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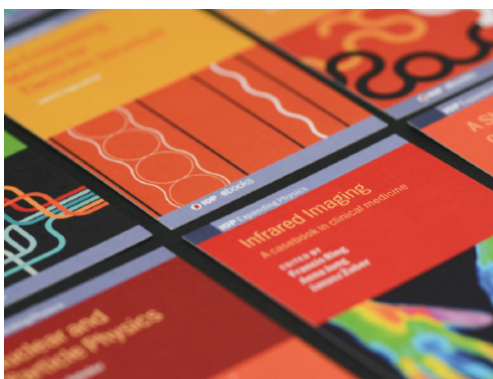
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Wronskian method for bound states

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Abstract

We propose a simple and straightforward method based on Wronskians for the calculation of bound-state energies and wavefunctions of one-dimensional quantum-mechanical problems. We explicitly discuss the asymptotic behaviour of the wavefunction and show that the allowed energies make the divergent part vanish. As illustrative examples we consider an exactly solvable model, the Gaussian potential well, and a two-well potential proposed earlier for the interpretation of the infrared spectrum of ammonia.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Wronskians (or Wronskian determinants) are most useful for the analysis of ordinary differential equations in general [1] and the Schrödinger equation in particular [2]. Whitton and Connor [3] applied a remarkable Wronskian formalism to resonance tunnelling reactions and we have recently proposed that a closely related method may be suitable for teaching quantum scattering in advanced undergraduate and graduate courses in quantum mechanics [4].

The purpose of this paper is to show that the Wronskian method is also useful for the study of bound states of one-dimensional quantum-mechanical models. We believe that this variant of the approach is also suitable for pedagogical purposes and enables a unified treatment of the discrete and continuous spectra of simple quantum-mechanical models.

In section 2, we convert the Schrödinger equation into a dimensionless eigenvalue equation and show how to apply the Wronskian method to bound states. In section 3, we illustrate the application of the approach by means of three suitable examples, one of them with an interesting physical application to vibrational spectroscopy. In section 4, we outline the main results of the paper and draw conclusions. Finally, in the appendix we outline the main properties of Wronskians that are relevant to the present discussion.

2. The Schrödinger equation

Before solving the Schrödinger equation it is a good practice to convert it into a dimensionless eigenvalue equation. In this way one removes all the physical constants and reduces the number of model parameters to a minimum. The time-independent Schrödinger equation for a particle of mass m that moves in one dimension ($-\infty < X < \infty$) under the effect of a potential $V(X)$ is

$$-\frac{\hbar^2}{2m}\psi''(X) + V(X)\psi(X) = E\psi(X) \quad (1)$$

where the prime indicates derivative with respect to the coordinate. If we define the dimensionless coordinate $x = X/L$, where L is an appropriate length scale, then we obtain the dimensionless eigenvalue equation

$$\begin{aligned} -\frac{1}{2}\varphi''(x) + v(x)\varphi(x) &= \epsilon\varphi(x) \\ \varphi(x) &= \sqrt{L}\psi(Lx), \quad v(x) = \frac{mL^2}{\hbar^2}V(Lx), \quad \epsilon = \frac{mL^2E}{\hbar^2}. \end{aligned} \quad (2)$$

The length unit L that renders both ϵ and $v(x)$ dimensionless is arbitrary and we can choose it in such a way that makes the Schrödinger equation simpler. We will see some examples in section 3.

It is well known that a general solution to the second-order differential equation (2) can be written as a linear combination of two linearly independent solutions. Here we write

$$\varphi(x) = A_2C(x) + B_2S(x) \quad (3)$$

where the solutions $C(x)$ and $S(x)$ satisfy

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

at a given point x_0 in $(-\infty, \infty)$. These conditions are sufficient to ensure that $C(x)$ and $S(x)$ are linearly independent [2].

