

ONE

Alternative Methods of Solution and Approximation Methods

It is a common practice to approach quantum mechanics through the study of a few, exactly soluble examples using the Schrödinger equation in position-space. The number of potential energy functions for which such closed-form solutions are available is, however, quite small. Luckily, many of them actually correspond reasonably well to actual physical systems; examples include the infinite well as a model of a free particle in a “box” (Chapters 5 and 7), the harmonic oscillator (Chapter 9), the rigid rotator (Chapter 16), and the Coulomb potential for the hydrogen atom (Chapter 17).

Nonetheless, it is important to recognize that other methods can be used to study the properties of a quantum system. Some of them are quite different from the Schrödinger equation approach, and many are amenable for use as numerical and approximation methods in problems for which analytic solutions are not available.

In this chapter, we focus on several methods which can be used to study the spectrum of energy eigenvalues and wavefunctions for time-independent systems and (more briefly) on the effects of time-dependent perturbations, not only as calculational tools for possible numerical analysis, but also as examples of very different ways of approaching quantum mechanical problems. We can make several general comments:

- Many (but by no means all) of the alternative approaches discussed here are most useful for the study of the ground state of the system. Because the structure of matter is ultimately determined by the lowest energy configuration, the determination of the properties of the ground state is arguably the most important; it is the very clearly “first among equals”.
- Any method which is to be used as a numerical approximation technique should be capable of increased precision (usually at the cost of increased

calculational difficulty) as well as providing an estimate of the errors made in the approximation. We will not focus extensively on these questions, but the reader should always keep in mind how each method can be extended in precision, as well as the possible effort involved in doing so.

- As our ultimate goal is to understand the physics behind the equations, we may well have to rethink what it means to “solve” a problem when we approach it numerically. For example, do we need an analytic functional form for $\psi(x)$ or is an array of numbers or an interpolating function enough? How precisely do we need to know the energy eigenvalues? When are we “done”?
- Finally, the use of numerical methods is often nicely complementary to the study of analytic examples. One often looks at a problem in a much different way when one approaches it expecting to write a computer program to “solve” it, and such new insights can be valuable. For example, the study of chaotic dynamics in classical mechanics owes much of its success to the application of numerical (as opposed to analytic) techniques to otherwise familiar problems.

In each section, we first discuss the formalism of each method and then give an example of its possible use as a computational tool.

10.1 Numerical Integration

Classical and quantum mechanics share the fact that their fundamental mathematical descriptions are given by second-order differential equations, Newton’s law for a point particle

$$m \frac{d^2 x(t)}{dt^2} = F(x) \quad (10.1)$$

and the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (10.2)$$

We are used to thinking of Eqn. (10.1) as being completely deterministic,¹ in that, if we are given the appropriate initial conditions, namely, $x_0 = x(0)$ and $v_0 = \dot{x}(0)$, the future time development of $x(t)$ is then predicted. To see how a particle “uses” Eqn. (10.1) to “know where it should be” at later times, we can

¹ We ignore any complications such as the extreme sensitivity to initial conditions present in chaotic systems.

use a conceptually simple method² to integrate Newton's law directly. We first approximate the acceleration (the second derivative) via

$$\begin{aligned}
 \frac{d^2x(t)}{dt^2} &= \ddot{x}(t) = \lim_{\delta \rightarrow 0} \left(\frac{\dot{x}(t + \delta) - \dot{x}(t)}{\delta} \right) \\
 &= \lim_{\delta \rightarrow 0} \left[\frac{\lim_{\delta \rightarrow 0} ((x(t + 2\delta) - x(t + \delta))/\delta) - \lim_{\delta \rightarrow 0} ((x(t + \delta) - x(t))/\delta)}{\delta} \right] \\
 &= \lim_{\delta \rightarrow 0} \left(\frac{x(t + 2\delta) - 2x(t + \delta) + x(t)}{\delta^2} \right) \\
 &\approx \frac{x(t + 2\delta) - 2x(t + \delta) + x(t)}{\delta^2}.
 \end{aligned} \tag{10.3}$$

With this approximation, Newton's law can be written as

$$x(t + 2\delta) \approx 2x(t + \delta) - x(t) + \delta^2 \frac{F(x(t))}{m} \tag{10.4}$$

which is now a *difference equation* for $x(t)$, evaluated at the discretized times $t = n\delta$.

Since

$$v_0 = \dot{x}(0) \approx \frac{x(\delta) - x(0)}{\delta} \quad \text{we have} \quad x(\delta) \approx x(0) + \delta \dot{x}(0) \tag{10.5}$$

and the values of $x(t)$ at the first two of the discretized times, $n = 0, 1$, are fixed by the initial conditions; for later times, the $x(t = n\delta)$ with $n \geq 2$ are then determined by Eqn. (10.4).

Example 10.1. Numerical integration of the classical harmonic oscillator

The classical equation for a mass and a spring is of the form

$$\ddot{x}(t) = -\omega^2 x(t) \tag{10.6}$$

where $\omega = \sqrt{K/m}$. For any numerical problem, we must specialize to definite values, for both the physical parameters of the problem, and for the initial conditions; as an example, we choose

$$\omega = 2\pi, \quad x(0) = 1, \quad \text{and} \quad v(0) = \dot{x}(0) = 0 \tag{10.7}$$

² Much more powerful techniques, such as the Runge–Kutta method, are discussed in all textbooks dealing with numerical methods.

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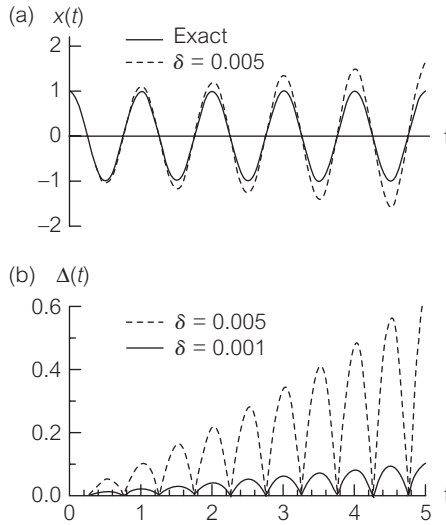


Figure 10.1. The exact (solid) and numerical (dashed) solutions of the harmonic oscillator differential equation are shown in (a). The differences between the numerical and exact solutions versus time for two different step sizes, δ , are plotted in (b).

which has the exact solution $x(t) = \cos(2\pi t)$. In Fig. 10.1(a), we show the result of a numerical solution of Eqn. (10.6) (dashed curve), using Eqn. (10.4), to be compared to the exact solution (solid curve). In Fig. 10.1(b) the difference between the numerical and exact solutions, $\Delta(t)$, is seen to increase with t , but it is also smaller for smaller step sizes, δ , as expected.

The same strategy can be used to solve the Schrödinger by approximating Eqn. (10.2) as

$$\psi(x + 2\delta) \approx 2\psi(x + \delta) - \psi(x) + \delta^2 \left[\frac{2m}{\hbar^2} (V(x) - E) \right] \psi(x) \quad (10.8)$$

and using

$$\psi(0) \quad \text{and} \quad \psi(\delta) \approx \psi(0) + \psi'(0)\delta \quad (10.9)$$

In this sense, Eqn. (10.2) is just as deterministic as Newton's laws; the chief differences are:

- The choice of $x = 0$ as the “initial” value is arbitrary.
- The differential equation can (and should) be integrated “to the left” as well to obtain $\psi(x)$ for $x < 0$.

- Most importantly, the Schrödinger equation can be integrated (solved) for any value of the energy eigenvalue, E ; the solutions so obtained, however, will not necessarily be physically acceptable, that is, square-integrable.

To illustrate the usefulness of this approach to the isolation of energy eigenvalues and their corresponding eigenfunctions, we restrict ourselves to the special case of a symmetric potential for reasons that will become clear. In that case, we know that the solutions will also be eigenfunctions of parity and hence satisfy

$$\text{even solutions: } \psi(0) = \text{arbitrary} \quad \text{and} \quad \psi'(0) = 0 \quad (10.10)$$

and

$$\text{odd solutions: } \psi(0) = 0 \quad \text{and} \quad \psi'(0) = \text{arbitrary} \quad (10.11)$$

The arbitrariness in $\psi(0)$ or $\psi'(0)$ present at this point is eventually removed when the wavefunction is properly normalized, but that is separate from the solution of the Schrödinger equation itself. The overall normalization does not affect the *shape* of the solution.

We now focus on the behavior of the wavefunction at large $|x|$ for various values of E . For the even case, for example, we can start at $x = 0$ with an arbitrary value of $\psi(0)$, use the oddness of $\psi'(x)$ to determine $\psi(\delta) = \psi(0)$, and then use Eqn. (10.8) to numerically integrate to arbitrarily large values of $x = n\delta$; we find the generic behavior shown in Fig. 10.2(a). If we call the lowest even energy eigenvalue $E_1^{(+)}$, then for values of $E < E_1^{(+)}$, the solutions diverge as $\psi(x) \rightarrow +\infty$ as $x \rightarrow +\infty$. When $E \gtrsim E_1^{(+)}$, the solutions are still poorly behaved at infinity, but now diverge with the opposite sign. Clearly, the energy of the physically acceptable square-integrable ground state solution lies between E_a and E_b ; this behavior is familiar from our study of the harmonic oscillator and Fig. 9.3.

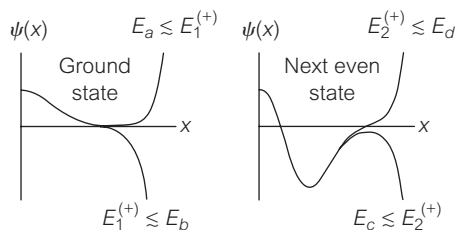


Figure 10.2. Numerical solutions of the Schrödinger equation for a symmetric potential. The energy parameters $E_a < E_1^{(+)} < E_b$ bracket the true ground state energy; $E_c < E_2^{(+)} < E_d$ bracket the first-excited even state.

Once such a pair of energy values which brackets the “acceptable” ground state solution is found, one can determine $E_1^{(+)}$ with increasing *precision* by a systematic exploration in the interval (E_a, E_b) , finding values of E , which bracket the “true value” with decreasing error; the resulting *accuracy* of the estimated value of E_0 , however, will still depend on the integration method used (Q10.2). As the energy parameter E is increased further, additional changes in sign of the wavefunction at infinity are encountered (Fig. 10.1(b)), and the energy spectrum can be systematically mapped out by finding pairs of energy values which bracket a “sign change.”

Example 10.2. Energy eigenvalues for the harmonic oscillator

The numerical solution of the Schrödinger equation for the harmonic oscillator potential is easy to implement using Eqn. (10.8) provided the problem is put into dimensionless form as in Section 9.2.1, namely

$$\frac{d^2\psi(y)}{dy^2} = (y^2 - \epsilon)\psi(y) \quad (10.12)$$

where the dimensionless eigenvalues are $\epsilon_n = 2E_n/\hbar\omega = (2n + 1)$. The even states have $\epsilon_n = 1, 5, 9, \dots$ and so forth. Values of E_a, E_b , which bracket the ground state ($E_1^{(+)}$) and first even excited state ($E_2^{(+)}$) energies for several values of δ are given by

δ	$E_a < E_1^{(+)} < E_b$	$E_a < E_2^{(+)} < E_b$
0.1	(1.191, 1.192)	(5.510, 5.511)
0.01	(1.0171, 1.0172)	(5.0431, 5.0432)
0.001	(1.00169, 1.00170)	(5.00423, 5.00424)

so that the effect of decreasing the step size on the reliability of the results is clear.

It is useful to keep in mind that before applying any numerical technique to a new problem, it is best to “test” it on a well-understood example if at all possible.

Once an approximate energy eigenvalue is found, the wavefunction for each energy eigenvalue is obtained from the numerical integration as the collection of points $\psi(x = n\delta)$, and can be fit to a smooth function using interpolation techniques if desired; in any case, it can be normalized and used to extract further information about the quantum system. The odd states are found in a similar way (Q10.4) by making use of Eqn. (10.11).

10.2 The Variational or Rayleigh–Ritz Method

Many branches of physics can be formulated in terms of a simple minimum principle using the methods of the calculus of variations. Examples include minimum surface problems (bubble problems and the like), Fermat’s formulation of geometrical optics using a principle of least time and, perhaps most importantly, the principle of least action approach to classical mechanics.

In each case, the object of study is a *functional*, so-called because it takes as its argument a function and returns a number as its output. The *classical action* in mechanics, $S[x(t)]$, is just such an example; it takes any possible classical path, $x(t)$, and returns the numerical value

$$S[x(t)] = \int_{t_a}^{t_b} dt \left(\frac{1}{2} m \dot{x}^2(t) - V(x(t)) \right) \quad (10.13)$$

and the trajectory realized in nature is the unique path which minimizes Eqn. (10.13).

It is perhaps then not surprising that quantum mechanics can also be formulated in such a manner. We will first discuss just such an approach and then discuss how it can be applied as a calculational tool to approximate energy eigenvalues and wavefunctions.

