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Integral Equations: A Tool to Solve the Schrodinger Equation*

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From the integral equation equivalent to the one-dimensional Schrodinger equation with the boundary conditions appropriate for a bound state problem, an exact three-point integration rule is derived. The approximate evaluation of this rule by means of the Euler–McLaurin sum rule gives rise to various $O(h^2)$ and $O(h^4)$ integration methods associated with the different ways of splitting the starting equation into a free part and an interaction term. The method is particularly useful to deal with the singularities of the potential.

1. INTRODUCTION

The problem of integrating numerically the one-dimensional Schrodinger equation and the radial equation corresponding to spherically symmetric three-dimensional systems is a subset of continued interest. Certainly there exists at present a number of computer codes both published or unpublished which almost automatically give the set of bound states for any potential with prescribed values of the error [1].

However, apart from the computation of the energy levels or the determination of the corresponding wave functions for specific systems (molecules, nuclei, solids, etc.) the mere question of the determination of new algorithms or the improvement of existing ones has a deep interest by itself in the field of numerical analysis where this problem is usually called the Sturm–Liouville problem.

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Among the various approaches we are particularly interested in the case where the relevant information (i.e., the potential or the wave functions) is known or has to be determined in a set of equally spaced points which constitute the integration mesh. In that case most of the algorithms are or can be described with the help of difference operators and most of them are related to the approximate relation between the second derivative operator and a polynomial or a rational form involving the second difference operator δ^2. In this form the original differential equation is converted into a set of (generally linear) equation involving both the eigenvalue and the discretized wave function.

The most pupular methods are known by the name of second difference method (where the second derivative is approximated by $D^2 \simeq \delta^2/h^2 + O(h^2)$) and the Numerov method (in which case $D^2 \simeq \delta^2/h^2/(1+\delta^2/12) + O(h^4)$). Both permit a simple coding [2], even using hand calculators or home computers [3]. When these methods are combined with the Richardson extrapolation [4] they become a simple, fast and accurate tool to determine in general the eigenvalues of a given potential.

A step beyond these simple algorithms is the determination of other algorithms whose dominant error term depends on higher powers of the intergration step h. We can mention in this sense the so called extended Numerov methods [5] which have been generalised by means of formal Padé approximants expansions [6], the Runge-Kutta-like extension of Numerov methods [7] and the perturbative corrections to the simpler algorithms [8]. In a different context, but deeply related to these methods, Calogero [9] obtained a very accurate integration rule which apparently has not received much attention. The clue of these algorithms is the determination of a new approximation to the second derivative operator in terms of the second differences operator or the approximation of the error term, proportional to a power of the second derivative, by using the starting differential equation.

In this work we seek approximation to (hermitian) operators others than the second derivative one. In practice this is done through the integral equation form equivalent to the Schrodinger equation which includes the appropriate boundary condition. In a first step we split the Schrodinger equation into two pieces, a *free* part and an *interaction* part. The first one contains the second derivative operator and may also contain other quantities which are explicitly present in the differential equation (namely, the energy or the centrifugal barrier or both) or which are arbitrarily introduced (like a constant energy shift or a part of the potential). The freedom in choosing this free part is the most attractive aspect of this approach and can be the clue for an accurate study of potentials which deviate only slightly from simpler, analytically solvable, forms.

Once the free Green function is determined and the integral equation is written down, the Euler–McLaurin sum rule is used to approximate this integral equation, getting several three-point integration rules which may be very simple coded. These rules include both the well known second differences and Numerov methods as well as other novel algorithms. One of the advantages of this approach is that it permits

a simple treatment of the troubles associated with the presence of singularities in the differential equation.

Finally we include three practical rules associated with the *natural* ways of splitting the Schrodinger equation.

2. Integral Equation

The objective is to determine stationary solutions of the two-point boundary value problem

$$\frac{d^2R}{dr^2} = (\tilde{V}(r) - E)\, R(r), \tag{1}$$

where $\tilde{V}$ contains both the potential and the centrifugal barrier, $\tilde{V}(r) = V(r) - l(l+1)/r^2$, subject to the boundary conditions

$$\begin{aligned} R(0) &= 0, \\ R(X) &= 0. \end{aligned} \tag{2}$$

In Eq. (2) X should be infinity. The three-point rules to be derived in the next section are independent of the actual value of X.

