

Application of Runge-Kutta Numerical Methods to Solve the Schrodinger Equation for Hydrogen and Positronium Atoms

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Abstract: In this study, the radial Schrodinger equation for central coulomb potential using numerical Runge-Kutta has been solved. Energy eigenvalues for hydrogen and positronium bound systems is derived -13.6056 and -6.803 eV, respectively. Numerical results of ground state modes of wave functions for hydrogen and positronium $R(r)$ and the presence probability function $|R(r)|^2$ has been presented. These results are in good agreement with analytical calculations of the hydrogen atom in modern physics and quantum mechanics. Therefore, numerical methods can be very useful and effective in solving physical problems.

Key words: Schrodinger wave equation, Runge-Kutta method, energy eigenvalues, wave function, quantum mechanics, positronium

INTRODUCTION

One of the most important eigenvalues equations in physics is Schrodinger wave equation and for atomic mass m in the potential V is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \quad (1)$$

In which $\psi(\vec{r})$ is particle wave function and E is an energy eigenvalues (Gasirowicz, 2003; Weidner and Sells, 1973). For one-dimensional potential equation above is as follows:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (2)$$

This equation has the answer for the few analytical potential functions and for many analytical potential it can not be solved. So in quantum mechanics, numerical solution of Schrodinger's wave equation is very important and so far, for the special cases has been solved numerically (Simos, 2001; Tremblay and Carrington, 2004).

APPROPRIATE UNITS AND BOUNDARY CONDITIONS

Before performing the numerical solution of this equation, we need to note that the use of units and appropriate boundary conditions. Planck's constant

$\hbar = 6.63 \times 10^{-34}$ j.s in the metric system SI, the number is too small to perform computation, therefore we use atomic units in which the length is Angstrom, energy terms of electron volts (eV):

$$\hbar = 7.6199682 m_e eV \text{Å}^2 \quad (3)$$

In the Eq. 3, m_e is mass inertia of electron and $m_e c^2 = 0.51101 \times 10^6$ eV also the amount;

$$\frac{e^2}{4\pi\epsilon_0} = 14.39998 eV \text{Å}$$

would be useful for the Coulomb potential. But boundary conditions are continuity the Schrodinger wave function and its derivatives at the boundary also the wave function approaches to zero at infinity:

$$\int_{-\infty}^{+\infty} \Psi^*(x)\Psi(x)dx = 1 \quad (4)$$

But the important point is that the boundary conditions to convert the initial conditions for numerical methods and this type of problem depend on the symmetry potential.

SCHRODINGER EQUATION FOR HYDROGEN ATOM AND POSITRONIUM

One of the most important problems of quantum mechanics, analysis of two body systems such as

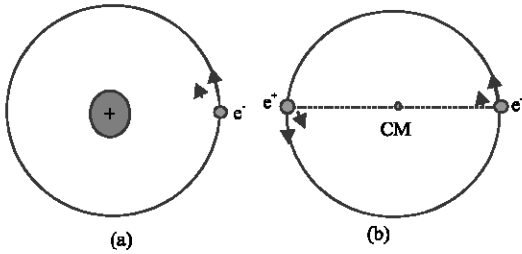


Fig. 1: a, b) hydrogen atom, positronium atom

hydrogen atom and positronium in which electron is in the Coulomb force constraint proton or positron (Fig. 1). Radial Schrodinger equation for the central potential $V(r)$ as follows:

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr}\right]R(r) + \frac{2\mu}{\hbar^2} [E + V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2}]R(r) = 0 \quad (5)$$

In which μ is reduced mass of two-body system, l is the orbital quantum number and $R(r)$ is radial wave function. However, the Coulomb potential in the hydrogen atom is $V(r) = e^2/4\pi\epsilon_0 r$, thus:

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr}\right]R + \frac{2\mu}{\hbar^2} \left[E + \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R = 0 \quad (6)$$

Where:

$$\mu = \frac{m_p m_e}{m_p + m_e} = \text{For hydrogen atom}$$

$$\mu = \frac{m_e m_e}{m_e + m_e} = \frac{m_e}{2} = \text{For positronium atom too}$$

RUNGE-KUTTA METHODS

For the first time, the methods were presented by Runge and Kutta two German mathematicians. These methods were very accurate and efficient and instead direct calculations of higher derivatives only function used for different values.

