aligned} \tag{2.10}$$

where $R = B^{-1}$. In our case we will also need the standard overlap with a delta function, which we have calculated in appendix B and has the form

$$\begin{aligned}\langle G' \,|\delta(\omega^T \mathbf{x} - \mathbf{y_0})|\, G \rangle &= \frac{M_0(B, \mathbf{v})}{(2\pi)^3} \exp\left(-\frac{1}{4\alpha}(\mathbf{q} - \mathbf{y_0})^2\right) \left(\sqrt{\frac{\pi}{\alpha}}\right)^3 \\ &\xrightarrow{\mathbf{v}=0} \frac{M_0(B, \mathbf{0})}{(2\pi)^3} \exp\left(-\frac{1}{4\alpha}\mathbf{y_0}^2\right) \left(\sqrt{\frac{\pi}{\alpha}}\right)^3,\end{aligned} \tag{B.11}$$

where $\mathbf{q} = \frac{1}{2}\omega^T R \mathbf{v}$ and $\alpha = \frac{1}{4}\omega^T R \omega$.

The Kinetic Matrix Element

When working with Hamiltonians, we will always have a kinetic term so this is also quite an important element. The kinetic operator has the general form

$$K = -\partial_{\mathbf{x}} \Lambda \partial_{\mathbf{x}^T} = -\sum_{i,j} \Lambda_{ij} \partial_i \partial_j, \quad \partial_i = \frac{\partial}{\partial \mathbf{x}_i}, \tag{2.11}$$

where Λ is a symmetric positive-definite matrix. Since we got no further restriction on Λ, we see that K, in principle, also can represent mixed second order partial derivatives, but physics tells us that when used in a Hamiltonian the Λ matrix will necessarily be a diagonal matrix with entries of the form $\Lambda_{ii} = \frac{1}{2m_i}$, where m_i is the mass of the i'th particle.

The matrix element has the form

$$\begin{aligned}\langle G' \,|K|\, G \rangle &= M_0(B, \mathbf{v}) \Big(6 \operatorname{Tr}\big(A' \Lambda A R\big) + \left(\mathbf{s}' - 2A'\mathbf{u}\right)^T \Lambda \left(\mathbf{s} - 2A\mathbf{u}\right)\Big) \\ &\xrightarrow{\mathbf{v}=0} 6 M_0(B, \mathbf{0}) \operatorname{Tr}\big(A' \Lambda A R\big),\end{aligned} \tag{B.23}$$

where $\mathbf{u} = \frac{1}{2}R\mathbf{v}$. As for the delta expression, we want an extra restriction in place: since we are effectively freezing a particle in place, we do not want it to contribute anything to the kinetic energy and if we require that $K\omega = \omega^T K = \mathbf{0}$ this will be

accomplished. Fortunately, this also greatly simplifies the calculation, as the deltas will no longer be effected by the differential operators in K, which makes us able to effectively split them up into the form

$$\begin{aligned}\langle G' | K\delta(\omega^T \mathbf{x} - y_0) | G \rangle &= \frac{\langle G' | K | G \rangle}{M_0(B, \mathbf{v})} \langle G' | \delta(\omega^T \mathbf{x} - \mathbf{y_0}) | G \rangle \\ &\xrightarrow{\mathbf{v}=0} \frac{\langle G' | K | G \rangle}{M_0(B, \mathbf{0})} \langle G' | \delta(\omega^T \mathbf{x} - \mathbf{y_0}) | G \rangle.\end{aligned} \tag{B.26}$$

Both of these have been fully calculated in appendix B.

Coulomb matrix element

For the Coulomb + delta term we have two constant vectors, ω and η, and two scenarios based on whether these are parallel or not. The reason for this is that normally the solution is a result of a Fourier transform of the coulomb potential, but when they are parallel, the delta function turns the Coulomb term into a constant, which has no bearing on the integral calculation; greatly simplifying everything. The full calculation can be found in appendix B and yields the expression

$$\langle G' | \frac{\delta(\omega^T \mathbf{x} - \mathbf{y_0})}{|\eta^T \mathbf{x}|} | G \rangle = \begin{cases} \frac{\langle G' | \delta(\omega^T \mathbf{x} - \mathbf{y_0}) | G \rangle}{c} \operatorname{erf}\left(\frac{c}{2\sqrt{a}}\right) & \eta \nparallel \omega \\ \frac{\langle G' | \delta(\omega^T \mathbf{x} - \mathbf{y_0}) | G \rangle}{|k||y_0|} & \eta = k \cdot \omega \end{cases} \tag{B.47}$$

$$\xrightarrow{\mathbf{v}=0} \mathbf{c} = \frac{\beta}{\alpha} \mathbf{y_0}, \tag{2.12}$$

where $\operatorname{erf}(x)$ is the special integral function, also called the error function, which is defined as

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \mathrm{d}t \ \exp\left(-t^2\right). \tag{2.13}$$

Unlike the other terms in this section,we decided just to show how the $\mathbf{c}$ changes for $\mathbf{v} \to \mathbf{0}$, as it would only muddy the equation to change the $\mathbf{c}$'s themselves. We have also introduced the new constants

$$\beta = \frac{1}{4}\omega^T R \eta, \quad \gamma = \frac{1}{4}\eta^T R \eta, \quad a = \gamma - \frac{\beta^2}{\alpha}, \tag{2.14}$$

and the vectors

$$\mathbf{p} = \frac{1}{2}\eta^T R \mathbf{v}, \quad \mathbf{c} = \mathbf{p} - \frac{\beta}{\alpha}(\mathbf{q} - \mathbf{y_0}). \tag{2.15}$$

2.2 Scattering theory

Scattering theory in quantum mechanics is built upon concepts that has their roots in classical scattering. This is not too surprising since the classical analogue has had quite a large head start, historically speaking, and they should both agree when looking at certain systems and regimes. Classically one would look at an incoming particle with energy E and with what is called the *impact parameter*, typically denoted

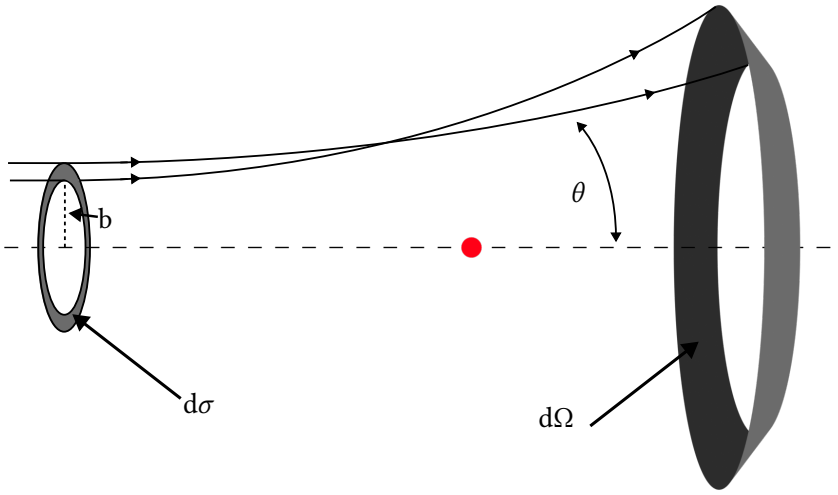

FIGURE 2.2: A picture depicting a classical scattering setup with the relevant quantities and their relations. The red dot represents the scattering center.

b, that measures the vertical displacement between the initial trajectory of the incoming particle and the scattering center (often consisting of/centered around some target – see figure 2.2 for illustration). The particle, when approaching the center, will then be measurably deflected by it, until it is far enough away to be locally in a free particle system where we know it will continue on a straight trajectory until it hits something; like a detector in the case of experimental physics. The angle between this deflected trajectory and the original one is what we call the *scattering angle*, θ, which is one of the quintessential quantities of the scatterings process, and a lot of classical scattering is about finding a relationship between E, b and θ.

Once this relation has been acquired, one can, as illustrated in figure 2.2, explore the relationship between the differential of cross section, $\mathrm{d}\sigma$, and the differential of solid angle, $\mathrm{d}\Omega$, which together form the *differential cross section*, $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}$, which is a very important and useful quantity. It is a sort of probabilistic measure of how likely a specific scattering event is to occur. Also, if one integrates over all of the solid angles they will get the total cross section (the total chance of the scattering event)

$$\sigma = \oint_{S^2} \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\, \mathrm{d}\Omega. \tag{2.16}$$

This framework of thinking of the differential cross section as a sort of probability goes even further, as it can be related to the *scattering amplitude*, f, in the following way

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(\theta)|^2, \tag{2.17}$$

which resembles the common Born rule for probabilities of quantum mechanics quite a lot. This result is of tremendous importance, as it allows us to relate an experimentally verifiable quantity (the cross section) to a strictly theoretical object (the scattering amplitude). This, in turn, allows us to test our interaction theories more carefully, which is especially practical considering most calculations in this field are forced to be approximated due to the complexity of the actual computations.

The relevant theoretical question then becomes how you calculate the scattering amplitude, and to this end we will introduce the notion of *partial waves*.

2.2.1 Partial wave expansion

Most of the math from this subsection can be found in "Physics and Molecules" by B.H Bransden & C.J. Joachain[9].

In physics we often work with two sorts of scattering: high-energy and low-energy. High-energy scattering is the sort most often encountered in accelerator physics, where we smash particles together at close to the speed of light, which makes the interaction time between particles extremely short. Low-energy scattering, also called s-wave scattering, on the other hand is what is typically found in nuclear physics and sensitive instruments. Fortunately, with each of these regimes also follow some natural approximations that we can use to get an answer to our calculation within a precision that suits the situation. For example, in high-energy we have the Born approximation and Born series[10], while low-energy has the partial wave expansion which is what we will look at now.

The idea is that when one has a central potential, such that the potential only depends on the magnitude of $\mathbf{r}$, we expect to see azimuthal symmetry and our solution[4], $\Psi^{(+)}_{\mathbf{k}_i}$, should be able to be expanded as a series of Legendre polynomials as:

$$\Psi^{(+)}_{\mathbf{k}_i}(k, r, \theta) = \sum_{\ell=0}^{\infty} R_\ell(k, r) P_\ell(\cos(\theta)), \tag{2.18}$$

where k is the wave number and $R_\ell(k, r)$ is a solution to the radial equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\ell(\ell+1)}{r} - U(r) + k^2\right] R_\ell(k, r) = 0, \tag{2.19}$$

where $U(r) = 2mV(r)$ in Hartree atomic units. Usually one solves this by first introducing a new radial function

$$u_\ell(k, r) = rR_\ell(k, r), \tag{2.20}$$

which removes the linear differential term from equation (2.19), leaving

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} - U(r) + k^2\right] u_\ell(k, r) = 0. \tag{2.21}$$

The radial function can then be expanded in a power series using the Frobenius method

$$u_\ell(k, r) = r^s \sum_{n=0}^{\infty} a_n r^n \tag{2.22}$$

which gives us the indicial equation for s. Going through the calculation yields two solutions, one which is *regular* at the origin and behaves like

$$u_\ell(k, r) \xrightarrow[r\to 0]{} r^{\ell+1} \tag{2.23}$$

4: The (+) stands for positive phase velocity which simply means the phases of all the frequency components travel together in the positive direction.

and one which is *irregular* and behaves like

$$u_\ell(k,r) \xrightarrow[r\to 0]{} r^{-\ell} \tag{2.24}$$

Since we need this to describe a physical process, it cannot be infinite anywhere, so near the origin we must make sure it is the regular solution for $u_\ell(k,r)$ that is chosen. Now, assuming that the potential only has a certain range a (after which it can be ignored) we can also solve the radial equation (equation (2.19)) in this region where it reduces to the much simpler

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \frac{2}{\rho}\frac{\mathrm{d}}{\mathrm{d}\rho} + 1 - \frac{\ell(\ell+1)}{\rho^2}\right] R_\ell(\rho) = 0, \qquad \rho = kr. \tag{2.25}$$

This equation is known as the *spherical Bessel differential equation* and the general solution is a linear combination of the spherical Bessel, j_ℓ, and Neumann, η_ℓ, function

$$j_\ell(\rho) = \left(\frac{\pi}{2\rho}\right)^{\frac{1}{2}} J_{\ell+1/2}(\rho), \quad \eta_\ell(\rho) = (-1)^{\ell+1}\left(\frac{\pi}{2\rho}\right)^{\frac{1}{2}} J_{-\ell-1/2}(\rho), \tag{2.26}$$

where $J_\nu(\rho)$ is a Bessel function of order ν. An interesting property of these spherical functions is their limiting behaviour, which for small values looks like[5]

$$j_\ell(\rho) \xrightarrow[\rho\to 0]{} \frac{\rho^\ell}{(2\ell+1)!!}\left[1 - \frac{\rho^2}{2(2\ell+3)} + \cdots\right], \tag{2.27}$$

$$\eta_\ell(\rho) \xrightarrow[\rho\to 0]{} -\frac{(2\ell+1)!!}{\rho^{\ell+1}}\left[1 - \frac{\rho^2}{2(1-2\ell)} + \cdots\right]. \tag{2.28}$$

So we see that just like $u_\ell(k,r)$, we have a regular and irregular solution for $r, \rho \to 0$. Likewise, for $\rho \to \infty$, although it still works well for values of ρ somewhat larger than $\frac{\ell(\ell+1)}{2}$, we have the asymptotic formulas

$$\begin{aligned} j_\ell(\rho) &\xrightarrow[\rho\to\infty]{} \frac{1}{\rho}\sin\left(\rho - \ell\frac{\pi}{2}\right), \\ \eta_\ell(\rho) &\xrightarrow[\rho\to\infty]{} -\frac{1}{\rho}\cos\left(\rho - \ell\frac{\pi}{2}\right), \end{aligned} \tag{2.29}$$

which will be useful shortly.

We now return to the radial functions $R_\ell(k,r)$ and $u_\ell(k,r)$. We see that in the external region ($r > a$) we have the solution

$$R_\ell(k,r) = B_\ell(k) j_\ell(kr) + C_\ell(k)\eta_\ell(kr), \tag{2.30}$$

5: $n!!$ is the double factorial, which is a product starting at n that then jumps down in steps of two

$$n!! = n(n-2)(n-4)\cdots\begin{cases} 1, & n \text{ odd} \\ 2, & n \text{ even} \end{cases}$$

which by using $A_\ell = \left[B_\ell^2(k) + C_\ell^2(k)\right]^{\frac{1}{2}}$, $\tan(\delta_\ell(k)) = -\frac{C_\ell(k)}{B_\ell(k)}$ as well as the asymptotic relations (equation (2.29)), gives us an asymptotic relation for $R_\ell(k,r)$ of the form

$$R_\ell(k,r) \xrightarrow[\rho\to\infty]{} \frac{A_\ell(k)}{kr} \sin\left(kr - \ell\frac{\pi}{2} + \delta_\ell(k)\right). \tag{2.31}$$

It is also possible to show that this relationship is true, as long as the potential vanishes faster than r^{-1}. The introduced quantity, $\delta_\ell(k)$, is called the *phase shift* and is a measure for how much the potential mixes the regular and irregular solutions through its interaction. That is, if one had zero potential everywhere, the shift would be 0 and our solution would be a pure spherical Bessel function. In the next section, we will discuss the importance of the phase shift through its connection to the scattering amplitude which is what we were trying to find.

What is the phase shift good for?

