# Analytic matrix elements of prefactor Gaussians, and their application to variational calculations

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Bachelor's project

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# Preface

This 10-ECTS bachelor's thesis is written by me, Asbjørn Teilmann, a third year physics student at Aarhus University. My prerequisites for writing this thesis are all mandatory courses. And no additional prerequisites are required to read this thesis.

This thesis is inspired by recent work on the pion-nucleon interaction by my supervisor, Dmitri Fedorov, who provided the ideas studied within. This thesis will focus on the development of theory behind an extension to a well known calculational tool within few-body physics, and thus I will not discuss any models of the pion-nucleon interaction in detail.

Weekly meetings were held with Fedorov and graduate students, Martin Cradock Østerlund and Nikolaj Leonhard Peters. Thanks to all for providing helpful guidance and assistance with double-checking the results of many calculations and derivations made during this project.

Thanks to fellow bachelor's student Frode Balling-Ansø who provided many helpful comments during the writing of this thesis.

## Summary

Within the field of few-body physics several atomic, molecular and nuclear models have been solved to high accuracy using the method of corrolated gaussians. This is a variational method where the trial wavefunction is expanded in a basis of wavefunctions that are gaussians in the distance between particles. In this thesis we consider a related basis, called prefactor ECG's, that are suitable for describing complicated angular structure, such as those encountered in angular momentum eigenstates. We show that the necessary matrix elements can be derived using the shifted corrolated gaussians as generating functions. Overlap, kinetic energy, coulomb potential and harmonic potential matrix elements are calculated. We compare the performance between prefactor ECG's and shifted corrolated gaussians in a numerical calculation of the spectrum of the hydrogen atom, and demonstrate a substantial improvement. For this case, it is found that for the non-spherically symmetric states, the size of the basis set can be reduced by a factor of 2-3 while achieving the same accuracy.


### Colophon

*Analytic matrix elements of prefactor Gaussians, and their application to variational calculations*


Bachelor's project by Asbjørn Frost Teilmann.

The project is supervised by Dmitri Fedorov.



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# Resumé

I feltet få-legeme fysik har forskellige atomiske, molekylære og kernemodeller blevet løst til høj præcision ved brug af metoden "The Method of Corrolated Gaussians". Dette er en metode der gør brug af variationsprincippet og bølgefunktionen bliver skrevet som en linear kombination af Gausser i afstanden mellem partikler. I dette projekt betragter vi en relateret basis, kaldet prefaktor ECG'er, der er velegnet til komplicerede vinkelafhængigheder, såsom dem i egentilstande af impulsmoment. Vi viser at de nødvendige matrix elementer kan regnes ved brug af skiftede korrolerede Gausser som generende funktioner. Overlap, kinetisk energy, coulomb potentialet og det harmoniske potentiale matrix elementer beregnes. Vi sammenligner præstationen af prefaktor ECG'er med skiftede korrolerede Gausser i en numerisk beregning af hydrogen spectret, og demonstrerer en substantiel forbedring. I dette tilfælde finder vi at for de ikke-sfærisk symmetriske tilstande kan størrelsen af vores basis reduceres med en faktor på 2-3 med præcisionen bibeholdt.

### Kolofon

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# Chapter 1

# Introduction

The field of quantum few-body physics concerns itself with physical systems consisting of a small number of particles which may be described by non-relativistic quantum mechanics. Examples of such systems are: small atoms, molecules and light nuclei, including the meson-nucleon interaction. These systems are sufficiently simple so as to be described by exact two-body interactions. A common method used to calculate the energies and wavefunctions of few-body systems is The Method Of Corrolated Gaussians. This is an application of the variational principle where the wavefunction is expanded in a basis set of wavefunctions that explicitly correlate the coordinates of the different particles,

$$\phi(\mathbf{r}) = \exp\left(-\mathbf{r}^{\intercal} A \mathbf{r}\right).$$

There are many modifcations of this basis used for different problems. Several spectra and wavefunctions have been calculated in nuclear [3, 5], atomic and molecular physics [2] using this method. In this thesis we will consider a modification of the Method Of Correlated Gaussians using basis functions that may be chosen as angular momentum eigenstates, and are particularly well suited to describe the meson-nucleon interaction. These functions are named prefactor ECG's (Explicitly Corrolated Gaussians). We will calculate several important matrix elements: Overlaps, kinetic energy, coulomb interaction and the harmonic potential. These results are then applied to a numerical calculation of the spectrum and wavefunctions of the hydrogen atom and compared to a similar calculation using another basis, shifted corrolated gaussians.

# Chapter 2

# Background

## 2.1 Notation

Systems with an arbitrary number of particles can be compactly described using the notation from 'Analytic matrix elements with shifted correlated Gaussians' by D.V. Fedorov [6]. We will consider an $N$ particle system. Normal 3-dimensional vectors will be denoted by a vector arrow: $\vec{r}$, $\vec{s}$, $\vec{a}$. Capital letters, e.g. $A$, $B$ and $R$, will denote $N \times N$-matrices. In our $N$-body system the positions of the particles is contained in the $N$-dimensional vector $\mathbf{r}$ given by:

$$\mathbf{r} = (\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)^\intercal .$$

Generally, $N$-dimensional vectors containing ordinary 3-d vectors are denoted by bold font.[1] In this notation, dot-products and products with matrices are defined by the following:

$$\begin{aligned}
\mathbf{a}^\intercal \mathbf{b} &= \sum_{i=1}^{N} \vec{a}_i \cdot \vec{b}_i \\
(A\mathbf{b})_i &= \sum_{j=1}^{N} A_{ij} \vec{b}_j \\
\mathbf{a}^\intercal A \mathbf{b} &= \sum_{i,j=1}^{N} A_{ij}\, \vec{a}_i \cdot \vec{b}_j .
\end{aligned}$$

It should be noted that most results from the algebra of matrices still apply in this notation, but not all. For example:[2]

$$(\mathbf{r}^\intercal \mathbf{a})\,(\mathbf{b}^\intercal \mathbf{r}) \neq \mathbf{r}^\intercal\,(\mathbf{a}\mathbf{b}^\intercal)\,\mathbf{r}.$$

1: In the case $N = 1$, we will not distinguish between the matrix/bold-font vector and its single entry.

2: $(\mathbf{a}\mathbf{b}^\intercal)_{ij} = \vec{a}_i \cdot \vec{b}_j$.

The generalization of the gradient is:[3]

$$\frac{\partial}{\partial \mathbf{r}} = \left( \frac{\partial}{\partial \vec{r}_1}, \frac{\partial}{\partial \vec{r}_2}, \ldots, \frac{\partial}{\partial \vec{r}_N} \right).$$

Most rules of derivatives can be straightforwardly verified. For example, the chain rule is ($f$ taking real values):

$$\frac{\partial}{\partial \mathbf{r}} f(g(\mathbf{r})) = f'(g(\mathbf{r})) \frac{\partial g}{\partial \mathbf{r}}.$$

The derivative of linear function[4]:

$$\frac{\partial}{\partial \mathbf{r}^\intercal} \mathbf{a}^\intercal A \mathbf{r} = A^\intercal \mathbf{a},$$

and the derivative of a quadratic function:

$$\frac{\partial}{\partial \mathbf{r}^\intercal} \mathbf{r}^\intercal A \mathbf{r} = \left( A + A^\intercal \right) \mathbf{r}.$$

Proofs of these identites are presented in Appendix A. The product rule generalizes in the natural way, which we will use repeatedly in section 3.2.

## 2.2 The method of correlated gaussians

In this section we outline the formalism of The Method of Correlated Gaussians [11]. The starting point of this method is the variational principle.

### The variational principle

The important result of the variational principle is the following statement: For a system with hamiltonian $\hat{H}$, ground state energy $E_0$ and arbitrary state vector $|\psi\rangle$:

$$E[\psi] \equiv \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0. \tag{2.1}$$

3: $\frac{\partial}{\partial \vec{r}} = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) = \nabla$ is the normal 3-gradient for $\vec{r} = (x, y, z)^\intercal$

4: $\frac{\partial}{\partial \mathbf{r}^\intercal} = \left( \frac{\partial}{\partial \mathbf{r}} \right)^\intercal$

If, in addition, $|\psi\rangle$ is orthogonal to the true ground state of the system, the variational principle states that $E[\psi]$ is greater than the energy of the first excited state. This generalizes to any excited state provided that $|\psi\rangle$ is orthogonal to all lower lying eigenstates of $\hat{H}$ [8, 11].

In The Method of Correlated Gaussians, the wavefunction $|\psi\rangle$ is expanded in a (non-orthogonal) basis of size $N_g$, $\{|\phi_i\rangle\,, i = 1, 2, \ldots N_g\}$:

$$|\psi\rangle = \sum_{i=1}^{N_g} c_i \,|\phi_i\rangle\,. \tag{2.2}$$

Using the Schrödinger equation,

$$\sum_{i=1}^{N_g} c_i \hat{H}\,|\phi_i\rangle = E \sum_{i=1}^{N_g} c_i \,|\phi_i\rangle \tag{2.3}$$

and multiplying by $\langle\phi_j|$ from the left, the equation takes the form

$$\mathcal{H}c = E\mathcal{N}c, \tag{2.4}$$

where $\mathcal{H}$ and $\mathcal{N}$ are $N_g \times N_g$ hermitian matrices:

$$\mathcal{H}_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle\,, \quad \mathcal{N}_{ij} = \langle\phi_i|\phi_j\rangle\,,$$
$$c = (c_1, c_2, \ldots, c_{N_g})^\intercal.$$

At this point minimizing the energy functional in Equation 2.1 wrt. to $c$ is straight forward. The functional becomes:

$$E[\psi] = \frac{c^\dagger \mathcal{H} c}{c^\dagger \mathcal{N} c}.$$

From which we get:

$$\begin{aligned}
\frac{\partial}{\partial c} E[\psi] &= \frac{1}{(c^\dagger \mathcal{N} c)^2} \left( c^\dagger \mathcal{N} c \frac{\partial}{\partial c} \left(c^\dagger \mathcal{H} c\right) - c^\dagger \mathcal{H} c \frac{\partial}{\partial c} \left(c^\dagger \mathcal{N} c\right) \right) \\
&= \frac{2}{(c^\dagger \mathcal{N} c)^2} \left(c^\dagger \mathcal{N} c \cdot c^\dagger \mathcal{H} - c^\dagger \mathcal{H} c \cdot c^\dagger \mathcal{N}\right) \\
&= \frac{2}{c^\dagger \mathcal{N} c} \left(\mathcal{H} c - E[\psi] \mathcal{N} c\right)^\dagger .
\end{aligned}$$

(We used that $\mathcal{H}$ and $\mathcal{N}$ are hermitian). This is zero exactly if $c$ and $E[\psi]$ are the eigenvector and eigenvalue of the generalized eigenvalue

problem Equation 2.4. It has been proven that the $n$'th lowest eigenvalue to the generalized eigenvalue problem is an upper bound to the exact $n$'th lowest eigenvalue of $\hat{H}$ [9]. Thus, minimizing the energy functional $E[\psi]$ wrt. $c$ is equivalent to solving Equation 2.4.

This is a very useful generalization of the variational principle, provided that $\mathcal{H}$ and $\mathcal{N}$ can be easily calculated. The generalized eigenvalue problem is typically solved numerically by one of many known algorithms.

