

Remembering that for $\mathcal{H}_p = 0$ we know the energy ($= E_n^{(0)}$) and the wave function ($= \psi_n^{(0)}(\mathbf{r})$) we can rewrite equation (6) as

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda_p/\varepsilon_1 + \lambda_p^2/\varepsilon_2 + \dots, \\ \psi_n(\mathbf{r}) &= \psi_n^{(0)}(\mathbf{r}) + \lambda_p/\chi_1(\mathbf{r}) + \lambda_p^2/\chi_2(\mathbf{r}) + \dots \end{aligned} \quad (7)$$

The second term on the right-hand side of equation (7) is called the first-order correction to the energy or wave function, the third term is called the second-order correction, etc. In principle, perturbation theory enables us to evaluate all the terms in these infinite series and hence to find E_n and $\psi_n(\mathbf{r})$ exactly. However, the complexity of evaluating the terms increases with their order and, in practice, the calculation is limited to the first few terms. Nevertheless, provided λ_p is small, only the first few terms in the series will be significant, and the results for E_n and $\psi_n(\mathbf{r})$ will be accurate.

2.3 The first-order correction to the energy

If \mathcal{H}_p is very small then $\psi_n(\mathbf{r})$ will be almost identical to $\psi_n^{(0)}(\mathbf{r})$. The first-order correction to the energy is found by assuming that any change in the wave function is negligible. The change in the energy will then be

$$\lambda_p \varepsilon_1 = E_n^{(1)} = E_n \approx E_n^{(0)} = \frac{\int_{\text{all space}} \psi_n^{(0)*}(\mathbf{r}) \mathcal{H}_p \psi_n^{(0)}(\mathbf{r}) d\mathbf{r}}{\int_{\text{all space}} \psi_n^{(0)*}(\mathbf{r}) \psi_n^{(0)}(\mathbf{r}) d\mathbf{r}} \quad (8)$$

which is the usual expression for the average value of an observable. (If you are unfamiliar with this type of expression then consider the following argument. Suppose \mathcal{H}_p is an extra contribution to the potential, say $V_p(\mathbf{r})$. If the wave function is $\psi_n^{(0)}(\mathbf{r})$ then the probability density at \mathbf{r} is $\psi_n^{(0)*}(\mathbf{r})\psi_n^{(0)}(\mathbf{r})$. The expression given above for the first-order correction to the energy is simply the probability density at \mathbf{r} , multiplied by the change in potential energy at \mathbf{r} , integrated, i.e. averaged, over all space, and divided by the total probability of the particle being anywhere in space.) It is convenient to choose $\psi_n^{(0)}(\mathbf{r})$ such that

$$\int_{\text{all space}} \psi_n^{(0)*}(\mathbf{r}) \psi_n^{(0)}(\mathbf{r}) d\mathbf{r} = 1 \quad (9)$$

and it will be assumed in the following that this is always the case. (The wave functions are then said to be normalized.) Then, to first order, equation (8) becomes

$$E_n \approx E_n^{(0)} + \int_{\text{all space}} \psi_n^{(0)*}(\mathbf{r}) \mathcal{H}_p \psi_n^{(0)}(\mathbf{r}) d\mathbf{r} \quad (10)$$

and, since $E_n^{(0)}$, $\psi_n^{(0)}(\mathbf{r})$, and \mathcal{H}_p' are known, the energy can be found to first order, provided that the integral can be evaluated.