The differential equation can be written in the generic form

$$L[R] = g(r)\, R(r) \tag{3}$$

and the differential form L will be taken as

$$L = \frac{d^2}{dr^2} - q(r) \tag{4}$$

so that the quantity $g(r)$ corresponds in our problem to

$$g(r) = \tilde{V}(r) - E - q(r). \tag{5}$$

The function $q(r)$ added to the differential equation is arbitrary, provided the *free* equation $L[R] = 0$ can be algebraically solved. The independent solutions of the free equation will be used to build up the integral equation to Eq. (1) and incorporating the boundary conditions (2). In other words, the various pieces entering in the differential equation (1) may be arbitrarily moved from the l.h.s. to the r.h.s. and the form of L depends only on our imagination.

The integral equation equivalent to our problem can be written using standard

methods [10]: Let $u(r)$ and $v(r)$ be two independent solutions of the free equation (4), such that

$$\begin{aligned} &\text{(i)} \quad L[u]=0, \qquad \text{and} \qquad u(0)=0, \\ &\text{(ii)} \quad L[v]=0, \qquad \text{and} \qquad v(X)=0, \end{aligned} \tag{6}$$

and define the Green function

$$G(r,s)=\begin{cases} \dfrac{1}{w}\,v(r)\,u(s), & s\leqslant r \\ \dfrac{1}{w}\,u(r)\,v(s), & s\geqslant r, \end{cases} \tag{7}$$

where w is the wronskian of u and v,

$$w=u(r)\,v'(r)-u'(r)\,v(r)=\text{constant}. \tag{8}$$

Then the integral equation

$$R(r)=\int_0^X G(r,s)\,g(s)\,R(s)\,ds \tag{9}$$

is equivalent to Eqs. (1) plus (2). The rest of the paper will be devoted to determine numerical approximations to Eq. (9), and for that purpose it is better to write Eq. (9) in the form

$$wR(r)=v(r)\int_0^r u(s)\,g(s)\,R(s)\,ds+u(r)\int_r^X v(s)\,g(s)\,R(s)\,ds. \tag{10}$$

From Eq. (10) it is possible to write a *three-point rule* relating the values of the function at three equally spaced points $r-h$, r and $r+h$. This task is easily carried out by writing Eq. (10) explicitly at these three points and determining a linear combination of these three equations so as to cancel the integrals extending from 0 to $r-h$ and from $r+h$ up to X. The corresponding rule is

$$\begin{aligned} &w[C_+R(r+h)+C_0R(r)+C_-R(r-h)] \\ &\quad=C_+\left[v(r+h)\int_r^{r+h}u(s)\,g(s)\,R(s)\,ds-u(r+h)\int_r^{r+h}v(s)\,g(s)\,R(s)\,ds\right] \\ &\qquad+C_-\left[-v(r-h)\int_{r-h}^{r}u(s)\,g(s)\,R(s)\,ds+u(r-h)\int_{r-h}^{r}v(s)\,g(s)\,R(s)\,ds\right], \end{aligned} \tag{11}$$

where C_+, C_0, and C_- are r-dependent quantities given by

$$\begin{aligned} C_+ &= v(r-h)\,u(r) - u(r-h)\,v(r), \\ C_0 &= v(r+h)\,u(r-h) - u(r+h)\,v(r-h), \\ C_- &= v(r)\,u(r+h) - u(r)\,v(r+h). \end{aligned} \tag{12}$$

Note that the three-point relation (11) is not valid at the boundaries, i.e., at $r = h$ or $r = X - h$. In these cases a two-point relation is easily obtained. Near the origin there results

$$\begin{aligned} &w[u(2h)\,R(h) - u(h)\,R(2h)] \\ &\quad = [u(2h)\,v(h) - u(h)\,v(2h)] \int_0^h u(s)\,g(s)\,R(s)\,ds \\ &\qquad + u(h)\,v(2h) \int_h^{2h} [v(s) - u(s)]\,g(s)\,R(s)\,ds. \end{aligned} \tag{13}$$

