

Regularized Relativistic Corrections for Molecular Systems

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1 Introduction

In recent decades, high-resolution spectroscopy has seen unprecedented growth and development, yielding experimental results for several few-body systems, reaching more than ten significant figures [1]. However, devising methods and calculations that can match this precision for molecular systems has been a long-standing problem in the field of theoretical chemistry. This difficulty can be attributed to the exponential increase in the computational resources required, as well as the large surge in the difficulty of calculations that arise with the added complexity of molecules. Even for small molecular systems, computations tied to high-precision spectroscopy are not readily performed as the general methodology is simply not available. Leading-order relativistic corrections require tedious manual adjusting, while tight energy lower bound calculations, indispensable for firm control of error convergence, are also the subject of much-needed research. One important obstacle preventing these implementations to small molecular systems is the square of the Hamiltonian operator $\hat{H}^2$ and the matrix elements it gives rise to. Evaluating these for molecules, with an accuracy demanded by high-resolution spectroscopy, has not yet been done and the exact calculations on the preferred basis are considered impossible [2].

In this research report, I will describe a newly developed method for evaluating the matrix elements of the square of the Hamiltonian using a very precise approximation and will detail its use concerning relativistic corrections. Regarding applications, this method has already been used to obtain relativistic corrections for several few-body systems using the in-house developed QUANTEN program, with promising results so far.

In the following, I will first provide the necessary theoretical framework in Section 2. After this, I will detail the origins of the incalculable matrix elements of $\hat{H}^2$ and showcase their integral part in relativistic corrections with a brief look at energy lower-bound calculations. In Section 4, I will discuss the background of the approximation used, whereas Section 5 will pertain to the direct application of this approximation and the evaluation of the matrix elements. The remainder of this report will focus on the numerical results obtained so far, as well as a brief summary and outlook on ongoing and future work. An article based on the contents of this report is also set to be published this year in the Communications section of The Journal of Chemical Physics [3].

2 Theoretical Background

2.1 Non-Relativistic Quantum Mechanics of Atoms and Molecules

One of the fundamental equations of non-relativistic quantum mechanics is the Schrödinger equation [4], which describes the energy levels of classical quantum-mechanical systems. For our purposes, dealing with stationary states, the time-independent version will suffice, which takes the form of an eigenvalue problem:

$$\hat{H}\Psi_n = E_n\Psi_n \quad n = 1, 2 \dots, \quad (2.1)$$

where $\hat{H}$ is the Hamiltonian operator, and E_n are the different energy levels, each corresponding to a Ψ_n eigenstate of the system. For the sake of clarity, the energies are labeled such as $E_1 \leq E_2 \leq E_3 \leq \dots$

The Hamiltonian operator $\hat{H}$ can be understood as being composed of the kinetic energies of the electrons and nuclei and the potential energies due to the Coulomb interactions between them. The Hamiltonian of this description is known as the molecular or non-relativistic Coulomb Hamiltonian $\hat{H}_{\text{mol}}$ and can be broken up into the following terms:

$$\hat{H}_{\text{mol}} = \hat{T}_e + \hat{T}_n + \hat{U}_{\text{nn}} + \hat{U}_{\text{en}} + \hat{U}_{\text{ee}}. \quad (2.2)$$

The operators $\hat{T}_e$ and $\hat{T}_n$ represent the kinetic energies of the electrons and the nuclei, respectively, while the $\hat{U}_{\text{nn}}$ term describes the nucleus-nucleus, the $\hat{U}_{\text{en}}$ term describes the electron-nucleus, and the $\hat{U}_{\text{ee}}$ term describes the electron-electron interactions. These can then be further expanded and expressed in atomic units as:

$$\hat{T}_e = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2, \quad (2.3)$$

$$\hat{T}_n = -\frac{1}{2} \sum_{a=1}^N \frac{1}{M_a} \nabla_a^2, \quad (2.4)$$

$$\hat{U}_{\text{ee}} = \frac{1}{2} \sum_{i=1}^n \sum_{j>i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = \frac{1}{2} \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}, \quad (2.5)$$

$$\hat{U}_{\text{en}} = -\sum_{i=1}^n \sum_{a=1}^N \frac{Z_a}{|\mathbf{r}_i - \mathbf{R}_a|} = -\sum_{i=1}^n \sum_{a=1}^N \frac{Z_a}{r_{ia}}, \quad (2.6)$$

$$\hat{U}_{\text{nn}} = \frac{1}{2} \sum_{a=1}^N \sum_{b>a}^N \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|} = \frac{1}{2} \sum_{a=1}^N \sum_{b>a}^N \frac{Z_a Z_b}{r_{ab}}. \quad (2.7)$$

In the above expressions and throughout this report, indices starting from i, j going to n correspond to electrons, whereas indices from a, b going to N correspond to the nuclei. The Cartesian coordinates of the electrons are represented by the $\mathbf{r}$ vector, and for the nuclei, the $\mathbf{R}$ vector. M will denote the mass of the nuclei, while the charge is denoted by Z . For later convenience, the following notation will also be often employed in this report: $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, $r_{ia} = |\mathbf{r}_i - \mathbf{R}_a|$ and $r_{ab} = |\mathbf{R}_a - \mathbf{R}_b|$.

Furthermore, we will also use the Born–Oppenheimer approximation [5], which states that due to the much larger mass of the nuclei relative to the electrons, it is meaningful to separate the quantum mechanical motion of the electrons and the nuclei. The Hamiltonian for the electrons in the electric field of the fixed nuclei is:

$$\hat{H}_{\text{el}} = \hat{T}_{\text{e}} + \hat{U}_{\text{nn}} + \hat{U}_{\text{en}} + \hat{U}_{\text{ee}} . \quad (2.8)$$

In this report, we will stay within the Born–Oppenheimer approximation and will consider the electronic Hamiltonian $\hat{H} = \hat{H}_{\text{el}}$. However, generalizations of the methodological developments presented here may be possible and could be relevant to future work.

Unfortunately, even if the form of the Hamiltonian is available, the analytic solution of the time-independent Schrödinger equation, seen in Eq. (2.1), is still unknown in most cases. Most common solution techniques in molecular quantum mechanics are based on the variational principle or perturbation theory techniques, which will be detailed in the following sections.

2.2 The Variational Method

One of the most widely used approaches to solve the Schrödinger equation in molecular quantum mechanics is the variational method, which fundamentally relies on the variational principle:

$$\frac{\langle \Psi_{\text{trial}} | \hat{H} | \Psi_{\text{trial}} \rangle}{\langle \Psi_{\text{trial}} | \Psi_{\text{trial}} \rangle} \geq E_1 . \quad (2.9)$$

For the ground state energy level, this approach replaces the Ψ_1 wave function corresponding to E_1 with a so-called trial function Ψ_{trial} . This artificially constructed function of a chosen form contains some parameters $\alpha_1, \alpha_2 \dots \alpha_k$ which can be varied and optimized to give the lowest value for the expectation value of $\hat{H}$ seen in Eq. (2.9).

This equation relies on the fact that the Hamiltonian operator is bounded from below [6, 7], thus no choice of Ψ_{trial} will give a lower expectation value than E_1 . Using this principle, the original

eigenvalue problem becomes one of minimizing the expectation value of the Hamiltonian operator by finding the best trial function.

In 1909, Ritz proposed [8] to construct the trial function as a linear combination of K fixed basis functions $\Phi(\alpha_i)$:

$$\Psi_{\text{trial}} = \sum_{i=1}^K c_i \Phi(\alpha_i) . \quad (2.10)$$

Combining this prescription for the trial function and the variational principle of Eq. (2.9), we can obtain the so-called generalized matrix eigenvalue problem:

$$\mathbf{H}\mathbf{c} = E_1\mathbf{S}\mathbf{c} , \quad (2.11)$$

where $\mathbf{c}$ denotes a K -dimensional vector containing the c_i constants, while $\mathbf{H}$ and $\mathbf{S}$ are the $K \times K$ -dimensional Hamiltonian and overlap matrices, respectively, which take the form:

$$H_{ij} = \langle \Phi(\alpha_i) | \hat{H} | \Phi(\alpha_j) \rangle , \quad S_{ij} = \langle \Phi(\alpha_i) | \Phi(\alpha_j) \rangle . \quad (2.12)$$

With this, we have simplified the original operator eigenvalue problem by restricting it into a $\mathcal{V}_K$ subspace of the original $\mathcal{H}$ Hilbert space, spanned by the $\Phi(\alpha_i)$ functions, as well as have introduced the matrix representation of the Hamiltonian operator H_{ij} . The specific choice for the basis functions as explicitly correlated Gaussian functions will be the subject of the next section.

2.3 Explicitly Correlated Gaussian Functions

2.3.1 A Brief Overview

Many different sets of functions have been explored and tested to serve as basis functions since the development of the variational approach for molecular quantum mechanics problems. The choice of exponential functions was first explored by Hylleraas in the late 1920s [9, 10, 11, 12], and have since been further developed into the Hylleraas-type functions, which have seen great success with accurate results for applications regarding few-body systems [13, 14]. However, calculations for larger systems using this basis set become increasingly difficult with each particle added, so their use remains mostly restricted to some three-body problems.

In 1960, Boys [15] and Singer [16], independently from each other, proposed a set of basis functions much better suited for calculations with molecular systems, namely explicitly correlated Gaussian

functions (ECGs). Originally, these functions took the form:

$$\varphi = \exp \left[- \sum_{i=1}^K \sum_{j>1}^K \alpha_{ij} (\mathbf{r}_i - \mathbf{r}_j)^2 \right] , \quad (2.13)$$

where $\mathbf{r}_i$ and $\mathbf{r}_j$ represent the coordinates of the i th and j th electrons, while α_{ij} is the variational parameter describing the falloff of the interaction between the two particles.

An explicitly correlated Gaussian basis set fulfills the fundamental requirement of a systematic convergence towards the exact eigenvalue as the number of basis functions is increased [17] while having two major advantages. As shown in Eq. (2.13), they have a form that accounts for all pairwise interactions between the particles of the system, which allows tight convergence of the energy (assuming a good parameterization can be found). Furthermore, unlike the Hylleraas-type exponential functions, the quadratic form of the interparticle distances gives rise to matrix elements that can be analytically evaluated [18]. This means that the algebraic difficulty of the calculations does not increase for systems with $N \geq 3$ particles. These highly desirable properties make them suitable for a wide range of applications in theoretical chemistry and many-body physics, which is reflected in their steadily growing use over the last couple of decades [18].

However, it should also be noted that the choice of ECGs do also come with certain drawbacks and difficulties. At large distances, $r_{ij} \rightarrow \infty$, they decay faster than expected due to the quadratic exponent, resulting in a slower convergence. Owing to their smoothness, they also behave incorrectly near the coalescence points of the Coulomb interaction close to zero, $r_{ij} \rightarrow 0$, as a result, not fulfilling Kato's cusp condition [17, 19].

2.3.2 Expanding the Trial Function

The basis function used for variational calculations can be understood as an (anti)symmetrized product of a spatial and a spin function:

$$\Phi_i^{[\lambda, \zeta]} = \hat{\mathcal{A}} \left\{ \varphi_i^{[\lambda]} \chi_i^{[\zeta]} \right\} , \quad (2.14)$$

where λ collects the spatial quantum numbers or symmetry labels (if any) and $\zeta = S_a, M_{S_a} \dots$ represents the spin quantum numbers. The (anti)symmetrization operator will take the form:

$$\hat{\mathcal{A}} = (N_p!)^{-\frac{1}{2}} \sum_{p=1}^{N_p!} \epsilon_p \hat{P}_p , \quad (2.15)$$

where N_p is the number of identical particles in the system, for which there exist $N_p!$ permutations that can be performed. In the above equation, $\hat{P}_p$ denotes the permutation operator, and ϵ_p is a factor, which for fermions equals -1, while for bosonic particles equals 1. This construct ensures that the basis function fulfills the Pauli principle.

With these considerations, the expectation value of the Hamiltonian using Eq. (2.10) can be expanded as [20]:

$$\langle \Psi_{\text{trial}} | \hat{H} | \Psi_{\text{trial}} \rangle = \sum_{i=1}^K \sum_{j=1}^K c_i^* c_j \langle \Phi_i | \hat{H} | \Phi_j \rangle = \sum_{i=1}^K \sum_{j=1}^K c_i^* c_j \langle \hat{\mathcal{A}}\{\varphi_i \chi_i\} | \hat{H} | \hat{\mathcal{A}}\{\varphi_j \chi_j\} \rangle . \quad (2.16)$$

Using the quasi-idempotency of the (anti)symmetrization operator $\hat{\mathcal{A}}^2 = (N_p!)^{\frac{1}{2}} \hat{\mathcal{A}}$, and substituting in Eq. (2.15), the following expansions can be made:

$$\begin{aligned} \langle \Psi_{\text{trial}} | \hat{H} | \Psi_{\text{trial}} \rangle &= \sum_{i=1}^K \sum_{j=1}^K c_i^* c_j (N_p!)^{\frac{1}{2}} \langle \varphi_i \chi_i | \hat{H} | \hat{\mathcal{A}}\{\varphi_j \chi_j\} \rangle \\ &= \sum_{i=1}^K \sum_{j=1}^K \sum_{p=1}^{N_p!} c_i^* c_j \epsilon_p \langle \varphi_i \chi_i | \hat{H} | \hat{P}_p \{\varphi_j \chi_j\} \rangle \\ &= \sum_{i=1}^K \sum_{j=1}^K \sum_{p=1}^{N_p!} c_i^* c_j \epsilon_p \langle \varphi_i | \hat{H} | \hat{P}_p \varphi_j \rangle \langle \chi_i | \hat{P}_p \chi_j \rangle . \end{aligned} \quad (2.17)$$

With this, we have successfully separated the spatial and spin functions of Eq. (2.14) into two factors. In this report, we will narrow our focus to the spatial function matrix elements, as the spin function integrals can be calculated with relative ease (and are already available in the QUANTEN program).

The permutation operator $\hat{P}_p$ in Eq. (2.17) can be dealt with by reparameterizing the spatial functions $\varphi_i(\mathbf{r}, \mathbf{A}_i, \mathbf{s}_i)$ [20]. To do this, we need to define the matrix representation of $\hat{P}_p$ acting on the spatial vector $\mathbf{r}$:

$$\hat{P}_p \mathbf{r} = (\mathbf{P}_p^r \otimes \mathbf{I}_3) \mathbf{r} . \quad (2.18)$$

The constructed $\mathbf{P}_p^r$ matrix contains only zeros except for a single one in each row and column corresponding to each of the possible permutations. It also needs to act on the three coordinates in the same manner, which is why the direct multiplication with the three-dimensional identity matrix $\mathbf{I}_3$ is necessary. With this in mind, we can make the following modifications:

$$\hat{P}_p \varphi_i(\mathbf{r}, \mathbf{A}_i, \mathbf{s}_i) = \varphi_i(\hat{P}_p^{-1} \mathbf{r}, \mathbf{A}_i, \mathbf{s}_i) = \varphi_i((\mathbf{P}_p^r \otimes \mathbf{I}_3)^{-1} \mathbf{r}, \mathbf{A}_i, \mathbf{s}_i) . \quad (2.19)$$

Following a linear transformation by $\mathbf{P}_p^r$, we arrive at the new spatial function:

$$\varphi_p(\mathbf{r}, \mathbf{A}_p, \mathbf{s}_p) \quad \text{where:} \quad \mathbf{s}_p = (\mathbf{P}_p^r \otimes \mathbf{I}_3)^T \mathbf{s}_i, \quad \mathbf{A}_p = (\mathbf{P}_p^r)^T \mathbf{A}_i \mathbf{P}_p^r. \quad (2.20)$$

For the sake of simplicity, we will continue using the notation $\varphi_i(\mathbf{r}, \mathbf{A}_i, \mathbf{s}_i)$ throughout this report, however, this simple reparameterization dealing with the permutation operator should be kept in mind.