In general the expansion in Equation 2.2 should contain spinors multiplied on the basis functions and be appropriately (anti-)symmetrized according to fermionic or bosonic statistics for identical particles. In this thesis these effects are neglected as they don't influence the matrix elements evaluated in chapter 3, nor the application to the simple hydrogen atom in chapter 4.

## Correlated Gaussians

In the method of correlated Gaussians the basis functions $|\phi\rangle$ are chosen as gaussians in the distance between particles, known as explicitly correlated Gaussians (Henceforth referred to as 'ECG'):

$$\begin{aligned}\langle \mathbf{r}|\phi\rangle = \phi(\mathbf{r}) &= \exp\left(-\sum_{i>j=1}^{N}\left(\frac{\vec{r}_i - \vec{r}_j}{b_{ij}}\right)^2\right) \\ &= \exp\left(-\sum_{i,j=1}^{N} A_{ij}\vec{r}_i \cdot \vec{r}_j\right) \\ &= e^{-\mathbf{r}^\intercal A \mathbf{r}}.\end{aligned}$$

Where the constants $b_{ij}$ are variational parameters and the matrix $A$ can be written in terms of $b_{ij}$ if desired. For calculations the expression in terms of the symmetric positive definite matrix $A$ is more convenient. The benefit of this choice of basis functions is that the matrix elements of $\mathcal{H}$ and $\mathcal{N}$ can be computed analytically in most important cases. Furthermore, the complexity of these expressions do not depend on the number of particles. These functions explicitly correlate the positions of different particles, which allow for high accuracy calculations for systems with $N \geq 3$ [11]. In fact the matrix elements are known for the more general form of $|\phi\rangle$ [6]:

$$\phi(\mathbf{r}) = e^{-\mathbf{r}^\intercal A\mathbf{r}+\mathbf{s}^\intercal\mathbf{r}},$$

known as shifted ECG's. Generally the kinetic energy matrix elements are calculated with the kinetic energy operator in the general form [6]:

$$\hat{T} = -\frac{\partial}{\partial\mathbf{r}}\Lambda\frac{\partial}{\partial\mathbf{r}^\intercal} = -\sum_{i,j=1}^{N}\Lambda_{ij}\frac{\partial}{\partial\vec{r}_i}\frac{\partial}{\partial\vec{r}_j^{\,\intercal}},$$

where $\Lambda$ is a symmetric positive definite matrix. The two body interaction between the two particles and any external potentials can be conveniently handled through an $N$-dimensional vector $w$, which for an interaction involving the $i$'th and $j$'th particle is given by:

$$\begin{aligned} w_k &= \delta_{ik} - \delta_{jk}, && \text{For two-body force,}\\ w_k &= \delta_{ik}, && \text{For external force.} \end{aligned}$$

Then any interaction $V$ depending on $\vec{r}_i$ or $\vec{r}_i - \vec{r}_j$ is represented by the function $V(w^\intercal\mathbf{r})$. In chapter 3 we will use the known matrix elements of the shifted ECG's to compute corrosponding matrix elements of $\mathcal{N}$ and $\mathcal{H}$ for ECG's with front factors that corrospond to non-zero angular momentum.

# Chapter 3

# Prefactor Correlated Gaussians

## 3.1 Properties

We are interested in a generalization of ECG's to a functional form that explicitly incorporates the angular structure of angular momentum eigenstates. The choice is labeled by one of the states: s-wave: $|A\rangle$, p-wave: $|\mathbf{a}A\rangle$ and d-wave: $|\mathbf{ba}A\rangle$. We refer to these as prefactor ECG's. They have the following wavefunctions:

$$\begin{aligned}\langle \mathbf{r}|A\rangle &= e^{-\mathbf{r}^\intercal A\mathbf{r}},\\ \langle \mathbf{r}|\mathbf{a}A\rangle &= (\mathbf{a}^\intercal\mathbf{r})e^{-\mathbf{r}^\intercal A\mathbf{r}},\\ \langle \mathbf{r}|\mathbf{ba}A\rangle &= (\mathbf{b}^\intercal\mathbf{r})(\mathbf{a}^\intercal\mathbf{r})e^{-\mathbf{r}^\intercal A\mathbf{r}}.\end{aligned}$$

This form is partly motivated by the nucleon-nucleon force, which is mediated by meson exchange. The dominating contribution comes from the pion, since it is the lightest. When modelling this exchange the QM operator creating a pion is sometimes be chosen to be [5]:

$$\hat{W} = (\vec{\tau}\cdot\vec{\pi})(\vec{\sigma}\cdot\vec{r})f(r),$$

where $\vec{\tau}$ is the isovector of pauli matrices acting on isospin-space, $\vec{\pi}$ is the isovector of pions, $\vec{\sigma}$ is the vector of pauli matrices, $\vec{r}$ is the relative nucleon pion coordinate and $f(r)$ is phenomenogical short range form factor. If the form factor is chosen to be a gaussian, applying this operator to an s-state nucleon creates a pion with a wavefunction like the p-wave above.

Another primary motivation is the description of states with complicated angular dependence. In fact, denoting the total angular momentum operator by $\vec{L}_{\text{tot}}$, it can be easily shown (see Appendix C):

$$\begin{aligned}L^2_{\text{tot}}\,|A\rangle &= 0,\\ L^2_{\text{tot}}\,|\mathbf{a}A\rangle &= 2\hbar^2\,|\mathbf{a}A\rangle\,,\end{aligned} \tag{3.1}$$

as we would like. The d-waves, however, are not eigenstates of angular momentum in general. In section 3.2 it is shown that $\langle A'|\mathbf{ab}A\rangle \neq 0$ in general. Thus, careful consideration has to be made if one wishes to describe pure d-states with this basis. But this is not always a problem. The deuterons wavefunction, for example, is an admixture of s- and d-waves, so a pure angular momentum description is not necessarily desirable [10]. We will label the shifted ECG's by $|A\mathbf{s}\rangle$:

$$\langle \mathbf{r}|A\mathbf{s}\rangle = e^{-\mathbf{r}^\intercal A\mathbf{r}+\mathbf{s}^\intercal\mathbf{r}}.$$

In addition we will need the functional forms of the prefactor ECG's multiplied by the factor $e^{\mathbf{s}^\intercal\mathbf{r}}$, these will be labeled by $|A\mathbf{s}\rangle$, $|\mathbf{a}A\mathbf{s}\rangle$ and $|\mathbf{ba}A\mathbf{s}\rangle$. An important property is that the prefactor ECG's can be obtained by differentiating (or equivalently series expanding) the shifted ECG's:

$$\langle \mathbf{r}|A\rangle = \langle \mathbf{r}|A\mathbf{s}\rangle\,|_{\mathbf{s}=0}, \tag{3.2}$$

$$\langle \mathbf{r}|\mathbf{a}A\rangle = \left(\mathbf{a}^\intercal\frac{\partial}{\partial\mathbf{s}^\intercal}\right)\langle \mathbf{r}|A\mathbf{s}\rangle\,\Big|_{\mathbf{s}=0}, \tag{3.3}$$

$$\langle \mathbf{r}|\mathbf{ba}A\rangle = \left(\mathbf{b}^\intercal\frac{\partial}{\partial\mathbf{s}^\intercal}\right)\left(\mathbf{a}^\intercal\frac{\partial}{\partial\mathbf{s}^\intercal}\right)\langle \mathbf{r}|A\mathbf{s}\rangle\,\Big|_{\mathbf{s}=0}. \tag{3.4}$$

Which means that we can compute matrix elements by differentiating the known matrix elements of shifted ECG's. Thus the shifted ECG's may be used essentially as generating functions for prefactor ECG's.

## The single particle system

In 1-dimension, $A$ is just a real positive number. The s-waves have spherical symmetry, and thus are angular momentum eigenstates with $l = 0$. In the case of p-waves, we can use the cartesian representation of the spherical harmonics (see Arfken And Weber [1]) and can pick out $\mathbf{a}$ such that the wave is proportional to any of the $L = 1$ spherical harmonics. For example, with $\mathbf{a} = (0, 0, 1)^\intercal$:

$$(\mathbf{a}^\intercal\mathbf{r}) = z = \sqrt{\frac{4\pi}{3}}Y_1^0 r.$$

For the other projections, and the projections for d-waves, see Table 3.1. It is impossible to obtain the $Y_2^0$ projection with a single prefactor ECG.

| vectors $(\mathbf{a}, \mathbf{b})$ | function |
|---|---|
| $(1, i, 0)^\intercal$ | $(\mathbf{a}^\intercal \mathbf{r}) = -\sqrt{\frac{8\pi}{3}} Y_1^1 r$ |
| $(0, 0, 1)^\intercal$ | $(\mathbf{a}^\intercal \mathbf{r}) = \sqrt{\frac{4\pi}{3}} Y_1^0 r$ |
| $(1, i, 0)^\intercal, (1, i, 0)^\intercal$ | $(\mathbf{a}^\intercal \mathbf{r})(\mathbf{b}^\intercal \mathbf{r}) = \sqrt{\frac{32\pi}{15}} Y_2^2 r^2$ |
| $(1, i, 0)^\intercal, (0, 0, 1)^\intercal$ | $(\mathbf{a}^\intercal \mathbf{r})(\mathbf{b}^\intercal \mathbf{r}) = -\sqrt{\frac{8\pi}{15}} Y_2^1 r^2$ |

TABLE 3.1: Choices of vectors that give spherical harmonics for 1-dimensional ECG's with explicit angular momentum. The spherical harmonics with negative $m$ can be obtained by conjugating the vectors $\mathbf{a}$ and $\mathbf{b}$.

In the case of 1 particle, we can evaluate matrix elements directly. In the special cases of $\mathbf{a} = (0, 0, 1)^\intercal$ and $\mathbf{b} = \mathbf{c} = (1, i, 0)^\intercal$ (which are applied to the hydrogen atom in chapter 4) the matrix elements are: Overlaps:

$$\langle A' | A \rangle = \left( \frac{\pi}{A + A'} \right)^{3/2}, \tag{3.5}$$

$$\langle \mathbf{a} A' | \mathbf{a} A \rangle = \frac{\pi^{3/2}}{2 \left( A + A' \right)^{5/2}}, \tag{3.6}$$

$$\langle \mathbf{cb} A' | \mathbf{cb} A \rangle = \frac{2\pi^{3/2}}{\left( A + A' \right)^{7/2}}. \tag{3.7}$$

Kinetic Energy:

$$\langle A' | \nabla^2 | A \rangle = -6 A A' \frac{\pi^{3/2}}{(A + A')^{5/2}}, \tag{3.8}$$

$$\langle \mathbf{a} A' | \nabla^2 | \mathbf{a} A \rangle = -5 A A' \frac{\pi^{3/2}}{(A + A')^{7/2}}, \tag{3.9}$$

$$\langle \mathbf{cb} A' | \nabla^2 | \mathbf{cb} A \rangle = -28 A A' \frac{\pi^{3/2}}{(A + A')^{9/2}}. \tag{3.10}$$

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Coulomb and harmonic potentials:

$$\left\langle A' \left| \frac{1}{r} \right| A \right\rangle = \frac{2\pi}{A + A'}, \tag{3.11}$$

$$\left\langle \mathbf{a}A' \left| \frac{1}{r} \right| \mathbf{a}A \right\rangle = \frac{2\pi}{3(A + A')^2}, \tag{3.12}$$

$$\left\langle \mathbf{cb}A' \left| \frac{1}{r} \right| \mathbf{cb}A \right\rangle = \frac{32\pi}{15(A + A')^3}, \tag{3.13}$$

$$\left\langle A' \left| r^2 \right| A \right\rangle = \frac{3\pi^{3/2}}{2(A + A')^{5/2}}, \tag{3.14}$$

$$\left\langle \mathbf{a}A' \left| r^2 \right| \mathbf{a}A \right\rangle = \frac{5\pi^{3/2}}{4(A + A')^{7/2}}, \tag{3.15}$$

$$\left\langle \mathbf{cb}A' \left| r^2 \right| \mathbf{cb}A \right\rangle = \frac{7\pi^{3/2}}{(A + A')^{9/2}}. \tag{3.16}$$

The calculation of these matrix elements is done in Appendix B. In the next section we'll generalize these results to an arbitrary number of particles.

