Properties of positronium hydride

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Properties of Positronium Hydride

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Abstract

The properties of the bound ground state composed of a hydrogen (p^+e^-) and a positronium (e^+e^-) (positronium hydride (PsH)) have been determined using the variational method in the Gaussian basis. Using significantly accurate wave function, the calculation of non-relativistic ground state energy of (PsH), the expectation values of inter-particle distances and their squares, and the two-,three- and four-particles coalescence probabilities are calculated. The expectation value of two-particles delta function converges slowly if we calculate it directly. Drachman proposed very important identities that ensures the convergence of this two-particle delta function even with small set of basis. We used these identities to determine the values of different two-particle delta functions by using the Gaussian wave functions for the ground state with 1000 basis. We find that for 1000 basis our results matches with the reported values in the literature.

Chapter 1

Introduction

The stable formation of positron systems through Coulomb interaction is a widely accepted fact. The most basic example of such a system is known as positronium (Ps) which is composed of an electron and a positron. This system can be considered similar to a hydrogen atom. Empirical confirmation of the The fact that Ps exist has been provided by Mohorovičić in 1934 [**1**]. Based upon the spin configuration of electron and positron, the positronium can exist in two possible spin states, i.e. para-positronium (spin-0) and ortho-positronium (spin-1). The positronium is unstable and annihilates into photons. Due to the parity conservation (a holy symmetry in QED), the para-positronium (ortho-poistronium) will decay to two (three) photons.

In this dissertation, we calculate the properties, such as the binding energy, coalescence probabilities, etc., of the positronium hydride (PsH). After the theoretical prediction of the stability of positronium molecule and positronium hydride [**1**, **2** , **3**], these exotic atoms become a subject of topical interest [**4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **15**, **16**, **17**, **18**, **19**, **20**] (and references therein). In comparison to the the Ps^- ion, the production of PsH is more challenging and for the very first time Pareja *et al.* reported the experimental existence of such a bound state of PsH in a condensed phase [**21**]. The first convincing evidence of PsH was reported by Schrader *et al.* [**22**] in the collision between the positrons and methane, i.e.,

$$e^+ + \mathrm{CH}_4 \to \mathrm{CH}_3^+ + \mathrm{PsH}, \qquad 7.55\mathrm{eV} - B_{\mathrm{PsH}} \tag{1.1}$$

giving an estimate of binding energy, $B_{\mathrm{PsH}} = 1.1 \pm 0.2$ eV which in line with most of the theoretical predictions. Apart from the production of PsH in the laboratory, this compound molecule can be produced and later annihilated inside and outside the hydrogen stars; therefore, these system play a definite role in certain astrophysical models [**23**] and also in a dense hydrogen plasma. Theoretically, these compound molecules serve as an important tool to test the various quantum mechanical methods and with the passage of time significant accuracy in theoretical calculations is achieved due to the rapid growth in the computational facilities. Including relativistic effects, one of the most accurate estimate of the ground state energy of PsH is given by Bubin and Verga [**24**].

Apart form the precision calculation of the binding energy of compound molecules, another very important problem is to evaluate the positron annihilation rates to different number of photons. In most of the cases, e.g., in Ps_2, the final state is not of the interest after positron annihilation, and the main focus is the calculation of annihilation rates $\Gamma_{n\gamma}$, where n means the number of emitted photons. This is different from the PsH where after the positron annihilation we have PsH $\to [\mathrm{H}^+,\ e^-] + n\gamma$, where $[\mathrm{H}^+,\ e^-]$ designates the final state that can be unbound H^+e^- state, or a bound state (hydrogen H). In case of an unbound final state, along with one- and zero-photon, the full QED calculation of the decay rate is performed in [**25**]. This was the first complete and correct result of these QED annihilations.

The relaxation of the daughter system, after positron annihilation to two photons in PsH, in one of the states of hydrogen is investigated for the first time by Schrader and Peterson [**26**]. They have calculated the probabilities of occupation of different final states after the positron annihilation and showed that the maximum probability is for the $1s$-state. Later, by considering different choices of the variational wave-function the same system was discussed by number of other authors [**27**, **28**].

In contrast to the two photon annihilation, the case of one photon along with the hydrogen like final state is also very important. In this particular case, one of the photon is absorbed by the final state electron (in which case we have unbound state) or by the H^+ for which we have either the bound or unbound state. The aim of the present study is to calculate the probabilities of different hydrogen states in case of both two- and one- photon annihilations when final state hydrogen atom is in i-th state. The purpose of this work is to calculate the binding energy of PsH using variational approach. By using the Gaussian basis for the position wave function, we calculate the kinetic energy and potential energy as a function of variational parameters. We use the numerical code developed by A. Czarnecki at al. to perform the numerical calculations. wave functions for the position [**29**].

This dissertation is organized as follows in chapter. In Chapter 2, first we will write the Hamiltonian in terms of the kinetic and potential (Coulomb) energies for the PsH. We calculate different properties of PsH such as inter-particle distances, kinetic energy and Coulomb potential and their expectation values by using variational principal and Gaussian basis [**29**]. As PsH is unstable, and it decays due to electron-positron annihilation. this corresponds to the coalescence probabilities of Dirac delta function. For the two particle delta function, the convergence of direct calculation of expectation values of two particle delta function requirers significant computational time. Without compromising it, the Drachman has given some identities to calculate these expectation values [**30**]. This we discuss in Chapter 3. Finally, in Chapter 4, we present our numerical results and conclusions.

Chapter 2

Positronium Hydride

2.1 PsH Wave Function and Hamiltonian

As a heart of the Variational Principle (VP) we have to chose the ground state wave function as a trial wave function. In case of our system of PsH it is the product of spatial and spin parts and is antisymmetrized with respect to the permutation of two electrons (the identical particles) in our system. In the Gaussian basis, for the ground state of PsH it can be written as [**29**]

$$\psi = \chi^1_\uparrow \chi^2_\uparrow \left(\chi^3_\downarrow \chi^4_\uparrow - \chi^3_\uparrow \chi^4_\downarrow\right)\left(1 \pm P_{34}\right)\phi_S \tag{2.1}$$

where, χ's deonote the spin part and ϕ_S is the S-wave spatial wavefunction and it can be written as

$$\phi_S = \sum_{i=1}^{N} c'^{S}_{i} \exp\left[-\sum_{a<b} w^{iS}_{ab} r^2_{ab}\right] \tag{2.2}$$

and in the spatial part w_{ab} are the real coefficients. In Eq. (2.2), N are the number of trial basis and P_{34} is the permutation operator for the two identical fermions. There is a factor of $\frac{1}{\sqrt{2}}$ with the permutation operator but that is absorbed in the normalization constant c'^{S}_{i}.

In order to write the Hamiltonian, there are different approaches adopted in the literature. In our case, we will follow the analogy of di-positronium molecule where the motion of all the four bodies is considered. Hamiltonian of this system can be written as

$$\begin{aligned}\hat{H} &= \sum_{i=1}^{4} \frac{\hat{p}_i^2}{2m_i} + \sum_{i<j} V\left(r_{ij}\right) \\ &= \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + \frac{\hat{p}_3^2}{2m_3} + \frac{\hat{p}_4^2}{2m_4} + \alpha \sum_{i<j}\left[\frac{z_i z_j}{r_{ij}}\right],\end{aligned} \tag{2.3}$$

where we have considered the indices $\{1,2\}$ for the $\{p^+,\ e^+\}$ and $\{3,4\}$ for $\{e^-,\ e^-\}$. The z_i correspond to the charge index which is -1 for e^- and $+1$ for $\{e^+,\ p\}$. We know that the masses of electron and positron are equal and we can write $m_2 = m_3 = m_4 = m$, but we will derive the expressions for the arbirary masses and at the end we will substitute these three masses to be equal.

Let $\vec{A}_i$ denote the Lab. coordinates and $\vec{r}_{ij}$ to be the relative coordinates. The inter-particle distances can be written as $r_{ij} = \sqrt{\left(\vec{A}_i - \vec{A}_j\right)^2}$. Thus in term of these coordinates, the Hamiltonian becomes $(\hbar = 1)$

$$\begin{aligned}\hat{H} = &-\frac{1}{2\mu_{12}}\left[\vec{\nabla}^2_{\vec{r}_{12}} + \vec{\nabla}^2_{\vec{r}_{13}} + \vec{\nabla}^2_{\vec{r}_{14}}\right] - \frac{1}{m_1}\left[\vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{13}} + \vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{14}} + \vec{\nabla}_{\vec{r}_{13}}\cdot\vec{\nabla}_{\vec{r}_{14}}\right] \\ &+ \alpha\left[\frac{z_1 z_2}{r_{12}} + \frac{z_3 z_4}{r_{34}} + \frac{z_1 z_3}{r_{13}} + \frac{z_1 z_4}{r_{14}} + \frac{z_2 z_3}{r_{23}} + \frac{z_2 z_4}{r_{24}}\right].\end{aligned} \tag{2.4}$$

where $\mu_{ij} = \frac{m_i m_j}{m_i + m_j}$ is the reduced mass and in our case, $m_1 = m_p$, $m_2 = m_3 = m_4 = m_e$, therefore, the reduced masses $\mu_{12} = \mu_{13} = \mu_{14}$. It is worth mentioning that while going from the Lab. coordinates to the relative coordinates, we have ignored the kinetic energy term of the centre-of-mass of the PsH system.

2.2 Calculation of Various Terms in the Hamiltonian

In our case, the trial wave functions depend on the relative coordinates, therefore, we will express the kinetic energy operator

$$\hat{T} = -\frac{1}{2}\left[\frac{\nabla^2_{\vec{A}_1}}{m_1} + \frac{\nabla^2_{\vec{A}_2}}{m_2} + \frac{\nabla^2_{\vec{A}_3}}{m_3} + \frac{\nabla^2_{\vec{A}_4}}{m_4}\right], \tag{2.5}$$

in term of these coordinates. To do this, let us introduce the centre of mass (CoM) coordinates

$$\vec{R} = \frac{1}{M}\left(m_1\vec{A}_1 + m_2\vec{A}_2 + m_3\vec{A}_3 + m_4\vec{A}_4\right), \tag{2.6}$$

where $M = m_1 + m_2 + m_3 + m_4$ is the total mass.

The three independent relative coordinates are

$$\begin{aligned} \vec{r}_{12} &= \vec{A}_2 - \vec{A}_1, \\ \vec{r}_{13} &= \vec{A}_3 - \vec{A}_1, \\ \vec{r}_{14} &= \vec{A}_4 - \vec{A}_1. \end{aligned} \tag{2.7}$$

In terms of these coordinates, one can write

$$\begin{aligned} \vec{\nabla}_{\vec{A}_1} &= \frac{\partial \vec{R}}{\partial \vec{A}_1}\frac{\partial}{\partial \vec{R}} + \frac{\partial \vec{r}_{12}}{\partial \vec{A}_1}\frac{\partial}{\partial \vec{r}_{12}} + \frac{\partial \vec{r}_{13}}{\partial \vec{A}_1}\frac{\partial}{\partial \vec{r}_{13}} + \frac{\partial \vec{r}_{14}}{\partial \vec{A}_1}\frac{\partial}{\partial \vec{r}_{14}} \\ &= \frac{m_1}{M}\vec{\nabla}_{\vec{R}} - \vec{\nabla}_{\vec{r}_{12}} - \vec{\nabla}_{\vec{r}_{13}} - \vec{\nabla}_{\vec{r}_{14}}. \end{aligned} \tag{2.8}$$

Similarly,

$$\begin{aligned} \vec{\nabla}_{\vec{A}_2} &= \frac{m_2}{M}\vec{\nabla}_{\vec{R}} - \vec{\nabla}_{\vec{r}_{12}}, \\ \vec{\nabla}_{\vec{A}_3} &= \frac{m_3}{M}\vec{\nabla}_{\vec{R}} - \vec{\nabla}_{\vec{r}_{13}}, \\ \vec{\nabla}_{\vec{A}_4} &= \frac{m_3}{M}\vec{\nabla}_{\vec{R}} - \vec{\nabla}_{\vec{r}_{14}}. \end{aligned} \tag{2.9}$$

As the motion of the CoM does not have any effect dynamics of the system, therefore, we can write

$$\begin{aligned} \vec{\nabla}^2_{\vec{A}_1} &= \vec{\nabla}^2_{\vec{r}_{12}} + \vec{\nabla}^2_{\vec{r}_{13}} + \vec{\nabla}^2_{\vec{r}_{14}} + 2\vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{13}} + 2\vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{14}} + 2\vec{\nabla}_{\vec{r}_{13}}\cdot\vec{\nabla}_{\vec{r}_{14}}, \\ \vec{\nabla}^2_{\vec{A}_2} &= \vec{\nabla}^2_{\vec{r}_{12}}, \\ \vec{\nabla}^2_{\vec{A}_3} &= \vec{\nabla}^2_{\vec{r}_{13}}, \\ \vec{\nabla}^2_{\vec{A}_4} &= \vec{\nabla}^2_{\vec{r}_{14}}. \end{aligned} \tag{2.10}$$

Thus, in term of relative coordinates Eq. (2.5) becomes

$$\begin{aligned} \hat{T} &= -\frac{1}{2}\left[\frac{\vec{\nabla}^2_{\vec{r}_{12}} + \vec{\nabla}^2_{\vec{r}_{13}} + \vec{\nabla}^2_{\vec{r}_{14}} + 2\vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{13}} + 2\vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{14}} + 2\vec{\nabla}_{\vec{r}_{13}}\cdot\vec{\nabla}_{\vec{r}_{14}}}{m_1} + \frac{\vec{\nabla}^2_{\vec{r}_{12}}}{m_2} + \frac{\vec{\nabla}^2_{\vec{r}_{13}}}{m_3} + \frac{\vec{\nabla}^2_{\vec{r}_{14}}}{m_4}\right], \qquad (2.11) \\ &= -\frac{1}{2}\left[\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\vec{\nabla}^2_{\vec{r}_{12}} + \left(\frac{1}{m_1} + \frac{1}{m_3}\right)\vec{\nabla}^2_{\vec{r}_{13}} + \left(\frac{1}{m_1} + \frac{1}{m_4}\right)\vec{\nabla}^2_{\vec{r}_{14}} + \frac{2}{m_1}\left(\vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{13}} + \vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{14}} + \vec{\nabla}_{\vec{r}_{13}}\cdot\vec{\nabla}_{\vec{r}_{14}}\right)\right], \\ &= -\frac{1}{2}\left[\frac{1}{\mu_{12}}\vec{\nabla}^2_{\vec{r}_{12}} + \frac{1}{\mu_{13}}\vec{\nabla}^2_{\vec{r}_{13}} + \frac{1}{\mu_{14}}\vec{\nabla}^2_{\vec{r}_{14}} + \frac{2}{m_1}\left(\vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{13}} + \vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{14}} + \vec{\nabla}_{\vec{r}_{13}}\cdot\vec{\nabla}_{\vec{r}_{14}}\right)\right], \end{aligned}$$

where $\mu_{ij} = \frac{m_i m_j}{m_i+m_j}$ is the reduced mass. In our case, $m_1 = m_p$, $m_4 = m_2 = m_3 = m_e$ and , therefore, the reduced masses $\mu_{12} = \mu_{13} = \mu_{14}$. Hence, Eq. (2.11) becomes

$$\hat{T} = -\frac{1}{2\mu_{12}}\left[\vec{\nabla}^2_{\vec{r}_{12}} + \vec{\nabla}^2_{\vec{r}_{13}} + \vec{\nabla}^2_{\vec{r}_{14}}\right] - \frac{1}{m_1}\left[\vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{13}} + \vec{\nabla}_{\vec{r}_{12}}\cdot\vec{\nabla}_{\vec{r}_{14}} + \vec{\nabla}_{\vec{r}_{13}}\cdot\vec{\nabla}_{\vec{r}_{14}}\right] \tag{2.12}$$

The trial wave function, in terms of these relative coordinates, can be written as

$$\begin{aligned}\left|\psi_i^{1234}\right\rangle &= \phi\left(a_i', b_i', c_i', d_i', e_i', f_i'\right) \\ &= \exp\left(-a_i' r_{12}^2 - b_i' r_{13}^2 - c_i' r_{14}^2 - d_i' r_{23}^2 - e_i' r_{24}^2 - f_i' r_{34}^2\right).\end{aligned} \tag{2.13}$$

The only permutation symmetry this wave function has is the swaping of two electrons, i.e., the $\{3 \leftrightarrow 4\}$ and it gives

$$\begin{aligned}\left|\psi_i^{1243}\right\rangle &= \exp\left(-a_i' r_{12}^2 - b_i' r_{14}^2 - c_i' r_{13}^2 - d_i' r_{24}^2 - e_i' r_{23}^2 - f_i' r_{34}^2\right) \\ &= \exp\left(-a_i' r_{12}^2 - c_i' r_{13}^2 - b_i' r_{14}^2 - e_i' r_{23}^2 - d_i' r_{24}^2 - f_i' r_{34}^2\right) \\ &= \phi\left(a_i', c_i', b_i', e_i', d_i', f_i'\right).\end{aligned} \tag{2.14}$$

The total wavefunction respecting all the symmetries is

$$|\psi_i\rangle = \left|\psi_i^{1234}\right\rangle + \left|\psi_i^{1243}\right\rangle = \phi\left(a_i', b_i', c_i', d_i', e_i', f_i'\right) + \phi\left(a_i', c_i', b_i', e_i', d_i', f_i'\right).$$

From Eqs. (2.13) and (2.14), we can see that all the results that we obtain using Eq. (2.13) can be obtanined for Eq. (2.14) just by the simultaneous interchange of $b \leftrightarrow c$ and $d \leftrightarrow e$.

Before, we apply the diffential operators, we know that not all the coordinates are independent. By fixing the orientation of the four-body system, we can write

$$\begin{aligned}\vec{r}_{12} + \vec{r}_{23} &= \vec{r}_{13}, \\ \vec{r}_{12} + \vec{r}_{24} &= \vec{r}_{14}, \\ \vec{r}_{13} + \vec{r}_{34} &= \vec{r}_{14}.\end{aligned} \tag{2.15}$$

Now, let's first write $\vec{r}_{23}$ and $\vec{r}_{24}$, in terms of $\vec{r}_{12}$ to calculate the differentials w.r.t. this parameter. We can write

$$\begin{aligned}r_{23}^2 &= r_{12}^2 + r_{13}^2 - 2\vec{r}_{12}\cdot\vec{r}_{13}, \\ r_{24}^2 &= r_{12}^2 + r_{14}^2 - 2\vec{r}_{12}\cdot\vec{r}_{14}, \\ r_{34}^2 &= r_{13}^2 + r_{14}^2 - 2\vec{r}_{13}\cdot\vec{r}_{14}\end{aligned} \tag{2.16}$$

$$\begin{aligned}\nabla_{\vec{r}_{12}}\left|\psi_i^{1234}\right\rangle &= \left[-2\left(a_i' + d_i' + e_i'\right)\vec{r}_{12} + 2d_i'\vec{r}_{13} + 2e_i'\vec{r}_{14}\right]\left|\psi_i^{1234}\right\rangle \\ \nabla_{\vec{r}_{13}}\left|\psi_i^{1234}\right\rangle &= \left[\nabla_{\vec{r}_{13}}\left(-a_i' r_{12}^2 - b_i' r_{13}^2 - c_i' r_{14}^2 - d_i' r_{23}^2 - e_i' r_{24}^2 - f_i' r_{34}^2\right)\right]\left|\psi_i^{1234}\right\rangle \\ &= \left[\left(-a_i'\nabla_{\vec{r}_{13}} r_{12}^2 - b_i'\nabla_{\vec{r}_{13}} r_{13}^2 - c_i'\nabla_{\vec{r}_{13}} r_{14}^2 - d_i'\nabla_{\vec{r}_{13}} r_{23}^2 - e_i'\nabla_{\vec{r}_{13}} r_{24}^2 - f_i'\nabla_{\vec{r}_{13}} r_{34}^2\right)\right]\left|\psi_i^{1234}\right\rangle \\ &= \left[-d_i'\left(\vec{r}_{13} - 2\vec{r}_{12}\right) - 2b_i'\vec{r}_{13} - f_i'\left(2\vec{r}_{13} - 2\vec{r}_{14}\right)\right]\left|\psi_i^{1234}\right\rangle \\ &= \left[-2\left(b_i' + d_i' + f_i'\right)\vec{r}_{13} + 2d_i'\vec{r}_{12} + 2f_i'\vec{r}_{14}\right]\left|\psi_i^{1234}\right\rangle,\end{aligned} \tag{2.17}$$

$$\begin{aligned}\nabla_{\vec{r}_{14}}\left|\psi_i^{1234}\right\rangle &= \left[\nabla_{\vec{r}_{14}}\left(-a_i' r_{12}^2 - b_i' r_{13}^2 - c_i' r_{14}^2 - d_i' r_{23}^2 - e_i' r_{24}^2 - f_i' r_{34}^2\right)\right]\left|\psi_i^{1234}\right\rangle \\ &= \left[-2c_i'\vec{r}_{14} - e_i'\left(2\vec{r}_{14} - 2\vec{r}_{12}\right) - f_i'\left(2\vec{r}_{14} - 2\vec{r}_{13}\right)\right]\left|\psi_i^{1234}\right\rangle \\ &= \left[-2\left(c_i' + e_i' + f_i'\right)\vec{r}_{14} + 2e_i'\vec{r}_{12} + 2f_i'\vec{r}_{13}\right]\left|\psi_i^{1234}\right\rangle.\end{aligned} \tag{2.18}$$

