Non-Adiabatic Calculations with Explicitly Correlated Gaussians

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Master's thesis

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Colophon

Non-Adiabatic Calculations with Explicitly Correlated Gaussians

— Ikke-Adiabatiske Beregninger med Eksplicitte Korrelerede Gausser

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Abstract

This master's thesis further builds upon the method examined in two previous master's theses [1, 2]. This method combines the use of explicitly correlated Gaussians (ECGs) as basis functions in the variational principle with the Born-Oppenheimer approximation. These studies established the foundation for the method, but did not obtain results that match other literature, and they did not reach the non-adiabatic calculations. In this thesis, we correct the derivations and implementation of the analytical matrix elements, thereby obtaining results consistent with other literature. Finally, we explicitly calculate the non-adiabatic terms and discuss their characteristics.

The implementation of the method is tested by performing numerical calculations with the H_2^+ system. Here, we solve the generalized eigenvalue problem for different distances between the hydrogen atom and the proton (y_0), which gives the potential energy surfaces (PES). We do this for both the ground state and the first excited state within the σ_g symmetry. Within the Born-Oppenheimer approximation, we obtain very satisfactory results, which are in agreement with other literature. The potential energy surface for the ground state converges fast, while the first excited state shows the need for a larger basis size to converge. However, going beyond the Born-Oppenheimer approximation is problematic, as the non-adiabatic terms have a very spiky nature. We tried to circumvent this by including a penalty term on the variational parameters of the ECGs in the minimization. This fixed the problem for the non-adiabatic term Q_{00}, but not for the terms coupling the ground state and the first excited state.

Resumé

Dette speciale bygger videre på metoden, som er undersøgt i to tidligere specialer [1, 2]. Denne metode kombinerer brugen af eksplicitte korrelerede Gausser som basisfunktioner i variationsprincippet med Born-Oppenheimer approksimationen. Disse undersøgelser etablerede grundlaget for metoden, men opnåede ikke resultater, der stemmer overens med anden litteratur, og de nåede ikke til de ikke-adiabatiske udregninger. I denne afhandling retter vi udledningerne og implementeringen af de analytiske matrix elementer, hvormed vi opnår resultater, som passer med anden litteratur. Til sidst beregner vi eksplicit de ikke-adiabatiske led og diskuterer deres karakteristikker.

Implementeringen af metoden er testet ved at lave numeriske beregninger med H_2^+ systemet. Her løser vi det generaliserede egenværdiproblem for forskellige afstande mellem hydrogenatomet og protonen (y_0), som giver de potentielle energioverflader (PES). Vi gør dette både for grundtilstanden samt den første exciterede tilstand inden for σ_g symmetrien. Inden for Born-Oppenheimer approksimationen opnår vi meget tilfredsstillende resultater, som er i overensstemmelse med anden litteratur. Den potentielle energioverflade for grundtilstanden konvergerer hurtigt, mens den første exciterede tilstand har brug for en større basis for at konvergere. Der er dog problemer, når vi går ud over Born-Oppenheimer approksimationen, da de ikke-adiabatiske led indeholder mange hop. Vi forsøgte at undgå dette ved at inkludere et strafled på ECG'ernes variationsparametre i minimeringsrutinen. Dette løste problemet for det ikke-adiabatiske led Q_{00}, men ikke for leddene, som kobler grundtilstanden og den første exciterede tilstand.

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Chapter 1

Introduction

The quantum few-body problem is one of the most important problems in quantum mechanics. Variational methods are some of the most widely used methods for describing few-body systems. In this thesis, we will test the method of using explicitly correlated Gaussians (ECGs) as basis functions in the variational principle combined with the Born-Oppenheimer approximation. The advantage of using explicitly correlated Gaussians is that they have analytical matrix elements that do not become more complex as the number of particles increases. The method will be tested using the H_2^+ system, as it is the simplest molecular system.

This thesis continues the work of two earlier master's theses [1, 2], which laid the groundwork for the method but were unable to obtain the correct potential energy surfaces (PES). Here, we will correct the derivations and implementation of the analytical matrix elements, which allows us to obtain the correct potential energy surfaces within the Born-Oppenheimer approximation. These are then used to compute the radial wave function as well as the ground state energy of H_2^+. We will then go one step further by going beyond the Born-Oppenheimer approximation and explicitly calculating the non-adiabatic terms. These are then used in the calculation of the energy in the non-Born-Oppenheimer approach, which will be compared to the energy in the Born-Oppenheimer approximation.

The thesis starts off with a chapter introducing the notation and theory used throughout. The results for the most relevant matrix elements can also be seen here, with the full calculations given in the appendix. We then implement the theory to the H_2^+ system. Next, we go through the numerical methods used in the simulations. We then show the results from the numerical calculations, starting with the results in the Born-Oppenheimer approximation before moving on to the non-adiabatic effects. Lastly, we discuss the results, comparing our results to the previous work on the method and to literature using other methods. We also discuss the future work that needs to be done on the method, focusing on the optimization and non-adiabatic terms.

Chapter 2

Theory

2.1 General notation

This section introduces the notation used in this thesis, which follows that of most other work on ECGs [2, 3, 4]. Throughout this thesis we will be working with different types of vectors. We will denote 3-dimensional vectors by a vector arrow and N-dimensional vectors with 3-dimensional vectors in the entries by bold font. The position vector of a system with N particles can then be written as

$$\mathbf{r} = \begin{pmatrix} \vec{r}_1 \\ \vec{r}_2 \\ \vdots \\ \vec{r}_N \end{pmatrix}, \tag{2.1}$$

where $\vec{r}_i$ is the 3-dimensional position vector for the i'th particle. The N-dimensional vectors with entries consisting of real numbers will be denoted by regular font. In particular, we will be working with vectors of the forms

$$\omega_i = (0, \dots, 1, \dots, 0)^\intercal, \tag{2.2}$$

and

$$\omega_{ij} = (0, \dots, 1, \dots, -1, \dots, 0)^\intercal. \tag{2.3}$$

These vectors then pick out the 3-dimensional vectors from $\mathbf{r}$ in the following ways

$$\omega_i^\intercal \mathbf{r} = \vec{r}_i, \tag{2.4}$$

and

$$\omega_{ij}^{\mathsf{T}}\mathbf{r} = \vec{r}_i - \vec{r}_j. \tag{2.5}$$

The N-dimensional vectors with vector entries have the properties

$$\mathbf{a}^{\mathsf{T}}\mathbf{b} = \sum_{i=1}^{N} \vec{a}_i \cdot \vec{b}_i, \tag{2.6}$$

and

$$\mathbf{a}^{\mathsf{T}}A\mathbf{b} = \sum_{i,j=1}^{N} A_{ij}\vec{a}_i \cdot \vec{b}_j, \tag{2.7}$$

where the central dot denotes the standard dot product between two vectors, and A is an $N \times N$ matrix with entries A_{ij}.

We will also work with gradients of the form

$$\frac{\partial}{\partial \mathbf{r}} = \left(\frac{\partial}{\partial \vec{r}_1}, \ldots, \frac{\partial}{\partial \vec{r}_N} \right), \tag{2.8}$$

where $\frac{\partial}{\partial \vec{r}_i}$ denotes the standard 3-dimensional gradient given by

$$\frac{\partial}{\partial \vec{r}_i} = \left(\frac{\partial}{\partial (\vec{r}_i)_1}, \frac{\partial}{\partial (\vec{r}_i)_2}, \frac{\partial}{\partial (\vec{r}_i)_3} \right), \tag{2.9}$$

and $\frac{\partial}{\partial (\vec{r}_i)_j}$ is the partial derivative with respect to the j'th component of $\vec{r}_i$. Introducing the notation

$$\frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}} \equiv \left(\frac{\partial}{\partial \mathbf{r}} \right)^{\mathsf{T}}, \tag{2.10}$$

the kinetic energy operator can be written as

$$\hat{K} = -\frac{\partial}{\partial \mathbf{r}} \Lambda \frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}} = -\sum_{i,j=1}^{N} \Lambda_{ij} \frac{\partial}{\partial \vec{r}_i} \cdot \frac{\partial}{\partial \vec{r}_j}, \tag{2.11}$$

where Λ is an $N \times N$ matrix. In our case, we will be working with a diagonal Λ matrix, which has entries related to the masses of the particles.

2.2 Variational theory

A very important approach when solving quantum few-body problems is the use of variational methods, which allow one to approximate the energies and wave functions of the system. In this section, we introduce the variational principle and the Rayleigh-Ritz method, where the derivation mainly follows that of [5, 6, 7]. Finally, we will also introduce explicitly correlated Gaussians (ECGs), which are the basis functions that we will be using in the Rayleigh-Ritz method.

2.2.1 The Variational Principle

In the variational principle, we consider a quantum system with a time-independent, Hermitian Hamiltonian $\hat{H}$. Here, we are interested in the discrete eigenvalue spectrum

$$\hat{H}\psi_n = E_n\psi_n, \qquad n = 0, 1, 2\dots \tag{2.12}$$

where the energies E_n are arranged in ascending order such that $E_0 \leq E_1 \leq E_2 \dots$. For any normalizable trial wave function Ψ, the variational principle states that

$$E \equiv \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0, \tag{2.13}$$

where $\Psi(\{\alpha\})$ is parametrized by a finite set of parameters $\{\alpha\}$. In other words, the variational principle provides an upper bound to the true ground state energy of the system, and the energy $E = E_n$ if and only if $\Psi = \psi_n$. If the trial wave function Ψ is chosen so that it is orthogonal to the energy eigenfunctions $\psi_0, \dots, \psi_{i-1}$, then we get an upper bound for the i'th eigenvalue E_i.

2.2.2 The Rayleigh-Ritz Method

The variational principle is the basis for the Rayleigh-Ritz method, where the trial function is constructed as a linear combination of N linearly independent functions

$$\Psi = \sum_{i=0}^{N-1} c_i\varphi_i(\{\alpha_i\}). \tag{2.14}$$

Here, the coefficients c_i are linear variational parameters, and the φ_i's are parametrized by the variable parameters $\{\alpha_i\}$. We can then substitute the above trial function into equation 2.13 to obtain

$$E = \frac{\sum_{i,j=0}^{N-1} c_i^* c_j \langle\varphi_i|\hat{H}|\varphi_j\rangle}{\sum_{i,j=0}^{N-1} c_i^* c_j \langle\varphi_i|\varphi_j\rangle} = \frac{\sum_{i,j=0}^{N-1} c_i^* c_j \mathcal{H}_{ij}}{\sum_{i,j=0}^{N-1} c_i^* c_j \mathcal{N}_{ij}} = \frac{c^\dagger\mathcal{H}c}{c^\dagger\mathcal{N}c}, \tag{2.15}$$

where c denotes the vector $(c_0, \dots, c_{N-1})^\mathsf{T}$, and the $N \times N$ overlap and Hamiltonian matrices $\mathcal{N}$ and $\mathcal{H}$ have entries

$$\mathcal{N}_{ij} = \langle\varphi_i|\varphi_j\rangle, \tag{2.16}$$

$$\mathcal{H}_{ij} = \langle\varphi_i|\hat{H}|\varphi_j\rangle, \tag{2.17}$$

respectively.

The idea now is to differentiate equation 2.15 with respect to the c_i's and then find the vector c that minimizes the energy E. In other words, we require that

$$\frac{\partial E}{\partial c_i^*} = 0, \qquad i = 0, 1, \dots, N-1 \tag{2.18}$$

or equivalently

$$\frac{\partial E}{\partial c^*} = 0. \tag{2.19}$$

Inserting the expression in equation 2.15 into the above equation, we get

$$\begin{aligned} \frac{\partial E}{\partial c^*} &= \frac{\partial}{\partial c^*}\left(\frac{c^\dagger \mathcal{H} c}{c^\dagger \mathcal{N} c}\right) && (2.20) \\ &= \frac{(\mathcal{H} c)\, c^\dagger \mathcal{N} c - c^\dagger \mathcal{H} c \left(\mathcal{N} c\right)}{\left(c^\dagger \mathcal{N} c\right)^2} && (2.21) \\ &= \frac{\mathcal{H} c - E \mathcal{N} c}{c^\dagger \mathcal{N} c} && (2.22) \\ &= 0, && (2.23) \end{aligned}$$

where we have used that $\frac{\partial}{\partial c^*}\left(c^\dagger \mathcal{H} c\right) = \mathcal{H} c$ and $\frac{\partial}{\partial c^*}\left(c^\dagger \mathcal{N} c\right) = \mathcal{N} c$. These gradients can be easily shown by looking at the k'th entry

$$\begin{aligned} \left(\frac{\partial}{\partial c^*} c^\dagger \mathcal{H} c\right)_k &= \frac{\partial}{\partial c_k^*} \sum_{i,j=0}^{N-1} c_i^* \mathcal{H}_{ij} c_j && (2.24) \\ &= \sum_{i,j=0}^{N-1} \delta_{ik} \mathcal{H}_{ij} c_j && (2.25) \\ &= \sum_{i,j=0}^{N-1} \mathcal{H}_{kj} c_j && (2.26) \\ &= (\mathcal{H} c)_k\,. && (2.27) \end{aligned}$$

From equation 2.22 above, we obtain the generalized eigenvalue problem

$$\mathcal{H} c = E \mathcal{N} c, \tag{2.28}$$

which can also be written in component form as

$$\sum_{j=0}^{N-1} \left(\mathcal{H}_{ij} - E \mathcal{N}_{ij}\right) c_j = 0. \qquad i = 0, 1, \dots, N-1 \tag{2.29}$$

This is a set of N linear and homogeneous equations in the coefficients c_j. Non-trivial solutions to this equation exist only when the secular determinant vanishes

$$\det\left(\mathcal{H} - E\mathcal{N}\right) = 0. \tag{2.30}$$

If we let $\varepsilon_0^{(N)}, \varepsilon_1^{(N)}, \dots, \varepsilon_{N-1}^{(N)}$ be the roots of the determinant above and assume that they are arranged in ascending order, we have the following inequalities

$$E_0 \leq \varepsilon_0^{(N)}, E_1 \leq \varepsilon_1^{(N)}, \dots, E_{N-1} \leq \varepsilon_{N-1}^{(N)}, \tag{2.31}$$

where the superscript (N) indicates the size of the basis. Hence, the lowest root $\varepsilon_0^{(N)}$ provides an upper bound to the ground state energy. Similarly, the next root $\varepsilon_1^{(N)}$ serves as an upper bound to the first excited state energy and so on. We can also look at what happens if we add an additional basis function to the existing trial function. The new trial function then becomes

$$\Psi = \sum_{i=0}^{N} c_i \varphi_i\left(\{\alpha_i\}\right), \tag{2.32}$$

which will have $N+1$ roots $\varepsilon_0^{(N+1)}, \varepsilon_1^{(N+1)}, \dots, \varepsilon_N^{(N+1)}$ in equation 2.30. It can be shown that these roots obey

$$\varepsilon_0^{(N+1)} \leq \varepsilon_0^{(N)} \leq \varepsilon_1^{(N+1)} \leq \varepsilon_1^{(N)} \leq \dots \leq \varepsilon_{N-1}^{(N+1)} \leq \varepsilon_{N-1}^{(N)} \leq \varepsilon_N^{(N+1)}. \tag{2.33}$$

That is, adding an additional element to the basis will never result in worse upper bounds for the energies of the system.

2.2.3 Explicitly Correlated Gaussians

The basis functions we want to use in the variational principle are explicitly correlated Gaussians (ECGs). We will use $|A\rangle$ as the notation for a general ECG, which in position space takes the form [8]

$$\langle \mathbf{r}|A\rangle = \exp\left(-\sum_{j>i=1}^{N}\left(\frac{\vec{r}_i - \vec{r}_j}{b_{ij}}\right)^2\right), \tag{2.34}$$

where b_{ij} are variational parameters. In this form, the particle correlation is clear, as the function depends directly on the relative coordinates $\vec{r}_i - \vec{r}_j$. An equivalent way of writing an ECG is

$$\langle \mathbf{r}|A\rangle = \exp\left(-\mathbf{r}^{\mathsf{T}} A \mathbf{r}\right), \tag{2.35}$$

where A is the correlation matrix. If we let the correlation matrix A be given as [8]

$$A = \sum_{j>i=1}^{N} \frac{\omega_{ij}\omega_{ij}^{\mathsf{T}}}{b_{ij}^2}, \tag{2.36}$$

it becomes clear that the two forms are equivalent since

$$\mathbf{r}^{\mathsf{T}} \left(\omega_{ij}\omega_{ij}^{\mathsf{T}}\right) \mathbf{r} = \left(\mathbf{r}^{\mathsf{T}}\omega_{ij}\right) \cdot \left(\omega_{ij}^{\mathsf{T}}\mathbf{r}\right) = \left(\vec{r}_i - \vec{r}_j\right) \cdot \left(\vec{r}_i - \vec{r}_j\right) = \left(\vec{r}_i - \vec{r}_j\right)^2. \tag{2.37}$$

The ECGs can be generalized by introducing a shift vector of the form $\mathbf{s}_a = \left((\vec{s}_a)_1, (\vec{s}_a)_2, \dots, (\vec{s}_a)_N\right)^{\mathsf{T}}$. In position space, the shifted ECGs are given by [9]

$$\langle \mathbf{r}|A, \mathbf{s}_a\rangle = \exp\left(-\mathbf{r}^{\mathsf{T}}A\mathbf{r} + \mathbf{s}_a^{\mathsf{T}}\mathbf{r}\right), \tag{2.38}$$

which is the form we will use in the matrix element calculations. Using shifted ECGs allows for a more general treatment of the matrix element, while the quadratic form representation simplifies the calculations compared to using the form in equation 2.34. From now on, we will drop the term "shifted" and just call these functions ECGs.

As we want to use ECGs as basis functions in the Rayleigh-Ritz method, they must be normalizable. In other words, they must satisfy

$$\langle A, \mathbf{s}_a|A, \mathbf{s}_a\rangle = \int d\mathbf{r}\langle A, \mathbf{s}_a|\mathbf{r}\rangle\langle \mathbf{r}|A, \mathbf{s}_a\rangle < \infty, \tag{2.39}$$

which is true if and only if the correlation matrix A is positive-definite [5]. Using the equivalence of equations 2.34 and 2.35, we see that $\mathbf{r}^{\mathsf{T}}A\mathbf{r} \geq 0$ since all terms in the sum in equation 2.34 are non-negative. The correlation matrix in equation 2.36 is therefore only positive semi-definite. It can also be noted that $\mathbf{r}^{\mathsf{T}}A\mathbf{r} = 0$ if and only if we have the coordinate configuration where

$$\vec{r}_1 = \vec{r}_2 = \dots = \vec{r}_N, \tag{2.40}$$

which can also be written as

$$\mathbf{r} = \left(\vec{r}_1, \vec{r}_1, \dots, \vec{r}_1\right)^{\mathsf{T}} = \vec{r}_1 \left(1, 1, \dots, 1\right)^{\mathsf{T}}. \tag{2.41}$$

This particular configuration will be discussed further in section 2.3.

There are several advantages to using ECGs as basis functions. The main advantage is that the matrix elements of $\mathcal{N}$ and $\mathcal{H}$ are analytical, which makes the numerical computations much simpler. Furthermore, the complexity of the analytical expressions does not increase for systems with more than 3 particles, meaning we can easily generalize to N-body systems. Since the ECGs also form a complete basis in the limit of a large basis size, the energy will converge to the exact eigenvalue as the number of basis functions increases. The biggest issue with ECGs is that they do not describe the asymptotic form of the wave function at large distances particularly well [4, 5].

2.3 Jacobi coordinate transformation

When working with a system that is not acted upon by any external forces, we are only interested in the intrinsic interactions. We can then ignore the center-of-mass (COM) motion, which is done by making a coordinate transformation from the single particle coordinates $\mathbf{r} = \left(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N\right)^\mathsf{T}$ to the coordinates $\mathbf{x} = \left(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N\right)^\mathsf{T}$. Here, $\{\vec{x}_1, \dots, \vec{x}_{N-1}\}$ is a set of relative coordinates and $\vec{x}_N$ is the COM coordinate. A common choice of relative coordinates is the Jacobi coordinates, which we will use in this thesis. For a system of N particles, the i'th Jacobi coordinate is defined as [8]

$$\vec{x}_i = \frac{1}{M_i}\sum_{j=1}^{i} m_j\vec{r}_j - \vec{r}_{i+1}, \qquad i = 1, 2, \dots N-1, \tag{2.42}$$

with the last coordinate being the COM coordinate defined by

$$\vec{x}_N = \frac{1}{M_N}\sum_{j=1}^{N} m_j\vec{r}_j. \tag{2.43}$$

Here, M_i is defined as the sum of the masses of the first i particles

$$M_i = \sum_{j=1}^{i} m_j. \tag{2.44}$$

Figure 2.1 shows an example of the Jacobi coordinates for the case of three particles. The Jacobi coordinate transformation is a linear transformation which can be written in matrix form as [5]

$$\mathbf{r} \to \mathbf{x} = J\mathbf{r}, \tag{2.45}$$

with the matrix J given as

$$J = \begin{pmatrix} 1 & -1 & 0 & \dots & 0 \\ \frac{m_1}{M_2} & \frac{m_2}{M_2} & -1 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{m_1}{M_{N-1}} & \frac{m_2}{M_{N-1}} & \frac{m_3}{M_{N-1}} & \dots & -1 \\ \frac{m_1}{M_N} & \frac{m_2}{M_N} & \frac{m_3}{M_N} & \dots & \frac{m_N}{M_N} \end{pmatrix}, \tag{2.46}$$

and with inverse

$$U = \begin{pmatrix} \frac{m_2}{M_2} & \frac{m_3}{M_3} & \dots & \frac{m_N}{M_N} & 1 \\ -\frac{m_1}{M_2} & \frac{m_3}{M_3} & \dots & \frac{m_N}{M_N} & 1 \\ 0 & -\frac{M_2}{M_3} & \ddots & \vdots & \vdots \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \dots & -\frac{M_{N-1}}{M_N} & 1 \end{pmatrix}. \tag{2.47}$$

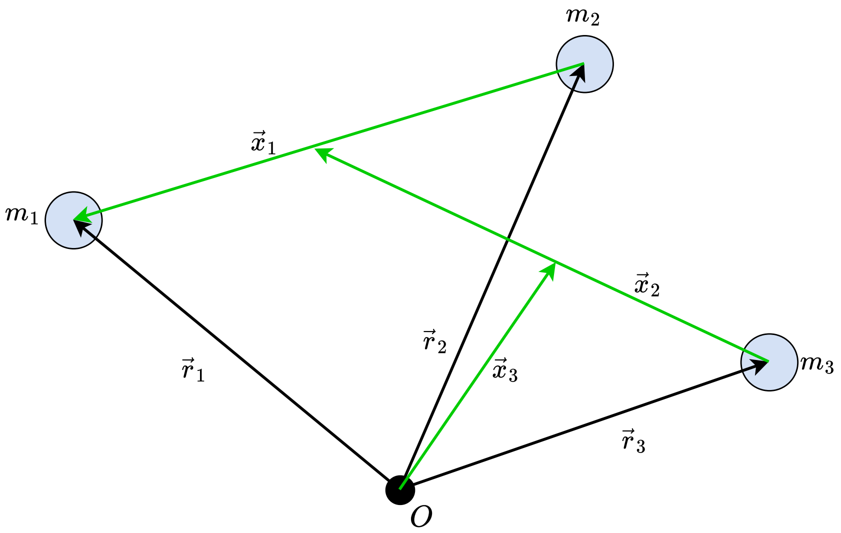

Figure 2.1: Example of the Jacobi coordinates and single particle coordinates for a system of 3 particles. The r_i coordinates show the single particle coordinates, while x_i show the Jacobi coordinates.

From equation 2.45 it is clear that we can ignore the COM coordinate simply by removing the last row of J and the last column of U [8]. This reduces the dimensionality of the computational problem by 1, thereby reducing the computational cost. The matrices obtained by removing the last row of J and the last column of U will be denoted by J' and U', respectively.

We are also interested in how the kinetic energy and the vectors ω_i and ω_{ij} transform under the Jacobi coordinate transformation. These transformation laws have the form

$$\omega_i \to U^\intercal \omega_i, \tag{2.48}$$

$$\Lambda \to J \Lambda J^\intercal, \tag{2.49}$$

and are shown in Appendix A.

In section 2.2.3 we found that the quadratic form $r^\intercal A r$ satisfies the relation $r^\intercal A r \geq 0$, so that the correlation matrix A in equation 2.36 is only positive semi-definite. Here we looked at the configuration given by the vector $\mathbf{r} = \vec{r}_1 (1, 1, \dots, 1)^\intercal$, which is the only configuration for which the quadratic form is not strictly positive. It then follows from the Jacobi matrix in equation 2.46 that this configuration in Jacobi coordinates is given by

$$\mathbf{x} = J\mathbf{r} = J\vec{r}_1 (1, 1, \dots, 1)^\intercal = \vec{r}_1 J (1, 1, \dots, 1)^\intercal = \vec{r}_1 (0, 0, \dots, 0, 1)^\intercal . \tag{2.50}$$

However, the last entry in the Jacobi coordinates is just the COM coordinate, meaning the quadratic form becomes strictly positive by removing the COM coordinate. Since the quadratic form can be written as

$$\mathbf{r}^\intercal A\mathbf{r} = (U\mathbf{x})^\intercal A(U\mathbf{x}) = \mathbf{x}^\intercal U^\intercal AU\mathbf{x}, \tag{2.51}$$

it follows from the discussion above that the matrix $U'^\intercal AU'$ is a positive-definite matrix. Using the correlation matrix in equation 2.36, this matrix can be written as

$$U'^\intercal AU' = \sum_{j>i=1}^{N} \frac{\left(U'^\intercal \omega_{ij}\right)\left(\omega_{ij}^\intercal U'\right)}{b_{ij}^2}, \tag{2.52}$$

which is the form we will use in the numerical calculations.

