An Adiabatic Study of the Positronium Negative Ion and Other Three-Particle Systems.

Javier Botero
Louisiana State University and Agricultural & Mechanical College

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AN ADIABATIC STUDY OF THE
POSITRONIUM NEGATIVE ION AND
OTHER THREE-PARTICLE SYSTEMS

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in
The Department of Physics and Astronomy

by
Javier Botero
C.E., Escuela Colombiana de Ingenieria, 1981
May 1986
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The novel methods introduced in this dissertation for the solution of the adiabatic eigenvalue equation and the calculation of the probability density are the product of a close collaboration between Dr. Greene and myself.

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ABSTRACT

In an effort to unravel the dependence of the dynamics of three-bound-particle systems on the relative masses of the particles, an adiabatic treatment in hyperspherical coordinates is used to study the ground state and some doubly excited states of $\text{Ps}^-$ (positronium negative ion) and other three-particle systems, including $\text{H}^-$ and $\text{M}^-$ (muonium negative ion). Two different methods for the solution of the adiabatic eigenvalue equation are presented; one uses a "prediagonalized" basis of hyperspherical harmonics, and the other uses an asymptotic basis which consists of hydrogenic functions for the positronium. Potential curves for $\text{Ps}^-$ and $\text{M}^-$ in the $^1\text{S}_{\text{e}}$, $^1\text{P}_{\text{e}}$, $^3\text{P}_{\text{e}}$, $^3\text{P}_{\text{o}}$ and $^1\text{D}_{\text{e}}$ states and for $\text{H}^-$ in the $^1\text{P}_{\text{o}}$ states are presented. A method for calculating the probability density as a function of the hyperspherical coordinates $(R, \alpha, \theta_{12})$ is introduced and used for the $\text{P}$ states of $\text{Ps}^-$. This helps to understand the different symmetries and to distinguish among them. A remarkable linear dependence of the binding energy of the ground state and of the doubly excited states on the reduced mass of the atom, discovered in this study, is presented and discussed.
I. INTRODUCTION

The problem of three bodies is the most celebrated of all dynamical problems. It has attracted the attention of many of the greatest physicists and mathematicians since the Eighteenth century. The practical importance of this problem arose initially from its applications to celestial mechanics. The problem is enunciated classically as follows: Given the positions and velocities of three particles whose masses are $m_1, m_2$ and $m_3$ and which move in space under the action of their gravitational attraction, the positions of the particles are to be determined at any subsequent time. This problem has no known exact solution in general. A similar problem is the one of three particles interacting via the Coulomb force. This is a purely quantum mechanical problem since the coupling constant of the electromagnetic interaction $(e^2/\hbar c = 1 \text{ a.u.})$ is of the order of $10^{-2}$ and the distances and masses involved are in the atomic scale, while the coupling constant of the gravitational interaction $(GM/c^2)$ is of the order of $10^{-45}$ and the distances and masses involved are on a macroscopic scale.

There are two different cases in the general problem of three bodies. First, there is the scattering case, in which at least one particle can escape to infinity. This is the case of a collision of a particle, free at infinity,
with two bound particles. An example of this case is the scattering of an electron by a hydrogen atom. The second case is when the three particles are bound, which means that none of the particles can escape to infinity. An example of this case is the $H^-\text{ ion}$. Neither one of these two problems has a known exact solution in classical or in quantum mechanics in general.

The solution of the problem of three-bound particles interacting via Coulomb forces in quantum mechanics consists of finding the spectrum of the system, e.g. finding the energies at which the system is either bound or has a resonance; the latter means that even though one particle can escape to infinity, the interaction of the particles keeps the system bound during a finite length of time. These energies depend strongly on the relative masses of the particles, of course. Concerning this mass dependence, there are two limiting regimes which are the most known and discussed in the literature. One limit, realized physically by the $H_2^+$ molecular ion, consists of one light particle ($e^-$) and two heavy particles ($p,p$). It is accurately characterized by an adiabatic treatment of the heavy particle motion. The opposite limit, realized physically by the $H^-\text{ ion}$, consists of two light particles ($e^-,e^-$) undergoing correlated motion in the central field of a massive proton. It is usually assumed that the proton is infinitely massive, in which case the center of mass of
the system coincides with the position of the proton. The problem then becomes one of two interacting particles in a central field. Here one sees a whole range of approximations, starting with the crude model that neglects the Coulomb interaction between the two electrons, in which case the Schrödinger equation can be solved exactly but results far from the exact values are obtained, to very extensive variational calculations (with hundreds of trial functions) and the formulation of the Breit equation in the relativistic theory. Still, doubly excited states of two-electron atoms are an open field of research. Some intermediate systems, like $^+e^-e^-$ (M$^-$ throughout this dissertation) and other molecular-type systems, fall close to either one of these limiting cases, and are, therefore, treated within the same approximations.

When the three particles are of comparable masses, the system does not fall into either one of the limiting cases, and a different approach must be followed. That is the case in the positronium negative ion (Ps$^-$ throughout this dissertation), where the three particles, one positron and two electrons, have the same mass. An adiabatic study in hyperspherical coordinates of Ps$^-$ is the main subject of this dissertation. This approach has the great advantage that intermediate results (the potential curves) bring much information about how different processes, like excitation and photodetachment, should occur.
There are two main reasons for pursuing this work: i) it is well known\textsuperscript{6-9} that both the ground state energy of \textit{Ps}\textsuperscript{-} and its one-electron binding energy in the ground state are approximately one half the corresponding values for \textit{H}\textsuperscript{-}. Since the reduced mass of \textit{Ps} is half that of \textit{H} and since both \textit{Ps}\textsuperscript{-} and \textit{H}\textsuperscript{-} are weakly bound, the scaling of the total energy is reasonable. Apparently no simple explanation is known for the scaling of the binding energy, which depends more strongly on the amount of correlation between the particles. Comparison between known results for \textit{H}\textsuperscript{-} and those calculated here for \textit{Ps}\textsuperscript{-} and \textit{M}\textsuperscript{-} should give a better understanding of the dependence of the dynamics of three-bound-particle systems on the relative masses of the particles; and ii) in the last few years there has been growing interest in the study of systems that contain positrons. One such system, known to be bound since the 1950's, is \textit{Ps}\textsuperscript{-}. While there are many calculations of the ground state of \textit{Ps}\textsuperscript{-}, there are very few of its doubly excited states. I present here the results of a series of calculations of doubly excited states of \textit{Ps}\textsuperscript{-} with total angular momentum \textit{L} = 0, 1, and 2, and different states of spin (singlets and triplets) and of parity (even and odd).

Chapter II of this dissertation presents the problem and the coordinate system to be used. Chapter III presents a brief review of the hyperspherical coordinates and the
adiabatic treatment. Chapter IV describes the solution of the adiabatic equation for arbitrary total angular momentum using hyperspherical harmonics as basis functions. Chapter V presents the results for Ps\(^-\). Five different symmetries are discussed. Potential curves and probability density plots are also presented. Chapter VI derives an alternative method for solving the adiabatic eigenvalue equation which uses an asymptotic basis. It is used to study \(^1S^e\) states of Ps\(^-\). At the end of Chapter VI a set of Euler angles to rotate from the body-fixed frame to the laboratory frame is also discussed. In Chapter VII I present results for other three-particle systems, including H\(^-\) and M\(^-\). Chapter VIII consists of some concluding remarks and future applications.
II. THE COORDINATE SYSTEM AND THE SCHRODINGER EQUATION

Different coordinate systems have been used to describe three particle systems depending mainly on the relative masses of the particles. For two-electron atoms, independent-particle type coordinates \((\vec{r}_1, \vec{r}_2)\) are usually used, where \(\vec{r}_1\) represents the position vector of electron 1 relative to the nucleus, and \(\vec{r}_2\) represents that of electron 2. (These coordinates can in turn be replaced by hyperspherical coordinates, as will be explained in the next chapter.) The full Hamiltonian in independent particle coordinates is:

\[
H = -\frac{1}{2\mu} \vec{\nabla}_1^2 - \frac{1}{2\mu} \vec{\nabla}_2^2 - \frac{m}{M} \vec{\nabla}_1 \cdot \vec{\nabla}_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (II.1)
\]

where \(\mu\) is the reduced mass of the electron-nucleus pair, \(m\) is the mass of the electron, \(M\) is the mass of the nucleus and \(Z\) is the nuclear charge. In the usual case of a heavy nucleus, \(m/M\) is small, and this term may be treated in perturbation theory\(^1\).

When the three particles are of comparable masses, as is the case in Ps\(^-\), the cross term \(\vec{\nabla}_1 \cdot \vec{\nabla}_2\) is as important as the other two terms of the kinetic energy operator and cannot be treated perturbatively. In order to avoid the complications involved with this term, I describe the three-particle configuration space in terms of symmetric
Jacobi coordinates \((\dot{r}_1, \dot{x})\) defined as followed:

\[
\dot{r}_1 = \dot{r}_{m_2} - \dot{r}_{m_1}
\]

\[
\dot{x} = -\frac{1}{2} (\dot{r}_{m_1} + \dot{r}_{m_2}) + \dot{r}_{m_3}
\]  

(II.2)

where \(\dot{r}_{m_1}, \dot{r}_{m_2}, \) and \(\dot{r}_{m_3}\) are the position vectors of particles 1, 2, and 3, respectively (see Figs. 1a and 1b).

The Hamiltonian of the system in these coordinates is:

\[
H = T + V
\]

(II.3)

where

\[
T = -\frac{1}{2m_1} \nabla^2 r_{m_1} - \frac{1}{2m_2} \nabla^2 r_{m_2} - \frac{1}{2m_3} \nabla^2 r_{m_3}
\]

(II.4)

\[
T = -\frac{1}{2\mu_{12}} \nabla^2 r_1 - \frac{1}{2\mu_{12,3}} \nabla^2 x
\]

and

\[
V = \frac{1}{|\dot{r}_1|} - \frac{1}{|\frac{1}{2} \dot{r}_1 + \dot{x}|} - \frac{1}{|\frac{1}{2} \dot{r}_1 - \dot{x}|}
\]

(II.5)

are the kinetic and potential energy operators in the center of mass frame. Here \(\mu_{12}\) is defined as the reduced mass of particles 1 and 2, and \(\mu_{12,3}\) as the reduced mass of particle 3 relative to particles 1 and 2.
Fig. 1. Coordinate systems used to describe three-particle systems in their center-of-mass frame. (a) shows the independent-particle coordinates and (b) shows the Jacobi coordinates ($\vec{r}_1, \vec{x}$) and ($\vec{r}_1', \vec{x}'$) used in the present study.
\[ \mu_{12} = \frac{m_1 m_2}{m_1 + m_2} \quad (II.6) \]

\[ \mu_{12,3} = \frac{(m_1 + m_2) m_3}{m_1 + m_2 + m_3} \]

In the latter equations, and hereafter, the two particles with equal charge \((e^-e^-)\) are particles 1 and 2 while the opposite charged particle (nucleus) is particle number 3.

This choice of coordinates has two main advantages:

1) The kinetic energy operator is simple, and can be separated in hyperspherical coordinates.

2) When two of the three particles are identical, as is the case in \(\text{Ps}^-\) and the other systems studied here, \(\hat{r}_1\) is chosen as the separation between the identical particles, so that the effect of the exchange operator is simple:

\[ P_{12} f(\hat{r}_1, \hat{x}) = f(-\hat{r}_1, \hat{x}) \quad (II.7) \]

Two different choices for the angular coordinates are discussed here. One set of coordinates uses three "Euler type" angles to describe the body-fixed frame of the particles and a fourth angle \(\theta_{12} = \cos^{-1}(\hat{r}_1 \cdot \hat{x})\). A brief presentation of these angles is given in Chapter VI. The other set of angles, which is the one used in most of this work, uses the spherical angles \((\theta_1 \phi_1)\) and \((\theta_2 \phi_2)\) of the
unit vectors $\hat{r}_1$ and $\hat{x}$. 
III. HYPERSPHERICAL COORDINATES AND THE ADIABATIC TREATMENT

Hyperspherical coordinates \((R, \alpha)\) were first used in atomic physics to study the wave function of the helium atom in the limiting regime \(r_1 \rightarrow 0\) and \(r_2 \rightarrow 0\) \(^{11}\) (where \(r_1\) and \(r_2\) are independent-electron coordinates). They are defined by:

\[
R = (r_1^2 + r_2^2)^{1/2} \tag{III.1}
\]

\[
\alpha = \tan^{-1} \left( \frac{r_2}{r_1} \right) .
\]

The only radial coordinate, \(R\), represents the "size" of the system, while the mock angle \(\alpha\) characterizes the radial correlation of the two electrons. Fock\(^{12}\) showed later that the expansion of the ground state wave function near \(R = 0\), the Fock expansion, contains terms which are powers of \(\ln R\); this has been discussed more recently by Feagin and Macek\(^{13}\). Wannier\(^{14}\) also used these coordinates in his study of electron-impact ionization of atoms near threshold. Starting with Macek's\(^{15}\) adiabatic treatment of helium, hyperspherical coordinates have been used extensively and successfully for describing electron correlation and doubly excited states of atoms\(^{4}\). Lin's study of \(H^-\) and helium\(^{16}\), its extension to alkaline-earth elements (Be, Mg, Ca, Sr, ...) and their isoelectronic ions (Li\(^-\), Na\(^-\), Sr\(^-\), ...) by Greene\(^{17}\), the study of three-
electron atoms by Greene and Clark\textsuperscript{18}, the study of He\textsuperscript{-} by Watanabe\textsuperscript{19}, the more recent study of HD\textsuperscript{+} by Macek and Jerjian\textsuperscript{20} and the study of molecular dynamics by Kupperman and others\textsuperscript{21}, are a few examples of the broad range of application of hyperspherical coordinates in atomic and molecular physics.

