LETTER TO THE EDITOR

A new treatment of enclosed quantum mechanical systems

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Abstract. A simple and helpful method for calculating approximate eigenvalues corresponding to an enclosed quantum mechanical system is presented. The hydrogen atom enclosed within a spherical surface is chosen as an illustrative example. Numerical comparison with exact results shows very good agreement.

Quantum mechanical systems subjected to non-trivial boundary conditions have a marked usefulness in several branches of physics. Special interest has been shown during the last few years in the harmonic oscillator model (Vawter 1973, and references cited therein, Consortini and Frieden 1976, Rotbar 1978, Aguilera-Navarro et al 1980, Fernández and Castro 1981a, b) and the hydrogen atom enclosed within boxes with impenetrable walls.

The purpose of this communication is to present a simple and helpful method that allows one to calculate, in an approximate way, eigenvalues corresponding to enclosed systems, whenever the solutions of the same model controlled by trivial boundary conditions are known.

As an illustrative example, we consider the ground state of the hydrogen atom model enclosed inside a spherical surface with impenetrable walls.

The radial function $f(r)$ of the total wavefunction is determined by the following differential equation (in atomic units):

$$-\tfrac{1}{2}f'' - (1/r)f' - (1/r)f = Ef \tag{1}$$

with the boundary condition

$$f(R) = 0. \tag{2}$$

The method consists in proposing a solution with the particular form

$$f(r) = F(r)\exp[-G(r)], \tag{3}$$

$$G(r) = \sum_{s=1}^{\infty} g_s r^s. \tag{4}$$

The appropriate expression of $F(r)$ for the ground state of our model is

$$F(r) = r - R. \tag{5}$$

The substitution of equations (3)–(5) in equation (1) permits us to obtain the coefficients

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g_s as a function of E:

$$-R(s+1)(s+2)g_{s+1}+s(s+3)g_s-\sum_{t=0}^{s}(s-t)tg_{s-t}g_t+R\sum_{t=0}^{s+1}(s+1-t)g_{s+1-t}g_t$$

$$=2E\delta_{s2}+2(1-RE)\delta_{s1}+2(1-R)\delta_{s0}. \tag{6}$$

A particular example of the propounded solution allows us to arrive at exact values when $R=2$ and $R=\infty$, because of the following:

$$g_s(R=\infty)=\delta_{s1}, \qquad E(R=\infty)=-\tfrac{1}{2}, \tag{7}$$

$$g_s(R=2)=\tfrac{1}{2}\delta_{s1}, \qquad E(R=2)=-\tfrac{1}{8}. \tag{8}$$

For different R-values we can obtain successive approximations $E(s,R)$ for the energy eigenvalue via the general condition

$$g_{s+1}(R)=0. \tag{9}$$

The first two approximations are

$$E(1,R)=3/2R^2-\tfrac{1}{2}, \tag{10}$$

$$E(2,R)=-\tfrac{1}{2}-3/2R^2+9/R^2(R+1). \tag{11}$$

Numerical results calculated with formulae (10)–(11) are displayed in table 1, together with those values reported by Ludeña (1977, and references cited therein). It can be seen that values given by equation (11) are noticeably near to exact ones associated with the ground state of the enclosed hydrogen atom for the whole range of R-values. The

Table 1. Ground state energy for the hydrogen atom enclosed within a sphere of radius R.

R	E (equation (10))	E (equation (11))	E (Ludeña)
0.8100	1.786	4.792	4.392
1.0100	0.970	2.419	2.301
1.4480	0.215	0.538	0.540
1.7110	0.012	0.122	0.126
1.9020	−0.085	−0.057	−0.056
2.0000	−0.125	−0.125	−0.125
2.2005	−0.190	−0.229	−0.232
2.4720	−0.255	−0.321	−0.327
2.6000	−0.278	−0.352	−0.359
2.8070	−0.310	−0.390	−0.398
3.0413	−0.338	−0.421	−0.428
3.2130	−0.355	−0.438	−0.445
3.5287	−0.380	−0.461	−0.466
3.7592	−0.394	−0.472	−0.476
4.0062	−0.407	−0.481	−0.483
4.4153	−0.423	−0.492	−0.491
4.7916	−0.435	−0.498	−0.493
5.0200	−0.440	−0.500	−0.496
5.3706	−0.448	−0.503	−0.498
5.8010	−0.455	−0.505	−0.499
6.2253	−0.461	−0.507	−0.499
∞	−0.500	−0.500	−0.500

only inconvenience posed by this analytic expression consists in the fact that

$$\{\partial E / \partial R\}(2, R) > 0$$

for large R-values. However from a theoretical viewpoint it is well known that $E(R)$ is a decreasing monotonic function. The present method can be applied without further modifications in order to study the bounded isotropic harmonic oscillator and the one-dimensional oscillator model (Vawter 1973, and references cited therein, Consortini and Frieden 1976, Rotbar 1978, Aguilera-Navarro *et al* 1980, Fernández and Castro 1981a, b).

The analysis of excited states makes it necessary to carry out some changes. The first excited level of our illustrative model is the 2p ($n = 2$; $l = 1$). In this case the difficulty is solved by choosing the pre-exponential function

$$F_{21}(r) = r(r - R). \tag{12}$$

This choice ensures the attainment of the correct result when $R = 6$ or $R = \infty$.

The next excited state is the 2s ($n = 2$; $l = 0$), whose eigenfunction has an interior zero $R_1 < R$. Then

$$F_{20}(r) = (r - R_1)(r - R). \tag{13}$$

This new parameter R_1 can be written as an R function, taking into account that

$$E_{10}(R_1) = E_{20}(R). \tag{14}$$

Higher excited states may be studied in a similar fashion.

Although mathematical formulae for eigenvalues become more complicated with increasing quantum numbers n and l, the treatment is very simple, as shown above. There is an easy procedure to check the goodness of a given approximate function. When $f(r)$ is the normalised radial function of the Schrödinger equation for a central field problem subjected to boundary conditions (2), then the fulfilment of the relation

$$\partial E / \partial R = -\tfrac{1}{2} R^2 |f'(R)|^2 \tag{15}$$

is verified at once. This equation enables us to examine the value of $E(R)$ and its slope for those particular R-values where the exact solution is known. For the hydrogen atom we obtain the following results:

$$\partial E_{\text{exact}}(R = 2)/\partial R = -1/4(e^2 - 7) = -0.642\,580,$$

$$\partial E(1, R = 2)/\partial R = -\tfrac{3}{8} = -0.375, \qquad \partial E(2, R = 2)/\partial R = -\tfrac{5}{8} = -0.625.$$

These results explain why the graph $E(2, R)$ is nearer to the exact function than $E(1, R)$.

We deem that the displayed results show in a plain manner that the method presented in this Letter seems to be very promising for studying lower states of any bounded quantum mechanical system. At present, work along these lines is being carried out in our laboratory and results will be given elsewhere.

References

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