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Abstract. The partial-wave Schrödinger equation with real boundary conditions is recast as an equation for the probability density. When a small additional potential is included, the changes in the bound-state energy eigenvalues are obtained, up to third order in the perturbation, purely in terms of the perturbing potential and the unperturbed probability density. Although the approach is different, our results are equivalent to those derived by Bender (Bender C M 1978 *Advanced Mathematical Methods for Scientists and Engineers* (New York: McGraw-Hill) p 330). Knowledge of neither the unperturbed energy spectrum nor the wavefunctions of excited states is required. Evaluations of the second-order energy shift are given for some soluble *S*-wave problems.

1. The probability equation

Almost all calculations in non-relativistic quantum mechanics are carried out within the framework of the Schrödinger equation. However, for bound-state problems, or more generally for any stationary problem where the wavefunction can be taken to be real, it is possible to work directly with an equation for the probability density [1]‡. To see how this comes about, consider the reduced *S*-wave time-independent Schrödinger equation for the motion of a particle of mass m and energy E in a spherically symmetric potential $U(r)$:

$$u''(r) = [U(r) - E]u(r) \tag{1.1}$$

where E and $U(r)$ are measured in units of $\hbar^2/2m$. Provided that the wavefunction $u(r)$ is real, it is related to the probability density $P(r)$ by

$$P(r) = [u(r)]^2. \tag{1.2}$$

Multiplying the Schrödinger equation by $2u^3$ and adding a term $2u^2u'^2$ to both sides, we find that $P(r)$ satisfies the second-order nonlinear equation:

$$PP'' = \tfrac{1}{2}(P')^2 + 2P^2(U - E). \tag{1.3}$$

Although we shall mainly work with equation (1.3), it is of interest that one can derive from this a third-order linear equation for P by differentiating equation (1.3) and dividing by P:

$$P''' - 4(U - E)P' - 2U'P = 0. \tag{1.4}$$

After the inclusion of a centrifugal barrier term in an effective potential $U_{\mathrm{eff}}(r)$, the derivation for higher angular momenta follows through in a similar manner. The bound-state spectrum

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‡ The probability equation was used without citation, though it must be much older than this.

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and probability densities may be obtained by resolving equation (1.4), though at the expense of imposing one extra boundary condition as compared to the Schrödinger equation.

It is the aim of this paper to develop time-independent perturbation theory for spherically symmetric perturbations within the framework of the probability equation. It is important to note that in the probability approach one cannot exploit directly the orthogonality of different wavefunctions. As a consequence, one should not obtain the standard second and higher-order perturbation theory results, which involve sums over intermediate states. However, Bender [2] has derived a form of perturbation theory where the changes in the energy and wavefunction of a state can be obtained without requiring information on any of the other states. Although our approach is completely different, our results for the energy shifts of bound states are equivalent to those of Bender, though the connection between the probability densities is less transparent because of the different normalizations employed.

In section 2 we discuss some of the properties of the probability function in the bound state case. Perturbation theory up to third order in the energy eigenvalue is developed in section 3 for spherically symmetric perturbations to spherically symmetric systems. The first-order energy shift depends only upon the unperturbed probability distribution and the perturbing potential. The surprising result is that this is also true in higher order. Direct information is *not* required on the unperturbed potential or energy levels and, of course, unperturbed eigenfunctions of other states are not employed. Second-order perturbation theory is investigated in detail in section 4, where different equivalent forms are obtained for the energy shift E_2. Values of E_2 are obtained explicitly for simple soluble S-wave examples. For the ground state, where the probability density has no nodes, it is easy to rederive the standard result that the second-order shift is negative. This allows one to establish that the variational functional, with the true probability density, corresponds to a local minimum, and this is discussed in section 5. Bender's formalism is contrasted with ours in section 6 and our conclusions are drawn in section 7.

It will be shown in a later paper that the same ideas can be used in the continuum to evaluate the change in the phase shift when the potential or the energy is perturbed.