Here this approach is extended to the general case of three particles of masses \(m_1, m_2,\) and \(m_3\), two of which \((m_1, m_2)\) are identical. In this case, the hyperspherical coordinates \(R\) and \(\alpha\) are defined as:

\[
R = (r_1^2 + r_2^2)^{1/2} \quad \text{(III.2)}
\]

\[
\alpha = \tan^{-1}(r_2/r_1) \quad \text{(III.3)}
\]

where

\[
\dot{r}_2 = c \dot{x},
\]

\(\dot{r}_1\) and \(\dot{x}\) are the Jacobi coordinates defined in the previous section, and the constant \(c\) is introduced so that the squared hyperspherical radius is proportional to the trace of the moment-of-inertia tensor of the system; this is a necessary condition for the kinetic energy to be separable in these coordinates\textsuperscript{22,23}

\[
c = \left( \frac{\mu_{12,3}}{\mu_{12}} \right)^{1/2}. \quad \text{(III.4)}
\]

The kinetic and potential energy operators are then:
where $\Lambda^2$ is the Casimir operator for the group $0^\circ$, usually called the "grand angular momentum operator":

$$\Lambda^2 = -\frac{1}{2} \frac{d}{d\alpha} \sin^2 \alpha \cos^2 \alpha \frac{d}{d\alpha} + \frac{\lambda_1^2}{\sin \alpha \cos \alpha} + \frac{\lambda_2^2}{\sin \alpha} - \frac{1}{4}.$$  (III.6)

The Schrödinger equation is then:

$$\left\{ -\frac{\hbar^2}{2\mu_{12}} \left[ \frac{\partial^2}{\partial R^2} - \frac{1}{R} \frac{\partial^2}{\partial \alpha^2} - \frac{1}{4R^2} + \frac{\lambda_1}{R \cos \alpha} + \frac{\lambda_2}{R \sin \alpha} \right] 
+ V(R,\Omega)-E \right\} \psi(R,\Omega) = 0.$$  (III.7)

Here the usual wave function $\psi(R,\Omega)$ has been renormalized by setting

$$\psi(R,\Omega) = \psi(R,\Omega) R^{5/2} \sin \alpha \cos \alpha$$  (III.8)

in order to remove first derivative terms in the kinetic energy operator both in $R$ and in $\alpha$. $\Omega$ stands for the
angular variables

\[ \Omega = (\alpha, \hat{r}_1, \hat{r}_2) \]  \hspace{1cm} \text{(III.9)}

The \( R \) dependence of the potential energy in these coordinates factors out, so that \( C(\Omega) \) is independent of \( R \),

\[ C(\Omega) = R V(R, \Omega) . \]

This fact will prove to be very important as the calculation of the matrix \( C \) can be done once and then be used at all \( R \) values to calculate \( V \), if an \( R \)-independent basis set is used.

Figure 2 shows a plot of \( V(R, \Omega) \) as a function of \( \alpha \) and \( \theta_{12} \), the angle between \( \hat{r}_1 \) and \( \hat{r}_2 \) for \( \text{Ps}^- \). We see two potential wells at \( \alpha = \pi/6 \) and \( \theta_{12} = 0 \) and \( \pi \) where either electron approaches the positron, and a divergence at \( \alpha = \pi/2 \) where the two electrons approach each other. Some properties of the potential function may not be as clear here as they are in Lin's more symmetric surface. For example, the saddle point of the \( H^- \) potential at \( \alpha = \pi/4, \cos \theta_{12} = -1 \) (in Macek's coordinate system\(^4\)), which is so important in the study of double-electron escape, here becomes the line \( \alpha = 0 \).

**Adiabatic Expansion**

A prototype of an adiabatic approach is the Born-Oppenheimer separation for diatomic molecules. It consists
Fig. 2. The potential energy surface of Ps\(^-\) is shown at one R value as a function of the two hyperspherical angles \(\alpha\) and \(\theta_{12}\). (From ref. 6)
of solving the Schrödinger equation first at fixed internuclear separation $R$, obtaining electronic wave functions. These form a complete set at each value of $R$ and are orthonormal. Therefore, the total wave function can be expanded into a basis of these electronic wave functions, with expansion coefficients that depend on $R$.

The Born-Oppenheimer approximation consists of further neglecting terms that involve derivatives with respect to $R$ of the electronic wave function. This is based on the slow, i.e. adiabatic, variation of the electronic wave function as a function of $R$.

In the hyperspherical approach, the adiabatic treatment consists of solving the Schrödinger equation at fixed hyperspherical radius $R$ in order to obtain the so-called adiabatic wavefunctions $\Phi_\mu(R,\Omega)$ and the adiabatic potential curves $U_\mu(R)$ as follows:

$$\left[ \frac{1}{2\mu_1 R^2} \left[ - \frac{a^2}{2} - \frac{1}{4} + \frac{l_1^2}{\cos^2 \alpha} + \frac{l_2^2}{\sin^2 \alpha} \right] + V(R,\Omega) \right] \Phi_\mu(R,\Omega)$$

$$= U_\mu(R) \Phi_\mu(R,\Omega)$$

(III.10)

The wavefunction is then expanded as

$$\psi(R,\Omega) = \sum_\mu F_\mu(R) \Phi_\mu(R,\Omega)$$

(III.11)

When this expansion is entered into the Schrödinger
equation, and is projected onto each of the $\phi_v(R,Q)$, one gets a system of equations for the radial functions $F_\mu(R)$.

$$\frac{1}{2\mu_{12}} \left\{ -\frac{\partial^2}{\partial R^2} F_\mu(R) - \sum <\phi_v|\frac{2\partial F_\mu}{\partial R} \frac{\partial}{\partial R} + F_\mu \frac{\partial^2}{\partial R^2}|\phi_\mu> \right\}$$

$$+ (U_v(R) - E) F_v(R) = 0 . \quad (\text{III.12})$$

where $<|>$ implies integration over all angular variables.

This is a system of $n$ equations (if the complete set is retained) coupled through the terms

$$W_{\mu\nu} = -<\phi_\mu|\frac{\partial^2}{\partial R^2}\phi_\nu> = \frac{dP_{\mu\nu}}{dR} - (P_{\mu\nu})^2 \quad (\text{III.13})$$

and

$$P_{\mu\nu} = <\phi_\mu|\frac{\partial}{\partial R}\phi_\nu> \quad (\text{III.14})$$

Previous studies$^{4,5,24}$ have shown that the off-diagonal elements of the coupling matrix $P_{\mu\nu}$ ($P_{\mu\mu} = 0$) are small everywhere in $R$ except in the regions where two adiabatic curves try to cross, the so-called avoided-crossing regions. In this region the coupling term $P_{\mu\nu}$ becomes a leading term in the radial equation. Based on this fact, I have neglected the coupling between different channels everywhere except in the avoided-crossing regions, where I have either forced the curves to cross diabatically when it is known, based on symmetry considerations, that the curves should cross, or neglect
the effects produced by this "avoided-crossing" and interpolate the curves adiabatically when it is known that the curves should not cross. This will also be confirmed by the probability density plots.

The radial equation is then:

\[
\frac{1}{2\mu_{12}} \left\{ - \frac{d^2}{dR^2} + \frac{d}{dR} W_{\mu\mu}(R) + U_{\mu}(R) - E \right\} F_{\mu}(R) = 0 . \quad (III.15)
\]

This equation can be integrated in order to obtain either resonance energy positions or scattering phase-shifts, depending on the energy range of interest. Here the Numerov method has been used.
IV. SOLUTION OF THE ADIABATIC EQUATION

1. Introduction

One of the most important intermediate results of the adiabatic-hyperspherical treatment is the set of potential curves. They are analogous to the Born-Oppenheimer potential curves obtained in the study of diatomic molecules, except that the internuclear separation is replaced by the hyperspherical radius. These potential curves have permitted previous studies of three-particle systems to gain a deeper understanding of the dynamics.\(^4\)

The potential curve \(U_\mu(R) + W_{\mu\mu}(R)\) is the eigenvalue of the fixed-R Hamiltonian in addition to the adiabatic correction term \(W_{\mu\mu}(R)\) at each hyperradius \(R\). Therefore, the most important step in the adiabatic-hyperspherical treatment is the solution of the adiabatic eigenvalue equation. Different approaches have been presented in the literature. Here I shall review briefly a method introduced by Macek\(^{15}\) in his study of doubly excited states of helium \((\mu_{12}=1)\), and used later in several studies.\(^{17,22}\) It consists of expanding the adiabatic wavefunctions \(\Phi_\mu(R,\Omega)\) as

\[
\Phi_\mu(R,\Omega) = \sum_{\ell_1 \ell_2} g^\mu_{\ell_1 \ell_2}(R,\alpha) Y_{\ell_1 \ell_2}^{LM}(\hat{r}_1,\hat{r}_2) \quad (IV.1)
\]
where the $Y_{\lambda \lambda_1 l_2 LM}(\hat{r}_1, \hat{r}_2)$ are standard coupled spherical harmonics. Substituting this equation into the adiabatic eigenvalue equation leads to a system of differential equations for $g^\mu_{\lambda_1 \lambda_2}(R, \alpha)$

$$
\left\{ \frac{1}{2} \frac{d^2}{d \alpha^2} - \frac{1}{4} \frac{\lambda_1(\lambda_1+1)}{\cos^2 \alpha} + \frac{\lambda_2(\lambda_2+1)}{\sin^2 \alpha} \right\} - U_\mu(R) \right\} g^\mu_{\lambda_1 \lambda_2}(R, \alpha)
$$

$$
= \sum_{\lambda_1 \lambda_2} V_{\lambda_1 \lambda_2, \lambda_1 \lambda_2} g^\mu_{\lambda_1 \lambda_2}(R, \alpha) \quad (IV.2)
$$

where

$$
V_{\lambda_1 \lambda_2, \lambda_1 \lambda_2} = \langle Y_{\lambda_1 \lambda_2 LM}(\hat{r}_1, \hat{r}_2) | V | Y_{\lambda_1 \lambda_2 LM}(\hat{r}_1, \hat{r}_2) \rangle \quad (IV.3)
$$

is an integral only over $\hat{r}_1$ and $\hat{r}_2$. When many partial waves have to be included, this method becomes inefficient, for one has to solve a large system of coupled differential equations. A different approach, used first by Lin\textsuperscript{16}, consists of expanding the adiabatic function in a basis of eigenfunctions of the grand angular momentum operator $\hat{\lambda}^2$. A substantially modified version of this method is used in most of this work. A detailed discussion of it is made in the next section. In Chapter VI a third method is presented, introduced in Ref. 6, in which an asymptotic basis is used for the expansion of the adiabatic function in the study of $^1S^e$ states of $\text{Ps}^-$.
2. Expansion in Hyperspherical Harmonics

The fixed-R Hamiltonian is:

\[ \hat{U} = \frac{\hat{A}^2(\Omega) + C(\Omega)}{2\mu_{12}R^2} \]  \hspace{1cm} (IV.4)

where \( \hat{A}^2 \) is the grand angular momentum operator with the first derivative terms removed by rescaling the wavefunction in equation (III.4). The eigenfunctions of \( \hat{A}^2 \) in this coordinate system are hyperspherical harmonics,\(^4\),\(^2\)\(^5\) which form a complete set in \((\alpha, \hat{r}_1, \hat{r}_2)\):

\[ y_{m\ell_1 \ell_2}(\Omega) = N_{m\ell_1 \ell_2}(\cos \alpha)^{\ell_1+1}(\sin \alpha)^{\ell_2+1} \]

\[ \times F(-m, m+\ell_1+\ell_2+2, \frac{3}{2}; \sin^2 \alpha) \]  \hspace{1cm} (IV.5)

\[ \times Y_{\ell_1 \ell_2 LM}(\hat{r}_1, \hat{r}_2) \chi_{SM_S} \]

These correspond to eigenvalues

\[ (\lambda + 2)^2 - \frac{1}{4} = (2m + \ell_1 + \ell_2 + 2)^2 - \frac{1}{4}, \]

where \( m = 0, 1, 2, \ldots \) is the number of nodes of (IV.5) in \( \alpha \).