2.4 Born-Oppenheimer approximation

In this section, we will go through the theory behind the Born-Oppenheimer approximation [6, 7] and how to go beyond it by including non-adiabatic effects [10]. The Born-Oppenheimer approximation, also called the adiabatic approximation, is based on the great mass difference between electrons and nuclei. The electrons can therefore adjust almost immediately to any displacements of the nuclei. We can then separate the electronic and nuclear motions, and instead of solving the Schrödinger equation for all particles, we solve the Schrödinger equation for the electrons with the nuclei being fixed. In the following, we will use $\mathbf{R} = (\vec{R}_1, \ldots)^\intercal$ and $\mathbf{r} = (\vec{r}_1, \ldots)^\intercal$ to denote nuclear and electronic coordinates, respectively, and we will not consider any spin interactions. We now consider the time-independent Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}), \tag{2.53}$$

where

$$\hat{H} = \hat{K}_N + \hat{K}_e + V(\mathbf{r}, \mathbf{R}). \tag{2.54}$$

Here, $\hat{K}_N$ is the kinetic energy operator of the nuclei, $\hat{K}_e$ is the kinetic energy operator of the electrons and $V(\mathbf{r}, \mathbf{R})$ is the potential energy of the whole system. We now want to separate the electronic and nuclear motion, which is done by expanding the total wave function as

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_n f_n(\mathbf{R})\phi_n(\mathbf{r}; \mathbf{R}), \tag{2.55}$$

where $f_n(\mathbf{R})$ are the nuclear wave functions and $\phi_n(\mathbf{r};\mathbf{R})$ are the electronic wave functions. The semicolon notation signifies that the electronic wave function depends parametrically on $\mathbf{R}$. We now consider the electronic Schrödinger equation, which for a fixed $\mathbf{R}$ is given by

$$\left(\hat{K}_e + V(\mathbf{r},\mathbf{R})\right) \phi_n(\mathbf{r};\mathbf{R}) = \varepsilon_n(;\mathbf{R})\phi_n(\mathbf{r};\mathbf{R}), \tag{2.56}$$

where $\varepsilon_n(;\mathbf{R})$ is the potential energy surface (PES). Using these two relations and noting that $\hat{K}_N$ acts on both the electronic and nuclear wave functions, while $\hat{K}_e$ and $V(\mathbf{r},\mathbf{R})$ act only on the electronic part, we obtain

$$\left(\hat{K}_e + \hat{K}_N + V(\mathbf{r},\mathbf{R})\right) \sum_n f_n(\mathbf{R})\phi_n(\mathbf{r};\mathbf{R}) = E \sum_n f_n(\mathbf{R})\phi_n(\mathbf{r};\mathbf{R}) \tag{2.57}$$

$$\Downarrow$$

$$\sum_n \hat{K}_N f_n(\mathbf{R})\phi_n(\mathbf{r};\mathbf{R}) + \sum_n f_n(\mathbf{R}) \left[\hat{K}_e + V(\mathbf{r},\mathbf{R})\right] \phi_n(\mathbf{r};\mathbf{R}) = E \sum_n f_n(\mathbf{R})\phi_n(\mathbf{r};\mathbf{R}) \tag{2.58}$$

$$\Downarrow$$

$$\sum_n \left[\hat{K}_N + \varepsilon_n(;\mathbf{R})\right] f_n(\mathbf{R})\phi_n(\mathbf{r};\mathbf{R}) = E \sum_n f_n(\mathbf{R})\phi_n(\mathbf{r};\mathbf{R}). \tag{2.59}$$

We now multiply the above equation by $\langle\phi_{n'}(\mathbf{r};\mathbf{R})|$ from the left, giving us

$$\begin{aligned}&\sum_n \langle\phi_{n'}(\mathbf{r};\mathbf{R})|\hat{K}_N f_n(\mathbf{R})|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}} + \sum_n \varepsilon_n(;\mathbf{R}) f_n(\mathbf{R})\langle\phi_{n'}(\mathbf{r};\mathbf{R})|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}} \\ &= E \sum_n f_n(\mathbf{R})\langle\phi_{n'}(\mathbf{r};\mathbf{R})|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}}.\end{aligned} \tag{2.60}$$

The subscript $-\mathbf{R}$ on the inner product indicates that we do not integrate over $\mathbf{R}$, as it is kept fixed. The electronic wave functions form a complete orthonormal basis set

$$\langle\phi_{n'}(\mathbf{r};\mathbf{R})|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}} = \delta_{n'n}. \tag{2.61}$$

Using this, we can write equation 2.60 as

$$\sum_n \langle\phi_{n'}(\mathbf{r};\mathbf{R})|\hat{K}_N f_n(\mathbf{R})|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}} + \varepsilon_{n'}(;\mathbf{R}) f_{n'}(\mathbf{R}) = E f_{n'}(\mathbf{R}). \tag{2.62}$$

The next step is to do the Born-Oppenheimer approximation, which is based on the very slow nuclear motion compared to the electronic motion. The electronic wave function will then vary slowly as we vary $\mathbf{R}$. Therefore, we can let $\hat{K}_N$ act only on $f_n(\mathbf{R})$, meaning the final equation then becomes

$$\left[\hat{K}_N + \varepsilon_{n'}(;\mathbf{R})\right] f_{n'}(\mathbf{R}) = E f_{n'}(\mathbf{R}). \tag{2.63}$$

The idea now is to first solve equation 2.56 using the Rayleigh-Ritz method with ECGs as basis functions to obtain $\varepsilon_n(;\mathbf{R})$. We can then solve equation 2.63 for each of these potential energy surfaces, which we will go through in section 4.3. From this we obtain the real energies of the system as well as the corresponding nuclear wave functions $f_{n'}$.

There are multiple cases where the Born-Oppenheimer approximation can break down. It breaks down near avoided crossings between potential energy surfaces or if the nuclei move fast [11]. It can also break down in the case of higher excited states [7].

2.4.1 Beyond the Born-Oppenheimer approximation

If we do not make the Born-Oppenheimer approximation in equation 2.62, we cannot simply pull $\hat{K}_N$ out of the inner product. Instead, we use the fact that $\hat{K}_N$ can be written as

$$\hat{K}_N = -\frac{1}{2\mu}\nabla_{\mathbf{R}}^2, \tag{2.64}$$

where μ is the reduced mass of the proton-hydrogen system. Using this, we can write

$$\begin{aligned}\nabla_{\mathbf{R}}^2\left(f_n(\mathbf{R})\phi_n(\mathbf{r};\mathbf{R})\right) &= \left(\nabla_{\mathbf{R}}^2 f_n(\mathbf{R})\right)\phi_n(\mathbf{r};\mathbf{R}) + f_n(\mathbf{R})\left(\nabla_{\mathbf{R}}^2\phi_n(\mathbf{r};\mathbf{R})\right)\\ &+ 2\left(\nabla_{\mathbf{R}} f_n(\mathbf{R})\right)\left(\nabla_{\mathbf{R}}\phi_n(\mathbf{r};\mathbf{R})\right).\end{aligned} \tag{2.65}$$

Inserting this back into equation 2.62 gives

$$\begin{aligned}&-\frac{1}{2\mu}\sum_n\Big(\langle\phi_{n'}(\mathbf{r};\mathbf{R})|\left(\nabla_{\mathbf{R}}^2 f_n(\mathbf{R})\right)|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}} + \langle\phi_{n'}(\mathbf{r};\mathbf{R})|f_n(\mathbf{R})\nabla_{\mathbf{R}}^2|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}}\\ &+2\langle\phi_{n'}(\mathbf{r};\mathbf{R})|\left(\nabla_{\mathbf{R}} f_n(\mathbf{R})\right)\nabla_{\mathbf{R}}|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}}\Big) + \varepsilon_{n'}(;\mathbf{R})f_{n'}(\mathbf{R}) = Ef_{n'}(\mathbf{R})\end{aligned} \tag{2.66}$$

$$\Downarrow$$

$$\begin{aligned}&\left[\hat{K}_N + \varepsilon_{n'}(;\mathbf{R})\right]f_{n'}(\mathbf{R}) - \frac{1}{2\mu}\sum_n\Big(f_n(\mathbf{R})\langle\phi_{n'}(\mathbf{r};\mathbf{R})|\nabla_{\mathbf{R}}^2|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}}\\ &+2\left(\nabla_{\mathbf{R}} f_n(\mathbf{R})\right)\langle\phi_{n'}(\mathbf{r};\mathbf{R})|\nabla_{\mathbf{R}}|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}}\Big) = Ef_{n'}(\mathbf{R})\end{aligned} \tag{2.67}$$

$$\Downarrow$$

$$\left[\hat{K}_N + \varepsilon_{n'}(;\mathbf{R})\right]f_{n'}(\mathbf{R}) - \frac{1}{2\mu}\sum_n\left(f_n(\mathbf{R})Q_{n'n}(\mathbf{R}) + 2\left(\nabla_{\mathbf{R}} f_n(\mathbf{R})\right)P_{n'n}(\mathbf{R})\right) = Ef_{n'}(\mathbf{R}), \tag{2.68}$$

where we have introduced the non-adiabatic terms

$$P_{n'n}(\mathbf{R}) = \langle\phi_{n'}(\mathbf{r};\mathbf{R})|\nabla_{\mathbf{R}}|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}}, \tag{2.69}$$

$$Q_{n'n}(\mathbf{R}) = \langle\phi_{n'}(\mathbf{r};\mathbf{R})|\nabla_{\mathbf{R}}^2|\phi_n(\mathbf{r};\mathbf{R})\rangle_{-\mathbf{R}}. \tag{2.70}$$

Equation 2.68 is a more complicated differential equation for the energy and nuclear wave functions, as it is a system of coupled differential equations. Here, we can have transitions between different states, unlike in the Born-Oppenheimer approximation, where there are no transitions between states.

2.4.2 Born-Huang approximation

Instead of doing the full non-adiabatic correction to the Born-Oppenheimer approximation, one can do the Born-Huang approximation [12]. The Born-Huang approximation only considers diagonal non-adiabatic effects, meaning the electronic states are still uncoupled. In the Born-Huang approximation, the equation for the f_n's then becomes

$$\left[\hat{K}_N + \varepsilon_n(;\mathbf{R}) - \frac{1}{2\mu}Q_{nn}(\mathbf{R})\right] f_n(\mathbf{R}) = E f_n(\mathbf{R}), \tag{2.71}$$

where the quantity $(\varepsilon_n(;\mathbf{R}) - \frac{1}{2\mu}Q_{nn}(\mathbf{R}))$ can be seen as a new effective PES.

2.5 Matrix elements

One of the main advantages of ECGs is that the matrix elements are analytical. In the following, we present the results of all the matrix elements needed for the numerical computations. The full derivations can be seen in Appendix C along with other matrix elements that are introduced to ease the calculations.

Although we only consider s-waves in the numerical computations, the matrix elements are derived with general shift vectors $\mathbf{s}_a$ and $\mathbf{s}_b$. One can then obtain the s-wave matrix elements by simply setting the shift vectors equal to zero. The matrix elements can also be extended to p-waves, d-waves and so on by performing a Taylor expansion with respect to the shift vectors [3, 13].

The Born-Oppenheimer approximation, or adiabatic approximation, is implemented by including a delta function $\delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right)$ in the matrix elements. Here, ω_0 picks out the slow coordinate, which we will indicate with the subscript 0. By fixing the slow coordinate to $\vec{y}_0$, the integration can be extended to go over all variables.

Overlap

The most essential matrix element is the standard overlap between two ECGs, as it forms the overlap matrix $\mathcal{N}$ and appears in all other matrix elements. If we let $|A, \mathbf{s}_a\rangle$ and $|B, \mathbf{s}_b\rangle$ denote two shifted ECGs, the overlap between them is given by

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle = \exp\left(\frac{1}{4}\mathbf{v}^\intercal C^{-1}\mathbf{v}\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2} \equiv M\left(C, \mathbf{v}\right), \tag{2.72}$$

where $C = A + B$ and $\mathbf{v} = \mathbf{s}_a + \mathbf{s}_b$. For s-waves, the matrix element can be obtained simply by letting $\mathbf{s}_a = \mathbf{s}_b = 0$ or equivalently $\mathbf{v} = 0$. In this case, the overlap becomes

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle \overset{\mathbf{v}=0}{=} \left(\frac{\pi^N}{\det(C)}\right)^{3/2} \equiv M_0. \tag{2.73}$$

Delta function matrix element

In order to include the adiabatic approximation, we will need the overlap between two ECGs with a delta function $\delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right)$. For this calculation, we will express the delta function using its Fourier transform

$$\delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) = \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(i\vec{k}\cdot\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right)\right). \tag{2.74}$$

The resulting matrix element is then

$$\langle B, \mathbf{s}_b | \delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) | A, \mathbf{s}_a \rangle = \frac{M\left(C, \mathbf{v}\right)}{(2\pi)^3} \exp\left(-\frac{1}{4\alpha}\left(\vec{q} - \vec{y}_0\right)^2\right)\left(\frac{\pi}{\alpha}\right)^{3/2}, \tag{2.75}$$

where we have introduced

$$\alpha = \frac{1}{4}\omega_0^\intercal C^{-1}\omega_0, \qquad \vec{q} = \frac{1}{2}\omega_0^\intercal C^{-1}\mathbf{v}. \tag{2.76}$$

For s-waves this reduces to

$$\langle B, \mathbf{s}_b | \delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) | A, \mathbf{s}_a \rangle \overset{\mathbf{v}=0}{=} \frac{M_0}{(2\pi)^3} \exp\left(-\frac{y_0^2}{4\alpha}\right)\left(\frac{\pi}{\alpha}\right)^{3/2}, \tag{2.77}$$

such that the matrix element only depends on the magnitude of $\vec{y}_0$.

Kinetic energy matrix element

Here we are interested in the matrix element of the kinetic energy operator, which can be written in the general form

$$\hat{K} = -\frac{\partial}{\partial \mathbf{r}}\Lambda\frac{\partial}{\partial \mathbf{r}^\intercal} = -\sum_{i,j=1}^{N} \Lambda_{ij}\frac{\partial}{\partial \vec{r}_i}\cdot\frac{\partial}{\partial \vec{r}_j}, \tag{2.78}$$

with Λ being an $N \times N$ matrix independent of $\mathbf{r}$. The final result for this matrix element has the form

$$\langle B, \mathbf{s}_b | \hat{K} | A, \mathbf{s}_a \rangle = M\left(C, \mathbf{v}\right) \left[6 \operatorname{Tr}\left(B \Lambda A C^{-1} \right) + \left(\mathbf{s}_b - B C^{-1} \mathbf{v} \right)^{\mathsf{T}} \Lambda \left(\mathbf{s}_a - A C^{-1} \mathbf{v} \right) \right], \tag{2.79}$$

which for s-waves is given by

$$\langle B, \mathbf{s}_b | \hat{K} | A, \mathbf{s}_a \rangle \overset{\mathbf{v}=0}{=} 6 M_0 \operatorname{Tr}\left(B \Lambda A C^{-1} \right). \tag{2.80}$$

Kinetic energy with delta function matrix element

The matrix element of interest is

$$\langle B, \mathbf{s}_b | \hat{K} \delta^3 \left(\omega_0^{\mathsf{T}} \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle. \tag{2.81}$$

As the slow coordinate should not contribute any kinetic energy, we require that Λ is diagonal and that $\Lambda \omega_0 = 0$ (and equivalently $\omega_0^{\mathsf{T}} \Lambda = 0$). There are now two cases. If A and B are diagonal, the matrix element is given by

$$\langle B, \mathbf{s}_b | \hat{K} \delta^3 \left(\omega_0^{\mathsf{T}} \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle \tag{2.82}$$

$$= \frac{1}{M\left(C, \mathbf{v}\right)} \langle B, \mathbf{s}_b | \hat{K} | A, \mathbf{s}_a \rangle \langle B, \mathbf{s}_b | \delta^3 \left(\omega_0^{\mathsf{T}} \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle, \tag{2.83}$$

which for s-waves becomes

$$\langle B, \mathbf{s}_b | \hat{K} \delta^3 \left(\omega_0^{\mathsf{T}} \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle \overset{\mathbf{v}=0}{=} 6 \operatorname{Tr}\left(B \Lambda A C^{-1} \right) \frac{M_0}{(2\pi)^3} \exp\left(-\frac{y_0^2}{4\alpha} \right) \left(\frac{\pi}{\alpha} \right)^{3/2}. \tag{2.84}$$

In the other case where A and B are not diagonal, the resulting matrix element can be written as

$$\langle B, \mathbf{s}_b | \hat{K} \delta^3 \left(\omega_0^{\mathsf{T}} \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle \tag{2.85}$$

$$= \langle B, \mathbf{s}_b | \delta^3 \left(\omega_0^{\mathsf{T}} \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle \left[\frac{\langle B, \mathbf{s}_b | \hat{K} | A, \mathbf{s}_a \rangle}{M\left(C, \mathbf{v}\right)} - \frac{\vec{c}_1 \cdot \left(\vec{q} - \vec{y}_0 \right)}{2\alpha} + c_2 \left(\frac{3}{2\alpha} - \frac{\left(\vec{q} - \vec{y}_0 \right)^2}{4\alpha^2} \right) \right], \tag{2.86}$$

where

$$\vec{c}_1 = -\mathbf{s}_b^{\mathsf{T}} \Lambda A C^{-1} \omega_0 + \mathbf{v}^{\mathsf{T}} C^{-1} B \Lambda A C^{-1} \omega_0 - \omega_0^{\mathsf{T}} C^{-1} B \Lambda \mathbf{s}_a + \omega_0^{\mathsf{T}} C^{-1} B \Lambda A C^{-1} \mathbf{v}, \tag{2.87}$$

and

$$c_2 = -\omega_0^{\mathsf{T}} C^{-1} B \Lambda A C^{-1} \omega_0. \tag{2.88}$$

For s-waves the matrix element reduces to

$$\langle B, \mathbf{s}_b | \hat{K} \delta^3 \left(\omega_0^{\mathsf{T}} \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle \tag{2.89}$$

$$\overset{\mathbf{v}=0}{=} \frac{M_0}{(2\pi)^3} \exp\left(-\frac{y_0^2}{4\alpha} \right) \left(\frac{\pi}{\alpha} \right)^{3/2} \left[6 \operatorname{Tr}\left(B \Lambda A C^{-1} \right) + c_2 \left(\frac{3}{2\alpha} - \frac{y_0^2}{4\alpha^2} \right) \right]. \tag{2.90}$$

Coulomb potential matrix element

The idea in this matrix element is to use the Fourier transform of the Coulomb potential, which has the following form

$$\frac{1}{|\omega_{ij}^{\mathsf{T}}\mathbf{r}|} = \int \frac{d^3\vec{k}}{(2\pi)^3}\frac{4\pi}{k^2}\exp\left(i\vec{k}\cdot\omega_{ij}^{\mathsf{T}}\mathbf{r}\right). \tag{2.91}$$

Inserting this into the matrix element and switching to spherical coordinates then leads to the following result

$$\left\langle B,\mathbf{s}_b\middle|\frac{1}{|\omega_{ij}^{\mathsf{T}}\mathbf{r}|}\middle|A,\mathbf{s}_a\right\rangle = \frac{M(C,\mathbf{v})}{p}\operatorname{erf}\left(\frac{p}{2\sqrt{\beta}}\right), \tag{2.92}$$

where

$$\beta = \frac{1}{4}\omega_{ij}^{\mathsf{T}}C^{-1}\omega_{ij}, \qquad \vec{p} = \frac{1}{2}\omega_{ij}^{\mathsf{T}}C^{-1}\mathbf{v}. \tag{2.93}$$

The matrix element for s-waves is given by

$$\left\langle B,\mathbf{s}_b\middle|\frac{1}{|\omega_{ij}^{\mathsf{T}}\mathbf{r}|}\middle|A,\mathbf{s}_a\right\rangle \overset{\mathrm{v}=0}{=} \frac{M_0}{\sqrt{\beta\pi}}. \tag{2.94}$$

Coulomb potential with delta function matrix element

The matrix element we want to calculate here is

$$\left\langle B,\mathbf{s}_b\middle|\frac{\delta^3\left(\omega_0^{\mathsf{T}}\mathbf{r}-\vec{y}_0\right)}{|\omega_{ij}^{\mathsf{T}}\mathbf{r}|}\middle|A,\mathbf{s}_a\right\rangle, \tag{2.95}$$

where we note that i and j cannot be equal to each other. We again use the Fourier transform of the Coulomb potential, which yields the result

$$\left\langle B,\mathbf{s}_b\middle|\frac{\delta^3\left(\omega_0^{\mathsf{T}}\mathbf{r}-\vec{y}_0\right)}{|\omega_{ij}^{\mathsf{T}}\mathbf{r}|}\middle|A,\mathbf{s}_a\right\rangle \tag{2.96}$$

$$= \langle B,\mathbf{s}_b|\delta^3\left(\omega_0^{\mathsf{T}}\mathbf{r}-\vec{y}_0\right)|A,\mathbf{s}_a\rangle\frac{1}{q_3}\operatorname{erf}\left(\frac{q_3}{2\sqrt{\alpha_3}}\right). \tag{2.97}$$

In the case of s-waves the matrix element reduces to

$$\left\langle B,\mathbf{s}_b\middle|\frac{\delta^3\left(\omega_0^{\mathsf{T}}\mathbf{r}-\vec{y}_0\right)}{|\omega_{ij}^{\mathsf{T}}\mathbf{r}|}\middle|A,\mathbf{s}_a\right\rangle \tag{2.98}$$

$$\overset{\mathrm{v}=0}{=} \frac{M_0}{(2\pi)^3}\exp\left(-\frac{y_0^2}{4\alpha_1}\right)\left(\frac{\pi}{\alpha_1}\right)^{3/2}\frac{2\alpha_1}{\gamma y_0}\operatorname{erf}\left(\frac{\gamma y_0}{4\alpha_1\sqrt{\alpha_3}}\right). \tag{2.99}$$

Modified overlap

In the numerical calculations of the non-adiabatic terms, we need the overlap between two ECGs, where the slow variable is not integrated over. The full derivations are given in Appendix D. The matrix element of interest is then given by

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle_{-k} = \int d^3\vec{r}_1 \dots d^3\vec{r}_{k-1} d^3\vec{r}_{k+1} \dots d^3\vec{r}_N \exp\left(-\mathbf{r}^\mathsf{T} C \mathbf{r} + \mathbf{v}^\mathsf{T} \mathbf{r}\right), \tag{2.100}$$

where k denotes the slow variable. The idea is then to separate out all terms in the exponent that depend on the slow variable, which gives

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle_{-k} = \exp\left(-C_{kk} r_k^2 + \vec{v}_k \cdot \vec{r}_k\right) M\left(C_{-k}, \boldsymbol{\eta}_{-k}\right), \tag{2.101}$$

where

$$M\left(C_{-k}, \boldsymbol{\eta}_{-k}\right) = \exp\left(\frac{1}{4} \boldsymbol{\eta}_{-k}^\mathsf{T} W \boldsymbol{\eta}_{-k}\right) \left(\frac{\pi^{N-1}}{\det(C_{-k})}\right)^{3/2}, \tag{2.102}$$

with $W = (C_{-k})^{-1}$ and $\boldsymbol{\eta}$ being the vector with entries $\vec{\eta}_i = \vec{v}_i - 2C_{ik}\vec{r}_k$. For s-waves this can be written as

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle_{-k} \overset{\mathrm{v}=0}{=} \exp\left(-C_{kk} r_k^2\right) M\left(C_{-k}, \boldsymbol{\eta}_{-k}^{(0)}\right). \tag{2.103}$$

We will also need the modified overlap between two ECGs found at two different values of $\vec{r}_k$. This matrix element is given by

$$\begin{aligned} &\langle B, \mathbf{s}_b|_{\vec{r}_k} \big| A, \mathbf{s}_a|_{\vec{r}_k + \Delta\vec{r}_k} \rangle_{-k} && (2.104) \\ &= \exp\left(-C_{kk} r_k^2 - A_{kk}(\Delta r_k)^2 - 2A_{kk}\vec{r}_k \cdot \Delta\vec{r}_k + \vec{v}_k \cdot \vec{r}_k + (\mathbf{s}_a)_k \cdot \Delta\vec{r}_k\right) M\left(C_{-k}, \boldsymbol{\eta}_{-k}\right), && (2.105) \end{aligned}$$

where $\boldsymbol{\eta}_{-k}$ has entries $\vec{\eta}_i = \vec{v}_i - 2C_{ik}\vec{r}_k - 2A_{ik}\Delta\vec{r}_k$. Here, A is the correlation matrix found at $\vec{r}_k + \Delta\vec{r}_k$, while B is the correlation matrix found at $\vec{r}_k$. For s-waves the matrix element reduces to

$$\begin{aligned} &\langle B, \mathbf{s}_b|_{\vec{r}_k} \big| A, \mathbf{s}_a|_{\vec{r}_k + \Delta\vec{r}_k} \rangle_{-k} && (2.106) \\ &\overset{\mathrm{v}=0}{=} \exp\left(-C_{kk} r_k^2 - A_{kk}(\Delta r_k)^2 - 2A_{kk}\vec{r}_k \cdot \Delta\vec{r}_k\right) M\left(C_{-k}, \boldsymbol{\eta}_{-k}^{(0)}\right). && (2.107) \end{aligned}$$

Chapter 3

Model Implementation

3.1 Implementation of theory to our system

The system we will be working with is H_2^+, as it is the simplest molecular system. This means that we have a three particle system with coordinates $\mathbf{r} = (\vec{r}_1, \vec{r}_2, \vec{r}_3)^\intercal$, where we let $\vec{r}_1$ denote the position of the electron. We will be using atomic units, where $m_e = e = \hbar = 4\pi\epsilon_0 = 1$, so that the ratio between the proton and electron masses is given by

$$\kappa \equiv \frac{m_p}{m_e} \approx 1836. \tag{3.1}$$

Using this along with the notation introduced earlier, the Hamiltonian can be written as

$$\hat{H} = -\frac{1}{2}\nabla^2_{\vec{r}_1} - \frac{1}{2\kappa}\nabla^2_{\vec{r}_2} - \frac{1}{2\kappa}\nabla^2_{\vec{r}_3} - \frac{1}{\left|\vec{r}_1 - \vec{r}_2\right|} - \frac{1}{\left|\vec{r}_1 - \vec{r}_3\right|} + \frac{1}{\left|\vec{r}_2 - \vec{r}_3\right|} \tag{3.2}$$

$$= -\frac{\partial}{\partial \mathbf{r}}\Lambda\frac{\partial}{\partial \mathbf{r}^\intercal} - \frac{1}{|\omega_{12}^\intercal \mathbf{r}|} - \frac{1}{|\omega_{13}^\intercal \mathbf{r}|} + \frac{1}{|\omega_{23}^\intercal \mathbf{r}|}, \tag{3.3}$$

with Λ given as

$$\Lambda = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2\kappa} & 0 \\ 0 & 0 & \frac{1}{2\kappa} \end{pmatrix}. \tag{3.4}$$

Following the treatment in section 2.3, we may switch to Jacobi coordinates and ignore the COM coordinate. Our new coordinates will be denoted by $\mathbf{x} = (\vec{x}, \vec{y})^\intercal$, where $\vec{x}$ is the coordinate between the electron and the proton in the hydrogen atom, and $\vec{y}$ is the coordinate between the other proton and the COM of the hydrogen atom. These coordinates can be seen in figure 3.1.

