Wronskian method and the Schrödinger eigenvalue march

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Abstract

We compare the Wronskian method (WM) and the Schrödinger eigenvalue march or canonical function method (SEM–CFM) for the calculation of the energies and eigenfunctions of the Schrödinger equation. The Wronskians between linearly independent solutions of the Schrödinger equation provide a rigorous basis for some of the assumptions of the SEM–CFM, like, for example, the concept of “saturation”. We compare the performance of both approaches on a simple one-dimensional model and suggest that taking into account the asymptotic behavior of the wavefunction (as is already done in the WM) may make the SEM–CFM more efficient from a numerical point of view.

1 Introduction

In a recent paper Tannous and Langlois [1] proposed the Schrödinger eigenvalue march (SEM) for the calculation of eigenvalues of the Schrödinger equation. The SEM was developed by Kobeissi [2] under the name of canonical function method.
function method (CFM) and even Tannous and Langlois \cite{3} and Tannous et al \cite{1} used to call it that way before renaming it. According to the authors, the SEM compares favourably to the well-known Numerov and shooting methods \cite{1}. Leubner \cite{5} argued that the underlying idea of the CFM is very old and can be found in standard textbooks on differential equations as the reduction of two–point boundary value problems to initial value problems. In addition to it, he also proved the equivalence between the CFM and the widely used shooting method. In a rather late reply, Kobeissi \cite{6} tried to show that the CFM is considerably more accurate than the shooting method and other algorithms. However, Tellinghuisen \cite{7} confirmed Leubner’s conclusions and showed that the apparent numerical advantage found by Kobeissi \cite{6} was merely due to different numerical precision in the results compared by this author. Leubner’s and Tellinghuisen’s papers have been utterly omitted in all later applications of the CFM \cite{4}. It is worth quoting Tellinghuisen’s comment that ‘Although the CFM is fundamentally less efficient than the Cooley algorithm, it does offer some advantages in practical applications, as it avoids unnecessary integration in the nonclassical region’.

We have recently discussed a method for the calculation of bound states and transmission probabilities for one–dimensional wells and barriers \cite{8–10}. It is based on the fact that the coefficients of the linearly independent asymptotic contributions to the wavefunction can be easily expressed in terms of Wronskians. Those papers were mainly focused on the pedagogical value of the Wronskian method (WM) that is already known since long ago (see the references cited there \cite{8–10}). Since the WM is also based on the so called canonical functions \cite{2–4, 6} (or normalized solutions \cite{1}) we think that it may be interesting and fruitful from a pedagogical point of view to compare it with the SEM (or CFM). In Sec. 2 we outline the main ideas behind the WM. In Sec. 3 we discuss the SEM–CFM and provide a rigorous basis for some of its equations by means of the WM. In Sec. 4 we test, discuss and verify the
general results by means of simple examples. Finally, in Sec. 5 we summarize
the main results and draw conclusions.

2 The Wronskian method

In order to introduce the main ideas of the WM we consider the second–order
differential equation

\[ L(y) = y''(x) + Q(x)y(x) = 0 \] (1)

If \( y_1 \) and \( y_2 \) are two solutions to this equation then we have

\[ y_1L(y_2) - y_2L(y_1) = \frac{d}{dx}W(y_1, y_2) = 0 \] (2)

where

\[ W(y_1, y_2) = y_1y_2' - y_2y_1' \] (3)

is the Wronskian (or Wronskian determinant). If \( y_1 \) and \( y_2 \) are linearly inde-
dependent then the Wronskian (3) is a nonzero constant. For practical purposes
it is convenient to choose two solutions \( C(x) \) and \( S(x) \) that satisfy

\[ C(x_0) = S'(x_0) = 1, \quad C'(x_0) = S(x_0) = 0 \] (4)

at a given point \( x_0 \), so that \( W(C, S) = 1 \) for all \( x \).