An analogous relation can be written for $R(X-2h)$ and $R(X-h)$. However, given that it will not be used it is not necessary to write it. The reason of this different treatment of the points near the origin and the points near the cut-off distance is that later we will consider the case where the effective potential entering in $g(s)$ can be singular at the origin. This is the case, for example, of the centrifugal barrier. Then the integrals appearing in (13) need to be carefully treated. On the contrary, the two-point relation corresponding to $r = X - h$ can be considered like in Eq. (11) just putting $R(X) = 0$ and $v(X) = 0$.

In the following section we will consider several approximations to the integrals appearing in (11) and (13). There will result a system of homogeneous equations in $R(r)$ whose solution requires the solution of an eigenvalue or generalized eigenvalue problem, i.e., we will end up with a well posed algebraic problem.

However, relations (11) and (13) can also be used within the spirit of other approaches to solve the Schrodinger equation, such as a piece-wise approximation of the potential by some simple forms in small intervals (i.e., a constant value [8] or a polynomial form [11]).

3. Numerical Methods: The Euler–McLaurin Sum Rule

To get a true three-point relation from (11) the definite integrals must be approximated so as to involve $R(r)$ only at the points $r - h$, r and $r + h$. To this end we have found the Euler–McLaurin sum rule to be a very useful tool. For a single interval h, the Euler–McLaurin rule is given by [12]

$$\int_a^{a+h} F(x)\,dx = \frac{1}{2}h[F(a)+F(b)] + \sum_{m=1}^{n-1} \frac{(-)^m B_m h^{2m}}{(2m)!}[F^{(2m-1)}(a+h) - F^{(2m-1)}(a)] + R_n, \quad (14)$$

where B_m are the Bernouilli numbers $B_1 = \frac{1}{6}$, $B_2 = \frac{1}{30}$, $B_3 = \frac{1}{42}$, etc. The only condition for the validity of this formula is that $F(x)$ must be analytic along a straight line joining a and $a+h$.

Equation (14) involves the odd derivatives of the integrand at the boundaries. Due to the particular form of our integrands, Eq. (11), it turns out that we can manage in a simple form the cases where we consider on the r.h.s. of (14) the integrated term and the first ($m=1$) Euler–McLaurin correction, getting the three point rule formula

$$C_+\left[1-\frac{h^2}{12}g(r+h)\right]R(r+h) + C_0\left[1-\frac{h^2}{12}g(r)\right]R(r) + C_-\left[1-\frac{h^2}{12}g(r-h)\right]R(r-h) = -\frac{h}{w}C_+C_-g(r)R(r). \quad (15)$$

This is an extension of the well-known Numerov method [13]. The energy eigenvalues are hidden in $g(r)$ or in the functions $u(r)$ and $v(r)$, depending on the criterium used to split the original equation into a *free* and an *interacting* part. The solution of Eq. (15) gives the energy eigenvalues with an error proportional to h^4, the first term neglected in the Euler–McLaurin sum rule.

If the terms with coefficient $h^2/12$ in Eq. (15) are removed there results the extension to the simplest second differences rule, with an error proportional to h^2.

In Table I we present several natural forms of splitting the complete differential equation into a free and an interacting part, with the corresponding $u(r)$ and $v(r)$ functions and the value of the wronskian. Note that the form called ENERGY which incorporates a constant $E = \pm\lambda^2$ into the free equation may be interpreted in two ways: one can consider the constant E to be exactly the stationary value of the energy (thus giving rise to a nonlinear equation for the eigenvalue) or just like a displacement constant to be added afterwards to the energy.

In addition to the cases shown in Table I one can also consider the case appropriately called COMPLETE, in which the free form contains both the centrifugal barrier and the energy $E = \pm\lambda^2$. The generating functions of the free Green function are related in that case to the spherical Bessel functions $j_n(\lambda r)$ and $y_n(\lambda r)$, or the corresponding spherical Bessel functions of imaginary argument.