In eq. (IV.5) \( N_{m\ell_1 \ell_2} \) is a normalization constant.
\[ N_{m_1l_1l_2} = \left( \frac{8}{\pi} \right)^{1/2} \frac{\begin{pmatrix} l_1 + l_2 \\ 2 \end{pmatrix}}{(2l_2+1)!} \]

\[ x \left[ \frac{(l_1 + l_2 + 2m + 2) (m + l_1 + l_2 + 1)! (2m + 2l_2 + 1)! (m + l_1)!}{m! (m + l_2)! (2m + 2l_1 + 1)!} \right]^{1/2} \]

... is a hypergeometric polynomial, \( Y \) is a standard coupled spherical harmonic and \( \chi \) is a two-electron spinor. Some properties of these functions in this coordinate system are: under interchange of particles 1 and 2,

\[ P_{12} y_{m_1l_1l_2}(\alpha, \hat{r}_1, \hat{r}_2) = y_{m_1l_1l_2}(\alpha, -\hat{r}_1, \hat{r}_2) \]

\[ P_{12} y_{m_1l_1l_2}(\alpha, \hat{r}_1, \hat{r}_2) = (-1)^{l_1} y_{m_1l_1l_2}(\alpha, \hat{r}_1, \hat{r}_2) \]

and under the parity operator,

\[ \pi y_{m_1l_1l_2}(\alpha, \hat{r}_1, \hat{r}_2) = (-1)^{l_1 + l_2} y_{m_1l_1l_2}(\alpha, \hat{r}_1, \hat{r}_2) \]

so that antisymmetry of the wavefunction under electron exchange is enforced by

\[ S^{+l_1+1} (-1)^{l_1+1} = 1 \]

The method introduced by Lin\textsuperscript{16} diagonalizes \( \hat{U} \) in a basis set consisting of these eigenfunctions of \( \hat{A}^2 \). This
basis set has two advantageous properties: (i) $\hat{U}$ is almost diagonal in the limit $R \to 0$, where $C/R$ is negligible compared to $[(\lambda + 2)^2 - 1/4]/R^2$; and (ii) the basis functions $\mathbf{y}_{m\lambda_1\lambda_2}(\Omega)$, like $\mathbf{C}(\Omega)$, are independent of $R$, so that $C$ must be calculated only once and can then be used to calculate matrix elements of $\hat{U}$ at all $R$-values. Since the calculation of $C$ is the most difficult and time-consuming part of the calculation, this is a very important property. This set also has a well-known disadvantage: its convergence at large $R$ is extremely slow. The reason for this slow convergence is the fact that the adiabatic wavefunction $\hat{\Phi}_\mu$ becomes confined into a very small portion of the $(\alpha, \theta_{12})$ plane, where it describes an atomic bound state wavefunction. This is illustrated in Fig. 13 (p. 56) where I plot the probability density corresponding to $P_s^-$ in the $1^P_o$ "+" state at $R = 42$ a.u. Similar plots are obtained for different symmetries and different systems. The wavefunction is confined in the region $\alpha \approx \pi/6$, $\theta_{12} \approx 0, \pi$. These regions correspond to either electron being close to the positron and far from the other electron $[(e^- - e^+) - e^-]$. This slow convergence implies that a large number of harmonics are needed; actually, as $R \to \infty$ an infinite number of harmonics would be required to reach convergence. In order to speed up this slow convergence, ref. 25 (called BG2 hereafter) introduced a method which selects linear combinations of hyperspherical
harmonics that are relevant to the physical configuration. This is accomplished by a "prediagonalization" of the matrix of the potential $C$ in fixed-$\lambda$ subspaces.

3. Prediagonalization

In this and the next sections I shall present in detail a method introduced by BG2 for the solution of the adiabatic eigenvalue equation when a basis of hyperspherical harmonics is used. As mentioned above, the main problem of this basis set is its extremely slow convergence. That means that large values of $\lambda$ must be included. The dimensionality of the space increases rapidly as $\lambda$ increases. For odd parity (with $L = 1$), each successive eigenvalue contains one additional degenerate state $(m, \ell_1, \ell_2 = \eta)$, the actual degeneracy being $(\lambda + 1)/2$ (see Fig. 3a); for even parity (with $L = 1$), every two successive eigenvalues contain one additional degenerate state (see Fig. 3b). Therefore, the dimensionality of the space increases in direct proportion to $\lambda_{\max}^2$. A way to circumvent this problem emerged in BG2 upon consideration of Fig. 4, which shows the absolute value of the eigenvector of $\hat{U}$ corresponding to the lowest eigenvalue $U_1$ at $R = 20$ a.u. for the $^1P^oPs^-$ system (analogous plots are obtained for each of the different
Fig. 3(a). Degeneracy of the eigenvalues of $\lambda^2$ for an odd parity singlet state with $L = 1$. Each successive eigenvalue contains one additional degenerate state.
Fig. 3(b). Degeneracy of the eigenvalues of $\hat{\Lambda}^2$ for an even parity triplet state with $L = 1$. Every two successive eigenvalues contain one additional degenerate state.
systems studied here). Fig. 4(a) shows the eigenvector \( |z_{\eta,\mu} \rangle \) in the "primitive" basis of hyperspherical harmonics. Notice how the components are distributed among most of the \( \eta \)'s. Fig. 4(b) shows eigenvector components \( |z_{\lambda,\nu,\mu} \rangle \) of this same adiabatic eigenstate \((\mu = 1)\), but transformed into a different representation in which submatrices of the potential matrix \( C \) within a fixed \( \lambda \) subspace are made diagonal. It is clear that only the eigenstates corresponding to the two or three lowest eigenvalues of each submatrix contributes appreciably to the adiabatic wave function. The reason why this prediagonalization sorts out the linear combination of harmonics physically relevant can be understood by considering the probability density plots corresponding to these states. The method used in calculating the density is presented in a later section. Fig. 5 shows primitive basis functions corresponding to \( \lambda = 9 \) and \( \ell_1 = 4, \ell_2 = 5, m = 0 \) in (a) and \( \ell_1 = 2, \ell_2 = 3, \) and \( m = 2 \) in (b), and \( \ell_1 = 0, \ell_2 = 1 \) and \( m = 4 \) in (c). Notice how the density is distributed over the whole \((\alpha, \theta_{12})\) plane without any pattern relevant to physical considerations. Fig. 6 shows prediagonalized basis functions in the \( \lambda = 19 \) subspace. Fig. 6(a) shows the density corresponding to the lowest eigenvalue. Notice how most of the density is distributed over the portions of the \((\alpha, \theta_{12})\) plane corresponding to physical configurations like
Fig. 4. Absolute values of the expansion coefficients of the lowest $^1P^0$ adiabatic eigenstate of $Ps^-$ at $R = 20$. Each dot corresponds to the coefficient of a single hyperspherical harmonic. In (a), the representation of harmonics used is that of Eq. (IV.4). In (b) instead, the "prediagonalized" representation is adopted. (See text) (From ref. 25)
Fig. 5. Primitive squared basis functions (hyperspherical harmonics) in the $^1P^0 \lambda = 9$ subspace. In (a) $\lambda_1 = 4$, $\lambda_2 = 5$, and $m = 0$; in (b) $\lambda_1 = 2$, $\lambda_2 = 3$, and $m = 2$; in (c) $\lambda_1 = 0$, $\lambda_2 = 1$, and $m = 4$. 
Fig. 6. Probability density corresponding to $P^0$ prediagonalized basis functions. In (a) is the density corresponding to the lowest eigenvalue. In (f) is the one corresponding to the highest eigenvalue. (See text)
\( e^- e^+ - e^- (\alpha = \pi/2, \theta_{12} = 0, \pi) \). Fig. 6(b) shows the density corresponding to the second lowest eigenvalue. Fig. 6(f) shows the one corresponding to the highest eigenvalue. In this last case most of the density is in the region \( \alpha = \pi/2 \), which corresponds to the unphysical configuration \( e^- - e^- - e^+ \).

I have therefore truncated the basis set accordingly, retaining only the lower eigenstates in each \( \lambda \)-subspace. Details concerning the computational aspects of the method are presented in section 4 of this chapter.

Next consider the nodal structure in \( \theta_{12} \) that appears to be present in these "prediagonalized" eigenstates, even though this is a nonseparable problem, which means that the nodal structure in \( \theta_{12} \) should not be independent of \( \alpha \) in general. Nevertheless, such a pattern seems to exist. Fig. 6 shows plots of the density corresponding to states in the \( \lambda = 19 \) subspace. The states correspond to the lowest, second, fourth, sixth, eighth and highest eigenvalues in (a), (b), (c), (d), (e) and (f) respectively. The state corresponding to the highest eigenvalue has no nodes in \( \theta_{12} \), and the number of nodes increases as the eigenvalue decreases down to a point where that "symmetry" is broken. This pattern is the same in all \( \lambda \)-subspaces. An analogous pattern is observed when one plots all the eigenvalues in an energy-versus \( \lambda \) plot.26 Fig. 7 shows this plot for the \( ^1P^0 \) \( Ps^- \) system up to
Fig. 7. Each line corresponds to the position of one eigenvalue of \( c^\lambda \) in the corresponding \( \lambda \)-subspace. (See text)
\[ \lambda = 35. \] Each line corresponds to the position of one eigenvalue in the corresponding \( \lambda \)-subspace. The upper half of the "spectrum" follows some regularity while the lower part apparently does not. Notice that the eigenstate in which the nodal structure is lost, is apparently the same state where the regularity in the \( E - \lambda \) plot is lost (for example when \( \lambda = 19 \), this occurs in the third lowest eigenstate). The reason why this regularity in the nodal structure exists is still not understood but suggests that the problem may be quasi-separable, at least for those states that have large amplitude in the high "prediagonalized" eigenstates. This kind of regular and chaotic behavior of the spectrum of the Hamiltonian has been studied by Stefanski and Taylor\(^{27} \) for a classical Hamiltonian. A similar "prediagonalization" was introduced, parallel to BG2, in the problem of a hydrogen atom in a magnetic field.\(^{28} \) There, the prediagonalization was made in subspaces with \( n \) fixed, where \( n \) is the principal quantum number of the hydrogen atom.

4. **Large R Limit of the Potential Curves**

In the limit \( R \to \infty \), the physical configuration of the system is an electron far from a neutral atom. In the Jacobi coordinates described in Chapter II, this limit implies that both \( r_1 \) and \( r_2 \) go to infinity. This suggests
that, in this limiting region, a different set of coordinates in which the physical configuration is represented more clearly should be chosen. In this new set of coordinates $\mathbf{r}_j'$ is the position vector of electron 1 with respect to the nucleus and $\mathbf{x}'$ is the position vector of electron 2 with respect to the center of mass of the atom. Notice that this new set is identical to the independent-particle coordinate system mentioned before, when the nucleus is infinitely massive.

A new set of hyperspherical coordinates analogous to $R$ and $\alpha$ is defined as follows:

\[ R'^2 = r_1'^2 + r_2'^2 \]

\[ \alpha' = \tan^{-1} \left( \frac{r_2'}{r_1'} \right) \]

where $\mathbf{r}'_2 = \mathbf{c}' \mathbf{x}'$

\[ c' = \left[ \frac{\mu_1^{1/2}}{\mu_1} \right]^{1/2} \]  

Since the squared hyperspherical radius is defined such that it is proportional to the trace of the moment-of-inertia tensor of the systems, $R'^2$ must be proportional to $R^2$, i.e. $R'^2 = d R^2$. The constant of proportionality was found to be

\[ d = \frac{1}{c^2} + \frac{1}{4} \]
by expressing $R'$ in terms of $r_1^2$ and $r_2^2$. The hyperspherical radius $R$ enters the adiabatic equation only as a parameter. Therefore the only effect of this transformation of coordinates is a scaling of the abscissas of the potential curves by a factor $(d)^{1/2}$.

The asymptotic limit of these new coordinates is:

$$<r_1' > \rightarrow \text{constant}$$
$$r_2' \rightarrow R'$$

$$(IV.12)$$

$$(a') \rightarrow \pi/2 ; (a'') = (a' - \pi/2) \rightarrow 0$$

as $R \rightarrow \infty$, provided the total energy is negative.

In order to see the asymptotic limit of the adiabatic equation, I set $\rho = R'a''$ and expand in powers of $1/R'$, obtaining:15

$$
\left\{ \left[ \frac{1}{2\mu_{13}} \left( - \frac{\partial^2}{\rho} + \frac{L_1'^2}{\rho} \right) - \frac{1}{\rho} \right] + \frac{1}{R'} \left[ \frac{1}{2\mu_{13}} \left( - \frac{1}{4} + \frac{L_1'^2}{3} + L_2'^2 \right) \right.
$$

$$
+ \left. c' \rho \hat{r}_1' \hat{r}_2' - \frac{\rho}{6} \right] + \mathcal{O}\left( \frac{1}{R'} \right) \Phi_\mu(R',\Omega')
$$

$$= U_\mu(R') \Phi_\mu(R',\Omega').$$

(IV.13)

The terms inside the first square bracket coincide with the atomic Hamiltonian when I set $r_1 = \rho$. It has been proved in the appendix of Ref. 15 that, to order $1/R^2$, the
potential in the large R limit is the same as that obtained from the close-coupling equations for states of the same principal quantum number. This means that, when including the adiabatic correction in eq. (IV.12), the term proportional to \(1/R^2\) is:

\[
\frac{1}{2\mu_{13}} \mathbf{L}_{1}^{'2} + c' \mathbf{r}_{1}^{'} \cdot \mathbf{r}_{2}^{'} ,
\]

where I have also set \(r_{1}^{'} \approx r\). The effect of this term on the adiabatic potential curve can be calculated using degenerate perturbation theory. This requires finding the eigenvalues of the operator

\[
\hat{D} = \frac{1}{2\mu_{13}} \mathbf{L}_{2}^{'2} + c' \mathbf{r}_{1}^{'} \cdot \mathbf{r}_{2}^{'}
\]

in the corresponding \(n-L\) subspace. Here \(n\) is the principal quantum number of the atom and \(L\) is the total angular momentum of the system. In order to illustrate this, I show explicitly the matrix elements of \(\hat{D}\) in the \(n = 2, L = 1\) subspace.

\[
D = \begin{pmatrix}
2s\epsilon p & 2p\epsilon s & 2p\epsilon d \\
2s\epsilon p & D_{11} & D_{12} & D_{13} \\
2p\epsilon s & D_{21} & D_{22} & D_{23} \\
2p\epsilon d & D_{31} & D_{23} & D_{33}
\end{pmatrix}
\]

where
\[ D_{11} = < 2s\varepsilon p|D|2s\varepsilon p > = \frac{1}{\mu_{13}} \]

\[ D_{21} = D_{12} = < 2p\varepsilon s|D|2s\varepsilon p > = R_{1s}^{2p} < Y_{1010}|P_1|Y_{0110} > \]

\[ D_{31} = D_{13} = < 2p\varepsilon d|D|2s\varepsilon p > = R_{1s}^{2p} < Y_{1210}|P_1|Y_{0112} > \]

\[ D_{22} = < 2p\varepsilon s|D|2p\varepsilon s > = 0 \]

\[ D_{23} = D_{32} = < 2p\varepsilon s|D|2p\varepsilon d > = 0 \]

\[ D_{33} = < 2p\varepsilon d|D|2p\varepsilon d > = \frac{3}{\mu_{13}} \]

where

\[ |2\ell_1\ell_2> = R_{2\ell_1}(r_1) Y_{\ell_1 \ell_2} LM (r_1, r_2) \]

and \( R_{n\ell}(r) \) are hydrogenic wavefunctions, and

\[ R_{2s}^{2p}(r) = \int_0^\infty r^3 R_{2s}(r) R_{2p}(r) \, dr \]

This is the standard procedure of Seaton\textsuperscript{29} and of Gailitis and Damburg\textsuperscript{30}.