For every value of the dimensionless energy ϵ , we know that

$$\varphi(x) \rightarrow \begin{cases} A_1L_c(x) + B_1L_d(x), & x \rightarrow -\infty \\ A_3R_c(x) + B_3R_d(x), & x \rightarrow \infty \end{cases} \quad (5)$$

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

It follows from the Wronskian properties outlined in the appendix that

$$\begin{aligned} B_1W(L_c, L_d) &= A_2W(L_c, C) + B_2W(L_c, S), & x \rightarrow -\infty \\ B_3W(R_c, R_d) &= A_3W(R_c, C) + B_2W(R_c, S), & x \rightarrow \infty. \end{aligned} \quad (6)$$

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

$$W(L_c, C)W(R_c, S) - W(R_c, C)W(L_c, S) = 0. \quad (7)$$

The roots of this equation ϵ_n , $n = 0, 1, \dots$ are the energies of the bound states (discrete spectrum).

When the potential is parity invariant

$$v(-x) = v(x) \quad (8)$$

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

$$\begin{aligned} W(L_c, S) &= W(R_c, S) \\ W(L_c, C) &= -W(R_c, C) \end{aligned} \quad (9)$$

and determinant (7) 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

$$\begin{aligned} W(R_c, C) &= 0 \\ W(R_c, S) &= 0, \end{aligned} \quad (10)$$

respectively. Besides, we need to consider only the interval $0 \leq x < \infty$.

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 equation (7). This problem is easily solved by means of, for example, a suitable numerical integration method [5]. If $y(x)$ stands for either $C(x)$ or $S(x)$, then such an approach gives us its values at a set of points $x_0 - N_L h, x_0 - N_L h + h, \dots, x_0, x_0 + h, \dots, x_0 + N_R h$ 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.

3. Examples

3.1. Exactly solvable problem

In order to test the accuracy of the Wronskian method we first choose the exactly solvable problem given by the potential $V(X) = -V_0/\cosh^2(\alpha X)$, where $V_0 > 0$ and $\alpha > 0$. If we set $L = 1/\alpha$, we are led to the dimensionless Schrödinger equation (2) where

$$\begin{aligned} v(x) &= -\frac{v_0}{\cosh^2(x)}, \\ v_0 &= \frac{mV_0}{\hbar^2\alpha^2}, \quad \epsilon = \frac{mE}{\hbar^2\alpha^2}. \end{aligned} \quad (11)$$

Note that the dimensionless energy ϵ depends on only one independent potential parameter v_0 . The units of length and energy are $1/\alpha$ and $\hbar^2\alpha^2/m$, respectively, and we do not have to bother about the mass of the particle and the Planck constant when solving the differential equation. The allowed dimensionless energies are given by [6]

$$\begin{aligned} \epsilon_n &= -\frac{1}{2}(\lambda - 1 - n)^2, \quad n = 0, 1, \dots, \leq \lambda - 1 \\ \lambda &= \frac{1}{2}(1 + \sqrt{1 + 8v_0}) \end{aligned} \quad (12)$$

and the spectrum is continuous for all $\epsilon > 0$. It is clear that $\lambda \rightarrow 1$ as $v_0 \rightarrow 0$ 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 $v_{0,n} = \lambda_n(\lambda_n - 1)/2 = n(n + 1)/2$.

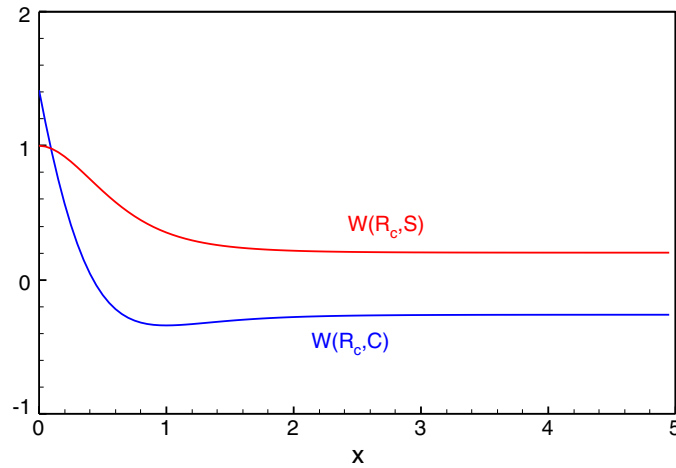


Figure 1. Wronskians for the exactly solvable problem with $\epsilon = -1$ and $v_0 = 2.5$.

