Bound states of $dt\mu$, $pd\mu$ and $tp\mu$ mesomolecules

A. V. Eskin[1,*], *V. I.* Korobov[1,2,**], *A. P.* Martynenko[1,***], and *V. V.* Sorokin[1,****]

[1]Samara National Research University named after S. P. Korolev, 443086, Samara, Russia
[2]Joint Institute for Nuclear Research, BLTP, 141980, Moscow region, Dubna, Russia

Abstract. The energy spectrum of excited bound states of muonic molecules $pt\mu$, $pd\mu$, and $dt\mu$ is calculated on the basis of the stochastic variational method. The basis wave functions of the muonic molecule are taken in the Gaussian form. The matrix elements of the Hamiltonian are calculated analytically. For numerical calculation, a computer code was written in the MATLAB system. As a result, the numerical values of bound state energies for excited P-states of muonic molecules $pt\mu$, $pd\mu$ and $dt\mu$ were obtained.

1 Introduction

In recent years, due to the appearance of the experimental results of the CREMA collaboration [1, 2], there has been an increasing interest in the study of the energy spectra of muonic atoms. In the case of two-particle muonic atoms and ions, there are reliable analytical methods for calculating the fine and hyperfine structure of the spectrum in the framework of quantum electrodynamics [3, 4]. In the transition to three-particle muon systems, it is also possible to carry out analytical calculations of energy levels in the framework of perturbation theory in a number of cases [5–7]. On the other hand, for many decades, methods have been developed to study mesomolecules based on the variational approach and adiabatic approach in the three-body problem [8–11]. Of particular note is the variational method, in which the problem of bound states for a three-particle system allows one to get ultra-precise numerical solutions on modern computers [12, 13]. Knowledge of the exact values of the energy levels of mesomolecules is important when calculating the rates of resonant formation of mesomolecules in muon catalysis reactions [14–19]. Since the rates of resonance formation are strongly dependent on the binding energy of weakly bound states of mesomolecules, it is necessary to improve the accuracy of calculating the binding energies.

Muonic molecules $pt\mu$, $pd\mu$, and $dt\mu$ include different hydrogen isotopes which lead to a different energy structure. The lighter ones $pt\mu$ and $pd\mu$ have only two bound states: one $S(L = 0)$ and one $P(L = 1)$, where L is the total orbital angular momentum of a three-particle system. None of these states are weakly bound. The heavier $dt\mu$ has five bound states: two $S(L = 0)$, two $P(L = 1)$ and one $D(L = 2)$ [9, 10, 14]. Excited $P^*(L = 1)$-state is weakly bound. In our work we investigate states with $L = 1$. Note that there are several different approaches to classify the bound states in mesomolecular ions. One of them originates from

*e-mail: eskinalexey1992@gmail.com
**e-mail: korobov@theor.jinr.ru
***e-mail: a.p.martynenko@samsu.ru
****e-mail: wws63rus@yandex.ru

the adiabatic approach and involves a pair of two quantum numbers L and ν, where L is a rotational quantum number and ν is a vibrational quantum number [9, 10]. For example, the ground state in this approach is designated as (0,0), while the excited $P^*(L = 1)$-state becomes (1,1). Aside from the states with "normal" spacial parity $(-1)^L$ described above there are metastable states with $L = 1$ and "odd" spacial parity $(-1)^{L+1}$ [14]. In the framework of the variational method, either an exponential basis [9, 10] or Gaussian one [11] is usually used. In this work, we apply the Gaussian form for the wave function of the mesomolecule in the framework of the stochastic variational method and calculate the energy levels of the ground and excited states for mesomolecules consisting of different particles.