We are now interested in the *stationary state wave function*, denoted $\Psi^{(+)}_{\mathbf{k}_i}(\mathbf{r})$, which is a particular solution to the differential equation

$$\left(\nabla^2 + k^2 - U(\mathbf{r})\right)\Psi(\mathbf{r}) = 0 \tag{2.32}$$

that satisfies the asymptotic boundary condition

$$\Psi^{(+)}_{\mathbf{k}_i}(\mathbf{r}) \xrightarrow[r\to\infty]{} A\left[\exp(i\mathbf{k}_i\cdot\mathbf{r}) + f(k,\theta,\phi)\frac{\exp(ikr)}{r}\right] \tag{2.33}$$

where $\mathbf{k}_i$ is some initial wave vector. If we rewrite equation (2.33) using the well-known expansion of a plane wave in Legendre polynomials, $P_\ell(x)$,

$$A\exp(ikz) = A\exp(ikr\cos(\theta)) = A\sum_{\ell=0}^{\infty}(2\ell+1)i^\ell j_\ell(kr)P_\ell(\cos(\theta)) \tag{2.34}$$

where i is the imaginary unit, we can then compare it to the asymptotic form of the radial function $R_\ell(k,r)$, through their connection in equation (2.18), which after some coefficient comparisons gives us

$$f(k,\theta) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\exp(i\delta_\ell(k))\sin(\delta_\ell(k))P_\ell(\cos(\theta)). \tag{2.35}$$

We now have a direct relation between the desired scattering amplitude and the phase shift, but we can also find an expression for the total cross-section based on the connection between it and the amplitude

$$\sigma_{\text{tot}}(k) = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2(\delta_\ell(k)). \tag{2.36}$$

Now, in general, the idea of the partial wave method is that, the lower the energy of the incident particle, the less terms in the sum will be needed. This can be explained by looking back at equation (2.21) and writing an effective potential by adding a centrifugal barrier term to the potential

$$U_{\text{eff}}(r) = U(r) + \frac{\ell(\ell+1)}{r^2}. \tag{2.37}$$

When ℓ increases, the second term becomes more prominent and the incident particle will need more energy to overcome this repulsion in order to probe the interaction region. Consequently, as we are only interested in low-energy scattering; s-wave scattering, we only need the lowest order possible, $\ell = 0$. Therefore we will be particularly interested in the expressions (using that $P_0(x) = 1$)

$$f(k) = \frac{1}{k}\exp(i\delta_0(k))\sin(\delta_0(k)), \quad \sigma_{\text{tot}}(k) = \frac{4\pi}{k^2}\sin^2(\delta_0(k)). \tag{2.38}$$

2.2.2 Our system

To try out the ECG method, we are going to use one of the simplest non-trivial systems, that being low-energy proton-hydrogen scattering which would fall within the theory of 'non-relativistic scattering by a real potential'. As with most things in quantum mechanics, the place to begin is with Schrödinger's equation which states

$$H\Psi(\mathbf{x},t) = [T(\mathbf{x}) + V(\mathbf{x})]\,\Psi(\mathbf{x},t) = E\Psi(\mathbf{x},t) \tag{2.39}$$

where H is our Hamiltonian, $T(\mathbf{x})$ describes the kinetic energy of the system and $V(\mathbf{x})$ is the potential of our system. As is conventional in this field, we will be using Hartree atomic units, in which our Hamiltonian will have the form the

$$H = T_{p_H} + T_{p_i} + T_e - \frac{1}{|\mathbf{x}_e - \mathbf{x}_{p_H}|} - \frac{1}{|\mathbf{x}_e - \mathbf{x}_{p_i}|} + \frac{1}{|\mathbf{x}_{p_H} - \mathbf{x}_{p_i}|} \tag{2.40}$$

where $\mathbf{x}_{p_H}$ is the position vector corresponding to the hydrogen proton, $\mathbf{x}_{p_i}$ is the incident proton, $\mathbf{x}_e$ is the electron and $T_i = -\frac{1}{2m_i}\partial^2_{\mathbf{x}_i}$ are the kinetic energies.

At first glance it might seem like our entire analysis in section 2.2.1 was in vain considering that:

1) *We are not dealing with a central potential*

2) *We only have coulomb terms, which do not satisfy the vanishing requirement*

but luckily, we have a workaround for both of these. As will be discussed further in section 2.2.3, our strategy will be to use the Born-Oppenheimer approximation to separate the system into two parts which will net us an effective potential energy, $\epsilon(\mathbf{y})$. Other than greatly simplifying the calculation, this also has the added benefit of turning it into a central potential problem; solving the first complication. As for the vanishing requirement, we have to think about the system electrodynamically. The hydrogen atom does not have an electric monopole so when far away the potential is effectively immediately 0. Meanwhile, as the incident proton moves closer, the best place for the electron to be, energetically speaking, is in-between the two protons; creating an ion-induced dipole, which, as luck would have it, has an inverse square potential[11], r^{-2}. Therefore our analysis is still valid for our system and, by the theory of this section, we should eventually be able to fit a sine wave far away and find the phase shift as we wanted.

2.2.3 Born-Oppenheimer approximation

One of the primary methods for calculation we are going to utilise is the Born-Oppenheimer (BO) approximation which is a sort of adiabatic approximation where we separate our system into a fast moving, and slow moving, part and assume that these can be solved separately. Normally, this comes in the form of separating the nuclear and electronic motion, but in our case we have the fast relative motion between the hydrogen proton and its electron and the slow relative motion between the hydrogen proton and incident proton. As such, if we denote the slow moving position coordinate with $\mathbf{y}$ and the fast moving with $\mathbf{x}$ we can then rewrite our solution as

$$\Psi(\mathbf{x},\mathbf{y}) = \sum_{n=1}^{N} f_n(\mathbf{y})\phi_n(\mathbf{x},\mathbf{y}) \tag{2.41}$$

where the $\phi_n(\mathbf{x},\mathbf{y})$s form an orthonormal basis and satisfy

$$[T_x + V(\mathbf{x},\mathbf{y})]\phi_n(\mathbf{x},\mathbf{y}) = \epsilon_n(\mathbf{y})\phi_n(\mathbf{x},\mathbf{y}) \tag{2.42}$$

if we insert these two conditions into equation (2.39) we obtain:

$$\begin{aligned}[T_x + T_y + V(\mathbf{x},\mathbf{y})] &\sum_{n=1}^{N} f_n(\mathbf{y})\phi_n(\mathbf{x},\mathbf{y}) \\ &= T_y \sum_{n=1}^{N} f_n(\mathbf{y})\phi_n(\mathbf{x},\mathbf{y}) + \sum_{n=1}^{N} f_n(\mathbf{y})[T_x + V(\mathbf{x},\mathbf{y})]\phi_n(\mathbf{x},\mathbf{y}) \\ &= [T_y + \epsilon_n(\mathbf{y})] \sum_{n=1}^{N} f_n(\mathbf{y})\phi_n(\mathbf{x},\mathbf{y}) = E \sum_{n=1}^{N} f_n(\mathbf{y})\phi_n(\mathbf{x},\mathbf{y})\end{aligned} \tag{2.43}$$

We then do the classic trick of applying $\langle\, \phi_m(\mathbf{x},\mathbf{y}) \,|$, or rather $\int \mathrm{d}^3x\phi_m^*$, since we are keeping $\mathbf{y}$ constant, on both sides giving us:

$$\sum_{n=1}^{N} \langle\, \phi_m \,|T_y f_n(\mathbf{y})|\, \phi_n \,\rangle + \sum_{n=1}^{N} \epsilon_n(\mathbf{y}) f_n(\mathbf{y}) \langle\, \phi_m \,|\, \phi_n \,\rangle = E \sum_{n=1}^{N} f_n(\mathbf{y}) \langle\, \phi_m \,|\, \phi_n \,\rangle \tag{2.44}$$

where orthogonalisation then allows us to write it as

$$\sum_{n=1}^{N} \langle\, \phi_m \,|T_y f_n(\mathbf{y})|\, \phi_n \,\rangle + \epsilon_m(\mathbf{y}) f_m(\mathbf{y}) = E f_m(\mathbf{y}). \tag{2.45}$$

If we now assume that y is slow enough, such that the operator T_y will not influence ϕ_n too much, we can do another BO approximation to simply pull T_y outside like the other terms, giving us the equation

$$[T_y + \epsilon(\mathbf{y})] f(\mathbf{y}) = E f(\mathbf{y}). \tag{2.46}$$

This is another sort of Hamiltonian relation, but for $f(\mathbf{y})$. So the plan is to rewrite the $\phi_n(\mathbf{x},\mathbf{y})$ using the method of ECGs and then solve equation (2.42) to get an 'effective potential' depending only on y, $\epsilon(\mathbf{y})$. We then use this potential to solve equation (2.46) via the grid method, described in appendix C, which should give us our f_n's, as well as the real energy of the system.

2.2.4 Non-Born-Oppenheimer approximation

If we instead choose not to do the second BO approximation, we need another way to deal with the summation term of equation (2.45). Since we know that $T_y = \frac{1}{2m_y}\partial_y^2$, we can simply just insert ∂_y^2 into $\langle\, \phi_m \,|T_y f_n(\mathbf{y})|\, \phi_n \,\rangle$ and use it to the right, which should give us 3 terms

$$\partial_y \left(f(\mathbf{y})\phi_n(\mathbf{x},\mathbf{y})\right) = \partial_y^2(f(\mathbf{y}))\phi_n(\mathbf{x},\mathbf{y}) + f(\mathbf{y})\partial_y^2\phi_n(\mathbf{x},\mathbf{y}) + 2\left(\partial_y f(\mathbf{y})\right)\left(\partial_y\phi_n(\mathbf{x},\mathbf{y})\right). \tag{2.47}$$

Inserting equation (2.47) back into equation (2.45) gives us:

$$T_y f_m(\mathbf{y}) + \frac{1}{2m_y}\sum_{n=1}^{N}\left(2\partial_y f_n(\mathbf{y})\langle\, \phi_m \,|\, \partial_y\phi_n \,\rangle + f_n(\mathbf{y})\langle\, \phi_m \,|\, \partial_y^2\phi_n \,\rangle\right) + \epsilon_m(\mathbf{y})f_m(\mathbf{y}) = E f_m(\mathbf{y}). \tag{2.48}$$

We can now introduce the scattering coefficients, P_{mn} and Q_{mn}

$$P_{mn}(\mathbf{y}) = \langle\, \phi_m \,|\, \partial_y\phi_n \,\rangle, \quad Q_{mn}(\mathbf{y}) = \langle\, \phi_m \,|\, \partial_y^2\phi_n \,\rangle, \tag{2.49}$$

and get

$$T_y f_m(\mathbf{y}) + \frac{1}{2m_y}\sum_{n=1}^{N}\left(2\partial_y f_n(\mathbf{y})P_{mn}(\mathbf{y}) + f_n(\mathbf{y})Q_{mn}(\mathbf{y})\right) + \epsilon_m(\mathbf{y})f_m(\mathbf{y}) = E f_m(\mathbf{y}), \tag{2.50}$$

which is a more difficult differential equation for $f_m(\mathbf{y})$. The next step is then to find an explicit form of P_{mn} and Q_{mn}. This, like all our other matrix elements from 2.1.2, will be done through ECGs, but we keep in mind that the inner product is specifically not integrating over the slow variable, from how we introduced it in the previous section. So if we assume that the basis functions, ϕ_i, have the form

$$\phi_n = \exp\left(-\mathbf{x}^T A\mathbf{x}\right), \quad \phi_m = \exp\left(-\mathbf{x}^T A'\mathbf{x}\right), \tag{2.51}$$

then the scattering coefficients will have the following form[6]

$$P_{mn} = -2\left(\tilde{\mathbf{u}}_k^T\,[A]^{\tilde{k}} + A_{kk}\mathbf{x}_k^T\right)\tilde{M}_k, \tag{D.27}$$

$$\begin{aligned} Q_{mn} = 4\Bigg(&\left(A'\Lambda_k A\right)_{kk}\mathbf{x}_k^2 + \tilde{\mathbf{u}}_k^T\left(\left[A'\Lambda_k A\right]^{\tilde{k}} + \left(\left[A'\Lambda_k A\right]_{\tilde{k}}\right)^T\right)\mathbf{x}_k + \\ &\frac{3}{2}\,\mathrm{Tr}\left(\widetilde{(A'\Lambda_k A)}_k\tilde{R}_k\right) + (\tilde{\mathbf{u}}_k)^T\,\widetilde{(A'\Lambda_k A)}_k\tilde{\mathbf{u}}_k\Bigg)\tilde{M}_k, \end{aligned} \tag{D.28}$$

where k denotes the index of the slow changing variable of $\mathbf{x}$; that is, in our prior notation we would write $\mathbf{y} = \mathbf{x}_k$. If our object is adorned by a $\tilde{\circ}_k$, it will imply the removal of all indices of the object having to do with k (The k'th row and column for matrices, and for column and row vectors, respectively), Λ_k is the matrix that has a value of 1 at index kk and is 0 everywhere else. $[\circ]_n$ or $[\circ]^n$ being either a row or column vector respectively created from the n'th row or column of the matrix in the

6: Although, only the reduced forms without shift vectors. For more general coefficients see appendix E.

brackets. If the n has a tilde on it, like so $[\circ]^{\tilde{n}}$, it will mean the vector created from this operation with the n'th index removed. Lastly we have the symbols:

$$\tilde{\mathbf{u}}_k = \frac{1}{2} W_k \tilde{\xi}_{\tilde{\mathbf{k}}}, \quad W_k = (\tilde{B}_k)^{-1}, \quad \xi_i = 2B_{ki}\mathbf{x}_k, \tag{2.52}$$

$$\tilde{M}_k = \exp\left(-B_{kk}\mathbf{x}_k^2\right) \exp\left(\frac{1}{4}\left(\tilde{\xi}_{\tilde{\mathbf{k}}}\right)^T W_k \tilde{\xi}_{\tilde{\mathbf{k}}}\right) \left(\frac{\pi^{N-1}}{\det\left(\tilde{B}_k\right)}\right)^{3/2}. \tag{D.12}$$

If one wishes to see explicit, written-out examples of the notation in action, they can check out the designated section in appendix D.

The scattering coefficients, Q and P, are alternating and decreasing in nature[12]. Therefore we will overshoot and undershoot our target by less and less as we add more terms. Thus, the 'real value' will lie somewhere between the zeroth term (double BO) and first term approximation, which just adds Q_{01},

$$T_y f_0(\mathbf{y}) + \frac{1}{2m_y} f_1(\mathbf{y}) Q_{01}(\mathbf{y}) + \epsilon_0(\mathbf{y}) f_0(\mathbf{y}) = E f_0(\mathbf{y}). \tag{2.53}$$

This enables us to find both a lower and upper bound on our calculations with a bit more effort.

2.3 Optimization

Looking back at the ansatz used in the Ritz method from equation (2.2),

$$\Psi = \sum_{i=1}^{N} c_i \psi_i(\{a_i\}), \tag{2.2}$$

in light of the discussion of the ECGs, it should now be clear that the coefficients a_i, in our case, represent the matrices, A_i, used in the complete description of our Gaussian basis elements as per their reduced form in equation (2.6),

$$G(A, \mathbf{x}) = \exp\left(-\mathbf{x}^T A \mathbf{x}\right). \tag{2.6}$$

However, while the c_i's are given to us "for free" when we solve the generalized eigenvalue problem, equation (2.3),

$$\mathcal{H}\mathbf{c} = E\mathcal{N}\mathbf{c}, \tag{2.3}$$

we still need to generate some positive-definite A_i's before we get to the optimization process. So the question becomes both how should we generate them and how should we optimize them. Overall we will have two different optimization strategies to choose between: we can either optimise everything at once or generate the A_i's stochastically before optimizing the c_i's via the generalized eigenvalue problem. Both of these options will be discussed below.

2.3.1 The generation of A matrices

As noted during the definition of the ECGs, we need the A matrices to be symmetric and positive-definite. This is simply to ensure that all our integrals will be convergent. The naive, but obvious, approach to generating the A matrices would be the following process:

1. Create a random $N \times N$ matrix
2. Symmetrize it
3. Check if it is positive-definite[7] (if not return to step 1).