## 3.2 Matrix elements

In this section we will compute overlaps and matrix elements for kinetic energy. We also compute the matrix elements of the coulomb potential, a very important potential as it appears in all atomic and most nuclear applications of the Method of Corrolated Gaussians. These calculations are based on the known results for shifted ECG's and are given in the relevant sections. The matrix elements for the harmonic potential will be calculated in the final section using a slightly different approach. We will assume that $A$ and $A'$ are real $N \times N$ matrices and $\mathbf{s}$ and $\mathbf{s}'$ are real vectors. The vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and $\mathbf{d}$ are complex in general. All the operators we consider preserve parity, therefore the matrix elements between s- and p-waves or p- and d-waves are all zero since they have opposite parity. Central to the calculations is the following fact we noted earlier: For any operator $\hat{K}$,

$$\langle \mathbf{c}A'|\hat{K}|\mathbf{a}A\rangle = \left(\mathbf{c}^\dagger \frac{\partial}{\partial \mathbf{s}'^\intercal}\right)\left(\mathbf{a}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right) \langle A'\mathbf{s}'|\hat{K}|A\mathbf{s}\rangle \Big|_{\mathbf{s}=\mathbf{s}'=0}, \tag{3.17}$$

$$\langle \mathbf{dc}A'|\hat{K}|\mathbf{ba}A\rangle = \Delta^2 \langle A'\mathbf{s}'|\hat{K}|A\mathbf{s}\rangle \big|_{\mathbf{s}=\mathbf{s}'=0}, \tag{3.18}$$

where,[1]

$$\Delta^2 = \left(\mathbf{d}^\dagger \frac{\partial}{\partial \mathbf{s}'^\intercal}\right)\left(\mathbf{c}^\dagger \frac{\partial}{\partial \mathbf{s}'^\intercal}\right)\left(\mathbf{b}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right)\left(\mathbf{a}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right).$$

Thus we can in principle calculate any matrix element of prefactor ECG's if the same matrix elements is known analytically for shifted ECG's.

## Overlaps

In this section we compute the overlaps of prefactor ECG's. The overlap integral of shifted ECG's is [6]:

$$\langle A'\mathbf{s}'|A\mathbf{s}\rangle = e^{\frac{1}{4}\mathbf{v}^\intercal B^{-1}\mathbf{v}}\left(\frac{\pi^N}{\det(B)}\right)^{3/2} = e^{\frac{1}{4}\mathbf{v}^\intercal B^{-1}\mathbf{v}} M_0 \equiv M, \quad (3.19)$$

where: $B = A + A'$, $\mathbf{v} = \mathbf{s} + \mathbf{s}'$ and $M_0 = \left(\frac{\pi^N}{\det(B)}\right)^{3/2}$.

Carrying out the derivative in Equation 3.17 we get, setting $R = B^{-1}$:

$$\begin{aligned}\langle \mathbf{c}A'\mathbf{s}'|\mathbf{a}A\mathbf{s}\rangle &= \left(\mathbf{c}^\dagger \frac{\partial}{\partial \mathbf{s}'^\intercal}\right)\left(\mathbf{a}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right) M \\ &= \left(\mathbf{c}^\dagger \frac{\partial}{\partial \mathbf{s}'^\intercal}\right)\frac{1}{4}(2\mathbf{a}^\intercal R\mathbf{v})M \\ &= \left(2\mathbf{c}^\dagger R\mathbf{a} + \mathbf{c}^\dagger R\mathbf{v}\cdot\mathbf{a}^\intercal R\mathbf{v}\right)\frac{M}{4}. \end{aligned} \quad (3.20)$$

Note that we obtained a formula for the single and double derivative of $M$. We can repeat this calculation for d-waves, using the product rule multiple times:

$$\begin{aligned}\langle \mathbf{dc}A'\mathbf{s}'|\mathbf{ba}A\mathbf{s}\rangle &= \left(\mathbf{d}^\dagger \frac{\partial}{\partial \mathbf{s}'^\intercal}\right)\left(\mathbf{b}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right)\left(2\mathbf{c}^\dagger R\mathbf{a} + \mathbf{c}^\dagger R\mathbf{v}\cdot\mathbf{a}^\intercal R\mathbf{v}\right)\frac{M}{4} \\ &= \left(2\mathbf{c}^\dagger R\mathbf{a} + \mathbf{c}^\dagger R\mathbf{v}\cdot\mathbf{a}^\intercal R\mathbf{v}\right)\left(2\mathbf{d}^\dagger R\mathbf{b} + \mathbf{d}^\dagger R\mathbf{v}\cdot\mathbf{b}^\intercal R\mathbf{v}\right)\frac{M}{16} \\ &\quad + (\mathbf{c}^\dagger R\mathbf{b}\cdot\mathbf{d}^\dagger R\mathbf{a} + \mathbf{c}^\dagger R\mathbf{d}^*\cdot\mathbf{a}^\intercal R\mathbf{b})\frac{M}{4} \\ &\quad + (\mathbf{c}^\dagger R\mathbf{b}\cdot\mathbf{a}^\intercal R\mathbf{v} + \mathbf{c}^\dagger R\mathbf{v}\cdot\mathbf{a}^\intercal R\mathbf{b})(\mathbf{d}^\dagger R\mathbf{v})\frac{M}{8} \\ &\quad + (\mathbf{c}^\dagger R\mathbf{d}^*\cdot\mathbf{a}^\intercal R\mathbf{v} + \mathbf{c}^\dagger R\mathbf{v}\cdot\mathbf{d}^\dagger R\mathbf{a})(\mathbf{b}^\intercal R\mathbf{v})\frac{M}{8}. \end{aligned} \quad (3.21)$$

1: For any matrix $\mathbf{a}$, $\mathbf{a}^\dagger = (\mathbf{a}^*)^\intercal$.

Analytic matrix elements of prefactor Gaussians, and their application to variational calculations

Equations 3.20 and 3.21 will be useful when calculating the matrix elements of the harmonic potential. Plugging in $\mathbf{s} = \mathbf{s}' = 0$ into 3.19, 3.20 and 3.21 we obtain the desired overlaps:

$$\langle A|A'\rangle = M_0, \tag{3.22}$$

$$\langle \mathbf{c}A'|\mathbf{a}A\rangle = \mathbf{c}^\dagger R\mathbf{a}\frac{M_0}{2} \tag{3.23}$$

$$\begin{aligned}\langle \mathbf{dc}A'|\mathbf{ba}A\rangle = (&\mathbf{b}^\intercal R\mathbf{a}\cdot\mathbf{d}^\dagger R\mathbf{c}^* + \mathbf{c}^\dagger R\mathbf{a}\cdot\mathbf{d}^\dagger R\mathbf{b} \\ &+ \mathbf{c}^\dagger R\mathbf{b}\cdot\mathbf{d}^\dagger R\mathbf{a})\frac{M_0}{4}.\end{aligned} \tag{3.24}$$

An expression for the overlap between s- and d-waves can be obtained by noting that the integral is identical to that between p-waves. (up to a complex conjugate) Thus:

$$\langle A'|\mathbf{ba}A\rangle = \mathbf{b}^\intercal R\mathbf{a}\frac{M_0}{2}. \tag{3.25}$$

## Kinetic energy

In this section we calculate the matrix elements of kinetic energy in the general form for a symmetric positive definite real matrix $\Lambda$:

$$\hat{T} = -\frac{\partial}{\partial\mathbf{r}}\Lambda\frac{\partial}{\partial\mathbf{r}^\intercal}.$$

The kinetic energy matrix element for shifted ECG's is [6]:

$$\left\langle A'\mathbf{s}'\left|\hat{T}\right|A\mathbf{s}\right\rangle = \left(L + (\mathbf{s}' - A'R\mathbf{v})^\intercal\Lambda(\mathbf{s} - AR\mathbf{v})\right)M, \tag{3.26}$$

where $L = 6\,\mathrm{Tr}(A'\Lambda AB^{-1})$. We will compute the matrix elements of the kinetic energy in a similar way to the overlaps. To make the differentiation managable, we first note a bunch of formulae derived from the product rule. Let $F$ and $G$ be $N \times N$ matrices. The matrix element for s-waves is simply obtained by putting $\mathbf{s} = \mathbf{s}' = 0$ in Equation 3.26:

$$\langle A'|\hat{T}|A\rangle = LM_0. \tag{3.27}$$

For p-waves and matrix elements between s- and d-states, we need the 4 following results which are easily verified:[2]

$$\left(\mathbf{c}^\dagger \frac{\partial}{\partial \mathbf{s}'^\intercal}\right)\left(\mathbf{a}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right)\mathbf{s}^\intercal F \mathbf{s} M\big|_{\mathbf{s}=\mathbf{s}'=0} = 0, \tag{3.28}$$

$$\left(\mathbf{b}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right)\left(\mathbf{a}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right)\mathbf{s}^\intercal F \mathbf{s} M\big|_{\mathbf{s}=\mathbf{s}'=0} = \mathbf{b}^\intercal \left(F + F^\intercal\right)\mathbf{a} M_0, \tag{3.29}$$

$$\left(\mathbf{c}^\dagger \frac{\partial}{\partial \mathbf{s}'^\intercal}\right)\left(\mathbf{a}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right)\mathbf{s}'^\intercal F \mathbf{s} M\big|_{\mathbf{s}=\mathbf{s}'=0} = \mathbf{c}^\dagger F \mathbf{a} M_0, \tag{3.30}$$

$$\left(\mathbf{b}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right)\left(\mathbf{a}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal}\right)\mathbf{s}'^\intercal F \mathbf{s} M\big|_{\mathbf{s}=\mathbf{s}'=0} = 0. \tag{3.31}$$

Applying Equation 3.17 (with $\hat{K} = \hat{T}$), we see that the first term in Equation 3.26 just gives the overlap rescaled by $L$. Using the formulae 3.28 and 3.30, we see that the second term gives 2 contributions from the terms involving both $\mathbf{s}$ and $\mathbf{s}'$:

$$\begin{aligned}\langle \mathbf{c}A'|\hat{T}|\mathbf{a}A\rangle = L\langle \mathbf{c}A'|\mathbf{a}A\rangle + \mathbf{c}^\dagger\big((1-RA')\Lambda(1-AR) \\ +RA\Lambda A'R\big)\mathbf{a}M_0.\end{aligned} \tag{3.32}$$