As mentioned above, the choice for the spatial functions will be explicitly correlated Gaussians, particularly the floating-type (FECG), which take the form:

$$\varphi_i(\mathbf{r}, \mathbf{A}_i, \mathbf{s}_i) = \exp \left[-(\mathbf{r} - \mathbf{s}_i)^T (\mathbf{A}_i \otimes \mathbf{I}_3) (\mathbf{r} - \mathbf{s}_i) \right], \quad (2.21)$$

where $\mathbf{A}_i \in \mathbb{R}^{n \times n}$ is a positive-definite, symmetric matrix (to ensure its square-integrability), the elements of which are related to the α variational parameters by a linear transformation, while T denotes the transpose operation. The multiplication with $\mathbf{I}_3$ is done for the same reason as with $\mathbf{P}_p^r$, to ensure all three coordinates of each particle are treated the same. It is also important to note that the $\mathbf{r}$ vector here, without any indices, represents a $3n$ -dimensional vector that contains all the Cartesian coordinates of the electrons in the system. The coordinates of the i th electron are found at the i th position of this general $\mathbf{r}$ vector and are thus denoted as $\mathbf{r}_i \in \mathbb{R}^3$. This notation will become especially important during the calculations of Section 5.

In comparison to the origin-centered explicitly correlated Gaussians, FECGs also contain an additional $\mathbf{s}_i \in \mathbb{R}^{3n}$ parameter known as the shift vector. As their name suggests, these vectors allow for the displacement of the origin of the Gaussian functions, which is indispensable for describing the multiple peaks around the nuclei in molecules [18]. However, it should also be duly noted that while these shift vectors allow for the highly precise description of molecules using ECGs, they can also make calculations especially difficult. For atoms, $\mathbf{s}_i = 0$, all of the $\langle \varphi | \hat{H}^2 | \varphi \rangle$ matrix elements are known in a closed analytic form [21]. At the same time, it is necessary to allow for $\mathbf{s}_i \neq 0$ to perform molecular computations, however, many of the $\hat{H}^2$ matrix elements that arise this way are considered incalculable [2], as we shall see later.

While not expanded upon in this report, it should also be noted that FECGs are also related by a constant factor to the g generator function of explicitly correlated Gaussians in a global vector representation (ECG-GVR). These basis functions have been successfully used outside the

Born–Oppenheimer paradigm, known as pre-Born–Oppenheimer quantum mechanics [20, 22]:

$$\varphi_i(\mathbf{r}, \mathbf{A}_i, \mathbf{s}_i) = \exp[-\mathbf{s}_i(\mathbf{A}_i \otimes \mathbf{I}_3)\mathbf{s}_i] \cdot g(\mathbf{r}, \mathbf{A}_i, (\mathbf{A}_i \otimes \mathbf{I}_3)\mathbf{s}_i) . \quad (2.22)$$

2.4 Perturbation Theory Approaches

Another important family of methods in molecular quantum mechanics includes perturbative approaches. In this section, we will focus on a specific branch of this larger field, namely Rayleigh–Schrödinger perturbation theory [23]. This technique is built on a known, solvable eigenvalue problem, which, in general, can be written as:

$$\hat{H}^{(0)}\Psi_k^{(0)} = E_k^{(0)}\Psi_k^{(0)} , \quad (2.23)$$

and is known as the unperturbed or zeroth order equation, denoted by the (0) superscripts. It is important to note that all $\Psi_k^{(0)}$ eigenstates and $E_k^{(0)}$ eigenvalues have to be known for the method to work. This system is then built upon by introducing correctional terms which help create a more and more accurate picture of the original, complex system. To achieve this, the Hamiltonian operator $\hat{H}^{(0)}$ is fitted with a hermitian perturbation operator $\hat{W}$ and perturbation parameter λ , which are both known and will allow us to describe our system of interest as:

$$\left(\hat{H}^{(0)} + \lambda\hat{W}\right)\Psi_k = E_k\Psi_k , \quad \text{where: } 0 \leq \lambda \leq 1 . \quad (2.24)$$

The unknown parameters Ψ_k and E_k are then expanded into a series in terms of λ :

$$\Psi_k = \Psi_k^{(0)} + \lambda\Psi_k^{(1)} + \lambda^2\Psi_k^{(2)} \dots , \quad (2.25)$$

$$E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} \dots . \quad (2.26)$$

Performing these substitutions, we get:

$$\left(\hat{H}^{(0)} + \lambda\hat{W}\right)\left(\Psi_k^{(0)} + \lambda\Psi_k^{(1)} \dots\right) = \left(E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} \dots\right)\left(\Psi_k^{(0)} + \lambda\Psi_k^{(1)} \dots\right) . \quad (2.27)$$

Next, by exploiting the hermiticity of the $\hat{H}^{(0)}$ Hamiltonian operator, $\langle\Psi_k^{(0)}|\Psi_l^{(0)}\rangle = \delta_{kl}$, and employing a so-called intermediate normalization $\langle\Psi_k|\Psi_k^{(0)}\rangle = 1$, we can formulate an equation based on each order of λ and, theoretically, express all the correctional terms of the series in

Eqs. (2.25) and (2.26). For example, the first-order terms can be written as:

$$E_k^{(1)} = \left\langle \Psi_k^{(0)} \left| \hat{W} \right| \Psi_k^{(0)} \right\rangle , \quad (2.28)$$

$$\Psi_k^{(1)} = \sum_{j=0}^{\infty} \frac{\left\langle \Psi_j^{(0)} \left| \hat{W} \right| \Psi_k^{(0)} \right\rangle}{E_k^{(0)} - E_j^{(0)}} \Psi_j^{(0)} , \quad (2.29)$$

where the condition $j \neq k$ has to be fulfilled to comply with the intermediate normalization. Each order of corrections relies on all of the preceding perturbative terms; due to this, in most practical cases, only the first few correction terms are usually calculated.

Other perturbation theory approaches have been proposed in the past and are used in different fields of molecular quantum mechanics. In relativistic quantum mechanics, which will be the topic of Section 3.2, the perturbation theory approach employed is known as the Foldy–Wouthuysen perturbation theory [24]. This technique is based on constructing a similarity transform of the original problem so that the coupling of the ‘full’ and the ‘unperturbed’ parts can be made smaller at every perturbative order.

3 Motivation behind the Present Work

The main topic of this report focuses on evaluating the matrix elements of the Hamiltonian operator squared $\hat{H}^2$ within an FECG basis set. As mentioned in Section 2.3.2, the introduction of the shift vectors of the FECGs, which are necessary for the description of molecular systems, also leads to the expectation value of $\hat{H}^2$ becoming analytically in calculable. In this section, we shall dissect the $\langle \varphi | \hat{H}^2 | \varphi \rangle$ matrix elements into their further parts and identify three operator expressions for which no analytic integrals are known. After this step, in the following two sections, we will see how these matrix elements appear in calculations of relativistic corrections, as well as lower bounds to the exact energy.

3.1 The Hamiltonian Squared

The aim of this section is to derive all of the constituting matrix elements of the square of the electronic Hamiltonian. To achieve this, as a first step, we will employ the expression seen in Eq. (2.8):

$$\begin{aligned}
\hat{H}_{\text{el}}^2 &= \left(\hat{T}_e + \hat{U}_{\text{nn}} + \hat{U}_{\text{en}} + \hat{U}_{\text{ee}} \right) \cdot \left(\hat{T}_e + \hat{U}_{\text{nn}} + \hat{U}_{\text{en}} + \hat{U}_{\text{ee}} \right) \\
&= \left(\hat{T}_e \hat{T}_e + \hat{T}_e \hat{U}_{\text{nn}} + \hat{T}_e \hat{U}_{\text{en}} + \hat{T}_e \hat{U}_{\text{ee}} \right) + \left(\hat{U}_{\text{nn}} \hat{T}_e + \hat{U}_{\text{nn}} \hat{U}_{\text{nn}} + \hat{U}_{\text{nn}} \hat{U}_{\text{en}} + \hat{U}_{\text{nn}} \hat{U}_{\text{ee}} \right) \\
&+ \left(\hat{U}_{\text{en}} \hat{T}_e + \hat{U}_{\text{en}} \hat{U}_{\text{nn}} + \hat{U}_{\text{en}} \hat{U}_{\text{en}} + \hat{U}_{\text{en}} \hat{U}_{\text{ee}} \right) + \left(\hat{U}_{\text{ee}} \hat{T}_e + \hat{U}_{\text{ee}} \hat{U}_{\text{nn}} + \hat{U}_{\text{ee}} \hat{U}_{\text{en}} + \hat{U}_{\text{ee}} \hat{U}_{\text{ee}} \right) \\
&= \left(\hat{T}_e \hat{T}_e + 2 \cdot \hat{T}_e \hat{U}_{\text{nn}} + \hat{T}_e \hat{U}_{\text{en}} + \hat{U}_{\text{en}} \hat{T}_e + \hat{T}_e \hat{U}_{\text{ee}} + \hat{U}_{\text{ee}} \hat{T}_e \right) \\
&+ \left(\hat{U}_{\text{nn}} \hat{U}_{\text{nn}} + 2 \cdot \hat{U}_{\text{en}} \hat{U}_{\text{nn}} + \hat{U}_{\text{en}} \hat{U}_{\text{en}} + 2 \cdot \hat{U}_{\text{en}} \hat{U}_{\text{ee}} + \hat{U}_{\text{ee}} \hat{U}_{\text{ee}} + 2 \cdot \hat{U}_{\text{ee}} \hat{U}_{\text{nn}} \right) , \tag{3.1}
\end{aligned}$$

where in the last step, we considered the fact that while the kinetic and potential energy operators do not commute, $[\hat{T}\hat{U}] \neq 0$, the different $\hat{U}$ -operators do. It should also be noted that as in this report we will stay within the bounds of the Born–Oppenheimer approximation, the $\hat{U}_{\text{nn}}$ -operator essentially equals a multiplication by a constant factor. With this in mind, we can express the 12 unique matrix elements identified above using Eqs. (2.3)–(2.7):

$$\langle \varphi_k | \hat{T}_e \hat{T}_e | \varphi_l \rangle = \frac{1}{4} \sum_{i=1}^n \sum_{j=1}^n , \langle \varphi_k | \nabla_i^2 \nabla_j^2 | \varphi_l \rangle , \tag{3.2}$$

$$\langle \varphi_k | \hat{T}_e \hat{U}_{\text{nn}} | \varphi_l \rangle = -\frac{1}{4} \sum_{i=1}^n \sum_{a=1}^N \sum_{b>a}^N \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|} \langle \varphi_k | \nabla_i^2 | \varphi_l \rangle , \tag{3.3}$$

$$\langle \varphi_k | \hat{T}_e \hat{U}_{\text{en}} | \varphi_l \rangle = \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n \sum_{a=1}^N Z_a \langle \varphi_k | \nabla_i^2 \frac{1}{|\mathbf{r}_j - \mathbf{R}_a|} | \varphi_l \rangle , \tag{3.4}$$

$$\langle \varphi_k | \hat{T}_e \hat{U}_{ee} | \varphi_l \rangle = -\frac{1}{4} \sum_{i=1}^n \sum_{j=1}^n \sum_{k>j}^n \langle \varphi_k | \nabla_i^2 \frac{1}{r_{jk}} | \varphi_l \rangle , \quad (3.5)$$

$$\langle \varphi_k | \hat{U}_{en} \hat{T}_e | \varphi_l \rangle = \frac{1}{2} \sum_{i=1}^n \sum_{a=1}^N \sum_{j=1}^n Z_a \langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \nabla_j^2 | \varphi_l \rangle , \quad (3.6)$$

$$\langle \varphi_k | \hat{U}_{ee} \hat{T}_e | \varphi_l \rangle = -\frac{1}{4} \sum_{i=1}^n \sum_{j>i}^n \sum_{k=1}^n \langle \varphi_k | \frac{1}{r_{ij}} \nabla_k^2 | \varphi_l \rangle , \quad (3.7)$$

$$\langle \varphi_k | \hat{U}_{nn} \hat{U}_{nn} | \varphi_l \rangle = \frac{1}{4} \sum_{a=1}^N \sum_{b>a}^N \sum_{c=1}^N \sum_{d>c}^N \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|} \frac{Z_c Z_d}{|\mathbf{R}_c - \mathbf{R}_d|} \langle \varphi_k | \varphi_l \rangle , \quad (3.8)$$

$$\langle \varphi_k | \hat{U}_{en} \hat{U}_{nn} | \varphi_l \rangle = -\frac{1}{2} \sum_{i=1}^n \sum_{a=1}^N \sum_{b=1}^N \sum_{c>b}^N \frac{Z_a Z_b Z_c}{|\mathbf{R}_b - \mathbf{R}_c|} \langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle , \quad (3.9)$$

$$\langle \varphi_k | \hat{U}_{ee} \hat{U}_{nn} | \varphi_l \rangle = \frac{1}{4} \sum_{i=1}^n \sum_{j>i}^n \sum_{a=1}^N \sum_{b>a}^N \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|} \langle \varphi_k | \frac{1}{r_{ij}} | \varphi_l \rangle , \quad (3.10)$$

$$\langle \varphi_k | \hat{U}_{en} \hat{U}_{en} | \varphi_l \rangle = \sum_{i=1}^n \sum_{a=1}^N \sum_{j=1}^N \sum_{b=1}^N Z_a Z_b \langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_j - \mathbf{R}_b|} | \varphi_l \rangle , \quad (3.11)$$

$$\langle \varphi_k | \hat{U}_{en} \hat{U}_{ee} | \varphi_l \rangle = -\frac{1}{2} \sum_{i=1}^n \sum_{a=1}^N \sum_{j=1}^n \sum_{k>j}^n Z_a \langle \varphi_k | \frac{1}{r_{jk}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle , \quad (3.12)$$

$$\langle \varphi_k | \hat{U}_{ee} \hat{U}_{ee} | \varphi_l \rangle = \frac{1}{4} \sum_{i=1}^n \sum_{j>i}^n \sum_{p=1}^n \sum_{q>p}^n \langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle . \quad (3.13)$$

Of these, the last three integrals, Eqs. (3.11)–(3.13), are of particular interest to us, as these are the ones thought to have no analytic solutions on an FECG basis set. To solve this problem, in Section 4, we will introduce an approximation that can express one of the $\frac{1}{r}$ factors in the integrand by a linear combination of Gaussian functions. However, before doing that, let us see where these elements occur in practice and why their evaluation is so important.

3.2 Relativistic Corrections

3.2.1 Non-Relativistic Quantum Electrodynamics

As discussed before, there is an urgent need for highly precise theoretical results that can match and verify those obtained through experiments. When it comes to the accurate calculations of energy levels, the preferred method involves the so-called non-relativistic quantum electrodynamics (QED) expansion of the energy [25, 26]:

$$E = \sum_k \alpha^k E_k , \quad (3.14)$$

where the expansion happens in terms of the fine-structure constant α . This approach takes the non-relativistic energy E_0 , obtained through solving the Schrödinger equation, and adds correc-

tional terms, some of which can be attributed a physical meaning. The αE_1 term is missing; the $\alpha^2 E_2$ term corresponds to the so-called leading-order relativistic effects, the $\alpha^3 E_3$ term describes the leading-order QED effects, while the rest of the terms are referred to as higher-order relativistic and QED effects. Using this approach, each part of the expansion can be evaluated perturbatively with the same non-relativistic wave function [18].