But it turns out that there is a pretty big bottleneck hidden in plain sight in the form of step number 3. It turns out that positive-definite matrices are actually quite scarce once the dimensionality is increased, which is discussed further in appendix E. Therefore it quickly becomes an impractical solution for even small systems, but luckily, in this section, we will argue for the existence of a method for generating positive *semi*-definite matrices[8], which we can then massage into proper definite matrices. The idea is that if we can somehow find a way to rewrite $\mathbf{x}^T A \mathbf{x}$ as $\sum_{i<j}^{N} \left(\frac{\mathbf{x}_i - \mathbf{x}_j}{b_{ij}} \right)^2$ then we are guaranteed to get a non-negative result for all choices of $\mathbf{x}$'s. It turns out that the choice of A, which makes this possible is

$$A = \sum_{i<j} \frac{\mathbf{w}(i,j)\mathbf{w}(i,j)^T}{b_{ij}^2}, \tag{2.54}$$

where $\mathbf{w}(i,j)$ is the vector that has a 1 in entry i, a -1 in entry j and 0 otherwise. It is quite easy to show this works as $\mathbf{w}(i,j)^T \mathbf{x} = \mathbf{x}_i - \mathbf{x}_j$

$$\mathbf{x}^T A \mathbf{x} = \mathbf{x}^T \left(\sum_{i<j} \frac{\mathbf{w}(i,j)\mathbf{w}(i,j)^T}{b_{ij}^2} \right) \mathbf{x} = \sum_{i<j} \frac{\left(\mathbf{x}^T \mathbf{w}(i,j)\right)\left(\mathbf{w}(i,j)^T \mathbf{x}\right)}{b_{ij}^2} = \sum_{i<j} \frac{\left(\mathbf{x}_i - \mathbf{x}_j\right)^2}{b_{ij}^2}. \tag{2.55}$$

However, the semi-definiteness turns out not just to be a possibility, but a consequence, as one might notice that a vector that has identical entries in i and j has a zero inner product with a given $\mathbf{w}(i,j)$ and therefore the vector containing all 1's, let us call it $\mathbf{m}$, satisfies:

$$\mathbf{w}(i,j)^T \mathbf{m} = 0, \forall i, j. \tag{2.56}$$

If this is true, then $\mathbf{m}$ must necessarily also be an eigenvector of A with eigenvalue 0

$$A\mathbf{m} = \sum_{i<j} \frac{\mathbf{w}(i,j)\left(\mathbf{w}(i,j)^T \mathbf{m}\right)}{b_{ij}^2} = \sum_{i<j} 0 = 0, \tag{2.57}$$

7: This would be done through a diagonalisation routine by checking if all the eigenvalues are positive which is an equivalent criteria.

8: Semi-definiteness simply means that $\mathbf{x}^T A \mathbf{x} \geq 0$ instead of $\mathbf{x}^T A \mathbf{x} > 0$.

so all matrices generated this way are guaranteed to be positive semi-definite, which is not quite strict enough for our purpose. Fortunately, we know that this eigenstate corresponds to the center of mass coordinate, when we have transformed it to Jacobi coordinates, and it has an eigenvalue of 0 exactly because there are no external forces acting on our system. Therefore, there is not a problem, as we are disregarding the center of mass coordinate completely by removing it after the transformation. Thus, we have ensured that our A's are positive-definite as we wanted.

Another advantage of this rewritten form is that it gives us a clear thing to use in the optimization, that being the $\frac{N(N+1)}{2}$ b_{ij}-coefficients making up A.

2.3.2 The stochastic method

As for the actual optimization, a more exotic method one could use is a stochastic one. In this method, we have two parameters to change the quality of the fit: the amount of repeats and the amount of iterations, t. The repeats is how many times we iterate through the entire basis set, as the first element we found might not be as good as it could be, once the entire basis has been created. Iterations, on the other hand, is just how many elements we test per position in the basis. The algorithm is then as follows (for a basis of k elements)

1. Generate the proper amount of b_{ij}'s, using some suitable random distribution, and use them to create t candidates for your first basis element, A_1.

2. Out of the t candidates, pick the A_1 which minimizes the energy, using equation (2.2), on its own and move on to your second basis element, A_2.

3. Do the same procedure as for A_1, except when you compare the candidates, you do it with respect to the two-element basis, $\{A_1, A_2\}$. Pick the A_2 which made $\{A_1, A_2\}$ yield the lowest energy, and you have a provisional basis of two elements.

4. Continue this procedure until the basis is full: $\{A_1, A_2, \cdots, A_k\}$.

5. Now, for each repeat, we start over at A_1 and go through the same thing again, except now all the choices have to be weighed against a full basis.

6. After all the repeats, we should now have a basis set which has been properly minimized. The energy here will be used as our ground state energy of the system.

We then do this for different y's, as described in section 2.2.3, and this should give us an effective energy curve as a function of y. This method has a lot of advantages when compared to its competition. First of all, it reduces the amount of objects to optimize over significantly which is usually the bottleneck of most other methods. It also does not require us to recalculate the Hamiltonian at every iteration nor to fully rediagonalize it every time we select a new basis element.

However, the method is not without problems. Since it only takes on one element at a time in the beginning there is a high probability that it ends up in a local minima instead of a global minima. This is not always fixed by further repeats since

by then the other elements will have been picked to minimize inside this minima. This problem is by no means unique to this method however. Another problem is that its efficiency is very dependent on the random distribution we choose. This is analogous to how a good starting guess and region of search is very important for other optimization strategies. If the matrix is big enough, corresponding to having a system with a lot of particles, this method is also not particularly faster than the direct approach, since the amount of numbers one needs to generate each time grows as N^2, which quickly adds up when including all the repeats and iterations on top.

We also had problems with getting it to converge properly, but this has been a general issue that we will discuss in section 2.3.4. In any case, after a lot of trouble, we chose to do what seemed to be a more direct approach.

2.3.3 The direct approach

Instead of doing the stochastic method, one could simply optimize everything at once which we decided to do instead. After much trouble and many attempts, we ended up settling on the 'Nelder-Mead' (NM) method, also called the *downhill simplex method*, which has be implemented using the Python library SciPy through a function called 'optimize.minimize'. Like the stochastic method this routine also has a chance of only finding a local minima since it is a local search heuristic[13], but it is also a lot easier to set up. For most calculations, except for the purposes of comparison, we usually chose to only optimize 3 ECGs which, as we will see later in section 3.2, seemed to be sufficient.

2.3.4 Problems with convergence

The biggest problem with the numerical aspect of this thesis, when using the methods presented in section 2.3.2 and 2.3.3, has been getting the optimization to act as we wanted it to. A lot of it probably boils down to poor implementation, but oftentimes we would simply end up with ground state energy lower, *much lower*, than what should be allowed through the variational method. It is almost as though the optimization would run into an algebraic error and then just insert random values. The running hypothesis for where this numerical problem arises is the from the fact that the double-precision floating-point format has very limited resolution when working with both large and small numbers at the same time; especially during division. This is further supported by equation (B.26) in which we have a variable a, which we proved in appendix B could not be equal to 0 unless we had collinearity between the constant vectors in the delta function and Coulomb potential. However, despite this analytical impossibility of 0, "`ZeroDivisionError: division by zero`" was by far the most common error in my script, and it always referred back to that very same equation. If nothing else, this tells us that if a robust numerical calculation is required, then we would need to use another datatype for our variables with higher precision, or rewrite the equations in a more numerically friendly way, which is outside my area of expertise.

After much hassle we did manage to get it to behave a little bit, for 3 ECGs specifically, but the limiting behaviour was still giving us values that were way too small. After having a discussion with my supervisor, who did not seem experience

the same complication, we found out the difference in our approaches was that he had set the off-diagonal elements, of the A matrices, to 0. After we did the same, we obtained the same result, but we have still yet to figure out what went wrong with the off-diagonal elements, and why they allowed for ground state values lower than physically possible. Only using diagonals thankfully also reduced the amount division errors, although they did not remove them completely.

Chapter 3

The Scattering System

In this section we will go into greater detail about the scattering system using most of the things derived in the previous chapter. A lot of preliminary numerical results will also be presented to check that the matrix elements are working as intended.

3.1 The system

As mentioned in section 2.2.2, the scattering problem we are going to try to look at is proton-hydrogen scattering, which means we are going to have a three-particle system. The reason for this choice is that we are only going to test whether or not this ECG method even makes sense to use, and for this purpose we deemed it useful to start with what seemed to be one of the simplest non-trivial scattering examples. First we want to rewrite our Hamiltonian, previously seen in equation (2.40); which we will write below for ease of access

$$H = T_{p_H} + T_{p_i} + T_e - \frac{1}{|\mathbf{x}_e - \mathbf{x}_{p_H}|} - \frac{1}{|\mathbf{x}_e - \mathbf{x}_{p_i}|} + \frac{1}{|\mathbf{x}_{p_H} - \mathbf{x}_{p_i}|}. \tag{2.40}$$

To rewrite it, we will introduce the variable and matrix

$$\mathbf{r} = \left[\mathbf{x}_e, \mathbf{x}_{p_H}, \mathbf{x}_{p_i}\right]^T, \quad \Lambda = \begin{bmatrix} \frac{1}{2m_e} & 0 & 0 \\ 0 & \frac{1}{2m_p} & 0 \\ 0 & 0 & \frac{1}{2m_p} \end{bmatrix}, \tag{3.1}$$

while reintroducing the notation $\mathbf{w}(i, j)$ from section 2.3.1 and K from section 2.1.2, allowing us to write it more succinctly as

$$H = K - \frac{1}{|\mathbf{w}(1,2)^T\mathbf{r}|} - \frac{1}{|\mathbf{w}(1,3)^T\mathbf{r}|} + \frac{1}{|\mathbf{w}(2,3)^T\mathbf{r}|}. \tag{3.2}$$

This is a more useful form when considering the shape of the calculated matrix elements. We can then Jacobi coordinate transform the system into the form seen in figure 3.1.

This reduces the complexity quite a bit since we now only have two variables, that being the fast variable, $\mathbf{x}$, and our slow variable, $\mathbf{y}$ (as per the discussion in section

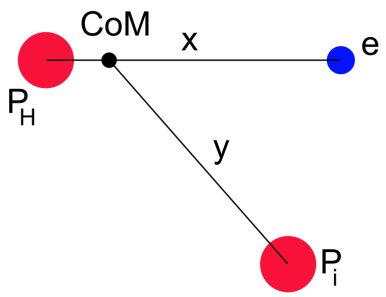

FIGURE 3.1: An illustration of our transformed system with the relevant variables noted. We note that we have reduced the degrees of freedom by one. We also note that when reducing y, which we are using as our slow variable, p_i comes way closer to p_H than to e, since it goes through the COM of hydrogen and p_H is more than 1800 heavier than e. This is relevant for the analysis we do in section 3.2. The credit for the image goes to its creator Martin C. Østerlund.

2.2.3). We also note that since the proton is about 1800 times more massive than the electron, the CoM of hydrogen is effectively right next to the hydrogen proton. This will be relevant when we have to test the limits of our matrix elements.

3.2 The limit test

To make sure we obtained the correct matrix elements, we thought it would be fruitful to reduce the complexity of the system by disregarding the repulsion between the protons, since, in this system, we have two recognizable limits for y. In one end, when the incident proton is far away, corresponding to large y values, all we have left is a single unperturbed hydrogen atom and we know that in our unit system this has a ground state energy of $-\frac{1}{2}$. Meanwhile, for small y, we just have a hydrogen atom with a nucleus of twice the mass and, more importantly, charge. One can show[14] that the energy of a hydrogen-like (one electron) atom with charge Z, in our units, is:

$$E_n = -\frac{Z^2}{2n^2}. \tag{3.3}$$

That is to say, in this particular situation the ground state energy is simply $E_1 = -\frac{Z^2}{2}$ and therefore we expect the other limit to approach $-\frac{2^2}{2} = -2$.

This result can be seen in figure 3.2, and it also supports the choice of using only 3 ECGs, as mentioned during section 2.3.3. This is because it seems noticeably better as a choice than 2, while not being significantly worse than 4, even though it is *a lot* quicker for my program to calculate. To see this comparison more clearly, we also made a plot comparing the differences between the 5 functions in figure 3.3.

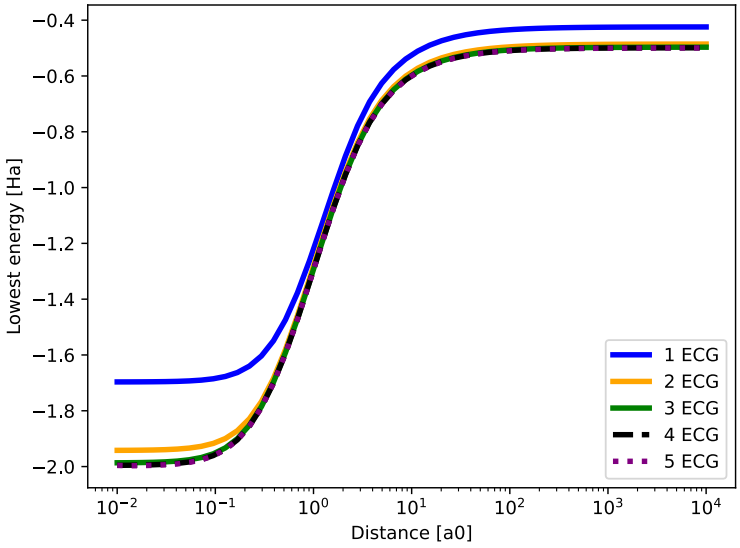

FIGURE 3.2: A semi-logarithmic plot showing the limiting behaviour of our proton-hydrogen wave functions, where we have disregarded the repulsion term between the protons, for a variable amount of ECGs in our basis. We see that in one end it quickly approaches -2 while in the other it approaches $-\frac{1}{2}$ as we expected theoretically from the discussion in section 3.2. It can also be seen, although it is made more clear in figure 3.2, that 3 ECGs seems to be the sweet spot as it is still noticeably better than 2, but not seemingly much worse than 4. The units of the x-axis are Bohr radii, a_0, and the units of the y-axis are Hartree energy units, Ha.

3.3 The actual calculation

The problems first become apparent when having to do the calculation with the repulsion included. Before the limit test, when doing the calculations with a non-diagonal matrix, we managed to make the curves seen in figure 3.4,

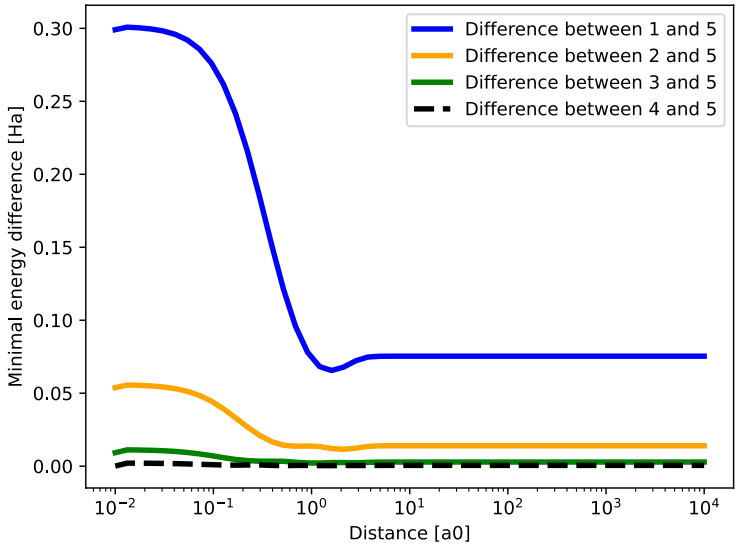

FIGURE 3.3: A semi-logarithmic plot showing the value difference between the wave functions of figure 3.2. This supports the choice of 3 ECGs being sufficient for the calculations. The units of the x-axis are Bohr radii, a_0, and the units of the y-axis are Hartree energy units, Ha.