2. Properties of the probability equation

Since the reduced wavefunction $u(r)$ vanishes at the origin, there are two boundary conditions on equation (1.4) at this point:

$$P(0) = 0$$
$$P'(0) = 0. \tag{2.1}$$

It is the imposition of the second of these which makes the bound-state spectrum correspond to that of the Schrödinger equation. It should be noted that for the nonlinear equation (1.3), which is equivalent to the Schrödinger equation, the vanishing of $P'(r)$ at the origin is guaranteed by the equation itself.

Furthermore, the localizable density corresponding to a bound state is normalized by

$$\int_0^\infty P(r)\, dr = 1. \tag{2.2}$$

These boundary conditions are sufficient to fix the solutions of the third-order equation in equation (1.4) and determine the corresponding energy eigenvalues.

In the classical limit of $\hbar \to 0$, both $E, U \to \infty$, so equation (1.4) then reduces to

$$(U - E)P' + \tfrac{1}{2}U'P = O(\hbar^2) \tag{2.3}$$

which has the correct classical solution of

$$P(r) \approx \frac{C}{\sqrt{E - U(r)}}.$$ (2.4)

It is also easy to show that any zero of $P(r)$ is of even order so, if the probability is positive at small distances, then it remains non-negative for all r. $u'(r)$ is continuous at these zeros and so one can deduce uniquely the form of $u(r)$ from the solution for $P(r)$. It is straightforward to solve the probability equation for such standard potentials as the Coulomb or square well and, if desired, deduce the wavefunctions by taking a square root [3].

3. Bound state perturbation theory

The standard formula for second-order non-degenerate time-independent perturbation theory [4] involves a sum over excited states and depends upon the orthogonality of the different wavefunctions. Neither of these features is appropriate when treating equations (1.3) or (1.4), where the wavefunction can only be constructed in a secondary step. A different approach is therefore required.

Suppose that the probability equation is soluble for some potential $U_0(r)$ with solution $P_0(r)$. Introduce a spherically symmetric perturbation $\lambda W(r)$, such that $U(r) = U_0(r) + \lambda W(r)$, and expand the probability and energies in power series in λ:

$$\begin{aligned} P(r) &\to P_0(r) + \lambda P_1(r) + \lambda^2 P_2(r) + \lambda^3 P_3(r) + \cdots \\ E &\to E_0 + \lambda E_1 + \lambda^2 E_2 + \lambda^3 E_3 + \cdots. \end{aligned}$$ (3.1)

Since the probability must remain normalized to unity for all values of λ, equation (2.2) requires that

$$\int_0^\infty P_n(r) \, \mathrm{d}r = \delta_{n0}.$$ (3.2)

Furthermore, the boundary conditions of equation (2.1) at the origin apply separately to each of the $P_n(r)$, which must also decrease exponentially at large r.

Although the nonlinearity means that one is multiplying more sums together, because there is one fewer differentiation, it is easiest to insert equations (3.1) into the second-order equation of equation (1.3) and compare different powers of λ. The order λ^0 terms give the unperturbed equation

$$P_0 P_0'' = \tfrac{1}{2}(P_0')^2 + 2P_0^2(U_0 - E_0).$$ (3.3)

3.1. First-order corrections

The order λ^1 terms from equation (1.3) yield

$$P_0'' P_1 + P_1'' P_0 - P_0' P_1' - 4(U_0 - E_0) P_1 P_0 = 2(W - E_1) P_0^2.$$ (3.4)

Substituting for $(U_0 - E_0)$, from equation (3.3), gives

$$P_0'' P_1 + P_1'' P_0 - P_0' P_1' - \frac{2P_1}{P_0} \left[P_0'' P_0 - \frac{1}{2}(P_0')^2 \right] = 2(W - E_1) P_0^2.$$ (3.5)

After dividing both sides by P_0, one recognizes the left-hand side to be an exact derivative, and therefore

$$\frac{\mathrm{d}}{\mathrm{d}r} \left[P_1' - \frac{P_1 P_0'}{P_0} \right] = 2(W - E_1) P_0.$$ (3.6)

