

Some Comments on the Hydrogen Atom in a Spherical Enclosure*

V. C. AGUILERA-NAVARRO, E. LEY KOO** and A. H. ZIMMERMAN

Instituto de Física Teórica, São Paulo

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We discuss some properties of the ground state energy solutions for the hydrogen atom in a spherical enclosure. We consider also the application of the many-point Padé approximants to this kind of systems inside a box.

Discutimos algumas propriedades das soluções que correspondem ao estado fundamental de um átomo de hidrogênio dentro de uma caixa esférica. Consideramos também a aplicação dos aproximantes de Padé de muitos pontos para este tipo de sistemas dentro de uma caixa.

1. INTRODUCTION

The hydrogen atom within a spherical box with unpenetrable walls has been investigated in many occasions¹⁻⁴. More recently it has been also considered the hydrogen atom within spherical boxes with penetrable walls⁵.

The application of the Rayleigh-Schrödinger perturbation theory to the hydrogen atom in a spherical box has also been discussed⁶⁻⁹ and, in particular, the ground-state energy up to the fifth order in e^2 has been obtained¹⁰, namely,

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$$E(R) = \pi^2/2R^2 - 2.4377/R - 1.0796/\pi^2 - 1.2112R/\pi^4 - 1.1928R^2/\pi^6 - 0.752R^3/\pi^8 \quad (1)$$

in atomic units. R is the radius of the spherical box. It has been argued¹¹ that this formula can be very useful for the obtention of the ground-state energy for *sufficiently small* R , where the *previous calculations*³ have presented numerical errors (for $R \lesssim 1.4$ a.u.); therefore the perturbation expansion would be useful for the H atom subject to high pressure.

Ley-Koo and Rubinstein⁵ have also improved the numerical calculations by de Groot and Ten Seldam³ even for small R , for the ground state energy of the hydrogen atom in spherical box with unpenetrable walls.

The hydrogen atom enclosed in a spherical box has also been studied in an application of a variational approach to perturbation theory¹².

In section 2, we discuss some properties of the solutions of the hydrogen atom within a spherical box and in section 3 we discuss the application of the many-point Padé approximants to this kind of problem.

2. PROPERTIES OF THE SOLUTIONS

The radial equation for the s-state reads⁵

$$\left(\frac{d^2}{dx^2} + \frac{2}{x} \frac{d}{dx} + \frac{2\nu}{x} - 1 \right) \phi_\nu(x) = 0 \quad (2)$$

with

$$x = r/\nu a_0, \quad E = -e^2/2a_0\nu^2, \quad (3)$$

$a_0 = \hbar^2/me^2$ being the Bohr radius. The solution to Eq. (2) is

$$\phi_\nu(x) = e^{-x/\nu a_0} M(1-\nu, 2, 2x/\nu a_0), \quad (4)$$

where $M(a, b, z)$ is a Kummer or confluent hypergeometric function. For large r and small β , with $\nu = 1+\beta$, it behaves like¹³

$$M(-\beta, 2, 2r/\alpha_0) \xrightarrow{r \rightarrow \infty} \frac{1}{\Gamma(2)} + \frac{e^{2r/\alpha_0} (2r/\alpha_0)^{-2}}{\Gamma(-\beta)} . \quad (5)$$

As for $r = R$, $\phi_v = 0$, the expression (5) gives, by keeping only terms in first order in β ,

$$\beta = (2R/\alpha_0)^2 \exp(-2R/\alpha_0) , \quad (6)$$

and, therefore, introducing this value of β in (3), we have for the energy that

$$E = -e^2/2\alpha_0 + (2R/\alpha_0)^2 \exp(-2R/\alpha_0) e^2/\alpha_0 \quad (7)$$

(This expression is very similar to that one conjectured by Wigner⁶, but it is valid only for large R).

The second term in expression (7) decays exponentially with R and explains why with not so large R, like $R = 5$ or $6\alpha_0$, we already reach the value -0.5 (in units of e^2/α_0), as the exact numerical calculations have indicated (see Table I).

Let us observe that

$$M(-\beta, 2, 2R/\alpha_0) = \sum_{k=0}^{\infty} \frac{(-\beta)_k (2R/\alpha_0)^k}{k! (k+1)!} ,$$

which for small β gives

$$M(-\beta, 2, 2R/\alpha_0) = 1 - \beta \sum_{k=0}^{\infty} \frac{(2R/\alpha_0)^k}{k(k+1)!}$$

Now, the condition $M(R) = 0$, gives³

$$\beta \approx 1 / \sum_{k=0}^{\infty} \frac{(2R/\alpha_0)^k}{k(k+1)!} . \quad (8)$$

It is not difficult to see that expression (7) is consistent with (6) for large R.