In taking these gradients we used

$$
\begin{aligned}
\frac{\partial r_k}{\partial r_j} &= \delta_{kj}, \\
\frac{\partial}{\partial r_1^j} r_1^2 &= \frac{\partial}{\partial r_1^j}\left(r_1^k r_1^k\right) = 2r_1^k \delta^{jk} = 2r_1^j, \\
\frac{\partial}{\partial r_1^j}\left(r_1 \cdot r_2\right) &= \frac{\partial}{\partial r_1^j}\left(r_1^k r_2^k\right) = \delta^{jk} r_2^k = r_2^j.
\end{aligned}
\tag{2.19}
$$

where δ_{ij} correspond to the kronecker delta. As the terms in kinetic energy involve the second gradient for all the terms, therefore, in the next step we have to calculate it. Let's calculate $\nabla^2_{\vec{r}_{12}} \left|\psi^{1234}\right\rangle$ and do to so, we will use the first line of Eq. (2.17). Writing

$$
\begin{aligned}
\nabla^2_{\vec{r}_{12}} \left|\psi_i^{1234}\right\rangle &= \vec{\nabla}_{\vec{r}_{12}} \cdot \vec{\nabla}_{\vec{r}_{12}} \left|\psi_i^{1234}\right\rangle, \\
&= \vec{\nabla}_{\vec{r}_{12}} \cdot \left[\left(-2\left(a_i' + d_i' + e_i'\right)\vec{r}_{12} + 2d_i'\vec{r}_{13} + 2e_i'\vec{r}_{14}\right)\left|\psi_i^{1234}\right\rangle\right], \\
&= -6\left(a_i' + d_i' + e_i'\right)\left|\psi_i^{1234}\right\rangle + \left[-2\left(a_i' + d_i' + e_i'\right)\vec{r}_{12} + 2d_i'\vec{r}_{13} + 2e_i'\vec{r}_{14}\right] \cdot \vec{\nabla}_{\vec{r}_{12}} \left|\psi_i^{1234}\right\rangle, \because \delta_{ii} = 3, \\
&= -6\left(a_i' + d_i' + e_i'\right)\left|\psi_i^{1234}\right\rangle + \left[-2\left(a_i' + d_i' + e_i'\right)\vec{r}_{12} + 2d_i'\vec{r}_{13} + 2e_i'\vec{r}_{14}\right] \cdot \\
&\quad \left[-2\left(a_i' + d_i' + e_i'\right)\vec{r}_{12} + 2d_i'\vec{r}_{13} + 2e_i'\vec{r}_{14}\right]\left|\psi_i^{1234}\right\rangle \\
&= -6\left(a_i' + d_i' + e_i'\right)\left|\psi_i^{1234}\right\rangle \\
&\quad + 4\Big[\left(a_i' + d_i' + e_i'\right)^2 r_{12}^2 + d_i'^2 r_{13}^2 + e_i'^2 r_{14}^2 - 2d_i'\left(a_i' + d_i' + e_i'\right)\vec{r}_{12} \cdot \vec{r}_{13} \\
&\quad - 2e_i'\left(a_i' + d_i' + e_i'\right)\vec{r}_{12} \cdot \vec{r}_{14} + 2d_i'e_i'\vec{r}_{13} \cdot \vec{r}_{14}\Big]\left|\psi_i^{1234}\right\rangle,
\end{aligned}
\tag{2.20}
$$

$$
\begin{aligned}
\nabla^2_{\vec{r}_{13}} \left|\psi_i^{1234}\right\rangle &= \vec{\nabla}_{\vec{r}_{13}} \cdot \left[\left(-2\left(b_i' + d_i' + f_i'\right)\vec{r}_{13} + 2d_i'\vec{r}_{12} + 2f_i'\vec{r}_{14}\right)\left|\psi_i^{1234}\right\rangle\right], \\
&= -6\left(b_i' + d_i' + f_i'\right)\left|\psi_i^{1234}\right\rangle \\
&\quad + 4\Big[\left(b_i' + d_i' + f_i'\right)^2 r_{13}^2 + d_i'^2 r_{12}^2 + f_i'^2 r_{14}^2 - 2d_i'\left(b_i' + d_i' + f_i'\right)\vec{r}_{12} \cdot \vec{r}_{13} \\
&\quad - 2f_i'\left(b_i' + d_i' + f_i'\right)\vec{r}_{13} \cdot \vec{r}_{14} + 2d_i'f_i'\vec{r}_{12} \cdot \vec{r}_{14}\Big]\left|\psi_i^{1234}\right\rangle,
\end{aligned}
\tag{2.21}
$$

$$
\begin{aligned}
\nabla^2_{\vec{r}_{14}} \left|\psi_i^{1234}\right\rangle &= -6\left(c_i' + e_i' + f_i'\right)\left|\psi_i^{1234}\right\rangle + \left[\left(-2\left(c_i' + e_i' + f_i'\right)\vec{r}_{14} + 2e_i'\vec{r}_{12} + 2f_i'\vec{r}_{13}\right) \cdot \right. \\
&\quad \left.\left(-2\left(c_i' + e_i' + f_i'\right)\vec{r}_{14} + 2e_i'\vec{r}_{12} + 2f_i'\vec{r}_{13}\right)\right]\left|\psi_i^{1234}\right\rangle
\end{aligned}
\tag{2.22}
$$

As the kinetic energy term also involve the gradient terms like $\vec{\nabla}_{\vec{r}_{12}} \cdot \vec{\nabla}_{\vec{r}_{13}}$, $\vec{\nabla}_{\vec{r}_{12}} \cdot \vec{\nabla}_{\vec{r}_{14}}$, $\vec{\nabla}_{\vec{r}_{13}} \cdot \vec{\nabla}_{\vec{r}_{14}}$, the next task is to calculate these terms.

$$
\begin{aligned}
\vec{\nabla}_{\vec{r}_{12}} \cdot \vec{\nabla}_{\vec{r}_{13}} \left|\psi_i^{1234}\right\rangle &= \vec{\nabla}_{\vec{r}_{12}} \cdot \left[\left(-2\left(b_i' + d_i' + f_i'\right)\vec{r}_{13} + 2d_i'\vec{r}_{12} + 2f_i'\vec{r}_{14}\right)\left|\psi_i^{1234}\right\rangle\right] \\
&= \left[6d_i' + \left(-2\left(b_i' + d_i' + f_i'\right)\vec{r}_{13} + 2d_i'\vec{r}_{12} + 2f_i'\vec{r}_{14}\right) \cdot \left(-2\left(a_i' + d_i' + e_i'\right)\vec{r}_{12} + 2d_i'\vec{r}_{13} + 2e_i'\vec{r}_{14}\right)\right]\left|\psi_i^{1234}\right\rangle \\
&= \Big[6d_i' + 4\Big[-d_i'\left(a_i' + d_i' + e_i'\right)r_{12}^2 - d_i'\left(b_i' + d_i' + f_i'\right)r_{13}^2 + e_i'f_i'r_{14}^2 \\
&\quad \left[d_i'^2 + \left(b_i' + d_i' + f_i'\right)\left(a_i' + d_i' + e_i'\right)\right]\vec{r}_{12} \cdot \vec{r}_{13} + \left[d_i'f_i' - e_i'\left(b_i' + d_i' + f_i'\right)\right]\vec{r}_{13} \cdot \vec{r}_{14} \\
&\quad \left[d_i'e_i' - f_i'\left(a_i' + d_i' + e_i'\right)\right]\vec{r}_{12} \cdot \vec{r}_{14}\Big]\Big]\left|\psi_i^{1234}\right\rangle.
\end{aligned}
\tag{2.23}
$$

$$
\begin{aligned}
\vec{\nabla}_{\vec{r}_{12}} \cdot \vec{\nabla}_{\vec{r}_{14}} \left|\psi_i^{1234}\right\rangle &= \vec{\nabla}_{\vec{r}_{12}} \cdot \left[\left(-2\left(c_i'+e_i'+f_i'\right)\vec{r}_{14} + 2e_i'\vec{r}_{12} + 2f_i'\vec{r}_{13}\right)\left|\psi_i^{1234}\right\rangle\right] \\
&= \left[6e_i' + \left(-2\left(c_i'+e_i'+f_i'\right)\vec{r}_{14} + 2e_i'\vec{r}_{12} + 2f_i'\vec{r}_{13}\right)\cdot\left(-2\left(a_i'+d_i'+e_i'\right)\vec{r}_{12} + 2d_i'\vec{r}_{13} + 2e_i'\vec{r}_{14}\right)\right]\left|\psi_i^{1234}\right\rangle \\
&= \Big[6e_i' + 4\Big[-e_i'\left(a_i'+d_i'+e_i'\right)r_{12}^2 + d_i'f_i'r_{13}^2 - e_i'\left(c_i'+e_i'+f_i'\right)r_{14}^2 \\
&\quad \left[d_i'e_i' - f_i'\left(a_i'+d_i'+e_i'\right)\right]\vec{r}_{12}\cdot\vec{r}_{13} + \left[e_i'f_i' - d_i'\left(c_i'+e_i'+f_i'\right)\right]\vec{r}_{13}\cdot\vec{r}_{14} \\
&\quad \left[e_i'^2 + \left(a_i'+d_i'+e_i'\right)\left(c_i'+e_i'+f_i'\right)\right]\vec{r}_{12}\cdot\vec{r}_{14}\Big]\Big]\left|\psi_i^{1234}\right\rangle .
\end{aligned} \tag{2.24}
$$

$$
\begin{aligned}
\vec{\nabla}_{\vec{r}_{13}} \cdot \vec{\nabla}_{\vec{r}_{14}} \left|\psi_i^{1234}\right\rangle &= \vec{\nabla}_{\vec{r}_{13}} \cdot \left[\left(-2\left(c_i'+e_i'+f_i'\right)\vec{r}_{14} + 2e_i'\vec{r}_{12} + 2f_i'\vec{r}_{13}\right)\left|\psi_i^{1234}\right\rangle\right] \\
&= \left[6f_i' + \left(-2\left(c_i'+e_i'+f_i'\right)\vec{r}_{14} + 2e_i'\vec{r}_{12} + 2f_i'\vec{r}_{13}\right)\cdot\left(-2\left(b_i'+d_i'+f_i'\right)\vec{r}_{13} + 2d_i'\vec{r}_{12} + 2f_i'\vec{r}_{14}\right)\right]\left|\psi_i^{1234}\right\rangle \\
&= \Big[6f_i' + 4\Big[d_i'e_i'r_{12}^2 - f_i'\left(b_i'+d_i'+f_i'\right)r_{13}^2 - f_i'\left(c_i'+e_i'+f_i'\right)r_{14}^2 \\
&\quad \left[d_i'f_i' - e_i'\left(b_i'+d_i'+f_i'\right)\right]\vec{r}_{12}\cdot\vec{r}_{13} + \left[f_i'^2 + \left(b_i'+d_i'+f_i'\right)\left(c_i'+e_i'+f_i'\right)\right]\vec{r}_{13}\cdot\vec{r}_{14} \\
&\quad \left[e_i'f_i' - d_i'\left(c_i'+e_i'+f_i'\right)\right]\vec{r}_{12}\cdot\vec{r}_{14}\Big]\Big]\left|\psi_i^{1234}\right\rangle .
\end{aligned} \tag{2.25}
$$

Comment: All these terms agreed with the McGrath thesis [**31**] except the first term in the final expression of Eq. (2.25) where $6d_i'$ is written instead of $6f_i'$. To me it seems that it is just a typo as the expression based on these results given in first line of kinetic energy expression (c.f. Eq. (120) in [**31**]) is correct. The law of cosine will help us to simplify the dot products between different inter-particle displacements. For example, from Eq. (2.16), we can write

$$
\begin{aligned}
2\vec{r}_{12}\cdot\vec{r}_{13} &= r_{12}^2 + r_{13}^2 - r_{23}^2, \\
2\vec{r}_{12}\cdot\vec{r}_{14} &= r_{12}^2 + r_{14}^2 - r_{24}^2, \\
2\vec{r}_{13}\cdot\vec{r}_{14} &= r_{13}^2 + r_{14}^2 - r_{34}^2.
\end{aligned} \tag{2.26}
$$

In order to calculate the expression of $\hat{T}$, let's assemble the terms corresponding to different inter-particle distances i.e., r_{ij}^2.

Constant Terms:

$$
\begin{aligned}
-\frac{1}{2\mu_{12}}&\left[-6\left(a_i'+d_i'+e_i'\right) - 6\left(b_i'+d_i'+f_i'\right) - 6\left(c_i'+e_i'+f_i'\right)\right] - \frac{1}{m_1}\left[6d_i' + 6e_i' + 6f_i'\right] \\
&= -\frac{1}{2\mu_{12}}\left[-6\left(a_i'+b_i'+c_i'+2d_i'+2e_i'+2f_i'\right)\right] - \frac{1}{m_1}\left[6\left(d_i'+e_i'+f_i'\right)\right] \\
&= \frac{3}{\mu_{12}}\left(a_i'+b_i'+c_i'+2d_i'+2e_i'+2f_i'\right) - \frac{6}{m_1}\left(d_i'+e_i'+f_i'\right).
\end{aligned} \tag{2.27}
$$

$\mathbf{r_{12}^2}$ Terms: [Mathematica is used to simplify different terms]

$$
-\frac{2}{\mu_{12}}\left(a_i'^2 + a_i'd_i' - b_i'd_i' + a_i'e_i' - c_i'e_i'\right) - \frac{2}{m_1}\left(a_i'b_i' + a_i'c_i' - a_i'd_i' + b_i'd_i' - a_i'e_i' + c_i'e_i'\right).
$$

$\mathbf{r_{13}^2}$ Terms:

$$
-\frac{2}{\mu_{12}}\left(b_i'^2 - a_i'd_i' + b_i'd_i' + b_i'f_i' - c_i'f_i'\right) - \frac{2}{m_1}\left(a_i'b_i' + b_i'c_i' + a_i'd_i' - b_i'd_i' - b_i'f_i' + c_i'f_i'\right).
$$

$\mathbf{r_{14}^2}$ Terms:

$$
-\frac{2}{\mu_{12}}\left(c_i'^2 - a_i'e_i' + c_i'e_i' - b_i'f_i' + c_i'f_i'\right) - \frac{2}{m_1}\left(a_i'c_i' + b_i'c_i' + a_i'e_i' - c_i'e_i' + b_i'f_i' - c_i'f_i'\right).
$$

$\mathbf{r_{23}^2}$ Terms:

$$
-\frac{2}{\mu_{12}}\left(2d_i'^2 + a_i'd_i' + b_i'd_i' + d_i'e_i' + d_i'f_i' - e_i'f_i'\right) + \frac{2}{m_1}\left(2d_i'^2 + a_i'b_i' + a_i'd_i' + b_i'd_i' + d_i'e_i' + d_i'f_i' - e_i'f_i'\right).
$$

$\mathbf{r_{24}^2}$ Terms:

$$-\frac{2}{\mu_{12}}\left(2e_i'^2+a_i'e_i'+c_i'e_i'+d_i'e_i'-d_i'f_i'-e_i'f_i'\right)+\frac{2}{m_1}\left(2e_i'^2+a_i'c_i'+a_i'e_i'+c_i'e_i'+d_i'e_i'-d_i'f_i'-e_i'f_i'\right).$$

$\mathbf{r_{34}^2}$ **Terms:**

$$-\frac{2}{\mu_{12}}\left(2f_i'^2-d_i'e_i'+b_i'f_i'+c_i'f_i'+d_i'f_i'+e_i'f_i'\right)+\frac{2}{m_1}\left(2f_i'^2+b_i'c_i'-d_i'e_i'+b_i'f_i'+c_i'f_i'+d_i'f_i'+e_i'f_i'\right).$$

Finally, the expression for the average kinetic energy for the states $\left|\psi^{1234}\right\rangle$ becomes

$$\begin{aligned}
\left\langle\psi_i^{1234}\left|\hat{T}\right|\psi_j^{1234}\right\rangle=&\left[\frac{3}{\mu_{12}}\left(a_i'+b_i'+c_i'+2d_i'+2e_i'+2f_i'\right)-\frac{6}{m_1}\left(d_i'+e_i'+f_i'\right)\right]\left\langle\psi_i^{1234}\mid\psi_j^{1234}\right\rangle\\
&-2\left[\frac{1}{\mu_{12}}\left(a_i'^2+a_i'd_i'-b_i'd_i'+a_i'e_i'-c_i'e_i'\right)+\frac{1}{m_1}\left(a_i'b_i'+a_i'c_i'-a_i'd_i'+b_i'd_i'-a_i'e_i'+c_i'e_i'\right)\right]\left\langle r_{12}^2\right\rangle\\
&-2\left[\frac{1}{\mu_{12}}\left(b_i'^2-a_i'd_i'+b_i'd_i'+b_i'f_i'-c_i'f_i'\right)+\frac{1}{m_1}\left(a_i'b_i'+b_i'c_i'+a_i'd_i'-b_i'd_i'-b_i'f_i'+c_i'f_i'\right)\right]\left\langle r_{13}^2\right\rangle\\
&-2\left[\frac{1}{\mu_{12}}\left(c_i'^2-a_i'e_i'+c_i'e_i'-b_i'f_i'+c_i'f_i'\right)+\frac{1}{m_1}\left(a_i'c_i'+b_i'c_i'+a_i'e_i'-c_i'e_i'+b_i'f_i'-c_i'f_i'\right)\right]\left\langle r_{14}^2\right\rangle\\
&-2\left[\frac{1}{\mu_{12}}\left(2d_i'^2+a_i'd_i'+b_i'd_i'+d_i'e_i'+d_i'f_i'-e_i'f_i'\right)\right.\\
&\left.-\frac{1}{m_1}\left(2d_i'^2+a_i'b_i'+a_i'd_i'+b_i'd_i'+d_i'e_i'+d_i'f_i'-e_i'f_i'\right)\right]\left\langle r_{23}^2\right\rangle\\
&-2\left[\frac{1}{\mu_{12}}\left(2e_i'^2+a_i'e_i'+c_i'e_i'+d_i'e_i'-d_i'f_i'+e_i'f_i'\right)\right.\\
&\left.-\frac{1}{m_1}\left(2e_i'^2+a_i'c_i'+a_i'e_i'+c_i'e_i'+d_i'e_i'-d_i'f_i'+e_i'f_i'\right)\right]\left\langle r_{24}^2\right\rangle\\
&-2\left[\frac{1}{\mu_{12}}\left(2f_i'^2-d_i'e_i'+b_i'f_i'+c_i'f_i'+d_i'f_i'+e_i'f_i'\right)\right.\\
&\left.-\frac{1}{m_1}\left(2f_i'^2+b_i'c_i'-d_i'e_i'+b_i'f_i'+c_i'f_i'+d_i'f_i'+e_i'f_i'\right)\right]\left\langle r_{34}^2\right\rangle,
\end{aligned}\tag{2.28}$$

where $\left\langle r_{ij}^2\right\rangle=\left\langle\psi^{1234}\left|r_{ij}^2\right|\psi^{1234}\right\rangle$ correspond to the expectation value of the square of inter-particle distances.

Comment: We can see that under the limit $\mu_{12}\to m_1/2$ that is, when PsH become the Ps_2 the results given in the McGrath thesis [**31**] can be reproduced except one typo in the coefficient of $\left\langle r_{24}^2\right\rangle$ where the second term is $a_i'c_i'$ instead of $a_i'e_i'$ (c.f. Eq. (120) of [**31**]).

