

# EXACT SOLUTION OF THE RESTRICTED THREE-BODY SANTILLI-SHILLADY MODEL OF $H_2$ MOLECULE

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## Abstract

In this paper, we study the exact solution of the restricted isochemical model of  $H_2$  molecule with fixed nuclei recently proposed by Santilli and Shillady in which the two electrons are assumed to be bonded/correlated into a quasiparticle called the *isoelectronium*. Under the conditions that: 1) the isoelectronium is stable; 2) the effective size of the isoelectronium is ignorable, in comparison to internuclear distance; and 3) the two nuclei are at rest, the Santilli-Shillady model of the  $H_2$  molecule is reduced to a restricted *three-body* system essentially similar to a neutral version of the  $H_2^+$  ion, which, as such, admits exact solution. Our main result is that the restricted three-body Santilli-Shillady approach to  $H_2$  is capable to fit the experimental binding energy, at the isoelectronium mass parameter  $M = 0.308381m_e$ , although under optimal internuclear distance about 19.6% bigger than the conventional experimental value, indicating an approximate character of the three-body model.

# 1 Introduction

In this paper, we study isochemical model of the  $H_2$  molecule recently introduced by R. M. Santilli and D. D. Shillady [1], which is characterized by the conventional  $H_2$  model set up plus a short-range attractive Hulthen potential interaction between the two electrons originating from the deep overlapping of their wave functions at mutual distances of the order of 1 fm; see also [2]. If one assumes that this attractive potential is strong enough to overcome Coloumb repulsion between the two electrons, they can form electron-electron system called *isoelectronium*. The isoelectronium is characterized by "bare" mass  $M = 2m_e$ , as a sum of masses of two constituent electrons, charge  $-2e$ , radius about  $10^{-11}$  cm, and null magnetic moment. The used Hulthen potential contains two real parameters, one of which is the isoelectronium correlation length parameter  $r_c$ , which can be treated as an effective radius of isoelectronium.

The main structural difference between the Santilli-Shillady isochemical model and the conventional quantum chemical model of the  $H_2$  molecule, is that the former admits additional nonlinear, nonlocal, and nonpotential, thus nonunitary effects due to the deep overlapping of the wavepackets of valence electrons at short distances, which are responsible for the strong molecular bond. In a first nonrelativistic approximation, Santilli and Shillady [1] derived the following characteristics of the isoelectronium: total rest mass  $M = 2m_e$ , charge  $-2e$ , magnetic moment zero, and radius  $6.84323 \times 10^{-11} cm$ . The value  $M = 2m_e$  of the rest mass was derived via the assumption of a contact, *nonpotential* interactions due to the mutual wave-overlapping sufficiently strong to overcome the repulsive Coulomb force. The nonpotential character of the bond was then responsible for the essential lack of binding energy in the isoelectronium, and the resulting value  $M = 2m_e$ . However, the authors stressed in [1] that the isoelectronium is expected to have a non-null binding energy, and, therefore, a rest mass smaller than  $2m_e$ . One argument presented in [1] is that, when coupled in singlet at very short distances, the two electrons eventually experience very strong *attractive* forces of magnetic type, due to the two pairs of opposing magnetic polarities, resulting in a bond. The potential origin of the bond then implies the existence of a binding energy, resulting in a rest mass of the isoelectronium smaller than  $2m_e$ . Also, in the subsequent paper [3], Santilli pointed out that the isoelectronium can at most admit a small instability.

As a result of a correlation/bonding between the two electrons, Santilli and Shillady were able to reach, for the first time, representations of the binding energy and other characteristics of  $H_2$  molecule which are accurate to the *seventh digit*, within the framework of numerical Hartree-Fock approach to  $H_2$  molecule viewed as a four-body system with fixed nuclei, and with the use of Gaussian screened Coloumb potential taken as an approximation to the Hulten potential [1].

On the other hand, the above mentioned strong short-range character of the electron-electron interaction suggests the use of approximation of *stable* isoelectronium of *ignorably small* size, in comparison to the internuclear distance [1]. Indeed, under these two assumptions one can reduce the conventional *four-body* structure of the  $H_2$  molecule to a *three-body* system (the two electrons are viewed as a single point-like particle). Furthermore, in the Born-Oppenheimer approximation, i.e. at fixed nuclei, we have a *restricted* three-body system, the Shrödinger equation for which admits *exact* analytic solution.

So, we have the original four-body Santilli-Shillady model of  $H_2$  molecule, and the three-body Santilli-Shillady model of  $H_2$ , which is an approximation to it. The former is characterized by, in general, unstable isoelectronium and, thus, sensitivity to details of the electron-electron interaction, while the latter deals with a single point-like particle (stable isoelectronium of ignorable size) moving around two fixed nuclei.

Clearly, the three-body Santilli-Shillady model of  $H_2$  molecule can be viewed as  $H_2^+$  ion like system. For the sake of brevity and to avoid confusion with the  $H_2^+$  ion itself, we denote  $H_2$  molecule, viewed as the restricted three-body system, as  $\hat{H}_2$ . Note that  $\hat{H}_2$  is a neutral  $H_2^+$  ion like system.

The quantum mechanical problem of the restricted  $H_2^+$  ion like systems, associated differential equation, and its exact analytic solution have been studied in the literature by various authors [6]-[14].

In this paper we present the exact analytic solution of the above indicated restricted three-body Santilli-Shillady isochemical model of the hydrogen molecule, study its asymptotic behavior, and analyze the ground state energy, presenting numerical results in the form of tables and plots. Our analysis is based on the analytical results obtained for thoroughly studied  $H_2^+$  ion.

In Sec. 2, we review some features of the four-body Santilli-Shillady model of  $H_2$  necessary for our study, and introduce our separation of variables in

the Schrödinger equation under the assumption that the isoelectronium is a stable quasiparticle of ignorable size.

In Sec. 3, we review the exact analytic solution of the  $H_2^+$  ion like systems (which includes the  $\hat{H}_2$  system), and study their asymptotic behavior at large and small distances between the two nuclei.

In Sec. 4, we use the preceding solution to find the binding energy of  $\hat{H}_2$  system. We then develop a scaling method and use Ritz's variational approach to check the results. Both the cases of the isoelectronium "bare" mass  $M = 2m_e$  and of variable mass parameter,  $M = \eta m_e$  have been studied. All the data and basic results of this Section have been collected in Table 1.

In Sec. 5, we introduce a preliminary study on the application of Ritz's variational approach to the general four-body Santilli-Shillady model of  $H_2$ , where the isoelectronium is an *unstable* composite particle, in which case the model re-acquires its *four-body* structure, yet preserves a strong bonding/correlation between the electrons.

In the Appendix, we present the results of our numerical calculations of the ground state energy of  $H_2^+$  ion and of  $\hat{H}_2$  system, for different values of the isoelectronium mass parameter  $M$ , based on their respective exact solutions, in the form of tables and plots.

Our main result is that *the restricted three-body Santilli-Shillady isochemical model of the hydrogen molecule does admit exact analytic solution capable of an essentially exact representation of the binding energy, although under internuclear distance about 19.6% bigger than the conventional experimental value.* The mass parameter  $M$  of isoelectronium has been used here to fit the experimental value of the binding energy, with the result  $M = 0.308381m_e$  (i.e. about 7 times less than the "bare" mass  $M = 2m_e$ ). In this paper, we assume that some defect of mass effect may have place leading to decrease of the "bare" mass  $M = 2m_e$ .

We also note that the value  $M = 0.308381m_e$  implies a binding energy of about 1.7 MeV, which is admittedly rather large. Recent studies by Y. Rui [4] on the correct force law among spinning charges have indicated the existence of a critical distance below which particles with the same charge attract each others. If confirmed, these studies imply that the repulsive Coulomb force itself between two electrons in singlet coupling can be attractive at a sufficiently small distance, thus eliminating the need to postulate an attractive force sufficiently strong to overcome the repulsive Coulomb force. As a result, a binding energy in the isoelectronium structure of the order of 1.7

MeV cannot be excluded on grounds of our knowledge at this time.

Clearly, however, that due to the current lack of dynamical description of the above mentioned defect of mass, and the obtained result that the predicted internuclear distance is about 19.6% bigger than the experimental value, our study is insufficient to conclude that the isoelectronium is permanently stable, and one needs for additional study on the four-body Santilli-Shillady isochemical model of  $H_2$ , which is conducted in a subsequent paper by one of the authors [5].

## 2 Santilli-Shillady model of $H_2$ molecule

### 2.1 General equation

The Santilli-Shillady iso-Schrödinger's equation for  $H_2$  molecule with short-range attractive Hulten potential between the two electrons can be reduced to the following form [1]:

$$\left( -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 - V_0 \frac{e^{-r_{12}/r_c}}{1 - e^{-r_{12}/r_c}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1a}} - \frac{e^2}{r_{2a}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2b}} + \frac{e^2}{R} \right) |\phi\rangle = E|\phi\rangle, \quad (2.1)$$

where  $V_0$  and  $r_c$  are positive constants, and  $R$  is distance between nuclei  $a$  and  $b$ . By using vectors of center-of-mass system of electrons 1 and 2,  $\vec{r}_a$  and  $\vec{r}_b$ , originated at nuclei  $a$  and  $b$ , respectively, we have

$$r_{1a} = \left| \vec{r}_a - \frac{m_2}{m_1 + m_2} \vec{r}_{12} \right|, \quad r_{2a} = \left| \vec{r}_a + \frac{m_1}{m_1 + m_2} \vec{r}_{12} \right|. \quad (2.2)$$

$$r_{1b} = \left| \vec{r}_b - \frac{m_2}{m_1 + m_2} \vec{r}_{12} \right|, \quad r_{2b} = \left| \vec{r}_b + \frac{m_1}{m_1 + m_2} \vec{r}_{12} \right|, \quad (2.3)$$

(for electrons we have  $m_1 = m_2 = m_e$ ). The Lagrangian of the system can be written

$$\mathcal{L} = \frac{m_1 \dot{r}_1^2}{2} + \frac{m_2 \dot{r}_2^2}{2} - V(r_{12}) - W(r_{1a}, r_{1b}, r_{2a}, r_{2b}, R), \quad (2.4)$$

Here,  $V$  is the potential energy of interaction between the electrons 1 and 2,

$$V(r_{12}) = \frac{e^2}{r_{12}} - V_0 \frac{e^{-r_{12}/r_c}}{1 - e^{-r_{12}/r_c}}, \quad (2.5)$$

and  $W$  is the potential energy of interaction between electrons and nuclei, and between two nuclei,

$$W(r_{1a}, r_{1b}, r_{2a}, r_{2b}, R) = -\frac{e^2}{r_{1a}} - \frac{e^2}{r_{2a}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2b}} + \frac{e^2}{R}. \quad (2.6)$$

Notice that  $\dot{r}_1 = \dot{r}_{1a} = \dot{r}_{1b}$ , and  $\dot{r}_2 = \dot{r}_{2a} = \dot{r}_{2b}$ , because  $\vec{r}_{1a} = \vec{r}_{1b} + \vec{R}$  and  $\vec{r}_{2a} = \vec{r}_{2b} + \vec{R}$ , where  $\vec{R}$  is constant vector. Similarly,

$$\vec{r}_a = \vec{r}_b + \vec{R}, \quad \vec{r}_a = \frac{m_1 \vec{r}_{1a} + m_2 \vec{r}_{2a}}{m_1 + m_2}, \quad \vec{r}_b = \frac{m_1 \vec{r}_{1b} + m_2 \vec{r}_{2b}}{m_1 + m_2}. \quad (2.7)$$

Then, Lagrangian (2.4) can be rewritten as  $\mathcal{L} = \mathcal{L}(r_a, r_b, r_{12})$ ,

$$\mathcal{L} = \frac{M \dot{r}_a^2}{2} + \frac{m \dot{r}_{12}^2}{2} - V(r_{12}) - W(r_a, r_b, r_{12}, R). \quad (2.8)$$

Here,  $M = m_1 + m_2$  is the total mass of the electrons, and  $m = m_1 m_2 / (m_1 + m_2)$  is the reduced mass. Corresponding generalized momenta take the form

$$\vec{P}_M = \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_A} = M \dot{\vec{r}}_A, \quad \vec{p}_m = \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_{12}} = m \dot{\vec{r}}_{12}. \quad (2.9)$$

The system reveals axial symmetry, with the axis connecting two nuclei. Also, for identical nuclei we have reflection symmetry in respect to the plane perpendicular to the above axis and lying on equal distances from the two nuclei.

## 2.2 Separation of variables

Santilli and Shillady [1] then assume that, as a particular case under study in this paper (not to be confused with the general four-body case), the two valence electrons of the  $H_2$  molecule can form a stable quasi-particle of small size due to short-range attractive Hulten potential, such that

$$r_{12} \ll r_a, \quad r_{12} \ll r_b. \quad (2.10)$$

Therefore, we can ignore  $r_{12}$  in Eqs.(2.2) and (2.3),

$$\vec{r}_{1a} \approx \vec{r}_{2a} \approx \vec{r}_a, \quad \vec{r}_{1b} \approx \vec{r}_{2b} \approx \vec{r}_b. \quad (2.11)$$

The Hamiltonian of the system then becomes

$$\hat{H} = \frac{\hat{P}_M^2}{2M} + \frac{\hat{p}_m^2}{2m} + V(r_{12}) + W(r_a, r_b, R), \quad (2.12)$$

where

$$W(r_a, r_b, R) = -\frac{2e^2}{r_a} - \frac{2e^2}{r_b} + \frac{2e^2}{R}. \quad (2.13)$$

In this approximation, it is possible to *separate* the variables  $r_{a,b}$  and  $r_{12}$ . Namely, inserting  $|\phi\rangle = \psi(r_a, r_b, R)\chi(r_{12})$  into the equation [1]

$$\left( -\frac{\hbar^2}{2M} \nabla_{ab}^2 - \frac{\hbar^2}{2m} \nabla_{12}^2 - V_0 \frac{e^{-r_{12}/r_c}}{1 - e^{-r_{12}/r_c}} + \frac{e^2}{r_{12}} - \frac{2e^2}{r_a} - \frac{2e^2}{r_b} + \frac{e^2}{R} \right) |\phi\rangle = E|\phi\rangle \quad (2.14)$$

we obtain

$$-\frac{\hbar^2}{2M} \frac{\nabla_{ab}^2 \psi}{\psi} - \frac{\hbar^2}{2m} \frac{\nabla_{12}^2 \chi}{\chi} + V(r_{12}) + W(r_a, r_b, R) - E = 0. \quad (2.15)$$

By separating the variables, we have the following two equations:

$$-\frac{\hbar^2}{2m} \nabla_{12}^2 \chi + V(r_{12}) \chi = \varepsilon \chi. \quad (2.16)$$

and

$$-\frac{\hbar^2}{2M} \nabla_{ab}^2 \psi + W(r_a, r_b, R) \psi = (E - \varepsilon) \psi. \quad (2.17)$$

In this way, under approximation (2.10), the original four-body problem is reduced to a three-body problem characterized by two differential equations:

1) Equation (2.16), which describes the electron-electron system forming the bound quasi-particle state called isoelectronium, with "bare" total mass  $M = 2m_e$  and charge  $-2e$ . This equation will not be studied in this paper, since we assume that the isoelectronium is permanently stable.

2) Equation (2.17), which is the structural equation of the restricted three-body Santilli-Shillady isochemical model  $\hat{H}_2$ , in which the stable isoelectronium with "bare" mass  $M = 2m_e$ , charge  $-2e$ , null magnetic moment and

ignorable size orbits around the two nuclei, hereon assumed to have infinite mass (the Born-Oppenheimer approximation).

This paper is devoted to the study of the exact analytic solution of the latter equation, and its capability to represent the experimental data on the binding energy, bond length, and other characteristics of the hydrogen molecule.

### 3 Exact solution for $H_2^+$ ion like system

In this Section, we present analytical solution of the Schrödinger equation for  $H_2^+$  ion-like systems in Born-Oppenheimer approximation, we analyze the associated recurrence relations, and asymptotic behavior of the solutions at large and small distances between the two nuclei. As it was indicated [1], this problem arises when Santilli-Shillady model of  $H_2$  is reduced to the restricted *three-body* problem characterized by Eq. (2.17), which possesses exact solution under appropriate separation of variables.