In this paper we are interested in the dimensionless Schrödinger equation

\[ -\frac{1}{2}\varphi''(x) + v(x)\varphi(x) = \epsilon\varphi(x) \] (5)

where \( \epsilon \) and \( v(x) \) are the dimensionless energy and potential, respectively. In
earlier papers we have discussed a systematic way of converting the standard
Schrödinger equation into its dimensionless form \([8–10]\) and we do not repeat it here. In order to facilitate the discussion below we assume that \(-\infty < x < \infty\), keeping in mind that the main results can be extended to other cases if necessary. If \(C(x)\) and \(S(x)\) are two solutions satisfying (4) then we can write a general solution as

\[
\varphi(x) = A_2 C(x) + B_2 S(x) \quad (6)
\]

where, obviously,

\[
A_2 = \varphi(x_0) = W(\varphi, S) \\
B_2 = \varphi'(x_0) = W(C, \varphi) \quad (7)
\]

For notation simplicity we write \(C(x)\) and \(S(x)\) instead of the more detailed expressions \(C(\epsilon, x_0, x)\) and \(S(\epsilon, x_0, x)\), respectively, that explicitly indicate the dependence of the linearly independent solutions on the dimensionless energy \(\epsilon\) and the chosen coordinate point \(x_0\).

It is well known that for an arbitrary value of the dimensionless energy \(\epsilon\) the wavefunction behaves asymptotically as

\[
\varphi(x) \rightarrow \begin{cases} 
A_1 L_c(x) + B_1 L_d(x), & x \rightarrow -\infty \\
A_3 R_c(x) + B_3 R_d(x), & x \rightarrow \infty
\end{cases} \quad (8)
\]

where \(L\) and \(R\) stand for left and right and \(c\) and \(d\) for convergent and divergent, respectively. It means that, for arbitrary \(\epsilon\), the wavefunction is a linear combination of a convergent and a divergent function when \(|x| \rightarrow \infty\). If, for a particular value of \(\epsilon\), \(B_1 = B_3 = 0\) then the resulting wavefunction is square integrable. This condition determines the energies of the discrete spectrum.

It follows from the well known properties of the Wronskians \([8–10]\) (and references therein) that
\[
B_1 W(L_c, L_d)_- = A_2 W(L_c, C)_- + B_2 W(L_c, S)_- \\
B_3 W(R_c, R_d)_+ = A_2 W(R_c, C)_+ + B_2 W(R_c, S)_+ 
\] (9)

where the subscripts \(-\) and \(\,+\) indicate that the Wronskians are calculated in the limits \(x \to -\infty\) and \(x \to \infty\), respectively (where they become constants). Therefore, when \(B_1 = B_3 = 0\) we have a linear homogeneous system of two equations with two unknowns: \(A_2\) and \(B_2\). There will be nontrivial solutions provided that its determinant vanishes

\[
W(L_c, C)_- W(R_c, S)_+ - W(R_c, C)_+ W(L_c, S)_- = 0 
\] (10)

The roots of this equation \(\epsilon_n, n = 0, 1, \ldots\), are the energies of the bound states.

When the potential is parity invariant

\[
v(-x) = v(x) \] (11)

and \(x_0 = 0\) then \(C(x)\) and \(S(x)\) are even and odd functions, respectively. In this case we have

\[
W(L_c, S)_- = W(R_c, S)_+ \\
W(L_c, C)_- = -W(R_c, C)_+ 
\] (12)

and the determinant (10) takes a simpler form: \(W(R_c, C)_+ W(R_c, S)_+ = 0\). We appreciate that the even and odd solutions are clearly separate and their eigenvalues are given by

\[
W(R_c, C)_+ = 0 \\
W(R_c, S)_+ = 0 
\] (13)

respectively. Besides, we need to consider only the interval \(0 \leq x < \infty\).
3 The canonical–function method or Schrödinger eigenvalue march

In order to compare the results of Sec. 3 with the SEM–CFM [1–4] we simply note the following equivalence between the main functions \( \phi(x) \rightarrow y(x) \), \( C(x) \rightarrow \alpha(x) \) and \( S(x) \rightarrow \beta(x) \). It follows from equation (7) that

\[
\frac{\phi'(x_0)}{\phi(x_0)} = \frac{W(C, \phi)}{W(\varphi, S)} = \frac{C\varphi' - C'\varphi}{\varphi' S - \varphi S'}
\]  

In the SEM–CFM one defines

\[
l_-(\epsilon) = \lim_{x \to -\infty} \frac{W(C, \phi)}{W(\varphi, S)} = \frac{W(C, \phi)_-}{W(\varphi, S)_-}
\]

\[
l_+(\epsilon) = \lim_{x \to \infty} \frac{W(C, \phi)}{W(\varphi, S)} = \frac{W(C, \phi)_+}{W(\varphi, S)_+}
\]

and obtains the eigenvalues from the roots of [1–4]

\[
F(\epsilon) = l_+(\epsilon) - l_-(\epsilon) = 0
\]

Note that Eqs. (15) are identical to Eqs (4) of Tannous and Langlois [1]. Therefore, the WM is quite similar to SEM except for some slight differences that we will discuss later on.