2.4 The first-order correction to the wave function and the second-order correction to the energy

As explained above, the first-order correction to the energy is derived from the uncorrected ('zeroth-order') wave function. The second-order correction to the energy is derived from the first-order corrected wave function, and so on. The first-order correction to the wave function consists of an appropriate linear combination of all the *other* unperturbed wave functions, i.e. to first order:

$$\psi_n(\mathbf{r}) = \psi_n^{(0)}(\mathbf{r}) + \sum_{\substack{m \neq n \\ m=1}}^{\infty} a_m \psi_m^{(0)}(\mathbf{r}). \quad (11)$$

It is possible to show that the coefficients a_m , which determine the amount of wave function $\psi_m^{(0)}(\mathbf{r})$ to be added, are given by

$$a_m = \frac{\int_{\text{all space}} \psi_m^{(0)*}(\mathbf{r}) \mathcal{H}_p \psi_n^{(0)}(\mathbf{r}) d\mathbf{r}}{(E_n^{(0)} - E_m^{(0)})}, \quad (12)$$

and the resultant second-order correction to the energy is given by

$$\lambda_p^2 \varepsilon_2 = E_n^{(2)} = E_n - E_n^{(0)} - E_n^{(1)} = \sum_{\substack{m \neq n \\ m=1}}^{\infty} \frac{\left| \int_{\text{all space}} \psi_m^{(0)*}(\mathbf{r}) \mathcal{H}_p \psi_n^{(0)}(\mathbf{r}) d\mathbf{r} \right|^2}{(E_n^{(0)} - E_m^{(0)})}. \quad (13)$$

The full expression for the perturbed energy, correct to second order is therefore

$$E_n = E_n^{(0)} + \int_{\text{all space}} \psi_n^{(0)*}(\mathbf{r}) \mathcal{H}_p \psi_n^{(0)}(\mathbf{r}) d\mathbf{r} + \sum_{\substack{m \neq n \\ m=1}}^{\infty} \frac{\left| \int_{\text{all space}} \psi_m^{(0)*}(\mathbf{r}) \mathcal{H}_p \psi_n^{(0)}(\mathbf{r}) d\mathbf{r} \right|^2}{(E_n^{(0)} - E_m^{(0)})}. \quad (14)$$

Note that the first-order term for the energy only involves a single integral; its evaluation is therefore much simpler than that of the second-order term which is an infinite series of integrals involving all the unperturbed states.

3. A PARTICLE IN A ONE-DIMENSIONAL INFINITE POTENTIAL WELL

3.1 Unperturbed potential well

In one dimension the Schrödinger equation for a particle of mass M_p in a region $0 < x < L_3$, say, where $V(x) = 0$, is

$$\frac{-\hbar^2}{2M_p} \frac{d^2}{dx^2} \psi_n^{(0)}(x) = E_n^{(0)} \psi_n^{(0)}(x). \quad (15)$$

Because \hbar is very small, quantum effects are usually only important in systems with atomic dimensions and masses. (A mass of 1 kg in an infinite potential well of width 1 m would have a ground state energy of 5.5×10^{-63} J, which corresponds to a r.m.s. velocity of 3.3×10^{-34} m s $^{-1}$; an electron of mass 9.11×10^{-31} kg in an infinite potential well of width 0.1 nm—typical of atomic dimensions—would have a ground state energy of 1.19×10^{-17} J = 75 eV, which corresponds to a r.m.s. velocity of 5.1×10^6 m s $^{-1}$.) Rather than enter numbers such as 9.11×10^{-31} (the mass of an electron in kg) into the computer for M_p we will use the atomic system of units in the following.

If lengths are expressed as multiples of the Bohr radius (1 Bohr radius = $4\pi\epsilon_0\hbar^2/m_e e^2 = 5.29 \times 10^{-11}$ m) and energies and potentials are expressed as multiples of the Rydberg (1 Rydberg = -the ground state energy of the electron in the hydrogen atom = $m_e e^4/32\pi\epsilon_0^2\hbar^2 = 2.19 \times 10^{-18}$ J = 13.6 eV) then equation (1), in dimensionless form, is

$$\left[-\frac{1}{M_p'} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad (16)$$

where $M_p' = M_p/m_e$. For the one-dimensional infinite potential well (see Figure 2) equation (16) becomes (dropping the prime on M_p')

$$-\frac{1}{M_p} \frac{d^2}{dx^2} \psi_n^{(0)}(x) = E_n^{(0)} \psi_n^{(0)}(x). \quad (17)$$

The general solution to (17) is

$$\psi_n^{(0)}(x) = A e^{ikx} + B e^{-ikx}, \quad (18)$$

where $k^2 = E_n^{(0)} M_p$.