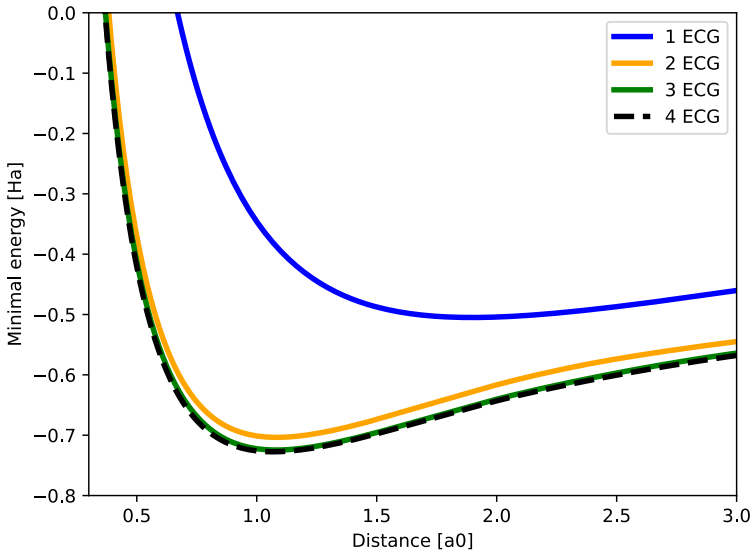

FIGURE 3.4: An energy curve plot for the proton-hydrogen scattering system when using non-diagonal PD matrices. We notice that it has a valley of minimum energy as is typical for bound systems like ours. The units of the x-axis are Bohr radii, a_0, and the units of the y-axis are Hartree energy units, Ha.

which matches the sort of curve one would want to find during these sorts of calculations. The issue is that using non-diagonal positive-definite matrices always

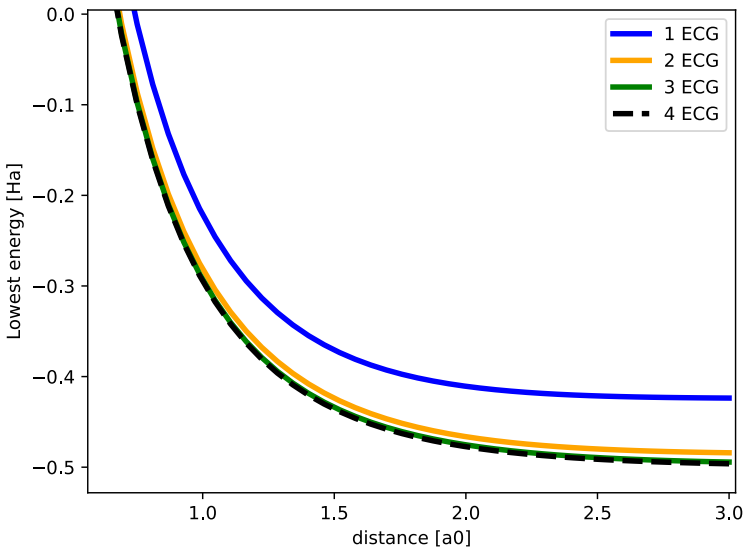

FIGURE 3.5: Typical energy curve plot for the proton-hydrogen scattering system when using diagonal matrices only. We notice that there is no valley this time unlike figure 3.4. The units of the x-axis are Bohr radii, a_0, and the units of the y-axis are Hartree energy units, Ha.

yielded the wrong limits, when performing the test afterwards, as mentioned in section 2.3.4. On the other hand, if we change to diagonal matrices we can obtain the limits just fine, but then when going back to calculate these energy curves, we can no longer reproduce the energy valleys that we expect, as seen in figure 3.5.

This is a problem since we know that H_2^+ exists, which would indicate a bound state solution exists somewhere, when moving the incident proton closer to the hydrogen atom. We have been discussing possible explanation for this difference. One possibility is that our figure 3.5 indeed contains the right minimum energies, but not for the ground state; making this an issue of ending up in some local minimum for a higher s-state. To test this, one could try getting closer to the global optimum right out of the gate by choosing a global optimization algorithm, like 'simulated annealing'; which is also available in SciPy's 'optimize' package, and let that find the global minimum for some initial choice of y, y_0. Then as we slowly vary y away from y_0, it should only move the minimum slightly in response. Therefore, we could use the global minimum for y_0 as a starting condition for the NM method for the reminder of the optimization. We do not know if this would work in practice, however, as we only tried changing the starting conditions manually, and sadly only ended up with errors or analogous plots to figure 3.5.

3.3.1 The grid plot

Considering that we did not end up with a proper result in the previous section, it is not surprising that the same holds true for the grid plot, but we will still go through the methodology as based on the description in appendix C, where one can also see

an example of it working in practice. Like so many times before, we start out with the general Hamiltonian equation

$$H = T + V, \tag{3.4}$$

where our potential, in this case, is the effective energy curve from figure 3.5, denoted $\epsilon(y)$, and the kinetic energy is discretely rewritten like in appendix C by using the symmetric central-difference approximation equation[15]

$$u_i'' = \frac{u_{i-1} - 2u_i + u_{i+1}}{(\Delta r)^2}. \tag{C.4}$$

In the end, we effectively end up with a Hamiltonian of the form

$$H = \begin{bmatrix} -\frac{1}{\mu(\Delta r)^2} + \epsilon(y_1) & 1 & 0 & \cdots & 0 \\ 1 & -\frac{1}{\mu(\Delta r)^2} + \epsilon(y_2) & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & 1 & -\frac{1}{\mu(\Delta r)^2} + \epsilon(y_{N-1}) & 1 \\ 0 & \cdots & 0 & 1 & -\frac{1}{\mu(\Delta r)^2} + \epsilon(y_N) \end{bmatrix}, \tag{3.5}$$

where $\mu = \frac{m_e}{m_p + m_e}$. We can solve this via diagonalisation and then pick the eigenvector corresponding to the lowest energy/eigenvalue as our ground state.

Chapter 4

Results and Discussion

In this section we would have compared the results of the direct ECG method, for both BO and non-BO proton-hydrogen scattering, to some experimental values, but since we did not get any numerical results to compare, we will simply discuss the efficiency of the method, and some possible further explorations one could do if so desired.

4.1 Efficiency of the method

Even though we failed to the desired numerical result, we can still comment on whether we expect the method to be particularly efficient. If we disregard the actual coding aspect, the final step will be to approximate the asymptotic sinusoidal behaviour of the outgoing radial wave function, as seen from partial waves. One could then rightfully ask if we even expect a finite amount of Gaussian functions to be especially well-suited to mimic sinusoidal behaviour at all. On the same topic of asymptotic behaviour, the people behind the initial review paper[2] also comment on the fact that the scattering wave function changing to a simple product form, once the incoming particle is far enough away, is one of the reasons for ECGs to be considered unfavorable for approximating asymptotic behaviour. The reason for this is that they implicitly assume all the vectors/particles are to be treated equally, mathematically speaking, which does not mesh well with shifts in the system where one, or more, particles suddenly can be considered completely disconnected from the rest. This change to product form can be illustrated mathematically by letting $\mathbf{R}$ be the collection of coordinate vectors used in the wave function describing the object at the wave center and $\mathbf{r}$ being the coordinate vectors of the incoming/outgoing particle

$$\Psi_{\text{in}} = \psi_i(\mathbf{R}, \mathbf{r}) \to \Psi_{\text{out}} = \psi_o(\mathbf{R})\phi(\mathbf{r}). \tag{4.1}$$

To mitigate the efficiency reduction from the asymptotic behaviour, they created an *asymptotic basis*, which is a reduced ECG where the wave center and the outgoing particle have their own ECG basis, that they could mix in with the normal basis

$$\Psi_o = \sum_n c_n \exp\left(-\mathbf{R}^T A_n \mathbf{R}\right), \quad \phi(\mathbf{r}) = \sum_n d_n \exp\left(-\mathbf{r}^T B_n \mathbf{r}\right). \tag{4.2}$$

A natural consequence this mixing of both types, is that it only saves computation time if one already has a large basis to begin with[9], as otherwise one would need to expand their own to make room, which might not be feasible to do without more computational power than what is available on an average laptop. In any case, whoever wants to continue with this method might want to look into how to best represent the asymptotic behaviour once they get to that part.

4.2 Future work

The obvious step forward is for someone to make some code that actually works properly and consistently to make sure that this semi-classical ECG approach is actually worth pursuing despite its numerical annoyances and huge algebraic expressions. Once this has been confirmed, one can begin mixing it with other theories and systems to check the boundaries of its application. One notable scattering problem is that of strong force nucleon-nucleon scattering, which would allow one to check how compatible it is with different nuclear models; in particular the explicit pion model which my supervisor has worked with a lot previously[10].

9: As an example, for a e^--He ($^2S^e$) (s-wave scattering of electrons from the helium ground state) phase shift calculation[16], they could get better convergence from 800 three-electron ECGs supplemented by 40 additional asymptotic basis functions than a basis of 1600 three-electron ECG by themselves.

10: As an example, see previously mentioned Østerlund [7] or his own article [17].

Chapter 5

Conclusion

In this thesis, we set out to develop and test a more classical method of low-energy scattering calculations using ECGs. First, the mathematical and theoretical groundwork was laid and explored in great detail, primarily through the calculation of various matrix elements; the results of which can be found primarily in sections 2.1.2 and 2.2.4 (or, for the full calculation, in appendix B and appendix D). Then we moved on to questions about the methodology for numerical implementation which we described in great detail with a lot of focus on the 'whys' which one might not initially consider. The following preliminary tests of the formulas we found showed a promising agreement between the theoretical expectations and numerical results, but further troubles with convergence in the code limited the scope of the project from that point forward.

However, even with this limited scope, future prospects were still discussed and the possibility for a future numerical investigation, that even includes other models as well, might still be possible, and will be even easier to instigate now that the foundation has been laid down entirely.

Appendix A

Jacobi Transform

In this appendix we will quickly derive the Jacobi basis transformation relations as seen in equation (A.4) on page 10. The only thing we will use is that we have a transformation matrix, J, which gives us the following relation

$$\mathbf{r} = J\mathbf{x} \iff \mathbf{x} = J^{-1}\mathbf{r}. \tag{A.1}$$

- **The kinetic term**

  The general kinetic term of the Hamiltonian of a N-particle system can be written as $K = -\partial_{\mathbf{x}}\Lambda\partial_{\mathbf{x}^T}$ where $\partial_{\mathbf{x}} = (\partial_{x_1}, \cdots, \partial_{x_N})$ and Λ is a $N \times N$ positive-definite matrix, which means a general ij'th term has the form

  $$\frac{\partial}{\partial x_i}\Lambda_{ij}\frac{\partial}{\partial x_j}, \tag{A.2}$$

  which through the chain rule and transformation becomes

  $$\frac{\partial}{\partial r_k}\frac{\partial r_k}{\partial x_i}\Lambda_{ij}\frac{\partial}{\partial r_\ell}\frac{\partial r_\ell}{\partial x_j} = \frac{\partial}{\partial r_k}J_{ki}\Lambda_{ij}J_{\ell j}\frac{\partial}{\partial r_\ell}, \tag{A.3}$$

  from which we can infer that the general matrix transformation has the form

  $$K \to JKJ^T. \tag{A.4}$$

- **Vectors**

  We will also come across a lot of terms of the form $\omega^T\mathbf{x}$, which will be transformed like above

  $$\omega^T\left(J^{-1}\mathbf{r}\right) = \left(\left(J^{-1}\right)^T\omega\right)^T\mathbf{r}, \tag{A.5}$$

  from which we infer that the general vector transformation has the form

  $$\omega \to \left(J^{-1}\right)^T\omega. \tag{A.6}$$

Appendix B

Calculation of Matrix Elements

In this appendix we will calculate some of the matrix elements seen on page 10. As a shorthand we will write

$$G' = G(\mathbf{s}'; A', \mathbf{x}), \quad G = G(\mathbf{s}; A, \mathbf{x}), \quad \partial_a = \frac{\partial}{\partial a}. \tag{B.1}$$

B.1 The Delta Function Matrix Element

For this calculation we will only be requiring two well-known formulas, that being the overlap between two ECGs for a 3-dimensional system with N particles[8]

$$\langle G' \,|\, G \rangle = M_0(B, \mathbf{v}) = \exp\left(\frac{1}{4}\mathbf{v}^T R \mathbf{v}\right)\left(\frac{\pi^N}{\det(B)}\right)^{3/2}, \tag{B.2}$$

where $R = B^{-1}$, $B = A + A'$ and $\mathbf{v} = \mathbf{s} + \mathbf{s}'$, and the Fourier transform of the (three dimensional) delta function

$$\delta(\mathbf{y} - \mathbf{y_0}) = \frac{1}{(2\pi)^3}\int \exp\left(i\mathbf{k}^T(\mathbf{y} - \mathbf{y_0})\right) \mathrm{d}^3\mathbf{k}. \tag{B.3}$$

As equation (B.3) alludes to, we want to work with a Fourier transform at some point. Therefore we first want to look at the matrix element for $\exp\left(i\mathbf{k}^T\left(\omega^T\mathbf{x}\right)\right)$, as it will allow us to generalise the matrix elements of functions of the form $f(\omega^T\mathbf{x})$ later

$$\begin{aligned}
\langle G' \,|\, \exp\left(i\mathbf{k}^T\left(\omega^T\mathbf{x}\right)\right) \,|\, G \rangle &= M_0(B, \mathbf{v} + i\mathbf{k}\omega) \\
&= \exp\left(\frac{1}{4}(\mathbf{v} + i\mathbf{k}\omega)^T R (\mathbf{v} + i\mathbf{k}\omega)\right)\left(\frac{\pi^N}{\det(B)}\right)^{3/2} \\
&= M_0(B, \mathbf{v}) \cdot \exp\left(-\alpha\mathbf{k}^2 + i\mathbf{k}^T\mathbf{q}\right),
\end{aligned} \tag{B.4}$$

where

$$\alpha = \frac{1}{4}\omega^T R \omega, \quad \mathbf{q} = \frac{1}{2}\omega^T R \mathbf{v}. \tag{B.5}$$

In the calculation we used the fact that $\exp\left(i\mathbf{k}^T\left(\omega^T\mathbf{x}\right)\right)$ was linear in $\mathbf{x}$ and therefore only affected the final shift term. As an important remark, we will just point out

that $\alpha > 0$ since R is a positive-definite matrix. We now define $F(\mathbf{k})$ as the Fourier transform of the function $f(\omega^T\mathbf{x})$ and look at the matrix element of the function via the transform

$$\begin{aligned}\langle G'|f(\omega^T\mathbf{x})|G\rangle &= \langle G'|\int \frac{d^3\mathbf{k}}{(2\pi)^3}F(\mathbf{k})\exp\left(i\mathbf{k}^T(\omega^T\mathbf{x})\right)|G\rangle \\ &= \int \frac{d^3\mathbf{k}}{(2\pi)^3}F(\mathbf{k})\langle G'|\exp\left(i\mathbf{k}^T(\omega^T\mathbf{x})\right)|G\rangle \\ &= \frac{M_0(B,\mathbf{v})}{(2\pi)^3}\int d^3\mathbf{k}\ F(\mathbf{k})\exp\left(-\alpha\mathbf{k}^2+i\mathbf{k}^T\mathbf{q}\right).\end{aligned} \tag{B.6}$$

