# On the Numerical Integration of the Schrödinger Equation in the Finite-Difference Schemes

R. GUARDIOLA

*Departamento de Física Nuclear,*
*Universidad de Granada, Granada, Spain*

AND

J. ROS

*Departamento de Física Teórica,*
*Universidad de Granada, Granada, Spain*

Formulae for the integration of the Schrödinger equation for bound states based on the scheme of central differences are generated from the Taylor expansion with the help of formal Padé approximants. These methods are studied in matrix form, and a limiting formula—the best for a given discretization—is obtained.

## 1. INTRODUCTION

With the exception of a few cases, the Schrödinger equation is not analytically integrable, and very frequently one has to resort to numerical methods for the (approximate) solution of the eigenvalue problem. The determination of bound states corresponds to a two-point boundary value problem such that the solution is zero at $r = 0$ and at $r \to \infty$ (in the case of the reduced radial equation for potentials with spherical symmetry) or at $x \to \pm \infty$ (in one-dimensional problems). The question is to determine those values of the energy compatible with the prescribed boundary conditions. Three frequently used methods for the numerical integration are the following.

(a)  The step-by-step methods (referred to also as "shooting" methods). These methods are based on the finite-difference scheme, and consist of an approximation to the second derivative of the wave function at $x$ in terms of the wave function at $x$, $x \pm h$, $x \pm 2h$,.... In practical applications one assumes (shoots) a value for the energy and then integrates from the origin up to a maximum value of $r$, $R$. The value of the energy is varied so as to fulfill the boundary condition at $R$. One of the most

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widely used shooting methods is known as the Numerov method [1]. A general description and generalizations can be found in [2–8].

(b)   The finite-element method. The integration region is divided into domains where the potential does not change too much, and the potential is approximated in these domains by forms simple enough to have analytical solutions of the Schrödinger equation (e.g., the potential is substituted by a staircaselike form). The actual solutions are obtained by satisfying the boundary conditions at $r = 0$ and $r \to \infty$, supplemented by the matching of the logarithmic derivative at the borders of the domains [9–11].

(c)   The Rayleigh–Ritz–Galerkin [12] or spectral method [11]. The solution is expanded in a (not necessarily orthogonal) basis and the corresponding secular equation is solved. The basis is usually chosen so that the matrix elements of the potential and kinetic energy operators are fairly simple to compute (such as harmonic oscillator, sine basis [13], splines [14], Gaussians [15]). All these methods have been empirically tested [16] and compared with finite-difference methods for the case of the Morse potential. The main disadvantage is the need for the exact analytic computation of the matrix elements of the potential, but this can be avoided through the use of special quadrature formulae [17–18]. The strong relation between the use of splines and the finite-element method should also be stressed.

The finite-element and the Rayleigh–Ritz–Galerkin methods cannot be considered as universal methods, because they require a good knowledge of the potential for the decomposition into domains or for selecting the basis. When applicable, they are very accurate. Methods based on finite differences are more general, and usually, a very good knowledge of the potential is not necessary, being (for this reason) particularly convenient in Hartree–Fock-like calculations.

Finite-difference scheme methods for the solution of the Schrödinger equation have frequently been formulated in matrix (or global) form [16, 19–21], so that one should no longer refer to these methods as "shooting" methods. Certainly, the eigenvalues and eigenvectors are the same regardless of the procedure followed for their solution.

This paper is concerned with the methods based on the finite-difference scheme from a global or matrix point of view. Section 2 is devoted to a unified presentation of (constant step) finite-difference methods (Taylor expansion, Numerov-like methods [2], extended-Numerov methods [18], and other methods not yet described), all of them related to Padé approximants in the variable $\delta^2$. The generating method is fairly simple (cf. [8]), and even the determination of the error involved is simple.

In Section 3 all these methods are written in matrix form, using the simple properties of the matrix associated with $\delta^2$, giving rise to a generalized matrix-eigenvalue problem. It then appears that the transformation to a discretized plane-wave basis is the correct way to transform the generalized eigenvalue problem into a standard matrix-eigenvalue problem. The plane-wave representation suggests a mechanism to sum up the whole Taylor expansion, and this gives the optimal integration rule within the finite-difference scheme. This step is carried out in Section 4.

We should remark that the use of Padé approximants for the expansion of the second derivative in terms of $\delta^2$ is by no means related to the numerical approximation with Padé algorithm [22]. (It may be related, however, to the extrapolation techniques to null step [23].) Furthermore, the presence of the discretized plane-wave basis does not imply that the same basis is the best one for Rayleigh–Ritz–Galerkin methods. Finally, the use of optimal as adjective of our plane-wave method only means that this is the best method within the finite-difference schemes. It may well happen that other approaches give better results with the same or less computational work.

Although we will refer to the radial Schrödinger equation, i.e., the differential equation obtained after the change $\psi(r) = R(r) \, Y_{lm}(\hat{r})/r$ extending from 0 to $\infty$, all our results are also valid for the one-dimensional equation.