For relativistic corrections, the part that concerns us primarily is the simplest, leading-order $\alpha^2 E_2$ term. It is well established [27, 28, 29] that this can be obtained by calculating the expectation value of the Breit-Pauli Hamiltonian [24, 30, 31], which, for our calculations with fixed nuclei and singlet electronic states, takes the form [18, 32]:

$$E_2 = \langle \Psi | \hat{H}_{\text{BP}} | \Psi \rangle , \quad (3.15)$$

$$\hat{H}_{\text{BP}} = -\frac{1}{8} \sum_{i=1}^n \nabla_i^2 \nabla_i^2 + \frac{\pi}{2} \sum_{i=1}^n \sum_{a=1}^N Z_a \delta(\mathbf{r}_{ia}) + \pi \sum_{i=1}^n \sum_{j>i}^n \delta(\mathbf{r}_{ij}) - \frac{1}{2} \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} \left(\mathbf{p}_i \mathbf{p}_j + \frac{\mathbf{r}_{ij} (\mathbf{r}_{ij} \mathbf{p}_i) \mathbf{p}_j}{r_{ij}^2} \right) , \quad (3.16)$$

where the parts of the Breit-Pauli Hamiltonian are known as the mass-velocity, Darwin I., Darwin II. (combined with the spin-spin Fermi contact interaction expression) and orbit-orbit terms, respectively. Of these, the first three are of particular interest to us, as these are singular operators. Due to the inaccurate behavior of ECGs near the coalescence points, the expectation values of such operators tend to converge overly slowly, in terms of the number of basis functions used, to a point where the desired spectroscopic accuracy is not achievable. To combat this issue, two regularization techniques have been developed to reexpress these terms in a more favourable form through operator identities.

3.2.2 Integral Transformation Technique

The first regularization method I would like to discuss is the integral transformation technique developed by Pachucki, Cencek and Komasa in 2005 [33]. The general idea of this approach is to perform a transformation, which relocates the singularity of the Dirac delta function from its original place near zero into the asymptotic tail of the new transformed function. As a result, for short distances, the expectation values in the Darwin terms can be accurately described with the smooth ECGs using the following formula:

$$\langle \Psi | \delta(\mathbf{r}) | \Psi \rangle = \frac{1}{2\pi^{3/2}} \int_0^\infty \langle \Psi | 2t^2 (3 - 2t^2 r^2) e^{-t^2 r^2} | \Psi \rangle dt . \quad (3.17)$$

For larger distances, to where the singularity was essentially displaced, an analytically obtained asymptotic formula is employed:

$$f(t) = \frac{4Z}{\sqrt{\pi}t^2} \langle \Psi | \delta(\mathbf{r}) | \Psi \rangle \left(1 + \frac{A_1}{t} + \frac{A_2}{t^2} + \frac{A_3}{t^3} + \dots \right), \quad (3.18)$$

where the parameters A_i are defined to help with the fitting of the short-range formula, and the Z parameter denotes the nuclear charge. For the theoretical details of the derivation of this method, see [34].

While this method is applicable to both atomic and molecular systems, it leads to having to perform tedious manual balancing of the previous two equations, deciding where to place the cut-offs, which, unfortunately, makes it prone to mistakes and becomes unfeasible in an automated evaluation procedure, *e.g.*, at many points over a potential energy surface [34, 35].

3.2.3 Drachmanization Technique

The second regularization method I would like to consider is colloquially known as Drachmanization after Drachman, who first proposed it in 1981 [36]. This is the technique that will be further expanded upon in this paper, and where the incalculable matrix elements of $\hat{H}^2$ appear for molecular calculations. Due to this reason, the great drawback of this method until now was its limited use for atomic systems.

This method relies on an exact identity for the Dirac delta function, which will be derived in the following equations. First, let us consider a two-electron system, from which the results will be generalized for n particles. To begin, we consider the following notations for the expectation value, which hold true for the real wave functions used in our calculations:

$$\langle \delta(\mathbf{r}_{12}) \rangle = \langle \Psi | \delta(\mathbf{r}_{12}) | \Psi \rangle = \int_{\mathbb{R}^6} d\mathbf{r} \, \Psi \, \delta(\mathbf{r}_{12}) \, \Psi = \int d\mathbf{r} \, \delta(\mathbf{r}_{12}) \, \Psi^2. \quad (3.19)$$

The Dirac delta associated with the two-electron interaction $\delta(\mathbf{r}_{12})$ can be expressed in the following two ways using the Poisson equation:

$$\nabla_1^2 \frac{1}{r_{12}} = -4\pi\delta(\mathbf{r}_{12}), \quad (3.20)$$

$$\nabla_2^2 \frac{1}{r_{12}} = -4\pi\delta(\mathbf{r}_{12}). \quad (3.21)$$

Adding the above two equations together and taking the expectation value, we arrive at the four-

dation of the coming transformations:

$$-8\pi\langle\delta(\mathbf{r}_{12})\rangle = \int d\mathbf{r} \left[(\nabla_1^2 + \nabla_2^2) \frac{1}{r_{12}} \right] \Psi^2 . \quad (3.22)$$

Next, we will make use of integration by parts twice, with the consideration that we are working with fixed boundaries, thus the terms pulled out of the integral can be set to zero. Examining one term of the addition, we get:

$$\int d\mathbf{r} \left[\nabla_1^2 \frac{1}{r_{12}} \right] \Psi^2 = (0) - \int d\mathbf{r} \left[\nabla_1 \frac{1}{r_{12}} \right] (\nabla_1 \Psi^2) = (0) + \int d\mathbf{r} \frac{1}{r_{12}} \nabla_1^2 \Psi^2 . \quad (3.23)$$

Performing the same transformations with the other Laplacian as well, we arrive at an expression where the $\frac{1}{r_{12}}$ and Ψ^2 terms have swapped places relative to Eq. (3.22):

$$\langle\delta(\mathbf{r}_{12})\rangle = -\frac{1}{8\pi} \int d\mathbf{r} \left[(\nabla_1^2 + \nabla_2^2) \Psi^2 \right] \frac{1}{r_{12}} . \quad (3.24)$$

To develop this expression further, we need to first expand the Schrödinger equation for the two-electron case by directly substituting in the kinetic and potential energy operators of Eqs. (2.3)–(2.7):

$$\hat{H}_{\text{el}}\Psi = E\Psi , \quad (3.25)$$

$$\left[\underbrace{-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2}_{\hat{T}} + \underbrace{\frac{1}{r_{12}} - \sum_{a=1}^N \left(\frac{Z_a}{r_{1a}} + \frac{Z_a}{r_{2a}} \right) + \sum_{a=1}^N \sum_{b>a}^N \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}}_{\hat{V}} \right] \Psi = E\Psi , \quad (3.26)$$

where in the last equation, we introduced the notation $\hat{T}$ and $\hat{V}$ for grouping the kinetic and potential energy operators together. With this in mind, we can construct the following expression by comparing Eqs. (3.24) and (3.26):

$$[(\nabla_1^2 + \nabla_2^2) \Psi] = -2 \cdot \hat{T} \Psi = -2 \cdot (E - \hat{V}) \Psi . \quad (3.27)$$

To be able to use the above equation, we first need to rewrite the Ψ^2 term in Eq. (3.24). For this, we exploit the hermiticity of the Laplacian and employ the identity [36]:

$$\nabla^2 \Psi^2 = 2\Psi(\nabla^2 \Psi) + 2(\nabla \Psi)(\nabla \Psi) , \quad (3.28)$$

substituting it into Eq. (3.24), we finally get:

$$\langle \delta(\mathbf{r}_{12}) \rangle = -\frac{1}{8\pi} \left[2 \int d\mathbf{r} \Psi \frac{1}{r_{12}} [(\nabla_1^2 + \nabla_2^2)\Psi] + 2 \sum_{i=1}^2 \int d\mathbf{r} \frac{1}{r_{12}} (\nabla_i \Psi)(\nabla_i \Psi) \right] \quad (3.29)$$

$$= \frac{1}{4\pi} \left[2 \langle \Psi | \frac{1}{r_{12}} (E - \hat{V}) | \Psi \rangle - \sum_{i=1}^2 \langle \nabla \Psi_i | \frac{1}{r_{12}} | \nabla \Psi_i \rangle \right]. \quad (3.30)$$

Generalizing this equation for the n -electron case, we arrive at the final result of:

$$\langle \delta(\mathbf{r}_{ij}) \rangle = \frac{1}{4\pi} \left[2 \langle \Psi | \frac{1}{r_{ij}} (E - \hat{V}) | \Psi \rangle - \sum_{i=1}^n \langle \nabla \Psi_i | \frac{1}{r_{ij}} | \nabla \Psi_i \rangle \right]. \quad (3.31)$$

For the Dirac delta function of the Darwin I. term, the derivation is almost identical, with the only change being that the starting Poisson equations are:

$$\nabla_1^2 \frac{1}{r_{1a}} = -4\pi\delta(\mathbf{r}_{1a}), \quad (3.32)$$

$$\nabla_2^2 \frac{1}{r_{1a}} = 0. \quad (3.33)$$

In the end, this change results in $\frac{1}{2}$ factor difference compared to Eq. (3.31):

$$\langle \delta(\mathbf{r}_{ia}) \rangle = \frac{1}{2\pi} \left[2 \langle \Psi | \frac{1}{r_{ia}} (E - \hat{V}) | \Psi \rangle - \sum_{i=1}^n \langle \nabla \Psi_i | \frac{1}{r_{ia}} | \nabla \Psi_i \rangle \right]. \quad (3.34)$$

Lastly, the mass-velocity term can also be reexpressed in a similar way, resulting in the following equation:

$$\left\langle \sum_{i=1}^n \nabla_i^2 \nabla_i^2 \right\rangle = 4 \left\langle \Psi \left| (E - \hat{V})^2 \right| \Psi \right\rangle - 2 \sum_{i=1}^n \sum_{j>i}^n \langle \nabla_i^2 \Psi | \nabla_j^2 \Psi \rangle. \quad (3.35)$$

It should be noted, that for these generalized cases the potential energy operator $\hat{V}$ is written as:

$$\hat{V} = \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} - \sum_{i=1}^n \sum_{a=1}^N \frac{Z_a}{|\mathbf{r}_i - \mathbf{R}_a|} + \sum_{a=1}^N \sum_{b>a}^N \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}. \quad (3.36)$$

To summarize, through the derivation detailed in this section, we have arrived at three new expressions for the expectation values of the mass-velocity, Darwin I. and Darwin II. terms needed for relativistic corrections; these can be seen in Eqs. (3.31), (3.34) and (3.35). While the expectation value of the Hamiltonian squared does not explicitly appear in any of these equations, it is clear that all three of the incalculable matrix elements would appear in the terms $\frac{1}{r_{ij}} \hat{V}$, $\frac{1}{r_{is}} \hat{V}$ and $\hat{V}^2$ when the general wave function Ψ got condensed down to the spatial FECG functions.

3.3 Lower Bounds

In Section 2.2, with the variational principle of Eq. (2.9), we have defined a method to accurately approach the exact energy level of a few-body system from above. Similarly constructing a method to obtain lower bounds of the exact energy would prove immensely useful, as by using the combination of these two limits, we could definitively establish a region within which the precise energy of the system lies [37]. Amongst others, this could, for example, help accurately verify experimental results. Unfortunately, most of the current methods of establishing lower bounds are orders of magnitude less accurate compared to their upper counterparts, making them essentially useless in most cases. Owing to this fact, this area is still the subject of active research.

Most of the methods devised are founded upon two classical ways of defining lower bounds. The simpler of the two is known as Weinstein’s criterion [38], taking the form:

$$E - \sigma \leq E_0 , \quad (3.37)$$

where E is the expectation value obtained for the upper bound, E_0 is the exact ground state energy and σ is the variance of energy, defined as:

$$\sigma^2 = \frac{\langle \Psi | \hat{H}^2 | \Psi \rangle}{\langle \Psi | \Psi \rangle} - E^2 . \quad (3.38)$$

The other important lower bound is called Temple’s bound [39]:

$$E - \frac{\sigma^2}{\varepsilon - E} \leq E_0 , \quad (3.39)$$

where ε is a parameter which fulfils $E \leq \varepsilon \leq E_1$. This means that this method requires some knowledge about the energy of the first excited state E_1 as well.

Many methods used for calculating lower bounds, which build on these early equations, have so far been limited to atomic systems due to their use of σ and, indirectly, the expectation value of $\hat{H}^2$. For molecules, such calculations would require the evaluation of the three analytically unknown matrix elements. In this report, I will not further flesh out the topic of lower bounds, as my research so far has exclusively concentrated on the previously discussed relativistic corrections. However, it should be noted that tight lower bound calculations are another direct application of the method detailed in this report.

4 The Beylkin method

4.1 The Background of the Approximation

In 2005, G. Beylkin and L. Monzón published an article [40] containing several approximations of different functions using exponential sums, including a general $r^{-\alpha}$ -family of functions, where α is a positive real number. Using this proposed method with $\alpha = 1$, we can approximate one of the $\frac{1}{r}$ terms in the analytically in calculable matrix elements to still evaluate it and expand the applications of Section 3 to molecular systems. This direct calculation will be the subject of Section 5. In this section, I will give a more descriptive derivation of the proposed approximation formula, partly, to gain a more comprehensive understanding of where its parameters come from. However, I will not complete the proof as it is rather tedious and the resulting set of equations for the parameters is not used in our calculations. The theorem proposed is:

$$\left| r^{-\alpha} - \sum_{m=1}^M w_m e^{-p_m r^2} \right| \leq r^{-\alpha} \varepsilon \quad \text{for all } \delta \leq r \leq 1, \quad (4.1)$$

where parameter ε denotes the desired accuracy, while δ is a small step parameter generally chosen to be $\delta \approx 10^2 \cdot \varepsilon$. To begin the proof, we will have to restructure the well-known definition of the gamma function:

$$\Gamma(z) = \int_0^\infty x^{z-1} e^{-x} dx \quad \text{Re}(z) > 0. \quad (4.2)$$

We first have to make the substitutions $z = \frac{\alpha}{2}$ and $t = \ln \frac{x}{r^2}$, which result in:

$$x = r^2 e^t, \quad (4.3)$$

$$dx = x dt = r^2 e^t dt, \quad (4.4)$$

with the integration limits changing to:

$$\lim_{x \rightarrow 0} \ln \frac{x}{r^2} = -\infty, \quad (4.5)$$

$$\lim_{x \rightarrow \infty} \ln \frac{x}{r^2} = \infty. \quad (4.6)$$

Completing these changes, the gamma function takes on the form:

$$\Gamma\left(\frac{\alpha}{2}\right) = r^\alpha \int_{-\infty}^{\infty} e^{-r^2 e^t + \frac{1}{2}\alpha t} dt. \quad (4.7)$$

With the final substitution of $s = \frac{t}{2}$ and some further rearrangements, we get the following expression:

$$\frac{\Gamma\left(\frac{\alpha}{2}\right)}{2} r^{-\alpha} = \int_{-\infty}^{\infty} e^{-r^2 e^{2s} + \alpha s} ds . \quad (4.8)$$

The essence of the approximation is the discretization of the integral seen above by using the sum provided by the trapezoidal rule:

$$T_h^M = h \cdot \left[\sum_{k=1}^{M-1} f(a + m \cdot h) + \frac{f(a) + f(b)}{2} \right], \quad \text{where: } h = \frac{b-a}{M}, \quad (4.9)$$

and the calculation is narrowed down to a domain $[a, b]$, instead of $[-\infty, \infty]$. In our case, as seen in Eq. (4.8), the function of the integral we want to approximate is:

$$f_{\alpha,r}(s) = e^{-r^2 e^{2s} + \alpha s} . \quad (4.10)$$

In general, the error of this approximation can be given by the Euler–Maclaurin formula of the appropriate form [41, 42]:

$$\begin{aligned} \int_a^b f(s) ds - T_h^M &= h^{2N+1} \int_0^M \frac{B_{2N}(s - [s])}{2N!} D^{2N} f(a + sh) ds \\ &\quad - \sum_{n=1}^N \frac{b_{2n}}{2n!} h^{2n} (D^{2n-1} f(b) - D^{2n-1} f(a)) , \end{aligned} \quad (4.11)$$

where N is a positive integer determined by the desired accuracy ε , D^{2N} denotes the $2N$ th derivative, $B_{2N}(s)$ are Bernoulli polynomials, b_{2n} are Bernoulli numbers, and $[s]$ represents the integer part of the real number s .