We can now work with the delta function, $\delta(\omega^T\mathbf{x}-\mathbf{y_0})$, with $\omega^T\mathbf{x}=\mathbf{y}$, for which we know $F(\mathbf{k}) = \exp\left(-i\mathbf{k}^T\mathbf{y_0}\right)$ due to equation (B.3), and we get

$$\begin{aligned}\langle G'|\delta(\mathbf{y}-\mathbf{y_0})|G\rangle &= \frac{M_0(B,\mathbf{v})}{(2\pi)^3}\int d^3\mathbf{k}\exp\left(-i\mathbf{k}^T\mathbf{y_0}\right)\exp\left(-\alpha\mathbf{k}^2+i\mathbf{k}^T\mathbf{q}\right) \\ &= \frac{M_0(B,\mathbf{v})}{(2\pi)^3}\int d^3\mathbf{k}\exp\left(-\alpha\left(\mathbf{k}^2-\frac{i}{\alpha}\mathbf{k}^T(\mathbf{q}-\mathbf{y_0})\right)\right).\end{aligned} \tag{B.7}$$

To calculate this, we simply complete the square in the exponential, which is done by multiplying and dividing by $\exp\left(\frac{1}{4\alpha}(\mathbf{q}-\mathbf{y_0})^2\right)$, giving us

$$\langle G'|\delta(\mathbf{y}-\mathbf{y_0})|G\rangle = \frac{M_0(B,\mathbf{v})}{(2\pi)^3}\exp\left(-\frac{1}{4\alpha}(\mathbf{q}-\mathbf{y_0})^2\right)\int d^3\mathbf{k}\exp\left(-\alpha\left(\mathbf{k}-\frac{i}{\alpha}(\mathbf{q}-\mathbf{y_0})\right)^2\right). \tag{B.8}$$

Since we can split the square of a vector into the square of its constituents, $\mathbf{v}^2 = v_1^2+\cdots+v_N^2$, and the exponential and integral satisfies:

$$\exp(x+y)=\exp(x)\exp(y), \qquad \iint \mathrm{d}x\mathrm{d}y f(x)g(y) = \int \mathrm{d}y\ g(y)\int \mathrm{d}x\ f(x), \tag{B.9}$$

what we have left is a product of three integrals of the well-known form[18]

$$\int_{-\infty}^{\infty}\mathrm{d}x\exp\left(-a(x-b)^2\right)=\sqrt{\frac{\pi}{a}}. \tag{B.10}$$

This leaves us with the final result

$$\begin{aligned}\langle G'|\delta(\mathbf{y}-\mathbf{y_0})|G\rangle &= \frac{M_0(B,\mathbf{v})}{(2\pi)^3}\exp\left(-\frac{1}{4\alpha}(\mathbf{q}-\mathbf{y_0})^2\right)\left(\sqrt{\frac{\pi}{\alpha}}\right)^3 \\ &\xrightarrow{\mathbf{v}=0} \frac{M_0(B,\mathbf{0})}{(2\pi)^3}\exp\left(-\frac{1}{4\alpha}\mathbf{y_0}^2\right)\left(\sqrt{\frac{\pi}{\alpha}}\right)^3\end{aligned} \tag{B.11}$$

B.2 The Delta Function + Kinetic Matrix Element

In this section, we will calculate the kinetic matrix element that includes a delta function

$$\langle G'|K\delta(\omega^T\mathbf{x}-\mathbf{y_0})|G\rangle, \quad K=-\partial_{\mathbf{x}}\Lambda\partial_{\mathbf{x}^T}=-\sum_{i,j}\Lambda_{ij}\partial_{\mathbf{x}_i}\partial_{\mathbf{x}_j}, \quad \partial_{\mathbf{x}_i}=\frac{\partial}{\partial\mathbf{x}_i}, \tag{B.12}$$

where Λ is another symmetric positive-definite matrix, and

$$\partial_{\mathbf{x}^T} = \left[\partial_{\mathbf{x}_1}, \partial_{\mathbf{x}_2}, \cdots, \partial_{\mathbf{x}_N}\right]^T, \quad \partial_{\mathbf{x}} = \left[\partial_{\mathbf{x}_1}, \partial_{\mathbf{x}_2}, \cdots, \partial_{\mathbf{x}_N}\right]. \tag{B.13}$$

First we want to calculate the kinetic energy matrix element, $\langle G' | K | G \rangle$, by itself. In order to do this we need to calculate some differentiation identities. The simplest is that if $\mathbf{x}_i$ is d-dimensional for all i then

$$\partial_{\mathbf{x}}\mathbf{x} = \sum_{i=1}^{N} \partial_{\mathbf{x}_i}\mathbf{x}_i = \sum_{i=1}^{N}\sum_{j=1}^{d} \left(\partial_{\mathbf{x}_i}\right)_j (\mathbf{x}_i)_j = \sum_{i=1}^{N}\sum_{j=1}^{d} = d \cdot n. \tag{B.14}$$

If M is a symmetric positive-definite matrix then we can generalize this result further by looking at the differential $\partial_{\mathbf{x}} M\mathbf{x}$, which can transform via diagonalization into

$$\partial_{\mathbf{x}} M\mathbf{x} = (\partial_{\mathbf{r}} Q)\, M\left(Q^T\mathbf{r}\right) = \partial_{\mathbf{r}} D\mathbf{r} = \sum_{i=1}^{N} D_{ii}\partial_{\mathbf{x}_i}\mathbf{x}_i = d \cdot \sum_{i=1}^{N} D_{ii} = d \cdot \mathrm{Tr}(D) = d \cdot \mathrm{Tr}(M). \tag{B.15}$$

We see that it reduces to the result above when we set M as the $N \times N$ identity matrix, as we expected. We can also show that if we have another vector of vectors, $\mathbf{b}$, then

$$\partial_{\mathbf{x}}\left(\mathbf{b}^T\mathbf{x}\right) = \left[\partial_{\mathbf{x}_1}\left(\mathbf{b}_1^T\mathbf{x}_1 + \cdots\right), \cdots, \partial_{\mathbf{x}_N}\left(\mathbf{b}_1^T\mathbf{x}_1 + \cdots\right)\right] = \left[\mathbf{b}_1^T, \cdots, \mathbf{b}_N^T\right] = \mathbf{b}^T, \tag{B.16}$$

as well as the important quadratic identity

$$\begin{aligned}\partial_{\mathbf{x}}\left(\mathbf{x}^T M\mathbf{x}\right) = \partial_{\mathbf{x}}\left(\mathbf{r}^T D\mathbf{r}\right) &= \left[\partial_{\mathbf{x}_1}\left(D_1\mathbf{r}_1^2 + \cdots\right), \cdots, \partial_{\mathbf{x}_N}\left(D_1\mathbf{r}_1^2 + \cdots\right)\right] \\ &= \left[\sum_i D_{ii}\left(\partial_{\mathbf{r}_i}\mathbf{r}_i^2\right)\frac{\partial \mathbf{r}_i}{\partial_{\mathbf{x}_1}}, \cdots, \sum_i D_{ii}\left(\partial_{\mathbf{r}_i}\mathbf{r}_i^2\right)\frac{\partial \mathbf{r}_i}{\partial_{\mathbf{x}_N}}\right].\end{aligned} \tag{B.17}$$

Using the transformation $\mathbf{r} = Q\mathbf{x}$ again, we can rewrite one of these sums as:

$$\begin{aligned}\sum_i D_{ii}\left(\partial_{\mathbf{r}_i}\mathbf{r}_i^2\right)\frac{\partial \mathbf{r}_i}{\partial_{\mathbf{x}_m}} &= 2\sum_i D_{ii}\mathbf{r}_i^T Q_{im} = 2\sum_{i,j} D_{ii}\left(Q_{ij}\mathbf{x}_j\right)^T Q_{im} \\ &= 2\sum_j \mathbf{x}_j^T \sum_i Q_{ij}^T D_{ii} Q_{im} = 2\sum_j \mathbf{x}_j^T M_{jm} = 2\left[x^T M\right]_m,\end{aligned} \tag{B.18}$$

and if we reinsert this back into the equation, it will give us

$$\partial_{\mathbf{x}}\left(\mathbf{x}^T M\mathbf{x}\right) = 2\left[\left[\mathbf{x}^T M\right]_1, \left[\mathbf{x}^T M\right]_2, \cdots, \left[\mathbf{x}^T M\right]_N\right] = 2\mathbf{x}^T M. \tag{B.19}$$

One could use the exact same methods to show the analogous identities for $\partial_{\mathbf{x}^T}$, although they are the exact same except for a transposition.

Armed with these identities, we are now ready to calculate the matrix element of the kinetic energy. This will be done by first calculating $\langle G' | \mathbf{x} | G \rangle$, using that we have an exponential factor of the form $\exp\left(\mathbf{v}^T\mathbf{x}\right)$ when calculating the standard matrix element $\langle G' | G \rangle$ since then

$$\partial_{\mathbf{v}^T}\exp\left(\mathbf{v}^T\mathbf{x}\right) = \mathbf{x}\exp\left(\mathbf{v}^T\mathbf{x}\right). \tag{B.20}$$

Using that as well as equation (B.2) gives us

$$\begin{aligned}\langle G' |\mathbf{x}| G \rangle = \partial_{\mathbf{v}^T} \langle G' | G \rangle &= \left(\frac{\pi^N}{\det(B)}\right)^{3/2} \partial_{\mathbf{v}^T} \exp\left(\frac{1}{4}\mathbf{v}^T R\mathbf{v}\right) \\ &= M_0(B,\mathbf{v})\partial_{\mathbf{v}^T}\left(\frac{1}{4}\mathbf{v}^T R\mathbf{v}\right) = \frac{M_0(B,\mathbf{v})}{2} R\mathbf{v} = M_0(B,\mathbf{v})\mathbf{u},\end{aligned} \tag{B.21}$$

where we have introduced the new vector $u = \frac{1}{2}R\mathbf{v}$. We can then go on to show the matrix element for the quadratic form

$$\begin{aligned}\langle G' |\mathbf{x}^T F\mathbf{x}| G \rangle &= \partial_{\mathbf{v}} F \partial_{\mathbf{v}^T} \langle G' | G \rangle = \partial_{\mathbf{v}} F\mathbf{u} M_0(B,\mathbf{v}) \\ &= \partial_{\mathbf{v}} \left(F\mathbf{u}\right) M_0(B,\mathbf{v}) + \left(\partial_{\mathbf{v}} M_0(B,\mathbf{v})\right) F\mathbf{u} \\ &= \left(\frac{d}{2}\operatorname{Tr}(FR) + \mathbf{u}^T F\mathbf{u}\right) M_0(B,\mathbf{v}),\end{aligned} \tag{B.22}$$

and with this we can finally calculate $\langle G' |K| G \rangle$ (for $d = 3$)

$$\begin{aligned}&\langle G' |K| G \rangle = \langle G' | - \partial_{\mathbf{x}} \Lambda \partial_{\mathbf{x}^T} | G \rangle = \langle G' | \left(\left(\mathbf{s}'\right)^T \Lambda - 2A'\mathbf{x}\right)^T \Lambda\left(\mathbf{s} - 2A\mathbf{x}\right) | G \rangle \\ &= \left(\mathbf{s}'\right)^T \Lambda\mathbf{s} \langle G' | G \rangle - 2\left(\left(\mathbf{s}'\right)^T \Lambda A \langle G' |\mathbf{x}| G \rangle + \langle G' |\mathbf{x}^T | G \rangle A'\Lambda\mathbf{s}\right) + 4\langle G' |\mathbf{x}^T \left(A'\Lambda A\right)\mathbf{x}| G \rangle \\ &= M_0(B,\mathbf{v})\left(6\operatorname{Tr}\left(A'\Lambda AR\right) + \left(\mathbf{s}' - 2A'\mathbf{u}\right)^T \Lambda\left(\mathbf{s} - 2A\mathbf{u}\right)\right) \xrightarrow{\mathbf{v}=0} 6M_0(B,\mathbf{0})\operatorname{Tr}\left(A'\Lambda AR\right).\end{aligned} \tag{B.23}$$

It would seem that it should be annoying to calculate the matrix element when we introduce the delta function, $\delta(\omega^T\mathbf{x} - \mathbf{y}_0)$, but since we intend to use it to keep a particle in place, that particle should effectively not contribute any kinetic energy to the system. In practice this means that we want the condition $\Lambda\omega = \omega^T\Lambda = 0$ to hold. However, this makes it very easy to calculate the matrix element since (we remember that $\mathbf{k}$ is a standard vector while $\mathbf{x}$ is a vector of vectors)

$$\Lambda\partial_{\mathbf{x}^T}\left(\exp\left(i\mathbf{k}^T\left(\omega^T\mathbf{x}\right)\right) f(\mathbf{x})\right) = \Lambda\left(i\omega\mathbf{k}f(\mathbf{x}) + f'(\mathbf{x})\right)\exp\left(i\mathbf{k}\omega^T\mathbf{x}\right) = \Lambda\exp\left(i\mathbf{k}\omega^T\mathbf{x}\right) f'(\mathbf{x}). \tag{B.24}$$

So, in a sense, the exponential factor we get from the delta function does not interact with the differential from the kinematic operator at all. This means what we will get is the kinetic matrix element as usual, but with a shift from $\exp\left(i\mathbf{k}\omega^T\mathbf{x}\right)$ in the Gaussians by the end. Therefore the result will simply be the kinetic matrix element multiplied by $M_0(B, \mathbf{v} + i\mathbf{k}\omega)$, which we already calculated in equation (B.4)

$$\langle G' |K\exp\left(i\mathbf{k}\omega^T\mathbf{x}\right)| G \rangle = \langle G' |K| G \rangle \exp\left(-\alpha\mathbf{k}^2 + i\mathbf{k}^T\mathbf{q}\right). \tag{B.25}$$

But we already did the Fourier calculation with that exponential so our final result can be written as the separation

$$\langle G' |K\delta(\mathbf{y} - \mathbf{y_0})| G \rangle = \frac{\langle G' |K| G \rangle}{M_0(B,\mathbf{v})} \langle G' |\delta(\mathbf{y} - \mathbf{y_0})| G \rangle. \tag{B.26}$$

B.3 The Delta Function + Coulomb Matrix Element

In this section, we will calculate the matrix element of the combined delta function and Coulomb interaction

$$\langle G' | \frac{\delta(\mathbf{y} - \mathbf{y_0})}{|\eta^T \mathbf{x}|} | G \rangle. \tag{B.27}$$

First we need to do the same trick as the standard overlap and look at the matrix element of a delta function with another complex exponential $\exp\left(i\mathbf{k}^T \left(\eta^T \mathbf{x}\right)\right)$ so we can set up another Fourier transform. Like before, the exponential only affects the shift, leaving us with the delta function overlap we calculated in equation (B.11) with an extra shift:

$$\langle G' | \delta(\mathbf{y} - \mathbf{y_0}) \exp\left(i\mathbf{k}^T \left(\eta^T \mathbf{x}\right)\right) | G \rangle = \frac{M_0(B, \mathbf{v} + i\mathbf{k}\eta)}{(2\pi)^3} \exp\left(-\frac{1}{4\alpha}(\mathbf{q}' - \mathbf{y_0})^2\right) \left(\sqrt{\frac{\pi}{\alpha}}\right)^3. \tag{B.28}$$

