Comment on “Bidimensional bound states for charged polar nanoparticles”

Paolo Amore
Facultad de Ciencias, CUICBAS, Universidad de Colima,
Bernal Díaz del Castillo 340, Colima, Colima, Mexico

Francisco M. Fernández
INIFTA (CONICET), División Química Teórica,
Blvd. 113 y 64 (S/N), Sucursal 4, Casilla de Correo 16,
1900 La Plata, Argentina

June 16, 2020

Abstract

In a recent paper Castellanos-Jaramillo and Castellanos-Moreno proposed a simple quantum-mechanical model for an electron in the vicinity of an ionized nanostructure with a permanent electric dipole. They chose the interaction of the electron with the charge and the dipole in such a way that the resulting Schrödinger equation is separable into radial and angular parts. In this comment we show that those authors did not solve the angular eigenvalue equation with proper periodic boundary conditions and that they also made a mistake in the elimination of the first derivative in the radial equation. Such errors invalidate their results of the Einstein coefficients for the \((GaAs)_3\) system considered.

*paolo.amore@gmail.com
†framfer@gmail.com
1 Introduction

In a recent paper Castellanos-Jaramillo and Castellanos-Moreno [1] (CC from now on) put forward a simple quantum-mechanical model for an electron in the vicinity of an ionized nanostructure with a permanent electric dipole. They chose the interaction of the electron with the charge and the dipole in such a way that the resulting Schrödinger equation is separable into radial and angular parts. At first they state that the solutions to the latter eigenvalue equation should be periodic of period $2\pi$ but later they turn to somewhat different boundary conditions.

The purpose of this paper is to solve the Schrödinger equation for the model proposed by those authors with true periodic boundary conditions in order to determine to which extent this change may affect their results. In section 2 we transform the Schrödinger equation into a dimensionless eigenvalue equation and calculate the eigenvalues of the angular part when the eigenfunctions a periodic functions of period $2\pi$. We compare present results with those obtained by CC. Finally, in section 2 we discuss the results and draw conclusions.

2 The model

The model Hamiltonian chosen by CC [1] is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \frac{qQ}{4\pi\epsilon_0 \vert \mathbf{r} - \mathbf{r}_0 \vert} + \frac{qD \cos \theta}{4\pi\epsilon_0 \vert \mathbf{r} - \mathbf{r}_0 \vert^2} + Be^{-r^2/\sigma^2}$$

(1)

where $\mathbf{r} = (x, y)$, $q = -e$ and $Q = Ze$ are the charges of the electron and the nanostructure, respectively, $D$ is the dipole of the latter, $\epsilon_0$ is the vacuum permittivity and $\sigma$ is related to the radius of the nanoparticle (note that we write $\sigma^2$ instead of $\sigma$ in the Gaussian term).

In order to facilitate the treatment of the Schrödinger equation it is convenient to transform it into a dimensionless eigenvalue equation. CC do it in a rather confuse way; therefore, we proceed differently. By means of the change
of variables

\[ r = L \rho, \quad L = -\frac{4 \pi \epsilon_0 \hbar^2}{mqQ} \]  

(2)

the Schrödinger equation \( H \psi = E \psi \) becomes

\[ H' \Phi = E \Phi \]

\[ H' = -\frac{1}{2} \nabla^2 - \frac{1}{|\rho - \rho_0|} + \frac{\xi \cos \theta}{|\rho - \rho_0|^2} + Ae^{-\alpha^2 \rho^2} \]

\[ \xi = \frac{mqD}{4 \pi \epsilon_0 \hbar^2}, \quad A = \frac{mL^2 B}{\hbar^2}, \quad \alpha = \frac{L}{\sigma}, \quad \rho_0 = \frac{r_0}{L} \]

\[ E = \frac{mL^2E}{\hbar^2} \]  

(3)