We must impose the boundary conditions that $\psi_n^{(0)}(x) \rightarrow 0$, both for $x \rightarrow 0$ and $x \rightarrow L_3$, because the particle would require an infinite energy to penetrate the region of infinite potential. Thus $B = -A$ and $\psi_n^{(0)}(x) =$

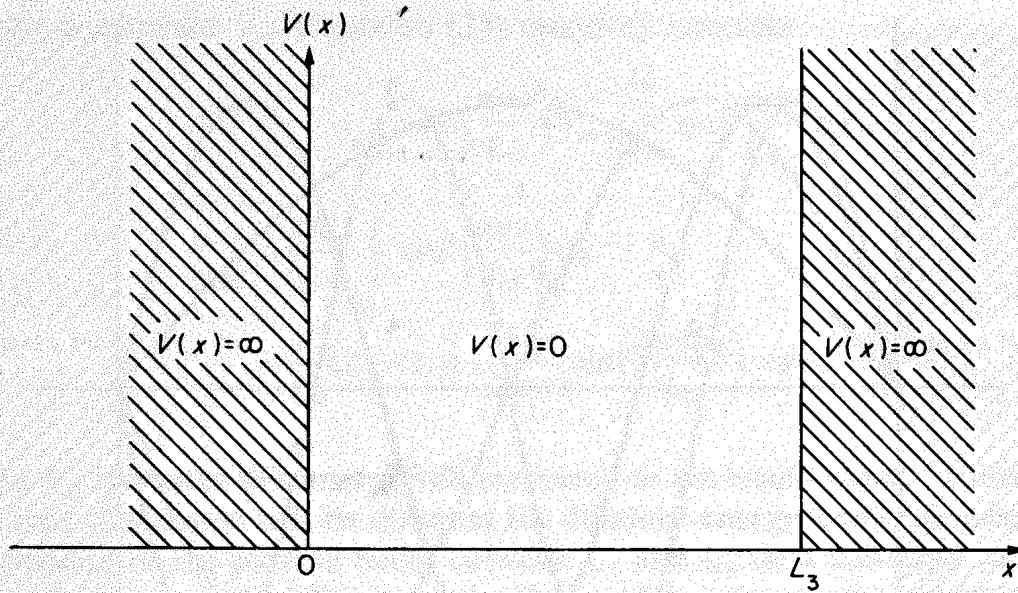


Figure 2. The unperturbed infinite potential well

$C \sin kx$ with $C = 2iA$. But $\psi_n^{(0)}(L_3) = C \sin(kL_3) = 0$, hence

$$\begin{aligned} k &= \frac{n\pi}{L_3}, \quad n = 1, 2, 3, \dots, \\ E_n^{(0)} &= \frac{k^2}{M_p} = \frac{n^2 \pi^2}{M_p L_3^2}, \\ \psi_n^{(0)}(x) &= C \sin\left(\frac{n\pi x}{L_3}\right). \end{aligned} \quad (19)$$

These are the results for the unperturbed energies and wave functions (see Figure 3). The expressions given earlier for first- and second-order perturbation theory required normalized wave functions so C must be adjusted to ensure this. This is done quite simply by requiring that

$$\int_0^{L_3} C^* \sin\left(\frac{n\pi x}{L_3}\right) C \sin\left(\frac{n\pi x}{L_3}\right) dx = C^2 \left[\frac{x}{2} - \frac{L_3}{4n\pi} \sin \frac{2n\pi x}{L_3} \right]_0^{L_3} = C^2 \frac{L_3}{2} = 1, \quad (20)$$

i.e.

$$\psi_n^{(0)}(x) = \sqrt{\frac{2}{L_3}} \sin\left(\frac{n\pi x}{L_3}\right) \quad n = 1, 2, 3, \dots \quad (21)$$

