EXPECTATION VALUES OF SINGULAR OPERATORS IN VARIATIONAL CALCULATIONS OF ATOMIC P-STATES

by

Toreniyaz Shomenov

A Thesis Submitted to the Faculty of the

DEPARTMENT OF PHYSICS

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE IN PHYSICS

In the School of Sciences and Humanities

NAZARBAYEV UNIVERSITY

2020

NAZARBAYEV UNIVERSITY, SCHOOL OF SCIENCES AND HUMANITIES

As members of the thesis committee, we certify that we have read the thesis prepared by Toreniyaz Shomenov entitled

EXPECTATION VALUES OF SINGULAR OPERATORS IN VARIATIONAL CALCULATIONS OF ATOMIC P-STATES

and recommend that it be accepted as fulfilling the thesis requirement for the degree of Master of Science in Physics.

_____ Date: May 5, 2020

Sergiy Bubin

_____ Date: May 5, 2020

Thomas Oikonomou

_____ Date: May 5, 2020

Michael Good

Final approval and acceptance of this thesis is contingent upon the candidate's submission of the final copies of the thesis to the Department of Physics.

I hereby certify that I have read this thesis prepared under my direction and recommend that it be accepted as fulfilling the thesis requirement.

_____ Date: May 5, 2020

Thesis Director: Sergiy Bubin

Table of contents

ABSTRACT

Expectation values of singular operators evaluated in the framework of the Rayleigh-Ritz variational method in quantum mechanics may show slow convergence with increasing the number of basis functions, K. An example of such commonly used operator in the case of high-accuracy calculations of few-electron atoms and molecules is the Dirac delta function dependent on interparticle distances, $\delta(\mathbf{r}_{ij})$. One way to improve the convergence is to adopt the expectation value identities, in which the singular operator is replaced by an certain non-singular operator so that the expectation value is the same in the limit when the trial wave function approaches the exact solution to the Schrödinger equation. However, when the wave function is approximate, which takes place for any finite K, the convergence of the expectation value of this equivalent non-singular operator is usually improved, often by orders of magnitude. In this thesis, we provide the derivation of formulas for such expectation value identities and implement them into a computer code for the case of atomic P-states, whose wave function is expanded in terms of all-particle explicitly correlated Gaussian basis functions.

Acknowledgment

I am sincerely thankful to my supervisor S. Bubin for his constant help, kindness and patience. I am thankful to postdoctoral researchers I. Hornyak and S. Nasiri for useful conversations. I am also very thankful to kind and helpful people working at NU physics department.

1 Introduction

The few-body problem is encountered in many areas of physics. Solving the few-body problem, especially for quantum systems, is a non-trivial task. Common examples of few-body systems in quantum mechanics are the helium and lithium atoms. They are composed of electrons that interact with each other via Coulomb forces. The solutions to the Schrödinger equation for such systems cannot be obtained in analytical form. Instead one has to resort to numerical approaches. Since the adoption of electronic computers in scientific research in 1960s, a number of techniques have been developed to solve the Schrödinger equation numerically with high accuracy. These include quantum Monte Carlo (QMC) [1, 2], configuration-interaction (CI) [3], many body perturbation theory (MBPT) [4, 5], coupled-cluster (CC) [6], method of hyperspherical harmonics (HH) [7], multi-component Hartree-Fock (MCHF)[8], and other techniques.

A commonly used approach to approximate the solutions to the Schrödinger equation is the Rayleigh-Ritz variational method, which approximates the wave function as a linear combination of some basis functions. Given a basis set that can effectively mimic the wave function of the system, one can obtain highly accurate solutions to the Schrödinger equation for atomic and molecular systems. The Hartree-Fock, variational quantum Monte-Carlo, configuration-interaction, and the method of hyperspherical harmonics are partial cases of the variational method.

Choosing appropriate basis functions is a crucial point in variational calculations [9]. When the calculations target very high accuracy (e.g. in theoretical spectroscopy of few-electron atoms) these basis functions should be capable of describing important features of the wave function of the system very well. At the same time it is highly desirable that all the necessary matrix elements with these functions can be evaluated analytically. There are some popular choices that include Hylleraas-type basis functions, Slater-type functions, James-Coolidge-type functions and explicitly correlated Gaussians. The Hylleraas-type basis functions, which include the inter-particle distances r_{ij} were first introduced by Hylleraas back in 1929 [10] to calculate the energy of the Helium atom. The Slater-type basis functions [11] could be considered as a modification to the Hylleraas type functions. They include the inter-electronic distances in the argument of the

exponent. Both the Hylleraas and Slater type basis functions can be used for systems containing no more than 3-4 particles because of the difficulty of calculating the Hamiltonian and overlap matrix elements analitically. Another commonly used basis functions in variational calculations of various few-particle systems are explicitly correlated Gaussians (ECGs) [12]. They also explicitly depend on the distances between particles in the system and can provide very accurate solutions to the Schrödinger equation. ECGs were first introduced in the works of Boys and Singer [13, 14]. For a general N-particle system in a state with zero total orbital angular momentum they have the following form

$$\psi_k = \exp\left[-\sum_{i>j=1}^{N} \alpha_{ij}^{(k)}(\mathbf{r}_i - \mathbf{r}_j)^2\right], \tag{1.1}$$

where $\alpha_{ij}^{(k)}$ are some adjustable parameters. The main advantage of using ECGs is that all matrix elements with them can be calculated analytically for an arbitrary number of particles in the system [12].

After constructing an accurate trial wave function by expanding it in terms of some basis set, one can evaluate expectation values of operators that correspond to various properties of the system. Some of those that represent particular interest are singular operators, in the sense that they are highly localized in the coordinate space. The expectation values of these operators may show slow convergence with the increase of the number of basis functions. This general behavior is illustrated in Table 1, where the convergence of the expectation values of $\langle\delta(\mathbf{r}_{ij})\rangle$ is compared with the expectation values of the nonrelativistic energy and the interparticle distance r_{ij} for Helium atom.

Table 1: Convergence of the expectation values of $\langle\delta(\mathbf{r}_{ij})\rangle$ for the lowest P-state of helium atom. All quantities are in a.u.

Basis size	Energy	$\langle r_{ij}\rangle$	$\langle\delta(\mathbf{r}_{ij})\rangle$
100	−2.12384297654	5.138326834	0.000742402
200	−2.12384307541	5.138328140	0.000737019
500	−2.12384308642	5.138328346	0.000735331
1000	−2.12384308649	5.138328371	0.000735210

It should be noted that the expectation values of $\delta(\mathbf{r}_i)$ and $\delta(\mathbf{r}_{ij})$ are not of purely technical interest. They are needed in calculations of many important properties. In

particular, in order to achieve high accuracy in the calculations and good agreement with experiment for atoms and molecules with small Z's (nuclear charges), one must take into account the relativistic corrections and quantum electrodynamic (QED) effects. It can be done in the framework of the perturbation theory [15]. The operator representing the total relativistic correction can be decomposed into several contributions commonly referred to as the mass-velocity (MV), Darwin (D), orbit-orbit (OO), spin-spin (SS) and spin-orbit (SO) interactions [9]. Many of them contain the Dirac delta-functions depending on interparticle distances. The QED correction also includes the expectation values of $\delta(\mathbf{r}_i)$ and $\delta(\mathbf{r}_{ij})$. The expectation values of the Dirac delta-functions are also needed in the calculations of electron-positron annihilation rates in positronic systems [16]. Therefore, finding a way to accelerate the convergence rate of the expectation values of the Dirac delta-function may bring many practical benefits and reduce the size of the basis in variational calculations.

There is another singular operator found in the relativistic correction, which is proportional to the fourth power of linear momenta. It is commonly referred to as the mass-velocity Hamiltonian [9] and has the following form

$$H_{MV} = -\frac{1}{8}\sum_{i=1}^{n}\frac{\mathbf{P}_i^4}{M_i^3}, \tag{1.2}$$

where M_i is the mass and $\mathbf{P}_i$ is the momentum of the ith particle in the laboratory coordinate frame. In order to understand the nature of the singularity due to the presence of $\mathbf{P}_i^4$ ($\propto \nabla_i^4$) in H_{MV}, one may consider the expectation value of ∇^4 with the exact ground state wave function of the hydrogen atom, ψ. First acting with ∇^2 on ψ one obtains $\nabla^2\psi \propto (E-1/r)\psi$, which behaves as ψ/r when r approaches zero. The subsequent application of ∇^2 will then yield terms containing the Dirac delta-function because $\nabla^2(1/r) = -4\pi\delta(\mathbf{r})$.

The singular operators are very demanding with respect to local properties of the trial wave function. More specifically, the expectation values of singular operators are accurate only to the first order in error, since the variational trial wave function is sampled locally rather than globally when the corresponding integrals are computed. While it is known that the expectation values of energy are accurate to the second order [17]. This implies that the convergence of the singular operator's expectation value is much slower compared to the energy. For example, as we can see in Table 1, the number of converged

digits in the expectation values of delta function is around twice fewer than the energy. Approximately the same accuracy as in the energy estimation can be expected when evaluating the expectation values of operators which depend on the same region of space that determines the energy [18].

Several approaches have been proposed to improve the accuracy of the expectation values of singular operators. These include the expectation value identity of Drachman [19], integral transform [20], the Hiller-Sucher-Feinberg (HSF) approach [21], and using basis functions with linear prefactors that improve the description of the cusp region [22]. In work [19], Drachman proposed an expectation value identity for $\langle\delta(\mathbf{r}_{ij})\rangle$ and demonstrated that it provides a significant improvement in terms of accuracy for the helium isoelectronic sequence. His approach is based on the idea of replacing a singular operator by another global non-singular operator, so that its expectation value with the exact wave function is the same as the expectation value of the corresponding singular operator. In this thesis, we adopt the Drachman's approach and apply it for the calculations of $\langle\delta(\mathbf{r}_{i})\rangle$ and $\langle\delta(\mathbf{r}_{ij})\rangle$ in few-electron atoms, while for the fourth powers of momenta we apply somewhat different regularization scheme, which will be discussed later. An expectation value identity is relation that can be cast in the following form:

$$\langle\psi|\delta(\mathbf{r}_{ij})|\psi\rangle = \langle\psi|\hat{O}|\psi\rangle, \tag{1.3}$$

where $\hat{O}$ is certain global non-singular operator (the explicit form of it will be derived later) and ψ is the exact wave function. It is important to note that expression (1.3) is valid *only* for the exact wave function of the system ψ, not for any function. In the case of the Dirac delta-function, matrix elements of the global operator $\hat{O}$ for the case of atoms can be computed analytically, while for molecular systems it becomes difficult to implement. Instead, one can apply the integral tranform (IT) approach [20], which works for both atoms and molecules.

2 The variational principle

The main idea of the variaitonal principle is based on the Ritz theorem [23], which states that the expectation value of the Hamiltonian with some normalized trial wave function Ψ (such that $\langle\Psi|\Psi\rangle = 1$) gives an upper bound to the exact ground state energy of the system

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

Adjusting the trial wave function Ψ allows one to approximate the wave function of the system, essentially, with any accuracy, limited only by the computational power available. In practice, the trial wave function Ψ is expanded in terms of some basis set

$$|\Psi\rangle = \sum_{l=1}^{N} c_l|\psi_l(\alpha_l)\rangle, \tag{2.2}$$

where basis functions $\psi_l(\alpha_l)$ may contain some adjustable parameters α_l. Coefficients c_l and parameters α_l in the trial wave function are adjusted to minimize the expectation value of the Hamiltonian. Minimizing the energy with respect to the linear coefficients c_l results in a generalized eigenvalue problem

$$H\mathbf{c} = \epsilon S\mathbf{c}, \tag{2.3}$$

where $\mathbf{c}$ is a column vector, which consists of coefficients c_l, while H and S are $N \times N$ Hamiltonian and overlap matrices respectively, whose matrix elements are

$$H_{lk} = \langle\psi_l|H|\psi_k\rangle, \quad S_{lk} = \langle\psi_l|\psi_k\rangle. \tag{2.4}$$

Minimizing the energy with respect to parameters α_l leads to a nonlinear optimization problem. The generalized eigenvalue problem (2.3) with hermitian (or symmetric if basis functions are real) matrices H and S has N solutions – eigenvalues $\epsilon^{(i)}$ and the corresponding eigenvectors $\mathbf{c}^{(i)}$. According to the mini-max theorem, if eigenvalues $\epsilon^{(i)}$ are sorted in an increasing order, then the first eigenvalue, $\epsilon^{(1)}$ gives an upper bound to the exact ground state energy of the system. The second eigenvalue, $\epsilon^{(2)}$, gives an upper bound to the the first excited state energy of the system and so on [24]. In other words, by minimizing the eigenvalues of above generalized eigenvalue problem with respect to parameters α_l, one can target a specific bound state of the system.

3 Notations

The notation scheme used in this thesis is adopted from the works on explicitly correlated complex Gaussians [25, 26]. Let us list the conventions used in this notation scheme:

- Lower-case Greek letters (β, γ etc.) denote scalars.
- Lower-case Latin letters (a, b, c etc.) denote n-component column vectors.
- Bold lower-case Greek letters ($\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, $\boldsymbol{\gamma}$, etc.) denote 3-component vectors, i.e. vectors in 3D space.
- Bold lower-case Latin letters ($\mathbf{x}$, $\mathbf{y}$, $\mathbf{j}$, etc.) denote $3n$-component vectors.
- Upper case Greek letters (Λ, Ξ, Θ etc.) denote 3×3 matrices.
- Upper case Latin letters (A, B, C, etc.) denote $N \times N$ matrices.
- Bold upper case Latin letters ($\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$, etc.) denote $3N \times 3N$ matrices.
- Prime after the letters (r', A', $\mathbf{v}'$, etc.) stands for the matrix or vector transpose.
- A^{-1}, $\mathbf{A}^{-1}$ denotes the inverse matrix.
- $A^*, \mathbf{A}^*, a^*, \beta^*$, etc. - denotes the complex conjugate of a matrix or vector.
- $A^\dagger, \mathbf{A}^\dagger, a^\dagger, \beta^\dagger$, etc. - denotes the transpose of a matrix or vector followed by the complex conjugation.
- Vertical bars with the vector in between ($|\mathbf{r}|$, $|v|$, etc.) stands for the absolute value of the vector.
- Vertical bars with the matrix in between ($|A|$, $|\mathbf{A}|$, etc.) stands for the determinant of the matrix.
- tr(A), tr($\mathbf{A}$) denotes the trace of the matrix.
- $A \otimes B$, $a \otimes b$, etc., denotes the Kronecker product of matrices or vectors.

- Upper case Latin letters $\mathtt{A}, \mathtt{B}$, and etc., written in typewriter font denotes the matrices in basis functions space. For example, in the case of basis size K, these becomes $K \times K$ matrices.

- The letter I is used to denote the identity matrices. For example, I_3 and I_n denote the 3×3 and $n \times n$ identity matrices respectively.

In some derivations we will need to take the differentials of matrix expressions. In particular, for an arbitrary matrix X the following relations take place [27]:

$$d|X| = |X|\mathrm{tr}[X^{-1}dX],$$

$$d(X^{-1}) = -X^{-1}(dX)X^{-1}.$$

Lastly, let us give the value of the n-dimensional Gaussian integral

$$\int \exp(-x'Ax + y'x)dx = \exp\left(\frac{1}{4}y'A^{-1}y\right)\frac{(\pi)^{n/2}}{|A|^{1/2}}, \tag{3.1}$$

where x is a n-component vector of variables, y is a n-component constant vector, and A is a complex symmetric $n \times n$ matrix with a positive definite real part. The derivation of the above integral and some other related integrals are given in subsection Gaussian integrals.

4 Separation of the center of mass motion

4.1 The nonrelativistic Hamiltonian

Let us consider a general quantum system of N particles with Coulomb interaction between the particles. Let $\mathbf{R}_i$, M_i and Q_i be the position vector, mass and charge of the ith particle in the laboratory Cartesian coordinate frame. Then, the nonrelativistic Hamiltonian of the system is

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2M_i} \nabla^2_{\mathbf{R}_i} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Q_i Q_j}{R_{ij}}. \tag{4.1}$$

Here $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$ is the distance between ith and jth particles and $\nabla_{\mathbf{R}_i}$ is the gradient with respect to the position vector of the ith particle.

4.2 Separating the center of mass motion

In the bound state calculations of quantum systems it is necessary to separate out the motion of the center of mass from the laboratory frame Hamiltonian [9]. In this procedure we place one particle (usually the heaviest one) at the origin of the internal reference frame and we will define the coordinates of other particles with respect to this new reference particle. The relation between the internal and laboratory coordinates is given by

$$\mathbf{r}_i = -\mathbf{R}_1 + \mathbf{R}_{i+1}, \quad i = 1, 2, \ldots, N-1. \tag{4.2}$$

The total mass of the system is $m_t = \sum_{i=1}^{N} m_i$ and the coordinate of the center of mass is defined as follows:

$$\mathbf{r}_0 = \sum_{i=1}^{N} \frac{m_i \mathbf{r}_i}{m_t}. \tag{4.3}$$

Starting from the laboratory Cartesian coordinate with N particles, we will move to the new internal coordinate system with $n = N - 1$ pseudo-particles, with masses $m_i = M_{i+1}$ and charges $q_i = Q_{i+1}$.

Writing the gradient $\nabla^2_{\mathbf{R}_i}$ in equation (4.1) in terms of the internal coordinates $\mathbf{r}_i$ and using the reduced masses $\mu_i = m_0 m_i/(m_0 + m_i)$, the laboratory frame Hamiltonian becomes:

$$\hat{H} = -\frac{1}{2m_t}\nabla^2_0 - \sum_{i=1}^{n} \frac{1}{2\mu_i}\nabla^2_i - \sum_{i\neq j}^{n} \frac{1}{2m_0}\nabla'_i \nabla_j + \sum_{i=1}^{n} \frac{q_0 q_i}{r_i} + \sum_{i=1}^{n}\sum_{j>i}^{n} \frac{q_i q_j}{r_{ij}}. \tag{4.4}$$

The first term describes the motion of the center of mass (center of mass Hamiltonian $\hat{H}_{cm}$), while other terms are called an "internal" Hamiltonian:

$$\hat{H}_{cm} = -\frac{1}{2m_t}\nabla_0^2, \tag{4.5}$$

$$\hat{H}_{internal} = -\sum_{i=1}^{n}\frac{1}{2\mu_i}\nabla_i^2 - \sum_{i\neq j}^{n}\frac{1}{2m_0}\nabla_i'\nabla_j + \sum_{i=1}^{n}\frac{q_0 q_i}{r_i} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{q_i q_j}{r_{ij}}. \tag{4.6}$$

The internal Hamiltonian describes the motion of the n pseudo-particles with the origin of the internal coordinate system r_i and contains $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ term, which is the relative distance between the ith and jth pseudo-particles.

4.3 Matrix form of the internal Hamiltonian

Hamiltonian (4.6) can be written in the matrix form in order to make further derivations simple and convenient. For that purpose, we will write the position and gradients of n pseudo-particles as $3n$-component vectors

$$\mathbf{r} = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \dots \\ \mathbf{r}_n \end{pmatrix}; \qquad \nabla_r = \begin{pmatrix} \nabla_{\mathbf{r}_1} \\ \nabla_{\mathbf{r}_2} \\ \dots \\ \nabla_{\mathbf{r}_n} \end{pmatrix} = \begin{pmatrix} \nabla_1 \\ \nabla_2 \\ \dots \\ \nabla_n \end{pmatrix}. \tag{4.7}$$

With above short notations we have

$$\hat{H}_{internal} = -\nabla_{\mathbf{r}}'\mathbf{M}\nabla_{\mathbf{r}} + \sum_{i=1}^{n}\frac{q_0 q_i}{r_i} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{q_i q_j}{r_{ij}}, \tag{4.8}$$

where $\mathbf{M} = M \otimes I_3$ is the Kronecker product between $n \times n$ matrix M and the 3×3 identity matrix I. Matrix elements of M are

$$M_{ij} = \begin{cases} \frac{1}{2\mu_i}, & i = j \\ \frac{1}{m_0}, & \text{otherwise} \end{cases} \tag{4.9}$$

4.4 Mass-velocity Hamiltonian

The mass-velocity Hamiltonian, which in the laboratory coordinates is proportional to the sum of the fourth power of linear momenta,

$$H_{MV} = -\frac{1}{8}\sum_{i=1}^{n}\frac{\mathbf{P}_i^4}{M_i^3}$$

in the internal coordinate frame can be written in the following form:

$$H_{MV} = -\frac{1}{8}\left[\frac{1}{m_0^3}\left(\sum_{i=1}^{n}\nabla_{\mathbf{r}_i}\right)^4 + \sum_{i=1}^{n}\frac{1}{m_i^3}\nabla_{\mathbf{r}_i}^4\right]. \tag{4.10}$$

In order to evaluate the matrix elements of the internal mass-velocity Hamiltonian, we will write the above expression in the matrix form. For this purpose, we define new matrices $\mathbf{J} = J \otimes I_3$ and $\mathbf{J}_{ii} = J_{ii} \otimes I_3$, J is a $n \times n$ matrix with all its elements equal to 1, while matrix J_{ii} is a $n \times n$ matrix with only one nonzero element, which is set to 1. With these notations, the matrix form of the internal mass-velocity Hamiltonian is given by:

$$H_{MV} = -(\nabla'_{\mathbf{r}}\beta_0\mathbf{J}\nabla_{\mathbf{r}})^2 - \sum_{i=1}^{n}(\nabla'_{\mathbf{r}}\beta_i\mathbf{J}_{ii}\nabla_{\mathbf{r}})^2, \tag{4.11}$$

where we defined $\beta_0 = 1/\sqrt{8m_0^3}$ and $\beta_i = 1/\sqrt{8m_i^3}$.