2 General formalism

All variational methods have common properties: the use of any complete set of basis functions with the calculation of representations on these sets of Hamiltonian and overlapping integrals and the subsequent solution of the generalized eigenvalue problem. In this work to calculate the energy spectrum of the ground and excited bound states of muonic molecules $pt\mu$, $pd\mu$, and $dt\mu$ we have used the stochastic variational method [11]. The wave function of the three-particle system with zero angular momentum is expanded as following:

$$\Psi = \sum_{i=1}^{K} c_i \psi_{S M_S}(\mathbf{x}_i, A_i), \tag{1}$$

where S, M_S are spin quantum numbers, K is a number of basis functions. An upper bound for the ground state energy of the system is given by the lowest eigenvalue of the generalized eigenvalue problem:

$$HC = E_K BC, \quad H_{ij} = (\psi_{S M_S}(\mathbf{x}_i, A_i, H\psi_{S M_S}(\mathbf{x}_j, A_j), \quad B_{ij} = (\psi_{S M_S}(\mathbf{x}_i, A_i, \psi_{S M_S}(\mathbf{x}_j, A_j). \tag{2}$$

The trial wave function $\psi_{S M_S}(\mathbf{x}_i, A_i)$ of the muonic molecule in this approach has the Gaussian form. The Gaussian-type basis function with non-zero angular momentum for nonidentical particles can be written as follows:

$$\phi_L(\boldsymbol{x}, A) = e^{-\frac{1}{2}\widetilde{\boldsymbol{x}} A \boldsymbol{x}} \theta_L(\boldsymbol{x}), \tag{3}$$

where $\boldsymbol{x} = (\boldsymbol{x}_1, ..., \boldsymbol{x}_{N-1})$ are Jacobi coordinates (N is a number of bound particles), A is a $(N-1)\times(N-1)$ positive-defined matrix of variational parameters, $\widetilde{\boldsymbol{x}} A \boldsymbol{x} = \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} A_{ij} \boldsymbol{x}_i \cdot \boldsymbol{x}_j$

$$\theta_L(\boldsymbol{x}) = [[[\mathbb{Y}_{l_1}(\boldsymbol{x}_1)\mathbb{Y}_{l_2}(\boldsymbol{x}_2)]_{L_{12}} \mathbb{Y}_{l_3}(\boldsymbol{x}_3)]_{L_{123}} ...]_{LM}, \tag{4}$$

where $\mathbb{Y}_{l_m}(\boldsymbol{x}) = r^l Y_{lm}(\boldsymbol{x})$. In the case of three nonidentical particles in P-state ($L = 1$, where L is the total angular momentum of particles) there are three possible wave functions [10, 20–22]:

$$\phi_{10}(\boldsymbol{\rho}, \boldsymbol{\lambda}, A) = e^{-\frac{1}{2}[A_{11}\rho^2 + A_{22}\lambda^2 + 2A_{12}(\rho\lambda)]}(\boldsymbol{\epsilon}\boldsymbol{\rho}), \tag{5}$$

$$\phi_{01}(\boldsymbol{\rho}, \boldsymbol{\lambda}, A) = e^{-\frac{1}{2}[A_{11}\rho^2 + A_{22}\lambda^2 + 2A_{12}(\rho\lambda)]}(\boldsymbol{\epsilon}\boldsymbol{\lambda}), \tag{6}$$

$$\phi_{11}(\boldsymbol{\rho}, \boldsymbol{\lambda}, A) = e^{-\frac{1}{2}[A_{11}\rho^2 + A_{22}\lambda^2 + 2A_{12}(\rho\lambda)]}(\boldsymbol{\epsilon}[\boldsymbol{\rho} \times \boldsymbol{\lambda}]), \tag{7}$$

where we use the tensor representation for the angular part of wave functions with polarization vector $\boldsymbol{\varepsilon}$, and $\boldsymbol{\rho}$, $\boldsymbol{\lambda}$ are the Jacobi coordinates of three particles which are related with the particle radius vectors:

$$\boldsymbol{\rho} = \boldsymbol{r_1} - \boldsymbol{r_2}, \quad \boldsymbol{\lambda} = \frac{\boldsymbol{r_1} m_1 + \boldsymbol{r_2} m_2}{m_1 + m_2} - \boldsymbol{r_3}. \tag{8}$$

First two wave functions have "normal" spacial parity $(-1)^L$ while the third one has the "odd" parity $(-1)^{L+1}$. We investigate both of these cases. To construct basis functions, one has to take a superposition of (5) and (6) as $\psi_{P-state}(\boldsymbol{\rho},\boldsymbol{\lambda},A) = c_1\phi_{10}(\boldsymbol{\rho},\boldsymbol{\lambda},A) + c_2\phi_{01}(\boldsymbol{\rho},\boldsymbol{\lambda},A)$ for the state with $(-1)^L$ parity and (7) for the "odd" parity. Knowing the basis functions we can perform analytical calculations of matrix elements of Hamiltonian, which is an advantage of Gaussian basis.