## 2. Finite Differences

a. *The Taylor Expansion*

Consider the set $\{f_n\}$, where $f_n = f(x_0 + nh)$, which corresponds to a discretization of the function $f(x)$ at the points $x_0, x_0 + h,..., x_0 + Nh$. The value of $f$ at the point $x_0 + (n + 1) h$ is related to the value at the point $x_0 + nh$ by the Taylor series

$$f_{n+1} = \{1 + hD + (h^2/2!) \, D^2 + \cdots\} f_n, \tag{1}$$

where $D$ is the operator $d/dx$. In a symbolic form we may write

$$f_{n+1} = \exp\{hD\} f_n. \tag{2}$$

The central differences are defined as

$$\delta f_n = f(x_0 + nh + \tfrac{1}{2}h) - f(x_0 + nh - \tfrac{1}{2}h) \tag{3}$$

and by using the symbolic equation (2) we obtain the formal representation of $\delta$

$$\delta = \exp\{\tfrac{1}{2}hD\} - \exp\{-\tfrac{1}{2}hD\} = 2 \sinh(\tfrac{1}{2}hD). \tag{4}$$

This equation is the clue of numerical methods for the solution of differential equations in the finite-difference scheme. If the equation is inverted it becomes

$$hD = 2 \sinh^{-1}\{\delta/2\} \tag{5}$$

and, insofar as we are mainly concerned with the radial part of the Schrödinger equation, we shall refer to the square of Eq. (5), namely,

$$h^2D^2 = 4\{\sinh^{-1}(\delta/2)\}^2. \tag{6}$$

The expansion in powers of $\delta/2$ is the inversion of the square of Eq. (4), and corresponds to

$$h^2D^2 = \delta^2\{1 - \tfrac{1}{12}\delta^2 + \tfrac{1}{90}\delta^4 - \tfrac{1}{560}\delta^6 + \tfrac{1}{3150}\delta^8$$
$$- \tfrac{1}{16,632}\delta^{10} + \tfrac{1}{84,084}\delta^{12} - \tfrac{1}{411,840}\delta^{14} + \tfrac{1}{1,969,110}\delta^{16} + \cdots\}. \tag{7}$$

It is important to observe the absence of odd powers of $\delta$ in this expansion. This is a very important property because $\delta f_n$ does not belong to our space $\{f_n\}$ defined above, but to $\{f_{n+1/2}\}$, whereas, $\delta^2 f_n$ is in our space.

Even if the discretization step $h$ is not explicitly present in the r.h.s. of Eq. (7), it is implicitly present in $\delta$, so that if we retain powers of $\delta$ up to $\delta^{2N}$ in the r.h.s. of (7), then the second derivative is computed to order $h^{2N+2}$ (i.e., the term $h^{2N+2}$ is the first term not included in the calculation of the second derivative). The formal equations (5)–(7) are well known in numerical analysis and have been used as generating formulae for both differentiation and integration methods [24].

The utility of Eq. (7) for the numerical solution of the Schrödinger equation is a consequence of the particular form of the latter,

$$\frac{d^2}{dx^2}\psi = (V - E)\psi$$

or, in the symbolic form used above

$$D^2\psi = (V - E)\psi. \tag{8}$$

Then Eq. (7) gives a set of relations between $(V_n - E)\psi_n$ and the even differences $\delta^{2p}\psi_n$ and once boundary conditions have been imposed the referred set of equations may be solved by iteration for any value of $E$. This is known as a "shooting method": the eigenvalues $E$ are adjusted so that the solution $\{\psi_n\}$ satisfies the required boundary conditions. We shall deal with the question of boundary conditions later on.

b. *Padé Approximants*

In practical applications Eq. (7) is terminated at a given power of $\delta$. The series expansion (7) is difficult to analyze because it is acting on a (unknown) set of values $\{\psi_n\}$ and may be asymptotic [7, 19]. Certainly, if $\delta$ were simply a number, the convergence radius of expansion (7) would be limited to $|\delta/2| < 1$, which is the radius of convergence of the Taylor expansion for $\sinh^{-1}(x)$ [25]. A general procedure for extending the radius of convergence is the use of techniques based on Padé approximants [26]. We apply this procedure to expansion (7) to obtain the following formulae (the notation $h^2D^2[N/M]$ means that $h^2D^2$ is expressed as a quotient of polynomials in $\delta^2$ of degree $N$ and $M$, respectively):

$$h^2D^2[1/0] = \delta^2 - \tfrac{1}{12}h^4D^4$$
$$h^2D^2[2/0] = \delta^2(1 - \tfrac{1}{12}\delta^2) + \tfrac{1}{90}h^6D^6$$

$$h^2D^2[1/1] = \frac{\delta^2}{1 + \frac{1}{12}\delta^2} + \frac{1}{240}h^6D^6$$

$$h^2D^2[3/0] = \delta^2(1 - \frac{1}{12}\delta^2 + \frac{1}{90}\delta^4) + \frac{1}{560}h^8D^8$$

$$h^2D^2[2/1] = \frac{\delta^2(1 + \frac{1}{20}\delta^2)}{1 + \frac{2}{15}\delta^2} - \frac{23}{75,600}h^8D^8$$

$$h^2D^2[1/2] = \frac{\delta^2}{1 + \frac{1}{12}\delta^2 - \frac{1}{240}\delta^4} - \frac{31}{60,480}h^8D^8$$

$$h^2D^2[4/0] = \delta^2(1 - \frac{1}{12}\delta^2 + \frac{1}{90}\delta^4 - \frac{1}{560}\delta^6) + \frac{1}{3150}h^{10}D^{10} \tag{9}$$