In order to find the exception values of the potential energy, we can write

$$\begin{aligned}
\left\langle\psi_i^{1234}\left|\hat{V}\right|\psi_j^{1234}\right\rangle=\alpha&\left[\left\langle\psi_i^{1234}\left|\frac{1}{r_{12}}\right|\psi_j^{1234}\right\rangle+\left\langle\psi_i^{1234}\left|\frac{1}{r_{34}}\right|\psi_j^{1234}\right\rangle-\left\langle\psi_i^{1234}\left|\frac{1}{r_{13}}\right|\psi_j^{1234}\right\rangle\right.\\
&\left.-\left\langle\psi_i^{1234}\left|\frac{1}{r_{14}}\right|\psi_j^{1234}\right\rangle-\left\langle\psi_i^{1234}\left|\frac{1}{r_{23}}\right|\psi_j^{1234}\right\rangle-\left\langle\psi_i^{1234}\left|\frac{1}{r_{24}}\right|\psi_j^{1234}\right\rangle\right].
\end{aligned}\tag{2.29}$$

In order to calculate different matrix elements, we need to calculate the Gaussian integrals. Let's solve them one by one and first consider

$$\left\langle\psi_i^{1234}\mid\psi_j^{1234}\right\rangle.$$

In the reference [**31**] it is shown that going from Lab. coordinates $\vec{A}_i$ to the relative coordinates, the Jacobian for the transformation is equal to 1. This is actually a two step process, where at the first step, we shift from Lab. to centre of mass coordinates and then from centre of mass to the relative coordinates.

Just for the simplicity, we will remove the indices of $a'_i \cdots f'_i$. Consider

$$\begin{aligned}\left\langle \psi_i^{1234} \mid \psi_j^{1234} \right\rangle &= I\left(a', b', c', d', e', f', \right) \\ &= \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \exp\left(-a' r_{12}^2 - b' r_{13}^2 - c' r_{14}^2 - d' r_{23}^2 - e' r_{24}^2 - f' r_{34}^2\right). \end{aligned} \tag{2.30}$$

In order to evaluate these integrals first consider the coordinate shift

$$\begin{aligned}\vec{r}_{12} &= \vec{x} + \alpha_1 \vec{y} + \alpha_2 \vec{z}, \\ \vec{r}_{13} &= \vec{y} + \alpha_3 \vec{z}, \\ \vec{r}_{14} &= \vec{z}.\end{aligned} \tag{2.31}$$

Again the Jacobian corresponding to these transformations is unit and the α_1, α_2 and α_3 are the constants and these will be determined later.

$$\begin{aligned}\vec{r}_{23} &= \vec{r}_{13} - \vec{r}_{12} = -\vec{x} + (1-\alpha_1)\vec{y} + (\alpha_3 - \alpha_2)\vec{z}, \\ \vec{r}_{24} &= \vec{r}_{14} - \vec{r}_{12} = -\vec{x} - \alpha_1 \vec{y} + (1-\alpha_2)\vec{z}, \\ \vec{r}_{34} &= \vec{r}_{14} - \vec{r}_{13} = -\vec{y} + (1-\alpha_3)\vec{z}.\end{aligned} \tag{2.32}$$

In these coordinates

$$\begin{aligned}-a' r_{12}^2 &= -a' \left(\vec{x} + \alpha_1 \vec{y} + \alpha_2 \vec{z}\right)^2 = -a'\left(x^2 + \alpha_1^2 y^2 + \alpha_2^2 z^2 + 2\alpha_1 \vec{x}\cdot\vec{y} + 2\alpha_2 \vec{x}\cdot\vec{z} + 2\alpha_1\alpha_2 \vec{y}\cdot\vec{z}\right), \\ -b' r_{13}^2 &= -b'\left(\vec{y} + \alpha_3 \vec{z}\right)^2 = -b'\left(y^2 + \alpha_3^2 z^2 + 2\alpha_3 \vec{y}\cdot\vec{z}\right), \\ -c' r_{14}^2 &= -c'\left(\vec{z}\right)^2 = -c' z^2, \\ -d' r_{23}^2 &= -d'\left(-\vec{x} + (1-\alpha_1)\vec{y} + (\alpha_3-\alpha_2)\vec{z}\right)^2 = -d'\Big[x^2 + (1-\alpha_1)^2 y^2 + (\alpha_3-\alpha_2)^2 z^2 - 2(1-\alpha_1)\vec{x}\cdot\vec{y} \\ &\quad -2(\alpha_3-\alpha_2)\vec{x}\cdot\vec{z} + 2(1-\alpha_1)(\alpha_3-\alpha_2)\vec{y}\cdot\vec{z}\Big], \\ -e' r_{24}^2 &= -e'\left(-\vec{x} - \alpha_1\vec{y} + (1-\alpha_2)\vec{z}\right)^2 = -e'\Big[x^2 + \alpha_1^2 y^2 + (1-\alpha_2)^2 z^2 + 2\alpha_1 \vec{x}\cdot\vec{y} \\ &\quad -2(1-\alpha_2)\vec{x}\cdot\vec{z} - 2\alpha_1(1-\alpha_2)\vec{y}\cdot\vec{z}\Big], \\ -f' r_{34}^2 &= -f'\left(-\vec{y} + (1-\alpha_3)\vec{z}\right)^2 = -f'\left[y^2 + (1-\alpha_3)^2 z^2 - 2(1-\alpha_3)\vec{y}\cdot\vec{z}\right].\end{aligned} \tag{2.33}$$

In line with reference [**31**], let's put $\alpha_4 = 1-\alpha_2$, $\alpha_5 = 1-\alpha_3$, $\alpha_3 - \alpha_2 = \alpha_4 - \alpha_5$ and collect the coefficients of different dot products in Eq. (2.33) set them equal to zero as it will not lose the generality.

$$\begin{aligned}(\vec{x}\cdot\vec{y})\left[-2a'\alpha_1 + 2d'(1-\alpha_1) - 2e'\alpha_1\right] &= 0, \\ (\vec{x}\cdot\vec{z})\left[-2a'(1-\alpha_4) + 2d'(\alpha_4-\alpha_5) + 2e'\alpha_4\right] &= 0, \\ (\vec{y}\cdot\vec{z})\left[-2a'\alpha_1(1-\alpha_4) - 2b'(1-\alpha_5) - 2d'(1-\alpha_1)(\alpha_4-\alpha_5) + 2e'\alpha_1\alpha_4 + 2f'\alpha_5\right] &= 0.\end{aligned} \tag{2.34}$$

Solving the equation in (2.34), for α_1, α_4 and α_5 gives

$$\alpha_1\left(a' + d' + e'\right) = d, \implies \alpha_1 = \frac{d'}{a'+d'+e'}. \tag{2.35}$$

From second line of Eq. (2.34)

$$\begin{aligned}-\left(a'+d'+e'\right)\alpha_4 &= -d'\left(\alpha_5 + \frac{a'}{d'}\right), \\ \alpha_4 \equiv 1-\alpha_2 &= \frac{d'}{a'+d'+e'}\left(\alpha_5 + \frac{a'}{d'}\right), \\ &= \alpha_1\left(\alpha_5 + \frac{a'}{d'}\right).F_2\left(a', b', c', d', e', f'\right)\end{aligned} \tag{2.36}$$

Using Eqs. (2.35) and (2.36) in Eq. (2.34) and solving for α_5 gives

$$\alpha_5 \equiv 1-\alpha_3 = \frac{b'd' + 2\alpha_1 a'd' - \alpha_1^2 a' \left(a'+d'+e'\right)}{d'\left(b'+d'+f'-2d'\alpha_1 + \alpha_1^2\left(a'+d'+e'\right)\right)},$$

and using $a'+d'+e' = \frac{d'}{\alpha_1}$, we get

$$\begin{aligned}\alpha_5 &= \frac{b'd' + 2\alpha_1 a'd' - \alpha_1 a'd'}{d'\left(b'+d'+f'-2d'\alpha_1+\alpha_1 d'\right)},\\ &= \frac{\alpha_1 a' + b'}{\left(b'+d'+f'-d'\alpha_1\right)}.\end{aligned} \tag{2.37}$$

Hence, from Eq. (2.33), we can write

$$\begin{aligned}-a'r_{12}^2 - \ldots - f'r_{34}^2 &= -a'\left(x^2+\alpha_1^2 y^2+\alpha_2^2 z^2\right) - b'\left(y^2+\alpha_3^2 z^2\right) - c'z^2\\ &- d'\left(x^2 + \left(1-\alpha_1\right)^2 y^2 + \left(\alpha_3-\alpha_2\right)^2 z^2\right)\\ &- e'\left(x^2+\alpha_1^2 y^2 + \left(1-\alpha_2\right)^2 z^2\right)\\ &- f'\left(y^2 + \left(1-\alpha_3\right)^2 z^2\right)\\ &= -x^2\left(a'+d'+e'\right) - y^2\left(a'\alpha_1^2 + b' + d'\left(1-\alpha_1\right)^2 + e'\alpha_1^2 + f'\right)\\ &- z^2\left(a'\alpha_2^2 + b'\alpha_3^2 + c' + d'\left(\alpha_3-\alpha_2\right)^2 + e'\left(1-\alpha_2\right)^2 + f\left(1-\alpha_3\right)^2\right).\end{aligned} \tag{2.38}$$

Let's solve the different coefficients one by one.

$$\begin{aligned}&x^2: \left(a'+d'+e'\right) = \alpha_x\\ &y^2: \left(a'\alpha_1^2 + b' + d'\left(1-\alpha_1\right)^2 + e'\alpha_1^2 + f'\right) = \alpha_1^2\left(a'+d'+e'\right) + b'+d'+f' - 2\alpha_1 d'\\ &\quad = \frac{d'^2}{\left(a'+d'+e'\right)^2}\left(a'+d'+e'\right) + b'+d'+f' - 2\frac{d'^2}{\left(a'+d'+e'\right)}\\ &\quad = \frac{\left(b'+d'+f'\right)\left(a'+d'+e'\right) - d'^2}{\left(a'+d'+e'\right)} = \frac{F_2\left(a',b',c',d',e',f'\right)}{\alpha_x} \equiv \alpha_y\\ &z^2: \left(a'\alpha_2^2 + b'\alpha_3^2 + c' + d'\left(\alpha_3-\alpha_2\right)^2 + e'\left(1-\alpha_2\right)^2 + f'\left(1-\alpha_3\right)^2\right)\\ &\quad = \left(a'\left(1-\alpha_4\right)^2 + b'\left(1-\alpha_5\right)^2 + c' + d'\left(\alpha_4-\alpha_5\right)^2 + e'\alpha_4^2 + f'\alpha_5^2\right)\\ &\quad = \left(\alpha_4^2\left(a+d+e\right) + \alpha_5^2\left(b+d+f\right) + a+b+c - 2a\alpha_4 - 2b\alpha_5 - 2d\alpha_4\alpha_5\right)\\ &\quad = \left(\alpha_1\left(\alpha_5+\frac{a'}{d'}\right)^2 d' + \alpha_5^2\left(b'+d'+f'\right) + a'+b'+c' - 2a'\alpha_1\left(\alpha_5+\frac{a'}{d'}\right) - 2b\alpha_5 - 2d\alpha_1\left(\alpha_5+\frac{a}{d}\right)\alpha_5\right)\end{aligned} \tag{2.39}$$

$$\quad = \frac{F_1\left(a',b',c',d',e',f'\right)}{F_2\left(a',b',c',d',e',f'\right)} \equiv \alpha_z,$$

where

$$\begin{aligned}F_1\left(a',b',c',d',e',f'\right) &= a'b'c' + a'b'e' + a'b'f' + a'c'd' + a'd'e' + a'c'f' + a'd'f' + a'e'f'\\ &+ b'c'd' + b'c'e' + b'd'e' + b'd'f' + b'e'f' + c'd'e' + c'd'f' + c'e'f',\end{aligned} \tag{2.40}$$

and

$$\begin{aligned}F_2\left(a',b',c',d',e',f'\right) &= \left(b'+d'+f'\right)\left(a'+d'+e'\right) - d'^2\\ &= a'b' + a'd' + a'f' + b'd' + b'e' + d'e' + d'f' + e'f'.\end{aligned} \tag{2.41}$$

Thus,

$$-a'r_{12}^2 - \ldots - f'r_{34}^2 = -\alpha_x x^2 - \alpha_y y^2 - \alpha_z z^2. \tag{2.42}$$

2.2.1 Matrix Elements

Overlap Integral

From Eq. (2.30), we can write

$$\begin{aligned}
I\left(a', b', c', d', e', f'\right) &= \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \exp\left(-a'r_{12}^2 - b'r_{13}^2 - c'r_{14}^2 - d'r_{23}^2 - e'r_{24}^2 - f'r_{34}^2\right), \\
I\left(\alpha_x, \alpha_y, \alpha_z\right) &= \int d^3\vec{x} d^3\vec{y} d^3\vec{z} \exp\left(-\alpha_x x^2 - \alpha_y y^2 - \alpha_z z^2\right), \\
&= \int d^3\vec{x} \exp\left(-\alpha_x x^2\right) \int d^3\vec{y} \exp\left(-\alpha_y y^2\right) \int d^3\vec{z} \exp\left(-\alpha_z z^2\right), \\
I\left(\alpha_x, \alpha_y, \alpha_z\right) &= \frac{\pi^{9/2}}{\left(\alpha_x \alpha_y \alpha_z\right)^{3/2}} \because \int dx \exp\left(-\gamma x^2\right) = \frac{1}{2}\sqrt{\frac{\pi}{\gamma}}, \\
&= \frac{\pi^{9/2}}{\left[F_1\left(a', b', c', d', e', f'\right)\right]^{3/2}}.
\end{aligned} \tag{2.43}$$

This is one of the overlap matrix. We know that the full over lap matrix element has four terms as there is a symmetry between the last two indices. Therefore, the four matrix elements can be obtained by using the permutation symmetry i.e., swapping the different parameters.the four matrix elements can be obtained by using the permutation symmetry i.e., swapping the different parameters. To be more specific, these are summarized here

$$I_1\left(a', b', c', d', e', f'\right) = \left\langle \psi_i^{1234} \mid \psi_j^{1234} \right\rangle = \frac{\pi^{9/2}}{\left[F_1\left(a', b', c', d', e', f'\right)\right]^{3/2}} \tag{2.44}$$

where $a' = a_i' + a_j',\ b' = b_i' + b_j',\ c' = c_i' + c_j',\ d' = d_i' + d_j',\ e' = e_i' + e''_j,\ f' = f_i' + f_j'$.

$$I_2\left(a', b', c', d', e', f'\right) = \left\langle \psi_i^{1243} \mid \psi_j^{1243} \right\rangle = \frac{\pi^{9/2}}{\left[F_1\left(a', b', c', d', e', f'\right)\right]^{3/2}} \tag{2.45}$$

Again, $a' = a_i' + a_j',\ b' = b_i' + b_j',\ c' = c_i' + c_j',\ d' = d_i' + d'^{j,\ e'=e_i'+e''_j,\ f'=f_i'+f_j'}$. Now the cross term

$$I_3\left(a', b', c', d', e', f'\right) = \left\langle \psi_i^{1234} \mid \psi_j^{1243} \right\rangle = \frac{\pi^{9/2}}{\left[F_1\left(a', b', c', d', e', f'\right)\right]^{3/2}} \tag{2.46}$$

where in this case, $a' = a_i' + a_j',\ b' = b_i' + c_j',\ c' = c_i' + b_j',\ d' = d_i' + e''_j,\ e' = e_i' + d_j',\ f' = f_i' + f_j'$. Similarly

$$I_4\left(a', b', c', d', e', f'\right) = \left\langle \psi_i^{1243} \mid \psi_j^{1234} \right\rangle = \frac{\pi^{9/2}}{\left[F_1\left(a', b', c', d', e', f'\right)\right]^{3/2}} \tag{2.47}$$

with the arguments of F_1 in this case can be obtained by interchanging the indices $i \leftrightarrow j$ in the subscripts of Eq. (2.46) i.e,. $a' = a_i' + a_j',\ b' = b_j' + c_i',\ c' = c_j' + b_i',\ d' = d_j' + e_i',\ e' = e_j' + d_i',\ f' = f_i' + f_j'$.

2.2.2 Coulomb Potential

$\left\langle \psi_i^{1234} \middle| \hat{V} \middle| \psi_j^{1234} \right\rangle$

Just like above, we will work out with matrix elements with one of the wave functions, say $\left\langle \psi_i^{1234} \middle| \hat{V} \middle| \psi_j^{1234} \right\rangle$ and calculate different terms given in Eq. (2.29). The other three terms that correspond to the permutation can be calculated just by swapping the parameters as we did in Eqs. (2.44-2.47). Consider the potential energy term between proton-electron $(p^+ - e^-)$

$$V_{14}\left(a',b',c',d',e',f'\right) = \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\frac{1}{r_{14}}\exp\left(-a'r_{12}^2 - b'r_{13}^2 - c'r_{14}^2 - d'r_{23}^2 - e'r_{24}^2 - f'r_{34}^2\right),$$

where

$$a' = a_i' + a_j',\ b' = b_i' + b_j',\ c' = c_i' + c_j',\ d' = d_i' + d_j',\ e' = e_i' + e_j',\ f = f_i' + f_j'. \tag{2.48}$$

This becomes

$$\begin{aligned} V_{14}\left(\alpha_x,\alpha_y,\alpha_z\right) &= \int d^3\vec{x}d^3\vec{y}d^3\vec{z}\left(\frac{1}{z}\right)\exp\left(-\alpha_x x^2 - \alpha_y y^2 - \alpha_z z^2\right), \\ &= \frac{\pi^3}{\left(\alpha_x\alpha_y\right)^{3/2}}\int d^3\vec{z}\left(\frac{1}{z}\right)\exp\left(-\alpha_z z^2\right), \\ &= \frac{\pi^3}{\left(\alpha_x\alpha_y\right)^{3/2}}\int_0^\infty F_1\left(a',b',c',d',e',f'\right)y4\pi z\exp\left(-\alpha_z z^2\right), \\ &= \frac{4\pi^4}{\left(\alpha_x\alpha_y\right)^{3/2}}\times\frac{1}{2\alpha_z}, \\ V_{14}\left(a',b',c',d',e',f'\right) &= \frac{2\pi^4}{F_1\left(a',b',c',d',e',f'\right)\left[F_2\left(a',b',c',d',e',f'\right)\right]^{1/2}}, \\ V_{14}\left(a',b',c',d',e',f'\right) &= \frac{2\pi^{9/2}}{\sqrt{\pi}F_1\left(a',b',c',d',e',f'\right)\left[F_2\left(a',b',c',d',e',f'\right)\right]^{1/2}} \end{aligned} \tag{2.49}$$

where we have multiplied and divided by $\sqrt{\pi}$. This is due to the fact that when we divide the expectation values with over-lap factor, this common factor cancels.

Now for proton-positron $(p^+ - e^+)$

$$V_{12}\left(a',b',c',d',e',f'\right) = \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\frac{1}{r_{12}}\exp\left(-a'r_{12}^2 - b'r_{13}^2 - c'r_{14}^2 - d'r_{23}^2 - e'r_{24}^2 - f'r_{34}^2\right)$$

Let's try to express it interms of the $V_{14}\left(a',b',c',d',e',f'\right)$ by swaping the parameters/indices. We use the bold indices just to specify what is needed to be interchanged.

$$\begin{aligned} V_{12}\left(\mathbf{a}',b',\mathbf{c}',\mathbf{d}',e',\mathbf{f}'\right) &= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\frac{1}{r_{12}}\exp\left(-\mathbf{a}'r_{12}^2 - b'r_{13}^2 - \mathbf{c}'r_{14}^2 - \mathbf{d}'r_{23}^2 - e'r_{24}^2 - \mathbf{f}'r_{34}^2\right) \\ &= \int d^3\vec{r}_{14}d^3\vec{r}_{13}d^3\vec{r}_{12}\frac{1}{r_{14}}\exp\left(-\mathbf{a}'r_{14}^2 - b'r_{13}^2 - \mathbf{c}'r_{12}^2 - \mathbf{d}'r_{34}^2 - e'r_{24}^2 - \mathbf{f}'r_{23}^2\right),\ 2\leftrightarrow 4 \\ &= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\frac{1}{r_{14}}\exp\left(-\mathbf{c}'r_{12}^2 - b'r_{13}^2 - \mathbf{a}'r_{14}^2 - \mathbf{f}'r_{23}^2 - e'r_{24}^2 - \mathbf{d}'r_{34}^2\right) \\ &\equiv V_{14}\left(\mathbf{c}',b',\mathbf{a}',\mathbf{f}',e',\mathbf{d}'\right). \end{aligned} \tag{2.50}$$

where coefficients $a_i',\cdots,f_i'$ are given in Eq. (2.48). The potential energy between proton-(second) electron $(p^+ - e^-)$

$$\begin{aligned} V_{13}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\frac{1}{r_{13}}\exp\left(-a'r_{12}^2 - \mathbf{b}'r_{13}^2 - \mathbf{c}'r_{14}^2 - \mathbf{d}'r_{23}^2 - \mathbf{e}'r_{24}^2 - f'r_{34}^2\right) \\ &= \int d^3\vec{r}_{12}d^3\vec{r}_{14}d^3\vec{r}_{13}\frac{1}{r_{14}}\exp\left(-a'r_{12}^2 - \mathbf{b}'r_{14}^2 - \mathbf{c}'r_{13}^2 - \mathbf{d}'r_{24}^2 - \mathbf{e}'r_{23}^2 - f'r_{34}^2\right),\ 3\leftrightarrow 4 \\ &= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\frac{1}{r_{14}}\exp\left(-a'r_{12}^2 - \mathbf{c}'r_{13}^2 - \mathbf{b}'r_{14}^2 - \mathbf{e}'r_{23}^2 - \mathbf{d}'r_{24}^2 - f'r_{34}^2\right) \\ &\equiv V_{14}\left(a',\mathbf{c}',\mathbf{b}',\mathbf{e}',\mathbf{d}',f'\right), \end{aligned} \tag{2.51}$$

i.e., the elements $2\leftrightarrow 3$ and $4\leftrightarrow 5$ interchanged in the result of Eq. (2.49). The coulomb interaction between positron-electron $(e^+ - e^-)$

$$V_{23}(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f') = V_{13}(a', \mathbf{d}', \mathbf{e}', \mathbf{b}', \mathbf{c}', f') = V_{14}(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'). \tag{2.52}$$

i.e. in the first step we have changed $1 \leftrightarrow 2$ in the expression (c.f. Eq. (2.51) line one) and then $1 \leftrightarrow 2$, $3 \leftrightarrow 4$ in the result to relate it to V_{14}. Similarly for positron-(second) electron $(e^+ - e^-)$

$$V_{24}(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f') = V_{23}(a', \mathbf{c}', \mathbf{b}', \mathbf{e}', \mathbf{d}', f') = V_{14}(a', \mathbf{d}', \mathbf{e}', \mathbf{b}', \mathbf{c}', f') \tag{2.53}$$

This can be obtained from V_{23} by swapping $3 \leftrightarrow 4$ in Eq. (2.52).