Let us calculate the overlap matrix elements first. The integral for the wave function (5) has the following form:

$$< \phi' | \phi >^{10} = \int\int d\boldsymbol{\rho} d\boldsymbol{\lambda} e^{-\frac{1}{2}[B_{11}\rho^2 + B_{22}\lambda^2 + 2B_{12}(\boldsymbol{\rho}\boldsymbol{\lambda})]} (\boldsymbol{\epsilon}^*\boldsymbol{\rho})(\boldsymbol{\epsilon}\boldsymbol{\rho}), \tag{9}$$

where the index (10) corresponds to the wave function (5). After the analytical integration and averaging over polarizations we obtain:

$$< \phi' | \phi >^{10} = \frac{1}{3}\int\int d\boldsymbol{\rho} d\boldsymbol{\lambda} e^{-\frac{1}{2}[B_{11}\rho^2 + B_{22}\lambda^2 + 2B_{12}(\boldsymbol{\rho}\boldsymbol{\lambda})]} \frac{3}{4\pi}\delta_{ij}\rho_i\rho_j = \frac{6\pi^2 B_{22}}{(\det B)^{5/2}}. \tag{10}$$

For other states the integration can be performed in a similar manner with the following results (the indices (01), (11) correspond to functions (6), (7)):

$$< \phi' | \phi >^{01} = \frac{6\pi^2 B_{11}}{(\det B)^{5/2}}, \quad < \phi' | \phi >^{11} = \frac{12\pi^2}{(\det B)^{5/2}}. \tag{11}$$

We also calculate "off-diagonal" matrix elements of the form $< \phi_{01} | \phi_{10} >$ (this matrix element is indicated by the index (01|10)):

$$< \phi' | \phi >^{(01|10)} = -\frac{6\pi^2 B_{12}}{(\det B)^{5/2}}. \tag{12}$$

For the calculation of matrix elements of Hamiltonian we use explicit expressions for potential and kinetic energy operators. The kinetic energy operator in Jacobi coordinates is

$$\hat{T} = -\frac{\hbar^2}{2\mu_1}\Delta_\rho - \frac{\hbar^2}{2\mu_2}\Delta_\lambda, \tag{13}$$

where $\mu_1 = \frac{m_1 m_2}{m_1+m_2}$, $\mu_2 = \frac{(m_1+m_2)m_3}{m_1+m_2+m_3}$. After the analytical integration the matrix elements of kinetic energy operator can be presented as follows (designations are the same as in the above formulae):

$$< \phi' | \hat{T} | \phi >^{10,01,11,(01|10)} = -\frac{6\pi^2}{(\det B)^{7/2}} \left\{ \frac{\hbar^2}{2\mu_1} I_\rho^{10,01,11,(01|10)} + \frac{\hbar^2}{2\mu_2} I_\lambda^{10,01,11,(01|10)} \right\}, \tag{14}$$

$$I_\rho^{10} = 5A_{11}B_{22}[B_{12}^2 + (A_{11} - B_{11})B_{22}] - 2A_{12}B_{12}(B_{12}^2 + 5A_{11}B_{22} - B_{11}B_{22}) + \\ + A_{12}^2(2B_{12}^2 + 3B_{11}B_{22}), \tag{15}$$

$$I_\lambda^{10} = 5A_{12}^2B_{22}^2 + A_{22}B_{22}(-10A_{12}B_{12} + 3B_{12}^2 - 3B_{11}B_{22}) + A_{22}^2(2B_{12}^2 + 3B_{11}B_{22}),$$