$$h^2D^2[3/1] = \frac{\delta^2(1 + \frac{13}{168}\delta^2 - \frac{23}{10080}\delta^4)}{1 + \frac{9}{56}\delta^2} + \frac{3}{1,411,200}h^{10}D^{10}$$

$$h^2D^2[2/2] = \frac{\delta^2(1 + \frac{31}{252}\delta^2)}{1 + \frac{13}{63}\delta^2 + \frac{23}{3780}\delta^4} + \frac{79}{4,762,800}h^{10}D^{10}$$

$$h^2D^2[1/3] = \frac{\delta^2}{1 + \frac{1}{12}\delta^2 - \frac{1}{240}\delta^4 + \frac{31}{60,480}\delta^6} + \frac{289}{725,760}h^{10}D^{10}$$

$$h^2D^2[5/0] = \delta^2(1 - \frac{1}{12}\delta^2 + \frac{1}{90}\delta^4 - \frac{1}{560}\delta^6 + \frac{1}{3150}\delta^8) - 6.01 \times 10^{-5}h^{12}D^{12}$$

$$h^2D^2[4/1] = \frac{\delta^2(1 + \frac{17}{180}\delta^2 - \frac{1}{270}\delta^4 + \frac{43}{226,800}\delta^6)}{1 + \frac{8}{45}\delta^2} - 3.688 \times 10^{-6}h^{12}D^{12}$$

$$h^2D^2[3/2] = \frac{\delta^2(1 + \frac{49}{276}\delta^2 + \frac{79}{28980}\delta^4)}{1 + \frac{6}{23}\delta^2 + \frac{43}{3,220}\delta^4} - 1.156 \times 10^{-6}h^{12}D^{12}$$

$$h^2D^2[2/3] = \frac{\delta^2(1 - \frac{641}{6360}\delta^2)}{1 - \frac{37}{2120}\delta^2 - \frac{959}{76,320}\delta^4 + \frac{29891}{32,054,400}\delta^6} - 3.287 \times 10^{-5}h^{12}D^{12}$$

$$h^2D^2[1/4] = \frac{\delta^2}{1 + \frac{1}{12}\delta^2 - \frac{1}{240}\delta^4 + \frac{31}{60,480}\delta^6 - \frac{289}{725,760}\delta^8} - 1.265 \times 10^{-5}h^{12}D^{12}.$$

We have included only a small subset of all the possible formulae. The Padé forms [N/0] correspond to the three-, five-,... point integration formulae for $N = 1, 2,...$. One may also recognize the three-, five-,... point Numerov's formulae [2] which correspond to the Padé forms [1/1], [1/2],..., [1/N], respectively. Another subset of interest is that of the diagonal Padé approximants [1/1], [2/2],..., [N/N] which have been recently studied [8] and called "extended Numerov methods." (Note that there is a misprint in Eq. (43) of [8]: the coefficient of $f''_i$ should be 2358 instead of 2538.)[1]

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[1] The extension of the Numerov method of [27], Eq. (12), is not an $O(h^8)$ method. Actually, the error is $h^6D^6/1980$. So that even if there is an error in the derivation of the integration formula, the resulting integration formula is better, as the authors conclude, than the three-point Numerov method, its error being $h^6D^6/240$. The quotient form of Eq. (12), [27] is $\delta^2(1 + \frac{1}{4}\delta^2)/(1 + \frac{1}{3}\delta^2 + \frac{1}{60}\delta^4)$, which is not a Padé approximant to Eq. (7) and furthermore is a five-point formula.

In general, the approximant $h^2D^2[N/M]$ is valid to order $h^{2(N+M+1)}$ and the explicit form of the correction has been included in Eqs. (9). This is a simple consequence of the way Padé approximants are constructed. Because of that property, all forms with $N + M$ constant should have essentially the same accuracy for the integration of the differential equation. Padé approximants have unusual properties of a not well-known origin so that the accuracy is not a function of $N + M$ only: in fact, the three-point Numerov formula [1/1] gives more precise results than the five-point Taylor formula [2/0].

A look at the correction terms shows that, for a given value of $N + M$, the coefficient of $(hD)^{2(N+M+1)}$ has the smaller value in the cases $M = N$ or $M = N - 1$. This subset of the Padé table, namely, $[N/N]$ and $[N + 1/N]$, corresponds to the stepwise path followed by the convergents of the continuous-fraction expansion [26].

From a practical point of view, the best formula is the one containing the smaller powers of $\delta$ for the same value of $N + M$ because $\delta^{2n}$ corresponds to a $(2n + 1)$-point integration formula. Accordingly, the optimal formulae from the computational point of view are the $[N/N]$ forms, i.e., the extended Numerov formulae of Burke and the $[N + 1/N]$ forms. Finally, note that Eqs. (9) do not have the usual form: currently the operator in the denominator is acting on the lhs, and the difference operators $\delta^n$ are written in the explicit form

$$\delta^{2n}f_p = \sum_k \begin{pmatrix} 2n \\ k \end{pmatrix} (-)^k f_{p+n-k}. \tag{10}$$