We already know how $M_0(B, \mathbf{v} + i\mathbf{k}\eta)$ changes, from equation (B.4), so we just need to look a $\mathbf{q}'$

$$\mathbf{q}' = \frac{1}{2}\omega^T R (\mathbf{v} + i\mathbf{k}\eta) = \mathbf{q} + \frac{i}{2}\left(\omega^T R \eta\right)\mathbf{k} = \mathbf{q} + i2\beta\mathbf{k}, \tag{B.29}$$

$$\begin{aligned} \left(\mathbf{q}' - \mathbf{y_0}\right)^2 = (\mathbf{q} + 2i\beta\mathbf{k} - \mathbf{y_0})^2 &= (\mathbf{q} - \mathbf{y_0})^2 - (2\beta\mathbf{k})^2 + 4i\beta\mathbf{k}(\mathbf{q} - \mathbf{y_0}) \\ &= (\mathbf{q} - \mathbf{y_0})^2 - (2\beta\mathbf{k})^2 + 4i\mathbf{w} \cdot \mathbf{k}, \end{aligned} \tag{B.30}$$

where $\beta = \frac{1}{4}\omega^T R \eta$ and $\mathbf{w} = \beta(\mathbf{q} - \mathbf{y_0})$. This means we can write our expression as

$$\begin{aligned} \langle G' | \delta(\mathbf{y} - \mathbf{y_0}) \exp\left(i\mathbf{k}^T \left(\eta^T \mathbf{x}\right)\right) | G \rangle &= \langle G' | \delta(\mathbf{y} - \mathbf{y_0}) | G \rangle \exp\left(-\left(\gamma - \frac{\beta^2}{\alpha}\right)\mathbf{k}^2 + i\left(\mathbf{p} - \frac{\mathbf{w}}{\alpha}\right) \cdot \mathbf{k}\right) \\ &= \langle G' | \delta(\mathbf{y} - \mathbf{y_0}) | G \rangle \exp\left(-a\mathbf{k}^2 + i\mathbf{c} \cdot \mathbf{k}\right), \end{aligned} \tag{B.31}$$

where $\gamma = \frac{1}{4}\eta^T R \eta$, $\mathbf{p} = \frac{1}{2}\eta^T R \mathbf{v}$, $a = \gamma - \frac{\beta^2}{\alpha}$ and $\mathbf{c} = \mathbf{p} - \frac{\mathbf{w}}{\alpha}$. Since we are eventually going to integrate over this exponential factor, it would be a good idea to discuss when it actually gives us something convergent. All that is required is that $a > 0$, which means we want:

$$\alpha\gamma - \beta^2 > 0 \rightarrow \left(\eta^T R \eta\right)\left(\omega^T R \omega\right) - \left(\omega^T R \eta\right)^2 > 0, \tag{B.32}$$

since $\alpha > 0$. Because $|\langle a, Mb \rangle|$ defines an inner product norm when M is positive-definite[19], we can use the Cauchy-Schwartz inequality[20]

$$|\langle \mathbf{u}, \mathbf{v} \rangle|^2 \leq \langle \mathbf{u}, \mathbf{u} \rangle \cdot \langle \mathbf{v}, \mathbf{v} \rangle, \tag{B.33}$$

to say that

$$\left(\omega^T R \eta\right)^2 \leq \left(\eta^T R \eta\right)\left(\omega^T R \omega\right). \tag{B.34}$$

We can then utilise that $Q^T RQ = D$, for some orthogonal matrix[11], Q, and set $\omega = Q\omega'$ and $\eta = Q\eta'$ after which we see that the equality is only satisfied when ω' and η' are collinear, $\omega' \parallel \eta'$ (as the inequality reduces to the normal Cauchy-Schwarz inequality for vectors), but since the transformation Q preservers inner products, we can say that the only requirement for convergence is that $\omega \nparallel \eta$. However this is expected since when $\omega \parallel \eta$ we can write $\eta = k \cdot \omega$, for $k \in \mathbb{R}/\{0\}$, and then

$$|\eta^T \mathbf{x}| = |k| \cdot |\omega^T \mathbf{x}| = |k||\mathbf{y}| \to \frac{\delta(\mathbf{y} - \mathbf{y_0})}{|k||\mathbf{y}|} = \frac{\delta(\mathbf{y} - \mathbf{y_0})}{|k||\mathbf{y_0}|}, \tag{B.35}$$

and since we used the Fourier transformation of $\frac{1}{|\mathbf{x}|}$ in the calculation, it is only natural it breaks down when we turn it into a constant. This also makes the collinear case quite trivial to calculate

$$\langle G' | \frac{\delta(\mathbf{y} - \mathbf{y_0})}{|\eta^T \mathbf{x}|} | G \rangle = \frac{1}{|k| \cdot y_0} \langle G' | \delta(\mathbf{y} - \mathbf{y_0}) | G \rangle. \tag{B.36}$$

With those considerations explored, we can now move onto the actual matrix element, which we will calculate like we did (B.11), but with $f(\eta^T \mathbf{x}) = \frac{1}{|\eta^T \mathbf{x}|}$ instead. As can be shown pretty easily, using the distribution form $\exp(-a|x|)/|x|$ with $a \to 0$, the Fourier transform of the Coulomb potential is $F(\mathbf{k}) = \frac{4\pi}{\mathbf{k}^2}$, and inserting this gives us the integral:

$$\langle G' | \frac{\delta(\mathbf{y} - \mathbf{y_0})}{|\eta^T \mathbf{x}|} | G \rangle = \frac{\langle G' | \delta(\mathbf{y} - \mathbf{y_0}) | G \rangle}{(2\pi)^3} \int \mathrm{d}^3\mathbf{k} \frac{4\pi}{\mathbf{k}^2} \exp\left(-a\mathbf{k}^2 + i\mathbf{c} \cdot \mathbf{k}\right). \tag{B.37}$$

In order to solve this, we first change to spherical coordinates, (k, θ, ϕ), and rotate it such that one of our vectors are along the z-axis, allowing us to write $\mathbf{c} \cdot \mathbf{k} = |\mathbf{c}| \cdot |\mathbf{k}| \cdot \cos(\theta)$, leaving us the integral ($\mathbf{k}^2 = k^2$)

$$\int_0^\infty \mathrm{d}k \exp\left(-ak^2\right) \int_0^{2\pi} \mathrm{d}\phi \int_0^\pi \mathrm{d}\theta \sin(\theta) \exp\left(ick\cos(\theta)\right). \tag{B.38}$$

First we calculate the θ-integral separately

$$\int_0^\pi \mathrm{d}\theta \sin(\theta) \exp\left(ick\cos(\theta)\right) = \int_{-1}^1 \mathrm{d}t \exp\left(ickt\right) = \frac{2i}{ick} \sin(ck) = \frac{2}{c} \cdot \frac{\sin(ck)}{k}, \tag{B.39}$$

by way of substitution by $t = \cos(\theta)$. Since the total integral does not depend on the other angle, ϕ, we just get a factor of 2π from the ϕ-integral. This leaves us with the total k-integral

$$\langle G' | \frac{\delta(\mathbf{y} - \mathbf{y_0})}{|\eta^T \mathbf{x}|} | G \rangle = \frac{\langle G' | \delta(\mathbf{y} - \mathbf{y_0}) | G \rangle}{(2\pi)^3} \frac{16\pi^2}{c} \int_0^\infty \mathrm{d}k \exp\left(-ak^2\right) \cdot \frac{\sin(ck)}{k}. \tag{B.40}$$

This particular integral can be solved through two uses of Feynman's trick[12]. First we write the integral as a function, $J(a, c)$, of the coefficients we do not integrate

11: An orthogonal matrix satisfies $Q^T = Q^{-1}$.

12: Feynman's trick is when you differentiate an integral with respect to some integral parameter, that you are **not** integrating over, and then exchange the differentiation and integral operation to get an easier integral

$$\partial_t \int \mathrm{d}x f(x,t) \to \int \mathrm{d}x \left(\partial_t f(x,t)\right)$$

This allows you to solve integrals as differential equations instead.

over, and then differentiate with respect to c to obtain a more familiar integral, which we denote $I(a,c)$

$$\partial_c J(a,c) = \partial_c \left(\int_0^\infty \mathrm{d}k \exp\left(-ak^2\right) \cdot \frac{\sin(ck)}{k} \right) = \int_0^\infty \mathrm{d}k \exp\left(-ak^2\right) \cdot \cos(ck) = I(a,c). \tag{B.41}$$

This integral can also be solved via Feynman's trick and partial integration

$$\begin{aligned} \partial_c I(a,c) &= -\int_0^\infty \mathrm{d}k \; k \cdot \exp\left(-ak^2\right) \cdot \sin(ck) \\ &= \left[\frac{\exp\left(-ak^2\right)}{2a} \cdot \sin(ck) \right]_{k=0}^{k=\infty} - \frac{c}{2a} \int_0^\infty \mathrm{d}k \; \exp\left(-ak^2\right) \cdot \cos(ck) \\ &= -\frac{c}{2a} I(a,c), \end{aligned} \tag{B.42}$$

where we used that $\int \mathrm{d}x \; x \cdot \exp\left(-ax^2\right) = -\frac{\exp\left(-ax^2\right)}{2a} + C$ which is easily shown through substitution. As can be seen, this use of differentiation gave us a differential equation of the form (the boundary condition, $I(a,0)$, stems from equation (B.10) for $b = 0$)

$$\partial_c I(a,c) = -\frac{c}{2a} I(a,c), \quad I(a,0) = \frac{\sqrt{\pi}}{2\sqrt{a}}, \tag{B.43}$$

which is a separable differential equation[13] with the solution

$$I(a,c) = \int_0^\infty \mathrm{d}k \exp\left(-ak^2\right) \cdot \cos(ck) = \frac{\sqrt{\pi}}{2\sqrt{a}} \exp\left(-\frac{c^2}{4a}\right). \tag{B.44}$$

Therefore the original integral solves the differential equation

$$\partial_c J(a,c) = \frac{\sqrt{\pi}}{2\sqrt{a}} \exp\left(-\frac{c^2}{4a}\right), \quad J(a,0) = 0, \tag{B.45}$$

from which we can obtain the answer by simply integrating both sides with respect to c. This means our original integral has the solution

$$J(a,c) = \int_0^\infty \mathrm{d}k \exp\left(-ak^2\right) \cdot \frac{\sin(ck)}{k} = \frac{\pi}{2} \operatorname{erf}\left(\frac{c}{2\sqrt{a}}\right), \tag{B.46}$$

where $\operatorname{erf}(x)$ denotes the error function as defined in equation (2.13). Lastly, we just insert equation (B.46) into equation (B.40) and we get the final result:

$$\langle G' | \frac{\delta(\mathbf{y} - \mathbf{y_0})}{|\eta^T \mathbf{x}|} | G \rangle = \frac{\langle G' | \delta(\mathbf{y} - \mathbf{y_0}) | G \rangle}{c} \operatorname{erf}\left(\frac{c}{2\sqrt{a}}\right). \tag{B.47}$$

13: This means it can be written in the form $y' = f(x)g(y)$.

Appendix C

The Grid/Lattice Method

In this appendix we will be looking at a numerical finite difference method called the grid/lattice method that is often used to solve boundary value problems. The idea is that when solving a differential equation, we are looking for a function that changes continuously in a certain way when we vary the input. But, as it turns out, this action can be broken down into smaller steps where the value at each step is influenced by the values around it. We can then use these values to draw a graph and we expect the limiting behaviour of this graph to equal the original solution to our differential equation as the amount of steps increase.

To demonstrate its usefulness we can use it to solve the Hydrogen atom. In Hartree atomic units, the lowest order radial solution of the Schrödinger equation for the hydrogen atom has the following form

$$-\frac{1}{2}u''(r) - \frac{1}{r}u(r) = \epsilon u(r), \quad u(r) = r \cdot \Psi(r) \tag{C.1}$$

where our boundary conditions are

$$\lim_{r\to 0} u(r) \to 0, \quad \lim_{r\to\infty} u(r) \to 0 \tag{C.2}$$

The next step is to make the grid. The simplest way is to make all the points equidistant using a fixed step size of Δr, and then our wave function will simply be a vector $\mathbf{u}$ with indices, u_i, evaluated at these points

$$r_i = i \cdot \Delta r, \quad i \in \{1, \cdots, N\} \quad N = \frac{r_{\max}}{\Delta r} - 1, \quad u_i = u(r_i). \tag{C.3}$$

We point out that neither r_0 nor $r_{\max}$ will be a part of our steps. This is due to our boundary conditions where we are using $r_{\max}$ as a stand-in for ∞ which is fine since we expect our real function to fall off quite quickly; doing it like this allows us to build the boundary conditions into our Hamiltonian. The next step is to use the finite difference to transform the second-order derivative into a discrete object like so (equation (C.4) is also called the *symmetric central-difference approximation* [15])

$$u_i'' = \frac{u_{i-1} - 2u_i + u_{i+1}}{(\Delta r)^2}. \tag{C.4}$$

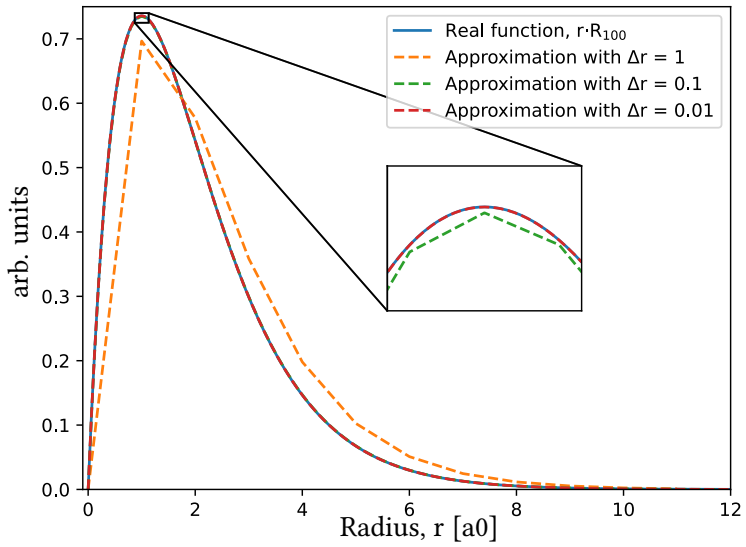

FIGURE C.1: Comparison between three radial numerical eigenstate approximations, using different step sizes, compared to the analytically known radial ground state solution, $r \cdot R_{100}$. These eigenstates have been created using the grid method. The red, green and blue line are all pretty close, so a zoomed window has been added for visual clarity. The units of the x-axis are Bohr radii, a_0.

With all of this, we are ready to write down the Hamiltonian

$$H = K + V, \tag{C.5}$$

where

$$V = -\begin{bmatrix} \frac{1}{r_1} & 0 & \cdots & 0 & 0 \\ 0 & \frac{1}{r_2} & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & 0 & \frac{1}{r_{N-1}} & 0 \\ 0 & \cdots & 0 & 0 & \frac{1}{r_N} \end{bmatrix}, \quad K = -\frac{1}{2(\Delta r)^2}\begin{bmatrix} -2 & 1 & 0 & 0 & \cdots & 0 \\ 1 & -2 & 1 & 0 & \cdots & 0 \\ 0 & 1 & -2 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & 0 & 1 & -2 & 1 \\ 0 & \cdots & 0 & 0 & 1 & -2 \end{bmatrix}, \tag{C.6}$$

giving us the eigenvalue equation

$$H\mathbf{u} = \epsilon\mathbf{u}, \tag{C.7}$$

which we can solve with any standard diagonalization routine. In figure C.1 is a plot comparing[14] the analytic solution of the radial ground state of Hydrogen, denoted $r \cdot R_{100}$, to the one we get from the grid for different step sizes.

Since the step size of $\Delta r = 0.01$ is not noticeably slower than 0.1 to calculate, but still gives a better result, it will be the one we typically use. For good measure, we have also included how the eigenvalue changes for different step sizes in figure C.2.

14: When comparing, it is important to properly scale the eigenstate one obtains from the diagonalization. One can show this normalization constant will be equal to $\frac{1}{\sqrt{\Delta r}}$.