Following CC we choose \( r_0 = 0 \) so that the equation is separable in polar coordinates

\[ H = -\frac{1}{2 \rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} - \frac{1}{2 \rho^2} \frac{\partial^2}{\partial \theta^2} - \frac{1}{\rho} + \frac{\xi \cos \theta}{\rho^2} + Ae^{-\alpha^2 \rho^2} \]  

(4)

Upon setting \( \Phi(\rho, \theta) = f(\rho)g(\theta) \) and choosing \( g(\theta) \) so that

\[ \left( -\frac{1}{2} \frac{d^2}{d \theta^2} + \frac{\xi \cos \theta}{\rho^2} \right) g = \lambda g \]  

(5)

then

\[ \left( -\frac{1}{2 \rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} - \frac{1}{\rho} + \frac{\lambda}{\rho^2} + Ae^{-\alpha^2 \rho^2} \right) f = E f \]  

(6)

CC first state that the solutions to equation (5) should be periodic of period 2\( \pi \) \((g(\theta + 2\pi) = g(\theta))\) but later they turn to different boundary conditions.

The eigenvalue equation (5) with periodic boundary conditions has discrete eigenvalues \( \lambda = \lambda_m, \quad m = 0, 1, \ldots \) \((\lambda_0 < \lambda_1 < \ldots)\) and those of (6) will be \( \mathcal{E}_{nm}, \quad n = 0, 1, \ldots \) In order to compare present results with those of CC \([1]\) note that

\[ 2\xi = gp \quad \text{and} \quad 2\lambda = \lambda^{CC}. \]

For \( \lambda \geq 0 \) the behaviour of the solution to the radial equation (6) at the origin is \( f(\rho) \approx \rho^{-\sqrt{2\lambda}} \). On the other hand, when \( \lambda < 0 \) this function goes through infinitely many zeroes when \( \rho \to 0 \) and the spectrum becomes continuous and unbounded from below. In order to overcome this difficulty one may define a self-adjoint extension of the Hamiltonian by specifying a particular boundary condition at \( \rho = 0 \) \([2]\). We will not discuss this aspect of the problem in detail.
here because we will not need to solve the radial equation. In order to be square integrable the behaviour of the solution to the radial equation at infinity should be \( f(\rho) \approx e^{-\sqrt{-2E}\rho} \). Consequently, there are simple suitable solutions \( \Phi_{nm}(\rho, \theta) \) for the bound-states of the Schrödinger equation when \( \lambda \geq 0 \) and \( E < 0 \) and some additional care is required for \( \lambda < 0 \). CC [1] bypassed the problem of negative eigenvalues \( \lambda_m \) by postulating that they are physically unacceptable.

For large values of \( \xi \) the eigenvalues of the angular equation behave as

\[
\lambda_m \approx -\xi + \sqrt{\xi}\left(m + \frac{1}{2}\right) + \mathcal{O}(1) \tag{7}
\]

Therefore, there are values \( \xi = \xi_{m_c} \) such that \( \lambda_{m_c} = 0 \) and, consequently, \( \lambda_m < 0 \) for all \( m < m_c \). In order to obtain the critical values \( \xi_{m_c} \) it is only necessary to solve equation (5) for \( \lambda = 0 \).

The even and odd solutions to the angular equation (5) can be expanded in Fourier series of period \( 2\pi \)

\[
g^e(\theta) = \sum_{j=0}^{\infty} a_j \cos(j\theta)
\]

\[
g^o(\theta) = \sum_{j=1}^{\infty} b_j \sin(j\theta) \tag{8}
\]

respectively. The coefficients \( a_j \) and \( b_j \) can be easily obtained as polynomial functions of \( \lambda \) from simple three-term recurrence relations:

\[
2\lambda a_0 - \xi a_1 = 0, \quad (2\lambda - 1) a_1 - \xi (2a_0 + a_2) = 0
\]

\[
(2\lambda - n^2) a_n - \xi (a_{n-1} + a_{n+1}) , \quad n = 2, 3, \ldots
\]

\[
(2\lambda - n^2) b_n - \xi (b_{n-1} + b_{n+1}) , \quad n = 1, 2, \ldots , \quad b_0 = 0 \tag{9}
\]