5 Expectation Value Identities

5.1 Example of derivation

We will derive the simplest form of the expectation value identity by considering the Hamiltonian of a nonrelativistic Coulombic system consisting of N particles

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2m_i} \nabla^2_{\mathbf{r}_i} + V(\mathbf{r}).$$

Let $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ be the wave function of the system. Using the following identities

$$\nabla^2_j (1/r_{jk}) = -4\pi\delta(\mathbf{r}_{jk})$$

$$\nabla^2_k (1/r_{jk}) = -4\pi\delta(\mathbf{r}_{jk}), \tag{5.1}$$

where $r_{jk} = |\mathbf{r}_j - \mathbf{r}_k|$, and hermicity of ∇^2 operator we can write

$$\int dr^N \frac{1}{r_{jk}} \left[\frac{1}{2m_j} \nabla^2_j + \frac{1}{2m_k} \nabla^2_k \right] |\psi|^2 = \int dr^N |\psi|^2 \left[\frac{1}{2m_j} \nabla^2_j + \frac{1}{2m_k} \nabla^2_k \right] \frac{1}{r_{jk}} =$$

$$= -2\pi \int dr^N |\psi|^2 \left[\frac{1}{m_k} + \frac{1}{m_j} \right] \delta(\mathbf{r}_{jk}) = -\frac{2\pi}{\mu_{jk}} \int dr^N |\psi|^2 \delta(\mathbf{r}_{jk}) = -\frac{2\pi}{\mu_{jk}} \langle \delta(\mathbf{r}_{jk}) \rangle. \tag{5.2}$$

Now, from equation (5.2):

$$\int dr^N |\psi|^2 \left[\frac{1}{2m_j} \nabla^2_j + \frac{1}{2m_k} \nabla^2_k \right] \frac{1}{r_{jk}} = -\frac{2\pi}{\mu_{jk}} \langle \delta(\mathbf{r}_{jk}) \rangle \Rightarrow$$

$$\Rightarrow \langle \delta(\mathbf{r}_{jk} \rangle = -\frac{\mu_{jk}}{4\pi} \int dr^N |\psi|^2 \left[\frac{1}{m_j} \nabla^2_j + \frac{1}{m_k} \nabla^2_k \right] \frac{1}{r_{jk}}. \tag{5.3}$$

Using the Schrödinger equation

$$\hat{H}\psi = E\psi \Rightarrow$$

$$\Rightarrow \left[-\sum_{i=1}^{N} \frac{1}{2m_i} \nabla^2_{\mathbf{r}_i} + V(\mathbf{r}) \right] \psi = E\psi$$

$$\Rightarrow -\sum_{i=1}^{N} \frac{1}{2m_i} \nabla^2_{\mathbf{r}_i} \psi = (E - V)\psi. \tag{5.4}$$

After multiplying both sides of equation (5.4) by ψ, we can obtain

$$-\sum_{i=1}^{N} \frac{1}{2m_i} \psi^* \nabla^2_{\mathbf{r}_i} \psi = (E - V)\psi^2. \tag{5.5}$$

There is a neat way of applying the property of ∇^2 operator, which is

$$\nabla^2\psi^2 = 2\psi^*\nabla^2\psi + 2(\nabla\psi)^2 \Rightarrow$$
$$\Rightarrow \psi^*\nabla^2\psi = \frac{\nabla^2\psi^2}{2} - (\nabla\psi)^2. \tag{5.6}$$

Substituting the above identity into equation (5.5), we have

$$-\sum_{i=1}^{N}\frac{1}{m_i}\left[\frac{\nabla^2_{\mathbf{r}_i}\psi^2}{2} - (\nabla_{\mathbf{r}_i}\psi)^2\right] = 2(E-V)\psi^2 \Rightarrow$$
$$\Rightarrow \sum_{i=1}^{N}\frac{1}{m_i}\frac{\nabla^2_{\mathbf{r}_i}\psi^2}{2} = \sum_{i=1}^{N}\frac{1}{m_i}(\nabla_{\mathbf{r}_i}\psi)^2 - 2(E-V)\psi^2 \Rightarrow$$
$$\Rightarrow \sum_{i=1}^{N}\frac{\nabla^2_{\mathbf{r}_i}\psi^2}{m_i} = \sum_{i=1}^{N}\frac{2}{m_i}(\nabla_{\mathbf{r}_i}\psi)^2 - 4(E-V)\psi^2. \tag{5.7}$$

In order to substitute equation (5.7) in equation (5.3), we will use the following relation:

$$\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2\left[\frac{1}{r_{jk}}\right] = \left[\frac{1}{m_j}\nabla_j^2 + \frac{1}{m_k}\nabla_k^2\right]\frac{1}{r_{jk}}. \tag{5.8}$$

Substituting the equation (5.8) back to equation (5.3) yields

$$\langle\delta(\mathbf{r}_{jk}\rangle = -\frac{\mu_{jk}}{4\pi}\int dr^N|\psi|^2\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2\left[\frac{1}{r_{jk}}\right]. \tag{5.9}$$

Using the hermiticity of the Laplace operator and equation (5.7), we have

$$\langle\delta(\mathbf{r}_{jk}\rangle = -\frac{\mu_{jk}}{4\pi}\int dr^N\frac{1}{r_{jk}}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2|\psi|^2 = -\frac{\mu_{jk}}{4\pi}\int dr^N\frac{1}{r_{jk}}\left[\sum_{i=1}^{N}\frac{2}{m_i}(\nabla_{\mathbf{r}_i}\psi)^2 - 4(E-V)\psi^2\right]$$
$$\Rightarrow \langle\delta(\mathbf{r}_{jk})\rangle = \frac{\mu_{jk}}{\pi}\int dr^N\frac{1}{r_{jk}}\left[(E-V)|\psi|^2 - \sum_{i=1}^{N}\frac{1}{2m_i}\nabla_i^2|\psi|^2\right]. \tag{5.10}$$

The same procedure between equation (5.1) and (5.10) can be easily used for the internal Hamiltonian (4.6) described in the previous section.

5.2 Expectation value identity for the internal Hamiltonian

Before going into detail, we will rewrite the internal Hamiltonian (4.6) in a different form for convenience:

$$\hat{H}_{internal} = -\sum_{i=1}^{n}\frac{1}{2\mu_i}\nabla_i^2 - \sum_{i\neq j}^{n}\frac{1}{2m_0}\nabla_i'\nabla_j + \sum_{i=1}^{n}\frac{q_0q_i}{r_i} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{q_iq_j}{r_{ij}} =$$

$$= -\frac{1}{2}\left[\sum_{i=1}^{n}\frac{1}{\mu_i}\nabla_i^2 + \sum_{i\neq j}^{n}\frac{1}{m_0}\nabla_i'\nabla_j\right] + V(\mathbf{r}) =$$

$$= -\frac{1}{2}\left[\sum_{i=1}^{n}\frac{1}{m_i}\nabla_i^2 + \sum_{i=1}^{n}\frac{1}{m_0}\nabla_i^2 + \sum_{i\neq j}^{n}\frac{1}{m_0}\nabla_i'\nabla_j\right] + V(\mathbf{r}) =$$

$$= -\frac{1}{2}\left[\sum_{i=1}^{n}\frac{1}{m_i}\nabla_i^2 + \frac{1}{m_0}\sum_{i=1}^{n}\sum_{j=1}^{n}\nabla_i\nabla_j\right] + V(\mathbf{r}) = \hat{H}_{internal}, \tag{5.11}$$

where $V(\mathbf{r}) = \sum_{i=1}^{n}\frac{q_0 q_i}{r_i} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{q_i q_j}{r_{ij}}$. Now, we substitute $\hat{H}_{internal}$ in the stationary Schrödinger equation

$$-\frac{1}{2}\left[\sum_{i=1}^{n}\frac{1}{m_i}\nabla_i^2 + \frac{1}{m_0}\sum_{i=1}^{n}\sum_{j=1}^{n}\nabla_i\nabla_j\right]\psi + V(\mathbf{r})\psi = E\psi \Rightarrow$$

$$\Rightarrow -\sum_{i=1}^{n}\frac{1}{m_i}\nabla_i^2\psi = 2[E - V(\mathbf{r})]\psi + \frac{1}{m_0}\sum_{i=1}^{n}\sum_{j=1}^{n}\nabla_i\nabla_j\psi. \tag{5.12}$$

Let us multiply both sides by ψ

$$-\sum_{i=1}^{n}\frac{1}{m_i}\psi^*\nabla_i^2\psi = 2[E - V(\mathbf{r})]|\psi|^2 + \frac{1}{m_0}\sum_{i=1}^{n}\sum_{j=1}^{n}\psi^*\nabla_i\nabla_j\psi. \tag{5.13}$$

As we can see from equation (5.13), we can use the properties of Laplace operator regarding the term on the left ($\psi^*\nabla_i^2\psi$) and the second term on the right ($\psi^*\nabla_i\nabla_j\psi$). As before, the first term using identity $\nabla^2\psi^2 = 2\psi^*\nabla^2\psi + 2(\nabla\psi)^2$, can be written

$$\psi^*\nabla^2\psi = \frac{\nabla^2\psi^2}{2} - (\nabla\psi)^2, \tag{5.14}$$

while the second term, can be rearranged using the following identity

$$\nabla_i\nabla_j|\psi|^2 = \psi\nabla_i\nabla_j\psi^* + \psi^*\nabla_i\nabla_j\psi + \nabla_i\psi\nabla_j\psi^* + \nabla_i\psi^*\nabla_j\psi \Rightarrow$$

$$\Rightarrow \nabla_i\nabla_j|\psi|^2 = 2\psi^*\nabla_i\nabla_j\psi + 2(\nabla_i\psi)^*\nabla_j\psi. \tag{5.15}$$

Using identity (5.15), we can replace the last term in equation (5.13):

$$\psi^*\nabla_i\nabla_j\psi = \frac{\nabla_i\nabla_j|\psi|^2}{2} - (\nabla_i\psi)^*\nabla_j\psi. \tag{5.16}$$

Substituting (5.14) and (5.16) back to (5.13), we have

$$-\sum_{i=1}^{n}\frac{1}{m_i}\left[\frac{\nabla_i^2\psi^2}{2} - (\nabla_i\psi)^2\right] = 2[E - V(\mathbf{r})]|\psi|^2 + \frac{1}{m_0}\sum_{i=1}^{n}\sum_{j=1}^{n}\left[\frac{\nabla_i\nabla_j|\psi|^2}{2} - (\nabla_i\psi)^*\nabla_j\psi\right]$$

$$\Rightarrow -\sum_{i=1}^{n}\frac{1}{m_i}\nabla_i^2\psi^2 =$$

$$= 4[E-V(\mathbf{r})]|\psi|^2 + \frac{1}{m_0}\sum_{i=j=1}^{n}\nabla_i\nabla_j|\psi|^2 - \frac{2}{m_0}\sum_{i=j=1}^{n}(\nabla_i\psi)^*\nabla_j\psi - \sum_{i=1}^{n}\frac{2}{m_i}(\nabla_i\psi)^2. \quad (5.17)$$

As before, we use the relation involving the sum:

$$\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2\left[\frac{1}{r_{kl}}\right] = \left[\frac{1}{m_k}\nabla_k^2 + \frac{1}{m_l}\nabla_l^2\right]\frac{1}{r_{kl}}. \quad (5.18)$$

Now we will rewrite the equation (5.3) by changing the index j to l and reversing k and l for convenience (as in equation (5.18)). This is because we already have index j in equation (5.17) and that may cause a confusion.

$$\langle\delta(\mathbf{r}_{kl})\rangle = -\frac{\mu_{kl}}{4\pi}\int dr^N|\psi|^2\left[\frac{1}{m_k}\nabla_k^2 + \frac{1}{m_l}\nabla_l^2\right]\frac{1}{r_{kl}} = -\frac{\mu_{kl}}{4\pi}\int dr^N|\psi|^2\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2\left[\frac{1}{r_{kl}}\right] =$$

$$= -\frac{\mu_{kl}}{4\pi}\int dr^N\frac{1}{r_{kl}}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2|\psi|^2 = \langle\delta(\mathbf{r}_{kl})\rangle. \quad (5.19)$$

Now we substitute equation (5.17) in equation (5.19) and use the hermicity of the Laplace operator one more time:

$$\langle\delta(\mathbf{r}_{kl})\rangle = \frac{\mu_{kl}}{4\pi}\int dr^N\left[4[E-V(\mathbf{r})]|\psi|^2 + \frac{1}{m_0}\sum_{i=j=1}^{n}\nabla_i\nabla_j|\psi|^2\right.$$

$$\left. -\frac{2}{m_0}\sum_{i=j=1}^{n}(\nabla_i\psi)^*\nabla_j\psi - \sum_{i=1}^{n}\frac{2}{m_i}(\nabla_i\psi)^2\right]\frac{1}{r_{kl}} \Rightarrow$$

$$\langle\delta(\mathbf{r}_{kl})\rangle = \frac{\mu_{kl}}{\pi}\int dr^N\frac{1}{r_{kl}}\left[(E-V(\mathbf{r}))|\psi|^2 - \frac{1}{2m_0}\sum_{i=j=1}^{n}(\nabla_i\psi)^*\nabla_j\psi - \sum_{i=1}^{n}\frac{1}{2m_i}(\nabla_i\psi)^2\right]. \quad (5.20)$$

In the above procedure, the tricky part was the term $\frac{1}{m_0}\sum_{i=j=1}^{n}\nabla_i\nabla_j|\psi|^2\frac{1}{r_{kl}}$, which is essentially equal to 0 in our situation. We can prove this by considering (also by considering equation (5.18)):

$$\frac{1}{m_0}\frac{1}{r_{kl}}\sum_{i=j=1}^{n}\nabla_i\nabla_j|\psi|^2 = \frac{1}{m_0}|\psi|^2\sum_{i=j=1}^{n}\nabla_i\nabla_j\frac{1}{r_{kl}} \Rightarrow$$

$$\Rightarrow \nabla_i\nabla_j\frac{1}{r_{kl}} = \begin{cases} 0, & kl \neq ij \\ -4\pi\delta(\mathbf{r}_{kl}), & kl = ij; \quad i = j \\ 4\pi\delta(\mathbf{r}_{kl}), & kl = ij; \quad i \neq j \end{cases} \quad (5.21)$$

Equation (5.20) in the matrix form in terms of expectation values becomes:

$$\langle\delta(\mathbf{r}_{kl})\rangle = \frac{\mu_{kl}}{\pi}\left[\left\langle\psi\left|\frac{E-V}{r_{kl}}\right|\psi\right\rangle - \left\langle\nabla_r\psi\left|\frac{\mathbf{M}}{r_{kl}}\right|\nabla_r\psi\right\rangle\right]. \tag{5.22}$$

If we derive everything using i and j instead of k and l, this becomes:

$$\langle\delta(\mathbf{r}_{ij})\rangle = \frac{\mu_{ij}}{\pi}\left[\left\langle\psi\left|\frac{E-V}{r_{ij}}\right|\psi\right\rangle - \left\langle\nabla_r\psi\left|\frac{\mathbf{M}}{r_{ij}}\right|\nabla_r\psi\right\rangle\right]. \tag{5.23}$$

In the case of the internal mass-velocity Hamiltonian (4.10) one can use the following identity

$$\langle\psi|H_{MV}|\psi\rangle = -\lambda^2\langle\psi|(E-V)^2|\psi\rangle - \lambda^2\langle\psi|(E-V)(\nabla'_{\mathbf{r}}\mathbf{B}\nabla_{\mathbf{r}})|\psi\rangle + \lambda^2\langle\psi|(\nabla'_{\mathbf{r}}\mathbf{M}\nabla_{\mathbf{r}})^2|\psi\rangle +$$

$$\lambda^2\langle\psi|(\nabla'_{\mathbf{r}}\mathbf{M}\nabla_{\mathbf{r}})(\nabla'_{\mathbf{r}}\mathbf{B}\nabla_{\mathbf{r}})|\psi\rangle - \beta_0\langle\psi|(\nabla'_{\mathbf{r}}\mathbf{J}\nabla_{\mathbf{r}})^2|\psi\rangle - \sum_{i=1}^{n}\beta_i\langle\psi|(\nabla'_{\mathbf{r}}\mathbf{J}_{ii}\nabla_{\mathbf{r}})^2|\psi\rangle. \tag{5.24}$$

Matrix $\mathbf{B} = B \otimes I_3$ and parameter λ in the above identity are chosen in the following manner:

$$\lambda^2 = \frac{\beta_0^2+\beta_k^2}{(M)_{kk}^2};\ (B)_{ii} = \frac{\beta_0^2+\beta_k^2}{\lambda^2(M)_{ii}} - (M)_{ii}, \tag{5.25}$$

where k is the lightest particle in the system. When there is a huge difference between the lightest mass m_k and the masses of other particles, the right hand side of the above equation converges much faster towards the complete basis set limit.

6 Expectation values in ECGs basis

6.1 ECGs basis

The basis set we used in this thesis are explicitly correlated Gaussian functions with complex parameters [25, 26]:

$$\phi_k = z_{m_k} \exp[-\mathbf{r}'\mathbf{C}_k\mathbf{r}] \equiv z_{m_k} \exp[-\mathbf{r}'((A_k + iB_k) \otimes I_3)\mathbf{r}], \tag{6.1}$$

where m_k is an integer with k values from 1 to n, while k subscript of these matrices means that they are unique for each basis function. A_k, B_k are $n \times n$ symmetric matrices, but they do not have to be symmetric, since one can always make their elements in a way that they become symmetric. We recall that trial basis functions used in bound state calculations have to be square integrable, hence this imposes the restriction on the elements of A_k. The restriction is matrix A_k must be positive definite, which means that this matrix can be represented in a Cholesky-factored form $A_k = L_k L_k'$, with a triangular matrix L_k. Consequently, during the variational optimization of the basis functions, the elements of L_k can be varied without any restriction in the range $[-\infty, \infty]$ [25].

Wave function (6.1) can be represented in an alternative form for the derivation of matrix elements:

$$\phi_k = \lim_{\alpha_k \to\, 0} \frac{\partial}{\partial \alpha_k} \exp[-\mathbf{r}'\mathbf{C}_k\mathbf{r} + \alpha_k z_{m_k}] = \lim_{\alpha_k \to\, 0} \frac{\partial}{\partial \alpha_k} \exp[-\mathbf{r}'\mathbf{C}_k\mathbf{r} + \alpha_k (\mathbf{v}^k)'\mathbf{r}], \tag{6.2}$$

where α_k is a parameter and $\mathbf{v}_k = v_k \otimes w$ with $w' = (0, 0, 1)$. Hence, $\mathbf{v}_k$ is the vector with only one non-zero $3m_k$-th component, which is 1. For convenience, we define a generating function φ_k from equation (6.2):

$$\phi_k = \lim_{\alpha_k \to\, 0} \frac{\partial}{\partial \alpha_k} \varphi_k \quad \Rightarrow \quad \varphi_k = \exp[-\mathbf{r}'\mathbf{C}_k\mathbf{r} + \alpha_k (\mathbf{v}^k)'\mathbf{r}]. \tag{6.3}$$

Before providing the answers to the question of why we chose the basis function (6.1), first we will provide general information. Constructing the basis set is the main part in the bound state calculations when the Born-Oppenheimer (BO) approximation is not assumed [9]. In the BO approximation the nuclei are considered much heavier than electrons and thus, are placed in some fixed positions. Then the electronic wave function is determined treating the fixed positions of nuclei as parameters. For example, in the case of atoms,

the BO approximation is used to describe the motion of electrons in the static field of the nucleus located at the origin. Since we want to describe the atomic systems with high accuracy by taking into account the coupled motions of both electrons and nucleus, we do not assume the BO approximation. This means that our basis functions should depend not only on the inter-electronic distances, but also on the distances between the electrons and nucleus. After separating the center-of-mass motion from the laboratory frame Hamiltonian and considering the nucleus as the center of the coordinate system, the internal Hamiltonian describes the motion of pseudo-electrons in the central field of the nucleus (positive charge) located in the origin of the internal coordinate system. (In this case we can say that the finite nuclear mass (FNM) is explicitly included in the internal Hamiltonian (4.8) in a nonperturbative way). Consequently, the basis set we should choose in this case have to accurately describe only the electronic correlation effect and the distribution of the electrons around the positively charged central nucleus.

The choice of basis functions (6.1) is motivated by the following properties. First, the exponential part of this function is spherically symmetric (rotationally invariant or does not change under 3D rotations) as required by the symmetry of the problem. The rotationally invariant function means that the function is invariant with respect to any orthogonal transformation. To see this, let U be any 3×3 orthogonal matrix that rotates vectors $\mathbf{r}_i$ in the 3D space. We can use the property of the Kronecker product which reads that if $A = Q\otimes U$, where Q and U are orthogonal (or unitary) matrices, then A is also an orthogonal matrix [27]. The identity matrix I_n is a special case of a unitary matrix with its determinant equal to unity. Now we act on our basis function by an orthogonal matrix $I_n \otimes U$ (since the Kronecker product between orthogonal matrices is also orthogonal) to show the spherical symmetry:

$$\phi_k = \exp[-((I_n\otimes U)\mathbf{r})'((A_k+iB_k)\otimes I_3)(I_n\otimes U)\mathbf{r}] = \exp[-\mathbf{r}'(I_n\otimes U')((A_k+iB_k)\otimes I_3)(I_n\otimes U)\mathbf{r}]$$

$$= \exp[-\mathbf{r}'((A_k+iB_k)\otimes U'U)\mathbf{r}] = \exp[-\mathbf{r}'((A_k+iB_k)\otimes I_3)\mathbf{r}].$$

Second, basis functions (6.1) have complex exponential parameters. Using ECGs with complex exponential parameters facilitates an adequate description of the radial nodes in the ground and excited state wave functions of atomic and molecular systems. Such complex functions are more flexible than real Gaussians (one-center correlated Gaus-

sians $\phi_k = \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}]$) and if put together in a certain combinations (to simulate periodic functions namely sine or cosine functions), they should correctly describe the radial nodes (oscillations) in the wave function in atomic also molecular excited states [25, 26]. It is also worth mentioning a big advantage of using Gaussians as a basis function compared to the other basis functions: all matrix elements with Gaussians can be evaluated analytically for an arbitrary number of particles.

Third, there is another concern regarding the excited states in atomic calculations. In particular, it is related to describing the radial and angular nodes in the wave functions. We already showed the one way of describing the radial nodes with use of complex Gaussians, while both radial and angular nodes can be described by using premultipliers to the complex Gaussian we defined above. Let us describe about premultipliers in detail.