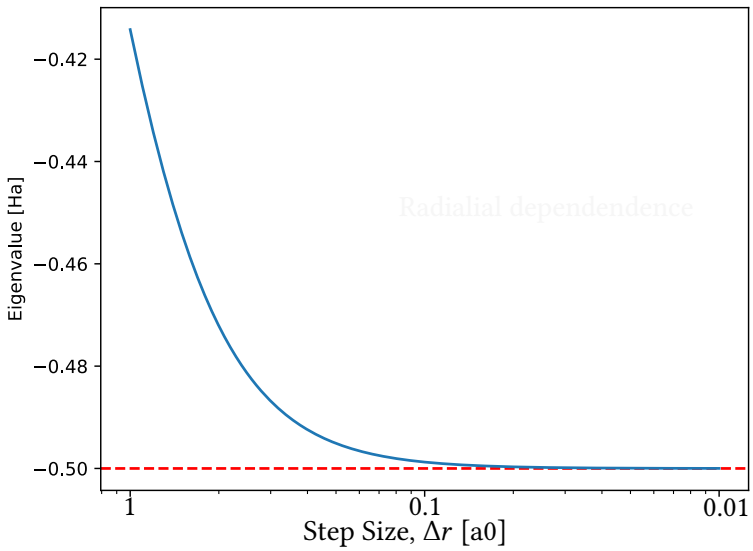

FIGURE C.2: Eigenvalue for different step lengths in logarithmic scale. The three values used for figure C.1 are noted. As it can be seen, the value of ϵ quickly converges to a value of $-\frac{1}{2}$, which is also what we expect theoretically. The units of the x-axis are Bohr radii, a_0, and the units of the y-axis are Hartree energy units, Ha.

Appendix D

The Scattering Coefficients

In this appendix we will derive the general formulas for $P_{mn}(y)$ and $Q_{mn}(y)$ as seen in equation (2.53). Both of these will be solved in the same fashion and therefore a bigger focus will be placed on the overall methodology, starting with the notation that will be used.

Let $\langle G' \,|\, G \rangle_{\mathbf{k}}$ denote the overlap between two ECGs, but where we do not integrate over the variable $\mathbf{x}_k$. Then we can write

$$P = \langle G' \,|\partial_{\mathbf{k}}|\, G \rangle_{\mathbf{k}}, \qquad Q = \langle G' \,|\partial_{\mathbf{k}}^2|\, G \rangle_{\mathbf{k}} \qquad \partial_{\mathbf{k}} = \partial_{\mathbf{x}_k}. \tag{D.1}$$

To calculate these we will first have to calculate $\langle G' \,|\, G \rangle_{\mathbf{k}}$, $\langle G' \,|\mathbf{x}_i|\, G \rangle_{\mathbf{k}}$, $\langle G' \,|\mathbf{x}_i^T \mathbf{x}_j|\, G \rangle_{\mathbf{k}}$ and $\langle G' \,|\mathbf{x}^T F \mathbf{x}|\, G \rangle_{\mathbf{k}}$, but before any of that, we want to quickly go through the notation that will be used since it is a bit hairy.

D.1 The Notation

In the calculations to come, the strategy will generally be to separate out the variable we are not integrating over, which will be denoted $x_{\mathbf{k}}$, and then using formulas we have already calculated on whatever is left. Therefore it will be useful to introduce notation that deals with the absence of this variable and its index, so we do not have to drag summations all over the place, and so that this connection to the already calculated formulas becomes more apparent.

We will let vectors and matrices equipped with a $\tilde{\circ}_k$ denote the same vector and matrix after the removal of the k'th index and the k'th column and row, respectively. For example:

$$\mathbf{x} = \begin{bmatrix} \mathbf{x}_1 \\ \mathbf{x}_2 \\ \mathbf{x}_3 \end{bmatrix} \to \tilde{\mathbf{x}}_2 = \begin{bmatrix} \mathbf{x}_1 \\ \mathbf{x}_3 \end{bmatrix}, \quad M = \begin{bmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{bmatrix} \to \tilde{M}_2 = \begin{bmatrix} M_{11} & M_{13} \\ M_{31} & M_{33} \end{bmatrix}. \tag{D.2}$$

The reason it is very useful notation is because it allows for the following shorthand notation

$$\tilde{x}_{\mathbf{k}}^T \tilde{B}_k \tilde{x}_{\mathbf{k}} = \sum_{i,j} (\tilde{x}_{\mathbf{k}})_i^T \left(\tilde{B}_k\right)_{ij} (\tilde{x}_{\mathbf{k}})_j = \sum_{i,j \neq k} x_i B_{ij} x_j, \tag{D.3}$$

which will be useful in turning our summations back into quadratic expressions so we can better match old expressions. However, there are some issues with this simple notation. The first one has probably already been noticed, which is that it sort of steps over the toes of index notation since $\mathbf{x}_k$ and $\tilde{\mathbf{x}}_k$ could easily be mistaken for each other, although they are entirely different objects. Also, that the index notation for the tilded parameters will either be potentially confusing, $\tilde{x}_{\mathbf{k},i}$, $\tilde{M}_{k,ij}$, or a bit clunky; with two sets of indexes, as in equation (D.3), $(\tilde{x}_{\mathbf{k}})_i$, $\left(\tilde{B}_k\right)_{ij}$. As we feel it is more clear, the second of these options have been chosen for the calculations, but we are also sure that one could come up with something better if needed.

The bigger problem comes from the indexing differences between the regular and tilded parameters when one changes from one to the other, which will be useful in quite a lot of the calculations. This is because we have to work around the missing index which means that

$$\mathbf{x}_i = (\tilde{\mathbf{x}}_k)_{i-\mathrm{H}(i-k)}\,, \quad i \neq k, \quad \mathrm{H}(i-k) = \begin{cases} 1, & i \geq k \\ 0, & i < k \end{cases}, \tag{D.4}$$

where $\mathrm{H}(x)$ is the Heaviside step function. It will clutter too much to have the entire thing in the subscript, so we will use the notation $h(i) = i - \mathrm{H}(i-k)$ as a placeholder, $(\tilde{\mathbf{x}}_k)_{h(i)}$. Even though it is technically also dependant on k, we will never sum over that in calculations, and it will be tied to the subscript of the variable itself, $\tilde{\mathbf{x}}_k$, so it will probably be fine to omit it explicitly.

We also want some notation to represent the n'th column or row of a matrix as a vector; this is for the sake of removing some ugly summations and more accurately representing how the expression will look in the code. The chosen notation is square brackets with a subscript n for rows and superscript n for columns. For example:

$$M = \begin{bmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{bmatrix} \to [M]_3 = \begin{bmatrix} M_{31} & M_{32} & M_{33} \end{bmatrix}, \quad [M]^3 = \begin{bmatrix} M_{13} \\ M_{23} \\ M_{33} \end{bmatrix}. \tag{D.5}$$

Lastly, to better distinguish between $\widetilde{[M]}_n$ and $\left[\tilde{M}\right]_n$, and not using to many subscripts, we will use $[M]_{\tilde{n}}$ as a shorthand for 'the n'th row vector of matrix M with the n'th index removed'. For example:

$$M = \begin{bmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{bmatrix} \to [M]_{\tilde{3}} = \begin{bmatrix} M_{31} & M_{32} \end{bmatrix}, \quad [M]^{\tilde{3}} = \begin{bmatrix} M_{13} \\ M_{23} \end{bmatrix}. \tag{D.6}$$

With all this notation in our possession, we are now ready to tackle the actual calculations starting with the standard overlap.

D.2 The Modified Standard Overlap

Reusing the notation from section 2.1.2, we can write out the result of the product of two Gaussian terms $\exp\left(-\mathbf{x}^T A'\mathbf{x} + \mathbf{s}'\mathbf{x}\right)\exp\left(-\mathbf{x}^T A\mathbf{x} + \mathbf{s}\mathbf{x}\right) = \exp\left(-\mathbf{x}^T B\mathbf{x} + \mathbf{v}\mathbf{x}\right)$ as such

$$-\mathbf{x}^T B\mathbf{x} + \mathbf{v}^T\mathbf{x} = -\sum_{i,j} B_{ij}\mathbf{x}_i^T\mathbf{x}_j + \sum_i \mathbf{v}_i^T\mathbf{x}_i. \tag{D.7}$$

We want to separate out everything that has to do with $\mathbf{x}_k$ leaving us with

$$\begin{aligned} &= -B_{kk}\mathbf{x}_k^2 + \mathbf{v}_k^T\mathbf{x}_k - \sum_{i\neq k, j\neq k} B_{ij}\mathbf{x}_i^T\mathbf{x}_j + 2\sum_{i\neq k} B_{ki}\mathbf{x}_k^T\mathbf{x}_i + \sum_{i\neq k}\mathbf{v}_i^T\mathbf{x}_i \\ &= -B_{kk}\mathbf{x}_k^2 + \mathbf{v}_k^T\mathbf{x}_k - \sum_{i\neq k, j\neq k} B_{ij}\mathbf{x}_i^T\mathbf{x}_j + \sum_{i\neq k}\left(\mathbf{v}_i + 2B_{ki}\mathbf{x}_k\right)^T\mathbf{x}_i. \end{aligned} \tag{D.8}$$

We now introduce $\tilde{B}_k$ and $\tilde{\mathbf{x}}_k$; the reduced B matrix and $\mathbf{x}$ vector, as explained in section D.1, as well as the vector ξ, with indices $\xi_i = \mathbf{v}_i + 2B_{ki}\mathbf{x}_k$, as a shorthand. We can now simplify the above expression by use of equation (D.3)

$$= -B_{kk}\mathbf{x}_k^2 + \mathbf{v}_k\mathbf{x}_k - \tilde{\mathbf{x}}_k^T\tilde{B}_k\tilde{\mathbf{x}}_k + \left(\tilde{\xi}_{\mathbf{k}}\right)^T\tilde{\mathbf{x}}_k. \tag{D.9}$$

But the first two terms of the expression are not affected by the integral, since we do not integrate over $\mathbf{x}_k$, and the last two terms have the standard form of the product of two Gaussians, as seen in equation (2.10), but with a modified matrix and shift vector (both of one index less, $N-1$). Therefore we expect our integral to have the form

$$\begin{aligned} \langle G' \,|\, G \rangle_k &= \exp\left(-B_{kk}\mathbf{x}_k^2 + \mathbf{v}_k\mathbf{x}_k\right) M_0(\tilde{B}_k, \tilde{\xi}_{\mathbf{k}}) \\ &\xrightarrow{\mathbf{v}=0} = \exp\left(-B_{kk}\mathbf{x}_k^2\right) M_0(\tilde{B}_k, \tilde{\xi}_{\mathbf{k}}), \end{aligned} \tag{D.10}$$

$$\begin{aligned} M_0(\tilde{B}_k, \tilde{\xi}_{\mathbf{k}}) &= \exp\left(\frac{1}{4}\left(\tilde{\xi}_{\mathbf{k}}\right)^T W_k \tilde{\xi}_{\mathbf{k}}\right)\left(\frac{\pi^{N-1}}{\det\left(\tilde{B}_k\right)}\right)^{3/2} \\ &\xrightarrow{\mathbf{v}=0} \xi_i = 2B_{ki}\mathbf{x}_k, \end{aligned} \tag{D.11}$$

with $W_k = \left(\tilde{B}_k\right)^{-1}$. For the sake of mathematical brevity in future calculations, we will use the notation:

$$\tilde{M}_k = \langle G' \,|\, G \rangle_k = \exp\left(-B_{kk}\mathbf{x}_k^2 + \mathbf{v}_k\mathbf{x}_k\right) M_0(\tilde{B}_k, \tilde{\xi}_{\mathbf{k}}). \tag{D.12}$$

The last thing we need to make sure of, is that the matrix remains positive-definite if we delete a row and column because otherwise we cannot always use the above calculation. This can be easily shown by noticing that there exists a non-diagonal matrix, Q_k, such that:

$$Q_k\mathbf{x} = \tilde{\mathbf{x}}_k, \qquad Q_k B Q_k^T = \tilde{B}_k, \tag{D.13}$$

that has the form of the identity matrix with the k'th row deleted. Here is an example for three indices:

$$Q_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{D.14}$$

This means we can write:

$$\tilde{\mathbf{x}}_k^T\tilde{B}_k\tilde{\mathbf{x}}_k = (Q_k\mathbf{x})^T\left(Q_k B Q_k^T\right)(Q_k\mathbf{x}) = \left(Q_k^T Q_k\mathbf{x}\right)^T B\left(Q_k^T Q_k\mathbf{x}\right)\mathbf{x} = (N_k\mathbf{x})^T B\,(N_k\mathbf{x}), \tag{D.15}$$

or, all in all

$$\tilde{\mathbf{x}}_k^T \tilde{B}_k \tilde{\mathbf{x}}_k = (N_k \mathbf{x})^T B (N_k \mathbf{x}), \tag{D.16}$$

and by simple calculations, one can show these N_k matrices are simply identity matrices where the k'th diagonal element is equal to 0. That means $N_k\mathbf{x}$ is just $\mathbf{x}$ with the k'th index equal to 0. Since we already know B is positive-definite, we know the RHS will be strictly positive as long as $N_k\mathbf{x}$ is not the zero vector, but this will only happen if all elements, except for $\mathbf{x}_k$, are $\mathbf{0}$ which will correspond to the case where $\tilde{\mathbf{x}}_k$ itself is the zero vector. This means that the LHS is also different from 0, as long as $\tilde{\mathbf{x}}_k$ is not the zero vector, which implies that our $\tilde{B}_k$ matrix is also positive-definite, as we wanted to show.