5. Computation of \( U_{m\ell_1 \ell_2, m' \ell_1' \ell_2'} \)

As explained above, the diagonalization of \( \hat{U} \) is made here in two steps. First, the potential matrix \( C \) is diagonalized within degenerate \( \lambda \)-subspaces in the primitive basis, e.g. the hyperspherical harmonics of equation IV.5. This amounts to diagonalizing submatrices \( c^\lambda \) with dimensions given by the degeneracy of the corresponding
$\lambda$-subspace. This is illustrated here by showing the lowest three such matrices corresponding to an odd parity:

$$
c_1 = \langle 001 | C | 001 \rangle
$$

$$
c_3 = \begin{pmatrix}
\langle 021 | C | 021 \rangle & \langle 021 | C | 101 \rangle \\
\langle 101 | C | 021 \rangle & \langle 101 | C | 101 \rangle
\end{pmatrix}
$$

$$
c_5 = \begin{pmatrix}
\langle 023 | C | 023 \rangle & \langle 023 | C | 121 \rangle & \langle 023 | C | 201 \rangle \\
\langle 121 | C | 023 \rangle & \langle 121 | C | 121 \rangle & \langle 121 | C | 201 \rangle \\
\langle 201 | C | 023 \rangle & \langle 201 | C | 121 \rangle & \langle 201 | C | 201 \rangle
\end{pmatrix}
$$

Here, $\langle \cdot | \cdot \rangle$ corresponds to integration over the five angular coordinates and the numbers follow the order $| m \lambda_1 \lambda_2 \rangle$.

In order to calculate these matrix elements, $C$ was expanded as follows:

$$
C = RV = \frac{1}{\cos \alpha} - \frac{R}{\left| \frac{1}{2} \mathbf{r}_1 + \frac{1}{c} \mathbf{r}_2 \right|} - \frac{R}{\left| \frac{1}{2} \mathbf{r}_1 - \frac{1}{c} \mathbf{r}_2 \right|}
$$

$$
C = \frac{1}{\cos \alpha} - 2 \sum_{k=0}^{\infty} \frac{r_<}{r_>^{k+1}} P_k(\cos \theta_{12})
$$

where $r_<(r_>)$ is the lesser(greater) of $\frac{1}{2} \cos \alpha$ and $\frac{1}{c} \sin \alpha$, and $\Sigma'$ implies summation over even values of $k$ only. Then

$$
c_{\eta, \eta'}^{\lambda} = \langle \eta | C | \eta' \rangle^{\lambda}
$$
\[ c_{\eta, \eta}' = N_{m, \lambda_1, \lambda_2} \int_0^{\pi/2} d\alpha \ F(-m, \ m + \lambda_1 + \lambda_2 + 2, \ \lambda_2 + \frac{3}{2}, \ \sin^2 \alpha) \]

\[ \times \ F(-m', \ m' + \lambda_1 + \lambda_2 + 2, \ \lambda_2' + \frac{3}{2}, \ \sin^2 \alpha) \]  

(IV.18)

\[ x(\cos \alpha) \{ \frac{1}{\cos \alpha} \delta_{\lambda_1 \lambda_1} \delta_{\lambda_2 \lambda_2} \}
\]

\[ - 2 \sum' \ \frac{\beta(\lambda_1 \lambda_2 \lambda_1 \lambda_2; kLM)}{r_{12}^k} \]

with\[ 2m + \lambda_1 + \lambda_2 = \lambda \]

and where I have defined an integral over \( \hat{r}_1 \) and \( \hat{r}_2 \) to be

\[ \beta(\lambda_1 \lambda_2 \lambda_1 \lambda_2; kLM) = \left< Y_{\lambda_1 \lambda_2 LM} | \mathbf{P}_k(\cos \theta_{12}) | Y_{\lambda_1' \lambda_2' LM} \right> \]

(IV.19)

\[ \beta(\lambda_1 \lambda_2 \lambda_1 \lambda_2; kLM) = (-1)^{\lambda_1 + \lambda_2 + L} \begin{vmatrix} \lambda_1 & \lambda_2 & L \\ \lambda_2 & \lambda_1 & k \end{vmatrix} \]

\[ \times (\lambda_1 || \beta^k || \lambda_1') (\lambda_2 || \beta^k || \lambda_2') \]

with\[ (\lambda_1 || \beta^k || \lambda_2) = (-1)^{\lambda_1} [(2\lambda_1 + 1)(2\lambda_2 + 1)]^{1/2} \]

(IV.20)

\[ \times \begin{pmatrix} \lambda_1 & k & \lambda_2 \\ 0 & 0 & 0 \end{pmatrix} \]
The coefficient $\beta$ appears to depend on the total magnetic quantum number $M$. But since the matrix elements that are being calculated are scalar quantities, they are independent of $M$. Therefore, one is able to choose the most convenient $M$-value for computational purposes, which is $M = 0$. The Wigner three-j and six-j coefficients are calculated using the expressions given in ref. 32.

The expansion of the hypergeometric polynomials used for the computation of $c^{\lambda}_{\eta, \eta'}$ is:

$$ F(-m, m+\ell_1+\ell_2+2, \ell_2+\frac{3}{2}; \sin^2 \alpha) $$

$$ = \frac{\Gamma(m+1) \Gamma(\ell_2+3/2)}{\Gamma(m+\ell_2+3/2)} \sum_{s=0}^{m} (-1)^{m-s} \binom{m+\ell_2+1/2}{s} \binom{m+\ell_1+1/2}{m-s} $$

$$ \times (\cos \alpha)^{2s} (\sin \alpha)^{2(m-s)} \quad (IV.21) $$

This expression becomes unstable at $\sin^2 \alpha \approx 1$ when $m > 20$. For this reason, I use the expression:

$$ F(-m, m+\ell_1+\ell_2+2, \ell_2+\frac{3}{2}; \sin^2 \alpha) $$

$$ = (-1)^m \frac{\Gamma(m+\ell_1-1/2) \Gamma(\ell_2-1/2)}{\Gamma(m+\ell_2-1/2) \Gamma(\ell_1-1/2)} \quad (IV.22) $$

$$ \times F(-m, m+\ell_1+\ell_2+2, \ell_1+\frac{3}{2}; 1-\sin^2 \alpha) $$
for all values of \( m \) where \( \sin^2 \alpha > 0.5 \). When \( m \geq 27 \),
this expression is unstable as well in the region
\( \sin^2 \alpha \approx 0.5 \). In this regime, I then used an asymptotic
expression for the hypergeometric function\(^{34} \) for values
of \( \alpha \) in the region \( 0.1 < \sin^2 \alpha < 0.9 \):

\[
F(-m, m+l_1+l_2+2; \ t_2+\frac{3}{2}; \ \sin^2 \alpha)
\]

(IV.23)

\[
= \frac{1}{(m+l_2+1/2)^m} \frac{\cos[(2m+l_1+l_2+2)\alpha - (l_2+1/2)\pi]}{(\pi m)^{1/2} \ (\cos \alpha) \ (\sin \alpha)}
\]

The diagonalization of each submatrix of \( C \) gives then
eigenvalues \( c_\lambda^\eta \) and eigenvectors \( a_\lambda^\eta \). As mentioned above,
only the lowest eigenstates are retained in each
\( \lambda \)-subspace. In the actual calculation, the lowest four
eigenstates are retained up to \( \lambda = 41 \) (this comes from the
fact that for low \( \lambda \)'s, the third and fourth eigenstate
contributes to the second lowest potential curve, the "+"
channel in the \( 1^1P^0 \) symmetry). The lowest two were then
used from \( \lambda = 43 \) to \( \lambda = 59 \), and the lowest one
from \( \lambda = 59 \) to \( \lambda = 71 \), when an odd parity was being
studied. Instead when an even parity was being studied,
the lowest three such eigenstates were used up to \( \lambda = 66 \).
These eigenstates were then used as a basis to finally
diagonalize \( \hat{U} \), so that the matrix elements are given by:
The diagonalization determines eigenvalues \( U \) and their corresponding eigenvectors \( z_{\lambda, \nu} \).

6. **Computation of the Body Frame Probability Density**

In this section a method for calculating the density as a function of the angular variables \( \alpha \) and \( \theta_{12} \) is presented. This will help to understand the different symmetries and to distinguish among them. In order to have a density independent of the space-fixed coordinate system, I calculate the scalar quantity \( \rho^\mu(R; \alpha, \theta_{12}) \):

\[
\rho_L^\mu(R; \alpha, \theta_{12}) = \sum_M |\psi_{LM}^\mu|^2
\]

(IV.25)

In order to do so, the wave function at any particular \( R \)-value is written as:

\[
\psi_{LM}^\mu = \sum_{\lambda_1 \lambda_2} \frac{1}{\sqrt{2^{\lambda_1 + \lambda_2}} \Gamma(\lambda_1 + \lambda_2 + \frac{1}{2})} \langle \lambda_1 \lambda_2 | \hat{r}_1 | \hat{r}_2 \rangle \phi_{\lambda_1 \lambda_2}(\alpha) Y_{\lambda_1 \lambda_2}^{\mu} \left( \hat{r}_1, \hat{r}_2 \right)
\]

(IV.26)
\[ G_{l_1 l_2}^{\alpha} = \sum_{\lambda, \nu} N_{m_{l_1 l_2}} \alpha^{\lambda} \eta_{\nu} (\cos \alpha)^{l_1+1} (\sin \alpha)^{l_2+1} \]

\[ F(-m, m+l_1+l_2+2, l_2+\frac{3}{2}; \sin \alpha) \chi_{SM} \]

So that

\[ \rho_{L}^{\mu}(\alpha, \theta_1, \theta_2) = \sum_{l_1, l_2} G_{l_1 l_2}^{\mu}(\alpha) G_{l_1 l_2}^{\mu}(\alpha) Y_{l_1 l_2 L M}(\hat{r}_1, \hat{r}_2) \]

\[ \times Y_{l_1 l_2 L M}^{*}(\hat{r}_1, \hat{r}_2) \]

The summation over the magnetic quantum number \( M \) is:

\[ \sum_{M} Y_{l_1 l_2 L M}(\hat{r}_1, \hat{r}_2) Y_{l_1 l_2 L M}^{*}(\hat{r}_1, \hat{r}_2) = \sum_{M} Y_{l_1 m_1}(\hat{r}_1) Y_{l_2 m_2}(\hat{r}_2) Y_{l_1 m_1}^{*}(\hat{r}_1) Y_{l_2 m_2}^{*}(\hat{r}_2) \]

Consider now the sum over \( M \) of the Clebsh-Gordan coefficients:
\[
\sum_{M} (\lambda_1 m_1, \lambda_2 m_2 | LM) (LM | \lambda_1 m_1, \lambda_2 m_2)
\]

\[
= \sum_{M} (2L + 1) \begin{pmatrix} \lambda_1 & \lambda_2 & L \\ -m_1 & -m_2 & M \end{pmatrix} \begin{pmatrix} \lambda_1 & \lambda_1 & L \\ m_2 & m_1 & M \end{pmatrix}
\]

\[
= (2L + 1) \sum_{kq} \begin{pmatrix} \lambda_1 & \lambda_2 & L \\ \lambda_2 & \lambda_1 & k \end{pmatrix} \begin{pmatrix} \lambda_1 & \lambda_1 & k \\ m_2 & -m_2 & q \end{pmatrix} (-1)^{L+k+m_2-m_1}
\]

\[
x (2k + 1) \begin{pmatrix} \lambda_2 & \lambda_2 & k \\ m_2 & -m_2 & q \end{pmatrix} \begin{pmatrix} \lambda_1 & \lambda_1 & k \\ -m_1 & m_1 & -q \end{pmatrix}
\]

In the last line an identity given in ref. 35 has been used. Then
\[ \rho_{L}^{\mu}(R;\alpha,\theta_{12}) = \sum_{l_{1}l_{2}} G_{l_{1}l_{2}}^{\mu}(\alpha) G_{l_{1}l_{2}}^{\mu}, (\alpha) (-1)^{L+k} \]

\[ \times (2L+1)(2k+1) \begin{pmatrix} l_{1} & l_{2} & L \\ l_{2} & l_{1} & k \end{pmatrix} \]

\[ \times \sum_{m_{1}m_{2}} \begin{pmatrix} l_{1} & l_{2} & k \\ -m_{2} & m_{2} & -q \end{pmatrix} \begin{pmatrix} l_{1} & l_{1} & k \\ -m_{1} & m_{1} & -q \end{pmatrix} \]

\[ \times Y_{l_{2}m_{2}}(r_{2}) Y_{l_{1}m_{1}}^{*}(r_{1}) Y_{l_{1}m_{1}}^{*}(r_{1}) Y_{l_{2}m_{2}}(r_{2}) \]