#### 3.1 Differential equations

In Born-Oppenheimer approximation, i.e., at fixed nuclei, the equation for  $H_2^+$  ion-like system for a particle of mass  $M$  and charge  $q$  is

$$\nabla^2\psi + 2M(E + \frac{q}{r_a} + \frac{q}{r_b})\psi = 0. \quad (3.1)$$

In spheroidal coordinates,

$$x = \frac{r_a + r_b}{R}, \quad 1 < x < \infty, \quad (3.2)$$

$$y = \frac{r_a - r_b}{R}, \quad -1 < y < 1, \quad (3.3)$$

$$\varphi, \quad 0 < \varphi < 2\pi, \quad (3.4)$$

where  $R$  is a fixed separation distance between the nuclei  $a$  and  $b$ , and

$$\begin{aligned} \nabla^2 = \frac{4}{R^2(x^2 - y^2)} & \left( \frac{\partial}{\partial x}(x^2 - 1)\frac{\partial}{\partial x} + \frac{\partial}{\partial y}(1 - y^2)\frac{\partial}{\partial y} \right) \\ & + \frac{1}{R^2(x^2 - 1)(1 - y^2)} \frac{\partial^2}{\partial \varphi^2}. \end{aligned} \quad (3.5)$$



We then have from Eq.(3.1)

$$\left[ \frac{\partial}{\partial x}(x^2 - 1) \frac{\partial}{\partial x} + \frac{\partial}{\partial y}(1 - y^2) \frac{\partial}{\partial y} + \frac{x^2 - y^2}{4(x^2 - 1)(1 - y^2)} \frac{\partial^2}{\partial \varphi^2} + \frac{MER^2}{2}(x^2 - y^2) + 2MqRx \right] \psi = 0. \quad (3.6)$$

Here, we have used

$$\frac{1}{r_a} + \frac{1}{r_b} = \frac{4}{R} \frac{x}{x^2 - y^2}. \quad (3.7)$$

Obviously, Equation (3.6) can be *separated* by the use of the representation

$$\psi = f(x)g(y)e^{im\varphi}, \quad (3.8)$$

under which we have two second-order *ordinary* differential equations,

$$\frac{d}{dx} \left( (x^2 - 1) \frac{d}{dx} f \right) - \left( \lambda - 2MqRx - \frac{MER^2}{2} x^2 + \frac{m^2}{x^2 - 1} \right) f = 0, \quad (3.9)$$

$$\frac{d}{dy} \left( (1 - y^2) \frac{d}{dy} g \right) + \left( \lambda - \frac{MER^2}{2} y^2 - \frac{m^2}{1 - y^2} \right) g = 0, \quad (3.10)$$

where  $\lambda$  is a separation constant (cf. [6]). So, the problem is to identify solutions for  $f$  and  $g$ .

## 3.2 Recurrence relations

By introducing the re-formulations

$$f \rightarrow (x^2 - 1)^{m/2} f, \quad (3.11)$$

$$g \rightarrow (1 - y^2)^{m/2} g, \quad (3.12)$$

to handle singularities at  $x = \pm 1$  and  $y = \pm 1$  in Eqs.(3.9) and (3.10), respectively, we reach the following final form of the equations to be solved:

$$(x^2 - 1)f'' + 2(m + 1)f' - (\lambda + m(m + 1) - \tilde{a}x - c^2x^2)f = 0 \quad (3.13)$$

and

$$(1 - y^2)g'' - 2(m + 1)g' + (\lambda - m(m + 1) - c^2y^2)g = 0, \quad (3.14)$$

where we have denoted

$$c^2 = \frac{MER^2}{2}, \quad \tilde{a} = 2MqR. \quad (3.15)$$

We shall look for solutions in the form of power series. Substituting the power series

$$f = \sum f_k x^k, \quad (3.16)$$

$$g = \sum g_k y^k, \quad (3.17)$$

into Eqs. (3.13) and (3.14), we obtain the recurrence relations,

$$c^2 f_{n-2} + \tilde{a} f_{n-1} - (\lambda - (m+n)(m+n+1)) f_n \quad (3.18)$$

$$-(n+1)(n+2) f_{n+2} = 0$$

and

$$c^2 g_{n-2} - (\lambda - (m+n)(m+n+1)) g_n - (n+1)(n+2) g_{n+2} = 0, \quad (3.19)$$

from which coefficients  $f_k$  and  $g_k$  must be found. Here,  $f_0$  and  $g_0$  are fixed by normalization of the general solution. Note that the recurrence relation (3.18) contains term  $2MqR f_{n-1}$  raised from the linear term  $2MqRx$  in Eq.(3.9).

In the next two Sections we consider some particular cases of interest prior to going into details of the general solution. These particular solutions are important for the study of the general case.

### 3.3 The particular case $R = 0$

In the particular case  $R = 0$ , the two nuclei are superimposed, so that the system is reduced to a helium-like system,

$$\frac{d}{dx} \left( (x^2 - 1) \frac{d}{dx} f \right) - \left( \lambda + \frac{m^2}{x^2 - 1} \right) f = 0, \quad (3.20)$$

$$\frac{d}{dy} \left( (1 - y^2) \frac{d}{dy} g \right) + \left( \lambda - \frac{m^2}{1 - y^2} \right) g = 0. \quad (3.21)$$

From recurrence relations (3.18) and (3.19) we obtain the following particular recurrence sequences,

$$(\lambda - (m+n)(m+n+1)) f_n - (n+1)(n+2) f_{n+2} = 0 \quad (3.22)$$

and

$$(\lambda - (m + n)(m + n + 1))g_n - (n + 1)(n + 2)g_{n+2} = 0, \quad (3.23)$$

which are equivalent to each other, and can be *stopped* by putting the separation constant

$$\lambda = (m + n)(m + n + 1) = l(l + 1), \quad (3.24)$$

with  $m = -l, \dots, l$ . This gives us well known solution for  $g$  in terms of Legendre polynomials,

$$g = (1 - y^2)^{m/2} \frac{d}{dy^m} P_l(y), \quad (3.25)$$

where  $m = |m|$ , and

$$P_l = \frac{1}{2^l l!} \frac{d^l}{dy^l} (y^2 - 1)^l. \quad (3.26)$$

The solution is the well known spherical harmonic function

$$Y_{lm} = N_{lm} P_l^m(y) e^{im\varphi}, \quad (3.27)$$

with normalization constant

$$N_{lm} = \sqrt{\frac{(l - m)!(2l + 1)}{(l + m)!4\pi}}. \quad (3.28)$$

This solution corresponds to the case of an ellipsoid degenerated into a sphere, and we can put  $y = \cos \theta$  for identification with the angular spherical coordinates  $(\theta, \varphi)$ . Equation in  $x$  corresponds to the radial part of the well known solution expressed in terms of Laguerre polynomials.

### 3.4 The particular case $q = 0$

In the particular case of zero charge,  $q = 0$ , we have from Eqs.(3.9) and (3.10)

$$\frac{d}{dx} \left( (x^2 - 1) \frac{d}{dx} f \right) - \left( \lambda - c^2 x^2 + \frac{m^2}{x^2 - 1} \right) f = 0, \quad (3.29)$$

$$\frac{d}{dy} \left( (1 - y^2) \frac{d}{dy} g \right) + \left( \lambda - c^2 y^2 - \frac{m^2}{1 - y^2} \right) g = 0. \quad (3.30)$$

One can see that these equations originate straightforwardly also from the standard wave equation  $\nabla^2\psi + k^2\psi = 0$ , in the spheroidal coordinates  $(x, y, \varphi)$ . Recurrence relations (3.18) and (3.19) then become

$$c^2 f_{n-2} - (\lambda - (m+n)(m+n+1))f_n - (n+1)(n+2)f_{n+2} = 0 \quad (3.31)$$

and

$$c^2 g_{n-2} - (\lambda - (m+n)(m+n+1))g_n - (n+1)(n+2)g_{n+2} = 0, \quad (3.32)$$

which are equivalent to each other.

A general solution for  $f$  is given by linear combinations of radial spheroidal functions  $R_{mn}^{(p)}(c, x)$  of first,  $p = 1$ , and second,  $p = 2$ , kind [7],

$$R_{mn}^{(p)}(c, x) = \left\{ \sum_{r=0,1}^{\infty'} \frac{(2m+r)!}{r!} d_r^{mn} \right\}^{-1} \left( \frac{x^2-1}{x^2} \right)^{m/2} \times \quad (3.33)$$

$$\times \sum_{r=0,1}^{\infty'} i^{r+m-n} \frac{(2m+r)!}{r!} d_r^{mn} Z_{m+r}^{(p)}(cx),$$

where,

$$Z_n^{(1)}(z) = \sqrt{\frac{\pi}{2z}} J_{n+1/2}(z), \quad (3.34)$$

$$Z_n^{(2)}(z) = \sqrt{\frac{\pi}{2z}} Y_{n+1/2}(z), \quad (3.35)$$

and  $J_{n+1/2}(z)$  and  $Y_{n+1/2}(z)$  are Bessel functions of first and second kind, respectively. The sum in (3.33) is made over either even or odd values of  $r$  depending on the parity of  $n - m$ . Asymptotics of  $R_{mn}^{(1)}(c, x)$  and  $R_{mn}^{(2)}(c, x)$  are

$$R_{mn}^{(1)}(c, x) \xrightarrow{cx \rightarrow \infty} \frac{1}{cx} \cos \left[ cx - \frac{1}{2}(n+1)\pi \right], \quad (3.36)$$

$$R_{mn}^{(2)}(c, x) \xrightarrow{cx \rightarrow \infty} \frac{1}{cx} \sin \left[ cx - \frac{1}{2}(n+1)\pi \right]. \quad (3.37)$$

Particularly, to have well defined limit at  $x = 0$  we should use only spheroidal function of first kind,  $R_{mn}^{(1)}(c, x)$ , because Bessel function of second kind,  $Y_n(z)$ , has logarithmic divergence at  $z = 0$ .

General solution for  $g$  is given by linear combination of angular spheroidal functions of first and second kind [7],

$$S_{mn}^{(1)}(c, y) = \sum_{r=0,1}^{\infty'} d_r^{mn}(c) P_{m+r}^m(y), \quad (3.38)$$

$$S_{mn}^{(2)}(c, y) = \sum_{r=-\infty}^{\infty'} d_r^{mn}(c) Q_{m+r}^m(y), \quad (3.39)$$

where  $P_n^m(y)$  and  $Q_n^m(y)$  are the associated Legendre polynomials of first and second kind, respectively.

Expressions for radial and angular spheroidal functions, and corresponding eigenvalues  $\lambda$ , for particular values of  $m$  and  $n$ , are presented in Ref. [7].

Coefficients  $d_k^{mn}(c)$  are calculated with the help of the following recurrence relation:

$$\alpha_k d_{k+2} + (\beta_k - \lambda_{mn}) d_k + \gamma_k d_{k-2} = 0, \quad (3.40)$$

where

$$\alpha_k = \frac{(2m+k+2)(2m+k+1)c^2}{(2m+2k+3)(2m+2k+5)}, \quad (3.41)$$

$$\beta_k = (m+k)(m+k+1) + \frac{2(m+k)(m+k+1) - 2m^2 - 1}{(2m+2k-1)(2m+2k+3)} c^2, \quad (3.42)$$

$$\gamma_k = \frac{k(k-1)c^2}{(2m+2k-3)(2m+2k-1)}. \quad (3.43)$$

The calculation is made by the following procedure. First, one calculates  $N_r^m$ ,

$$N_{r+2}^m = \gamma_r^m - \lambda_{mn} - \frac{\beta_r^m}{N_r^m} \quad (r \geq 2), \quad (3.44)$$

$$N_2^m = \gamma_0^m - \lambda_{mn}; \quad N_3^m = \gamma_1^m - \lambda_{mn}, \quad (3.45)$$

$$\gamma_r^m = (m+r)(m+r+1) + \frac{1}{2}c^2 \left[ 1 - \frac{4m^2 - 1}{(2m+2r-1)(2m+2r+3)} \right] \quad (r \geq 0). \quad (3.46)$$

Second, one calculates the fractions  $d_0/d_{2r}$  and  $d_1/d_{2p+1}$  with the use of

$$\frac{d_0}{d_{2r}} = \frac{d_0}{d_2} \frac{d_2}{d_4} \dots \frac{d_{2r-2}}{d_{2r}}, \quad (3.47)$$

$$\frac{d_1}{d_{2p+1}} = \frac{d_1}{d_3} \frac{d_3}{d_5} \dots \frac{d_{2p-1}}{d_{2p+1}}, \quad (3.48)$$

and

$$N_r^m = \frac{(2m+r)(2m+r-1)c^2}{(2m+2r-1)(2m+2r+1)} \frac{d_r}{d_{r-2}} \quad (3.49)$$

The coefficients  $d_0$ , for even  $r$ , and  $d_1$ , for odd  $r$ , are determined via the normalization of the solution.

### 3.5 The general case

In this Section, we consider the general solution of our basic equations (3.9) and (3.10). To have more general set up, we consider the case of different charges of nuclei,  $Z_1$  and  $Z_2$ . This leads to appearance of additional linear in  $y$  term in Eq.(3.10), so that both the ordinary differential equations become of similar structure. Also, we restrict consideration by analyzing discrete spectrum, i.e. we assume that the energy  $E < 0$ .

Let us denote

$$p = \frac{R}{2} \sqrt{-2E}, \quad a = R(Z_2 + Z_1), \quad b = R(Z_2 - Z_1). \quad (3.50)$$

Then, Eqs.(3.9) and (3.10), for the general case of different charges of nuclei, can be written as

$$\begin{aligned} & \frac{d}{dx} \left( (x^2 - 1) \frac{d}{dx} f_{mk}(p, a; x) \right) \\ & + \left( -\lambda_{mk}^{(x)} - p^2(x^2 - 1) + ax - \frac{m^2}{x^2 - 1} \right) f_{mk}(p, a; x) = 0, \end{aligned} \quad (3.51)$$

$$\begin{aligned} & \frac{d}{dy} \left( (1 - y^2) \frac{d}{dy} g_{mq}(p, b; y) \right) \\ & + \left( \lambda_{mq}^{(y)} - p^2(1 - y^2) + by - \frac{m^2}{1 - y^2} \right) g_{mq}(p, b; y) = 0, \end{aligned} \quad (3.52)$$

where we assume that the solutions obey

$$|f_{mk}(p, a; 1)| < \infty, \quad \lim_{x \rightarrow \infty} f_{mk}(p, a; x) = 0, \quad |g_{mq}(p, b; \pm 1)| < \infty. \quad (3.53)$$

The eigenvalues  $\lambda$  in Eqs.(3.51) and (3.52) should be equal to each other,

$$\lambda_{mk}^{(x)}(p, a) = \lambda_{mq}^{(y)}(p, b). \quad (3.54)$$

The general solution  $\psi(x, y, \varphi)$  of Eq.(3.6) is represented in the following factorized form:

$$\psi_{kqm}(x, y, \varphi; R) = N_{kqm}(p, a, b) f_{mk}(p, a; x) g_{mq}(p, b; y) \frac{\exp(\pm im\varphi)}{\sqrt{2\pi}}. \quad (3.55)$$

The normalization coefficients  $N_{kqm}(p, a, b)$  in Eq.(3.55) are represented with the help of derivatives of the eigenvalues,  $\lambda_{mk}^{(x)}(p, a)$  and  $\lambda_{mq}^{(y)}(p, b)$ , namely,

$$N_{kqm}^2(p, a, b) = \frac{16p}{R^3} \left[ \frac{\partial \lambda_{mq}^{(y)}(p, b)}{\partial p} - \frac{\partial \lambda_{mk}^{(x)}(p, a)}{\partial p} \right]^{-1}. \quad (3.56)$$

For a given indices  $k, q, m$ , and fixed values of  $Z_1, Z_2$ , and  $R$ , the discrete energy spectrum  $E$  can be determined from Eq.(3.54). This equation has unique solution,  $p = p_{kqm}(a, b)$ . Then, by solving the relation stemming from (3.50)

$$p_{kqm}(R(Z_2 + Z_1), R(Z_2 - Z_1)) = \frac{R}{2} \sqrt{-2E} \quad (3.57)$$

in respect to  $E$ , we can find the discrete spectrum of energy,

$$E_j(R) = E_{kqm}(R, Z_1, Z_2). \quad (3.58)$$

Number of zeroes,  $k, q$ , and  $m$ , of the functions  $g(y)$ ,  $f(x)$ , and  $\exp \pm im\varphi$  are the angular, radial and azimuthal quantum numbers, respectively. However, instead of  $k, q$ , and  $m$  one can use their linear combinations, namely,  $N = k + q + m + 1$  is main quantum number and  $l = q + m$  is orbital quantum number.