We know that when there is no external fields are present the Hamiltonian commutes with the total orbital angular momentum operator $\hat{L}^2$ and with the projection of it on a selected axis $\hat{L}_z$ [23]. Hence, the exact solutions of the corresponding Schrödinger equation must also be eigenfunctions of these operators. Because of the degeneracy of the energy levels corresponding to different quantum numbers M (eigenvalues of $\hat{L}_z$), it is not required that basis functions must correspond to a particular M value. In addition to this, according to the Wigner-Eckardt theorem, the energy of the system described by a spherically symmetric Hamiltonian is independent of M.

In short, it becomes necessary to construct basis functions that are eigenfunctions of the square of the total angular momentum operator with angular momentum L. Since the eigenfunctions of L^2 and L_z are nothing but the old spherical harmonics [23], and including the electron-nucleus distances powers in the wave function for better presentation of the radial nodes, a common approach to building basis functions of proper rotational symmetry, is to multiply $\exp[-\mathbf{r}'\mathbf{C}_k\mathbf{r}]$ by a generalized solid spherical harmonic $\Theta_{LM}(\mathbf{r})$,

$$\phi_k = \Theta_{LM}(\mathbf{r}) \exp[-\mathbf{r}'\mathbf{C}_k\mathbf{r}].$$

$\Theta_{LM}(\mathbf{r})$ can be formed by successively coupling solid spherical harmonics,

$$\Theta_{LM}(\mathbf{r}) = r_1^{l_1} \cdots r_n^{l_n} [[[Y_{l_1 m_1}(\hat{\mathbf{r}}_1) Y_{l_2 m_2}(\hat{\mathbf{r}}_2)]_{L_{12} M_{12}} Y_{l_3 m_3}(\hat{\mathbf{r}}_3)]_{L_{123} M_{123}} \cdots Y_{l_n m_n}(\hat{\mathbf{r}}_n)]_{LM}.$$

Using above equation, it is possible to build basis functions for any value of the total orbital angular momentum and its z projection. For $L = 1$, $M = 0$ states, with a single

Cartesian coordinate, in which the dominant configuration corresponds to one particle with $l = 1$ and all others with $l = 0$ (i.e., $l_k = 1, l_i = 0, k \neq i$), which lead to the $r_k Y_{10}(\mathbf{r}_k)$, so that the ECGs have the following form:

$$\phi_k = z_{m_k} \exp[-\mathbf{r}'\mathbf{C}_k\mathbf{r}].$$

In addition to this, in the case of high values of total angular momentum L, implementing the above procedure is complicated, instead one can use the following general form:

$$\Theta_{LM}(\mathbf{r}) = v^{2K+L} Y_{LM}(\hat{\mathbf{v}}),$$

where $\mathbf{v} = \sum_{i=1}^{n} u_i \mathbf{r}_i$, and $v = |\mathbf{v}|$ is defined as a linear combination of all pseudoparticle coordinates. The integer variational parameter K, which can take any non-negative value, introduces an additional flexibility that can be used to improve the short-range behavior of the basis functions [28].

6.2 Gaussian integrals

The Gaussian integral:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} \exp(-\frac{1}{2}x'Ax)dx_1dx_2...dx_n,$$

where x' is a transpose of a n dimensional x column vector and A is a symmetric, non-singular(determinant is non-zero) $n \times n$ matrix, can be solved in the following way. Let us transform the vector x to some other vector y with an orthogonal matrix S ($S' = S^{-1}$), whose determinant is unity $|S|$=1. Next requirement to solve this integral is that matrix S should be diagonalizing matrix, which means that $S_{-1}AS$ be a diagonal matrix D (all elements are zeros, except diagonal terms) with diagonal elements $d_1, d_2, ..., d_n$, which are eigenvalues of a matrix A.

$$\mathbf{x} = Sy,\ dx = Sdy,\ dx_1dx_2... = |S|dy_1dy_2...$$

$$\int \exp(-\frac{1}{2}y'Dy)dy = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} \exp(-\frac{1}{2}[d_1y_1^2 + d_2y_2^2 + ... + d_ny_n^2])dy_1dy_2...dy_n =$$

$$= \sqrt{\frac{2\pi}{d_1}} \cdot \sqrt{\frac{2\pi}{d_2}} \cdots \sqrt{\frac{2\pi}{d_n}} = \prod_{i=1}^{n} \sqrt{\frac{(2\pi)^n}{d_i}} = \left(\frac{(2\pi)^n}{|D|}\right)^{1/2} = \left(\frac{(2\pi)^n}{|A|}\right)^{1/2} \Rightarrow$$

$$\Rightarrow \int \exp(-\frac{1}{2}x'Ax)dx = \left(\frac{(2\pi)^n}{|A|}\right)^{1/2}. \tag{6.4}$$

In addition, the following integral

$$\int \exp(-\frac{1}{2}x'Ax + J'x)dx,$$

where additional J is a vector, whose elements are constants, can be solved using the property of non-singular positive symmetric matrix A and rule of transpose, which are:

$$A^{-1} = (A^{-1})',\ (xA)' = A'x'.$$

Using only above properties and noting that $d(x - A^{-1}J)$ is the same as dx, since both A and J has no x components, we can easily calculate the integral as follows:

$$\int \exp(-\frac{1}{2}x'Ax + J'x)dx = \int \exp\left[-\frac{1}{2}(x - A^{-1}J)'A(x - A^{-1}J) + \frac{1}{2}J'A^{-1}J\right]dx =$$

$$= \exp\left(\frac{1}{2}J'A^{-1}J\right)\int \exp\left[-\frac{1}{2}(x - A^{-1}J)'A(x - A^{-1}J)\right]d(x - A^{-1}J) \Rightarrow$$

$$\Rightarrow \int \exp(-\frac{1}{2}x'Ax + J'x)dx = \exp\left(\frac{1}{2}J'A^{-1}J\right)\sqrt{\frac{(2\pi)^n}{|A|}}. \tag{6.5}$$

6.3 Overlap Integral

The overlap integral can be calculated by noting that $\mathbf{C}_{kl} = \mathbf{C}_k + \mathbf{C}_l$:

$$\langle\varphi_k|\varphi_l\rangle = \int e^{[-\mathbf{r}'\mathbf{C}_k\mathbf{r} + \alpha_k(\mathbf{v}^k)'\mathbf{r}]}e^{[-\mathbf{r}'\mathbf{C}_l\mathbf{r} + \alpha_l(\mathbf{v}^l)'\mathbf{r}]}d\mathbf{r} =$$

$$= \int d\mathbf{r}\exp[-\mathbf{r}'(\mathbf{C}_k + \mathbf{C}_l)\mathbf{r} + (\alpha_k\mathbf{v}'_k + \alpha_l\mathbf{v}'_l)\mathbf{r}] = \int d\mathbf{r}\exp[-\mathbf{r}'(\mathbf{C}_{kl})\mathbf{r} + (\alpha_k\mathbf{v}'_k + \alpha_l\mathbf{v}'_l)\mathbf{r}] \Rightarrow$$

$$\Rightarrow \langle\varphi_k|\varphi_l\rangle = \frac{\pi^{3n/2}}{|\mathbf{C}_{kl}|^{1/2}}\exp[\frac{1}{4}(\alpha_k\mathbf{v}_k + \alpha_l\mathbf{v}_l)'\mathbf{C}_{kl}^{-1}(\alpha_k\mathbf{v}_k + \alpha_l\mathbf{v}_l)].$$

By substituting the definitions $\mathbf{v}_k = v_k \otimes w$ and $\mathbf{C}_{kl} = C_{kl} \otimes I_3$ as well as using the fact that $|\mathbf{C}_{kl}| \equiv |C_{kl} \otimes I_3| = |C_{kl}|^3$, and $(a' \otimes w')(C_{kl} \otimes I_3)(a \otimes w) = a'C_{kl}a \otimes w'I_3w = a'C_{kl}a$, above integral reduces to the following form:

$$\langle\varphi_k|\varphi_l\rangle = \frac{\pi^{3n/2}}{|C_{kl}|^{3/2}}\exp[\frac{1}{4}(\alpha_k v_k + \alpha_l v_l)'C_{kl}^{-1}(\alpha_k v_k + \alpha_l v_l)].$$

In order to find the overlap integral, we still need to take the derivative followed by the limit from above integral:

$$\langle\phi_k|\phi_l\rangle = \lim_{\alpha_k\to\ 0}\frac{\partial}{\partial\alpha_k}\lim_{\alpha_l\to\ 0}\frac{\partial}{\partial\alpha_l}\langle\varphi_k|\varphi_l\rangle;$$

$$\Rightarrow \lim_{\alpha_l\to\ 0}\frac{\pi^{3n/2}}{|C_{kl}|^{3/2}}\left[\frac{1}{2}C_{kl}^{-1}(\alpha_k v_k+\alpha_l v_l)v_l\right]\exp[\frac{1}{4}C_{kl}^{-1}(\alpha_k v_k+\alpha_l v_l)^2] =$$

$$= \frac{\pi^{3n/2}}{|C_{kl}|^{3/2}}\left[\frac{1}{2}C_{kl}^{-1}(\alpha_k v_k)v_l\right]\exp[\frac{1}{4}C_{kl}^{-1}(\alpha_k v_k)^2].$$

$$\Rightarrow \lim_{\alpha_k\to\ 0}\frac{\pi^{3n/2}}{|C_{kl}|^{3/2}}\frac{1}{2}\left[C_{kl}^{-1}v_k v_l\exp[\frac{1}{4}C_{kl}^{-1}(\alpha_k v_k)^2] + C_{kl}^{-1}\alpha_k v_k v_l[\frac{1}{2}\alpha_k v_k^2]\exp[\frac{1}{4}C_{kl}^{-1}(\alpha_k v_k)^2]\right] =$$

$$= \frac{\pi^{3n/2}}{|C_{kl}|^{3/2}}\frac{1}{2}C_{kl}^{-1}v_k v_l \Rightarrow \langle\phi_k|\phi_l\rangle = \frac{\pi^{3n/2}}{|C_{kl}|^{3/2}}\frac{1}{2}v_k' C_{kl}^{-1}v_l. \tag{6.6}$$

Finally, the normalized overlap matrix elements are:

$$\mathtt{S}_{kl} = \frac{\langle\phi_k|\phi_l\rangle}{\sqrt{\langle\phi_k|\phi_k\rangle\langle\phi_l|\phi_l\rangle}} = \frac{(|C_{kk}|^{3/2}|C_{ll}|^{3/2})^{1/2}}{|C_{kl}|^{3/2}}\frac{v_k' C_{kl}^{-1}v_l}{(v_k' C_{kk}^{-1}v_k v_l' C_{ll}^{-1}v_l)^{1/2}} =$$

$$= 2^{3n/2}\left(\frac{\big||L_k|\big|\big||L_l|\big|}{|C_{kl}|^{3/2}}\right)^{3/2}\frac{v_k' C_{kl}^{-1}v_l}{(v_k' C_{kk}^{-1}v_k v_l' C_{ll}^{-1}v_l)^{1/2}}, \tag{6.7}$$

where we used $C_k = L_k L_k' = |L_k|^2 \to C_{kk} = C_k + C_k = 2|L_k|^2$.

6.4 $\left\langle\psi\left|\frac{1}{r_{ij}}\right|\psi\right\rangle$ integral

In order to derive the matrix elements of necessary operators, we need to calculate $\left\langle\psi\left|\frac{1}{r_{ij}}\right|\psi\right\rangle$ integral first, since we will use this integral several times. We start by using the following Gaussian integral:

$$\int_{-\infty}^{\infty}d\beta\exp[-\beta^2 r_{ij}^2] = 2\int_0^{\infty}d\beta\exp[-\beta^2 r_{ij}^2] = \frac{\sqrt{\pi}}{r_{ij}} \Rightarrow$$

$$\Rightarrow \frac{1}{r_{ij}} = \frac{2}{\sqrt{\pi}}\int_0^{\infty}d\beta\exp[-\beta^2 r_{ij}^2].$$

Substituting the new form of $\frac{1}{r_{ij}}$ we have

$$\left\langle\phi_k\left|\frac{1}{r_{ij}}\right|\phi_l\right\rangle = \frac{2}{\sqrt{\pi}}\int_0^{\infty}d\beta\langle\phi_k|\exp[-\beta^2 r_{ij}^2]|\phi_l\rangle. \tag{6.8}$$

In addition, we introduce matrix $\mathbf{J}_{ij} = J_{ij} \otimes I_3$ for further calculations:

$$r_{ij}^2 = \mathbf{r}'\mathbf{J}_{ij}\mathbf{r}, \quad r_i^2 = \mathbf{r}'\mathbf{J}_{ii}\mathbf{r}, \quad J_{ij} = j^{ij'}j^{ij}, \quad J_{ii} = j^i, \tag{6.9}$$

where $j^{ij} = j^i - j^j$. j^i is the vector with all zero elements except the i-th term, which is set to one. Then equation (6.8) can be re-expressed as

$$\left\langle \phi_k \middle| \frac{1}{r_{ij}} \middle| \phi_l \right\rangle = \frac{2}{\sqrt{\pi}} \lim_{\alpha_k \to 0} \frac{\partial}{\partial \alpha_k} \lim_{\alpha_l \to 0} \frac{\partial}{\partial \alpha_l} \int_0^\infty d\beta \int_\infty^\infty d\mathbf{r} \exp\left[-\mathbf{r}'(\mathbf{C}_{kl} + \beta^2 \mathbf{J}_{ij})\mathbf{r} + (\alpha_k \mathbf{v}_k + \alpha_l \mathbf{v}_l)'\mathbf{r} \right].$$

The above integral is the same as overlap integral with $C_{kl} + \beta^2 J_{ij}$ instead of C_{kl}, so we just substitute the result from the overlap integral

$$\left\langle \phi_k \middle| \frac{1}{r_{ij}} \middle| \phi_l \right\rangle = \pi^{\frac{3N-1}{2}} \int_0^\infty d\beta \frac{v_k'(C_{kl} + \beta^2 J_{ij})^{-1} v_l}{|C_{kl} + \beta^2 J_{ij}|^{\frac{3}{2}}}. \tag{6.10}$$

In order to calculate the integral above, the following transformations should be applied

$$v_k'(C_{kl} + \beta^2 J_{ij})^{-1} v_l = \mathrm{tr}[(C_{kl} + \beta^2 J_{ij})^{-1} v_l v_k'],$$

$$\frac{\mathrm{tr}[(C_{kl} + \beta^2 J_{ij})^{-1} v_l v_k']}{|C_{kl} + \beta^2 J_{ij}|^{\frac{3}{2}}} = -\frac{2}{3} \frac{\partial}{\partial \epsilon} \frac{1}{|C_{kl} + \epsilon v_l v_k' + \beta^2 J_{ij}|^{\frac{3}{2}}} \bigg|_{\epsilon=0},$$

where we used shorthand notation for limit, which is $\Big|_{\epsilon=0}$. Now integral (6.10) turns to

$$\left\langle \phi_k \middle| \frac{1}{r_{ij}} \middle| \phi_l \right\rangle = -\frac{2\pi^{\frac{3N-1}{2}}}{3} \frac{\partial}{\partial \epsilon} \int_0^\infty d\beta \frac{1}{|C_{kl} + \epsilon v_l v_k' + \beta^2 J_{ij}|^{\frac{3}{2}}} \bigg|_{\epsilon=0}. \tag{6.11}$$

For symmetric square matrix A we can use the following relation [27]

$$|A + xy'| = |A|\big[1 + \mathrm{tr}(A^{-1}xy')\big]. \tag{6.12}$$

From (6.12) determinant turns into

$$|C_{kl} + \epsilon v_l v_k' + \beta^2 J_{ij}| = |C_{kl} + \epsilon v_l v_k'| \Big(1 + \mathrm{tr}\big[\beta^2 (C_{kl} + \epsilon v_l v_k')^{-1} J_{ij}\big] \Big). \tag{6.13}$$

Substituting (6.13) into (6.11) we have

$$\left\langle \phi_k \middle| \frac{1}{r_{ij}} \middle| \phi_l \right\rangle = -\frac{2\pi^{\frac{3N}{2}}}{3\sqrt{\pi}} \frac{\partial}{\partial \epsilon} |C_{kl} + \epsilon v_l v_k'|^{-\frac{3}{2}} \int_0^\infty d\beta \frac{1}{\Big(1 + \mathrm{tr}\big[\beta^2 (C_{kl} + \epsilon v_l v_k')^{-1} J_{ij}\big]\Big)^{\frac{3}{2}}} \bigg|_{\epsilon=0} =$$

$$= -\frac{2\pi^{\frac{3N}{2}}}{3\sqrt{\pi}} \frac{\partial}{\partial \epsilon} |C_{kl} + \epsilon v_l v_k'|^{-\frac{3}{2}} \big[\mathrm{tr}(C_{kl} + \epsilon v_l v_k')^{-1} J_{ij}\big]^{-\frac{1}{2}} \Big|_{\epsilon=0}.$$

Evaluation of the derivative leads to

$$\frac{\partial}{\partial\epsilon}|C_{kl}+\epsilon v_l v'_k|^{-\frac{3}{2}}\left[\mathrm{tr}(C_{kl}+\epsilon v_l v'_k)^{-1}J_{ij}\right]^{-\frac{1}{2}}\Big|_{\epsilon=0}=$$

$$=\left[\mathrm{tr}(C_{kl}^{-1}J_{ij})\right]^{-\frac{1}{2}}\frac{\partial}{\partial\epsilon}|C_{kl}+\epsilon v_l v'_k|^{-\frac{3}{2}}\Big|_{\epsilon=0}+|C_{kl}|^{-\frac{3}{2}}\frac{\partial}{\partial\epsilon}\left[\mathrm{tr}(C_{kl}+\epsilon v_l v'_k)^{-1}J_{ij}\right]^{-\frac{1}{2}}\Big|_{\epsilon=0}=$$

$$=-\frac{3}{2}\left[\mathrm{tr}(C_{kl}^{-1}J_{ij})\right]^{-\frac{1}{2}}|C_{kl}|^{-\frac{5}{2}}|C_{kl}|\mathrm{tr}(C_{kl}^{-1}v_l v'_k)-\frac{1}{2}|C_{kl}|^{-\frac{3}{2}}\left[\mathrm{tr}(C_{kl}^{-1}J_{ij})\right]^{-\frac{3}{2}}\mathrm{tr}(-C_{kl}^{-1}v_l v'_k C_{kl}^{-1}J_{ij})$$

$$=-\frac{3}{2}|C_{kl}|^{-\frac{3}{2}}\left[\mathrm{tr}(C_{kl}^{-1}v_l v'_k)\left[\mathrm{tr}(C_{kl}^{-1}J_{ij})\right]^{-\frac{1}{2}}-\frac{1}{3}\mathrm{tr}(C_{kl}^{-1}v_l v'_k C_{kl}^{-1}J_{ij})\left[\mathrm{tr}(C_{kl}^{-1}J_{ij})\right]^{-\frac{3}{2}}\right].$$

Substituting it back we get

$$\left\langle\phi_k\left|\frac{1}{r_{ij}}\right|\phi_l\right\rangle=\frac{\pi^{\frac{3N-1}{2}}}{|C_{kl}|^{\frac{3}{2}}}\left[\frac{\mathrm{tr}(C_{kl}^{-1}v_l v'_k)}{\mathrm{tr}(C_{kl}^{-1}J_{ij})^{\frac{1}{2}}}-\frac{1}{3}\frac{\mathrm{tr}(C_{kl}^{-1}v_l v'_k C_{kl}^{-1}J_{ij})}{\mathrm{tr}(C_{kl}^{-1}J_{ij})^{\frac{3}{2}}}\right].\tag{6.14}$$

Using normalized basis functions, (6.14) becomes

$$\left\langle\phi_k\left|\frac{1}{r_{ij}}\right|\phi_l\right\rangle=\frac{2}{\sqrt{\pi}}\frac{\mathtt{S}_{kl}}{\mathrm{tr}(C_{kl}^{-1}J_{ij})^{\frac{1}{2}}}\left[1-\frac{1}{3\mathrm{tr}(C_{kl}^{-1}J_{ij})}\frac{v'_k C_{kl}^{-1}J_{ij}C_{kl}^{-1}v_l}{v'_k C_{kl}^{-1}v_l}\right].\tag{6.15}$$

6.5 $\left\langle\nabla_r\psi\left|\frac{\mathbf{M}}{r_{ij}}\right|\nabla_r\psi\right\rangle$ term

First step is to take gradient ∇_r of the generating function $\varphi_k=\exp[\mathbf{r}'\mathbf{C}_k\mathbf{r}+\alpha_k\mathbf{v}'_k\mathbf{r}]$, which is simply $(-2\mathbf{C}_k\mathbf{r}+\alpha_k\mathbf{v}_k)\varphi_k$.

$$\left\langle\nabla_r\varphi_k\left|\frac{\mathbf{M}}{r_{ij}}\right|\nabla_r\varphi_l\right\rangle=\left\langle(-2\mathbf{C}_k\mathbf{r}+\alpha_k\mathbf{v}_k)\varphi_k\left|\frac{\mathbf{M}}{r_{ij}}\right|(-2\mathbf{C}_l\mathbf{r}+\alpha_l\mathbf{v}_l)\varphi_l\right\rangle=$$

$$=4\left\langle\varphi_k\left|\frac{\mathbf{r}'\mathbf{C}_k^\dagger\mathbf{M}\mathbf{C}_l\mathbf{r}}{r_{ij}}\right|\varphi_l\right\rangle-2\alpha_l\left\langle\varphi_k\left|\frac{\mathbf{r}'\mathbf{C}_k^\dagger\mathbf{M}\mathbf{v}_l}{r_{ij}}\right|\varphi_l\right\rangle$$
$$-2\alpha_k\left\langle\varphi_k\left|\frac{\mathbf{v}'_k\mathbf{M}\mathbf{C}_l\mathbf{r}}{r_{ij}}\right|\varphi_l\right\rangle+\alpha_k\alpha_l\mathbf{v}'_k\mathbf{M}\mathbf{v}_l\left\langle\varphi_k\left|\frac{1}{r_{ij}}\right|\varphi_l\right\rangle.$$

Since the derivation of these expectation values are lengthy, it is convenient to consider above four different expectation values separately as four different terms and combine them at the end.