The s-d matrix element results from the terms involving only $\mathbf{s}$:

$$\begin{aligned}\langle A'|\hat{T}|\mathbf{b}\mathbf{a}A\rangle = L\langle A'|\mathbf{b}\mathbf{a}A\rangle + \mathbf{b}^\intercal\big(RA'\Lambda AR + RA\Lambda A'R \\ -RA\Lambda - \Lambda AR\big)\mathbf{a}M_0,\end{aligned} \tag{3.33}$$

for d-waves we can start by writing Equation 3.26 as:

$$\begin{aligned}\left\langle A'\mathbf{s}'\left|\hat{T}\right|A\mathbf{s}\right\rangle =& LM + \big(\mathbf{s}'^\intercal\Lambda\mathbf{s} - \mathbf{s}'^\intercal\Lambda AR\mathbf{v} \\ &-\mathbf{v}^\intercal RA'\Lambda\mathbf{s} + \mathbf{v}^\intercal RA'\Lambda AR\mathbf{v}\big)M\end{aligned} \tag{3.34}$$

Applying Equation 3.18 we obtain many terms to organize, to this end the following result is useful:

$$\begin{aligned}\Delta^2\left(\mathbf{s}^\intercal F\mathbf{s}M\right)|_{\mathbf{s}=\mathbf{s}'=0} =& \left(\mathbf{a}^\intercal\frac{\partial}{\partial\mathbf{s}^\intercal}\right)\left(\mathbf{b}^\intercal\frac{\partial}{\partial\mathbf{s}^\intercal}\right)\mathbf{s}^\intercal F\mathbf{s} \\ &\cdot\left(\mathbf{c}^\dagger\frac{\partial}{\partial\mathbf{s}'^\intercal}\right)\left(\mathbf{d}^\dagger\frac{\partial}{\partial\mathbf{s}'^\intercal}\right)M|_{\mathbf{s}=\mathbf{s}'=0} \\ =& \left(\mathbf{a}^\intercal F\mathbf{b} + \mathbf{b}^\intercal F\mathbf{a}\right)\langle\mathbf{d}\mathbf{c}A'|A\rangle\,.\end{aligned} \tag{3.35}$$

2: In 3.29 we use that $\mathbf{a}^\intercal F\mathbf{b} = (\mathbf{a}^\intercal F\mathbf{b})^\intercal = \mathbf{b}^\intercal F^\intercal\mathbf{a}$.

An almost identical calculation gives:

$$\Delta^2 \left(\mathbf{s}'^{\intercal} F \mathbf{s} M\right)|_{\mathbf{s}=\mathbf{s}'=0} = \mathbf{c}^\dagger F \mathbf{a} \left\langle \mathbf{d}A'|\mathbf{b}A\right\rangle + \mathbf{d}^\dagger F \mathbf{a} \left\langle \mathbf{c}A'|\mathbf{b}A\right\rangle + \mathbf{c}^\dagger F \mathbf{b} \left\langle \mathbf{d}A'|\mathbf{a}A\right\rangle + \mathbf{d}^\dagger F \mathbf{b} \left\langle \mathbf{c}A'|\mathbf{a}A\right\rangle, \quad (3.36)$$

with similar formulae for $\mathbf{s}$ and $\mathbf{s}'$ swapped. We can now compute the d-wave matrix element. From the first term in the parentheses in Equation 3.34 we get the four terms from Equation 3.36. The next two terms each contribute 6 terms to the final result. And the last term contributes with 12 terms. The final result can be written out:

$$\begin{aligned}
\langle \mathbf{d}\mathbf{c}A'|\hat{T}|\mathbf{b}\mathbf{a}A\rangle &= L\left\langle \mathbf{d}\mathbf{c}A'|\mathbf{b}\mathbf{a}A\right\rangle + \frac{M_0}{2}\big[\mathbf{c}^\dagger R\mathbf{b}\cdot\mathbf{d}^\dagger\Lambda\mathbf{a} \\
&+ \mathbf{d}^\dagger R\mathbf{b}\cdot\mathbf{c}^\dagger\Lambda\mathbf{a} + \mathbf{c}^\dagger R\mathbf{a}\cdot\mathbf{d}^\dagger\Lambda\mathbf{b} + \mathbf{d}^\dagger R\mathbf{a}\cdot\mathbf{c}^\dagger\Lambda\mathbf{b} \\
&- \mathbf{c}^\dagger R\mathbf{b}\cdot\mathbf{d}^\dagger RA\Lambda\mathbf{a} - \mathbf{d}^\dagger R\mathbf{b}\cdot\mathbf{c}^\dagger RA\Lambda\mathbf{a} - \mathbf{c}^\dagger R\mathbf{a}\cdot\mathbf{d}^\dagger RA\Lambda\mathbf{b} \\
&- \mathbf{d}^\dagger R\mathbf{a}\cdot\mathbf{c}^\dagger RA\Lambda\mathbf{b} - \mathbf{b}^\intercal R\mathbf{a}\cdot\mathbf{c}^\dagger RA\Lambda\mathbf{d}^* - \mathbf{b}^\intercal R\mathbf{a}\cdot\mathbf{d}^\dagger RA\Lambda\mathbf{c}^* \\
&- \mathbf{c}^\dagger R\mathbf{b}\cdot\mathbf{d}^\dagger RA'\Lambda\mathbf{a} - \mathbf{d}^\dagger R\mathbf{b}\cdot\mathbf{c}^\dagger RA'\Lambda\mathbf{a} - \mathbf{c}^\dagger R\mathbf{a}\cdot\mathbf{d}^\dagger RA'\Lambda\mathbf{b} \\
&- \mathbf{d}^\dagger R\mathbf{a}\cdot\mathbf{c}^\dagger RA'\Lambda\mathbf{b} - \mathbf{c}^\dagger R\mathbf{d}^*\cdot\mathbf{b}^\intercal RA'\Lambda\mathbf{a} - \mathbf{c}^\dagger R\mathbf{d}^*\cdot\mathbf{a}^\intercal RA'\Lambda\mathbf{b} \\
&+ \mathbf{c}^\dagger R\mathbf{b}\cdot\mathbf{d}^\dagger RA'\Lambda AR\mathbf{a} + \mathbf{d}^\dagger R\mathbf{b}\cdot\mathbf{c}^\dagger RA'\Lambda AR\mathbf{a} \\
&+ \mathbf{c}^\dagger R\mathbf{a}\cdot\mathbf{d}^\dagger RA'\Lambda AR\mathbf{b} + \mathbf{d}^\dagger R\mathbf{a}\cdot\mathbf{c}^\dagger RA'\Lambda AR\mathbf{b} \\
&+ \mathbf{b}^\intercal R\mathbf{a}\cdot\mathbf{d}^\dagger RA\Lambda A'R\mathbf{c}^* + \mathbf{b}^\intercal R\mathbf{a}\cdot\mathbf{d}^\dagger RA'\Lambda AR\mathbf{c}^* \\
&+ \mathbf{c}^\dagger R\mathbf{b}\cdot\mathbf{d}^\dagger RA\Lambda A'R\mathbf{a} + \mathbf{d}^\dagger R\mathbf{b}\cdot\mathbf{c}^\dagger RA\Lambda A'R\mathbf{a} \\
&+ \mathbf{c}^\dagger R\mathbf{a}\cdot\mathbf{d}^\dagger RA\Lambda A'R\mathbf{b} + \mathbf{d}^\dagger R\mathbf{a}\cdot\mathbf{c}^\dagger RA\Lambda A'R\mathbf{b} \\
&+ \mathbf{c}^\dagger R\mathbf{d}^*\cdot\mathbf{b}^\intercal RA'\Lambda AR\mathbf{a} + \mathbf{c}^\dagger R\mathbf{d}^*\cdot\mathbf{b}^\intercal RA\Lambda A'R\mathbf{a}\big]. \qquad (3.37)
\end{aligned}$$

This is a rather cumbersome result, but is structured in such a way that it is relatively easy to implement directly into numerical calculations. In total the results are the following equations:

| | |
|---|---|
| $\langle A'\|\hat{T}\|A\rangle$ | Equation 3.27 |
| $\langle \mathbf{c}A'\|\hat{T}\|\mathbf{a}A\rangle$ | Equation 3.32 |
| $\langle A'\|\hat{T}\|\mathbf{b}\mathbf{a}A\rangle$ | Equation 3.33 |
| $\langle \mathbf{d}\mathbf{c}A'\|\hat{T}\|\mathbf{b}\mathbf{a}A\rangle$ | Equation 3.37 |

## The Coulomb Interaction

In this section we compute the matrix element of the coulomb interaction $V_C = |w^\intercal \mathbf{r}|^{-1}$. The matrix element between shifted ECG's is

given [6]:

$$\langle A'\mathbf{s}' \left| V_C \right| A\mathbf{s} \rangle = \frac{\text{erf}(\sqrt{\beta}q)}{q} M, \tag{3.38}$$

with: $\beta = \left(w^\intercal B^{-1} w\right)^{-1}$ and $\vec{q} = \frac{1}{2} w^\intercal R\mathbf{v}$. In anticipation of differentiating and putting $\mathbf{s} = \mathbf{s}' = 0$, we series expand the error function in Equation 3.38 to fourth order in $\mathbf{v}$, since all higher order terms will not contribute to the matrix elements.

$$\langle A'\mathbf{s}' \left| V_C \right| A\mathbf{s} \rangle = 2\sqrt{\frac{\beta}{\pi}} \left( 1 - \frac{\beta}{12} \mathbf{v}^\intercal \tilde{R} \mathbf{v} + \frac{\beta^2}{160} \left( \mathbf{v}^\intercal \tilde{R} \mathbf{v} \right)^2 \right) M, \tag{3.39}$$

where $\tilde{R} = Rww^\intercal R$. We can now obtain the result for s-waves:

$$\langle A' \left| V_C \right| A \rangle = 2\sqrt{\frac{\beta}{\pi}} M_0. \tag{3.40}$$

As is usual by now, we differentiate to obtain results for p- and d-waves. For p-waves we see that only the first two terms in Equation 3.39 contribute, using Equation 3.28 and 3.30:

$$\begin{aligned} \langle \mathbf{c}A' \left| V_C \right| \mathbf{a}A \rangle = 2\sqrt{\frac{\beta}{\pi}} \Bigg[ & \left( \mathbf{c}^\dagger \frac{\partial}{\partial \mathbf{s}'^\intercal} \right) \left( \mathbf{a}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal} \right) M \\ & - \frac{\beta}{12} M_0 \left( \mathbf{c}^\dagger \frac{\partial}{\partial \mathbf{s}'^\intercal} \right) \left( \mathbf{a}^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal} \right) \mathbf{v}^\intercal \tilde{R} \mathbf{v} \Bigg] \Bigg|_{\mathbf{s}=0} \\ = \mathbf{c}^\dagger & \left( R - \frac{\beta}{3} \tilde{R} \right) \mathbf{a} \sqrt{\frac{\beta}{\pi}} M_0, \end{aligned} \tag{3.41}$$

where we used the p-wave overlap. The s-d matrix element then follows immediately like the overlap:

$$\langle A' \left| V_C \right| \mathbf{ba}A \rangle = \mathbf{b}^\intercal \left( R - \frac{\beta}{3} \right) \mathbf{a} \sqrt{\frac{\beta}{\pi}} M_0. \tag{3.42}$$

