



Highly accurate calculation of the resonances in the Stark effect in hydrogen



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ABSTRACT

We obtained accurate resonances for the Stark effect in hydrogen by means of three independent methods. Two of them are based on complex rotation of the coordinates and diagonalization of the Hamiltonian matrix (CRLM and CRCH). The other one is based on the Riccati equations for the logarithmic derivatives of factors of the wavefunction (RPM). The latter approach enabled us to obtain the most accurate results and extremely sharp resonances.

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1. Introduction

The Stark effect in hydrogen is an old problem in atomic spectroscopy and one of the first triumphs of wave mechanics [1,2] (and references therein). The Schrödinger equation is separable in parabolic and squared parabolic coordinates which facilitates the application of most approximate methods [2].

In a recent paper Fernández-Menchero and Summers [3] obtained the complex eigenvalues and eigenfunctions of the Hamiltonian operator for the hydrogen atom in a uniform electric field. They resorted to the Lagrange-mesh basis set, proposed by Lin and Ho [4] for the treatment of the Yukawa potential in a uniform electric field, and the complex-rotation method [5]. They compared their results with those obtained by Lin and Ho [4], Kolosov [6], Rao and Li [7] and Ivanov [8] and overlooked the earlier impressive calculations of Benassi and Grecchi [9] and the accurate results obtained by Fernández [10]. Benassi and Grecchi resorted to complex scaling and a basis set of confluent hypergeometric functions that is suitable when the Schrödinger equation is written in squared parabolic coordinates. On the other hand, Fernández applied the straightforward Riccati–Padé method (RPM) that does not require the use of complex coordinates.

The purpose of this paper is to calculate the Stark resonances as accurately as possible by means of the methods proposed by Fernández-Menchero and Summers [3], Benassi and Grecchi [9] and Fernández [10] and compare the results with those obtained by the authors already mentioned and also by Damburg and Kolosov [11]. There is a vast literature on the hydrogen atom in a uniform electric field but we restrict present discussion to some of the available calculations that we deem are suitable for comparison.

In Section 2 we outline the main ideas about separating the Schrödinger equation in parabolic and squared parabolic coordinates. In Sections 3–5 we briefly introduce the methods of Fernández-Menchero and Summers [3], Benassi and Grecchi [9] and Fernández [10], respectively. In Section 6 we compare the results of various approaches and in Section 7 we summarize the main results and draw conclusions.

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2. Stark effect in hydrogen

The Schrödinger equation in atomic units is

$$H\psi = E\psi$$

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r} + Fz, \quad (1)$$

where F is the intensity of the uniform electric field assumed to be directed along the z axis.

This equation is separable in parabolic coordinates

$$x = \sqrt{\xi\eta} \cos \phi, \quad y = \sqrt{\xi\eta} \sin \phi, \quad z = \frac{\xi - \eta}{2}$$

$$\xi \geq 0, \quad \eta \geq 0, \quad 0 \leq \phi \leq 2\pi. \quad (2)$$

If we write

$$\psi(x, y, z) = (\xi\eta)^{-1/2} u(\xi)v(\eta)e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots, \quad (3)$$

then we obtain two equations of the form

$$\left(\frac{d^2}{dx^2} + \frac{1-m^2}{4x^2} + \frac{E}{2} - \sigma \frac{F}{4}x + \frac{A_\sigma}{x} \right) \Phi(x) = 0, \quad (4)$$

where $\sigma = \pm 1$ and $A_+ = A$ and $A_- = 1 - A$ are separation constants. When $\sigma = 1$, $x = \xi$ and $\Phi(\xi) = u(\xi)$; when $\sigma = -1$, $x = \eta$ and $\Phi(\eta) = v(\eta)$.

The Schrödinger equation (1) is also separable in squared parabolic coordinates

$$x = \mu\nu \cos \phi, \quad y = \mu\nu \sin \phi, \quad z = \frac{\mu^2 - \nu^2}{2}$$

$$\mu \geq 0, \quad \nu \geq 0, \quad 0 \leq \phi \leq 2\pi. \quad (5)$$

If in this case we write

$$\psi(x, y, z) = (\mu\nu)^{-1/2} u(\mu)v(\nu)e^{im\phi}, \quad (6)$$

then we obtain two equations of the form

$$\left(\frac{d^2}{dx^2} + \frac{1-4m^2}{4x^2} + 2Ex^2 - \sigma Fx^4 + Z_\sigma \right) \Phi(x) = 0, \quad (7)$$

where, $\sigma = \pm 1$ and $Z_+ = Z$ and $Z_- = 4 - Z$ are the separation constants. When $\sigma = 1$, $x = \mu$ and $\Phi(\mu) = u(\mu)$; when $\sigma = -1$, $x = \nu$ and $\Phi(\nu) = v(\nu)$.

The solutions to the equations in either set of coordinates are commonly labeled by the quantum numbers $n_1, n_2 = 0, 1, 2, \dots$ and $m = 0, 1, \dots$, and the notation $|n_1, n_2, m\rangle$ is suitable for referring to them. We will sometimes resort to the principal quantum number $n = n_1 + n_2 + |m| + 1$ to denote a set of states. Obviously, m is the only good quantum number; the other ones refer to the states of the hydrogen atom and are valid when $F = 0$.

3. Complex rotation and Laguerre-mesh basis set

Fernández-Menchero and Summers [3] decided to treat the Schrödinger equation as nonseparable. The Hamiltonian operator in parabolic coordinates reads

$$H = -\frac{2}{\xi + \eta} \left[\frac{\partial}{\partial \xi} \left(\xi \frac{\partial}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left(\eta \frac{\partial}{\partial \eta} \right) \right] - \frac{1}{2\xi\eta} \frac{\partial^2}{\partial \phi^2} - \frac{2}{\xi + \eta} + F \frac{\xi - \eta}{2}, \quad (8)$$

and the authors proposed the variational ansatz

$$\psi(\xi, \eta, \phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \sum_{k=1}^N \sum_{l=1}^N c_{klm} e^{-\frac{\xi+\eta}{2}} (\xi\eta)^{\frac{|m|}{2}} \Lambda_{Nk}(\xi) \Lambda_{Nl}(\eta) \quad (9)$$

$$\Lambda_{Nk}(x) = (-1)^k \sqrt{x_k} \frac{L_N(x)}{x - x_k}, \quad (10)$$

where $L_N(x)$ is the Laguerre polynomial of degree N and x_k its k th zero. In order to obtain the resonances they resorted to the well-known complex rotation method [5] that in this case is given by the transformation $(\xi, \eta) \rightarrow (e^{i\theta}\xi, e^{i\theta}\eta)$, where θ is the rotation angle. The eigenvalues and expansion coefficients are given by the secular equation

$$(\mathbf{H} - E\mathbf{S})\mathbf{C} = 0, \quad (11)$$

where the elements of the $N^2 \times N^2$ matrices \mathbf{H} and \mathbf{S} are explicitly shown elsewhere [3] and the elements of the column vector \mathbf{C} are the coefficients c_{klm} . Note that the integrals appearing in the matrix elements of both \mathbf{H} and \mathbf{S} should be calculated numerically and when we increase N we have to calculate all those integrals again. For brevity we will call this method CRLM.

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