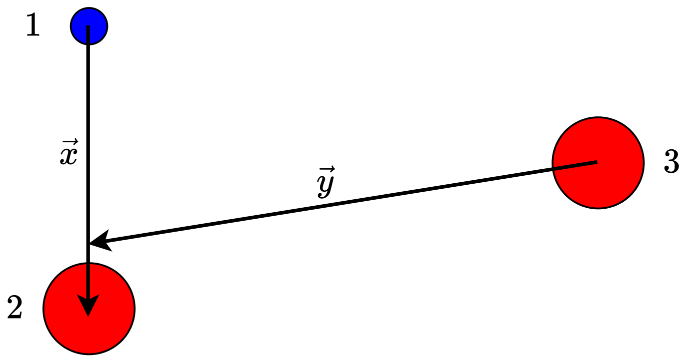

FIGURE 3.1: Illustration showcasing the Jacobi coordinates for the H_2^+ system, where the first particle is the electron, the second particle is the proton in the hydrogen atom and the third particle is the last proton.

In these coordinates, the Hamiltonian is

$$\hat{H} = -\frac{\partial}{\partial \mathbf{x}} \Lambda' \frac{\partial}{\partial \mathbf{x}^{\intercal}} - \frac{1}{\left|\omega_{12}'^{\intercal}\mathbf{x}\right|} - \frac{1}{\left|\omega_{13}'^{\intercal}\mathbf{x}\right|} + \frac{1}{\left|\omega_{23}'^{\intercal}\mathbf{x}\right|}, \tag{3.5}$$

where we have introduced

$$\Lambda' = J'\Lambda J'^{\intercal}, \tag{3.6}$$

$$\omega_{ij}' = U'^{\intercal}\omega_{ij}. \tag{3.7}$$

For the H_2^+ molecule, the J' and U' matrices take the forms

$$J' = \begin{pmatrix} 1 & -1 & 0 \\ \frac{1}{1+\kappa} & \frac{\kappa}{1+\kappa} & -1 \end{pmatrix}, \tag{3.8}$$

and

$$U' = \begin{pmatrix} \frac{\kappa}{1+\kappa} & \frac{\kappa}{1+2\kappa} \\ -\frac{1}{1+\kappa} & \frac{\kappa}{1+2\kappa} \\ 0 & -\frac{1+\kappa}{1+2\kappa} \end{pmatrix}. \tag{3.9}$$

We now want to implement the Born-Oppenheimer approximation. This is done by considering the H_2^+ system as a low-energy proton-hydrogen scattering system, where the incident proton has a low energy. When we introduced the Born-Oppenheimer approximation in section 2.4, it was based on the large difference in mass between electrons and nuclei, meaning the electrons move much faster than the nuclei. This differs from our case, where it is the motion of the incident proton that is slow, while the particles of the hydrogen atom can adjust quickly. That is, $\vec{x}$ is the fast moving coordinate and $\vec{y}$ is the slow moving coordinate. Since we do not want the $\vec{y}$-coordinate to contribute any kinetic energy, we impose the condition

$$\Lambda'_{22} = \left(J'\Lambda J'^{\intercal}\right)_{22} = 0. \tag{3.10}$$

We now want to solve equation 2.56, where we will use the Rayleigh-Ritz method, which means that we must solve the generalized eigenvalue problem $\mathcal{H}c = E\mathcal{N}c$. This will be solved with ECGs as basis functions, where the correlation matrices are given by

$$A_n = \sum_{j>i=1}^{3} \frac{\omega'_{ij}\omega'^{\intercal}_{ij}}{b_{ij}^2}, \tag{3.11}$$

as described in section 2.2.3. The Born-Oppenheimer approximation is then implemented by including a delta function $\delta^3\left(\omega_0^{\intercal}\mathbf{x} - \vec{y}_0\right)$ in the matrix elements of the overlap and Hamiltonian matrices. In Jacobi coordinates without the COM coordinate, the ω'_0 vector can be written as

$$\omega'_0 = U'^{\intercal}\omega_0 = U'^{\intercal}\begin{pmatrix}\frac{1}{1+\kappa}\\ \frac{\kappa}{1+\kappa}\\ -1\end{pmatrix} = \begin{pmatrix}0\\1\end{pmatrix}, \tag{3.12}$$

where ω_0 is the vector in the $\mathbf{r}$ coordinates.

We will check our model by doing tests where we assume that the coordinates $\vec{x}$ and $\vec{y}$ are uncorrelated. In other words, the ECGs should not contain cross terms of the form

$$\vec{x}\cdot\vec{y}. \tag{3.13}$$

However, these terms are a result of the off-diagonal entries in the correlation matrices. The motion between $\vec{x}$ and $\vec{y}$ will then be uncorrelated if A_n is chosen to be diagonal. The A_n matrix can then be parametrized as

$$A_n = \begin{pmatrix}\frac{1}{b_1^2} & 0\\ 0 & \frac{1}{b_2^2}\end{pmatrix}. \tag{3.14}$$

where b_1 and b_2 are the new variational parameters.

3.2 Permutation symmetry of protons

When working with systems that contain identical particles, we must consider the symmetry under the exchange of these. In our case, we have to consider the symmetry when the two protons are exchanged. Since the protons are identical fermions, the total wave function must be antisymmetric under the exchange of the two protons. That is

$$P_{23}\Psi_{\text{total}} = -\Psi_{\text{total}}, \tag{3.15}$$

where P_{23} is the permutation operator. The total wave function can be written as

$$\Psi_{\text{total}} = \psi^{(\text{p})}_{\text{spin}}\psi_{\text{spatial}}(\vec{r}_1, \vec{r}_2, \vec{r}_3), \tag{3.16}$$

and so

$$P_{23}\Psi_{\text{total}} = (P_{23}\psi^{(\text{p})}_{\text{spin}})(P_{23}\psi_{\text{spatial}}). \tag{3.17}$$

For the total proton spin, we use $S = 0$, implying that

$$P_{23}\psi^{(\text{p})}_{\text{spin}} = -\psi^{(\text{p})}_{\text{spin}}. \tag{3.18}$$

In order for the total wave function to then be antisymmetric, the spatial part must be symmetric

$$P_{23}\psi_{\text{spatial}} = +\psi_{\text{spatial}}. \tag{3.19}$$

We can then write

$$\psi_{\text{spatial}} \to \psi_{\text{spatial}}(\vec{r}_1, \vec{r}_2, \vec{r}_3) + \psi_{\text{spatial}}(\vec{r}_1, \vec{r}_3, \vec{r}_2). \tag{3.20}$$

We also have to consider how the particle coordinates, ECGs, and matrix elements transform under the permutation of the protons. The particle coordinates transform as

$$\mathbf{r} = \begin{pmatrix} \vec{r}_1 \\ \vec{r}_2 \\ \vec{r}_3 \end{pmatrix} \to \mathbf{r}' = P_{23}\mathbf{r} = \begin{pmatrix} \vec{r}_1 \\ \vec{r}_3 \\ \vec{r}_2 \end{pmatrix}, \qquad P_{23} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}. \tag{3.21}$$

Inserting this into the general expression for the ECGs, we find that

$$\exp(-\mathbf{r}^{\mathsf{T}}A\mathbf{r}) \to \exp(-(P_{23}\mathbf{r})^{\mathsf{T}}A(P_{23}\mathbf{r})) = \exp(-\mathbf{r}^{\mathsf{T}}(P_{23}^{\mathsf{T}}AP_{23})\mathbf{r}), \tag{3.22}$$

from which it is apparent that the correlation matrices transform in the following way

$$A \to A + P_{23}^{\mathsf{T}}AP_{23} = \tilde{A}. \tag{3.23}$$

The matrix elements can then be written as

$$\langle B|\hat{H}|A\rangle \rightarrow \langle\tilde{B}|\hat{H}|\tilde{A}\rangle = \langle B + P_{23}^{\intercal}BP_{23}|\hat{H}|A + P_{23}^{\intercal}AP_{23}\rangle \tag{3.24}$$

$$= \langle B|\hat{H}|A\rangle + \langle B|\hat{H}|P_{23}^{\intercal}AP_{23}\rangle + \langle P_{23}^{\intercal}BP_{23}|\hat{H}|A\rangle + \langle P_{23}^{\intercal}BP_{23}|\hat{H}|P_{23}^{\intercal}AP_{23}\rangle, \tag{3.25}$$

with a similar expression for the overlap matrix element. Now we want to find P_{23} in Jacobi coordinates, which we do by utilizing the relations between $\mathbf{x}$ and $\mathbf{r}$, where we get

$$\mathbf{x}' = J\mathbf{r}' = JP_{23}\mathbf{r} = JP_{23}U\mathbf{x}. \tag{3.26}$$

From here it is evident that the permutation matrix in Jacobi coordinates is given by

$$P_{23}^{(\mathrm{Jac})} = JP_{23}U, \tag{3.27}$$

and the correlation matrix then becomes

$$\tilde{A} = A + (JP_{23}U)^{\intercal} A (JP_{23}U). \tag{3.28}$$

Exchanging the two nuclei in a homonuclear diatomic molecule is equivalent to an inversion through the molecular center. Equation 3.19 therefore implies that the spatial wave function must have gerade (g) symmetry.

Since we are working with ECGs without shifts, they do not have any angular dependence. The ECGs are therefore rotationally invariant around the axis connecting the protons, meaning only σ states are possible. This together with the previous argument means that we can only obtain σ_g states.

Having gerade symmetry is the same as saying that the parity is $\pi = +1$. We can then use that the parity under inversion is given by

$$\pi = (-1)^l, \tag{3.29}$$

meaning only even l's are allowed. The only possible states that we can get are then $s\sigma_g$, $d\sigma_g$, $g\sigma_g$ and so on.

CHAPTER 4

Numerical Methods

This section covers the different methods used in the numerical simulations. This includes a detailed description of the optimization routine and how the energy is minimized. The numerical implementation of the non-adiabatic terms is also covered, and finally we show how to obtain the radial wave function using the finite difference method.

4.1 Optimization

We will solve the generalized eigenvalue problem using scipy.linalg.eigh, which can be used since both $\mathcal{N}$ and $\mathcal{H}$ are real and symmetric matrices. This function returns the eigenvalues sorted in ascending order and the corresponding eigenvectors, which are normalized according to $c^\dagger \mathcal{N} c = 1$.

4.1.1 Minimization methods

For the actual minimization of the energy, it is essential to find the optimal parameters for the ECGs. The parameters we need to optimize are the b_{ij} variational parameters in equation 3.11. There are several different ways of finding the optimal parameters. One possible method is the stochastic variational method, where the parameters are generated from a pseudo-random or quasi-random distribution. Here, it is important to choose a suitable distribution so that the size of the random parameters matches the inherent scale of the system. The idea is to generate a large amount of random parameters and then use these to construct a large set of candidates for the basis elements. For the first basis element, we then pick the candidate that minimizes the energy. While keeping the first basis element fixed, the second basis element is then chosen from the remaining pool of candidate, such that the energy is minimized with respect to the full basis. This procedure can then be continued until the basis has the required size. Each time a basis element is added, it only gives an additional row and column in the $\mathcal{N}$ and $\mathcal{H}$ matrices with the rest of the matrices being the same. Thus, it is not necessary to recompute the entire overlap and Hamiltonian matrices, and one does not have to solve the full generalized eigenvalue problem [5]. A problem with this method can occur if two basis elements are nearly identical. The overlap matrix may then be non-invertible, meaning the generalized eigenvalue problem is not solvable. Another reason to avoid having nearly identical basis elements is that it barely gives any improvements in the energy. This problem is less likely to occur when using a quasi-random distribution due to its low discrepancy [14]. Another option when adding a new basis element is to calculate the overlap with all other basis elements, and then throw it away if the quantity

$$\frac{\langle B|A\rangle}{\sqrt{\langle A|A\rangle\langle B|B\rangle}} \tag{4.1}$$

is above a prescribed limit.

Another method is the full optimization, where all parameters are optimized at once. Instead of generating many random basis elements and choosing the best one, this method uses a minimizing function such as scipy.optimize.minimize. The initial guess for the minimization function will again be generated from a suitable random distribution. In the case of N basis function, the initial guess requires $3N$ parameters. As we minimize $3N$ parameters at a time, this method quickly becomes computationally expensive when N becomes large. This method also has a problem regarding local minima, as there is a risk of the minimizer ending up in a local minimum instead of finding the global minimum. Then, there is no guarantee that the energy becomes lower as the size of the basis increases. A strategy to reduce this issue is to test multiple initial guesses for the minimizer and then choose the one that yields the lowest energy.

The method we ended up using throughout this thesis mixes the two approaches above. The minimization procedure largely follows the same steps as the stochastic variational method, but instead of minimizing the energy by trying many random basis elements, the energy is minimized using scipy.optimize.minimize as in the full optimization. The optimization algorithm is as follows

Optimization of ground state energy

- First ECG
  - Start by generating three random parameters from a suitable distribution. These are then used as an initial guess for the minimization function, where the optimized parameters are saved.
- Adding an ECG
  - Again start by generating three random parameters. These will be our initial guess along with the optimal parameters from the previous ECGs, which will be kept fixed.
- Refinement
  - Vary the three parameters belonging to the first ECG, and let the initial guess be the optimal parameters from the earlier minimization. Keep the parameters for the other ECGs fixed to the optimal parameters from the minimization.
  - Repeat the above step for all elements of the basis.
  - If necessary, perform additional refinement loops.

This method only optimizes three parameters at a time compared to the $3N$ parameters in the full optimization, greatly reducing the total computational cost. We also expect that the energy converges faster using a minimization function compared to randomly generating the basis elements. For the minimization function we found that both the Nelder-Mead downhill simplex method and the conjugate gradient method worked relatively well.

4.1.2 Potential energy surfaces

The optimization of the potential energy surfaces is slightly more challenging compared to the optimization of the ground state energy, since the energy must be minimized for every y_0. The optimization procedure is as follows

Optimization of PES

- First ECG
  - Start with the smallest value of y_0 and generate three random parameters from a suitable distribution. Use these as an initial guess for the minimization routine, and save the optimized parameters and energy.

  - Use the optimal parameters from the previous y_0 value as a start guess for the next y_0 value, and again save the optimized parameters and energy.
  - Do this for all values of y_0, so that we have the energies and optimal parameters for every y_0.

- Adding an ECG
  - Again start with the smallest value of y_0 and generate three random parameters. We now optimize only these three parameters and fix the parameters for the other ECGs to the earlier obtained optimal parameters at the same y_0 value. Save the energy and the optimized parameters for the added ECG.
  - For the next y_0 value we use the optimized parameters for the added ECG from the previous value of y_0 as a start guess. As in the last step, the other parameters are fixed to the earlier obtained optimal parameters for the same value of y_0.
  - Continue in this way for every y_0 value.
  - Run one or more refinement loops.

The procedure of fixing the already optimized ECGs and optimizing only the added ECG ensures, as per the discussion in section 2.2.2, that the energy for each y_0 does not get worse. This guarantees that the PES corresponding to different numbers of ECGs do not cross.

4.1.3 Excited states

In order to solve the non-adiabatic equation 2.68 with higher order non-adiabatic terms, we need the PES for the excited states. Now, in order to obtain the i'th eigenvalue, the basis must at minimum be i-dimensional. As described in section 2.2.2, the i'th eigenvalue obtained by solving the generalized eigenvalue problem is an upper bound for the energy of the $i-1$'th excited state. In this thesis, we will only consider the first excited state, but higher excited states can be included similarly. In this thesis, we will use the term first excited state to denote the second lowest state within the symmetry specified in section 3.2.

ECGs that describe one state well will not necessarily describe other states well. For example, a basis function optimized for the ground state may not minimize the energy of the first excited state very well. In general, it is best to first optimize the basis until the ground state energy is relatively stable before optimizing the energy of the first excited state [5]. The PES for the first excited state is then optimized by minimizing the second lowest eigenvalue from the generalized eigenvalue problem. Another method is to minimize the sum of the ground state energy and the energy of the first excited state. Here, it is important to note that if the basis only contains one element, only the ground state energy can be optimized.

4.2 Non-adiabatic terms

In order to implement the non-adiabatic terms into the numerical calculation, we need to rewrite them. The first order non-adiabatic term is defined by

$$P_{mn}(y_0) = \left\langle \phi_m(y_0) \middle| \frac{\partial}{\partial y_0} \middle| \phi_n(y_0) \right\rangle_{-y}. \tag{4.2}$$

We will approximate this numerically by approximating the derivative using the central finite difference formula given by [15]

$$\frac{\partial}{\partial y_0}\phi_n(y_0) \approx \frac{\phi_n(y_0+\Delta y_0) - \phi_n(y_0-\Delta y_0)}{2\Delta y_0}, \tag{4.3}$$

such that

$$P_{mn}(y_0) \approx \frac{\langle \phi_m(y_0)|\phi_n(y_0+\Delta y_0)\rangle_{-y} - \langle \phi_m(y_0)|\phi_n(y_0-\Delta y_0)\rangle_{-y}}{2\Delta y_0}. \tag{4.4}$$

Similarly, the second order non-adiabatic term is defined by

$$Q_{mn}(y_0) = \left\langle \phi_m(y_0) \middle| \frac{\partial^2}{\partial y_0^2} \middle| \phi_n(y_0) \right\rangle_{-y}. \tag{4.5}$$

Using the symmetric central-difference formula, the second order derivative can be approximated as [15]

$$\frac{\partial^2}{\partial y_0^2}\phi_n(y_0) \approx \frac{\phi_n(y_0-\Delta y_0) - 2\phi_n(y_0) + \phi_n(y_0+\Delta y_0)}{(\Delta y_0)^2}, \tag{4.6}$$

so that

$$Q_{mn}(y_0) \approx \frac{\langle \phi_m(y_0)|\phi_n(y_0-\Delta y_0)\rangle_{-y} - 2\langle \phi_m(y_0)|\phi_n(y_0)\rangle_{-y} + \langle \phi_m(y_0)|\phi_n(y_0+\Delta y_0)\rangle_{-y}}{(\Delta y_0)^2}. \tag{4.7}$$

We can now look at the overlaps in equations 4.4 and 4.7. The ϕ_n states can be written as

$$\phi_n(y_0) = \sum_{i=1}^{N} c_{n,i}(y_0) A_i(y_0), \tag{4.8}$$

where A_i are ECGs. The overlap then becomes

$$\langle \phi_m(y_0)|\phi_n(y_0+\Delta y_0)\rangle_{-y} = c_m^\dagger(y_0)S(y_0, y_0+\Delta y_0)c_n(y_0+\Delta y_0), \tag{4.9}$$

where c_n is an N-dimensional vector and S is an $N \times N$ matrix with elements

$$S_{ij}(y_0, y_0+\Delta y_0) = \langle A_i(y_0)|A_j(y_0+\Delta y_0)\rangle_{-y}, \tag{4.10}$$

with analogous expressions for $\langle \phi_m(y_0)|\phi_n(y_0-\Delta y_0)\rangle_{-y}$ and $\langle \phi_m(y_0)|\phi_n(y_0)\rangle_{-y}$. For the elements of S it is important to implement the permutation symmetry described in section 3.2. When computing P_{mn} and Q_{mn} it is important to make sure that the c-coefficients are normalized according to $c_m^\dagger(y_0)S(y_0, y_0)c_m(y_0) = 1$ for every y_0.

4.3 Radial wave function

In order to find the radial wave function, we must solve the reduced radial Schrödinger equation. For the case of no angular momentum, this is given by

$$\left[-\frac{1}{2\mu}\frac{d^2}{dr^2} + V(r)\right]u(r) = Eu(r), \tag{4.11}$$

where μ is the reduced mass of the system. For a solution to be physical, it must satisfy boundary conditions

$$\lim_{r\to 0} u(r) = 0, \qquad \lim_{r\to\infty} u(r) = 0. \tag{4.12}$$

These boundary conditions can be implemented by requiring our solution to be zero at a lower and upper limit, which we will call r_{min} and r_{max}. We will solve equation 4.11 using the finite difference method. The general principle of the finite difference method is to approximate the derivatives with finite difference formulas. The first step is to divide the r-axis into N steps of length Δr, so that the wave function is the N-dimensional vector $\vec{u}$ with $u_i = u(r_i)$, where

$$N = \frac{r_{max} - r_{min}}{\Delta r} - 1, \qquad r_i = i \cdot \Delta r + r_{min}, \qquad i \in \{1, 2, \dots, N\}. \tag{4.13}$$

Here, we note that r_{min} and r_{max} are not part of the steps. In this way, the boundary conditions in equation 4.12 are incorporated directly into the Hamiltonian. Next, we can rewrite the second-order derivative with the symmetric central-difference formula as [15]

$$\frac{d^2u_i}{dr^2} = \frac{u_{i-1} - 2u_i + u_{i+1}}{(\Delta r)^2}. \tag{4.14}$$

Applying this to the case of H_2^+, where our potential is the PES we obtained by solving equation 2.56, the Hamiltonian becomes

$$H = T + V, \tag{4.15}$$

where

$$T = -\frac{1}{2\mu(\Delta r)^2}\begin{pmatrix} -2 & 1 & 0 & 0 & \dots & 0 \\ 1 & -2 & 1 & 0 & \dots & 0 \\ 0 & 1 & -2 & 1 & \dots & 0 \\ \vdots & \ddots & \ddots & \ddots & \ddots & \vdots \\ 0 & \dots & 0 & 1 & -2 & 1 \\ 0 & \dots & 0 & 0 & 1 & -2 \end{pmatrix}, \tag{4.16}$$

$$V = \begin{pmatrix} \varepsilon(y_1) & 0 & 0 & \dots & 0 \\ 0 & \varepsilon(y_2) & 0 & \dots & 0 \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & \dots & 0 & \varepsilon(y_{N-1}) & 0 \\ 0 & \dots & 0 & 0 & \varepsilon(y_N) \end{pmatrix}, \tag{4.17}$$

with $\mu = \frac{m_p m_H}{m_p + m_H}$. The reduced radial Schrödinger equation then becomes the following eigenvalue equation

$$H\vec{u} = E\vec{u}, \tag{4.18}$$

which can be solved with a diagonalization routine such as numpy.linalg.eigh.