Consider a Hamiltonian, \hat{H} , defining the bound state spectra of some system. We assume that it will have a discrete spectrum of bound state energies, E_n , with corresponding, already normalized wavefunctions $\psi_n(x)$. We can define an *energy functional* for *any* trial wavefunction, $\psi(x)$, via

$$\begin{aligned} E[\psi] &\equiv \langle \psi | \hat{H} | \psi \rangle = \langle \psi | \hat{T} | \psi \rangle + \langle \psi | V(x) | \psi \rangle \\ &= \int_{-\infty}^{+\infty} dx \psi^*(x) \hat{H} \psi(x) \\ &= \frac{1}{2m} \int_{-\infty}^{+\infty} dx \psi^*(x) \hat{p}^2 \psi(x) + \int_{-\infty}^{+\infty} dx V(x) |\psi(x)|^2 \end{aligned} \quad (10.14)$$

This is defined whether $\psi(x)$ is an eigenfunction or not. It is often convenient to use the “alternative” form of the average value of kinetic energy (as in

Eqn. (4.65)), that is,

$$\langle \psi | \hat{T} | \psi \rangle = \langle \hat{T} \rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} dx \left| \frac{d\psi(x)}{dx} \right|^2 \quad (10.15)$$

If for some reason the trial wavefunction ψ is not already normalized, we can simply write

$$E[\psi] \equiv \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (10.16)$$

It is easy to see that this functional simply returns an energy eigenvalue when its argument is a normalized eigenstate, since

$$E[\psi_n] = \int_{-\infty}^{+\infty} dx \psi_n^*(x) \hat{H} \psi_n(x) = \int_{-\infty}^{+\infty} dx \psi_n^*(x) E_n \psi_n(x) = E_n \quad (10.17)$$

For a general wavefunction, $\psi(x)$, we assume we can use the expansion theorem and write $\psi(x) = \sum_{n=0}^{\infty} a_n \psi_n(x)$ and we find that

$$\begin{aligned} E[\psi] &= \langle \psi | \hat{H} | \psi \rangle = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} a_m^* a_n \langle \psi_m | \hat{H} | \psi_n \rangle \\ &= \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} a_m^* a_n E_n \delta_{n,m} \\ &= \sum_{n=0}^{\infty} |a_n|^2 E_n \end{aligned} \quad (10.18)$$

This derivation is similar to that of Section 6.4 for the average value of the energy operator, \hat{E} , in a general state, but the quantity that appears in the energy functional here is the expectation value of the appropriate Hamiltonian for the problem, which in general acts only on spatial degrees of freedom.

We assume that the energy eigenvalues are ordered, that is, $\cdots \geq E_2 \geq E_1 \geq E_0$ so that

$$E[\psi] = \sum_{n=0}^{\infty} |a_n|^2 E_n \geq \sum_{n=0}^{\infty} |a_n|^2 E_0 = E_0 \quad \text{or} \quad E[\psi] \geq E_0 \quad (10.19)$$

because the expansion coefficients, when squared, sum to unity, since $\psi(x)$ is assumed normalized. The lower bound is only “saturated” when $\psi(x) = \psi_0(x)$ in which case $a_n = \delta_{n,0}$ and only the ground state energy term contributes.

This is then the desired minimum principle, namely that:

- The energy functional, $E[\psi]$, defined via Eqn. (10.14), always gives an energy at least as large as the true ground state energy, that is, $E[\psi] \geq E_0$ for all ψ .

To use this property as a calculational tool, we first note that if the wavefunction used in the functional has an arbitrary parameter, for example, $\psi(x) = \psi(x; a)$, then the energy functional yields a function of one variable, namely

$$E[\psi(x; a)] = E(a) \quad (10.20)$$

An example of this would be the family of Gaussian variational wavefunctions, $\psi(x; a) = \exp(-x^2/2a^2)/\sqrt{a\sqrt{\pi}}$, with a variable width.

Because the functional satisfies the minimum principle for each value of the parameter, one can minimize the variational function $E(a)$ and be assured that the resulting minimum is still greater than the true ground state energy. Thus, one can find the trial wavefunction, in the one parameter family considered, which has the lowest energy. The minimizing wavefunction accomplishes this by somehow “adjusting” to as similar as possible to the exact ground state solution. This approach is similar in spirit to the “zero-point energy” argument of P1.14, but is more powerful because:

- The guaranteed lower bound of Eqn. (10.19) provides a method of assessing the reliability of the approximations.

— Of two variational estimates of the ground state energy, the lower one is always closer to the true value.

In this context, “lower is always better” as we know that we can never “undershoot” E_0 on the negative side.

- It also provides an approximation to the wavefunction as well as to the energy; one can then use it to estimate expectation values and to find the approximate momentum-space wavefunction. As an aside, because the argument leading to Eqn. (10.18) is not specific to a position-space representation, one can also use the variational method with momentum-space wavefunctions (P10.5).

For illustrative purposes, we will sometimes calculate $|a_0|^2$ as a measure of the “overlap” of the trial solution with the exact ground state wavefunction (if known); it can be used as a quantitative measure of the similarity of any two functions. We reiterate, however, that the trial wavefunction of a given class which minimizes the energy is not necessarily the one which has the largest overlap with the true ground state wavefunction, that is, it does not necessarily maximize $|a_0|^2$ (see, for example, P10.9).

Example 10.3. Variational estimate for the harmonic oscillator I

As an example of the method, consider approximating the ground state energy and eigenfunction of the simple harmonic oscillator by using the family of trial wavefunctions $\psi(x; a) = \exp(-x^2/2a^2)/\sqrt{a\sqrt{\pi}}$ mentioned above. Because the true ground state solution is also Gaussian, we expect to find the exact answer. We have to evaluate Eqn. (10.14) with $V(x) = m\omega^2 x^2/2$ and we find that

$$E[\psi(x; a)] = E(a) = \langle \hat{T} \rangle + \langle V(x) \rangle = \frac{\hbar^2}{4ma^2} + \frac{1}{4}m\omega^2 a^2 \quad (10.21)$$

Minimizing this expression we find

$$\frac{dE(a)}{da} = -\frac{\hbar^2}{2ma^3} + \frac{1}{2}m\omega^2 a = 0 \quad (10.22)$$

which yields $a_{\min} = \sqrt{\hbar/m\omega}$ and $E(a_{\min}) = \hbar\omega/2$ as expected.

Example 10.4. Variational estimate for the harmonic oscillator II

To illustrate the principle in the case where the form of the ground state wavefunction is not known, consider as a trial wavefunction for the simple harmonic oscillator (SHO) the wavefunction

$$\psi(x; a) = \begin{cases} 0 & \text{for } |x| > a \\ N(a^2 - x^2)^2 & \text{for } |x| < a \end{cases} \quad (10.23)$$

where the variational parameter is again a and the normalization constant is given by $N = \sqrt{315/256a^9}$. A similar calculation to the one above shows (P10.3) that the energy function is

$$E[\psi] = E(a) = \frac{3\hbar^2}{2ma^2} + \frac{m\omega^2 a^2}{22}. \quad (10.24)$$

This has a minimum value at $a_{\min}^2 = \sqrt{33}\hbar/m\omega$ yielding

$$E(a_{\min}) = \frac{\hbar\omega}{2} \sqrt{\frac{12}{11}} = (0.522)\hbar\omega \quad (10.25)$$

which is only 4.4% greater than the exact value.

The trial wavefunctions, along with their corresponding energies for several choices of a are shown in Fig. 10.3 along with the value of $|a_0|^2$. We plot in Fig. 10.4 the fractional difference between the variational energy and the exact ground state value $(E(\text{var}) - E(\text{exact}))/E(\text{exact})$ as well as the probability that the variational wavefunction is *not* in the ground state, that is, $1 - |a_0|^2$, versus the variational parameter a . We note

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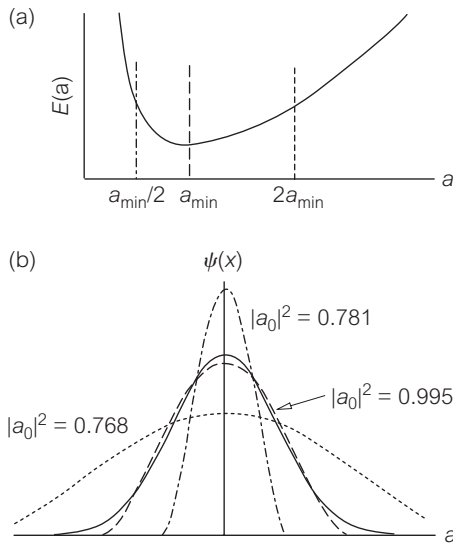
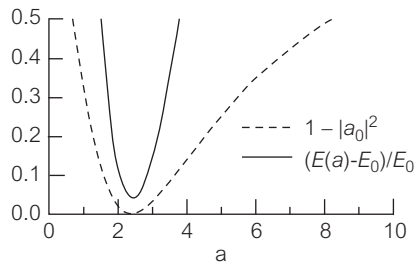


Figure 10.3. (a) The variational energy, $E(a)$ versus a , showing the value of a_{min} which minimizes the energy functional (vertical dashed line) and two other values (dotted and dot-dash). (b) The corresponding variational wavefunctions (same dashing) along with the exact ground state (solid curve). Values of the overlap, given by $|a_0|^2$, for each variational waveform are also shown.

Figure 10.4. The fractional energy error (solid curve) and the degree of “non-overlap” (dashed curve) versus variational parameter a for Example 10.4. This illustrates that first-order changes in the wavefunction give second-order changes in the energy functional.



that variations in the parameter a seem to have a much larger effect on the energy functional than on the wavefunction itself.

To formalize this last observation further, let us imagine making small variations around the exact ground state wavefunction, $\psi_0(x)$, parameterized by $\psi_0(x) \rightarrow \psi_0(x) + \lambda\phi(x)$ so that $\phi(x)$ represents a first-order change in the wavefunction; we use λ to keep track of the expansion.

Consider then the energy functional (where we use Eqn. (10.16) since the new wavefunction is not properly normalized) and we find

$$\begin{aligned}
 E[\psi_0 + \lambda\phi] &= \frac{\langle \psi_0 + \lambda\phi | \hat{H} | \psi_0 + \lambda\phi \rangle}{\langle \psi_0 + \lambda\phi | \psi_0 + \lambda\phi \rangle} \\
 &= \frac{E_0 \langle \psi_0 | \psi_0 \rangle + \lambda(\langle \psi_0 | \hat{H} | \phi \rangle + \langle \phi | \hat{H} | \psi_0 \rangle) + \lambda^2 \langle \phi | \hat{H} | \phi \rangle}{\langle \psi_0 | \psi_0 \rangle + \lambda \langle \psi_0 | \phi \rangle + \lambda \langle \phi | \psi_0 \rangle + \lambda^2 \langle \phi | \phi \rangle} \\
 &= E_0 \left(\frac{1 + \lambda(\langle \psi_0 | \phi \rangle + \langle \phi | \psi_0 \rangle) + \lambda^2 \langle \phi | \hat{H} | \phi \rangle / E_0}{1 + \lambda(\langle \psi_0 | \phi \rangle + \langle \phi | \psi_0 \rangle) + \lambda^2 \langle \phi | \phi \rangle} \right) \\
 &= E_0 (1 + \mathcal{O}(\lambda^2))
 \end{aligned} \tag{10.26}$$

since the zeroth-order and $\mathcal{O}(\lambda)$ terms are identical. This shows that, in general,

- *First-order changes* ($\mathcal{O}(\lambda)$) in the trial wavefunction, away from the true ground state solution, give rise to *second-order changes* ($\mathcal{O}(\lambda^2)$) in the corresponding energy functional.

This fact is reflected in Fig. 10.4 as the fractional change in energy does seem to vary quadratically with deviations away from the minimum value of the variational parameter, while the deviation in the wavefunction itself (as measured by $1 - |a_0|^2$) seems to vary much more weakly on a . This is a typical feature of problems involving the calculus of variations.

If the variational method is to be useful as an approximation method there should be some possibility of further refinement of the estimation of the ground state energy. This can be accomplished by simply taking as a trial wavefunction one with a larger number of variational parameters. For example, one might consider

$$\psi(x; a, b) = e^{-x^2/2a^2} (1 + bx^2) \tag{10.27}$$

which has an additional parameter, b , but which reduces to the original choice in some limit (namely, $b = 0$). In this case, we are guaranteed to have

$$E(a_{\min}) \equiv E[\psi(x; a_{\min})] > E(a_{\min}, b_{\min}) \equiv E[\psi(x; a_{\min}, b_{\min})] \geq E_0 \tag{10.28}$$

because any variational energy must be larger than the true ground state and because the minimum with nonzero values of b will be at least as small as for

$b = 0$. The new minimum value will be determined by

$$\frac{\partial E(a, b)}{\partial a} = \frac{\partial E(a, b)}{\partial b} = 0 \tag{10.29}$$

By adding more and more variational parameters, we can allow the trial wavefunction to conform as closely as possible to the exact ground state.

Example 10.5. Variational estimate for the harmonic oscillator III

We illustrate the improvement possible with multi-parameter trial wavefunctions by using the (unnormalized) function

$$\psi(x; a, b) = \begin{cases} 0 & \text{for } |x| > a \\ (a^2 - x^2)^2(1 + bx^2) & \text{for } |x| < a \end{cases} \tag{10.30}$$

as a trial solution for the ground state of the SHO. We plot in Fig. 10.5 a contour plot of $E(a, b)$ versus a, b ; the small star on the dotted line indicates the minimum for the $b = 0$ case, while the small $+$ indicates the new global minimum which does indeed have somewhat lower energy. The values of the exact, one-parameter, and two-parameter fits for various quantities are shown below:

quantity	exact	$\psi(x; a)$	$\psi(x; a, b)$
$E_0/(\hbar\omega/2)$	1	1.0445	1.0198
$ a_0 ^2$	1	0.9951	0.9977
$\langle x^2 \rangle/\rho^2$	1/2	0.5222	0.5099
$\langle x^4 \rangle/\rho^4$	3/4	0.6923	0.6884

(10.31)

The energy is lower and the overall fit is better ($|a_0|^2$ is closer to 1) than in the one-parameter case; it is clear, however, that various higher moments (i.e. average values of x^{2n}) are never fit very well with this particular form which is not surprising given its lack of a realistic ‘tail’ for large $|x|$.