Since $\lim_{|x| \rightarrow \infty} v(x) = 0$, then in this case $R_c(x) = e^{-kx}$ and $R_d(x) = e^{kx}$, 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

$$\begin{aligned} W(R_c, C) &= [C'(x) + kC(x)]e^{-kx} = 0, & x \rightarrow \infty \\ W(R_c, S) &= [S'(x) + kS(x)]e^{-kx} = 0, & x \rightarrow \infty \end{aligned} \quad (13)$$

for even and odd states, respectively.

Since the potential (11) is parity invariant, we integrate the Schrödinger equation from $x_0 = 0$ to $x_R = N_R h$. Figure 1 shows the Wronskians $W(R_c, C)$ and $W(R_c, S)$ for the arbitrary values $\epsilon = -1$ and $v_0 = 2.5$. We appreciate that $x = x_R = 5$ is large enough to have constant asymptotic Wronskians and we choose this coordinate value from now on. This numerical test also shows that it is sufficient for the present purposes to set $h = 0.01$ and $N_R = 500$ in the fourth-order Runge–Kutta method [5] built in the computer algebra system Derive (<http://www.chartwellyorke.com/derive.html>).

Figure 2 shows both $W(R_c, C)$ and $W(R_c, S)$ for $x = 5$ and $v_0 = 6$ as functions of ϵ . We see that the Wronskians vanish at the exact eigenvalues given by equation (12). This is a confirmation of our earlier assumption that the number of steps and their size are suitable for obtaining reasonable results.

Figure 3 shows $W(R_c, C)$ and $W(R_c, S)$ for $x = 5$ and $\epsilon = 0$ as functions of v_0 . In this case the Wronskians vanish at the exact critical values $v_{0,n} = n(n+1)/2$.

Those results for the exactly solvable problem suggest that the Wronskian method is successful for all bound-state energies and all well depths.

3.2. Gaussian well

As a second example, in what follows we try the nontrivial problem provided by the Gaussian well $V(x) = -V_0 e^{-\alpha X^2}$, where $V_0 > 0$, and $\alpha > 0$, that we easily convert into the

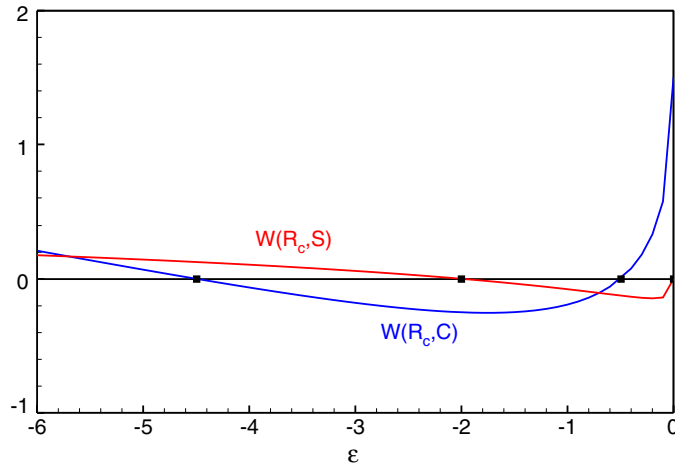


Figure 2. Wronskians for the exactly solvable problem with $v_0 = 6$ as functions of ϵ . The squares mark the exact eigenvalues.