For d-waves all three terms contribute,

$$\begin{aligned} \langle \mathbf{dc}A' \left| V_C \right| \mathbf{ba}A \rangle = & 2\sqrt{\frac{\beta}{\pi}} \langle \mathbf{dc}A' \left| \right. \mathbf{ba}A \rangle \\ & - \frac{\beta}{6} \sqrt{\frac{\beta}{\pi}} \cdot \Delta^2 \left[ \mathbf{v}^\intercal \tilde{R} \mathbf{v} M \right] |_{\mathbf{s}=\mathbf{s}'=0} \\ & + M_0 \frac{\beta^2}{80} \sqrt{\frac{\beta}{\pi}} \cdot \Delta^2 \left[ \mathbf{v}^\intercal \tilde{R} \mathbf{v} \right]^2 |_{\mathbf{s}=\mathbf{s}'=0}. \end{aligned} \tag{3.43}$$

The first parentheses contains the term: $\mathbf{a}^\intercal\tilde{R}\mathbf{b}\cdot\mathbf{c}^\dagger R\mathbf{d}^*/4$ and all permutations of $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and $\mathbf{d}$, all derived from Equation 3.35 and 3.36. Noting that $R$ and $\tilde{R}$ are symmetric, we see there are 6 different terms each counted 4 times. Similarly, for the last parentheses we use the product rule repeatedly to obtain three different terms like: $\mathbf{a}^\intercal\tilde{R}\mathbf{b}\cdot\mathbf{c}^\dagger\tilde{R}\mathbf{d}^*$, each counted 8 times (using the symmetry properties again). The total result is:

$$\begin{aligned}\langle\mathbf{dc}A'\,|V_C|\,\mathbf{ba}A\rangle &= 2\sqrt{\frac{\beta}{\pi}}\,\langle\mathbf{dc}A'\,|\,\mathbf{ba}A\rangle - \frac{\beta^{3/2}M_0}{6\sqrt{\pi}}\times\\ &\Big[\mathbf{c}^\dagger R\mathbf{d}^*\cdot\mathbf{a}^\intercal\tilde{R}\mathbf{b} + \mathbf{d}^\dagger R\mathbf{b}\cdot\mathbf{c}^\dagger\tilde{R}\mathbf{a} + \mathbf{c}^\dagger R\mathbf{b}\cdot\mathbf{d}^\dagger\tilde{R}\mathbf{a}\\ &+\mathbf{d}^\dagger R\mathbf{a}\cdot\mathbf{c}^\dagger\tilde{R}\mathbf{b} + \mathbf{c}^\dagger R\mathbf{a}\cdot\mathbf{d}^\dagger\tilde{R}\mathbf{b} + \mathbf{a}^\intercal R\mathbf{b}\cdot\mathbf{c}^\dagger\tilde{R}\mathbf{d}^*\Big] + \frac{\beta^{5/2}M_0}{10\sqrt{\pi}}\times\\ &\Big[\mathbf{a}^\intercal\tilde{R}\mathbf{b}\cdot\mathbf{c}^\dagger\tilde{R}\mathbf{d}^* + \mathbf{c}^\dagger\tilde{R}\mathbf{a}\cdot\mathbf{d}^\dagger\tilde{R}\mathbf{b} + \mathbf{d}^\dagger\tilde{R}\mathbf{a}\cdot\mathbf{c}^\dagger\tilde{R}\mathbf{b}\Big]. \qquad (3.44)\end{aligned}$$

The results are the following:

| | |
|---|---|
| $\langle A'\|V_C\|A\rangle$ | Equation 3.40 |
| $\langle\mathbf{c}A'\|V_C\|\mathbf{a}A\rangle$ | Equation 3.41 |
| $\langle A'\|V_C\|\mathbf{ba}A\rangle$ | Equation 3.42 |
| $\langle\mathbf{dc}A'\|V_C\|\mathbf{ba}A\rangle$ | Equation 3.44 |

## The Harmonic Potential

In this section we compute the matrix element of the harmonic potential,

$$V_H(w^\intercal\mathbf{r}) = \mathbf{r}^\intercal ww^\intercal\mathbf{r}.$$

This can computed more easily by differentiating the overlap integrals, for example:

$$\langle\mathbf{c}A'|V_H|\mathbf{a}A\rangle = \left\langle\mathbf{c}A'\left|\frac{\partial}{\partial\mathbf{s}}ww^\intercal\frac{\partial}{\partial\mathbf{s}^\intercal}\right|\mathbf{a}A\mathbf{s}\right\rangle\Bigg|_{\mathbf{s}=0}.$$

We need 2 simple identities to carry out this computation

$$\begin{aligned}\frac{\partial}{\partial\mathbf{s}}F\frac{\partial}{\partial\mathbf{s}^\intercal}\,(\mathbf{s}^\intercal B\mathbf{s}) &= 6\,\mathrm{Tr}\,(FB),\\ \frac{\partial}{\partial\mathbf{s}}F\frac{\partial}{\partial\mathbf{s}^\intercal}\,(\mathbf{a}^\intercal B\mathbf{s}\cdot\mathbf{b}^\intercal C\mathbf{s}) &= \mathbf{a}^\intercal BFC\mathbf{b} + \mathbf{b}^\intercal CFB\mathbf{a}.\end{aligned}$$

For symmetric matrices $F$, $B$ and $C$. The second of these is easily derived using the product rule. The first is less trivial, and is proven in Appendix A. From this we derive

$$\begin{aligned}\langle A'|V_H|A\rangle &= \frac{\partial}{\partial \mathbf{s}} ww^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal} \langle A'|A\mathbf{s}\rangle \Big|_{\mathbf{s}=0} \\ &= \frac{3}{2} \operatorname{Tr}(ww^\intercal R) M_0 \\ &= \frac{3}{2} w^\intercal R w \cdot M_0. \end{aligned} \tag{3.45}$$

Where we use that $\operatorname{Tr}(ABC) = \operatorname{Tr}(BCA)$. Similarly:

$$\begin{aligned}\langle \mathbf{c}A'|V_H|\mathbf{a}A\rangle &= \frac{\partial}{\partial \mathbf{s}} ww^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal} \langle \mathbf{c}A'|\mathbf{a}A\mathbf{s}\rangle \Big|_{\mathbf{s}=0} \\ &= \frac{1}{2}\mathbf{c}^\dagger R\mathbf{a} \frac{\partial}{\partial \mathbf{s}} ww^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal} M\Big|_{\mathbf{s}=0} \\ &+ \frac{M_0}{4} \frac{\partial}{\partial \mathbf{s}} ww^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal} \left(\mathbf{c}^\dagger R\mathbf{s} \cdot \mathbf{a}^\intercal R\mathbf{s}\right) \\ &= (3\mathbf{c}^\dagger R\mathbf{a} \cdot w^\intercal R w + 2\mathbf{c}^\dagger \tilde{R}\mathbf{a}) \frac{M_0}{4}, \end{aligned} \tag{3.46}$$

with $\tilde{R} = Rww^\intercal R$. We obtain immediately:

$$\langle A'|V_H|\mathbf{b}\mathbf{a}A\rangle = (3\mathbf{b}^\intercal R\mathbf{a} \cdot w^\intercal R w + 2\mathbf{c}^\dagger \tilde{R}\mathbf{a}) \frac{M_0}{4}. \tag{3.47}$$

To calculate the matrix element for d-waves, we can differentiate Equation 3.21 while noticing that the derivatives on $M$ result in exactly Equation 3.45. Carrying out the differentiation and collecting like terms the matrix element is

$$\begin{aligned}\langle \mathbf{d}\mathbf{c}A'|V_H|\mathbf{b}\mathbf{a}A\rangle &= \frac{\partial}{\partial \mathbf{s}} ww^\intercal \frac{\partial}{\partial \mathbf{s}^\intercal} \langle \mathbf{d}\mathbf{c}A'|\mathbf{b}\mathbf{a}A\mathbf{s}\rangle \Big|_{\mathbf{s}=0} \\ &= \frac{3}{2} w^\intercal R w \langle \mathbf{d}\mathbf{c}A'|\mathbf{b}\mathbf{a}A\rangle + \\ &\quad \frac{M_0}{4}(\mathbf{c}^\dagger R\mathbf{a} \cdot \mathbf{d}^\dagger \tilde{R}\mathbf{b} + \mathbf{d}^\dagger R\mathbf{a} \cdot \mathbf{c}^\dagger \tilde{R}\mathbf{b} \\ &\quad + \mathbf{c}^\dagger R\mathbf{b} \cdot \mathbf{d}^\dagger \tilde{R}\mathbf{a} + \mathbf{d}^\dagger R\mathbf{b} \cdot \mathbf{c}^\dagger \tilde{R}\mathbf{a} \\ &\quad + \mathbf{c}^\dagger R\mathbf{d}^* \cdot \mathbf{a}^\intercal \tilde{R}\mathbf{b} + \mathbf{b}^\intercal R\mathbf{a} \cdot \mathbf{d}^\dagger \tilde{R}\mathbf{c}^*). \end{aligned} \tag{3.48}$$

If we specialize to $N = 1$ in these matrix elements and plug in the correct vectors ($(0, 0, 1)$ for p-waves and $(1, i, 0)$ for d-waves). Every one of these matrix elements reduce to those listed in section 3.1, confirming our results.

# Chapter 4

# The Hydrogen Atom

In this chapter we apply the method of correlated gaussians and the calculated matrix elements to compute the spectrum and wavefunctions of the hydrogen atom. In this chapter we will exclusively work in atomic units (described in [7]). In this system the spinless hydrogen atom has the hamiltonian:

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

approximating the mass of the nucleus as infinite.[1] In our notation this corresponds to $\Lambda = 1/2$ and the coulomb potential as in section 3.2 with $w = 1$. The solutions of Schrödingers equation, $\hat{H}\,|\psi\rangle = E\,|\psi\rangle$, are well known [8]:

$$E_n = -\frac{1}{2n^2}. \tag{4.1}$$

## 4.1 Single Gaussian optimization

To check our numerical procedure we minimize the energy functional Equation 2.1 analytically by hand for a single gaussian. In this case the problem reduces to a single parameter, $A$. Using the matrix elements we derived in section 3.1 and putting $A = A'$, the energy functional

1: Instead of using the infinite mass approximation and atomic units, one can change coordinates $\vec{r} = a_0\vec{x}$ and energy $E = \alpha^2\mu c^2 \cdot \varepsilon$. Where $a_0$ is the Bohr radius, $\alpha$ is the fine structure constant and $\mu$ is the reduced mass of the system. In this case the Schrödinger equation becomes $\hat{H}_{\vec{x}}\psi(\vec{x}) = \varepsilon\psi(\vec{x})$ with $\hat{H}$ as above, avoiding any approximations.

becomes:

$$E_s(A) = -\frac{\langle A|\nabla^2|A\rangle}{2\langle A|A\rangle} - \frac{\langle A|r^{-1}|A\rangle}{\langle A|A\rangle} = \frac{3}{2}A - \sqrt{\frac{8A}{\pi}},$$
$$E_p(A) = -\frac{\langle \mathbf{a}A|\nabla^2|\mathbf{a}A\rangle}{2\langle \mathbf{a}A|\mathbf{a}A\rangle} - \frac{\langle \mathbf{a}A|r^{-1}|\mathbf{a}A\rangle}{\langle \mathbf{a}A|\mathbf{a}A\rangle} = \frac{5}{2}A - \frac{4}{3}\sqrt{\frac{2A}{\pi}},$$
$$E_d(A) = -\frac{\langle \mathbf{cb}A|\nabla^2|\mathbf{cb}A\rangle}{2\langle \mathbf{cb}A|\mathbf{cb}A\rangle} - \frac{\langle \mathbf{cb}A|r^{-1}|\mathbf{cb}A\rangle}{\langle \mathbf{cb}A|\mathbf{cb}A\rangle} = \frac{7}{2}A - \frac{16}{15}\sqrt{\frac{2A}{\pi}}.$$

These expressions can be easily minimized. The results are:

$$A_{\min,s} = \frac{8}{9\pi} \approx 0.283, \qquad E_s(A_{\min,s}) = -\frac{4}{3\pi} \approx -0.424,$$
$$A_{\min,p} = \frac{32}{225\pi} \approx 0.0453, \qquad E_p(A_{\min,p}) = -\frac{16}{45\pi} \approx -0.113,$$
$$A_{\min,d} = \frac{512}{11025\pi} \approx 0.0148, \qquad E_d(A_{\min,d}) = -\frac{256}{1575\pi} \approx -0.0517.$$

These are exactly the numerical values attained in Table 4.1.