To construct the general solution  $u(z)$ , which is called *Coloumb spheroidal function* [8] (CSF), in terms of *angular* CSF  $g(y)$  and *radial* CSF  $f(x)$ , let us, again, use the form which accounts for singularities at the points  $z = \pm 1$  and  $z = \infty$ ,

$$u(z) = (1 - z^2)^{m/2} \exp[-p(1 \pm z)] v(z). \quad (3.59)$$

Then, we represent  $v(z)$  as an expansion,

$$v(z) = \sum_{s=0}^{\infty} a_s(p, b, \lambda) w_s(z), \quad (3.60)$$

in some set of basis functions  $w_s(z)$ .

Now, the complexity of the recurrence relations depends on the basis. In the preceding sections, where the particular cases,  $R = 0$  and  $q = 0$ , have been considered, we used a power series representation. One can try other forms of the representation as well. For a good choice of the basis functions  $w_s(z)$ , we can obtain *three-term* recurrence relation of the form

$$\alpha_s a_{s+1} - \beta_s a_s + \gamma_s a_{s-1} = 0, \quad (3.61)$$

where  $\alpha_s$ ,  $\beta_s$ , and  $\gamma_s$  are some polynomials in  $p$ ,  $b$ , and  $\lambda$ . Then, using the tridiagonal matrix  $\hat{A}$  consisting of the coefficients  $\alpha_s$ ,  $\beta_s$ , and  $\gamma_s$  entering Eq.(3.61), we can write down the equation to find out eigenvalues  $\lambda_{mk}^{(x)}(p, a)$  and  $\lambda_{mq}^{(y)}(p, b)$ . Namely,

$$\det \hat{A} = F(p, b, \lambda) = 0. \quad (3.62)$$

The matrix  $\hat{A}$  has a tridiagonal form. This leads directly to one-to-one correspondence between  $\det \hat{A}$  and the *infinite chain fraction*,

$$F(p, b, \lambda) = \beta_0 - \frac{\alpha_0 \gamma_1}{\beta_1 - \frac{\alpha_1 \gamma_2}{\beta_2 - \dots \frac{\alpha_N \gamma_{N+1}}{\beta_{N+1} - \dots}}} = \beta_0 - \frac{\alpha_0 \gamma_1}{\beta_1} \frac{\alpha_1 \gamma_2}{\beta_2} \dots \simeq \frac{Q_N}{P_N}. \quad (3.63)$$

In numerical computations, this relation allows one to find out eigenvalues  $\lambda$  in an easier way due to simpler algorithm provided by the chain fraction. Consequently, one can compute the energy and coefficients  $a_s$  of the expansion of eigenfunctions  $g(y)$  and  $f(x)$  by using the chain fraction.

The result of this approach in constructing of the solutions depends on the convergence of the chain fraction. Analysis of the convergence can be made from a general point of view. Sufficient conditions of the convergence of the chain (3.63), and of the expansion (3.60), are the following two relations:

$$\left| \frac{\alpha_{s-1} \gamma_s}{\beta_{s-1} \beta_s} \right| < \frac{1}{4}, \quad \frac{a_{s+1}}{a_s} \Big|_{s \rightarrow \infty} \sim \frac{\beta_s}{2\alpha_s} \left[ 1 - \left( 1 - 4 \frac{\alpha_s \gamma_s}{\beta_s^2} \right)^{1/2} \right]. \quad (3.64)$$

Further analysis of the convergence depends on specific choice of the basis functions  $u_s(z)$ .



(i) Series expansion,  $v_s(z) = z^s$ . In this case, the radius,  $Z_v$ , of convergence is

$$Z_v = \lim_{s \rightarrow \infty} \left| \frac{a_s}{a_{s+1}} \right|. \quad (3.65)$$

Particularly, when  $a_{s+1}/a_s \rightarrow 0$  at  $s \rightarrow \infty$  the series (3.60) converges at any  $z$ .

(ii) For the choice of basis function  $v_s(z)$  in the form of orthogonal polynomials, the sufficient condition for convergence of Fourier series (3.60) is

$$\left| \frac{a_s}{a_{s+1}} \right|_{s \rightarrow \infty} \leq 1 - \frac{1}{s}. \quad (3.66)$$

Below, we consider separately angular and radial CSF entering the general solution.

### 3.5.1 The angular Coloumb spheroidal function

For the angular Coloumb spheroidal function (ACSF), it is natural to choose the basis functions  $v_s(y)$  in the form of associated Legendre polynomials,  $P_{s+m}^m(y)$ . Indeed, they form complete system in the region  $y \in [-1, 1]$ , and reproduce ACSF at  $p = b = 0$  (see Sec. 3.3). Inserting of the expansion

$$g_{mq}(p, b; y) = \sum_{s=0}^{\infty} c_s P_{s+m}^m(y) \quad (3.67)$$

into Eq.(3.52) entails five-term recurrence relation. However, this relation, which is sometimes used, is not so suitable as the three-term relation. This is because the determinant of the corresponding pentadiagonal matrix can not be represented as a chain fraction. Nevertheless, in the case  $b = 0$ , i.e. for  $Z_1 = Z_2$ , this five-terms recurrence relation is reduced to two three-terms recurrence relations, separately for even ( $c_{-2} = 0$ ,  $c_0 = 1$ ) and odd ( $c_{-1} = 0$ ,  $c_1 = 1$ ) solutions of Eq.(3.52) presented in previous Section.

For the general case  $b \neq 0$ , the expansions of  $g(p, b; y)$ , handling singularities at the points  $y = \pm 1$  and  $y = \infty$ , respectively, as considered by Baber and Hasse [9], are

$$g_{mq}(p, b; y) = \exp[-p(1+y)] \sum_{s=0}^{\infty} c_s P_{s+m}^m(y), \quad (3.68)$$

$$g_{mq}(p, b; y) = \exp[-p(1 - y)] \sum_{s=0}^{\infty} c'_s P_{s+m}^m(y), \quad (3.69)$$

These expansions yield three-terms recurrence relation,

$$\rho_s c_{s+1} - \kappa_s c_s + \delta_s c_{s-1} = 0, \quad c_{-1} = 0, \quad (3.70)$$

where the coefficients for the case of expansion (3.68) have the following form:

$$\begin{aligned} \rho_s &= \frac{(s + 2m + 1)[b - 2p(s + m + 1)]}{2(s + m) + 3}, \\ \kappa_s &= (s + m)(s + m + 1) - \lambda, \\ \delta_s &= \frac{s[b + 2p(s + m)]}{2(s + m) - 1}. \end{aligned} \quad (3.71)$$

To estimate convergence of these expansions, one can use the above made estimation of the convergence, with the following replacements:  $\alpha_s \rightarrow \rho_s$ ,  $\beta_s \rightarrow \kappa_s$ ,  $\gamma_s \rightarrow \delta_s$ , and  $a_s \rightarrow c_s$ . For the expansion (3.79) we have

$$\left| \frac{\rho_{s-1} \delta_s}{\kappa_{s-1} \kappa_s} \right|_{s \rightarrow \infty} \sim \left( \frac{p}{s} \right)^2, \quad (3.72)$$

i.e., at  $p > 1$ , convergence takes place only at  $s > 2p$ . We should take into account this condition when choosing *minimal* number of terms in the chain fraction (3.73) which is sufficient to calculate  $\lambda$ , to a required accuracy.

The recurrence relation for the coefficients  $c'_s$  of the expansion (3.69) differs from that of Eq.(3.70) by the replacement  $p \rightarrow -p$  in formulas (3.71). Clearly, this replacement does not change the form of the chain fraction,

$$F^{(y)}(p, b, \lambda) = \kappa_0 - \frac{\rho_0 \delta_1}{\kappa_1 -} \frac{\rho_1 \delta_2}{\kappa_2 -} \dots \quad (3.73)$$

So, in both the cases, (3.68) and (3.69), the eigenvalues  $\lambda$  can be found from one and the same equation,

$$F^{(y)}(p, b, \lambda) = 0. \quad (3.74)$$

In practical calculations with the help of this algorithm, the infinite chain fraction (3.63) is, of course, replaced by the *finite* one,  $F_{N+1}^{(y)}(p, b, \lambda)$ , in which

one retains a sufficiently big number  $N$  of terms. Typically,  $N > 10$  provides very good accuracy. So, the eigenvalues are computed as the roots of the polynomial  $Q_{N+1}(p, b, \lambda)$  of degree  $N + 1$ , namely,

$$F_{N+1}^{(y)}(p, b, \lambda) = \frac{Q_{N+1}(p, b, \lambda)}{P_{N+1}(p, b, \lambda)}. \quad (3.75)$$

Such a representation allows one to exclude singularities, associated to zeroes of the polynomial  $P_{N+1}(p, b, \lambda)$ , from Eq.(3.74). Further, from the definitions (3.63) and (3.75) we obtain the following recurrence relation for the polynomial  $Q_k(p, b, \lambda)$ :

$$Q_{k+1} = Q_k \bar{\kappa}_{N-k} - Q_{k-1} \bar{\rho}_{N-k} \bar{\delta}_{N-k+1}, \quad Q_{-1} = 0, \quad Q_0 = 1, \quad (3.76)$$

with the use of which one can find  $Q_{N+1}$ . Here, the coefficients  $\bar{\kappa}_s$ ,  $\bar{\rho}_s$ , and  $\bar{\delta}_s$  differ from that of Eq.(3.71) by the factor  $(1 + \kappa_s^2)^{-1/2}$ . This factor does not change the recurrence relation (3.70). However, it makes possible to avoid accumulating of big numbers at intermediate computations. Indeed, from Eq.(3.71) for  $\kappa_s$  it follows that the leading coefficients of the polynomials  $Q_k$  would behave as  $k^{4k}$ , for example, for  $k = 4$  we would have  $4^{16}$ , if we would not made the above mentioned renormalization of the coefficients  $\rho_s$ ,  $\kappa_s$ , and  $\delta_s$ . The eigenvalue is found as an appropriate root of the polynomial  $Q_{N+1}(p, b, \lambda^{(y)})$ . Clearly, for big  $N$ , there is no way to represent in general the roots of  $Q_{N+1}$  analytically so one is forced to use numerical computations.

In the numerical computations, to pick up the appropriate eigenvalue  $\lambda_{mq}^{(y)}(p, b)$  among  $N + 1$  roots of the polynomial  $Q_{N+1}$  it is necessary to choose some starting value of  $\lambda$ . For example, one can put the starting value at the point  $p = b = 0$ , where  $\lambda_{mq}^{(y)}(0, 0) = (q + m)(q + m + 1)$ . The first step is to increase discretely  $p \rightarrow p + \Delta p$  and  $b \rightarrow b + \Delta b$  beginning from the starting point  $p = b = 0$ , at fixed values of  $m$  and  $q$ , and the second step is to find  $\lambda_{mq}^{(y)}(p + \Delta p, b + \Delta b)$  with the help of Eq.(3.74). Repeating these steps one can find  $\lambda_{mq}^{(y)}$  numerically as a function of  $p$  and  $b$  in some interval of interest.

Also, asymptotics of  $\lambda$  which will be studied in Sec. 3.6 are of much help here to choose the appropriate root. For example, for  $b = 0$  and  $N = 5$  we obtain numerically from the determinant of the tridiagonal matrix consisting of the coefficients defined by Eq.(3.71), with  $-\kappa_s$  on the main diagonal, and  $\rho_s$  and  $\delta_s$  on the upper and lower adjacent diagonals respectively, the

polynomial,

$$\det \hat{A} = 0.003\lambda^6 - 0.2\lambda^5 + (0.2p^2 + 5.5)\lambda^4 - (6.3p^2 + 56)\lambda^3 + (1.5p^4 + 66p^2 + 231)\lambda^2 - (19p^4 + 226p^2 + 277)\lambda + p^6 + 44p^4 + 186p^2. \quad (3.77)$$

Only one of its six roots has asymptotics,

$$\lambda_{|p \rightarrow 0} = 0.667p^2 - 0.0148p^4 + O(p^5), \quad (3.78)$$

which reproduces, to a good accuracy, the asymptotics (3.124). So, this is the desired root to be used in subsequent calculations. Also, observe the decrease of the numerical coefficients at higher degrees of  $\lambda$  which control the convergence.

Note that, at  $p \gg 1$ , the ACSF is concentrated around the points  $y = \pm 1$  so that expansion (3.68) converges slowly. In this case one uses another, more appropriate, expansions,

$$g_{mq}(p, b; y) = (1 - y^2)^{m/2} \exp[-p(1 + y)] \sum_{s=0}^{\infty} c_s (1 + y)^s, \quad (3.79)$$

$$g_{mq}(p, b; y) = (1 - y^2)^{m/2} \exp[-p(1 - y)] \sum_{s=0}^{\infty} c'_s (1 - y)^s. \quad (3.80)$$

Evidently, expansion (3.79) converges faster in the region  $[-1, 0]$  while the expansion (3.80) converges faster in the region  $[0, 1]$ . Here, the coefficients  $c_s$  of the expansion (3.79) obey the three-term recurrence sequence (3.70), with

$$\begin{aligned} \rho_s &= 2(s + 1)(s + m + 1), \\ \kappa_s &= s(s + 1) + (2s + m + 1)(2p + m) + b - \lambda, \\ \delta_s &= b + 2p(s + m). \end{aligned} \quad (3.81)$$

It is remarkable to note that expansions (3.79) and (3.80) converge at any  $y$ , and the corresponding chain fractions (3.63) converge at any  $p$  since

$$\frac{c_{s+1}}{c_s} \Big|_{s \rightarrow \infty} \sim \frac{2p}{s}, \quad \left| \frac{\rho_{s-1} \delta_s}{\kappa_{s-1} \kappa_s} \right|_{s \rightarrow \infty} \sim \frac{4p}{s}. \quad (3.82)$$

Similarly, the coefficients  $c'_s$  obey the same relation, with the replacement  $b \rightarrow -b$  in Eq.(3.81).

In practical calculations, one can use a combination of expansions (3.68) and (3.79). Namely, the procedure is: from expansion (3.68) one finds eigenvalues while the eigenfunctions are calculated from to Eq.(3.79). Of course, both solutions (3.79) and (3.80) should be sewed, for example, at the point  $y = 0$ , because the recurrence relations do not determine, in this case, a general normalization of the coefficients  $c_s$  and  $c'_s$ . Particularly, the sewing condition, which defines the normalization of  $c_s$  and  $c'_s$ , has the form

$$\sum_{s=0} c_s = \sum_{s=0} c'_s. \quad (3.83)$$

To derive the asymptotics of ACSF and its eigenvalues we can use an expansion in Laguerre polynomials,

$$g_{mq}(p, b; y) = (1 - y^2)^{m/2} \exp[-p(1 \pm y)] \sum_{s=0}^{\infty} c_s L_{s+m}^m(2p(1 \pm y)), \quad (3.84)$$

$$L_n^m(z) = \frac{e^z z^{-m}}{n!} \frac{d^n}{dz^n} (e^{-z} z^{n+m}). \quad (3.85)$$

The insertion of this expansion into Eq.(3.52) and the use of the differential equation for Laguerre polynomials,

$$z \frac{d^2}{dz^2} L_n^m(z) + (1 - z + m) \frac{d}{dz} L_n^m(z) + n L_n^m(z) = 0 \quad (3.86)$$

yield recurrence relation (3.70). For the case of positive sign in Eq.(3.84), we should put

$$\begin{aligned} \rho_s &= -(s + m + 1) \left( s + 1 + \frac{b}{2p} \right), \\ \kappa_s &= -(2s + m + 1) \left( s + m + 1 + \frac{b}{2p} - 2p \right) + (s + m)(m + 1) + b - \lambda, \\ \delta_s &= -s \left( s + m + \frac{b}{2p} \right). \end{aligned} \quad (3.87)$$

### 3.5.2 The radial Coloumb spheroidal function

The radial Coloumb spheroidal function (RCSF) obviously should be written in a form suitable to handle singularities at the points  $x = 1$  and  $x = \infty$ , namely,

$$f_{mk}(p, a; x) = (1 - x^2)^{m/2} \exp[-p(x - 1)]f(x). \quad (3.88)$$

So, the equation for  $f(x)$  takes the form

$$(x^2 - 1)f''(x) + [-2p(x^2 - 1) + 2(m + 1)x]f'(x) + [-\lambda + m(m + 1) + 2p\sigma x]f(x) = 0, \quad (3.89)$$

where we have denoted  $\sigma = \frac{a}{2p} - (m + 1)$ . In the case when the expansion

$$f(x) = \sum_{s=0} a_s u_s(x) \quad (3.90)$$

implies a three-terms recurrence relation, the eigenvalues  $\lambda_{mk}^{(x)}(p, a)$  can be found from the chain fraction equation,

$$F^{(x)}(p, a; \lambda) = 0. \quad (3.91)$$

Also, the expansion which is of practical use has been considered by Jaffe [10]. In this case, the expansion series (3.90) becomes

$$f(x) = (x + 1)^\sigma \sum_{s=0} a_s \chi^s, \quad (3.92)$$

where  $\chi = (x - 1)/(x + 1)$  is Jaffe's variable. By inserting (3.92) into the equation for the function  $f(x)$ , we get recurrence relation (3.61), where the coefficients are

$$\begin{aligned} \alpha_s &= (s + 1)(s + m + 1), \\ \beta_s &= 2s^2 + (2s + m + 1)(2p - \sigma) - a - m(m + 1) + \lambda = \\ &= 2s(s + 2p - \sigma) - (m + \sigma)(m + 1) - 2p\sigma + \lambda, \\ \gamma_s &= (s - 1 - \sigma)(s - m - 1 - \sigma). \end{aligned} \quad (3.93)$$

Also, for Jaffe series expansion, we have

$$\left| \frac{\alpha_{s-1}\gamma_s}{\beta_{s-1}\beta_s} \right|_{s \rightarrow \infty} = \frac{1}{4} \left( 1 - \frac{4p}{s} \right) + O\left( \frac{p^2}{s^2} \right), \quad (3.94)$$

i.e., the chain fraction converges at  $p > 0$ . One can see also that the Jaffe expansion converges at any  $x$ .