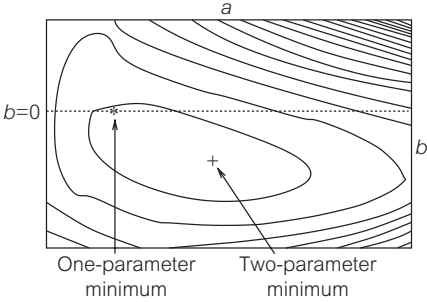


Figure 10.5. Contour plot of two-parameter variational energy $E(a, b)$ versus (a, b) ; the dotted line corresponds to the one-parameter family, $E(a)$ versus a . The minimum energy for the two-parameter family of trial wavefunctions is lower than for the one-parameter set.

The process can be continued with as many variational parameters as one can handle, presumably improving the agreement with experiment, if not providing much more useful insight into the basic physics.³ One of the most famous *tour de force* calculations of this type are variational calculations of the ground state of the helium atom which use trial wavefunctions with hundreds of parameters.⁴

In some cases, it is also possible to extend the variational method to give rigorous lower bounds for excited states as well as the ground state. Suppose, for example, that one could choose a trial wavefunction which was somehow known to be orthogonal to the true ground state, that is, $\langle \psi | \psi_0 \rangle = 0$; this would guarantee that $a_0 = 0$ in the expansion theorem. The standard argument would then give

$$\psi = \sum_{n=1}^{\infty} a_n \psi_n \implies E[\psi] = \sum_{n=1}^{\infty} |a_n|^2 E_n \geq \sum_{n=1}^{\infty} |a_n|^2 E_1 = E_1 \quad (10.32)$$

Thus, all the trial wavefunctions in this restricted class would have energies at least as great as the first excited state.

Various symmetries of the problem can often be used to restrict the form of the trial wavefunction so as to satisfy this constraint. For example, in a one-dimensional problem with a symmetric potential, $V(x) = V(-x)$, we know that the ground state will be an even function; therefore any odd trial wavefunction will have $a_0 = 0$ and hence satisfy Eqn. (10.32) and give a good estimate of the first excited state energy. Less prosaically, in three-dimensional problems with spherical symmetry, the ground state will have no angular momentum (i.e. $l = 0$) and excited states with higher values of l are automatically orthogonal to the ground state.

10.3 The WKB method

The variational method is best suited to evaluating the properties of the ground state solution, that is, for $n = 0$. It is useful to have a complementary approach, which is more appropriate for the quasi-classical regime where $n \gg 1$; we have argued that this limit is also attained, in some sense, when $\hbar \rightarrow 0$. Such an

³ It is said that, when confronted with the result of an impressive numerical calculation, Eugene Wigner said “*It is nice to know that the computer understands the problem. But I would like to understand it too.*”; See Nussenzveig (1992).

⁴ See Bethe and Jackiw (1968) or Park (1992) for discussions.

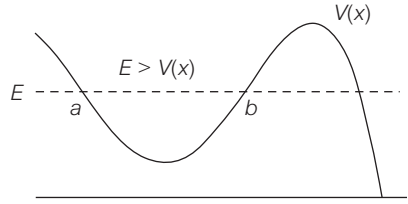


Figure 10.6. Generic potential with classical turning points for the WKB approximation.

approach was first discussed in the context of quantum mechanics by Wentzel, Kramers, and Brillouin⁵ and is therefore often called the WKB method.

10.3.1 WKB Wavefunctions

Motivated by the simple form for a free-particle de Broglie wave, that is,

$$\psi(x) = A e^{i2\pi x/\lambda} = A e^{ikx} = A e^{ipx/\hbar} \quad (10.33)$$

we attempt a solution of the time-independent Schrödinger equation of the form

$$\psi(x) = A(x) e^{iF(x)/\hbar} \quad (10.34)$$

where $A(x)$ and $F(x)$ are an amplitude and phase term, respectively. We retain the explicit factor of \hbar and will use it to parameterize the smallness of various terms. We also assume, for the moment, that we are in the classically allowed region so that $E > V(x)$, as in Fig. 10.6, so that $a < x < b$.

With the *ansatz*⁶ in Eqn. (10.34), the Schrödinger equation becomes

$$\begin{aligned} 0 = A(x) & \left[\frac{1}{2m} \left(\frac{dF(x)}{dx} \right)^2 - (E - V(x)) \right] \\ & - \hbar \left(\frac{i}{2m} \right) \left[2 \frac{dA(x)}{dx} \frac{dF(x)}{dx} + A(x) \frac{d^2 F(x)}{dx^2} \right] \\ & - \hbar^2 \left[\frac{1}{2m} \frac{d^2 A(x)}{dx^2} \right] \end{aligned} \quad (10.35)$$

At this point, we can either consider \hbar as an arbitrary small parameter and set the first two terms (of order $\mathcal{O}(\hbar^0)$ and $\mathcal{O}(\hbar^1)$, respectively) separately to zero or else we can require that both the real and imaginary parts of Eqn. (10.35) are satisfied; in either case, we neglect the last term (being of order $\mathcal{O}(\hbar^2)$) and discuss the validity of this approximation below.

⁵ It was also studied independently by Jeffries; the name WKBJ approximation is therefore sometimes used.

⁶ The German term *ansatz*, often defined as *formulation* or *setup*, is often taken to mean something like “assumed form of the solution” in the context of a physics or math problem.

The $\mathcal{O}(\hbar^0)$ equation (or real part) is easily written as

$$\frac{dF(x)}{dx} = \pm \sqrt{2m(E - V(x))} \equiv \pm p(x) \quad (10.36)$$

or

$$F(x) = \pm \int^x p(x) dx \quad (10.37)$$

where $p(x)$ is simply the classical momentum. The $\mathcal{O}(\hbar^1)$ (or imaginary part) then gives

$$2 \frac{dA(x)}{dx} p(x) + A(x) \frac{dp(x)}{dx} = 0 \quad (10.38)$$

which can be multiplied on both sides by $A(x)$ to obtain

$$\left(2A(x) \frac{dA(x)}{dx} \right) p(x) + [A(x)]^2 \frac{dp(x)}{dx} \equiv \frac{d}{dx} ([A(x)]^2 p(x)) = 0 \quad (10.39)$$

or

$$[A(x)]^2 p(x) = C \quad (10.40)$$

where C is a constant. The two linearly independent solutions (corresponding to right (+) and left-moving (−) waves) are then given by

$$\psi_{\pm}(x) = \frac{C_{\pm}}{\sqrt{p(x)}} e^{\pm i \int^x p(x) dx / \hbar} \propto \frac{1}{\sqrt{v(x)}} e^{\pm i \int^x k(x) dx} \quad (10.41)$$

where $p(x) = \hbar k(x)$ defines the “local wavenumber” $k(x)$, and $v(x)$ is the local speed. This remarkably simple solution has several obvious features:

- The corresponding probability density, $|\psi(x)|^2$, satisfies

$$|\psi(x)|^2 \propto \frac{1}{p(x)} \propto \frac{1}{v(x)} \quad (10.42)$$

which is exactly of the form of the *classical probability distribution* first discussed in Section 5.1. This implies (recall Fig. 9.7) that the wavefunctions for the low-lying energy levels will be *poorly* described by the WKB solutions; the quantum wavefunctions for large quantum numbers will, however, approach these semiclassical solutions when suitably locally averaged.

- The phase of the wavefunction can be written as

$$\int^x k(x) dx = \int^x d\phi(x) \quad (10.43)$$

where

$$d\phi(x) = k(x) dx = \frac{2\pi}{\lambda(x)} dx \quad \text{or} \quad \frac{d\phi}{2\pi} = \frac{dx}{\lambda(x)} \quad (10.44)$$

Thus, as the particle moves a distance dx , or a fraction of a “local” wavelength, $df = dx/\lambda(x)$, through the potential, it acquires a phase $d\phi = 2\pi df$.

- The solutions can be easily extended to the case where $E < V(x)$, that is, in the classically disallowed regions by appropriate changes in sign giving

$$\psi_{\pm} = \frac{\tilde{C}_{\pm}}{\sqrt{p(x)}} \exp\left(\pm \sqrt{2m/\hbar^2} \int^x \sqrt{V(x) - E} dx\right) \quad (10.45)$$

which are the exponentially suppressed solutions discussed in Section 8.2.2; these give rise to quantum tunneling effects. The WKB wavefunction thus has features of both the classical probability distribution, arising from averaging over the trajectory, and the quantum wavefunction.

With this form of the solution, we can examine the effect of neglecting the $\mathcal{O}(\hbar^2)$ term in Eqn. (10.35). Taking the ratio of the last term to the first we find something of the order

$$\frac{\hbar^2}{F'(x)^2} \left(\frac{A''(x)}{A(x)} \right) \propto \frac{\hbar^2}{p(x)^2} \frac{1}{l^2} \propto \frac{1}{[lk(x)]^2} \propto \left(\frac{\lambda(x)}{2\pi l} \right)^2 \quad (10.46)$$

where l is a typical distance scale over which $E - V(x)$ changes. Thus, if the “local de Broglie wavelength,” $\lambda(x)$, is much shorter than the distance scale over which the potential changes, the semiclassical approximation is a good one. This is obviously not the case near the classical turning points where the explicit $1/\sqrt{p(x)}$ factors in Eqn. (10.41) actually diverge, indicating that the solution is poorly behaved there.

To obtain a complete description of the wavefunction, the solutions inside and outside the well must be smoothly matched onto each other. The formalism for doing this is not beyond the level of this text, but we choose to only quote the results.⁷ For example, we can take linear combinations of the complex exponential solutions near the left turning point to write

$$\psi_L(x) = \frac{A_L}{\sqrt{p(x)}} \cos\left(\int_a^x k(x) dx - C_L\pi\right) \quad (10.47)$$

⁷ See, for example, Park (1992); I also like the discussion in Migdal and Krainov (1969).

For an infinite wall type boundary condition, it is easy to see that $C_L = 1/2$ since we require that

$$\psi_L(a) \propto \cos(-C_L\pi) = 0 \quad (10.48)$$

For a smoother potential, one for which one can approximate $V(x)$ near $x = a$ by a linear function,⁸ the appropriate value of C_L turns out to be $1/4$. This can be interpreted as saying that the quantum wavefunction penetrates $\pi/4 = 2\pi/8$ or $\sim 1/8$ of a local wavelength into the classically disallowed region.

10.3.2 WKB Quantized Energy Levels

One of the most useful results arising from the WKB method is a semiclassical estimate for the quantized energy levels in a potential. Matching the WKB wavefunctions at each of the two classical turning points yields two, presumably equivalent descriptions of $\psi(x)$ inside the well, namely

$$\psi_L(x) = \frac{A_L}{\sqrt{p(x)}} \cos\left(\int_a^x k(x) dx - C_L\pi\right) \quad (10.49)$$

and

$$\psi_R(x) = \frac{A_R}{\sqrt{p(x)}} \cos\left(\int_x^b k(x) dx - C_R\pi\right) \quad (10.50)$$

If these two solutions are to agree, we must clearly have $|A_L| = |A_R|$; then comparing the arguments of the cosines we find that

$$\int_a^b k(x) dx - (C_L + C_R)\pi = n\pi \quad \text{for } n = 0, 1, 2, \dots \quad (10.51)$$

This implies that

$$\int_a^b k(x) dx = (n + C_L + C_R)\pi \quad \text{for } n = 0, 1, 2, \dots \quad (10.52)$$

or

$$\int_a^b \sqrt{2m(E - V(x))} dx = (n + C_L + C_R)\pi\hbar \quad (10.53)$$

Recalling that $k(x) = 2\pi/\lambda(x)$, we see that Eqn. (10.52) is simply a more sophisticated version of “fitting an integral number of de Broglie half-wavelengths in a box” and generalizes the Bohr–Sommerfeld quantization condition. The value of n can be seen to count the number of nodes in the quantum wavefunction.

⁸ In this case, the solution which interpolates between the inside and outside can be described by an Airy function (See Appendix E.2).

Example 10.6. Infinite well and harmonic oscillator

For the standard infinite well, we have $C_L = C_R = 1/2$ (infinite wall boundary conditions) and $k(x) = \sqrt{2mE/\hbar^2}$, so that the WKB quantization condition gives

$$\int_0^a \sqrt{2mE} dx = (n+1)\pi \quad (10.54)$$

or

$$E_n = \frac{\hbar^2(n+1)^2\pi^2}{2ma^2} \quad \text{for } n = 0, 1, 2, \dots \quad (10.55)$$

which is the exact answer.