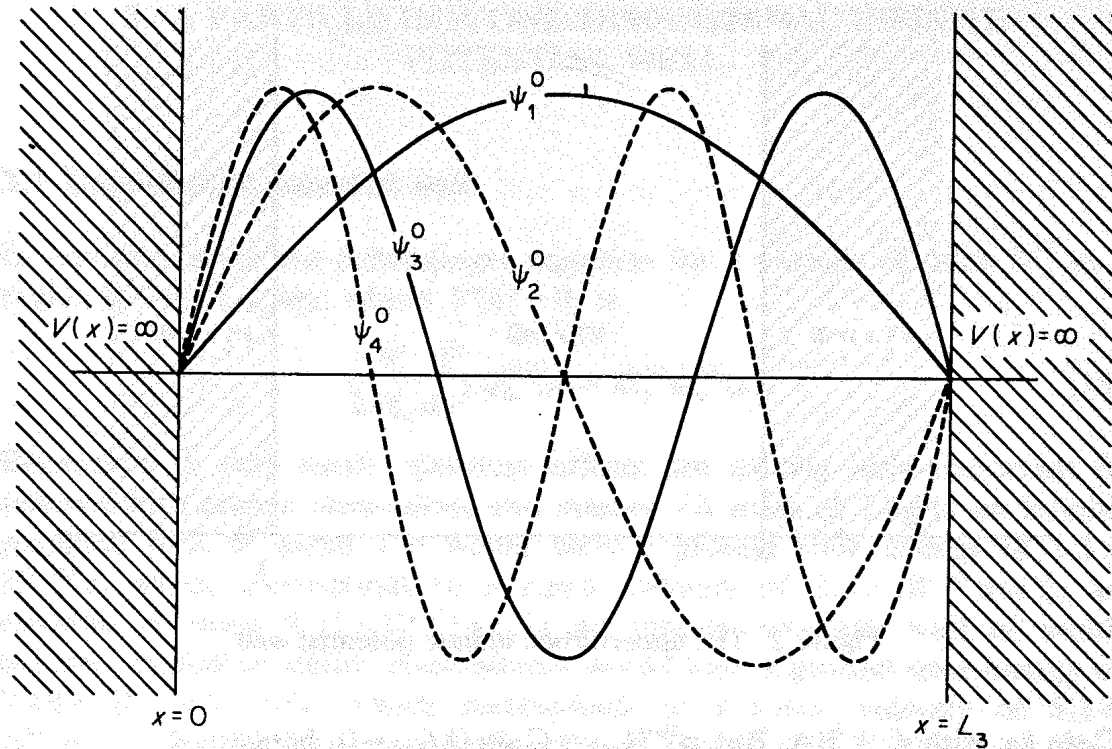


Figure 3. The unperturbed wave functions.

The case $V_p=0$ should be tried, when running the computer program, detailed in section 4, to check that the computed energies agree with the standard expression

$$E_n^{(0)} = \frac{n^2 \pi^2}{M_p L_3^2}, \quad n = 1, 2, 3, \dots \quad (22)$$

for your chosen values of M_p and L_3 .

3.2 The first-order correction to the energy for a particle in an infinite one-dimensional potential well with a perturbation V_p

The general expression for the first-order correction to the n th energy level is

$$E_n^{(1)} = \int_{\text{all space}} \psi_n^{(0)*}(\mathbf{r}) \mathcal{H}_p \psi_n^{(0)}(\mathbf{r}) d\mathbf{r}. \quad (23)$$