After smaller modifications to Eq. (4.11) and substituting in Eq. (4.8), we arrive at the following symbolic expression:

$$\left| \frac{\Gamma\left(\frac{\alpha}{2}\right)}{2} r^{-\alpha} - T_h^M \right| \leq I_a + I_b + S_a + S_b + I . \quad (4.12)$$

In this equation, I_a and I_b account for the restriction of the domain from $[-\infty, \infty]$ to $[a, b]$:

$$I_a = \int_{-\infty}^a f_{\alpha,r}(s) ds \quad I_b = \int_b^{\infty} f_{\alpha,r}(s) ds , \quad (4.13)$$

while the other three parameters come from the Euler–Maclaurin formula.

The rest of the proof pertains to proving that $I_a + I_b + S_a + S_b + I \leq \frac{\Gamma(\frac{\alpha}{2})}{2} r^{-\alpha} \varepsilon$ with the right choice of parameters a, b and M (and an appropriate inner variable N), thus resulting in:

$$\left| \frac{\Gamma(\frac{\alpha}{2})}{2} r^{-\alpha} - T_h^M \right| \leq \frac{\Gamma(\frac{\alpha}{2})}{2} r^{-\alpha} \varepsilon . \quad (4.14)$$

The final parts of the proof can be found in [40]. We decided not to detail these final steps here as the system of equations it gives to determine the values of a, b , and M were generally not followed in our applications, rather mainly used as starting points. This was done because, after some numerical testing, better final results were obtained with values that did not strictly follow these recommended boundaries. The details of these tests are the subject of the next section.

To arrive at a practical version of Eq. (4.14), we continue by substituting in Eq. (4.10) into Eq. (4.9), so we can express T_h^M as:

$$T_h^M = h \sum_{m=1}^M \exp \left[-r^2 e^{2 \cdot (a+m \cdot h)} + \alpha \cdot (a + m \cdot h) \right] , \quad (4.15)$$

which, after some rearrangement leads us to the final expression:

$$\left| r^{-\alpha} - \frac{2}{\Gamma(\frac{\alpha}{2})} h \sum_{m=1}^M \exp \left[-r^2 e^{2 \cdot (a+m \cdot h)} + \alpha \cdot (a + m \cdot h) \right] \right| \leq r^{-\alpha} \varepsilon . \quad (4.16)$$

Comparing Eq. (4.16) and the originally proposed theorem in Eq. (4.1), we get the expressions for the parameters w_m and p_m :

$$w_m = \frac{2}{\Gamma(\frac{\alpha}{2})} h \cdot \exp [\alpha \cdot (a + m \cdot h)] , \quad (4.17)$$

$$p_m = \exp [2 \cdot (a + m \cdot h)] . \quad (4.18)$$

As mentioned in the beginning, α will equal 1 in our applications, so w_m is better expressed as:

$$w_m = \frac{2}{\sqrt{\pi}} h \cdot \exp [a + m \cdot h] . \quad (4.19)$$

4.2 Choosing Parameters and Investigating the Approximation

As detailed previously, the final steps of the proof result in a set of equations designed to help assign the a, b , and M parameters to achieve the desired accuracy ε . However, for our applications, we decided to investigate this issue further and search for better-performing parameters.

We did this by carrying out trial calculations of this approximation using arbitrary FECG basis functions. These computations were primarily concentrated on evaluating the matrix elements of an electron-electron interaction potential energy:

$$U_e^{kl} = \langle \varphi_k | \frac{1}{r_{ij}} | \varphi_l \rangle , \quad (4.20)$$

for which the analytic formula is known [21], allowing us to compare our results and accuracy. Accordingly, we performed many calculations for these matrix elements, each time gradually changing the approximation parameters a, b , and M . For the sake of convenience, we also made the inconsequential limitation of $|a| = |b|$, which is not a requirement of the original paper. With this in mind, we can define the relative error of the approximation as:

$$\delta = \left| \frac{U_{e, \text{exact}}^{kl} - U_{e, \text{approx.}}^{kl}}{U_{e, \text{approx.}}^{kl}} \right| . \quad (4.21)$$

To serve as an example, a result of this investigation can be nicely showcased through the following typical plot of the relative error in terms of the approximation parameters, computed with Wolfram Mathematica, Figure 1.

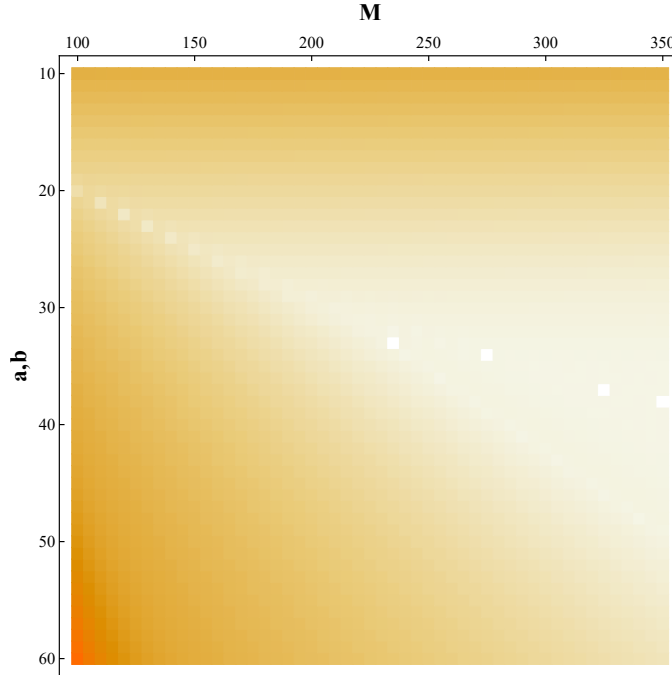


Figure 1: The relative error of the approximation for the given calculation in terms of a, b and M approximation parameters

In the above figure, the darker colors represent higher values of the relative error, while the lighter

shades represent lower ones, with the highest accuracy being around 10^{-17} near the lightest parts of the image. Fortunately, this result is entirely consistent with expectations: the M number of terms of the summation has to be increased in parallel with the a, b bounds of the approximation in order to achieve the best results. Moreover, the darker areas in the left-hand corner are explained by the fact that increasing the a, b boundaries with a constant M only worsens the resolution of the approximation.

Through similar investigations with a handful of FECG functions, taking into account the computational resources as well, we decided on using $M = 200$ points of summation with boundaries $b = 31$, and $a = -31$. Admittedly, these parameters could be further refined, which should be the subject of future considerations. However, the numerical results obtained with this choice were already excellent with an affordable computational cost. The improvement observed with $M = 400$ was not significant.

Due to the incorrect behavior of ECGs at short distances, discussed in Section 2.3.1, we decided to examine the effect of the shape of the basis functions used as well. The rudimentary method devised was again based on calculating the matrix element of Eq. (4.20), however, this time focusing on the zero-shift case, where the basis function takes on the form:

$$\varphi_k = \exp \left[-\mathbf{r}^T \underline{\mathbf{A}}_k \mathbf{r} \right] . \quad (4.22)$$

We also chose to condense down the $\mathbf{A}_k$ -matrix to a one-dimensional form, *i.e.*, a simple number A . This way, we could elegantly study the effects of the shape of the ECG basis function by increasing the A parameter and observing its effects on the relative error. With this technique, the following logarithmic plot was produced in Mathematica, Figure 2.

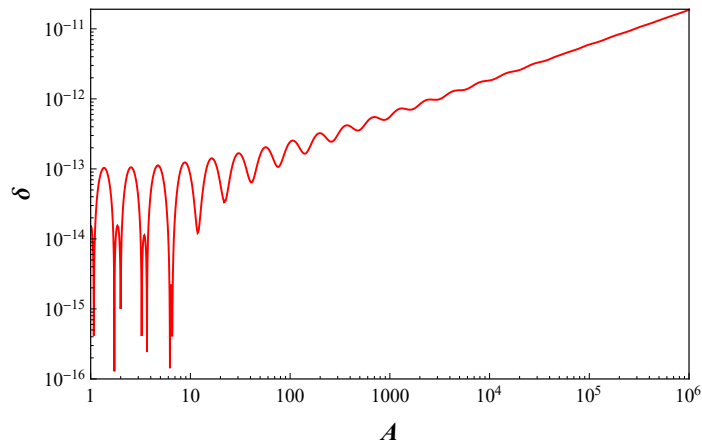


Figure 2: The relative error of the approximation in terms of A , representing the shape of the basis function used

On the x-axis, we have increased A from 1 to 1 million, which only resulted in a loss of three orders of accuracy. While this may seem significant, the elements of the positive-definite $\mathbf{A}_k$ matrix rarely exceed the order of 10^4 , with negative numbers further dampening this magnitude. In this sense, the one-dimensional plot of Figure 2 could be taken as a worst-case scenario. This is further backed by subsequent investigations of similar plots with different arrangements of two-dimensional $\mathbf{A}_k$ matrices, some of which had the initial stability, seen in Figure 2 near the A values of 1-10, extending into the 10^6 range. With this understanding, these results can certainly be considered promising.

5 Deriving the Matrix Elements

In this section, several derivations will be presented by applying the approximation of Section 4 to calculate the three analytically unknown matrix elements first discussed in Section 3.1. While incorporating the sum provided by Beylkin and Monzón's method into the expectation values may seem straightforward at first glance, multiple obstacles and difficulties need to be accounted for, which will all be detailed here. Some of these considerations and calculations done in the following could seem somewhat tedious, however, it should be noted that the resulting methodology is exceedingly robust, and can be used without any prior knowledge of these inner workings. As we shall see in Section 6, during our calculations of relativistic corrections, there was no need to change or adjust the starting parameters of the approximation: $M = 200$ and $a = -31$, $b = 31$.

5.1 Common Notations

Some common notations, of which we will make extensive use in the following sections:

$$\underline{\mathbf{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3 , \quad (5.1)$$

$$\mathbf{A}_{kl} = \mathbf{A}_l + \mathbf{A}_k , \quad (5.2)$$

$$\mathbf{e} = \underline{\mathbf{A}}_l \mathbf{s}_l + \underline{\mathbf{A}}_k \mathbf{s}_k , \quad (5.3)$$

$$\eta = \mathbf{s}_l^T \underline{\mathbf{A}}_l \mathbf{s}_l + \mathbf{s}_k^T \underline{\mathbf{A}}_k \mathbf{s}_k , \quad (5.4)$$

$$\gamma = \mathbf{e}^T \underline{\mathbf{A}}_{kl}^{-1} \mathbf{e} - \eta , \quad (5.5)$$

$$\mathbf{s} = \underline{\mathbf{A}}_{kl}^{-1} \mathbf{e} , \quad (5.6)$$

$$S_{kl} = \exp[\gamma] \frac{\pi^{3n/2}}{|\mathbf{A}_{kl}|^{3/2}} . \quad (5.7)$$

5.2 The $\langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle$ Matrix Element

In this section, we will derive the general formula for the incalculable matrix element, which contains two electron-electron interaction energy terms: $\frac{1}{r_{ij}}$ and $\frac{1}{r_{pq}}$, where, as a reminder: $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $r_{pq} = |\mathbf{r}_p - \mathbf{r}_q|$. In practice, the approximation introduced in Eq. (4.1) will take on the following form (with $\alpha = 1$):

$$\frac{1}{r_{pq}} \cong \sum_{m=1}^M w_m \exp[-p_m r_{pq}^2] . \quad (5.8)$$

Applying this to the matrix element, we get:

$$\langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle \cong \sum_{m=1}^M w_m \langle \varphi_k | \frac{1}{r_{ij}} \exp[-p_m r_{pq}^2] | \varphi_l \rangle . \quad (5.9)$$

As previously detailed, φ_k and φ_l denote FECG spatial basis functions of the form:

$$\varphi_k = \exp [-(\mathbf{r} - \mathbf{s}_k)^T \underline{\mathbf{A}}_k (\mathbf{r} - \mathbf{s}_k)] , \quad (5.10)$$

$$\varphi_l = \exp [-(\mathbf{r} - \mathbf{s}_l)^T \underline{\mathbf{A}}_l (\mathbf{r} - \mathbf{s}_l)] , \quad (5.11)$$

where we have employed the notation of Eq. (5.1). It should also be restated that $\mathbf{r} \in \mathbb{R}^{3n}$ represents a vector that contains all the coordinates of the electrons in the system; at its i th position are the coordinates of the i th electron, which can be denoted by the three-dimensional vector $\mathbf{r}_i$.

Substituting these FECG basis functions into Eq. (5.9), we get the following expression:

$$\begin{aligned} \langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle &= \sum_{m=1}^M w_m \int_{-\infty}^{\infty} d\mathbf{r} \frac{1}{r_{ij}} \exp[-p_m r_{pq}^2] \\ &\cdot \exp [-(\mathbf{r} - \mathbf{s}_k)^T \underline{\mathbf{A}}_k (\mathbf{r} - \mathbf{s}_k)] \exp [-(\mathbf{r} - \mathbf{s}_l)^T \underline{\mathbf{A}}_l (\mathbf{r} - \mathbf{s}_l)] . \end{aligned} \quad (5.12)$$

If we introduce the new parameters of $\underline{\mathbf{A}}_{kl}$, η and $\mathbf{e}$, which can be understood through Eqs. (5.1)–(5.4), we can make the following contraction:

$$\exp [-(\mathbf{r} - \mathbf{s}_k)^T \underline{\mathbf{A}}_k (\mathbf{r} - \mathbf{s}_k)] \exp [-(\mathbf{r} - \mathbf{s}_l)^T \underline{\mathbf{A}}_l (\mathbf{r} - \mathbf{s}_l)] = \exp[-\eta] \exp [-\mathbf{r}^T \underline{\mathbf{A}}_{kl} \mathbf{r} + 2 \mathbf{e}^T \mathbf{r}] . \quad (5.13)$$

We are also going to make the well-known substitution of the one-dimensional Gaussian integral for the $\frac{1}{r_{ij}}$ term [21, 43]:

$$\frac{1}{r_{ij}} = \frac{2}{\sqrt{\pi}} \int_0^{\infty} dt \exp[-r_{ij}^2 t^2] . \quad (5.14)$$

Making use of both of the previous two identities, we arrive at the following form:

$$\langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle = \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \exp[-\eta] \int_0^{\infty} dt \int_{-\infty}^{\infty} d\mathbf{r} \exp [-p_m r_{pq}^2 - t^2 r_{ij}^2] \exp [-\mathbf{r}^T \underline{\mathbf{A}}_{kl} \mathbf{r} + 2 \mathbf{e}^T \mathbf{r}] . \quad (5.15)$$

Next, we need to rewrite the r_{ij}^2 and r_{pq}^2 parts using the general $\mathbf{r}$ vector in order to make further contractions to the equation. To do this, we introduce the first type of the $\mathbf{J} \in \mathbb{R}^{n \times n}$ matrices,

which will cut out the coordinates of the two chosen electrons from $\mathbf{r}$ and subtract them from each other, like such:

$$\mathbf{r}^T \underline{\mathbf{J}}_{ij} \mathbf{r} = r_{ij}^2 . \quad (5.16)$$

Multiplication with the three-dimensional identity matrix is required here as well, which as per Eq. (5.1), is denoted by underlining.