For concreteness we assume that the acceptable solutions to the dimensionless Schrödinger equation (5) satisfy the boundary conditions

\[
\lim_{|x| \to \infty} \phi(x) = 0
\]  

In such a case it is customary to simplify the SEM–CFM equations (15) as follows [1–4]

\[
l_-(\epsilon) = \lim_{x \to -\infty} \frac{C(x)}{S(x)}
\]

\[
l_+(\epsilon) = \lim_{x \to \infty} \frac{C(x)}{S(x)}
\]
In order to provide a rigorous proof for these equations we take into account that

\[ C(x) = a_1 L_c(x) + b_1 L_d(x), \quad x \to -\infty \]
\[ S(x) = a'_1 L_c(x) + b'_1 L_d(x), \quad x \to -\infty \]
\[ C(x) = a_3 R_c(x) + b_3 R_d(x), \quad x \to \infty \]
\[ S(x) = a'_3 R_c(x) + b'_3 R_d(x), \quad x \to \infty \]  \hspace{1cm} (19)

so that

\[ l_- = \lim_{x \to -\infty} \frac{C(x)}{S(x)} = \frac{b_1}{b'_1} \]
\[ l_+ = \lim_{x \to \infty} \frac{C(x)}{S(x)} = \frac{b_3}{b'_3} \]  \hspace{1cm} (20)

We can thus give a precise meaning to the word “saturation” often used in connection with the SEM–CFM [1, 3, 4]. It simply points to the obvious fact that the divergent functions dominate when \( |x| \) is sufficiently large and \( l_\pm \) tend to the ratios of their coefficients in the expansion of the functions \( C(x) \) and \( S(x) \). Besides, the WM gives us expressions for the coefficients in equation (19) and their ratios read

\[ \frac{b_1}{b'_1} = \frac{W(C, L_c)_-}{W(S, L_c)_-} \]
\[ \frac{b_3}{b'_3} = \frac{W(C, R_c)_+}{W(S, R_c)_+} \]  \hspace{1cm} (21)

Consequently equation (16) leads to (10) that has been rigorously proved in Sec. 2. Obviously, the right-hand sides of equation (20) do not change if we substitute \( C'(x)/S'(x) \) for \( C(x)/S(x) \) as pointed out by Kobeissi [2] without giving a rigorous proof. More precisely, if we substitute any pair of linearly independent solutions for \( C(x) \) and \( S(x) \) in equations (20) and (21) we should obtain a similar result. It does not mean that all the pairs of solutions will be equally efficient from a numerical point of view. We simply want to point out that the WM provides a rigorous proof for the main equations commonly used in the SEM–CFM.
If we require that \( \varphi(x_L) = \varphi(x_R) = 0 \) for \( x_L \ll x_0 \ll x_R \) then we have an homogeneous system of two equations with two unknowns

\[
\begin{align*}
A_2C(x_L) + B_2S(x_L) &= 0 \\
A_2C(x_R) + B_2S(x_R) &= 0
\end{align*}
\]

that has nontrivial solutions only if

\[
C(x_L)S(x_R) - C(x_R)S(x_L) = 0
\]

This determinantal equation, derived earlier by Leubner [5], is equivalent to

\[
l_+(\epsilon) - l_-(\epsilon) = 0
\]

since \( l_+(\epsilon) = C(x_R)/S(x_R) \) and \( l_-(\epsilon) = C(x_L)/S(x_L) \) in the right and left asymptotic regions, respectively.

In the case of a symmetric potential and \( x_0 = 0 \) we have \( C(-x) = C(x) \) and \( S(-x) = -S(x) \) and the approximate eigenvalues are roots of the simpler equation \( C(x_R)S(x_R) = 0 \); that is to say \( C(x_R) = 0 \) or \( S(x_R) = 0 \) for the even or odd solutions, respectively.