For example, the [1/1] form is usually written as

$$-24f_n + 12(f_{n+1} + f_{n-1}) = h^2(10f_n'' + f_{n+1}'' + f_{n-1}'') \tag{11}$$

and the [2/2] form becomes

$$-4770f_n + 1920(f_{n+1} + f_{n-1}) + 465(f_{n+2} + f_{n-2})$$
$$= h^2(2358f_n'' + 688(f_{n+1}'' + f_{n-1}'') + 23(f_{n+2}'' + f_{n-2}'')). \tag{12}$$

## 3. MATRIX FORM OF THE FINITE-DIFFERENCE SCHEME

### a. *Boundary Conditions*

Matrix forms for the previous difference schemes are obtained by a very simple procedure: let us consider the solution of the Schrödinger equation as a column vector of components $\psi_1, \psi_2, ..., \psi_N$, where $\psi_p = \psi(ph)$. This vector is the position representation of the solution $\psi(r)$ in the discretized coordinate basis $\{x_1, ..., x_N\}$ with $x_p = ph$. When assuming that representation of $\psi(r)$ we are implicitly imposing the boundary conditions

$$\psi(r = 0) = 0$$
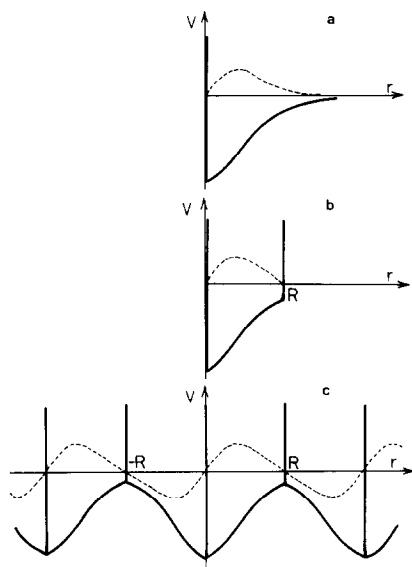$$\psi(R = (N + 1) h) = 0. \tag{13}$$

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FIG. 1. Schematic representation of the numerical solution of the Schrödinger equation with boundary conditions $f(0) = f(R) = 0$. (a) The potential to be solved (thick line) and the exact wave function (dashed line). (b) The effect of the inclusion of an infinite barrier at $r = R$. (c) The periodicity conditions implied in the numerical methods.

The first condition is satisfied by the radial solution of the Schrödinger equation (note that the simple form Eq. (8) of the Schrödinger equation results from the separation of variables $\phi(r) = \psi(r) Y_{lm}(r)/r$, and that the behaviour of $\psi(r)$ at the origin turns out to be $r^{l+1}$ for the regular solution, at least for well-behaved potentials). The second condition (13) is an approximation: in order that the wave function be normalizable it must satisfy the condition $\psi(r) \to 0$ at $r \to \infty$, so that the second equation of (13) assumes that $R = (N + 1) h$ is already very large.

The meaning of the boundary conditions (13) is illustrated in Fig. 1. Figure 1a represents the potential to be studied (thick line) and the eigenfunction (dashed line). This potential is changed according to Eq. (13) as shown in Fig. 1b, by adding two infinite barriers at $r = 0$ and $r = R$. Certainly, if $R$ is large enough one expects to have both energy and wave functions very close to the exact values.

In this representation the second difference operator $\delta^2$ has the matrix form

$$\delta^2 = \begin{bmatrix} -2 & 1 & & & & & \\ 1 & -2 & 1 & & & & \\ & 1 & -2 & 1 & & & \\ & & \ddots & \ddots & \ddots & & \\ & & & 1 & -2 & 1 \\ & & & & 1 & -2 \end{bmatrix}. \tag{14}$$

This tridiagonal matrix appears in many different fields in numerical analysis and has the following interesting properties.

(1)   It is diagonalized by the orthogonal and symmetric transformation

$$A_{pq} = \sqrt{\frac{2}{N+1}} \sin \frac{pq\pi}{N+1}. \tag{15}$$

(2)   Its eigenvalues are

$$(\delta^2)_p = -4 \sin^2 \frac{p\pi}{2(N+1)}. \tag{16}$$

(3)   The corresponding eigenvectors are the columns of matrix $A$.

Note that since all eigenvalues are different, the eigenvectors are uniquely defined apart from a phase factor.

The matrix representation for the fourth-, sixth-,... difference operators is obtained by computing the successive powers of $\delta^2$. We will not be interested in their explicit form for the subsequent development but some aspects are of interest. Consider

$$\delta^4 = \begin{bmatrix} 5 & -4 & 1 & & & \\ -4 & 6 & -4 & 1 & & \\ 1 & -4 & 6 & -4 & 1 & \\ & 1 & -4 & 6 & -4 & 1 \\ & & \ddots & \ddots & \ddots & \ddots & \ddots \end{bmatrix}. \tag{14'}$$