I can now use the identity\textsuperscript{36}:

\[ \sum_{m_{1}m_{2}} \begin{pmatrix} l_{1} & l_{2} & l \\ m_{1} & m_{2} & m \end{pmatrix} Y_{l_{1}m_{1}}(r) Y_{l_{2}m_{2}}(r) \]

\[ = \left[ \frac{(2l_{1}+1)(2l_{2}+1)}{4\pi(2l+1)} \right]^{1/2} Y_{lm}^{*}(r) \begin{pmatrix} l_{1} & l_{2} & l \\ 0 & 0 & 0 \end{pmatrix} \]

and the fact that

\[ \sum_{q} Y_{kq}^{*}(r_{2}) Y_{kj}(r_{1}) = \frac{2k+1}{4\pi} P_{k}(\cos\theta_{12}) \]

to obtain the final expression:
\[ \rho^\mu_L(R; \alpha, \theta_{12}) = \sum_{\ell_1 \ell_2} (-1)^{L+k} \frac{(2L+1)(2k+1)}{(4\pi)^2} \]

\[ \times [(2\ell_1 + 1)(2\ell_2 + 1)(2\ell_1^{\prime} + 1)(2\ell_2^{\prime} + 1)]^{1/2} \]

\[ G^\mu_{\ell_1 \ell_2}(\alpha) G^\mu_{\ell_1^{\prime} \ell_2^{\prime}}(\alpha) \begin{pmatrix} \ell_1 & \ell_2 & L \\ \ell_1^{\prime} & \ell_2^{\prime} & k \end{pmatrix} \]

\[ \times \begin{pmatrix} \ell_1 & \ell_1^{\prime} & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_2 & \ell_2^{\prime} & k \\ 0 & 0 & 0 \end{pmatrix} P_k(\cos \theta_{12}) . \]
V. THE POSITRONIUM NEGATIVE ION

1. Introduction

The positronium negative ion is a three particle system that consists of one positron and two electrons. The existence of this simple system was first predicted by Wheeler and recently confirmed experimentally by Mills by partially transmitting a beam of 400 eV positrons through a carbon film in vacuum. Mills also measured its lifetime. In the last few years there has been much theoretical interest in the excited states of Ps and in the study of electron scattering by positronium atoms. The main reason for this is the recent advances in experimental techniques for studying systems containing positrons. These include not only Ps but also electron-positron plasmas and positronium molecules. There have been several studies of the ground state of Ps, but very few of the doubly excited states, especially those with angular momentum greater than 0.

In this chapter I present the results of a series of calculations of the Ps ground state and its doubly excited states using the method described in previous chapters. I analyze here five different symmetries, the $^1S_e$, $^1P_o$, $^3P_o$, $^3P_e$, and $^1D_e$, and obtain the corresponding potential curves converging to the $n = 1$ and $n = 2$ thresholds of the positronium atom. Resonance energy
positions are calculated along with the probability density for the P states.

Numerical values of the constants involved in the calculation for Ps\(^-\) are:

\[ c = \left( \frac{\mu_{12}^3}{\mu_{12}} \right)^{1/2} = \left( \frac{4}{3} \right)^{1/2} \]

\[ c' = \left( \frac{\mu_{13}^2}{\mu_{13}} \right)^{1/2} = c = \left( \frac{4}{3} \right)^{1/2} \]

\[ d = \left( \frac{1}{c^2} + \frac{1}{4} \right)^{1/2} = 1 \, . \]

Accordingly, \( R = R' \) for Ps\(^-\).

2. \( ^1S^e \) Symmetry

The ground state of Ps\(^-\) is a \( ^1S^e \) state. This requires \( \lambda_1 \) and \( \lambda_2 \) to be even and equal, so that \( \lambda \) is also even (including \( \lambda = 0 \)). The ground state potential curve, \( U_1(R) + W_{11}(R) \) is shown in Fig. 8(a). It can be proved (see Appendix of reference 45) that the solution of the radial equation (Equation III.15) gives a lower bound on the lowest exact energy for each symmetry when the adiabatic correction term \( W_{11}(R) \) is not included, and gives an upper bound when the adiabatic correction term is included. At large \( R \), \( R \geq 15 \), the curve was smoothly connected to the one calculated using the method presented
Fig. 8. The lowest two $^1S^e$ hyperspherical potential curves of $\text{Ps}^-$ converging to the (a) $n = 1$ and (b) $n = 2$ threshold of $\text{Ps}$.
in the next chapter, in which an asymptotic basis is used. The asymptotic basis helps to obtain a better converged curve in this region with a much smaller number of basis functions. At small $R$, $R < 15$ a.u., the two curves are almost exactly the same. The lower and upper bounds on the ground state energy obtained were $E_l = -0.2646$ a.u. and $E_u = -0.2597$ a.u., which bracket the best calculated value $E = -0.2620$ a.u. (Ref. 9).

The lowest $^1S^e$ potential curve converging to the $n = 2$ threshold of $Ps$ is shown in Fig. 10(b). It has a minimum at $R = 20$ a.u. and behaves asymptotically as $-7.06/R^2$ below threshold. It supports an infinite number of Feshbach resonances, owing to the long-range dipole attraction, the lowest of which was calculated to be $E = -0.0763$ a.u., in good agreement with a previous calculation using the complex-coordinate rotation method\textsuperscript{46} $E = -0.07602$ a.u. There is a second curve converging to the same threshold which is completely repulsive and behaves asymptotically as $10.06/R^2$ above threshold.

3. $^1P^0$ Symmetry

Photodetachment of the ground state of $Ps^{-}$ leads to $^1P^0$ symmetry in the final state, since the transition

$$hv + Ps^{-} (1s\ 1^3S^e) \rightarrow Ps^{-} (1P^0) + e + Ps$$
is the only allowed dipole transition. By analyzing the potential curves obtained with the method described in earlier chapters, BG2 was able to predict the main resonance features which should be seen in Ps\(^-\) photodetachment. The results obtained there will be discussed here along with probability density plots, which corroborate the diabatic interpolation of the "+" and "-" potential curves.

This symmetry requires \( l_1 \) to be even and \( l_2 \) to be odd, so that \( \lambda \) is odd as well. The potential curves \( U_\mu \mu (R) + W_\mu \mu (R) \) are shown in Fig. 9. (The ground state, a completely repulsive curve converging to the ground state of Ps, is not shown.) As explained in Section 4 of Chapter V, these potential curves were connected smoothly to their asymptotic form at \( R > 45 \) a.u.

These potential curves and those for H\(^-\) calculated by Lin\(^46\) and by Klar and Klar\(^47\) and also in the present study (see Chapter VIII) are qualitatively similar, apart from numerical values, so the same classification ("+", "-", and "pd") introduced by Cooper, Fano, and Prats\(^48\) is used here.

The von Neumann-Wigner non-crossing rule states that adiabatic potential curves belonging to the same symmetry cannot cross.\(^49\) The "+" and "-" curves do not strictly have different symmetry, so they cannot cross. In fact, they show an avoided crossing at \( R = 35.5 \) a.u. with a
Fig. 9. The $^1P^o$ hyperspherical potential curves of $Ps^-$ converging to the $Ps$ (n = 2) threshold. (From ref. 25)
minimum separation of $\Delta U = 0.0012$ a.u. The diabatic interpolation in the region $28 < R < 42$ made in Fig. 9 is based on the fact that the system does not behave adiabatically in regions of avoided crossings where two adiabatic channels interact strongly. In order to corroborate this, I present plots of the probability density corresponding to the "+" and "-" states before and after the crossing. Fig. 10 shows the density plot corresponding to the "+" state at $R = 20$ a.u. (before the crossing), and Fig. 11 shows the one corresponding to the "-" state at $R = 25$ a.u. (also, before the crossing). Notice the big difference between these two plots. The "-" character is mainly expressed by the presence of a node at $\theta_{12} = \pi/2$ (this corresponds to a node at $\alpha = \pi/4$, e.g. $r_1 = r_2$ in the independent-particle coordinates), and the "+" character by the absence of this node (at small $R$, there is an antinode at $\theta_{12} = \pi/2$). Fig. 12 shows the "-" potential curve (e.g. the potential curve corresponding to the second, not the third, eigenvalue) at $R = 42$ a.u. Notice that the node at $\theta_{12} = \pi/2$ is still present. Fig. 13 shows the "+" potential curve at the same $R$ value. Notice the absence of a node at $\theta_{12} = \pi/2$. This strongly suggests that the diabatic interpolation is correct.

Even though the "+" potential curve is the most attractive at small $R$, it is not sufficiently deep to support a quasi-bound state below $P_s$ ($n = 2$). The
Fig. 10. Probability density of the $^1P^o$ "+" channel of Ps$^-$ at $R = 20$ a.u. (before the crossing between the "+" and "-" potential curves).
Fig. 11. Probability density of the $^1P^o$ "-" channel of Ps" at $R = 25$ a.u. (before the crossing between the "+" and "-" potential curves).
Fig. 12. Probability density of the $^1P^0$ "-" channel of Ps$^-$ at $R = 42$ a.u. (after the crossing between the "+" and "-" potential curves). In (b), the plot has been cut at $\rho = 0.025$ in order to see more clearly the approximate node at $\theta_{12} = \pi/2$. 
Fig. 13. Probability density of the $^1\text{p}^\text{o}$ "+" channel of Ps at $R = 42$ a.u. (after the crossing between the "+" and "-" potential curves). In (b), the plot has been cut at $p = 0.025$ in order to see the absence of a node at $\theta_{12} = \pi/2$. 
presence of a potential barrier that decays asymptotically as \( 2/R^2 \), enables the curve to support a shape resonance at an energy we estimated to be \( E = 4 \times 10^{-4} \) a.u. above threshold. Fig. 14 shows the elastic scattering phaseshift and its derivative with respect to energy, the time delay, corresponding to this "+" channel. The width of the resonance can be obtained from the time delay; it is then estimated to be \( \Gamma = 4 \times 10^{-4} \) a.u. It originates primarily from tunnelling through the barrier.

The "-" channel, attractive at small \( R \) but with a long-range dipole attraction which decays as \( -5.544/R^2 \), has an infinite series of Feshbach resonances, guaranteed by this long-range dipole field. The lowest such resonance was obtained by numerically integrating Eq. III.15, giving \( E = 8.7 \times 10^{-5} \) a.u. below the \( n = 2 \) threshold. The next resonance lies at \( 6 \times 10^{-6} \) a.u., and the binding energy of successive levels converges exponentially to zero. The "pd" potential curve is completely repulsive and behaves as \( 11.544/R \) above the \( n = 2 \) threshold at large \( R \), and can accordingly support no resonance features.

4. \(^3\text{P}^e\) Symmetry

The existence of a metastable \( 2p\ ^2\ ^3\text{P}^e \) state of \( \text{Ps}^- \) would have many experimental implications, for it would
Fig. 14. The elastic scattering phase shift and its energy derivative just above the Ps (n = 2) threshold for the $^1P_0^+$ channel of Ps$^-$. These indicate a shape resonance at an energy of $4 \times 10^{-4}$ above threshold. (From ref. 25)
not decay by electron-positron annihilation (in first order) but rather by a slow radiative transition to an autoionizing state. Two previous studies have not found such a state. In this calculation I confirm these studies, and find the reason for the absence of such a state: it has become a shape resonance. In this case, \( J_{l_1} \) is odd, \( l_2 \) is odd and \( \lambda \) is even (excluding 0).

Fig. 15 shows the lowest potential curve corresponding to the \( 3P_e \) symmetry converging to the \( n = 2 \) threshold of Ps. Much like the \( 1P^0 \) "+" channel, the \( 3P_e \) potential curve is not sufficiently deep to support a metastable state, but it does support a shape resonance at an energy \( E = 3.8 \times 10^{-4} \) a.u. above threshold. Fig. 16 shows the calculated elastic scattering phase shifts and the time delay, from which the width of the resonance, (coming also from tunneling through the barrier), can be obtained, \( \Gamma = 3.6 \times 10^{-4} \) a.u. Fig. 17 shows the probability density at \( R = 20 \) a.u. (at about the minimum of the potential curve). The results of this calculation agrees with the supermultiplet classification of Herrick, et al., in which the \( 3P_e \) and the \( 1P^0 \) are part of a supermultiplet in \( H^- \), since the position of the \( 1P^0 \) "+" resonance is very close to the one of the \( 3P_e \). The same resemblance exists in the probability density as can be seen in Fig. 17 and Fig. 10, even though a remarkable difference exists at \( \theta_{12} = 0 \).
Fig. 15. The lowest hyperspherical potential curve for
Ps, $^3\text{P}^\circ$ symmetry, converging to the Ps (n = 2)
threshold.
Fig. 16. The elastic scattering phase shift and its energy derivative just above the Ps (n = 2) threshold for \( ^3P_e \) symmetry of Ps\(^-\). These indicate a shape resonance at an energy of \( 3.7 \times 10^{-4} \) a.u. above threshold.
Fig. 17. Probability density of the lowest \(^3\!\!p_e\) state of Ps\(^-\) at \(R = 20\) a.u.
and π, where the density corresponding to the \(^3P_e\) state vanishes while that corresponding to the \(^1P^o\) "++" state does not. This can be understood by analogy with the exclusion of parity unfavored transitions in forward (or backward) scattering collisions, explained by Pano in 1964.\(^5^1\) The transition operator \(T\), as defined in reference 51, is

\[
T = \sum_{ll'LM} T_{ll'LM} Y_{ll'LM}(k,k')
\]

analogous to Eq. IV.26. Ref. 51 proves that

\[
Y_{ll'LM}(k,k') = 0
\]

when the angle between \(\hat{k}\) and \(\hat{k}'\) is \(\theta_{12} = 0\) or \(\pi\) when \(M = 0\) and \(l+l'\) is odd (parity-unfavored transitions).