Now the final task is to obtained the matrix elements for $\left\langle \psi_i^{1234} \left| V_{34} \right| \psi_j^{1234} \right\rangle$ i.e., the Coulomb interaction term between two electrons $(e^- - e^-)$

$$\begin{aligned} V_{34}(\mathbf{a}', \mathbf{b},' \mathbf{c}', \mathbf{d}', \mathbf{e}', \mathbf{f}') &= \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \frac{1}{r_{34}} \exp\left(-\mathbf{a}' r_{12}^2 - \mathbf{b}' r_{13}^2 - \mathbf{c}' r_{14}^2 - \mathbf{d}' r_{23}^2 - \mathbf{e}' r_{24}^2 - \mathbf{f}' r_{34}^2\right) \\ &= \int d^3\vec{r}_{13} d^3\vec{r}_{12} d^3\vec{r}_{14} \frac{1}{r_{24}} \exp\left(-\mathbf{a}' r_{13}^2 - \mathbf{b}' r_{12}^2 - \mathbf{c}' r_{14}^2 - \mathbf{d}' r_{23}^2 - \mathbf{e}' r_{34}^2 - \mathbf{f}' r_{24}^2\right), \ 2 \leftrightarrow 3 \\ &= V_{24}(\mathbf{b}', \mathbf{a}', \mathbf{c}', \mathbf{d}', \mathbf{f}', \mathbf{e}'), \end{aligned} \tag{2.54}$$

and from Eq. (2.53), we get

$$V_{34}(\mathbf{a}', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', \mathbf{f}') = V_{14}(\mathbf{b}', \mathbf{d}', \mathbf{f}', \mathbf{a}', \mathbf{c},' \mathbf{e}') \tag{2.55}$$

In Eqs. (2.49 - 2.55) the definition of $a', \cdots, f'$ is the one given in Eq. (2.48) and the bold indices are the same as unbold.

$\left\langle \psi^{1243} \left| \hat{V} \right| \psi^{1243} \right\rangle$

From Eq. (2.45), we can see that these matrix elements can be written in terms of the $\left\langle \psi_i^{1234} \left| \hat{V} \right| \psi_j^{1234} \right\rangle$ by interchange $b \leftrightarrow c$ and $d \leftrightarrow e$.

$$\begin{aligned} V_{14}^{1243}(a', b', c', d', e', f') &= V_{14}^{1234}(a', c', b', e', d', f'), \\ V_{12}^{1243}(\mathbf{a}', b', \mathbf{c}', \mathbf{d}', e', \mathbf{f}') &= V_{12}^{1234}(\mathbf{a}', \mathbf{c}', b', \mathbf{e}', d', \mathbf{f}'), \\ V_{13}^{1243}(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f') &= V_{13}^{1234}(a', \mathbf{c}', \mathbf{b}', \mathbf{e}', \mathbf{d}', f'), \\ V_{23}^{1243}(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f') &= V_{23}^{1234}(a', \mathbf{c}', \mathbf{b}', \mathbf{e}', \mathbf{d}', f'), \\ V_{24}^{1243}(a', \mathbf{b}', \mathbf{c}', \mathbf{d},' \mathbf{e}', f') &= V_{24}^{1234}(a', \mathbf{c}', \mathbf{b}', \mathbf{e}', \mathbf{d}', f'), \\ V_{34}^{1243}(\mathbf{a}', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', \mathbf{f}') &= V_{34}^{1234}(\mathbf{a}', \mathbf{c}', \mathbf{b}', \mathbf{e}', \mathbf{d}', \mathbf{f}') \end{aligned} \tag{2.56}$$

where in Eqs. (2.56) the definition of $a', \cdots f'$ is the one given in Eq. (2.48).

$\left\langle \psi_i^{1234} \middle| \hat{V} \middle| \psi_j^{1243} \right\rangle$

The goal here is the calculate the cross terms i.e. $\left\langle \psi_i^{1234} \middle| \hat{V} \middle| \psi_j^{1243} \right\rangle$,

$$\begin{aligned}
V_{14}^{1234(43)}\left(a', b', c', d', e', f'\right) &= V_{14}^{1234}\left(a', b', c', d', e', f'\right), \\
V_{12}^{1234(43)}\left(\mathbf{a}', b', \mathbf{c}', \mathbf{d}', e', \mathbf{f}'\right) &= V_{12}^{1234}\left(\mathbf{a}', b', \mathbf{c}', \mathbf{d}', e', \mathbf{f}'\right), \\
V_{13}^{1234(43)}\left(a, \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) &= V_{13}^{1234}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right), \\
V_{23}^{1234(43)}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) &= V_{23}^{1234}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right), \\
V_{24}^{1234(43)}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) &= V_{24}^{1234}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right), \\
V_{34}^{1234(43)}\left(\mathbf{a}', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', \mathbf{f}'\right) &= V_{34}^{1234}\left(\mathbf{a}', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', \mathbf{f}'\right),
\end{aligned} \tag{2.57}$$

where, in this case the definition of $a_i', \cdots f_i'$ is

$$a' = a_i' + a_j',\ b' = b_i' + c_j',\ c' = c_i' + b_j',\ d' = d + e''_j,\ e' = e_i' + d_j',\ f' = f_i' + f_j'. \tag{2.58}$$

$\left\langle \psi^{1243} \middle| \hat{V} \middle| \psi^{1234} \right\rangle$

$$\begin{aligned}
V_{14}^{1243(34)}\left(a', b', c', d', e', f'\right) &= V_{14}^{1234}\left(a', b', c', d', e', f'\right), \\
V_{12}^{1243(34)}\left(\mathbf{a}', b', \mathbf{c}', \mathbf{d}', e', \mathbf{f}'\right) &= V_{12}^{1234}\left(\mathbf{a}', b', \mathbf{c}', \mathbf{d}', e', \mathbf{f}'\right), \\
V_{13}^{1243(34)}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) &= V_{13}^{1234}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right), \\
V_{23}^{1243(34)}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) &= V_{23}^{1234}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f\right), \\
V_{24}^{1243(34)}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) &= V_{24}^{1234}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right), \\
V_{34}^{1243(34)}\left(\mathbf{a}', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', \mathbf{f}'\right) &= V_{34}^{1234}\left(\mathbf{a}', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', \mathbf{f}'\right),
\end{aligned} \tag{2.59}$$

where in this case

$$a' = a_i' + a_j',\ b' = b_j' + c_i',\ c' = c_j' + b_i',\ d' = d_j' + e_i',\ e' = e''_j + d_i',\ f' = f_i' + f_j'. \tag{2.60}$$

2.2.3 Inter Particle Distances

In order to calculate the inter particle distances, we have to calculate the matrix elements of the type

$$\langle r_{ab} \rangle = \left\langle \psi_j^{1234} \left| \hat{r}_{ab} \right| \psi_i^{1234} \right\rangle .$$

Again, we will start with r_{14} and write the others in terms of it

$$\begin{aligned}
\langle r_{14} \rangle &= \left\langle \psi_j^{1234} \left| \hat{r}_{14} \right| \psi_i^{1234} \right\rangle \\
&= \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} r_{14} \exp\left(-a' r_{12}^2 - b' r_{13}^2 - c' r_{14}^2 - d' r_{23}^2 - e' r_{24}^2 - f' r_{34}^2\right), \\
&= \int d^3\vec{x} \exp\left(-\alpha_x x^2\right) \int d^3\vec{y} \exp\left(-\alpha_y y^2\right) \int d^3\vec{z}\,(z) \exp\left(-\alpha_z z^2\right), \\
&= 2\pi^{9/2} \frac{\left[F_2\left(a', b', c', d', e', f'\right)\right]^{1/2}}{\sqrt{\pi}\left[F_1\left(a', b', c', d', e', f'\right)\right]^2} \equiv \langle r_{14} \rangle \left(a', b', c', d', e', f'\right).
\end{aligned} \tag{2.61}$$

Similarly, using the scheme as did for the calculation of potential energy, we have

$$\begin{aligned}
\langle r_{12}\rangle\left(a',b',c',d',e',f'\right) &= \langle r_{14}\rangle\left(c',b',a',f',e',d'\right),\\
\langle r_{13}\rangle\left(a',b',c',d',e',f'\right) &= \langle r_{14}\rangle\left(a',c',b',e',d',f'\right),\\
\langle r_{23}\rangle\left(a',b',c',d',e',f'\right) &= \langle r_{14}\rangle\left(a',e',d',c',b',f'\right),\\
\langle r_{24}\rangle\left(a',b',c',d',e',f'\right) &= \langle r_{14}\rangle\left(a',d',e',b',c',f'\right),\\
\langle r_{34}\rangle\left(a',b',c',d',e',f'\right) &= \langle r_{14}\rangle\left(b',d',f',a',c',e'\right).
\end{aligned} \tag{2.62}$$

The definition of $a, \cdots, f$ is the one given in Eq. (2.48). The matrix elements for the other states can also be calculated in the similar fashion to exhaust all the permutations.

Matrix elements for inverse Square of Inter-particle distances

Here we will calculate the matrix elements for the inverse square of the inter-particle distances, i.e., the matrix elements of the type $\left\langle \psi_j^{1234} \middle| \frac{1}{r_{ab}^2} \middle| \psi_i^{1234} \right\rangle$. To do it, let us follow our old foot-steps

$$\left\langle \psi_j^{1234} \middle| \frac{1}{r_{14}^2} \middle| \psi_i^{1234} \right\rangle = \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \left(r_{14}^2\right) \exp\left(-a'r_{12}^2 - b'r_{13}^2 - c'r_{14}^2 - d'r_{23}^2 - e'r_{24}^2 - f'r_{34}^2\right)$$

which in terms of $(\vec{x}, \vec{y}, \vec{z})$ and following the procedure of Eq. (2.49), we have

$$\begin{aligned}
\left\langle \frac{1}{r_{14}^2} \right\rangle (a,b,c,d,e,f) &= \int d^3\vec{x} d^3\vec{y} d^3\vec{z} \left(\frac{1}{z^2}\right) \exp\left(-\alpha_x x^2 - \alpha_y y^2 - \alpha_z z^2\right)\\
&= \frac{4\pi^4}{\left(\alpha_x \alpha_y\right)^{3/2}} \int dz \exp\left(-\alpha_z z^2\right)\\
&= \frac{2\pi^{9/2}}{F_2\left(a',b',c',d',e',f'\right)\left[F_1\left(a',b',c',d',e',f'\right)\right]^{1/2}}.
\end{aligned} \tag{2.63}$$

Likewise, the others can be expressed in terms of above matrix elements as

$$\begin{aligned}
\left\langle \frac{1}{r_{12}^2} \right\rangle \left(a',b',c',d',e',f'\right) &= \left\langle \frac{1}{r_{14}^2} \right\rangle \left(c',b',a',f',e',d'\right),\\
\left\langle \frac{1}{r_{13}^2} \right\rangle \left(a',b',c',d',e',f'\right) &= \left\langle \frac{1}{r_{14}^2} \right\rangle \left(a',c',b',e',d',f'\right),\\
\left\langle \frac{1}{r_{23}^2} \right\rangle \left(a',b',c',d',e',f'\right) &= \left\langle \frac{1}{r_{14}^2} \right\rangle \left(a',e',d',c',b',f'\right),\\
\left\langle \frac{1}{r_{24}^2} \right\rangle \left(a',b',c',d',e',f'\right) &= \left\langle \frac{1}{r_{14}^2} \right\rangle \left(a',d',e',b',c',f'\right),\\
\left\langle \frac{1}{r_{34}^2} \right\rangle \left(a',b',c',d',e',f'\right) &= \left\langle \frac{1}{r_{14}^2} \right\rangle \left(b',d',f',a',c',e'\right).
\end{aligned} \tag{2.64}$$

The definition of $a', \cdots, f'$ is the one given in Eq. (2.48). The matrix elements for the other states can also be calculated in the similar fashion to exhaust all the permutations which is just the swapping of parameters.

Kinetic Energy matrix elements

$\left\langle \psi_i^{1234} \left| T \right| \psi_j^{1234} \right\rangle$

In order to do so, first let us calculate

$$\left\langle r_{14}^2 \right\rangle \left(a',b',c',d',e',f'\right) = \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \left(r_{14}^2\right) \exp\left(-a'r_{12}^2 - b'r_{13}^2 - c'r_{14}^2 - d'r_{23}^2 - e'r_{24}^2 - f'r_{34}^2\right), \tag{2.65}$$

which in terms of $(\vec{x}, \vec{y}, \vec{z})$ and following the procedure of Eq. (2.49), we have

$$\begin{aligned}
\left\langle r_{14}^2 \right\rangle (a', b', c', d', e', f') &= \int d^3\vec{x} d^3\vec{y} d^3\vec{z} \left(z^2\right) \exp\left(-\alpha_x x^2 - \alpha_y y^2 - \alpha_z z^2\right) \\
&= \frac{\pi^3}{\left(\alpha_x \alpha_y\right)^{3/2}} \int d^3\vec{z} \left(z^2\right) \exp\left(-\alpha_z z^2\right) \\
&= \frac{4\pi^4}{\left(\alpha_x \alpha_y\right)^{3/2}} \int dz\, z^4 \exp\left(-\alpha_z z^2\right).
\end{aligned} \tag{2.66}$$

We know that

$$\begin{aligned}
\int dx e^{-ax^2} &= \frac{1}{2}\sqrt{\frac{\pi}{a}} \\
\frac{d}{da}\int dx e^{-ax^2} &= \int dx x^2 e^{-ax^2} = \frac{1}{4}\frac{\sqrt{\pi}}{a^{3/2}} \\
\frac{d}{da}\int dx x^2 e^{-ax^2} &= \int dx x^4 e^{-ax^2} = \frac{3}{8}\frac{\sqrt{\pi}}{a^{5/2}}.
\end{aligned} \tag{2.67}$$

Thus

$$\begin{aligned}
\left\langle r_{14}^2 \right\rangle (a', b', c', d', e', f') &= \frac{4\pi^4}{\left(\alpha_x \alpha_y\right)^{3/2}} \frac{3}{8} \frac{\sqrt{\pi}}{\alpha_z^{5/2}} \\
&= \frac{3\pi^{9/2}}{2\alpha_z \left(\alpha_x \alpha_y \alpha_z\right)^{3/2}} \\
&= \frac{3\pi^{9/2} F_2 (a', b', c', d', e', f')}{2\left(F_1 (a', b', c', d', e', f')\right)^{5/2}}
\end{aligned} \tag{2.68}$$

where $a, \cdots, f$ are given in Eq. (2.48).

$$\begin{aligned}
\left\langle r_{12}^2 \right\rangle (\mathbf{a}', b', \mathbf{c}', \mathbf{d}', e', \mathbf{f}') &= \left\langle r_{14}^2 \right\rangle (\mathbf{c}', b', \mathbf{a}', \mathbf{f}', e', \mathbf{d}'), \\
\left\langle r_{13}^2 \right\rangle (a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f') &= \left\langle r_{14}^2 \right\rangle (a', \mathbf{c}', \mathbf{b}', \mathbf{e}', \mathbf{d}', f'), \\
\left\langle r_{23}^2 \right\rangle (a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f') &= \left\langle r_{14}^2 \right\rangle (a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'), \\
\left\langle r_{24}^2 \right\rangle (a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f') &= \left\langle r_{14}^2 \right\rangle (a', \mathbf{d}', \mathbf{e}', \mathbf{b}', \mathbf{c}', f'), \\
\left\langle r_{34}^2 \right\rangle (\mathbf{a}', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', \mathbf{f}') &= \left\langle r_{14}^2 \right\rangle (\mathbf{b}', \mathbf{d}', \mathbf{f}', \mathbf{a}', \mathbf{c}', \mathbf{e}').
\end{aligned} \tag{2.69}$$

The corresponding expressions for the kinetic energy are

$$\begin{aligned}
T_{14}\left(a',b',c',d',e',f'\right) &= -2\left[\frac{1}{\mu_{12}}\left(c_j'^{\,2}-a_j'e_j'+c_j'e_j'-b_j'f_j'+c_j'f_j'\right)\right. \\
&\left.+\frac{1}{m_1}\left(a_j'c_j'+b_j'c_j'+a_j'e_j'-c_j'e_j'+b_j'f_j'-c_j'f_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(a',b',c',d',e',f'\right) \\
T_{12}\left(\mathbf{a}',b',\mathbf{c}',\mathbf{d}',e',\mathbf{f}'\right) &= -2\left[\frac{1}{\mu_{12}}\left(a_j'^{\,2}+a_j'd_j'-b_j'd_j'+a_j'e_j'-c_j'e_j'\right)\right. \\
&\left.+\frac{1}{m_1}\left(a_j'b_j'+a_j'c_j'-a_j'd_j'+b_j'd_j'-a_j'e_j'+c_j'e_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(\mathbf{c}',b',\mathbf{a}',\mathbf{f}',e',\mathbf{d}'\right) \\
T_{13}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= -2\left[\frac{1}{\mu_{12}}\left(b_j'^{\,2}-a_j'd_j'+b_j'd_j'+b_j'f_j'-c_j'f_j'\right)\right. \\
&\left.+\frac{1}{m_1}\left(a_j'b_j'+b_j'c_j'+a_j'd_j'-b_j'd_j'-b_j'f_j'+c_j'f_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(a',\mathbf{c}',\mathbf{b}',\mathbf{e}',\mathbf{d}',f'\right) \quad (2.70) \\
T_{23}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= -2\left[\frac{1}{\mu_{12}}\left(2d_j'^{\,2}+a_j'd_j'+b_j'd_j'+d_j'e_j'+d_j'f_j'-e_j'f_j'\right)\right. \\
&\left.-\frac{1}{m_1}\left(2d_j'^{\,2}+a_j'b_j'+a_j'd_j'+b_j'd_j'+d_j'e_j'+d_j'f_j'-e_j'f_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(a',\mathbf{e}',\mathbf{d}',\mathbf{c}',\mathbf{b}',f'\right) \\
T_{24}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= -2\left[\frac{1}{\mu_{12}}\left(2e_j'^{\,2}+a_j'e_j'+c_j'e_j'+d_j'e_j'-d_j'f_j'+e_j'f_j'\right)\right. \\
&\left.-\frac{1}{m_1}\left(2e_j'^{\,2}+a_j'c_j'+a_j'e_j'+c_j'e_j'+d_j'e_j'-d_j'f_j'+e_j'f_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(a',\mathbf{d}',\mathbf{e}',\mathbf{b}',\mathbf{c}',f'\right) \\
T_{34}\left(\mathbf{a}',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',\mathbf{f}'\right) &= -2\left[\frac{1}{\mu_{12}}\left(2f_j'^{2}-d_j'e_j'+b_j'f_j'+c_j'f_j'+d_j'f_j'+e_j'f_j'\right)\right. \\
&\left.-\frac{1}{m_1}\left(2f_j'^{2}+b_j'c_j'-d_j'e_j'+b_j'f_j'+c_j'f_j'+d_j'f_j'+e_j'f_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(\mathbf{b}',\mathbf{d}',\mathbf{f}',\mathbf{a}',\mathbf{c}',\mathbf{e}'\right).
\end{aligned}$$

In Eq. (2.70), the coefficients $a',\cdots,f'$ are the the same defined in Eq. (2.48).