This is a pentadiagonal matrix whose rows are $(0, 0,..., 0, 1, -4, 6, -4, 1, 0,..., 0)$ as corresponds to Eq. (10) with the exception of the two first and last rows. The fourth difference $\delta^4 f_1$ should be

$$\delta^4 f_1 = f_{-1} - 4f_0 + 6f_1 - 4f_2 + f_3 \tag{14''}$$

and to have a matrix form for $\delta^4$ it is necessary to add a supplementary boundary condition, namely, the value of $f_{-1} = f(-h)$ (note that $f_0 = 0$, Eq. (13)). This boundary condition can be obtained by comparing the first row of matrix (14') with Eq. (14'') and it becomes

$$f_{-1} = -f_1.$$

Analogously, $f_{N+2} = -f_N$. If the same reasoning is carried out for $\delta^6, \delta^8,...$, then the following set of boundary conditions results:

$$\begin{aligned} f_{-p} &= -f_p \\ f_{N+p} &= -f_{N-p+2} \end{aligned} \tag{17}$$

which correspond to periodicity of the wave function at $r = 0, 2R, 4R,...$ and antisymmetry around $R, 3R,....$ This is illustrated in Fig. 1c. Periodicity is not surprising; actually, it is well known that the $s$-wave solutions of the radial equation are the odd solutions of the corresponding one-dimensional potential. The condition of antisymmetry at $R$ results from the limitation of the space $[0, \infty]$ to $[0, R]$.

Consider the origin and the practical applications of symmetry properties Eq. (17). When the finite-difference schemes are used to solve the two-point boundary value problem by the shooting method, there is always the question of how to start. In the case where only second differences are involved the solution is trivial: take $y_0 = 0$ and $y_1 = c$, any constant value, and the second difference determines the value of $y_2$. The process is repeated up to $y_{N+1}$, where the outer boundary condition $(y_{N+1} = 0)$ determines how good our guess for the eigenvalue is. When $\delta^4, \delta^6,...$ differences are involved, however, it is necessary to have 4, 6,... initial values, which are usually determined from second differences with a smaller step or by using the (hopefully) known asymptotic properties of the solution near the origin. All of these troubles disappear in the matrix formulation, the problem being reduced to the solution of a generalized matrix-eigenvalue problem (see Eq. (20)) which is easily converted into a standard matrix-eigenvalue problem (see Eq. (25)).

### b. Matrix Form for the Finite Difference Equations

Equation (9) and all other generalized finite-difference equations may be written in matrix form after the substitution of $D^2\psi$ by $(V - E)\psi$, giving rise to a generalized eigenvalue problem of the form

$$\mathbf{N}\psi = h^2\mathbf{M}(\mathbf{V} - E\mathbf{I})\psi, \tag{18}$$

where $\mathbf{N}$ and $\mathbf{M}$ are the matrices corresponding to the numerator and denominator of Eq. (9), and $\mathbf{V}$ is the diagonal matrix

$$V_{pq} = \delta_{pq}V(ph). \tag{19}$$

The matrix form of the generalized finite-difference scheme has been used quite frequently [2, 16]. If Eq. (18) is written in the standard form

$$\mathbf{H}\psi = E\mathbf{\Omega}\psi, \tag{20}$$

then the "overlap" matrix $\mathbf{\Omega}$ is always real and symmetric, but $\mathbf{H}$ is no longer symmetric so that there is no guarantee that the resulting eigenvalues are real (with the exception of the cases $M = 1$, i.e., the $[N/0]$ Padé form which corresponds to the Taylor expansion). This is an unwanted feature of Eq. (20). Another problem in the use of Eq. (20) is that the practical solution of the generalized eigenvalue problem is more time consuming than the solution of the standard eigenvalue problem.

In the present case, however, Eq. (18) may be written in a very simple form just by considering the particularly simple properties of the matrix representation of $\delta^2$. By carrying out the basis transformation

$$\tilde{\psi} = \mathbf{A}\psi \tag{21}$$

with $A$ given by Eq. (15), Eq. (18) turns out to be

$$\mathbf{n}\tilde{\psi} = h^2\mathbf{m}(\tilde{\mathbf{V}} - E\mathbf{I})\,\tilde{\psi}, \tag{22}$$

where $\mathbf{n}$ and $\mathbf{m}$ are the corresponding diagonal forms of $\mathbf{N}$ and $\mathbf{M}$. Given that both $\mathbf{N}$ and $\mathbf{M}$ are a sum of powers of $\delta^2$, e.g.,

$$\mathbf{N} = \sum_n \lambda_n \delta^{2n},$$

then the corresponding diagonal matrices are

$$n_{pq} = \delta_{pq} \sum_n \lambda_n (-)^n \, 4^n \sin^{2n} \frac{p\pi}{2(N+1)} \tag{23}$$

and an analogous result for $\mathbf{m}$. Finally, the potential matrix $\tilde{V}$ is given by

$$\tilde{V}_{pq} = \frac{2}{N+1} \sum_l \sin\left(\frac{pl\pi}{N+1}\right) V(lh) \sin\left(\frac{ql\pi}{N+1}\right). \tag{24}$$

The next step is to divide both sides of Eq. (22) by $\mathbf{m}$ (provided none of the eigenvalues of $\mathbf{m}$ is null[2]) so as to convert the generalized eigenvalue problem into

$$(\tilde{\mathbf{T}} + \tilde{\mathbf{V}})\,\tilde{\psi} = E\tilde{\psi}, \tag{25}$$

where $\tilde{\mathbf{T}}$ is a diagonal matrix given by

$$T_{pq} = -\delta_{pq}\, n_{pp}/h^2 m_{pp}. \tag{26}$$

There is a very important consequence of Eq. (25): the matrix in the lhs is real and symmetric (note that $\tilde{V}$ is symmetric) so that the solution of the eigenvalue equation (25) provides us with $N$ real eigenvalues. A large number of these eigenvalues will not correspond to physical bound states and are a consequence of the inclusion of the two infinite walls at $r = 0$ and $r = R$, but the lowest eigenvalues are expected to correspond to true eigenvalues of the Schrödinger equation provided $R$ is large enough and $h$ small enough.