The first term: $4\left\langle \varphi_k \left| \frac{\mathbf{r}'\mathbf{C}_k^\dagger \mathbf{M}\mathbf{C}_l\mathbf{r}}{r_{ij}} \right| \varphi_l \right\rangle$

Using the following relation for a symmetric matrix $\mathbf{W} = W \otimes I_3$:

$$\mathbf{r}'\mathbf{W}\mathbf{r} = -\frac{\partial}{\partial\gamma}\exp[-\gamma\mathbf{r}'\mathbf{W}\mathbf{r}]\Big|_{\gamma=0}, \tag{6.16}$$

and equations (6.8, 6.9), as well as adopting new notation $\frac{\mathbf{C}_k^\dagger\mathbf{M}\mathbf{C}_l+(\mathbf{C}_k^\dagger\mathbf{M}\mathbf{C}_l)'}{2} = \frac{\mathbf{C}_k^\dagger\mathbf{M}\mathbf{C}_l+\mathbf{C}_l\mathbf{M}\mathbf{C}_k^\dagger}{2} = \mathbf{K}$, $\mathbf{K} = K \otimes I_3$, we can write:

$$\left\langle \varphi_k \left| \frac{\mathbf{r}'\mathbf{K}\mathbf{r}}{r_{ij}} \right| \varphi_l \right\rangle = -\frac{2}{\sqrt{\pi}} \int_0^\infty d\beta \frac{\partial^3}{\partial\gamma\partial\alpha_k\partial\alpha_l} \times$$

$$\times \int d\mathbf{r} \exp[-\mathbf{r}'(\mathbf{C}_{kl} + \gamma\mathbf{K} + \beta^2\mathbf{J}_{ij})\mathbf{r} + (\alpha_k\mathbf{v}_k + \alpha_l\mathbf{v}_l)'\mathbf{r}]\Big|_{\gamma,\alpha_k,\alpha_l=0} =$$

$$= -\pi^{(3n-1)/2} \int_0^\infty d\beta \frac{\partial}{\partial\gamma} \frac{v_k'(C_{kl} + \gamma K + \beta^2 J_{ij})^{-1} v_l}{|C_{kl} + \gamma K + \beta^2 J_{ij}|^{2/3}}\Big|_{\gamma=0}. \tag{6.17}$$

In order to calculate the integral above, the following transformations should be applied

$$v_k'(C_{kl} + \gamma K + \beta^2 J_{ij})^{-1} v_l = \mathrm{tr}[(C_{kl} + \gamma K + \beta^2 J_{ij})^{-1} v_l v_k'],$$

$$\frac{\mathrm{tr}[(C_{kl} + \gamma K + \beta^2 J_{ij})^{-1} v_l v_k']}{|C_{kl} + \gamma K + \beta^2 J_{ij}|^{\frac{3}{2}}} = -\frac{2}{3}\frac{\partial}{\partial\epsilon} \frac{1}{|C_{kl} + \epsilon v_l v_k' + \gamma K + \beta^2 J_{ij}|^{\frac{3}{2}}}\Big|_{\epsilon=0}.$$

Now integral (6.17) turns to

$$\left\langle \varphi_k \left| \frac{\mathbf{r}'\mathbf{K}\mathbf{r}}{r_{ij}} \right| \varphi_l \right\rangle = \frac{2\pi^{(3n-1)/2}}{3} \frac{\partial}{\partial\gamma}\frac{\partial}{\partial\epsilon} \int_0^\infty d\beta \frac{1}{|C_{kl} + \epsilon v_l v_k' + \gamma K + \beta^2 J_{ij}|^{\frac{3}{2}}}\Big|_{\gamma,\epsilon=0}. \tag{6.18}$$

For symmetric square matrix A we can use the following relation

$$|A + xy'| = |A|\big[1 + \mathrm{tr}(A^{-1}xy')\big]. \tag{6.19}$$

Recall that J_{ij} is the rank 1 matrix, and using the fact that matrix multiplication with rank 1 matrix gives another rank 1 matrix, which have only one eigenvalue, determinant in (6.18) can be rearranged using the relation (6.18)

$$|C_{kl} + \gamma K + \epsilon v_l v_k' + \beta^2 J_{ij}| = |C_{kl} + \gamma K + \epsilon v_l v_k'||I_N + \beta^2 (C_{kl} + \gamma K + \epsilon v_l v_k')^{-1} J_{ij}| \Rightarrow$$

$$|I_N + \beta^2 (C_{kl} + \gamma K + \epsilon v_l v_k')^{-1} J_{ij}| = \prod_{k=1}^{N} (1 + \lambda_k) = 1 + \lambda,$$

where λ is an eigenvalue of rank 1 matrix $\beta^2(C_{kl}+\gamma K+\epsilon v_l v_k')^{-1}J_{ij}$. From the fact of trace-eigenvalue dependence

$$\mathrm{tr}[\beta^2(C_{kl}+\gamma K+\epsilon v_l v_k')^{-1}J_{ij}]=\sum_{k=1}^{N}\lambda_k=\lambda,$$

$$\Rightarrow |I_N+\beta^2(C_{kl}+\gamma K+\epsilon v_l v_k')^{-1}J_{ij}|=\Big(1+\mathrm{tr}[\beta^2(C_{kl}+\gamma K+\epsilon v_l v_k')^{-1}J_{ij}]\Big).$$

Finally, the determinant in equation (6.18) turns to

$$|C_{kl}+\gamma K+\epsilon v_l v_k'+\beta^2 J_{ij}|=|C_{kl}+\gamma K+\epsilon v_l v_k'|\Big(1+\mathrm{tr}\big[\beta^2(C_{kl}+\gamma K+\epsilon v_l v_k')^{-1}J_{ij}\big]\Big). \quad (6.20)$$

Substituting (6.20) into (6.18) yields

$$\Big\langle\phi_k\Big|\frac{1}{r_{ij}}\Big|\phi_l\Big\rangle=$$

$$=\frac{2\pi^{\frac{3n-1}{2}}}{3}\frac{\partial}{\partial\gamma}\frac{\partial}{\partial\epsilon}|C_{kl}+\gamma K+\epsilon v_l v_k'|^{-\frac{3}{2}}\int_0^\infty d\beta\frac{1}{\Big(1+\mathrm{tr}\big[\beta^2(C_{kl}+\gamma K+\epsilon v_l v_k')^{-1}J_{ij}\big]\Big)^{\frac{3}{2}}}\Bigg|_{\gamma,\epsilon=0}=$$

$$=\frac{2\pi^{\frac{3n-1}{2}}}{3}\frac{\partial}{\partial\gamma}\frac{\partial}{\partial\epsilon}|C_{kl}+\gamma K+\epsilon v_l v_k'|^{-\frac{3}{2}}\Big(\mathrm{tr}([C_{kl}+\gamma K+\epsilon v_l v_k')^{-1}J_{ij}]\Big)^{-\frac{1}{2}}\Bigg|_{\gamma,\epsilon=0}.$$

In the β integral we used the fact that $\mathrm{tr}(a\mathbf{A})=a\mathrm{tr}(\mathbf{A})$ and $\int_0^\infty\frac{1}{(1+ax^2)^{3/2}}dx=\frac{1}{\sqrt{a}}$. Evaluation of the derivative with respect to ϵ:

$$\frac{\partial}{\partial\epsilon}|C_{kl}+\gamma K+\epsilon v_l v_k'|^{-\frac{3}{2}}\big[\mathrm{tr}((C_{kl}+\gamma K+\epsilon v_l v_k')^{-1}J_{ij})\big]^{-\frac{1}{2}}\Big|_{\epsilon=0}=$$

$$=\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{1}{2}}\frac{\partial}{\partial\epsilon}|C_{kl}+\gamma K+\epsilon v_l v_k'|^{-\frac{3}{2}}\Big|_{\epsilon=0}+$$

$$+|C_{kl}+\gamma K|^{-\frac{3}{2}}\frac{\partial}{\partial\epsilon}\big[\mathrm{tr}((C_{kl}+\gamma K+\epsilon v_l v_k')^{-1}J_{ij})\big]^{-\frac{1}{2}}\Big|_{\epsilon=0}=$$

$$=-\frac{3}{2}\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{1}{2}}|C_{kl}+\gamma K|^{-\frac{5}{2}}|C_{kl}+\gamma K|\mathrm{tr}((C_{kl}+\gamma K)^{-1}v_l v_k')$$

$$-\frac{1}{2}|C_{kl}+\gamma K|^{-\frac{3}{2}}\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{3}{2}}\mathrm{tr}(-(C_{kl}+\gamma K)^{-1}v_l v_k'(C_{kl}+\gamma K)^{-1}J_{ij})=$$

$$=-\frac{3}{2}|C_{kl}+\gamma K|^{-\frac{3}{2}}\Bigg[\mathrm{tr}((C_{kl}+\gamma K)^{-1}v_l v_k')\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{1}{2}}$$

$$-\frac{1}{3}\mathrm{tr}((C_{kl}+\gamma K)^{-1}v_l v_k'(C_{kl}+\gamma K)^{-1}J_{ij})\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{3}{2}}\Bigg].$$

One note here is that, we could substitute $C_{kl}+\gamma K$ in stead of C_{kl}, and write the equation (6.14) directly. Now it is time to take derivative with respect to γ. Derivatives are strightforward, but a bit lengthy:

$$-\frac{3}{2}\left[\mathrm{tr}(C_{kl}^{-1}v_l v_k')\big[\mathrm{tr}(C_{kl}^{-1}J_{ij})\big]^{-\frac{1}{2}}-\frac{1}{3}\mathrm{tr}(C_{kl}^{-1}v_l v_k' C_{kl}^{-1}J_{ij})\big[\mathrm{tr}(C_{kl}^{-1}J_{ij})\big]^{-\frac{3}{2}}\right]\frac{\partial}{\partial\gamma}|C_{kl}+\gamma K|^{-\frac{3}{2}}\Big|_{\gamma=0}$$

$$-\frac{3}{2}|C_{kl}|^{-\frac{3}{2}}\frac{\partial}{\partial\gamma}\left[\mathrm{tr}((C_{kl}+\gamma K)^{-1}v_l v_k')\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{1}{2}}\right.$$

$$\left.-\frac{1}{3}\mathrm{tr}((C_{kl}+\gamma K)^{-1}v_l v_k'(C_{kl}+\gamma K)^{-1}J_{ij})\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{3}{2}}\right]\Big|_{\gamma=0};$$

For the sake of convenience, let us consider the each derivative separately, then we will substitute it back. First, considering $d|X|=|X|\mathrm{tr}[X^{-1}dX]$,

$$\frac{\partial}{\partial\gamma}|C_{kl}+\gamma K|^{-\frac{3}{2}}\Big|_{\gamma=0}=-\frac{3}{2}|C_{kl}+\gamma K|^{-\frac{5}{2}}|C_{kl}+\gamma K|\mathrm{tr}[(C_{kl}+\gamma K)^{-1}K]\Big|_{\gamma=0}=-\frac{3}{2}|C_{kl}|^{-3/2}\mathrm{tr}[C_{kl}^{-1}K].$$

Second term derivative is longer:

$$\frac{\partial}{\partial\gamma}\left[\mathrm{tr}((C_{kl}+\gamma K)^{-1}v_l v_k')\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{1}{2}}\right.$$

$$\left.-\frac{1}{3}\mathrm{tr}((C_{kl}+\gamma K)^{-1}v_l v_k'(C_{kl}+\gamma K)^{-1}J_{ij})\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{3}{2}}\right]\Big|_{\gamma=0}=$$

$$\Big[\mathrm{tr}(C_{kl}^{-1}J_{ij})\Big]^{-1/2}\frac{\partial}{\partial\gamma}\mathrm{tr}((C_{kl}+\gamma K)^{-1}v_l v_k')\Big|_{\gamma=0}+\mathrm{tr}(C_{kl}^{-1}v_l v_k')\frac{\partial}{\partial\gamma}\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{1}{2}}\Big|_{\gamma=0}$$

$$-\frac{1}{3}\big[\mathrm{tr}(C_{kl}^{-1}J_{ij})\big]^{-\frac{3}{2}}\frac{\partial}{\partial\gamma}\mathrm{tr}((C_{kl}+\gamma K)^{-1}v_l v_k'(C_{kl}+\gamma K)^{-1}J_{ij})\Big|_{\gamma=0}$$

$$-\frac{1}{3}\mathrm{tr}(C_{kl}^{-1}v_l v_k' C_{kl}^{-1}J_{ij})\frac{\partial}{\partial\gamma}\big[\mathrm{tr}((C_{kl}+\gamma K)^{-1}J_{ij})\big]^{-\frac{3}{2}}\Big|_{\gamma=0}=$$

By noting that $d\mathrm{tr}(A)=\mathrm{tr}(dA)$ and $d(C_{kl}+\gamma K)^{-1}=-(C_{kl}+\gamma K)^{-1}K(C_{kl}+\gamma K)^{-1}$, we have

$$=\Big[\mathrm{tr}(C_{kl}^{-1}J_{ij})\Big]^{-1/2}\mathrm{tr}(-C_{kl}^{-1}KC_{kl}^{-1}v_l v_k')-\frac{1}{2}\mathrm{tr}(C_{kl}^{-1}v_l v_k')(\mathrm{tr}(C_{kl}^{-1}J_{ij}))^{-2/3}\mathrm{tr}(-C_{kl}^{-1}KC_{kl}^{-1}J_{ij})$$

$$-\frac{1}{3}\big[\mathrm{tr}(C_{kl}^{-1}J_{ij})\big]^{-\frac{3}{2}}\mathrm{tr}\Big(-C_{kl}^{-1}KC_{kl}^{-1}v_l v_k' C_{kl}^{-1}J_{ij}-C_{kl}^{-1}v_l v_k' C_{kl}^{-1}KC_{kl}^{-1}J_{ij}\Big)$$

$$+\frac{1}{2}\mathrm{tr}(C_{kl}^{-1}v_l v_k' C_{kl}^{-1}J_{ij})(\mathrm{tr}(C_{kl}^{-1}J_{ij}))^{-5/2}\mathrm{tr}(-C_{kl}^{-1}KC_{kl}^{-1}J_{ij}).$$

Now it is remained to substitute everything into (6.18), which was our initial purpose, but equations are getting messy, unless we introduce some new notations. Taking into account of our previous definitions $J_{ij} = j^{ij'} j^{ij}$ and $\frac{\mathbf{C}_k^\dagger \mathbf{M} \mathbf{C}_l + \mathbf{C}_l \mathbf{M} \mathbf{C}_k^\dagger}{2} = \mathbf{K} \Rightarrow K = (C_k^\dagger M C_l + C_l M C_k^\dagger)/2$ as well as $\mathrm{tr}(-X) = -\mathrm{tr}(X)$

$$a = \mathrm{tr}(C_{kl}^{-1} J_{ij}) = j^{ij'} C_{kl}^{-1} j^{ij},$$

$$g = \mathrm{tr}(C_{kl}^{-1} v_l v_k') = v_k' C_{kl}^{-1} v_l,$$

$$d = \mathrm{tr}(C_{kl}^{-1} v_l v_k' C_{kl}^{-1} J_{ij}) = v_k' C_{kl}^{-1} J_{ij} C_{kl}^{-1} v_l,$$

$$e = \mathrm{tr}(C_{kl}^{-1} K C_{kl}^{-1} v_l v_k') = v_k' C_{kl}^{-1} K C_{kl}^{-1} v_l,$$

$$b = \mathrm{tr}(C_{kl}^{-1} K C_{kl}^{-1} J_{ij}) = j^{ij'} C_{kl}^{-1} K C_{kl}^{-1} j^{ij},$$

$$p = \mathrm{tr}(C_{kl}^{-1} K),$$

$$f = \mathrm{tr}\left(C_{kl}^{-1} K C_{kl}^{-1} v_l v_k' C_{kl}^{-1} J_{ij} + C_{kl}^{-1} v_l v_k' C_{kl}^{-1} K C_{kl}^{-1} J_{ij} \right) =$$
$$= v_k' C_{kl}^{-1} J_{ij} C_{kl}^{-1} K C_{kl}^{-1} v_l + v_k' C_{kl}^{-1} K C_{kl}^{-1} J_{ij} C_{kl}^{-1} v_l. \tag{6.21}$$

Using above short notations the first term integral (ignoring 4 in front) becomes

$$\left\langle \phi_k \left| \frac{\mathbf{r}' \mathbf{C}_k^\dagger \mathbf{M} \mathbf{C}_l \mathbf{r}}{r_{ij}} \right| \phi_l \right\rangle =$$

$$\frac{2\pi^{(3n-1)/2}}{3} |C_{kl}|^{-3/2} \left[\frac{9}{4} p \left(g a^{-1/2} - \frac{1}{3} d a^{-3/2} \right) - \frac{3}{2} \left(-a^{-1/2} e + \frac{1}{2} g a^{-3/2} b + \frac{1}{3} a^{-3/2} f - \frac{1}{2} d a^{-5/2} b \right) \right] =$$
$$\frac{\pi^{(3n-1)/2}}{|C_{kl}|^{3/2}} \left[\frac{3}{2} p g a^{-1/2} - \frac{1}{2} p d a^{-3/2} + a^{-1/2} e - \frac{1}{2} g a^{-3/2} b - \frac{1}{3} f a^{-3/2} + \frac{1}{2} d b a^{-5/2} \right].$$

The second term:$-2\alpha_l \left\langle \varphi_k \left| \frac{\mathbf{r}' \mathbf{C}_k^\dagger \mathbf{M} \mathbf{v}_l}{r_{ij}} \right| \varphi_l \right\rangle$ integral

Let us start solving this integral as follows:

$$\frac{\partial^2}{\partial \alpha_k \partial \alpha_l} \left(\alpha_l \left\langle \varphi_k \left| \frac{\mathbf{r}' \mathbf{C}_k^\dagger \mathbf{M} \mathbf{v}_l}{r_{ij}} \right| \varphi_l \right\rangle \right) = \frac{\partial}{\partial \alpha_k} \left[\left\langle \varphi_k \left| \frac{\mathbf{r}' \mathbf{C}_k^\dagger \mathbf{M} \mathbf{v}_l}{r_{ij}} \right| \varphi_l \right\rangle \Big|_{\alpha_l = 0} + 0 \right] \Big|_{\alpha_k = 0} =$$

$$= \frac{\partial}{\partial \alpha_k} \int d\mathbf{r} \frac{\mathbf{r}' \mathbf{C}_k^\dagger \mathbf{M} \mathbf{v}_l}{r_{ij}} \exp[-\mathbf{r}'(\mathbf{C}_{kl})\mathbf{r} + (\alpha_k \mathbf{v}_k' + \alpha_l \mathbf{v}_l')\mathbf{r}] \Big|_{\alpha_l, \alpha_k = 0}$$

$$\frac{\partial}{\partial \alpha_k} \int d\mathbf{r} \left[\frac{\mathbf{r}' \mathbf{C}_k^\dagger \mathbf{M} \mathbf{v}_l}{r_{ij}} \right] \exp[-\mathbf{r}'(\mathbf{C}_{kl})\mathbf{r} + (\alpha_k \mathbf{v}_k')\mathbf{r}] \Big|_{\alpha_k = 0} =$$

$$= \int d\mathbf{r}\left[\frac{(\mathbf{v}_k'\mathbf{r})(\mathbf{r}'\mathbf{C}_k^\dagger\mathbf{M}\mathbf{v}_l)}{r_{ij}}\right]\exp[-\mathbf{r}'(\mathbf{C}_{kl})\mathbf{r}] = \int d\mathbf{r}\left[\frac{(\mathbf{v}_k'\mathbf{r})(\mathbf{C}_k^\dagger\mathbf{M}\mathbf{v}_l)'\mathbf{r}}{r_{ij}}\right]\exp[-\mathbf{r}'(\mathbf{C}_{kl})\mathbf{r}]. \tag{6.22}$$

Using the definition of $1/r_{ij}$ and denoting $\mathbf{C}_k^\dagger\mathbf{M} = \mathbf{F}$ or $C_k^\dagger M = F$, and using the Kronecker product property to make argument of exponent consistent $(F \otimes I_3)(v_l \otimes \epsilon) = (Fv_l) \otimes (I_3\epsilon) = (Fv_l) \otimes \epsilon$, we have

$$\frac{2}{\sqrt{\pi}}\int_0^\infty d\beta \frac{\partial^2}{\partial\alpha\partial\gamma}\int d\mathbf{r}\exp[-\mathbf{r}'(\mathbf{C}_{kl}+\beta^2\mathbf{J}_{ij})\mathbf{r} + (\alpha\mathbf{v}_k + \gamma\mathbf{F}\mathbf{v}_l)'\mathbf{r}]\Big|_{\alpha,\gamma=0}.$$

Above integral is the same with the $\langle\phi_k|\frac{1}{r_{ij}}|\phi_l\rangle$, the only difference is that we substitute Fv_l or $C_k^\dagger M v_l$ instead of v_l and solution is directly from (6.14):

$$\alpha_l\left\langle\phi_k\left|\frac{\mathbf{r}'\mathbf{C}_k^\dagger\mathbf{M}\mathbf{v}_l}{r_{ij}}\right|\phi_l\right\rangle = \frac{\pi^{\frac{3N-1}{2}}}{|C_{kl}|^{\frac{3}{2}}}\left[\frac{\mathrm{tr}(C_{kl}^{-1}C_k^\dagger M v_l v_k')}{\mathrm{tr}(C_{kl}^{-1}J_{ij})^{\frac{1}{2}}} - \frac{1}{3}\frac{\mathrm{tr}(C_{kl}^{-1}C_k^\dagger M v_l v_k' C_{kl}^{-1}J_{ij})}{\mathrm{tr}(C_{kl}^{-1}J_{ij})^{\frac{3}{2}}}\right]. \tag{6.23}$$

Let us define the following short notations:

$$k = \mathrm{tr}(C_{kl}^{-1}C_k^\dagger M v_l v_k'),$$

$$h = \mathrm{tr}(C_{kl}^{-1}C_k^\dagger M v_l v_k' C_{kl}^{-1}J_{ij}).$$

Taking into account the initial factor -2 in front of the integral, which we ignored for convenience we have:

$$-2\alpha_l\left\langle\phi_k\left|\frac{\mathbf{r}'\mathbf{C}_k^\dagger\mathbf{M}\mathbf{v}_l}{r_{ij}}\right|\phi_l\right\rangle = -2\frac{\pi^{\frac{3N-1}{2}}}{|C_{kl}|^{\frac{3}{2}}}\left[a^{-1/2}k - \frac{1}{3}a^{-3/2}h\right]. \tag{6.24}$$