In Runge-Kutta second order method, instead of the Taylor series expansion up to second derivative for numerical solution:

$$\begin{cases} y' = f(x, y) \\ y(x_0) = y_0 \end{cases} \quad (7)$$

The following formula was introduced:

$$\begin{cases} k_1 = hf(x_n, y_n) \\ k_2 = hf(x_n + \alpha h, y_n + \beta k_1) \\ y_{n+1} = y_n + \alpha k_1 + \beta k_2 \end{cases} \quad (8)$$

We note in this method L local error is defined as follows:

$$L = y(x_{n+1}) - y_{n+1} \quad (9)$$

Thus α, β, α and β are selected so that the error is small as possible. We have:

$$y(x_{n+1}) = y(x_n + h) = y(x_n) + hf'(x_n) + \frac{h^2}{2!} y''(x_n) + \dots \quad (10)$$

With helping relationship Eq. 8, the results are:

$$y_{n+1} = y_n + ahf(x_n, y_n) + bhf((x_n + \alpha h), h_n + \beta hf(x_n, y_n)) \quad (11)$$

But we know:

$$f(x + h) = f(x) + hf'(x) + \frac{h^2}{2} f''(x) + \dots \quad (12)$$

Now, consider the Taylor expand for the function with two variables:

$$f(x + h, y + k) = f(x, y) + h \frac{\delta f(x, y)}{\delta x} + k \frac{\delta f(x, y)}{\delta y} + \frac{h^2}{2} \frac{\delta^2 f(x, y)}{\delta x^2} + \frac{2hk}{2\delta x \delta y} \frac{\delta^2 f}{\delta x \delta y} + \frac{k^2}{2\delta y^2} \frac{\delta^2 f}{\delta y^2} + \dots \quad (13)$$

And finally put in the Eq. 11 we have:

$$y_{n+1} = y_n + ahf_n + bh \left[f_n + \alpha h \frac{\delta f_n}{\delta y} + \beta hf_n \frac{\delta f_n}{\delta y} + o(h^2) \right]$$

Or

$$y_{n+1} = y_n + (a + b)hf_n + \alpha bh^2 \frac{\delta f_n}{\delta x} + \beta bh^2 f_n \frac{\delta f_n}{\delta y} + o(h^3) \quad (14)$$

If we write Eq. 10 also based on the partial derivatives, the result is the following relationships:

$$\left\{ \begin{aligned} y' &= f(x, y) \\ y'' &= \frac{d}{dx} f(x, y) = \frac{\delta f}{\delta x} + \frac{\delta f}{\delta y} \frac{dy}{dx} = \frac{\delta f}{\delta x} + f \frac{\delta f}{\delta y} \\ y''' &= \frac{d}{dx} y'' = \dots \\ &\vdots \\ y(x_{n+1}) &= y(x_n) + hf(x_n, y(x_n)) + \frac{h^2}{2!} \\ &\left[\frac{\delta f(x_n, y(x_n))}{\delta x} + f(x_n, y(x_n)) \frac{\delta f(x_n, y(x_n))}{\delta y} \right] + o(h^3) \end{aligned} \right. \quad (15)$$

And the error position is:

$$L = y(x_{n+1}) - y_{n+1} \quad (16)$$

We try to choose a, b, α and β so that the left side of this relationship is small as possible. In case of equality including the first four we have:

$$\left\{ \begin{aligned} y_n &= y(x_n) \\ (a + b)h &= h \Rightarrow a + b = 1 \\ \alpha bh^2 \frac{\delta f_n}{\delta x} + \beta bh^2 f_n \frac{\delta f_n}{\delta y} &= \frac{h^2}{2} \frac{\delta f}{\delta x} + \frac{h^2}{2} f_n \frac{\delta f_n}{\delta y} \Rightarrow \begin{cases} \alpha b = \frac{1}{2} \\ \alpha b = \frac{1}{2} \end{cases} \end{aligned} \right. \quad (17)$$

From two recent relationships, three equations with four unknowns are obtained so should the one unknown arbitrary to select:

$$\begin{aligned} \alpha = \beta = \frac{1}{2}, \quad b = 1, \quad a = 0 \\ \alpha = \beta = 1, \quad b = \frac{1}{2}, \quad a = \frac{1}{2} \\ \alpha = \beta = \frac{2}{3}, \quad b = \frac{3}{4}, \quad a = \frac{1}{4} \end{aligned} \quad (18)$$

In each of these selections, the local order is of order o (h³) and is known as Runge-Kutta method of second order. The two scientists had extended their previous methods and now are famous as Runge-Kutta method of fourth order and mostly are used in numerical calculations:

$$\begin{aligned} y_{n+1} &= y_n + ak_1 + bk_2 + ck_3 + dk_4 \\ k_1 &= hf(x_n, y_n) \\ k_2 &= hf(x_n + \alpha h, y_n + \beta k_1) \\ k_3 &= hf(x_n + \gamma h, y_n + \ell k_1 + \theta k_2) \\ k_4 &= hf(x_n + \delta h, y_n + \rho k_1 + \mu k_2 + \eta k_3) \end{aligned} \quad (19)$$