## 4 Examples

As a first illustrative example, Tannous and Langlois [1] considered a particle of mass \( m \) in a box with impenetrable walls at \( x = 0 \) and \( x = a \)

\[
-\frac{\hbar^2}{2m}\psi''(X) = E\psi(X), \quad \psi(0) = \psi(a) = 0
\]

as a model for an electron in a one–dimensional metallic rod of finite length. The electron moves freely inside \( (V(x) = 0) \) and cannot escape from the rod \( (V(x) = \infty \ if \ x < 0 \ or \ x > a) \). They applied the SEM and obtained the well known energies. However, their choice of the model parameter \( a \) is rather atypical. Here, on the other hand, we transform the Schrödinger equation (24) into a dimensionless eigenvalue equation by means of the change of variables
\( X = ax \) and \( \varphi(x) = \sqrt{a}\psi(ax) \) that leads to \( \varphi''(x) = -2\epsilon\varphi(x) \), where \( \epsilon = ma^2E/\hbar^2 \). Note that the boundary conditions for the dimensionless solutions are \( \varphi(0) = \varphi(1) = 0 \).

Tannous and Langlois mention the problem of defining proper self-adjoint extensions of the operators for the infinite-well potential [11]. This mathematical subtlety is of great importance in the discussion of physical observables but it is not an issue with regard to the calculation of the eigenvalues by means of a numerical method like the SEM-CFM.

The particle in an infinite square well is suitable for the pedagogical analysis of the performance of the shooting methods. If we consider a set of discrete coordinate points \( x_j = jh, \ j = 0, 1, \ldots, N \) such that \( x_N = Nh = 1 \) and define the approximate finite-difference first and second derivatives

\[
\delta_h \varphi(x) = \frac{\varphi(x + h) - \varphi(x - h)}{2h} = \varphi'(x) + \frac{h^2\varphi'''(x)}{6} + \ldots
\]

\[
\delta_h^2 \varphi(x) = \frac{\varphi(x + 2h) - 2\varphi(x) + \varphi(x - 2h)}{4h^2} = \varphi''(x) + \frac{h^2\varphi^{IV}(x)}{3} + \ldots \quad (25)
\]

then the Schrödinger equation becomes a three-term recurrence relation

\[
\varphi_{j+2} + \left( 8h^2\epsilon - 2 \right) \varphi_j + \varphi_{j-2} = 0 \quad (26)
\]

where \( \varphi_j = \varphi(x_j) \) and \( j = 1, 2, \ldots, N - 1 \). On substituting the solution \( \varphi_j = e^{ij\theta} \) we obtain

\[
\epsilon = \frac{1 - \cos(2\theta)}{4h^2} \quad (27)
\]

Since \( \varphi_j = e^{-ij\theta} \) is also a solution, then the general one will be \( \varphi_j = Ae^{ij\theta} + Be^{-ij\theta} \). From the boundary conditions \( \varphi_0 = \varphi_N = 0 \) we obtain \( \varphi_j = 2Ai \sin(j\theta) \), where \( \theta = n\pi/N, \ n = 1, 2, \ldots, N - 1 \) (note that \( N \to \infty \) as \( h \to 0 \)). Therefore,
the approximate eigenvalues are

\[
\epsilon_n = \frac{1 - \cos(2n\pi h)}{4h^2} = \frac{n^2\pi^2}{2} - \frac{n^4\pi^4h^2}{6} + \ldots
\]  

(28)

This expression shows that the error in the numerical calculation of the eigenvalues decreases quadratically with the step size \(h\) and increases with the quantum number \(n\). A method is called \(k^{th}\) order if its error term is of order \(h^{k+1}\) \[12\]. The naive shooting method just outlined is first order. There are other well-known numerical integration algorithms of greater order like the fourth-order Runge-Kutta method \[12\] that we will use in the calculations below.