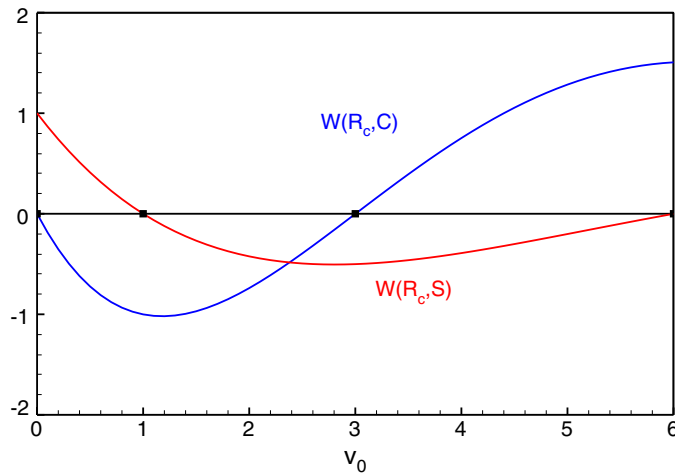


Figure 3. Wronskians for the exactly solvable problem with $\epsilon = 0$ as functions of v_0 . The squares mark the exact critical parameters.

dimensionless potential

$$\begin{aligned}
 v(x) &= -v_0 e^{-x^2}, \\
 v_0 &= \frac{m V_0}{\hbar^2 \alpha}, \quad \epsilon = \frac{m E}{\hbar^2 \alpha}
 \end{aligned}
 \tag{14}$$

by means of the length unit $L = 1/\sqrt{\alpha}$. This potential is also parity invariant and vanishes asymptotically as $|x| \rightarrow \infty$ so that the calculation is similar to the preceding example. In order to show that the Wronskian method also applies successfully to this model, we first obtain some critical values of the potential parameter v_0 . Figure 4 shows $W(R_c, C)$ and $W(R_c, S)$

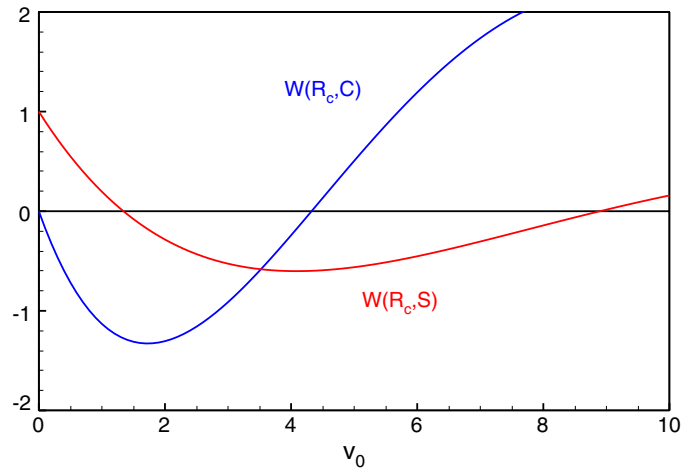


Figure 4. Wronskians for the Gaussian well with $\epsilon = 0$ as functions of v_0 .

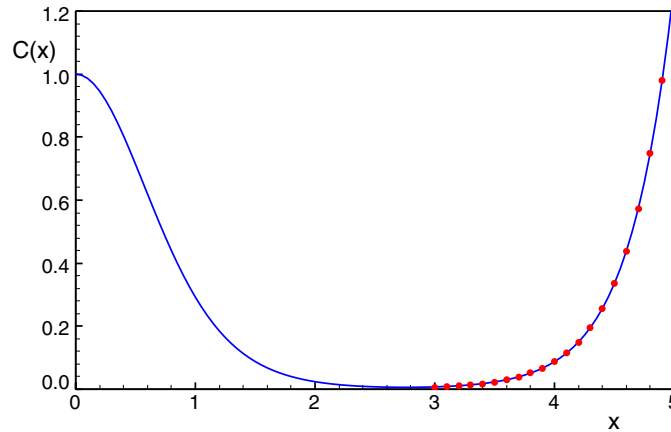


Figure 5. Unnormalized ground-state wavefunction for the Gaussian well with $v_0 = 5$.

for $x = 5$ and $\epsilon = 0$ as functions of v_0 . The three zeros of the Wronskians shown in the figure appear at $v_{0,1} = 1.342$, $v_{0,2} = 4.325$ and $v_{0,3} = 8.898$.