In addition, the function  $f(x)$  can be expanded in associated Laguerre polynomials,

$$f(x) = (x+1)^\sigma \sum_{s=0}^{\infty} a_s L_{s+m}^m(\bar{x}), \quad \bar{x} = 2p(x-1). \quad (3.95)$$

In this case, the recurrence relation is of three-terms form, and the coefficients are

$$\begin{aligned} \alpha_s &= -(s+m+1) \left[ \frac{a}{2p} - (s+1) \right] = (s+m+1)(s-m-\sigma), \\ \beta_s &= -(2s+m+1) \left[ \frac{a}{2p} - (s+m+1) \right] + \\ &+ 2p(2s+m+1) - (s+m)(m+1) - a + \lambda, \\ \gamma_s &= -s \left[ \frac{a}{2p} - (s+m) \right] = s(s-1-\sigma). \end{aligned} \quad (3.96)$$

As to numerical computation of the eigenvalues  $\lambda^{(x)}$ , expansions (3.92) and (3.95) are equivalent because the chain fraction depends, in fact, only on  $\beta_s$  and  $\alpha_s \gamma_{s+1}$ . Indeed, by comparing Eq.(3.93) and Eq.(3.96), one can easily see that in both cases  $\beta_s$  and  $\alpha_s \gamma_{s+1}$  are the same. Evidently, it then follows that the associated chain fractions are equivalent to each other.

However, we should note that Jaffe's recurrence sequence, in general, is more stable, while Laguerre expansion (3.95) is more suitable to find out the asymptotics of  $f_{mk}(p, a; x)$ .

Also, we note that the associated "radial" polynomials  $Q_{N+1}$ , the root  $\lambda^{(x)}(p, a)$  of which should be found, contain a much bigger number of terms, in comparison to the "angular" case. So, practically finding of radial eigenvalues is much harder than that of angular eigenvalues.

At equal charges of nuclei,  $Z_1 = Z_2$ , the equation for  $g$ , and the recurrence relation for  $g_k$ , are the same as they are in the particular case  $q = 0$  considered in Sec. 3.4. A general solution for  $g$  is then given by ACSF (3.38) and (3.39), with coefficients  $d_r^{mn}$  given by recurrence relation (3.40).

In the reminder of this Section we would like to note that, in general, solving the recurrence relations can be made equivalent to solving associated

ordinary differential equations by making the  $z$  transform. In many cases the  $z$  transform helps to solve recurrence relations. Namely, one defines the function

$$Z(z) = \sum_{s=0}^{\infty} \frac{a_s}{z^n} \quad (3.97)$$

associated to the coefficients  $a_s$  entering Eq.(3.61) viewed as a function of discrete variable  $s$ . For  $\alpha_s$ ,  $\beta_s$ , and  $\gamma_s$  given by Eq.(3.93) we obtain from Eq.(3.61)

$$\begin{aligned} z(z-1)^2 Z'' + \left[ (1-m)z^2 + 2(2p-\sigma-1)z + 2\sigma + m + 1 \right] Z' + \\ + \left[ (\sigma+m)(m+1) + 2p\sigma - \lambda + \frac{(m+\sigma)\sigma}{z} \right] Z = 0. \end{aligned} \quad (3.98)$$

For the coefficients  $c_s$ , we define

$$Y(z) = \sum_{s=0}^{\infty} \frac{c_s}{z^n}. \quad (3.99)$$

and for  $\rho_s$ ,  $\kappa_s$ , and  $\delta_s$  given by Eq.(3.81) we obtain from Eq.(3.70)

$$\begin{aligned} z(z-1)^2 Y'' + \left[ (\tau-2)z^2 + 2(2p-\tau+1)z + \tau \right] Y' + \\ + \left[ (m(m+1) - m\tau)z - 2p(m+1) + (\tau+m)(m+1) + b - \lambda - \frac{\tau}{z} \right] Y - \\ - m(m-\tau+1)c_0 z = 0, \end{aligned} \quad (3.100)$$

where we have denoted

$$\tau = \frac{b}{2p} + m + 1. \quad (3.101)$$

If one has solved these differential equations for  $Z(z)$  and  $Y(z)$ , then, by making the inverse  $z$  transform, one can find the expansion coefficients  $a_s$  and  $c_s$  (and thus the general solution of the problem).

### 3.6 Asymptotics of CSF and their eigenvalues

To analyze the exact solution, which is of rather complicated *nonclosed* form (infinite series) given in the previous Sections, it is much instructive to derive its asymptotics, which can be represented in a closed form. In this Section, we present the asymptotics at large ( $R \rightarrow \infty$ ) and small ( $R \rightarrow 0$ ) distances between the nuclei, with a particular attention paid to the ground state.



### 3.6.1 Asymptotics at $R \rightarrow \infty$

For increasing distances  $R$  between the nuclei, at fixed quantum numbers  $k$ ,  $q$ , and  $m$ , we have increasing values of the parameters  $p$ ,  $a$ , and  $b$ ,

$$p = (-2E)^{1/2}R/2 \rightarrow \infty, \quad a = (Z_2 + Z_1)R \rightarrow \infty, \quad b = (Z_2 - Z_1)R \rightarrow \pm\infty. \quad (3.102)$$

Let us introduce the notation

$$\alpha = \frac{a}{2p} = \frac{Z_2 + Z_1}{\sqrt{-2E}}, \quad \beta = \frac{b}{2p} = \frac{Z_2 - Z_1}{\sqrt{-2E}} \quad (3.103)$$

and assume that  $\alpha \sim 1$  and  $\beta \sim 1$ .

**ACSF at  $R \rightarrow \infty$ .**

Let us consider the asymptotic expansion of ACSF. In this case, the equation for the Whittaker function,  $M_{\kappa,\mu}(y)$ , builds ansatz around the poles  $y = \pm 1$ . Here, the solution is constructed in two overlapping intervals,  $\mathcal{D}_- = [-1, y_1]$  and  $\mathcal{D}_+ = [y_2, 1]$ , with  $y_2 < y_1$ . Then, the asymptotics of ACSF  $g_{mq}(p, 2p\beta; y)$  in the interval  $\mathcal{D}_-$  have the form

$$g_{mq}(p, 2p\beta; y) = \frac{d_-}{\Gamma(m+1)} \left[ \frac{2\Gamma\left(\kappa + \frac{1+m}{2}\right)}{\Gamma\left(\kappa + \frac{1-m}{2}\right)} \right]^{1/2} \times \\ \times \frac{M_{\kappa,m/2}\left(2p(1+y) + 2(\kappa + \beta) \ln \frac{1+y}{2}\right)}{\sqrt{1-y^2}} [1 + O(p^{-1})], \quad y \in \mathcal{D}_-. \quad (3.104)$$

while in the interval  $\mathcal{D}_+$  it is

$$g_{mq}(p, 2p\beta; y) = \frac{d_+}{\Gamma(m+1)} \left[ \frac{2\Gamma\left(\kappa' + \frac{1+m}{2}\right)}{\Gamma\left(\kappa' + \frac{1-m}{2}\right)} \right]^{1/2} \times \\ \times \frac{M_{\kappa',m/2}\left(2p(1-y) + 2(\kappa' + \beta) \ln \frac{1+y}{2}\right)}{\sqrt{1-y^2}} [1 + O(p^{-1})], \quad y \in \mathcal{D}_+. \quad (3.105)$$

Here, the coefficients  $d_-$  and  $d_+$  ( $d_-^2 + d_+^2 = 1$ ) are defined by the relations

$$d_- = \left| \frac{\sin \pi(2\kappa' - m - 1)}{\sin \pi(2\kappa - m - 1) + \sin \pi(2\kappa' - m - 1)} \right|^{1/2} \times \quad (3.106)$$

$$\begin{aligned}
& \times \text{sgn} \left[ \frac{-\cos \pi(\kappa - (m+1)/2)}{\sin \pi(\kappa' - (m+1)/2)} \right] \\
d_+ = & \left| \frac{\sin \pi(2\kappa - m - 1)}{\sin \pi(2\kappa - m - 1) + \sin \pi(2\kappa' - m - 1)} \right|^{1/2}. \quad (3.107)
\end{aligned}$$

**RCSF at  $R \rightarrow \infty$ .**

Now, let us consider the asymptotic expansion of RCSF. The replacements  $x \rightarrow -y$ ,  $p \rightarrow -p$ ,  $\alpha \rightarrow -\beta$  convert the radial equation around the point  $x = 1$  to the angular equation around the point  $y = -1$ . Thus, the corresponding asymptotics of RCSF are directly related to the above found asymptotics of ACSF.

The RCSF, normalized to the first order in  $p$ , has the form

$$\begin{aligned}
f_{mk}(p, 2p\alpha; x) = & \frac{1}{m!} \left[ \frac{2(k+m)!}{k!(x^2-1)} \right]^{1/2} \times \\
& \times M_{\kappa, m/2}(2p(x-1)) [1 + O(p^{-1})]. \quad (3.108)
\end{aligned}$$

Since the first index of Whittaker function in Eq.(3.108) is  $\kappa = k + (m+1)/2$ , the function can be expressed in terms of Laguerre polynomials.

**Energy at  $R \rightarrow \infty$ .**

In the limit  $R \rightarrow \infty$ , the Coloumb two-center problem is evidently reduced to two separate problems of Coloumb centers, with the charges  $Z_1$  and  $Z_2$ . Each of the atoms,  $eZ_1$  and  $eZ_2$ , is characterized by a set of parabolic quantum numbers,  $[n, n_1, n_2, m]$  and  $[n', n'_1, n'_2, m]$ , which are related to each other by the relations

$$n = n_1 + n_2 + m + 1, \quad n' = n'_1 + n'_2 + m + 1. \quad (3.109)$$

The number  $k$  of zeroes of RCSF coincides with the number  $n_1$ , for the angular functions of the left center,  $eZ_1$ , and with the number  $n'_1$ , for the angular functions of the right center,  $eZ_2$ .

A series expansion in inverse power of  $R$  can be obtained in the form

$$E_{[nn_1n_2m]}(Z_1, Z_2, R) = -\frac{Z_1^2}{2n^2} - \frac{Z_2}{R} + \frac{3Z_2n\Delta}{2R^2Z_1} - \frac{Z_2n^2}{2R^3Z_1^2}(6\Delta^2 - n^2 + 1) + \quad (3.110)$$

$$\begin{aligned}
& + \frac{Z_2 n^3}{16R^4 Z_1^4} [Z_1 \Delta (109\Delta^2 - 39n^2 - 9m^2 + 59) - Z_2 n (17n^2 - 3\Delta^2 - 9m^2 + 19)] + \\
& + \frac{\varepsilon_5}{R^5} + \frac{\varepsilon_6}{R^6} + O\left(\frac{1}{R^7}\right),
\end{aligned}$$

where  $\Delta = n_1 - n_2$ , and  $\varepsilon_{5,6}$  are defined via the expressions,

$$\varepsilon_5 = -\frac{n^3}{64Z_1^3} [n_Z (1065\Delta^4 - 594n^2\Delta^2 + 1230\Delta^2 - 234m^2\Delta^2 + 9m^4 + (3.111)$$

$$+ 33n^4 - 18n^2m^2 - 18m^2 + 105 - 138n^2) + 4n_Z^2 \Delta (21\Delta^2 - 111n^2 + 63m^2 - 189)].$$

$$\varepsilon_6 = -\frac{n^4}{64Z_1^4} [n_Z \Delta (-2727\Delta^4 + 2076n^2\Delta^2 - 5544\Delta^2 + 1056m^2\Delta^2 - 93m^4 - (3.112)$$

$$\begin{aligned}
& - 273n^4 + 78n^2m^2 + 450m^2 - 1533 + 1470n^2) + 2n_Z^2 (-207\Delta^4 + 1044n^2\Delta^2 + \\
& + 2436\Delta^2 - 576\Delta^2m^2 - 42n^2 + 371 - 162m^2 + 42m^2n^2 - 89n^4 + 15m^4) + \\
& + 2n_Z^3 \Delta (3\Delta^2 - 69n^2 - 117 - 33m^2)],
\end{aligned}$$

where  $n_Z = nZ_2/Z_1$ .

Eq.(3.110) gives the multipole expansion in the electrostatic energy of the interaction between the atom  $eZ_1$  and the far-distant charge  $Z_2$  (so called  $eZ_1$ -terms).

Note that expansion (3.110) can be obtained by ordinary perturbation techniques as well. Indeed, the degrees of  $Z_1$  display the orders of the multipole moment of the atom  $eZ_1$ .

The series of terms corresponding to the other atom,  $eZ_2$ , is obtained from Eq.(3.110) with the use of self-evident replacements,  $Z_1 \leftrightarrow Z_2$ ,  $n \rightarrow n'$ ,  $\Delta \rightarrow \Delta'$ , and  $n_2 \rightarrow n'_2$ .

Finally, the energy of the ground state  $1s\sigma_g$  of the molecular ion, for which  $Z_1 = Z_2 = 1$  (equal charges of nuclei), can be written, to a high accuracy, as

$$E_{1000}(1, 1, R) = -\frac{1}{2} - \frac{9}{4R^4} - \frac{15}{2R^6} - \frac{213}{4R^7} - \frac{7755}{64R^8} - \frac{1733}{2R^9} - \frac{86049}{16R^{10}} - O\left(\frac{1}{R^{11}}\right). \quad (3.113)$$

### 3.6.2 Asymptotics at $R \rightarrow 0$

#### Energy at $R \rightarrow 0$ .

In the case of positive total charge,  $Z = Z_1 + Z_2 > 0$ , and at  $R \rightarrow 0$ , we can use perturbative approach to  $Z_1 e Z_2$  problem, without using a separation of variables. Namely, the Hamiltonian of the system  $Z_1 e Z_2$  is represented as the sum

$$\hat{H} = \hat{H}^{UA} + \hat{W} = \frac{\hat{P}^2}{2m} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}. \quad (3.114)$$

The operator  $\hat{H}^{UA}$  is usually chosen as the Hamilton operator of the so called *united atom*,

$$\hat{H}^{UA} = \frac{\hat{P}^2}{2m} - \frac{Z}{r_c}, \quad (3.115)$$

which is placed on the  $z$ -axis at the point  $z = z_0$ ,

$$z_0 = \left( -\frac{1}{2} + \frac{Z_2}{Z} \right) R = \left( \frac{1}{2} + \frac{Z_1}{Z} \right) R. \quad (3.116)$$

The point  $(0, 0, z_0)$  is called *center of charges* due to the fact that it lies at the distances

$$R_1 = \frac{Z_2}{Z} R \quad \text{and} \quad R_2 = \frac{Z_1}{Z} R, \quad (3.117)$$

from the left and right atoms, respectively.