These forms of the free function are the *standard* forms. However, and for some particular potentials, a part of that potential could be included into the Green function, in a manner similar to perturbation theory.

For the three cases shown in Table I we have the following three-point rules:

TABLE I

The Natural Ways of Defining the Free Equation and the Corresponding Functions $u(r)$ and $v(r)$ as Well as the Value of the Wronskians.

Free Green Function	Free Equation	$u(r)$	$v(r)$	Wronskian
Simple	$L = d^2/dr^2$	r	$r/X - 1$	1
Energy	$L = d^2/dr^2 - \lambda^2 \quad E = -\lambda^2$	$e^{\lambda r} - e^{-\lambda r}$	$e^{\lambda(r-X)} - e^{-\lambda(r-X)}$	$4\lambda \sinh(\lambda X)$
	$L = d^2/dr^2 + \lambda^2 \quad E = \lambda^2$	$\sin(\lambda r)$	$\sin \lambda(r - X)$	$\lambda \sin(\lambda X)$
Centrifugal	$L = d^2/dr^2 - l(l+1)/r^2$	r^{l+1}	$r^{l+1}/X^{2l+1} - r^{-l}$	$2l+1$

(1) Green function SIMPLE

$$\left[1 - \frac{h^2}{12} U_{n-1}\right] R_{n-1} - 2\left[1 - \frac{h^2}{12} U_n\right] R_n + \left[1 - \frac{h^2}{12} U_{n+1}\right] R_{n+1} = h^2 U_n R_n \tag{16}$$

with $U(r) = V(r) + l(l+1)/r^2 - E$.

(2) Green function including the ENERGY

$$\left[1 - \frac{h^2}{12} U_{n-1}\right] R_{n-1} - 2\cosh(\lambda h)\left[1 - \frac{h^2}{12} U_n\right] R_n + \left[1 - \frac{h^2}{12} U_{n+1}\right] R_{n+1} = \frac{h}{\lambda} \sinh(\lambda h)\, U_n R_n \tag{17}$$

with $U(r) = V(r) + l(l+1)/r^2$

(3) Green function including the CENTRIFUGAL barrier

$$\begin{aligned}
&\left[\left[\frac{n+1}{n}\right]^l (n+1) - \left[\frac{n}{n+1}\right]^l n\right]\left(1 - \frac{h^2}{12} U_{n-1}\right) R_{n-1} \\
&\quad + \left[\left[\frac{n-1}{n+1}\right]^l (n-1) - \left[\frac{n+1}{n-1}\right]^l (n+1)\right]\left(1 - \frac{h^2}{12} U_n\right) R_n \\
&\quad + \left[\left[\frac{n}{n-1}\right]^l n - \left[\frac{n-1}{n}\right]^l (n-1)\right]\left(1 - \frac{h^2}{12} U_{n+1}\right) R_{n+1} \\
&= \frac{h}{2l+1}\left[\left[\frac{n}{n-1}\right]^l n - \left[\frac{n-1}{n}\right]^l (n-1)\right] \\
&\quad \times \left[\left[\frac{n+1}{n}\right]^l (n+1) - \left[\frac{n}{n+1}\right]^l n\right](U_n - E)\, R_n.
\end{aligned}$$

with $U(r) = V(r) - E$.

Equations (16), (17), and (18) correspond to the Numerov-like forms, and the error in the determination of the energy is proportional to the fourth power of the step length. In all these formulae, if the factors of the type $(1-h^2/12U_n)$ are substituted just by 1 we get the second-differences-like forms, with an error proportional to h^2.

In all cases presented, there results a linear homogeneous system involving a symmetric tridiagonal matrix (Eq. (15) has not been written explicitly in symmetric form because of typographical reasons). The cases called *simple* and *centrifugal* correspond to a standard eigenvalue problem (in the $O(h^2)$ approximation) or to a generalized eigenvalue problem ($O(h^4)$ case). Any of the usual methods of solution of these problems may be used, e.g., constructing the adequate Sturm sequence plus a bisection algorithm [14] or using the popular shooting method, to determine or isolate the eigenvalues. On the contrary, the dependence on the energy in the case called *energy* is not trivial, because the square root of the energy is present in the linear problem through the $\cosh(\lambda h)$ and $\sinh(\lambda h)$ functions. However, the simple shooting method can again be used.