The $\psi_n^{(0)}(\mathbf{r})$ are the normalized unperturbed wave functions found above. The integration is carried out over all space where \mathcal{H}_p is finite—in this case between L_1 and L_2 . \mathcal{H}_p itself is the extra term in the Hamiltonian—here

simply a constant V_p . Equation (23) therefore becomes

$$\begin{aligned}
 E_n^{(1)} &= \int_{L_1}^{L_2} \sqrt{\frac{2}{L_3}} \sin\left(\frac{n\pi x}{L_3}\right) V_p \sqrt{\frac{2}{L_3}} \sin\left(\frac{n\pi x}{L_3}\right) dx \\
 &= \frac{2V_p}{L_3} \int_{L_1}^{L_2} \sin^2\left(\frac{n\pi x}{L_3}\right) dx \\
 &= \frac{V_p}{L_3}(L_2 - L_1) - \frac{V_p}{2n\pi} \left\{ \sin\left(\frac{2\pi n L_2}{L_3}\right) - \sin\left(\frac{2\pi n L_1}{L_3}\right) \right\}. \quad (24)
 \end{aligned}$$

As V_p increases this energy will increase—as we would expect. However, the rate of increase will be different for different energy levels, because the probability of the particle being between L_1 and L_2 (and therefore ‘seeing’ V_p) will change with n . For example, if L_1 and L_2 are near the centre of the well the perturbation will affect the $n = 1$ level (in which the particle has a high probability of being near the centre) much more than the $n = 2$ level (where the particle has a low probability of being near the centre).

3.3 The second-order correction to the energy for a particle in an infinite one-dimensional potential well with a perturbation V_p

The general expression for the second-order correction to the energy of the n th level is

$$E_n^{(2)} = \sum_{\substack{m \neq n \\ m=1}}^{\infty} \frac{\left| \int_{\text{all space}} \psi_m^{(0)*}(\mathbf{r}) \mathcal{H}_p \psi_n^{(0)}(\mathbf{r}) d\mathbf{r} \right|^2}{(E_n^{(0)} - E_m^{(0)})} = \sum_{\substack{m \neq n \\ m=1}}^{\infty} E_{mn}^{(2)} \quad (25)$$

In the present case

$$\begin{aligned}
 I_{mn} &= \int_{\text{all space}} \psi_m^{(0)*}(\mathbf{r}) \mathcal{H}_p \psi_n^{(0)}(\mathbf{r}) d\mathbf{r} \\
 &= \int_{L_1}^{L_2} \sqrt{\frac{2}{L_3}} \sin\left(\frac{m\pi x}{L_3}\right) V_p \sqrt{\frac{2}{L_3}} \sin\left(\frac{n\pi x}{L_3}\right) dx \\
 &= \frac{2V_p}{L_3} \int_{L_1}^{L_2} \sin\left(\frac{m\pi x}{L_3}\right) \sin\left(\frac{n\pi x}{L_3}\right) dx \\
 &= \frac{V_p}{L_3} \left\{ \frac{\sin(\alpha L_2) - \sin(\alpha L_1)}{\alpha} - \frac{\sin(\beta L_2) - \sin(\beta L_1)}{\beta} \right\}, \quad (26)
 \end{aligned}$$

where $\alpha = \pi(n - m)/L_3$, $\beta = \pi(n + m)/L_3$ and $|m| \neq |n|$.

4. THE COMPUTER PROGRAM

4.1 Basic features

The computer program calculates, to very high accuracy, the four lowest energy states of a particle of mass M_p , in a one-dimensional infinite potential well with an extra constant potential V_p in part of it. The program allows you to choose the particle mass M_p , the width of the finite potential well ($=L_3$), the position where the potential V_p starts ($=L_1$) and ends ($=L_2$), and the potential V_p itself. The basic procedure used to obtain the exact results is outlined below.