These $\mathbf{J}$ matrices can be exactly defined using Kronecker deltas as:

$$J_{ij,\alpha\beta} = \delta_{\alpha\beta}(\delta_{\alpha i} + \delta_{\alpha j}) - (\delta_{\alpha i}\delta_{\beta j} + \delta_{\beta i}\delta_{\alpha j})(1 - \delta_{\alpha\beta}) , \quad (5.17)$$

or more intuitively, as an example, the matrix subtracting the coordinates of first and second electrons in a three-electron system, $\mathbf{J}_{12}$, will take on the form:

$$\mathbf{J}_{12} = \begin{pmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} .$$

Using this method for both r_{ij}^2 and r_{pq}^2 and defining two $\mathbf{J}$ matrices, we get:

$$\langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle = \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \exp[-\eta] \int_0^\infty dt \int_{-\infty}^\infty d\mathbf{r} \exp \left[-\mathbf{r}^T (\underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{pq} + t^2 \underline{\mathbf{J}}_{ij}) \mathbf{r} + 2 \mathbf{e}^T \mathbf{r} \right] . \quad (5.18)$$

In this equation both the $\underline{\mathbf{A}}_{kl}$ and $p_m \underline{\mathbf{J}}_{pq}$ terms are considered constants when it comes to the integrals, and thus can be contracted as:

$$\underline{\mathbf{A}}'_{kl} = \underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{pq} . \quad (5.19)$$

Later it will become important that p_m parameters are hidden within these 'dashed' variables. By performing this substitution, we can directly use the well-known identity seen below [21, 43]:

$$\int_{-\infty}^\infty d^n \mathbf{x} \exp[-\mathbf{x}^T \mathbf{M} \mathbf{x} + \mathbf{y}^T \mathbf{x}] = \frac{\pi^{n/2}}{|\mathbf{M}|^{1/2}} \exp \left[\frac{1}{4} \mathbf{y}^T \mathbf{M}^{-1} \mathbf{y} \right] , \quad (5.20)$$

to obtain the following result:

$$\langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle = \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \pi^{3n/2} \exp[-\eta] \int_0^\infty dt |\mathbf{A}'_{kl} + t^2 \mathbf{J}_{ij}|^{-3/2} \exp \left[\mathbf{e}^T (\mathbf{A}'_{kl} + t^2 \mathbf{J}_{ij})^{-1} \mathbf{e} \right], \quad (5.21)$$

where the powers of three result from the multiplications by the $\mathbf{I}_3$ matrix, and n denotes the number of electrons in the system. Next, we need to use the two important identities of rank one matrices [21, 43], which when applied to Eq. (5.21), give us:

$$|\mathbf{I} + a\mathbf{B}| = 1 + a \operatorname{Tr} \mathbf{B}, \quad (5.22)$$

$$\begin{aligned} |\mathbf{A}'_{kl} + t^2 \mathbf{J}_{ij}|^{-3/2} &= |\mathbf{A}'_{kl}|^{-3/2} |\mathbf{I} + t^2 \mathbf{A}'_{kl}{}^{-1} \mathbf{J}_{ij}|^{-3/2} \\ &= |\mathbf{A}'_{kl}|^{-3/2} (1 + t^2 \operatorname{Tr}(\mathbf{A}'_{kl}{}^{-1} \mathbf{J}_{ij}))^{-3/2}, \end{aligned} \quad (5.23)$$

$$(\mathbf{A} + \mathbf{B})^{-1} = \mathbf{A}^{-1} - \frac{\mathbf{A}^{-1} \mathbf{B} \mathbf{A}^{-1}}{1 + \operatorname{Tr}(\mathbf{B} \mathbf{A}^{-1})}, \quad (5.24)$$

$$(\mathbf{A}'_{kl} + t^2 \mathbf{J}_{ij})^{-1} = \mathbf{A}'_{kl}{}^{-1} - \frac{t^2 \mathbf{A}'_{kl}{}^{-1} \mathbf{J}_{ij} \mathbf{A}'_{kl}{}^{-1}}{1 + t^2 \operatorname{Tr}(\mathbf{A}'_{kl}{}^{-1} \mathbf{J}_{ij})}. \quad (5.25)$$

Substituting these in, we get the following:

$$\begin{aligned} \langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle &= \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \pi^{3n/2} |\mathbf{A}'_{kl}|^{-3/2} \exp[\mathbf{e}^T \mathbf{A}'_{kl}{}^{-1} \mathbf{e} - \eta] \int_0^\infty dt \\ &\cdot (1 + t^2 \operatorname{Tr}(\mathbf{A}'_{kl}{}^{-1} \mathbf{J}_{ij}))^{-3/2} \exp \left[\mathbf{e}^T \left(\frac{-t^2 \mathbf{A}'_{kl}{}^{-1} \mathbf{J}_{ij} \mathbf{A}'_{kl}{}^{-1}}{1 + t^2 \operatorname{Tr}(\mathbf{A}'_{kl}{}^{-1} \mathbf{J}_{ij})} \right) \mathbf{e} \right]. \end{aligned} \quad (5.26)$$

In order to make the following transformations more easily understandable, we introduce three temporary parameters:

$$S'_{kl} = \pi^{3n/2} |\mathbf{A}'_{kl}|^{-3/2} \exp[\mathbf{e}^T \mathbf{A}'_{kl}{}^{-1} \mathbf{e} - \eta], \quad (5.27)$$

$$a' = \operatorname{Tr}(\mathbf{A}'_{kl}{}^{-1} \mathbf{J}_{ij}), \quad (5.28)$$

$$\beta' = \mathbf{e}^T \mathbf{A}'_{kl}{}^{-1} \mathbf{J}_{ij} \mathbf{A}'_{kl}{}^{-1} \mathbf{e}. \quad (5.29)$$

Using these three notations, Eq. (5.26) can be elegantly simplified to:

$$\langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle = \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} S'_{kl} \int_0^\infty dt (1 + t^2 a')^{-3/2} \exp \left[\frac{-t^2 \beta'}{1 + t^2 a'} \right]. \quad (5.30)$$

In the next, almost final steps, we would like to apply the following definition of the error function, to get a clear, computationally favorable equation:

$$\operatorname{erf} x = \frac{\operatorname{sgn} x}{\sqrt{\pi}} \gamma\left(\frac{1}{2}, x^2\right), \quad (5.31)$$

$$\gamma\left(\frac{1}{2}, x^2\right) = \int_0^{x^2} y^{-1/2} \exp[-y] dy. \quad (5.32)$$

where γ is the lower incomplete gamma function. To achieve this, we employ a substitution of:

$$z = \frac{t^2 \beta'}{1 + t^2 a'}, \quad (5.33)$$

$$dt = dz \cdot \frac{(1 + t^2 a')^2}{2 \cdot t \beta'}, \quad (5.34)$$

which also changes the boundaries of the integral:

$$\lim_{t \rightarrow 0} \frac{t^2 \beta'}{1 + t^2 a'} = 0, \quad (5.35)$$

$$\lim_{t \rightarrow \infty} \frac{t^2 \beta'}{1 + t^2 a'} = \frac{\beta'}{a'}. \quad (5.36)$$

Employing these changes, we arrive at the following form:

$$\langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle = \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} S'_{kl} \frac{1}{2\sqrt{\beta'}} \int_0^{\frac{\beta'}{a'}} dz z^{-1/2} \exp[-z]. \quad (5.37)$$

In this form, we can directly apply the definitions of Eqs. (5.31) and (5.32), to get the following succinct equation:

$$\langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle \cong \sum_{m=1}^M w_m \frac{S'_{kl}}{\sqrt{\beta'}} \operatorname{erf} \left(\sqrt{\frac{\beta'}{a'}} \right), \quad (5.38)$$

where the $\operatorname{sgn} x$ could be left out, as we are dealing with real numbers. This elegant result is completely identical to that of the single electron-electron interaction case $\langle \varphi_k | \frac{1}{r_{ij}} | \varphi_l \rangle$, except here we use ‘dashed’ parameters as we needed to introduce the $\underline{A}'_{kl}$ matrix.

While it is tempting to leave this equation like so, we have to dissect these ‘dashed’ variables of Eqs. (5.27)–(5.29) and directly see the p_m parameters in order to arrive at a form that can actually be computationally implemented.

5.2.1 Breaking down the Equation

Before we begin dissecting this result, for future reference, it will be very useful to define the following seven new parameters:

$$t_1 = \text{Tr}(\mathbf{A}_{kl}^{-1} \mathbf{J}_{ij}) , \quad (5.39)$$

$$t_2 = \text{Tr}(\mathbf{A}_{kl}^{-1} \mathbf{J}_{pq}) , \quad (5.40)$$

$$t_3 = \text{Tr}(\mathbf{A}_{kl}^{-1} \mathbf{J}_{pq} \mathbf{A}_{kl}^{-1} \mathbf{J}_{ij}) , \quad (5.41)$$

$$\kappa_1 = \mathbf{s}^T \underline{\mathbf{J}}_{ij} \mathbf{s} , \quad (5.42)$$

$$\kappa_2 = \mathbf{s}^T \underline{\mathbf{J}}_{ij} \underline{\mathbf{A}}_{kl}^{-1} \underline{\mathbf{J}}_{pq} \mathbf{s} , \quad (5.43)$$

$$\kappa_3 = \mathbf{s}^T \underline{\mathbf{J}}_{pq} \underline{\mathbf{A}}_{kl}^{-1} \underline{\mathbf{J}}_{ij} \underline{\mathbf{A}}_{kl}^{-1} \underline{\mathbf{J}}_{pq} \mathbf{s} , \quad (5.44)$$

$$\kappa_4 = \mathbf{s}^T \underline{\mathbf{J}}_{pq} \mathbf{s} . \quad (5.45)$$

With these in mind, let us examine the S'_{kl} parameter of Eq. (5.27):

$$\begin{aligned} |\mathbf{A}'_{kl}|^{-3/2} &= |\mathbf{A}_{kl} + p_m \mathbf{J}_{pq}|^{-3/2} = |\mathbf{A}_{kl}|^{-3/2} |\mathbf{I} + p_m \mathbf{A}_{kl}^{-1} \mathbf{J}_{pq}|^{-3/2} \\ &= |\mathbf{A}_{kl}|^{-3/2} (1 + p_m \text{Tr}(\mathbf{A}_{kl}^{-1} \mathbf{J}_{pq}))^{-3/2} = |\mathbf{A}_{kl}|^{-3/2} (1 + p_m t_2)^{-3/2} , \end{aligned} \quad (5.46)$$

$$\begin{aligned} \mathbf{e}^T \underline{\mathbf{A}}_{kl}^{-1} \mathbf{e} &= \mathbf{e}^T \underline{\mathbf{A}}_{kl}^{-1} \mathbf{e} - \mathbf{e}^T \left[\frac{p_m \underline{\mathbf{A}}_{kl}^{-1} \underline{\mathbf{J}}_{pq} \underline{\mathbf{A}}_{kl}^{-1}}{1 + p_m t_2} \right] \mathbf{e} = \mathbf{e}^T \underline{\mathbf{A}}_{kl}^{-1} \mathbf{e} - \left[\frac{p_m \mathbf{s}^T \underline{\mathbf{J}}_{pq} \mathbf{s}}{1 + p_m t_2} \right] \\ &= \mathbf{e}^T \underline{\mathbf{A}}_{kl}^{-1} \mathbf{e} - \frac{p_m \kappa_4}{1 + p_m t_2} , \end{aligned} \quad (5.47)$$

where we have used the identities of Eqs. (5.22) and (5.24), and the common notation of the $\mathbf{s}$ vector from Eq. (5.6). Applying these, S'_{kl} becomes:

$$\begin{aligned} S'_{kl} &= \pi^{3n/2} |\mathbf{A}_{kl}|^{-3/2} \exp[\gamma] (1 + p_m t_2)^{-3/2} \exp \left[\frac{-p_m \kappa_4}{1 + p_m t_2} \right] \\ &= S_{kl} (1 + p_m t_2)^{-3/2} \exp \left[\frac{-p_m \kappa_4}{1 + p_m t_2} \right] , \end{aligned} \quad (5.48)$$

where we also employed the common notations from Eqs. (5.5) and (5.7). Here, S_{kl} denotes the matrix element of the overlap matrix on an ECG basis [17].

Next, we examine a' and β' :

$$\begin{aligned} a' &= \text{Tr}(\mathbf{A}'_{kl}^{-1} \mathbf{J}_{ij}) = \text{Tr}((\mathbf{A}_{kl} + p_m \mathbf{J}_{pq})^{-1} \mathbf{J}_{ij}) = \text{Tr} \left[\left(\mathbf{A}_{kl} - \frac{p_m \mathbf{A}_{kl}^{-1} \mathbf{J}_{pq} \mathbf{A}_{kl}^{-1}}{1 + p_m \text{Tr}(\mathbf{A}_{kl}^{-1} \mathbf{J}_{pq})} \right) \mathbf{J}_{ij} \right] \\ &= t_1 - \frac{p_m t_3}{1 + p_m t_2} = \frac{t_1 + p_m (t_1 t_2 - t_3)}{1 + p_m t_2} , \end{aligned} \quad (5.49)$$

$$\begin{aligned}
\beta' &= \mathbf{e}^T (\mathbf{A}_{kl} + p_m \mathbf{J}_{pq})^{-1} \mathbf{J}_{ij} (\mathbf{A}_{kl} + p_m \mathbf{J}_{pq})^{-1} \mathbf{e} \\
&= \mathbf{e}^T \left(\mathbf{A}_{kl}^{-1} - \frac{p_m \mathbf{A}_{kl}^{-1} \mathbf{J}_{pq} \mathbf{A}_{kl}^{-1}}{1 + p_m \text{Tr}(\mathbf{A}_{kl}^{-1} \mathbf{J}_{pq})} \right) \mathbf{J}_{ij} \left(\mathbf{A}_{kl}^{-1} - \frac{p_m \mathbf{A}_{kl}^{-1} \mathbf{J}_{pq} \mathbf{A}_{kl}^{-1}}{1 + p_m \text{Tr}(\mathbf{A}_{kl}^{-1} \mathbf{J}_{pq})} \right) \mathbf{e} \\
&= \mathbf{s} \mathbf{J}_{ij} \mathbf{s} - \frac{2 \cdot p_m}{1 + p_m t_2} \mathbf{s} \mathbf{J}_{ij} \mathbf{A}_{kl}^{-1} \mathbf{J}_{pq} \mathbf{s} + \frac{p_m^2}{(1 + p_m t_2)^2} \mathbf{s} \mathbf{J}_{pq} \mathbf{A}_{kl}^{-1} \mathbf{J}_{ij} \mathbf{A}_{kl}^{-1} \mathbf{J}_{pq} \mathbf{s} \\
&= \kappa_1 - \frac{2 \cdot p_m}{1 + p_m t_2} \kappa_2 + \frac{p^2}{(1 + p_m t_2)^2} \kappa_3 \\
&= \frac{1}{(1 + p_m t_2)^2} (\kappa_1 + 2 \cdot p_m (t_2 \kappa_1 - \kappa_2) + p_m^2 (t_2^2 \kappa_1 - 2 \cdot t_2 \kappa_2 + \kappa_3)) . \tag{5.50}
\end{aligned}$$

Regarding the β' parameter, it should be noted that grouping the terms by the powers of p_m has been observed to help with the numerical stability of the computations.