The third term: $-2\alpha_k\left\langle\varphi_k\left|\frac{\mathbf{v}_k'\mathbf{M}\mathbf{C}_l\mathbf{r}}{r_{ij}}\right|\varphi_l\right\rangle$ integral

Calculation of this term is very similar to the previous subsections integral.

$$\frac{\partial^2}{\partial\alpha_k\partial\alpha_l}\left(\alpha_k\left\langle\varphi_k\left|\frac{\mathbf{v}_k'\mathbf{M}\mathbf{C}_l\mathbf{r}}{r_{ij}}\right|\varphi_l\right\rangle\right) = \frac{\partial}{\partial\alpha_l}\left[\left\langle\varphi_k\left|\frac{\mathbf{v}_k'\mathbf{M}\mathbf{C}_l\mathbf{r}}{r_{ij}}\right|\varphi_l\right\rangle\Big|_{\alpha_k=0} + 0\right]\Big|_{\alpha_l=0} =$$

$$\frac{\partial}{\partial\alpha_l}\int d\mathbf{r}\frac{\mathbf{v}_k'\mathbf{M}\mathbf{C}_l\mathbf{r}}{r_{ij}}\exp[-\mathbf{r}'(\mathbf{C}_{kl})\mathbf{r} + (\alpha_k\mathbf{v}_k' + \alpha_l\mathbf{v}_l')\mathbf{r}]\Big|_{\alpha_l,\alpha_k=0} =$$

$$\frac{\partial}{\partial\alpha_l}\int d\mathbf{r}\left[\frac{\mathbf{v}_k'\mathbf{M}\mathbf{C}_l\mathbf{r}}{r_{ij}}\right]\exp[-\mathbf{r}'(\mathbf{C}_{kl})\mathbf{r}+(\alpha_l\mathbf{v}_l')\mathbf{r}]\Big|_{\alpha_l=0} = \int d\mathbf{r}\left[\frac{(\mathbf{v}_k'\mathbf{M}\mathbf{C}_l\mathbf{r})(\mathbf{v}_l'\mathbf{r})}{r_{ij}}\right]\exp[-\mathbf{r}'(\mathbf{C}_{kl})\mathbf{r}].$$

Using the definition of $1/r_{ij}$ and denoting $\mathbf{M}\mathbf{C}_l = \mathbf{G}$ or $MC_l = G$,

$$= \frac{2}{\sqrt{\pi}}\int_0^\infty d\beta\frac{\partial^2}{\partial\alpha\partial\gamma}\int d\mathbf{r}\exp[-\mathbf{r}'(\mathbf{C}_{kl}+\beta^2\mathbf{J}_{ij})\mathbf{r} + (\alpha\mathbf{v}_k\mathbf{G} + \gamma\mathbf{v}_l)'\mathbf{r}]\Big|_{\alpha,\gamma=0}.$$

Above integral is the same with the $\langle\phi_k|\frac{1}{r_{ij}}|\phi_l\rangle$, the only difference is that we substitute $v_k'G$ or $v_k'MC_l$ instead of v_k' and solution is directly from (6.14):

$$\alpha_k\left\langle\phi_k\left|\frac{\mathbf{v}_k'\mathbf{M}\mathbf{C}_l\mathbf{r}}{r_{ij}}\right|\phi_l\right\rangle=\frac{\pi^{\frac{3N-1}{2}}}{|C_{kl}|^{\frac{3}{2}}}\left[\frac{\mathrm{tr}(v_lv_k'MC_lC_{kl}^{-1})}{\mathrm{tr}(C_{kl}^{-1}J_{ij})^{\frac{1}{2}}}-\frac{1}{3}\frac{\mathrm{tr}(C_{kl}^{-1}v_lv_k'MC_lC_{kl}^{-1}J_{ij})}{\mathrm{tr}(C_{kl}^{-1}J_{ij})^{\frac{3}{2}}}\right].\quad(6.25)$$

Introducing new notations for convenience:

$$n=\mathrm{tr}(v_lv_k'MC_lC_{kl}^{-1}),$$

$$m=\mathrm{tr}(C_{kl}^{-1}v_lv_k'MC_lC_{kl}^{-1}J_{ij}).$$

Taking into account the initial -2 factor in front of integral, that we ignored for convenience we have:

$$-2\alpha_k\left\langle\phi_k\left|\frac{\mathbf{v}_k'\mathbf{M}\mathbf{C}_l\mathbf{r}}{r_{ij}}\right|\phi_l\right\rangle=-2\frac{\pi^{\frac{3N-1}{2}}}{|C_{kl}|^{\frac{3}{2}}}\left[a^{-1/2}n-\frac{1}{3}a^{-2/3}m\right].\quad(6.26)$$

The forth term: $\alpha_k\alpha_l\mathbf{v}_k'\mathbf{M}\mathbf{v}_l\langle\varphi_k|\frac{1}{r_{ij}}|\varphi_l\rangle$ integral

Before solving this integral, let us recall how expectation value with trial basis function ϕ_k looks like in terms of our defined function φ_k:

$$\langle\phi_k|\phi_l\rangle=\frac{\partial^2}{\partial\alpha_k\partial\alpha_l}\langle\varphi_k|\varphi_l\rangle\Big|_{\alpha_k,\alpha_l=0}.\quad(6.27)$$

Considering prefactor $\mathbf{v}_k'\mathbf{M}\mathbf{v}_l=v_k'Mv_l$ as constant (since it does not contain any α dependent value), our forth term becomes:

$$\frac{\partial^2}{\partial\alpha_k\partial\alpha_l}\left[\alpha_k\alpha_l\langle\varphi_k|\frac{1}{r_{ij}}|\varphi_l\rangle\right]\Big|_{\alpha_k,\alpha_l=0}=$$

$$=\frac{\partial}{\partial\alpha_k}\left[\left(\alpha_k\langle\varphi_k|\frac{1}{r_{ij}}|\varphi_l\rangle\right)\Big|_{\alpha_l=0}+\left(\alpha_l\alpha_k\frac{\partial}{\partial\alpha_l}\langle\varphi_k|\frac{1}{r_{ij}}|\varphi_l\rangle\right)\Big|_{\alpha_l=0}\right]\Big|_{\alpha_k=0}.$$

Since the second term is zero anyway, we ignore the second term and substitute the necessary part:

$$\frac{\partial}{\partial\alpha_k}\left[\left(\frac{2}{\sqrt{\pi}}\alpha_k\int_0^\infty d\beta\int_{-\infty}^\infty d\mathbf{r}\exp[\mathbf{r}'(\mathbf{C}_{kl}+\beta^2\mathbf{J}_{ij})\mathbf{r}+(\alpha_k\mathbf{v}_k+\alpha_l\mathbf{v}_l)'\mathbf{r}]\right)\Big|_{\alpha_l=0}\right]\Big|_{\alpha_k=0}=$$

$$\frac{\partial}{\partial\alpha_k}\left[\frac{2}{\sqrt{\pi}}\alpha_k\int_0^\infty d\beta\int_{-\infty}^\infty d\mathbf{r}\exp[\mathbf{r}'(\mathbf{C}_{kl}+\beta^2\mathbf{J}_{ij})\mathbf{r}+(\alpha_k\mathbf{v}_k)'\mathbf{r}]\right]\Big|_{\alpha_k=0}.$$

In the same way as above, we will ignore the second term, since it is zero:

$$\frac{2}{\sqrt{\pi}}\int_0^\infty d\beta\int_{-\infty}^\infty d\mathbf{r}\exp[\mathbf{r}'(\mathbf{C}_{kl}+\beta^2\mathbf{J}_{ij})\mathbf{r}]=\frac{2}{\sqrt{\pi}}\int_0^\infty d\beta\frac{\pi^{3n/2}}{|C_{kl}+\beta^2 J_{ij}|^{3/2}}.$$

We have already encountered this situation before. So we will make the same manipulation here: $|C_{kl}+\beta^2 J_{ij}|=|C_{kl}|(1+\beta^2\mathrm{tr}(C_{kl}^{-1}J_{ij}))$. In addition, $\int_0^\infty dx\frac{1}{(1+ax^2)^{2/3}}=\frac{1}{\sqrt{a}}$. By these, we have

$$\frac{2\pi^{(3n-1)/2}}{|C_{kl}|^{3/2}}\int_0^\infty d\beta\frac{1}{(1+\beta^2\mathrm{tr}(C_{kl}^{-1}J_{ij}))^{3/2}}=\frac{2\pi^{(3n-1)/2}}{|C_{kl}|^{3/2}}[\mathrm{tr}(C_{kl}^{-1}J_{ij})]^{-1/2}=\frac{2\pi^{(3n-1)/2}}{|C_{kl}|^{3/2}}(a)^{-1/2}.$$

To sum up, the forth integral is:

$$\alpha_k\alpha_l\mathbf{v}_k'\mathbf{M}\mathbf{v}_l\langle\varphi_k|\frac{1}{r_{ij}}|\varphi_l\rangle=\frac{2\pi^{(3n-1)/2}}{|C_{kl}|^{3/2}}a^{-1/2}q, \tag{6.28}$$

where $a=\mathrm{tr}(C_{kl}^{-1}J_{ij})$ as our previous definition and $q=v_k'Mv_l$.

All terms together

Recall that in the first term, we have 4 in front, we did not include it into derivation for convenience, so including 4 in the first term:

$$\frac{4\pi^{(3n-1)/2}}{|C_{kl}|^{3/2}}\left[a^{-1/2}e-\frac{1}{2}ga^{-3/2}b-\frac{1}{3}a^{-3/2}f+\frac{1}{2}da^{-5/2}b+\frac{3}{2}pga^{-1/2}-\frac{1}{2}pda^{-3/2}\right]$$

$$-2\pi^{(3n-1)/2}|C_{kl}|^{-3/2}(ka^{-1/2}-\frac{1}{3}ha^{-3/2})-2\pi^{(3n-1)/2}|C_{kl}|^{-3/2}(na^{-1/2}-\frac{1}{3}ma^{-3/2})+$$

$$+\frac{2\pi^{(3n-1)/2}}{|C_{kl}|^{3/2}}a^{-1/2}q\Rightarrow\frac{2\pi^{(3n-1)/2}}{|C_{kl}|^{3/2}}\left[2a^{-1/2}e-ga^{-3/2}b-\frac{2}{3}a^{-3/2}f+da^{-5/2}b+3pga^{-1/2}-pda^{-3/2}\right.$$

$$\left.-ka^{-1/2}+\frac{1}{3}ha^{-3/2}-na^{-1/2}+\frac{1}{3}ma^{-3/2}+a^{-1/2}q\right]\Rightarrow$$

$$\frac{2\pi^{(3n-1)/2}}{|C_{kl}|^{3/2}}\left[a^{-1/2}(2e+3pg-k-n+q)-a^{-3/2}(gb+\frac{2}{3}f+pd-\frac{1}{3}h-\frac{1}{3}m)+a^{-5/2}db\right]=$$

$$\Rightarrow\frac{4\mathtt{S}_{kl}}{g\sqrt{\pi}}\left[a^{-1/2}(2e+3pg-k-n+q)-a^{-3/2}(gb+\frac{2}{3}f+pd-\frac{1}{3}h-\frac{1}{3}m)+a^{-5/2}db\right]. \tag{6.29}$$

where $\mathtt{S}_{kl}\equiv\langle\phi_k|\phi_l\rangle=\frac{\pi^{3n/2}}{2}\frac{v_k'C_{kl}^{-1}v_l}{|C_{kl}|^{3/2}}=\frac{\pi^{3n/2}}{2}\frac{g}{|C_{kl}|^{3/2}}$. So, the final result is:

$$\left\langle\nabla_r\phi_k\left|\frac{\mathbf{M}}{r_{ij}}\right|\nabla_r\phi_l\right\rangle=$$

$$=\frac{4\mathtt{S}_{kl}}{g\sqrt{\pi}}\left[a^{-1/2}(2e+3pg-k-n+q)-a^{-3/2}(gb+\frac{2}{3}f+pd-\frac{1}{3}h-\frac{1}{3}m)+a^{-5/2}db\right]. \tag{6.30}$$

One note here is that terms $2e, k, n, q$ can be manipulated as follows:

$$2e-k-n-q = 2\frac{v_k' C_{kl}^{-1}(C_k^\dagger M C_l + C_l M C_k^\dagger)C_{kl}^{-1}v_l}{2} - \mathrm{tr}(C_{kl}^{-1}C_k^\dagger M v_l v_k') =$$

$$-\mathrm{tr}(MC_lC_{kl}^{-1}v_l v_k') + \mathrm{tr}(Mv_l v_k') = 2\mathrm{tr}(C_{kl}^{-1}C_l M C_k^\dagger C_{kl}^{-1}v_l v_k') = 2\lambda. \tag{6.31}$$

6.6 $\langle\psi|\frac{1}{r_{ij}r_{pq}}|\psi\rangle$ term

Another required integral for computing the expectation value of regularization identity (5.23) for the Dirac delta function is the integral $\langle\psi|\frac{V_{int}}{r_{ij}}|\psi\rangle$, which can be split into several integrals of the form $\langle\psi|\frac{1}{r_{ij}r_{pq}}|\psi\rangle$. By applying equations (6.8) and (6.9), and using the overlap integral (6.6), we have

$$\langle\phi_k|\frac{1}{r_{ij}r_{pq}}|\phi_l\rangle = \frac{4}{\pi}\int_0^\infty\int_0^\infty d\alpha d\beta \langle\phi_k|\exp[-\alpha^2 r_{ij}^2 - \beta^2 r_{pq}^2]|\phi_l\rangle \Rightarrow$$

$$\Rightarrow 2\pi^{3N/2-1}\int_0^\infty\int_0^\infty d\alpha d\beta \frac{\mathrm{tr}[(C_{kl}+\alpha^2 J_{ij}+\beta^2 J_{pq})^{-1}v_l v_k']}{|C_{kl}+\alpha^2 J_{ij}+\beta^2 J_{pq}|^{3/2}}. \tag{6.32}$$

We will use the same transformation as in the previous subsections:

$$\frac{\mathrm{tr}[(C_{kl}+\alpha^2 J_{ij}+\beta^2 J_{pq})^{-1}v_l v_k']}{|C_{kl}+\alpha^2 J_{ij}+\beta^2 J_{pq}|^{3/2}} = -\frac{2}{3}\frac{\partial}{\partial\epsilon}\frac{1}{|C_{kl}+\alpha^2 J_{ij}+\beta^2 J_{pq}+\epsilon v_l v_k'|^{3/2}}\bigg|_{\epsilon=0},$$

and the relation for symmetric square matrix A:

$$|A+xy'| = |A|\big[1+\mathrm{tr}(A^{-1}xy')\big]. \tag{6.33}$$

By applying the integral $\int_0^\infty \frac{dx}{(1+ax^2)^{3/2}} = \frac{1}{\sqrt{a}}$, equation (6.32) becomes

$$\langle\phi_k|\frac{1}{r_{ij}r_{pq}}|\phi_l\rangle = -\frac{4}{3}\pi^{\frac{3N}{2}-1}\frac{\partial}{\partial\epsilon}\int_0^\infty d\alpha \frac{|C_{kl}+\alpha^2 J_{ij}+\epsilon v_l v_k'|^{-3/2}}{(\mathrm{tr}[(C_{kl}+\alpha^2 J_{ij}+\epsilon v_l v_k')^{-1}J_{pq}])^{1/2}}\bigg|_{\epsilon=0}. \tag{6.34}$$

Using formula (6.33) for the determinant, in the right hand side of (6.34) we get

$$|C_{kl}+\alpha^2 J_{ij}+\epsilon v_l v_k'| = |C_{kl}+\epsilon v_l v_k'|(1+\beta^2\mathrm{tr}[(C_{kl}+\epsilon v_l v_k')^{-1}J_{ij}]), \tag{6.35}$$

and for invertable square matrices $C_{kl}+\epsilon v_l v_k'$ and J_{ij}, we can use the Sherman-Morrison formula:

$$(C_{kl}+\epsilon v_l v_k'+\alpha^2 J_{ij})^{-1} = (C_{kl}+\epsilon v_l v_k')^{-1} - \frac{\alpha^2(C_{kl}+\epsilon v_l v_k')^{-1}J_{ij}(C_{kl}+\epsilon v_l v_k')^{-1}}{1+\alpha^2\mathrm{tr}[(C_{kl}+\epsilon v_l v_k')^{-1}J_{ij}]}. \tag{6.36}$$

To simplify our calculations, we define new notations:

$$a = \mathrm{tr}[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{ij}],$$

$$b = \mathrm{tr}[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{pq}],$$

$$c = \mathrm{tr}[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{ij} (C_{kl} + \epsilon v_l v'_k)^{-1} J_{pq}].$$

Using these notations and formulas (6.35) and (6.36) term $\mathrm{tr}[(C_{kl} + \alpha^2 J_{ij} + \epsilon v_l v'_k)^{-1} J_{pq}]$ becomes:

$$\mathrm{tr}[(C_{kl} + \alpha^2 J_{ij} + \epsilon v_l v'_k)^{-1} J_{pq}] = b - \frac{\alpha^2 c}{1 + \alpha^2 a}. \tag{6.37}$$

Using above notations, equation (6.34) can be written in a compact form as

$$\left\langle \phi_k \right| \frac{1}{r_{ij} r_{pq}} \left| \phi_l \right\rangle = -\frac{4}{3} \pi^{\frac{3N}{2}-1} \frac{\partial}{\partial \epsilon} \frac{1}{|C_{kl} + \epsilon v_l v'_k|^{3/2}} \int_0^\infty d\alpha \frac{1}{(1 + \alpha^2 a)(b - \alpha^2 c + \alpha^2 b a)^{1/2}} =$$

$$= -\frac{4}{3} \pi^{\frac{3N}{2}-1} \frac{\partial}{\partial \epsilon} \frac{1}{|C_{kl} + \epsilon v_l v'_k|^{3/2}} \left[\frac{1}{\sqrt{c}} \arccos\left(\sqrt{1 - \frac{c}{ab}} \right) \right], \tag{6.38}$$

where a, b, c are constant parameters with $b > 0, a > 0, c \geq 0, ab - c \geq 0$. Let us find the derivative in (6.38) separately

$$\frac{\partial}{\partial \epsilon} \frac{\arccos\left[\sqrt{1 - \frac{\mathrm{tr}\left[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{ij} (C_{kl} + \epsilon v_l v'_k)^{-1} J_{pq} \right]}{\mathrm{tr}\left[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{ij} \right] \mathrm{tr}\left[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{pq} \right]} } \right]}{|C_{kl} + \epsilon v_l v'_k|^{\frac{3}{2}} \sqrt{\mathrm{tr}\left[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{ij} (C_{kl} + \epsilon v_l v'_k)^{-1} J_{pq} \right]}} \Bigg|_{\epsilon=0} =$$

$$= -\frac{3}{2} \frac{\arccos\left[\sqrt{1 - \frac{\mathrm{tr}(C_{kl}^{-1} J_{ij} C_{kl}^{-1} J_{pq})}{\mathrm{tr}(C_{kl}^{-1} J_{ij}) \mathrm{tr}(C_{kl}^{-1} J_{pq})} } \right]}{|C_{kl}|^{\frac{3}{2}} \sqrt{\mathrm{tr}(C_{kl}^{-1} J_{ij} C_{kl}^{-1} J_{pq})}} \mathrm{tr}(C_{kl}^{-1} v_l v'_k) +$$

$$+ \frac{1}{2} \frac{\arccos\left[\sqrt{1 - \frac{\mathrm{tr}(C_{kl}^{-1} J_{ij} C_{kl}^{-1} J_{pq})}{\mathrm{tr}(C_{kl}^{-1} J_{ij}) \mathrm{tr}(C_{kl}^{-1} J_{pq})} } \right]}{|C_{kl}|^{\frac{3}{2}}} \frac{\mathrm{tr}(C_{kl}^{-1} v_l v'_k C_{kl}^{-1} J_{ij} C_{kl}^{-1} J_{pq} + C_{kl}^{-1} J_{ij} C_{kl}^{-1} v_l v'_k C_{kl}^{-1} J_{pq})}{\left[\mathrm{tr}(C_{kl}^{-1} J_{ij} C_{kl}^{-1} J_{pq}) \right]^{\frac{3}{2}}} +$$

$$+ \frac{|C_{kl}|^{-\frac{3}{2}}}{\sqrt{\mathrm{tr}(C_{kl}^{-1} J_{ij} C_{kl}^{-1} J_{pq})}} \frac{\partial}{\partial \epsilon} \arccos\left[\sqrt{1 - \frac{\mathrm{tr}\left[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{ij} (C_{kl} + \epsilon v_l v'_k)^{-1} J_{pq} \right]}{\mathrm{tr}\left[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{ij} \right] \mathrm{tr}\left[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{pq} \right]} } \right] \Bigg|_{\epsilon=0}.$$

