Complex Molecular Integral Evaluation using Long range Short range separation of nuclear-electron attraction integral

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Certificate of Examination

This is to certify that the dissertation titled "**Complex Molecular Integral Evaluation using Long range Short range separation of nuclear-electron attraction integral**" submitted by **Mr. Shivam Abhineet Meena (Reg. No. MS14124)** for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Professor K.S. Viswanathan   Dr. R. Ramachandran   Dr. P. Balanarayan

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Declaration

The work presented in this dissertation has been carried out by me with Dr. P. Balanarayan at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma or a fellowship to any other university or institute. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Shivam Abhineet Meena

(Candidate)

Dated: April 24, 2019

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. P. Balanarayan

(Supervisor)

Acknowledgements

"Electricity is actually made up of extremely tiny particles called electrons, that you cannot see with the naked eye unless you have been drinking."

<div align="right">Dave Barry</div>

"People Live their Lives bound by what they accept as correct and true. That is how they define "Reality" . But what does it mean to be "correct" or "true"? They are merely vague concepts... Their "Reality" may all be a mirage. Can we consider them to be simply living in their own world, shaped by their beliefs?"

<div align="right">Itachi Uchiha</div>

"When you are courting a nice girl an hour seems like a second. When you sit on a red-hot cinder a second seems like an hour. That's relativity."

<div align="right">Albert Einstein</div>

Dedicated to My Parents, Brother, Sister, Teachers and my close friends

For love, support and encouragement

Contents

List of Figures

List of Tables

Abbreviations

erf	**E**rror **F**unction
erfc	**C**omplimentary **E**rror **F**unction
NAI	**N**uclear **A**ttraction **I**ntegral
GPT	**G**aussian **P**roduct **T**heorem
GTO	**G**aussian **T**ype **O**rbitals
CAP	**C**omplex **A**bsorbing **P**otential

Symbols

T_{ab}	kinetic energy integral
S_{ab}	overlap integral
$\hat{S}$	complex scaling operator
$L(c;a,b)$	intermediate functions for NAIs
Z_c	Nuclear charge
ϕ	wave functions
ζ	orbital exponent

Abstract

The main objective for this work was to calculate complex scaled nuclear attraction integral for atoms and molecules. By splitting the one electron Coulomb interaction into long-range and short-range components, the energy of a quantum electronic system is decomposed into long-range and short-range contributions using error function. We used Gaussian basis and the analytical form was solved using Gaussian product theorem and Fourier transformation. This form is then complex scaled using appropriate rotations in the complex plane for which Weierstrass transformation is performed to get a smooth function. Now, after getting the appropriate function Gaussian integral is modified to get all the analytical forms. Configuration interaction calculations are performed to get the correlation energies for He atom using the basis "coemd-ref" for s, p and d Cartesian Gaussian function is used because it gives us a good mix of high and low exponents of Gaussian function which is useful to capture the resonances. We constructed the plots for ground, first and doubly excited state for He atom.

Chapter 1

Introduction

In the standard electronic-structure methods of quantum chemistry, the electronic wave function is expressed in terms of Slater determinants, either to describe interacting systems or non-interacting systems. The electronic structure is treated in such a way that the wave function depends explicitly on the electronic separation term. The interaction term $< \phi_1 | \frac{1}{r} | \phi_2 >$ is split into a singular short-ranged term and a nonsingular but slowly decaying long-ranged term [1]. A modification is done on the latter term while splitting: the inclusion of an error function, which is very useful as the integral is in the form of Gaussian functions. The Gaussian product rule which states that the product of two Gaussians is another Gaussian centered somewhere on the line connecting the original Gaussians, is applied for further simplification to get the atomic resonances.

One of the more attractive pictures of atomic resonances can be found through the method of complex scaling. The dilation operator is considered in complex scaling. If H is an atomic Hamiltonian then the discrete energy levels of H remain as discrete energies of $H(\theta)$, where θ is the angle by which wavefunction is rotated during complex scaling. Afterwards the continuum is rotated down around each atomic threshold by an angle of $-2Im\theta$. As the continuum rotates down it traces eigenvalues, whose real parts are associated with the position and the imaginary parts with the width of atomic resonances.[2]

Gaussian product theorem (GPT) is used for futher simplification of products for two Gaussian functions. One electron integral splitting is considered using the error function which gave Gaussian function on which GPT can be applied. This later got transformed

through complex scaling and subsequently Weierstrass transformation to get the appropriate analytical form for our function. The form was then used in the configuration interaction (CI) calculation for He atom to get the correlation energy and ultimately our atomic resonances.

1.1 One electron integrals

There are many types of one-electron integrals in quantum chemistry like:

1. The Overlap integral:

$$S_{ab} = < a|b > = \int \chi_a(r)\chi_b(r)dr, \tag{1.1}$$

2. Kinetic energy integral:

$$T_{ab} = -\frac{1}{2} < a|\nabla^2|b > = -\frac{1}{2}\int \chi_a(r)\nabla^2\chi_b(r)dr \tag{1.2}$$

3. Potential energy integral:

$$< a|r_{1C}^{-1}|b > = \int \frac{\chi_a(r)\chi_b(r)}{r_C}dr \tag{1.3}$$

where S_{ab} is an overlap integral, T_{ab} is a kinetic energy integral and $< a|r_{1C}^{-1}|b >$ is a nuclear-electron attraction integral.[2]

The one electron nuclear-electron attraction integral is modified as follows:

$$V = \int dx \phi_1 r_{ne}^{-1} \phi_2 = (\chi_1|r_{ne}^{-1}|\chi_2) \approx \lim_{\mu \to \infty} \left(\chi_1|\frac{erf(\mu r_{ne})}{r_{ne}}|\chi_2 \right) \tag{1.4}$$