In order to study the solution around $E=0$, it is useful to rewrite $\phi_\nu(x)$ of Eq. (4) in the form

$$\phi_\nu(x) = \sum_{t=0}^{\infty} f_{2t}(x/a) v^{-2t} \quad (9)$$

where

$$f_0(x/a_0) = \sum_{s=0}^{\infty} \frac{(-2)^s}{s!(s+1)!} \left(\frac{x}{a_0}\right)^s = \left(\frac{v_0}{2x}\right)^{1/2} J_1 \left[\left(\frac{8x}{a_0}\right)^{1/2} \right] \quad (10)$$

$$f_2(x/a_0) = \frac{1}{2} \sum_{s=2}^{\infty} \frac{(-2)^{s-1}}{s!(s+1)!} \left[s(s-1) + (s-1)(s-2) + (s-2)(s-3) \right] \left(\frac{x}{a_0}\right)^s \quad (11)$$

and so on.

We see that for $E=0$, the radius R of our box corresponds to the zero of the Bessel function of the right hand side of expression (10). As the first zero occurs at 3.8317, we obtain the known value $R_0 = 1.8353400 \sqrt{2}$. It is easy to see that expression (10) is a solution of Eq. (2) for $E=0$.

3. APPLICATION OF THE MANY-POINT PADÉ APPROXIMANTS

The purpose of this section is to discuss the application of the many-point Padé approximants to systems inside a box. It has been observed in Ref. (10) that if we construct the one-point Padé approximants¹⁴ with the help of expression (1), then we obtain very bad results for the ground-state energy, for sufficiently large R . But we can consider the two-point Padé approximants¹⁴ by means of the use of the behaviour given in expression (1) around $R = 0$ and the behaviour around $R = \infty$, given in expression (7). In table I, we reproduce $E[4/2]$ and $E[5/3]$ which have been obtained by considering two-point Padé approximants for the function $f(R) = R^2 E(R)$. For comparison, we also reproduce the exact numerical values for $E(R)$ as given in Ref.5 and the perturbative values obtained from expression (1).

We see that for $R \leq 3\alpha_0$, the perturbation expansion (1) gives very good results compared to the exact ones, while for larger R the two-point Padé approximants give a somewhat better tendency (for $R \rightarrow \infty$, the perturbative expansion diverges, while the two-point Padé approximants tend to the exact result = 0.5, by construction).

The two-point Padé approximant for the ground-state energy of the hydrogen atom inside a spherical box of radius R writes

$$E[5/3] = \frac{1}{R^2} \cdot \frac{4.9348 - 1.979R - 0.2788R^2 - 0.0464R^3 - 0.0057R^4 - 0.00043R^5}{1 + 0.093R + 0.0115R^2 + 0.00086R^3}, \quad (12)$$

in atomic units. This formula reproduces reasonably well (Table I) the ground-state energy of the H atom over the entire range of values for R . Evidently, if we want a better fitting, we can use a three-point Padé ap

R	E_{exact}	E_{pert}	$E[4/2]$	$E[5/3]$
6.53399	-0.4997	-0.523	-0.470	-0.484
5.37065	-0.4980	-0.507	-0.477	-0.487
4.93358	-0.4960	-0.501	-0.478	-0.487
3.04187	-0.42865	-0.429	-0.423	-0.426
2.0000	-0.1250	-0.125	-0.123	-0.124
1.90192	-0.0555	-0.055	-0.054	-0.055
1.83524	0.0000	0.000	0.001	0.001
1.41279	0.6173	0.617	0.618	0.618
1.05486	2.000	2.000	2.000	2.000
0.91333	3.1250	3.125	3.125	3.125
0.52622	12.500	12.500	12.500	12.500

Table I - R is given in units of α_0 . The energies are given in units of e^2/α_0 .

proximant¹⁴, which uses also an expansion of $E(R)$ around some other point besides the ones used. For instance, with the help of expression (9), we can obtain the expansion of $E(R)$ around $R = R_0$, where $E(R_0) = 0$.

The pressure calculated with the help of the perturbative expansion Eq. (1), coincides within few percent with the exact one for $R \leq 3\alpha_0$. For the hyperfine splitting constant A , the perturbative expansion gives results which are comparable with the exact ones within 10% for $R \leq 2\alpha_0$. For larger values of R , the perturbative expansion for A gives very bad results, while the two-points Padé approximants $A[4/1]$ constructed from the behaviour of A around $R = 0$ and $R = \infty$, gives results which are comparable to the exact ones within 10%.

Recently^{15,16}, exact numerical calculations have been done for the energy levels of quantum oscillator systems inside a box. We can show that perturbative expansions like expression (1) are very easy to be obtained and are very useful for this kind of problems. Specially when, with the help of the behaviour of $E(R)$ for large R also, we construct the two-point Padé approximants. In this way we obtain interpolating formulae similar to expression (12) which reproduce very well the energy levels for the entire range of values of R .

Other problems of systems inside a box are being treated by the very same methods.

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