The numerical methods, although as accurate as one may desire (or the computer allows), are not exact; therefore, we can make the coefficient of the divergent part of the wavefunction very small but never exactly equal to zero. To illustrate this point we consider the ground state of the Gaussian well with $v_0 = 5$ and obtain the approximate energy $\epsilon_0 = -3.6077$ by means of a naive bracketing algorithm. The Wronskian method gives us the coefficient of the divergent part of the wavefunction $B_3 = W(R_c, C)/W(R_c, R_d) = W(R_c, C)/(2k) = 1.886 \times 10^{-6}$ as a by-product of the calculation at $x = 5$. Note that in this case $A_2 = 1$ and $B_2 = 0$ so that $C(x)$ is the unnormalized approximation to φ_0 . Figure 5 shows that the wavefunction decreases as $A_3 e^{-kx}$ to almost zero and then increases as $B_3 e^{kx}$. For intermediate values of the coordinate, the convergent part dominates because A_3 is much larger than B_3 but for larger values of x , R_d dominates as shown in figure 5. The points in this figure are the values of

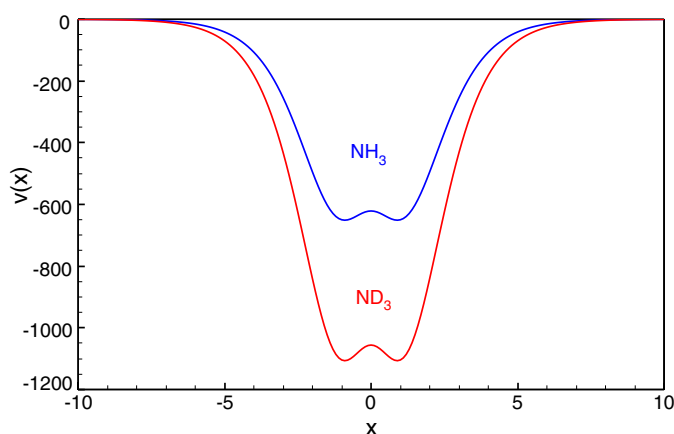


Figure 6. Manning's potential for NH_3 and ND_3 .

$B_3 R_d(x) = 1.886 \times 10^{-6} e^{2.686x}$. We can improve the calculation and make B_3 as small as desired, but it will never be exactly zero because the numerical calculation is approximate and the spurious divergent part will always be present. However, in order to normalize the wavefunction and calculate expectation values, we judiciously truncate the coordinate interval at a convenient point and obtain finite accurate values for those quantities. The Wronskian method is clearly suitable for deciding on the truncation point and estimating the error.

3.3. Double well

As an interesting application of the Wronskian method to an actual physical problem we consider the Manning potential that has been suitable for the interpretation of the infrared spectra of ammonia [7], formamide [8] and cyanamide [9] as well as their deuterated species. In order to study one of the vibrational normal modes of NH_3 and ND_3 , Manning [7] proposed the Schrödinger equation

$$\frac{d^2 R}{dr^2} + k \left[E + \frac{(\beta/2)(\beta/2 + 1/2) + D}{k\rho^2} \operatorname{sech}^2\left(\frac{r}{2\rho}\right) - \frac{D}{k\rho^2} \operatorname{sech}^4\left(\frac{r}{2\rho}\right) \right] R = 0 \quad (15)$$

where $k = 8\pi^2 c \mu / h$, μ is the reduced mass of the molecule for the type of vibration considered, E is the energy in cm^{-1} and β , D and ρ are potential parameters chosen to fit the observed spectra. If we define $x = r/\rho$, then we obtain the dimensionless Schrödinger equation (2) with

$$v(x) = -\frac{\beta(\beta + 1)}{8} \operatorname{sech}^2\left(\frac{x}{2}\right) - \frac{D}{2} \left[\operatorname{sech}^2\left(\frac{x}{2}\right) - \operatorname{sech}^4\left(\frac{x}{2}\right) \right] \quad (16)$$

and $\epsilon = k\rho^2 E/2$. This potential exhibits two minima at $x = \pm x_w$ ($v_w = v(\pm x_w)$) and a barrier with maximum at $x = 0$ ($v_0 = v(0)$).