Taking into account the differential $d \arccos(x) = \frac{-1}{\sqrt{1-x^2}}$, where $x \neq \pm 1$, we find the derivative of arccosine function separately

$$\frac{\partial}{\partial \epsilon} \arccos\left[\sqrt{1 - \frac{\mathrm{tr}\left[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{ij} (C_{kl} + \epsilon v_l v'_k)^{-1} J_{pq} \right]}{\mathrm{tr}\left[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{ij} \right] \mathrm{tr}\left[(C_{kl} + \epsilon v_l v'_k)^{-1} J_{pq} \right]} } \right] \Bigg|_{\epsilon=0} =$$

$$= \frac{-1}{2\sqrt{\frac{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}C_{kl}^{-1}J_{pq}\right]}{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}\right]\mathrm{tr}\left[C_{kl}^{-1}J_{pq}\right]}}} \frac{1}{\sqrt{1-\left|\frac{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}C_{kl}^{-1}J_{pq}\right]}{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}\right]\mathrm{tr}\left[C_{kl}^{-1}J_{pq}\right]}\right|}} \times$$

$$\times \frac{\partial}{\partial\epsilon}\left[1-\frac{\mathrm{tr}\left[(C_{kl}+\epsilon v_l v_k')^{-1}J_{ij}(C_{kl}+\epsilon v_l v_k')^{-1}J_{pq}\right]}{\mathrm{tr}\left[(C_{kl}+\epsilon v_l v_k')^{-1}J_{ij}\right]\mathrm{tr}\left[(C_{kl}+\epsilon v_l v_k')^{-1}J_{pq}\right]}\right]\Bigg|_{\epsilon=0} =$$

$$= \frac{1}{2\sqrt{\frac{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}C_{kl}^{-1}J_{pq}\right]}{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}\right]\mathrm{tr}\left[C_{kl}^{-1}J_{pq}\right]}}} \frac{1}{\sqrt{1-\left|\frac{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}C_{kl}^{-1}J_{pq}\right]}{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}\right]\mathrm{tr}\left[C_{kl}^{-1}J_{pq}\right]}\right|}} \times$$

$$\times\left[\frac{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}C_{kl}^{-1}J_{pq}\right]}{\mathrm{tr}\left[C_{kl}^{-1}J_{pq}\right]}\frac{\mathrm{tr}\left[C_{kl}^{-1}v_l v_k' C_{kl}^{-1}J_{ij}\right]}{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}\right]^2}+\frac{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}C_{kl}^{-1}J_{pq}\right]}{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}\right]}\frac{\mathrm{tr}\left[C_{kl}^{-1}v_l v_k' C_{kl}^{-1}J_{pq}\right]}{\mathrm{tr}\left[C_{kl}^{-1}J_{pq}\right]^2}-\right.$$

$$\left.-\frac{\mathrm{tr}(C_{kl}^{-1}v_l v_k' C_{kl}^{-1}J_{ij}C_{kl}^{-1}J_{pq}+C_{kl}^{-1}J_{ij}C_{kl}^{-1}v_l v_k' C_{kl}^{-1}J_{pq})}{\mathrm{tr}\left[C_{kl}^{-1}J_{ij}\right]\mathrm{tr}\left[C_{kl}^{-1}J_{pq}\right]}\right].$$

Keeping in mind the definition $J_{ij} = j^{ij\prime}j^{ij}$, we can introduce the following short notations:

$$a = \mathrm{tr}(C_{kl}^{-1}J_{ij}) = j^{ij\prime}C_{kl}^{-1}j^{ij},$$

$$b = \mathrm{tr}(C_{kl}^{-1}J_{pq}) = j^{pq\prime}C_{kl}^{-1}j^{pq},$$

$$c = \mathrm{tr}(C_{kl}^{-1}J_{ij}C_{kl}^{-1}J_{pq}) = j^{pq\prime}C_{kl}^{-1}j^{ij}j^{ij\prime}C_{kl}^{-1}j^{pq},$$

$$d = \mathrm{tr}(C_{kl}^{-1}J_{ij}C_{kl}^{-1}v_l v_k') = v_k'C_{kl}^{-1}J_{ij}C_{kl}^{-1}v_l,$$

$$e = \mathrm{tr}(C_{kl}^{-1}J_{pq}C_{kl}^{-1}v_l v_k') = v_k'C_{kl}^{-1}J_{pq}C_{kl}^{-1}v_l,$$

$$f = \mathrm{tr}(C_{kl}^{-1}J_{ij}C_{kl}^{-1}J_{pq}C_{kl}^{-1}v_l v_k' + C_{kl}^{-1}J_{pq}C_{kl}^{-1}J_{ij}C_{kl}^{-1}v_l v_k') =$$

$$= v_k'C_{kl}^{-1}J_{ij}C_{kl}^{-1}J_{pq}C_{kl}^{-1}v_l + v_k'C_{kl}^{-1}J_{pq}C_{kl}^{-1}J_{ij}C_{kl}^{-1}v_l,$$

$$g = \mathrm{tr}(C_{kl}^{-1}v_l v_k') = v_k'C_{kl}^{-1}v_l. \tag{6.39}$$

Using these we can write equation (6.38) as follows:

$$\left\langle\phi_k\right|\frac{1}{r_{ij}r_{pq}}\left|\phi_l\right\rangle = -\frac{4}{3|C_{kl}|^{3/2}}\pi^{\frac{3N}{2}-1}\left[-\frac{3}{2}\frac{g\arccos(\sqrt{1-\frac{c}{ab}})}{c^{1/2}}+\frac{f\arccos(\sqrt{1-\frac{c}{ab}})}{2c^{3/2}}+\right.$$

$$\left.+\frac{1}{c^{1/2}}\left(\frac{1}{2\sqrt{\frac{c}{ab}}}\frac{1}{\sqrt{1-\left|\frac{c}{ab}\right|}}\left(\frac{c}{b}\frac{d}{a^2}+\frac{c}{a}\frac{e}{b^2}-\frac{f}{ab}\right)\right)\right] = -\frac{2}{3|C_{kl}|^{3/2}}\pi^{\frac{3N}{2}-1}\times$$

$$\times\left[\arccos\left(\sqrt{1-\frac{c}{ab}}\right)\left[\frac{f}{c^{3/2}}-\frac{3g}{c^{1/2}}\right]+\frac{\sqrt{ab}}{\sqrt{1-\left|\frac{c}{ab}\right|}}\left(\frac{d}{ba^2}+\frac{e}{ab^2}-\frac{f}{cab}\right)\right].$$

Using the normalized wave function, we have

$$\langle\phi_k|\frac{1}{r_{ij}r_{pq}}|\phi_l\rangle = \frac{4S_{kl}}{3\pi g}\left[\arccos\left(\sqrt{1-\frac{c}{ab}}\right)\left[\frac{3g}{c^{1/2}}-\frac{f}{c^{3/2}}\right]+\frac{1/\sqrt{ab}}{\sqrt{1-\left|\frac{c}{ab}\right|}}\left(\frac{f}{c}-\frac{d}{a}-\frac{e}{b}\right)\right]. \quad (6.40)$$

6.7 Matrix elements with the Dirac delta function

If we consider some arbitrary function $f(\mathbf{r}_{ij})$, then using the property of Dirac delta-function we can write it as

$$f(\mathbf{r}_{ij}) = \int \delta(\boldsymbol{\theta}-\mathbf{r}_{ij})f(\boldsymbol{\theta})d\boldsymbol{\theta}, \quad (6.41)$$

where the integration over $\boldsymbol{\theta}$ takes place in $3D$ space, and $\delta(\boldsymbol{\theta}-\mathbf{r}_{ij})$ is $3D$ Dirac delta-function. Using this relation the expectation value of f can be written as follows:

$$\langle\phi_k|f(\mathbf{r}_{ij})|\phi_l\rangle = \int f(\boldsymbol{\theta})d\boldsymbol{\theta}\langle\phi_k|\delta(\boldsymbol{\theta}-\mathbf{r}_{ij})|\phi_l\rangle. \quad (6.42)$$

In order to proceed with the resultant expectation value, we will use the representation of the delta function in the form of a Gaussian with infinitely narrow width:

$$\delta(\boldsymbol{\theta}-\mathbf{r}_{ij}) = \lim_{\beta\to\infty}(\beta/\pi)^{3/2}\exp(-\beta(\boldsymbol{\theta}-\mathbf{r}_{ij})^2). \quad (6.43)$$

We can make a substitution $\mathbf{r}_{ij} = (b\otimes I_3)'\mathbf{r}$, where $b = j^j - j^i$ (j^i is an n-component vector whose ith element is one, while all others are zero) and use the property of the Kronecker product, which transforms the the right hand side of equation (6.42) as follows:

$$\langle\phi_k|\delta(\boldsymbol{\theta}-\mathbf{r}_{ij})|\phi_l\rangle = \lim_{\beta\to\infty}\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}}\exp[-\beta\boldsymbol{\theta}^2]\frac{\partial^2}{\partial\alpha_k\partial\alpha_l}\times$$

$$\times\int d\mathbf{r}\exp[-\mathbf{r}'(\mathbf{C}_{kl}+\beta bb')\mathbf{r}+(\alpha_k\mathbf{v}_k+\alpha_l\mathbf{v}_l+2\beta((b\otimes I_3)\boldsymbol{\theta}))'\mathbf{r})]\Big|_{\alpha_k\alpha_l=0}. \quad (6.44)$$

As one can notice immediately, the integral in the last expression is similar to the overlap integral, so the result is:

$$\langle\phi_k|\delta(\boldsymbol{\theta}-\mathbf{r}_{ij})|\phi_l\rangle = \lim_{\beta\to\infty}\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}}\exp[-\beta\boldsymbol{\theta}^2]\frac{\pi^{\frac{3N}{2}}}{|C_{kl}+\beta bb'|^{3/2}}\times$$

$$\times\frac{\partial^2}{\partial\alpha_k\partial\alpha_l}\exp[\frac{1}{4}(\alpha_k\mathbf{v}_k+\alpha_l\mathbf{v}_l+2\beta((b\otimes I_3)\boldsymbol{\theta}))'((C_{kl}+\beta bb')^{-1}\otimes I_3)]\times$$

$$\times(\alpha_k\mathbf{v}_k+\alpha_l\mathbf{v}_l+2\beta((b\otimes I_3)\boldsymbol{\theta}))]\Big|_{\alpha_k,\alpha_l=0}. \quad (6.45)$$

Using the following relations

$$|C_{kl} + \beta bb'| = |C_{kl}|(1 + \beta \mathrm{tr}(C_{kl} bb')),$$

$$(A + B)^{-1} = A^{-1} - \frac{A^{-1} B A^{-1}}{1 + \mathrm{tr}(A^{-1} B)},$$

and taking the limit followed by taking the derivatives with respect to parameters α_k and α_l (which is rather lengthy to write it here explicitly), we obtain the final result:

$$\langle \phi_k | \delta(\boldsymbol{\theta} - \mathbf{r}_{ij}) | \phi_l \rangle = \frac{\mathtt{S}_{kl}}{(\pi \mathrm{tr}(C_{kl}^{-1} bb'))^{3/2}} \exp\left[- \frac{\boldsymbol{\theta}^2}{\mathrm{tr}(C_{kl}^{-1} bb')} \right] \times$$

$$\times \left[1 + \frac{v_k' C_{kl}^{-1} bb' C_{kl}^{-1} v_l}{\mathrm{tr}(C_{kl}^{-1} bb') \mathrm{tr}(C_{kl}^{-1} v_l v_k')} \left(\frac{2\boldsymbol{\theta}^2}{\mathrm{tr}(C_{kl}^{-1} bb')} - 1 \right) \right]. \tag{6.46}$$

It should be noted that in actual numerical applications it is better to write terms containing the trace in terms of only matrix multiplications as in (6.21) as this is more efficient from the computational point of view. Using $b = j^j - j^i$, $j^{ij} = j^i - j^j$ and $j^{ij} j^{ij'} = J_{ij}$, we have

$$bb' = (j^j - j^i)(j^j - j^i)' = j^j j^{j'} - j^i j^{j'} - j^j j^{i'} + j^i j^{i'} = E_{jj} - E_{ij} - E_{ji} + E_{ii} = J_{ij},$$

where E_{ij} is a matrix with 1 in the i, jth position and 0's everywhere. We came up with the old matrix J_{ij} , which is very useful to write the equation (6.46) in a more compact form using the notations (6.21). So, the compact form is:

$$\langle \phi_k | \delta(\boldsymbol{\theta} - \mathbf{r}_{ij}) | \phi_l \rangle = \frac{\mathtt{S}_{kl}}{(\pi a)^{3/2}} \exp\left[- \frac{\boldsymbol{\theta}^2}{a} \right] \left(1 + \frac{d}{ag} (2\boldsymbol{\theta}^2/a - 1) \right). \tag{6.47}$$

Expressions (6.41) and (6.47) allow to calculate the expectation value of any desired function $f(\mathbf{r}_{ij})$.

7 Matrix elements for the mass-velocity identity

The expectation value identity for the case of the mass-velocity Hamiltonian is written as in equation (5.24)

$$\langle\psi|H_{MV}|\psi\rangle = -\lambda^2\langle\psi|(E-V)^2|\psi\rangle - \lambda^2\langle\psi|(E-V)(\nabla'_{\mathbf{r}}\mathbf{B}\nabla_{\mathbf{r}})|\psi\rangle + \lambda^2\langle\psi|(\nabla'_{\mathbf{r}}\mathbf{M}\nabla_{\mathbf{r}})^2|\psi\rangle +$$

$$\lambda^2\langle\psi|(\nabla'_{\mathbf{r}}\mathbf{M}\nabla_{\mathbf{r}})(\nabla'_{\mathbf{r}}\mathbf{B}\nabla_{\mathbf{r}})|\psi\rangle - \beta_0\langle\psi|(\nabla'_{\mathbf{r}}\mathbf{J}\nabla_{\mathbf{r}})^2|\psi\rangle - \sum_{i=1}^{n}\beta_i\langle\psi|(\nabla'_{\mathbf{r}}\mathbf{J}_{ii}\nabla_{\mathbf{r}})^2|\psi\rangle. \tag{7.1}$$

One can notice that only four types of integrals appear here: one is overlap integral, second is $\langle\phi|\mathbf{r}'\mathbf{X}\mathbf{r}|\phi\rangle$ type integral, which is very similar to the overlap integral, the third type is derived in Section 6.5, while the last one is derived in the next subsection.

7.1 $\langle\psi|(\nabla'_{\mathbf{r}}\mathbf{M}\nabla_{\mathbf{r}})(\nabla'_{\mathbf{r}}\mathbf{B}\nabla_{\mathbf{r}})|\psi\rangle$ integral

This integral is similar to other integrals, e.g. $\langle\psi|(\nabla'_{\mathbf{r}}\mathbf{J}_{ii}\nabla_{\mathbf{r}})^2|\psi\rangle$ integral. So we only chose the arbitrary one to show the derivation. Before starting to solve the integral, for convenience we write the following derivatives of generating function φ_k:

$$\nabla_{\mathbf{r}}\varphi_k = \nabla_{\mathbf{r}}\exp[-\mathbf{r}'\mathbf{C}_k\mathbf{r} + \alpha_k(\mathbf{v}^k)'\mathbf{r}] = [-2\mathbf{C}_k\mathbf{r} + \alpha_k\mathbf{v}_k]\exp[-\mathbf{r}'\mathbf{C}_k\mathbf{r} + \alpha_k(\mathbf{v}^k)'\mathbf{r}] \Rightarrow$$

$$\nabla_{\mathbf{r}}\varphi_k = [-2\mathbf{C}_k\mathbf{r} + \alpha_k\mathbf{v}_k]\varphi_k,$$

$$\nabla'_{\mathbf{r}}\varphi_k = [-2\mathbf{r}'\mathbf{C}_k + \alpha_k\mathbf{v}'_k]\varphi_k. \tag{7.2}$$

Using the following property

$$\langle\varphi_k|(\nabla'_{\mathbf{r}}\mathbf{M}\nabla_{\mathbf{r}})(\nabla'_{\mathbf{r}}\mathbf{B}\nabla_{\mathbf{r}})|\varphi_l\rangle = \langle\nabla'_{\mathbf{r}}\mathbf{M}\nabla_{\mathbf{r}}\varphi_k|\nabla'_{\mathbf{r}}\mathbf{B}\nabla_{\mathbf{r}}\varphi_l\rangle, \tag{7.3}$$

we see that, we also need the following derivatives

$$\mathbf{M}\nabla_{\mathbf{r}}\varphi_k = [-2\mathbf{M}\mathbf{C}_k\mathbf{r} + \alpha_k\mathbf{M}\mathbf{v}_k]\varphi_k,$$

$$\nabla'_{\mathbf{r}}\mathbf{M}\nabla_{\mathbf{r}}\varphi_k = \nabla'_{\mathbf{r}}([-2\mathbf{M}\mathbf{C}_k\mathbf{r} + \alpha_k\mathbf{M}\mathbf{v}_k]\varphi_k) = -2\mathrm{tr}[\mathbf{M}\mathbf{C}_k] + (-2\mathbf{M}\mathbf{C}_k\mathbf{r} + \alpha_k\mathbf{M}\mathbf{v})(-2\mathbf{r}'\mathbf{C}_k +$$

$$+ \alpha_k\mathbf{v}'_k)\varphi_k = [-2\mathrm{tr}[\mathbf{M}\mathbf{C}_k] + 4(\mathbf{r}'\mathbf{C}_k\mathbf{M}\mathbf{C}_k\mathbf{r}) - 4\alpha_k(\mathbf{v}'_k\mathbf{M}\mathbf{C}_k\mathbf{r}) + \alpha_k^2(\mathbf{v}'_k\mathbf{M}\mathbf{v}_k)]\varphi_k. \tag{7.4}$$

Similarly

$$\nabla'_{\mathbf{r}}\mathbf{B}\nabla_{\mathbf{r}}\varphi_l = [-2\mathrm{tr}[\mathbf{C}_l\mathbf{B}] + 4(\mathbf{r}'\mathbf{C}_l\mathbf{B}\mathbf{C}_l\mathbf{r}) - 4\alpha_l(\mathbf{v}'_l\mathbf{B}\mathbf{C}_l\mathbf{r}) + \alpha_l^2(\mathbf{v}'_l\mathbf{B}\mathbf{v}_l)]\varphi_l. \tag{7.5}$$

In order to calculate the expectation value $\langle \nabla'_{\mathbf{r}} \mathbf{M} \nabla_{\mathbf{r}} \varphi_k | \nabla'_{\mathbf{r}} \mathbf{B} \nabla_{\mathbf{r}} \varphi_l \rangle$, we need to multiply equations (7.4) and (7.5) term by term by ignoring the α^2 terms (because its expectation value becomes zero when we take the limit with respect to α's and set the α equal to zero):

$$[-2\mathrm{tr}[\mathbf{MC}_k] + 4(\mathbf{r}'\mathbf{C}_k\mathbf{MC}_k\mathbf{r}) - 4\alpha_k(\mathbf{v}'_k\mathbf{MC}_k\mathbf{r})][-2\mathrm{tr}[\mathbf{C}_l\mathbf{B}] + 4(\mathbf{r}'\mathbf{C}_l\mathbf{BC}_l\mathbf{r}) - 4\alpha_l(\mathbf{v}'_l\mathbf{BC}_l\mathbf{r})]$$

$$= 4\mathrm{tr}[\mathbf{MC}_k]\mathrm{tr}[\mathbf{C}_l\mathbf{B}] - 8\mathrm{tr}[\mathbf{MC}_k](\mathbf{r}'\mathbf{C}_l\mathbf{BC}_l\mathbf{r}) + 8\alpha_l\mathrm{tr}[\mathbf{MC}_k](\mathbf{v}'_l\mathbf{BC}_l\mathbf{r}) -$$

$$-8\mathrm{tr}[\mathbf{C}_l\mathbf{B}](\mathbf{r}'\mathbf{C}_k\mathbf{MC}_k\mathbf{r}) + 16(\mathbf{r}'\mathbf{C}_k\mathbf{MC}_k\mathbf{r})(\mathbf{r}'\mathbf{C}_l\mathbf{BC}_l\mathbf{r}) - 16\alpha_l(\mathbf{r}'\mathbf{C}_k\mathbf{MC}_k\mathbf{r})(\mathbf{v}'_l\mathbf{BC}_l\mathbf{r})$$

$$+8\alpha_k\mathrm{tr}[\mathbf{C}_l\mathbf{B}](\mathbf{v}'_k\mathbf{MC}_k\mathbf{r}) - 16\alpha_k(\mathbf{v}'_k\mathbf{MC}_k\mathbf{r})(\mathbf{r}'\mathbf{C}_l\mathbf{BC}_l\mathbf{r}) + 16\alpha_k\alpha_l(\mathbf{v}'_k\mathbf{MC}_k\mathbf{r})(\mathbf{v}'_l\mathbf{BC}_l\mathbf{r}).$$

Now we can proceed to writing the above expressions in terms of the expectation values (since taking the limit with respect to α_k and α_l and setting it zero is straightforward, we write the result at once)

$$\langle \nabla'_{\mathbf{r}} \mathbf{M} \nabla_{\mathbf{r}} \phi_k | \nabla'_{\mathbf{r}} \mathbf{B} \nabla_{\mathbf{r}} \phi_l \rangle = 36\mathrm{tr}[C_k M]\mathrm{tr}[C_l B]\langle \phi_k | \phi_l \rangle - 24\mathrm{tr}[C_k M]\langle \phi_k | \mathbf{r}'\mathbf{C}_l\mathbf{BC}_l\mathbf{r} | \phi_l \rangle$$

$$-24\mathrm{tr}[C_l B]\langle \phi_k | \mathbf{r}'\mathbf{C}_k\mathbf{MC}_k\mathbf{r} | \phi_l \rangle + 16\langle \phi_k | (\mathbf{r}'\mathbf{C}_k\mathbf{MC}_k\mathbf{r})(\mathbf{r}'\mathbf{C}_l\mathbf{BC}_l\mathbf{r}) | \phi_l \rangle$$

$$+24\mathrm{tr}[C_k M]\langle \varphi_k | (\mathbf{v}'_k\mathbf{r})(\mathbf{v}'_l\mathbf{BC}_l\mathbf{r}) | \varphi_l \rangle - 16\langle \varphi_k | (\mathbf{v}'_k\mathbf{r})(\mathbf{r}'\mathbf{C}_k\mathbf{MC}_k\mathbf{r})(\mathbf{v}'_l\mathbf{BC}_l\mathbf{r}) | \varphi_l \rangle$$

$$+24\mathrm{tr}[C_l B]\langle \varphi_k | (\mathbf{v}'_k\mathbf{MC}_k\mathbf{r})(\mathbf{v}'_l\mathbf{r}) | \varphi_l \rangle - 16\langle \varphi_k | (\mathbf{v}'_k\mathbf{MC}_k\mathbf{r})(\mathbf{r}'\mathbf{C}_l\mathbf{BC}_l\mathbf{r})(\mathbf{v}'_l\mathbf{r}) | \varphi_l \rangle$$

$$+ 16\langle \varphi_k | (\mathbf{v}'_k\mathbf{MC}_k\mathbf{r})(\mathbf{v}'_l\mathbf{BC}_l\mathbf{r}) | \varphi_l \rangle. \tag{7.6}$$

Integrals that are similar to the one above were derived in Subsection 6.5, while the remaining third and the seventh terms still need to be computed. Hence, we will show how these terms can be calculated and give the final expression in the end.