## 4.2 Numerical procedure

We are now able to calculate the spectrum and wavefunctions of hydrogen. For ECG's with explicit angular momentum, we can fix $\mathbf{a}$ and $\mathbf{b}$ in accordance with Table 3.1. This will pick out s, p and d-states which therefore give the ground state and two lowest lying excited states when the lowest eigenvalue of Equation 2.4 is minimized. We fix the prefactors such that the angular dependence of the wavefunctions is $Y_1^0$ or $Y_2^2$ for all gaussians of the same type.

For comparison we also compute these energies using shifted ECG's. In this case, the 2p and 3d states are computed by minimizing the second and sixth lowest eigenvalues of the generalized eigenvalue problem. For the $n = 3$ states we have to pick the sixth lowest eigenvalue because, as we know in advance, the $n = 2$ states are four-fold degenerate. In addition, this implies that at least 6 shifted ECG's are needed to describe the d-states and 2 to describe the p-states. In a central problem with no analytical solution, we only expect degeneracy in the $m$ quantum number, therefore we can only hope any additional (exact or approximate) degeneracy would be revealed by the calculation itself.

Analytic matrix elements of prefactor Gaussians, and their application to variational calculations

The non-linear parameters $A$ (and the components of $\mathbf{s}$ for the shifted ECG's) are optimized deterministically.[2] The initial conditions for $A$ are chosen as:

$$A_i = (b \cdot i/N_g)^{-2}, \qquad i = 1, 2, \ldots N_g,$$

where $N_g$ is the number of gaussians and $b$ is parameter chosen to be 5 for s and p waves and 10 for d-waves. For p-waves the initial conditions for $\mathbf{s}$ are chosen as:

$$\mathbf{s} = (0, 0, \frac{2i/N_g - 1}{2b}), \qquad i = 0, 1, \ldots N_g - 1. \tag{4.2}$$

To describe the $n = 3$ states we paramaterize $\mathbf{s}$ in spherical coordinates:

$$\mathbf{s} = s \cdot (\sin\theta \cdot \cos\phi, \sin\theta \cdot \sin\phi, \cos\theta)^\intercal \tag{4.3}$$

With initial conditions:

$$\begin{aligned} \theta &= \pi/2 \\ \phi_i &= 2\pi \cdot i/N_g \quad \text{for} \quad i = 0, 1, \ldots N_g - 1. \\ s &= 1/b \end{aligned}$$

We can exploit some of our knowledge of the states in the calculations using shifted ECG's. For instance we only optimize the z-component of $\mathbf{s}$ when calculating the p-wave energies. We can do this since we already know that the p-states with $m = 0$ have nonspherical components that only depend on the z-coordinate. Similarly $\mathbf{s} = 0$ is chosen for the s-state.

The linear parameters $c$ are optimized by solving the generalized eigenvalue problem,

$$\mathcal{H}c = E\mathcal{N}c,$$

as described in section 2.2. This problem was solved numerically using the QR-algorithm which is $O(N_g^3)$ [4].

2: This problem is simple enough to be solvable with most numerical optimization algorithms. The Nelder-Mead method was used for this optimization.

## 4.3 Energies

The numerically calculated energies can be seen in Table 4.1. Energy convergence plots can be seen in Figure 4.1. We can consistently and easily attain 4 digits of precision. At $N_g \geq 10$ the calculation of the $n = 3$ energies with shifted ECG's begin increasing. This suggests that the numerical calculation becomes unstable as $\mathcal{N}$ may become approximately singular, and therefore the values are not usable.

We also see that the prefactor ECG's attain almost 2 orders of magnitude better precision with fewer Gaussians than shifted ECG's, for the states with non-zero angular momentum. It should be noted that the accuracy is best for the d-waves.

| Prefactor ECG's | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $n = 1$ | | | $n = 2$ | | | $n = 3$ | |
| $N_g$ | $E$ | % Error | $N_g$ | $E$ | % Error | $N_g$ | $E$ | % Error |
| 1 | $-0.4244$ | 15 | 1 | $-0.11318$ | 9.5 | 1 | $-0.05174$ | 6.9 |
| 2 | $-0.4858$ | 2.8 | 2 | $-0.12329$ | 1.4 | 2 | $-0.05508$ | 0.86 |
| 3 | $-0.4970$ | 0.60 | 3 | $-0.12473$ | 0.22 | 3 | $-0.05549$ | 0.11 |
| 4 | $-0.4993$ | 0.14 | 4 | $-0.12495$ | 0.039 | 4 | $-0.05554$ | 0.016 |
| 5 | $-0.4998$ | 0.038 | 5 | $-0.12499$ | 0.008 | 5 | $-0.05555$ | 0.003 |
| Shifted ECG's | | | | | | | | |
| | $n = 1$ | | | $n = 2$ | | | $n = 3$ | |
| $N_g$ | $E$ | % Error | $N_g$ | $E$ | % Error | $N_g$ | $E$ | % Error |
| 1 | $-0.4244$ | 15 | 2 | $-0.1168$ | 6.5 | 6 | $-0.0519$ | 6.6 |
| 2 | $-0.4858$ | 2.8 | 3 | $-0.1237$ | 1.0 | 7 | $-0.0550$ | 1.0 |
| 3 | $-0.4970$ | 0.60 | 4 | $-0.1246$ | 0.30 | 8 | $-0.0553$ | 0.48 |
| 4 | $-0.4993$ | 0.14 | 5 | $-0.1246$ | 0.30 | 9 | $-0.0554$ | 0.22 |
| 5 | $-0.4998$ | 0.038 | 6 | $-0.1248$ | 0.17 | | | |

TABLE 4.1: Energies calculated numerically as described in section 4.2. The size of the basis set is denoted by $N_g$. Convergence plots using these results are given Figure 4.1.

## 4.4 Radial wavefunctions

we can examine the radial wavefunctions resulting from the variational calculations. Calculating the radial wavefunctions from the ECG's with explicit angular momentum is very easy. Indeed we simply remove the $Y_l^m$ from the wavefunctions. For example, given that $\mathbf{a}$

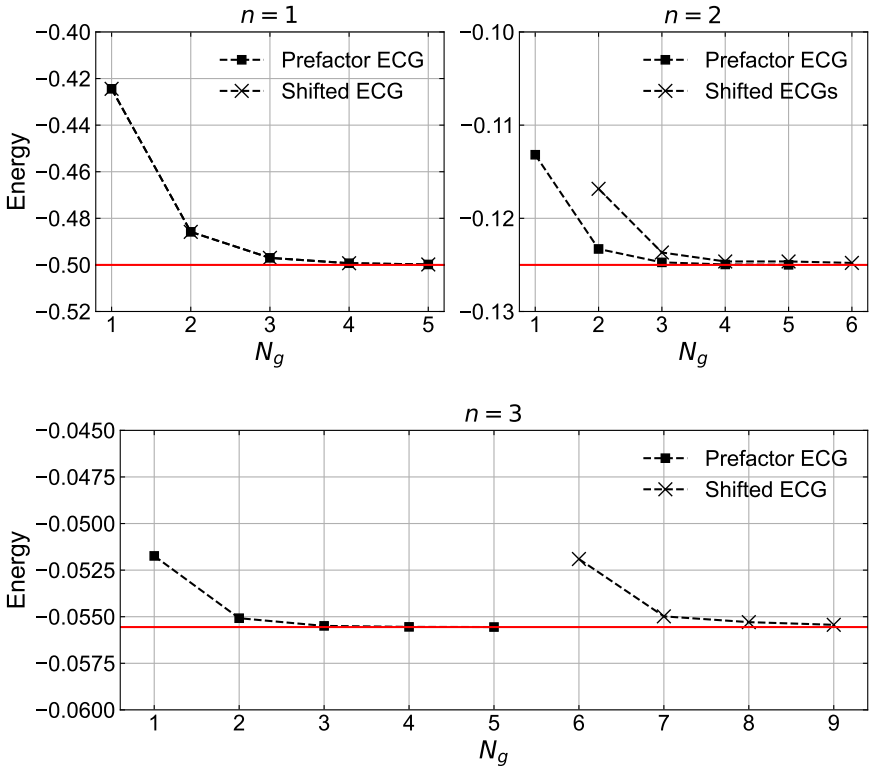


FIGURE 4.1: Energy convergence the variational calculation using both ECG's with explicit angular momentum and shifted ECG's. For explicit angular momentum states, $\mathbf{a}$ and $\mathbf{b}$ are fixed according to the second and third entry of Table 3.1 for p- and d-states respectively. The red lines are the analytic energies and $N_g$ is the number of gaussians in the calculation. The numerical value of the energies can be seen in Table 4.1.

and $\mathbf{b}$ are fixed for each gaussian:

$$R_d(r) = \sqrt{\frac{32\pi}{15}} \sum_{i=1}^{N_g} c_i r^2 e^{-A_i r^2},$$

with only normalization to be determined. We normalize according to $\int_0^\infty r^2 R^2 dr = 1$. This is equivalent to normalizing $c$ according to

$$c^\dagger \mathcal{N} c = 1.$$

These wavefunctions are plotted along with the exact wavefunctions in Figure 4.2 for the choices described in section 4.2.