For $0 < x < L_1$ and $L_2 < x < L_3$, $V(x) = 0$ and

$$\psi(x) = A \exp(ik_1x) + B \exp(-ik_1x), \quad k_1 = \sqrt{M_p E}. \quad (27)$$

Similarly, for $L_1 < x < L_2$, $V(x) = V_p$ and

$$\psi(x) = A' \exp(ik_2x) + B' \exp(-ik_2x), \quad k_2 = \sqrt{M_p(E - V_p)}. \quad (28)$$

Here, $\psi(0) = 0$ is a necessary boundary condition, but this still leaves the assignment of $[d\psi(x)/dx]_{x=0}$. It is chosen to be unity, which is a compromise value resulting in $\psi(x)$ and $d\psi(x)/dx$ being of reasonable size over the whole system. (Note that in this computer method of solution, $\psi(x)$ is not, and need not, be normalized. Also this choice of $d\psi(x)/dx$ is reasonable only provided V_p has not a very extreme value.)

If E is then given $\psi(x)$ and $d\psi(x)/dx$ can be matched at L_1 and L_2 and hence $\psi(L_3)$ can be found. The subroutine PL3FEN, which finds $\psi(L_3)$ in this way, also returns the number of nodes of $\psi(x)$. The eigenvalues of the system will correspond to those values of E for which $\psi(L_3) = 0$. The problem is therefore equivalent to the determination of the roots of the complex determinantal transcendental equation which can be set up by conventional methods. However, the method adopted here is thought to possess some pedagogical advantages. An example of the variation of $\psi(L_3)$ with energy is shown in Figure 4.

The eigenvalues are first estimated using perturbation theory. Then, with these as a guide, by repeated doubling and halving, two energies, one above and one below the true n th energy level, are found where the number of nodes are $n - 1$ and n respectively. The function EFPL30 is next employed to determine an accurate zero of $\psi(L_3)$ using a combination of the methods of linear extrapolation, linear interpolation, and bisection.

4.2 Running the program

Input the position where the perturbation starts (L_1) and ends (L_2), the width of the infinite potential well (L_3) and the mass of the particle (M_p).

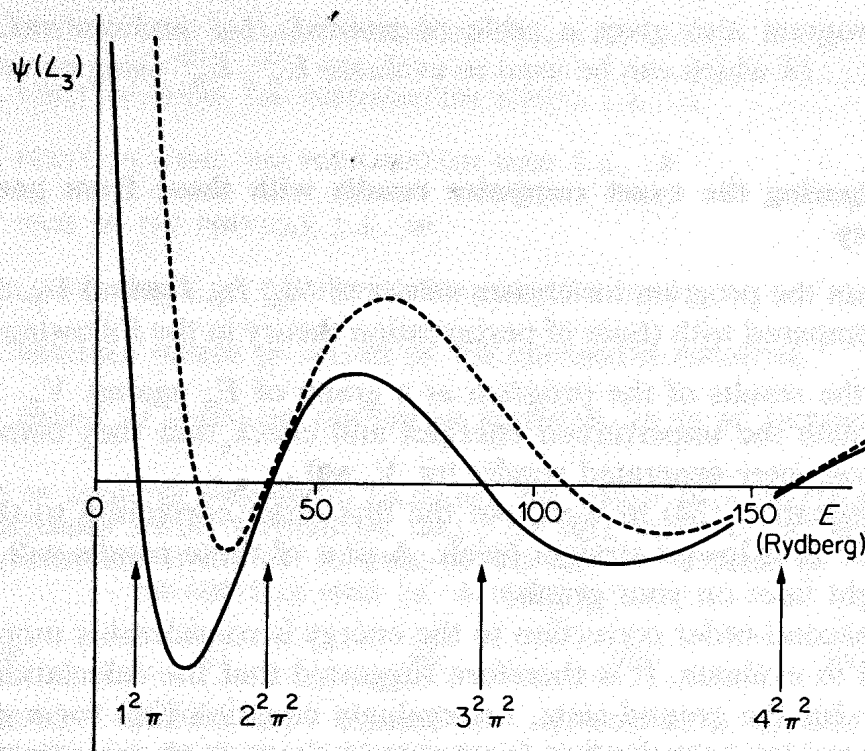


Figure 4. The variation of $\psi(L_3)$ with E , as returned by PL3FEN for $L_3 = 1.0$, $M_p = 1.0$. The solid curve shows the results for $V_p = 0$; the values of E for which $\psi(L_3) = 0$ coincide with the theoretical values for the energy: $E_n^0 = \pi^2 n^2 / M_p L_3^2 = \pi^2 n^2$. The dashed curve shows the result for $L_1 = 0.49$, $L_2 = 0.51$, $V_p = 500.0$. As we would expect from first-order perturbation theory, the ground state and second excited state energies are modified much more than the energies of the first and third excited states.