We will also need to find the radial wave function with the non-adiabatic effects included. Here, we will look at the example where we only consider the two lowest states. The radial wave function will then have two components

$$\mathbf{u} = \begin{pmatrix} \vec{u}_0 \\ \vec{u}_1 \end{pmatrix}, \tag{4.19}$$

where $\vec{u}_0$ and $\vec{u}_1$ correspond to the ground state and the first excited state, respectively. The Hamiltonian matrix then turns into a block matrix of the form

$$H = \begin{pmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{pmatrix}, \tag{4.20}$$

where

$$H_{nn} = T + V_n - \frac{1}{2\mu}\left(Q_{nn} + 2P_{nn}\frac{d}{dr}\right), \tag{4.21}$$

and

$$H_{mn} = -\frac{1}{2\mu}\left(Q_{mn} + 2P_{mn}\frac{d}{dr}\right). \qquad m \neq n \tag{4.22}$$

The first order derivative is approximated using the central finite difference formula [15], such that it can be written as

$$\frac{d\vec{u}_i}{dr} = \frac{1}{2\Delta r}\begin{pmatrix} 0 & 1 & 0 & \cdots & 0 \\ -1 & 0 & 1 & \ddots & \vdots \\ 0 & -1 & 0 & \ddots & 0 \\ \vdots & \ddots & \ddots & \ddots & 1 \\ 0 & \cdots & 0 & -1 & 0 \end{pmatrix}. \tag{4.23}$$

The reduced radial Schrödinger equation can now be written as

$$H\mathbf{u} = E\mathbf{u}, \tag{4.24}$$

which we will solve with numpy.linalg.eigh. In our case, we will not consider the Q_{11} and P_{11} terms.

Chapter 5

Results

In this section, we present the results of this thesis. We start by recreating some of the results obtained in [1] and [2]. This includes a convergence plot of the ground state energy of H_2^+, which is used to verify that the method has been correctly implemented. We then move on to the potential energy surfaces, which we calculate for both correlated and non-correlated coordinates, and with and without proton-proton repulsion. This leads to the reduced radial wave function, where we analyze the bound states of H_2^+.

We then move on to the results beyond those in [1, 2]. Here, we first find the PES of the first excited state. The non-adiabatic terms are then found using the method described in section 4.2. These are then used to solve the non-adiabatic equation 2.68, from which the ground state energy is obtained. Finally, we compare this energy with the energy from both the Born-Oppenheimer approximation and the Born-Huang approximation.

5.1 Ground state energy

We will test the method of ECGs by calculating the ground state energy of H_2^+ using the optimization procedure from section 4.1. This is to ensure that the energy converges to the correct value. In this way, we check both that our calculated matrix elements are correct and that the optimization procedure is correctly implemented. The results can be seen in figure 5.1, where we see that the energy converges reasonably fast towards the real ground state energy of -0.597 Ha [16].

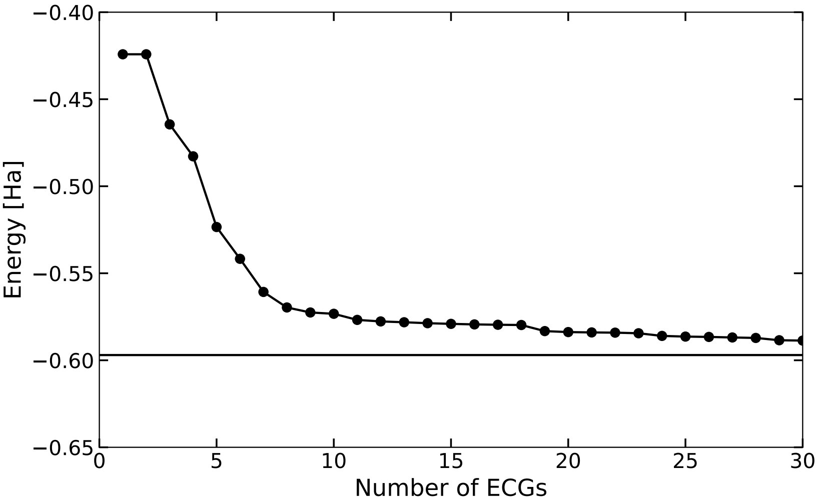

FIGURE 5.1: Convergence plot of the ground state energy of H_2^+. The real ground state energy is -0.597 Ha, which is indicated by the horizontal line.

5.2 Ground state potential energy surfaces

We will test the implementation of the Born-Oppenheimer approximation into the method of ECGs by excluding the proton-proton repulsion and only using diagonal correlation matrices, as described in section 3.1. As y_0 basically represents the distance between the proton, we have two well-known limits for y_0. For large y_0 values, where the protons are far apart, we simply have a hydrogen atom and a free proton. Thus, we expect the energy to converge to the ground state energy of a hydrogen atom, which in our units has an energy of $-\frac{1}{2}$ Ha. For small y_0 values, the protons are close together and we have a hydrogen atom with twice the mass and charge. In atomic units, the energy of a hydrogen-like atom with Z protons is given by [17]

$$E_n = -\frac{Z^2}{2(n+1)^2}, \tag{5.1}$$

such that the ground state energy in our case is $E_0 = \frac{-2^2}{2} = -2$ Ha. The result can be seen in figure 5.2, where we see that the energy converges to the expected values. We also note that the energy converges fast to the correct limits and that reasonable convergence is already achieved with a basis of two ECGs.

We now calculate the PES with the proton-proton repulsion included, while still using only diagonal correlation matrices. The results are shown in figure 5.3. As expected, we see that the energy now diverges for small y_0 values due to the repulsion between the protons, and that it still converges

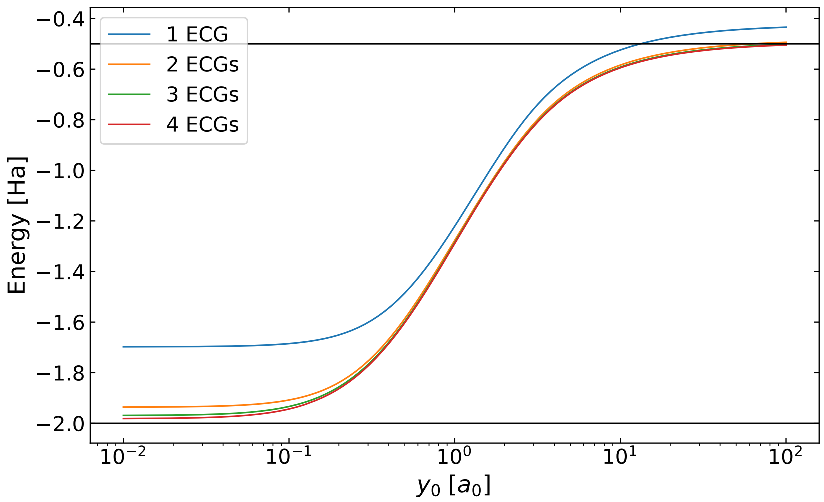

FIGURE 5.2: PES for the ground state showcasing the limiting behavior of the energy. This is done for a different number of ECGs in the basis, where the energy is computed with diagonal correlation matrices and without the proton-proton repulsion. The two horizontal lines show the limits of small and large proton-hydrogen separation.

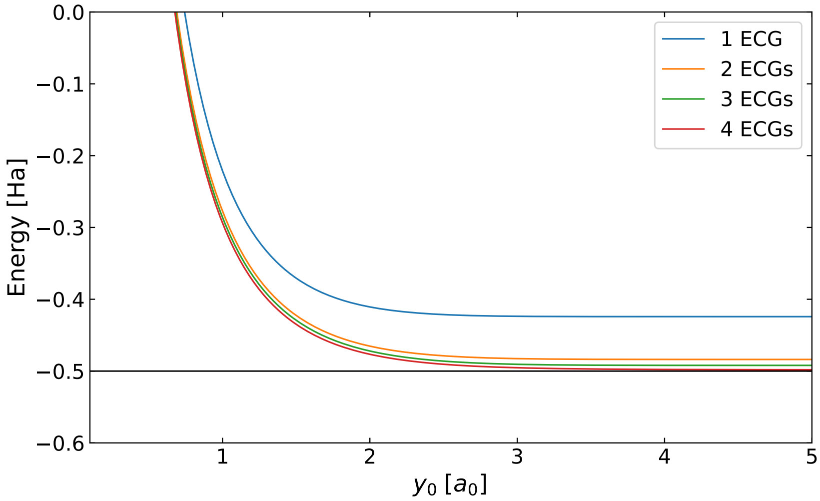

FIGURE 5.3: PES for the ground state calculated with diagonal correlation matrices and with the proton-proton repulsion included. This is done for a varying number of ECGs in the basis. The asymptotic limit of a large distance between the proton and hydrogen atom is shown by the horizontal line.

to the ground state energy of hydrogen for large y_0 values. We also see that there is no energy minimum. This indicates that uncorrelated coordinates do not produce any bound states.

The results of the computations with non-diagonal correlation matrices are given in figure 5.4. With a basis consisting of four ECGs, the PES has a minimum of -0.601 Ha at a distance of 1.99 a_0. We also note that the energy converges quite fast and does not improve significantly after the second ECG has been added.

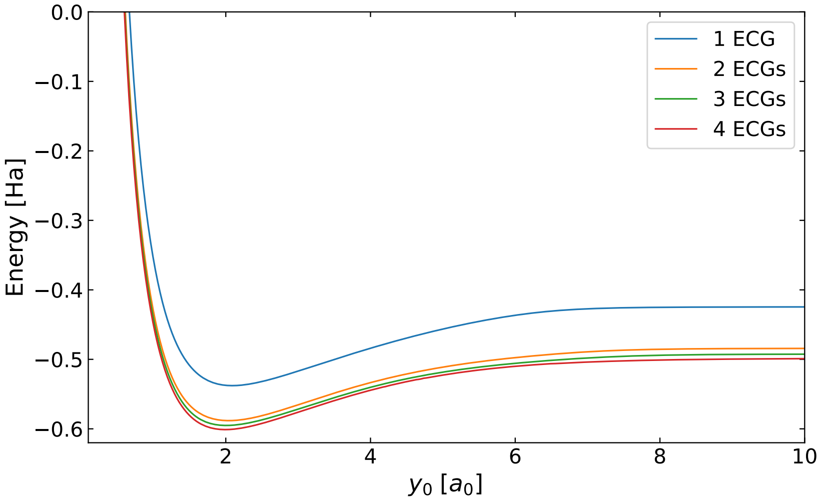

FIGURE 5.4: PES for the ground state calculated with non-diagonal correlation matrices and with the proton-proton repulsion included. This is done for a varying number of ECGs in the basis.

5.3 Excited states

We will also calculate the PES of the first excited state, as this is needed in the calculations of the non-adiabatic coupling terms. For the actual optimization, we start by optimizing the first two ECGs to the ground state and then optimize the next two ECGs to the first excited state. At large y_0 values, we expect the PES of the first excited state to go to the energy of the first excited state of a hydrogen atom. The energies of the excited states of hydrogen are given by [17]

$$E_n = -\frac{1}{2(n+1)^2}, \tag{5.2}$$

meaning the energy of the first excited state is $E_1 = -\frac{1}{2\cdot 2^2} = -0.125$ Ha. The result of the calculation is shown in figure 5.5. The PES for the first excited state has a minimum of -0.164 Ha at a distance of 9.4 a_0. As expected, we see that the PES goes to -0.125 Ha at large values of y_0. The PES for the first excited state obtained with the three and four ECG basis practically lie on top of each other. This indicates either that the PES is already converged or that

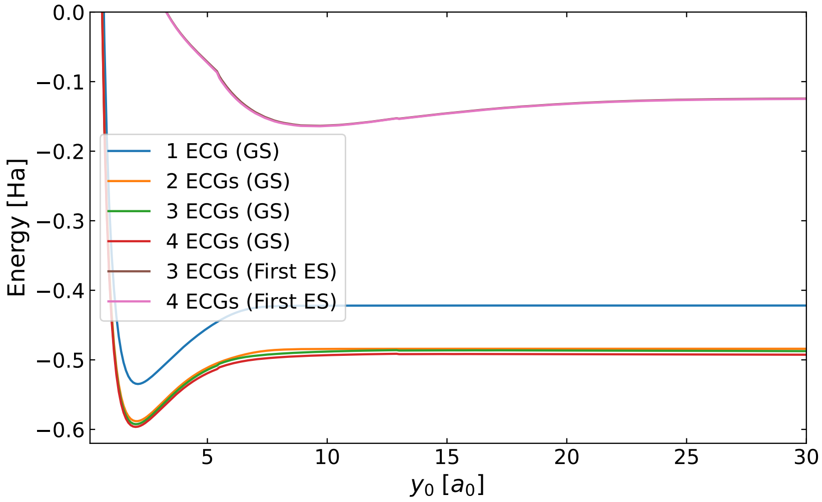

FIGURE 5.5: PES for the ground state and first excited state. The first two ECGs are optimized for the ground state (GS) and the next two are optimized for the first excited state (ES).

a much larger basis is needed for the energy to converge, the latter being the most likely case. We also see that the PES for the first excited state makes a kink just above $y_0 = 5\,\mathrm{a}_0$. This kink is caused by an avoided crossing between the PES for two different states. Finally, we note that the ground state energy does not improve by much when adding the third and fourth basis element, as these are optimized to the first excited state. The PES for the ground state obtained with this optimization scheme only has a minimum of −0.596 Ha, compared to the minimum of −0.601 Ha when all the ECGs are optimized to the ground state.

5.4 Reduced radial wave function

The reduced radial wave function can be obtained by following the method outlined in section 4.3. The solutions with energies below −0.5 Ha correspond to bound states. Using the lowest PES in figure 5.4, we obtain figure 5.6 where the three bound states with the lowest energies are plotted. In total, we get 17 bound states, where the lowest has an energy of −0.596 Ha. A similar plot can be made for the first excited state, where we find 34 bound states, that is, states with an energy below −0.125 Ha. Here, the lowest lying state has an energy of −0.163 Ha.

In this thesis, we focus on the bound states, but one can also solve for the scattered states, which for the ground state are solutions with energies above

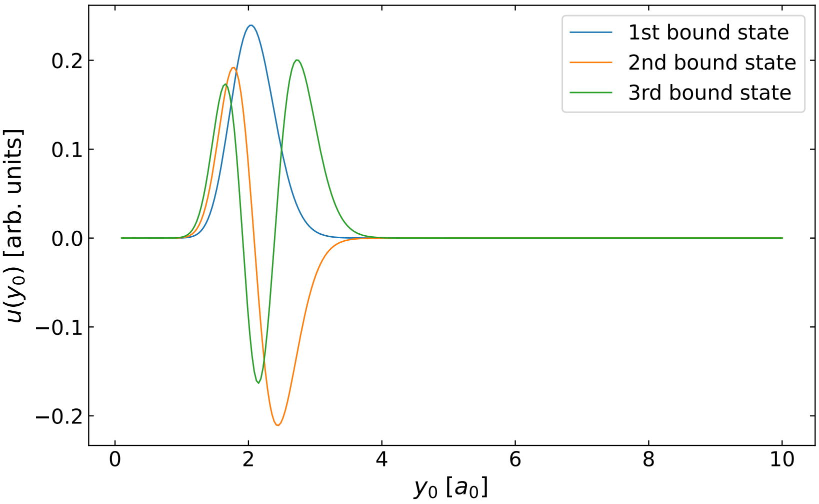

FIGURE 5.6: The reduced radial wave function plotted as a function of the distance between the proton and hydrogen atom, where the 3 lowest-lying bound states are shown. The energy of the lowest bound state is −0.596 Ha.

−0.5 Ha. These can then be used to calculate scattering observables, such as the scattering length, effective range, and phase shift.

5.5 Non-adiabatic terms

The non-adiabatic terms are calculated with the method described in section 4.2 using the optimized ECG basis from figure 5.5. The Q_{00} term is only related to the ground state. We therefore set the c-coefficients corresponding to the third and fourth ECG in our basis equal to zero when calculating this term. We expect that this will only have a minor impact on the value of Q_{00}, since the ECGs that are optimized to the first excited state should not contribute much to the ground state. Figure 5.7 shows a plot of Q_{00} as a function of y_0. Here, we see that Q_{00} is not a smooth curve but instead spikes at many different values of y_0. This could indicate that the ECGs jump from one local minimum to another during the optimization procedure, meaning that we are in different local minima at different values of y_0. One possible way to avoid these jumps between local minima is to set some restrictions on the variational b-parameters in the ECGs. In our case, instead of purely minimizing the energy, we try to minimize the expression

$$E + \lambda \left\| \frac{b_{\text{new}} - b_{\text{prev}}}{b_{\text{prev}}} \right\|^2, \tag{5.3}$$

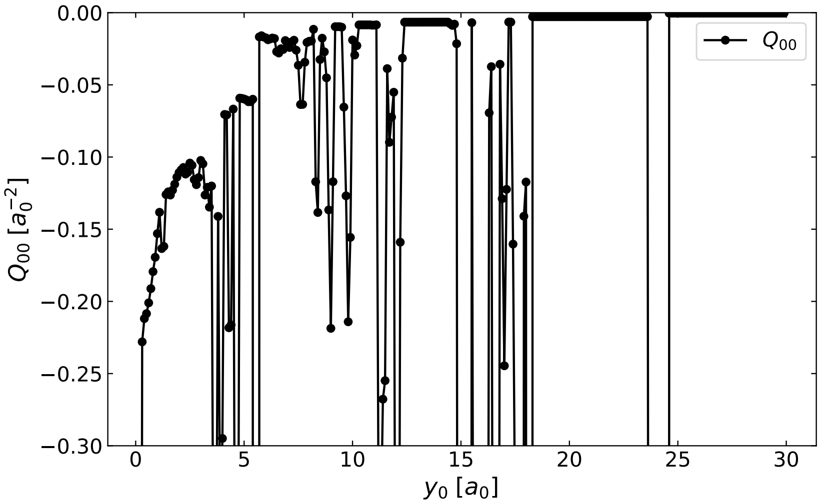

FIGURE 5.7: The non-adiabatic term Q_{00} calculated as a function of y_0 with no restrictions on the variational b-parameters. The PES used in the calculation are those obtained by optimizing the first two ECGs for the ground state and the next two for the first excited state.

where b_{new} is the vector containing the parameters we want to optimize, b_{prev} is the vector containing the optimized parameters from the previous value of y_0 and λ is a small number. This makes it less likely for the b-parameters to change drastically from one value of y_0 to another, and we should therefore see fewer spikes in the non-adiabatic terms. However, minimizing expression 5.3 rather than just the energy does give a higher risk of not finding the best minima. The value of λ must therefore be chosen such that we both obtain good energies and that the b-parameters do not change significantly between y_0 values. We found that $\lambda = 0.01$ gave nearly the same energies as before, while also significantly reducing the amount of spikes. Using this when calculating the PES, we obtain the Q_{00} term seen in figure 5.8. This is again calculated with the c-coefficients corresponding to the third and fourth ECG set to zero as discussed above. This is to avoid the spike that could arise from the avoided crossing in the PES of the first excited state. Here, we see that including a penalty on the b-parameters gives a smooth Q_{00} curve, which generally has a low value. This suggests that the non-adiabatic effects in our system are small. The curve also goes to zero at large y_0's. This is as expected, since the PES is flat at large y_0 values. The value of Q_{00} is also negative at every y_0 as it should be. Comparing the figures, we see that even without the penalty on the b-parameters in figure 5.7, it still shows trends similar to those in figure 5.8.

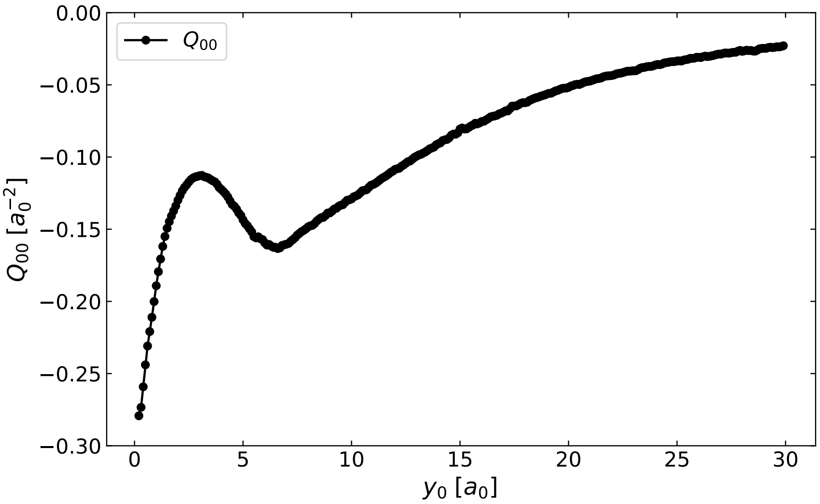

FIGURE 5.8: The non-adiabatic term Q_{00} calculated as a function of y_0 with penalty on the variational b-parameters during the minimization. The PES used in the calculation are those obtained by optimizing the first two ECGs for the ground state and the next two for the first excited state.

We obtain Q_{01} and Q_{10} similarly, this time using the full c-coefficient, as these terms couple the ground state and the first excited state. The results can be seen in figure 5.9 and 5.10, respectively.

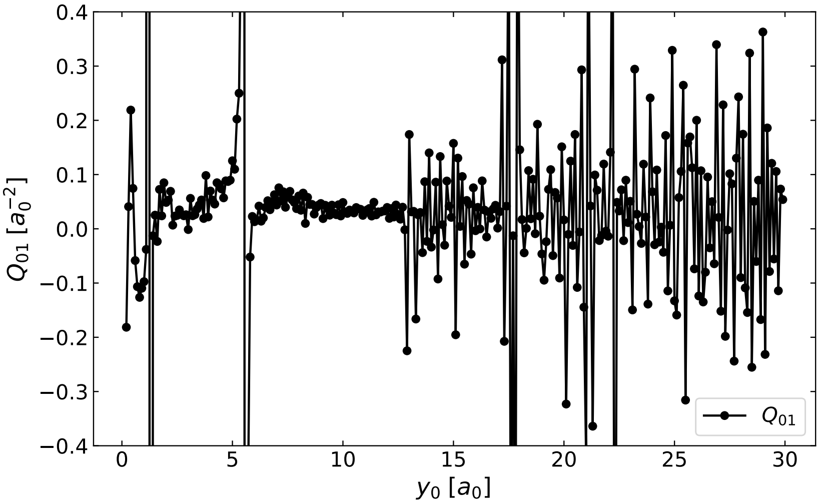

FIGURE 5.9: The non-adiabatic coupling term Q_{01} calculated as a function of y_0 with penalty on the variational b-parameters during the minimization.

Here, we do not obtain smooth curves as we did for Q_{00}. It could therefore seem that the b-parameters are more likely to jump when optimizing the

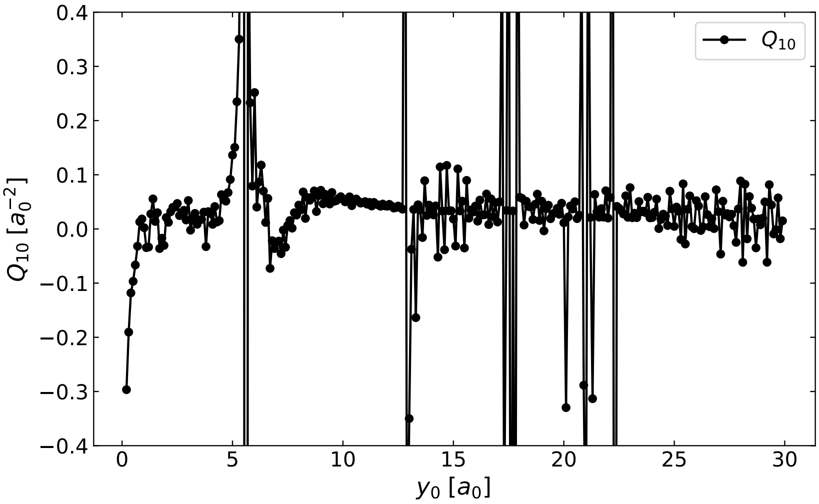

FIGURE 5.10: The non-adiabatic coupling term Q_{10} calculated as a function of y_0 with penalty on the variational b-parameters during the minimization.

first excited state compared to the ground state. In both Q_{01} and Q_{10} we see a large spike just above $y_0 = 5$ a$_0$. This is likely caused by the avoided crossing in the PES for the first excited state, which gives a natural cause for the b-parameters to change significantly.

We now move on to the P terms with P_{00} depicted in figure 5.11. Here, we see that it is equal to zero for all y_0, which is as expected [18].