From the termination conditions \( a_N(\lambda, \xi) = 0 \) or \( b_N(\lambda, \xi) = 0 \) we obtain \( \lambda(\xi) \) or \( \xi(\lambda) \) with any desired accuracy provided that \( N \) is large enough. Setting \( \lambda = 0 \) we obtain the critical values \( \xi_{m_c} \) mentioned above; the first of them are \( \xi_0 = 0 \), \( \xi_1 = 1.894922593 \), \( \xi_2 = 5.324657803 \). Note that \( \lambda_0(\xi) \) is negative for all \( \xi > 0 \). Fig. [1] shows the first eigenvalues \( \lambda_m \) for a range of \( \xi \) values.

CC [1] chose a set of model parameters that appear to be suitable for \((GaAs)_3\) and obtained \( 4\wp = 0.8147872 \). Table II shows that our results \( \lambda^{CC} = \)
2\lambda for \xi = 0.8147872/8 do not agree with those in Table 1 of CC. The reason is probably that CC did not use proper periodic angular eigenfunctions; note that they claim to have used equation (33) \((y(z) = e^{i\nu z}\phi(z))\) instead of the correct one \(y(z) = e^{i\nu z}\phi(z)\).

If we define \(z = \theta/2\) then \(u(z) = g(2z)\) is a periodic function of period \(\pi\) that we may rewrite as \(u(z) = e^{i\nu z}v(z)\), where \(v(z)\) is periodic of period \(\pi\). Note that \(u(z)\) will be periodic of period \(\pi\) provided that \(\nu = 0, 2, \ldots\). If we solve the eigenvalue equation for \(v(z)\) by means of its expansion in the basis set \(\phi_j = \frac{1}{\sqrt{\pi}} e^{2ijz}, j = 0 \pm 1, \pm 2, \ldots\) we obtain the eigenvalues \(\lambda_m(\nu)\) shown in figure 2. Note that \(\lambda_m(\nu = 0) = \lambda_m(\nu = 2)\) as expected and the interesting fact that the eigenvalues exhibit avoided crossings at \(\nu = 1\). The left panel shows the first 6 eigenvalues. If we just consider the first two ones (right panel) then we realize that the discontinuity in CC’s figure 1 may probably come from choosing the lowest eigenvalue for \(0 < \nu < 1\) and the first excited one for \(\nu > 1\).

We now briefly turn to the radial equation. If we write \(f(\rho) = u(\rho)/\sqrt{\rho}\) we obtain

\[ u''(\rho) + \left[ 2E + \frac{2}{\rho} - 2Ae^{a^2\rho^2} - \frac{2\lambda - \frac{1}{4}}{\rho^2} \right] u(\rho) = 0 \quad (10) \]

Note that this expression differs from equation (28) in CC’s paper in the centrifugal term. They obtained \(\lambda^{CC} + 1/4\) while here we have \(\lambda^{CC} - 1/4\). If CC already used their equation (28), then their results for the Einstein coefficients cannot be correct.

### 3 Further comments and conclusions

Throughout this paper we solved the eigenvalue equation for an oversimplified quantum-mechanical model for an electron in the vicinity of an ionized nanostructure with a permanent electric dipole proposed recently [1]. Our results suggest that the authors did not solve the angular part with the intended physical periodic boundary conditions. One may think that there is just a typo in CC’s equation (33) but the fact is that our results, based on actual functions of
period $2\pi$ (present Table 1), do not agree with those in CC’s Table 1.

We do not solve the radial part because it is sufficient to show that CC’s $\lambda$ values are not correct to conclude that their Einstein’s coefficients are surely wrong. However, one can easily show, as we did above, that the centrifugal term in their equations (28) and (29) should be $\frac{\lambda - \frac{1}{4}}{\eta^2}$ instead $\frac{\lambda + \frac{1}{4}}{\eta^2}$. We believe that our analysis is correct and that CC’s results may well be meaningless. For example, the Einstein coefficients calculated by those authors do not correspond with the intended model of $(GaAs)_3$.