The nuclear-electron interaction is decomposed in the following way as the long ranged part contains information of atomic resonance states since it plays a part in charge changing processes:

$$\frac{1}{r} = \nu_{ne}^{\mu}(r) + \bar{\nu}_{ne}^{\mu}(r) \tag{1.5}$$

where $\nu_{ne}^{\mu}(r)$ is long- range interaction, $\bar{\nu}_{ne}^{\mu}(r)$ is the complement short range interaction and μ is a parameter controlling the length and width of the curve. [4]

The nuclear attraction integral for potential experienced at a point r due to a set of atoms and electrons with nucleus located at C is [5]:

$$< a|\frac{1}{r}|b >= \int dr \phi_a \frac{1}{|r - C|} \phi_b \qquad (1.6)$$

where ϕ_a and ϕ_b are normalized Gaussian functions of the form $Ne^{-\alpha|r-r_a|^2}$ where N is the normalization constant. Using Gaussian product rule it reduces to:

$$< a|\frac{1}{r}(0)|b >= \frac{2}{\pi^{\frac{1}{2}}} \int_0^\infty du < a|0_C|b >, \qquad (1.7)$$

where;

$$< a|0_C|b >= \int dr \phi_a \phi_b \times e^{-u^2(r-C)^2} \qquad (1.8)$$

Here, nuclear attraction integral is defined with a non-negative integer m, which satisfies the recurrence formula. The integral considering s-type functions is:

$$< 0_A|\frac{1}{r}(0)|0_B >^{(m)} = \frac{2}{\pi^{\frac{1}{2}}} \int_0^\infty du \left(\frac{u^2}{\zeta + u^2} \right)^m \left(\frac{u^2}{\zeta + u^2} \right)^{\frac{3}{2}} < 0_A||0_B > \times e^{-\zeta(P-C)^2 \frac{u^2}{+u^2}} \qquad (1.9)$$

where $\zeta = \zeta_a + \zeta_b$ and $P = \frac{\alpha_a r_A + \alpha_b r_B}{\alpha_a + \alpha_b}$

Therefore,

$$< 0_A|\frac{1}{r}(0)|0_B >^{(m)} = 2(\frac{\zeta}{\pi})^{\frac{1}{2}} < 0_A||0_B > F_m(U) \qquad (1.10)$$

where $U = \zeta(P - C)^2$ and C is the atomic center.

This analytical form of the integral $< \phi_1|\frac{1}{r}|\phi_2 >$ is modified to get the analytical form of our function:

$$< \phi_1|\frac{erf(\mu r_{ne})}{r_{ne}}|\phi_2 > \qquad (1.11)$$

1.2 Splitting the interaction term

For the analytical term, the basis "coemd-ref" [6] for s, p and d Cartesian Gaussian function is used because it gives us a good mix of high and low exponents of Gaussian function which is useful to capture the resonances. The long ranged potential and the

Gaussian product rule yield an analytical form of integral for our function. The final form of the function is now computed for different μ values which is the parameter controlling the height and width of the curve. The total energies are plotted in which no cusp is observed for He atom.

The interaction term is in the following manner: [7]

$$\frac{1}{|\vec{r}|} = \frac{erf(r)}{|\vec{r}|} + \frac{1 - erf(r)}{|\vec{r}|} \tag{1.12}$$

where $erf(R)$ is the error function.

Here $\frac{erf(r)}{|\vec{r}|}$ is a long ranged function while the other one $\frac{1-erf(r)}{|\vec{r}|}$ is a short ranged function. Now, they can be treated separately. Only the long ranged part is considered as not only does it contain information of the resonance states and it does not have any singularity point, instead yielding a slowly decaying function as seen in the plot.
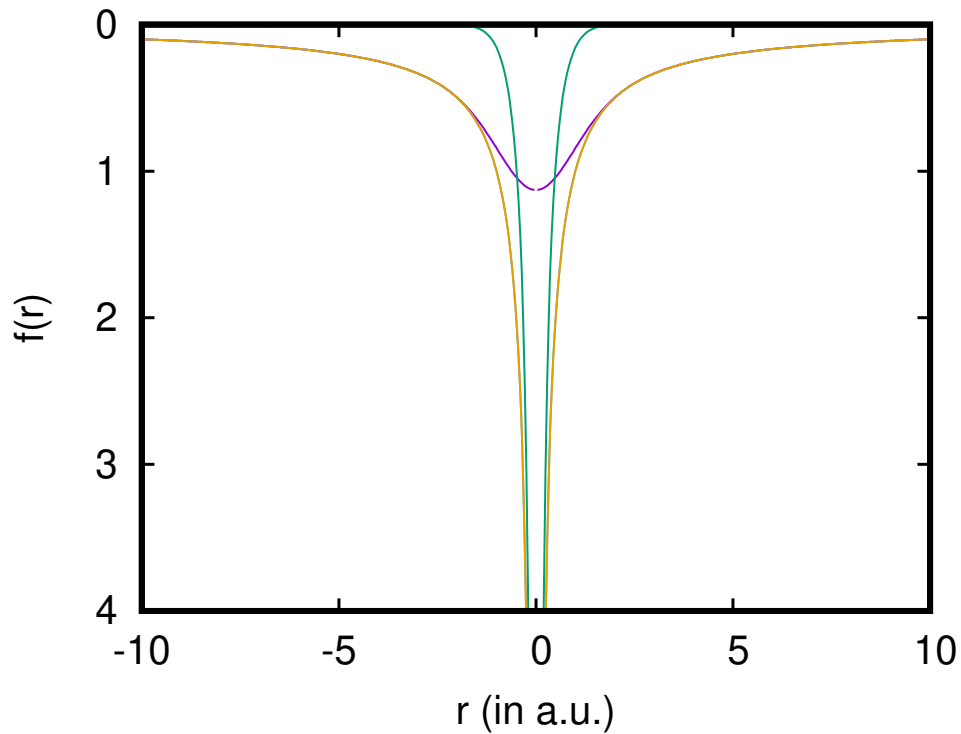

FIGURE 1.1: The given figure shows us the plot of $|r|$ vs $f(r) = \frac{1}{|r|}$ and its splitting terms using error function.