$$I_\rho^{01} = 5A_{12}^2B_{11}^2 + A_{11}B_{11}(-10A_{12}B_{12} + 3B_{12}^2 - 3B_{22}B_{11}) + A_{11}^2(2B_{12}^2 + 3B_{22}B_{11}),$$

$$I_\lambda^{01} = 5A_{22}B_{11}[B_{12}^2 + (A_{22} - B_{22})B_{11}] - 2A_{12}B_{12}(B_{12}^2 + 5A_{22}B_{11} - B_{22}B_{11}) + \\ + A_{12}^2(2B_{12}^2 + 3B_{22}B_{11}),$$

$$I_\rho^{11} = A_{12}^2B_{11} - 2A_{11}A_{12}B_{12} + A_{11}[B_{12}^2 + (A_{11} - B_{11})B_{22}],$$

$$I_{\lambda}^{11} = A_{12}^2 B_{22} - 2A_{22}A_{12}B_{12} + A_{22}[B_{12}^2 + (A_{22} - B_{22})B_{11}],$$
$$I_{\rho}^{(01|10)} = -B_{12}[-2A_{12}B_{12}(4A_{11} + B_{11}) + 5A_{11}B_{12}^2 + 5A_{12}^2 B_{11}] -$$
$$-B_{22}(A_{11} - B_{11})(5A_{11}B_{12} - 2A_{12}B_{11}),$$
$$I_{\lambda}^{(01|10)} = 5A_{12}^2 B_{12}B_{22} - A_{22}(2A_{12}B_{11}B_{22} + 8A_{12}B_{12}^2 + 3B_{11}B_{12}B_{22} - 3B_{12}^3) + 5A_{22}^2 B_{11}B_{12}.$$

The potential energy of Coulomb interaction of particles has the form:

$$\hat{V} = \frac{e_1 e_2}{|\boldsymbol{r_{12}}|} + \frac{e_1 e_3}{|\boldsymbol{r_{13}}|} + \frac{e_2 e_3}{|\boldsymbol{r_{23}}|}, \tag{16}$$

where $\boldsymbol{r_{12}} = \boldsymbol{r_1} - \boldsymbol{r_2} = \boldsymbol{\rho}$, $\boldsymbol{r_{13}} = \boldsymbol{r_1} - \boldsymbol{r_3} = \boldsymbol{\lambda} + \frac{m_2}{m_{12}}\boldsymbol{\rho}$, $\boldsymbol{r_{23}} = \boldsymbol{r_2} - \boldsymbol{r_3} = \boldsymbol{\lambda} - \frac{m_1}{m_{12}}\boldsymbol{\rho}$, e_1, e_2, e_3 are charges of particles. To find the matrix elements of second and third terms of potential (16), we introduce a new variable $\boldsymbol{k^{13,23}} = \boldsymbol{\lambda} \pm \frac{m_2^{13,23}}{m_{12}}\boldsymbol{\rho}$, $m_{2,1}^{13,23}$ coincides with the mass m_2 for the integral I_{13} or with the mass m_1 for the integral I_{23}, $m_{12} = m_1 + m_2$.

After the integration we obtain the following analytical expressions of matrix elements:

$$< \phi' | \hat{V} | \phi >^{10,01,11,(01|10)} = e_1 e_2 I_{12}^{10,01,11,(01|10)} + e_1 e_3 I_{13}^{10,01,11,(01|10)} + e_2 e_3 I_{23}^{10,01,11,(01|10)}, \tag{17}$$

$$I_{12}^{10} = \frac{4\sqrt{2}\pi^{3/2}\sqrt{B_{22}}}{(\det B)^2}, \quad I_{13,23}^{10} = \frac{2\sqrt{2}\pi^{3/2}(3B_{22}F_1^{13,23} - (F_2^{13,23})^2)}{(F_1^{13,23})^{3/2}[B_{22}F_1^{13,23} - (F_2^{13,23})^2]^2}, \tag{18}$$