The explicit form of the matrix $\tilde{T}$, Eq. (26), is very easily obtained from Eq. (9) by the formal replacement

$$\delta^2 \to -4\sin^2\left(\frac{p\pi}{2(N+1)}\right) \tag{27}$$

so that the construction of Eq. (26) is very simple.

[2] Empirical calculations show a strong relation among the poles of Padé approximants and the singularities of the function (see [26], particularly Chapter 10), and probably all poles of the successive Padé approximants are outside the circle of convergence of $\sinh^{-1} z$, i.e., the circle of radius $\delta^2 = 4$. There is, however, no proof of this statement.

## 4. The Momentum Representation and a New Integration Rule

The process carried out in the preceding section is equivalent to expressing all finite-difference schemes in the basis of discretized plane waves. The columns of the matrix $A$, Eq. (15), are a discrete set of plane waves in a box of infinite walls extending from $r = 0$ to $r = R$. The $l$th state is represented by $N$ components which are the (discrete) position representation of $\sqrt{2/(N+1)} \sin(lr\pi/R)$. Furthermore, the vector $\tilde{\psi}$ is the representation of the radial wave function in the same discretized momentum basis, and $\tilde{V}$ is the matrix corresponding to the potential in the same basis. We will refer to the set of orthogonal vectors which constitute the matrix $A$ as PW, acronym of plane waves.

Let $|p\rangle$, $|q\rangle$,... represent vectors of the set PW, and $|n\rangle$, $|m\rangle$,... basis vectors of the position representation. Then

$$\langle n | p \rangle = \sqrt{\frac{2}{N+1}} \sin \frac{np\pi}{N+1} \tag{28}$$

and the matrix $\tilde{V}$ in momentum representation is

$$\tilde{V}_{pq} = \langle p | V | q \rangle = \sum_n \langle p | n \rangle \langle n | V | n \rangle \langle n | q \rangle, \tag{29}$$

because $\langle n | V | m \rangle$ is diagonal in position representation, its value being $V_n \delta_{mn}$. Then

$$\tilde{V}_{pq} = \sum_n \langle p | n \rangle V_n \langle n | q \rangle \tag{30}$$

which is exactly Eq. (24). We have computed $\tilde{V}$ carefully to realize that $\tilde{V}$ is *exactly* computed in the discretized basis, even if Eq. (24) looks like a trapezoidal integration rule. If the latter were true, i.e., if the potential were computed through a trapezoidal rule, all finite-difference methods would have accuracy $O(h^2)$. Note also that in Eq. (24) the value of the matrix $\tilde{V}$ is the same for any method based on finite differences, the difference among the various integration rules being only in the value used for the kinetic part $\tilde{T}$.

It is important to realize that the PW basis has appeared naturally in our development, this basis being the only one which diagonalizes $\delta^2$. If, however, we were working from the very beginning with the PW basis, then for the kinetic term, we would have used a matrix very different from the matrices related to Eq. (9), namely,

$$\tilde{T}_{pq} = h^{-2} \delta_{pq} \left( \frac{p\pi}{N+1} \right)^2 \tag{31}$$

which corresponds to the discretized form of the kinetic energy operator in the momentum representation. It is then natural to conjecture that the PW form for

kinetic energy equation (31) is the limiting form for any $[N/M]$ family of the Padé table, and this may be formally proved as follows: From the diagonal representation of $\delta^2$, Eq. (27), we may write

$$\delta_{pp} = 2i \sin \frac{p\pi}{2(N+1)}$$

so that the inverse of Eq. (5) says

$$\left( \sinh \frac{hD}{2} \right)_{pp} = i \sin \frac{p\pi}{2(N+1)}$$

i.e.,

$$\left( \frac{hD}{2} \right)_{pp} = i \frac{p\pi}{2(N+1)}$$

and

$$(D^2)_{pp} = -h^{-2} \left( \frac{p\pi}{N+1} \right)^2.$$

The proof is purely formal because $\delta$ extends outside our space: the central differences, according to Eq. (3) need the values of the function at half-integer points, which are not included in the space. Appendix A includes a proof of Eq. (31).