Acknowledgements

Paolo Amore acknowledges support from Sistema Nacional de Investigadores (México)

Addendum

After the Comment [3] and Reply [4] were published we could finally reproduce CC’s results [1,4] by simply solving the eigenvalue equation for the Mathieu function as shown by Coisson et al [5]. Table 2 shows $a(\nu)$ for $q = 0.8147872$ and $\nu = 1, 2, 3, 4$. Boldface entries indicate the values of $a(\nu)$ reported by CC [1]. We conjecture that the algorithm used by those authors does not yield the eigenvalues orderly and for that reason they have been picking out the eigenvalues randomly which explains the discontinuity in CC’s figure 1 [1] that does not appear in our more careful calculation given in figure 2 of our comment [3]. Figure 3 shows present results $\lambda(\nu)$ (blue, continuous line) and those given by CC [4] in their reply (red circles). It is clear that the discontinuity in the figure 1 of their first paper [1] is due to a jump from the lowest eigenvalue to the next higher one as conjectured in our Comment [3].

The errors in the calculation of $\lambda$ will obviously affect the results obtained later from the solutions of the radial eigenvalue equation [6].
Table 1: Eigenvalues of the angular eigenvalue equation (5) for $\xi = 0.8147872/8$

| $m$ | $2\lambda_m$            |
|-----|-------------------------|
| 0   | -0.02038332             |
| 1   | 0.9965447876            |
| 2   | 1.016922136             |
| 3   | 4.001380556             |
| 4   | 4.001386528             |
| 5   | 9.000592776             |
| 6   | 9.000592776             |

References

[1] A. Castellanos-Jaramillo and A. Castellanos-Moreno, “Bidimensional bound states for charged polar nanoparticles”, J. Nanopart. Res. 21, 141 (2019).

[2] S. A. Coon and B. R. Holstein, “Anomalies in quantum mechanics: The $1/r^2$ potential”, Am. J. Phys. 70, 513-519 (2002).

[3] P. Amore and F. M. Fernández, “Comment on “Bidimensional bound states for charged polar nanoparticles””, J. Nanopart. Res. 22, 16 (2020).

[4] A. Castellanos-Jaramillo and A. Castellanos-Moreno, “Response to Amore and Fernández”, J. Nanopart. Res. 22, 149 (2020).

[5] R. Coisson, G. Vernizzi, and X. Yang, “Mathieu functions and numerical solutions of the Mathieu equation,” 2009 IEEE International Workshop on Open-source Software for Scientific Computation (OSSC), Guiyang, 2009, pp. 3-10, doi: 10.1109/OSSC.2009.5416839
Table 2: Eigenvalues \( a \) of the Mathieu equation for \( q = 0.8147872 \) and \( \nu = 1, 2, 3, 4 \)

\[
\begin{array}{|c|c|c|c|c|}
\hline
\nu & a & 1.723195887 & 9.033407277 & 9.050089309 & 25.01383463 \\
2 & -0.3109361980 & 3.944835174 & 4.255390446 & 16.02196863 & 16.02234952 \\
3 & 0.1103083812 & 1.723195887 & 9.033407277 & 9.050089309 & 25.01383463 \\
4 & -0.3109361980 & 3.944835174 & 4.255390446 & 16.02196863 & 16.02234952 \\
\hline
\end{array}
\]

Figure 1: Eigenvalues \( \lambda_m \) of the angular equation for a range of \( \xi \) values. The continuous (blue) and broken (red) curves denote even and odd solutions, respectively.
Figure 2: First eigenvalues $\lambda_m(\nu)$ for $\xi = 0.8147872/8$

Figure 3: Present results (blue, continuous line) and those of CC [4] for $\lambda(\nu)$ and $q = 4gp = 0.8147872$. 