On recent calculations of resonances for the Stark effect in hydrogen

Francisco M. Fernández and Javier García
INIFTA (UNLP, CCT La Plata-CONICET), Blvd. 113 y 64 S/N,
Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina

We show that the resonances of the Stark effect in hydrogen reported in Phys. Rev. A 88, 022509 (2013) are considerably less accurate than the number of digits appear to suggest. In particular, the imaginary part of the lowest resonance is several orders of magnitude greater than it should be. We compare the results of that paper with those provided by the Riccati-Padé method, perturbation theory and an asymptotic expansion for the resonance width. The inaccuracy of those results can be traced back to the lack of precision in the calculation of the matrix elements of the secular equation. We carry out a more accurate calculation with the same method and show that the agreement with earlier results of other authors is greatly improved.

PACS numbers: 31.15.ac, 32.60.+i, 52.70.Ds

In a recent paper Fernández-Menchero and Summers obtained the complex eigenvalues and eigenfunctions of the Hamiltonian operator for the hydrogen atom in a uniform electric field. They resorted to the Laguerre-mesh basis set proposed by Lin and Ho for the treatment of the Yukawa potential in a uniform electric field and the complex-rotation method. For brevity we will refer to this method as CRLM from now on. They compared their results with those obtained by Lin and Ho, Kolosov, Rao and Li and Ivanov and overlooked the earlier impressive calculations of Benassi and Grecchi and the accurate results obtained by Fernández. Benassi and Grecchi resorted to 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 Riccati-Padé method (RPM) that does not require the use of complex coordinates.

The results of Fernández-Menchero and Summers for the excited states deviate somewhat from the other ones that appear to be in closer agreement among them. On the other hand, they were unable to compare their estimate of the lowest resonance for the field strength $F = 0.005 \text{ a.u}$ because there does not appear to be any independent calculation available.

Fernández-Menchero and Summers stressed that perturbation theory (PT) is unsound because the Stark effect does not fulfill the conditions for the application of such an approach. They are obviously unaware of the fact that the straightforward perturbation series is asymptotic to the real part of the resonances which in some cases can be obtained with reasonable accuracy by judicious truncation to a suitable number of terms. Besides, Adams calculated the real and imaginary parts of the lowest resonance by means of analytic continuation and Padé summation and Jentschura resorted to Borel-Padé summation for obtaining several selected resonances.

The purpose of this comment is to show that the resonances reported by those authors are considerably less accurate than the number of digits appear to indicate while the width for the lowest resonance is several orders of magnitude greater than it should be. The inaccuracy of their results, which accounts for the discrepancy with respect to those of other authors mentioned above, can be traced back to the lack of precision in the calculation of the matrix elements in
the secular equation. To verify this conjecture we carry out a more accurate calculation with the CRLM. In addition to it, we also resort to the RPM, PT and the asymptotic formula for the width of the lowest resonance derived by Benassi and Grecchi\[7\].

The Schrödinger equation in atomic units is

$$H\psi = E\psi$$

$$H = \frac{1}{2} \nabla^2 + \frac{1}{r} - F z,$$  \hspace{1cm} (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

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

$$\xi \geq 0, \quad \eta \geq 0, \quad 0 \leq \phi \leq 2\pi,$$  \hspace{1cm} (2)

but the authors decided to treat the Schrödinger equation for the resulting Hamiltonian

$$H = -\frac{2}{\xi + \eta} \left[ \frac{\partial}{\partial \xi} \left( \xi \frac{\partial}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left( \eta \frac{\partial}{\partial \eta} \right) \right] - \frac{1}{2} \frac{\partial^2}{\xi \eta \partial \phi^2} - \frac{2}{\xi + \eta} + F \frac{\xi - \eta}{2},$$  \hspace{1cm} (3)

as nonseparable. To this end they proposed the variational ansatz

$$\psi(\xi, \eta, \phi) = \frac{1}{\sqrt{2\pi}} \sum_{k=1}^{N} \sum_{l=1}^{N} c_{klm} e^{-\frac{i}{4} (\xi \eta)^{\frac{m}{2}}} \Lambda_{Nk}(\xi) \Lambda_{Nl}(\eta)$$

$$\Lambda_{Nk}(x) = (-1)^k \sqrt{\frac{L_N(x)}{x - x_k}},$$  \hspace{1cm} (4)

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\[3\] that in this case is given by the particular complex-scaling transformation $(\xi, \eta) \rightarrow (e^{i\theta} \xi, e^{i\theta} \eta)$. The eigenvalues and expansion coefficients are given by the secular equation

$$(H - ES)C = 0,$$  \hspace{1cm} (6)

where the elements of the $N^2 \times N^2$ matrices $H$ and $S$ are explicitly shown elsewhere\[1\] and the elements of the column vector $C$ are the coefficients $c_{klm}$. Note that the integrals appearing in the matrix elements of both $H$ and $S$ should be calculated numerically and when we increase $N$ we have to calculate all those integrals again.