D.3 The Modified Linear Operator Overlap

Continuing on from the prior calculation, we will now calculate $\langle G' | \mathbf{x}_i | G \rangle_k$ in pretty much the same way, but with an added trick to deal with the linear operator in front of the integral. If $i = k$ then there is no problem since our integral does not depend on $\mathbf{x}_k$. As such, we simply reduce to our prior calculation

$$\langle G' | \mathbf{x}_k | G \rangle_k = \mathbf{x}_k \langle G' | G \rangle_k. \tag{D.17}$$

Let us now look at the situation where $i \neq k$. In this case we can write $\mathbf{x}_i = \rho_{h(i)}^T \tilde{\mathbf{x}}_k$, where $\rho_{h(i)}$ is simply the vector that picks out the index of a vector corresponding to $i - \mathrm{H}(i-k)$. With this we can now write

$$\langle G' | \mathbf{x}_i | G \rangle_k = \rho_{h(i)}^T \langle G' | \tilde{\mathbf{x}}_k | G \rangle_k, \tag{D.18}$$

and if we write the Gaussian in terms of the modified matrix and shift vector like above, we now have a matrix element that looks exactly like $\langle G' | \mathbf{x} | G \rangle$. This is an element we have already calculated, in equation (B.21), giving us

$$\begin{aligned} \langle G' | \mathbf{x}_i | G \rangle_k &= \rho_{h(i)}^T \exp\left(-B_{kk}\mathbf{x}_k^2 + \mathbf{v}_k \mathbf{x}_k\right) M_0(\tilde{B}_k, \tilde{\xi}_{\mathbf{k}}) \tilde{\mathbf{u}}_k \\ &= \tilde{M}_k \left(\rho_{h(i)}^T \tilde{\mathbf{u}}_k\right) = \tilde{M}_k \left(\tilde{\mathbf{u}}_k\right)_{h(i)}, \end{aligned} \tag{D.19}$$

where $\tilde{\mathbf{u}}_k = \frac{1}{2} W_k \tilde{\xi}_{\mathbf{k}}$. From this we also get that

$$\begin{aligned} \langle G' | \mathbf{a}^T F \mathbf{x} | G \rangle_k &= \sum_{ij} F_{ij} \mathbf{a}_i^T \langle G' | \mathbf{x}_j | G \rangle_k \\ &= \sum_i F_{ik} \mathbf{a}_i^T \mathbf{x}_k \langle G' | G \rangle_k + \sum_i \sum_{j \neq k} F_{ij} \mathbf{a}_i^T \langle G' | \mathbf{x}_j | G \rangle_k \\ &= \left(\sum_i F_{ik} \mathbf{a}_i^T \mathbf{x}_k + \sum_i \sum_{j \neq k} F_{ij} \mathbf{a}_i^T \left(\tilde{\mathbf{u}}_k\right)_{h(j)} \right) \tilde{M}_k \\ &= \left(\left(\sum_i F_{ik} \mathbf{a}_i^T \right) \mathbf{x}_k + \mathbf{a}_k^T \sum_{j \neq k} F_{kj} \left(\tilde{\mathbf{u}}_k\right)_{h(j)} + \sum_{i,j \neq k} F_{ij} \mathbf{a}_i^T \left(\tilde{\mathbf{u}}_k\right)_{h(j)} \right) \tilde{M}_k, \end{aligned} \tag{D.20}$$

and if we then introduce $\tilde{\mathbf{a}}_k$ and $\tilde{F}_k$, as well as the matrix row and column vector notation, we can rewrite this more succinctly as:

$$\langle G' | \mathbf{a}^T F \mathbf{x} | G \rangle_k = \left(\left(\mathbf{a}^T \left[F\right]^k \right) \mathbf{x}_k + \mathbf{a}_k^T \left(\left[F\right]_{\tilde{k}} \tilde{\mathbf{u}}_k \right) + \tilde{\mathbf{a}}_k^T \tilde{F}_k \tilde{u}_k \right) \tilde{M}_k. \tag{D.21}$$

D.4 The Modified Quadratic Operator Overlap

Now we look at the general quadratic operator $\langle G' | \mathbf{x}_i^T \mathbf{x}_j | G \rangle_k$ which will be calculated much like the linear one. Assuming $i, j \neq k$ we have

$$\langle G' | \mathbf{x}_i^T \mathbf{x}_j | G \rangle_k = \langle G' | (\rho_{h(i)}^T \tilde{\mathbf{x}}_k)^T \rho_{h(j)}^T \tilde{\mathbf{x}}_k | G \rangle_k = \langle G' | \tilde{\mathbf{x}}_k^T \left(\rho_{h(i)} \rho_{h(j)}^T \right) \tilde{\mathbf{x}}_k | G \rangle_k, \quad \text{(D.22)}$$

we can now utilise equation (B.22), with $F = \rho_{h(i)} \rho_{h(j)}^T$, giving us

$$\begin{aligned} \langle G' | \mathbf{x}_i^T \mathbf{x}_j | G \rangle_k &= \left(\frac{3}{2} \operatorname{Tr}\left(\rho_{h(i)} \rho_{h(j)}^T W_k \right) + \tilde{\mathbf{u}}_k^T \left(\rho_{h(i)} \rho_{h(j)}^T \right) \tilde{\mathbf{u}}_k \right) \tilde{M}_k \\ &= \left(\frac{3}{2} (W_k)_{h(j)h(i)} + (\tilde{\mathbf{u}}_k)_{h(i)}^T (\tilde{\mathbf{u}}_k)_{h(j)} \right) \tilde{M}_k, \end{aligned} \quad \text{(D.23)}$$

where we utilised that $\rho_{h(i)} \rho_{h(j)}^T$ will be a $(N-1) \times (N-1)$ matrix with a 1 in row $h(i)$ and column $h(j)$. When we multiply such a matrix onto any other matrix, it has the effect of moving row $h(j)$ to row $h(i)$ and setting everything else to 0. That means the trace of the product of these matrices will necessarily be the element in the $h(i)$'th column of row $h(j)$, which is why we have $(W_k)_{h(j)h(i)}$.

D.5 The Modified Quadratic Matrix Operator Overlap

While this calculation brings nothing new to the table, as it is simply a combination of the three calculations above, the result is still going to be used when calculating Q, so we thought it would be worth noting separately as well. Underway, we will be utilising equation (B.22), like above, and we are still assuming $d = 3$ like in prior calculations

$$\begin{aligned} &\langle G' | \mathbf{x}^T F \mathbf{x} | G \rangle_k = \sum_{ij} F_{ij} \langle G' | \mathbf{x}_i^T \mathbf{x}_j | G \rangle_k \\ &= F_{kk} \mathbf{x}_k^2 \langle G' | G \rangle_k + \sum_{i \neq k} F_{ik} \langle G' | \mathbf{x}_i^T | G \rangle_k \mathbf{x}_k + \sum_{j \neq k} F_{kj} \mathbf{x}_k^T \langle G' | \mathbf{x}_j | G \rangle_k + \sum_{i,j \neq k} F_{ij} \langle G' | \mathbf{x}_i \mathbf{x}_j | G \rangle_k \\ &= F_{kk} \mathbf{x}_k^2 \langle G' | G \rangle_k + \left(\sum_{i \neq k} F_{ik} (\tilde{\mathbf{u}}_k)_{h(i)}^T \right) \mathbf{x}_k \tilde{M}_k + \mathbf{x}_k^T \left(\sum_{j \neq k} F_{kj} (\tilde{\mathbf{u}}_k)_{h(j)} \right) \tilde{M}_k + \langle G' | \tilde{\mathbf{x}}_k^T \tilde{F}_k \tilde{\mathbf{x}}_k | G \rangle_k \\ &= \left(F_{kk} \mathbf{x}_k^2 + \left(\tilde{\mathbf{u}}_k^T [F]^{\tilde{k}} \right) \mathbf{x}_k + \mathbf{x}_k^T \left([F]_{\tilde{k}} \tilde{\mathbf{u}}_k \right) + \frac{3}{2} \operatorname{Tr}\left(\tilde{F}_k W_k \right) + (\tilde{\mathbf{u}}_k)^T \tilde{F}_k \tilde{\mathbf{u}}_k \right) \tilde{M}_k, \end{aligned} \quad \text{(D.24)}$$

all in all:

$$\langle G' | \mathbf{x}^T F \mathbf{x} | G \rangle_k = \left(F_{kk} \mathbf{x}_k^2 + \tilde{\mathbf{u}}_k^T \left([F]^{\tilde{k}} + \left([F]_{\tilde{k}} \right)^T \right) \mathbf{x}_k + \frac{3}{2} \operatorname{Tr}\left(\tilde{F}_k W_k \right) + (\tilde{\mathbf{u}}_k)^T \tilde{F}_k \tilde{\mathbf{u}}_k \right) \tilde{M}_k. \quad \text{(D.25)}$$

D.6 The Calculation of P

Using the differentiation rules of section B.2 and the expressions above, we have everything we need to calculate the first differential overlap, P.

$$
\begin{aligned}
P &= \langle G' \,|\partial_k|\, G\rangle_k = \langle G' \,|\partial_k \left(-\mathbf{x}^T A\mathbf{x} + \mathbf{s}^T\mathbf{x}\right)|\, G\rangle_k = \langle G' \,|-2\sum_i A_{ik}\mathbf{x}_i^T + \mathbf{s}_k^T|\, G\rangle_k \\
&= -2\sum_{i\neq k} A_{ik}\langle G' \,|\mathbf{x}_i^T|\, G\rangle_k + \left(-2A_{kk}\mathbf{x}_k^T + \mathbf{s}_k^T\right)\langle G' \,|\, G\rangle_k \\
&= \left(-2\sum_{i\neq k} A_{ik}\left(\tilde{\mathbf{u}}_k\right)_{h(i)}^T - 2A_{kk}\mathbf{x}_k^T + \mathbf{s}_k\right)\tilde{M}_k = \left(-2\tilde{\mathbf{u}}_k^T\left[A\right]^{\tilde{k}} - 2A_{kk}\mathbf{x}_k^T + \mathbf{s}_k\right)\tilde{M}_k,
\end{aligned}
\tag{D.26}
$$

which means that for $\mathbf{s}, \mathbf{v} \to \mathbf{0}$ we obtain

$$
P = -2\left(\tilde{\mathbf{u}}_k^T\left[A\right]^{\tilde{k}} + A_{kk}\mathbf{x}_k^T\right)\tilde{M}_k. \tag{D.27}
$$

D.7 The Calculation of Q

For this, we can pretty much reuse our calculation for the kinetic matrix element, as well as section B.2, but with the identities above instead. Although this time we do not have to be as general since we will necessarily have a lambda matrix with only the k'th entry equal to 1 which, most importantly, means it is symmetric. For this reason we will denote it Λ_k throughout the calculation. Writing it out we have:

$$
\begin{aligned}
Q &= \langle G' \,|\partial_k^2|\, G\rangle_k = \langle G' \,|\partial_{\mathbf{x}}\Lambda_k\partial_{\mathbf{x}^T}|\, G\rangle_k = \langle G' \,|\left(\mathbf{s}' - 2A'\mathbf{x}\right)^T\Lambda_k\left(\mathbf{s} - 2A\mathbf{x}\right)|\, G\rangle_k \\
&= \left(\mathbf{s}'\right)^T\Lambda_k\mathbf{s}\langle G' \,|\, G\rangle_k - 2\langle G' \,|\left(\mathbf{s}'\right)^T\Lambda_k A\mathbf{x}|\, G\rangle_k - 2\langle G' \,|\mathbf{x}^T A'\Lambda_k\mathbf{s}|\, G\rangle_k + 4\langle G' \,|\mathbf{x}^T\left(A'\Lambda_k A\right)\mathbf{x}|\, G\rangle_k,
\end{aligned}
\tag{D.28}
$$

we will utilise that $\mathbf{x}^T A'\Lambda_k\mathbf{s} = (A'\Lambda_k\mathbf{s})^T x = \mathbf{s}^T\Lambda_k A'x$, since it is a constant. We now have one constant term, two terms of the form $\mathbf{a}^T F\mathbf{x}$ and one of the form $\mathbf{x}^T F\mathbf{x}$ so we can insert our formulas above

$$
\begin{aligned}
&= \Bigg(\left(\mathbf{s}'\right)^T\Lambda_k\mathbf{s} - 2\left(\left(\left(\mathbf{s}'\right)^T\left[\Lambda_k A\right]^k\right)\mathbf{x}_k + \left(\mathbf{s}'\right)_k^T\left(\left[\Lambda_k A\right]_{\tilde{k}}\tilde{\mathbf{u}}_k\right) + (\tilde{\mathbf{s}'})_k^T\left(\widetilde{\Lambda_k A}\right)_k\tilde{u}_k\right) - \\
&\quad 2\left(\left(\mathbf{s}^T\left[\Lambda_k A'\right]^k\right)\mathbf{x}_k + \mathbf{s}_k^T\left(\left[\Lambda_k A'\right]_{\tilde{k}}\tilde{\mathbf{u}}_k\right) + \tilde{\mathbf{s}}_k^T\left(\widetilde{\Lambda_k A'}\right)_k\tilde{u}_k\right) + 4\Bigg(\left(A'\Lambda_k A\right)_{kk}\mathbf{x}_k^2 + \\
&\quad \tilde{\mathbf{u}}_k^T\left(\left[A'\Lambda_k A\right]^{\tilde{k}} + \left(\left[A'\Lambda_k A\right]_{\tilde{k}}\right)^T\right)\mathbf{x}_k + \frac{3}{2}\mathrm{Tr}\left((\widetilde{A'\Lambda_k A})_k W_k\right) + (\tilde{\mathbf{u}}_k)^T(\widetilde{A'\Lambda_k A})_k\tilde{\mathbf{u}}_k\Bigg)\Bigg)\tilde{M}_k.
\end{aligned}
\tag{D.29}
$$

This is quite a long and complicated expression, but luckily we are only looking at the Gaussians without shifts, reducing our expression down to

$$
\begin{aligned}
Q = 4\Bigg(&\left(A'\Lambda_k A\right)_{kk}\mathbf{x}_k^2 + \tilde{\mathbf{u}}_k^T\left(\left[A'\Lambda_k A\right]^{\tilde{k}} + \left(\left[A'\Lambda_k A\right]_{\tilde{k}}\right)^T\right)\mathbf{x}_k + \\
&\frac{3}{2}\mathrm{Tr}\left((\widetilde{A'\Lambda_k A})_k W_k\right) + (\tilde{\mathbf{u}}_k)^T(\widetilde{A'\Lambda_k A})_k\tilde{\mathbf{u}}_k\Bigg)\tilde{M}_k,
\end{aligned}
\tag{D.30}
$$

which is a bit more manageable. Sadly it does not simplify as much as the kinetic case since we also have a shift from the linear $\mathbf{x}_k$ terms back when we rewrote the Gaussians, such that $\tilde{u}_k \neq \mathbf{0}$.

Appendix E

The Construction of Positive-definite Matrices

In this appendix we will be discussing the fundamental issue of generating positive-definite matrices using a random matrix approach. Naively, one would think the most computationally heavy part of checking if a matrix is positive-definite should be finding its eigenvalues, which can be done through procedures such as numpy.linalg.eig. However, if such a program is actually created, it is immediately obvious that it takes longer than one would expect. This observation is supported by figure E.1.

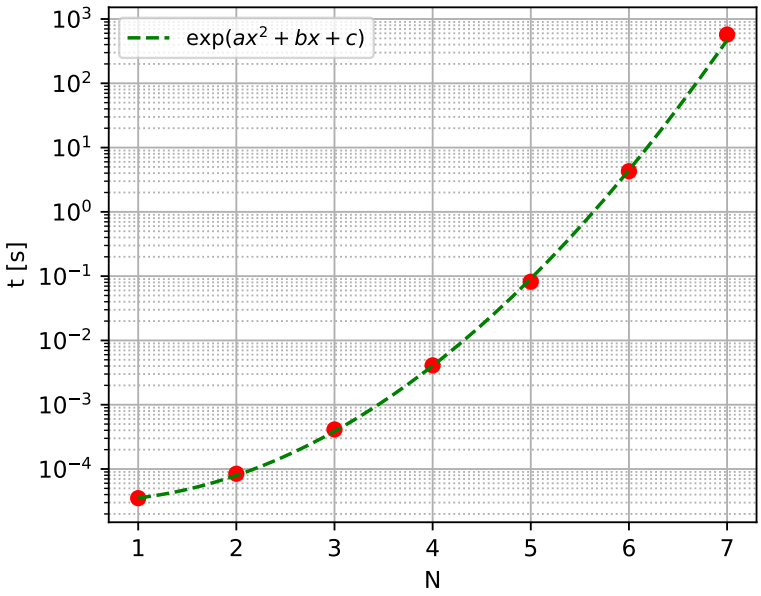

Figure E.1: Semi-log plot of the average time, t, it takes my algorithm to find a random positive-definite matrix as a function of the matrix size, N. The values of the fitted constants are $(a, b, c) = (0.38, -0.35, -10.29)$.

As it turns out, the problem is not one of computational complexity, but of probability, as it is exceedingly rare for a random symmetric matrix to also be positive-definite. More specifically, the chance for an $N \times N$ matrix to be positive-definite asymptotically approaches $p_N \sim e^{-\frac{\ln(3)}{4}N^2}$ [21] which matches pretty well with what is observed in the figure. This means that if our calculations require significant amounts of large positive-definite matrices (corresponding to a big particle systems), then it would be wise to explore other avenues.

The random matrix approach is of course only relevant if one wishes to do the stochastic optimization method, because otherwise you would have nothing to optimize over, but it still shows the superiority of the approach that was developed in its stead using the $\left(\mathbf{x}_i - \mathbf{x}_j\right)^2$ formalism from section 2.3.1.

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