To find the first-order correction to the energy, integrate both sides between zero and infinity:

$$\left[P_1' - \frac{P_1 P_0'}{P_0} \right]_0^\infty = 2 \int_0^\infty (W - E_1) P_0 \, dr. \tag{3.7}$$

Near the origin, $P_0'/P_0 \approx 1/r$ and P_1 vanishes at least as fast as r^2, so the left-hand side vanishes at $r = 0$. Similarly, as $r \to \infty$, $P_1 \to 0$, and P_0'/P_0 is bounded, which means that the whole of the left-hand side is zero. As a consequence we recover the standard first-order energy shift

$$E_1 = \int_0^\infty W P_0 \, dr. \tag{3.8}$$

The first-order change in the probability may be found from an indefinite integration of equation (3.6)

$$\left[P_1' - \frac{P_1 P_0'}{P_0} \right]_0^r = 2 \int_0^r P_0 (W - E_1) \, dr' \tag{3.9}$$

which can be rewritten, as before, as an exact derivative,

$$\frac{d}{dr} [P_1 P_0^{-1}] = 2 P_0^{-1} \int_0^r P_0 (W - E_1) \, dr'. \tag{3.10}$$

Integrating with respect to r,

$$P_1 = 2 P_0 \int_0^r \frac{1}{P_0} \int_0^{r'} P_0 (W - E_1) \, dr'' \, dr' + C P_0. \tag{3.11}$$

To find the constant of integration C, we insist that the integral of P_1 over all r vanishes, as required by equation (3.2). The first-order perturbation to the probability density function therefore takes the form

$$P_1 = 2 P_0 \int_0^r \frac{1}{P_0} \int_0^{r'} P_0 (W - E_1) \, dr'' \, dr'$$
$$- 2 P_0 \int_0^\infty P_0 \int_0^r \frac{1}{P_0} \int_0^{r'} P_0 (W - E_1) \, dr'' \, dr' \, dr. \tag{3.12}$$

This is very different in structure to the formula of standard perturbation theory where the first correction to the wavefunction involves an infinite sum over all the excited states. It is clear from equation (3.12) that the correction actually depends only upon the form of the perturbation and the unperturbed probability density.

3.2. Second-order corrections

In evaluating the first-order corrections to both the energy and probability density, it proved useful to rearrange the equations such that certain combinations of terms became exact differentials. This is also true in second and higher orders. The coefficient of the λ^2 terms, after some manipulation, can be put into the following form:

$$P_1 (E_1 - W) + 2 E_2 P_0 = \frac{d}{dr} \left[\frac{P_2 P_0'}{P_0} - P_2' - \frac{P_1^2 P_0'}{2 P_0^2} + \frac{P_1 P_1'}{2 P_0} \right]. \tag{3.13}$$

Integrating this from zero to infinity, the integrated term on the right-hand side drops out, and we are left with

$$2 E_2 \int_0^\infty P_0 \, dr + E_1 \int_0^\infty P_1 \, dr - \int_0^\infty P_1 W \, dr = 0. \tag{3.14}$$

Since the integral of P_1 vanishes, the second-order change in the energy becomes

$$E_2 = \tfrac{1}{2} \int_0^\infty W P_1 \, \mathrm{d}r. \tag{3.15}$$

Inserting into this the expression for P_1, we obtain the final result

$$E_2 = \int_0^\infty (W(r) - E_1) P_0(r) \, \mathrm{d}r \int_0^r \frac{1}{P_0(r')} \, \mathrm{d}r' \int_0^{r'} (W(r'') - E_1) P_0(r'') \, \mathrm{d}r'' \tag{3.16}$$

where the integration variables are explicitly indicated. This is probably the most important result of our work.

The second-order corrections to the probability density are found by evaluating the indefinite integral of equation (3.13). With judicious rearrangement, this leads to

$$\frac{1}{P_0} \int_0^r (E_1 P_1 - W P_1 + 2 E_2 P_0) \, \mathrm{d}r' = \frac{\mathrm{d}}{\mathrm{d}r} \left[\frac{P_1^2}{4 P_0^2} - \frac{P_2}{P_0} \right]. \tag{3.17}$$

An expression for P_2 is found by integrating with respect to r:

$$P_2 = P_0 \int_0^r \frac{1}{P_0} \, \mathrm{d}r' \int_0^{r'} (W P_1 - E_1 P_1 - 2 E_2 P_0) \, \mathrm{d}r'' + \frac{1}{4} \frac{P_1^2}{P_0} + C P_0 \tag{3.18}$$

where the integration constant C is found by demanding that the integral of P_2 over all r vanishes.