We obtain Taylor series expansion of y (x_n+h) up to the fourth derivative order and Taylor expansion for functions with two variables k₂, k₃ and k₄ and put the result in y_{n+1}. With comparison of the two expansions, we reach to 9 equations with 13 unknown and local error is order of o (h⁵). Of course, we must first choose 4 unknowns as the desired unknown and nine other unknown are calculated. A set of optional unknowns include:

$$\ell = 0, \quad \rho = 0, \quad \alpha = \frac{1}{2}\mu \quad (20)$$

In this case, the answer is the following result:

$$\left\{ \begin{aligned} y_{n+1} &= y_n + \frac{1}{6} (k_1 + 2k_2 + 2k_3 + k_4) \\ k_1 &= hf(x_n, y_n) \\ k_2 &= hf(x_n + \frac{1}{2}h, y_n + \frac{1}{2}k_1) \\ k_3 &= hf(x_n + \frac{1}{2}h, y_n + \frac{1}{2}k_2) \\ k_4 &= hf(x_n + h, y_n + h_3) \end{aligned} \right. \quad (21)$$

At the end of this study, a computer program for Runge-Kutta method of fourth order that has been used in numerical computations is presented.

NUMERICAL RESULTS FROM RUNGE-KUTTA METHOD

Because the potential is proportional to the inverse radius and is infinity at r→0, therefore, we use the initial conditions:

$$R(r)|_{r=0.0001} = 10^{-6}$$

and

$$\left. \frac{dR}{dr} \right|_{r=0.0001} = -1000$$

in Runge-Kutta method (Lampert, 1994; Lxaru, 1984; Press *et al.*, 1992). Near the coordinates origin, r = 0.0001Å and wave function has a small amount of 10⁻⁶. But because of severe changes in the wave function, we consider a great value -1000 for wave function derivative.

Thus with choosing the initial amount of energy with try and error test until wave function will be convergent. The answer obtained for l = 0 i.e., ground state of hydrogen (S wave) is -13.6056 eV and for positronium atom is -6.803 eV which is half amount of hydrogen atom. These results are in good agreement with analytical calculations for the hydrogen atom results in modern

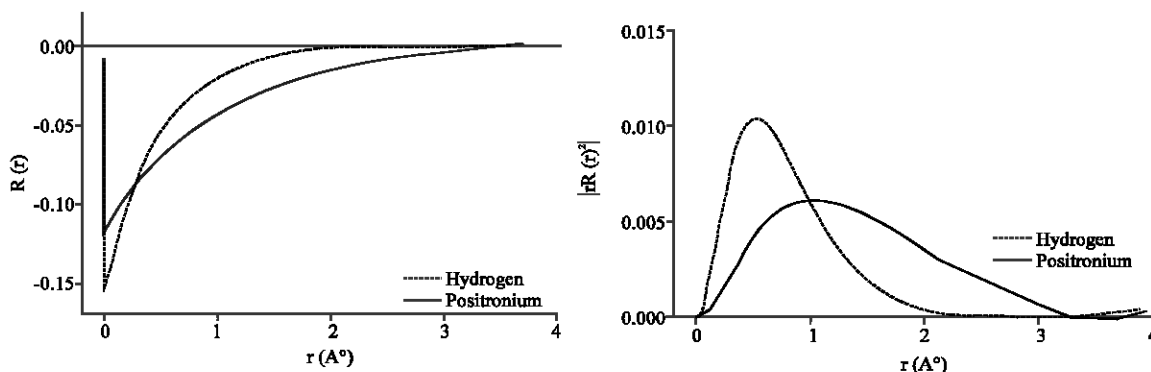


Fig. 2: Results obtained from numerical Runge-Kutta method for the ground state wave functions of hydrogen and positronium and the presence probability function $|rR(r)|^2$

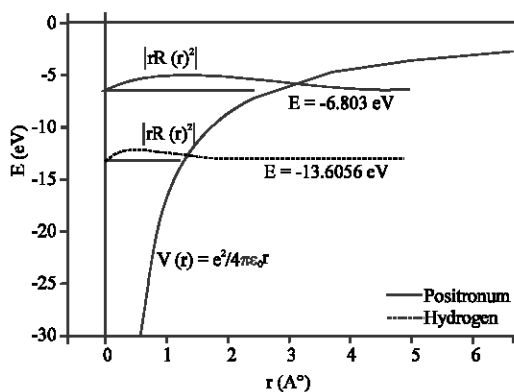


Fig. 3: The presence probability functions for atoms of hydrogen and positronium in the Coulomb potential well

physics and quantum mechanics (Gasiorowicz, 2003; Weidner and Sells, 1973). Ground states of wave functions for hydrogen and positronium and the presence probability function are shown in Fig. 2. Also, the presence probability function in Coulomb potential wells for these atoms is shown in Fig. 3.