More interestingly, the WKB quantization also gives the correct answer for the harmonic oscillator. In that case we have

$$p(x) = \sqrt{2m(E - m\omega^2 x^2/2)} \quad \text{or} \quad k(x) = \frac{m\omega}{\hbar} \sqrt{A^2 - x^2} \quad (10.56)$$

where $E = m\omega^2 A^2/2$. Since $C_L = C_R = 1/4$ in this case (noninfinite walls) we find

$$\int_{-A}^{+A} k(x) dx = \frac{m\omega}{\hbar} \int_{-A}^{+A} \sqrt{A^2 - x^2} dx = (n+1/2)\pi \quad (10.57)$$

or

$$E_n = (n+1/2)\hbar\omega. \quad (10.58)$$

Once again, the harmonic oscillator problem can be solved exactly with seemingly every method brought to bear.

We have noted that we have dropped terms of order $\mathcal{O}(\hbar^2)$ or $1/(lk)^2$; since typically we find $k_n \propto n/l$, we expect the WKB estimates of the energies to have errors of order $\mathcal{O}(1/n^2)$. This is consistent with our keeping the C_L, C_R terms in Eqn. (10.52), which, in this language, are of order $\mathcal{O}(1/n)$.

10.4 Matrix Methods

The variational method relies on the expansion of a general quantum state in terms of energy eigenstates. In this section, we describe a matrix approach, which also uses the algebraic structure inherent in the Schrödinger equation, but in a rather different way.

Suppose that we have solved for the energy eigenstates of some Hamiltonian operator, \hat{H} . We call them $\psi_n(x)$ where we let the label n start with $n = 1$ for

notational convenience; with this labeling, the ground state is $\psi_1(x)$, the first excited state $\psi_2(x)$, and so on.

We know that a general wavefunction can be expanded in such eigenstates via $\psi(x) = \sum_{n=1}^{\infty} a_n \psi_n(x)$ and from Section 6.4 we know that the information content in $\psi(x)$ and the expansion coefficients, $\{a_n\}$, is the same. We can write the collected $\{a_n\}$ as an (infinite-dimensional) vector \mathbf{a}

$$\psi(x) \Longleftrightarrow \{a_n\} \Longleftrightarrow \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \Longleftrightarrow \mathbf{a} \quad (10.59)$$

where we demand that $\sum_n |a_n|^2 = 1$ for proper normalization. In this language, individual energy eigenstates are written as

$$\psi_1(x) \Longleftrightarrow \{a_1 = 1, a_{n>1} = 0\} \Longleftrightarrow \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} \Longleftrightarrow \mathbf{e}_1 \quad (10.60)$$

and so forth. The set of vectors, \mathbf{e}_i , corresponding to eigenfunctions are said to form a *basis* for the infinite-dimensional vector space; they are like the unit vectors of a more physical vector space. We then have $\mathbf{a} = \sum_i a_i \mathbf{e}_i$.

The Schrödinger equation $\hat{H}\psi = E\psi$ can be written in the form

$$\hat{H} \left(\sum_m a_m \psi_m(x) \right) = E \left(\sum_m a_m \psi_m(x) \right) \quad (10.61)$$

so that if we multiply both sides by $\psi_n^*(x)$ (on the left, as usual) and integrate we find that

$$\sum_m \langle \psi_n | \hat{H} | \psi_m \rangle a_m = E \sum_m \langle \psi_n | \psi_m \rangle a_m = E \sum_m \delta_{n,m} a_m = E a_n \quad (10.62)$$

We then choose to identify

$$\langle \psi_n | \hat{H} | \psi_m \rangle \equiv \mathbf{H}_{nm} \quad (10.63)$$

with the n, m th element of a *matrix* \mathbf{H} in which case the Schrödinger equation takes the form of a matrix eigenvalue problem (see Appendix F.1), namely

$$\begin{pmatrix} \mathbf{H}_{11} & \mathbf{H}_{12} & \mathbf{H}_{13} & \cdots \\ \mathbf{H}_{21} & \mathbf{H}_{22} & \mathbf{H}_{23} & \cdots \\ \mathbf{H}_{31} & \mathbf{H}_{32} & \mathbf{H}_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \quad (10.64)$$

or

$$\mathbf{H}\mathbf{a} = E\mathbf{a} \quad (10.65)$$

for short. The H_{nm} are called the *matrix elements* of the Hamiltonian and are said to form a *matrix representation* of the operator \hat{H} .

We note that \mathbf{H} can always be evaluated using a particular set of basis vectors, namely the eigenfunctions of \hat{H} itself. In this particular case, the matrix takes an especially simple form namely, because

$$H_{nm} = \langle \psi_n | \hat{H} | \psi_m \rangle = \langle \psi_n | E_m | \psi_m \rangle = E \delta_{nm} \quad (10.66)$$

so that the matrix \mathbf{H} is *diagonal*. Thus, Eqn. (10.64) takes the form

$$\begin{pmatrix} E_1 & 0 & 0 & \cdots \\ 0 & E_2 & 0 & \cdots \\ 0 & 0 & E_3 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \quad (10.67)$$

The only way Eqn. (10.67) can be satisfied is if

$$\det(\mathbf{H} - E \mathbf{1}) = \det \begin{vmatrix} E_1 - E & 0 & 0 & \cdots \\ 0 & E_2 - E & 0 & \cdots \\ 0 & 0 & E_3 - E & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0 \quad (10.68)$$

where $\mathbf{1}$ is the unit matrix. This is equivalent to

$$(E_1 - E)(E_2 - E)(E_3 - E) \cdots = \prod_{n=1}^{\infty} (E_n - E) = 0 \quad (10.69)$$

so that the energy eigenvalues are simply the E_n , as we knew; the corresponding eigenvectors of the matrix equation are then simply the \mathbf{e}_i (Why?).

We then say that:

- The matrix representation of a Hamiltonian, when evaluated using its eigenfunctions as a basis, is diagonal and the diagonal entries are just its energy eigenvalues.

Matrix representations of other operators can also be generated. For example, the position and momentum operators, x and \hat{p} , have matrix counterparts denoted by \mathbf{x} and \mathbf{p} and are defined via

$$\mathbf{x}_{nm} = \langle \psi_n | x | \psi_m \rangle \quad \text{and} \quad \mathbf{p}_{nm} = \langle \psi_n | \hat{p} | \psi_m \rangle \quad (10.70)$$

Such matrix representations satisfy the usual rules of matrix algebra, namely

$$(\mathbf{x}^2)_{nm} = \sum_k \mathbf{x}_{nk} \mathbf{x}_{km} \quad (10.71)$$

or more explicitly

$$\begin{pmatrix} \mathbf{x}_{11}^2 & \mathbf{x}_{12}^2 & \cdots \\ \mathbf{x}_{21}^2 & \mathbf{x}_{22}^2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} = \begin{pmatrix} \mathbf{x}_{11} & \mathbf{x}_{12} & \cdots \\ \mathbf{x}_{21} & \mathbf{x}_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \cdot \begin{pmatrix} \mathbf{x}_{11} & \mathbf{x}_{12} & \cdots \\ \mathbf{x}_{21} & \mathbf{x}_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (10.72)$$

The matrix representation for the kinetic energy operator is, for example, $\mathbf{T} = \mathbf{p}^2/2m$ or

$$\mathbf{T}_{nm} = \frac{1}{2m} \sum_k \mathbf{p}_{nk} \mathbf{p}_{km} \quad (10.73)$$

Example 10.7. Matrix representation of the harmonic oscillator

We can make use of the results of Chapter 9 to evaluate many of these matrix representations for the specific case of the harmonic oscillator. Using the standard energy eigenvalues we find that

$$\mathbf{H} = \frac{\hbar\omega}{2} \begin{pmatrix} 1 & 0 & 0 & \cdots \\ 0 & 3 & 0 & \cdots \\ 0 & 0 & 5 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (10.74)$$

Using the results in Section 9.2.1, we then find that

$$\mathbf{x}_{nm} = \sqrt{\frac{\hbar}{2m\omega}} \left(\delta_{n,m-1} \sqrt{m} + \delta_{n,m+1} \sqrt{m+1} \right) \quad (10.75)$$

and we also quote the result

$$\begin{aligned} \mathbf{x}_{nm}^2 = \frac{\hbar}{2m\omega} & \left(\delta_{n,m+2} \sqrt{(m+1)(m+2)} + (2n+1)\delta_{n,m} \right. \\ & \left. + \delta_{n,m-2} \sqrt{m(m-1)} \right) \end{aligned} \quad (10.76)$$

We can check that the matrix equation

$$\mathbf{x}_{nm}^2 = \sum_k \mathbf{x}_{nk} \mathbf{x}_{km} \quad (10.77)$$

(Continued)

holds explicitly by comparing

$$\frac{\hbar}{2m\omega} \begin{pmatrix} 1 & 0 & \sqrt{1 \cdot 2} & 0 & \dots \\ 0 & 3 & 0 & \sqrt{2 \cdot 3} & \dots \\ \sqrt{1 \cdot 2} & 0 & 5 & 0 & \dots \\ 0 & \sqrt{2 \cdot 3} & 0 & 7 \dots & \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (10.78)$$

$$\sqrt{\frac{\hbar}{2m\omega}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \dots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \dots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \dots \\ 0 & 0 & \sqrt{3} & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \cdot \sqrt{\frac{\hbar}{2m\omega}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \dots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \dots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \dots \\ 0 & 0 & \sqrt{3} & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

Similar results hold for p and p^2 and one can show (P10.16) that

$$H_{nm} = \frac{1}{2m} p_{nm}^2 + \frac{m\omega^2}{2} x_{nm}^2 \quad (10.79)$$

holds as a matrix equation.

The *average* or *expectation value* of an operator in any state can also be written in this language. For example, we have

$$\begin{aligned} \langle x \rangle &= \langle \psi | x | \psi \rangle = \left\langle \sum_n a_n \psi_n \left| x \right| \sum_m a_m \psi_m \right\rangle \\ &= \sum_{n,m} a_n^* \langle \psi_n | x | \psi_m \rangle a_m \\ &= \sum_{n,m} a_n^* x_{nm} a_m \end{aligned} \quad (10.80)$$

with similar expressions for other operators. We can also easily include the time-dependence for any state via

$$\mathbf{a}(t) \Longleftrightarrow \sum_i a_i \mathbf{e}_i e^{-iE_i t/\hbar} \Longleftrightarrow \begin{pmatrix} a_1 e^{-iE_1 t/\hbar} \\ a_2 e^{-iE_2 t/\hbar} \\ \vdots \end{pmatrix} \quad (10.81)$$

The expectation value of the energy operator can be checked to satisfy

$$\langle \hat{E} \rangle_t = \sum_n |a_n|^2 E_n \quad (10.82)$$

independent of time because the energy matrix is diagonal; other average values have less trivial time-dependence (P10.17) in agreement with earlier examples.

Thus far we have only considered the case in which we already know the energy eigenfunctions and eigenvalues of the Hamiltonian operator \hat{H} . In this instance, the discussion above is interesting, but provides little new information; we have just provided yet another representation of the solution space. If, on the other hand, we did not know the stationary states we could still proceed as follows:

1. Pick a convenient set of energy eigenfunctions to *some* problem, called $\zeta_n(x)$; we immediately know that they form a complete set so that the expansion theorem will work.
2. Evaluate the Hamiltonian matrix using this set of basis functions, that is calculate

$$\mathbf{H}_{nm} \equiv \langle \zeta_n | \hat{H} | \zeta_m \rangle = \frac{1}{2m} \langle \zeta_n | \hat{p}^2 | \zeta_m \rangle + \langle \zeta_n | V(x) | \zeta_m \rangle \quad (10.83)$$

In this case, \mathbf{H} will no longer be diagonal.

3. The Schrödinger equation in matrix form is still an eigenvalue problem of the form in Eqn. (10.64); its eigenvalues are determined by the condition that $\det(\mathbf{H} - E \mathbf{1}) = 0$.
4. If the eigenvalues are labeled via E_i and the corresponding eigenvectors by $\mathbf{a}^{(i)}$, the position-space wavefunctions are given by $\psi_i(x) = \sum_n^\infty a_n^{(i)} \zeta_n(x)$.

Since finding the *exact* eigenvalues and eigenvectors of an infinite-dimensional matrix is only possible in very special cases, to use this method as a real calculational tool we most often restrict ourselves to a truncated version of the problem. More specifically, we try to diagonalize the $N \times N$ submatrix in the upper left-hand corner for some finite value of N . As N is made larger, we expect to obtain an increasingly good representation of the exact result. Because there exist powerful techniques for diagonalizing large matrices, especially if they happen to have large numbers of vanishing components (so-called sparse matrices), this technique is well suited for numerical computations.

Example 10.8. Infinite well plus δ -function I: Matrix methods

As an example of this method, consider the potential discussed in P8.8, namely, a symmetric infinite well defined via

$$V(x) = \begin{cases} 0 & \text{for } |x| < a \\ +\infty & \text{for } |x| > a \end{cases} \quad (10.84)$$

plus a δ -function potential spike at the origin,

$$V_g(x) = g\delta(x) \quad (10.85)$$

This problem can be solved exactly and hence is useful as a testing ground for various approximation techniques. (For a thorough discussion, see Lapidus (1987).)