3.3. Third- and higher-order corrections

The higher-order terms become progressively more involved and it becomes harder to find linear combinations which are exact differentials. We shall only show the result for the third-order energy change:

$$E_3 = \tfrac{1}{3} \int_0^\infty W P_2 \, \mathrm{d}r. \tag{3.19}$$

Inserting the expression for P_2 from equation (3.18), the third-order shift becomes

$$\begin{aligned}
E_3 = \frac{1}{3} \int_0^\infty (W(r) - E_1) P_0(r) \, \mathrm{d}r \int_0^r \frac{1}{P_0(r')} \, \mathrm{d}r' \\
\times \int_0^{r'} (W(r'') P_1(r'') - E_1 P_1(r'') - 2 E_2 P_0(r'')) \, \mathrm{d}r'' \\
+ \frac{1}{12} \int_0^\infty (W(r) - E_1) \frac{P_1(r)^2}{P_0(r)} \, \mathrm{d}r.
\end{aligned} \tag{3.20}$$

Since the formulae do not involve the unperturbed potential, which might contain a centrifugal barrier term, they are equally valid for all angular momenta ℓ, provided that the unperturbed probability density is appropriate. For a well behaved potential this should vary as $r^{2\ell+2}$ at the origin.

The results for the changes in energy and probability distributions have been tested by changing the spring constant in the harmonic oscillator or the electronic charge in the Coulomb problem. Excited states in these problems are handled just as easily as the ground state [3].

4. Second-order perturbation theory

4.1. Formalism

In practical terms, it is the second-order energy shift of equation (3.16) which is potentially the most valuable result, and this may be recast in several alternative forms. Thus

$$E_2 = \int_0^\infty (W(r) - E_1)\,\mathrm{d}r \int_0^r (W(r') - E_1)K(r', r)\,\mathrm{d}r' \tag{4.1}$$

where the kernel,

$$K(r', r) = P_0(r)P_0(r') \int_{r'}^r \frac{1}{P_0(r'')}\,\mathrm{d}r'' \tag{4.2}$$

depends only upon the unperturbed probability density. It should be noted that the kernel is singular both at $r' = 0$ and as $r \to \infty$, but that these divergences are more than compensated by the zeros in $P_0(r')$ and $P_0(r)$.

A simpler-looking formula may be obtained by integrating either equations (3.16) or (4.1) by parts. Defining

$$Q(r) = \int_0^r (W(r') - E_1)P_0(r')\,\mathrm{d}r' \tag{4.3}$$

then, from equation (3.16),

$$E_2 = Q(r) \int_0^r \frac{1}{P_0(r')} Q(r')\,\mathrm{d}r' \Big|_{r=0}^{r=\infty} - \int_0^\infty Q(r)\frac{1}{P_0(r)} Q(r)\,\mathrm{d}r. \tag{4.4}$$

The integrated term vanishes and we are left with

$$E_2 = -\int_0^\infty [Q(r)]^2 \frac{1}{P_0(r)}\,\mathrm{d}r. \tag{4.5}$$

Provided that $P_0(r)$ does not vanish, other than at zero or infinity, then the integrand is positive and finite so E_2 is negative. This is still true for non-zero angular momentum, where $P_0(r)$ goes to zero faster in the vicinity of $r = 0$. The negative nature of E_2 is a well known result for the ground state of a system [4], the ground state here being defined as the one where the wavefunction has no nodes.