Tannous and Langlois \[1\] do not indicate the value of \(x_0\) chosen for their calculation on the infinite square well. More precisely, they appear to be rather inconsistent about this important point. They first state that if the potential is symmetric in the interval \([x_1, x_2]\) they choose \(x_0 = (x_1 + x_2)/2\). However, in the discussion of the boundary conditions, they say that if the potential is symmetric in an interval of length \(a\) they set \(x_1 = 0\) and \(x_2 = a/2\) in which case we expect a different value of this coordinate point: \(0 < x_0 < a/2\). Therefore, in order to illustrate the application of the method to this trivial model we choose an arbitrary value \(0 < x_0 < 1\) and do not exploit the symmetry of the equation about \(x = 1/2\). The two linearly independent solutions that satisfy Eq. (4) are \(C(x) = \cos[k(x - x_0)]\) and \(S(x) = k^{-1}\sin[k(x - x_0)]\), where \(k = \sqrt{2\epsilon}\). Obviously, in this case we do not have to bother about reaching constant values of \(l_\pm\) (saturation) because the coordinate interval is finite. Upon substituting the Dirichlet boundary conditions into equations (16) and (18) (adapted to the finite interval) we obtain

\[
F(\epsilon) = l_+(\epsilon) - l_-(\epsilon) = -k\frac{\sin(k)}{\sin(kx_0)\sin[k(1 - x_0)]}
\]  

(29)
Fig. 1 shows $F(\epsilon)$ for $0 < \epsilon < 10$ and $x_0 = 1/8, 1/4, 2/5$. Note that $F(\epsilon)$ vanishes at $k = n\pi$, $n = 1, 2, \ldots$ thus giving the well known eigenvalues disregarding the chosen value of $x_0$. We also appreciate the effect of $x_0$ on the form of the characteristic function $F(\epsilon)$.

Commonly, it is not difficult to derive approximate expressions for the convergent and divergent asymptotic forms of the wavefunction because they are straightforwardly determined by the asymptotic behaviour of the potential $v(x)$. Therefore, it only remains to have sufficiently accurate expressions for $C(x)$ and $S(x)$ and their derivatives in order to obtain the eigenvalues by means of the equations developed in sections 2 and 3. This problem is easily solved by means of, for example, a suitable numerical integration method \[12\]. If $y(x)$ stands for either $C(x)$ or $S(x)$ then such an approach gives us its values at a set of points $x_0 - N_L h, x_0 - N_L h + h, \ldots, x_0, x_0 + h, \ldots, x_0 + N_R h$ where $N_L$ and $N_R$ are the number of steps of size $h$ to the left and right of $x_0$, respectively. The number of steps should be sufficiently large so that $y(x)$ reaches its asymptotic value at both $x_L = x_0 - N_L h$ and $x_R = x_0 + N_R h$ and $h$ should be sufficiently small to provide a good representation of $y(x)$. The numerical integration methods also yield the derivative of the function $y'(x)$ at the same set of points which facilitates the calculation of the Wronskians.

If the potential is parity invariant we only need to integrate the Schrödinger equation from $x_0 = 0$ to $x_R = N_R h$.

In Sec. 3 we provided a rigorous basis for the SEM–CFM that is one of the goals of this paper. In what follows we illustrate those mathematical results by means of another exactly solvable problem. For concreteness we choose

$$v(x) = -\frac{v_0}{\cosh^2(x)}, \quad (30)$$

where $-\infty < x < \infty$. The allowed dimensionless energies are given by \[8, 13\].
\[ \epsilon_n = -\frac{1}{2}(\lambda - 1 - n)^2, \quad n = 0, 1, \ldots \leq \lambda - 1 \]

\[ \lambda = \frac{1}{2} \left(1 + \sqrt{1 + 8v_0}\right) \]  \quad (31)

and the spectrum is continuous for all \( \epsilon > 0 \). It is clear that \( \lambda \to 1 \) as \( v_0 \to 0 \) and there is only one bound state when \( 1 < \lambda < 2 \) (\( 0 < v_0 < 1 \)). As \( v_0 \) increases more bound states appear. As a result there are critical values of the potential parameter for which \( \epsilon_n = 0 \) that are given by the condition \( \lambda_n = n + 1 \) or \( v_{0,n} = \lambda_n(\lambda_n - 1)/2 = n(n + 1)/2 \).