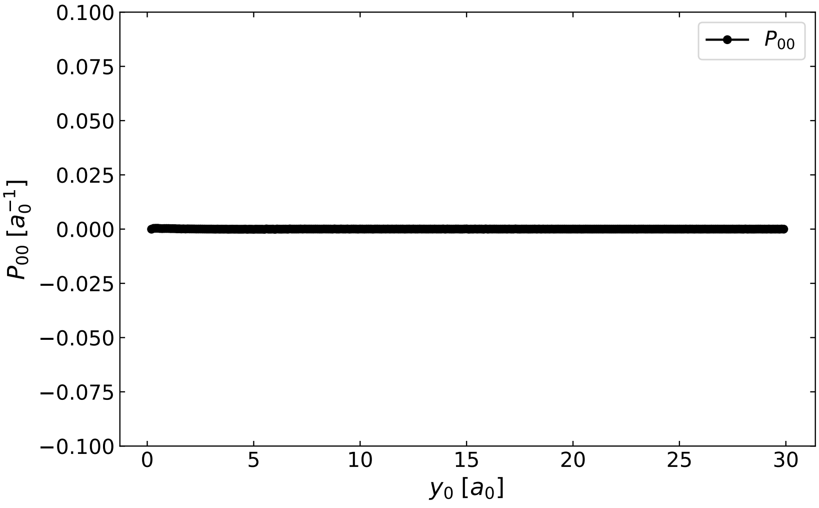

FIGURE 5.11: The non-adiabatic term P_{00} calculated as a function of y_0 with penalty on the variational b-parameters during the minimization.

The P_{01} and P_{10} terms are shown in figure 5.12 and 5.13, respectively. These show features similar to those seen in Q_{01} and Q_{10}. Although they are smoother, they still contain spikes, and we again have a large spike just above $y_0 = 5$ a$_0$ due to the avoided crossing, as we did for Q_{01} and Q_{10}.

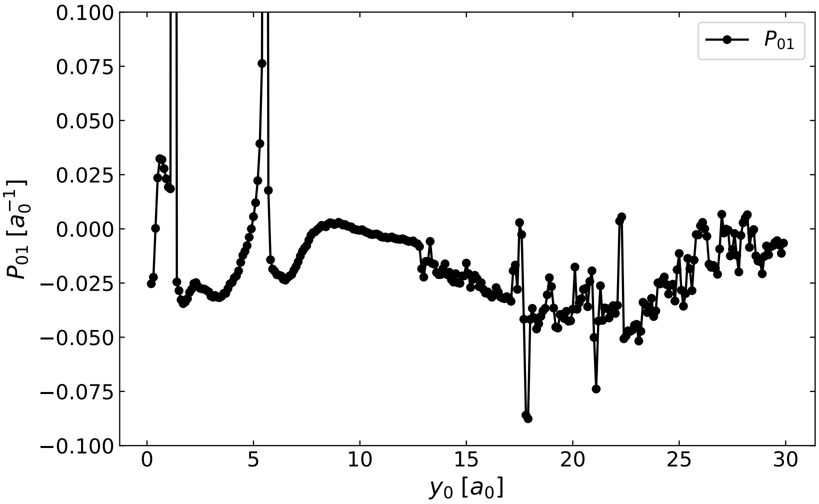

FIGURE 5.12: The non-adiabatic coupling term P_{01} calculated as a function of y_0 with penalty on the variational b-parameters during the minimization.

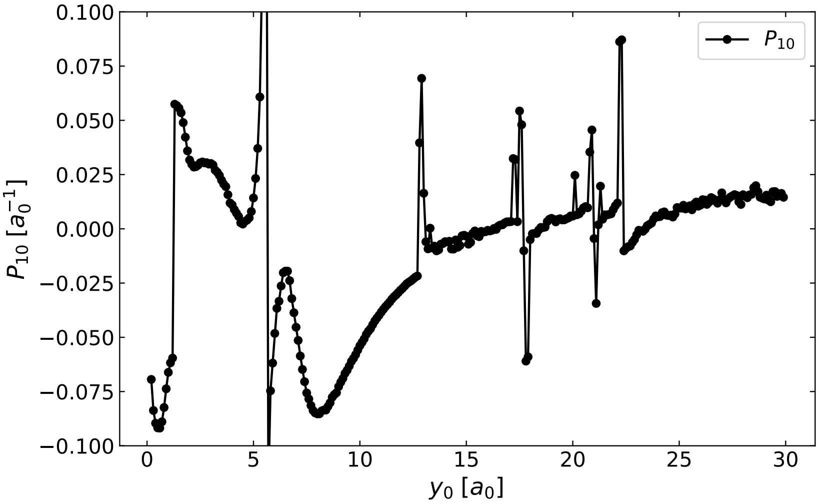

FIGURE 5.13: The non-adiabatic coupling term P_{10} calculated as a function of y_0 with penalty on the variational b-parameters during the minimization.

The next step is to find the ground state energy of H_2^+ in the Born-Oppenheimer approximation, Born-Huang approximation, and non-Born-Oppenheimer approach. This is done by solving equations 2.63, 2.71 and 2.68, respectively, using the potential energy surfaces and non-adiabatic terms from above. The difference between the Born-Oppenheimer and Born-Huang approximation is showcased in figure 5.14. Here, we have calculated the PES of the ground state for a basis with two ECGs, and plotted it with and without $-\frac{1}{2\mu}Q_{00}$ added. We can see $(\varepsilon_n(;\mathbf{R}) - \frac{1}{2\mu}Q_{00}(\mathbf{R}))$ as an effective PES, which is the one we use in the Born-Huang approximation. We see that the Q_{00} term only raises the PES very slightly, so we expect that including the non-adiabatic terms will only have a very small impact of the final energy.

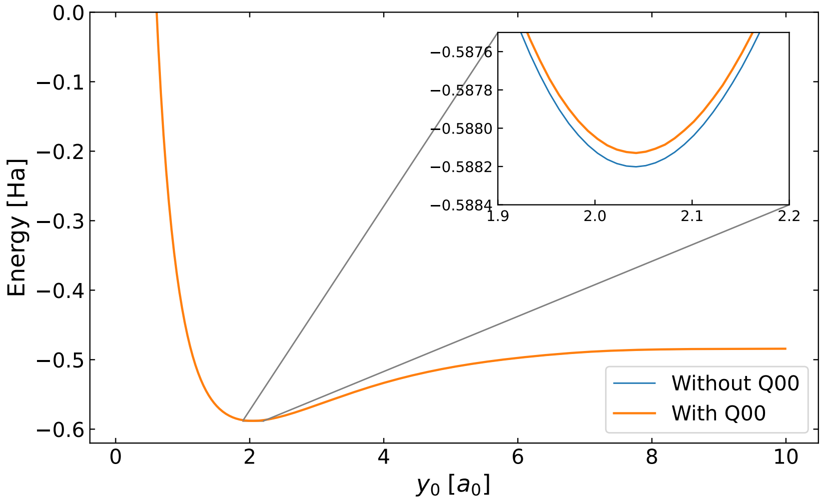

FIGURE 5.14: PES of the ground state with and without Q_{00} added. The plotted PES is optimized with two ECGs both optimized to the ground state.

The ground state energies for H_2^+, calculated for the different approaches using the four ECG basis described in section 5.3, are given in table 5.1. Here we see that including the Q_{00} term as expected gives a slightly higher energy. Including more non-adiabatic terms only has a negligible effect on the energy. However, this could be related to the fact that we were unable to obtain smooth curves for Q_{01}, Q_{10}, P_{01} and P_{10}. Overall, the energies in table 5.1 indicate that the Born-Oppenheimer approximation describes the H_2^+ system very accurately.

	BO	BH	Beyond BO
Energy	−0.58973148 Ha	−0.58966159 Ha	−0.58966160 Ha

TABLE 5.1: Ground state energy of H_2^+ in the Born-Oppenheimer approximation, Born-Huang approximation and beyond the Born-Oppenheimer approximation. For these calculations we have used the non-adiabatic terms found with a penalty on the b-parameters.

Chapter 6

Discussion

The implementation of our method is tested with a convergence plot of the ground state energy of H_2^+, which shows a reasonably fast convergence towards the true ground state energy. This suggests that both the derived matrix elements are correct and that the optimization procedure works correctly.

6.1 Adiabatic results

The implementation of the Born-Oppenheimer approximation, that is, including the delta function in the matrix elements, is tested by using only diagonal correlation matrices and excluding the proton-proton repulsion. This yields the expected limits for the PES of the ground state with reasonable convergence already achieved with a basis consisting of two ECGs.

Including the proton-proton repulsion only gives an energy minimum if non-diagonal correlation matrices are used. For the ground state, we find a minimum of -0.601 Ha at a distance of 1.99 a_0 with a basis consisting of four ECGs. This is in great agreement with other literature that calculates the PES of H_2^+ in the Born-Oppenheimer approximation, which finds a minimum of -0.6026 Ha at a distance of 1.997 a_0 for the ground state [19]. This is in contrast to the previous master's theses [1, 2], which combine the method of ECGs with the Born-Oppenheimer approximation. Both of these found a lower minimum in the PES at a closer distance of around 1 a_0. This is likely caused by the fact that [1] does not consider the c_2 term in the kinetic energy with a delta function matrix element, while [2] sets it to zero. We again see that the convergence as a function of the basis size is relatively quick.

The PES of the first excited state goes to the expected limit at large distances. The first excited state in our calculations corresponds to the $3d\sigma_g$

state [20]. For this state, other numerical calculations [19, 20] using other methods find a minimum in the PES of around −0.175 Ha at a distance of 8.8 a_0. This is considerably lower than our minimum of −0.164 Ha, indicating that a much larger basis is needed for the energy of the first excited state to converge. This is probably also what causes our minimum to be positioned at a slightly higher y_0 value. We also find that the PES of the first excited state contains a kink just above $y_0 = 5\ \mathrm{a}_0$, which is caused by an avoided crossing between the $3d\sigma_g$ and $2s\sigma_g$ states. This is in relatively good agreement with other literature [20], which finds the avoided crossing between these states at 4 a_0. The difference in the positions of the avoided crossing is again likely due to our calculated PES not being fully converged.

The reduced radial wave functions are then found with the finite difference method using our calculated PES. For the ground state, we obtain a total of 17 bound states. This is close to the true number of 19 bound states for the ground state [21, 22]. The reason for us having fewer bound states is likely that our potential energy surface is not accurate enough and that a larger basis size is needed. The lowest lying bound state we obtain has an energy of −0.596 Ha, which is very close to the true value of −0.597 Ha [16].

6.2 Non-adiabatic effects

The non-adiabatic terms are calculated numerically using finite difference formulas. In general, the calculated non-adiabatic terms show a non-smooth nature as a function of y_0, which is evident from figure 5.7. The spikes indicate that the variational b-parameters in the ECGs change significantly between y_0 values, jumping from one local minimum to another during the optimization procedure. One solution to this problem is to restrict the b-parameters from varying too much between y_0 values, which we do by minimizing the quantity in equation 5.3. Using this, we managed to obtain a smooth curve for Q_{00} that follows the expected trends. That is, it remains negative at all points and approaches zero as y_0 becomes large. However, even when restricting the b-parameters in this way, the Q_{01}, Q_{10}, P_{01} and P_{10} terms do not become smooth. Thus, the b-parameters seem more prone to making large jumps when optimizing the first excited state than when optimizing the ground state.

Generally, we expect the first order coupling terms P_{mn} $(m \neq n)$ to be neither very small nor very large. Only near avoided crossings should these terms become large [18, 23]. This somewhat matches our findings, as we see a clear spike in all the coupling terms just around the y_0 value of the avoided crossing.

Including the non-adiabatic effects in the radial equation for the energy only has a small impact on the final energy. As expected, the addition of the Q_{00} term slightly increases the energy. However, including more non-adiabatic terms only has a negligible effect on the energy, which most likely is a consequence of us only obtaining a smooth curve for Q_{00}. The non-smooth behavior of the Q_{01}, Q_{10}, P_{01} and P_{10} terms means that one should be careful drawing any meaningful conclusions from these. Nevertheless, the overall small effect of the non-adiabatic terms on the final energy indicates that the H_2^+ system can be described very well within the Born-Oppenheimer approximation.

6.3 Future work

The next step in combining the Born-Oppenheimer approximation with the method of ECGs is to further investigate the non-adiabatic terms. Here, the focus should be on investigating whether the non-smooth behavior of these is an intrinsic characteristic of the ECGs, or if it is related to the optimization procedure. One possibility is to try using deterministic global optimization instead of the stochastic type used in this thesis. This way, we should not end up in local minima, reducing the risk that the b-parameters make large jumps between different values of y_0. Another option is to further refine the optimization procedure used here by finding a better way to restrict how the b-parameters vary between y_0 values. This could include coming up with a more complex penalty term on the b-parameters in expression 5.3.

Chapter 7

Conclusion

In this thesis, we further investigated the method of explicitly correlated Gaussians combined with the Born-Oppenheimer approximation, building upon two earlier master's theses [1, 2]. These laid the groundwork for the method but did not reach the calculations of the non-adiabatic terms, which we have calculated and discussed in this thesis.

We started out by going through the relevant theory, including the derivations of the analytical matrix elements, where we corrected the calculations and the implementation of these. We then described the methods used in the numerical implementation. The method was tested with the H_2^+ system, where we first calculated the ground state energy. We then successfully implemented the Born-Oppenheimer approximation, where our results are consistent with literature that uses different methods. This is in contrast to the previous studies using the method of ECGs [1, 2], which were unable to obtain the correct minimum in the potential energy surface. This is probably caused by them missing a term in the kinetic energy with a delta function matrix element in the numerical implementation. The potential energy surfaces for the ground state converged fast, while the first excited state shows the need for a larger basis size to converge. The potential energy surface for the first excited state displays an avoided crossing, as is the case in other literature. Solving the radial equation for the ground state with the calculated potential energy surface gave results very close to the expected values.

However, going beyond the Born-Oppenheimer approximation turned out to be problematic. The calculated non-adiabatic terms had a non-smooth nature due to the variational b-parameters of the ECGs making large jumps between y_0 values. We tried to circumvent this by adding a penalty term on the b-parameters in the minimization, making them less likely to vary significantly between y_0 values. Using this, we were able to obtain a smooth curve for the non-adiabatic term Q_{00}. However, this did not fix the problem for the non-adiabatic terms coupling the ground state and the first excited state, as these still contained many spikes. As expected, all these coupling terms have a large spike at the avoided crossing. Including the non-adiabatic terms when solving the radial equation only has a small effect on the final energy. As expected, the energy in the Born-Huang approximation lies slightly above the energy in the Born-Oppenheimer approximation. Including more non-adiabatic terms only has a negligible effect on the energy, which may be due to their non-smooth nature. We then discussed future work on the method, focusing on potential solutions to the problems with the non-adiabatic terms.

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Appendix A

Transformation Laws

In this appendix, we will show the transformation laws seen in equations 2.48 and 2.49. In order to do this, we will use the Jacobi coordinate transformation

$$\mathbf{x} = J\mathbf{r} \Leftrightarrow \mathbf{r} = U\mathbf{x}. \tag{A.1}$$

Vectors

Here we look at the expression $\omega_i^\top \mathbf{r}$, where making the change to Jacobi coordinates gives

$$\omega_i^\top \mathbf{r} \rightarrow \omega_i^\top (U\mathbf{x}) = (U^\top \omega_i)^\top \mathbf{x}, \tag{A.2}$$

from which it follows that the transformation law for ω_i is

$$\omega_i \rightarrow U^\top \omega_i. \tag{A.3}$$

Similarly, the transformation law for ω_{ij} is

$$\omega_{ij} \rightarrow U^\top \omega_{ij}. \tag{A.4}$$

Kinetic energy

We now use that we can write the kinetic energy operator as

$$\hat{K} = -\frac{\partial}{\partial \mathbf{r}} \Lambda \frac{\partial}{\partial \mathbf{r}^\top} = -\sum_{i,j=1}^{N} \Lambda_{ij} \frac{\partial}{\partial \vec{r}_i} \cdot \frac{\partial}{\partial \vec{r}_j^\top}. \tag{A.5}$$

Using the chain rule and the Jacobi coordinate transformation on this expression gives

$$\begin{aligned}
\hat{K} = -\sum_{i,j=1}^{N} \Lambda_{ij} \frac{\partial}{\partial \vec{r}_i} \cdot \frac{\partial}{\partial \vec{r}_j^{\mathsf{T}}} &\to -\sum_{i,j=1}^{N} \sum_{k,l=1}^{N} \Lambda_{ij} \frac{\partial}{\partial \vec{x}_k} \frac{\partial \vec{x}_k}{\partial \vec{r}_i} \cdot \frac{\partial}{\partial \vec{x}_l} \frac{\partial \vec{x}_l}{\partial \vec{r}_j} && \text{(A.6)} \\
&= -\sum_{i,j=1}^{N} \sum_{k,l=1}^{N} \Lambda_{ij} J_{ki} J_{lj} \frac{\partial}{\partial \vec{x}_k} \cdot \frac{\partial}{\partial \vec{x}_l} && \text{(A.7)} \\
&= -\sum_{k,l=1}^{N} (J \Lambda J^{\mathsf{T}})_{kl} \, \frac{\partial}{\partial \vec{x}_k} \cdot \frac{\partial}{\partial \vec{x}_l} && \text{(A.8)} \\
&= -\frac{\partial}{\partial \mathbf{x}} J \Lambda J^{\mathsf{T}} \frac{\partial}{\partial \mathbf{x}^{\mathsf{T}}}, && \text{(A.9)}
\end{aligned}$$

where it becomes clear that the transformation law for the Λ matrix is

$$\Lambda \to J \Lambda J^{\mathsf{T}}. \tag{A.10}$$

Appendix B

Positive-Definite Matrices and Differentiation Identities

This appendix covers the definition of positive-definite matrices, as well as their most important properties, which we will need in the derivations of the matrix elements. We will also show some general differentiation identities that will also be used in the calculations of the matrix elements.

B.1 Positive-definite matrices

The theory in this section is based on multiple sources [24, 25].

Definition of quadratic form
Let $M \in \mathbb{R}^{N\times N}$ and $\mathbf{x} \in \mathbb{R}^N$. The quadratic form of M is given by the expression

$$\mathbf{x}^\intercal M\mathbf{x}. \tag{B.1}$$

Definition of a positive-definite matrix
A matrix $M \in \mathbb{R}^{N\times N}$ is said to be positive-definite if

$$\mathbf{x}^\intercal M\mathbf{x} > 0 \tag{B.2}$$

for all $\mathbf{x} \in \mathbb{R}^N \setminus \{\mathbf{0}\}$.

Properties of positive-definite matrices
Let $M \in \mathbb{R}^{N\times N}$ be positive-definite. The matrix M then has the following properties.

1. Without loss of generality, M can be assumed to be symmetric.
2. The diagonal elements satisfy $M_{ii} > 0$ for $i = 1, 2, \dots N$.
3. M is invertible and its inverse M^{-1} is also positive-definite.
4. The sum of positive-definite matrices is also positive-definite.

B.2 Differentiation identities

The simplest derivative is that of a vector $\mathbf{r}$, which is given by

$$\frac{\partial}{\partial \mathbf{r}}\mathbf{r} = \sum_{i=1}^{N} \frac{\partial}{\partial \vec{r}_i}\vec{r}_i = \sum_{i=1}^{N}\sum_{j=1}^{3}\left(\frac{\partial}{\partial \vec{r}_i}\right)_j \left(\vec{r}_i\right)_j = \sum_{i=1}^{N}\sum_{j=1}^{3} 1 = 3N. \tag{B.3}$$

The next derivative we need is that of $M\mathbf{r}$, where M is an $N \times N$ matrix that does not depend on $\mathbf{r}$. This derivative is given by

$$\frac{\partial}{\partial \mathbf{r}} M\mathbf{r} = \sum_{i=1}^{N}\sum_{j=1}^{N} \frac{\partial}{\partial \vec{r}_i} M_{ij}\vec{r}_j = 3\sum_{i=1}^{N}\sum_{j=1}^{N} M_{ij}\delta_{ij} = 3\sum_{i=1}^{N} M_{ii} = 3\,\mathrm{Tr}\left(M\right). \tag{B.4}$$

We now show the derivative of the form $\mathbf{v}^\mathsf{T}\mathbf{r}$, which can be written as

$$\frac{\partial}{\partial \mathbf{r}}\mathbf{v}^\mathsf{T}\mathbf{r} = \left(\frac{\partial}{\partial \vec{r}_1}\sum_{i=1}^{N}\vec{v}_i\cdot\vec{r}_i, \dots, \frac{\partial}{\partial \vec{r}_N}\sum_{i=1}^{N}\vec{v}_i\cdot\vec{r}_i\right) = \left(\vec{v}_1, \dots, \vec{v}_N\right) = \mathbf{v}^\mathsf{T}. \tag{B.5}$$

In a similar way, one finds

$$\frac{\partial}{\partial \mathbf{r}^\mathsf{T}}\mathbf{v}^\mathsf{T}\mathbf{r} = \mathbf{v}. \tag{B.6}$$

We now consider the derivative of the expression $\mathbf{r}^\mathsf{T}M\mathbf{r}$. If M is symmetric, then the i'th entry in the derivative is given by

$$\left(\frac{\partial}{\partial \mathbf{r}}\mathbf{r}^\mathsf{T}M\mathbf{r}\right)_i = \frac{\partial}{\partial \vec{r}_i}\sum_{j=1}^{N}\sum_{k=1}^{N} M_{jk}\vec{r}_j\cdot\vec{r}_k \tag{B.7}$$

$$= \sum_{j=1}^{N}\sum_{k=1}^{N} M_{jk}\left(\delta_{ij}\vec{r}_k + \vec{r}_j\delta_{ik}\right) \tag{B.8}$$

$$= \sum_{k=1}^{N} M_{ik}\vec{r}_k + \sum_{j=1}^{N} M_{ji}\vec{r}_j \tag{B.9}$$

$$= 2\sum_{j=1}^{N} M_{ji}\vec{r}_j \tag{B.10}$$

$$= 2\left(\mathbf{r}^\mathsf{T}M\right)_i, \tag{B.11}$$

such that

$$\frac{\partial}{\partial \mathbf{r}} \mathbf{r}^{\mathsf{T}} M \mathbf{r} = 2\mathbf{r}^{\mathsf{T}} M. \tag{B.12}$$

Similarly, one can obtain the transposed derivative

$$\frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}} \mathbf{r}^{\mathsf{T}} M \mathbf{r} = 2M\mathbf{r}. \tag{B.13}$$

If we let $f(g(\mathbf{r}))$ be a scalar function, we are interested in the second order derivative of this expression. It can be shown that the second order derivative of this scalar function is [2]

$$\frac{\partial}{\partial \mathbf{r}} M \frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}} f(g(\mathbf{r})) = f''(g(\mathbf{r})) \frac{\partial g(\mathbf{r})}{\partial \mathbf{r}} M \frac{\partial g(\mathbf{r})}{\partial \mathbf{r}^{\mathsf{T}}} + f'(g(\mathbf{r})) \frac{\partial}{\partial \mathbf{r}} M \frac{\partial g(\mathbf{r})}{\partial \mathbf{r}^{\mathsf{T}}}. \tag{B.14}$$

Appendix C

Matrix Element Calculations

Overlap matrix element

The overlap between two ECGs can be written as

$$\begin{aligned}
\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle &= \int_{\mathbb{R}^{3N}} d\mathbf{r} \, \langle B, \mathbf{s}_b | \mathbf{r} \rangle \langle \mathbf{r} | A, \mathbf{s}_a \rangle && \text{(C.1)} \\
&= \int d^3\vec{r}_1 \ldots d^3\vec{r}_N \exp\left(-\mathbf{r}^\intercal B \mathbf{r} + \mathbf{s}_b^\intercal \mathbf{r}\right) \exp\left(-\mathbf{r}^\intercal A \mathbf{r} + \mathbf{s}_a^\intercal \mathbf{r}\right) && \text{(C.2)} \\
&= \int d^3\vec{r}_1 \ldots d^3\vec{r}_N \exp\left(-\mathbf{r}^\intercal (A + B) \mathbf{r} + \left(\mathbf{s}_a^\intercal + \mathbf{s}_b^\intercal\right) \mathbf{r}\right) && \text{(C.3)} \\
&= \int d^3\vec{r}_1 \ldots d^3\vec{r}_N \exp(-\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}), && \text{(C.4)}
\end{aligned}$$

where $C = A + B$ and $\mathbf{v} = \mathbf{s}_a + \mathbf{s}_b$. From property 1 both A and B can be assumed to be symmetric. The matrix C is then also symmetric by property 4. By the spectral theorem we can then write $C = QDQ^\intercal$, with Q an orthogonal matrix and D a diagonal matrix [26]. The above expression can then be written as

$$\begin{aligned}
\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle &= \int d^3\vec{r}_1 \ldots d^3\vec{r}_N \exp(-\mathbf{r}^\intercal QDQ^\intercal \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}) && \text{(C.5)} \\
&= \int d^3\vec{x}_1 \ldots d^3\vec{x}_N \exp\left(-\mathbf{x}^\intercal D \mathbf{x} + \mathbf{v}'^\intercal \mathbf{x}\right), && \text{(C.6)}
\end{aligned}$$

where $\mathbf{x} = Q^\intercal \mathbf{r}$ and $\mathbf{v}'^\intercal = \mathbf{v}^\intercal Q$. Here, we have changed coordinates from $\mathbf{r}$ to $\mathbf{x}$, which we can do without introducing any Jacobian factor or changing the integration region [2]. Writing out the exponent in component form gives