Coupled spherical harmonics transform from one coordinate system to another according to the equation:

\[
Y_{l_1l_2LM}^{\phi_1\phi_2\phi_3}(k,k') = \sum_Q Y_{l_1l_2LQ}^{\phi_1\phi_2\phi_3}(\hat{k}',\hat{k}''') D_{Q}\left(\phi_3,\phi_2,\phi_1\right) \tag{V.1}
\]

Here \(D_{Q}\) is a rotation matrix.\(^5^2\) Only the \(Q = 0\) term is different from zero when \(k'' = 0\) and \(k''' = 0\) or \(\pi\), therefore

\[
Y_{l_1l_2LM}^{\phi_1\phi_2\phi_3}(k,k' = \pm k) = Y_{l_1l_2L0}^{\phi_1\phi_2\phi_3}(\hat{k}'',\hat{k}''') D_{0}\left(\phi_3,\phi_2,\phi_1\right) \tag{V.2}
\]

\[
D_{0}(\phi,\theta,\psi) = \left(\frac{4\pi}{2L+1}\right)^{1/2} Y_{LM}(\theta,\psi) .
\]
then

\[ Y_{\ell_1 \ell_2 LM}(\hat{k}, \hat{k'} = \pm \hat{k'}) = (\frac{4\pi}{2L+1})^{1/2} Y_{\ell_1 \ell_2 LO}(\hat{k''}, \hat{k'''}) Y_{LM}(\theta, \psi) \]

But Ref. 51 proves that

\[ Y_{\ell_1 \ell_2 LO}(\hat{k''}, \hat{k'''} = 0 \]

when the angle between \( \hat{k''} \) and \( \hat{k'''} \) is 0 or \( \pi \), and

\( \ell_1 + \ell_2 - L \) is odd, therefore,

\[ Y_{\ell_1 \ell_2 LM}(\hat{k}, \hat{k'}) = 0 \]

where \( \hat{k} = \pm \hat{k'} \) for all \( M \) when \( \ell_1 + \ell_2 - L \) is odd. In this case, \( L = 1 \) and \( \ell_1 + \ell_2 \) is even (even parity) therefore the probability density vanishes when \( \theta_{12} \) is 0 or \( \pi \).

A second difference between the probability density plots corresponding to the \( ^1\text{P}^O \) "+" and the \( ^3\text{P}^e \) states is the presence of an extra node in the \( ^1\text{P}^O \) state. This can be understood with the help of the independent electron picture, where the \( ^1\text{P}^O \) is a linear combination of \( 2s2p + 2p^2 \) with some \( 2p^2 \) and has a node in the \( 2s \) function, while the \( ^3\text{P}^e \) is a \( 2p^2 \) and has no nodes.
5. $^3\text{P}^o$ Symmetry

Both in He and H$^-$, the $^3\text{P}^o$ symmetry holds a quasibound state which has the strongest binding of all of the P doubly excited states near the n = 2 threshold. The same is expected for Ps$^-$. This symmetry requires $l_1$ to be odd and $l_2$ to be even so that $\lambda$ is also odd.

The two lowest potential curves converging to the n = 2 threshold of Ps are shown in Fig. 18. The "+" channel is much more attractive than in the $^1\text{P}^o$ "+" case; the minimum of the $^3\text{P}^o$ potential curve is $U_2 + W_{22} = -0.085$ a.u. at $R = 20$ a.u. compared to $U_2 + W_{22} = -0.069$ at $R = 20$ for $^1\text{P}^o$. This is consistent with Hund's rule, which states that all else being equal, triplet atomic states lie lower than singlets, since the Pauli principle keeps the electrons farther apart in the triplet state. The coupling between the "+" and "-" channels in the avoided crossing region, $R = 45$, is much smaller for the $^3\text{P}^o$ than for $^1\text{P}^o$, and the system therefore behaves adiabatically. This can again be illustrated with the probability density. Fig. 19 shows the density corresponding to the "+" channel at $R = 20$ a.u., before the avoided crossing region, in (a) and at $R = 50$ a.u., after the avoided crossing region, in (b).

Fig. 20 shows the density corresponding to the "-" channel at $R = 25$ a.u. in (a) and at $R = 50$ a.u. in (b). Notice how the characteristic properties of each channel are
Fig. 18. Lowest two of the three $^3P^0$ hyperspherical potential curves of $Ps^-$ which converge to the $Ps$ ($n = 2$) threshold.
Fig. 19. Probability density of the $^3P^0$ $^+$ channel of Ps$^-$. In (a) $R = 20$ a.u. while in (b) $R = 50$ a.u. (See text)
Fig. 20. Probability density of the $^3P^o$ "-" channel. In (a) $R = 25$ a.u. while in (b) $R = 50$ a.u. (See text)
conserved through the avoided crossing region, strongly suggesting that the two potential curves do not cross. Therefore the potential curves were adiabatically interpolated in the region $38 < R < 50$. At large $R$, the potential curves were smoothly connected with the asymptotic curves, just as in the $^1P^o$ case.

The "+" potential curve, the only attractive one, is now deep enough to support quasi-bound states below the $n = 2$ threshold of Ps. It actually supports an infinite number of resonances. The three lowest ones were found by numerically integrating the radial equation giving:

\[ E_1 = 1.03 \times 10^{-2} \text{ a.u., } E_2 = 4.5 \times 10^{-4} \text{ a.u., and } \]

\[ E_3 = 9 \times 10^{-5} \text{ a.u. below the } n = 2 \text{ threshold, the lowest two of which are in good agreement with another calculation.}^8 \]

The binding energy of successive resonances goes exponentially to zero. The "-" potential curve is in this case completely repulsive, as is the "pd" curve (which is not shown in Fig. 18), and does not hold any resonance.

6. $^1D^e$ Symmetry

In $H^-$ the symmetry holding the most deeply bound resonant state after $^3P^o$ is $^1D^e$. In view of all of the similarities seen thus far, the same is expected in Ps$^-$. Symmetry requires $\lambda_1$ and $\lambda_2$ to be even so that $\lambda$ is also
even (excluding 0). The degeneracy in each $\lambda$-subspace is even higher in this case, since the orbital angular momentum is $L = 2$. Fig. 21 shows how the degeneracy increases as $\lambda$ increases. In this case, the use of the "prediagonalized" basis is even more necessary, since the number of "primitive" basis functions required to reach convergence was more than 800.

The potential curves converging to the $n = 2$ threshold of $\text{Ps}$ are shown in Fig. 22. (The ground state curve, a completely repulsive curve converging to the $n = 1$ threshold of $\text{Ps}$, is not shown.) These curves are like those corresponding to the $^3\text{P}^0$ symmetry, but not as deep. The lowest curve shown (the "+" curve) has a minimum $U_2 + W_2 = -0.078$ a.u. at $R = 20$ a.u. In this case there is no avoided crossing at large $R$ and the curves behave adiabatically. At small $R$ there is an avoided crossing at $R = 10$ a.u. (It does not appear in Fig. 21 because it is at higher energy). At large $R$, the curves were smoothly connected to their asymptotic limit. In this case, $L=2$, the three channels in the $n=2$ subspace in the independent-electron picture are $2s\epsilon d$, $2p\epsilon p$, and $2p\epsilon f$. Like in the $^3\text{P}^0$ symmetry, the only attractive curve is the one corresponding to $\mu = 2$. It supports an infinite number of resonances, guaranteed by the long-range dipole attraction which behaves as $-1.44/R^2$, the lowest one of which was calculated to be $E_1 = 0.067243$ a.u. by numerically
integrating the radial equation. The other two curves are completely repulsive and behave asymptotically as $6/R^2$ and $9.44/R^2$, respectively.
Fig. 21. Degeneracy of the eigenvalues of $\Lambda^2$ for an even parity singlet state with $L = 2$. 
Fig. 22. Lowest two of the three $^1D^e$ hyperspherical potential curves of Ps$^-$ which converge to the Ps (n = 2) threshold.
VI. AN ALTERNATIVE APPROACH FOR $^1S^e$ States of Ps$^-$

1. Introduction

This chapter presents the results of a calculation of $^1S^e$ states of Ps$^-$ using a variational method for the solution of the adiabatic eigenvalue equation. It is based on ref. 6, hereafter called BG1. This calculation was not aimed at improving the accuracy of known results, instead, it was a starting point for the study of doubly excited states of Ps$^-$ presented in previous chapters, in the sense that it showed that this adiabatic-hyperspherical treatment can be extended to systems with different particle masses by the use of the Jacobi coordinates presented in Chapter II. This method solves the adiabatic eigenvalue equation variationally by expanding the adiabatic wavefunction in a basis consisting of hydrogenic wavefunctions for the positronium, which become exact at large $R$.

2. Presentation of the Method and the Results

The adiabatic eigenvalue equation is

$$\left[ \frac{\Delta^2}{R^2} + V \right] \phi_{\mu}(R, \Omega) = U_{\mu}(R) \phi_{\mu}(R, \Omega)$$

(VI.1)

where

$$\Delta^2 = -\frac{\partial^2}{\partial \alpha^2} + \frac{l_1^2}{\cos^2 \alpha} + \frac{l_2^2}{\sin^2 \alpha} - \frac{1}{4}$$

(VI.2)
and

\[ V = \frac{1}{R \cos \alpha} \frac{2}{R(\cos^2 \alpha + \sqrt{3} \sin(2\alpha) \cos \theta_{12} + 3 \sin^2 \alpha)^{1/2}} - \frac{2}{R(\cos^2 \alpha - \sqrt{3} \sin(2\alpha) \cos \theta_{12} + 3 \sin^2 \alpha)^{1/2}}. \]  

(VI.3)

The adiabatic wavefunction is expanded as:\(^5\)

\[ \phi_{\mu}(R, \Omega) = \sum_{n, l} C_{nl} \phi_{nl} \]

\[ \phi_{nl} = A(r_1 \cdot r_2) R_{nl}(r_1) r_1^l Y_{\lambda_1 \lambda_2 \lambda}(r_1, r_2) \]  

(VI.4)

Where \( R_{nl} \) is a hydrogenic function for the positronium, \( Y \) is a coupled spherical harmonic, and \( \bar{A} \) denotes antisymmetrization with respect to electron exchange. The total angular momentum studied by BG1 is \( L = 0 \), in which case \( \lambda_1 = \lambda_2 = \lambda \), and

\[ Y_{\lambda \lambda \lambda 00}(\hat{r}_1, \hat{r}_2) = \frac{(-1)^\lambda 4\pi}{(2\lambda+1)^{1/2}} P_\lambda(\cos \theta_{12}), \]  

(VI.5)

So that the angular part of the kinetic energy is simple:\(^5\)

\[ \frac{\lambda_1^2}{\cos \alpha} + \frac{\lambda_2^2}{\sin \alpha} = \frac{1}{\sin \alpha \cos \alpha} \frac{2}{\sin \theta_{12}} \frac{1}{\sin \theta_{12}} \frac{\partial}{\partial \theta_{12}} \frac{\partial}{\partial \theta_{12}}. \]  

(VI.6)

When the total angular momentum is greater than zero, the angular part of the kinetic energy becomes more complicated. Besides, four angular coordinates are
required to represent the system, as opposed to only one in the $L = 0$ case. A brief presentation of the Euler angles is given at the end of this chapter.

Substituting the expansion of VI.4 into the adiabatic eigenvalue equation and applying the variational principle,

$$\frac{\delta U_\mu(R)}{\delta C_{n\ell}} = 0 . \quad (VI.7)$$

we get, in matrix form

$$U \phi_\mu(R,\Omega) = U_\mu(R) S \phi_\mu(R,\Omega) \quad (VI.8)$$

where

$$U_{n\ell,n'\ell'} = \int \phi_{n\ell}^* \left[ \frac{\hbar^2}{2R} + V \right] \phi_{n'\ell'} \, d\alpha \, d(\cos \theta_{12})$$

$$S_{n\ell,n'\ell'} = \int \phi_{n\ell}^* \phi_{n'\ell'} \, d\alpha \, d(\cos \theta_{12}) \quad (VI.9)$$

These equations involve two dimensional integrals, over $\alpha$ and $\theta_{12}$, which must be evaluated numerically. This is the most time consuming part of the calculation, especially at large $R$ where the wavefunction is confined into a small region on the $(\alpha, \theta_{12})$ plane, as discussed above. A large number of mesh points was required in order to ensure convergence of the Gauss-Legendre quadrature. Figs. 23(a) and (b) show the potential curves corresponding to the
Fig. 23. The lowest two $^1s_e$ hyperspherical potential curves of $\text{Ps}^-$ converging to the (a) $n = 1$ and (b) $n = 2$ threshold of $\text{Ps}$. (From ref. 6)
ground state and the lowest $^1S^e$ doubly excited state, converging to the $n = 1$ and $n = 2$ thresholds of $Ps$ respectively.