1.3 Error Function (erf)

The normal distribution was introduced by De Moivre (1733) as an attempt to approximate certain binomial distributions for large n. Laplace first used normal distribution in analysis of errors of experiments in 1774.

The error function and the complimentary error functions are special functions that appear in probability theory, the theory of errors and various other branches of mathematical physics. The error function has a direct connection with the Gaussian function and normalized Gaussian function (bell curve).

J.W.L Glaisher gave the term and the abbreviation for error function in 1871 because of its connection with "the theory of Probability" [8]. The fundamental solution of the Schrödinger equation is Gaussian, so the probabilities of the fundamental solution will be the magnitude of integrated Gaussian, which is basically our error function.The error function is defined as :

$$erf(x) = \frac{1}{\sqrt{\pi}} \int_{-x}^{x} e^{-t^2} dt = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} dt \qquad (1.13)$$
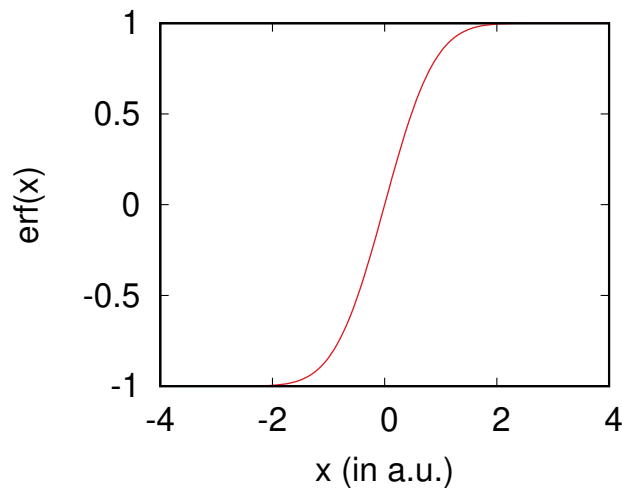

FIGURE 1.2: The plot of error function.

The complementary error function denoted by $erfc$ is defined as:

$$erfc(x) = 1 - erf(x) = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-t^2} dt \qquad (1.14)$$

1.3.1   Properties of error functions

1. Error function is an odd function as the integrand of e^{-t^2} is an even function.

$$erf(-z) == erf(z)$$

2. For a complex number z,

$$erf(\overline{z}) = \overline{erf(z)}$$

where $\overline{z}$ is complex conjugate of z.

3. The Taylor series expansion of error function always converges.

$$erf(z) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n z^{2n+1}}{n!(2n+1)}$$

4. The derivative of error function is given as:

$$\frac{d}{dz} erf(z) = \frac{2}{\sqrt{\pi}} e^{-z^2}$$

and the integration is obtained by using integration by parts.[9]

$$\int erf(z) = z erf(z) + \frac{e^{-z^2}}{\sqrt{\pi}}$$

1.4   Complex Scaling

Resonance is a common phenomenon in various areas of atomic physics and chemical physics. A method known as complex coordinate rotation (complex scaling) or the method of dilation analyticity was developed to calculate atomic resonances which was based on the mathematical developments by Aguilar and Combes (1971) [10], Balsve and Combes (1971) [11] and Simon (1972) [12].

It is a convenient and efficient method to calculate observables: it basically diverts the divergent resonance wavefunctions into the physical domain of square integrable wavefunctions [13]. Using this, the coordinate along which the divergence occurs which

is rotated into the complex plane and thus evaluation of observables is achieved. The transformation is:

$$r \rightarrow re^{i\theta} \tag{1.15}$$

When the coordinate is rotated into the complex plane, it is scaled by a complex phase:

$$\hat{S} = e^{i\frac{\theta}{2}} e^{i\theta \frac{\partial}{\partial x}} \tag{1.16}$$

For a many-particle three-dimensional system the scaling operator is defined by the scaling of all the different spatial coordinates of all the particles:

$$\hat{S} = \prod_{j} e^{i\frac{\theta}{2}} e^{i\theta r_j \cdot \nabla_j} \tag{1.17}$$

Complex scaling operator can be applied only if the potential $\hat{V}$ is an analytic function for which all the high-order derivatives are well defined.

For atoms, the complex scaled Hamiltonian operator becomes:

$$\hat{H}_{atom} = e^{-2i\theta}\hat{T}_e + e^{-i\theta}(\hat{V}_{eN} + \hat{V}_{ee}) \tag{1.18}$$

where $\hat{T}_e$ is the kinetic energy operator scaled by $e^{(-2i\theta)}$ whereas $\hat{V}_{eN}$ and $\hat{V}_{ee}$ are electron-nuclear and electron-electron potential energy operators respectively, both scaled by $e^{(-i\theta)}$.

1.4.1 Problem with molecules

It is not possible to complex scale molecular resonances by this method as we require the potential to be an analytic function within the spatial region where the resonance wavefunctions are localized, but the coupling between electronic and nuclear coordinates through the electron-nuclei potential energy terms are non-analytic operators. Therefore, it is not possible to otain complex potential energy surface by applying the transformation $r_j \rightarrow e^{i\theta}r_j$ while keeping the nuclei position R_α fixed and unscaled.

Molecular autoionization resonances can be calculated within the framework of the Born-Oppenheimer approximation using analytical continuation of the Hamiltonian matrix elements.[13]

1.5   Weierstrass Transformation

1.5.1   *Calculation of molecular resonances by complex scaling.* [2]
(by John D Morgan III and Barry Simon)

Weierstrass transform of a function $f(x)$ is a smoothed version of that function by averaging the values of function $f(x)$ weighted with a Gaussian centered at x. It is named after Karl Weierstrass.