$\left\langle\psi_i^{1243}\left|T\right|\psi_j^{1243}\right\rangle$

These can be obtained from Eq. (2.70) by swapping $b\leftrightarrow c$ and $d\leftrightarrow e$ thus in this case

$$\begin{aligned}
T_{14}^{1243}\left(a',b',c',d',e',f'\right) &= T_{14}\left(a',c',b',e',d',f'\right) \\
T_{12}^{1243}\left(\mathbf{a}',b',\mathbf{c}',\mathbf{d}',e',\mathbf{f}'\right) &= T_{12}\left(\mathbf{a}',\mathbf{c}',b',\mathbf{e}',d',\mathbf{f}'\right) \\
T_{13}^{1243}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= T_{13}\left(a',\mathbf{c}',\mathbf{b}',\mathbf{e}',\mathbf{d}',f'\right) \qquad (2.71) \\
T_{23}^{1243}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= T_{23}\left(a',\mathbf{c}',\mathbf{b}',\mathbf{e}',\mathbf{d}',f'\right) \\
T_{34}^{1243}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= T_{34}\left(a',\mathbf{c}',\mathbf{b}',\mathbf{e}',\mathbf{d}',f'\right)
\end{aligned}$$

Again, the coefficients $a',\cdots,f'$ are the the same defined in Eq. (2.48).

$\left\langle\psi_i^{1243}\left|T\right|\psi_j^{1234}\right\rangle$

$$\begin{aligned}
T_{14}^{1243(34)}\left(a',b',c',d',e',f'\right) &= T_{14}\left(a',b',c',d',e',f'\right) \\
T_{12}^{1243(34)}\left(\mathbf{a}',b',\mathbf{c}',\mathbf{d}',e',\mathbf{f}'\right) &= T_{12}\left(\mathbf{a}',b',\mathbf{c}',\mathbf{d}',e',\mathbf{f}'\right) \\
T_{13}^{1243(34)}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= T_{13}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) \qquad (2.72) \\
T_{23}^{1243(34)}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= T_{23}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) \\
T_{24}^{1243(34)}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= T_{24}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) \\
T_{34}^{1243(34)}\left(\mathbf{a}',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',\mathbf{f}'\right) &= T_{34}\left(\mathbf{a}',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',\mathbf{f}'\right)
\end{aligned}$$

where the arguments of T_{ij} i.e., $a',\cdots,f'$ are the the same defined in Eq. (2.60).

$\left\langle \psi_i^{1234} \left| T \right| \psi_j^{1243} \right\rangle$

$$
\begin{aligned}
T_{14}\left(a',b',c',d',e',f'\right) &= -2\left[\frac{1}{\mu_{12}}\left(b_j'^{\,2} - a_j'd_j' + b_j'd_j' - c_j'f_j' + b_j'f_j'\right)\right. \\
&\left. + \frac{1}{m_1}\left(a_j'b_j' + c_j'b_j' + a_j'd_j' - c_j'd_j' + c_j'f_j' - b_j'f_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(a',b',c',d',e',f'\right) \\
T_{12}\left(\mathbf{a}',b',\mathbf{c}',\mathbf{d}',e',\mathbf{f}'\right) &= -2\left[\frac{1}{\mu_{12}}\left(a_j'^{\,2} + a_j'e_j' - c_j'e_j' + a_j'd_j' - b_j'd_j'\right)\right. \\
&\left. + \frac{1}{m_1}\left(a_j'c_j' + a_j'b_j' - a_j'e_j' + c_j'e_j' - a_j'd_j' + b_j'd_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(\mathbf{c}',b',\mathbf{a}',\mathbf{f}',e',\mathbf{d}'\right) \\
T_{13}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= -2\left[\frac{1}{\mu_{12}}\left(c_j'^{\,2} - a_j'e_j' + c_j'e_j' + c_j'f_j' - b_j'f_j'\right)\right. \\
&\left. + \frac{1}{m_1}\left(a_j'c_j' + c_j'b_j' + a_j'e_j' - b_j'e_j' - c_j'f_j' + b_j'f_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(a,\mathbf{c}',\mathbf{b}',\mathbf{e}',\mathbf{d}',f'\right) \qquad (2.73) \\
T_{23}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= -2\left[\frac{1}{\mu_{12}}\left(2e_j'^{\,2} + a_j'e_j' + c_j'e_j' + e_j'd_j' + e_j'f_j' - d_j'f_j'\right)\right. \\
&\left. - \frac{1}{m_1}\left(2e_j'^{\,2} + a_j'c_j' + a_j'e_j' + c_j'e_j' + e_j'd_j' + e_j'f_j' - d_j'f_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(a',\mathbf{e}',\mathbf{d}',\mathbf{c}',\mathbf{b}',f'\right) \\
T_{24}\left(a',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',f'\right) &= -2\left[\frac{1}{\mu_{12}}\left(2d_j'^{\,2} + a_j'd_j' + b_j'd_j' + e_j'd_j' - e_j'f_j' - d_j'f_j'\right)\right. \\
&\left. - \frac{1}{m_1}\left(2d_j'^{\,2} + a_j'b_j' + a_j'd_j' + c_j'd_j' + e_j'd_j' - e_j'f_j' - d_j'f_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(a',\mathbf{d}',\mathbf{e}',\mathbf{b}',\mathbf{c}',f'\right) \\
T_{34}\left(\mathbf{a}',\mathbf{b}',\mathbf{c}',\mathbf{d}',\mathbf{e}',\mathbf{f}'\right) &= -2\left[\frac{1}{\mu_{12}}\left(2f_j'^{2} - e_j'd_j' + c_j'f_j' + b_j'f_j' + e_j'f_j' + d_j'f_j'\right)\right. \\
&\left. - \frac{1}{m_1}\left(2f_j'^{2} + c_j'b_j' - e_j'd_j' + c_j'f_j' + b_j'f_j' + e_j'f_j' + d_j'f_j'\right)\right]\left\langle r_{14}^2\right\rangle\left(\mathbf{b}',\mathbf{d}',\mathbf{f}',\mathbf{a}',\mathbf{c}',\mathbf{e}'\right)
\end{aligned}
$$

where the arguments of T_{ij} i.e., $a', \cdots, f'$ are the the same defined in Eq. (2.58).

2.2.4 Kinetic Energy of Positron

The kinetic energy of positron can be written as

$$
\begin{aligned}
\left\langle T_{e^+}\right\rangle_{ij} &= -\frac{1}{2m_2}\left\langle \psi_j^{1234}\left|\nabla_{\vec{A}_2}^2\right|\psi_i^{1234}\right\rangle \\
&= -\frac{1}{2m_2}\left\langle \psi_j^{1234}\left|\nabla_{\vec{r}_{12}}^2\right|\psi_i^{1234}\right\rangle .
\end{aligned}
$$

From Eq. (2.20), we know that

$$
\begin{aligned}
\nabla_{\vec{r}_{12}}^2\left|\psi_i^{1234}\right\rangle &= -6\left(a_i' + d_i' + e_i'\right)\left|\psi_i^{1234}\right\rangle + 4\left[\left(a_i' + d_i' + e_i'\right)^2 r_{12}^2 + d_i'^{\,2} r_{13}^2 + e_i'^{\,2} r_{14}^2 - 2d_i'\left(a_i' + d_i' + e_i'\right)\vec{r}_{12}\cdot\vec{r}_{13}\right. \\
&\left. -2e_i'\left(a_i' + d_i' + e_i'\right)\vec{r}_{12}\cdot\vec{r}_{14} + 2d_i'e_i'\vec{r}_{13}\cdot\vec{r}_{14}\right]\left|\psi_i^{1234}\right\rangle, \\
&= -6\left(a_i' + d_i' + e_i'\right)\left|\psi_i^{1234}\right\rangle \\
&+ 4\left[\left(a_i' + d_i' + e_i'\right)^2 r_{12}^2 + d_i'^{\,2} r_{13}^2 + e_i'^{\,2} r_{14}^2 - d_i'\left(a_i' + d_i' + e_i'\right)\left(r_{12}^2 + r_{13}^2 - r_{23}^2\right)\right. \\
&\left. -e_i'\left(a_i' + d_i' + e_i'\right)\left(r_{12}^2 + r_{14}^2 - r_{24}^2\right) + d_i'e_i'\left(r_{13}^2 + r_{14}^2 - r_{34}^2\right)\right]\left|\psi_i^{1234}\right\rangle \\
&= -6\left(a_i' + d_i' + e_i'\right)\left|\psi_i^{1234}\right\rangle + 4\left[\left(a_i'^{2} + a_i'd_i' + a_i'e_i'\right) r_{12}^2 - a_i'd_i' r_{13}^2 - a_i'e_i' r_{14}^2 + d_i'\left(a_i' + d_i' + e_i'\right) r_{23}^2\right. \\
&\left. +e_i'\left(a_i' + d_i' + e_i'\right) r_{24}^2 - d_i'e_i' r_{34}^2\right]\left|\psi_i^{1234}\right\rangle .
\end{aligned}
$$

Thus

$$
\begin{aligned}
\langle T_{e^+}\rangle_{ij} &= -\frac{1}{2m_2}\left\langle \psi_j^{1234}\left|\nabla^2_{\vec{r}_{12}}\right|\psi_i^{1234}\right\rangle \\
&= -\frac{1}{2m_2}\left[-6\left(a_i'+d_i'+e_i'\right)\left\langle \psi_j^{1234}\mid \psi_i^{1234}\right\rangle + 4\left[\left(a_i'^2+a_i'd_i'+a_i'e_i'\right)\left\langle r_{12}^2\right\rangle - a_i'd_i'\left\langle r_{13}^2\right\rangle - a_i'e_i'\left\langle r_{14}^2\right\rangle\right.\right. \\
&\quad \left.\left.+d_i'\left(a_i'+d_i'+e_i'\right)\left\langle r_{23}^2\right\rangle + e_i'\left(a_i'+d_i'+e_i'\right)\left\langle r_{24}^2\right\rangle - d_i'e_i'\left\langle r_{34}^2\right\rangle\right]\right]. \qquad (2.74)
\end{aligned}
$$

2.2.5 Kinetic Energy of electron (say at position 3)

In the PsH, there are two electrons in spin-singlet state. We can write the kinetic energy fo electron at position 3 as:

$$
\begin{aligned}
\langle T_{e^-}\rangle_{ij} &= -\frac{1}{2m_3}\left\langle \psi_j^{1234}\left|\nabla^2_{\vec{A}_3}\right|\psi_i^{1234}\right\rangle \\
&= -\frac{1}{2m_3}\left\langle \psi_j^{1234}\left|\nabla^2_{\vec{r}_{13}}\right|\psi_i^{1234}\right\rangle,
\end{aligned}
$$

and from Eq. (2.21), we know that

$$
\begin{aligned}
\nabla^2_{\vec{r}_{13}}\left|\psi_i^{1234}\right\rangle &= -6\left(b_i'+d_i'+f_i'\right)\left|\psi_i^{1234}\right\rangle + 4\left[\left(b_i'+d_i'+f_i'\right)^2 r_{13}^2 + d_i'^2 r_{12}^2 + f_i'^2 r_{14}^2 - 2d_i'\left(b_i'+d_i'+f_i'\right)\vec{r}_{12}\cdot\vec{r}_{13}\right. \\
&\quad \left.-2f_i'\left(b_i'+d_i'+f_i'\right)\vec{r}_{13}\cdot\vec{r}_{14} + 2d_i'f_i'\vec{r}_{12}\cdot\vec{r}_{14}\right]\left|\psi_i^{1234}\right\rangle, \\
&= -6\left(b_i'+d_i'+f_i'\right)\left|\psi_i^{1234}\right\rangle \\
&\quad + 4\left[\left(b_i'+d_i'+f_i'\right)^2 r_{13}^2 + d_i'^2 r_{12}^2 + f_i'^2 r_{14}^2 - d_i'\left(b_i'+d_i'+f_i'\right)\left(r_{12}^2+r_{13}^2-r_{23}^2\right)\right. \\
&\quad \left.+d_i'f_i'\left(r_{12}^2+r_{14}^2-r_{24}^2\right) - f_i'\left(b_i'+d_i'+f_i'\right)\left(r_{13}^2+r_{14}^2-r_{34}^2\right)\right]\left|\psi_i^{1234}\right\rangle \\
&= -6\left(b_i'+d_i'+f_i'\right)\left|\psi_i^{1234}\right\rangle + 4\left[-b_i'd_i'r_{12}^2 + \left(b_i'^2+b_i'd_i'+b_i'f_i'\right)r_{13}^2 - b_i'f_i'r_{14}^2 + d_i'\left(b_i'+d_i'+f_i'\right)r_{23}^2\right. \\
&\quad \left.-d_i'f_i'r_{24}^2 + f_i'\left(b_i'+d_i'+f_i'\right)r_{34}^2\right]\left|\psi_i^{1234}\right\rangle.
\end{aligned}
$$

Thus

$$
\begin{aligned}
\langle T_{e^-}\rangle_{ij} &= -\frac{1}{2m_3}\left\langle \psi_j^{1234}\left|\nabla^2_{\vec{r}_{12}}\right|\psi_i^{1234}\right\rangle \\
&= -\frac{1}{2m_3}\left[-6\left(b_i'+d_i'+f_i'\right)\left|\psi_i^{1234}\right\rangle\left\langle \psi_j^{1234}\mid \psi_i^{1234}\right\rangle\right. \\
&\quad + 4\left[\left(-b_i'd_i'\right)\left\langle r_{12}^2\right\rangle + \left(b_i'^2+b_i'd_i'+b_i'f_i'\right)\left\langle r_{13}^2\right\rangle - b_i'f_i'\left\langle r_{14}^2\right\rangle\right. \\
&\quad \left.\left.+d_i'\left(b_i'+d_i'+f_i'\right)\left\langle r_{23}^2\right\rangle - d_i'f_i'\left\langle r_{24}^2\right\rangle + f_i'\left(b_i'+d_i'+f_i'\right)\left\langle r_{34}^2\right\rangle\right]\right]. \qquad (2.75)
\end{aligned}
$$

Chapter 3

Coalescence Probabilities

The electron and positron in PsH annihilate producing even (in spin zero) and odd (in spin-1) number of photons. This annihilation corresponds to the coalescence probability of electron-positron which is just the expectation value of the Dirac delta function. Compared to the kinetic and potential energy discussed in previous chapter, its convergence is slow. To cure this problem, Drachman has proposed some identities [**30**] and in this is the major topic of this Chapter.

3.1 Derivation of Drachman Global Identity

Consider a system of N particles described by the Hamiltonian (in Rydberg units with masses in units of m_e: actually we write in Rydberg units $2m = m$)

$$H = -\sum_{i=1}^{N} \frac{1}{m_i} \nabla_i'^2 + V\left(\vec{r}_1, \cdots, \vec{r}_N\right) \tag{3.1}$$

and the wave function is $\psi\left(\vec{r}_1, \cdots, \vec{r}_N\right)$ and this is well behaved and are the eigen functions of the Hamiltonian. In our case, it is Gaussian and so this condition is satisfied [**30**]. We know that

$$\begin{aligned} \nabla_j'^2 \left(\frac{1}{r_{jk}}\right) &= -4\pi\delta\left(\vec{r}_{jk}\right), \\ \nabla_k^2 \left(\frac{1}{r_{jk}}\right) &= -4\pi\delta\left(\vec{r}_{jk}\right), \end{aligned} \tag{3.2}$$

where $\vec{r}_{jk} = \vec{r}_j - \vec{r}_k$. We can write

$$\begin{aligned} \int d\vec{r}^N \psi^2 \left(\frac{1}{m_j}\nabla_j'^2 + \frac{1}{m_k}\nabla_k^2\right)\left(\frac{1}{r_{jk}}\right) &= -4\pi\left(\frac{1}{m_j} + \frac{1}{m_k}\right)\int d\vec{r}^N \psi^2 \delta\left(\vec{r}_{jk}\right), \\ &= -4\pi\frac{1}{\mu_{jk}}\left\langle\delta\left(\vec{r}_{jk}\right)\right\rangle, \end{aligned} \tag{3.3}$$

with the reduced mass $\mu_{jk} = m_j m_k / \left(m_j + m_k\right)$. As ∇^2 is a Hermition operator, therefore, we can write

$$\begin{aligned} \nabla^2\psi^2 &= \vec{\nabla}\cdot\vec{\nabla}\psi^2 = 2\vec{\nabla}\cdot\psi\vec{\nabla}\psi, \\ &= 2\vec{\nabla}\psi\cdot\vec{\nabla}\psi + 2\psi\nabla^2\psi, \\ &= 2\psi\nabla^2\psi + 2\left(\vec{\nabla}\psi\right)^2. \end{aligned} \tag{3.4}$$

Thus from Eq. (3.3), we have

$$\int d\vec{r}^N \left(\frac{1}{r_{jk}}\right)\left(\frac{1}{m_j}\left[2\psi\nabla_j'^2\psi + 2\left(\vec{\nabla}_j\psi\right)^2\right] + \frac{1}{m_k}\left[2\psi\nabla_k^2\psi + 2\left(\vec{\nabla}_k\psi\right)^2\right]\right) = -4\pi\frac{1}{\mu_{jk}}\left\langle\delta\left(\vec{r}_{jk}\right)\right\rangle,$$

$$\int d\vec{r}^N \left(\frac{1}{r_{jk}}\right)\left(\psi\left[\frac{\nabla_j'^2}{m_j} + \frac{\nabla_k^2}{m_k}\right]\psi + \frac{1}{m_j}\left(\vec{\nabla}_j\psi\right)^2 + \frac{1}{m_k}\left(\vec{\nabla}_k\psi\right)^2\right) = -2\pi\frac{1}{\mu_{jk}}\left\langle\delta\left(\vec{r}_{jk}\right)\right\rangle. \quad (3.5)$$

Using Eq. (3.1), along with the fact that $H\psi = E\psi$, therefore,

$$\left\langle\delta\left(\vec{r}_{jk}\right)\right\rangle = \frac{\mu_{jk}}{2\pi}\int d\vec{r}^N\left(\frac{1}{r_{jk}}\right)\left(\left[E-V\right]\psi^2 - \sum_{i=1}^{N}\frac{1}{m_i}\left(\vec{\nabla}_i\psi\right)^2\right). \quad (3.6)$$

This is the Drachman identity that we are going to use to calculate the annihilation probability of different particles. In our case, we will write it in the form

$$4\pi\delta^3\left(r_{ab}\right)\phi_1\phi_2 \to \frac{2}{r_{ab}}\left(E-V\right)\phi_1\phi_2 - \sum_c \frac{\left(\nabla_c^i\phi_1\right)\left(\nabla_c^i\phi_2\right)}{r_{ab}} \quad (3.7)$$

where V is the potential energy defined in Eq. (2.3).

We have almost all the tools to calculate it as it involve the matrix elements of potential energy, overlap matrix and that of the gradient w.r.t. to the interparticle distances. For the off-diagonal terms, in Eq. (3.6) we will write $\left(\vec{\nabla}\psi\right)^2$ as $\vec{\nabla}\psi_i\cdot\vec{\nabla}\psi_j$, $\psi^2 = \psi_i\psi_j$ and $E = \frac{1}{2}\left(e_i' + e_j'\right)$. We will adopt this method and later put $i = j$ when needed.