We know that the odd states are unaffected by $V_g(x)$ since they all possess nodes at $x = 0$. We thus only consider the even states only for which the energy eigenvalue condition can be written as

$$\lambda = -2y \cot(y) \quad (10.86)$$

where

$$\lambda \equiv \frac{2mag}{\hbar^2} \quad \text{and} \quad E = \frac{\hbar^2 y^2}{2ma^2} \quad (10.87)$$

We naturally choose as a set of basis functions the even solutions of the symmetric well *without* the δ -function potential, that is,

$$\psi_n(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{(n-1/2)\pi x}{a}\right) \quad (10.88)$$

Evaluating the Hamiltonian matrix with this basis set, we find

$$H = \begin{pmatrix} \hbar^2\pi^2/8ma^2 + g/a & g/a & g/a & \cdots \\ g/a & 9\hbar^2\pi^2/8ma^2 + g/a & g/a & \cdots \\ g/a & g/a & 25\hbar^2\pi^2/8ma^2 + g/a & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (10.89)$$

or

$$H = \left(\frac{\hbar^2\pi^2}{8ma^2}\right) \begin{pmatrix} 1 + \epsilon & \epsilon & \epsilon & \cdots \\ \epsilon & 9 + \epsilon & \epsilon & \cdots \\ \epsilon & \epsilon & 25 + \epsilon & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (10.90)$$

where $\epsilon \equiv 4\lambda/\pi^2$. Since we rely on matrix diagonalization methods ("canned" packages exist in many programming languages which will find the eigenvalues and eigenvectors of

(Continued)

matrices), we must choose some specific numerical values. For $\lambda = 5$, the exact even energy eigenvalues (in terms of $\hbar^2\pi^2/8ma^2$) obtained from Eqn. (10.86) are

$$2.2969 \text{ (1)} \quad 10.8048 \text{ (9)} \quad 26.9303 \text{ (25)} \quad 50.9743 \text{ (49)} \quad (10.91)$$

where the terms in parentheses are the values without the δ -function term.

Using an available package (in this case *Mathematica*®), we find the eigenvalues for increasingly large $N \times N$ truncated basis sets:

$$\begin{array}{ccccc} 1 \times 1 & 3.02642 & \text{---} & \text{---} & \text{---} \\ 2 \times 2 & 2.54241 & 11.5104 & \text{---} & \text{---} \\ 3 \times 3 & 2.44832 & 11.1412 & 27.4898 & \text{---} \\ 4 \times 4 & 2.40672 & 11.0335 & 27.2396 & 51.4298 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 10 \times 10 & 2.33857 & 10.8861 & 27.0277 & 51.07991 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 50 \times 50 & 2.30506 & 10.8204 & 26.9487 & 50.9937 \end{array} \quad (10.92)$$

It does seem that the eigenvalues of the truncated set approach the exact values at N is increased. Such programs also give the eigenvectors as well; we display the components corresponding to the ground state solution below:

$$\begin{array}{cc} 1 \times 1 & (1) \\ 2 \times 2 & (0.97264, -0.23232) \\ 3 \times 3 & (0.97451, -0.21543, -0.06258) \\ 4 \times 4 & (0.97575, -0.20818, -0.06075, -0.02946) \end{array} \quad (10.93)$$

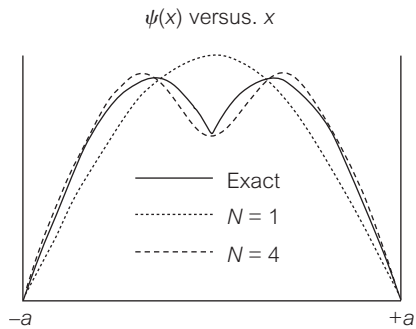


Figure 10.7. The exact (solid) and two approximate solutions for Example 10.8.

Using these values, we illustrate in Fig. 10.7 the approximations to the ground state wave-function for the first four approximations, comparing them to the exact solution, with the cusp expected from the singular δ -function; the convergence to the exact solution is not particularly rapid.

10.5 Perturbation Theory

We now turn to what is undoubtedly the most widely used approximation method we will discuss, perturbation theory. We are certainly used to the notion of the systematic expansion of some quantity in terms of a small parameter; a familiar example is the series expansion of a function,

$$f(x) = f(0) + f'(0)x + \frac{1}{2!}f''(0)x^2 + \dots \quad (10.94)$$

Such an expansion may well formally converge for all values of x (such as for the series for $\exp(x)$), but is often most useful as a calculational tool when $|x| \ll 1$.

Perturbation theory extends this notion to quantum mechanics in cases where the system under study can be described by an “unperturbed” Hamiltonian, \hat{H}_0 , for which the energy eigenstates can be obtained exactly, that is,

$$\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \quad (10.95)$$

We began this chapter with the observation that many important systems such as the hydrogen atom or the harmonic oscillator can actually be solved exactly. One can then imagine “turning on” an additional perturbing interaction, \hat{H}' , which will change the spectrum and wavefunctions; examples include the addition of an electric field acting on a charged particle (via a term $\hat{H}' = V(x) = -qEx$ in one dimension) or a magnetic field acting on a magnetic moment ($\hat{H}' = -\mu \cdot \mathbf{B}$). (While we will most often consider the case where the perturbation is a (small) additional potential energy function, other cases are possible (P10.20).) We can then write

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \quad (10.96)$$

where we introduce a dimensionless parameter λ (which can be set equal to unity at the end of the calculation) to act as an expansion parameter. Our goal is then to solve the Schrödinger equation for the complete system,

$$\hat{H} \psi_n = E_n \psi_n \quad (10.97)$$

as a series in λ .

We focus in the next two sections on time-independent problems, but briefly discuss problems involving perturbations which evolve in time in Section 10.5.3.

10.5.1 Nondegenerate States

We will begin by making the assumption that the energy levels of the unperturbed system are all distinct, that is, that there are no degeneracies where $E_n^{(0)} \approx E_l^{(0)}$

for some pair l, n . Then, as we imagine $\lambda \rightarrow 0$, we can unambiguously write

$$\psi_n \xrightarrow{\lambda \rightarrow 0} \psi_n^{(0)} \quad \text{and} \quad E_n \xrightarrow{\lambda \rightarrow 0} E_n^{(0)} \quad (10.98)$$

and make a unique identification of each perturbed state with its unperturbed counterpart. Motivated by these assumptions, we first write

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (10.99)$$

as a series in λ . Then, since the unperturbed eigenstates form a complete set, we always have

$$\psi_n = \sum_{j=0}^{\infty} a_{nj} \psi_j^{(0)} = a_{nn} \psi_n^{(0)} + \sum_j' a_{nj} \psi_j^{(0)} \quad (10.100)$$

where \sum_j' denotes the infinite sum with the $j = n$ term removed. The new (perturbed) eigenstates can always be written as a linear combination of the old (unperturbed) eigenstates.

The coefficients have slightly different expansions in λ ,

$$a_{nn} = a_{nn}^{(0)} + \lambda a_{nn}^{(1)} + \lambda^2 a_{nn}^{(2)} + \dots \quad (10.101)$$

$$a_{nj} = \lambda a_{nj}^{(1)} + \lambda^2 a_{nj}^{(2)} + \dots \quad \text{for } j \neq n \quad (10.102)$$

because Eqn. (10.98) implies that

$$\lim_{\lambda \rightarrow 0} a_{nj} = \delta_{nj} \quad (10.103)$$

We can constrain the expansion coefficients of Eqn. (10.100) further by noting that the normalization condition

$$\sum_{j=1}^{\infty} |a_{nj}|^2 = 1 \quad \text{for all } n \quad (10.104)$$

implies that

$$1 = |a_{nn}|^2 + \sum_j' |a_{nj}|^2 = |a_{nn}|^2 + \sum_j' \left(\lambda a_{nj}^{(1)} + \dots \right)^2 = |a_{nn}|^2 + \mathcal{O}(\lambda^2) \quad (10.105)$$

so that

$$a_{nn} \approx 1 \quad \text{to } \mathcal{O}(\lambda^2) \quad \text{which implies that } a_{nn}^{(1)} = 0 \quad (10.106)$$

The Schrödinger equation can now be written (to $\mathcal{O}(\lambda^2)$) in the form

$$\begin{aligned} (\hat{H}_0 + \lambda \hat{H}') \left(\psi_n + \lambda \sum_j' a_{nj} \psi_j^{(0)} + \dots \right) = \\ (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) \left(\psi_n + \lambda \sum_j' a_{nj} \psi_j^{(0)} + \dots \right) \end{aligned} \quad (10.107)$$

We first multiply Eqn. (10.107) by $(\psi_n^{(0)})^*$ on the left and integrate to obtain

$$\begin{aligned} \left\langle \psi_n^{(0)} \left| \hat{H}_0 + \lambda \hat{H}' \right| \left(\psi_n + \lambda \sum_j' a_{nj} \psi_j^{(0)} + \dots \right) \right\rangle \\ = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) \left\langle \psi_n^{(0)} \left| \left(\psi_n + \lambda \sum_j' a_{nj} \psi_j^{(0)} + \dots \right) \right\rangle \right\rangle \end{aligned} \quad (10.108)$$

Equating powers of λ and making extensive use of the orthogonality of the unperturbed wavefunctions, namely that $\langle \psi_n^{(0)} | \psi_j^{(0)} \rangle = \delta_{nj}$, we find

$$\mathcal{O}(\lambda^0) : E_n^{(0)} = \langle \psi_n^{(0)} | \hat{H}_0 | \psi_n^{(0)} \rangle \quad (10.109)$$

$$\mathcal{O}(\lambda^1) : E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \equiv H'_{nn} \quad (10.110)$$

$$\mathcal{O}(\lambda^2) : E_n^{(2)} = \sum_j' a_{nj}^{(1)} \langle \psi_n^{(0)} | \hat{H}' | \psi_j^{(0)} \rangle \equiv \sum_j' a_{nj}^{(1)} H'_{nj} \quad (10.111)$$

These expressions all require the *matrix elements* of the *perturbing Hamiltonian*, evaluated using the *unperturbed eigenfunctions*, H'_{nk} .

The $\mathcal{O}(\lambda^0)$ term ($E_n^{(0)}$) simply reproduces the unperturbed energy spectrum. The equation for $E_n^{(1)}$ in Eqn. (10.110) is a very important result as it states that:

- The first-order shift in the energy of level n due to a (small) perturbation is given by the diagonal matrix element of the perturbing Hamiltonian, H'_{nn} , evaluated with the unperturbed wavefunctions, that is,

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = H'_{nn} \quad (10.112)$$

which we repeat because of its extreme importance.

Using Eqn. (10.112) we see that it can sometimes happen that the first-order energy shift vanishes identically because of symmetry. For example, a charged

particle in the infinite symmetric well subject to a weak electric field, given by a potential of the form $V(x) = -qEx$, would have a first-order energy shift given by

$$E_n^{(1)} = \begin{cases} -qE\langle u_n^{(+)} | x | u_n^{(+)} \rangle & \text{for even states} \\ -qE\langle u_n^{(-)} | x | u_n^{(-)} \rangle & \text{for odd states} \end{cases} \quad (10.113)$$

which vanishes for all states. In such cases, the second-order term $E_n^{(2)}$ is the leading correction.

The form of Eqn. (10.111) also suggests the more general result:

- The k th order correction to the energy levels requires knowledge of the $(k - 1)$ th order wavefunctions

so that to determine $E^{(2)}$ we require the leading-order expansion coefficients, $a_{nj}^{(1)}$.

To obtain information on the expansion coefficients, we multiply Eqn. (10.107) by $(\psi_j^{(0)})^*$ with $j \neq n$ and integrate. The $\mathcal{O}(\lambda^0)$ terms are absent, while the $\mathcal{O}(\lambda^1)$ terms require that

$$a_{nk}^{(1)} = \frac{\langle \psi_k^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} = \frac{H'_{nk}}{(E_n^{(0)} - E_k^{(0)})} \quad (10.114)$$

The first-order wavefunction thus receives contributions from every state for which the *off-diagonal* matrix elements are nonvanishing, that is, $H'_{nk} \neq 0$. Combining Eqns. (10.114) and (10.111), we find that the second-order corrections to the energies are given by

$$\begin{aligned} E_n^{(2)} &= \sum_j' a_{nk}^{(1)} H'_{nk} \\ &= \sum_k' \left[\frac{\langle \psi_k^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} \right] \langle \psi_n^{(0)} | \hat{H}' | \psi_k^{(0)} \rangle \\ &= \sum_k' \frac{|\langle \psi_n^{(0)} | \hat{H}' | \psi_k^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})} \\ E_n^{(2)} &= \sum_k' \frac{|H'_{nk}|^2}{(E_n^{(0)} - E_k^{(0)})} \end{aligned} \quad (10.115)$$

In the last step, we have made use of the fact that \hat{H}' is Hermitian to write $H'_{nk} = (H'_{kn})^*$; this form makes it clear that the second-order shift in energy is manifestly real. This result has many interesting consequences:

- The second-order shift depends on the off-diagonal matrix elements, but inversely weighted by the “distance in energy” to the state in question; thus, in general, states nearby in energy have a larger effect.
- This form also implies that the spacing in energy levels must be larger than the matrix elements of the perturbation for the expansion to be valid, that is, we demand that

$$H'_{nk} \ll |E_n^{(0)} - E_k^{(0)}| \quad (10.116)$$

This shows that degenerate energy levels must clearly be handled in a different way.

- States with energy below (above) a given level induce a second-order energy shift which is positive (negative); this effect is often referred to as “level repulsion”.
- In particular, the second-order shift in the ground state energy is clearly always negative as all the other states lie above it. For many problems for which there are large numbers of levels, one can argue heuristically that the second-order shift for any fixed energy level will be negative due to the large number of states above it; this can be motivated on more physical grounds⁹ and is often observed.