We choose a spherical coordinate system,  $(r_c, \vartheta_c, \varphi)$ , with the origin at point  $(0, 0, z_0)$ , and the angle  $\vartheta_c$  measured from  $z$ -axis. Then, the eigenstates  $\psi_{Nlm}^{UA}$  of the operator  $\hat{H}^{UA}$  are

$$\psi_{Nlm}^{UA}(\vec{r}_c) = R_{Nl}(r_c) Y_l^m(\vartheta_c, \varphi), \quad (3.118)$$

while the eigenvalues are given by

$$E_{Nlm}^{UA} = -\frac{Z^2}{2N^2}. \quad (3.119)$$

The matrix  $W_{Nlm}^{N'l'm'}$  of the perturbation operator  $\hat{W}$  is diagonal on the functions  $\psi_{Nlm}^{UA}(\vec{r}_c)$  of the atom if  $z_0$  is defined by Eq.(3.116). Below, the first two terms of the expansion of energy in powers of  $R$  are given,

$$E_{Nlm}(Z_1, Z_2, R) =$$

$$-\frac{Z^2}{2N^2} - \frac{2Z_1Z_2[l(l+1) - 3m^2]}{N^3l(l+1)(2l-1)(2l+1)(2l+3)}(ZR)^2 + O((ZR)^3). \quad (3.120)$$

For the ground state of the  $Z_1eZ_1$  system, with equal values of the charges, one can find the following expression for the energy, up to the second order of perturbation:

$$E_{000}^{(2)}(Z_1, Z_1, R) = Z^2 \left[ -\frac{1}{2} + \frac{1}{6}(ZR)^2 - \frac{1}{6}(ZR)^3 + \frac{43}{2160}(ZR)^4 - \frac{1}{36}(ZR)^5 \ln ZR + \dots \right]. \quad (3.121)$$

**CSF at  $R \rightarrow 0$ .**

For fixed quantum numbers we have, at  $R \rightarrow 0$ ,

$$p = (-2E)^{1/2}R/2 \rightarrow 0, \quad a = (Z_2 + Z_1)R \rightarrow 0, \quad b = (Z_2 - Z_1)R \rightarrow 0. \quad (3.122)$$

Let us denote

$$\alpha = \frac{a}{2p} = \frac{Z_2 + Z_1}{\sqrt{-2E}} = \sigma + m + 1, \quad \beta = \frac{b}{2p} = \frac{Z_2 - Z_1}{\sqrt{-2E}}. \quad (3.123)$$

In this notation, the energy is  $E = -Z^2/(2\alpha)^2$ . Let us consider asymptotics of CSF of the ground state of the molecular ion.

**ACSF at  $R \rightarrow 0$ .**

The power series expansion of ACSF  $g_{00}(p, 2p\beta; y)$  in small parameter  $p$  can be obtained by expanding it in the Legendre polynomials. For the eigenvalue  $\lambda_{00}^{(y)}(p, 2p\beta)$ , we then get

$$\lambda_{00}^{(y)}(p, 2p\beta) = (1 - \beta^2) \left[ \frac{2}{3}p^2 - \frac{2}{135}p^4(1 + 11\beta^2) + O(p^6) \right]. \quad (3.124)$$

**RCSF at  $R \rightarrow 0$ .**

To expand RCSF  $f_{00}(p, 2p(1 + \sigma); x)$ , at  $p \rightarrow 0$ ,  $\sigma = O(p^2)$ , we use Jaffe's expansion,

$$f_{00}(p, 2p(1 + \sigma); x) = \exp(-px)(1 + x)^\sigma \sum_{s=0}^{\infty} a_s \chi^s, \quad \chi = \frac{x-1}{x+1}, \quad (3.125)$$

where  $a_s$ 's obey three-term recurrence relation with the coefficients (3.93).

For the eigenvalue  $\lambda_{00}^{(x)}(p, 2p(1 + \sigma))$ , we get

$$\lambda_{00}^{(x)}(p, 2p(1 + \sigma)) = \sigma(1 + 2p) + \sigma^2(1 + 4p \ln 4p\gamma) + o(p^5). \quad (3.126)$$

RCSF of the ground state of the molecular ion,  $Z_1 = Z_2 = 1$ , can be presented as

$$f_{00}(p, 2p(1 + \sigma); x) = \exp(-px)(1 + x)^\sigma [1 + \sigma^2 \text{Li}_2(\chi) + o(p^4)], \quad (3.127)$$

where  $\chi = (x-1)/(x+1)$  is Jaffe's variable and  $\text{Li}_2(\chi)$  is dilogarithm function,

$$\text{Li}_2(\chi) = \sum_{n=1}^{\infty} \frac{\chi^n}{n^2} = - \int_0^{\chi} \ln(1 - \xi) \frac{d\xi}{\xi}. \quad (3.128)$$

The ground state energy is defined as a function of three parameters,  $Z_1$ ,  $Z_2$ , and  $R$ ,

$$\lambda_{00}^{(y)}(p, 2p\beta) = \lambda_{00}^{(x)}(p, 2p(1 + \sigma)) \quad (3.129)$$

Combining Eqs.(3.124), (3.126) and (3.129), we get series expansion for the ground state energy of the  $Z_1 e Z_2$  system in the form

$$\begin{aligned} E_{000}(Z_1, Z_2, R) = & \\ & -\frac{1}{2}Z^2 + \frac{2}{3}Z_1 Z_2 (ZR)^2 - \frac{2}{3}Z_1 Z_2 (ZR)^3 + \frac{2}{5}Z_1 Z_2 \left(1 - \frac{64Z_1 Z_2}{27Z^2}\right) (ZR)^4 - \\ & - \frac{8}{45}Z_1 Z_2 \left[\frac{5Z_1 Z_2}{Z^2} \ln(2RZ\gamma) + 1 - \frac{199Z_1 Z_2}{12Z^2}\right] (ZR)^5 + o((ZR)^5). \end{aligned} \quad (3.130)$$

Comparing Eqs.(3.121) and (3.130) we see that the terms proportional to  $(ZR)^2$  and  $(ZR)^3$  coincide. The next order corrections makes a difference; Eq.(3.121) obtained by the second-order perturbation is of less accuracy. A practically achieved accuracy of the first-order perturbation (3.120) and of Eq.(3.130) is the same; at  $ZR < 0.1$ , the discrepancy is not bigger than 1%, and becomes sharply smaller with the increase of the parameter  $ZR$ .

### 3.6.3 Quasiclassical asymptotics

At  $R \rightarrow \infty$ , for  $eZ_1$  solutions we have

$$\lambda_{mk}^{(x)}(p, 2p\alpha) = -2p(2\kappa - \alpha) - \kappa(2\kappa - \alpha - m) + \quad (3.131)$$

$$\begin{aligned}
& + \frac{\kappa}{2p}(2\kappa^2 - 3\kappa\alpha + \alpha^2 - m^2) + o(p^{-2}), \\
\lambda_{mq}^{(y)}(p, 2p\beta) &= 2p(2\chi + \beta) - \chi(2\chi + 2\beta - m) - \\
& - \frac{\chi}{2p}(2\chi^2 + 3\chi\beta + \beta^2 - m^2) + o(p^{-2}).
\end{aligned} \tag{3.132}$$

From the equality  $\lambda_{mk}^{(x)} = \lambda_{mq}^{(y)}$ , we get the expansion for  $E_j(R)$  which coincides with the asymptotics (3.110), up to terms of the order of  $R^{-2}$ .

In the limit  $R \rightarrow 0$ , the following expansions are justified,

$$\lambda_{mk}^{(x)} = \left[ \frac{a}{2p} - (k + 1/2) \right]^2 + O(p^2), \tag{3.133}$$

$$\lambda_{mq}^{(y)} = (l + 1/2)^2 + \frac{p^2}{2} - \frac{b^2}{8(l + 1/2)^2} + O(p^4). \tag{3.134}$$

and we get, by using the equation  $\lambda^{(x)} = \lambda^{(y)}$ ,

$$E_{Nlm}(R) = -\frac{1}{2} \left( \frac{Z_1 + Z_2}{N} \right)^2 - R^2 \frac{Z_1 Z_2 (Z_1 + Z_2)^2}{4N^3(l + 1/2)^5} [(l + 1/2)^2 - 3m^2]. \tag{3.135}$$

Expression (3.135) for the energy coincides with the asymptotics (3.120), up to  $O(l^{-2})$ . Clearly, an accuracy of the quasiclassical Eqs.(3.131)-(3.135) becomes higher for a greater number of zeroes of the solutions,  $k$  and  $q$ . However, even for the ground state,  $k = q = m = 0$ , these equations give a good approximation for the energy in both limiting cases,  $R \rightarrow 0$  and  $R \rightarrow \infty$ . Also, we note that corresponding numerical calculations showed that for the intermediate values of  $R$  the terms  $E_j(R)$  can be determined within the quasiclassical approach with accuracy of about 5%, or more [11].

## 4 Scaling method and binding energy of three-body Santilli-Shillady isochemical model $\hat{H}_2$

To find the ground state energies of  $H_2^+$  and  $\hat{H}_2$ , we use computations of the  $1s\sigma$  terms of  $H_2^+$  ion and of  $\hat{H}_2$  based on the above presented exact CSF solution by solving the corresponding equations  $\lambda^{(x)} = \lambda^{(y)}$ .

The angular and radial eigenvalues  $\lambda$  are found as solutions of the equations containing infinite chain fractions presented in previous Sections which should be interrupted and then solved numerically, to a required accuracy.

Our primary interest is the study of Santilli-Shillady model  $\hat{H}_2$  system. However, we present the results for  $H_2^+$  ion as well to check our calculations and to use them in the scaling method described below.

Also, the reader should keep in mind that we are primarily interested in ascertaining whether there exist a non-zero value of  $R$  for which a fully stable and point-like isoelectronium permits an exact representation of the binding energy of  $H_2$  molecule.

It should be noted that the ground state electronic energy is obtained as a function of the parameter  $R$  due to Eq.(3.58). By adding to it the internuclear potential energy  $1/R$ , we obtain the *total* ground state energy of the system, so that at some value  $R = R_{min}$ , the total energy  $E$  necessarily has a *minimum*, if the system is *stable*. This is the way to determine uniquely the internuclear distance under an exact representation of the total energy  $E$ .

To have an independent check of the result for the total ground state energy of  $\hat{H}_2$  (with the stable and point-like isoelectronium) obtaining from the exact solution, we develop a scaling method based on the original Schrödinger equation for  $H_2^+$  ion like system. Namely, it appears that one is able to calculate the ground state energy as a function of  $R$  for *any*  $H_2^+$  ion like system with equal charges of nuclei,  $Z_1 = Z_2$ , provided that one knows the ground state energy as a function of  $R$  for the  $H_2^+$  ion itself. It should be pointed out that the scaling method does not depend on the obtained solution because it reflects, in fact, the scaling properties of the Schrödinger equation itself.

In addition, we use below Ritz's variational approach to  $H_2^+$  like systems to find out the *approximate* value of the ground state energy of  $\hat{H}_2$ , as well as to check the result provided by the exact solution, and to demonstrate the accuracy of the variational approximation.

Our general remark is that in both approaches, the exact solution and Ritz's variational solution, we use Born-Oppenheimer approximation (fixed nuclei). Clearly, taking into account the first order correction, i.e., zero harmonic oscillations of the nuclei in  $H_2$  around their equilibrium positions, we achieve greater accuracy.

But we still have a significant inaccuracy in the value of dissociation energy due to the fact that  $H_2$  system has the lightest possible nuclei (two



single protons).

To estimate this inaccuracy, one can invoke Morse's potential customarily used for diatomic molecules. In particular, the analysis for  $H_2$  molecule shows that the ground state energy of harmonic oscillations of the nuclei receives 1.4% correction due to the first anharmonic term.

#### 4.1 Exact representation of binding energies of $H_2^+$ ion and three-body $\hat{H}_2$ system

The CSF based computations for  $H_2^+$  ion were presented, for example, by Teller [12], Bates *et al.* [13], and Wind [14], and we do not repeat this study here for brevity, while we shall just describe the procedure and present our final numerical results in Appendix, Table 2.

In particular, Teller presented a plot of the resulting function  $E_{1s\sigma}(R)$  which provides a good accuracy, and Wind used the exact solution to present a table of energy values in seven decimal places for distance values of  $R$  up to 20 a.u. in steps of 0.05 a.u. However, these results cannot be used directly in our case since the repulsive potential between the nuclei,  $1/R$ , has not been accounted for, and, as the main reason, we have the isoelectronium instead of one single electron.

In the Appendix, we present the results obtained from the CSF based recurrence relations by numerical calculations for ordinary  $H_2^+$  ion and for  $\hat{H}_2$  system, at  $M = 2m_e$ . These results are presented in Tables 2 and 4. Tables 3 and 5 have been derived from Tables 2 and 4, respectively, by simple adding internuclear potential energy  $1/R$ , to obtain the *total* energy of the system.

In Table 2, we present the  $1s\sigma_g$  electronic term of  $H_2^+$ . In Table 3, we present the total energy of  $H_2^+$ . In Table 4, we present the  $1s\sigma_g$  term of  $\hat{H}_2$ , at the mass  $M = 2m_e$ . In Table 5, we present the total energy of  $\hat{H}_2$ , at the mass  $M = 2m_e$ . Also, in Table 6, we present the total *minimal* energies of  $\hat{H}_2$  and *optimal* distances  $R$ , for various values of the isoelectronium mass parameter,  $M = \eta m_e$ . All the data of these Tables are purely theoretical and, additionally, we plot them in Figures 1–8, for the reader convenience. Figures 6 and 8 give more detailed view on the interval  $0.26 < \eta < 0.34$ .

The analysis of the data in Tables 2–5 is simple. Namely, one should identify the *minimal* value of the energy in each Table. One can use Figures 1–4

for visual identification of the minima, and then turn to the corresponding Tables 2–5, to reach a higher numerical accuracy.

Let us consider, as an example, Table 2. One can see that the energy minimum for  $H_2^+$  is

$$E_{1s\sigma} = -2.0 \text{ a.u. at } R = 0 \text{ a.u.} \quad (4.1)$$

Note that  $E_{1s\sigma}$  is the electronic energy, i.e. the internuclear repulsion has not been taken into account here. Our remark is that this energy value corresponds to  $He^+$  ion due to the fact that two  $H_2^+$  nuclei are superimposed and form  $He$  nucleus at  $R = 0$ .

Let us consider now Table 3. In this Table, one can find the line  $|2.0 | - 0.602634|$  corresponding to visual minimal value of the energy. To identify a *more precise* value of the minimal energy, one should use the *interpolation* of the data. This gives us the minimum of the total energy of  $H_2^+$ ,

$$E = -0.6026346 \text{ a.u. at } R = 1.9971579 \text{ a.u.} \quad (4.2)$$

This theoretical value represents rather accurately the known experimental value  $E_{\text{exper}}[H_2^+] = -0.6017 \text{ a.u.}$  [15] for  $H_2^+$  ion, thus establishing the validity of our CSF based calculations. For completeness, we note that the experimental dissociation energy of  $H_2^+$  ion is  $D_{\text{exper}}[H_2^+] \simeq 0.0974 \text{ a.u.} = 2.65 \text{ eV}$ , and the internuclear distance  $R_{\text{exper}}[H_2^+] \simeq 2.00 \text{ a.u.} = 1.0584 \text{ \AA}$ .

Let us now consider Table 4. One can see that the energy minimum for  $\hat{H}_2$ , at  $M = 2m_e$ , is

$$E_{1s\sigma} = -16.0 \text{ a.u. at } R = 0 \text{ a.u.} \quad (4.3)$$

Note that  $E_{1s\sigma}$  only yields the isoelectronium's energy, i.e. the internuclear repulsion has not been taken into account here. Our remark is that this energy value corresponds to the  $He$  atom, where the two electrons form a stable point-like isoelectronium of mass  $M = 2m_e$ .

Let us consider now Table 5 which is of striking interest for our study. In this Table, one can find the line  $|0.250 | - 7.61428940411169996|$  corresponding to the visual minimal value of the energy. To identify a more precise value of the minimal energy, one should use the interpolation of the data given in this Table. This gives us the minimum of the total energy of  $\hat{H}_2$ ,

$$E = -7.617041 \text{ a.u. at } R = 0.258399 \text{ a.u.} \quad (4.4)$$

This theoretical value is in quite good agreement with the preceding theoretical result by Santilli and Shillady obtained via structurally different variational numerical method,  $E_{var} = -7.61509174$  at  $R_{var} = 0.2592$  (see third column of Table 1 in Ref.[1]). It is quite naturally to observe that this variational energy is a bit higher (by 0.002 a.u.) than the above one obtained from the exact solution (as it is expected to be for any variational solution).

However, this exact theoretical value (4.4) does not meet the experimental value  $E_{exper}[H_2] = -1.17$  a.u. [15] known for  $H_2$  molecule. Indeed, adopted approximation that the isoelectronium is point-like, stable, and has mass  $M = 2m_e$  leads us to the theoretical value (4.4) while the known experimental value,  $E_{exper}[H_2] = -1.17$  a.u., differs much from it.

Essentially the same conclusion is due to numerical program SASLOBE by Santilli and Shillady [1], where Gaussian screened Coloumb potential interaction between the electrons, rather than the stable point-like isoelectronium approximation, has been used to achieve final precise fit of  $E = -1.174474$  a.u., with the obtained bond length  $R = 1.4011$  a.u., at the isoelectronium correlation length  $r_c = 0.01125$  a.u. (see Table 1 in Ref.[1]). We discuss on this issue in Sec. 5.