Let's first calculate for the wave function ψ_j^{1234}:

$$\left\langle\frac{1}{r_{jk}}\sum_{l=1}^{4}\frac{\left(\vec{\nabla}_l\psi\right)^2}{m_l}\right\rangle = \left\langle\frac{1}{r_{jk}}\left[\frac{\left(\vec{\nabla}_1\psi\right)^2}{m_1} + \frac{\left(\vec{\nabla}_2\psi\right)^2}{m_2} + \frac{\left(\vec{\nabla}_3\psi\right)^2}{m_3} + \frac{\left(\vec{\nabla}_4\psi\right)^2}{m_4}\right]\right\rangle \quad (3.8)$$

where in terms of the relative coordinates $\vec{\nabla}_1, \cdots, \vec{\nabla}_4$ are the one given in Eqs. (2.8, 2.9). Ignoring the motion of centre of mass, they can be summarized as

$$\begin{aligned}\vec{\nabla}_1 &= -\vec{\nabla}_{\vec{r}_{12}} - \vec{\nabla}_{\vec{r}_{13}} - \vec{\nabla}_{\vec{r}_{14}},\\ \vec{\nabla}_2 &= -\vec{\nabla}_{\vec{r}_{12}},\\ \vec{\nabla}_2 &= -\vec{\nabla}_{\vec{r}_{13}},\\ \vec{\nabla}_3 &= -\vec{\nabla}_{\vec{r}_{14}}.\end{aligned} \quad (3.9)$$

Now writing

$$\left(\vec{\nabla}_1\psi\right)^2 = \left(\vec{\nabla}_1\psi_i\right)\cdot\left(\vec{\nabla}_1\psi_j\right)$$

where in our case if we take the wave function to be ψ^{1234} then ψ_i and ψ_j will be the same and we can always put $i = j$ at the end, we get

$$\begin{aligned}\left(\vec{\nabla}_1\psi_i\right)\cdot\left(\vec{\nabla}_1\psi_j\right) &= \left[\left(\vec{\nabla}_{\vec{r}_{12}} + \vec{\nabla}_{\vec{r}_{13}} + \vec{\nabla}_{\vec{r}_{14}}\right)\psi_i\right]\cdot\left[\left(\vec{\nabla}_{\vec{r}_{12}} + \vec{\nabla}_{\vec{r}_{13}} + \vec{\nabla}_{\vec{r}_{14}}\right)\psi_j\right]\\ &= \left(\vec{\nabla}_{\vec{r}_{12}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{12}}\psi_j\right) + \left(\vec{\nabla}_{\vec{r}_{13}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{13}}\psi_j\right) + \left(\vec{\nabla}_{\vec{r}_{14}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{14}}\psi_j\right)\\ &+ \left(\vec{\nabla}_{\vec{r}_{12}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{13}}\psi_j\right) + \left(\vec{\nabla}_{\vec{r}_{13}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{12}}\psi_j\right) + \left(\vec{\nabla}_{\vec{r}_{12}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{14}}\psi_j\right)\\ &+ \left(\vec{\nabla}_{\vec{r}_{14}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{12}}\psi_j\right) + \left(\vec{\nabla}_{\vec{r}_{13}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{14}}\psi_j\right) + \left(\vec{\nabla}_{\vec{r}_{14}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{13}}\psi_j\right), \quad (3.10)\\ \left(\vec{\nabla}_2\psi_i\right)\cdot\left(\vec{\nabla}_2\psi_j\right) &= \left(\vec{\nabla}_{\vec{r}_{12}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{12}}\psi_j\right),\\ \left(\vec{\nabla}_3\psi_i\right)\cdot\left(\vec{\nabla}_3\psi_j\right) &= \left(\vec{\nabla}_{\vec{r}_{13}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{13}}\psi_j\right),\\ \left(\vec{\nabla}_4\psi_i\right)\cdot\left(\vec{\nabla}_4\psi_j\right) &= \left(\vec{\nabla}_{\vec{r}_{14}}\psi_i\right)\cdot\left(\vec{\nabla}_{\vec{r}_{14}}\psi_j\right).\end{aligned}$$

Using Eqs. (2.17, 2.18), we can calculate all the terms given in Eq. (3.10). We have used MATHEMATICA to simplify the algebra involved here and to collect the coefficients of r_{ij}^2. These are

$$r_{12}^2 : \frac{1}{m_1}\left(4a_i'a_j' + 2a_i'b_j' + 2b_i'a_j' + 2a_i'c_j' + 2c_i'a_j'\right) + \frac{1}{m_2}\left(4a_i'a_j' + 2a_i'd_j' + 2d_i'a_j' + 2a_i'e_j' + 2e_i'a_j'\right)$$
$$- \frac{1}{m_3}\left(2b_i'd_j' + 2d_i'b_j'\right) - \frac{1}{m_4}\left(2c_i'e_j' + 2e_i'c_j'\right). \tag{3.11}$$

$$r_{13}^2 : \frac{1}{m_1}\left(4b_i'b_j' + 2a_i'b_j' + 2b_i'a_j' + 2b_i'c_j' + 2c_i'b_j'\right) - \frac{1}{m_2}\left(2a_i'd_j' + 2d_i'a_j'\right)$$
$$+ \frac{1}{m_3}\left(4b_i'b_j' + 2b_i'd_j' + 2d_i'b_j' + 2b_i'f_j' + 2f_i'b_j'\right) - \frac{1}{m_4}\left(2c_i'f_j' + 2f_i'c_j'\right). \tag{3.12}$$

$$r_{14}^2 : \frac{1}{m_1}\left(4c_i'c_j' + 2a_i'c_j' + 2c_i'a_j' + 2b_i'c_j' + 2c_i'b_j'\right) - \frac{1}{m_2}\left(2a_i'e_j' + 2e_i'a_j'\right) \tag{3.13}$$
$$- \frac{1}{m_3}\left(2b_i'f_j' + 2f_i'b_j'\right) + \frac{1}{m_4}\left(4c_i'c_j' + 2c_i'e_j' + 2e_i'c_j' + 2c_i'f_j' + 2f_i'c_j'\right).$$

$$r_{23}^2 : -\frac{1}{m_1}\left(2a_i'b_j' + 2b_i'a_j'\right) + \frac{1}{m_2}\left(4d_i'd_j' + 2a_i'd_j' + 2d_i'a_j' + 2d_i'e_j' + 2e_i'd_j'\right)$$
$$+ \frac{1}{m_3}\left(4d_i'd_j' + 2b_i'd_j' + 2d_i'b_j' + 2d_i'f_j' + 2f_i'd_j'\right) - \frac{1}{m_4}\left(2e_i'f_j' + 2f_i'e_j'\right). \tag{3.14}$$

$$r_{24}^2 : -\frac{1}{m_1}\left(2a_i'c_j' + 2c_i'a_j'\right) + \frac{1}{m_2}\left(4e_i'e_j' + 2a_i'e_j' + 2e_i'a_j' + 2d_i'e_j' + 2e_i'd_j'\right)$$
$$- \frac{1}{m_3}\left(2d_i'f_j' + 2f_i'd_j'\right) + \frac{1}{m_4}\left(4e_i'e_j' + 2c_i'e_j' + 2e_i'c_j' + 2e_i'f_j' + 2f_i'e_j'\right). \tag{3.15}$$

$$r_{34}^2 : -\frac{1}{m_1}\left(2b_i'c_j' + 2c_i'b_j'\right) + \frac{1}{m_2}\left(2e_i'd_j' + 2d_i'e_j'\right) + \frac{1}{m_3}\left(4f_i'f_j' + 2b_i'f_j' + 2f_i'b_j' + 2d_i'f_j' + 2f_i'd_j'\right) \tag{3.16}$$
$$+ \frac{1}{m_4}\left(4f_i'f_j' + 2c_i'f_j' + 2f_i'c_j' + 2e_i'f_j' + 2f_i'e_j'\right).$$

Hence,

$$\begin{aligned}
\left\langle \frac{1}{r_{jk}} \sum_{l=1}^{4} \frac{\left(\vec{\nabla}_l \psi\right)^2}{m_i} \right\rangle &= \left\langle \frac{r_{12}^2}{r_{jk}} \right\rangle \left[\frac{1}{m_1} \left(4a_i'a_j' + 2a_i'b_j' + 2b_i'a_j' + 2a_i'c_j' + 2c_i'a_j'\right) \right. \\
&+ \left. \frac{1}{m_2} \left(4a_i'a_j' + 2a_i'd_j' + 2d_i'a_j' + 2a_i'e_j' + 2e_i'a_j'\right) - \frac{1}{m_3} \left(2b_i'd_j' + 2d_i'b_j'\right) - \frac{1}{m_4} \left(2c_i'e_j' + 2e_i'c_j'\right) \right] \\
&\left\langle \frac{r_{13}^2}{r_{jk}} \right\rangle \left[\frac{1}{m_1} \left(4b_i'b_j' + 2a_i'b_j' + 2b_i'a_j' + 2b_i'c_j' + 2c_i'b_j'\right) - \frac{1}{m_2} \left(2a_i'd_j' + 2d_i'a_j'\right) \right. \\
&+ \left. \frac{1}{m_3} \left(4b_i'b_j' + 2b_i'd_j' + 2d_i'b_j' + 2b_i'f_j' + 2f_i'b_j'\right) - \frac{1}{m_4} \left(2c_i'f_j' + 2f_i'c_j'\right) \right] \\
&\left\langle \frac{r_{14}^2}{r_{jk}} \right\rangle \left[\frac{1}{m_1} \left(4c_i'c_j' + 2a_i'c_j' + 2c_i'a_j' + 2b_i'c_j' + 2c_i'b_j'\right) - \frac{1}{m_2} \left(2a_i'e_j' + 2e_i'a_j'\right) \right. \\
&- \left. \frac{1}{m_3} \left(2b_i'f_j' + 2f_i'b_j'\right) + \frac{1}{m_4} \left(4c_i'c_j' + 2c_i'e_j' + 2e_i'c_j' + 2c_i'f_j' + 2f_i'c_j'\right) \right] \\
&\left\langle \frac{r_{23}^2}{r_{jk}} \right\rangle \left[-\frac{1}{m_1} \left(2a_i'b_j' + 2b_i'a_j'\right) + \frac{1}{m_2} \left(4d_i'd_j' + 2a_i'd_j' + 2d_i'a_j' + 2d_i'e_j' + 2e_i'd_j'\right) \right. \\
&+ \left. \frac{1}{m_3} \left(4d_i'd_j' + 2b_i'd_j' + 2d_i'b_j' + 2d_i'f_j' + 2f_i'd_j'\right) - \frac{1}{m_4} \left(2e_i'f_j' + 2f_i'e_j'\right) \right] \qquad (3.17) \\
&\left\langle \frac{r_{24}^2}{r_{jk}} \right\rangle \left[-\frac{1}{m_1} \left(2a_i'c_j' + 2c_i'a_j'\right) + \frac{1}{m_2} \left(4e_i'e_j' + 2a_i'e_j' + 2e_i'a_j' + 2d_i'e_j' + 2e_i'd_j'\right) \right. \\
&- \left. \frac{1}{m_3} \left(2d_i'f_j' + 2f_i'd_j'\right) + \frac{1}{m_4} \left(4e_i'e_j' + 2c_i'e_j' + 2e_i'c_j' + 2e_i'f_j' + 2f_i'e_j'\right) \right] \\
&\left\langle \frac{r_{34}^2}{r_{jk}} \right\rangle \left[-\frac{1}{m_1} \left(2b_i'c_j' + 2c_i'b_j'\right) - \frac{1}{m_2} \left(2e_i'd_j' + 2d_i'e_j'\right) \right. \\
&+ \left. \frac{1}{m_3} \left(4f_i'f_j' + 2b_i'f_j' + 2f_i'b_j' + 2d_i'f_j' + 2f_i'd_j'\right) + \frac{1}{m_4} \left(4f_i'f_j' + 2c_i'f_j' + 2f_i'c_j' + 2e_i'f_j' + 2f_i'e_j'\right) \right].
\end{aligned}$$

Now to calculate the expectation values of $\left\langle \frac{r_{il}^2}{r_{jk}} \right\rangle$, we use the trick (say for $\left\langle \frac{r_{12}^2}{r_{jk}} \right\rangle$,

$$\left\langle \frac{r_{12}^2}{r_{jk}} \right\rangle = -\frac{\partial}{\partial a'} \left\langle \frac{1}{r_{jk}} \right\rangle. \qquad (3.18)$$

As we are considering the annihilation of the electron and positron i.e., say $\delta\left(\vec{r}_{23}\right)$. We know that the expectation value of $\frac{1}{r_{13}}$ is depicted in Eq. (2.52) i.e.,

$$\begin{aligned}
V_{23}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) &= V_{14}\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right) \\
&= \frac{2\pi^4}{F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f\right) \left[F_2\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^{1/2}},
\end{aligned}$$

where $F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)$ and $F_2\left(a, \mathbf{e}, \mathbf{d}, \mathbf{c}, \mathbf{b}, f\right)$ can be obtained from Eq. (2.40) and Eq. (2.41), respectively, by swapping the parameters and these will take the form

$$\begin{aligned}
F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right) &= a'b'c' + a'b'e' + a'c'd' + a'b'f' + a'c'f' + a'd'e + a'd'f' + a'e'f' \\
&+ b'c'd' + b'c'e' + b'd'e' + b'd'f' + b'e'f' + c'd'e' + c'd'f' + c'e'f', \qquad (3.19) \\
F_2\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right) &= a'c' + a'e' + a'f' + b'c' + b'e' + b'f' + c'e' + c'f'.
\end{aligned}$$

$$
\begin{aligned}
\left\langle \frac{r_{12}^2}{r_{23}} \right\rangle &= -\frac{\partial}{\partial a'} V_{23}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) = 2\pi^4 \left[\frac{b'c' + b'e' + b'f' + c'd' + c'f' + d'e' + d'f' + e'f'}{\left[F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^2 \left[F_2\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^{1/2}} \right. \\
&\quad \left. + \frac{1}{2} \frac{c + e + f}{F_1\left(a, \mathbf{e}, \mathbf{d}, \mathbf{c}, \mathbf{b}, f\right) \left[F_2\left(a, \mathbf{e}, \mathbf{d}, \mathbf{c}, \mathbf{b}, f\right)\right]^{3/2}} \right] \\
\left\langle \frac{r_{13}^2}{r_{23}} \right\rangle &= -\frac{\partial}{\partial b'} V_{23}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) = 2\pi^4 \left[\frac{a'c' + a'e' + a'f' + c'd' + c'e' + d'e' + d'f' + e'f'}{\left[F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^2 \left[F_2\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^{1/2}} \right. \\
&\quad \left. + \frac{1}{2} \frac{c + e + f}{F_1\left(a, \mathbf{e}, \mathbf{d}, \mathbf{c}, \mathbf{b}, f\right) \left[F_2\left(a, \mathbf{e}, \mathbf{d}, \mathbf{c}, \mathbf{b}, f\right)\right]^{3/2}} \right], \\
\left\langle \frac{r_{14}^2}{r_{23}} \right\rangle &= -\frac{\partial}{\partial c'} V_{23}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) = 2\pi^4 \left[\frac{a'b' + a'd' + a'f' + b'd' + b'e' + d'e' + d'f' + e'f'}{\left[F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^2 \left[F_2\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^{1/2}} \right. \\
&\quad \left. + \frac{1}{2} \frac{a + b + e + f}{F_1\left(a, \mathbf{e}, \mathbf{d}, \mathbf{c}, \mathbf{b}, f\right) \left[F_2\left(a, \mathbf{e}, \mathbf{d}, \mathbf{c}, \mathbf{b}, f\right)\right]^{3/2}} \right], \\
\left\langle \frac{r_{23}^2}{r_{23}} \right\rangle &= -\frac{\partial}{\partial d'} V_{23}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) = 2\pi^4 \left[\frac{a'c' + a'e' + a'f' + b'c' + b'e' + b'f' + c'e' + c'f'}{\left[F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^2 \left[F_2\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^{1/2}} \right], \qquad (3.20) \\
\left\langle \frac{r_{24}^2}{r_{23}} \right\rangle &= -\frac{\partial}{\partial e'} V_{23}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) = 2\pi^4 \left[\frac{a'b' + a'd' + a'f' + b'c' + b'd' + b'f' + c'd' + c'f'}{\left[F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^2 \left[F_2\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^{1/2}} \right. \\
&\quad \left. + \frac{1}{2} \frac{a' + b' + c'}{F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right) \left[F_2\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^{3/2}} \right], \\
\left\langle \frac{r_{34}^2}{r_{23}} \right\rangle &= -\frac{\partial}{\partial f'} V_{23}\left(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f'\right) = 2\pi^4 \left[\frac{a'b' + a'c' + a'd' + a'e' + b'd' + b'e' + c'd' + c'e'}{\left[F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^2 \left[F_2\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^{1/2}} \right. \\
&\quad \left. + \frac{1}{2} \frac{a' + b' + c'}{F_1\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right) \left[F_2\left(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'\right)\right]^{3/2}} \right].
\end{aligned}
$$

Here the definition of $a', \cdots, f'$ is the same as given in Eq. (2.48). We will multiply and divide these expressions with $\sqrt{\pi}$ so that we can take $\pi^{9/2}$ to be common that cancels with that in the over-lap matrix.

Calculation of $\left\langle \frac{1}{r_{ij} r_{kl}} \right\rangle$

In order to calculate $\left\langle \frac{1}{r_{ij} r_{kl}} \right\rangle$, thanks to the identity (c.f. Eq. (7) of [**30**])

$$
\frac{1}{r} = \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{e^{-ur^2}}{\sqrt{u}} du.
$$

Put $\sqrt{u} = q, \implies u = q^2$

$$
du = 2q dq, \implies 2dq = \frac{du}{q} = \frac{du}{\sqrt{u}}.
$$

Thus

$$
\frac{1}{r} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-q^2 r^2} dq, \qquad (3.21)
$$

therefore, we can see that it is converted to a Gaussian integral.

$$
\begin{aligned}
V_{14}\left(a', b', c', d', e', f'\right) \equiv \left\langle \frac{1}{r_{14}} \right\rangle &= \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \frac{1}{r_{14}} \exp\left(-a' r_{12}^2 - b' r_{13}^2 - c' r_{14}^2 - d' r_{23}^2 - e' r_{24}^2 - f' r_{34}^2\right), \\
\left\langle \frac{1}{r_{12} r_{14}} \right\rangle &= \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \frac{1}{r_{12}} \frac{1}{r_{14}} \exp\left(-a' r_{12}^2 - b' r_{13}^2 - c' r_{14}^2 - d' r_{23}^2 - e' r_{24}^2 - f' r_{34}^2\right), \\
&= \frac{2}{\sqrt{\pi}} \int_0^\infty dq \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \frac{1}{r_{14}} \exp\left(-(a' + q^2) r_{12}^2 - b' r_{13}^2 - c' r_{14}^2 - d' r_{23}^2 - e' r_{24}^2 - f' r_{34}^2\right), \\
&= \frac{2}{\sqrt{\pi}} \int_0^\infty dq V_{14}\left(a' + q^2, b', c', d', e', f'\right) \qquad (3.22)
\end{aligned}
$$

where $V_{14}\left(a'+q^2,b',c',d',e',f'\right)$ is the same as given in Eq. (2.49) with $a' \to a'+q^2$. Putting everything, we can write Eq. (3.22) as

$$\left\langle \frac{1}{r_{12}r_{14}} \right\rangle = \frac{2}{\sqrt{\pi}} \int_0^\infty dq \frac{2\pi^4}{F_1\left(a'+q^2,b',c',d',e',f'\right)\left[F_2\left(a'+q^2,b',c',d',e',f'\right)\right]^{1/2}},$$

with $F_1\left(a'+q^2,b',c',d',e',f'\right)$ and $F_2\left(a'+q^2,b',c',d',e',f'\right)$ can be taken from Eq. (2.40) and Eq. (2.41) with $a' \to a'+q^2$ i.e.,

$$\begin{aligned}
F_1\left(a'+q^2,b',c',d',e',f\right) &= F_1\left(a',b',c',d',e',f'\right) + \left(b'c'+b'e'+b'f'+c'd'+c'f'+d'e'+d'f'+e'f'\right)q^2,\\
&= A' + B'q^2,\\
F_2\left(a'+q^2,b',c',d',e',f'\right) &= F_2\left(a',b',c',d',e',f'\right) + \left(b'+d'+f'\right)q^2,\\
&= C' + D'q^2.
\end{aligned}$$

$$\begin{aligned}
\left\langle \frac{1}{r_{12}r_{14}} \right\rangle &= 4\pi^{7/2} \int_0^\infty dq \frac{1}{\left[A'+B'q^2\right]\left[C'+D'q^2\right]^{1/2}},\\
&= 4\pi^{7/2} \frac{\cos^{-1}\left(\sqrt{\frac{A'D'}{B'C'}}\right)}{\sqrt{A'\left(B'C'-A'D'\right)}}
\end{aligned} \tag{3.23}$$

As $B'C'-A'D'$ is either greater or less than zero, therefore, it is better to give it a form so that we can avoid the complet value. Writing $x = \frac{A'D'}{B'C'}$

$$\begin{aligned}
\cos^{-1} x = t &\implies x = \cos t\\
\sec^2 t = \frac{1}{x^2} &\implies 1 + \tan^2 t = \frac{1}{x^2}\\
\tan^2 t &= \frac{1}{x^2} - 1\\
t = \cos^{-1} x &= \tan^{-1}\left(\sqrt{\frac{B'C'-A'D'}{A'D'}}\right)
\end{aligned} \tag{3.24}$$

Thus for $(B'C'-A'D) \geqq 0$,

$$\left\langle \frac{1}{r_{12}r_{14}} \right\rangle = \frac{4\pi^{7/2}}{\sqrt{A'\left(B'C'-A'D'\right)}} \tan^{-1}\left(\sqrt{\frac{B'C'-A'D'}{A'D'}}\right). \tag{3.25}$$