The second-order expansion coefficients (the $a_{nj}^{(2)}$) are too complicated to reproduce here but, for reference, we state without proof that the result for the third-order shift in energies is

$$E_n^{(3)} = \sum_k' \sum_j' \frac{H'_{nk} H_{kj} H'_{jn}}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_j^{(0)})} - H'_{nn} \sum_k' \frac{|H'_{nk}|^2}{(E_n^{(0)} - E_k^{(0)})^2} \quad (10.117)$$

We see that the work required to continue the perturbation theory expansion increases rapidly, so that often only the first- and second-order corrections are calculated. We now turn to some examples.

⁹ See the nice discussion by Saxon (1968).

Example 10.9. Harmonic oscillator with applied electric field

The problem of a charged oscillator in a constant electric field, described by the Hamiltonian

$$\hat{H} = \frac{1}{2}m\omega^2 x^2 - Fx \quad (10.118)$$

(where $F = qE$) was investigated in P9.9 where it was shown that it could be solved exactly; the resulting energy spectrum is

$$E_n = (n + 1/2)\hbar\omega - \frac{F^2}{2m\omega^2} \quad (10.119)$$

Let us approach this problem by considering the electric field interaction to be a small perturbation about the unperturbed oscillator, that is, $\hat{H}' = -Fx$; we can then use F as an expansion coefficient to count powers in perturbation theory. We have $E_n^{(0)} = (n + 1/2)\hbar\omega$, of course, while the first-order correction vanishes (because of symmetry) since

$$E_n^{(1)} = \langle \psi_n | \hat{H}' | \psi_n \rangle = -qE \langle \psi_n | x | \psi_n \rangle = 0 \quad (10.120)$$

The second-order correction is given by

$$E_n^{(2)} = F^2 \sum_k' \frac{|\langle \psi_n | x | \psi_k \rangle|^2}{(E_n^{(0)} - E_k^{(0)})} = F^2 \sum_k' \frac{|\langle n | x | k \rangle|^2}{(n - k)\hbar\omega} \quad (10.121)$$

Using the results in Section 9.2.2, we know that

$$\langle n | x | k \rangle = \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{n} \delta_{k,n-1} + \sqrt{n+1} \delta_{k,n+1} \right) \quad (10.122)$$

Inserting this result into Eqn. (10.121), we find that

$$\begin{aligned} E_n^{(2)} &= \frac{F^2}{\hbar\omega} \left(\frac{\hbar}{2m\omega} \right) \sum_k' \frac{(n\delta_{k,n-1} + (n+1)\delta_{k,n+1})}{(n-k)} \\ &= \frac{F^2}{2m\omega^2} \left(\frac{n}{1} + \frac{(n+1)}{-1} \right) \\ &= -\frac{F^2}{2m\omega^2} \end{aligned} \quad (10.123)$$

which reproduces the exact answer. One would then expect that all of the higher-order corrections to the energy would then vanish identically and one can confirm explicitly (P10.21) that the third-order correction in Eqn. (10.117) is indeed zero in this case. It is also an example where the second-order corrections are, in fact, negative for all energy levels.

This does not imply, however, that the expansion coefficients have a similarly simple series behavior. To see this, we can make use of the exact ground state solution to the complete problem (see P9.9 again)

$$\psi(x; F) = \frac{1}{\sqrt{\rho\sqrt{\pi}}} e^{-(x-x_0)^2/2\rho^2} \quad (10.124)$$

(Continued)

where $x_0 = F/m\omega^2$ and $\rho = \sqrt{\hbar/m\omega}$. The expansion coefficient a_{00} is then given by

$$a_{00} \equiv \int [\psi(x; F=0)]^* \psi(x; F) dx = e^{-x_0^2/4\rho^2} = e^{-F^2/F_0^2} \quad (10.125)$$

where $F_0 \equiv 2\sqrt{\hbar m\omega}$. Expanding a_{00} in powers of F we find that

$$a_{00} = 1 - \frac{F^2}{F_0^2} + \frac{1}{2} \frac{F^4}{F_0^4} + \dots \quad (10.126)$$

Thus, while the perturbation series for the energies terminates at second-order, the expansion coefficients require the full series to converge to the exact answer.

Example 10.10. Infinite well plus δ -function II: Perturbation theory

Consider the problem, discussed in P8.8, of the symmetric infinite square well potential plus a δ -function potential at the origin; in this case, let the δ -function constitute the perturbation so that $\hat{H}' = g\delta(x)$.

For the odd case, the explicit application of the boundary conditions for the full problem require that the $u_n^{(-)}(x)$ vanish at the origin and gives the same energy eigenvalue condition as for the infinite well alone. This can be confirmed to any order in perturbation theory since all of the relevant matrix elements in Eqns (10.112), (10.115), and (10.117) vanish explicitly. (See P10.22.)

For the even case, the exact eigenvalue condition was given by $\lambda = -2y \cot(y)$ where $\lambda \equiv 2mag/\hbar^2$ and $E = \hbar^2 y^2/2ma^2$. Focusing only on the ground state, this eigenvalue condition can be expanded to second order (see P10.23) to yield

$$y = \frac{\pi}{2} + \frac{\lambda}{\pi} - 2\frac{\lambda^2}{\pi^3} + \mathcal{O}(\lambda^3) = \frac{\pi}{2} \left(1 + \frac{2\lambda}{\pi^2} - \frac{4\lambda^2}{\pi^4} \right) + \dots \quad (10.127)$$

or

$$\begin{aligned} E_1^{(+)} &\approx \frac{\hbar^2}{2ma^2} \frac{\pi^2}{4} \left(1 + \frac{2\lambda}{\pi^2} - \frac{4\lambda^2}{\pi^4} + \dots \right)^2 \\ &\approx \frac{\hbar^2 \pi^2}{8ma^2} + \lambda \left(\frac{\hbar^2}{2ma^2} \right) - \lambda^2 \left(\frac{\hbar^2}{2\pi^2 ma^2} \right) + \dots \end{aligned} \quad (10.128)$$

The first-order perturbation result for even states is simply

$$(E_n^{(+)})^{(1)} = \langle u_n^{(+)} | g\delta(x) | u_n^{(+)} \rangle = \frac{g}{a} = \lambda \left(\frac{\hbar^2}{2ma^2} \right) \quad (10.129)$$

(Continued)

independent of n for all even states; this obviously agrees with the explicit expansion of the eigenvalue condition for the ground state in Eqn. (10.128). The second-order correction is then

$$\begin{aligned}
 E_n^{(+)}{}^{(2)} &= \sum_{k=2}^{\infty} \frac{|\langle u_n^{(+)} | g\delta(x) | u_k^{(+)} \rangle|^2}{(\hbar^2\pi^2/8ma^2)((1 - (2k - 1)^2))} \\
 &= -\lambda^2 \frac{2\hbar^2}{m\pi^2 a^2} S \quad \text{where } S \equiv \sum_{k=2}^{\infty} \frac{1}{(2k - 1)^2 - 1} = \frac{1}{4} \\
 &= -\lambda^2 \left(\frac{\hbar^2}{2\pi^2 ma^2} \right) \tag{10.130}
 \end{aligned}$$

which also agrees with the expansion of the exact result. (See Epstein (1960) for a nice discussion of the subtleties of this problem.)

While the technical details of the calculation are beyond our level, it is appropriate to note here that one of the most spectacularly successful predictions in all of physics makes use of perturbation theory. The magnetic moment of both the electron and the muon can be calculated in the theory of quantum electrodynamics,¹⁰ using more advanced perturbation theory methods. A recent theoretical result for the electron magnetic moment (expressed as a dimensionless number) is

$$g_e(\text{theory}) = 2.0023193048 \text{ (8)} \tag{10.131}$$

where the uncertainty is indicated in the last significant digit. Amazingly, it can also be measured to a similar precision with the result

$$g_e(\text{experiment}) = 2.0023193048 \text{ (4)} \tag{10.132}$$

10.5.2 Degenerate Perturbation Theory

When two (or more) energy levels of the unperturbed system are degenerate, any linear combinations of the corresponding wavefunctions, $\psi_n^{(0)}(x)$ and $\psi_l^{(0)}(x)$, still give same energy eigenvalue. (Such combinations can still be made orthogonal to each other, of course.) This implies, however, that the unique identification of each perturbed state with an unperturbed counterpart as in Eqn. (10.98) is not possible. The breakdown of the perturbation method in this case is clearly signaled by the appearance of small energy denominators

¹⁰ See Perkins (2000) and references therein for a discussion at an undergraduate level.

in Eqn. (10.114); states nearby in energy can play an important role and have to be considered on a more equal footing.

In this limit, it is convenient to return to the matrix formulation of the eigenvalue problem and consider the 2×2 submatrix involving the states in question, namely

$$\begin{pmatrix} E_n^{(0)} + \lambda H'_{nn} & \lambda H'_{nl} \\ \lambda H'_{ln} & E_l^{(0)} + \lambda H'_{ll} \end{pmatrix} \begin{pmatrix} a_n \\ a_l \end{pmatrix} = E \begin{pmatrix} a_n \\ a_l \end{pmatrix} \quad (10.133)$$

where the a_n, a_l are the expansion coefficients. In general, for a case with N degenerate levels, the corresponding $N \times N$ submatrix must be considered.

This system of linear equations (for the $a_{n,l}$) will only have a nontrivial solution if the appropriate determinant vanishes, that is,

$$\det \begin{pmatrix} E_n^{(0)} + \lambda H'_{nn} - E & \lambda H'_{nl} \\ \lambda H'_{ln} & E_l^{(0)} + \lambda H'_{ll} - E \end{pmatrix} = 0 \quad (10.134)$$

The special case of an exact degeneracy where $E_n^{(0)} = E_l^{(0)} \equiv \mathcal{E}$ is easiest to treat; in this case, the energy eigenvalues are determined by the condition

$$(E - [\mathcal{E} + \lambda H'_{nn}]) (E - [\mathcal{E} + \lambda H'_{ll}]) - \lambda^2 H'_{ln} H'_{nl} = 0 \quad (10.135)$$

or

$$E_{\pm} = \mathcal{E} + \frac{\lambda}{2} (H'_{nn} + H'_{ll}) \pm \frac{\lambda}{2} \sqrt{(H'_{nn} - H'_{ll})^2 + 4H'_{ln} H'_{nl}} \quad (10.136)$$

The first term is obviously the (common) value of the unperturbed energy while the second is the average of the first-order energy shifts in each level, consistent with the non-degenerate case; the third term, however, can split the two levels and generally removes the degeneracy.

Substituting the result of Eqn. (10.136) into the matrix equation Eqn. (10.133), we find that the expansion coefficients are given by

$$\frac{a_n^{(\pm)}}{a_l^{(\pm)}} = \frac{2H'_{nl}}{(H'_{ll} - H'_{nn}) + \sqrt{(H'_{nn} - H'_{ll})^2 + 4H'_{ln} H'_{nl}}} \quad (10.137)$$

so that the appropriate (unnormalized) eigenfunctions are given by

$$\psi^{(\pm)}(x) \propto a_n^{(\pm)} \psi_n(x) + a_l^{(\pm)} \psi_l(x) \quad (10.138)$$

The actual energy splitting in Eqn. (10.136) clearly depends on λ , that is, on the *magnitude* of the perturbation; the appropriate linear combinations, however, do not, but are determined by the *form* of the perturbation, that is the *relative* sizes of the matrix elements H'_{nn} , H'_{ll} , and H'_{ln} (P10.26).

Because degeneracy of energy levels is far more common in multi-particle or multidimensional systems, we postpone presenting examples until later chapters.

10.5.3 Time-Dependent Perturbation Theory

The problem of determining the future time-development of a given quantum mechanical state, if one knows the exact energy eigenvalues and eigenfunctions of the system, is usually straightforward, since if we have $\hat{H}^{(0)}\psi_n^{(0)} = E_n\psi_n^{(0)}$, then

$$\psi^{(0)}(x, 0) = \sum_{n=0}^{\infty} a_n \psi_n^{(0)} \longrightarrow \psi^{(0)}(x, t) = \sum_{n=0}^{\infty} a_n e^{-iE_n t/\hbar} \psi_n^{(0)} \quad (10.139)$$

A similar problem arises in *time-dependent perturbation theory* when the system is subject to a (small) time-dependent change, so that the resulting Hamiltonian is given by

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}'(t), \quad (10.140)$$

just as in Eqn. (10.96), but now with \hat{H}' depending explicitly on time. We wish to see how the introduction of the perturbing potential changes the time-development of a quantum state, since we now must satisfy

$$\left[\hat{H}^{(0)} + \lambda \hat{H}'(t) \right] \psi(x, t) = \hat{H} \psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad (10.141)$$

Because the eigenfunctions of $\hat{H}^{(0)}$ still form a complete set, we can always write

$$\psi(x, t) = \sum_{n=0}^{\infty} a_n(t) e^{-iE_n t/\hbar} \psi_n^{(0)} \quad (10.142)$$

where we now assume that the expansion coefficients, the $a_n(t)$, themselves depend on time. (We can choose this form without loss of generality, thereby defining the $a_n(t)$, but this form is convenient since for the case of no perturbation, it reduces to the standard result in Eqn. (10.139).) We can substitute a solution of the form in Eqn. (10.142) into the time-dependent Schrödinger equation (Eqn. (10.141)), giving the respective left- and right-hand sides

$$\hat{H} \psi(x, t) = \sum_n E_n a_n(t) e^{-iE_n t/\hbar} \psi_n^{(0)} + \sum_n a_n(t) e^{-iE_n t/\hbar} \left[\lambda \hat{H}' \psi_n \right] \quad (10.143)$$

$$\begin{array}{ccc} \Downarrow & & \Downarrow \\ i\hbar \frac{\partial \psi(x, t)}{\partial t} = i\hbar \sum_n \left[\frac{da_n(t)}{dt} - \frac{iE_n}{\hbar} a_n(t) \right] e^{-iE_n t/\hbar} \psi_n & & \end{array} \quad (10.144)$$

Equating these two, cancelling the terms proportional to E_n , and multiplying (on the left, as usual) by $(\psi_m^{(0)})^*$ and integrating, we can make use of the orthonormality properties of the eigenstates to write

$$i\hbar \frac{da_m(t)}{dt} e^{-iE_m t/\hbar} = \sum_n a_n(t) e^{-iE_n t/\hbar} \langle \psi_m^{(0)} | \hat{H}'(t) | \psi_n^{(0)} \rangle \quad (10.145)$$

or

$$\begin{aligned} \frac{da_m(t)}{dt} &= -\frac{i}{\hbar} \sum_n a_n(t) e^{i(E_m - E_n)t/\hbar} \langle \psi_m^{(0)} | \hat{H}'(t) | \psi_n^{(0)} \rangle \\ &\equiv -\frac{i}{\hbar} \sum_n a_n(t) e^{i\omega_{m,n}t} H'_{mn} \end{aligned} \quad (10.146)$$

where

$$\omega_{m,n} \equiv \frac{(E_m - E_n)}{\hbar} \quad \text{and} \quad H'_{mn} \equiv \langle \psi_m^{(0)} | \hat{H}'(t) | \psi_n^{(0)} \rangle \quad (10.147)$$

and H'_{nm} can be called in this context a *transition matrix element*. We recall that the frequency $\omega_{m,n}$ sets the characteristic timescale for any two-state system (Section 4.6). At this stage, the infinite set of coupled equations implied by Eqn. (10.146) is still completely equivalent to the time-dependent Schrödinger equation for the perturbed system, as no approximations have been made.