The solution of the radial equation (Eq. III.15) gives then the ground state energy and the position of a resonance for the $\mu = 2$ $^1S^e$ state. As mentioned in section 2 of Chapter V, we get either an upper or a lower bound on the ground state energy depending on whether the adiabatic correction term $W_{\mu\mu}$ is included or not. The results obtained for the ground state energy are, $E = -0.2597$ a.u. for the upper bound and $E = -0.2646$ a.u. for the lower bound. These are in good agreement with previous calculations ($E = -0.2620$ a.u.) for the $^1S^e$ doubly excited state, these are not true bounds, but they do show the validity of this approach, since the respective values are $E = -0.07635$ a.u. and $E = -0.07796$ a.u., in good agreement with a previous calculation, $E = -0.07602$ a.u.

3. Euler Angle Representation

As mentioned above, when the total angular momentum $L$ of the system is greater than zero, a set of four angular coordinates, besides the hyperangle $\alpha$, is required to describe the system. In this section I present a set of Euler angles that simplifies the transformation from the laboratory frame ($x,y,z$) to the body-fixed frame ($x',y',z'$)
when symmetric Jacobi coordinates are used to describe a
system of three particles, two of which are identical.
Different sets of angles have been used in earlier studies
of three-body systems. One commonly used is the one
introduced by Bhatia and Tempkin\textsuperscript{55} which uses three Euler angles to define the body-fixed frame, with the \( \hat{z}' \) axis perpendicular to the plane that contains the particles.
The fourth angle is the angle between the position vector
(with respect to the nucleus) of particles 1 and 2. This set was introduced for the treatment of the two-electron
fixed-nucleus problem. When this set is applied to a three
equal-mass particles using symmetric Jacobi coordinates, it
loses some of its advantages and the kinetic energy
operator and the angular part of the wavefunction become
rather complicated. A second set recently introduced by
Lin and Watanabe\textsuperscript{56} uses \( \hat{r}_{12} \) as the \( \hat{z}' \) axis, where \( \hat{r}_{12} \)
is the vector \( \hat{r}_2 - \hat{r}_1 \) (also independent particle
coordinates). I define here a set of Euler angles,
analogous to that of Lin and Watanabe in the sense that it
also uses the unit vector in the direction of the
interelectronic separation as the \( \hat{z}' \) axis. The body-fixed
frame is identified as follows:

\[
\begin{align*}
\hat{z}' &= \hat{r}_1 \\
\hat{x}' &= \hat{r}_1 \times (\hat{r}_1 \times \hat{r}_2) / |\hat{r}_1 \times \hat{r}_2| \\
\hat{y}' &= \hat{r}_1 \times \hat{x}'
\end{align*}
\]  
(VI.14)
The Euler angles are then defined as the angles needed to rotate from the body-fixed frame \((x',y',z')\) to the laboratory frame \((x,y,z)\). With this definition, the three particles are located in the \(x'-z'\) plane. Exchange is simple in this coordinate system since its only effect is to replace \(\hat{r}_1(z')\) by \(-\hat{r}_1(-z)\).

The angular part of the wavefunction can then be expressed as a function of these angles and coupled spherical harmonics in the primed system by using equation (V.1):

\[
Y_{\ell_1\ell_2LM}(\hat{r}_1,\hat{r}_2) = \sum_{Q} Y_{\ell_1\ell_2LQ}(\hat{r}_1',\hat{r}_2', \phi, \theta, \psi) D_{QM}^{L}(\phi, \theta, \psi) \tag{VI.15}
\]

The angular wavefunction in the body-fixed frame is:

\[
Y_{\ell_1\ell_2LQ}(\hat{r}_1',\hat{r}_2') = \sum_{m_1m_2} (\ell_1m_1, \ell_2m_2 | LQ) \times Y_{\ell_1m_1}(\hat{r}_1') Y_{\ell_2m_2}(\hat{r}_2') \tag{VI.16}
\]

with

\[
Y_{\ell_1m_1}(\hat{r}_1'=z') = Y_{\ell_1m_1}(0,0) = \left(\frac{2\ell_1 + 1}{4\pi}\right)^{1/2} \delta_{m,0}
\]

\[
Y_{\ell_2m_2}(\hat{r}_2) = Y_{\ell_2m_2}(\theta_{12},0) = (-1)^{-m_2} (2\ell_2+1)(\ell_2-m_2)! \left(\frac{4\pi (\ell_2+m_2)!}{-\frac{1}{4\pi (\ell_2+m_2)!}}\right)^{1/2} \times P_{\ell_2}^{m_2}(\cos \theta_{12}) \tag{VI.16}
\]
Therefore:

\[ Y_{\ell_1 \ell_2 L M=0}(\hat{r}_1, \hat{r}_2) = \sum_Q C_{\ell_1 \ell_2 Q} P_{\ell_2}^{-Q}(\cos \theta_{12}) Y_{LM}(\hat{r}_1) \]  

(VI.17)

where I have used the expression:

\[ D_{\ell \ell_2}^L(\alpha, \beta, \gamma) = (-1)^Q \left[ \frac{4\pi}{(2L+1)} \right]^{1/2} Y_{LM}(\beta, \alpha) \]

and have defined

\[ C_{\ell_1 \ell_2 Q} = (-1)^Q \left[ \frac{(2\ell_1+1)(2\ell_2+1)(\ell_2+Q)!'}{(2L+1)4\pi(\ell_2-Q)!} \right]^{1/2} \]  

(VI.18)

Equation VI.17 gives an analytic expression for transforming the angular part of the wave function from the body-fixed frame to the laboratory frame. It can be used in the study of three-particle systems with angular momentum greater than zero using the method described in section 2 of this chapter, although there still remain some complications such as the calculation of matrix elements between direct and exchange terms of the wavefunction. It also should prove very useful in an R-matrix calculation of Ps^- and other three particle systems as well.
VII. OTHER THREE-PARTICLE SYSTEMS

1. Introduction

In this chapter I present the results of a series of calculations of doubly excited states, and in some cases the ground state, of other three particle systems using the method described in Chapter IV. I start with the $^1P^0$ symmetry of the $H^-$ ion. This system was previously studied using hyperspherical coordinates by Lin and by Klar and Klar. A comparison of the results is made to ascertain the validity of the approach developed here. Next I discuss the muonium negative ion ($M^- = \mu^+e^-e^-$). The potential curves and resonance energy positions corresponding to five different symmetries, $^1S_e$, $^1P^0$, $^3P_e$, $^3P^0$, and $^1D_e$ are presented.

The use of the symmetric Jacobi coordinates facilitates the calculation of the potential curves of systems having different relative masses, since the reduced mass only enters the equations through the constants $c$ (eq. III.3) and $c'$ (eq. IV.10).

2. $^1P^0$ States of the $H^-$ Ion

In this case

$$m_3 = m_p = 1836 \text{ a.u.}$$
\[ c = \left( \frac{\mu_{12}}{\mu_{12}} \right)^{1/2} \approx 1.999 \]

\[ c' = \left( \frac{\mu_{13}}{\mu_{13}} \right)^{1/2} \approx 1.00054 \]

and

\[ d \approx 0.50025 \]

Fig. 24 shows the potential curves converging to the \( n = 2 \) threshold of \( H \). This plot is analogous to Fig. 1 of ref. 46 and to Fig. 4 of ref. 47 (in the latter, the potential curves were not explicitly crossed diabatically). Notice that the hyperspherical radius \( R \) of the present work is equal to \( R'/\sqrt{d} \), where \( R' \) is the hyperspherical radius used by Lin and by Klar and Klar.

The minimum separation between the "+" and "-" potential curves in this work is \( \Delta U = 0.0013 \) a.u. at \( R = 20 \) a.u. compared to \( \Delta U = 0.002 \) a.u. at \( R = 14 \) a.u. in ref. 47. The height of the barrier of the "+" potential curve obtained in this work is \( 3 \times 10^{-3} \) a.u., compared to \( 2.4 \times 10^{-3} \) a.u. in ref. 46. Following Lin's diabatic interpolation of the potential curves, and also based on the probability density as discussed before, the "+" and "-" potential curves are diabatically interpolated in the region \( 17 < R < 22 \) a.u. As in \( \text{Ps}^- \), the "+" potential curve is not deep enough to support a resonance below threshold, but the presence of the potential barrier, which decays as \( 2/R^2 \) as \( R \to \infty \), enables the curve to support a shape
Fig. 24. Lowest two of the three $^1P^0$ hyperspherical potential curves of $H^-$ which converge to the $H$ ($n = 2$) threshold.
resonance. This resonance was first predicted by Taylor and Burke,\textsuperscript{57} and later by Lin,\textsuperscript{46} and it was confirmed experimentally by Bryant, et al.\textsuperscript{58} Fig. 25 shows the elastic scattering phase shift and the time delay for this resonance as obtained in this work. Table 1 gives the position and width of the shape resonance calculated in the present study and those obtained in other calculations. The "-" potential curve supports an infinite number of resonances, the lowest of which was calculated at $E = -0.12596$ a.u., in reasonably good agreement with Lin's result $E = -0.125955$ a.u. and with other calculations (e.g. $E = -0.1260496$ a.u.).\textsuperscript{60} Since all coupling between different channels has been neglected in the present study, the width of the Feshbach resonance cannot be calculated.

Table 1. The $^1P_o$ Shape Resonance of $H^-$

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>$E$ (a.u.)</th>
<th>$\Gamma$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>Adiabatic-Hyperspherical</td>
<td>0.1234</td>
<td>$1.7\times10^{-3}$</td>
</tr>
<tr>
<td>Lin\textsuperscript{46}</td>
<td>Adiabatic-Hyperspherical</td>
<td>0.12382</td>
<td>$1.03\times10^{-3}$</td>
</tr>
<tr>
<td>Burke, et al.\textsuperscript{57}</td>
<td>Close coupling (3 state plus correlations)</td>
<td>0.124337</td>
<td>$1.11\times10^{-3}$</td>
</tr>
<tr>
<td>Callaway\textsuperscript{59}</td>
<td>Close coupling (18 state)</td>
<td>0.124395</td>
<td>$1.47\times10^{-3}$</td>
</tr>
</tbody>
</table>
Fig. 25. The elastic scattering phase shift ($\delta$) and its energy derivative just above the H ($n=2$) threshold. These indicate a shape resonance at an energy of $1.6 \times 10^{-3}$ above threshold.
The reason for the small difference between the results obtained by Lin and those obtained in this work stems mainly from the fact that even though the diabatic interpolation is qualitatively correct, it is not an exact procedure. Besides, a slight lack of convergence on the potential curve increases the height of the barrier and, therefore, raises the position of the shape resonance. The maximum of the potential curve, which determines the height of the barrier, is located far in $R$, $R \approx 25$ a.u., where the convergence of the potential curve is becoming poorer, and before it is joined to its asymptotic limit.

Both adiabatic calculations, Lin's and the present one, give a shape resonance higher than other more accurate theoretical calculations. This comes mainly from two facts: first, the problem of convergence mentioned above; and second, the fact that the adiabatic calculation neglects entirely interchannel coupling.

3. **Muonium Negative Ion**

The muonium negative ion, $M^- \equiv \mu^+e^-e^-$, is another three-particle system, which consists of a positive muon ($m_\mu = 210.7$ a.u.) and two electrons. It has been very recently observed by Arnold, et al. in a double electron pick-up reaction as a beam of positive muons passes through a foil. As expressed in the published abstract where the
existence of $M^-$ is reported, $M^-$ is a new three-body bound state which is now available for spectroscopy studies. Since the reduced mass of the muonium is very close to that of hydrogen, $\mu_M = 0.9953$ compared to $\mu_H = 1.0$, the spectrum of $M^-$ is expected to be very similar to the spectrum of $H^-$. The constants involved in this calculation are:

\[
\begin{align*}
  c &= 1.9905760 \\
  c' &= 1.000001 \\
  d &= 0.502372
\end{align*}
\]

Fig. 26(a) shows the ground state potential curve of $M^-$ converging to the ground state of the muonium atom ($E_\mu = -0.497639$ a.u.). As mentioned in chapters V and VI, this approach gives either an upper or a lower bound on the lowest state of each symmetry, depending on whether the adiabatic correction term $W_\mu$ is included or not. The calculated values are $E_\mu = -0.5234$ a.u. and $E_\xi = -0.5325$ a.u., respectively. The ground state of $H^-$ is $E_0 = -0.52756$ a.u.\(^63\) The elementary correction on this energy due to the mass of the nucleus\(^62\) ($m_\mu = 210.8$ a.u.) is $\Delta E = 0.00236$ a.u., so that the ground state of $M^-$ is about $E_0 = 0.52553$ a.u., which is bracketed by the two calculated values. Fig. 26(b) shows the potential curve corresponding to the $^1S^e$ doubly excited state of $M^-$ converging to the $n = 2$ threshold of the muonium atom ($E_2 = -0.12441$ a.u.). It supports an infinite number of resonances in the long-range dipole potential which decays
Fig. 26. The lowest two $1^eS^e$ hyperspherical potential curves of $M^-$ converging to (a) $n = 1$ and (b) $n = 2$ thresholds of $M$. 
as \(-5.08/R^2\), the lowest of which was calculated to lie at 
\[ E = -0.1484 \text{ a.u.} \]

Fig. 27 shows the \( ^1p^0 \) potential curves of \( M^- \). They are very similar to those of \( H^- \), and all of the features discussed in \( H^- \) are present here too. Fig. 28 shows the elastic scattering phase shift and the time delay for the "+" potential curve. It also shows a shape resonance at an energy \( E = 1.8 \times 10^{-3} \text{ a.u.} \) above threshold. The width of the resonance was obtained to be \( \Gamma = 1.7 \times 10^{-3} \text{ a.u.} \). The lowest Feshbach resonance of the "-" channel was calculated at \( E = -0.12537 \text{ a.u.} \).