Substituting all of these into Eq. (5.38) and making simplifications where possible, we arrive at the practically applicable final equation:

$$\begin{aligned}
\langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle &= S_{kl} \sum_{m=1}^M w_m \exp[x_1] \frac{1}{\sqrt{x_2}} \text{erf}(\sqrt{x_3}) \\
x_1 &= \frac{-p_m}{1 + p_m t_2} \kappa_4 \\
x_2 &= (1 + p_m t_2) [\kappa_1 + 2 \cdot p_m (t_2 \kappa_1 - \kappa_2) + p_m^2 (t_2^2 \kappa_1 - 2 \cdot t_2 \kappa_2 + \kappa_3)] \\
x_3 &= \frac{\kappa_1 + 2 \cdot p_m (t_2 \kappa_1 - \kappa_2) + p_m^2 (t_2^2 \kappa_1 - 2 \cdot t_2 \kappa_2 + \kappa_3)}{(1 + p_m t_2)(t_1 + p_m(t_1 t_2 - t_3))} . \tag{5.51}
\end{aligned}$$

5.2.2 Subcases

One important aspect we have to pay attention to is whether the β' variable in Eq. (5.38), or to put it another way, the x_2 and x_3 parameter in Eq. (5.51), can equal zero. Looking at the constituting parameters $\kappa_1 \dots \kappa_3$, it is easy to see that if the $\mathbf{s}$ vector were to equal zero, that would be the case. A convenient way to evaluate this occurrence is to take the limit $\beta' \rightarrow 0$:

$$\lim_{\beta' \rightarrow 0} \frac{1}{\sqrt{\beta'}} \text{erf} \left(\sqrt{\frac{\beta'}{a'}} \right) = \frac{2}{\sqrt{\pi}} \cdot \frac{1}{\sqrt{a'}} . \tag{5.52}$$

Thus the matrix element of Eq. (5.51) for the, $\mathbf{s} = 0$, zero-shift case becomes:

$$\langle \varphi_k | \frac{1}{r_{ij}} \frac{1}{r_{pq}} | \varphi_l \rangle = \frac{2}{\sqrt{\pi}} S_{kl} \sum_{m=1}^M w_m \frac{1}{(1 + p_m t_2) \sqrt{(t_1 + p_m(t_1 t_2 - t_3))}} . \tag{5.53}$$

Besides this, another crucial idea that has to be considered is the equivalence of the $\frac{1}{r}$ terms in the matrix element. The reason why this has to be evaluated is because this results in the two $\mathbf{J}$ matrices becoming equal: $\mathbf{J}_{ij} = \mathbf{J}_{pq}$. This seemingly unimportant factor gives rise to two

important groups of equivalences for the a' and β' parameters, which, as we shall see, have to be considered not out of elegance, but necessity.

First, let us take a look at the expanded a' parameter of Eq. (5.49):

$$a' = \frac{t_1 + p_m(t_1 t_2 - t_3)}{1 + p_m t_2} . \quad (5.54)$$

If the $\mathbf{J}$ matrices were to be equal, the following two sets of equations would hold true for the $t_1 \dots t_3$ trace parameters:

$$t_1 = t_2 \quad (5.55)$$

$$t_3 = t_1^2 = t_2^2 = t_1 t_2 \quad (5.56)$$

It is clear to see that using these, the expression for a' could be simplified to:

$$a' = \frac{t_1}{1 + p_m t_1} . \quad (5.57)$$

The reason why this simplification must be made in order for the calculations to work can be understood by examining the p_m variable introduced in Eq. (4.18). Its defined form results in computations with an exponential term inside another exponential term, which, in practice, means that with each step of the m summation index, p_m increases by about a factor of 10^5 . Unfortunately, instead of canceling out the $(t_1 t_2 - t_3)$ term in a' , computationally, it usually gets evaluated as a small number around the order of 10^{-19} , which might seem insignificant, but combined with the rapid growth of the p_m parameter, this error, within a couple of steps of m , evolves into an unfathomably large, incorrect result.

Before moving on, let us prove that the statements written above are correct. By definition, Eq. (5.55) holds true, whereas Eq. (5.56) needs further explanation. To prove this statement, we have to use the fact that the $\mathbf{J}$ matrices used are rank one and symmetric, meaning that they can be expressed as the outer product of two equivalent vectors:

$$\mathbf{J} = \mathbf{v} \otimes \mathbf{v} , \quad (5.58)$$

$$J_{ij} = v_i v_j . \quad (5.59)$$

Using this idea, the following derivation can be made:

$$\begin{aligned}
t_3 &= \text{Tr}(\mathbf{A}\mathbf{J}\mathbf{A}\mathbf{J}) = \sum_i (\mathbf{A}\mathbf{J}\mathbf{A}\mathbf{J})_{ii} = \sum_{ij} (\mathbf{A}\mathbf{J})_{ij} (\mathbf{A}\mathbf{J})_{ji} = \sum_{ijkl} A_{ik} J_{kj} A_{jl} J_{li} \\
&= \sum_{ijkl} A_{ik} v_k v_j A_{jl} v_l v_i = \sum_{ijkl} A_{ik} v_k v_i A_{jl} v_l v_j = \sum_{ijkl} A_{ik} J_{ki} A_{jl} J_{lj} \\
&= \sum_{ij} (\mathbf{A}\mathbf{J})_{ii} (\mathbf{A}\mathbf{J})_{jj} = t_1 \cdot t_1 .
\end{aligned} \tag{5.60}$$

Thus, we have proven our previous statement. For cases where the $\mathbf{J}$ matrices are not the same, the v_j and v_i terms cannot be switched to produce the same matrices, meaning the above equivalence does not apply.

Regarding the β' parameter, there is another set of equivalences, stemming from the fact $\mathbf{J}_{ij} = \mathbf{J}_{pq}$, which also completely breaks our calculations. These can be stated as follows:

$$\kappa_1 = \kappa_4 , \tag{5.61}$$

$$\kappa_3 = \kappa_2 t_1 = \kappa_1 t_1^2 . \tag{5.62}$$

Applying these to the β' parameter in Eq. (5.50), we arrive at the much simpler form of:

$$\beta' = \frac{\kappa_1}{(1 + p_m t_1)^2} . \tag{5.63}$$

In this case, Eq. (5.61) is once again true by definition, whereas a proof for Eq. (5.62) relies on the rank one property of the $\mathbf{J}$ matrices. Here, we will only prove the following:

$$\begin{aligned}
\mathbf{J}_{ij} \mathbf{A}_{kl}^{-1} \mathbf{J}_{ij} &= \mathbf{J} \mathbf{A} \mathbf{J} \\
(\mathbf{J} \mathbf{A} \mathbf{J})_{ij} &= \sum_{kl} J_{il} A_{lk} J_{kj} = \sum_{kl} v_i v_l A_{lk} v_k v_j = \sum_{kl} v_k v_l A_{lk} v_i v_j = \sum_{kl} J_{kl} A_{lk} J_{ij} \\
&= \sum_k (\mathbf{J} \mathbf{A})_{kk} J_{ij} = t_1 \cdot J_{ij} ,
\end{aligned} \tag{5.64}$$

where if we consider the whole matrix, we get:

$$\mathbf{J} \mathbf{A} \mathbf{J} = t_1 \cdot \mathbf{J} . \tag{5.65}$$

This derivation can be generalized, to obtain the following useful formula, where n denotes the

number of multiplications by the identical $\mathbf{JA}$ term:

$$(\mathbf{JA})_n \mathbf{J} = t_1^n \cdot \mathbf{J} . \quad (5.66)$$

Substituting in these equivalences, and employing Eqs. (5.57) and (5.63) for a' and β' , we get the following result for the matrix element:

$$\langle \varphi_k | \frac{1}{r_{ij}^2} | \varphi_l \rangle = S_{kl} \sum_{m=1}^M w_m \exp \left[\frac{-p_m}{1 + p_m t_1} \kappa_1 \right] \frac{1}{\sqrt{\kappa_1(1 + p_m t_1)}} \operatorname{erf} \left(\sqrt{\frac{\kappa_1}{t_1(1 + p_m t_1)}} \right) . \quad (5.67)$$

We also have to consider the zero-shift case here as well:

$$\langle \varphi_k | \frac{1}{r_{ij}^2} | \varphi_l \rangle = \frac{2}{\sqrt{\pi}} S_{kl} \sum_{m=1}^M w_m \frac{1}{(1 + p_m t_1) \sqrt{t_1}} . \quad (5.68)$$

To summarize, in this section, we have derived the general formula for the analytically incalculable matrix element concerning two electron-electron interactions using the Beylkin approximation. After this, we expanded the elegant result into a practically implementable one and identified two special aspects that needed to be accounted for, resulting in four separate formulae. The derivations, expressions and ideas contained within this lengthy section will serve as a basis for the evaluation of the other two matrix elements.

5.3 The $\langle \varphi_k | \frac{1}{r_{jk}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle$ Matrix Element

In this section, we will use the Beylkin approximation to calculate the matrix element containing one electron-electron interaction term $\frac{1}{r_{jk}}$ and one electron-nucleus interaction term $\frac{1}{|\mathbf{r}_i - \mathbf{R}_a|}$. For the sake of brevity, we will also heavily rely on the contents of the previous section for the derivations.

We can once again begin by approximating the electron-electron term:

$$\langle \varphi_k | \frac{1}{r_{jk}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle \cong \sum_{m=1}^M w_m \langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \exp[-p_m r_{jk}^2] | \varphi_l \rangle . \quad (5.69)$$

Next, we can use the definition of the FECG basis function and, in the same step, employ the identity of Eq. (5.13) to get:

$$\langle \varphi_k | \frac{1}{r_{jk}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle = \sum_{m=1}^M w_m \exp[-\eta] \int_{-\infty}^{\infty} d\mathbf{r} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \exp[-p_m r_{jk}^2] \exp[-r^T \underline{\mathbf{A}}_{kl} r + 2 \mathbf{e}^T \mathbf{r}] , \quad (5.70)$$

where the $\frac{1}{|\mathbf{r}_i - \mathbf{R}_a|}$ term can again be expressed using the one-dimensional Gaussian integral of Eq. (5.14):

$$\begin{aligned} \langle \varphi_k | \frac{1}{r_{jk}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle &= \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \exp[-\eta] \int_0^\infty dt \int_{-\infty}^\infty d\mathbf{r} \exp[-p_m r_{jk}^2 - t^2 |\mathbf{r}_i - \mathbf{R}_a|^2] \\ &\cdot \exp[-\mathbf{r}^T \underline{\mathbf{A}}_{kl} \mathbf{r} + 2 \mathbf{e}^T \mathbf{r}] . \end{aligned} \quad (5.71)$$

At this point in the previous section, the next step involves the introduction of the $\mathbf{J}$ matrices. For r_{jk}^2 , we can once again use $r_{jk}^2 = \mathbf{r}^T \underline{\mathbf{J}}_{jk} \mathbf{r}$; however, the $|\mathbf{r}_i - \mathbf{R}_a|^2$ term requires further attention, as we cannot use the same type of $\mathbf{J}$ matrix for it. With this term, the coordinates of the nucleus $\mathbf{R}_a$ are fixed, as per the Born–Oppenheimer approximation, and are not contained within the general vector $\mathbf{r}$. To solve this problem, we define a new $\mathbf{a}$ vector, which has the same dimension as $\mathbf{r} \in \mathbb{R}^{3n}$ and is repeatedly filled with the coordinates of the a nucleus: $(\mathbf{a})_{l\alpha} = R_{a,\alpha}$ with $l = 1, \dots, n$ and $\alpha = 1(x), 2(y), 3(z)$. If we construct an $(\mathbf{r} - \mathbf{a})$ vector this way, we can use a different $\mathbf{J}$ matrix to cut out the $|\mathbf{r}_i - \mathbf{R}_a|^2$ term from this vector. This matrix will contain only zeros, except for a one on the diagonal of the i th row: $\mathbf{J}_{ii,\alpha\beta} = \delta_{i\alpha}\delta_{i\beta}$. For instance, the matrix used for the $|\mathbf{r}_2 - \mathbf{R}_a|^2$ term of a three-electron system would look like:

$$\mathbf{J}_{22} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} .$$

In general, repeating indices such as $\mathbf{J}_{ii}$ denote a matrix of this form and are used for electron–nucleus interactions, while $\mathbf{J}_{ij}$ refers to the previously defined form of the $\mathbf{J}$ matrices needed for electron–electron interactions.

Using this new formulation, we can express $|\mathbf{r}_i - \mathbf{R}_a|^2$ as follows:

$$|\mathbf{r}_i - \mathbf{R}_a|^2 = (\mathbf{r} - \mathbf{a})^T \underline{\mathbf{J}}_{ii} (\mathbf{r} - \mathbf{a}) . \quad (5.72)$$

Employing these substitutions, we get:

$$\begin{aligned} \langle \varphi_k | \frac{1}{r_{jk}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle &= \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \exp[-\eta] \int_{-\infty}^\infty d\mathbf{r} \int_0^\infty dt \exp[-\mathbf{r}^T (\underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{jk}) \mathbf{r} + 2 \mathbf{e}^T \mathbf{r}] \\ &\cdot \exp[-(\mathbf{r} - \mathbf{a})^T t^2 \underline{\mathbf{J}}_{ii} (\mathbf{r} - \mathbf{a})] . \end{aligned} \quad (5.73)$$

To continue, we need to make further contractions by expressing the terms containing $\mathbf{r}$ vectors using the newly defined $(\mathbf{r} - \mathbf{a})$ vectors. Firstly, we can use the fact that the $\mathbf{J}$ matrix for the electron-electron term $\mathbf{J}_{jk}$ is not influenced by this change:

$$\mathbf{r}^T \underline{\mathbf{J}}_{jk} \mathbf{r} = (\mathbf{r} - \mathbf{a})^T \underline{\mathbf{J}}_{jk} (\mathbf{r} - \mathbf{a}) , \quad (5.74)$$

while the other terms need to be transformed as follows:

$$\begin{aligned} \exp[-\eta] \exp[-\mathbf{r}^T \underline{\mathbf{A}}_{kl} \mathbf{r} + 2\mathbf{e}^T \mathbf{r}] &= \exp[\gamma] \exp[-(\mathbf{s} - \mathbf{a})^T \underline{\mathbf{A}}_{kl} (\mathbf{s} - \mathbf{a}) - (\mathbf{r} - \mathbf{a})^T \underline{\mathbf{A}}_{kl} (\mathbf{r} - \mathbf{a})] \\ &\cdot \exp[2(\mathbf{s} - \mathbf{a})^T \underline{\mathbf{A}}_{kl} (\mathbf{r} - \mathbf{a})] . \end{aligned} \quad (5.75)$$

This leads us to the following equation:

$$\begin{aligned} \langle \varphi_k | \frac{1}{r_{jk}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle &= \frac{2}{\sqrt{\pi}} \sum_{m=1}^M w_m \exp[\gamma - (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{A}}_{kl} (\mathbf{s} - \mathbf{a})] \int_{-\infty}^{\infty} d\mathbf{r} \int_0^{\infty} dt \\ &\cdot \exp[-(\mathbf{r} - \mathbf{a})^T (\underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{jk} + t^2 \underline{\mathbf{J}}_{ii}) (\mathbf{r} - \mathbf{a}) + 2\mathbf{e}'^T (\mathbf{r} - \mathbf{a})] , \end{aligned} \quad (5.76)$$

where we have defined a new variable $\mathbf{e}' = \underline{\mathbf{A}}_{kl} (\mathbf{s} - \mathbf{a})$. Next, we will make the substitution of $\boldsymbol{\xi} = (\mathbf{r} - \mathbf{a})$, which leaves the integration boundaries unchanged:

$$\begin{aligned} \langle \varphi_k | \frac{1}{r_{jk}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle &= \frac{2}{\sqrt{\pi}} \sum_{m=1}^M w_m \exp[\gamma - (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{A}}_{kl} (\mathbf{s} - \mathbf{a})] \int_{-\infty}^{\infty} d\boldsymbol{\xi} \int_0^{\infty} dt \\ &\cdot \exp[-\boldsymbol{\xi}^T (\underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{jk} + t^2 \underline{\mathbf{J}}_{ii}) \boldsymbol{\xi} + 2\mathbf{e}'^T \boldsymbol{\xi}] . \end{aligned} \quad (5.77)$$

If we compare this equation to that of Eq. (5.18), we can see that their forms are practically identical. This means that we can perform the same steps to obtain a similar result:

$$\langle \varphi_k | \frac{1}{r_{jk}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle \cong \sum_{m=1}^M w_m \frac{S'_{kl}}{\sqrt{\beta'}} \operatorname{erf} \left(\sqrt{\frac{\beta'}{a'}} \right) , \quad (5.78)$$

where, in this case, the usual parameters are slightly modified to mean:

$$\underline{\mathbf{A}}'_{kl} = \underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{jk} , \quad (5.79)$$

$$S'_{kl} = \pi^{3n/2} |\underline{\mathbf{A}}'_{kl}|^{-3/2} \exp[\gamma + \mathbf{e}'^T \underline{\mathbf{A}}'^{-1}_{kl} \mathbf{e}' - (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{A}}_{kl} (\mathbf{s} - \mathbf{a})] , \quad (5.80)$$

$$a' = \operatorname{Tr}(\underline{\mathbf{A}}'^{-1}_{kl} \underline{\mathbf{J}}_{ii}) , \quad (5.81)$$

$$\beta' = \mathbf{e}'^T \underline{\mathbf{A}}'^{-1}_{kl} \underline{\mathbf{J}}_{ii} \underline{\mathbf{A}}'^{-1}_{kl} \mathbf{e}' . \quad (5.82)$$