Our remark is that, due to Table 5, the experimental value  $E = -1.17$  a.u. is fitted by the distance  $R = 0.072370$  a.u. However, this energy value is not minimal and thus can not be ascribed reasonable physical treatment in Table 5.

Our conclusion from the above analysis is that we have two main possibilities to overcome this sharp discrepancy between our theoretical and the experimental binding energy values which has place at  $M = 2m_e$ :

1. Consider unstable isoelectronium, i.e. the four-body Santilli-Shillady model of  $H_2$  molecule;
2. Treat the mass  $M$  of isoelectronium as a free parameter, instead of fixing it to  $M = 2m_e$ , assuming thus some defect of mass discussed in Introduction,

in order to fit the experimental data on  $H_2$  molecule.

The first possibility will be considered in a subsequent paper because it needs in application of different technique, while the second possibility can be studied within the *three-body* Santilli-Shillady model under consideration to which we turn below.

In the next Section, we develop simple formalism allowing one to deal with the mass and charge of isoelectronium viewed as free parameters, and arrive at the conclusion (see Table 6) that the restricted three-body Santilli-Shillady model of  $H_2$  molecule is capable to fit the experimental binding energy, with the total mass of isoelectronium equal to  $M = 0.308381m_e$ , although with the internuclear distance about 19.6% bigger than the experimental value.

## 4.2 The scaling method

In order to relate the characteristics of  $H_2^+$  ion like system to that of thoroughly studied  $H_2^+$  ion, we develop scaling method based on the Schrödinger equation. The neutral  $\hat{H}_2$  system with stable point-like isoelectronium is an example of  $H_2^+$  ion like system in which we are particularly interested here. Below, we develop scaling method for the case of arbitrary mass and charge of the particle.

Let us write the Schrödinger equation for a particle of the rescaled charge

$$e \rightarrow -\zeta e, \quad (4.5)$$

(we turn here from  $e = -1$  to  $-e = 1$  representation), and the rescaled mass

$$m_e \rightarrow \eta m_e, \quad (4.6)$$

with *equal* charges of nuclei,  $+eZ_1 = +eZ_2 = +eZ$ ,

$$\left[ -\frac{\hbar^2}{2\eta m_e} \nabla_r^2 - \frac{\zeta Z e^2}{r_a} - \frac{\zeta Z e^2}{r_b} + \frac{Z^2 e^2}{R_{ab}} \right] \psi = E \psi. \quad (4.7)$$

where  $\eta$  and  $\zeta$  are scaling parameters, and  $R_{ab}$  is distance between the nuclei. The condition  $Z_1 = Z_2$  is an essential point to stress here because owing to which we can successfully develop the scaling method. We introduce the unit of length,

$$r_0 = \frac{1}{\eta \zeta Z} r_B \equiv \frac{1}{\eta \zeta Z} \frac{\hbar^2}{m_e e^2}, \quad (4.8)$$

where  $r_B$  is Bohr's radius. Dividing Eq.(4.7) by  $\zeta Z e^2$ , and multiplying it by  $r_0$ , we get

$$\left[ -\frac{\hbar^2}{\eta \zeta Z m_e e^2} r_0 \frac{1}{2} \nabla_r^2 - r_0 \frac{1}{r_a} - r_0 \frac{1}{r_b} + r_0 \left( \frac{Z}{\zeta} \right) \frac{1}{R_{ab}} \right] \psi = \frac{r_0 E}{\zeta Z e^2} \psi. \quad (4.9)$$

We introduce dimensionless entities  $\rho = r/r_0$ ,  $\rho_a = r_a/r_0$ ,  $\rho_b = r_b/r_0$ , and  $\mathcal{R} = R_{ab}/r_0$ . Then, Laplacian in Eq.(4.9) becomes  $r_0^2 \nabla_r^2 = \nabla_\rho^2$ . Further, introducing unit of energy,

$$E_0 = \frac{\eta m_e \zeta^2 Z^2 e^4}{\hbar^2} \equiv \eta \zeta^2 Z^2 \frac{m_e e^4}{\hbar^2}, \quad (4.10)$$

we have dimensionless energy  $\varepsilon = E/E_0$  so that Eq.(4.9) can be rewritten as

$$\left[ -\frac{1}{2} \nabla_\rho^2 - \frac{1}{\rho_a} - \frac{1}{\rho_b} + \frac{1}{(\zeta/Z)\mathcal{R}} \right] \psi = \varepsilon \psi. \quad (4.11)$$

Note that, at  $\eta = 1$ ,  $\zeta = 1$ , and  $Z = 1$ , the constants  $r_0(\eta, \zeta, Z)$  and  $E_0(\eta, \zeta, Z)$  reproduce *ordinary* atomic units,

$$r_0(1, 1, 1) = r_B = \frac{\hbar^2}{m_e e^2}, \quad E_0(1, 1, 1) = 2E_B = \frac{m_e e^4}{\hbar^2}, \quad (4.12)$$

and we recover the case of  $H_2^+$  ion. On the other hand, in terms of dimensionless entities the original Schrödinger equation for  $H_2^+$  ion is

$$\left[ -\frac{1}{2} \nabla_\rho^2 - \frac{1}{\rho_a} - \frac{1}{\rho_b} + \frac{1}{R} \right] \psi_0 = \varepsilon(R) \psi_0, \quad (4.13)$$

where  $R = R_{ab}/r_B$ . Comparison of Eq.(4.11) and Eq.(4.13) shows that by putting  $R = (\zeta/Z)\mathcal{R}$  in Eq.(4.11), we obtain the equation,

$$\left[ -\frac{1}{2} \nabla_\rho^2 - \frac{1}{\rho_a} - \frac{1}{\rho_b} + \frac{1}{R} \right] \psi = \varepsilon(R) \psi, \quad (4.14)$$

which identically coincides with the original Eq.(4.13). The difference is that Eq.(4.14) is treated in terms of the *rescaled* units,  $r_0(\eta, \zeta, Z)$  and  $E_0(\eta, \zeta, Z)$ , instead of the ordinary Bohr's units,  $r_B$  and  $E_B$ . As the result, we have one and the same form of Schrödinger equation for any  $H_2^+$  like system characterized by equal charges of nuclei. This makes a general ground to calculate some characteristic entity of any  $H_2^+$  like system when one knows its value for  $H_2^+$  ion.

Particularly, one can easily derive  $R_{ab}$  and  $E$  for the system with arbitrary parameters  $\eta$ ,  $\zeta$ , and  $Z$  from their values,  $R_{ab}[H_2^+]$  and  $E[H_2^+] = 2E_B - \varepsilon(R)$ ,

obtained for  $H_2^+$  ion (for which  $\eta = 1$ ,  $\zeta = 1$ , and  $Z = 1$ ). Indeed, since for arbitrary  $\eta$ ,  $\zeta$ , and  $Z$

$$R = \frac{\zeta}{Z} \mathcal{R} = \frac{\zeta}{Z} \frac{R_{ab}}{r_0} = \frac{\zeta}{Z} \frac{R_{ab}}{r_B} \eta \zeta Z, \quad (4.15)$$

we can establish the following relationship between the distances corresponding to arbitrary  $Z\zeta Z$  system and  $H_2^+$  ion,

$$R_{ab} = \frac{R[H_2^+]}{\eta \zeta^2}. \quad (4.16)$$

It is remarkable to note that the dependence on  $Z$  disappeared in Eq.(4.16). In the case of isoelectronium of mass  $M = 2m_e$  and charge  $-2e$ , we have  $\eta = 2$  and  $\zeta = 2$ , so that

$$R_{ab} = \frac{R[H_2^+]}{8}. \quad (4.17)$$

Also, the energy  $E(R)$  of  $Z\zeta Z$  system and energy  $\varepsilon(R)$  of  $H_2^+$  ion are related to each other according to the equation,

$$E(R) = \eta \zeta^2 Z^2 \left( \frac{m_e e^4}{\hbar^2} \right) \varepsilon(R). \quad (4.18)$$

#### 4.2.1 The case $M = 2m_e$

So, in the case of isoelectronium of mass  $M = 2m_e$  and charge  $-2e$ , we get

$$E(R_{ab}) = 8\varepsilon(R). \quad (4.19)$$

Note however that the factor  $\zeta/Z = 2$  arised due to  $R = (\zeta/Z)\mathcal{R}$  is hidden here so that in order to calculate the values of  $E(R_{ab})$  and  $R_{ab}$  from  $\varepsilon(R)$  and  $R$  respectively one should multiply  $\varepsilon$  by 8 and  $R$  by 1/4.

As the result, in accordance with the scaling method the points can be calculated due to the following rule:

$$(R, E) \rightarrow (R, E + 1/R) \rightarrow (R/4, 8E) \rightarrow (R/4, 8E + 4/R), \quad (4.20)$$

for Tables  $2 \rightarrow 3 \rightarrow 4 \rightarrow 5$ . One can easily check numerically that these properties indeed hold true for the presented Tables. Thus, the scaling method

can be used *instead of* the independent numerical calculations for  $\hat{H}_2$  system if one has the data for  $H_2^+$  ion.

It is highly important to note here that the energy *minimum* in Table 3 is *not* rescaled to the energy *minimum* in Table 5 due to the absence of energy scaling between these Tables; see Eq.(4.20), from which one can observe that  $(8E + 4/R)$  can not be expressed as  $n(E + 1/R)$ , where  $n$  is a number. So one needs to identify minimum in Table 5 independently (after calculating all the points), rather than direct rescale the minimum from Table 3 to try to get minimum for Table 5.

#### 4.2.2 The case $M = \eta m_e$

For a more general case of isoelectronium mass,  $M = \eta m_e$ , and charge  $-2e$ , we should keep the following sequence of calculations:

$$(R, E) \rightarrow (R, E + 1/R) \rightarrow (\frac{R}{2\eta}, 4\eta E) \rightarrow (\frac{R}{2\eta}, 4\eta E + \frac{2\eta}{R}). \quad (4.21)$$

starting from Table 2 to obtain, at the last step, the table of values (similar to Table 5) from which we should extract a *minimal* value of the energy and the corresponding *optimal* distance, at *each given* value of mass  $\eta$ . The result of the analysis of a big number of such tables is collected in Table 6, where the interval  $0.26 < \eta < 0.34$  appears to be of interest;  $M = \eta$ , in atomic units. Plots of the data of Table 6 are presented in Figures 5 and 7 (Figures 6 and 8 give more detailed view on the interval of interest) show that

$$E_{min}(M) \simeq -3.808M, \quad R_{opt}(M) \simeq \frac{0.517}{M}, \quad (4.22)$$

to a good accuracy. Note that  $E_{min}(M)$  unboundedly decreases with the increase of  $M$  (there is no local minimum), so we can use a fit, instead of the minimization in respect with  $M$ . From this Table, we obtain the following final fit of the binding energy for the restricted *three-body* Santilli-Shillady model of  $H_2$  molecule:

$$M = 0.308381m_e, \quad E = -1.174475 \text{ a.u.}, \quad R = 1.675828 \text{ a.u.}, \quad (4.23)$$

where the mass parameter  $M$  of the isoelectronium has been varied in order to meet the experimental energy  $E_{exper}[H_2] = -1.174474 \text{ a.u.} = -31.9598 \text{ eV}$ .

Using this value of mass,  $M = 0.308381m_e$ , we computed the total energy as a function of the internuclear distance  $R$ , and depicted it in Figure 9 to illustrate that  $R = 1.675828$  a.u. indeed corresponds to a *minimal* value of the energy. Note that the predicted optimal distance  $R = 1.675828$  a.u. =  $0.886810\text{\AA}$  appears to be about 19.6% bigger than the conventional experimental value  $R_{\text{exper}}[H_2] = 1.4011$  a.u. =  $0.742\text{\AA}$ .

This rather big (19.6%) discrepancy can not be ascribed to the Born-Oppenheimer approximation used in this paper since it gives relatively small uncertainty in the energy value, even in the case of  $H_2$  molecule. We stress here that in the Born-Oppenheimer approximation, the three-body problem (the Schrödinger equation) can be given exact solution owing to separation of the electronic and nuclear degrees of freedom while the full three-body problem (accounting for the wave functions of the nuclei, etc.) can not be solved exactly.

In a strict consideration, we should calculate the *dissociation* energy of  $H_2$  molecule,  $D = 2E_0 - E - E^{\text{nucl}}$ , to make comparison to the experimental value,  $D_{\text{exper}}[H_2] \simeq 0.164$  a.u. = 4.45 eV [15]. Here,  $E_0 = -0.5$  a.u. = -13.606 eV is the ground state energy of separate  $H$ -atom and  $E^{\text{nucl}}$  is the energy of zero mode harmonic oscillations of the nuclei, with the experimental value  $E_{\text{exper}}^{\text{nucl}}[H_2] \simeq 0.01$  a.u. = 0.27 eV [15]. One can see that the zero mode energy  $E^{\text{nucl}}$  (which is taken to be  $E^{\text{nucl}} = 0$ , in the Born-Oppenheimer approximation) is estimated to be less than 1% of the predicted  $E$ . The leading anharmonic correction to the harmonic oscillation energy is estimated to be 1.4% of  $E^{\text{nucl}}$ , i.e. it is of the order of 0.00014 a.u. = 0.004 eV, in the case of  $H_2$  molecule. So, in total the Born-Oppenheimer approximation makes only up to 1% uncertainty, which is obviously insufficient to treat the predicted  $R = 1.675828$  a.u. as an acceptable value, from the experimental point of view.

Note that, at the given  $M$ , we can not "fix"  $R$  to be equal to the desired experimental value  $R_{\text{exper}} = 1.4011$  a.u. unless we shift  $E$  to some *nonminimal* value, which is, as such, meaningless. Conversely, if we would fit experimental  $R_{\text{exper}}$  by varying  $M$ , we were obtain  $E_{\text{min}}$  between -1.52 a.u. and -1.33 a.u. (see Table 6), which is much deviated from the experimental  $E_{\text{exper}}$ . In other words, the relation between  $E$  and  $R$ , governed by the Schrödinger equation, is such that at some value of  $R$  there is a minimum of  $E$  so that  $R$  is not some kind of free parameter here since the system tends to minimize its own energy. In accordance to the exact solution of the model,



our single free parameter,  $M$ , can not provide us with the exact fit of *both* the experimental values,  $E_{exper}$  and  $R_{exper}$ .

Thus, we arrive at the conclusion that the three-body Santilli-Shillady model of  $H_2$  molecule yields the result (4.23), which indicates that the assumption of stable point-like isoelectronium builds a crude *approximation* to the general (four-body) Santilli-Shillady model. This means that we are forced to possess that the isoelectronium is *not stable point-like* quasi-particle, to meet the experimental data on  $H_2$  molecule.

### 4.3 Variational solution

In studying  $H_2^+$  ion like systems, one can use Ritz variational approach to obtain the value of the ground state energy as well. This approach assumes analytical calculations, which are easier than that used in finding the above exact solution but they give *approximate* value of the energy. It is helpful in making simplified analysis of the system. This can be made for the general case of isoelectronium total mass, which eventually undergoes some "defect" while its "bare" total mass is assumed to be  $M = 2m_e$ . Ritz variational solution of the  $H_2^+$  like problem yields, of course, similar result for the energy of  $\hat{H}_2$ . Below, we present shortly results of our calculations. However, we stress that the variational solution is given here just to make some support to the exact solution, and to see the typical order of the variational approximation.