The Schrödinger equation for this problem was solved by means of a power-series approach that leads to acceptable solutions provided that the energy eigenvalues are roots of a continued fraction [7]. Here we resort to the Wronskian method and obtain the lowest energies. Following Manning [7] we choose $\beta = 70$ (91.4), $D = 1920$ (3261) and $k\rho^2 = 2.885 \times 10^{-2}$ (4.899×10^{-2}) for NH_3 (ND_3). Figure 6 shows the potentials for both sets of parameters. Although the barriers appear to be rather low, there are several energies between v_w and v_0 that

Table 1. Energies of the Manning potential for NH₃.

| n | ϵ_n | $\frac{2}{k\rho^2}(\epsilon_n - \epsilon_0)$ | Ref. [7] | ϵ_n (RPM) |
|-----|--------------|--|----------|-------------------------|
| 0 | -643.845 703 | 0 | 0 | -643.845 706 021 8018 |
| 1 | -643.835 02 | 0.74 | 0.83 | -643.834 992 157 913 09 |
| 2 | -630.4740 | 926.98 | 935 | -630.474 034 6309 |
| 3 | -630.041 077 | 956.993 | 961 | -630.041 088 563 88 |

Table 2. Energies of the Manning potential for ND₃.

| n | ϵ_n | $\frac{2}{k\rho^2}(\epsilon_n - \epsilon_0)$ | Ref. [7] | ϵ_n (RPM) |
|-----|---------------|--|----------|-----------------------|
| 0 | -1096.739 532 | 0 | 0 | -1096.739 502 998 22 |
| 1 | -1096.738 464 | 0.0436 | <0.2 | -1096.738 420 316 656 |
| 2 | -1078.470 184 | 745.840 | 746 | -1078.470 124 5670 |
| 3 | -1078.404 724 | 748.512 | 748.5 | -1078.404 795 0329 |
| 4 | -1062.958 557 | 1379.097 | 1379 | -1062.958 552 20 |
| 4 | -1061.637 298 | 1433.037 | 1434 | -1061.637 339 253 78 |

we have calculated by means of the Wronskian method and show in tables 1 and 2. Although the agreement between our results and Manning's ones [7] is reasonable, the discrepancy in the energy differences $2(\epsilon_n - \epsilon_0)/(k\rho^2)$ for NH₃ is greater than the accuracy of the present Wronskian calculation. For that reason we also calculated the eigenvalues by means of the Riccati–Padé method (RPM) [10] (a pedagogical discussion of the RPM is available elsewhere [11]) that is highly accurate for those energies. The remarkable agreement between the results of two completely independent approaches such as the Wronskian method and the RPM shows that the present calculation is sufficiently accurate. The discrepancy mentioned above is therefore attributable to inaccuracies in Manning's calculation or in the reported model parameters [7].

Tables 1 and 2 show that $\epsilon_1 - \epsilon_0 \ll \epsilon_n - \epsilon_0$ for all $n > 1$. One expects that a perturbation on the system will couple the first two (almost degenerate) states more strongly than any other pair of states. For that reason, it is customary to treat the inversion motion of those molecules as a two-level model [12]. Feynman *et al* [12] considered two states $|1\rangle$ and $|2\rangle$ when the nitrogen atom is left and right of the plane defined by the three hydrogen atoms. They assumed that $\langle 1|H|1\rangle = \langle 2|H|2\rangle = E_0$ and $\langle 1|H|2\rangle = \langle 2|H|1\rangle = -A < 0$. This two-level model has two stationary states $|I\rangle$ and $|II\rangle$ with energies $E_I = E_0 + A$ and $E_{II} = E_0 - A$, respectively. The state of the system is $|\psi\rangle = C_1(t)|1\rangle + C_2(t)|2\rangle$ where $|C_1|^2 + |C_2|^2 = 1$. If the system is initially in the state $|1\rangle$, then the probability that it will be in the state $|2\rangle$ at time t is simply given by $P(t) = |C_2(t)|^2$. It is not difficult to prove that [12]

$$P(t) = \sin^2\left(\frac{At}{\hbar}\right). \quad (17)$$

The frequency of the inversion motion is therefore $\nu = \Delta E/h = 2A/h$. The results in tables 1 and 2 enable us to estimate the frequency of the inversion motion as

$$\nu = \frac{2c(\epsilon_1 - \epsilon_0)}{k\rho^2} \quad (18)$$

where c is the speed of light.