While the newly introduced $\mathbf{e}'$ parameter might appear to complicate the calculations, it serves the same purpose as the $\mathbf{e}$ vector acting on the $\underline{\mathbf{A}}_{kl}^{-1}$ -matrix:

$$\underline{\mathbf{A}}_{kl}^{-1} \mathbf{e} = \mathbf{s} ,$$

$$\underline{\mathbf{A}}_{kl}^{-1} \mathbf{e}' = \underline{\mathbf{A}}_{kl}^{-1} [\underline{\mathbf{A}}_{kl}(\mathbf{s} - \mathbf{a})] = (\mathbf{s} - \mathbf{a}) .$$

Thus, it results in a simple change from $\mathbf{s}$ to $(\mathbf{s} - \mathbf{a})$. With this consideration in mind, it is clear to see that the expanded equation will also be identical to that of the two electron-electron interaction case seen in Eq. (5.51), except the $t_1 \dots t_3$ and $\kappa_1 \dots \kappa_4$ parameters will be modified to:

$$t_1 = \text{Tr}(\underline{\mathbf{A}}_{kl}^{-1} \mathbf{J}_{ii}) , \quad (5.83)$$

$$t_2 = \text{Tr}(\underline{\mathbf{A}}_{kl}^{-1} \mathbf{J}_{jk}) , \quad (5.84)$$

$$t_3 = \text{Tr}(\underline{\mathbf{A}}_{kl}^{-1} \mathbf{J}_{jk} \underline{\mathbf{A}}_{kl}^{-1} \mathbf{J}_{ii}) , \quad (5.85)$$

$$\kappa_1 = (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{J}}_{ii} (\mathbf{s} - \mathbf{a}) , \quad (5.86)$$

$$\kappa_2 = (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{J}}_{ii} \underline{\mathbf{A}}_{kl}^{-1} \underline{\mathbf{J}}_{jk} (\mathbf{s} - \mathbf{a}) , \quad (5.87)$$

$$\kappa_3 = (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{J}}_{jk} \underline{\mathbf{A}}_{kl}^{-1} \underline{\mathbf{J}}_{ii} \underline{\mathbf{A}}_{kl}^{-1} \underline{\mathbf{J}}_{jk} (\mathbf{s} - \mathbf{a}) , \quad (5.88)$$

$$\kappa_4 = (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{J}}_{jk} (\mathbf{s} - \mathbf{a}) . \quad (5.89)$$

The zero-shift case also has to be considered, which in this instance means $(\mathbf{s} - \mathbf{a}) = 0$ rather than $\mathbf{s} = 0$; the final equation will take on the form of Eq. (5.53).

With these two equations, all matrix elements of the form $\langle \varphi_k | \frac{1}{r_{jk}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} | \varphi_l \rangle$ can be evaluated. We do not need to consider the equivalence of the $\mathbf{J}$ matrices, as the one used for the electron-electron and electron-nucleus interaction terms are defined differently and thus can never be identical.

5.4 The $\langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_j - \mathbf{R}_b|} | \varphi_l \rangle$ Matrix Element

Finally, in this section, we will evaluate the matrix element containing two electron-nucleus interaction terms. For the most part, this can be done by using the ideas and derivation discussed in the previous two sections, except for a special case which will be dealt with separately.

As the derivation of the general formula is once again very similar to those detailed before, only the key parts will be showcased here. As per usual, we begin by approximating one of the terms

of the matrix element:

$$\langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_j - \mathbf{R}_b|} | \varphi_l \rangle \cong \sum_{m=1}^M w_m \langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \exp[-p_m |\mathbf{r}_j - \mathbf{R}_b|^2] | \varphi_l \rangle . \quad (5.90)$$

Employing the identities of Eqs. (5.13) and (5.14), we get:

$$\begin{aligned} \langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_j - \mathbf{R}_b|} | \varphi_l \rangle &= \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \exp[-\eta] \int_{-\infty}^{\infty} d\mathbf{r} \int_0^{\infty} dt \exp[-t^2 |\mathbf{r}_i - \mathbf{R}_a|^2] \\ &\cdot \exp[-p_m |\mathbf{r}_j - \mathbf{R}_b|^2] \exp[-\mathbf{r}^T \underline{\mathbf{A}}_{kl} \mathbf{r} + 2 \mathbf{e}^T \mathbf{r}] . \end{aligned} \quad (5.91)$$

After this, we need to express the $\frac{1}{r}$ terms as follows:

$$|\mathbf{r}_i - \mathbf{R}_a|^2 = (\mathbf{r} - \mathbf{c})^T \underline{\mathbf{J}}_{ii} (\mathbf{r} - \mathbf{c}) , \quad (5.92)$$

$$|\mathbf{r}_j - \mathbf{R}_b|^2 = (\mathbf{r} - \mathbf{c})^T \underline{\mathbf{J}}_{jj} (\mathbf{r} - \mathbf{c}) , \quad (5.93)$$

where the $\mathbf{c} \in \mathbb{R}^{3n}$ vector is a null vector except for the i th and j th places where it contains the coordinates of the a th and b th nuclei, respectively. This way, we can create the following vector:

$$(\mathbf{r} - \mathbf{c}) = \begin{pmatrix} r_{1,x} - 0 \\ \dots \\ r_{i,x} - R_{a,x} \\ r_{i,y} - R_{a,y} \\ r_{i,z} - R_{a,z} \\ \dots \\ r_{j,x} - R_{b,x} \\ r_{j,y} - R_{b,y} \\ r_{j,z} - R_{b,z} \\ \dots \\ r_{n,z} - 0 \end{pmatrix} . \quad (5.94)$$

With these changes, we can arrive at the following equation:

$$\begin{aligned} \langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_j - \mathbf{R}_b|} | \varphi_l \rangle &= \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \exp[-\eta] \int_{-\infty}^{\infty} d\mathbf{r} \int_0^{\infty} dt \exp[-\mathbf{r}^T \underline{\mathbf{A}}_{kl} \mathbf{r} + 2 \mathbf{e}^T \mathbf{r}] \\ &\cdot \exp[-(\mathbf{r} - \mathbf{c})^T (t^2 \underline{\mathbf{J}}_{ii} + p_m \underline{\mathbf{J}}_{jj}) (\mathbf{r} - \mathbf{c})] . \end{aligned} \quad (5.95)$$

Next, we can make the expansion of Eq. (5.75), and the substitution of $\boldsymbol{\xi} = (\mathbf{r} - \mathbf{c})$ to get:

$$\begin{aligned} \langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_j - \mathbf{R}_b|} | \varphi_l \rangle &= \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \exp[\gamma - (\mathbf{s} - \mathbf{c})^T \underline{\mathbf{A}}_{kl} (\mathbf{s} - \mathbf{c})] \int_{-\infty}^{\infty} d\boldsymbol{\xi} \int_0^{\infty} dt \\ &\cdot \exp\left[-\boldsymbol{\xi}^T (\underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{jj} + t^2 \underline{\mathbf{J}}_{ii}) \boldsymbol{\xi} + 2\mathbf{e}'^T \boldsymbol{\xi}\right]. \end{aligned} \quad (5.96)$$

This equation is once again of identical form to that of Eqs. (5.18) or (5.77), meaning that with the same steps, we can arrive at the result:

$$\langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_j - \mathbf{R}_b|} | \varphi_l \rangle \cong \sum_{m=1}^M w_m \frac{S'_{kl}}{\sqrt{\beta'}} \operatorname{erf}\left(\sqrt{\frac{\beta'}{a'}}\right), \quad (5.97)$$

where:

$$\underline{\mathbf{A}}'_{kl} = \underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{jj}, \quad (5.98)$$

$$S'_{kl} = \pi^{3n/2} |\underline{\mathbf{A}}'_{kl}|^{-3/2} \exp[\gamma + \mathbf{e}'^T \underline{\mathbf{A}}'^{-1}_{kl} \mathbf{e}' - (\mathbf{s} - \mathbf{c})^T \underline{\mathbf{A}}_{kl} (\mathbf{s} - \mathbf{c})], \quad (5.99)$$

$$a' = \operatorname{Tr}(\underline{\mathbf{A}}'^{-1}_{kl} \underline{\mathbf{J}}_{ii}), \quad (5.100)$$

$$\beta' = \mathbf{e}'^T \underline{\mathbf{A}}'^{-1}_{kl} \underline{\mathbf{J}}_{ii} \underline{\mathbf{A}}'^{-1}_{kl} \mathbf{e}'. \quad (5.101)$$

If we were to expand this familiar result, we would again arrive at the four cases seen in Eqs. (5.51), (5.53), (5.67) and (5.68), with the parameters of Eqs. (5.83)–(5.89), except $\underline{\mathbf{J}}_{jk}$ gets replaced by $\underline{\mathbf{J}}_{jj}$ and $\mathbf{c}$ is used instead of $\mathbf{a}$. Since the $\underline{\mathbf{J}}$ matrices are of the same form, we have to consider the possibility of their equivalence as well, resulting in the four separate equations. At first, this might seem like a complete description of the titular matrix element, however, there is one special case that has to be evaluated differently discussed in the following.

5.4.1 A Special Case

Suppose the matrix element were to take on the form $\langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_i - \mathbf{R}_b|} | \varphi_l \rangle$, with the same electron present for both terms, the method we had used so far could not be applied. This can be understood through the vector seen in Eq. (5.94), as if we were to subtract both the coordinates of nuclei a and b from the same $\mathbf{r}_i$ elements, we would arrive at the incorrect case of $\langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a - \mathbf{R}_b|} \frac{1}{|\mathbf{r}_i - \mathbf{R}_a - \mathbf{R}_b|} | \varphi_l \rangle$; thus we need a different approach.

We can start a new derivation based on Eq. (5.91):

$$\begin{aligned} \langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_i - \mathbf{R}_b|} | \varphi_l \rangle &= \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \exp[-\eta] \int_{-\infty}^{\infty} d\mathbf{r} \int_0^{\infty} dt \exp[-t^2 |\mathbf{r}_i - \mathbf{R}_a|^2] \\ &\cdot \exp[-p_m |\mathbf{r}_i - \mathbf{R}_b|^2] \exp[-\mathbf{r}^T \underline{\mathbf{A}}_{kl} \mathbf{r} + 2e^T \mathbf{r}] . \end{aligned} \quad (5.102)$$

However, we will have to employ a new method to continue from this point onward. First, we define the following two vectors with the same dimension as the $\mathbf{r} \in \mathbb{R}^{3n}$ vector:

$$\mathbf{a} = \begin{pmatrix} R_{a,x} \\ R_{a,y} \\ R_{a,z} \\ R_{a,x} \\ \dots \end{pmatrix} , \quad \mathbf{b} = \begin{pmatrix} R_{b,x} \\ R_{b,y} \\ R_{b,z} \\ R_{b,x} \\ \dots \end{pmatrix} . \quad (5.103)$$

With the help of these vectors, we can express the $|\mathbf{r}_i - \mathbf{R}_a|^2$ and $|\mathbf{r}_i - \mathbf{R}_b|^2$ terms as:

$$t^2 |\mathbf{r}_i - \mathbf{R}_a|^2 = (\mathbf{r} - \mathbf{a})^T t^2 \underline{\mathbf{J}}_{ii} (\mathbf{r} - \mathbf{a}) , \quad (5.104)$$

$$p_m |\mathbf{r}_i - \mathbf{R}_b|^2 = (\mathbf{r} - \mathbf{b})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{r} - \mathbf{b}) . \quad (5.105)$$

Now, for the key step in this derivation, we need to reconcile these two expressions by rewriting the latter as:

$$\begin{aligned} (\mathbf{r} - \mathbf{b})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{r} - \mathbf{b}) &= (\mathbf{r} - \mathbf{a})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{r} - \mathbf{a}) + \mathbf{b}^T p_m \underline{\mathbf{J}}_{ii} \mathbf{b} - \mathbf{a}^T p_m \underline{\mathbf{J}}_{ii} \mathbf{a} - 2\mathbf{r}^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{b} - \mathbf{a}) \\ &= (\mathbf{r} - \mathbf{a})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{r} - \mathbf{a}) + \mathbf{b}^T p_m \underline{\mathbf{J}}_{ii} \mathbf{b} - \mathbf{a}^T p_m \underline{\mathbf{J}}_{ii} \mathbf{a} - 2(\mathbf{r} - \mathbf{a})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{b} - \mathbf{a}) \\ &\quad - 2\mathbf{a}^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{b} - \mathbf{a}) \\ &= (\mathbf{r} - \mathbf{a})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{r} - \mathbf{a}) - 2(\mathbf{r} - \mathbf{a})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{b} - \mathbf{a}) + (\mathbf{a} - \mathbf{b})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{a} - \mathbf{b}) . \end{aligned} \quad (5.106)$$

If we also use Eq. (5.75), we can arrive at the following equation:

$$\begin{aligned} \langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_i - \mathbf{R}_b|} | \varphi_l \rangle &= \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \exp[\gamma - (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{A}}_{kl} (\mathbf{s} - \mathbf{a}) - (\mathbf{a} - \mathbf{b})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{a} - \mathbf{b})] \\ &\int_{-\infty}^{\infty} d\mathbf{r} \int_0^{\infty} dt \exp[-(\mathbf{r} - \mathbf{a})^T (\underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{ii} + t^2 \underline{\mathbf{J}}_{ii}) (\mathbf{r} - \mathbf{a})] \\ &\cdot \exp[2 \cdot ((\mathbf{s} - \mathbf{a}) \underline{\mathbf{A}}_{kl} + (\mathbf{b} - \mathbf{a}) p_m \underline{\mathbf{J}}_{ii})^T (\mathbf{r} - \mathbf{a})] . \end{aligned} \quad (5.107)$$

Observing the previous equation, we can once again use the substitution $\boldsymbol{\xi} = (\mathbf{r} - \mathbf{a})$ and define a new parameter $\mathbf{e}^p = (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{A}}_{kl} + (\mathbf{b} - \mathbf{a})^T p_m \underline{\mathbf{J}}_{ii}$ to get:

$$\langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_i - \mathbf{R}_b|} | \varphi_l \rangle = \sum_{m=1}^M w_m \frac{2}{\sqrt{\pi}} \exp[\gamma - (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{A}}_{kl} (\mathbf{s} - \mathbf{a}) - (\mathbf{a} - \mathbf{b})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{a} - \mathbf{b})] \int_{-\infty}^{\infty} d\boldsymbol{\xi} \int_0^{\infty} dt \exp[-\boldsymbol{\xi}^T (\underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{ii} + t^2 \underline{\mathbf{J}}_{ii}) \boldsymbol{\xi} + 2 \mathbf{e}^p{}^T \boldsymbol{\xi}] . \quad (5.108)$$

As we have seen before, an equation of this form is related to that of Eq. (5.18), and through the same steps can be expressed as:

$$\langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_i - \mathbf{R}_b|} | \varphi_l \rangle \cong \sum_{m=1}^M w_m \frac{S'_{kl}}{\sqrt{\beta'}} \operatorname{erf} \left(\sqrt{\frac{\beta'}{a'}} \right) , \quad (5.109)$$

where the usual parameters are:

$$\underline{\mathbf{A}}'_{kl} = \underline{\mathbf{A}}_{kl} + p_m \underline{\mathbf{J}}_{ii} , \quad (5.110)$$

$$S'_{kl} = \pi^{3n/2} |\mathbf{A}'_{kl}|^{-3/2} \exp[\gamma + \mathbf{e}^p{}^T \underline{\mathbf{A}}'^{-1}_{kl} \mathbf{e}^p - (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{A}}_{kl} (\mathbf{s} - \mathbf{a})] \cdot \exp[-(\mathbf{a} - \mathbf{b})^T p_m \underline{\mathbf{J}}_{ii} (\mathbf{a} - \mathbf{b})] , \quad (5.111)$$

$$a' = \operatorname{Tr}(\mathbf{A}'^{-1}_{kl} \underline{\mathbf{J}}_{ii}) , \quad (5.112)$$

$$\beta' = \mathbf{e}^p{}^T \underline{\mathbf{A}}'^{-1}_{kl} \underline{\mathbf{J}}_{ii} \underline{\mathbf{A}}'^{-1}_{kl} \mathbf{e}^p . \quad (5.113)$$