Similarly for $(B'C'-A'D) < 0$, we have

$$\begin{aligned}
\left\langle \frac{1}{r_{12}r_{14}} \right\rangle &= \frac{1}{i} \frac{4\pi^{7/2}}{\sqrt{A'\left(A'D'-B'C'\right)}} i \tanh^{-1}\left(\sqrt{\frac{A'D'-B'C'}{A'D'}}\right)\\
&= \frac{4\pi^{7/2}}{\sqrt{A'\left(A'D'-B'C'\right)}} \tanh^{-1}\left(\sqrt{\frac{A'D'-B'C'}{A'D'}}\right).
\end{aligned} \tag{3.26}$$

By following the same line of action, let's calculate the other combinations:

$$\begin{aligned}
\left\langle \frac{1}{r_{13}r_{14}} \right\rangle &= \frac{2}{\sqrt{\pi}} \int_0^\infty dq V_{14}\left(a',b'+q^2,c',d',e',f'\right)\\
&= \left\langle \frac{1}{r_{12}r_{14}} \right\rangle \text{with} \begin{cases} B' = a'c'+a'e'+a'f'+c'd'+c'e'+d'e'+d'f'+e'f' \\ D' = a'+d'+e' \end{cases}.
\end{aligned} \tag{3.27}$$

$$\left\langle \frac{1}{r_{23}r_{14}} \right\rangle = \frac{2}{\sqrt{\pi}} \int_0^\infty dq V_{14}\left(a', b', c', d' + q^2, e', f'\right)$$
$$= \left\langle \frac{1}{r_{12}r_{14}} \right\rangle \text{ with } \begin{cases} B' = a'c' + a'e' + a'f' + b'c' + b'e' + b'f' + c'e' + c'f' \\ D' = a' + b' + e' + f' \end{cases} . \quad (3.28)$$

$$\left\langle \frac{1}{r_{24}r_{14}} \right\rangle = \frac{2}{\sqrt{\pi}} \int_0^\infty dq V_{14}\left(a', b', c', d', e' + q^2, f'\right)$$
$$= \left\langle \frac{1}{r_{12}r_{14}} \right\rangle \text{ with } \begin{cases} B' = a'b' + a'd' + a'f' + b'c' + b'd' + b'f' + c'd' + c'f' \\ D' = b' + d' + f' \end{cases} . \quad (3.29)$$

$$\left\langle \frac{1}{r_{34}r_{14}} \right\rangle = \frac{2}{\sqrt{\pi}} \int_0^\infty dq V_{14}\left(a', b', c', d', e' + q^2, f'\right)$$
$$= \left\langle \frac{1}{r_{12}r_{14}} \right\rangle \text{ with } \begin{cases} B' = a'b' + a'c' + a'e' + a'd' + b'd' + b'e' + c'd' + c'e' \\ D' = a' + d' + e' \end{cases} . \quad (3.30)$$

Now if we have the term

$$\left\langle \frac{1}{r_{14}r_{14}} \right\rangle = \left\langle \frac{1}{r_{14}^2} \right\rangle = \frac{2}{\sqrt{\pi}} \int_0^\infty dq V_{14}\left(a', b', c' + q^2, d', e', f'\right)$$
$$= \left\langle \frac{1}{r_{12}r_{14}} \right\rangle \text{ with } \begin{cases} B' = a'b' + a'd' + a'f' + b'd' + b'e' + d'e' + d'f' + e'f' \\ D' = 0 \end{cases} . \quad (3.31)$$

We can see that the agrument of trignometric functions become ∞ in Eqs. (3.25, 3.26), therefore, this scheme is not applicable when we have both r's to be same in the denominator.

But we know that the calculation for involving 23 can be done from 14 by the interchange of the parameters. Therefore, we can write for $(B'C' - A'D) \geqq 0$,

$$\left\langle \frac{1}{r_{12}r_{23}} \right\rangle = \frac{1}{\sqrt{A'\left(B'C' - A'D'\right)}} \tan^{-1}\left(\sqrt{\frac{B'C' - A'D'}{A'D'}}\right)$$

similarly for $(B'C' - A'D) < 0$, we have

$$\left\langle \frac{1}{r_{12}r_{23}} \right\rangle = \frac{1}{\sqrt{A'\left(A'D' - B'C'\right)}} \tanh^{-1}\left(\sqrt{\frac{A'D' - B'C'}{A'D'}}\right)$$

where $B' = b'c' + b'e' + b'f' + c'd' + c'f' + d'e' + d'f' + e'f'$, $A' = F_1\left(a', e', d', c', b', f'\right)$, $C' = F_2\left(a', e', d', c', b', f'\right)$ and $D' = \left(c' + e' + f'\right)$.

But thanks to the Gaussian wave functions, this can be calculated easily

$$\begin{aligned} V_{14}^2\left(a', b', c', d', e', f'\right) \equiv \left\langle \frac{1}{r_{14}^2} \right\rangle &= \int d^3\vec{x} d^3\vec{y} d^3\vec{z} \left(\frac{1}{z^2}\right) \exp\left(-\alpha_x x^2 - \alpha_y y^2 - \alpha_z z^2\right), \\ &= \frac{\pi^3}{\left(\alpha_x \alpha_y\right)^{3/2}} \int_0^\infty d^3\vec{z} \left(\frac{1}{z^2}\right) \exp\left(-\alpha_z z^2\right), \\ &= \frac{4\pi^4}{\left(\alpha_x \alpha_y\right)^{3/2}} \int_0^\infty dz \exp\left(-\alpha_z z^2\right), \\ &= \frac{2\pi^{9/2}}{\left(\alpha_x \alpha_y\right)^{3/2} \left(\alpha_z\right)^{1/2}} \\ &= \frac{2\pi^{9/2}}{F_2\left(a', b', c', d', e', f'\right) \left[F_1\left(a', b', c', d', e', f'\right)\right]^{1/2}}. \end{aligned} \quad (3.32)$$

Here the definition of $a, \cdots, f$ is the same as given in Eq. (2.48).

As we are calculating the annihilation of the particle at position 2 and 3 i.e., $\delta(\vec{r}_{23})$, therefore, we have to start with the expression of $\left\langle \frac{1}{r_{23}} \right\rangle$ and apply the method described about. But we know that for ψ^{1234}

$$V_{23}(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f') = V_{14}(a', \mathbf{e}', \mathbf{d}', \mathbf{c}', \mathbf{b}', f'), \tag{3.33}$$

therefore, in Eqs. (3.25, 3.26, 3.27, 3.28, 3.29, 3.30, 3.31, 3.32), we have to do the swapping of $b' \leftrightarrow e'$ and $c' \leftrightarrow d'$, simultaneously.

Now, for the same wavefunction ψ^{1234} there is also a possibility that the positron (e^+) at position 2 annhilate with the electron (e^-) at position 4 and the corresponding delta-function is $\delta(\vec{r}_{24})$. This can be obtained by swapping $b \leftrightarrow c$ and $d \leftrightarrow e$ in the expressions of $\delta(\vec{r}_{23})$. This is because of the fact that

$$V_{24}(a', \mathbf{b}', \mathbf{c}', \mathbf{d}', \mathbf{e}', f') = V_{23}(a', \mathbf{c}', \mathbf{b}', \mathbf{e}', \mathbf{d}', f'). \tag{3.34}$$

Expectation value of H^+e^- contact density $\langle \delta(\vec{r}_{14}) \rangle$

In order to calculate the $\left\langle \frac{1}{r_{jk}} \sum_{l=1}^{4} \frac{(\vec{\nabla}_l \psi)^2}{m_i} \right\rangle$ part of the Drachman identity in this case, with $r_{ij} = r_{14}$ we will start with the Eq. (3.17) as the constants remains the same and the only change is in the expectation value where the denominator in the expectation values is replaced with r_{14}. We will make use of Eq. (3.18) on

$$V_{14}(a', b', c', d', e', f') = \frac{2\pi^4}{F_1(a', b', c', d', e', f') \left[F_2(a', b', c', d', e', f')\right]^{1/2}},$$

where $F_1(a', b', c', d', e', f')$ and $F_2(a', b', c', d', e', f')$ are given in Eqs. (2.40) and (2.41), respectively and are

$$\begin{aligned} F_1(a', b', c', d', e', f') = {} & a'b'c' + a'b'e' + a'b'f' + a'c'd' + a'd'e' + a'c'f' + a'd'f' + a'e'f' \\ & + b'c'd' + b'c'e' + b'd'e' + b'd'f' + b'e'f' + c'd'e' + c'd'f' + c'e'f', \end{aligned}$$

and

$$\begin{aligned} F_2(a', b', c', d', e', f') &= (b' + d' + f')(a' + d' + e') - d'^2 \\ &= a'b' + a'd' + a'f' + b'd' + b'e' + d'e' + d'f' + e'f'. \end{aligned}$$

Therefore,

$$\left\langle \frac{r_{12}^2}{r_{14}} \right\rangle = -\frac{\partial}{\partial a} V_{14}\left(a',b',c',d',e',f'\right) = 2\pi^4 \left[\frac{b'c'+b'e'+b'f'+c'd'+c'f'+d'e'+d'f'+e'f'}{\left[F_1\left(a',b',c',d',e',f'\right)\right]^2 \left[F_2\left(a',b',c',d',e',f'\right)\right]^{1/2}} \right.$$
$$\left. + \frac{1}{2} \frac{b'+d'+f'}{F_1\left(a',b',c',d',e',f'\right)\left[F_2\left(a',b',c',d',e',f'\right)\right]^{3/2}} \right]$$
$$\left\langle \frac{r_{13}^2}{r_{14}} \right\rangle = -\frac{\partial}{\partial b} V_{14}\left(a',b',c',d',e',f'\right) = 2\pi^4 \left[\frac{a'c'+a'e'+a'f'+c'd'+c'e'+d'e'+d'f'+e'f'}{\left[F_1\left(a',b',c',d',e',f'\right)\right]^2 \left[F_2\left(a',b',c',d',e',f'\right)\right]^{1/2}} \right.$$
$$\left. + \frac{1}{2} \frac{a'+d'+e'}{F_1\left(a',b',c',d',e',f'\right)\left[F_2\left(a',b',c',d',e',f'\right)\right]^{3/2}} \right],$$
$$\left\langle \frac{r_{14}^2}{r_{14}} \right\rangle = -\frac{\partial}{\partial c} V_{14}\left(a',b',c',d',e',f'\right) = 2\pi^4 \left[\frac{a'b'+a'd'+a'f'+b'd'+b'e'+d'e'+d'f'+e'f'}{\left[F_1\left(a',b',c',d',e',f'\right)\right]^2 \left[F_2\left(a',b',c',d',e',f'\right)\right]^{1/2}} \right]$$
$$\left\langle \frac{r_{23}^2}{r_{14}} \right\rangle = -\frac{\partial}{\partial d} V_{14}\left(a',b',c',d',e',f'\right) = 2\pi^4 \left[\frac{a'c'+a'e'+a'f'+b'c'+b'e'+b'f'+c'e'+c'f'}{\left[F_1\left(a',b',c',d',e',f'\right)\right]^2 \left[F_2\left(a',b',c',d',e',f'\right)\right]^{1/2}} \right.$$
$$\left. + \frac{1}{2} \frac{a'+b'+e'+f'}{F_1\left(a',b',c',d',e',f'\right)\left[F_2\left(a',b',c',d',e',f'\right)\right]^{3/2}} \right],$$
$$\left\langle \frac{r_{24}^2}{r_{14}} \right\rangle = -\frac{\partial}{\partial e} V_{14}\left(a',b',c',d',e',f'\right) = 2\pi^4 \left[\frac{a'b'+a'd'+a'f'+b'c'+b'd'+b'f'+c'd'+c'f'}{\left[F_1\left(a',b',c',d',e',f'\right)\right]^2 \left[F_2\left(a',b',c',d',e',f'\right)\right]^{1/2}} \right. \tag{3.35}$$
$$\left. + \frac{1}{2} \frac{b'+d'+f'}{F_1\left(a',b',c',d',e',f'\right)\left[F_2\left(a',b',c',d',e',f'\right)\right]^{3/2}} \right],$$
$$\left\langle \frac{r_{34}^2}{r_{14}} \right\rangle = -\frac{\partial}{\partial f} V_{14}\left(a',b',c',d',e',f'\right) = 2\pi^4 \left[\frac{a'b'+a'c'+a'd'+a'e'+b'd'+b'e'+c'd'+c'e'}{\left[F_1\left(a',b',c',d',e',f'\right)\right]^2 \left[F_2\left(a',b',c',d',e',f'\right)\right]^{1/2}} \right.$$
$$\left. + \frac{1}{2} \frac{a'+d'+e'}{F_1\left(a',b',c',d',e',f'\right)\left[F_2\left(a',b',c',d',e',f'\right)\right]^{3/2}} \right].$$

3.1.1 Delta Function: Direct Calculations

Last, we come to the matrix elements for the different contact densities i.e., $\langle \delta(\vec{r}_{ij}) \rangle$ not using the Drachman identities but by using the direct computation.

$$\begin{aligned} \langle \delta(\vec{r}_{14}) \rangle &= \left\langle \psi_i^{1234} \left| \delta(\vec{r}_{14}) \right| \psi_j^{1234} \right\rangle, \\ &= \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \delta(\vec{r}_{14}) \exp\left(-a'r_{12}^2 - b'r_{13}^2 - c'r_{14}^2 - d'r_{23}^2 - e'r_{24}^2 - f'r_{34}^2\right), \end{aligned} \tag{3.36}$$

as $\vec{r}_{14} = \vec{r}_4 - \vec{r}_1$, therefore,

$$\begin{aligned} \langle \delta(\vec{r}_{14}) \rangle &= \int d^3\vec{r}_{12} d^3\vec{r}_{13} \exp\left(-a'r_{12}^2 - b'r_{13}^2 - d'r_{23}^2 - e'r_{21}^2 - f'r_{31}^2\right), \\ &= \int d^3\vec{r}_{12} d^3\vec{r}_{13} \exp\left(-a'r_{12}^2 - b'r_{13}^2 - d'r_{23}^2 - e'r_{21}^2 - f'r_{31}^2\right), \\ &= \int d^3\vec{r}_{12} d^3\vec{r}_{13} \exp\left(-\left(a'+e'\right)r_{12}^2 - \left(b'+f'\right)r_{13}^2 - dr_{23}^2\right). \end{aligned} \tag{3.37}$$

This is just like the overlap matrix with $a' \to a'+e', b' \to b'+f',\ c'=e'=f'=0$ and the answer is

$$\langle \delta(\vec{r}_{14}) \rangle = \frac{\pi^3}{\left[\left(a'+e'\right)\left(b'+f'\right) + \left(a'+e'\right)d' + \left(b'+f'\right)d'\right]^{3/2}} \equiv D\left[a',b',c',d',e',f'\right] \tag{3.38}$$

where $a' = a_i' + a_j',\ b' = b_j' + c_i',\ c' = c_j' + b_i',\ d' = d_j' + e_i',\ e' = e_j' + d_i',\ f' = f_i' + f_j'$.

Next in line is the

$$\langle \delta(\vec{r}_{12}) \rangle = \langle \psi_i^{1234} | \delta(\vec{r}_{12}) | \psi_j^{1234} \rangle ,$$
$$= \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \delta(\vec{r}_{12}) \exp\left(-a' r_{12}^2 - b' r_{13}^2 - c' r_{14}^2 - d' r_{23}^2 - e' r_{24}^2 - f' r_{34}^2\right), \tag{3.39}$$

as $\vec{r}_{12} = \vec{r}_2 - \vec{r}_1$, therefore,

$$\langle \delta(\vec{r}_{12}) \rangle = \int d^3\vec{r}_{13} d^3\vec{r}_{14} \exp\left(-b' r_{13}^2 - c' r_{14}^2 - d' r_{13}^2 - e' r_{14}^2 - f' r_{34}^2\right),$$
$$= \int d^3\vec{r}_{13} d^3\vec{r}_{14} \exp\left(-(b' + d') r_{13}^2 - (c' + e') r_{14}^2 - f r_{34}^2\right). \tag{3.40}$$

This is just like Eq. (3.38) with $a' \leftrightarrow c',\ f' \leftrightarrow d'$ and the result is

$$\langle \delta(\vec{r}_{12}) \rangle = \frac{\pi^3}{\left[(c' + e')(b' + d') + (c' + e') f + (b' + d') f\right]^{3/2}}, \tag{3.41}$$

where $a' = a_i' + a_j',\ b' = b_j' + c_i',\ c' = c_j' + b_i',\ d' = d_j' + e_i',\ e' = e_j' + d_i',\ f' = f_i' + f_j'$.

Likewise

$$\langle \delta(\vec{r}_{13}) \rangle = \langle \psi_i^{1234} | \delta(\vec{r}_{13}) | \psi_j^{1234} \rangle ,$$
$$= \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} \delta(\vec{r}_{13}) \exp\left(-a' r_{12}^2 - b' r_{13}^2 - c' r_{14}^2 - d' r_{23}^2 - e' r_{24}^2 - f' r_{34}^2\right), \tag{3.42}$$

as $\vec{r}_{13} = \vec{r}_3 - \vec{r}_1$, therefore,

$$\langle \delta(\vec{r}_{13}) \rangle = \int d^3\vec{r}_{12} d^3\vec{r}_{14} \exp\left(-a' r_{12}^2 - c' r_{14}^2 - d' r_{21}^2 - e' r_{24}^2 - f' r_{14}^2\right),$$
$$= \int d^3\vec{r}_{12} d^3\vec{r}_{14} \exp\left(-(a' + d') r_{12}^2 - (c' + f') r_{14}^2 - e' r_{24}^2\right),$$
$$= \frac{\pi^3}{\left[(a' + d')(c' + f') + (a' + d') e' + (c' + f') e'\right]^{3/2}}. \tag{3.43}$$

This is just like Eq. (3.38) with $b' \leftrightarrow c',\ d' \leftrightarrow e'$.

Using the scheme of Eq. (2.52), we can write

$$\langle \delta(\vec{r}_{23}) \rangle = D\left[a', e', d', c', b', f'\right] = \frac{\pi^3}{\left[(a' + b')(e' + f') + (a' + b') c' + (e' + f') c'\right]^{3/2}}, \tag{3.44}$$

where the function $D\left[a', b', c', d', e', f'\right]$ is the result of $\langle \delta(\vec{r}_{23}) \rangle$ and is given in Eq. (3.38). Similarly from Eq. (2.53), we have

$$\langle \delta(\vec{r}_{24}) \rangle = D\left[a', d', e', b', c', f'\right] = \frac{\pi^3}{\left[(a' + c')(d' + f') + (c' + e') b + (d' + f') b'\right]^{3/2}}, \tag{3.45}$$

and from Eq. (2.54),

$$\langle \delta(\vec{r}_{34}) \rangle = D\left[b', d', f', a', c', e'\right] = \frac{\pi^3}{\left[(b' + c')(d' + e') + (b' + c') a' + (d' + e') a'\right]^{3/2}}. \tag{3.46}$$

For the other case, we just swap the parameters to fully exhaust the permutation symmetries. Remember, we have to multiply and divide it with $\pi^{3/2}$ to make a common factor of $\pi^{9/2}$ that will be cancelled with we divide its expectation value with overlap matrix.

Product of two delta functions

This will include the terms like $\delta\left(\vec{r}_{ij}\right)\delta\left(\vec{r}_{lm}\right)$ and $\delta\left(\vec{r}_{ij}\right)\delta\left(\vec{r}_{jl}\right)$, where the later determine the three particles coalescence probabilities. Here we will consider different possibilities corresponding to these delta functions and later pick the one that is required for the coalescence probability.