Since \( \lim_{|x| \to \infty} v(x) = 0 \) we have \( R_c(x) \to e^{-kx} \) and \( R_d(x) \to e^{kx} \), where \( k^2 = -2\epsilon \) (we only consider the interval \( 0 \leq x < \infty \) because the potential is parity invariant). Consequently, the allowed energies are determined by the conditions

\[ W(R_c, C)_+ = \lim_{x \to \infty} [C'(x) + kC(x)] e^{-kx} = 0 \]

\[ W(R_c, S)_+ = \lim_{x \to \infty} [S'(x) + kS(x)] e^{-kx} = 0 \]  \quad (32)

for even and odd states, respectively.

Since the potential (30) is parity invariant we integrate the Schrödinger equation from \( x_0 = 0 \) to \( x_R = N_Rh \). Fig. 2 shows the Wronskians \( W(R_c, C) \) and \( W(R_c, S) \) and the ratios \( C(x)/S(x) \) and \( W(R_c, C)/W(R_c, S) \) for the arbitrary values \( \epsilon = -1 \) and \( v_0 = 2.5 \). We appreciate that the ratios \( C(x)/S(x) \) and \( W(R_c, C)/W(R_c, S) \) approach the same constant value as \( x \to \infty \) as proved in Sec. 3. Note that the latter reaches the limit at smaller coordinate values because the Wronskians take into account the asymptotic form of the solution explicitly. In other words, the WM requires less integration steps for the same accuracy. We also appreciate that \( x_R = 5 \) is large enough for the WM and SEM–CFM calculations in this case. In order to compare both approaches we find it reasonable to set \( h = 0.01 \) and \( N_R = 500 \) in the fourth–order Runge–Kutta method \[12\] built in the computer algebra system Derive (http://www.chartwellyorke.com/derive.html) that we use in all our
calculations. The numerical integration routine for the WM and SEM–CFM is identical and the only difference is given by the functions that we choose for the construction of $F(\epsilon)$.

Fig. 2 shows the Wronskians and the ratios $C(x_R)/S(x_R)$ and $S(x_R)/C(x_R)$ for $-10 < \epsilon < 0$ and $v_0 = 10$. We see that both approaches yield the exact eigenvalues marked by black squares in the same figure. The main difference is that the Wronskians change much more smoothly than the canonical functions that cut the abscissae axis sharply at the eigenvalues.

In many cases it is not difficult to derive the asymptotic form of the convergent and divergent contributions to the wavefunction. As another example consider the anharmonic oscillator $v(x) = v_2 x^2 + v_4 x^4$ ($v_4 > 0$). A particular case is given by the double well discussed by Tannous and Langlois [1]. If we introduce the ansatz $\varphi(x) = e^{-f(x)}$ into the Schrödinger equation and keep only the dominant term we conclude that $R_c(x) \to \exp \left(-\frac{\sqrt{2} v_4}{3} x^3\right)$ and $R_d(x) \to \exp \left(\frac{\sqrt{2} v_4}{3} x^3\right)$ as $x \to \infty$. On inserting these asymptotic expansions into the WM or the SEM–CFM equations the saturation should appear at smaller values of the coordinate as illustrated above by means of the exactly solvable model potential [30]. Another interesting example is provided by the radial part of the dimensionless Schrödinger equation for a central–field potential $v(r)$:

$$-\frac{1}{2} \varphi''(r) + \left[\frac{l(l+1)}{2r^2} + v(r)\right] \varphi(r) = \epsilon \varphi(r)$$

(33)

where $l = 0, 1, \ldots$ is the angular–momentum quantum number and $\varphi(0) = 0$. If we assume that $\lim_{r \to 0} r^2 v(r) = 0$ and insert the asymptotic behaviour $\varphi(r) \to r^s$ at origin we conclude that $L_c(r) \to r^{l+1}$ and $L_d(r) \to r^{-l}$ are the regular and irregular contributions to the wavefunction. Taking into consideration these asymptotic behaviours in the WM or SEM–CFM equations will provide an advantage during the integration from $r_0$ towards origin. According to the
discussion above one expects that it will not be necessary to integrate too close to the origin to achieve saturation. On the other hand, the asymptotic behaviour for \( r \to \infty \) is determined by the form of \( v(r) \) as discussed above.

