Nonrelativistic energy spectra of three-particle systems calculated in the adiabatic approach by using finite difference method

P. Danev, H. Tonchev
Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences,
blvd. Tsarigradsko ch. 72, Sofia 1142, Bulgaria

Three-particle systems

The precise spectroscopy of light atomic and molecular systems gives us new insides in the fundamental laws and physical constants of nature [1, 2]. From theoretical point of view, development of accurate techniques like adiabatic and variational methods give us the tools to compute different atomic quantities with the needed precision [3].
The nonrelativistic Hamiltonian of a three-particle system in atomic units is

$$H = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + \frac{\mathbf{p}_3^2}{2m_3} + \frac{Z_1 Z_3}{r_1} + \frac{Z_2 Z_3}{r_2} + \frac{Z_1 Z_2}{R}$$

Here, $\mathbf{p}_i, m_i$, and $Z_i, i = 1, 2, 3$ are the particles momentum, mass, and charge and the distances between them are r_1, r_2, and $R = |\mathbf{r}_1 - \mathbf{r}_2|$ as shown on Fig. 1

Spheroidal coordinates

In the center-of-mass frame, in a coordinate system co-rotating with the plane containing the three particles, by using the following transformations:

$$\lambda = (r_1 + r_2)/R, \qquad 1 \le \lambda < \infty$$
$$\mu = (r_1 - r_2)/R, \quad -1 \le \mu \le 1$$
$$dV = \frac{R^3}{8}(\lambda^2 - \mu^2)\lambda d\mu d\varphi$$
$$M = \frac{m_3(m_1 + m_2)}{(m_1 + m_2 + m_3)}$$

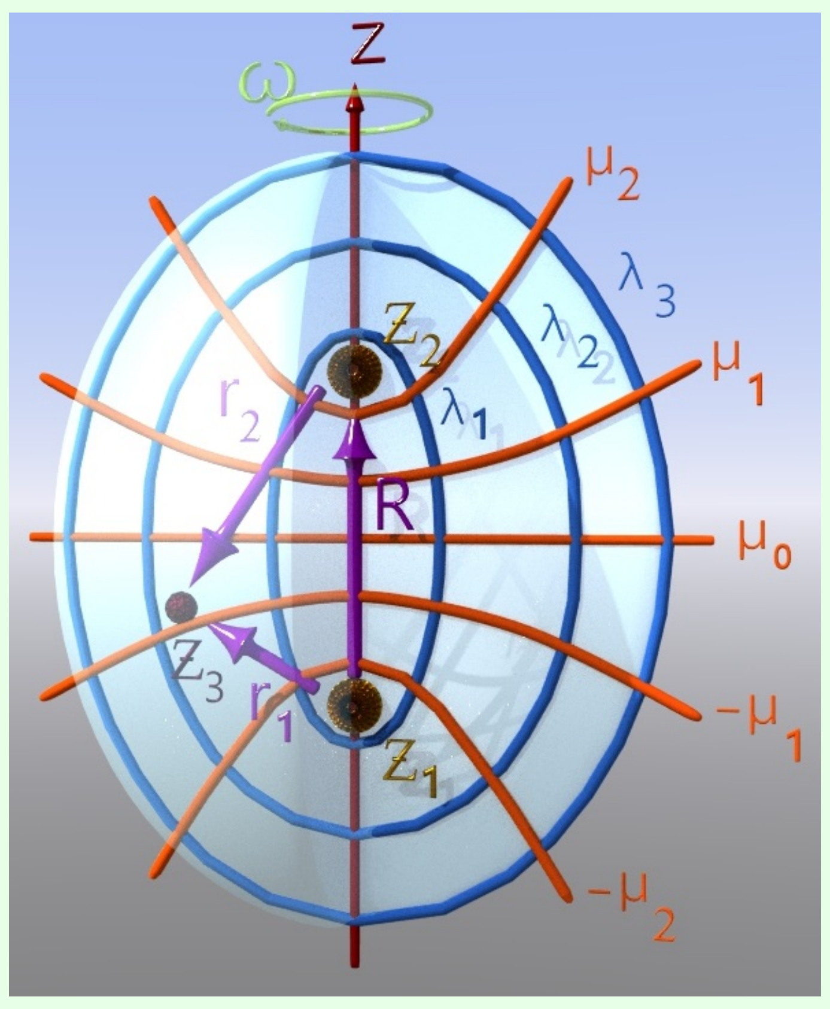

Figure 1: Three-particle system in prolate spheroidal coordinates.

The Hamiltonian can be written in spheroidal coordinates [4]:

$$H^{sph} = \frac{-2}{MR^2(\lambda^2 - \mu^2)} \left[\frac{\partial}{\partial \lambda}(\lambda^2 - 1)\frac{\partial}{\partial \lambda} + \frac{\partial}{\partial \mu}(1 - \mu^2)\frac{\partial}{\partial \mu} - \frac{m^2(\lambda^2 - \mu^2)}{(\lambda^2 - 1)(1 - \mu^2)} \right] + \frac{2 Z_1 Z_3}{R(\lambda^2 - \mu^2)} \left[\lambda \left(\frac{Z_2}{Z_1} + 1 \right) + \mu \left(\frac{Z_2}{Z_1} - 1 \right) \right]$$

The electronic terms $\varepsilon^{m,n_\lambda,n_\mu}$ are found by solving

$$H^{sph} \Phi^{m,n_\lambda,n_\mu}(R; \lambda, \mu) = \varepsilon^{m,n_\lambda,n_\mu} \Phi^{m,n_\lambda,n_\mu}(R; \lambda, \mu).$$

The separation constant $m = 0, 1, 2, ...$ is a solution to the equation $(d^2\Omega/d\omega^2) + m^2\Omega = 0, \quad 0 \le \omega \le 2\pi$.
The total electronic wavefunction is given by $\phi^{m,n_\lambda,n_\mu}(R; \lambda, \mu, \omega) = \Phi^{m,n_\lambda,n_\mu}(R; \lambda, \mu)\frac{\exp^{\pm im\omega}}{\sqrt{2\pi}}$.