$\langle \phi_k | (\mathbf{r}'\mathbf{C}_k\mathbf{MC}_k\mathbf{r})(\mathbf{r}'\mathbf{C}_l\mathbf{BC}_l\mathbf{r}) | \phi_l \rangle$ term

Before going into detail, let us define some useful symmetric matrices $\mathbf{P} = \mathbf{C}_k\mathbf{MC}_k$ and $Q = \mathbf{C}_l\mathbf{BC}_l$. In the same way as we did in the previous calculations, we solve the integral in the following way:

$$\langle \phi_k | (\mathbf{r}'\mathbf{Pr})(\mathbf{r}'\mathbf{Qr}) | \phi_l \rangle = \frac{\pi^{3n/2}}{2} \frac{\partial}{\partial\alpha} \frac{\partial}{\partial\beta} \frac{v'_k (C_{kl} + \alpha P + \beta Q)^{-1} v_l}{|C_{kl} + \alpha P + \beta Q|^{3/2}} \bigg|_{\alpha,\beta=0} =$$

$$= -\frac{\pi^{3n/2}}{2}\frac{\partial}{\partial\alpha}\left[\frac{v_k'(C_{kl}+\beta Q)^{-1}P(C_{kl}+\beta Q)^{-1}v_l}{|C_{kl}+\beta Q|^{3/2}} + \frac{3}{2}\frac{\mathrm{tr}[(C_{kl}+\beta Q)^{-1}P]v_k'(C_{kl}+\beta Q)^{-1}v_l}{|C_{kl}+\beta Q|^{3/2}}\right]$$

$$= -\frac{\pi^{3n/2}}{2}\left[(v_k'C_{kl}'PC_{kl}v_l + \frac{3}{2}\mathrm{tr}[C_{kl)}^{-1}P]v_k'C_{kl}^{-1}v_l)\left(\frac{3\mathrm{tr}[C_{kl}^{-1}Q]}{|C_{kl}|^{3/2}}\right) + \frac{1}{|C_{kl}|^{3/2}}\left(-v_k'C_{kl}^{-1}QC_{kl}^{-1}PC_{kl}^{-1}v_l\right.\right.$$

$$\left.\left. -v_k'C_{kl}^{-1}PC_{kl}^{-1}QC_{kl}^{-1}v_l + \frac{3}{2}\mathrm{tr}[C_{kl}^{-1}P]v_k'C_{kl}^{-1}QC_{kl}^{-1}v_l - \frac{3}{2}v_k'C_{kl}^{-1}v_l\mathrm{tr}[C_{kl}^{-1}QC_{kl}^{-1}P]\right)\right] =$$

$$= \langle\phi_k|\phi_l\rangle\left[\frac{3}{2}\mathrm{tr}[C_{kl}^{-1}Q]\frac{v_k'C_{kl}^{-1}PC_{kl}^{-1}v_l}{v_k'C_{kl}^{-1}v_l} + \frac{9}{4}\mathrm{tr}[C_{kl}^{-1}P]\mathrm{C_{kl}^{-1}Q} + \frac{v_k'C_{kl}^{-1}QC_{kl}^{-1}PC_{kl}^{-1}v_l}{v_k'C_{kl}^{-1}v_l} + \right.$$

$$\left. + \frac{v_k'C_{kl}^{-1}PC_{kl}^{-1}QC_{kl}^{-1}v_l}{v_k'C_{kl}^{-1}v_l} + \frac{3}{2}\frac{\mathrm{tr}[C_{kl}^{-1}P]v_k'C_{kl}^{-1}QC_{kl}^{-1}v_l}{v_k'C_{kl}^{-1}v_l} + \frac{3}{2}\mathrm{tr}[C_{kl}^{-1}QC_{kl}^{-1}P]\right].$$

Remaining terms

As it is mentioned, most of the terms in equation (7.6) are calculated in previous sections and very similar to the overlap and other elementary integrals, so we provide here only final results:

- $\langle\phi_k|\mathbf{r}'\mathbf{C}_l\mathbf{B}\mathbf{C}_l\mathbf{r}|\phi_l\rangle = \left(\frac{3}{2}\mathrm{tr}[C_{kl}^{-1}C_lBC_l] + \frac{v_k'C_{kl}^{-1}C_lBC_lC_{kl}^{-1}v_l}{v_k'C_{kl}^{-1}v_l}\right)\langle\phi_k|\phi_l\rangle.$
- $\langle\phi_k|\mathbf{r}'\mathbf{C}_k\mathbf{M}\mathbf{C}_k\mathbf{r}|\phi_l\rangle = \left(\frac{3}{2}\mathrm{tr}[C_{kl}^{-1}C_kMC_k] + \frac{v_k'C_{kl}^{-1}C_kMC_kC_{kl}^{-1}v_l}{v_k'C_{kl}^{-1}v_l}\right)\langle\phi_k|\phi_l\rangle.$
- $\langle\varphi_k|(\mathbf{v}_k'\mathbf{r})(\mathbf{v}_l'\mathbf{B}\mathbf{C}_l\mathbf{r})|\varphi_l\rangle = \frac{v_k'C_{kl}^{-1}C_lBv_l}{v_k'C_{kl}^{-1}v_l}\langle\phi_k|\phi_l\rangle.$
- $\langle\varphi_k|(\mathbf{v}_k'\mathbf{r})(\mathbf{r}'\mathbf{C}_k\mathbf{M}\mathbf{C}_k\mathbf{r})(\mathbf{v}_l'\mathbf{B}\mathbf{C}_l\mathbf{r})|\varphi_l\rangle = \langle\phi_k|\phi_l\rangle\left(\frac{3}{2}\mathrm{tr}[C_{kl}^{-1}C_kMC_k]v_k'C_{kl}^{-1}C_lBv_l + \frac{v_k'C_{kl}^{-1}C_kMC_kC_{kl}^{-1}C_lBv_l}{v_k'C_{kl}^{-1}v_l}\right).$
- $\langle\varphi_k|(\mathbf{v}_k'\mathbf{M}\mathbf{C}_k\mathbf{r})(\mathbf{v}_l'\mathbf{r})|\varphi_l\rangle = \frac{v_k'MC_kC_{kl}^{-1}v_l}{v_k'C_{kl}^{-1}v_l}\langle\phi_k|\phi_l\rangle.$
- $\langle\varphi_k|(\mathbf{v}_k'\mathbf{M}\mathbf{C}_k\mathbf{r})(\mathbf{r}'\mathbf{C}_l\mathbf{B}\mathbf{C}_l\mathbf{r})(\mathbf{v}_l'\mathbf{r})|\varphi_l\rangle = \langle\phi_k|\phi_l\rangle\left(\frac{3}{2}\mathrm{tr}[C_{kl}^{-1}C_lBC_l]v_k'MC_kC_{kl}^{-1}v_l + \frac{v_k'MC_kC_{kl}^{-1}C_lBC_lC_{kl}^{-1}v_l}{v_k'C_{kl}^{-1}v_l}\right).$
- $\langle\varphi_k|(\mathbf{v}_k'\mathbf{M}\mathbf{C}_k\mathbf{r})(\mathbf{v}_l'\mathbf{B}\mathbf{C}_l\mathbf{r})|\varphi_l\rangle = \frac{v_k'MC_kC_{kl}^{-1}C_lBv_l}{v_k'C_{kl}^{-1}v_l}\langle\phi_k|\phi_l\rangle.$

All terms together

Now let us write all the terms together in a compact form. For this purpose we use the formula $C_{kl} = C_k + C_l$, so that some terms can be canceled with each other. Here we will present the final result only:

$$\langle\phi_k|(\nabla'_{\mathbf{r}}\mathbf{M}\nabla_{\mathbf{r}})(\nabla'_{\mathbf{r}}\mathbf{B}\nabla_{\mathbf{r}})|\phi_l\rangle = 16\langle\phi_k|(\mathbf{r}'\mathbf{C}_k\mathbf{M}\mathbf{C}_k\mathbf{r})(\mathbf{r}'\mathbf{C}_l\mathbf{B}\mathbf{C}_l\mathbf{r})|\phi_l\rangle + \langle\phi_k|\phi_l\rangle\times$$
$$\times\Bigg[\mathrm{tr}[C_kM]\Big(36\,\mathrm{tr}[C_lB] - 36\,\mathrm{tr}[C_{kl}^{-1}C_lBC_l]\Big) - 36\,\mathrm{tr}[C_lB]\mathrm{tr}[C_{kl}^{-1}C_kMC_k]+$$
$$+\frac{8}{v'_kC_{kl}^{-1}v_l}\Big(3\,\mathrm{tr}[C_lM]v'_kC_{kl}^{-1}C_lBC_kC_{kl}^{-1}v_l + 3\,\mathrm{tr}[C_lB]v'_kC_{kl}^{-1}C_lMC_kC_{kl}^{-1}v_l -$$
$$-3\,\mathrm{tr}[C_{kl}^{-1}C_kMC_k]v'_kC_{kl}^{-1}C_lBv_l + 2v'_kC_{kl}^{-1}C_lMC_kC_{kl}^{-1}C_lBv_l -$$
$$-3\,\mathrm{tr}[C_{kl}^{-1}C_lBC_l]v'_kMC_kC_{kl}^{-1}v_l - 2v'_kMC_kC_{kl}^{-1}C_lBC_lC_{kl}^{-1}v_l\Big)\Bigg].$$

8 Numerical results

The analytic expressions obtained in Sections 6 and 7 have been implemented in FORTRAN computer code and interfaced with a larger program for parallel variational calculations of quantum-few body systems called ECG and maintained by Prof. Sergiy Bubin. To verify the quality of our implementation we have performed several test calculations of the expectation values for the lowest P-states of few-electron atoms as well as for the positronium molecule, Ps_2, consisting of two electrons and two positrons.

In our calculations of atoms we set the nucleus mass to infinity in order to compare our results with the available literature values. Apart from the numerical results in the form of tables, for each atomic system we also provide a plot illustrating the convergence of the regularized expectation values of the delta-functions and H_{MV} in comparison with direct evaluation. While in this work we present the calculations for the lowest P-states of atoms, our algorithm is general and can be applied for excited states as well, provided their wave function (a suitable ECG basis set) is available as an input.

8.1 He atom

The helium atom is composed of two electrons bound to nucleus containing two protons. In Table 2, for He in its lowest singlet P-state, it can be observed that the expectation value of one particle delta function $\delta(\mathbf{r}_i)$ converged to 6 significant figures, while its regularized version converged to 10 figures. In the case of two particle delta function $\delta(\mathbf{r}_{ij})$, the former converged to 4 significant figures, while the latter to 7 figures. The regularized expectation values agree with the available literature values. In particular, the values obtained are in very good agreement with the results of Yan and Drake [29]. Our $\langle\delta(\mathbf{r}_i)\rangle$ value reproduces that of all Yan and Drake in all 10 digits that they reported.

Table 2: Convergence of the expectation values of direct and regularized delta functions with the size of the basis set for He atom, with infinite mass of the nucleus, in the $2\,^1P$ state. All values are in atomic units. Label "Reg." stands for "Regularized".

Basis size	$\langle\delta(\mathbf{r}_i)\rangle$	Reg. $\langle\delta(\mathbf{r}_i)\rangle$	$\langle\delta(\mathbf{r}_{ij})\rangle$	Reg. $\langle\delta(\mathbf{r}_{ij})\rangle$
100	1.272831	1.2743910956	0.00074240	0.00073507509
200	1.274024	1.2743927656	0.00073701	0.00073516144
500	1.274355	1.2743928849	0.00073533	0.00073516877
1000	1.274385	1.2743928862	0.00073521	0.00073516887
Ref. [29]		1.274392886(1)		0.0007351691(3)
Ref. [30]		1.2743859		0.00073522038

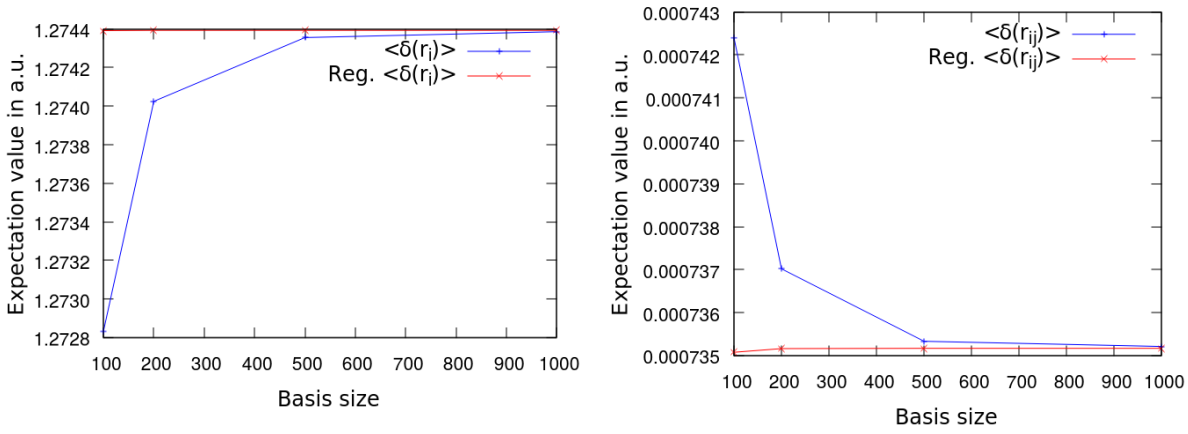

Figure 1: Graphical illustration of the data in Table 2.

Table 3: Convergence of the expectation values of direct and regularized mass-velocity with the size of the basis set for He atom, with infinite mass of the nucleus, in the $2\,^1P$ state. All values are in atomic units.

Basis size	$\langle H_{MV}\rangle$	Reg. $\langle H_{MV}\rangle$
100	−10.01949	−10.02924302
200	−10.02695	−10.02925297
500	−10.02901	−10.02925157
1000	−10.02921	−10.02925142
Ref. [29]		−10.029251357
Ref. [30]		−10.0292159

The convergence of the expectation values of regularized mass-velocity Hamiltonian is considerably higher reaching 9 significant figures in comparison with only 6 figures

obtained by the direct evaluation (see Table 3). As in the case of the Dirac delta function, the regularized values are also in good agreement with those reported in the work of Yan and Drake [29].

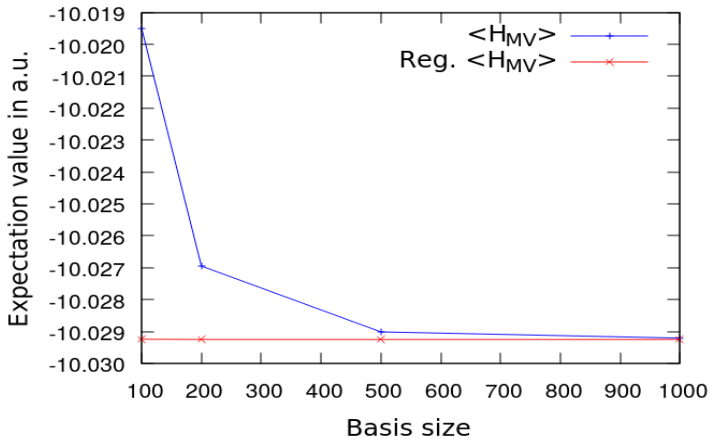

Figure 2: Graphical illustration of the data in Table 3.

8.2 Li atom

The lithium atom contains three electrons bound to the nucleus. In Table 4, the convergence of the regularized expectation values of one and two particle Dirac delta functions for Li atom is considerably higher in comparison with the case of direct evaluation. The accuracy increases from 7 to 11 and from 7 to 10 digits respectively. The results obtained in this case are in good agreement with the values obtained by Puchalski and Pachucki [31]. The leading 9 and 10 digits in the expectation values of the one and two-particle delta functions match those reported by Puchalski and Pachucki. The regularized expectation values of the mass-velocity Hamiltonian shown in Table 5 coincide in 7 significant figures. It should be noted that Puchalski and Pachucki used a very large Hylleraas basis set with the analytic integration and recursion relations for matrix elements in their work [31]. Their values are highly accurate and can serve as a reference.

Table 4: Convergence of the expectation values of direct and regularized delta functions for Li atom in the $2\,^1P_{1/2}$ state. All values are in atomic units.

Basis size	$\langle\delta(\mathbf{r}_i)\rangle$	Reg. $\langle\delta(\mathbf{r}_i)\rangle$	$\langle\delta(\mathbf{r}_{ij})\rangle$	Reg. $\langle\delta(\mathbf{r}_{ij})\rangle$
500	4.5562306	4.55873002783	0.17758132	0.177424454016
1000	4.5580211	4.55873213750	0.17747083	0.177424672382
2000	4.5585337	4.55873233559	0.17743459	0.177424697409
3000	4.5586621	4.55873234853	0.17743005	0.177424699470
4000	4.5586680	4.55873234941	0.17742773	0.177424699788
5000	4.5587036	4.55873234977	0.17742763	0.177424699786
6000	4.5587051	4.55873234980	0.17742707	0.177424699843
Ref. [32]		4.558612		0.177433
Ref. [31]		4.558732353		0.17742469963

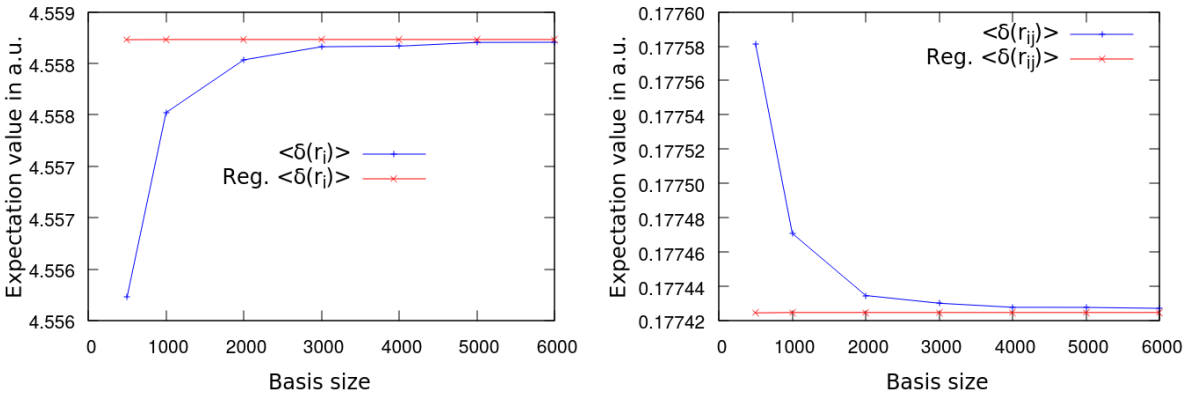

Figure 3: Graphical illustration of the data in Table 4

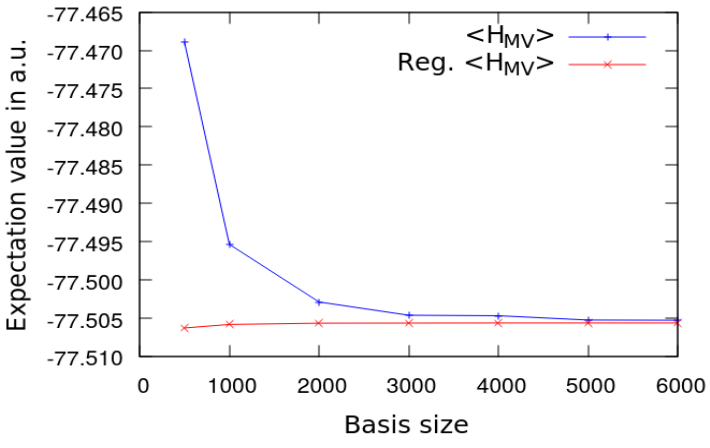

Figure 4: Graphical illustration of the data in Table 5

Table 5: Convergence of the expectation values of direct and regularized mass-velocity for Li atom in the $2\,^1P_{1/2}$ state. All values are in atomic units.

Basis size	$\langle H_{MV}\rangle$	Reg. $\langle H_{MV}\rangle$
500	−77.468927	−77.5062913
1000	−77.495357	−77.5058185
2000	−77.502889	−77.5056613
3000	−77.504618	−77.5056422
4000	−77.504686	−77.5056303
5000	−77.505243	−77.5056299
6000	−77.505268	−77.5056276
Ref. [31]		−77.505622125

8.3 Be atom

The regularized expectation values of singular operators obtained for Be atom, in the $2\,^1P$ state, are in good agreement with the calculations of Puchalski, Pachucki, and Komasa performed using the ECG basis set [33]. However, it should be mentioned that the number of converged figures is around 7, which is fewer than what we saw for He and Li atoms. This is expected as the overall accuracy of Be calculations (e.g. in terms of the total energy) is lower because the wave function of the four-electron system is much more complex.

Table 6: Convergence of the expectation values of direct and regularized delta functions for Be atom in the $2\,^1P$ state. All values are in atomic units.