On the other hand, in order to apply the RPM we write

$$\psi(\xi, \eta, \phi) = (\xi \eta)^{-1/2} u(\xi) v(\eta) e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots,$$  \hspace{1cm} (7)

and obtain two equations of the form

$$\left( \frac{d^2}{dx^2} + \frac{1 - m^2}{4x^2} + \frac{E}{2} - \sigma \frac{F}{4} x + \frac{A_\sigma}{x} \right) \Phi(x) = 0,$$  \hspace{1cm} (8)

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 regularized logarithmic derivative

\[ f(x) = \frac{s}{x} \frac{\Phi'(x)}{\Phi(x)}, \quad s = \frac{|m| + 1}{2}, \]  

(9)

can be expanded in a Taylor series

\[ f(x) = \sum_{j=0}^{\infty} f_j x^j, \]  

(10)

where the coefficients \( f_j \) are polynomial functions of \( E \) and \( A \). The details of the method are outlined elsewhere\cite{8}; here it suffices to say that we construct the Hankel determinant

\[
H_D^d(E, A, F) = \begin{vmatrix}
    f_{d+1} & f_{d+2} & \cdots & f_{D+d} \\
    f_{d+2} & f_{d+3} & \cdots & f_{D+d+1} \\
    \vdots & \vdots & \ddots & \vdots \\
    f_{D+d} & f_{D+d+1} & \cdots & f_{2D+d-1}
\end{vmatrix},
\]  

(11)

where \( D = 2, 3, \ldots \) and \( d = 0, 1, \ldots \) is kept fixed. The approximate eigenvalues are given by the set of nonlinear equations

\[ H_D^d(E, A, F) = H_D^d(E, A-1, F) = 0. \]  

(12)

The main advantage of the RPM is the enormous rate of convergence of the approximate eigenvalues \( E^{[D,d]} \) which enables us to obtain very accurate results with determinants of relatively small dimension. However, the great number of roots in the neighborhood of each eigenvalue makes it difficult to find the optimal sequence that converges to it. We can mention two other disadvantages of the RPM: first, it only applies to separable problems; second, it does not give the eigenfunction but its logarithmic derivative. Consequently, it is not practical for the calculation of physical properties that are defined in terms of the eigenfunctions. In spite of these disadvantages the RPM is an extremely useful tool to produce accurate results for benchmark purposes in those cases where it can be applied. The Stark effect in hydrogen is one such problem as shown in what follows.

In order to test the rate of convergence we calculate \( \log |(\alpha^{[D+1,d]} - \alpha^{[D,d]}) / \alpha^{[D+1,d]}| \) for \( \alpha = \text{Re}E \) or \( \alpha = \text{Im}E \). Here we restrict ourselves to \( d = 0 \). The results for the lowest resonance when \( F = 0.005 \) shown in Fig. 1 strongly suggest that present RPM calculation may be remarkably accurate.

The converged RPM resonance, truncated to a reasonable number of digits, is shown in Table II together with the CRLM one. The discrepancy between the real parts (1 in \( 10^6 \)) may not appear to be so serious at first sight, but the imaginary parts differ in many orders of magnitude predicting considerably different lifetimes for the same metastable state. Our estimated value of \( \text{Im}E \) is in perfect agreement with the analytic asymptotic formula derived by Benassi and Grecchi\cite{7}:

\[
\text{Im}E \sim -2F^{-1}e^{-2j(3F)} \left( 1 - 8.916F + 25.57F^2 + O(F^3) \right),
\]  

(13)

also shown in Table II. From a practical point of view this state may be considered stable because there is no experimental way of determining such a long lifetime. However, it is worth stressing the fact that the RPM enables us to calculate it.
In principle we expect that a properly truncated perturbation series will exhibit an accuracy of the order of $|\text{Im} E|$. On summing the first 130 terms of the perturbation series calculated by means of the hypervirial perturbative method\cite{11} we obtained the following result:

\[
E^{PT} = -0.5000562847937929693317739476914328819632509273188913726 \\
\text{Re}E^{RPM} = -0.50005628479379296933177394769143288196325092731889137262135731287267
\] (14)

that agrees with the RPM one to the last digit. Obviously, this result is more accurate than the CRLM one and most probably than any other calculation based on diagonalization and complex rotation.