We now specialize to the case where the initial state of the system is that of an energy eigenstate of the unperturbed Hamiltonian, namely, we assume that $\psi(x, 0) = \psi_k^{(0)}$. We then expect that for a small perturbation the expansion coefficients, $a_m(t)$, for states with $m \neq k$ will be small (since $a_{m \neq k}(t = 0) = \delta_{m,k} = 0$ to begin with), while the single $a_k(t)$ corresponding to the original eigenstate will be of order unity, namely

$$a_m(t) = \begin{cases} \mathcal{O}(\lambda) \ll 1 & \text{for } m \neq k \\ \mathcal{O}(1) & \text{for } m = k \end{cases} \quad (10.148)$$

Using this approximation in Eqn. (10.146), we find that

$$\frac{da_m(t)}{dt} \approx -\frac{i}{\hbar} e^{i\omega_{m,k}t} H'_{mk} \quad (10.149)$$

or

$$a_m(t) = -\frac{i}{\hbar} \int_{t_0}^t e^{i\omega_{m,k}t} H'_{mk}(t) dt \quad (10.150)$$

for $m \neq k$, if we assume that the perturbation is “turned on” at time $t = t_0$. This form is important since it implies that the probability that the particle will be

found in the m th state of the unperturbed system at a later time is given by

$$P_{k \rightarrow m}(t) = |a_m(t)|^2 = \frac{1}{\hbar^2} \left| \int_{t_0}^t e^{i\omega_{m,k}t} \mathbf{H}'_{mk}(t) dt \right|^2 \quad (10.151)$$

We expect that the chance of being excited (or decaying) into a different final state (the *transition probability*, $P_{k \rightarrow m}(t)$) will depend both on the transition matrix element (which includes information on the perturbation *and* its ability to “connect” the initial and final states) as well as on the detailed history of how the perturbation is applied in time, via the integral, which is weighted by the oscillatory exponential factor present in all two-state systems.

Example 10.11. Harmonic oscillator in a time-dependent electric field

Consider a particle of mass m and charge q in the ground state, $|0\rangle$, of the harmonic oscillator potential $V(x) = m\omega^2 x^2/2$. It is subject to an external time-dependent electric field of the form

$$\hat{H}'(t) = (-q\mathcal{E}_0 x) e^{-t^2/2\tau^2} \quad (10.152)$$

The perturbation is allowed to act over the time interval $(-\infty, +\infty)$ and we wish to evaluate the probability that the particle is eventually found in any excited state, $|n\rangle$.

The expansion coefficient from Eqn. (10.150) in this case is given by

$$a_m(t) = \frac{i}{\hbar} \langle n | q\mathcal{E}_0 x | 0 \rangle \int_{-\infty}^{+\infty} e^{i\omega_{n,0}t} e^{-t^2/2\tau^2} dt \quad (10.153)$$

The off-diagonal oscillator matrix element is given by Eqn. (9.50) as

$$\langle n | x | 0 \rangle = \sqrt{\frac{\hbar}{2m\omega}} \delta_{n,1} \quad (10.154)$$

while the integral over time is a standard Gaussian form. Combining these results, we find that the transition probability to any excited state is given by

$$P_{0 \rightarrow n}(t) = |a_n(t)|^2 = \frac{1}{\hbar^2} \left[\frac{q^2 \mathcal{E}_0^2 \hbar}{2m\omega} \delta_{n,1} \right] \left[2\pi\tau^2 e^{-(\omega_{n,0}\tau)^2} \right] \quad (10.155)$$

This result does show that transition probabilities in time-dependent perturbation theory can depend on *what* the perturbation is, to *which* states it is trying to couple, and *how* it is applied.

- The explicit form of the electric field potential in this case, for example, has implied that only adjacent levels can be excited (to this order of perturbation theory, at least) which is reminiscent of the selection rules discussed in Section 16.3.3. For an initial state $|k\rangle$, only the final states $|k \pm 1\rangle$ would be populated by this perturbation. The transition probability does, of course, also depend on the strength of the external field.

(Continued)

- The transition probability in this case is peaked at a value of $\omega_{n,0}\tau = 1$ so that application of the external perturbing potential at a rate (given by the timescale τ) which matches the natural frequency or period of the system gives the biggest effect. For the special case of the oscillator, $\omega_{n,0} \delta_{n,1} = \omega = 2\pi/T_{cl}$ is precisely the classical periodicity of the problem, so perturbations which occur on timescales much longer than this allow the system to accommodate itself to the change. This connection to the classical periodicity is much more general as we recall (P1.16 and Section 12.7)) that the classical period of a quantum system can be written as $T_{cl} = 2\pi\hbar/|dE_n/dn| \sim 2\pi/|\Delta E_{n,m}|$.

We can examine the result of applying the perturbation slowly over a long timescale in some detail, by writing Eqn. (10.150) in a way which includes information on the rate at which \hat{H}' is applied more directly. For example, using an identity and an integration-by-parts (IBP) trick, we have

$$\begin{aligned}
 a_m(t) &= -\frac{i}{\hbar} \int_{t_0}^t e^{i\omega_{m,k}t} H'_{mk}(t) dt \\
 &= -\frac{1}{\hbar\omega_{m,k}} \int_{t_0}^t \frac{d}{dt} \left[e^{i\omega_{m,k}t} \right] H'_{mk}(t) dt \\
 &\stackrel{\text{IBP}}{=} -\frac{1}{\hbar\omega_{m,k}} \left[-\int_{t_0}^t e^{i\omega_{m,k}t} \left(\frac{dH'_{mk}}{dt} \right) dt + e^{i\omega_{m,k}t} H'_{mk}(t) \right] \quad (10.156)
 \end{aligned}$$

If the rate at which the perturbation is applied, as encoded in the dH'_{mk}/dt term, is slow enough that that term can be neglected, we have the simplified result

$$a_m(t) = \frac{H'_{mk}(t)}{(E_k - E_m)} e^{i(E_m - E_k)t/\hbar} \quad (10.157)$$

Since $a_k(t) \sim \mathcal{O}(1) \cdot e^{-iE_k t/\hbar}$, the time-dependence of the perturbed state is simply

$$\begin{aligned}
 \psi(x, t) &= e^{-iE_k t/\hbar} \psi_k^{(0)} + \sum_{m \neq k} \left[\frac{H'_{mk}(t)}{(E_m - E_k)} e^{i(E_m - E_k)t/\hbar} \right] e^{-iE_m t/\hbar} \psi_m^{(0)} \\
 &= \left(\psi_k^{(0)} + \sum_{m \neq k} \frac{H'_{mk}(t)}{(E_m - E_k)} \psi_m^{(0)} \right) e^{-iE_k t/\hbar} \quad (10.158)
 \end{aligned}$$

We stress that the time-dependence of this state is simply that of a single eigenstate, while the form of the (spatial) wavefunction is that due to a first-order perturbation theory treatment of $\hat{H}'(t)$, as in Eqn. (10.114), evaluated at time t .

This implies that in the limit of slow application of the perturbation, the individual eigenstates of the old system “morph” into the corresponding eigenstates of the new system, in a state-by-state or quantum-number by quantum-number manner; thus the ground state of the new system corresponds to the ground state of the old system, the first excited state to the first excited state, and so forth. This limit of a slowly acting perturbation is called the *adiabatic approximation* and was used (implicitly) in P5.21.

The opposite extreme, where the system undergoes a very rapid change, is called the *sudden approximation* and in this case we have a discontinuous change in the Hamiltonian of the system. For example, if we have $\hat{H}_1 \rightarrow \hat{H}_2$ at $t = 0$, the eigenfunctions of the system can be written as

$$\hat{H}_1 \psi_n = E_n \psi_n \quad t < 0 \text{ (original system)} \quad (10.159)$$

$$\hat{H}_2 \phi_n = \mathcal{E}_n \phi_n \quad t > 0 \text{ (new system)} \quad (10.160)$$

In this case, if the initial state was that of an eigenstate of the original system (ψ_n) for $t < 0$, then in the new universe of solutions we have the standard expansion theorem result that

$$\psi(x, 0) = \psi_n = \sum_k c_k \phi_k \quad \text{with expansion coefficient } c_k = \langle \phi_k | \psi_n \rangle \quad (10.161)$$

and the future time-dependence of the original eigenstate in the new system will be given by

$$\psi(x, t) = \sum_k c_k e^{-i\mathcal{E}_k t/\hbar} \phi_k \quad (10.162)$$

We have also made implicit use of this method in earlier problems (Example 6.3 and P9.6) with a more physical use discussed in P17.8.

10.6 Questions and Problems

- Q10.1.** If you are given a numerical solution of the Schrödinger equation in the form of a list of values at discrete points, that is, $\psi(x = n\epsilon)$, how would you normalize the solution? How would you find $\langle x \rangle$? How about $\langle \hat{p} \rangle$? How would calculate the momentum-space wavefunction, $\phi(p)$?
- Q10.2.** Distinguish carefully between the *precision* and the *accuracy* of a measurement. For example, for a given approximation method, you can imagine determining

the range over which the solutions change their sign at infinity more and more precisely; is this increased precision or increased accuracy? Do you think that decreasing the step size ϵ or using a better integration method results in increased accuracy or increased precision?

- Q10.3.** Assume that you have a program which numerically integrates the Schrödinger equation and that you have found two energy values, E_a and E_b , which bracket an acceptable (i.e. square-integrable) solution of the SE. Describe an efficient strategy to get arbitrarily close to the “real” energy. Hint: If someone tells you they have a number between 1 and 1000, what is the optimal strategy to find their number using the minimum number of “yes–no” questions.
- Q10.4.** If you have a program which solves the Schrödinger equation for the even solutions in a symmetric potential, what lines of code would you have to change to let it solve for the odd solutions?
- Q10.5.** Assume that you have a quantum mechanical system with quantized energies E_i and probability densities $|\psi_i(x)|^2$. Suppose that you can add a δ -function perturbation at an arbitrary location. How could you then “map out” the wavefunction using the observed shifts in energy. Assume that the δ -function strengths are small enough that first-order perturbation theory can be used. This approach was followed by Salis *et al.* (1997).
- P10.1. Numerical integration—Newton’s law.** Pick some simple technique designed to numerically integrate second order differential equations, perhaps even the simple one used in Section 10.1. Write a short program (using a computer language, programmable calculator, or even a spread sheet program) to solve Newton’s laws for a general potential or force law.

(a) Apply it to the differential equation

$$\frac{d^2x(t)}{dt^2} = -x(t) \quad \text{where } x(0) = 1 \quad \text{and} \quad \dot{x}(0) = 0 \quad (10.163)$$

Compare your results for decreasing step size with the exact solution (which is, of course, $x(t) = \cos(t)$.) Try to reproduce Fig. 10.1.

(b) Try the same thing for the equation

$$\frac{d^2x(t)}{dt^2} = +x(t) \quad \text{where } x(0) = 1 \quad \text{and} \quad \dot{x}(0) = -1 \quad (10.164)$$

and also for the initial conditions $x(0) = +1$ and $\dot{x}(0) = +1$. What are the exact solutions, how well does your program work in these two cases, and why?

- P10.2. Numerical integration—The Schrödinger equation.** Using your experience from P10.1, modify your program to solve the Schrödinger equation for a symmetric potential.