Let's calculate

$$
\begin{aligned}
\left\langle \delta\left(\vec{r}_{13}\right)\delta\left(\vec{r}_{14}\right)\right\rangle &= \left\langle \psi_i^{1234}\left|\delta\left(\vec{r}_{13}\right)\delta\left(\vec{r}_{14}\right)\right|\psi_j^{1234}\right\rangle, \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\delta\left(\vec{r}_{13}\right)\delta\left(\vec{r}_{14}\right)\exp\left(-a'r_{12}^2-b'r_{13}^2-c'r_{14}^2-d'r_{23}^2-e'r_{24}^2-f'r_{34}^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}\delta\left(\vec{r}_{13}\right)\exp\left(-a'r_{12}^2-b'r_{13}^2-d'r_{23}^2-e'r_{21}^2-f'r_{31}^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}\delta\left(\vec{r}_{13}\right)\exp\left(-\left(a'+e'\right)r_{12}^2-\left(b'+f'\right)r_{13}^2-d'r_{23}^2\right), \\
&= \int d^3\vec{r}_{12}\exp\left(-\left(a'+d'+e'\right)r_{12}^2\right), \\
&= \left[\frac{\pi}{a'+d'+e'}\right]^{3/2}.
\end{aligned}
\tag{3.47}
$$

$$
\begin{aligned}
\left\langle \delta\left(\vec{r}_{12}\right)\delta\left(\vec{r}_{13}\right)\right\rangle &= \left\langle \psi_i^{1234}\left|\delta\left(\vec{r}_{12}\right)\delta\left(\vec{r}_{13}\right)\right|\psi_j^{1234}\right\rangle, \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\delta\left(\vec{r}_{12}\right)\delta\left(\vec{r}_{13}\right)\exp\left(-a'r_{12}^2-b'r_{13}^2-c'r_{14}^2-d'r_{23}^2-e'r_{24}^2-f'r_{34}^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{14}\delta\left(\vec{r}_{12}\right)\exp\left(-a'r_{12}^2-c'r_{14}^2-d'r_{21}^2-e'r_{24}^2-f'r_{14}^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{14}\delta\left(\vec{r}_{12}\right)\exp\left(-\left(a'+d'\right)r_{12}^2-\left(c'+f'\right)r_{14}^2-e'r_{24}^2\right), \\
&= \int d^3\vec{r}_{14}\exp\left(-\left(c'+e'+f'\right)r_{14}^2\right), \\
&= \left[\frac{\pi}{c'+e'+f'}\right]^{3/2}.
\end{aligned}
\tag{3.48}
$$

$$
\begin{aligned}
\left\langle \delta\left(\vec{r}_{12}\right)\delta\left(\vec{r}_{34}\right)\right\rangle &= \left\langle \psi_i^{1234}\left|\delta\left(\vec{r}_{12}\right)\delta\left(\vec{r}_{34}\right)\right|\psi_j^{1234}\right\rangle, \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\delta\left(\vec{r}_{12}\right)\delta\left(\vec{r}_{34}\right)\exp\left(-a'r_{12}^2-b'r_{13}^2-c'r_{14}^2-d'r_{23}^2-e'r_{24}^2-f'r_{34}^2\right), \\
&= \int d^3\vec{r}_{13}d^3\vec{r}_{14}\delta\left(\vec{r}_{34}\right)\exp\left(-b'r_{13}^2-c'r_{14}^2-d'r_{13}^2-e'r_{14}^2-f'r_{34}^2\right), \\
&= \int d^3\vec{r}_{13}d^3\vec{r}_{14}\delta\left(\vec{r}_{14}-\vec{r}_{13}\right)\exp\left(-\left(b'+d'\right)r_{13}^2-\left(c'+e'\right)r_{14}^2-d'\left(\vec{r}_{14}-\vec{r}_{13}\right)^2\right), \\
&= \int d^3\vec{r}_{13}\exp\left(-\left(b'+c'+d'+e'\right)r_{13}^2\right), \\
&= \left[\frac{\pi}{b'+c'+d'+e'}\right]^{3/2}.
\end{aligned}
\tag{3.49}
$$

$$
\begin{aligned}
\langle \delta(\vec{r}_{13})\,\delta(\vec{r}_{24})\rangle &= \left\langle \psi_i^{1234}\left|\delta(\vec{r}_{13})\,\delta(\vec{r}_{24})\right|\psi_j^{1234}\right\rangle, \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\delta(\vec{r}_{13})\,\delta(\vec{r}_{24})\exp\left(-a'r_{12}^2-b'r_{13}^2-c'r_{14}^2-d'r_{23}^2-e'r_{24}^2-f'r_{34}^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{14}\delta(\vec{r}_{24})\exp\left(-a'r_{12}^2-c'r_{14}^2-d'r_{21}^2-e'r_{24}^2-f'r_{14}^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{14}\delta(\vec{r}_{14}-\vec{r}_{12})\exp\left(-\left(a'+d'\right)r_{12}^2-\left(c'+f'\right)r_{14}^2-e'\left(\vec{r}_{14}-\vec{r}_{12}\right)^2\right), \\
&= \int d^3\vec{r}_{12}\exp\left(-\left(a'+c'+d'+f'\right)r_{12}^2\right), \\
&= \left[\frac{\pi}{a'+c'+d'+f'}\right]^{3/2}. \qquad (3.50)
\end{aligned}
$$

$$
\begin{aligned}
\langle \delta(\vec{r}_{23})\,\delta(\vec{r}_{24})\rangle &= \left\langle \psi_i^{1234}\left|\delta(\vec{r}_{23})\,\delta(\vec{r}_{24})\right|\psi_j^{1234}\right\rangle, \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\delta(\vec{r}_{13}-\vec{r}_{12})\,\delta(\vec{r}_{14}-\vec{r}_{12})\times \\
&\exp\left(-a'r_{12}^2-b'r_{13}^2-c'r_{14}^2-d'\left(\vec{r}_{13}-\vec{r}_{12}\right)^2-e'r_{24}^2-f'\left(\vec{r}_{14}-\vec{r}_{13}\right)^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{14}\delta(\vec{r}_{14}-\vec{r}_{12})\exp\left(-a'r_{12}^2-b'r_{12}^2-c'r_{14}^2-e'r_{24}^2-f\left(\vec{r}_{14}-\vec{r}_{12}\right)^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{14}\delta(\vec{r}_{14}-\vec{r}_{12})\exp\left(-\left(a'+b'\right)r_{12}^2-c'r_{14}^2-\left(e'+f'\right)\left(\vec{r}_{14}-\vec{r}_{12}\right)^2\right), \\
&= \int d^3\vec{r}_{12}\exp\left(-\left(a'+b'+c'\right)r_{12}^2\right), \\
&= \left[\frac{\pi}{a'+b'+c'}\right]^{3/2}. \qquad (3.51)
\end{aligned}
$$

$$
\begin{aligned}
\langle \delta(\vec{r}_{12})\,\delta(\vec{r}_{23})\rangle &= \left\langle \psi_i^{1234}\left|\delta(\vec{r}_{12})\,\delta(\vec{r}_{23})\right|\psi_j^{1234}\right\rangle, \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\delta(\vec{r}_{12})\,\delta(\vec{r}_{13}-\vec{r}_{12})\times \\
&\exp\left(-a'r_{12}^2-br_{13}'^2-c'r_{14}^2-d'r_{23}^2-e'r_{24}^2-f\left(\vec{r}_{14}-\vec{r}_{12}\right)^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{14}\delta(\vec{r}_{12})\exp\left(-a'r_{12}^2-b'r_{12}^2-c'r_{14}^2-e'r_{24}^2-f\left(\vec{r}_{14}-\vec{r}_{12}\right)^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{14}\delta(\vec{r}_{12})\exp\left(-\left(a'+b'\right)r_{12}^2-c'r_{14}^2-\left(e'+f'\right)\left(\vec{r}_{14}-\vec{r}_{12}\right)^2\right), \\
&= \int d^3\vec{r}_{14}\exp\left(-\left(c'+e'+f'\right)r_{12}^2\right), \\
&= \left[\frac{\pi}{c'+e'+f'}\right]^{3/2} \equiv \langle \delta(\vec{r}_{12})\,\delta(\vec{r}_{13})\rangle. \qquad (3.52)
\end{aligned}
$$

$$
\begin{aligned}
\langle \delta(\vec{r}_{23})\,\delta(\vec{r}_{34})\rangle &= \left\langle \psi_i^{1234}\left|\delta(\vec{r}_{23})\,\delta(\vec{r}_{34})\right|\psi_j^{1234}\right\rangle, \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\delta(\vec{r}_{13}-\vec{r}_{12})\,\delta(\vec{r}_{14}-\vec{r}_{13})\times \\
&\exp\left(-a'r_{12}^2-b'r_{13}^2-c'r_{14}^2-d'r_{23}^2-e'r_{24}^2-f'\left(\vec{r}_{14}-\vec{r}_{12}\right)^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{14}\delta(\vec{r}_{14}-\vec{r}_{12})\exp\left(-a'r_{12}^2-b'r_{12}^2-c'r_{14}^2-e'r_{24}^2-f'\left(\vec{r}_{14}-\vec{r}_{12}\right)^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{14}\delta(\vec{r}_{14}-\vec{r}_{12})\exp\left(-\left(a'+b'\right)r_{12}^2-c'r_{14}^2-\left(e'+f'\right)\left(\vec{r}_{14}-\vec{r}_{12}\right)^2\right), \\
&= \int d^3\vec{r}_{14}\exp\left(-\left(a'+b'+c'\right)r_{12}^2\right), \\
&= \left[\frac{\pi}{a'+b'+c'}\right]^{3/2} \equiv \langle \delta(\vec{r}_{23})\,\delta(\vec{r}_{23})\rangle. \qquad (3.53)
\end{aligned}
$$

Product of three delta functions

There are different possibilities of the four delta functions e.g.,

$$\begin{aligned}
\langle \delta(\vec{r}_{12})\,\delta(\vec{r}_{13})\,\delta(\vec{r}_{24})\rangle &= \left\langle \psi_i^{1234}\left|\delta(\vec{r}_{12})\,\delta(\vec{r}_{13})\,\delta(\vec{r}_{24})\right|\psi_j^{1234}\right\rangle, \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\delta(\vec{r}_{12})\,\delta(\vec{r}_{13})\,\delta(\vec{r}_{14}-\vec{r}_{12})\times \\
&\exp\left(-a'r_{12}^2 - b'r_{13}^2 - c'r_{14}^2 - d'r_{13}^2 - e'(\vec{r}_{14}-\vec{r}_{12})^2 - f'(\vec{r}_{14}-\vec{r}_{13})^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}\delta(\vec{r}_{12})\,\delta(\vec{r}_{13})\exp\left(-a'r_{12}^2 - b'r_{12}^2 - c'r_{12}^2 + d'r_{13}^2 - f'(\vec{r}_{12}-\vec{r}_{13})^2\right), \\
&= \int d^3\vec{r}_{12}\delta(\vec{r}_{12})\exp\left(-(a'+b'+c'+f')\,r_{12}^2\right), \\
&= \int d^3\vec{r}_{12}\delta(\vec{r}_{12})\exp\left(-(a'+b'+c'+f)\,r_{12}^2\right), \\
&= \text{Constant.} \equiv 1
\end{aligned} \tag{3.54}$$

In order to consider the four-particles coalescence probabilities we will consider the product of delta functions of the type $\delta(\vec{r}_{ij})\,\delta(\vec{r}_{jk})\,\delta(\vec{r}_{kl})$. The only possiblity that we are going to consider here is

$$\begin{aligned}
\langle \delta(\vec{r}_{12})\,\delta(\vec{r}_{23})\,\delta(\vec{r}_{34})\rangle &= \left\langle \psi_i^{1234}\left|\delta(\vec{r}_{12})\,\delta(\vec{r}_{23})\,\delta(\vec{r}_{34})\right|\psi_j^{1234}\right\rangle, \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}d^3\vec{r}_{14}\delta(\vec{r}_{12})\,\delta(\vec{r}_{23})\,\delta(\vec{r}_{14}-\vec{r}_{13})\times \\
&\exp\left(-a'r_{12}^2 - b'r_{13}^2 - c'r_{14}^2 - d'r_{23}^2 - e'(\vec{r}_{14}-\vec{r}_{12})^2 - f'(\vec{r}_{14}-\vec{r}_{13})^2\right), \\
&= \int d^3\vec{r}_{12}d^3\vec{r}_{13}\delta(\vec{r}_{12})\,\delta(\vec{r}_{13}-\vec{r}_{12})\times \\
&\exp\left(-a'r_{12}^2 - b'r_{12}^2 - c'r_{13}^2 + d'(\vec{r}_{13}-\vec{r}_{12})^2 - e(\vec{r}_{13}-\vec{r}_{12})^2\right), \\
&= \int d^3\vec{r}_{12}\delta(\vec{r}_{12})\exp\left(-(a'+b'+c')\,r_{12}^2\right), \\
&= \int d^3\vec{r}_{12}\delta(\vec{r}_{12})\exp\left(-(a'+b'+c')\,r_{12}^2\right), \\
&= \text{Constant.} \equiv 1
\end{aligned} \tag{3.55}$$

Chapter 4

Numerical Analysis and Conclusion

In our basic course on Quantum Mechanics we learned that hydrogen atom is a simplest two body system. Even such a simple system can be solved exactly for a Coulomb potential and one has to solve it numerically for the non-Coulomb like potentials. Replacing proton with a positron will give us a familiar bound state, i.e., positronium. If we add one more electron or position in the atom it will give us positronium ion ($Ps^{\pm}$. To solve this three body problem in Quantum Mechanics, variational approach is used. In this approach, Using the ground state wave function as a basis for a trial wave function. To study the different properties of $Ps^{\pm}$ using the trial wave function with Gaussian basis, a code is developed by A. Czarnecki et al. [**29**]. The same code is later used to find the ground state energy various coalesence probabilities of di-positronium or positronium molecule Ps_2.

In this dissertation we focused on the properties of PsH. One of most interesting features of the PsH is that it is somehow special class of Coulombic systems that lies between the H_2 molecule and the dipositronium molecule (Ps_2) as in the later case both nuclei are replaced with the positron. Since mass of one nuclei in the PsH is same as that of the electron, therefore, its motion can not be considered to be slow . Therefore, it is found that the electrons are cluster around the proton and, therefore, the PsH is essentially a four body system.

Some important properties of the PsH are: Its life time is 0.65 ns. The positronium in PsH is slightly swollen compared to the ordinary positronium atom with relative electron-positron distances ($\langle r_{e^-e^+}\rangle$) to be $3.48a_0$ and $3.0a_0$, respectively. The average distance of electrons from the proton ($\langle r_{e^-p^+}\rangle$) is $2.31a_0$ which is larger than the dihydrogen. The average distance between positron-proton $\left(\langle r_{e^+p^+}\rangle\right)$ is $3.66a_0$ which is much larger than $1.41a_0$ that is the average distance between two protons $\left(\langle r_{p^+p^+}\rangle\right)$ in the H_2.

When trying to identify the characteristics of complex quantum system it is not always feasible to obtain precise wave function. As a result, one may resort to variational calculation to estimate the wave function. Typically this involves a numerical computation, particularly when attempting to optimize wave function. If we strive to get a close approximation of our wave function using a set of even function as a basis, this could prove a significant benefit. The variational method provides a mean for approximating the ground state as well as certain excited states, of a system's lowest energy eigenstate. We use variational method to approximate wavefunction and to calculate expectation values of different properties of positronium hydride by using the code [**29**].

In Chapter 2, we have calculated the matrix elements of Hamiltonian in terms of these optimized parameters $a_i', .., f'$. We wrote a computer program based on FORTRAN to calculate expectation values of inter particle distances, Coulomb potential, matrix elements for inverse square of inter-particle distances, kinetic energy, matrix elements and total energy of PsH. By using the 1000 basis, the results are presented in Table 4.1. We can see that our results of binding energy $-0.788\ 870\ 345\ 206$ aligns well with the corresponding calculation. [**33**].

The radiative decays of PsH occurs through the annihilation of electron and positron, which is known as the coalescence probability. This corresponds to the expectation value of the Dirac delta function. In Table 4.1 we have calculated the expectation value of two-, three- and four-particles coalescence probabilities. There convergence will lead to the good estimate of the radiative decays and using the

$\langle r_{p^+e^+} \rangle$	$\langle r_{e^+e^-} \rangle$	$\langle r_{pe^-} \rangle$	$\langle r_{e^-e^-} \rangle$	$\langle r^2_{p^+e^+} \rangle$
3.663 501 879	3.481 175 784	2.313 161 069	3.577 021 997	16.272 155 569
3.663 471 893	3.481 158 108	2.313 146 873	3.576 994 110	16.271 617 005
$\langle r^2_{e^+e^-} \rangle$	$\langle r^2_{p^+e^-} \rangle$	$\langle r^2_{e^-e^-} \rangle$	$\langle 1/r^2_{p^+e^+} \rangle$	$\langle 1/r^2_{e^+e^-} \rangle$
15.593 537 619	7.824 794 250	15.895 938 518	0.172 013 647	0.349 072 614
15.593 216 798	7.824 543 786	15.895 434 519	0.172 015 799	0.349 067 937
$\langle 1/r^2_{p^+e^-} \rangle$	$\langle 1/r^2_{e^-e^-} \rangle$	$\langle 1/r_{p^+e^+} \rangle$	$\langle 1/r_{e^+e^-} \rangle$	$\langle 1/r_{p^+e^-} \rangle$
1.205 651 819	0.213 646 523	0.347 301 530	0.418 428 480	0.729 258 149
1.205 619 787	0.213 648 513	0.347 302 232	0.418 428 711	0.729 257 838
$\langle 1/r_{e^-e^-} \rangle$	$\langle T \rangle$	$\langle V \rangle$	$\langle H_{\text{non-rel.}} \equiv E_1 \rangle$	$\left\{ \begin{array}{l} \langle \delta_{e^+e_3^-}\delta_{e^+e_4^-} \rangle \\ \equiv \langle \delta_{e^+e_3^-}\delta_{e_3^-e_4^-} \rangle \end{array} \right.$
0.370 330 394	−−	−−	−0.788 870 685 002	3.7147×10^{-4}
0.370 330 979	0.788 869 542 262	−1.577 739 887 468	−0.788 870 345 206	3.7364×10^{-4}
$\left\{ \begin{array}{l} \langle \delta_{p^+e^+}\delta_{p^+e^-} \rangle \\ \equiv \langle \delta_{p^+e^+}\delta_{e^+e^-} \rangle \end{array} \right.$	$\langle \delta_{pe^+}\delta_{e_3^-e_4^-} \rangle$	$\langle \delta_{pe_3^-}\delta_{e^+e_4^-} \rangle$	$\langle \delta_{pe_3^-}\delta_{p^+e_4^-} \rangle$	$\langle \delta_{p^+e^+}\delta_{p^+e_3^-}\delta_{e^+e_4^-} \rangle$
8.5986×10^{-4}	3.1582×10^{-5}	6.3212×10^{-3}	7.5334×10^{-3}	1.9038×10^{-4}
8.8148×10^{-4}	3.1238×10^{-5}	6.0887×10^{-3}	7.3087×10^{-3}	1.8018×10^{-4}
$\langle \delta_{p^+e^+} \rangle$	$\langle \delta_{e^+e^-} \rangle$	$\langle \delta_{e^-e^-} \rangle$	$\langle \delta_{p^+e^-} \rangle$	$\langle \tilde{\delta}_{p^+e^+} \rangle$
0.001 626 822	0.024 458 106	0.004 366 761	0.176 973 054	0.001 622 883
0.001 646 266	0.024 407 634	0.004 388 427	0.176 142 839	0.001 624 232
$\langle \tilde{\delta}_{e^+e^-} \rangle$	$\langle \tilde{\delta}_{p^+e^-} \rangle$	$\langle \tilde{\delta}_{e^-e^-} \rangle$		
0.024 494 690	0.177 041 413	0.004 360 586		
0.024 492 580	0.177 031 923	0.004 361 544		

Table 4.1: Values of the parameter calculated by using our wave-function for the PsH and their comparision with [**33**]. The values of each parameter in the first row correspond to the one calculated in [**33**] and the second row in each case depicts the value calcualted here. In both cases the size of basis is considered to be 1000. The $\tilde{\delta}$ denotes the value using Drachman identity.

three- and four-particle delta functions the QED results of two and zero-photon annihilation of PsH are determined [**25**]. From Table 4.1, we can see that our results of various coalescence probabilities are in agreement with [**33**]. To achieve the good convergence of two-particle delta functions, we derived the corresponding results of the expectation using Drachman identities. Compared to the direct calculation of the expectation value of these two particle delta functions, we can see that the results obtained by Drachman identities show better agreement with the [**33**], and this is evident from Table 4.1.

To summarize: in the work presented here, we used the variational method in Gaussian basis and combine it with the algorithms for decomposing the Hamiltonian matrix elements and for optimizing the wave function for PsH. Using these optimized wave functions with 1000 basis, we calculated the various properties, such as inter-particle distances and the non-relativistic ground state energy and compare these quantities with the one calculated in [**33**]. The important problem in the PsH system is the study of electron-positron annihilation in this system which produce zero-, one-, two-, and in general n-photons where the decay rate to 2γ is the maximum. The electron-positron annihilation correspond to the coalescence probability of these two particles at one point and it corresponds to the the expectation value of $\delta_{e^+e^-}$. Knowing that the convergence of these expectation value is not very good in the Gaussian basis, we reported the values both by the direct calculation and also by using the Drachman identity and found a good agreement with their values reported in literature [**33**]. There is a possibility that one or both photons created due to electron-positron annihilations in the PsH are absorbed by the internal conversion that corresponds to the expectation value of the three particle and four particle δ-function. These coalescence probabilities of three- and four-particles at a single point and also calculated. However, the calculation of the decay rate of PsH to one- and zero-photon with free and bound (possible for one and two photons only) state of final proton and electron is beyond the scope of this work.

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