4. Conclusions

In our opinion the Wronskian method is sufficiently clear and straightforward for teaching an advanced undergraduate or graduate course in quantum mechanics. The mathematics requires no special background beyond an introductory calculus course. Since many available computer softwares offer numerical integration methods, the programming effort is relatively light.

From a purely theoretical point of view, the method is suitable for the discussion of the convergent and divergent asymptotic behaviours of the wavefunction and for illustrating how the allowed bound-state energies make the divergent part vanish leading to square-integrable wavefunctions. The students may try other quantum-mechanical models, derive the appropriate asymptotic behaviours analytically and then test their results by means of a suitable computer program. They can verify that the Wronskians already approach constants as the absolute value of the coordinate increases and that the wavefunction already looks like a square integrable function when the coefficient of the divergent contribution is almost zero. They can even estimate the remnants of the asymptotic divergent part because the Wronskian method provides the necessary coefficients. The lecturer may even look for interesting one-dimensional models with physical applications and offer them to the students as additional problems and exercises.

In addition, the Wronskian method is also suitable for quantum scattering [4] allowing a unified treatment of both the discrete and continuous spectra of the model.

Finally, we point out that computer algebra systems are remarkable aids for the teaching and learning process because they facilitate the algebraic treatment of the problem and even offer the possibility of straightforward numerical calculations (although they are considerably slower than specialized numerical programs).

Appendix. Wronskians

In order to make this paper sufficiently self-contained in this appendix, we outline some well-known results about the Wronskians that are useful for the study of ordinary differential equations in general [1] and also for the treatment of the Schrödinger equation in particular [2, 3]. To this end, we consider the ordinary second-order differential equation

$$L(y) = y''(x) + Q(x)y(x) = 0. \quad (\text{A.1})$$

If y_1 and y_2 are two linearly independent solutions to this equation, then we have

$$y_1 L(y_2) - y_2 L(y_1) = \frac{d}{dx} W(y_1, y_2) = 0 \quad (\text{A.2})$$

where

$$W(y_1, y_2) = y_1 y_2' - y_2 y_1' \quad (\text{A.3})$$

is the Wronskian (or Wronskian determinant [1]). The Wronskian is a skew-symmetric

$$W(f, g) = -W(g, f) \quad \Rightarrow \quad W(f, f) = 0 \quad (\text{A.4})$$

and the linear function of its arguments

$$\begin{aligned} W(f_1 + f_2, g) &= W(f_1, g) + W(f_2, g) \\ W(cf, g) &= cW(f, g) \end{aligned} \quad (\text{A.5})$$

where c is a constant.

By the linear combination of $y_1(x)$ and $y_2(x)$, we easily obtain two new solutions $C(x)$ and $S(x)$ satisfying

$$C(x_0) = S'(x_0) = 1, \quad C'(x_0) = S(x_0) = 0 \quad (\text{A.6})$$

at a given point x_0 so that $W(C, S) = 1$ for all x . If we write the general solution to equation (A.1) as

$$y(x) = AC(x) + BS(x), \quad (\text{A.7})$$

then

$$A = W(y, S), \quad B = W(C, y). \quad (\text{A.8})$$

This equation is quite useful for deriving relationships between the coefficients of the asymptotic expansions of the wavefunction in different regions of space as shown in sections 2 and 3. Additional mathematical properties of the Wronskians are available in Powell and Crasemann's book on quantum mechanics [2] and in the more rigorous discussion by Titchmarsh [13] where one also finds suitable generalizations of the functions $C(x)$ and $S(x)$.

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