Note that the quantity X used to determine the free solution $v(r)$ does not appear in the three-point rules, Eqs. (16)–(18). Nevertheless, in practical applications Eqs. (16)–(18) must be stopped somewhere and this means to introduce a large X as the outher boundary. Killingbeck [4] describes a clever method to decide where to stop just by recognizing when the exponential increase of the wave function starts. In any case, the question of determining the appropriate distance X is particularly difficult and important for bound levels near the edge of the potential well.

4. The Case of Singular Potentials

The algorithms presented in Section 3 may be used directly for the case of non-singular potentials. However, when the potential is singular, we must be careful. As we have already mentioned, the appropriate relation near the origin involves only two points (see Eq. (13)) and using again the Euler–McLaurin sum rule the equation of interest is now

$$w[u(2h)\,R(h)-u(h)\,R(2h)]-hC_-u(h)\,g(h)\,R(h)+\frac{1}{2}hC_-[u(r)\,g(r)\,R(r)]_{r=0}$$

$$=\frac{h^2}{12}w[u(2h)\,g(h)\,R(h)-u(h)\,g(2h)\,R(2h)]+\frac{h^2}{12}C_-[u(r)\,g(r)\,R(r)]'_{r=0}. \qquad (19)$$

This equation has been reordered so that the l.h.s. takes into account the contribution related to the trapezoidal approximation, whereas the r.h.s. is the part corresponding to the first Euler–McLaurin correction. In this equation $[u(r)\,g(r)\,R(r)]_{r=0}$ and $[u(r)\,g(r)\,R(r)]'_{r=0}$ are the limit of the product of the functions $u(r)\,g(r)\,R(r)$ at $r=0$ and the limit of its first derivative respectively.

There are two cases of particular interest: the case of an attractive potential with the behaviour at the origin α/r, (this is the case of Yukawa and Coulomb potentials), and the case of a repulsive potential with the behaviour $l(l+1)/r^2$, i.e., the centrifugal barrier. Certainly the first case assumes that the centrifugal barrier is not present.

In these two cases the behaviour at the origin of the regular solution is known ($R \to r$ in the first case, $R \to r^{l+1}$ in the second case) and thus the limits appearing in Eq. (19) can be determined.

In $O(h^2)$ rules, the limit $[u(r)\, g(r)\, R(r)]_{r=0}$ is always zero. In other words, there are not corrections and a straightforward shooting method is appropriate to determine the eigenvalues.

However, the term $[u(r)\, g(r)\, R(r)]'_{r=0}$ may be nonzero. Its value depends both on the kind of Green function chosen (because of the presence of $u(r)$) and on the kind of singularity of the potential, which is present in $g(r)$. We will work with some detail on the case of the correction related to Numerov's method, i.e., with the Green function called SIMPLE.

In the case of a Coulomb-like dominating behaviour of the potential we have the following behaviour near the origin

$$R(r) \to R'(0)r + R''(0)\, r^2/2! + \cdots,$$
$$R'(r) \to R'(0) + R''(0)r + \cdots,$$
$$g(r) \to \alpha/r,$$
$$u(r) \to r,$$

and

$$\lim_{r \to 0} [u(r)\, g(r)\, R(r)]' = \alpha R'(0) \tag{20}$$

so that we must determine a new quantity, $R'(0)$.

In the case of the centrifugal barrier ($l \neq 0$) we have

$$R(r) \to r^{l+1} R^{(l+1)}(0)/(l+1)!,$$
$$g(r) \to l(l+1)/r^2,$$

and the limit of $[u(r)\, g(r)\, R(r)]'$ is null unless $l = 1$, in which case its value is $R''(0)$.

In conclusion, the use of the standard Numerov method requires the knowledge of the quanties $R'(0)$ or $R''(0)$, depending on the kind of singularity.