For excited states, the zeros of $P_0(r)$ are of even order, normally second, and the integrands of equations (4.1) or (4.5) are apparently singular at such points, though Bender had already pointed out [2] that the energy shifts remain finite. To prove this, we choose to study an associated problem, where all the zeros of $P_0(r)$ are displaced into the lower half of the r-plane by an amount $-i\epsilon$. In this case the integrations can be displaced into the upper half r-plane and, at the end of the evaluation, the limit $\epsilon \to 0$ is taken. In the vicinity of a node at $r = a$, the singular part of the kernel in equation (4.2) is

$$K_{\mathrm{sing}}(r', r) = C(r-a+i\epsilon)^2(r'-a+i\epsilon)^2 \int_{r'}^r \frac{1}{(r''-a+i\epsilon)^2}\,\mathrm{d}r'' = C(r-a)(r'-a)(r-r') \tag{4.6}$$

where the answer is well behaved in the limit $\epsilon \to 0$. It is, however, important to note that for $r > a > r'$, $K_{\mathrm{sing}}(r', r)$ becomes negative in such a case and E_2 no longer has to be negative.

4.2. Results

As a concrete example of second-order perturbation theory, consider a particle moving freely in a box of radius 1. In such a case, the upper infinite integration limit is replaced by the box radius. The unperturbed probability for $r \leqslant 1$ is

$$P_0(r) = 2\sin^2(kr) \tag{4.7}$$

where $k = n\pi$, $n = 1, 2, 3, \ldots$. The corresponding energy levels, in units of $\hbar^2/2m$, are $E = n^2\pi^2$. Using the $-i\epsilon$ prescription, the kernel becomes

$$K(r', r) = \frac{1}{n\pi}[\sin(2n\pi r')\sin^2(n\pi r) - \sin(2n\pi r)\sin^2(n\pi r')]. \tag{4.8}$$

After rearranging equation (4.1), the two terms in (4.8) give the same result and

$$E_2(n) = \frac{2}{n\pi}\int_0^1 (W(r) - E_1)\sin^2(n\pi r)\,\mathrm{d}r \int_0^r (W(r') - E_1)\sin(2n\pi r')\,\mathrm{d}r'. \tag{4.9}$$

The perturbation $W(r) = r$ leads to $E_1(n) = \frac{1}{2}$ and, from equation (4.9),

$$E_2(n) = \frac{1}{48n^2\pi^2} - \frac{5}{16n^4\pi^4}. \tag{4.10}$$

Only for $n = 1$ is E_2 negative; the sum of E_2 over all values of n vanishes as required on general grounds.

This particular perturbation couples all the different states of the infinite square well but the same result could be derived using standard second-order perturbation theory by summing over an infinite number of intermediate states:

$$E_2(n) = \frac{64}{\pi^6} \sum_{m+n \,\mathrm{odd}} \frac{m^2 n^2}{(n^2 - m^2)^5}. \tag{4.11}$$

The probability density can be calculated to first order in λ from equation (3.12) but, for this perturbation, the mean value of position can be obtained directly from the energy shifts. Using equations (3.8) and (3.15), we see that to order λ

$$\langle x \rangle = \frac{E_1}{\lambda} + \frac{2E_2}{\lambda^2} = \frac{1}{2} + \frac{\lambda}{24n^2\pi^2} - \frac{5\lambda}{8n^4\pi^4} = \frac{1}{2} + \frac{\lambda}{24E_0} - \frac{5\lambda}{8E_0^2}. \tag{4.12}$$

For $\lambda > 0$, the expectation value falls in the left-hand side of the box only for the ground state. The potential is less repulsive here than the average, giving rise to an attractive second-order energy shift. On the other hand, in the classical limit the particle spends more time in regions where the potential is more repulsive. This suggests that $\langle x \rangle$ should be bigger than $\frac{1}{2}$ at large E_0 and that the second-order shift should be repulsive. This is indeed the case and the classical average position corresponding to purely radial motion, evaluated using equation (2.4), is $\frac{1}{2} + \lambda/24E_0$. This agrees with the classical limit of equation (4.12).