Using hydrogen ground state wave function and one-parameter Ritz variation, we obtain the following expression for the energy of  $H_2^+$  like system:

$$E(\rho) = -\frac{1}{2} \frac{e^2}{a_0} + \frac{e^2}{a_0} \frac{1}{\rho} \frac{(1+\rho)e^{-2\rho} + (1 - \frac{2}{3}\rho^2)e^{-\rho}}{1 + (1 + \rho + \frac{1}{3}\rho^2)e^{-\rho}}, \quad (4.24)$$

where  $\rho = R/a_0$  is variational parameter. For the general case of mass  $m$  and charge  $q = \zeta e$ , Eq.(4.24) can be rewritten in the following form:

$$E(\rho, \zeta) = \frac{Me^4\zeta^2}{\hbar^2} \left( -\frac{1}{2} + F(\rho) \right), \quad (4.25)$$

where

$$F(\rho) = \frac{1}{\rho} \frac{(1+\rho)e^{-2\rho} + (1 - \frac{2}{3}\rho^2)e^{-\rho}}{1 + (1 + \rho + \frac{1}{3}\rho^2)e^{-\rho}}. \quad (4.26)$$

Numerically, the function  $F(\rho)$  reaches minimum at the value  $\rho = 2.5$ , which should be used in the above expression for  $E(\rho, \zeta)$ . So, putting  $\zeta = 1$  we obtain the variational value of  $H_2^+$  ion energy,  $E(\rho) = -0.565$ . Note, to make a comparison, that we have the value  $E_{exact} = -0.6026$  due to the exact solution (4.2), and the value  $E_{exper}[H_2^+] = -0.6017$  as the experimental value of the energy of  $H_2^+$  ion. Thus, the optimal distance between the protons in  $H_2^+$  ion is  $R_m = a_0\rho = 2.5$  a.u., and the obtained variational energy  $E$  is slightly higher than both the values  $E_{exact}$  and  $E_{exper}$ , as it is normally expected to be in the variational approach. Now, we should replace electron by isoelectronium to describe the associated  $\hat{H}_2$  model. Substituting  $M = 2m_e$  and  $\zeta = 2$ , we see that the r.h.s. of Eq.(4.25) contains overall factor 8, in comparison to the  $H_2^+$  ion case ( $M = m_e$  and  $\zeta = 1$ ),

$$\tilde{E}(\rho) = 8|2E_B| \left( -\frac{1}{2} + F(\rho) \right), \quad (4.27)$$

The function  $F(\rho)$  remains the same, and its minimum is reached again at  $\rho = 2.5$ . Then, energy of  $H_2$  molecule due to Eq.(4.27) is  $\tilde{E}(\rho) = -8|2E_B|0.565 = -4.520$  a.u. This value should be compared with the one given by Eq.(4.4).

Below, we collect the above mentioned data and results of this Section in Table 1.

	$E$ , a.u.	$R$ , a.u.
$H_2^+$ ion, exact theory ( $N=16$ )	-0.6026346	1.9971579
$H_2^+$ ion, experiment [15]	-0.6017	2.00
3-body $\hat{H}_2$ , $M=2m_e$ , exact theory ( $N=16$ )	-7.617041	0.258399
3-body $\hat{H}_2$ , $M=2m_e$ , var. theory [1]	-7.61509174	0.2592
3-body $\hat{H}_2$ , $M=0.381m_e$ , exact theory ( $N=16$ )	-1.174475	1.675828
4-body $H_2$ , $r_c=0.01125$ a.u., var. theory [1]	-1.174474	1.4011
$H_2$ , experiment	-1.174474	1.4011

Table 1: The total ground state energy  $E$  and the internuclear distance  $R$ .

## 5 Concluding remarks

In this paper we have shown that the restricted three-body Santilli-Shillady isochemical model of the hydrogen molecule admits an exact analytic solution capable of representing the molecular binding energy in a way accurate to the sixth digit,  $E = -1.174475$  a.u., and the internuclear distance  $R = 1.675828$  a.u., which is about 19.6% bigger than the conventional experimental value,  $R_{\text{exper}}[H_2] = 1.4011$  a.u.

We should emphasize that the presented exact analytical solution includes infinite chain fractions. They still need numerical computation to reach the characteristic values of  $H_2^+$  ion like systems, such as the ground state energy, with the understanding that these values can be reached with any needed accuracy. For example, at the lengths of the chain fractions  $N = 100$  and  $N = 50$  for the angular and radial eigenvalues, one achieves accuracy of the ground state energy of about  $10^{-12}$ .

The general (four-body) Santilli-Shillady isochemical model of  $H_2$  cannot be, apparently, solved exactly, even in Born-Oppenheimer approximation, so that Ritz variational approach can be applied here to get the approximate values of the ground state energy and corresponding internuclear distance.

Ritz variational approach is a good instrument to analyze few-body problems, and restricted  $H_2$  molecule is such a system. It is wellknown that the variational solution of the ordinary model of  $H_2$  molecule includes rather complicated analytical calculations of the molecular integrals, with the hardest part of work being related to the exchange integral. Particularly, evaluated exchange integral for  $H_2$  molecule is expressed in terms of a special function (Sugiura's result, 1927). It is quite natural to expect that even more complications will arise when dealing with the Hulthén potential.

The reason to consider the general four-body Santilli-Shillady model of  $H_2$  molecule, after the made analysis of  $H_2^+$  like system approximate approach to it, is that the stable point-like isoelectronium  $\hat{H}_2$  model-based theoretical prediction does not meet the experimental data on  $H_2$  molecule, for the "bare" isoelectronium mass  $M = 2m_e$ , although we achieved essentially exact representation of the binding energy taking  $M = 0.308381m_e$ . Also, this stable point-like isoelectronium (three-body) model does not account for essential effect existing in the general (four-body) model. This effect is related to the potential barrier between the region associated to the attractive Hulthén potential,  $r_{12} < r_0$ , and the region associated to repulsive Coulomb poten-

tial,  $r_{12} > r_0$ , where  $r_0$  is the distance between the electrons at which Hulten potential is equal to Coloumb potential,  $V(r_{12}) = 0$ ; see Eq.(2.5). Characteristics of the barrier can be extracted from the function  $V(r_{12})$ . The barrier is finite for the used values of the parameters  $V_0$  and  $r_c$  so that the electrons penetrate it. The two  $1s$  electrons are thus simultaneously in two regimes, the first is strongly correlated regime due to short-range attractive Hulten potential (isoelectronium) and the second is weakly correlated regime due to the ordinary Coloumb repulsion. Also, there exist a transient regime corresponding to the region about the equilibrium point,  $r_{12} \simeq r_0$ , i.e. inside the barrier. Schematically, one could thought of that the electrons are, for instance, 10% in the isoelectronium regime, 1% in the transient regime, and 89% in the Coloumb regime. We stress that in the three-body approach to  $H_2$  molecule considered in this paper we have 100% for the isoelectronium regime.

Numerical computation by Santilli and Shillady [1] based on Gaussian transform techniques and SASLOBE computer program has shown *excellent* agreement of the general four-body model with experimental data on  $H_2$  molecule. They used *Gaussian screened Coloumb potential* as an approximation to the Hulten potential. It would be instructive to use Ritz variational approach, which deals with *analytical* calculations, in studying the four-body Santilli-Shillady model of  $H_2$  molecule. One can try it first for the Gaussian screened Coloumb potential, or exponential screened Coloumb potential in which case there is a hope to achieve exact analytical evaluation of the Coloumb and exchange integrals. Being a different approach, this would give a strong support to the numerical results on the ground state energy obtained by Santilli and Shillady. Also, having analytical set up one can make qualitative analysis of the four-body Santilli-Shillady model of  $H_2$  molecule. However, we should to note that these potentials, being approximations to the Hulten potential, will yield some approximate models, with corresponding approximate character of the results.

## Appendix

We use  $N = 16$  power degree approximation, the polynomials  $Q_N^{(x)}$  and  $Q_N^{(y)}$ , to find both the radial,  $\lambda^{(x)}(p, a)$ , and angular,  $\lambda^{(y)}(p, b)$ , eigenvalues of the CSF.  $Q_N$ 's are obtained by the use of recurrence relations (3.76) and definitions of the coefficients  $\alpha_s$ ,  $\beta_s$ ,  $\gamma_s$ ,  $\rho_s$ ,  $\kappa_s$ , and  $\delta_s$ , where we put  $b = 0$ , i.e.  $Z_1 = Z_2 = 1$ , and quantum number  $m = 0$ . Each of the two polynomials has 16 roots for  $\lambda$  from which we select one root which is appropriate due to its asymptotic behavior at  $R \rightarrow 0$ . Numerical solution of the equation  $\lambda^{(x)}(p, a) = \lambda^{(y)}(p, b)$  gives us the list of values of the electronic ground state energy  $E(R) = E_{1s\sigma}(R)$ , which corresponds to  $1s\sigma_g$  term of the  $H_2^+$  ion, as a function of the distance  $R$  between the nuclei. Table 2 presents the result, where no interpolation has been used. Numerical computation of each point in Table 2 took about 88 sec on ordinary Pentium desktop computer.

Below, we present some useful numerical values enabling one to convert atomic units, at which  $m_e = e = \hbar = 1$ , to the other units. Note also that for the energy 1 a.u.  $\equiv$  1 hartree, and for the length 1 a.u.  $\equiv$  1 bohr.

### Atomic units in terms of the other units

1 a.u. of mass, $m_e$	$9.10953 \cdot 10^{-28}$	gramms
1 a.u. of charge, $e$	$1.60219 \cdot 10^{-19}$	Coloumbs
1 a.u. of action, $\hbar$	$1.05459 \cdot 10^{-27}$	erg · sec
1 a.u. of length, $\frac{\hbar^2}{m_e e^2}$	$0.529177 \cdot 10^{-8}$	cm
1 a.u. of energy, $\frac{m_e e^4}{\hbar^2}$	27.2116	eV
1 a.u. of time, $\frac{\hbar^3}{m_e e^4}$	$2.41888 \cdot 10^{-17}$	sec
1 a.u. of velocity, $e^2/\hbar$	$2.18769 \cdot 10^8$	cm/sec
$\alpha = \frac{e^2}{\hbar c}$	1/137.0388	

### Conversion of the energy units

	a.u.	eV	Kcal·mole	cm <sup>-1</sup>
a.u.	1	27.212	$6.2651 \cdot 10^2$	$2.1947 \cdot 10^5$
eV	$3.6749 \cdot 10^{-2}$	1	23.061	8065.48
Kcal·mole	$1.5936 \cdot 10^{-3}$	$4.3364 \cdot 10^{-2}$	1	$3.4999 \cdot 10^2$
cm <sup>-1</sup>	$4.5563 \cdot 10^{-6}$	$1.2398 \cdot 10^{-4}$	$2.8573 \cdot 10^{-3}$	1

$R$ , a.u.	$E(R)$ , a.u.	$R$ , a.u.	$E(R)$ , a.u.
0.0	-1.99999999761099225	2.01	-1.10013870349441877
0.1	-1.97824134920757046	2.05	-1.09030214496519061
0.2	-1.92862028526774320	2.1	-1.07832542203506842
0.3	-1.86670393395684293	2.2	-1.05538508113994433
0.4	-1.80075405253452878	2.3	-1.03371349485820318
0.5	-1.73498799160719041	2.4	-1.01322030525887973
0.6	-1.67148471440012302	2.5	-0.99382351101203490
0.7	-1.61119720301672586	2.6	-0.97544858094023219
0.8	-1.55448006449772595	2.7	-0.95802766004904907
0.9	-1.50138158334624467	2.8	-0.94149886061738322
1.0	-1.45178630031448951	2.9	-0.92580563147803989
1.1	-1.40550252191841256	3.0	-0.91089619738235434
1.2	-1.36230785783351171	3.1	-0.89672306127076382
1.3	-1.32197139010318509	3.2	-0.88324255989570446
1.4	-1.28426925496894185	3.3	-0.87041447461742614
1.5	-1.24898987186705512	3.4	-0.85820167794222435
1.6	-1.21593722446146546	3.5	-0.84656982450508629
1.7	-1.18493139974611416	3.6	-0.83548707392472181
1.8	-1.15580915764590441	3.7	-0.82492384412924800
1.9	-1.12842156954614458	3.8	-0.81485259165546253
1.95	-1.11533575206408963	3.9	-0.80524772550750985
1.99	-1.10514450160298682	4.0	-0.79608496995054425
2.0	-1.10263415348745197	8.0	-0.62757022044109352

Table 2: The electronic energy of  $H_2^+$  ion (see Fig. 1).

Minimum of the energy  $E_{1s\sigma}(R)$  is  $E_{1s\sigma} = -1.9999999976$  a.u. at  $R = 0$ , which reproduces the known value  $E_{1s\sigma} = -2$  a.u. to a very high accuracy. Moreover, one can compare Table 2 and the table of Ref.[14] to see that each energy value in Table 2 does reproduce Wind's result up to seven decimal places. This means that our numerical calculations are correct.

We remark that Wind used  $N = 50$  approximation and presented seven decimal places while we use  $N = 16$  approximation and present seventeen decimal places. Alas, there is no need to keep such a high accuracy, and also Wind mentioned that even  $N = 10$  approximation gives the same result, up to seven digits.

By making 16th-order interpolation of the points in Table 2 and adding to it the potential of interaction between the nuclei,  $1/R$ , we obtain the list of values of the total energy presented in Table 3. It reveals the only minimum of the total energy,  $E(R) + R^{-1} = E_{min} = -0.6026346$  a.u. at the distance

$$R = R_{opt} = 1.9971579 \text{ a.u.}$$

$R, \text{ a.u.}$	$E(R) + R^{-1}, \text{ a.u.}$	$R, \text{ a.u.}$	$E(R) + R^{-1}, \text{ a.u.}$
0.1	+8.02176	2.1	-0.602135
0.2	+3.07138	2.2	-0.600840
0.3	+1.46663	2.3	-0.598931
0.4	+0.69924	2.4	-0.596554
0.5	+0.26501	2.5	-0.593824
0.6	-0.004818	2.6	-0.590833
0.7	-0.182626	2.7	-0.587657
0.8	-0.304480	2.8	-0.584356
0.9	-0.390270	2.9	-0.580978
1.0	-0.451786	3.0	-0.577563
1.1	-0.496412	3.1	-0.574142
1.2	-0.528975	3.2	-0.570743
1.3	-0.552741	3.3	-0.567384
1.4	-0.569984	3.4	-0.564084
1.5	-0.582323	3.5	-0.560856
1.6	-0.590937	3.6	-0.557709
1.7	-0.596696	3.7	-0.554654
1.8	-0.600254	3.8	-0.551695
1.9	-0.602106	3.9	-0.548837
2.0	-0.602634	4.0	-0.546085

Table 3: The total energy of  $H_2^+$  ion (see Fig. 2).

The results collected in Table 4 have been obtained directly by numerical calculations with the use of replacements  $p^2 \rightarrow 2p^2$  and  $a \rightarrow 4a$ , where  $p$  and  $a$  are defined by Eq.(3.50), in the coefficients  $\alpha_s$ ,  $\beta_s$ ,  $\gamma_s$ ,  $\rho_s$ ,  $\kappa_s$ , and  $\delta_s$  of the recurrence relations. These replacements have been made due to Eq.(3.15), with the mass parameter  $M = 2$  and the charge parameter  $q = -2$ , corresponding to the stable point-like isoelectronium of mass  $M = 2m_e$  and charge  $-2e$ . In addition, it turns out that Table 4 can be derived directly from Table 2 by the use of rescalements  $R \rightarrow R/4$  and  $E \rightarrow 8E$ . This remarkable property is confirmed by the scaling method developed in Sec. 4.2, and proves that the scaling method is correct. By adding  $1/R$  to the isoelectronic energy values of Table 4 we obtain Table 5 showing the total energy of the  $H_2$  system, at the mass  $M = 2m_e$ . The minimum of the total energy is found  $E(R) + R^{-1} = E_{min} = -7.617041 \text{ a.u.}$  at  $R = R_{opt} = 0.258399 \text{ a.u.}$

$R$ , a.u.	$E(R)$ , a.u.	$R$ , a.u.	$E(R)$ , a.u.
0.00	-16.000000000000008	0.50	-8.82107371596060652
0.05	-15.4289613540288446	0.55	-8.44308064942978475
0.10	-14.4060324481253427	0.60	-8.10576243870545276
0.15	-13.3718774940028106	0.65	-7.80358864752256309
0.20	-12.4358407555134897	0.70	-7.53199088488360768
0.225	-12.0110526341241952	0.75	-7.28716957910914597
0.25	-11.6142894041116995	0.80	-7.06594047783391143
0.275	-11.2440221722385613	0.85	-6.86561342351093717
0.30	-10.8984629511501962	0.90	-6.68389659171409977
0.35	-10.2741538838779300	0.95	-6.51882073404630535
0.40	-9.72749779604447084	1.00	-6.36867910416260141
0.45	-9.24647351730713928		

Table 4: The isoelectronium energy of the three-body  $\hat{H}_2$  system, at the mass  $M = 2m_e$  (see Fig. 3).