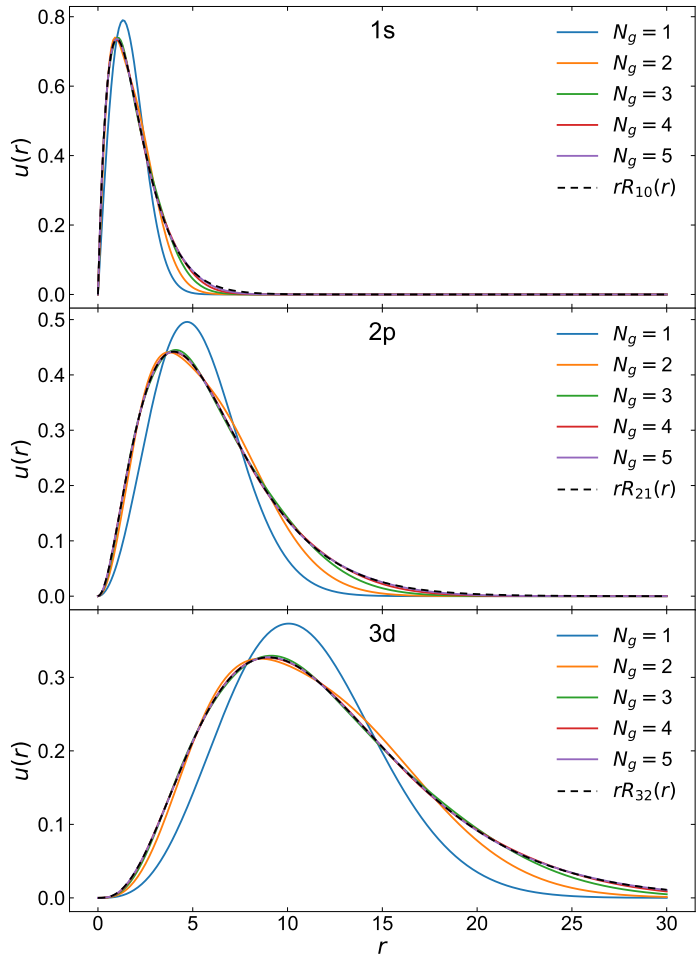


FIGURE 4.2: Approximate radial wavefunctions for s, p and d-states calculated using prefactor ECG's. These are plotted along with the exact radial wavefunctions. $N_g$ denotes the number of ECG's in the variational calculation. The wavefunctions are normalized according to $\int_0^\infty |u(r)|^2 dr = 1$.

It is clear that once energy convergence has been achieved (3-4 gaussians), the main deviation from the exact wavefunction stems from the incorrect asymptotic behaviour. The ECG's have a gaussian asymptotic dependence, whereas the coulomb potential gives rise to exponential asymptotic behaviour.[3] But note that, like with the energy convergence, this deviation is significantly smaller for the higher $l$ states than for the s-state.

3: For this reason exponential basis functions were sometimes preferred in the past, see Mitroy et al. [11].

# Chapter 5

# Discussion and generalization

## 5.1 Discussion

The matrix elements we calculated in section 3.2 were clearly analytic from the beginning. However, the results in Equation 3.37 and 3.44 show that these expressions quickly blow up in the number of terms. They are nevertheless managable, and their derivations straightforward if time consuming. This is a disadvantage that prefactor ECG's relative to shifted ECG's whose matrix elements are comparatively simple. For larger $N$ these terms likely become way less managable numerically as their computation time is significantly higher than for shifted ECG's.

The energy calculation of the hydrogen reveals that much greater accuracy are achieved significantly faster when describing non-zero angular momentum states using prefactor ECG's instead of shifted ECG's. The greatest benefit is accrued with the 3d-state. In this case in Table 4.1 we see that 9 shifted ECG's barely reach similar accuracy to 3 prefactor ECG's. Similarly, 6 shifted ECG's are needed to describe the 2p state to the same accuracy as 3 prefactor ECG's. This corresponds to 2-3 factor reduction in $N_g$, and since matrix diagonalization is $O(N_g^3)$, this is a factor of 8-27 times faster just in the matrix diagonalization. A rather significant improvement.

Another area of improvement is the reduced search space in the nonlinear parameters. If the angular structure of the studied system can be guessed beforehand, the prefactors can be fixed (as we did in the hydrogen atom), reducing the amount of nonlinear parameters to only the terms in the $A$-matrix. This is in contrast to shifted ECG's where the search space includes the shifts $\mathbf{s}$, which can be hard to optimize.

As noted in section 4.4, the main error in the wavefunction stems from the incorrect asymptotic behaviour of the basis functions as

$r \to \infty$. It is clear however, that this is not a significant hinderance when calculating energies. It may cause problems when evaluating expectation values which depend on arbitrarily large $r$, such as the dipole operator.

These prefactor ECG's can only describe states with angular momentum $l \leq 2$. One approach to generalize to higher $l$ is discussed in the next section.

## 5.2 More Prefactors

The form we have of prefactor ECG's naturally raise the question if we can generalize to a more general wavefunction with an arbitrary number of prefactors. One way to generalize is to consider a number, $l$, of vectors $\mathbf{a}_i$, and the wavefunction:

$$\langle \mathbf{r}|\phi\rangle = e^{-\mathbf{r}^\intercal A \mathbf{r}} \prod_{i=1}^{l} (\mathbf{a}_i^\intercal \mathbf{r})\,. \tag{5.1}$$

Ideally this would effectively describe more complicated angular structure, and maybe even fixed angular momentum eigenstates. Equation 5.1 may seem complicated to do analytic computations on, however, from Equation 3.24, Equation 3.37 and their derivations, we can geuss their the overlap and kinetic energy matrix elements. By $|\phi'\rangle$ we denote another prefactor ECG with same parity as $|\phi\rangle$. $|\phi'\rangle$ has matrix $A'$ and $l'$ prefactors $\mathbf{b}_i$. With this, we can generalize the overlap integral:

$$\langle \phi'|\phi\rangle = \frac{M_0}{2^{l+l'}(\frac{l+l'}{2})!} \sum_{\sigma} \prod_{i=1}^{(l+l')/2} \mathbf{c}_{\sigma(i)}^\intercal R \mathbf{c}_{\sigma\left(i+\frac{l+l'}{2}\right)},$$

where:

$$\mathbf{c}_i = \begin{cases} \mathbf{a}_i & \text{if } 0 < i \leq l \\ \mathbf{b}_{i-l}^* & \text{if } l < i \leq l + l' \end{cases}.$$

The sum is over all permutations $\sigma$ of the set $\{1, 2, \ldots l + l'\}$. Using the symmetry of $R$, we see that the number of terms in the overlap integral is $(l + l' - 1)!!$.

Similar expressions can be geussed for the kinetic energy and the potentials, although it is harder to derive the front factors of the

various sums. We haven't proven this expression, however it is clear that the method in section 3.2 will provide analytic expressions for any $N$ and $l$, and so the matrix elements can be calculated analytically. However, the number of terms in these matrix elements quickly blow up, thus their utility for calculations are restrained by computational limitations.

We saw earlier that the precision of the variational calculation seems to increase with $L$. If this trend continues, it may allieviate the complexity of the matrix elements by reducing the number of ECG's necessary to achieve convergence in the energy. However, this increase in precision is quite miniscule relative to the sheer number of terms in these matrix elements.

This choice of basis functions may still be an improvement over shifted ECG's, whose only advantage is the simpler matrix elements. This is almost certainly the case if the prefactors in Equation 5.1 are fixed in such a way that many of the terms in the matrix elements vanish. If this is not possible, other choices of ECG's may be preferred such as shifted ECG's or one of several known alternatives such as the global vector representation [12].

# Chapter 6

# Conclusion

In this thesis we considered an extension of the method of correlated gaussians appropriate for complicated angular dependecies. We have calculated the overlap integrals, kinetic energy, coulomb potential and harmonic potential matrix elements between prefactor ECG's using shifted ECG's as generating functions. We have seen that the resulting matrix elements are significantly more complicated for the prefactor ECG's corresponding to larger angular momentum than for shifted ECG's. We applied these basis functions to a numerical calculation of the hydrogen atom, reaching 0.1% precision with less than five ECG's, which is significantly better than shifted ECG's for the 2p and 3d states. This lead to a reduction of the necessary number of basis functions by a factor of 2-3 relative to shifted ECG's.

We argued that although most matrix elements are analytic in this basis and that this basis is better suited than shifted ECG's for non-zero angular momentum, the analytic complexity and computational load of these matrix elements may grow too fast to be generalizable to large angular momenta, in the most straightforward approach.

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# Appendix A Derivative identities

We denote the $i$'th component of a bold font vector, $\mathbf{a}$, by the notation $(\mathbf{a})_i$. With this, we derive the identities in section 2.1 componentwise. The chain rule can be derived using the normal chain rule for gradients:

$$\begin{aligned}\left(\frac{\partial}{\partial \mathbf{r}} f(g(\mathbf{r}))\right)_i &= \frac{\partial}{\partial \vec{r}_i} f(g(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N)) \\ &= f'(g(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N)) \frac{\partial g}{\partial \vec{r}_i}(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) \\ &= \left(f'(g(\mathbf{r})) \frac{\partial g}{\partial \mathbf{r}}(\mathbf{r})\right)_i .\end{aligned}$$

The linear derivative can be derived similarly:

$$\begin{aligned}\left(\frac{\partial}{\partial \mathbf{r}^\intercal} \mathbf{a}^\intercal A \mathbf{r}\right)_i &= \sum_{jk} \frac{\partial}{\partial \vec{r}_i^\intercal} A_{jk} \vec{a}_j \cdot \vec{r}_k \\ &= \sum_{jk} A_{jk} \vec{a_j} \delta_{ik} \\ &= \sum_j A_{ji} \vec{a_j} \\ &= (A^\intercal \mathbf{a})_i .\end{aligned}$$

For the quadratic function we use the product rule for ordinary gradients.

$$\begin{aligned}\left(\frac{\partial}{\partial \mathbf{r}^\intercal} \mathbf{r}^\intercal A \mathbf{r}\right)_i &= \sum_{jk} \frac{\partial}{\partial \vec{r}_i^\intercal} A_{jk} \vec{r_j} \cdot \vec{r}_k \\ &= \sum_{jk} A_{jk} \left(\delta_{ik} \vec{r_j} + \delta_{ij} \vec{r}_k\right) \\ &= \sum_j A_{ji} \vec{r_j} + \sum_k A_{ik} \vec{r}_k \\ &= (A^\intercal \mathbf{r} + A\mathbf{r})_i .\end{aligned}$$

A similar approach gives:

$$\begin{aligned}
\frac{\partial}{\partial \mathbf{s}} F \frac{\partial}{\partial \mathbf{s}^\intercal} \left(\mathbf{s}^\intercal B \mathbf{s}\right) &= \sum_{ijkl} F_{ij} B_{kl} \frac{\partial}{\partial \vec{r_i}} \cdot \frac{\partial}{\partial \vec{r_j}^\intercal} \left(\vec{r_k} \cdot \vec{r_l}\right) \\
&= \sum_{ijkl} F_{ij} B_{kl} \frac{\partial}{\partial \vec{r_i}} \cdot \left(\delta_{jk} \vec{r_l} + \delta_{jl} \vec{r_k}\right) \\
&= \sum_{ijkl} F_{ij} B_{kl} \cdot 3 \left(\delta_{jk} \delta_{il} + \delta_{jl} \delta_{ik}\right) \\
&= 3 \sum_{ij} F_{ij} B_{ji} + F_{ij} B_{ij} \\
&= 6 \operatorname{Tr}\left(FB\right).
\end{aligned}$$

Where we used that $B_{ij} = B_{ji}$. In the same way the product rule follows from the product rule for ordinary gradients:

$$\begin{aligned}
\mathbf{a}^\intercal \frac{\partial}{\partial \mathbf{r}^\intercal} f(\mathbf{r}) \cdot g(\mathbf{r}) &= \sum_i \vec{a}_i \cdot \frac{\partial}{\partial \vec{r_i}^\intercal} f(\mathbf{r}) g(\mathbf{r}) \\
&= \sum_i g(\mathbf{r}) \vec{a}_i \cdot \frac{\partial f}{\partial \vec{r_i}^\intercal} + f(\mathbf{r}) \vec{a}_i \cdot \frac{\partial g}{\partial \vec{r_i}^\intercal} \\
&= g(\mathbf{r}) \mathbf{a}^\intercal \frac{\partial f}{\partial \mathbf{r}^\intercal} + f(\mathbf{r}) \mathbf{a}^\intercal \frac{\partial g}{\partial \mathbf{r}^\intercal}.
\end{aligned}$$