As a more physical example, consider the evaluation of the energy shift of an s-wave pionic atom. Here one has to study the influence of a short-range potential on the energy levels of a π^- in a Coulomb orbit around a proton or heavier nucleus. This was investigated in a perturbation approach many years ago [5]. The unperturbed ground-state distribution is $P_0(r) = 4(r^2/a^3)\exp(-2r/a)$, where a is the pion Bohr radius. Taking as a perturbation $\lambda W = \lambda \exp(-2\beta r)$, the first-order shift is

$$E_1 = \left(\frac{1}{1 + \beta a}\right)^3 \tag{4.13}$$

and the auxiliary function

$$Q(r) = \left(\frac{1}{1 + \beta a} \right)^3 e^{-2(\beta + 1/a)r} [-2\beta^2 r^2 - 2\beta r(1 + 2r/a) + (e^{2\beta r} - 1)(1 + 2r/a + 2r^2/a^2)].$$
(4.14)

The second-order shift can then be evaluated analytically from equation (4.5) but we only quote the answer in the large-atom limit where

$$Q(r) \approx \frac{1}{\beta^3 a^3} [1 - e^{-2\beta r}(1 + 2\beta r + 2\beta^2 r^2)]$$
(4.15)

and $E_2 \approx -5/32\beta^5 a^3$. In this limit the perturbations to the energy are proportional to the successive Born approximations to the *free* scattering amplitude or, more correctly, free K-matrix element since we are using real boundary conditions. However, our approach allows higher-order Coulomb corrections to be evaluated and these might be significant for heavy targets.

In the estimation of the second-order shift in standard perturbation theory, the contribution from the bound intermediate S states is negligible in the large-a limit; all that then survive are the virtual transitions to the Coulomb continuum.

For explicitly soluble potentials, such as the square well, it is always possible to use the standard second-order approach. This is no longer straightforward if all that is known is a phenomenological unperturbed wavefunction. Consider for example the case where

$$P_0(r) = 30r^2(1 - r)^2 \Theta(1 - r).$$
(4.16)

With the same perturbation $W(r) = r$, one obtains $E_2 = \frac{1}{2}$ and $Q(r) = 5r^3(r - 1)^3$, which lead to

$$E_2 = -\frac{1}{756}.$$
(4.17)

This is about 20% larger than the corresponding square-well result, caused by the unperturbed probability being larger at the edges of the well.

5. Variational approach

The derivation of the variational method for the ground state eigenvalue starts from the ansatz that all other energies in the spectrum lie above it. We here establish a more modest local variational principle for the probability equation.

Consider the energy functional

$$F[P_\lambda] = \int_0^\infty \left[\frac{P_\lambda'(r)^2}{4P_\lambda(r)} + U_0(r)P_\lambda(r) \right] dr.$$
(5.1)

This corresponds to the standard form [4], provided that the trial probability density $P_\lambda(r)$ satisfies the boundary conditions discussed in section 2. If $P_\lambda(r)$ is close to the exact solution, then it satisfies the differential equation (1.4) with the potential $U(r) = U_0(r) + \lambda W(r)$, so that

$$E_\lambda = \int_0^\infty \left[\frac{P_\lambda'(r)^2}{4P_\lambda(r)} + (U_0(r) + \lambda W(r))P_\lambda(r) \right] dr.$$
(5.2)

Subtracting one equation from the other,

$$F[P_\lambda] - E_\lambda = \lambda \int_0^\infty W(r)P_\lambda(r) \, dr.$$
(5.3)

We now expand P_λ and E_λ in power series, as in equation (3.1). Using the expressions of equations (3.8), (3.15) derived for the first- and second-order energy shifts, we find that

$$F[P_\lambda] = E_0 - \lambda^2 E_2 + O(\lambda^3). \tag{5.4}$$

It is therefore seen that $F[P_\lambda]$ is stationary at $\lambda = 0$. Furthermore, in the case of the ground state where the density has no nodes, we have shown that the second-order shift E_2 is negative. For such a case the stationary point is therefore a *local* minimum. A different technique might be required to show that it is the expected *global* minimum.