$$I_{12}^{01} = \frac{2\sqrt{2}\pi^{3/2}(3B_{11}B_{22} - B_{12}^2)}{(B_{22})^{3/2}(\det B)^2}, \quad I_{13,23}^{01} = \frac{2\sqrt{2}\pi^{3/2}}{[B_{22}F_1^{13,23} - (F_2^{13,23})^2]^2}\Big\{2\sqrt{F_1^{13,23}} +$$
$$+\frac{(3B_{22}F_1^{13,23} - (F_2^{13,23})^2)}{(F_1^{13,23})^{3/2}}\frac{(m_{2,1}^{13,23})^2}{m_{12}^2} \pm \frac{4F_2^{13,23}}{\sqrt{F_1^{13,23}}}\frac{m_{2,1}^{13,23}}{m_{12}}\Big\},$$

$$I_{12}^{11} = \frac{8\sqrt{2}\pi^{3/2}}{\sqrt{B_{22}}(\det B)^2}, \; I_{13,23}^{11} = \frac{8\sqrt{2}\pi^{3/2}}{\sqrt{F_1^{13,23}}[B_{22}F_1^{13,23} - (F_2^{13,23})^2]^2}, \; I_{12}^{(01|10)} = -\frac{4\sqrt{2}\pi^{3/2}B_{12}}{\sqrt{B_{22}}(\det B)^2},$$

$$I_{13,23}^{(01|10)} = -\frac{2\sqrt{2}\pi^{3/2}}{[B_{22}F_1^{13,23} - (F_2^{13,23})^2]^2}\Big\{2\frac{F_2^{13,23}}{\sqrt{F_1^{13,23}}} \mp \frac{m_{2,1}^{13,23}}{m_{12}}\frac{(3B_{22}F_1^{13,23} - (F_2^{13,23})^2)}{(F_1^{13,23})^{3/2}}\Big\}.$$

As it has been previously mentioned we use the stochastic variational method to calculate energies of muonic molecules $pt\mu$, $pd\mu$ and $dt\mu$. The matrix of variational parameters in the framework of stochastic variational method is generated randomly, which prevents convergence of the result to a local minimum and eliminates the possibility of obtaining an incorrect result. Moreover, according to the Mini-Max theorem [11] in variational calculations the energies for excited states can be obtained along with the ground state energies.

For direct numerical calculations a computer code was written in the MATLAB system to solve the three-body Coulomb problem based on the Schrödinger equation. The program allows one not only to find the values of energy for the ground and excited states, but also to perform refinement cycles to improve the accuracy of previously calculated energies. For variational parameters the stochastic optimization procedure is used. In case of the $(-1)^L$ parity P-state the basis contains both (5) and (6) functions. As a result, the numerical values for the bound energy of ground and excited states of the muonic molecules $pt\mu$, $pd\mu$ and $dt\mu$ are obtained in muon atomic units (see Tab. 1). When writing the program, which helps to calculate the energy levels of the bound states of mesomolecules $td\mu$, $pd\mu$ and $tp\mu$, the Varga-Suzuki program [22] written in Fortran is taken as the basis, wherein we have made a number

Table 1. Energies of the bound states of muonic molecular ions in muon-atomic units. The results are compared with ones obtaned early by V.I. Korobov [9] and A.M. Frolov [10] using an exponential basis. The designation of states corresponds to those used in [8, 10, 22]

State	Ref.	$E(td\mu)$	$E(tp\mu)$	$E(dp\mu)$
(0,0)		-0.53859497060266	-0.519880084233196	-0.512711790250644
(0,0)	[9]	-0.53859497088114		
(0,0)	[10]	-0.53859497170948	-0.519880085704058	-0.512711792481703
(0,1)		-0.488056287316459	-0.481499142146054	-0.471905802356538
(0,1)	[9]	-0.488065353400705		
(0,1)	[10]	-0.488065354215765		
(1,0)		-0.523191450281939	-0.499492022668803	-0.490664161231777
(1,0)	[9]	-0.523191450934159		
(1,0)	[10]	-0.523191452003593	-0.499492024990190	-0.490664164603504
(1,1)		-0.481970439502052	-0.481277698317046	-0.471699625227238
(1,1)	[9]	-0.481991526590075		
(1,1)	[10]	-0.481991527054489		
$(1,1)^*$		-0.123867812294438	-0.120749575550362	-0.118989450178991
$(1,1)^*$	[9]	-0.123867812559127		