CONCLUSION

Numerical Runge-Kutta method to solve differential equations in physics is very efficient and accurate and can be very effective and is useful in solving physics problems. Numerical results from this study are in good agreement with analytical calculations for the hydrogen atom results in modern physics and quantum mechanics. Also, this method can be used in the analysis of quantum systems with different potentials.

APPENDIX

C Positronium atom bounding energy
dimension yscal(10),y(10),y1(200),y2(200)

```

common e,L
open(1,file='shor.dat')
n = 2
x = 0.0001
y(1) = -1E-3
y(2) = -1
write(*,*) 'E = ?, L = ?'
read(*,*)E,L
eps = 0.01
yscal(1) = 0.1
yscal(2) = 0.1
htry = 0.1
do 10 I = 1,800
call derivs(x,y,dydx)
call rkqc(Y,DYDX,N,X,HTRY,EPS,YSICAL,HDID,HNEXT)
y1(I) = y(1)
y2(I) = y(2)
write(*,*) x,y1(i)
write(1,*) x,y1(i)
10 continue
stop
end

c
-----
subroutine derivs(x,y,dydx)
dimension y(10),dydx(10)
common e,L
dydx(1) = y(2)
dydx(2) = -2*y(2)/x + L*y(1)/(x**2) -
(e+14.39998/x)*y(1)**2/7.6199682
return
end

c
-----
SUBROUTINE
RKQC(Y,DYDX,N,X,HTRY,EPS,YSICAL,HDID,HNEXT)
PARAMETER(NMAX = 10,FCOR = .066666667,
* ONE = 1.,SAFETY = 0.9,ERRCON = 6.E-4)
EXTERNAL DERIVS
DIMENSION
Y(N),DYDX(N),YSICAL(N),YTEMP(NMAX),YSAV(NMAX),DYSAV(
NMAX)
PGROW = -0.20
PSHRNK = -0.25
XSAV = X
DO 11 I = 1,N
YSAV(I) = Y(I)
DYSAV(I) = DYDX(I)
11 CONTINUE
H = HTRY
1 HH = 0.5*H
CALL RK4(YSAV,DYSAV,N,XSAV,HH,YTEMP)

```

```

X = XSAV+HH
CALL DERIVS(X,YTEMP,DYDX)
CALL RK4(YTEMP,DYDX,N,X,HH,Y)
X = XSAV+H
IF(X.EQ.XSAV)PAUSE 'Stepsize not significant in RKQC.'
CALL RK4(YSAV,DYSAV,N,XSAV,H,YTEMP)
ERRMAX = 0.
DO 12 I = 1,N
  YTEMP(I) = Y(I)-YTEMP (I)
ERRMAX = MAX(ERRMAX,ABS(YTEMP(I)/YSCAL(I)))
12 CONTINUE
ERRMAX = ERRMAX/EPS
IF(ERRMAX.GT.ONE) THEN
  H = SAFETY*H*(ERRMAX**PSHRNK)
  GOTO 1
ELSE
  HDID = H
  IF (ERRMAX.GT.ERRCON)THEN
    HNEXT = SAFETY*H*(ERRMAX**PGROW)
  ELSE
    HNEXT = 4.*H
  ENDIF
ENDIF
ENDIF
DO 13 I = 1,N
  Y(I) = Y(I)+YTEMP(I)*FCOR
13 CONTINUE
RETURN
END
SUBROUTINE RK4(Y, DYDX, N, X, H, YOUT)
PARAMETER (NMAX = 10)
DIMENSION
Y(N),DYDX(N),YOUT(N),YT(NMAX),DYT(NMAX),DYM (NMAX)
HH = H*0.5
H6 = H/6.
XH = X+HH
DO 11 I = 1,N
  YT(I) = Y(I)+HH*DYDX (I)
11 CONTINUE
CALL DERIVS(XH,YT,DYT)
DO 12 I = 1,N
  YT(I) = Y(I)+HH*DYT(I)
12 CONTINUE
CALL DERIVS(XH,YT,DYM)
DO 13 I = 1,N
  YT(I) = Y(I)+H*DYM(I)
  DYM(I) = DYT(I)+DYM(I)

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13 CONTINUE
CALL DERIVS(X+H,YT,DYT)
DO 14 I = 1,N
  YOUT(I) = Y(I)+H6*(DYDX(I)+DYT(I)+2.*DYM(I))
14 CONTINUE
RETURN
END

```

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