Three dimensional Gaussian for $\epsilon > 0$ is given by:

$$g_\epsilon(r) = (2\pi\epsilon)^{-\frac{3}{2}} exp\left(-\frac{|r|^2}{2\epsilon} \right) \tag{1.19}$$

which, as $\epsilon \downarrow 0$, approximates a δ function:

$$V^{(\epsilon)}(r) = \int g_\epsilon(x)|r - x|^{-1} d^3x \tag{1.20}$$

This convolution technique is known as Weierstrass transform. It maps functions $f(x)$ with $\int dx f(x) exp(-\alpha|x|^2) < \infty$ to analytic functions. For each $\epsilon > 0$, $V^{(\epsilon)}(r)$ will be an entire function of r :

$$V^{(\epsilon)}(r) = \frac{1}{|r|} erf\left(\frac{|r|}{\sqrt{2\epsilon}} \right) \tag{1.21}$$

where $erf(r)$ is the error function.

Smoothing effect of the Weierstrass transform can be seen in the momentum space as a singular kernel with exponential growth at infinity gets replaced as:

$$\frac{4\pi e^{-i\left(p - e^{-i}q\right)}}{|p - e^{-i\theta}q|^2} \rightarrow \frac{4\pi e^{-i\left(p - e^{-i}q\right)}}{|p - e^{-i\theta}q|^2} \left(\frac{2}{\pi}\right)^{\frac{3}{2}} e^{\left(-2\epsilon|p - e^{-i}q|^2\right)} \tag{1.22}$$

For $0 < |Im(\theta)| < \frac{\pi}{4}$ the new equation has exponential fall off as q becomes large. For fixed nuclear positions $R_1, ..., R_k$, let $H_{(\epsilon)}$ be the electronic Hamiltonian for the fixed nuclear positions with Coulomb potentials $|x - y|^{-1}$ replaced by $V^{(\epsilon)}(x - y)$. For $R_0 > max_j |R_j|$, consider the exterior scaled hamiltonian $H_{R_0}^{(\epsilon)}$. For $|Im(\theta)| < \frac{1}{4}\pi$, the potentials $V_{R_0}^{(\epsilon)}(\theta)$ converge uniformly to the Coulomb potential as $\epsilon \downarrow 0$:

$$||(H_{R_0}^{(\epsilon)}(\theta) - z)^{-1} - (H_{R_0}(\theta) - z)^{-1}|| \rightarrow 0 \qquad (1.23)$$

Thus, by general principles, eigenvalues $E^{(\epsilon)}$ of $H_{R_0}^{(\epsilon)}(\theta)$ converge to eigenvalues E of $H_{R_0}(\theta)$

For $N \times N$ approximations, let E_N and $E_N^{(\epsilon)}$ denote the corresponding eigenvalues. By the above mentioned convergence of potentials, the equations converge so that for any finite N:

$$E_N^{(\epsilon)} \rightarrow E_N \text{ as } \epsilon \downarrow 0$$

Now, $V^{(\epsilon)}$ is entire and has fall-off in the region $|arg(r)| < \frac{1}{4}\pi$. Thus, the usual complex scaling theory applies to the Hamiltonians $H^{(\epsilon)}$.

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Chapter 2

Methods Used

Complex scaling operator can be applied only if, the potential $\hat{V}$ is an analytic function for which all the high-order derivatives are well defined. For atoms, our Hamiltonian operator becomes:

$$\hat{H}_{atom} = \exp(-2i\theta)\hat{T}_e + \exp(-i\theta)(\hat{V}_{eN} + \hat{V}_{ee}) \tag{2.1}$$

where $\hat{T}_e$ is the kinetic energy operator scaled by $\exp(-2i\theta)$ whereas $\hat{V}_{eN}$ and $\hat{V}_{ee}$ are electron-nucleus and electron-electron potential energy operators respectively which are both scaled by $\exp(-i\theta)$.

It is not possible to complex scale molecular resonances by this method as we require the potential to be an analytic function within the spatial region where the resonance wavefunctions are localized, but the coupling between electronic and nuclear coordinates through the electron-nuclei potential energy terms are non-analytic operators. Therefore, it is not possible to obtain complex potential energy surface by applying the transformation $r_j \rightarrow \exp(i\theta)r_j$ while keeping the nuclei position R_α fixed and unscaled.[1] Weistrass transform averages the values of a function resulting in a smooth version of that function which leads to convergence.

2.1   Nuclear Attraction Integral

The Nuclear Arttraction Integral (NAIs) for the contracted Gaussian functions is written as [2] :

$$V_{ij}^C = Z_C \int d\tau_1 \phi_i(1) r_{1C}^{-1} \phi_j(2) \tag{2.2}$$

where, ϕ_i and ϕ_j are Gaussian functions for s, p and d orbitals, r_{1C} is the nuclear-electron distance and Z_C is the nuclear charge.

The Gaussian product theorem permits a separation in the Cartesian components of the Gaussian type functions (GTFs) and after normalization, the potential for the contracted Gaussian function is:

$$V_{ij}^C = Z_C \sum_{a,b} c_a c_b N_1 N_2 \int d\tau_1 \eta_a(1) r_{1C}^{-1} \eta_b(2) \tag{2.3}$$

The product for the functions in the equation 2.2 was simplified using the Gaussian product theorem. The product of two $1s$-type Gaussian type orbitals is another scaled $1s$-type Gaussian:

$$s_A s_B = e^{-\alpha|r-A|^2} e^{-\beta|r-B|^2} = k e^{-(\alpha+\beta)|r-P|^2} \tag{2.4}$$

It expresses the product as a multilinear combination of the functions that share a common center. The Gaussian product theorem gives us a final compact expression for the product of a number of Cartesian Gaussian type orbitals.