Fig. 29 shows the lowest potential curve of the \( ^3p^e \) symmetry of \( M^- \). There exists a \( 2p^2 \ ^3p^e \) quasibound state in \( H^- \), and the same is expected in \( M^- \). The potential curve shown does not support a resonance below the \( n = 2 \) threshold. It has a shape resonance at an energy \( E = 0.9 \times 10^{-4} \text{ a.u.} \) above threshold. Since this curve is the lowest one of the \( ^3p^e \) symmetry, this value is an upper bound on the exact energy. The lower bound on the resonance was found, by neglecting the adiabatic correction term \( W_{\mu\mu} \), to be \( E = -0.12623 \text{ a.u.} \). These two values bracket the value given in Fig. 1 of ref. 9, \( E = -0.12411 \text{ a.u.} \) (binding energy = \( 0.3 \times 10^{-3} \text{ a.u.} \)).

Fig. 30 shows the lowest two potential curves corresponding to the \( ^3p^0 \) symmetry of \( M^- \). As in \( Ps^- \), there is no crossing between the "+" and the "-" potential
Fig. 27. Lowest two of the three $^1P^0$ hyperspherical potential curves of M which converge to the M $(n = 2)$ threshold.
Fig. 28. The elastic scattering phase shift ($\delta$) and its energy derivative just above M (n=2) threshold. These indicate a shape resonance at an energy of $1.8 \times 10^{-3}$ a.u. above threshold.
Fig. 29. Lowest $^3P_e$ hyperspherical potential curve of $M^-$, converging to the $M$ ($n = 2$) threshold.
Fig. 30. Lowest two of the three $^3P^0$ hyperspherical potential curves of $M^-$ which converge to the $M$ ($n = 2$) threshold.
curves, and the curves behave adiabatically. Therefore, the only attractive potential curve is the "+", which behave as \(-3.71/R^2\) at large \(R\). The lowest resonance is calculated to lie at \(E = -0.14843\) a.u. Fig. 31 shows the potential curves of the \(^1\text{p}^\text{e}\) symmetry of \(M^-\). Again the potential curves behave adiabatically and the only attractive potential curve is the "+", which behaves as \(-0.24/R^2\) at large \(R\). It supports an infinite number of resonances, the lowest of which lies at \(E = -0.12692\) a.u.

4. A Hypothetical System with \(m_3 = 5\) a.u.

There is a large gap between the three-particle systems \(\text{Ps}^-\) and \(M^-\). In order to study the evolution of doubly excited states properties with the reduced mass of the atom, I discuss here an intermediate system, which of course does not exist, with a nuclear mass of 5 a.u. The reduced mass of the atom \(\mu_{13}\) is 0.83333 a.u., and the constants involved in the calculation are:

\[
\begin{align*}
c &= 1.690308 \\
c' &= 1.01485 \\
d &= 0.6
\end{align*}
\]

Fig. 32 shows the attractive potential curves converging to the \(n = 2\) threshold \((E_2 = -0.104166\) a.u.) corresponding to the \(^1\text{s}^\text{e}\), \(^3\text{p}^\text{o}\), and \(^1\text{p}^\text{e}\) symmetries. The binding energy of the ground state and of the doubly excited states are given in Table 2.
Fig. 31. Lowest two of the three $^1p_e$ hyperspherical potential curves of $M^-$ which converge to the $M$ ($n = 2$) threshold.
Fig. 32. $^1S^e$ (lower curve), $^3P^o$ (middle curve) and $^1D^e$ (upper curve) attractive hyperspherical potential curves of a hypothetical system with $m_3 = 5$ a.u.
VIII. CONCLUSIONS

The present analysis has shown for the first time the existence of many resonance states in Ps⁻ and M⁻. While most previous studies using hyperspherical coordinates were aimed at understanding features of electron correlations in doubly excited states which were obtained from more sophisticated calculations or from experiment, the present study relies only on the hyperspherical potential curves to predict these resonance features. From the ⁰¹potential curves, it can be concluded that photodetachment cross sections of Ps⁻ and M⁻ have the same pattern as in H⁻, e.g., a very sharp and narrow peak just below the n = 2 threshold, associated with the "-" Feshbach resonances, and a much wider "+" shape resonance just above threshold. It is also clear that the two resonances are qualitatively different, since the shape resonance decay width comes primarily from tunneling through the angular momentum barrier, while the Feshbach resonance decay width comes entirely from interchannel coupling. From the ³⁰potential curve of Ps⁻, it can now be understood why previous studies⁹,⁴⁰ have not found a quasibound state below the n = 2 threshold corresponding to the known 2p² ³pe metastable state of H⁻. The potential curve is not attractive enough to support it, and instead it supports a shape resonance. As for the ¹⁰shape resonance, the
$^3p^e$ shape resonance decay width comes primarily from tunneling through the barrier. The $^3p^e$ and $^1d^e$ potential curves show that there is no possible shape resonance in these symmetries, as there is none in $H^-$, since the "+" and "-" curves behave adiabatically, and therefore there is only one attractive curve ("+"), which supports an infinite number of Feshbach resonances. The spectrum of $Ps^-$ presented here is very similar to the spectrum of $H^-$, in the sense that it follows the same order: $^1s^e, ^3p^o, ^1d^e, ^1p^o"-", ^3p^e, ^1p^o"+"$.

All the features of $M^-$ parallel those of $H^-$ very closely, as expected. The results obtained here for the $^1s^e$ and $^3p^o$ resonances are lower than the expected values, from comparison to $H^-$, while the result for the $^1d^e$ resonance is slightly higher. The value of the energy found by Macek$^{17}$ for the $2s2p^3p^o$ state in helium was also lower than other calculated values. This can be explained, or at least partially justified, with the help of the post-adiabatic approximation of Klar and Fano.$^{63}$ Klar$^{64}$ gives an equation for the adiabatic potential corrected to leading order in the nonadiabatic coupling (eq. 16 of ref. 64):

$$u_v(R,E) = U_v(R) - \frac{1}{2} (\langle P^2 \rangle_v + 2(E-U_v(R)) \sum_{\mu} \frac{(P_{vv})^2}{U_v-U_{\mu}})$$
For the lowest channels, where \( U_\nu < E \), the contribution from all higher channels, with \( U_\mu > U_\nu \), is negative, while the contribution from lower channels, e.g., the contribution to the second channel from its coupling to the lowest one is positive, since \( U_\mu < U_\nu \), and since

\[
-\frac{1}{2} (P^2)_{\nu \nu} = \frac{1}{2} W_{\nu \nu} > 0 .
\]

Therefore, the correction to the second eigenvalue due to its coupling to the lowest channel would increase this eigenvalue.

Table 2 shows the binding energies of the ground state and the doubly excited states of the three systems studied here and those of \( \text{H}^- \). Fig. 33 shows how the binding energy of the ground state of three particles depend on the atomic reduced mass (\( \mu_{13} \)). The upper curve gives an upper bound on the binding energy (lower bound on the total energy), while the lower curve gives a lower bound on the binding energy. The curve in the middle, which has data points only at \( \mu_{13} = 0.5 \) and at \( \mu_{13} = 1.0 \) (\( \text{Ps}^- \) and \( \text{H}^- \) respectively) gives the exact values (from ref. 9 for \( \text{Ps}^- \) and from ref. 63 for \( \text{H}^- \)). This mass dependence is shown in Fig. 34 for the doubly excited states \( ^1S_e (\mu=2) \) (curve a), \( ^3P_0 \) (curve b), \( ^1D_e \) (curve c) and \( ^1P_0^\pi^- \) (curve d). All of them, including the binding energy of the ground state and of the doubly excited states, but excluding the points
Fig. 33. Mass dependence of the binding energy of the ground state for various three-particle systems having two identical particles. The lower curve gives a lower limit, the upper curve gives an upper limit, and the curve in the middle is the exact values. (See text). The abscissa is the atomic reduced mass ($\mu_{13}$).
Fig. 34. Mass dependence of the binding energy of doubly excited states, $^1S^e$ (curve a), $^3P^o$ (curve b), $^1D^e$ (curve c), and $^1P^o"-"$ (curve d) for various three-particle systems having two identical particles. The abscissa is the atomic reduced mass ($\mu_{13}$).
corresponding to $H^-$ which are exact values and were not calculated here, show a remarkable linear dependence. The slope of the line decreases as the total angular momentum of the system or the channel label $\mu$ increase. This means that even though there is a simple ratio of the binding energy of the ground state of $\text{Ps}^-$ to that of $H^-$, approximately equal to the ratio between the reduced masses of $\text{Ps}$ and $H$, this is not a general rule. There is also a simple dependence of the binding energy of doubly excited states on the atomic reduced mass. As pointed out in BG1 with respect to the ground state, this simple dependence of the binding energy on the atomic reduced mass is not a foregone conclusion, since $\text{Ps}^-$ consists of three particles of equal mass tumbling about their center of mass while $H^-$ consists of two electrons moving around a heavy proton. Doubly excited states of $H^-$, and to some extent of $\text{M}^-$, can be thought as truly "doubly" excited states, in the sense that the excitation energy is shared only by the two electrons with the proton being fixed in space, while doubly excited state of $\text{Ps}^-$ could be thought as "triply" excited states, in the sense that the excitation energy is shared by the three particles. The reason for this simple linear dependence of the binding energy on the reduced mass is still not understood and will be the subject of future investigations. In the case of $^1\text{De}^e$ states, the slope is negative. This appears to be correlated with fact that
Table 2. Binding energy of some three-particle systems in different symmetries (in a.u.)

<table>
<thead>
<tr>
<th></th>
<th>$^1S^e_\mu=1$</th>
<th>$^1S^e_\mu=2$</th>
<th>$^3p^o$</th>
<th>$^1D^e$</th>
<th>$^1p^o_{\pi,\sigma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01209</td>
<td>0.0139</td>
<td>0.0103</td>
<td>0.00493</td>
<td>0.000087</td>
</tr>
<tr>
<td></td>
<td>0.0191*</td>
<td>0.0204</td>
<td>0.0155</td>
<td>0.00352</td>
<td>0.000957</td>
</tr>
<tr>
<td></td>
<td>0.0257*</td>
<td>0.0240</td>
<td>0.0181</td>
<td>0.00251</td>
<td>0.0010460</td>
</tr>
<tr>
<td></td>
<td>0.0275663</td>
<td>0.023765</td>
<td>0.017165</td>
<td>0.0027865</td>
<td></td>
</tr>
</tbody>
</table>

* Lower bound

Table 3. Permanent dipole coefficients $D_1$ for different $L$ values (a.u.)

<table>
<thead>
<tr>
<th></th>
<th>$^1S^e_\mu=1$</th>
<th>$^1S^e_\mu=2$</th>
<th>$^3p^o$</th>
<th>$^1D^e$</th>
<th>$^1p^o_{\pi,\sigma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-7.06</td>
<td>-5.54</td>
<td>-5.52</td>
<td>-3.86</td>
<td>-1.44</td>
</tr>
<tr>
<td></td>
<td>-5.08</td>
<td>-3.71</td>
<td>-5.08</td>
<td>-3.71</td>
<td>-1.44</td>
</tr>
<tr>
<td></td>
<td>-0.289</td>
<td>-0.289</td>
<td>-0.289</td>
<td>-0.289</td>
<td>-1.44</td>
</tr>
</tbody>
</table>
the permanent dipole moment, the lowest eigenvalue of the
operator $\hat{D}$ (see eg. IV.15), is greater in $Ps^-$ than in the
other two systems. These eigenvalues are shown in Table
3. Note that the ratio of the coefficient for $Ps^-$ and $M^-$
in the $P$ state is only about 1.5, while it is about 5 in
the $D$ state. This means that the long-range dipole
attraction is stronger in $Ps^-$ than in $M^-$ in the
$^1D^e$ symmetry. The actual potential $D_1/R^2$ at the minimum
of each potential curve is $-0.0256$ for $M^-$ and $-0.01386$ for
$Ps^-$ in the $^3P^0$ symmetry while it is $-0.0036$ for $Ps^-$ and
0.002 for $M^-$ in the $^1D^e$ symmetry.

The "prediagonalization" discussed in Chapter IV and
used in most of the calculation, should prove very useful
in the study of many-particle systems, since it exploits
the degeneracy of the adiabatic eigenvalues in one region
of configuration space, say $R > 0$, by enabling one to
choose only the eigenstates in each degenerate subspace
which have a high density in the regions where the
potential is minimum. Lastly, the method introduced in
Chapter IV for calculating the probability density should
also prove useful in the study of other three-particle
systems, since it is not restricted in any way to the
Jacobi coordinates used in this work.
REFERENCES


3. Ibid., p. 155.


26. This plot was suggested by Professor A. R. P. Rau.
34. Ibid., p. 198, eq. 10.


42. Y. K. Ho, submitted to Phys. Rev. A.


52. A. R. Edmonds, as in ref. 36, p. 71, eq. (5.2.1).

53. There is a misprint in BG1. Equation 13 of BG1 should read as Eq. VI.4 of this work.


56. S. Watanabe, private communication.


62. H. A. Bethe and E. E. Salpeter, as ref. 3, p. 167.


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Date of Examination:

April 29, 1986