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle = \int d^3\vec{x}_1 \dots d^3\vec{x}_N \exp\left(-\mathbf{x}^\intercal D\mathbf{x} + \mathbf{v}'^\intercal \mathbf{x}\right) \tag{C.7}$$

$$= \int d^3\vec{x}_1 \dots d^3\vec{x}_N \exp\left(\sum_{i=1}^{N} -D_{ii}\vec{x}_i \cdot \vec{x}_i + \vec{v}_i' \cdot \vec{x}_i\right) \tag{C.8}$$

$$= \int d^3\vec{x}_1 \dots d^3\vec{x}_N \exp\left(\sum_{i=1}^{N}\sum_{j=1}^{3} -D_{ii}\left(\vec{x}_i\right)_j^2 + \left(\vec{v}_i'\right)_j\left(\vec{x}_i\right)_j\right), \tag{C.9}$$

where we have used the fact that D is diagonal when expanding the exponent. By completing the square, we obtain

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle = \int d^3\vec{x}_1 \dots d^3\vec{x}_N \exp\left(\sum_{i=1}^{N}\sum_{j=1}^{3} -D_{ii}\left[\left(\vec{x}_i\right)_j - \frac{\left(\vec{v}_i'\right)_j}{2D_{ii}}\right]^2 + \frac{\left(\vec{v}_i'\right)_j^2}{4D_{ii}}\right) \tag{C.10}$$

$$= \int d^3\vec{x}_1 \dots d^3\vec{x}_N \prod_{i=1}^{N} \exp\left(\sum_{j=1}^{3} -D_{ii}\left[\left(\vec{x}_i\right)_j - \frac{\left(\vec{v}_i'\right)_j}{2D_{ii}}\right]^2 + \frac{\left(\vec{v}_i'\right)_j^2}{4D_{ii}}\right) \tag{C.11}$$

$$= \prod_{i=1}^{N} \int_{\mathbb{R}^3} d^3\vec{x}_i \exp\left(\sum_{j=1}^{3} -D_{ii}\left[\left(\vec{x}_i\right)_j - \frac{\left(\vec{v}_i'\right)_j}{2D_{ii}}\right]^2 + \frac{\left(\vec{v}_i'\right)_j^2}{4D_{ii}}\right) \tag{C.12}$$

$$= \prod_{i=1}^{N} \int d^3\vec{x}_i \prod_{j=1}^{3} \exp\left(-D_{ii}\left[\left(\vec{x}_i\right)_j - \frac{\left(\vec{v}_i'\right)_j}{2D_{ii}}\right]^2 + \frac{\left(\vec{v}_i'\right)_j^2}{4D_{ii}}\right) \tag{C.13}$$

$$= \prod_{i=1}^{N}\prod_{j=1}^{3} \int_{-\infty}^{\infty} d\left(\vec{x}_i\right)_j \exp\left(-D_{ii}\left[\left(\vec{x}_i\right)_j - \frac{\left(\vec{v}_i'\right)_j}{2D_{ii}}\right]^2\right) \exp\left(\frac{\left(\vec{v}_i'\right)_j^2}{4D_{ii}}\right) \tag{C.14}$$

$$= \prod_{i=1}^{N}\prod_{j=1}^{3} \exp\left(\frac{\left(\vec{v}_i'\right)_j^2}{4D_{ii}}\right)\left(\frac{\pi}{D_{ii}}\right)^{1/2} \tag{C.15}$$

$$= \prod_{i=1}^{N} \exp\left(\frac{\vec{v}_i' \cdot \vec{v}_i'}{4D_{ii}}\right)\left(\frac{\pi}{D_{ii}}\right)^{3/2}, \tag{C.16}$$

where we have used the formula $\int_{-\infty}^{\infty} dx \exp\left(-a\left(x-b\right)^2\right) = \left(\frac{\pi}{a}\right)^{1/2}$ [27] and the fact that $D_{ii} > 0$ (see property 2). If we let $\mathbf{u} \neq 0$ be an arbitrary vector, then

$$\mathbf{u}^\intercal D\mathbf{u} = \mathbf{u}^\intercal Q^\intercal C Q\mathbf{u} = \mathbf{w}^\intercal C\mathbf{w} > 0, \tag{C.17}$$

since C is positive-definite. We also used the fact that $\mathbf{w} = Q\mathbf{u} \neq 0$, since Q is invertible. This shows that D is positive-definite and since it is diagonal, we get

$$\begin{aligned}\prod_{i=1}^{N} D_{ii} &= \det(D) = \det(Q^{\mathsf{T}})\det(C)\det(Q)\\ &= \det(Q^{\mathsf{T}}Q)\det(C) = \det(I)\det(C) = \det(C).\end{aligned} \tag{C.18}$$

Using this together with the fact that D^{-1} is diagonal with entries given by $\frac{1}{D_{ii}}$, the overlap becomes

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a\rangle = \exp\left(\sum_{i=1}^{N} \frac{\vec{v}_i' \cdot \vec{v}_i'}{4D_{ii}}\right)\left(\frac{\pi^N}{\det(D)}\right)^{3/2} \tag{C.19}$$

$$= \exp\left(\frac{1}{4}\sum_{i=1}^{N} (D_{ii})^{-1}\vec{v}_i' \cdot \vec{v}_i'\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2} \tag{C.20}$$

$$= \exp\left(\frac{1}{4}\mathbf{v}'^{\mathsf{T}} D^{-1}\mathbf{v}'\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2} \tag{C.21}$$

$$= \exp\left(\frac{1}{4}\mathbf{v}^{\mathsf{T}} Q\left(Q^{\mathsf{T}}C^{-1}Q\right)Q^{\mathsf{T}}\mathbf{v}\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2} \tag{C.22}$$

$$= \exp\left(\frac{1}{4}\mathbf{v}^{\mathsf{T}} C^{-1}\mathbf{v}\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2} \equiv M(C, \mathbf{v}). \tag{C.23}$$

The matrix element for s-waves is obtained by setting $\mathbf{s}_a = \mathbf{s}_b = 0$, which implies that $\mathbf{v} = 0$. The overlap in this case is then

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a\rangle \overset{\mathbf{v}=0}{=} \left(\frac{\pi^N}{\det(C)}\right)^{3/2} = M(C, \mathbf{v} = 0) \equiv M_0. \tag{C.24}$$

Position matrix element

The matrix element we want to calculate here is

$$\langle B, \mathbf{s}_b | \mathbf{r} | A, \mathbf{s}_a\rangle = \int d\mathbf{r}\ \langle B, \mathbf{s}_b | \mathbf{r}\rangle\ \mathbf{r}\ \langle \mathbf{r} | A, \mathbf{s}_a\rangle \tag{C.25}$$

$$= \int d^3\vec{r}_1 \dots d^3\vec{r}_N\ \mathbf{r}\exp\left(-\mathbf{r}^{\mathsf{T}}C\mathbf{r} + \mathbf{v}^{\mathsf{T}}\mathbf{r}\right) \tag{C.26}$$

$$= \int d^3\vec{r}_1 \dots d^3\vec{r}_N \frac{\partial}{\partial \mathbf{v}^{\mathsf{T}}}\exp\left(-\mathbf{r}^{\mathsf{T}}C\mathbf{r} + \mathbf{v}^{\mathsf{T}}\mathbf{r}\right) \tag{C.27}$$

$$= \frac{\partial}{\partial \mathbf{v}^{\mathsf{T}}}\int d^3\vec{r}_1 \dots d^3\vec{r}_N \exp\left(-\mathbf{r}^{\mathsf{T}}C\mathbf{r} + \mathbf{v}^{\mathsf{T}}\mathbf{r}\right) \tag{C.28}$$

$$= \frac{\partial}{\partial \mathbf{v}^{\mathsf{T}}}\langle B, \mathbf{s}_b | A, \mathbf{s}_a\rangle \tag{C.29}$$

$$= \frac{\partial}{\partial \mathbf{v}^{\mathsf{T}}}\exp\left(\frac{1}{4}\mathbf{v}^{\mathsf{T}}C^{-1}\mathbf{v}\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2}. \tag{C.30}$$

This derivative can be calculated using equation B.13, where we get

$$\langle B, \mathbf{s}_b | \mathbf{r} | A, \mathbf{s}_a \rangle = \exp\left(\frac{1}{4}\mathbf{v}^\intercal C^{-1}\mathbf{v}\right)\frac{\partial}{\partial \mathbf{v}^\intercal}\left(\frac{1}{4}\mathbf{v}^\intercal C^{-1}\mathbf{v}\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2} \tag{C.31}$$

$$= \frac{1}{2}C^{-1}\mathbf{v}M\left(C, \mathbf{v}\right). \tag{C.32}$$

Here we have also used the fact that since C is symmetric, so is C^{-1}. A similar calculation gives

$$\langle B, \mathbf{s}_b | \mathbf{r}^\intercal | A, \mathbf{s}_a \rangle = \frac{1}{2}\mathbf{v}^\intercal C^{-1}M\left(C, \mathbf{v}\right). \tag{C.33}$$

Both of these matrix elements vanish for s-waves, which is as expected due to spherical symmetry.

Quadratic form matrix element

The matrix element of interest is

$$\langle B, \mathbf{s}_b | \mathbf{r}^\intercal F \mathbf{r} | A, \mathbf{s}_a \rangle = \int d\mathbf{r}\, \langle B, \mathbf{s}_b | \mathbf{r} \rangle\, \mathbf{r}^\intercal F \mathbf{r}\, \langle \mathbf{r} | A, \mathbf{s}_a \rangle \tag{C.34}$$

$$= \int d^3\vec{r}_1 \dots d^3\vec{r}_N\ \mathbf{r}^\intercal F \mathbf{r} \exp\left(-\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}\right). \tag{C.35}$$

We first compute the second order derivative

$$\frac{\partial}{\partial \mathbf{v}} F \frac{\partial}{\partial \mathbf{v}^\intercal} \exp\left(-\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}\right), \tag{C.36}$$

using equation B.14 with $g(\mathbf{v}) = -\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}$, $f(x) = \exp(x)$ and $M = F$. From the identities in section B.2, we get

$$\frac{\partial g}{\partial \mathbf{v}^\intercal} = \frac{\partial}{\partial \mathbf{v}^\intercal}\left(-\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}\right) = \mathbf{r} \tag{C.37}$$

$$\frac{\partial g}{\partial \mathbf{v}} = \frac{\partial}{\partial \mathbf{v}}\left(-\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}\right) = \mathbf{r}^\intercal \tag{C.38}$$

$$\frac{\partial}{\partial \mathbf{v}} F \frac{\partial g}{\partial \mathbf{v}^\intercal} = \frac{\partial}{\partial \mathbf{v}}\left(F\mathbf{r}\right) = 0 \tag{C.39}$$

$$\Downarrow$$

$$\frac{\partial}{\partial \mathbf{v}} F \frac{\partial}{\partial \mathbf{v}^\intercal} \exp\left(-\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}\right) = \exp\left(-\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}\right) \mathbf{r}^\intercal F \mathbf{r}. \tag{C.40}$$

Inserting this result into the matrix element, we get

$$\langle B, \mathbf{s}_b | \mathbf{r}^\intercal F \mathbf{r} | A, \mathbf{s}_a \rangle = \int d^3\vec{r}_1 \dots d^3\vec{r}_N \frac{\partial}{\partial \mathbf{v}} F \frac{\partial}{\partial \mathbf{v}^\intercal} \exp\left(-\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}\right) \tag{C.41}$$

$$= \frac{\partial}{\partial \mathbf{v}} F \frac{\partial}{\partial \mathbf{v}^\intercal} \int d^3\vec{r}_1 \dots d^3\vec{r}_N \exp\left(-\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}\right) \tag{C.42}$$

$$= \frac{\partial}{\partial \mathbf{v}} F \frac{\partial}{\partial \mathbf{v}^\intercal} \langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle \tag{C.43}$$

$$= \frac{\partial}{\partial \mathbf{v}} F \frac{\partial}{\partial \mathbf{v}^\intercal} \left[\exp\left(\frac{1}{4} \mathbf{v}^\intercal C^{-1} \mathbf{v}\right) \left(\frac{\pi^N}{\det(C)}\right)^{3/2} \right]. \tag{C.44}$$

To calculate the above derivative, we again apply equation B.14, this time with $g(\mathbf{v}) = \frac{1}{4}\mathbf{v}^\intercal C^{-1}\mathbf{v}$, $f(x) = \exp(x)$ and $M = F$, which gives

$$\frac{\partial g}{\partial \mathbf{v}^\intercal} = \frac{\partial}{\partial \mathbf{v}^\intercal} \left(\frac{1}{4} \mathbf{v}^\intercal C^{-1} \mathbf{v}\right) = \frac{1}{2} C^{-1} \mathbf{v} \tag{C.45}$$

$$\frac{\partial g}{\partial \mathbf{v}} = \frac{\partial}{\partial \mathbf{v}} \left(\frac{1}{4} \mathbf{v}^\intercal C^{-1} \mathbf{v}\right) = \frac{1}{2} \mathbf{v}^\intercal C^{-1} \tag{C.46}$$

$$\frac{\partial}{\partial \mathbf{v}} F \frac{\partial g}{\partial \mathbf{v}^\intercal} = \frac{\partial}{\partial \mathbf{v}} \left(\frac{1}{2} F C^{-1} \mathbf{v}\right) = \frac{3}{2} \operatorname{Tr}\left(F C^{-1}\right) \tag{C.47}$$

$$\Downarrow$$

$$\frac{\partial}{\partial \mathbf{v}} F \frac{\partial}{\partial \mathbf{v}^\intercal} \exp\left(\frac{1}{4} \mathbf{v}^\intercal C^{-1} \mathbf{v}\right)$$

$$= \frac{1}{4} \exp\left(\frac{1}{4} \mathbf{v}^\intercal C^{-1} \mathbf{v}\right) \mathbf{v}^\intercal C^{-1} F C^{-1} \mathbf{v} + \exp\left(\frac{1}{4} \mathbf{v}^\intercal C^{-1} \mathbf{v}\right) \frac{3}{2} \operatorname{Tr}\left(F C^{-1}\right), \tag{C.48}$$

where we again have used the identities in section B.2. Inserting this into the matrix element gives

$$\langle B, \mathbf{s}_b | \mathbf{r}^\intercal F \mathbf{r} | A, \mathbf{s}_a \rangle = M(C, \mathbf{v}) \left[\frac{1}{4} \mathbf{v}^\intercal C^{-1} F C^{-1} \mathbf{v} + \frac{3}{2} \operatorname{Tr}\left(F C^{-1}\right) \right], \tag{C.49}$$

which for s-waves becomes

$$\langle B, \mathbf{s}_b | \mathbf{r}^\intercal F \mathbf{r} | A, \mathbf{s}_a \rangle \overset{\mathbf{v}=0}{=} \frac{3}{2} M_0 \operatorname{Tr}\left(F C^{-1}\right). \tag{C.50}$$

Plane wave matrix element

In this section, we calculate the matrix element of a plane wave with wave vector $\vec{k}$. This matrix element can be written as

$$\left\langle B, \mathbf{s}_b \middle| \exp\left(i\vec{k} \cdot \omega_0^\intercal \mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle \tag{C.51}$$

$$= \int d^3\vec{r}_1 \dots d^3\vec{r}_N \exp\left(-\mathbf{r}^\intercal C \mathbf{r} + \mathbf{v}^\intercal \mathbf{r}\right) \exp\left(i\vec{k} \cdot \omega_0^\intercal \mathbf{r}\right) \tag{C.52}$$

$$= \int d^3\vec{r}_1 \dots d^3\vec{r}_N \exp\left(-\mathbf{r}^\intercal C \mathbf{r} + \left(\mathbf{v} + i\vec{k}\omega_0\right)^\intercal \mathbf{r}\right). \tag{C.53}$$

This is just the standard overlap with a different shift vector $\mathbf{v} \to \mathbf{v} + i\vec{k}\omega_0$. It can be shown that the result in equation C.23 also holds for complex shift vectors [2], so we get

$$\left\langle B, \mathbf{s}_b \middle| \exp\left(i\vec{k} \cdot \omega_0^\mathsf{T}\mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle \tag{C.54}$$

$$= M\left(C, \mathbf{v} + i\vec{k}\omega_0\right) \tag{C.55}$$

$$= \exp\left(\frac{1}{4}\left(\mathbf{v} + i\vec{k}\omega_0\right)^\mathsf{T} C^{-1}\left(\mathbf{v} + i\vec{k}\omega_0\right)\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2} \tag{C.56}$$

$$= \exp\left(\frac{1}{4}\left[\mathbf{v}^\mathsf{T}C^{-1}\mathbf{v} - \vec{k}\cdot\vec{k}\omega_0^\mathsf{T}C^{-1}\omega_0 + i\vec{k}\cdot\mathbf{v}^\mathsf{T}C^{-1}\omega_0 + i\vec{k}\cdot\omega_0^\mathsf{T}C^{-1}\mathbf{v}\right]\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2}. \tag{C.57}$$

As a scalar is equal to its transpose, we have

$$\vec{k}\cdot\mathbf{v}^\mathsf{T}C^{-1}\omega_0 = \left(\vec{k}\cdot\mathbf{v}^\mathsf{T}C^{-1}\omega_0\right)^\mathsf{T} = \vec{k}\cdot\omega_0^\mathsf{T}C^{-1}\mathbf{v}. \tag{C.58}$$

The matrix element then becomes

$$\left\langle B, \mathbf{s}_b \middle| \exp\left(i\vec{k} \cdot \omega_0^\mathsf{T}\mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle \tag{C.59}$$

$$= \exp\left(\frac{1}{4}\left[\mathbf{v}^\mathsf{T}C^{-1}\mathbf{v} - k^2\omega_0^\mathsf{T}C^{-1}\omega_0 + 2i\vec{k}\cdot\omega_0^\mathsf{T}C^{-1}\mathbf{v}\right]\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2} \tag{C.60}$$

$$= \exp\left(\frac{1}{4}\mathbf{v}^\mathsf{T}C^{-1}\mathbf{v} - k^2\alpha + i\vec{k}\cdot\vec{q}\right)\left(\frac{\pi^N}{\det(C)}\right)^{3/2} \tag{C.61}$$

$$= M(C, \mathbf{v})\exp\left(-\alpha k^2 + i\vec{k}\cdot\vec{q}\right), \tag{C.62}$$

where $k = |\vec{k}|$ and

$$\alpha = \frac{1}{4}\omega_0^\mathsf{T}C^{-1}\omega_0, \qquad \vec{q} = \frac{1}{2}\omega_0^\mathsf{T}C^{-1}\mathbf{v}. \tag{C.63}$$

As $\vec{q} = 0$ for s-waves, the matrix element in this case becomes

$$\left\langle B, \mathbf{s}_b \middle| \exp\left(i\vec{k} \cdot \omega_0^\mathsf{T}\mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle \overset{\mathbf{v}=\mathbf{0}}{=} M_0 \exp\left(-\alpha k^2\right). \tag{C.64}$$

Delta function matrix element

In order to calculate the delta function matrix element, we express the delta function via its Fourier transform, which can be written as

$$\delta^3\left(\omega_0^\mathsf{T}\mathbf{r} - \vec{y}_0\right) = \int \frac{d^3\vec{k}}{(2\pi)^3}\exp\left(i\vec{k}\cdot\left(\omega_0^\mathsf{T}\mathbf{r} - \vec{y}_0\right)\right). \tag{C.65}$$

The matrix element then becomes

$$
\begin{aligned}
&\langle B, \mathbf{s}_b | \delta^3 \left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) | A, \mathbf{s}_a \rangle \qquad (C.66)\\
&= \left\langle B, \mathbf{s}_b \middle| \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(i\vec{k}\cdot\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right)\right) \middle| A, \mathbf{s}_a \right\rangle \qquad (C.67)\\
&= \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-i\vec{k}\cdot\vec{y}_0\right) \left\langle B, \mathbf{s}_b \middle| \exp\left(i\vec{k}\cdot\omega_0^\intercal \mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle \qquad (C.68)\\
&= \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-i\vec{k}\cdot\vec{y}_0\right) M(C, \mathbf{v}) \exp\left(-\alpha k^2 + i\vec{k}\cdot\vec{q}\right) \qquad (C.69)\\
&= \frac{M(C,\mathbf{v})}{(2\pi)^3} \int d^3\vec{k} \exp\left(-\alpha\left[k^2 - \frac{i}{\alpha}\vec{k}\cdot\left(\vec{q}-\vec{y}_0\right)\right]\right). \qquad (C.70)
\end{aligned}
$$

The exponential can then be written in component form, where completing the square gives

$$
\begin{aligned}
&\langle B, \mathbf{s}_b | \delta^3 \left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) | A, \mathbf{s}_a \rangle \qquad (C.71)\\
&= \frac{M(C,\mathbf{v})}{(2\pi)^3} \int d^3\vec{k} \exp\left(\sum_{j=1}^{3} -\alpha\left[(\vec{k})_j^2 - \frac{i}{\alpha}(\vec{k})_j \cdot \left((\vec{q})_j - (\vec{y}_0)_j\right)\right]\right) \qquad (C.72)\\
&= \frac{M(C,\mathbf{v})}{(2\pi)^3} \int d^3\vec{k} \exp\left(\sum_{j=1}^{3} -\alpha\left[(\vec{k})_j - \frac{i}{2\alpha}\left((\vec{q})_j - (\vec{y}_0)_j\right)\right]^2 - \frac{1}{4\alpha}\left((\vec{q})_j - (\vec{y}_0)_j\right)^2\right) \qquad (C.73)\\
&= \frac{M(C,\mathbf{v})}{(2\pi)^3} \exp\left(-\frac{1}{4\alpha}\left(\vec{q}-\vec{y}_0\right)^2\right) \prod_{j=1}^{3} \int d(\vec{k})_j \exp\left(-\alpha\left[(\vec{k})_j - \frac{i}{2\alpha}\left((\vec{q})_j - (\vec{y}_0)_j\right)\right]^2\right) \qquad (C.74)\\
&= \frac{M(C,\mathbf{v})}{(2\pi)^3} \exp\left(-\frac{1}{4\alpha}\left(\vec{q}-\vec{y}_0\right)^2\right) \left(\frac{\pi}{\alpha}\right)^{3/2}. \qquad (C.75)
\end{aligned}
$$

In the last line, we have used the same integral formula as in the calculation of the overlap, as it also holds for complex shifts [2]. Using property 3, the definition of positive-definite matrices, and the definition of α, one can easily see that $\alpha > 0$. In the case of s-waves the expression reduces to

$$
\langle B, \mathbf{s}_b | \delta^3 \left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) | A, \mathbf{s}_a \rangle \overset{\mathrm{v}=0}{=} \frac{M_0}{(2\pi)^3} \exp\left(-\frac{y_0^2}{4\alpha}\right) \left(\frac{\pi}{\alpha}\right)^{3/2}. \tag{C.76}
$$

Kinetic energy matrix element

We will be using the following derivatives in the calculation of the matrix element

$$\frac{\partial}{\partial \mathbf{r}}\left(\exp\left(-\mathbf{r}^{\mathsf{T}}B\mathbf{r}+\mathbf{s}_b^{\mathsf{T}}\mathbf{r}\right)\right)=\exp\left(-\mathbf{r}^{\mathsf{T}}B\mathbf{r}+\mathbf{s}_b^{\mathsf{T}}\mathbf{r}\right)\cdot\left(-2\mathbf{r}^{\mathsf{T}}B+\mathbf{s}_b^{\mathsf{T}}\right) \tag{C.77}$$

$$\frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}}\left(\exp\left(-\mathbf{r}^{\mathsf{T}}A\mathbf{r}+\mathbf{s}_a^{\mathsf{T}}\mathbf{r}\right)\right)=\exp\left(-\mathbf{r}^{\mathsf{T}}A\mathbf{r}+\mathbf{s}_a^{\mathsf{T}}\mathbf{r}\right)\cdot\left(-2A\mathbf{r}+\mathbf{s}_a\right), \tag{C.78}$$

which follow from the identities in section B.2. Another identity we will need is [28]

$$\left\langle B,\mathbf{s}_b\left|-\frac{\partial}{\partial \mathbf{r}}\Lambda\frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}}\right|A,\mathbf{s}_a\right\rangle=\left(\frac{\partial}{\partial \mathbf{r}}\langle B,\mathbf{s}_b|\right)\Lambda\left(\frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}}|A,\mathbf{s}_a\rangle\right). \tag{C.79}$$

The matrix element is then given by

$$\langle B,\mathbf{s}_b|\hat{K}|A,\mathbf{s}_a\rangle=\left\langle B,\mathbf{s}_b\left|-\frac{\partial}{\partial \mathbf{r}}\Lambda\frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}}\right|A,\mathbf{s}_a\right\rangle \tag{C.80}$$

$$=\left(\frac{\partial}{\partial \mathbf{r}}\langle B,\mathbf{s}_b|\right)\Lambda\left(\frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}}|A,\mathbf{s}_a\rangle\right) \tag{C.81}$$

$$=\langle B,\mathbf{s}_b|\left(\mathbf{s}_b^{\mathsf{T}}-2\mathbf{r}^{\mathsf{T}}B\right)\Lambda\left(\mathbf{s}_a-2A\mathbf{r}\right)|A,\mathbf{s}_a\rangle \tag{C.82}$$

$$\begin{aligned}&=\mathbf{s}_b^{\mathsf{T}}\Lambda\mathbf{s}_a\langle B,\mathbf{s}_b|A,\mathbf{s}_a\rangle-2\left(\mathbf{s}_b^{\mathsf{T}}\Lambda A\langle B,\mathbf{s}_b|\mathbf{r}|A,\mathbf{s}_a\rangle+\langle B,\mathbf{s}_b|\mathbf{r}^{\mathsf{T}}|A,\mathbf{s}_a\rangle B\Lambda\mathbf{s}_a\right)\\&+4\langle B,\mathbf{s}_b|\mathbf{r}^{\mathsf{T}}\left(B\Lambda A\right)\mathbf{r}|A,\mathbf{s}_a\rangle.\end{aligned} \tag{C.83}$$