In the following, we will again have to expand and break down the result of Eq. (5.109). The defining factors of this derivation will be the unusual form of the $\mathbf{e}^p$ variable, containing the p_m approximation parameter, as well as the equivalence of the $\underline{\mathbf{J}}$ matrices used. This means that due to the identities of Eqs. (5.55), (5.56) and (5.66) only a single trace parameter has to be defined:

$$t_1 = \operatorname{Tr}(\mathbf{A}_{kl}^{-1} \underline{\mathbf{J}}_{ii}) . \quad (5.114)$$

To begin, let us express the a' parameter, which will take on the expected form of:

$$\begin{aligned} a' &= \operatorname{Tr}((\mathbf{A}_{kl} + p_m \underline{\mathbf{J}}_{ii})^{-1} \underline{\mathbf{J}}_{ii}) = \operatorname{Tr} \left[\left(\mathbf{A}_{kl} - \frac{p_m \mathbf{A}_{kl}^{-1} \underline{\mathbf{J}}_{ii} \mathbf{A}_{kl}^{-1}}{1 + p_m \operatorname{Tr}(\mathbf{A}_{kl}^{-1} \underline{\mathbf{J}}_{ii})} \right) \underline{\mathbf{J}}_{ii} \right] \\ &= t_1 - \frac{p_m t_1^2}{1 + p_m t_1} = \frac{t_1}{1 + p_m t_1} . \end{aligned} \quad (5.115)$$

Next, examining the parts making up S'_{kl} , we can first use Eq. (5.46) to get:

$$|\mathbf{A}'_{kl}|^{-3/2} = |\mathbf{A}_{kl}|^{-3/2} (1 + p_m t_1)^{-3/2}. \quad (5.116)$$

The other part can be expanded as:

$$\begin{aligned} \mathbf{e}^p T \mathbf{A}'_{kl}{}^{-1} \mathbf{e}^p &= ((\mathbf{s} - \mathbf{a}) \mathbf{A}_{kl} + (\mathbf{b} - \mathbf{a}) p_m \mathbf{J}_{ii})^T \left(\mathbf{A}_{kl}^{-1} - \frac{p_m \mathbf{A}_{kl}^{-1} \mathbf{J}_{ii} \mathbf{A}_{kl}^{-1}}{1 + p_m t_1} \right) ((\mathbf{s} - \mathbf{a}) \mathbf{A}_{kl} + (\mathbf{b} - \mathbf{a}) p_m \mathbf{J}_{ii}) \\ &= (\mathbf{s} - \mathbf{a})^T \mathbf{A}_{kl} (\mathbf{s} - \mathbf{a}) - \frac{p_m (\mathbf{s} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{s} - \mathbf{a})}{1 + p_m t_1} + p_m^2 t_1 (\mathbf{b} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{b} - \mathbf{a}) \\ &\quad - \frac{p_m^3 t_1^2 (\mathbf{b} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{b} - \mathbf{a})}{1 + p_m t_1} + 2 \cdot p_m (\mathbf{s} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{b} - \mathbf{a}) - \frac{2 \cdot p_m^2 t_1 (\mathbf{s} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{b} - \mathbf{a})}{1 + p_m t_1} \\ &= (\mathbf{s} - \mathbf{a})^T \mathbf{A}_{kl} (\mathbf{s} - \mathbf{a}) + \frac{p_m [2 \cdot (\mathbf{s} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{b} - \mathbf{a}) + p_m t_1 (\mathbf{b} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{b} - \mathbf{a}) - (\mathbf{s} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{s} - \mathbf{a})]}{1 + p_m t_1} \\ &= (\mathbf{s} - \mathbf{a})^T \mathbf{A}_{kl} (\mathbf{s} - \mathbf{a}) + p_m (\mathbf{b} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{b} - \mathbf{a}) - \frac{p_m (\mathbf{s} - \mathbf{b})^T \mathbf{J}_{ii} (\mathbf{s} - \mathbf{b})}{1 + p_m t_1}. \end{aligned} \quad (5.117)$$

It should be noted that throughout this derivation, we made use of the identities in Eqs. (5.24) and (5.66). Combining all the parts of S'_{kl} , we get the following new expression:

$$\mathbf{S}'_{kl} = S_{kl} (1 + p_m t_1)^{-3/2} \exp \left[\frac{-p_m (\mathbf{s} - \mathbf{b})^T \mathbf{J}_{ii} (\mathbf{s} - \mathbf{b})}{1 + p_m t_1} \right]. \quad (5.118)$$

The expansion of the β' parameter is the most tedious, but the process is identical to that of Eq. (5.117); we employ Eqs. (5.24) and (5.66) and group similar terms together. Sparing the details, we can write the following:

$$\begin{aligned} \beta' &= \mathbf{e}^p T \mathbf{A}'_{kl}{}^{-1} \mathbf{J}_{ii} \mathbf{A}'_{kl}{}^{-1} \mathbf{e}^p \\ &= ((\mathbf{s} - \mathbf{a}) \mathbf{A}_{kl} + (\mathbf{b} - \mathbf{a}) p_m \mathbf{J}_{ii})^T \left(\mathbf{A}_{kl}^{-1} - \frac{p_m \mathbf{A}_{kl}^{-1} \mathbf{J}_{ii} \mathbf{A}_{kl}^{-1}}{1 + p_m t_1} \right) \mathbf{J}_{ii} \left(\mathbf{A}_{kl}^{-1} - \frac{p_m \mathbf{A}_{kl}^{-1} \mathbf{J}_{ii} \mathbf{A}_{kl}^{-1}}{1 + p_m t_1} \right) \\ &\quad \cdot ((\mathbf{s} - \mathbf{a}) \mathbf{A}_{kl} + (\mathbf{b} - \mathbf{a}) p_m \mathbf{J}_{ii}) \\ &= \frac{1}{(1 + p_m t_1)^2} [p_m^2 t_1^2 (\mathbf{b} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{b} - \mathbf{a}) + 2 \cdot p_m t_1 (\mathbf{s} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{b} - \mathbf{a}) + (\mathbf{s} - \mathbf{a})^T \mathbf{J}_{ii} (\mathbf{s} - \mathbf{a})]. \end{aligned} \quad (5.119)$$

Incorporating all of these changes, we arrive at the following final equation for this special case:

$$\begin{aligned}
\langle \varphi_k | \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} \frac{1}{|\mathbf{r}_i - \mathbf{R}_b|} | \varphi_l \rangle &= \sum_{m=1}^M w_m \exp[y_1] \frac{1}{\sqrt{y_2}} \operatorname{erf}(\sqrt{y_3}) \\
y_1 &= \frac{-p_m}{1 + p_m t_1} (\mathbf{s} - \mathbf{b})^T \underline{\mathbf{J}}_{ii} (\mathbf{s} - \mathbf{b}) \\
y_2 &= (1 + p_m t_1) [p_m^2 t_1^2 (\mathbf{b} - \mathbf{a})^T \underline{\mathbf{J}}_{ii} (\mathbf{b} - \mathbf{a}) + 2 \cdot p_m t_1 (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{J}}_{ii} (\mathbf{b} - \mathbf{a}) + (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{J}}_{ii} (\mathbf{s} - \mathbf{a})] \\
y_3 &= \frac{[p_m^2 t_1^2 (\mathbf{b} - \mathbf{a})^T \underline{\mathbf{J}}_{ii} (\mathbf{b} - \mathbf{a}) + 2 \cdot p_m t_1 (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{J}}_{ii} (\mathbf{b} - \mathbf{a}) + (\mathbf{s} - \mathbf{a})^T \underline{\mathbf{J}}_{ii} (\mathbf{s} - \mathbf{a})]}{t_1 (1 + p_m t_1)}. \quad (5.120)
\end{aligned}$$

With this, we have finished evaluating this special case of the matrix element containing two electron-nucleus interaction terms. Combined with the other equations and cases discussed in the previous three sections, we have successfully produced a method that can evaluate all three of the analytically incalculable matrix elements.

With these results, we can now employ this new technique to calculate the expectation value of $\hat{H}^2$, or expressions similar to it, on a spatial FECG basis. In the next section, we will detail the numerical results obtained using this method for the regularized relativistic corrections of Section 3.2.3.

6 Numerical Results

Equipped with the expressions of Section 5 to evaluate the analytically unknown matrix elements, in this section, we will directly apply this methodology to several few-body systems to obtain regularized relativistic corrections through the Drachmanization technique, detailed in Section 3.2.3. To reiterate, the three slowly converging singular terms, which will be calculated here, are the mass-velocity $\langle \sum_{i=1}^n \nabla_i^2 \nabla_i^2 \rangle$, Darwin I. $\langle \delta(\mathbf{r}_{ia}) \rangle$ and Darwin II. terms $\langle \delta(\mathbf{r}_{ij}) \rangle$.

First, let us look at the correction terms obtained for the ground state of the He atom. Being an atomic system, analytic calculations are also available for this example, allowing us to directly compare the exact results to the ones produced through the technique developed in this report. The following table contains the results of three different methods used to evaluate the previously mentioned singular operators with an increasing number of basis functions, allowing us to assess the speed of convergence for each case. The first one is the overly slowly converging direct method, where no regularization technique is employed, essentially being the ‘normal’ case. For the second and third cases, the Drachmanization method is used with the matrix elements in one calculated using the analytic formulae, while the other uses the methodology described in this work (with parameters $M = 200$ and $b = 31$, $a = -31$).

Table 1: Singular operators of the relativistic corrections for the He atom

Num. of basis func.	$\langle \sum_{i=1}^n \nabla_i^2 \nabla_i^2 \rangle$		
	<i>Direct</i>	<i>Analytic</i>	<i>This work</i>
20	10(5)	108.(1)	108.(1)
50	10(7)	108.(2)	108.(2)
100	108.(0)	108.1(8)	108.1(8)
200	108.1(3)	108.17(8)	108.17(8)
500	108.1(4)	108.17(7)	108.17(7)
Reference value [44]:	108.176 134 4(8)		

Num. of basis func.	$\langle \delta(\mathbf{r}_{ia}) \rangle$		
	<i>Direct</i>	<i>Analytic</i>	<i>This work</i>
20	3.(5)	3.6(1)	3.6(1)
50	3.6(0)	3.620(7)	3.620(7)
100	3.6(1)	3.6208(4)	3.6208(4)
200	3.6(1)	3.62085(7)	3.62085(7)
500	3.6(1)	3.62085(7)	3.62085(7)
Reference value [44]:	3.620 858 637 7(3)		

Num. of basis func.	$\langle \delta(\mathbf{r}_{ij}) \rangle$		
	<i>Direct</i>	<i>Analytic</i>	<i>This work</i>
20	0.1(1)	0.10(5)	0.10(5)
50	0.10(8)	0.106(2)	0.106(2)
100	0.106(9)	0.10634(2)	0.10634(2)
200	0.106(5)	0.10634(4)	0.10634(4)
500	0.106(4)	0.106345(2)	0.106345(2)
Reference value [33]:	0.106 345 370 636(2)		

It should be noted that the acceleration of the convergence by regularization does heavily depend on the quality of the basis functions and parameters used. Better results through identical use of Drachmanization have been obtained for the He atom (amongst other systems as well) [33] due to this reason. However, one aspect that needs to be highlighted is the remarkable similarity of the results produced by the analytic equations and the approximate method of this work. The above tables do not serve justice to this effect, as for each calculation, regardless of the value's correctness, the difference between the analytic and exact result was in the 10^{-12} range. This fact directly demonstrates the effectiveness of the approximation.

Finally, to properly use this method for its intended purpose of performing calculations for molecular systems for which no analytic approach exists, let us consider the H_3^+ -system, which is of outstanding importance to the field of astrochemistry. Following our calculations, the below table can be constructed containing the terms of the relativistic correction:

Table 2: Singular operators of the relativistic corrections for the H_3^+ cation ($R_{\text{pp}} = 1.65$ bohr, equilateral triangular geometry, ground electronic state)

Num. of basis func.	$\langle \sum_{i=1}^n \nabla_i^2 \nabla_i^2 \rangle$		$\langle \delta(\mathbf{r}_{ia}) \rangle$		$\langle \delta(\mathbf{r}_{ij}) \rangle$	
	<i>Direct</i>	<i>This work</i>	<i>Direct</i>	<i>This work</i>	<i>Direct</i>	<i>This work</i>
20	15.(0)	15.4(5)	1.0(5)	1.08(8)	$1.(9) \cdot 10^{-2}$	$1.8(2) \cdot 10^{-2}$
50	15.(3)	15.4(7)	1.08(2)	1.0896(0)	$1.(9) \cdot 10^{-2}$	$1.83(0) \cdot 10^{-2}$
100	15.(3)	15.46(8)	1.08(3)	1.0896(2)	$1.8(4) \cdot 10^{-2}$	$1.833(3) \cdot 10^{-2}$
200	15.4(4)	15.46(8)	1.08(8)	1.08965(2)	$1.8(4) \cdot 10^{-2}$	$1.8334(4) \cdot 10^{-2}$
500	15.4(5)	15.467(6)	1.08(8)	1.089654(2)	$1.83(5) \cdot 10^{-2}$	$1.83346(6) \cdot 10^{-2}$

In the above table, the acceleration of the convergence is especially pronounced, serving as a great final takeaway from this report. Unfortunately, no precise enough reference was found in

the literature to help ground our results, but very similar results were achieved with the integral transformation technique here: [34]. As previously detailed, this required manual inspection and adjustment of the transformation parameters, which would not be feasible at larger scales, for example, for the hundreds of points needed for potential energy surface computations.

Similar single-point calculations were also performed for systems of three- and four-electron atoms, as well as diatomic and triatomic molecular systems: Li, Be, H₂, HeH⁺, He²⁺, H₃ and He₂. Obtaining relativistic corrections for complete potential energy surfaces and curves is currently ongoing work and will be published later.

7 Summary and Conclusions

At the beginning of this report, we set out to improve the precision of theoretical calculations for small molecular systems, matching the results obtained through experiments. With the fundamental theoretical framework of Section 2, we detailed how the use of FECG basis functions is necessary to achieve this goal, and how their shift vectors lead to the square of the Hamiltonian $\hat{H}^2$ becoming analytically in calculable. We identified three general matrix elements at the root of this problem and saw how $\hat{H}^2$ plays a role in relativistic corrections, as well as tight lower bound calculations.

In Section 4, we introduced an approximation, developed by Beylkin and Monzón, which allowed us to transform parts of the unknown matrix elements into a usable form. We examined two aspects of this method and chose the parameters based on our own investigations. Next, we employed this approximation and saw through all the difficulties that arose along the way and had to be considered. The final result was, however, a complete, robust technique allowing us to evaluate matrix elements for the entire $\hat{H}^2$ operator for molecules. Finally, with this approach, we were able to calculate relativistic corrections for the H_3^+ -system amongst others, serving as a first step towards improving the precision of perturbative relativistic corrections of small, polyelectronic, polyatomic molecules.

As mentioned previously, calculations of relativistic corrections for complete potential energy curves and surfaces are currently in progress, with several other areas in consideration where this technique could be applied as well, such as lower bound calculations. An article based on the work discussed here is also set to be published this year in the Communications section of The Journal of Chemical Physics [3].

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