- (a) Apply it to the case of the harmonic oscillator written in dimensionless coordinates as

$$\frac{d^2\psi(y)}{dy^2} - y^2\psi(y) = -\epsilon\psi(y) \quad (10.165)$$

where ϵ are dimensionless eigenvalues. Try to reproduce the values in Example 10.2. Repeat for the odd case where the eigenvalues are $\epsilon = 3, 7, 11, \dots$

- (b) Apply your program to the case of a quartic potential, that is, $V(x) = Cx^4$. Write the Schrödinger equation in dimensionless variables and find the first two even and odd energy eigenvalues. Use your previous experience with the oscillator case to estimate the errors in your calculation.
- P10.3.** Show that the trial wavefunction in Example 10.4 yields the energy function in Eqn. (10.24). Try the problem with the nonzero piece of the wavefunction given by $N(a^2 - x^2)^n$ with $n = 1, 3, 4$ as well and compare your results.
- P10.4.** Estimate the ground state energy of the SHO by using the family of trial wavefunctions

$$\psi(x; a) = \sqrt{\frac{1}{a}} e^{-|x|/a} \quad (10.166)$$

Why is your answer so much worse than that using the cut-off polynomial expression of Example 10.4?

- P10.5.** The momentum-space wavefunction corresponding to P10.4 is

$$\phi(p) = \sqrt{\frac{2p_0}{\pi}} \left(\frac{p_0}{p^2 + p_0^2} \right) \quad (10.167)$$

where $p_0 \equiv \hbar/a$. Evaluate the energy functional in momentum space using this trial wavefunction for the SHO and show that you get the same result (for the energy and trial parameter) as in position space.

- P10.6.** Estimate the energy of the first excited state of the SHO potential by using a trial wavefunction of the form

$$\psi(x; a) = \begin{cases} 0 & \text{for } |x| > a \\ Nx(a^2 - x^2)^2 & \text{for } |x| < a \end{cases} \quad (10.168)$$

Is your answer guaranteed to be larger than the real answer?

- P10.7.** Use a Gaussian trial wavefunction to estimate the ground state energy for the quartic potential, $V(x) = gx^4$. Show that your answer is

$$E_{\min} = \left(\frac{3}{4}\right)^{4/3} \left(\frac{\hbar^4 g}{m}\right)^{1/3} \quad (10.169)$$

Compare this to the “exact” answer (determined by numerical integration) which has the prefactor 0.668.

- P10.8.** (a) Estimate the ground state energy of the symmetric infinite well using the family of trial wavefunctions

$$\psi(x) = \begin{cases} 0 & \text{for } |x| > a \\ N(a^\lambda - |x|^\lambda) & \text{for } |x| < a \end{cases} \quad (10.170)$$

where λ is the variational parameter and you must determine the normalization constant N

- (b) Estimate the energy of the first excited state by using the wavefunction in (a) multiplied by x to make an appropriate odd trial wavefunction. You will, of course, have to renormalize the wavefunction,

- P10.9.** (a) Estimate the ground state energy of the symmetric infinite well by using the wavefunction

$$\psi(x) = \begin{cases} 0 & \text{for } |x| > a \\ N(a^2 - x^2) & \text{for } |x| < a \end{cases} \quad (10.171)$$

Evaluate $E(\text{var})/E_0 - 1$ and $1 - |a_0|^2$ for this state. Note that this has no variational parameter.

- (b) Now consider the family of trial functions

$$\psi(x; b) = \begin{cases} 0 & \text{for } |x| > a \\ N'(a^2 - x^2)(1 + bx^2/L^2) & \text{for } |x| < a \end{cases} \quad (10.172)$$

which does have an additional parameter. Calculate both the variational energy $E(b) = E[\psi(x; b)]$ and $1 - |a_0|^2$. Find the values of b , which minimize each of these two quantities and show that they are slightly different. Specifically, show that

$$b_{\min} = \left(\frac{504 - 51\pi^2}{7\pi^2 - 72} \right) \approx -0.223216 \quad (10.173)$$

for the overlap maximum, while

$$b_{\min} = \frac{(-98 + 8\sqrt{133})}{26} \approx -0.22075 \quad (10.174)$$

for the energy minimum. This demonstrates that while there is a strong correlation between the wavefunction which minimizes the variational energy and the one which maximizes the overlap with the ground state wavefunction, the two criteria are ultimately independent.

- P10.10.** Using the variational method, show that any purely attractive potential in one dimension has at least one bound state. By purely attractive, we mean that $V(x) \leq 0$ for all x . We also assume that $V(x) \rightarrow 0$ as $x \rightarrow \pm\infty$. Hint: Show that we can find a (perhaps very shallow and narrow) finite square well

potential, $V_0(x)$, which satisfies $0 > V_0(x) > V(x)$ for all x and use the fact that a finite square well always has at least one bound state.

- P10.11.** Show that the matching of solutions leading to the WKB quantization condition implies that $C_L = C_R(-1)^n$.
- P10.12.** Apply the WKB quantization condition to the symmetric linear potential, $V(x) = F|x|$. The “exact” answers for the lowest lying even (+) and odd (−) states are given by

$$E_i^{(\pm)} = y_i^{(\pm)} \left(\frac{\hbar^2 F^2}{2m} \right)^{1/3} \quad (10.175)$$

where

$$\begin{aligned} y_1^{(+)} &= 1.0188 & y_1^{(-)} &= 2.3381 \\ y_2^{(+)} &= 3.2482 & y_2^{(-)} &= 4.0879 \\ y_3^{(+)} &= 4.8201 & y_3^{(-)} &= 5.5206 \\ y_4^{(+)} &= 6.1633 & y_4^{(-)} &= 6.7867 \end{aligned} \quad (10.176)$$

Does the agreement get better with increasing n as expected? Can you plot the WKB estimates and “exact” answers in such a way as to demonstrate that?

- P10.13.** Apply the WKB quantization condition to the “half-harmonic oscillator” potential, namely,

$$V(x) = \begin{cases} +\infty & \text{for } x < 0 \\ m\omega^2 x^2/2 & \text{for } x > 0 \end{cases} \quad (10.177)$$

What are the appropriate values of C_L , C_R and what are the WKB energies? What are the exact results for this problem? Hint: Recall P9.10.

- P10.14.** Apply the WKB quantization condition to estimate the bound state energies of the potential

$$V(x) = -\frac{V_0}{\cosh(x/a)^2} \quad (10.178)$$

- (a) Show that your results can be written in the form

$$E_n = -\left(\sqrt{V_0} - (n + 1/2)\sqrt{\frac{\hbar^2}{2ma^2}} \right)^2 \quad (10.179)$$

Hint: You might use the integral

$$\int_0^A \frac{\sqrt{A^2 - u^2}}{1 + u^2} du = \frac{\pi}{2} \left(\sqrt{1 + A^2} - 1 \right) \quad (10.180)$$

- (b) If $V_0 \gg \hbar^2/2ma^2$, show that your result approximates the harmonic oscillator approximation for this potential.
- (c) One might think that one could take the limit $V_0 \rightarrow \infty$ and $a \rightarrow 0$ in such a way as to reproduce an attractive δ -function potential. Discuss the WKB approximation to the energy levels in this limit; if it works, does it reproduce the result of Section 8.1.2? If it does not, why?

P10.15. Harmonic oscillator matrix elements.

- (a) Evaluate \mathbf{p}_{nm} for the harmonic oscillator using the methods in Example 10.7. Using your result, show that the commutator $[x, p] = i\hbar$ holds as a matrix equation.
- (b) Evaluate \mathbf{p}_{nm}^2 and use your result to show that Eqn. (10.79) holds by evaluating both sides as matrices.

P10.16. Infinite well matrix elements.

- (a) Evaluate the matrix elements \mathbf{p}_{nm} using the ‘standard’ infinite well energy eigenstates as a basis. How would you show that

$$\mathbf{H}_{nm} = \frac{1}{2m} \sum_k \mathbf{p}_{nk} \mathbf{p}_{km} \quad (10.181)$$

is the (diagonal) Hamiltonian matrix.

- (b) Evaluate the matrix elements \mathbf{x}_{nm} . Can you show that $[\mathbf{x}, \mathbf{p}] = i\hbar$ holds as a matrix equation?

P10.17. What is the expectation value, $\langle \hat{x} \rangle_t$, for a state vector in a matrix representation for general t , that is, how does Eqn. (10.80) generalize to $t \neq 0$? What does your expression look like for a state with only two components?

P10.18. Show that the wavefunction to second order in perturbation theory (assuming no degeneracies) is given by

$$\begin{aligned} \psi_n^{(2)} = & \sum_m' \sum_k' \frac{\mathbf{H}_{mk}' \mathbf{H}_{kn}'}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_m^{(0)})} \psi_m^{(0)} - \sum_m' \frac{\mathbf{H}_{mn}' \mathbf{H}_{mn}}{(E_n^{(0)} - E_m^{(0)})^2} \psi_m^{(0)} \\ & - \frac{1}{2} \psi_n^{(0)} \sum_m' \frac{|\mathbf{H}_{mn}'|^2}{(E_n^{(0)} - E_m^{(0)})^2} \end{aligned} \quad (10.182)$$

P10.19. We have seen in P6.4 that a constant shift in the potential energy function, that is, $V(x) \rightarrow V(x) + V_0$ can have no effect on the observable physics. Consider such a shift as a perturbation and evaluate (i) the first-, second-, and third-order changes in the energy of any state using Eqns. (10.112), (10.115), and (10.117) and (ii) the first-order shift in the wavefunction using Eqn. (10.114) and discuss your results. You can also use the results of P10.18 to check the second-order shift in the wavefunction.

P10.20. Relativistic effects in perturbation theory. The nonrelativistic series for the kinetic energy in Eqn. (1.8) is given by

$$T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots \quad (10.183)$$

Using first-order perturbation theory, value the effect of the second term in this expansion (with p replaced by the operator \hat{p}) on the n th level of a harmonic oscillator.

P10.21. Referring to Example 10.9, use Eqn. (10.117) to show that the third-order energy shift to the energy levels vanishes, as expected since the exact result is of second order.

P10.22. Referring to Example 10.10, evaluate the first-, second-, and third-order shifts in energy for the odd states due to the $\delta(x)$ perturbation and show that they vanish.

P10.23. Derive the expansion in Eqn. (10.127) for the ground state solution in Example 10.10 by writing

$$y = \frac{\pi}{2} + a\lambda + b\lambda^2 + \cdots \quad (10.184)$$

substituting this into the exact eigenvalue, $\lambda = -2y \cot(y)$ and equating powers of λ .

P10.24. A particle of mass m in a harmonic oscillator potential $V(x) = m\omega^2 x^2/2$ is subject to a small perturbing potential of the same type, namely, $V'(x) = \lambda x^2$.

(a) Show that the energy spectrum can be derived exactly with the result

$$E'_n = \left(n + \frac{1}{2}\right) \hbar \bar{\omega} \quad (10.185)$$

where $\bar{\omega} = \omega \sqrt{1 + 2\lambda/m\omega^2}$. Expand this for small λ to $\mathcal{O}(\lambda^2)$ for comparison with part (b).

(b) Evaluate the first- and second-order shifts in energy using Eqns (10.112) and (10.115) and compare your results to the exact answer in part (a). You will find the matrix elements of $\langle n|x^2|k\rangle$ in Example 10.7 useful.

P10.25. Anharmonic oscillator in perturbation theory. Evaluate the effect of a small anharmonic term of the form

$$V'(x) = -\lambda kx^3 \quad (10.186)$$

on the spectrum of the harmonic oscillator in first- and second-order perturbation theory. You may find the following matrix element useful:

$$\begin{aligned} \langle \psi_n | x^3 | \psi_k \rangle = & \left(\frac{\hbar}{2m\omega} \right)^{3/2} \left(\sqrt{(n+1)(n+2)(n+3)} \delta_{k,n+3} + 3(n+1)^{3/2} \delta_{k,n+1} \right. \\ & \left. + 3n^{3/2} \delta_{k,n-1} + \sqrt{n(n-1)(n-2)} \delta_{k,n-3} \right) \end{aligned} \quad (10.187)$$

P10.26. Degenerate states in perturbation theory

- (a) Show that the first-order shifts in energy in Eqn. (10.136) are real as they should be. Do the $a_{n,l}$ have to be real?
- (b) Using Eqn. (10.137), show that the linear combinations $\psi^{(+)}(x)$ and $\psi^{(-)}(x)$ are always orthogonal.
- (c) Discuss the energy levels and mixing of eigenstates in the case where $H'_{nm} = H'_{nl} = 0$ but $H'_{ln} = (H'_{nl})^* \neq 0$; show that the eigenfunctions are “completely mixed.”
- (d) Discuss the case where the degenerate states are not connected in the Hamiltonian to lowest order, that is for which $H'_{ln} = (H'_{nl})^* = 0$.

P10.27. Consider a particle of mass m and charge q in the ground state of the symmetric infinite well of Section 5.2.3. It is subject to a time-dependent electric field of the form

$$\hat{H}'(t) = (-q\mathcal{E}_0 x)e^{-|t|/\tau} \quad (10.188)$$

Find the probability that the particle will be excited to the first excited state if the perturbation is allowed to act over the time range $(-\infty, +\infty)$. Repeat for the probability that it is excited to the second-excited state.

P10.28. Consider a system in a general eigenstate ψ_k , which is subject to a time-dependent harmonic perturbation of the form

$$\hat{H}'(t) = 2V(x) \cos(\omega t) \quad (10.189)$$

If this perturbation is turned on at $t = 0$ and then removed at $t > 0$, find the probability that the system is in a new state, ψ_m . In the limit of long times, what states are most likely to be connected by this perturbation? Discuss what this might have to do with the emission or absorption of radiation.