Applying Gaussian product theorem in equation 2.2 gives:

$$V_{ij}^C = Z_C \sum_{ab} c_a c_b N(1) N(2) e^{\left(\frac{-1}{1} 2\overline{AB}^2\right)} \sum_{i=0}^{l_{x1}+l_{x2}} \sum_{j=0}^{l_{y1}+l_{y2}} \sum_{k=0}^{l_{z1}+l_{z2}} f(x)f(y)f(z) \int d_1 x_p^i y_p^j z_p^k r_{1C}^{-1} e^{(-\gamma_1 r_p^2)} \tag{2.5}$$

Now, Fourier transform for r_{1C}^{-1} is required for the evaluation of the integral above. In one dimension, the Fourier transform of a function $F(x)$ is defined as:

$$F(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk f(k) e^{ixk} \tag{2.6}$$

2.1.1 Modifications done

Weierstrass transform maps functions $f(x)$ with $\int dx f(x) exp(-\alpha|x|^2) < \infty$ to analytic functions. For each $\epsilon > 0$, $V^{(\epsilon)}(r)$ will be an entire function of r :

$$V^{(\epsilon)}(r) = \frac{1}{|r|} erf(\frac{|r|}{\sqrt{2\epsilon}}) \tag{2.7}$$

where $erf(z)$ is the error function. For $|Im(\theta)| < \frac{1}{4}\pi$, the potentials $V_{(R_0)}^{(\epsilon)}(\theta)$ converge uniformly to the Coulomb potential as $\epsilon \downarrow 0$:

$$||(H_{R_0}^{(\epsilon)}(\theta) - z)^{-1} - (H_{R_0}(\theta) - z)^{-1}|| \to 0 \tag{2.8}$$

Thus, by general principles eigenvalues $E^{(\epsilon)}$ of $H_{R_0}^{(\epsilon)}(\theta)$ converge to eigenvalues E of $H_{R_0}(\theta)$

For $N \times N$ approximations , let E_N and $E_N^{(\epsilon)}$ denote the corresponding eigenvalues. By the above mentioned convergence of potentials, our equation converge so that for any finite N;

$$E_N^{(\epsilon)} \to E_N \text{ as } \epsilon \downarrow 0$$

Now, $V^{(\epsilon)}$ is entire and has fall-off in the region $|arg(r)| < \frac{1}{4}\pi$. Thus, the usual complex scaling theory applies to the Hamiltonians $H^{(\epsilon)}$. [3]

The potential terms are:

$$V_r(r) = Z_C \int d\tau_1 \phi_i(1) \frac{1}{r} \phi_j(1) \tag{2.9}$$

and

$$V_{erf}(r) = Z_C \int d\tau_1 \phi_i(1) \frac{erf(\mu r)}{r} \phi_j(1) \tag{2.10}$$

The analytical form is taken from [1], checked using *GAMESS US* and the values for $\Delta = V_r^{code} - V_r^{GAMESS}$ are calculated with $\Delta \approx 10^{-6}$ or less. For these two analytical

forms it is observed that for large values of μ:

$$\lim_{\mu \to \infty} V_{erf}(r) \to V(r) \tag{2.11}$$

Modification is done to the analytical form $V(r)$ to get the value for $V_{erf}(r)$. The modification is done to the NAI integral for s, p and d functions where a factor of $\frac{1}{\mu}$ is added:

The overlap integral for V^{ss} is:

$$V^{ss}(a,b) = < S_a|S_b > = N_a N_b \left(\frac{\pi}{\alpha_p'}\right)^{\frac{3}{2}} exp\left(-\frac{ab}{\alpha_p'}\overline{AB}^2\right) F_0(t) \tag{2.12}$$

where $t = (A+B)(P-C)^2$; $P_x = \frac{aA_x + bB_x}{a+b}$; A, B are Gaussian centers & C is atomic center while a, b are exponents of Gaussian function and $F_0(t)$ are incomplete gamma function.

Now, the modification is done by replacing $\frac{1}{r}$ with $\frac{erf(\mu r)}{r}$ and, [4]

$$\frac{1}{\alpha_p'} \to \frac{1}{\alpha_p} + \frac{1}{\mu^2} \tag{2.13}$$

So, the analytical integral form needs to be multiplied by a factor of $\left(\frac{\alpha_p'}{\alpha_p}\right)^m$, where the value of m will be 0,1 and 2 for s, p and d respectively.
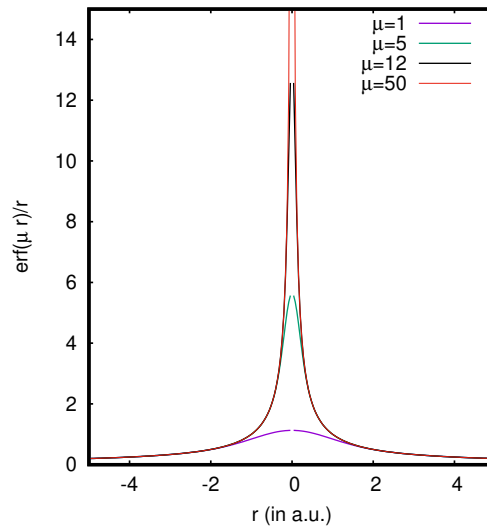

FIGURE 2.1: Plots for different μ values

From the plot above, it can be observed clearly that as the value of μ increases our analytical form converges to the one expected for $\frac{1}{r}$ and for smaller values it is different. This shows that the anallytical form is correct.