In Fig. 2 we compare the diagonal matrix elements of $\tilde{T}$ for the Numerov methods, the Taylor expansion, and the PW result Eq. (31) for $N = 20$. The tendency of these values toward the PW result is clear when the accuracy increases, and we may
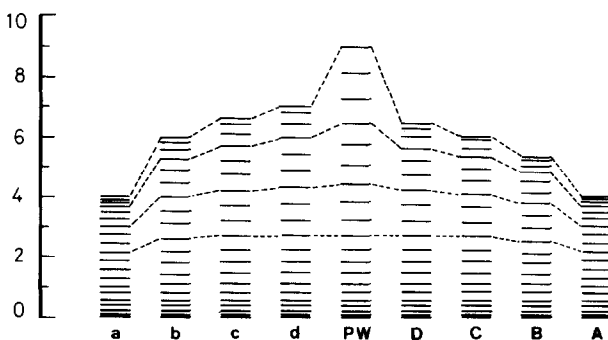


FIG. 2. The diagonal elements of the kinetic energy operator in several approximations (in units of $h^2$). The spectra labeled a, b, c, and d correspond to the 3-, 5-, 7-, and 9-point Numerov methods (Padé forms $1/n$). The spectra labeled A, B, C, and D correspond to the 3-, 5-, 7-, and 9-point Taylor methods (Padé forms $n/0$). **PW** corresponds to the discretized plane wave method. The number of mesh points is $N = 20$, and the dashed lines connect corresponding states.

conclude that the PW form is optimal for the calculation of the kinetic energy in the finite-difference schemes.

The PW form of the eigenvalue equation may be transformed back to position representation by computing the quantities

$$\mathbf{T}_{nm} = \frac{2}{N+1} \sum_p \sin \frac{pn\pi}{N+1} \sin \frac{pm\pi}{N+1} \frac{1}{h^2} \left( \frac{p\pi}{N+1} \right)^2$$

with the result

$$\mathbf{T}_{nm} = \frac{(-1)^{n+m}}{2h^2} \frac{\pi^2}{(N+1)^2} \left\{ \left[ \sin^2 \frac{(n-m)\pi}{2(N+1)} \right]^{-1} - \left[ \sin^2 \frac{(n+m)\pi}{2(N+1)} \right]^{-1} \right\}, \qquad n \neq m$$

$$\mathbf{T}_{nm} = \frac{1}{h^2} \frac{\pi^2}{(N+1)^2} \left\{ \tfrac{1}{3}N^2 + \tfrac{2}{3}N + \tfrac{1}{2} - \left[ 2 \sin^2 \frac{n\pi}{N+1} \right]^{-1} \right\}$$

(32)

and eigenvalue equation (25) may be solved in position representation using for **V** the diagonal coordinate form. Accordingly, we may bypass the computation of the Fourier transform of **V**. The position representation results in a noticeable saving of computing time in the case of extensive use of the numerical solution of the Schrödinger equation as, e.g., in Hartree–Fock calculations, because the kinetic energy matrix (32) may be computed and saved at the beginning, and only the diagonal values of $V$ need to be recomputed at each iteration.

## 5. CONCLUSIONS

The preceding sections present a unified description of numerical methods based upon the finite-difference schemes at constant step and the limit corresponding to the discretized plane-wave method. There are some results to be specifically mentioned.

(1)   Among methods accurate up to order $h^{2n}$, the best ones correspond to the Padé forms $[\tfrac{1}{2}n/\tfrac{1}{2}n]$ or $[\tfrac{1}{2}(n+1)/\tfrac{1}{2}(n-1)]$. Moreover, these methods are the simplest because they involve smaller powers of the difference operator $\delta$.

(2)   No special procedure is needed to determine the starting values of the function to carry out the integration.

(3)   Insofar as all methods give rise to a standard matrix-eigenvalue problem, the matrix being symmetric, they always provide a set of $N$ real eigenvalues.

(4)   In contrast with the conjecture of Mayers [7], expansion (7) of the second derivative is not asymptotic, but strictly convergent in the domain of functions with the boundary conditions $f(0) = f((N+1)h) = 0$, because the operator $\delta^2$ is bounded (Eq. (16)).

(5)   The exact summation is easily carried out and gives the best finite-difference integration method (PW method, Eq. (32)). The word "best" is correctly

applied in this context. All finite-difference based methods give rise to a matrix-eigenvalue problem $(T + V)\psi = E\psi$, where the potential matrix $V$ is independent of the method, and the kinetic energy $T$ has the best representation in the plane-wave limit.

There is a final remark which is worth considering. It is customary to classify the errors in the numerical integration of the Schrödinger equation into three groups [16]: *termination* errors coming from the use of a finite value of $R$, *roundoff* errors related to the finite-word length in computing machines, and *truncation* errors related to the approximation involved in the representation of a differential equation by a finite set of equations. We will only comment on the third kind of error. Truncation errors are due to truncation of the Taylor series expansion and decrease when the integration step decreases. These errors, however, do not disappear when the Taylor expansion is not truncated, as in the case of the PW limit. The use of a discretization in $N$ points is somehow equivalent to considering a basis of $N$ plane waves, and the lack of completeness of this basis is still the remaining source of error.

## APPENDIX A

The proof of Eq. (31) is carried out in the following manner: Start from the equation

$$h^2 D^2 = 4\{\sinh^{-1}(\delta/2)\}^2$$

at $\delta^2 = -4\sin^2(p\pi/2(N+1))$, corresponding to the $(p, p)$ diagonal element. The Taylor expansion of $\sinh^{-1}$ gives the result

$$h^2 D^2 = \delta^2 \left\{ \sum_{n=0}^{\infty} (-1)^n \frac{(2n)!}{2^{2n}(n!)^2 (2n+1)} \left(\frac{\delta}{2}\right)^{2n} \right\}^2, \qquad \delta^2 \leqslant 4, \qquad (A1)$$

where only $\delta^2$ is present, so that

$$h^2 D^2 = -4\sin^2\frac{p\pi}{2(N+1)} \left\{ \sum_{n=0}^{\infty} \binom{2n}{n} \frac{1}{(2n+1)} \frac{1}{2^{2n}} \sin^{2n}\frac{p\pi}{2(N+1)} \right\}^2. \quad (A2)$$