Rather than calculating the energy at a single value of V_p the program allows a range of values of V_p to be entered by reading the lowest required value of V_p (VP1)—which can be ≤ 0 or > 0 , the number of different values of V_p required (NVP) and the amount by which V_p is to be increased (DVP). Choose these parameters so that the case $V_p = 0$ is included.

An approximate graph of the results can be plotted on a line printer; the last input should be YES or NO as required.

The computer will set out the results for the four lowest energies E_1, E_2, E_3 , and E_4 as a function of V_p , in a table.

Remembering that the point of the exercise is to compare these computed results with perturbation theory, check that the chosen range of V_p is such that the energies change significantly (so that you can make the comparison) but not drastically (or otherwise V_p will be too large for perturbation theory to apply).

The program also gives a table of $\sin(n\pi L_1/L_3)$ and $\sin(n\pi L_2/L_3)$ for $n = 1, 2, \dots, 14$ which can be used to evaluate $E_n^{(1)}$, $E_n^{(2)}$ using equations (24) and (26).

4.3 Comparing the exact computer results with those from perturbation theory

Having run the program for chosen values of M_p , L_1 , L_2 , and L_3 , the results can be compared with those of perturbation theory in the following manner:

- (1) Plot the results of the program as a graph of E_n against V_p .
- (2) Calculate the unperturbed energies and check that they coincide with the computer-generated results for $V_p = 0$.
- (3) Use equation (24) to work out the first-order correction to the energy for the four lowest straight levels. A plot of these results will give four straight lines on your graph.
- (4) The second-order correction to the energy is considerably more complicated to evaluate. It is therefore suggested that the calculation only be made for the ground state, i.e. evaluate equation (26) for $n = 1$, $m \neq 1$ but consider only the first few terms in the second-order correction to the energy. You will find (as is generally the case) that these decrease quite rapidly because $|E_n^0 - E_m^0|$ increases rapidly with $|n - m|$, and so the series converges quickly. Plot the second-order correction to the ground state energy on the graph.
- (5) Can you make any general comments about the conditions for the validity of perturbation theory?

4.4 A Typical session

If the chosen parameters are:

L_1 (the position where the perturbation starts)	= 0.4	} (Bohr radii)
L_2 (the position where the perturbation ends)	= 0.5	
L_3 (the width of the infinite potential well)	= 1.0	
M_p (the mass of the particle)	= 1.0 (electron masses)	} (Rydbergs)
VP1 (the lowest value of the perturbation potential)	= -150.0	
DVP (the amount by which the perturbing potential is to be increased)	= 10.0	
NVP (the required number of values of the perturbing potential)	= 31	

and an approximate graph of the results on the line printer is requested, the results of the computer program are