These are just the previously calculated matrix elements, and by inserting our results found earlier, we obtain

$$\langle B,\mathbf{s}_b|\hat{K}|A,\mathbf{s}_a\rangle \tag{C.84}$$

$$\begin{aligned}&=\mathbf{s}_b^{\mathsf{T}}\Lambda\mathbf{s}_a M\left(C,\mathbf{v}\right)-\mathbf{s}_b^{\mathsf{T}}\Lambda A C^{-1}\mathbf{v}M\left(C,\mathbf{v}\right)-M\left(C,\mathbf{v}\right)\mathbf{v}^{\mathsf{T}}C^{-1}B\Lambda\mathbf{s}_a\\&+M\left(C,\mathbf{v}\right)\left[\mathbf{v}^{\mathsf{T}}C^{-1}B\Lambda A C^{-1}\mathbf{v}+6\operatorname{Tr}\left(B\Lambda A C^{-1}\right)\right]\end{aligned} \tag{C.85}$$

$$=M\left(C,\mathbf{v}\right)\left[6\operatorname{Tr}\left(B\Lambda A C^{-1}\right)+\left(\mathbf{s}_b-BC^{-1}\mathbf{v}\right)^{\mathsf{T}}\Lambda\left(\mathbf{s}_a-AC^{-1}\mathbf{v}\right)\right]. \tag{C.86}$$

For s-waves the matrix element becomes

$$\langle B,\mathbf{s}_b|\hat{K}|A,\mathbf{s}_a\rangle\overset{\mathbf{v}=0}{=}6M_0\operatorname{Tr}\left(B\Lambda A C^{-1}\right). \tag{C.87}$$

Kinetic energy with plane wave matrix element

In this calculation, we will need the following derivative

$$\frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}}\left(\exp\left(i\vec{k}\cdot\omega_0^{\mathsf{T}}\mathbf{r}\right)\exp\left(-\mathbf{r}^{\mathsf{T}}A\mathbf{r}+\mathbf{s}_a^{\mathsf{T}}\mathbf{r}\right)\right) \tag{C.88}$$

$$=\frac{\partial}{\partial \mathbf{r}^{\mathsf{T}}}\left(\exp\left(-\mathbf{r}^{\mathsf{T}}A\mathbf{r}+(\mathbf{s}_a+i\vec{k}\omega_0)^{\mathsf{T}}\mathbf{r}\right)\right) \tag{C.89}$$

$$=\exp\left(-\mathbf{r}^{\mathsf{T}}A\mathbf{r}+(\mathbf{s}_a+i\vec{k}\omega_0)^{\mathsf{T}}\mathbf{r}\right)\left(-2A\mathbf{r}+(\mathbf{s}_a+i\vec{k}\omega_0)\right). \tag{C.90}$$

Using this, the matrix element of interest can now be written as

$$\left\langle B, \mathbf{s}_b \middle| \hat{K} \exp\left(i\vec{k}\cdot\omega_0^{\mathsf{T}}\mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle \tag{C.91}$$

$$= \left\langle B, \mathbf{s}_b \middle| -\frac{\partial}{\partial\mathbf{r}}\Lambda\frac{\partial}{\partial\mathbf{r}^{\mathsf{T}}} \exp\left(i\vec{k}\cdot\omega_0^{\mathsf{T}}\mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle \tag{C.92}$$

$$= \left(\frac{\partial}{\partial\mathbf{r}}\langle B, \mathbf{s}_b|\right)\Lambda\left(\frac{\partial}{\partial\mathbf{r}^{\mathsf{T}}} \exp\left(i\vec{k}\cdot\omega_0^{\mathsf{T}}\mathbf{r}\right)|A, \mathbf{s}_a\rangle\right) \tag{C.93}$$

$$= \left\langle B, \mathbf{s}_b \middle| \left(\mathbf{s}_b^{\mathsf{T}} - 2\mathbf{r}^{\mathsf{T}}B\right)\Lambda\left((\mathbf{s}_a + i\vec{k}\omega_0) - 2A\mathbf{r}\right) \middle| A, \mathbf{s}_a + i\vec{k}\omega_0 \right\rangle . \tag{C.94}$$

But this is simply the kinetic energy matrix element where we have made the substitution $\mathbf{s}_a \to \mathbf{s}_a + i\vec{k}\omega_0$, so we get

$$\left\langle B, \mathbf{s}_b \middle| \hat{K} \exp\left(i\vec{k}\cdot\omega_0^{\mathsf{T}}\mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle = M\left(C, \mathbf{v} + i\vec{k}\omega_0\right)\times$$
$$\left[6\,\mathrm{Tr}\left(B\Lambda AC^{-1}\right) + \left(\mathbf{s}_b - BC^{-1}(\mathbf{v} + i\vec{k}\omega_0)\right)^{\mathsf{T}}\Lambda\left((\mathbf{s}_a + i\vec{k}\omega_0) - AC^{-1}(\mathbf{v} + i\vec{k}\omega_0)\right)\right]. \tag{C.95}$$

Now using that $M\left(C, \mathbf{v} + i\vec{k}\omega_0\right)$ is just the plane wave matrix element, and inserting our result from there gives us the following result

$$\left\langle B, \mathbf{s}_b \middle| \hat{K} \exp\left(i\vec{k}\cdot\omega_0^{\mathsf{T}}\mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle = M(C, \mathbf{v})\exp\left(-\alpha k^2 + i\vec{k}\cdot\vec{q}\right)\times$$
$$\left[6\,\mathrm{Tr}\left(B\Lambda AC^{-1}\right) + \left(\mathbf{s}_b - BC^{-1}(\mathbf{v} + i\vec{k}\omega_0)\right)^{\mathsf{T}}\Lambda\left((\mathbf{s}_a + i\vec{k}\omega_0) - AC^{-1}(\mathbf{v} + i\vec{k}\omega_0)\right)\right], \tag{C.96}$$

which for s-waves reduces to

$$\left\langle B, \mathbf{s}_b \middle| \hat{K} \exp\left(i\vec{k}\cdot\omega_0^{\mathsf{T}}\mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle \overset{\mathrm{v}=0}{=} M_0\exp\left(-\alpha k^2\right)\times$$
$$\left[6\,\mathrm{Tr}\left(B\Lambda AC^{-1}\right) + k^2\omega_0^{\mathsf{T}}BC^{-1}\Lambda\omega_0 - k^2\omega_0^{\mathsf{T}}BC^{-1}\Lambda AC^{-1}\omega_0\right]. \tag{C.97}$$

The matrix element can be simplified by setting some restrictions on Λ. Here, we require Λ to be diagonal and to satisfy $\Lambda\omega_0 = 0$ (and equivalently $\omega_0^{\mathsf{T}}\Lambda = 0$), since we do not want the slow coordinate to contribute any kinetic energy. If we also let A and B be diagonal, then C^{-1} will also be diagonal, and equation C.96 can be written as

$$\left\langle B, \mathbf{s}_b \middle| \hat{K} \exp\left(i\vec{k}\cdot\omega_0^{\mathsf{T}}\mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle = M(C, \mathbf{v})\exp\left(-\alpha k^2 + i\vec{k}\cdot\vec{q}\right)\times$$
$$\left[6\,\mathrm{Tr}\left(B\Lambda AC^{-1}\right) + \left(\mathbf{s}_b - BC^{-1}\mathbf{v}\right)^{\mathsf{T}}\Lambda\left((\mathbf{s}_a - AC^{-1}\mathbf{v}\right)\right] \tag{C.98}$$

$$= \exp\left(-\alpha k^2 + i\vec{k}\cdot\vec{q}\right)\langle B, \mathbf{s}_b|\hat{K}|A, \mathbf{s}_a\rangle, \tag{C.99}$$

where we have used the fact that diagonal matrices commute and that the terms containing $\Lambda\omega_0$ or $\omega_0^{\mathsf{T}}\Lambda$ are zero. For s-waves this becomes

$$\left\langle B, \mathbf{s}_b \middle| \hat{K} \exp\left(i\vec{k}\cdot\omega_0^{\mathsf{T}}\mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle \overset{\mathrm{v}=0}{=} 6M_0\,\mathrm{Tr}\left(B\Lambda AC^{-1}\right)\exp\left(-\alpha k^2\right). \tag{C.100}$$

Kinetic energy with delta function matrix element

We again express the delta function using its Fourier transform, and the matrix element then becomes

$$\langle B, \mathbf{s}_b | \hat{K} \delta^3 \left(\omega_0^\intercal \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle \tag{C.101}$$

$$= \left\langle B, \mathbf{s}_b \middle| \hat{K} \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(i\vec{k} \cdot \left(\omega_0^\intercal \mathbf{r} - \vec{y}_0 \right) \right) \middle| A, \mathbf{s}_a \right\rangle \tag{C.102}$$

$$= \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-i\vec{k} \cdot \vec{y}_0 \right) \left\langle B, \mathbf{s}_b \middle| \hat{K} \exp\left(i\vec{k} \cdot \omega_0^\intercal \mathbf{r} \right) \middle| A, \mathbf{s}_a \right\rangle . \tag{C.103}$$

Here we see that the matrix element inside the integral is the one we calculated above. In the case of diagonal A and B matrices, we can use equation C.99 and then get

$$\langle B, \mathbf{s}_b | \hat{K} \delta^3 \left(\omega_0^\intercal \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle \tag{C.104}$$

$$= \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-i\vec{k} \cdot \vec{y}_0 \right) \exp\left(-\alpha k^2 + i\vec{k} \cdot \vec{q} \right) \langle B, \mathbf{s}_b | \hat{K} | A, \mathbf{s}_a \rangle \tag{C.105}$$

$$= \langle B, \mathbf{s}_b | \hat{K} | A, \mathbf{s}_a \rangle \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-i\vec{k} \cdot \vec{y}_0 \right) \exp\left(-\alpha k^2 + i\vec{k} \cdot \vec{q} \right) \tag{C.106}$$

$$= \frac{1}{M\left(C, \mathbf{v}\right)} \langle B, \mathbf{s}_b | \hat{K} | A, \mathbf{s}_a \rangle \langle B, \mathbf{s}_b | \delta^3 \left(\omega_0^\intercal \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle , \tag{C.107}$$

where we in the last line have used that the integral is the same as the one in the delta function matrix element apart from a factor $M(C, \mathbf{v})$. For s-waves this becomes

$$\langle B, \mathbf{s}_b | \hat{K} \delta^3 \left(\omega_0^\intercal \mathbf{r} - \vec{y}_0 \right) | A, \mathbf{s}_a \rangle \overset{\mathrm{v}=0}{=} 6 \operatorname{Tr}\left(B \Lambda A C^{-1} \right) \frac{M_0}{(2\pi)^3} \exp\left(-\frac{y_0^2}{4\alpha} \right) \left(\frac{\pi}{\alpha} \right)^{3/2} . \tag{C.108}$$

We can then look at the other case, where A and B are not assumed to be diagonal. Here, the result in equation C.96 can be used and the matrix element becomes

$$\langle B, \mathbf{s}_b | \hat{K} \delta^3 \left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) | A, \mathbf{s}_a \rangle \tag{C.109}$$

$$= \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-i\vec{k} \cdot \vec{y}_0\right) M(C, \mathbf{v}) \exp\left(-\alpha k^2 + i\vec{k} \cdot \vec{q}\right) \times$$
$$\left[6 \operatorname{Tr}\left(B\Lambda A C^{-1}\right) + \left(\mathbf{s}_b - BC^{-1}(\mathbf{v} + i\vec{k}\omega_0)\right)^\intercal \Lambda \left((\mathbf{s}_a + i\vec{k}\omega_0) - AC^{-1}(\mathbf{v} + i\vec{k}\omega_0)\right)\right] \tag{C.110}$$

$$= \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-i\vec{k} \cdot \vec{y}_0\right) \exp\left(-\alpha k^2 + i\vec{k} \cdot \vec{q}\right) \left[\langle B, \mathbf{s}_b | \hat{K} | A, \mathbf{s}_a \rangle\right.$$
$$+ M(C, \mathbf{v}) \left((\mathbf{s}_b - BC^{-1}\mathbf{v} - BC^{-1} i\vec{k}\omega_0)^\intercal \Lambda (i\vec{k}\omega_0 - AC^{-1} i\vec{k}\omega_0)\right.$$
$$\left.\left. - (BC^{-1} i\vec{k}\omega_0)^\intercal \Lambda (\mathbf{s}_a - AC^{-1}\mathbf{v}\right)\right] \tag{C.111}$$

$$= \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-i\vec{k} \cdot \vec{y}_0\right) \exp\left(-\alpha k^2 + i\vec{k} \cdot \vec{q}\right) \times$$
$$\left[\langle B, \mathbf{s}_b | \hat{K} | A, \mathbf{s}_a \rangle + M(C, \mathbf{v}) \left(i\vec{c}_1 \cdot \vec{k} + c_2 k^2\right)\right], \tag{C.112}$$

where

$$\vec{c}_1 = -\mathbf{s}_b^\intercal \Lambda A C^{-1} \omega_0 + \mathbf{v}^\intercal C^{-1} B \Lambda A C^{-1} \omega_0 - \omega_0^\intercal C^{-1} B \Lambda \mathbf{s}_a + \omega_0^\intercal C^{-1} B \Lambda A C^{-1} \mathbf{v}, \tag{C.113}$$

and

$$c_2 = -\omega_0^\intercal C^{-1} B \Lambda A C^{-1} \omega_0. \tag{C.114}$$

Here, we again used the conditions $\Lambda\omega_0 = 0$ and $\omega_0^\intercal \Lambda = 0$, when expanding the brackets in equation C.111. The next step is to solve the integrals in equation C.112. We begin with the integral containing $\vec{c}_1$. If we let $\vec{z} = \vec{q} - \vec{y}_0$, this can be written as

$$\int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-i\vec{k} \cdot \vec{y}_0\right) \exp\left(-\alpha k^2 + i\vec{k} \cdot \vec{q}\right) M(C, \mathbf{v})\, i\vec{c}_1 \cdot \vec{k} \tag{C.115}$$

$$= iM(C, \mathbf{v})\, \vec{c}_1 \cdot \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(i\vec{k} \cdot \vec{z} - \alpha k^2\right) \vec{k} \tag{C.116}$$

$$= M(C, \mathbf{v})\, \vec{c}_1 \cdot \int \frac{d^3\vec{k}}{(2\pi)^3} \vec{\nabla}_{\vec{z}} \exp\left(i\vec{k} \cdot \vec{z} - \alpha k^2\right) \tag{C.117}$$

$$= M(C, \mathbf{v})\, \vec{c}_1 \cdot \vec{\nabla}_{\vec{z}} \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(i\vec{k} \cdot \vec{z} - \alpha k^2\right). \tag{C.118}$$

This is the same integral as the one we calculated in the delta function matrix element. Inserting the result from there gives the following result

$$M\left(C,\mathbf{v}\right)\vec{c}_1\cdot\vec{\nabla}_{\vec{z}}\left[\frac{1}{(2\pi)^3}\left(\frac{\pi}{\alpha}\right)^{3/2}\exp\left(-\frac{1}{4\alpha}z^2\right)\right] \tag{C.119}$$

$$=-\frac{M\left(C,\mathbf{v}\right)}{(2\pi)^3}\left(\frac{\pi}{\alpha}\right)^{3/2}\frac{\vec{c}_1\cdot\left(\vec{q}-\vec{y}_0\right)}{2\alpha}\exp\left(-\frac{1}{4\alpha}\left(\vec{q}-\vec{y}_0\right)^2\right). \tag{C.120}$$

The integral containing c_2 can be solved similarly

$$\int\frac{d^3\vec{k}}{(2\pi)^3}\exp\left(-i\vec{k}\cdot\vec{y}_0\right)\exp\left(-\alpha k^2+i\vec{k}\cdot\vec{q}\right)M\left(C,\mathbf{v}\right)c_2k^2 \tag{C.121}$$

$$=M\left(C,\mathbf{v}\right)c_2\int\frac{d^3\vec{k}}{(2\pi)^3}\exp\left(i\vec{k}\cdot\vec{z}-\alpha k^2\right)k^2 \tag{C.122}$$

$$=-M\left(C,\mathbf{v}\right)c_2\nabla^2_{\vec{z}}\int\frac{d^3\vec{k}}{(2\pi)^3}\exp\left(i\vec{k}\cdot\vec{z}-\alpha k^2\right) \tag{C.123}$$

$$=-M\left(C,\mathbf{v}\right)c_2\nabla^2_{\vec{z}}\left[\frac{1}{(2\pi)^3}\left(\frac{\pi}{\alpha}\right)^{3/2}\exp\left(-\frac{1}{4\alpha}z^2\right)\right] \tag{C.124}$$

$$=c_2\frac{M\left(C,\mathbf{v}\right)}{(2\pi)^3}\left(\frac{\pi}{\alpha}\right)^{3/2}\frac{1}{2\alpha}\vec{\nabla}_{\vec{z}}\left[\vec{z}\exp\left(-\frac{1}{4\alpha}z^2\right)\right] \tag{C.125}$$

$$=c_2\frac{M\left(C,\mathbf{v}\right)}{(2\pi)^3}\left(\frac{\pi}{\alpha}\right)^{3/2}\frac{1}{2\alpha}\left[3-\frac{z^2}{2\alpha}\right]\exp\left(-\frac{1}{4\alpha}z^2\right) \tag{C.126}$$

$$=c_2\frac{M\left(C,\mathbf{v}\right)}{(2\pi)^3}\left(\frac{\pi}{\alpha}\right)^{3/2}\left[\frac{3}{2\alpha}-\frac{\left(\vec{q}-\vec{y}_0\right)^2}{4\alpha^2}\right]\exp\left(-\frac{1}{4\alpha}\left(\vec{q}-\vec{y}_0\right)^2\right). \tag{C.127}$$

Inserting these results into equation C.112 gives the final expression

$$\langle B,\mathbf{s}_b|\hat{K}\delta^3\left(\omega_0^{\mathsf{T}}\mathbf{r}-\vec{y}_0\right)|A,\mathbf{s}_a\rangle \tag{C.128}$$

$$=\langle B,\mathbf{s}_b|\delta^3\left(\omega_0^{\mathsf{T}}\mathbf{r}-\vec{y}_0\right)|A,\mathbf{s}_a\rangle\left[\frac{\langle B,\mathbf{s}_b|\hat{K}|A,\mathbf{s}_a\rangle}{M\left(C,\mathbf{v}\right)}-\frac{\vec{c}_1\cdot\left(\vec{q}-\vec{y}_0\right)}{2\alpha}+c_2\left(\frac{3}{2\alpha}-\frac{\left(\vec{q}-\vec{y}_0\right)^2}{4\alpha^2}\right)\right]. \tag{C.129}$$

As each term in $\vec{c}_1$ contains a shift vector, we have $\vec{c}_1=0$ for s-waves. The matrix element in this case is then given by

$$\langle B,\mathbf{s}_b|\hat{K}\delta^3\left(\omega_0^{\mathsf{T}}\mathbf{r}-\vec{y}_0\right)|A,\mathbf{s}_a\rangle \tag{C.130}$$

$$\overset{\mathbf{v}=0}{=}\frac{M_0}{(2\pi)^3}\exp\left(-\frac{y_0^2}{4\alpha}\right)\left(\frac{\pi}{\alpha}\right)^{3/2}\left[6\,\mathrm{Tr}\left(B\Lambda AC^{-1}\right)+c_2\left(\frac{3}{2\alpha}-\frac{y_0^2}{4\alpha^2}\right)\right]. \tag{C.131}$$

Coulomb potential matrix element

In this section, we compute the matrix element of the Coulomb potential. For this calculation, we will need the Fourier transform of the Coulomb potential

$$\frac{1}{|\omega_{ij}^{\mathsf{T}}\mathbf{r}|} = \int \frac{d^3\vec{k}}{(2\pi)^3}\frac{4\pi}{k^2}\exp\left(i\vec{k}\cdot\omega_{ij}^{\mathsf{T}}\mathbf{r}\right). \tag{C.132}$$

The matrix element can now be written as

$$\begin{aligned}
\left\langle B,\mathbf{s}_b\middle|\frac{1}{|\omega_{ij}^{\mathsf{T}}\mathbf{r}|}\middle|A,\mathbf{s}_a\right\rangle &= \left\langle B,\mathbf{s}_b\middle|\int \frac{d^3\vec{k}}{(2\pi)^3}\frac{4\pi}{k^2}\exp\left(i\vec{k}\cdot\omega_{ij}^{\mathsf{T}}\mathbf{r}\right)\middle|A,\mathbf{s}_a\right\rangle & \text{(C.133)}\\
&= \int \frac{d^3\vec{k}}{(2\pi)^3}\frac{4\pi}{k^2}\left\langle B,\mathbf{s}_b\middle|\exp\left(i\vec{k}\cdot\omega_{ij}^{\mathsf{T}}\mathbf{r}\right)\middle|A,\mathbf{s}_a\right\rangle & \text{(C.134)}\\
&= \int \frac{d^3\vec{k}}{(2\pi)^3}\frac{4\pi}{k^2}M(C,\mathbf{v})\exp\left(-\beta k^2 + i\vec{k}\cdot\vec{p}\right) & \text{(C.135)}\\
&= \frac{4\pi}{(2\pi)^3}M(C,\mathbf{v})\int d^3\vec{k}\frac{1}{k^2}\exp\left(-\beta k^2 + i\vec{k}\cdot\vec{p}\right), & \text{(C.136)}
\end{aligned}$$

where we have used the result from the plane wave matrix element with

$$\beta = \frac{1}{4}\omega_{ij}^{\mathsf{T}}C^{-1}\omega_{ij}, \qquad \vec{p} = \frac{1}{2}\omega_{ij}^{\mathsf{T}}C^{-1}\mathbf{v}. \tag{C.137}$$

The integral in equation C.136 can be solved by switching to spherical coordinates (k,θ,ϕ), such that $d^3\vec{k} \to k^2\sin(\theta)dk\,d\theta\,d\phi$. The coordinate system can then be rotated so that $\vec{p}$ is aligned with the z-axis, meaning we can write

$$\vec{k}\cdot\vec{p} = kp\cos(\theta). \tag{C.138}$$

Using this, the integral in equation C.136 can be rewritten as

$$\int_0^\infty dk\,\exp\left(-\beta k^2\right)\int_0^{2\pi} d\phi\int_0^\pi d\theta\,\sin(\theta)\exp(ikp\cos(\theta)). \tag{C.139}$$

As the integrand does not depend on ϕ, the ϕ-integral only contributes a factor 2π. The θ-integral can be solved by making the substitution

$$t = \cos(\theta) \Rightarrow d\theta\,\sin(\theta) = -dt, \tag{C.140}$$

which then gives

$$\begin{aligned}
\int_0^\pi d\theta\,\sin(\theta)\exp(ikp\cos(\theta)) &= -\int_1^{-1} dt\,\exp(ikpt) & \text{(C.141)}\\
&= \int_{-1}^{1} dt\,\exp(ikpt) & \text{(C.142)}\\
&= \frac{1}{ikp}\left[\exp(ikp) - \exp(-ikp)\right] & \text{(C.143)}\\
&= \frac{2\sin(kp)}{kp}. & \text{(C.144)}
\end{aligned}$$

The integral in equation C.139 then becomes

$$\int_0^\infty dk\ \exp\left(-\beta k^2\right) \int_0^{2\pi} d\phi \int_0^\pi d\theta\ \sin(\theta) \exp\left(ikp\cos(\theta)\right) \tag{C.145}$$

$$= \frac{4\pi}{p} \int_0^\infty dk\ \exp\left(-\beta k^2\right) \frac{\sin(kp)}{k}. \tag{C.146}$$

This integral is given by [1]

$$\frac{4\pi}{p} \int_0^\infty dk\ \exp\left(-\beta k^2\right) \frac{\sin(kp)}{k} = \frac{4\pi}{p} \frac{\pi}{2} \operatorname{erf}\left(\frac{p}{2\sqrt{\beta}}\right), \tag{C.147}$$

for $\beta > 0$, which is the case since C^{-1} is positive-definite due to property 3. Inserting this into equation C.136, we obtain the final matrix element

$$\left\langle B, \mathbf{s}_b \middle| \frac{1}{|\omega_{ij}^\mathsf{T} \mathbf{r}|} \middle| A, \mathbf{s}_a \right\rangle = \frac{4\pi}{(2\pi)^3} M(C, \mathbf{v}) \frac{2\pi^2}{p} \operatorname{erf}\left(\frac{p}{2\sqrt{\beta}}\right) \tag{C.148}$$

$$= \frac{M(C, \mathbf{v})}{p} \operatorname{erf}\left(\frac{p}{2\sqrt{\beta}}\right). \tag{C.149}$$