Basis size	$\langle\delta(\mathbf{r}_i)\rangle$	Reg. $\langle\delta(\mathbf{r}_i)\rangle$	$\langle\delta(\mathbf{r}_{ij})\rangle$	Reg. $\langle\delta(\mathbf{r}_{ij})\rangle$
500	8.70047	8.72428604	0.2624096	0.261311960
1000	8.71296	8.72444021	0.2617699	0.261321198
2000	8.72111	8.72447613	0.2615228	0.261323468
3000	8.72241	8.72447979	0.2614415	0.261323867
4000	8.72331	8.72448080	0.2613896	0.261323965
5000	8.72340	8.72448107	0.2613676	0.261323999
6000	8.72369	8.72448124	0.2613647	0.261324009
Ref. [33]		8.7244787(2)		0.26132393(7)
Ref. [30]		8.724225		0.261345
Ref. [34]		8.72426480		0.26134390

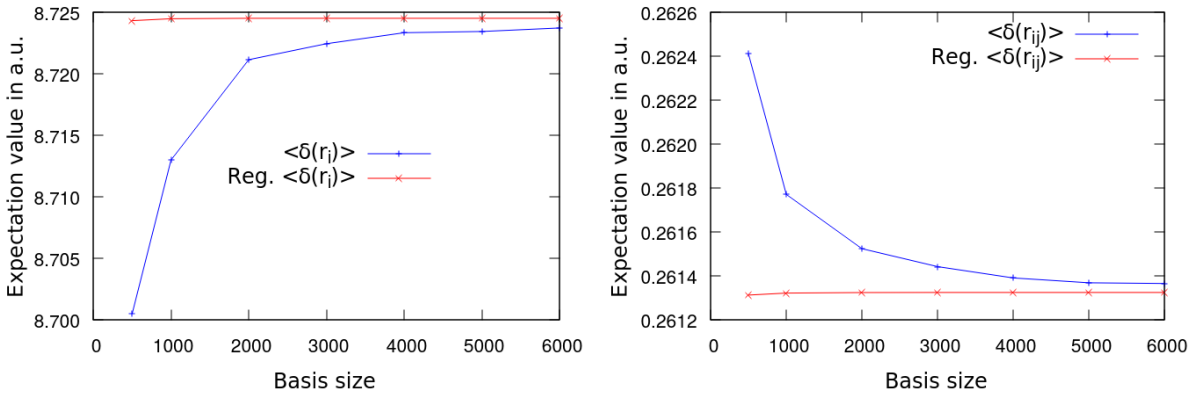

Figure 5: Graphical illustration of the data in Table 6

Table 7: Convergence of the expectation values of direct and regularized mass-velocity for Be atom in the $2\,^1P$ state. All values are in atomic units.

Basis size	$\langle H_{MV} \rangle$	Reg. $\langle H_{MV} \rangle$
500	−266.0816	−266.665236
1000	−266.3806	−266.666484
2000	−266.5891	−266.665892
3000	−266.6137	−266.665297
4000	−266.6363	−266.664855
5000	−266.6378	−266.664646
6000	−266.6442	−266.664629
Ref. [30]		−266.65862
Ref. [33]		−266.66514
Ref. [34]		−266.65902

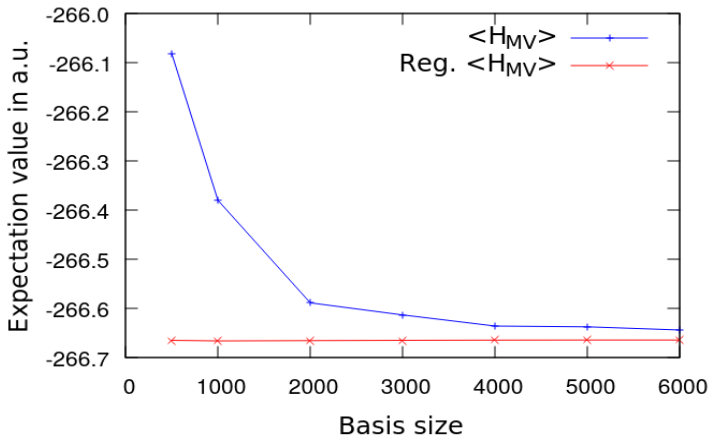

Figure 6: Graphical illustration of the data in Table 7

8.4 B atom

The largest system in our tests was the boron atom, which contains five electrons. Variational calculations with all-particle correlated Gaussians for B become more time consuming. Yet the method is capable of providing high accuracy results despite the high computational cost. It should be mentioned that it is very difficult to obtain results of spectroscopic accuracy for such larger system. The standard approaches that are based on single-electron functions, e.g. configuration interaction (CI) and coupled cluster (CC) methods struggle with this task. The expectation values of one-particle delta function $\delta(\mathbf{r}_i)$ we obtained in our tests have the same number of converged digits (around 6, see Table 8) as those reported by Puchalski, Komasa, and Pachucki [35]. The convergence of regularized version of two particle delta function $\delta(\mathbf{r}_{ij})$ is improved by almost 3 significant figures in comparison with the direct evaluation scheme. For the expectation value of the mass-velocity Hamiltonian (shown in Table 9) one can also observe the improvement by almost 3 orders of magnitude.

Table 8: Convergence of the expectation values of direct and regularized delta functions for B atom in the $2\,^2P$ state. All values are in atomic units.

Basis size	$\langle\delta(\mathbf{r}_i)\rangle$	Reg. $\langle\delta(\mathbf{r}_i)\rangle$	$\langle\delta(\mathbf{r}_{ij})\rangle$	Reg. $\langle\delta(\mathbf{r}_{ij})\rangle$
100	13.99852	14.355664	0.3643148	0.353393438
200	14.16340	14.365303	0.3590545	0.353612202
500	14.29217	14.371915	0.3566628	0.353786635
1000	14.34245	14.372701	0.3550145	0.353826851
2000	14.35894	14.372946	0.3545289	0.353840378
3000	14.36181	14.372982	0.3542649	0.353843269
4000	14.36445	14.372996	0.3540843	0.353844640
5000	14.36830	14.373002	0.3540453	0.353845094
Ref. [35]		14.372994		0.35384532

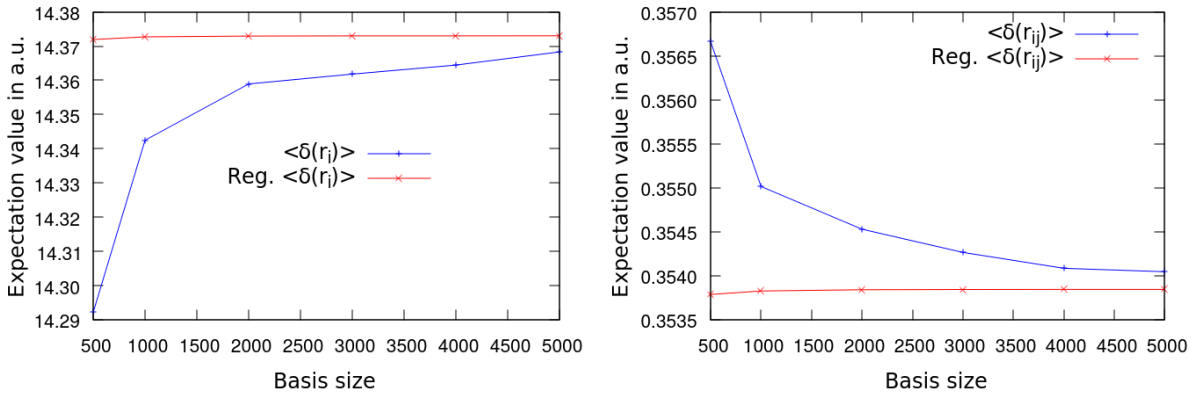

Figure 7: Graphical illustration of the data in Table 8

Table 9: Convergence of the expectation values of direct and regularized mass-velocity for B atom in the $2\,^2P$ state. All values are in atomic units.

Basis size	$\langle H_{MV} \rangle$	Reg. $\langle H_{MV} \rangle$
100	−677.993	−692.35691
200	−684.954	−692.92120
500	−690.179	−693.32619
1000	−692.249	−693.35720
2000	−692.813	−693.36774
3000	−692.919	−693.36638
4000	−693.036	−693.36449
5000	−693.182	−693.36437
Ref. [35]		−693.36550

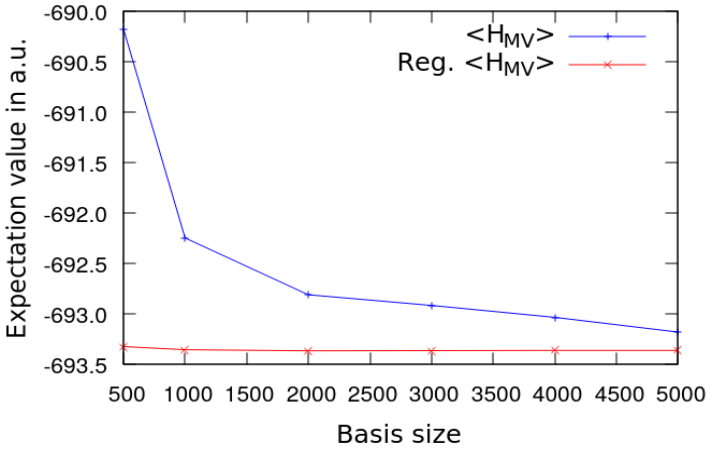

Figure 8: Graphical illustration of the data in Table 9

8.5 Ps_2 molecule

In addition to few-electron atoms, in this work we also performed calculation of the positronium molecule, Ps_2 – an exotic system consisting of two electrons and two positrons. The existence of bound state of the positronium molecule for the case of orbital angular momentum $L = 1$ (P-state) and negative parity was first predicted by Varga, Usukura and Suzuki in their work [36]. In this system, the spins of the positronium atoms are coupled to zero ($S = 0$). In this spin state, the positronium molecule can be separated into two positronium atoms provided that the relative orbital angular momentum is even. Hence, the positronium molecule with $L = 1$ and negative parity can not decay into the ground states of two positronium atoms [36]. It changes the dissociation threshold and allows the existence of a P state.

For the expectation values of the Dirac delta function and mass-velocity Hamiltonian, we observed a very significant improvement of the accuracy when we applied our regularization schemes. The improvement is even more significant than for He, Li, Be and B atoms. This can be attributed to the fact that the ECG basis is particularly suitable for the positronium molecule which possesses a high symmetry – the Hamiltonian is invariant not only with respect to the permutations of identical particles but also with respect to the charge conjugation (replacing all electrons with positrons and vice versa). Our results for Ps_2, agrees very well and improve upon those obtained by Puchalski and Czarnecki [37], where the authors also used the ECG basis and applied regularization schemes similar to those adopted in this work.

Table 10: Convergence of the expectation values of direct and regularized delta functions for Ps_2 molecule in the bound P-state. All values are in atomic units.

Basis size	$\langle\delta(\mathbf{r}_i)\rangle$	Reg. $\langle\delta(\mathbf{r}_i)\rangle$	$\langle\delta(\mathbf{r}_{ij})\rangle$	Reg. $\langle\delta(\mathbf{r}_{ij})\rangle$
500	0.01120304	0.011217212389	0.000146107	0.000145343016
1000	0.01121484	0.011217230077	0.000145599	0.000145349758
2000	0.01121633	0.011217231425	0.000145433	0.000145350734
3000	0.01121686	0.011217231526	0.000145378	0.000145350821
4000	0.01121689	0.011217231540	0.000145374	0.000145350834
5000	0.01121699	0.011217231549	0.000145365	0.000145350840
6000	0.01121709	0.011217231551	0.000145359	0.000145350842
Ref. [37]		0.0112172338		0.00014535127
Ref. [38]		0.0112091		0.00014591

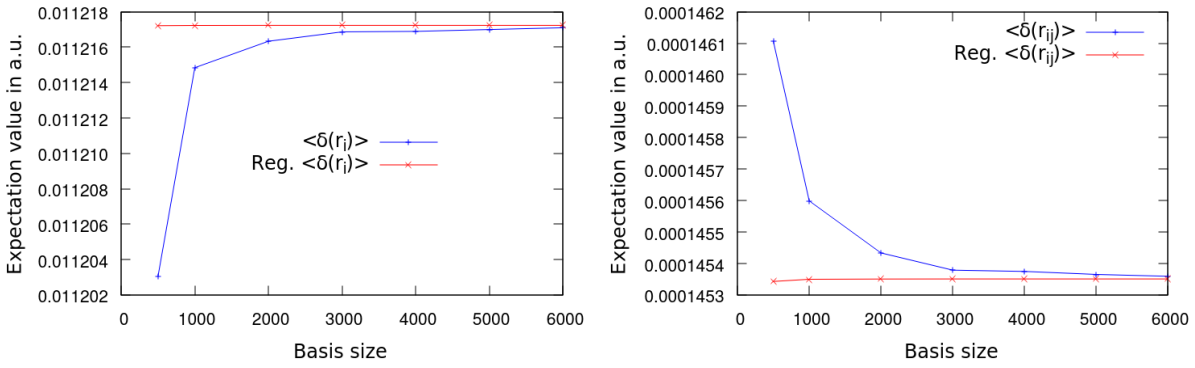

Figure 9: Graphical illustration of the data in Table 10

Table 11: Convergence of the expectation values of direct and regularized mass-velocity for Ps_2 molecule in the bound P-state. All values are in atomic units.

Basis size	$\langle H_{MV}\rangle$	Reg. $\langle H_{MV}\rangle$
500	−0.08967072	−0.08976220184
1000	−0.08975041	−0.08976239511
2000	−0.08975713	−0.08976241398
3000	−0.08976028	−0.08976241519
4000	−0.08976017	−0.08976241546
5000	−0.08976094	−0.08976241557
6000	−0.08976153	−0.08976241561
Ref. [37]		−0.0897629825

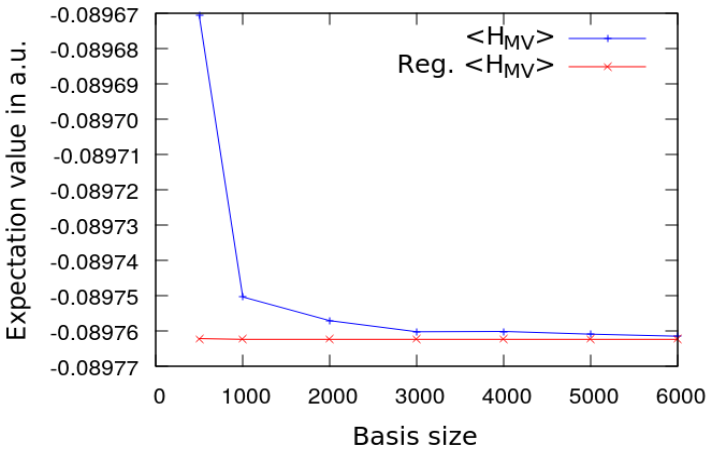

Figure 10: Graphical illustration of the data in Table 11

9 Conclusion

The variational method is a widely used approach in bound state calculations of atomic and molecular systems. In this method, the expectation values of singular operators (i.e. the operators that effectively sample the wave function within a small region of the total coordinate space or within a subspace) often suffer from slow convergence with the increase of the number of basis functions. In this thesis we applied regularization techniques to tackle this issue in the case of atomic P-states (states with the total orbital angular momentum $L = 1$), whose wave function is expanded in terms of all-particle explicitly correlated Gaussian basis set. We used the regularization scheme proposed by Drachman for the expectation values of the Dirac delta-function dependent on interparticle distances. We also regularized the expectation values of the mass-velocity Hamiltonian containing the fourth powers of linear momenta. All the necessary matrix elements involved in the expectation value identities were derived and implemented into a computer code. We performed test calculations for He, Be and B atoms in their lowest singlet P-states, for Li atom in its lowest doublet P-state as well as for the positronium molecule (Ps_2) in its bound P-state. We demonstrated that the regularized versions of the expectation values are considerably more accurate and converge faster to the complete basis set limit in comparison with the direct evaluation scheme. This is an important result because it allows us to increase the level of accuracy in determining the various properties of atoms and molecules, e.g. in computing the relativistic corrections and quantum electrodynamic (QED) effects. The results obtained in our test calculations agree well with the most accurate values available in the literature. While in this work we reported our computational results for the lowest P-states, our algorithm is general and can be applied for excited states as well. The future research may involve the extension of regularization techniques considered in this thesis for atomic D-states (states with the total orbital angular momentum $L = 2$). As the wave function corresponding to higher angular momentum is more complex compared to the lower ones, the derivation of the necessary matrix elements for such states is more challenging task. It should also be mentioned that reliable numerical calculations of the matrix elements may require a well thought out algorithms that are not prone to significant rounding errors, in particular in the case of highly excited states.

Bibliography

[1] D. Ceperley and B. Alder, "Quantum Monte Carlo," Science **231**, 555 (1986).

[2] B. L. Hammond, W. A. Lester, and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (WORLD SCIENTIFIC, 1994).

[3] C. D. Sherrill and H. F. Schaefer, "The Configuration Interaction Method: Advances in Highly Correlated Approaches," (Academic Press, 1999) pp. 143 – 269.

[4] C. Møller and M. S. Plesset, "Note on an Approximation Treatment for Many-Electron Systems," Phys. Rev. **46**, 618 (1934).

[5] R. J. Bartlett and G. D. Purvis, "Molecular Applications of Coupled Cluster and Many-Body Perturbation Methods," Phys. Scr. **21**, 255 (1980).

[6] R. J. Bartlett and G. D. Purvis, "Many-body perturbation theory, coupled-pair many-electron theory, and the importance of quadruple excitations for the correlation problem," Int. J. Quantum Chem. **14**, 561 (1978).

[7] R. Krivec, "FBS Colloquium Hyperspherical-Harmonics Methods for Few-Body Problems," Few-Body Syst. **25**, 199 (1998).

[8] C. F. Fischer and P. Jönsson, "MCHF calculations for atomic properties," Comput. Phys. Commun. **84**, 37 (1994).

[9] S. Bubin, M. Pavanello, W.-C. Tung, K. L. Sharkey, and L. Adamowicz, "Born-Oppenheimer and non-Born-Oppenheimer, atomic and molecular calculations with explicitly correlated Gaussians," Chem. Rev. **113**, 36—79 (2013).

[10] E. A. Hylleraas, "Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium," Z. Phys. **54**, 347 (1929).

[11] Z.-C. Yan and G. W. F. Drake, "Eigenvalues and expectation values for the $1s^2 2s^2$S, $1s^2 2p^2$P, and $1s^2 3d^2$D states of lithium," Phys. Rev. A **52**, 3711 (1995).

[12] J. Mitroy, S. Bubin, W. Horiuchi, Y. Suzuki, L. Adamowicz, W. Cencek, K. Szalewicz, J. Komasa, D. Blume, and K. Varga, "Theory and application of explicitly correlated Gaussians," Rev. Mod. Phys. **85**, 693 (2013).

[13] S. F. Boys and M. V. Wilkes, "The integral formulae for the variational solution of the molecular many-electron wave equation in terms of Gaussian functions with direct electronic correlation," Proc. R. Soc. London, Ser. A **258**, 402 (1960).

[14] K. Singer and M. V. Wilkes, "The use of Gaussian (exponential quadratic) wave functions in molecular problems - I. General formulae for the evaluation of integrals," Proc. R. Soc. London, Ser. A **258**, 412 (1960).

[15] K. Pachucki, "Effective Hamiltonian approach to the bound state: Positronium hyperfine structure," Phys. Rev. A **56**, 297 (1997).

[16] G. G. Ryzhikh and J. Mitroy, "Positronic Lithium, an Electronically Stable Li $- e^+$ Ground State," Phys. Rev. Lett. **79**, 4124 (1997).

[17] F. L. Pilar, *Elementary quantum chemistry* (McGraw-Hill, New York, NY, 1968).

[18] F. W. King, "Progress on high precision calculations for the ground state of atomic lithium," Comput. Theor. Chem. **400**, 7 (1997).

[19] R. J. Drachman, "A new global operator for two-particle delta functions," J. Phys. B **14**, 2733 (1981).

[20] K. Pachucki, W. Cencek, and J. Komasa, "On the acceleration of the convergence of singular operators in Gaussian basis sets," J. Chem. Phys. **122**, 184101 (2005).

[21] J. Hiller, J. Sucher, and G. Feinberg, "New techniques for evaluating parity-conserving and parity-violating contact interactions," Phys. Rev. A **18**, 2399 (1978).

[22] K. Pachucki and J. Komasa, "Gaussian basis sets with the cusp condition," Chem. Phys. Lett. **389**, 209 (2004).

[23] D. J. Griffiths and D. F. Schroeter, *Introduction to Quantum Mechanics*, 3rd ed. (Cambridge University Press, 2018).

[24] Y. Suzuki, M. Suzuki, and K. Varga, *Stochastic variational approach to quantum-mechanical few-body problems*, Vol. 54 (Springer Science & Business Media, 1998).

[25] S. Bubin and L. Adamowicz, "Matrix elements of N-particle explicitly correlated Gaussian basis functions with complex exponential parameters," J. Chem. Phys. **124**, 224317 (2006).

[26] S. Bubin and L. Adamowicz, "Energy and energy gradient matrix elements with N-particle explicitly correlated complex Gaussian basis functions with L=1," J. Chem. Phys. **128**, 114107 (2008).

[27] J. Magnus and H. Neudecker, *Matrix differential calculus with applications in statistics and econometrics* (Wiley, 1988).

[28] K. Varga, Y. Suzuki, and J. Usukura, "Global-Vector Representation of the Angular Motion of Few-Particle Systems," Few-Body Syst. **24**, 81 (1998).

[29] G. W. F. Drake and Z.-C. Yan, "Energies and relativistic corrections for the Rydberg states of helium: Variational results and asymptotic analysis," Phys. Rev. A **46**, 2378 (1992).

[30] M. Stanke, A. Bralin, S. Bubin, and L. Adamowicz, "Leading relativistic corrections for atomic P states calculated with a finite-nuclear-mass approach and all-electron explicitly correlated Gaussian functions," Phys. Rev. A **97**, 012513 (2018).

[31] M. Puchalski and K. Pachucki, "Relativistic, QED, and finite nuclear mass corrections for low-lying states of Li and Be^+," Phys. Rev. A **78**, 052511 (2008).

[32] S. Bubin and L. Adamowicz, "Explicitly correlated Gaussian calculations of the 2Po Rydberg spectrum of the lithium atom," J. Chem. Phys. **136**, 134305 (2012).

[33] M. Puchalski, K. Pachucki, and J. Komasa, "Isotope shift in a beryllium atom," Phys. Rev. A **89**, 012506 (2014).

[34] M. Stanke, S. Bubin, and L. Adamowicz, "Lowest ten 1 P Rydberg states of beryllium calculated with all-electron explicitly correlated Gaussian functions," J. Phys. B **52**, 155002 (2019).

[35] M. Puchalski, J. Komasa, and K. Pachucki, "Explicitly correlated wave function for a boron atom," Phys. Rev. A **92**, 062501 (2015).

[36] K. Varga, J. Usukura, and Y. Suzuki, "Second Bound State of the Positronium Molecule and Biexcitons," Phys. Rev. Lett. **80**, 1876 (1998).

[37] M. Puchalski and A. Czarnecki, "Dipole Excitation of the Positronium Molecule Ps_2," Phys. Rev. Lett. **101**, 183001 (2008).

[38] J. Usukura, K. Varga, and Y. Suzuki, "Signature of the existence of the positronium molecule," Phys. Rev. A **58**, 1918 (1998).