5 Conclusions

The main purpose of this paper is to show that the Wronskians provide a rigorous basis for the discussion of the SEM–CFM equations as well as concepts like saturation. We have seen in Fig. 2 that the Wronskians reach the asymptotic value or saturation at smaller values of \( |x| \) because they take the asymptotic behaviour of the wavefunction explicitly into account. However, the gain in numerical performance and efficiency derived from this result is not as important as giving the students the opportunity to discuss the asymptotic behaviour of the wavefunction for a given quantum–mechanical problem. The most general equations for both approaches developed in sections 2 and 3 suggest that they are essentially identical. If, for example, instead of substituting the boundary conditions in the SEM–CFM function \( F(\epsilon) \) we substitute the correct asymptotic behaviour of the wavefunction the SEM–CFM equation for the eigenvalues becomes the WM one. In such a case that one finds it rather laborious to develop a suitable analytical expression for the asymptotic behaviour of the wave function at some singular point (as, for example, in the case of the Lennard–Jones potential [4]) then it may be more convenient to resort to the raw boundary conditions satisfied by the wavefunction as discussed in Sec. 3 (for example, Eq. 23). In other words, we have the chance of using the SEM–CFM directly or improving it by explicitly using the asymptotic behaviour of the wavefunction.

In closing we want do discuss some points that may be of pedagogical value. In the first place Tannous and Langlois [11] state that the characteristic equation \( F(\epsilon) = 0 \) is not a matching condition but a dispersion relation. The matching
methods typically integrate the Schrödinger equation inwards from left and right and require that \((y_0)_- = (y_0)_+\) and \((y'_0)_- = (y'_0)_+\) at an intermediate point \(x_0\). Obviously, satisfying these equations is equivalent to obtaining the roots of \(F(\epsilon) = l_+ (\epsilon) - l_- (\epsilon)\). One can also integrate the logarithmic derivative \(y'(x)/y(x)\) inwards and obtain exactly the same equation. On the other hand, the SEM–CFM integrates the canonical functions (or normalized solutions) left and right from a given point \(x_0\) and then match the logarithmic derivative for each case at that intermediate point. The difference between both strategies is merely the direction of the integration (inwards or outwards). In fact, Kobeissi [2] explicitly refers to the continuity condition of the eigenfunction. The WM also proceeds outwards but does not focus on the logarithmic derivative. Instead it makes use of the Wronskians that become constant as the wavefunction approaches the asymptotic region to derive equations for the coefficients of the two linearly independent solutions.

The authors mention that the SEM evaluates the eigenvalues directly and avoids losing accuracy associated with rapidly oscillating wavefunctions of highly excited states. One should not forget that the calculation of the canonical functions is equivalent to the calculation of the wavefunction. Kobeissi [2] explicitly shows the oscillatory behaviour of such functions for an excited state of the Morse oscillator. It is customary to state that the CFM does not calculate the eigenfunctions explicitly [1–4,6] when it is obvious that the approach already does it through the numerical integration of the canonical functions. In other words, the numerical integration of the Schrödinger equation explicitly calculates two oscillatory functions but their ratios (or the appropriate Wronskians) do not reflect such oscillations as shown in Fig. [2].

In closing we want to discuss the statement that the SEM enables ‘full determination of the spectrum in a single run’ [1]. It is not clear what they mean because they calculate each root of \(F(\epsilon) = 0\) by means of the secant method. This algorithm requires the numerical evaluation of \(F(\epsilon)\) several times till \(\epsilon\) is
sufficiently close to the chosen root and each calculation of $F(\epsilon)$ requires an outward integration of the normalized solutions from $x_0$. In other words, just one eigenvalue requires many integrations.

References

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Fig. 1. Characteristic function $F(\epsilon)$ for the particle in a box for $x_0 = 1/8$ (blue squares), $x_0 = 1/4$, (red solid squares) and $x_0 = 2/5$ (green circles)

Fig. 2. Linearly independent solutions, Wronskians and their ratios for the potential (30) with $v_0 = 2.5$ and $\epsilon = -1$
Fig. 3. $W(R_c, C)(x_R)$ (red solid line), $W(R_c, S)(x_R)$ (blue dashed line), $C(x_R)/S(x_R)$ (red squares) and $S(x_R)/C(x_R)$ (blue circles) for the potential (30) with $v_0 = 10$.