As $p = 0$ for s-waves, equation C.139 reduces to

$$\int_0^\infty dk\ \exp\left(-\beta k^2\right) \int_0^{2\pi} d\phi \int_0^\pi d\theta\ \sin(\theta) = 4\pi \int_0^\infty dk\ \exp\left(-\beta k^2\right) \tag{C.150}$$

$$= \frac{4\pi}{\sqrt{\beta}} \int_0^\infty dt\ \exp\left(-t^2\right) \tag{C.151}$$

$$= \frac{4\pi}{\sqrt{\beta}} \frac{1}{2} \int_{-\infty}^\infty dt\ \exp\left(-t^2\right) \tag{C.152}$$

$$= \frac{4\pi}{\sqrt{\beta}} \frac{\sqrt{\pi}}{2}, \tag{C.153}$$

where we have made the substitution $t = \sqrt{\beta} k$ and used that the integrand is even. The matrix element for s-waves then becomes

$$\left\langle B, \mathbf{s}_b \middle| \frac{1}{|\omega_{ij}^\mathsf{T} \mathbf{r}|} \middle| A, \mathbf{s}_a \right\rangle \overset{\mathbf{v}=0}{=} \frac{4\pi}{(2\pi)^3} M_0 \frac{4\pi}{\sqrt{\beta}} \frac{\sqrt{\pi}}{2} = \frac{M_0}{\sqrt{\beta\pi}}. \tag{C.154}$$

Coulomb potential with delta function matrix element

We again use the Fourier transform of the Coulomb potential to write the matrix element as

$$\left\langle B, \mathbf{s}_b \middle| \frac{\delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right)}{|\omega_{ij}^\intercal \mathbf{r}|} \middle| A, \mathbf{s}_a \right\rangle \tag{C.155}$$

$$= \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{4\pi}{k^2} \left\langle B, \mathbf{s}_b \middle| \delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) \exp\left(i\vec{k} \cdot \omega_{ij}^\intercal \mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle, \tag{C.156}$$

noting that i and j cannot be equal to each other. The inner product in the integral is just the delta function matrix element with $\mathbf{s}_a \to \mathbf{s}_a + i\vec{k}\omega_{ij}$, so it can be written as

$$\left\langle B, \mathbf{s}_b \middle| \delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) \exp\left(i\vec{k} \cdot \omega_{ij}^\intercal \mathbf{r}\right) \middle| A, \mathbf{s}_a \right\rangle \tag{C.157}$$

$$= \langle B, \mathbf{s}_b | \delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) | A, \mathbf{s}_a + i\vec{k}\omega_{ij} \rangle \tag{C.158}$$

$$= \frac{M\left(C, \mathbf{v} + i\vec{k}\omega_{ij}\right)}{(2\pi)^3} \exp\left(-\frac{1}{4\alpha_1}\left(\vec{q}_1 + i\vec{k}\gamma - \vec{y}_0\right)^2\right)\left(\frac{\pi}{\alpha_1}\right)^{3/2}, \tag{C.159}$$

where

$$\vec{q}_1 = \frac{1}{2}\omega_0^\intercal C^{-1}\mathbf{v}, \qquad \gamma = \frac{1}{2}\omega_0^\intercal C^{-1}\omega_{ij}, \qquad \alpha_1 = \frac{1}{4}\omega_0^\intercal C^{-1}\omega_0. \tag{C.160}$$

If we now rewrite $M\left(C, \mathbf{v} + i\vec{k}\omega_{ij}\right)$ using the result from the plane wave matrix element, the expression above becomes

$$\frac{M(C, \mathbf{v})}{(2\pi)^3} \exp\left(-\alpha_2 k^2 + i\vec{k} \cdot \vec{q}_2\right) \exp\left(-\frac{1}{4\alpha_1}\left(\vec{q}_1 + i\vec{k}\gamma - \vec{y}_0\right)^2\right)\left(\frac{\pi}{\alpha_1}\right)^{3/2}, \tag{C.161}$$

where

$$\vec{q}_2 = \frac{1}{2}\omega_{ij}^\intercal C^{-1}\mathbf{v}, \qquad \alpha_2 = \frac{1}{4}\omega_{ij}^\intercal C^{-1}\omega_{ij}. \tag{C.162}$$

Writing out the square in the exponent then gives us

$$\left\langle B,\mathbf{s}_b \middle| \delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) \exp\left(i\vec{k}\cdot\omega_{ij}^\intercal\mathbf{r}\right) \middle| A,\mathbf{s}_a \right\rangle \tag{C.163}$$

$$\begin{aligned}&= \frac{M\left(C,\mathbf{v}\right)}{(2\pi)^3} \exp\left(-\alpha_2 k^2 + i\vec{k}\cdot\vec{q}_2\right)\left(\frac{\pi}{\alpha_1}\right)^{3/2} \times \\ &\exp\left(-\frac{1}{4\alpha_1}\left[(\vec{q}_1-\vec{y}_0)^2 - \gamma^2 k^2 + 2i\gamma\vec{k}\cdot(\vec{q}_1-\vec{y}_0)\right]\right)\end{aligned} \tag{C.164}$$

$$\begin{aligned}&= \frac{M\left(C,\mathbf{v}\right)}{(2\pi)^3} \exp\left(-\frac{1}{4\alpha_1}(\vec{q}_1-\vec{y}_0)^2\right)\left(\frac{\pi}{\alpha_1}\right)^{3/2} \times \\ &\exp\left(-\left(\alpha_2 - \frac{\gamma^2}{4\alpha_1}\right)k^2 + i\vec{k}\cdot\left(\vec{q}_2 - \frac{\gamma}{2\alpha_1}(\vec{q}_1-\vec{y}_0)\right)\right)\end{aligned} \tag{C.165}$$

$$= \langle B,\mathbf{s}_b|\delta^3\left(\omega_0^\intercal\mathbf{r} - \vec{y}_0\right)|A,\mathbf{s}_a\rangle \exp\left(-\alpha_3 k^2 + i\vec{k}\cdot\vec{q}_3\right), \tag{C.166}$$

where

$$\vec{q}_3 = \vec{q}_2 - \frac{\gamma}{2\alpha_1}\left(\vec{q}_1 - \vec{y}_0\right), \qquad \alpha_3 = \alpha_2 - \frac{\gamma^2}{4\alpha_1}. \tag{C.167}$$

Inserting this into equation C.156 gives

$$\left\langle B,\mathbf{s}_b \middle| \frac{\delta^3\left(\omega_0^\intercal\mathbf{r} - \vec{y}_0\right)}{|\omega_{ij}^\intercal\mathbf{r}|} \middle| A,\mathbf{s}_a \right\rangle \tag{C.168}$$

$$= \langle B,\mathbf{s}_b|\delta^3\left(\omega_0^\intercal\mathbf{r} - \vec{y}_0\right)|A,\mathbf{s}_a\rangle \frac{4\pi}{(2\pi)^3}\int d^3\vec{k}\,\frac{1}{k^2}\exp\left(-\alpha_3 k^2 + i\vec{k}\cdot\vec{q}_3\right). \tag{C.169}$$

This is exactly the integral, which we already calculated in the matrix element of the Coulomb potential. In order to make sure the integral is convergent, we must check if $\alpha_3 > 0$

$$\alpha_3 > 0 \tag{C.170}$$

$$\Downarrow \tag{C.171}$$

$$\alpha_2 - \frac{\gamma^2}{4\alpha_1} > 0 \tag{C.172}$$

$$\Downarrow \tag{C.173}$$

$$4\alpha_1\alpha_2 - \gamma^2 > 0 \tag{C.174}$$

$$\Downarrow \tag{C.175}$$

$$\left(\omega_0^\intercal C^{-1}\omega_0\right)\left(\omega_{ij}^\intercal C^{-1}\omega_{ij}\right) > \left(\omega_0^\intercal C^{-1}\omega_{ij}\right)^2. \tag{C.176}$$

As C^{-1} is positive-definite, it can be assumed to be symmetric, which then means that

$$\langle\mathbf{u},\mathbf{v}\rangle = \mathbf{u}^\intercal C^{-1}\mathbf{v}, \tag{C.177}$$

is an inner product [29]. We can then use the Cauchy-Schwarz inequality [30], which states that

$$|\langle \mathbf{u}, \mathbf{v} \rangle|^2 \leq \langle \mathbf{u}, \mathbf{u} \rangle \langle \mathbf{v}, \mathbf{v} \rangle, \tag{C.178}$$

with equality if and only if $\mathbf{u}$ and $\mathbf{v}$ are linearly dependent. If we let $\mathbf{u} = \omega_0$ and $\mathbf{v} = \omega_{ij}$, we find that equation C.176 is fulfilled as long as ω_0 and ω_{ij} are linearly independent, which follows by construction. Using the result from the Coulomb potential matrix element gives us the final result

$$\left\langle B, \mathbf{s}_b \middle| \frac{\delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right)}{|\omega_{ij}^\intercal \mathbf{r}|} \middle| A, \mathbf{s}_a \right\rangle \tag{C.179}$$

$$= \langle B, \mathbf{s}_b | \delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right) | A, \mathbf{s}_a \rangle \frac{1}{q_3} \operatorname{erf}\left(\frac{q_3}{2\sqrt{\alpha_3}}\right). \tag{C.180}$$

For s-waves we have $\vec{q}_3 = \frac{\gamma}{2\alpha_1}\vec{y}_0$ and the matrix element then reduces to

$$\left\langle B, \mathbf{s}_b \middle| \frac{\delta^3\left(\omega_0^\intercal \mathbf{r} - \vec{y}_0\right)}{|\omega_{ij}^\intercal \mathbf{r}|} \middle| A, \mathbf{s}_a \right\rangle \tag{C.181}$$

$$\overset{\mathrm{v}=0}{=} \frac{M_0}{(2\pi)^3} \exp\left(-\frac{y_0^2}{4\alpha_1}\right) \left(\frac{\pi}{\alpha_1}\right)^{3/2} \frac{2\alpha_1}{\gamma y_0} \operatorname{erf}\left(\frac{\gamma y_0}{4\alpha_1\sqrt{\alpha_3}}\right). \tag{C.182}$$

Appendix D

Calculation of Modified Overlap

Modified overlap

For the non-adiabatic terms P and Q, we need the overlap between two ECGs, where we do not integrate over the slow variable, which will be called $\vec{r}_k$. We now let the subscript $-k$ on vectors and matrices denote that the k'th entry and the k'th row and column have been removed, respectively. With this notation, we get the expression

$$\mathbf{r}_{-k}^{\mathsf{T}} C_{-k} \mathbf{r}_{-k} = \sum_{i,j} (C_{-k})_{ij} (\mathbf{r}_{-k})_i \cdot (\mathbf{r}_{-k})_j = \sum_{i,j\neq k} C_{ij} \vec{r}_i \cdot \vec{r}_j, \tag{D.1}$$

which will be useful in the following calculation. We are now ready to calculate the modified overlap. Doing the same steps as in the standard overlap, we see that the modified overlap can be written as

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle_{-k} = \int d^3\vec{r}_1 \ldots d^3\vec{r}_{k-1} d^3\vec{r}_{k+1} \ldots d^3\vec{r}_N \exp\left(-\mathbf{r}^{\mathsf{T}} C \mathbf{r} + \mathbf{v}^{\mathsf{T}} \mathbf{r}\right). \tag{D.2}$$

The idea now is to rewrite the exponent to separate out all terms that depend only on $\vec{r}_k$, which gives

$$\begin{aligned}
-\mathbf{r}^{\mathsf{T}} C \mathbf{r} + \mathbf{v}^{\mathsf{T}} \mathbf{r} &= -\sum_{i,j} C_{ij} \vec{r}_i \cdot \vec{r}_j + \sum_i \vec{v}_i \cdot \vec{r}_i &\text{(D.3)}\\
&= -C_{kk} r_k^2 - \sum_{i,j\neq k} C_{ij} \vec{r}_i \cdot \vec{r}_j - \sum_{i\neq k} C_{ik} \vec{r}_i \cdot \vec{r}_k - \sum_{j\neq k} C_{kj} \vec{r}_k \cdot \vec{r}_j + \vec{v}_k \cdot \vec{r}_k + \sum_{i\neq k} \vec{v}_i \cdot \vec{r}_i &\text{(D.4)}\\
&= -C_{kk} r_k^2 - \sum_{i,j\neq k} C_{ij} \vec{r}_i \cdot \vec{r}_j - 2\sum_{i\neq k} C_{ik} \vec{r}_i \cdot \vec{r}_k + \vec{v}_k \cdot \vec{r}_k + \sum_{i\neq k} \vec{v}_i \cdot \vec{r}_i &\text{(D.5)}\\
&= -C_{kk} r_k^2 + \vec{v}_k \cdot \vec{r}_k - \sum_{i,j\neq k} C_{ij} \vec{r}_i \cdot \vec{r}_j + \sum_{i\neq k} \left(\vec{v}_i - 2C_{ik}\vec{r}_k\right) \cdot \vec{r}_i &\text{(D.6)}\\
&= -C_{kk} r_k^2 + \vec{v}_k \cdot \vec{r}_k - \mathbf{r}_{-k}^{\mathsf{T}} C_{-k} \mathbf{r}_{-k} + \boldsymbol{\eta}_{-k}^{\mathsf{T}} \mathbf{r}_{-k}, &\text{(D.7)}
\end{aligned}$$

where we have introduced the vector $\boldsymbol{\eta}$ with entries $\vec{\eta}_i = \vec{v}_i - 2C_{ik}\vec{r}_k$. With this, the modified overlap can now be written as

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle_{-k} \tag{D.8}$$

$$= \int d^3\vec{r}_1 \dots d^3\vec{r}_{k-1} d^3\vec{r}_{k+1} \dots d^3\vec{r}_N \exp\left(-C_{kk} r_k^2 + \vec{v}_k \cdot \vec{r}_k - \mathbf{r}_{-k}^\mathsf{T} C_{-k} \mathbf{r}_{-k} + \boldsymbol{\eta}_{-k}^\mathsf{T} \mathbf{r}_{-k}\right) \tag{D.9}$$

$$= \exp\left(-C_{kk} r_k^2 + \vec{v}_k \cdot \vec{r}_k\right) \int d^3\vec{r}_1 \dots d^3\vec{r}_{k-1} d^3\vec{r}_{k+1} \dots d^3\vec{r}_N \exp\left(-\mathbf{r}_{-k}^\mathsf{T} C_{-k} \mathbf{r}_{-k} + \boldsymbol{\eta}_{-k}^\mathsf{T} \mathbf{r}_{-k}\right) \tag{D.10}$$

$$= \exp\left(-C_{kk} r_k^2 + \vec{v}_k \cdot \vec{r}_k\right) M\left(C_{-k}, \boldsymbol{\eta}_{-k}\right), \tag{D.11}$$

where we have used the result from the standard overlap and where

$$M\left(C_{-k}, \boldsymbol{\eta}_{-k}\right) = \exp\left(\frac{1}{4} \boldsymbol{\eta}_{-k}^\mathsf{T} W \boldsymbol{\eta}_{-k}\right) \left(\frac{\pi^{N-1}}{\det(C_{-k})}\right)^{3/2}, \tag{D.12}$$

with $W = (C_{-k})^{-1}$. For s-waves we have $\vec{v}_i = 0$, so that $\vec{\eta}_i = -2C_{ik}\vec{r}_k = \vec{\eta}_i^{(0)}$. The modified overlap for the case of s-waves can then be written as

$$\langle B, \mathbf{s}_b | A, \mathbf{s}_a \rangle_{-k} \overset{\mathrm{v}=0}{=} \exp\left(-C_{kk} r_k^2\right) M\left(C_{-k}, \boldsymbol{\eta}_{-k}^{(0)}\right). \tag{D.13}$$

In order to use the result from the standard overlap, we need to check whether the matrix remains positive-definite when removing the k'th row and column. Start by letting $A \in \mathbb{R}^{N \times N}$ be positive definite. We then want to show that A_{-k} is also positive definite. Let $\mathbf{y} \in \mathbb{R}^{N-1}$ be an arbitrary nonzero vector and construct a vector $\mathbf{x} \in \mathbb{R}^N$ with entries

$$x_i = \begin{cases} y_i, & i < k, \\ 0, & i = k, \\ y_{i-1}, & i > k. \end{cases} \tag{D.14}$$

If $\mathbf{y} \neq 0$ then $\mathbf{x} \neq 0$ and since A is positive definite, we get

$$0 < \mathbf{x}^\mathsf{T} A \mathbf{x} = \sum_{i,j \neq k} A_{ij} x_i x_j = \mathbf{y}^\mathsf{T} A_{-k} \mathbf{y}, \tag{D.15}$$

which shows that A_{-k} is positive definite.

Modified overlap between ECGs at different $\vec{r}_k$

For the non-adiabatic terms, we will also need the modified overlap between two ECGs that are found at two different values of $\vec{r}_k$. In the following, we will use the notation $\mathbf{r}^\mathsf{T}B\mathbf{r}|_{\vec{r}_k}$ and $\mathbf{r}^\mathsf{T}A\mathbf{r}|_{\vec{r}_k+\Delta\vec{r}_k}$ to denote that the quadratic form is evaluated at $\vec{r}_k$ and $\vec{r}_k + \Delta\vec{r}_k$, respectively. Using this notation, the modified overlap becomes

$$
\begin{aligned}
&\langle B, \mathbf{s}_b|_{\vec{r}_k} | A, \mathbf{s}_a|_{\vec{r}_k+\Delta\vec{r}_k}\rangle_{-k} && \text{(D.16)}\\
&= \int d^3\vec{r}_1 \dots d^3\vec{r}_{k-1} d^3\vec{r}_{k+1} \dots d^3\vec{r}_N \exp\left(-\mathbf{r}^\mathsf{T}B\mathbf{r}|_{\vec{r}_k} + \mathbf{s}_b^\mathsf{T}\mathbf{r}|_{\vec{r}_k}\right)\times \\
&\exp\left(-\mathbf{r}^\mathsf{T}A\mathbf{r}|_{\vec{r}_k+\Delta\vec{r}_k} + \mathbf{s}_a^\mathsf{T}\mathbf{r}|_{\vec{r}_k+\Delta\vec{r}_k}\right). && \text{(D.17)}
\end{aligned}
$$

From this point on, we let A and B be the ECGs found at $\vec{r}_k + \Delta\vec{r}_k$ and $\vec{r}_k$, respectively. Rewriting the second exponent in component form gives

$$
\begin{aligned}
&-\mathbf{r}^\mathsf{T}A\mathbf{r}|_{\vec{r}_k+\Delta\vec{r}_k} + \mathbf{s}_a^\mathsf{T}\mathbf{r}|_{\vec{r}_k+\Delta\vec{r}_k} && \text{(D.18)}\\
&= -A_{kk}(\vec{r}_k + \Delta\vec{r}_k)^2 - \sum_{i,j\neq k} A_{ij}\vec{r}_i\cdot\vec{r}_j - \sum_{i\neq k} A_{ik}\vec{r}_i\cdot(\vec{r}_k + \Delta\vec{r}_k)\\
&- \sum_{j\neq k} A_{kj}(\vec{r}_k + \Delta\vec{r}_k)\cdot\vec{r}_j + (\mathbf{s}_a)_k\cdot(\vec{r}_k + \Delta\vec{r}_k) + \sum_{i\neq k}(\mathbf{s}_a)_i\cdot\vec{r}_i && \text{(D.19)}\\
&= -A_{kk}r_k^2 - A_{kk}(\Delta r_k)^2 - 2A_{kk}\vec{r}_k\cdot\Delta\vec{r}_k - \sum_{i,j\neq k} A_{ij}\vec{r}_i\cdot\vec{r}_j\\
&- 2\sum_{i\neq k} A_{ik}\vec{r}_i\cdot(\vec{r}_k + \Delta\vec{r}_k) + (\mathbf{s}_a)_k\cdot(\vec{r}_k + \Delta\vec{r}_k) + \sum_{i\neq k}(\mathbf{s}_a)_i\cdot\vec{r}_i. && \text{(D.20)}
\end{aligned}
$$

In total, the two exponents can therefore be written as

$$
\begin{aligned}
&-\mathbf{r}^\mathsf{T}B\mathbf{r}|_{\vec{r}_k} + \mathbf{s}_b^\mathsf{T}\mathbf{r}|_{\vec{r}_k} - \mathbf{r}^\mathsf{T}A\mathbf{r}|_{\vec{r}_k+\Delta\vec{r}_k} + \mathbf{s}_a^\mathsf{T}\mathbf{r}|_{\vec{r}_k+\Delta\vec{r}_k} && \text{(D.21)}\\
&= -B_{kk}r_k^2 - \sum_{i,j\neq k} B_{ij}\vec{r}_i\cdot\vec{r}_j - 2\sum_{i\neq k} B_{ik}\vec{r}_i\cdot\vec{r}_k + (\mathbf{s}_b)_k\cdot\vec{r}_k + \sum_{i\neq k}(\mathbf{s}_b)_i\cdot\vec{r}_i\\
&- A_{kk}r_k^2 - A_{kk}(\Delta r_k)^2 - 2A_{kk}\vec{r}_k\cdot\Delta\vec{r}_k - \sum_{i,j\neq k} A_{ij}\vec{r}_i\cdot\vec{r}_j\\
&- 2\sum_{i\neq k} A_{ik}\vec{r}_i\cdot(\vec{r}_k + \Delta\vec{r}_k) + (\mathbf{s}_a)_k\cdot(\vec{r}_k + \Delta\vec{r}_k) + \sum_{i\neq k}(\mathbf{s}_a)_i\cdot\vec{r}_i && \text{(D.22)}\\
&= -C_{kk}r_k^2 - A_{kk}(\Delta r_k)^2 - 2A_{kk}\vec{r}_k\cdot\Delta\vec{r}_k + \vec{v}_k\cdot\vec{r}_k + (\mathbf{s}_a)_k\cdot\Delta\vec{r}_k\\
&- \sum_{i,j\neq k} C_{ij}\vec{r}_i\cdot\vec{r}_j + \sum_{i\neq k}\left(\vec{v}_i - 2C_{ik}\vec{r}_k - 2A_{ik}\Delta\vec{r}_k\right)\cdot\vec{r}_i && \text{(D.23)}\\
&= -C_{kk}r_k^2 - A_{kk}(\Delta r_k)^2 - 2A_{kk}\vec{r}_k\cdot\Delta\vec{r}_k + \vec{v}_k\cdot\vec{r}_k + (\mathbf{s}_a)_k\cdot\Delta\vec{r}_k\\
&- \mathbf{r}_{-k}^\mathsf{T}C_{-k}\mathbf{r}_{-k} + \boldsymbol{\eta}_{-k}^\mathsf{T}\mathbf{r}_{-k}, && \text{(D.24)}
\end{aligned}
$$

where $\boldsymbol{\eta}_{-k}$ has entries $\vec{\eta}_i = \vec{v}_i - 2C_{ik}\vec{r}_k - 2A_{ik}\Delta\vec{r}_k$. Inserting this into equation D.17, and pulling all $\vec{r}_k$ dependent terms outside the integral gives

$$\langle B, \mathbf{s}_b|_{\vec{r}_k} \big| A, \mathbf{s}_a|_{\vec{r}_k+\Delta\vec{r}_k} \rangle_{-k} \tag{D.25}$$

$$= \exp\left(-C_{kk}r_k^2 - A_{kk}(\Delta r_k)^2 - 2A_{kk}\vec{r}_k \cdot \Delta\vec{r}_k + \vec{v}_k \cdot \vec{r}_k + (\mathbf{s}_a)_k \cdot \Delta\vec{r}_k\right)\times$$

$$\int d^3\vec{r}_1 \dots d^3\vec{r}_{k-1} d^3\vec{r}_{k+1} \dots d^3\vec{r}_N \exp\left(-\mathbf{r}_{-k}^{\mathsf{T}} C_{-k}\mathbf{r}_{-k} + \boldsymbol{\eta}_{-k}^{\mathsf{T}}\mathbf{r}_{-k}\right) \tag{D.26}$$

$$= \exp\left(-C_{kk}r_k^2 - A_{kk}(\Delta r_k)^2 - 2A_{kk}\vec{r}_k \cdot \Delta\vec{r}_k + \vec{v}_k \cdot \vec{r}_k + (\mathbf{s}_a)_k \cdot \Delta\vec{r}_k\right) M\left(C_{-k}, \boldsymbol{\eta}_{-k}\right), \tag{D.27}$$

where the result of modified overlap has been used. For s-waves the matrix element is

$$\langle B, \mathbf{s}_b|_{\vec{r}_k} \big| A, \mathbf{s}_a|_{\vec{r}_k+\Delta\vec{r}_k} \rangle_{-k} \tag{D.28}$$

$$\overset{\mathrm{v=0}}{=} \exp\left(-C_{kk}r_k^2 - A_{kk}(\Delta r_k)^2 - 2A_{kk}\vec{r}_k \cdot \Delta\vec{r}_k\right) M\left(C_{-k}, \boldsymbol{\eta}_{-k}^{(0)}\right), \tag{D.29}$$

where $\vec{\eta}_i^{(0)} = -2C_{ik}\vec{r}_k - 2A_{ik}\Delta\vec{r}_k$.