2.2   Modified one electron Gaussian integral

1. For two $s - s$ type Gaussian attraction integral the analytical for NAI is [2] :

$$V_r^{ss}(a,b) = < S_a | \frac{1}{r_c} | S_b > = \Theta \sum_c S^{ss}(a,b) L^{ss}(c;a,b) \tag{2.14}$$

2. Similarly, For $s - p$ type Gaussian attraction integral the analytical for NAI is :

$$V_r^{p \times s}(a,b) = < P_{p \times a} | \frac{1}{r_c} | S_b > = \Theta \sum_c \left\{ S^{p \times s}(a,b) L^{ss}(c;a,b) + S^{ss}(a,b) L^{p \times s}(c;a,b) \right\} \tag{2.15}$$

3. For $p_x - p_y$ type Gaussian attraction integral the analytical for NAI is:

$$V^{p \times p y} = < P_{p \times a} | \frac{1}{r_c} | P_{p y b} > = \Theta \sum_c \left\{ S^{p \times p y}(a,b) L^{ss}(c;a,b) + S^{p \times s}(a,b) L^{s p y}(c;a,b) \right.$$
$$\left. + S^{s p y}(a,b) L^{p \times s}(c;a,b) + S^{ss}(a,b) L^{p \times p y}(c;a,b) \right\} \tag{2.16}$$

where: $\Theta = \frac{2}{\pi^{\frac{1}{2}}} (a+b)^{\frac{1}{2}}$, constant that depends on a, b.

The Overlap integrals $S(a,b)$ used in the analytical form for NAI is :

1. For $s - s$ type Gaussian function:

$$S^{ss}(a,b) = < S_a | S_b > = N_a N_b \left(\frac{\pi}{a+b} \right)^{\frac{3}{2}} e^{\left(-\frac{ab}{a+b} \overline{AB}^2 \right)} \tag{2.17}$$

2. For $p_x - s$ type Gaussian functon:

$$S^{p \times s}(a,b) = < P_{p \times a} | S_a > = -\frac{b}{a+b} (A_{p \times} - B_{p \times}) S^{ss}(a,b) \tag{2.18}$$

3. For $s - p_y$ type Gaussian function:

$$S^{s p y}(a,b) = < S_a | P_{p y b} > = \frac{a}{a+b} (A_{p y} - B_{p y}) S^{ss}(a,b) \tag{2.19}$$

4. For $p_x - p_y$ type Gaussian function:

$$S^{p_x p_y}(a,b) = <P_{p_x a}|P_{p_y b}> = \left\{ \frac{1}{2}(a+b)\delta_{p_x p_y} - \frac{ab}{a+b}^2 (A_s - B_s) \right.$$

$$\left. \cdot (A_{p_y - B_{py}}) \right\} S^{ss}(a,b) \qquad (2.20)$$

and, the intermediate functions $L(c; a, b)$ used in the calculations for NAI is:

1. For $s - s$ type Gaussian function:

$$L^{ss}(c; a, b) = F_0(t) \qquad (2.21)$$

where, $F_\nu(t)$ are incomplete gamma function which is defined as:

$$F_\nu(t) = \int_0^1 dx\, x^{2\nu} e^{-tx^2} \qquad (2.22)$$

and for $F_\nu(0) = (2\nu + 1)^{-1}$

2. For $p_x - s$ type Gaussian function:

$$L^{p_x s}(c; a, b) = L^{s p_x}(c; a, b) = (C_{p_x} - P_{p_x})F_1(t) \qquad (2.23)$$

3. For $p_x - p_y$ type Gaussian funcion:

$$L^{p_x p_y}(c; a, b) = (P_{p_x} - C_{p_x})(P_{p_y} - C_{p_y})F_2(t) - \frac{1}{2(a+b)}\delta_{p_x p_y}F_1(t) \qquad (2.24)$$

The analytical form for the function $< \phi(a)|\frac{erf(\mu r)}{r}|\phi(b) >$ is modified. For $< \phi(a)|\frac{1}{r}|\phi(b) >$ calculations we consider $\frac{1}{\alpha_p}$ which is $\alpha_p = a + b$, used in incomplete gamma function calculations. For $< \phi(a)|\frac{erf(\mu r)}{r}|\phi(b) >$ we use α_p':

$$\frac{1}{\alpha_p'} = \frac{1}{\alpha_p} + \frac{1}{\mu^2} \qquad (2.25)$$

which gives:

$$\alpha_p' = \frac{\alpha_p \mu^2}{\mu^2 + \alpha_p} \qquad (2.26)$$

and the Θ for our attraction integral is modified to $\dot{\Theta} = 2(\frac{\dot{\alpha_p}}{\pi})^{\frac{1}{2}}$.

The following table shows us the modifications done to the incomplete gamma functions.
Here $Y = \frac{(a+b)\mu^2}{(a+b)+\mu^2}$ and $Z = a+b$.

S.No.	$F_\nu(t)$ (for $\frac{1}{r}$)	$F_\nu(t)$ (for $\frac{erf(\mu r)}{r}$)
1.	$F_0(t)$	$(\frac{Y}{Z})^0 F_0(t')$
2.	$F_1(t)$	$(\frac{Y}{Z})^1 F_1(t')$
3.	$F_2(t)$	$(\frac{Y}{Z})^2 F_2(t')$
4.	$F_3(t)$	$(\frac{Y}{Z})^3 F_3(t')$
5.	$F_4(t)$	$(\frac{Y}{Z})^4 F_4(t')$

TABLE 2.1: Modified incomplete gamma functions

The final analytical form for the potential for different bases are:

S.No.		V_r	V_{erf}
1.	s-s	$\Theta \sum_c S^{ss}(a,b) F_0(t)$	$\dot\Theta \sum_c S^{ss}(a,b) F_0(t)$
2.	s-p_x	$\Theta \sum_c \left[S^{p,s}(a,b)F_0(t) + S^{ss}(a,b)(C_{p_x} - P_{p_x})F_1(t) \right]$	$\dot\Theta \sum_c \left[S^{p,s}(a,b)F_0(t) + S^{ss}(a,b)(C_{p_x} - P_{p_x})F_1(t)\left(\frac{Y}{Z}\right)^1 \right]$
3.	p_y-p_z	$\Theta \sum_c \begin{bmatrix} \left[S^{p,p_y}(a,b)F_0(t) + S^{p,s}(a,b)(C_{p_y} - P_{p_y})F_1(t) \right] + \\ \left[S^{s p_y}(a,b)(C_{p_x} - P_{p_x})F_1(t) \right] + \\ \left[S^{ss}(a,b)(P_{p_x} - C_{p_x})(P_{p_y} - C_{p_y})F_2(t) - \frac{1}{2(a+b)}\delta_{ij}F_1(t) \right] \end{bmatrix}$	$\dot\Theta \sum_c \begin{bmatrix} \left[S^{p,p_y}(a,b)F_0(t) + S^{p,s}(a,b)(C_{p_y} - P_{p_y})F_1(t)\left(\frac{Y}{Z}\right)^1 \right] + \\ \left[S^{s p_y}(a,b)(C_{p_x} - P_{p_x})F_1(t)\left(\frac{Y}{Z}\right)^1 \right] + \\ \left[S^{ss}(a,b)(P_{p_x} - C_{p_x})(P_{p_y} - C_{p_y})F_2(t)\left(\frac{Y}{Z}\right)^2 - \frac{1}{2(a+b)}\delta_{ij}F_1(t)\left(\frac{Y}{Z}\right)^1 \right] \end{bmatrix}$

FIGURE 2.2: Initial and modified potential functions

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Chapter 3

Configuration Interaction(CI) calculations for He atom with varying μ

3.1 Configuration Interaction

For the calculation of correlation energy the method of configuration interaction is used. In this method diagonalisation of an N-electron Hamiltonian is achieved in a basis of N-electron functions which will be the Slater determinants. This represents the wave functions as a linear combination of N-electron functions and the linear variation method follows. If the basis is complete then the exact energies can be obtained for ground state and for all excited states of the system. [1]

Due to the use of an average potential for the calculations of electron-electron interactions, even the best energies obtained using the Hartree-Fock are still inaccurate. Configuration Interaction that is, the interaction of different states, helps us overcome this limitation of Hartree-Fock energy calculations.

The motion of electrons in an atom is correlated due to the attractive and repulsive forces acting on them. When one electron comes close to the nucleus, the other one tends to move away. But, the exact wavefunction depends on the coordinates of both the electrons at the same time. In CI, while calculating energies, this correlation is neglected and the used wavefunctions that depend upon the coordinates of only one electron under the assumption that the electrons move independently. This approximation gives us reasonably good values for the energies which can later be correlated.

3.2   Plots for He atom

The long range nuclear-electron attraction integral is used for complex scaling and used for the calculation of resonances as it has a numerical advantage that they remain reflection-free even for large values of the complex scaling parameter. They are also effective for fast moving particles. The resonances is associated with a single cusp which is obtained when all parameters are held fixed and only θ is varied. In this θ trajectory calculation, each one of the resonances is associated with a single curve where the absolute value of the velocity of the θ trajectory achieves a minimal value. Almost cusp behavior is obtained in the θ trajectory and is very stable to variation of the parameter.

The reference orbitals for the configuration interaction calculations were obtained from a standard Hartree-Fock calculation on the ground state of the physical Hamiltonian. Using these Hartree-Fock orbitals determinants for full CI calculations of ground state, first and the doubly excited state was constructed. For kinetic energy and potential energy matrix elements of electronic hamiltonian full configuration interaction code was implemented in the *GAMESS US* quantum chemical package [2].
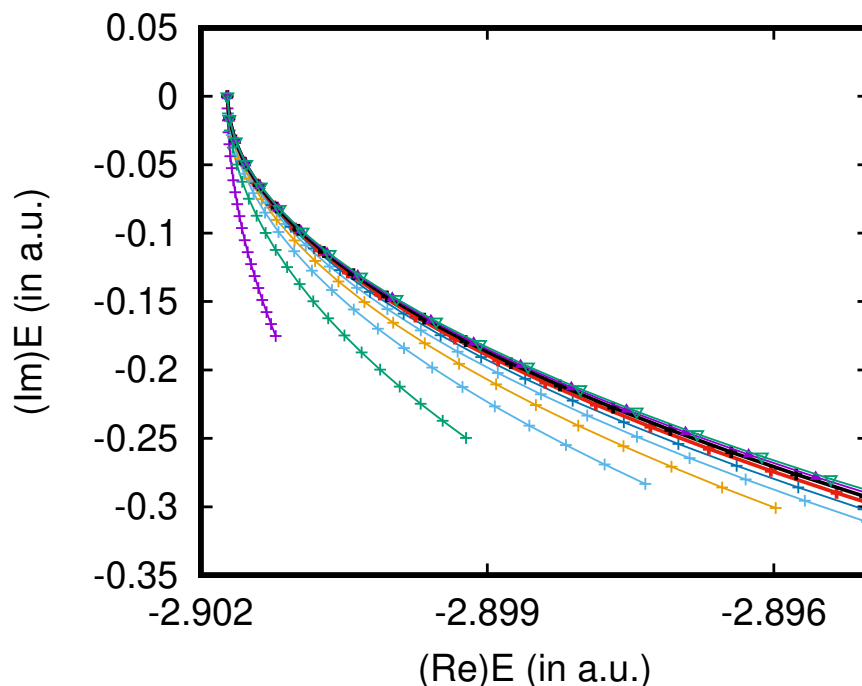
3.2.1   Ground State