The first derivative at the origin may be evaluated by using the integral equation (10),

$$R'(0) = \frac{u'(0)}{w} \int_0^x u(s)\, g(s)\, R(s)\, ds$$

and the Euler–McLaurin sum rule, with the result

$$\lim_{r\to 0}\,[u(r)\,g(r)\,R(r)]' = \frac{h}{1+\alpha h/2}\sum_{n=1}^{N-1} v(nh)[V(nh)-E]\,R(nh). \tag{21}$$

A simple way to take into account this correction is to evaluate the three point relation inwards. We assume a value for the eigenvalue E and compute $R(r)$ from $R(r+h)$ and $R(r+2h)$ using Eq. (16). At the same time the contributions to the sum in Eq. (21) are evaluated. This sum is only required in the last step, Eq. (19), which become the quantization condition for the energy. On the other hand, when the quantity required is $R''(0)$, i.e., in the p-wave case, we have not found a simple and direct method for its evaluation like Eq. (21). The problem, however, may be circumvented [15] by evaluating $R''(0)$ from the four nearest points $R(h)$ up to $R(4h)$.

The situation is better in the case of the centrifugal Green function. In that case the limits appearing in Eq. (19) are zero for Coulomb-like potentials, and there is no problem with the centrifugal barrier which is already included into the functions $u(r)$ and $v(r)$. In that case the step-by-step integration algorithm may again be carried out inwards by using repeteadly Eq. (18). The last step is to impose Eq. (19), without the special terms involving the limits, to determine the quantized levels.

Summarizing, we have the following situations related to singularities of the potential at $r=0$:

(a) Trapezoidal ($O(h^2)$) three point rules: no correction is necessary

(b) Numerov rule, corresponding to the Green function SIMPLE: the value of $R'(0)$ is required for Coulomb-like potentials, and this may be computed by means of Eq. (21).

The value of $R''(0)$ is required for p-waves. See [15] for an algorithm.

These conclusions also apply to the Green function called ENERGY.

(c) Numerov-like rule related to the Green function called CENTRIFUGAL: no corrections are necessary.

It is very important to stress the fact that if these corrections are not taken into account the goodness of the algorithm is lost, i.e., a $O(h^4)$ algorithm becomes a $O(h^2)$ algorithm.

5. Some Numerical Examples

In this section we present some simple calculations using the various algorithms described above with the aim of checking the main properties of these methods as well as the effect of the singularities of the potential. In all examples we have used the Coulomb potential, $V(r)=-2/r$, its bound states being given by $E_n=-1/n^2$.

This potential has been chosen because the standard Numerov method fails to give high quality results both in s and p-wave states. The reason of that failure is the singular character of the interaction. Moreover, the calculations carried out with the wide variety of high precision methods described in [6] give the same poor results as Numerov method.

To study the behaviour of the solutions with the integration step h we have included also the Richardson extrapolation corresponding to two calculations with step h and $h/2$. Then, if the dominant term of the error is of the form h^p, the combination $(2^p E_{1/2} - E_1)/(2^p - 1)$ should cancel that error term and because of the it should be a better approximation to the exact energy. In this expression $E_{1/2}$ and E_1 are respectively the eigenvalues determined with step $h/2$ and h.

Table II corresponds to the s-wave ground state. The first part contains the determination of the energy with the standard second differences rule, and the extrapolation shows a clear h^2 behaviour for the error. In the second part we have used the Numerov method without the corrections related to the singularity at the origin, and again the error shows a h^2 behaviour. Actually, the results in this case are worse than the results corresponding to the simplest rule. Finally, the third part includes the correction given by Eq. (21). Note that in this case the value of α is -2. The effect of this correction in impressive, particularly if we realize that it is only used in the last step of the calculation. The Richardson extrapolation shows the h^4 behaviour of the error term.