of changes. The matrix elements of the wave function normalization, kinetic and potential energies for the ground and excited states have been calculated analytically and introduced into the program. We have changed the way to set the function of generating random numbers. In our program, we use a combined version of random number generation, which uses the standard MATLAB function, as well as a function from the Varga-Suzuki program. The best value of the parameters is preserved. To calculate the excited states $(0,1)$ and $(1,1)$, the method of solving the eigenvalue problem has been changed by using the standard MATLAB function. In calculating the energies of the ground and excited states, different values are used for the intervals of random parameters. The running time of the program has been increased, but this allows one to find more accurate energy values for states $(0,1)$ and $(1,1)$.

Along with total energy E of a particular state of mesomolecular ion presented in Tab. 1 usually, the binding energy $\epsilon_{bind} = (Em_\mu\alpha^2 + \frac{m_r\alpha^2}{2n^2})$ (in eV) is introduced to characterize the binding energy of the quasi-nucleus, which is formed by the negative muon and the positive most heavy isotope of hydrogen, and the remaining isotope of hydrogen, where m_r is a reduced mass of a two-particle bound state $(t\mu)$ or $(d\mu)$, n is the principle quantum number of this bound state. For (1,0) and (1,1) states $n = 1$, while for the "odd" parity metastable P-state $n = 2$ [8, 9]. So, for example, in the case of the molecule $(td\mu)$ for the state $(1,1)$ our binding energy is equal to -0.541685 eV (we write it to six digits). For comparison, in [10] it is equal to -0.660330 eV. It is necessary to note that for the bound energy of quasi-nucleus $(t\mu)$ we can use the fine structure formula: $E(t\mu) = -(Z\alpha)^2/2n^2 - (Z\alpha)^4(1/(j+1/2) - 3/4n)/2n^3$. Then we obtain slightly different values for the binding energy: $\epsilon_{bind} = -0.505590$ eV (our result) and $\epsilon_{bind} = -0.624236$ eV [10]. For another three-particle molecule $(dp\mu)$ the variational approach also gives a negative value for the energy $(dp\mu)$ in the state (1,1) $E^{(1,1)}(dp\mu) = -0.471699625227238$ in muon-atomic units (-2653.995056 eV). Then the energy ε_{bind} is positive for the state (1,1). On this basis, it is usually concluded that a bound state of two clusters $(d\mu)$ and p is absent.

Comparing the results from Tab. 1 with previous calculations we can say that they are in good agreement with [9, 10]. The estimated accuracy of our calculations is 10^{-8} muon-atomic units based on the convergence of the total energy as the size of the basis increases.

The noticeable discrepancy for (1,1) states is related with a smaller basis size and the need for a more careful parameters optimization procedure. The results for the "odd" parity states coincide with [9]. It is worth mentioning that in our calculations we use double precision while in [10] quadruple precision is being used. This fact also contributes to the discrepancy of results.

3 Conclusion

In this work we have performed the investigation of the energy levels of muonic molecules $td\mu$, $tp\mu$, $dp\mu$ on the basis of stochastic variational method from [11, 22]. Our calculations have been made with the account of leading order terms in the particle interaction operator. They include nonrelativistic kinetic energy (13) and the Coulomb potential energy (16). The results obtained above (see Tab. 1) can be improved by calculating various corrections. Among them, the most important are corrections for vacuum polarization and relativistic corrections. It should be also taken into account that the formation of hydrogen mesic molecules occurs in various states of the hyperfine structure. For example, the energy level (1,1) splits into several sublevels due to the interaction of the spins of the particles and the orbital moment of the mesomolecule. The rates of formation of mesomolecules in each of the states of the hyperfine structure have their own values. Therefore, the calculation of the hyperfine structure of the excited states of mesomolecules is an important task. Work in this direction is in progress.

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