FIGURE 3.1: Ground state θ trajectory

The ground state of an atom is the state in which the total energy can not be lowered by transferring one or more electrons to different orbitals. It has a longer lifespan because of the stability. The given plot shows us the θ trajectory for Ground state of He atom. The state is bound so we do not observe any kind of cusp (transition between states) instead we get a continuum.
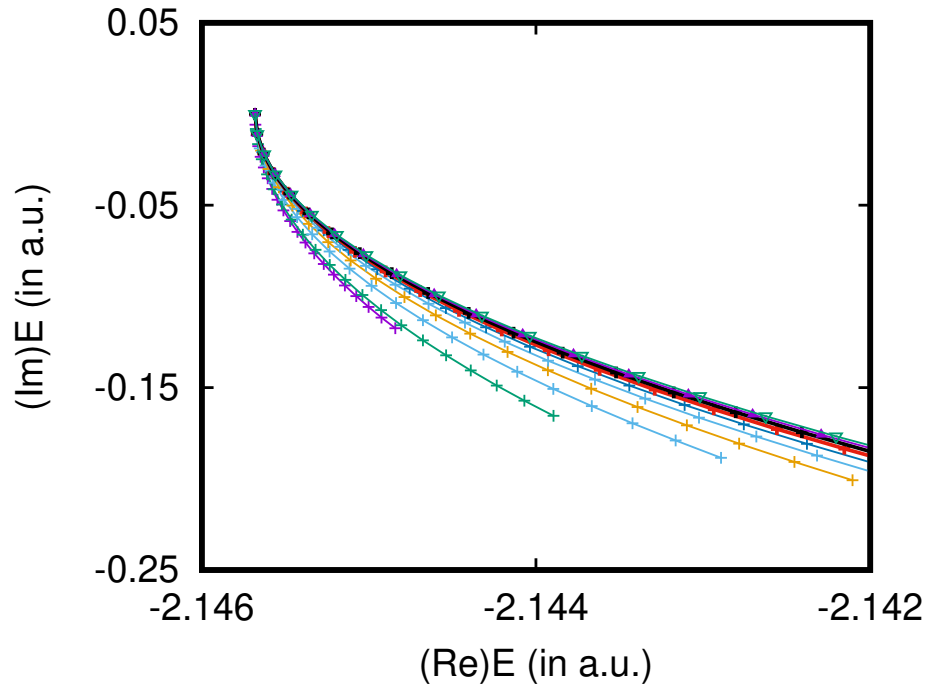
3.2.2   First Excited State

FIGURE 3.2: First excited state θ trajectory

First excited state is the lowest unoccupied energy level state after the ground state. First excited state for He is given as $1s$ $2s$. For this state the plot for θ trajectory, we gets a continuum curve and the cusp was not observed.

3.2.3   Doubly Excited State

Doubly excited state for He atom is given by $2s$ $2p$. In the θ trajectory calculations each resonance is associated with a single curve. Here, also a continuum was observed instead of cusp.
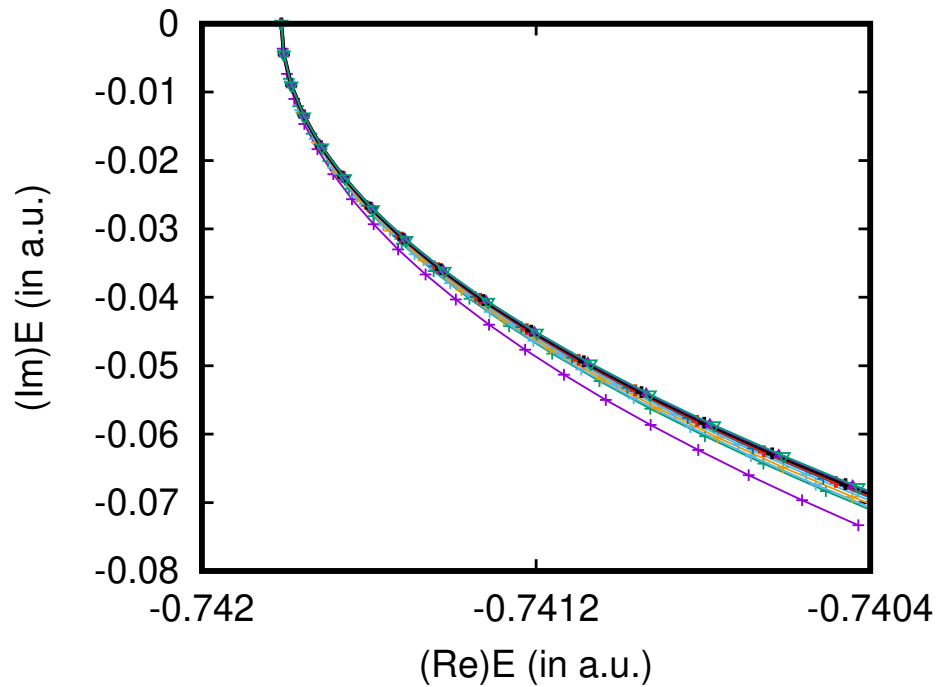
FIGURE 3.3: Doubly excited state θ trajectory

3.3   Observation and Conclusion

By using the Gaussian basis set, the complex scaling can be implemented and provides
the Feshbach resonances of the atom. Although the complex scaling depends on several
parameters, resonance is associated with the single point on the θ trajectory where the
absolute velocity of the trajectory gets a minimal value. There is a cusp associated with
a resonance state. The complex scaling should be introduced in the region where the
ionized electron does not feel the attractive force of Coulomb potential [2].

We did not get the cusp which would have given us the information about the resonances
instead we got a continuum for first and doubly excited states. For ground state as it is
a bound state the cusp won't be observed. Further calculations are going on to improve
the observations we got.

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