6. Comparison with Bender's formalism

Clearly, anything that can be achieved from the probability equation must also be obtainable from the Schrödinger equation. Expanding the wavefunction in powers of the potential strength λ,

$$u(r) \approx u_0(r) + \lambda u_1(r) + \lambda^2 u_2(r) + \lambda^3 u_3(r) + \cdots \tag{6.1}$$

Bender [2] shows that

$$\left[\frac{d^2}{dr^2} + U(r) - E_0\right] u_n(r) = -W(r)u_{n-1}(r) + \sum_{j=1}^{n} E_j u_{n-j}(r). \tag{6.2}$$

This can be simplified by introducing the auxiliary function $F_n(r)$ such that

$$u_n(r) = u_0(r) F_n(r). \tag{6.3}$$

The first-order correction can then be written as

$$\frac{d}{dr}\left[u_0^2(r)\frac{dF_1(r)}{dr}\right] = (W - E_1)u_0^2(r) \tag{6.4}$$

which corresponds to our equation (3.6) when we identify $F_1(r) = \frac{1}{2}P_1(r)/P_0(r) + C$. The second-order energy shift in this approach is therefore equivalent to that of equation (3.16). However, it is important to note that Bender does not impose the normalization condition on the wave functions, so that the integration constant C is not fixed by this physics, but rather by requiring $F_n(a) = 0$ at some arbitrary radius a. Fortunately, the value of E_2 turns out to be independent of the choice of C, and this remains true in higher order. The very different appearance of our form for E_3 in equation (3.20) from that of Bender is due to our imposing probability normalization order by order.

It should be noted that for certain simple potentials, such as $|x^p|$, it is possible to evaluate systematically the energy shifts to high order using the Bender technique [6]. On the other hand, a numerical evaluation of E_2 would require one to work out a triple integral in Bender's formalism, which is similar to our equations (3.16) or (4.1). This is to be compared to the two-dimensional mesh needed to calculate the more compact form of equation (4.5). A further advantage of our approach is that the $P_n(r)$ are directly the probability changes, whereas Bender's $F_n(r)$ remain to be normalized.

7. Conclusions

In the case of real stationary solutions to the time-independent Schrödinger equation, it is possible to derive a second-order nonlinear or a third-order linear equation for the corresponding probability density. For a single particle, moving under the influence of a central potential, this reality condition may be imposed for each partial wave, even in the continuum.

The probability equations do not involve transitions to other states and so normal perturbation theory, which requires an expansion in terms of a complete set of eigenfunctions, is clearly inapplicable. Nevertheless, we have developed a perturbative treatment of the equation to third order in the energy shift which, we subsequently found, coincides with the expressions derived in a different way by Bender from the Schrödinger equation. The expressions for the changes in the probability density are, however, rather different since Bender chose not to require the normalization condition, which we imposed separately in each order of perturbation. It is of course always possible to recover the correct forms of the perturbed wavefunctions by renormalizing Bender's full solution and, when this is done, our two methods become equivalent. However, our explicit formula for the second-order energy shift might be simpler to evaluate numerically.

Since we are working within a partial wave basis, we require the perturbation to have spherical symmetry so that equations do not couple different values of the angular momentum. If that happened in the scattering domain, it would not allow us to eliminate the complex phases so as to leave the real wavefunctions which are necessary for the probability approach. It is still possible to evaluate low-order perturbations by solving inhomogeneous differential equations [7].

In the computer age, perturbation theory is less important than it was and one has to give good arguments for going beyond second order unless, as in [6], one can evaluate the series to high order. We have given alternative forms of the second-order energy shift and applied equations (4.1) and (4.6) to simple physical problems. For the ground state one immediately deduces the standard result that E_2 should be negative. Care has to be taken in the vicinity of the nodes when treating excited states, but this may be handled by displacement into the complex plane.

In this paper we have only investigated the changes in the bound state spectrum when the potential is modified. Similar techniques, but with different boundary conditions, may be used to investigate the influence of an extra potential $\lambda W(r)$ on the scattering phase shifts. The energy variation of the scattering wavefunction and phase shift can also be studied by perturbing in the energy E. We wish to stress that all these effects depend purely upon the perturbation and the unperturbed density; explicit knowledge of the unperturbed potential is not necessary [3]. This exposition will be deferred to a later publication.

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