In our opinion it is quite difficult to obtain so small imaginary parts of resonances by means of standard methods based on diagonalization and complex rotation which may probably be the reason why it was not included in the earlier calculations chosen for comparison\cite{2,4–6}. This fact clearly shows that the RPM is a most valuable tool for testing other calculations on separable problems.

The discrepancy between the results of Fernández-Menchero and Summers and those chosen for comparison is probably due to insufficient accuracy in the calculation of the CRLM integrals. In order to test this conjecture we calculated those integrals with greater accuracy (15 digits) by means of a computer algebra system that enables, in principle, unlimited precision and then solved the CRLM secular equation in the usual way for $N = 30$. Present CRLM lowest resonance, also shown in Table I is in perfect agreement with the RPM result. Table II shows that present CRLM resonances are in better agreement with those of the other authors\cite{2,4–6} (for brevity we only show the results of Lin and Ho\cite{2}). In passing we mention that the width of the state $|210\rangle$ calculated by the other authors\cite{2,4–6} was incorrectly transcribed by Fernández-Menchero and Summers.

Typically the minimum value of $|\text{Im} E|$ that one can calculate by a diagonalization method is of the order of the accuracy of the eigenvalue. The accuracy of the results of Fernández-Menchero and Summers is roughly of the order of $10^{-6}$ which is the reason why they estimated such width for the lowest resonance. If we take into account that other physical effects (magnetic-field perturbation, fine structure, etc.) already mentioned by the authors are of the order of $10^{-4}$ we conclude that the lack of precision just mentioned may probably not be serious for most practical applications. However, we have clearly shown that the CRLM results can be considerably improved by increasing the accuracy of the integrals that provide the elements of the matrices in the secular equation.

We add that PT and the asymptotic formula\cite{7} are remarkably useful for the calculation of extremely sharp resonances. Unfortunately, while we have the perturbation series for all the resonances\cite{11} the asymptotic formula is only available for the lowest one\cite{7}. It should be mentioned that, even for the small field intensity considered here, PT is not so accurate for higher resonances unless one resorts to a suitable summation method\cite{9,10}. On the other hand, the RPM yields eigenvalues of similar accuracy to the one shown here.

\* Electronic address: fernande@quimica.unlp.edu.ar

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TABLE I: Lowest resonance for $F = 0.005$

|                | Re$E$       | $\Gamma$                        |
|----------------|-------------|---------------------------------|
| CRLM [1]       | $-0.5000553416$ | $0.8944475605 \times 10^{-7}$  |
| Present CRLM   | $-0.500056284793$ | $< 1 \times 10^{-13}$          |
| RPM            | $-0.5000562847938$ | $9.49802741674 \times 10^{-56}$ |
| Asymptotic     |             | $9.4983 \times 10^{-56}$       |

TABLE II: Resonances for $F = 0.005$

|                | Re$E$       | $\Gamma$                        |
|----------------|-------------|---------------------------------|
| $|2 - 1 0\rangle$ |             |                                 |
| CRLM [1]       | $-0.1426203564$ | $1.057292433 \times 10^{-4}$   |
| Present CRLM   | $-0.1426186076$ | $1.059444711 \times 10^{-4}$  |
| Ref. [2]       | $-0.1426186076$ | $1.059444711 \times 10^{-4}$  |
| $|2 1 0\rangle$ |             |                                 |
| CRLM [1]       | $-0.1120633027$ | $4.930560122 \times 10^{-6}$   |
| Present CRLM   | $-0.1120619240$ | $5.72936843930 \times 10^{-6}$ |
| Ref. [2]       | $-0.1120619240$ | $5.72939466 \times 10^{-6}$   |
| $|2 0 1\rangle$ |             |                                 |
| CRLM [1]       | $-0.127146612703972$ | $2.615285446 \times 10^{-5}$  |
| Present CRLM   | $-0.127146612703972$ | $2.615285446 \times 10^{-5}$  |
| Ref. [4]       | $-0.127146612703972$ | $2.615285446 \times 10^{-5}$  |

FIG. 1: Convergence of the RPM for the lowest resonance when $F = 0.005$