If this equation is compared with the series expansion of $\sin^{-1}(x)/x$, namely,

$$\frac{\sin^{-1}(x)}{x} = \sum_{n=0}^{\infty} \binom{2n}{n} \frac{1}{(2n+1)} \left(\frac{x}{2}\right)^{2n}, \qquad x^2 \leqslant 1, \qquad (A3)$$

then one concludes that

$$h^2 D^2 = -4\sin^2\frac{p\pi}{2(N+1)} \left\{ \left[\sin^{-1}\left(\sin\frac{p\pi}{2(N+1)}\right)\right] \middle/ \left[\sin\frac{p\pi}{2(N+1)}\right] \right\}^2 \cdot \cdot$$

There is no ambiguity when interpreting $\sin^{-1}(\sin x)$, because Eq. (A3) corresponds to $\sin^{-1} x$ in the $(-\pi/2, \pi/2)$ determination. Then Eq. (31) turns out.

There is also an important consequence of Eq. (A1). The expansion of $\sinh^{-1}$ is valid in the domain $x^2 \leqslant 1$, i.e., $\delta^2 \leqslant 4$, but the operator $\delta^2$ is strictly bounded by $-4$ (see Eq. (27)), so that all integration rules based upon Eq. (7) are well behaved, contrary to the conjecture of Mayers [7].

Probably, the instability related to the use of more-than-three-point integration formulae is a consequence of the inaccuracy in computing the starting points, this problem not occurring in the case of three-point formulae (see e.g., [2] and [27] on that question). We believe this is the explanation of Mayers' [7] and Blatt's [3] comments on the use of many-point integration rules. Note that the Numerov three-point formula is effectively a many-point integration formula: if one transforms the Numerov method back to coordinate representation (as we do with the PW method at the end of Section 4), then a full (not banded) $N \times N$ matrix results. The absence of instability of Numerov three-point formula supports our explanation.

## REFERENCES

1. B. NUMEROV, *Pub. Obs. Cent, Astrophys. Russ.* 2 (1933), 188.
2. C. FROESE-FISCHER, "The Hartree–Fock Method for Atoms," Wiley, New York, 1977.
3. J. M. BLATT, *J. Comput. Phys.* 1 (1967), 382.
4. J. W. COOLEY, *Math. Comput.* 15 (1961), 363.
5. B. R. JOHNSON, *J. Chem. Phys.* 67 (1977), 4086.
6. F. Y. HAJJ, *J. Phys.* B13 (1980), 4521.
7. D. F. MAYERS, Computational methods in the differential equations of atomic physics, *in* "New Directions in Atomic Physics" (E. U. Condon and O. Sinanoglu, Eds.), Vol. I, Yale Univ. Press, New Haven, Conn. 1972.
8. E. A. BURKE, *J. Math. Phys.* 21 (1980), 1366.
9. J. CANOSA AND R. G. DE OLIVEIRA, *J. Comput. Phys.* 5 (1970), 88.
10. R. G. GORDON, *J. Chem. Phys.* 51 (1969), 14.
11. M. DUFF, H. RABITZ, A. ASKAR, A. CAKMAK, AND M. ABLOWITZ, *J. Chem. Phys.* 72 (1980), 1543.
12. L. COLLATZ, "The Numerical Treatment of Differential Equations," Springer–Verlag, Berlin, 1966.
13. D. J. LOCKER, *J. Phys. Chem.* 75 (1971), 1756.
14. B. W. SHORE, *J. Phys.* B6 (1973), 1923.
15. J. P. CHESIEK, *J. Chem. Phys.* 49 (1968), 3772.
16. B. W. SHORE, *J. Chem. Phys.* 59 (1973), 6450.
17. D. O. HARRIS, G. ENGERHOLM, AND W. GWINN, *J. Chem. Phys.* 43 (1965), 1515.
18. A. S. DICKINSON AND R. P. CERTAIN, *J. Chem. Phys.* 49 (1968), 4209.
19. C. SCHWARTZ, *J. Comput. Phys.* 2 (1967), 90.
20. J. GARY AND R. HELGASON, *J. Comput. Phys.* 5 (1970), 169.
21. A. S. DICKINSON, *J. Comput. Phys.* 11 (1973), 458.

22. L. WUYTACK, Application of Padé approximants in numerical analysis, *in* "Approximation Theory" (R. Schaback and K. Scherer, Eds.), Springer–Verlag, Berlin, 1976.
23. H. W. CRATER AND G. W. REDDIEN, *J. Comput. Phys.* **19** (1975), 236.
24. F. B. HILDEBRAND, "Introduction to Numerical Analysis," Chapter 5, McGraw–Hill, New York, 1974.
25. M. ABRAMOWITZ AND I. STEGUN, "Handbook of Mathematical Functions," Dover, New York, 1964.
26. G. A. BAKER, "Essentials of Padé Approximants,"Academic Press, New York, 1975.
27. F. Y. HAJJ, H. KOBEISSE, AND N. R. NASSIF, *J. Comput. Phys.* **16** (1974), 150.