Finite difference method with logarithmic stencil

The wavefunctions $\Phi^{m,n_\lambda,n_\mu}(R; \lambda, \mu)$ and the corresponding eigenvalues $\varepsilon^{m,n_\lambda,n_\mu}$ for a number of low-excited electronic states with quantum numbers (m, n_λ, n_μ) are found by a two-dimensional finite difference method [5]. As an alternative to other calculations, to increase the precision, we use a logarithmic stencil. The N point stencil coefficients $a_i, i = 0, .., N-1$ for at the point $x_j = \alpha^{h_j}, h_j = h_0 + j\Delta$ are calculated by solving the system:

$$\begin{pmatrix} 1 & 1 & ... & 1 \\ \alpha^{p\Delta} - 1 & \alpha^{(p+1)\Delta} - 1 & ... & \alpha^{(p+N-1)\Delta} - 1 \\ & ... & ... & ... \\ (\alpha^{p\Delta} - 1)^{N-1} & (\alpha^{(p+1)\Delta} - 1)^{N-1} & ... & (\alpha^{(p+N-1)\Delta} - 1)^{N-1} \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ ... \\ a_{N-1} \end{pmatrix} = \frac{d!}{\alpha^{h_j}} \begin{pmatrix} \delta_{0d} \\ \delta_{1d} \\ ... \\ \delta_{N-1d} \end{pmatrix}$$

For example, to implement a five point central logarithmic stencil, we have to set the following numerical values in the equation above: $N = 5$ and $p = -2$. In this case the d^{th} order derivative of the function $f(x_j)$ is $f(x_j)^{(d)} = \sum_{k=0}^{4} a_k f(x_{j-2+k})$.

Solving electronic Schrödinger equation

The electronic wavefunctions and the corresponding eigenvalues for systems with charges $(Z_1 = 1, Z_2 = 1, Z_3 = -1)$ and $(Z_1 = 2, Z_2 = -1, Z_3 = -1)$ have been calculated. A few examples with both equally spaced (ES) and logarithmic stencil and comparison with existing results are given in the table.

$E, a.u.$ (H_2^+ like)		$E, a.u.$ ($\bar{p}$He like)	
$1s\sigma_g$		1σ	
−1.1026343945244	[ES]	− 1.5093601913	[ES]
−1.1026342144924	$[\mathrm{Log}_{10}]$	− 1.5093584825	$[\mathrm{Log}_{10}]$
−1.102634214497	Ref. [5]	− 1.5093585	Ref. [7]
−1.1026342144949	Ref. [6]		
$2p\sigma_u$		2σ	
−0.6675342981312	[ES]	− 0.2505320492	[ES]
−0.6675343922038	$[\mathrm{Log}_{10}]$	− 0.2505328701	$[\mathrm{Log}_{10}]$
−0.667534392205	Ref. [5]	− 0.2505329	Ref. [7]
−0.6675343922024	Ref. [6]		

Table 1: Energies, in atomic units, of the first electronic states of H_2^+ and $\bar{p}$He like systems at R = 2 a.u.

Nonrelativistic energy spectra

The nonrelativistic energy $E_{\nu J}$ for states, with vibrational and rotational quantum numbers ν and J, of a three-particle system are found in the adiabatic approach by solving a system of eigenvalue problems [4]:

$$\left\{ \frac{d^2}{dR^2} + 2ME_{\nu J} - U_{ii}^J(R) \right\} \chi_i(R) = \sum_{i \ne j}^{\infty} U_{ij}(R)\chi_j(R),$$
$$U_{ij} = (J(J+1) - 2m + 2MZ_1Z_2R)/R^2 + U_{ii}(R), \quad i, j \equiv (m, n_\lambda, n_\mu).$$

The potential $U_{ij}(R)$ is a combination of matrix elements $U_{ij}^k(R) = U_{ij}^k(R; \phi^i, \phi^j, d\phi^i/dR, d\phi^i/dR, \varepsilon^i, \varepsilon^j, d\varepsilon^i/dR, d\varepsilon^j/dR)$ as shown for example in [4]. When the electronic state mixing is ignored $(U_{ij}(R) = 0, \quad i \ne j)$ and $U_{ii}(R)$ includes only the electronic terms ε^i, the Born-Oppenheimer (BO) approximation is obtained. The diagonal matrix elements $U_{ii}(R)$ for lower electronic states of H_2^+ and $\bar{p}$He are computed by the finite difference method with logarithmic stencil.

State	$E, a.u.$		
(ν, J)	BO	DC	Ref. [8]
	H_2^+		
(0,0)	−0.597397	−0.597300	−0.597139063079
(0,1)	−0.597131	−0.597035	−0.596873738784
(1,0)	−0.587410	−0.587313	−0.587155679096
	$\bar{p}$He		
(0,38)	−2.724341	−2.724101	−2.72412478
(0,36)	−2.886792	−2.886490	−2.88668236
(5,36)	−2.643387	−2.643203	−2.64324803

Table 2: Nonrelativistic energies in atomic units of the H_2^+ and $\bar{p}$He states and $(\nu = 1, J = 0)$ in Born-Oppenheimer approximation (BO) and with diagonal adiabatic corrections (DC).

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