$R$ , a.u.	$E(R)$ , a.u.	$R$ , a.u.	$E(R)$ , a.u.
0.010	+84.0273769895390465	0.150	-6.70521082733614370
0.015	+50.7305619003569852	0.200	-7.43584075551348888
0.020	+34.1124961901906909	0.250	-7.61428940411169996
0.025	+24.1713076006601701	0.300	-7.56512961781686321
0.030	+17.5720885190207170	0.350	-7.41701102673507239
0.035	+12.8849357295675638	0.400	-7.22749779604447084
0.040	+9.39442987714794597	0.450	-7.02425129508491696
0.045	+6.70277469374505585	0.500	-6.82107371596060652
0.050	+4.57103864597115538	0.550	-6.62489883124796641
0.055	+2.84698239022676524	0.600	-6.43909577203878669
0.060	+1.42896579635860376	0.650	-6.26512710906102388
0.065	+0.24650856005471055	0.700	-6.10341945631217797
0.070	-0.75082137484248256	0.750	-5.95383624577581205
0.075	-1.60007720159364552	0.800	-5.81594047783391143
0.080	-2.32910343012903808	0.850	-5.68914283527564279
0.085	-2.95923562411244667	0.900	-5.57278548060298906
0.090	-3.50710131449860362	0.950	-5.46618915509893721
0.095	-3.98585308299203866	1.000	-5.36867910416260141
0.100	-4.40603244812534278		

Table 5: The total energy of the three-body  $\hat{H}_2$  system, at the mass  $M = 2m_e$  (see Fig. 4).



$M$ , a.u.	$E_{min}(M)$ , a.u.	$R_{opt}(M)$ , a.u.
0.10	-0.380852	5.167928
0.15	-0.571278	3.445291
0.20	-0.761704	2.583964
0.25	-0.952130	2.067171
0.26	-0.990215	1.987664
0.27	-1.028300	1.914050
0.28	-1.066385	1.845688
0.29	-1.104470	1.782044
0.30	-1.142556	1.722645
0.307	-1.169215	1.683367
0.308	-1.173024	1.677899
0.308381	-1.174475	1.675828
0.309	-1.176832	1.672471
0.31	-1.180641	1.667073
0.32	-1.218726	1.614977
0.33	-1.256811	1.566041
0.34	-1.294896	1.519981
0.35	-1.332982	1.476553
0.40	-1.523408	1.291982
0.45	-1.713834	1.148428
0.50	-1.904260	1.033585
0.75	-2.856390	0.689058
1.00	-3.808520	0.516792
1.25	-4.760650	0.413434
1.50	-5.712780	0.344529
1.75	-6.664910	0.295310
2.00	-7.617040	0.258396

Table 6: The minimal total energy  $E_{min}$  and the optimal internuclear distance  $R_{opt}$  of the three-body  $\hat{H}_2$  system as functions of the mass  $M$  of the stable point-like isoelectronium (see Figs. 5–8).

Table 6 presents result of calculations of the *minimal* total energies and corresponding *optimal* distances, at various values of the isoelectronium mass parameter  $M = \eta m_e$  ( $M = \eta$ , in atomic units). We have derived some 27 tables (such as Table 5) from Table 2 by the scaling method according to Eq.(4.21), and find minimum of the total energy in each table, together with the corresponding optimal distance. Then we collected all the obtained energy minima and optimal distances in Table 6. With the fourth order interpolation/extrapolation, the graphical representations of Table 6 show (see Figures 5–8) that the minimal total energy behaves as  $E_{min}(M) \simeq -3.808M$ ,

and the optimal distance behaves as  $R_{opt}(M) \simeq 0.517/M$ , to a good accuracy. One can see that at  $M = 2m_e$  we have  $E_{min}(M) = -7.617040$  a.u. and  $R_{opt}(M) = 0.258396$  a.u., which recover the earlier obtained values  $E_{min} = -7.617041$  a.u. and  $R_{opt} = 0.258399$  a.u. of Table 5, to a high accuracy, thus showing once again correctness of the used scaling method. In fact, the values of  $E$  and  $R$  for  $M = 1.50m_e$ ,  $M = 1.75m_e$ , and  $M = 2.00m_e$  in Table 6 have been obtained by extrapolation so they are not as much accurate as they are in Table 5. However, this is not of much importance here because we use them only to check the results of the scaling method.

The main conclusion following from Table 6 is that the mass parameter value  $M = 0.308381m_e$  fits the energy value  $E_{min}(M) = -1.174475$  a.u., with the corresponding  $R_{opt}(M) = 1.675828$  a.u., which appears to be about 19.6% bigger than the experimental value  $R_{exper}[H_2] = 1.4011$  a.u. The total energy as a function of internuclear distance, for this value of mass,  $M = 0.308381m_e$ , is shown in Figure 9 to illustrate that the obtained optimal distance  $R_{opt} = 1.675828$  a.u. corresponds to a minimal value of the total energy.

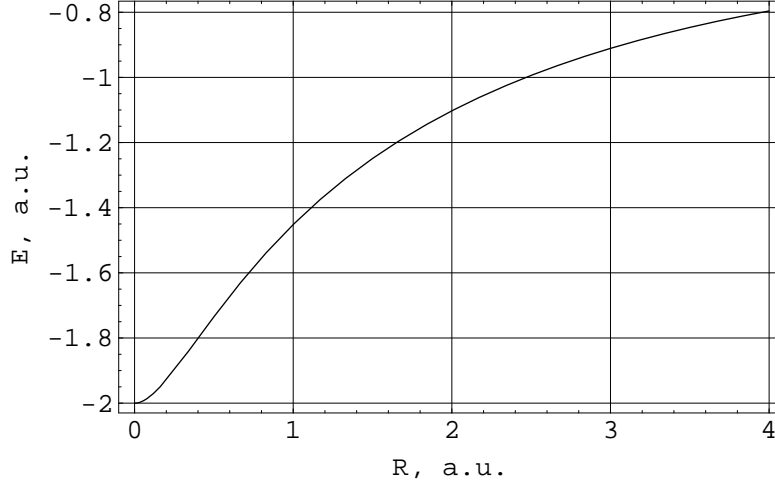


Figure 1: The electronic energy  $E(R)$  of  $H_2^+$  ion as a function of the internuclear distance  $R$ .

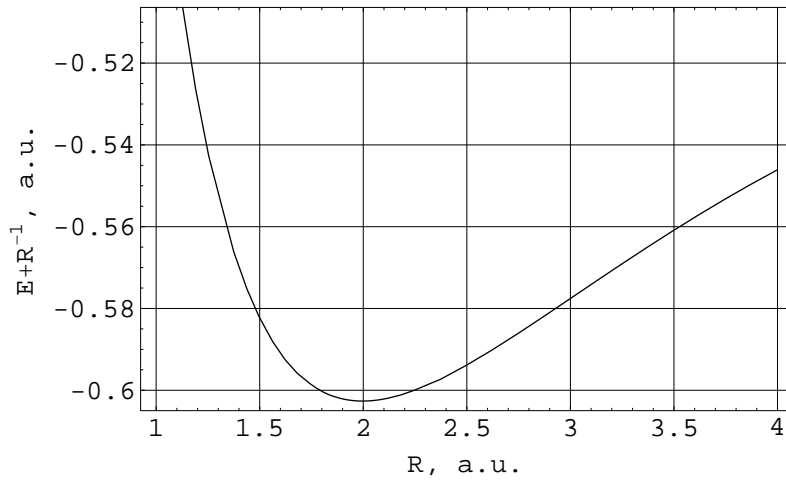


Figure 2: The total energy  $E(R) + R^{-1}$  of  $H_2^+$  ion as a function of the internuclear distance  $R$ .

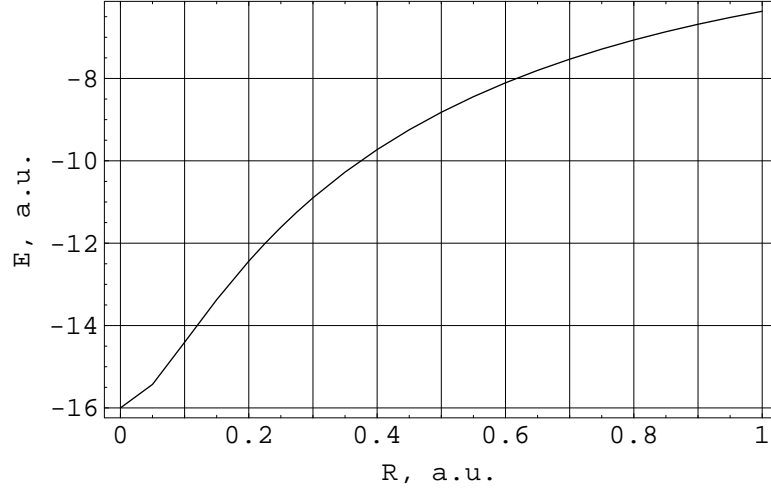


Figure 3: The isoelectronium energy  $E(R)$  of the  $\hat{H}_2$  system as a function of the internuclear distance  $R$ , at the isoelectronium mass  $M = 2m_e$ .

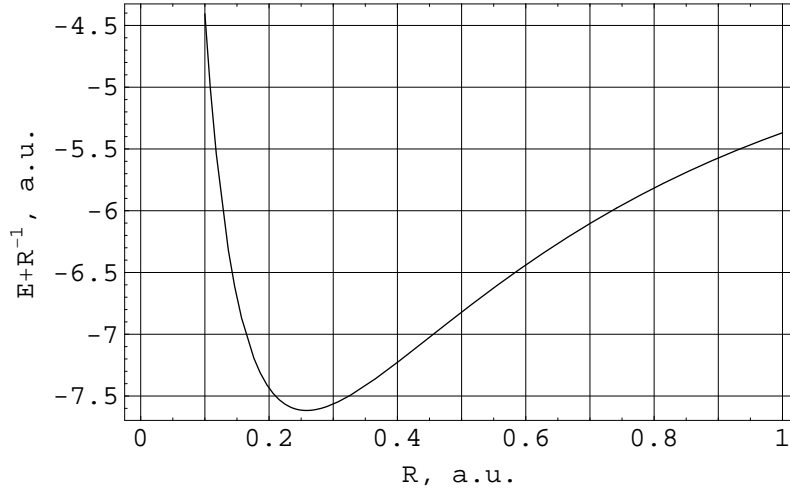


Figure 4: The total energy  $E(R) + R^{-1}$  of the  $\hat{H}_2$  system as a function of the internuclear distance  $R$ , at the isoelectronium mass  $M = 2m_e$ .

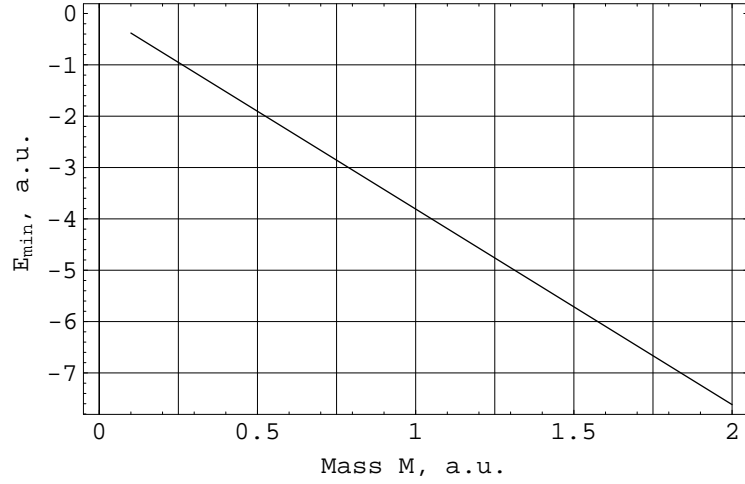


Figure 5: The minimal total energy  $E_{\min}(M)$  of the  $\hat{H}_2$  system as a function of the isoelectronium mass  $M$ .

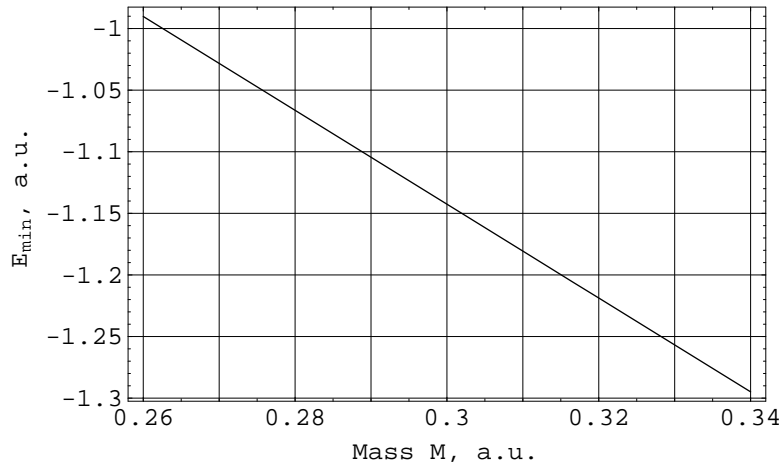


Figure 6: The minimal total energy  $E_{\min}(M)$  of the  $\hat{H}_2$  system as a function of the isoelectronium mass  $M$ . More detailed view.

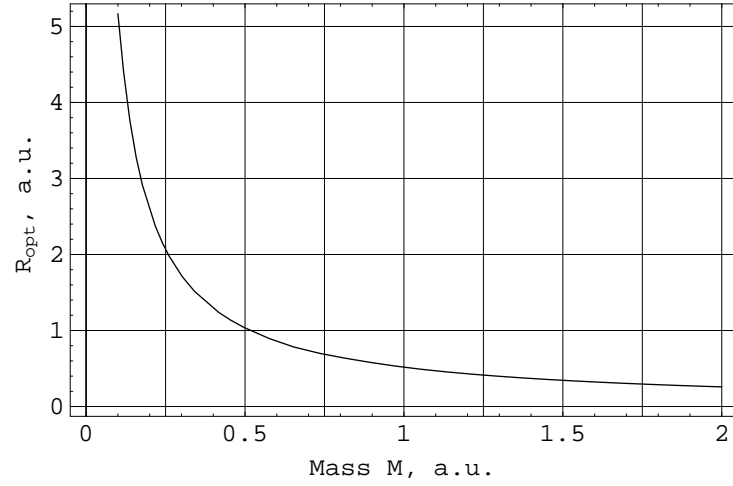


Figure 7: The optimal internuclear distance  $R_{opt}(M)$  of the  $\hat{H}_2$  system as a function of the isoelectronium mass  $M$ .

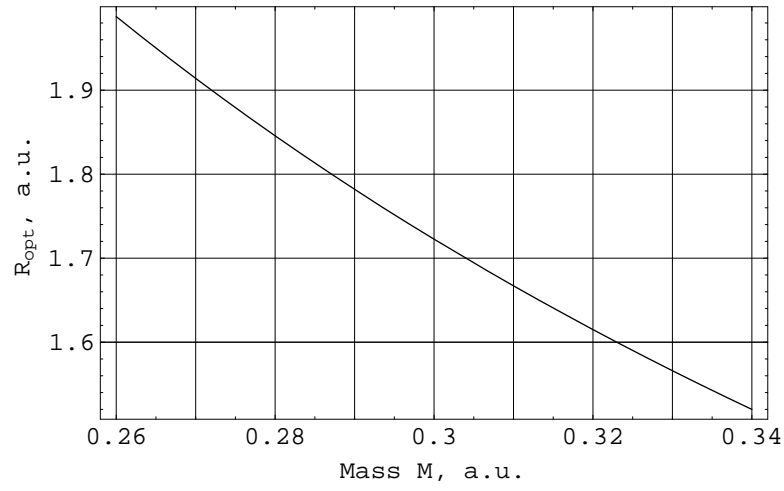


Figure 8: The optimal internuclear distance  $R_{opt}(M)$  of the  $\hat{H}_2$  system as a function of the isoelectronium mass  $M$ . More detailed view.

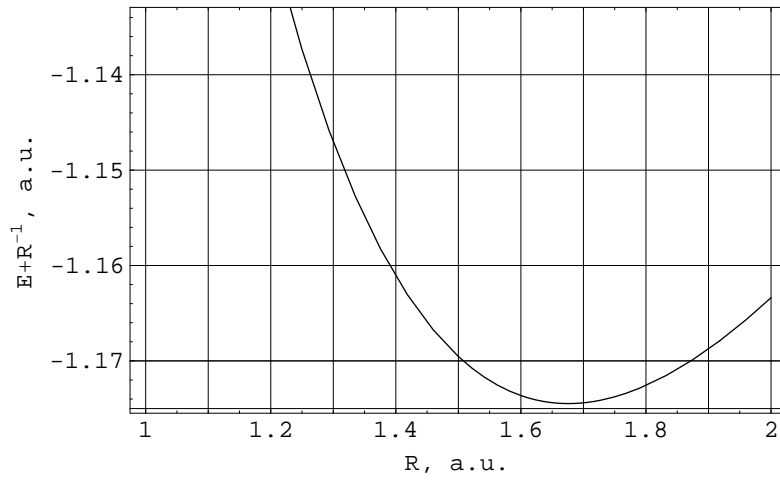


Figure 9: The total energy  $E(R) + R^{-1}$  of the  $\hat{H}_2$  system as a function of the internuclear distance  $R$ , at the isoelectronium mass  $M = 0.308381m_e$ .

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