# Appendix B Matrix elements for N = 1

We set $\mathbf{a} = (0, 0, 1)^\intercal$ and $\mathbf{b} = \mathbf{c} = (1, i, 0)^\intercal$ and use the results in Table 3.1. Using the well-known gaussian integrals:

$$\begin{aligned}
\int_0^\infty x^{2n} e^{-Ax^2} dx &= \frac{(2n)!}{n! \cdot 2^{2n+1} \cdot A^n} \sqrt{\frac{\pi}{A}}, \\
\int_0^\infty x^{2n+1} e^{-Ax^2} dx &= \frac{n!}{2A^{n+1}}.
\end{aligned}$$

The overlaps are calculated:

$$\langle A'|A\rangle = 4\pi \int_0^\infty r^2 e^{-(A'+A)r^2} dr = \left(\frac{\pi}{A+A'}\right)^{3/2}, \tag{B.1}$$

$$\begin{aligned}\langle \mathbf{a}A'|\mathbf{a}A\rangle &= \frac{4\pi}{3}\int_{\mathbb{R}^3} |Y_1^0|^2 \cdot r^2 e^{-(A'+A)r^2} d^3\vec{r} \\ &= \frac{4\pi}{3}\int_0^\infty r^4 e^{-(A'+A)r^2} dr = \frac{\pi^{3/2}}{2\left(A+A'\right)^{5/2}},\end{aligned} \tag{B.2}$$

$$\begin{aligned}\langle \mathbf{cb}A'|\mathbf{cb}A\rangle &= \frac{32\pi}{15}\int_{\mathbb{R}^3} |Y_2^2|^2 \cdot r^4 e^{-(A'+A)r^2} d^3\vec{r} \\ &= \frac{32\pi}{15}\int_0^\infty r^6 e^{-(A'+A)r^2} dr = \frac{2\pi^{3/2}}{(A+A')^{7/2}},\end{aligned} \tag{B.3}$$

where we have used the normalization of the $Y_l^m$. To compute the kinetic energy matrix element, we use the following form of the laplacian [8]:

$$\nabla^2 = \frac{1}{r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{\hbar^2}\right),$$

and the result:

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r} r^n e^{-Ar^2}\right) = \left(n(n+1) - 2A(2n+3)r^2 + 4A^2r^4\right) r^n e^{-Ar^2}.$$

Using this we can compute the matrix elements:

$$\begin{aligned}\langle A'|\nabla^2|A\rangle &= 4\pi\int_0^\infty (4A^2r^4 - 6Ar^2)e^{-(A+A')r^2}dr \\ &= \pi^{3/2}\left(\frac{6A^2}{(A+A')^{5/2}} - \frac{6A}{(A+A')^{3/2}}\right) \\ &= -6AA'\frac{\pi^{3/2}}{(A+A')^{5/2}}.\end{aligned} \tag{B.4}$$

For the p-waves the first term in the radial derivative cancels with the $L^2$ contribution, such that:

$$\begin{aligned}\langle \mathbf{a}A'|\nabla^2|\mathbf{a}A\rangle &= \frac{4\pi}{3}\int_0^\infty (4A^2r^6 - 10Ar^4)e^{-(A+A')r^2}dr \\ &= \pi^{3/2}\left(\frac{5A^2}{(A+A')^{7/2}} - \frac{5A}{(A+A')^{5/2}}\right) \\ &= -5AA'\frac{\pi^{3/2}}{(A+A')^{7/2}}.\end{aligned} \tag{B.5}$$

The calculation for d-waves is similar:

$$\begin{aligned}\langle \mathbf{cb}A'|\nabla^2|\mathbf{cb}A\rangle &= \frac{32\pi}{15}\int_0^\infty (4A^2r^8 - 14Ar^6)e^{-(A+A')r^2}dr \\ &= \pi^{3/2}\left(\frac{28A^2}{(A+A')^{9/2}} - \frac{28A}{(A+A')^{7/2}}\right) \\ &= -28AA'\frac{\pi^{3/2}}{(A+A')^{9/2}}. \end{aligned} \tag{B.6}$$

The kinetic matrix element is then obtained by multiplying these expressions by $-\hbar^2/2m$.

To finish off, we calculate the matrix element of the coulomb potential $V = r^{-1}$ and the harmonic potential, which is the same integrals as in equations B.1, B.2 and B.3 with integrands multiplied by $r^{-1}$ or $r^2$:
The Coulomb potential:

$$\left\langle A'\left|\frac{1}{r}\right|A\right\rangle = 4\pi\int_0^\infty re^{-(A'+A)r^2}dr = \frac{2\pi}{A+A'}, \tag{B.7}$$

$$\left\langle \mathbf{a}A'\left|\frac{1}{r}\right|\mathbf{a}A\right\rangle = \frac{4\pi}{3}\int_0^\infty r^3e^{-(A'+A)r^2}dr = \frac{2\pi}{3(A+A')^2}, \tag{B.8}$$

$$\left\langle \mathbf{cb}A'\left|\frac{1}{r}\right|\mathbf{cb}A\right\rangle = \frac{32\pi}{15}\int_0^\infty r^5e^{-(A'+A)r^2}dr = \frac{32\pi}{15(A+A')^3}. \tag{B.9}$$

The Harmonic potential:

$$\left\langle A'\left|r^2\right|A\right\rangle = 4\pi\int_0^\infty r^4e^{-(A'+A)r^2}dr = \frac{3\pi^{3/2}}{2(A+A')^{5/2}}, \tag{B.10}$$

$$\left\langle \mathbf{a}A'\left|r^2\right|\mathbf{a}A\right\rangle = \frac{4\pi}{3}\int_0^\infty r^6e^{-(A'+A)r^2}dr = \frac{5\pi^{3/2}}{4(A+A')^{7/2}}, \tag{B.11}$$

$$\left\langle \mathbf{cb}A'\left|r^2\right|\mathbf{cb}A\right\rangle = \frac{32\pi}{15}\int_0^\infty r^8e^{-(A'+A)r^2}dr = \frac{7\pi^{3/2}}{(A+A')^{9/2}}. \tag{B.12}$$

# Appendix C Proof of Equation 3.1

Let

$$\nabla_i = \left(\frac{\partial}{\partial \mathbf{r}^\intercal}\right)_i,$$

$$\vec{L}_{\text{tot}} = -i\hbar\sum_{i=1}^{N}\vec{r}_i \times \nabla_i.$$

Analytic matrix elements of prefactor Gaussians, and their application to variational calculations

We start by showing that

$$\vec{L}_{\text{tot}} e^{-\mathbf{r}^\intercal A \mathbf{r}} = 0. \tag{C.1}$$

From this, it follows immediately that

$$L^2_{\text{tot}} |A\rangle = 0. \tag{C.2}$$

By noting that $A$ is symmetric, the derivative is easy,

$$\begin{aligned} \vec{r}_i \times \nabla_i e^{-\mathbf{r}^\intercal A \mathbf{r}} &= -\vec{r}_i \times \left( \sum_{j,k} A_{jk} \left( \delta_{ij} \vec{r}_k + \delta_{ik} \vec{r}_j \right) \right) e^{-\mathbf{r}^\intercal A \mathbf{r}} \\ &= -2 \left( \sum_j A_{ij} \vec{r}_i \times \vec{r}_j \right) e^{-\mathbf{r}^\intercal A \mathbf{r}}. \end{aligned} \tag{C.3}$$

And thus,

$$\vec{L}_{\text{tot}} e^{-\mathbf{r}^\intercal A \mathbf{r}} = 2i\hbar \left( \sum_{ij} A_{ij} \vec{r}_i \times \vec{r}_j \right) e^{-\mathbf{r}^\intercal A \mathbf{r}} = 0. \tag{C.4}$$

The sum is zero because $A_{ij}$ is symmetric, and $\vec{r}_i \times \vec{r}_j$ is antisymmetric, such that each term cancels pairwise with the term that has $i$ and $j$ interchanged. using this result, we conlude:

$$L^2_{\text{tot}} \left( \mathbf{a}^\intercal \mathbf{r} \right) e^{-\mathbf{r}^\intercal A \mathbf{r}} = e^{-\mathbf{r}^\intercal A \mathbf{r}} L^2_{\text{tot}} \left( \mathbf{a}^\intercal \mathbf{r} \right). \tag{C.5}$$

Now let $r_{ik}$ denote the $k$'th component of $\vec{r}_i$, $\nabla_{ik}$ the $k$'th component of $\nabla_i$ and so on. It is clear that $\nabla_i \left( \mathbf{a}^\intercal \mathbf{r} \right) = \vec{a}_i$. The cross product can be written with the Levi-Civita symbol $\varepsilon_{ijk}$:

$$(\vec{a} \times \vec{b})_i = \sum_{j,k=1}^{3} \varepsilon_{ijk} a_j b_k. \tag{C.6}$$

Thus:

$$
\begin{aligned}
L^2_{\text{tot}}\left(\mathbf{a}^\intercal \mathbf{r}\right) &= -\hbar^2 \sum_{i,j=1}^{N} \left(\vec{r_j} \times \nabla_j\right) \cdot \left(\vec{r_i} \times \nabla_i\right) \left(\mathbf{a}^\intercal \mathbf{r}\right) \\
&= -\hbar^2 \sum_{i,j=1}^{N} \left(\vec{r_j} \times \nabla_j\right) \cdot \left(\vec{r_i} \times \vec{a}_i\right) \\
&= -\hbar^2 \sum_{i,j=1}^{N} \sum_{m,l,k,p,q=1}^{3} \varepsilon_{mlk}\varepsilon_{mpq} r_{jl} \nabla_{jk} r_{ip} a_{iq} \\
&= -\hbar^2 \sum_{i,j=1}^{N} \sum_{l,k,p,q=1}^{3} r_{jl} a_{iq} \delta_{ji} \delta_{kp} \left( \sum_{m=1}^{3} \varepsilon_{mlk}\varepsilon_{mpq} \right) \\
&= -\hbar^2 \sum_{i=1}^{N} \sum_{l,k,p,q=1}^{3} r_{il} a_{iq} \delta_{kp} \left(\delta_{lp}\delta_{kq} - \delta_{lq}\delta_{kp}\right) \\
&= -\hbar^2 \sum_{i=1}^{N} \sum_{l,p,q=1}^{3} r_{il} a_{iq} \left(\delta_{lp}\delta_{pq} - \delta_{lq}\right) \\
&= \hbar^2 \sum_{i=1}^{N} \left( \sum_{l,p=1}^{3} r_{il} a_{il} - \sum_{l=1}^{3} r_{il} a_{il} \right) \\
&= 2\hbar^2 \sum_{i=1}^{N} \vec{r}_i \cdot \vec{a}_i = 2\hbar^2 \left(\mathbf{a}^\intercal \mathbf{r}\right)
\end{aligned} \tag{C.7}
$$

Combining this result with Equation C.5 the result in Equation 3.1 is obtained.