In Table III we deal with the singularity associated with the centrifugal barrier for the case of p-wave states. This table shows a new feature: the standard second

TABLE II

The Determination of the Ground State of the Potential $V(r) = -2/r$

No. Points	Energy g.s.	Extrapolation h^2	Extrapolation h^4
	Extrapolation rule, Green function simple		
80	−0,9848500	−0.99988653	
160	−0,99612399	−0.99999238	
320	−0.99902528		
	Numerov rule, Green function simple, no corrections		
80	−0.96875846	−0.99833144	−0.99241685
160	−0.99093820	−0.99977413	−0.99800695
320	−0.99756515		
	Numerov rule, Green function simple, with corrections		
80	−1.00076422	−0.99980826	−0.99999945
160	−1.00004725	−0.99998817	−0.99999999
320	−1.00000294		

Note. The Exact Value is $E_{gs} = -1$ and the Integration algorithm has been extended from $r = 0$ up to $X = 20$.

Table III

Lowest P-Wave State of Coulomb Potential $V(r) = -2/r$. The Exact Value Is $E = -0.25$ and $X = 40$

Method	80 Points	160 Points	Extrapolation h^n	n
Trapezoidal SIMPLE	−0.25135236	−0.25032864	−0.24998740	2
Numerov SIMPLE	−0.25065776	−0.25008838	−0.25000704	3
Numerov CENTRIFUGAL	−0.25003640	−0.25000236	−0.25000009	4

Note. The method NUMEROV-SIMPLE does not include the correction related to the singularity at $r = 0$.

differences method has an error proportional to h^2, the Numerov method without corrections behaves like h^3 and the centrifugal Numerov method has a error proportional to h^4.

Finally Table IV shows the results of evaluating the lowest D-wave state by means of all methods discussed. In turns out, as expected, that all Numerov like algorithms have almost the same precision and that there is no special advantage in that case for any of these methods.

TABLE IV

D-Wave Lowest State of Coulomb Potential $V(r) = -2/r$

Method	80 Points	160 Points
Trapezoidal SIMPLE	−0.11122665	−0.11114004
Numerov SIMPLE	−0.11111289	−0.11111122
Numerov ENERGY	−0.11111301	−0.11111123
Numerov CENTRIFUGAL	−0.11110945	−0.11111101
Numerov COMPLETE	−0.11110524	−0.11111074

Note. The exact value is $E = -\frac{1}{9} = -0.11111...$ and $X = 60$.

6. SUMMARY

The integral equation formalism has been used to generate integration rules involving three points for the determination of eigenvalues and eigenfunctions of the one-dimensional Schrodinger equation. The generating formula is the exact three-point rule given in equation (11) from which one can derive a great deal of practical rules by using numerical approximations to the finite integrals. The cases presented have been obtained with the help of the Euler–McLaurin sum rule.

The main results and the extensions of our work can be summarized in the following points:

(1) The generality and flexibility of the method related to the freedom in choosing the free part of the equation and the interacting part.

(2) The ability to deal in a simple way with the problems associated with the singularities of the potential.

(3) The method goes beyond the usual approach of discretizing strictly the second derivative operator.

In the practical versions we have only presented the rules related to the use of the trapezoidal rule and the first Euler–McLaurin corrections. However, one can go beyond and include also higher corrections. In this manner a family of rules analogous (and including) the extended Numerov method [5] can be generated.

Some of the novel rules contain, at least in part, other methods which have been found very appropriate in some specialized cases. In particular, the rule associated with the *energy* Green function in the trapezoidal approximation integrates exactly the functions $\exp(\pm\lambda r)$ and $r\exp(\pm\lambda r)$ or the corresponding circular functions for a positive value of the energy, as it happens in the exponential-fitting methods of Raptis [16] and Raptis and Allison [17].

From a practical point of view, one can state the following results. When the potential has no singularities, the error of *any* of the methods derived in Section 3 has the same dependence on the step h, namely h^2 for trapezoidal rules or h^4 for Numerov-like formulae, so that all of them should be considered as equivalent. Moreover, in the case of a singularity of the kind $1/r$ (atractive), one should take into account the improvements discussed in section 4, particularly Eq. (21), and in the case of p-wave states one should use the centrifugal kernel, Eq. (18) to get the best method.

Nevertheless, we should not forget the freedom in the construction of the three-point rule, a consequence of the freedom in choosing the free and the interacting part of the kernel. This fact can be appropriately used so as to improve the goodness of the results in some specific problems.

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