TYPE THE WIDTH OF THE INFINITE POTENTIAL WELL, I.E. L3

1.0

TYPE THE POSITION WHERE THE PERTURBATION STARTS I.E. L1

0.4

TYPE THE POSITION WHERE THE PERTURBATION ENDS I.E. L2

0.5

TYPE THE MASS OF THE PARTICLE I.E. MP

1.0

TYPE THE LOWEST VALUE OF THE PERTURBING POTENTIAL UP

-150.0

TYPE THE REQUIRED NUMBER OF VALUES OF THE PERTURBING POTENTIAL

31

TYPE THE AMOUNT BY WHICH THE PERTURBING POTENTIAL IS TO BE INCREASED

10.0

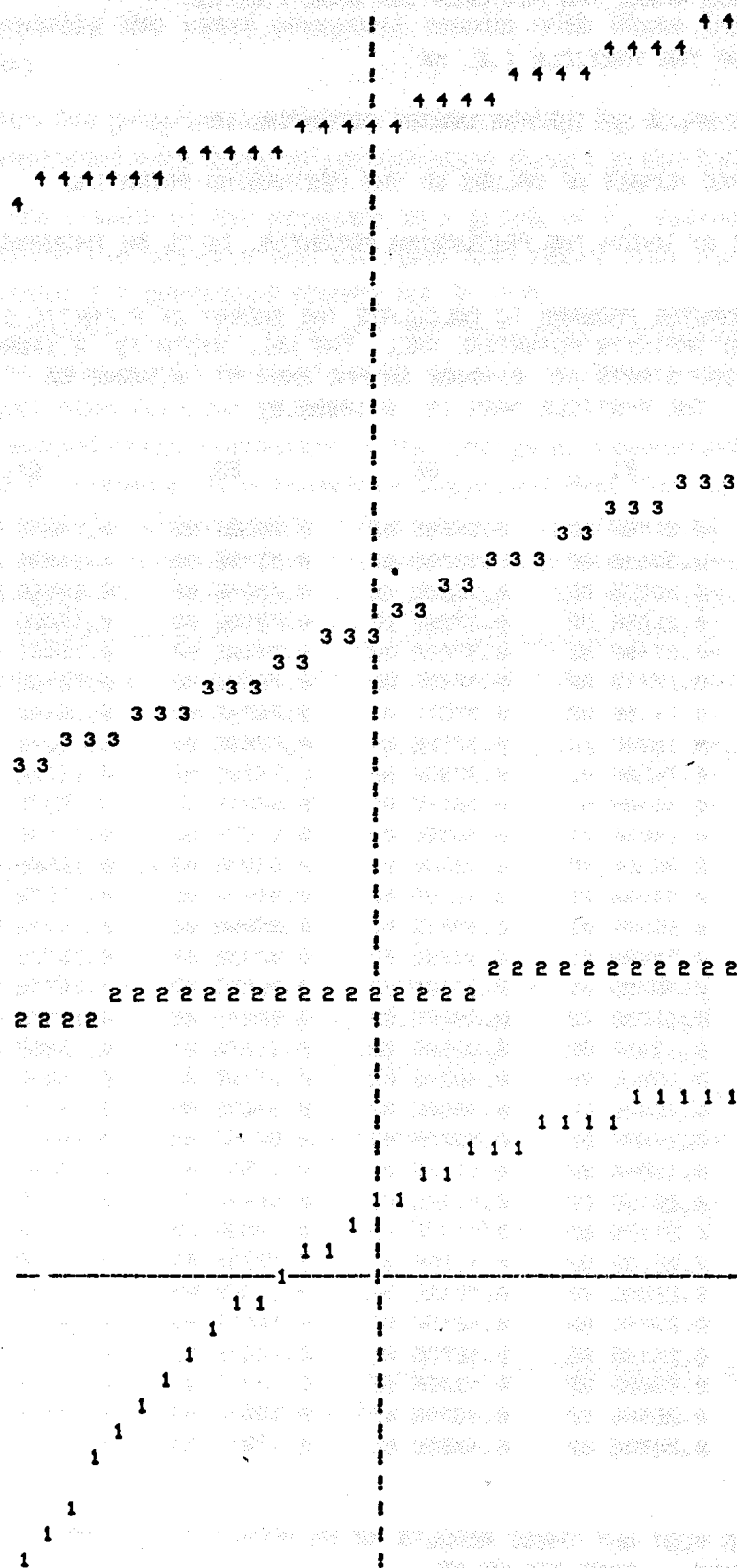
RESULTS OF COMPUTER PROGRAM TO CALCULATE THE ENERGY OF A PARTICLE
IN A PERTURBED INFINITE POTENTIAL WELL. THE WELL WIDTH IS 0.1000E 01
THE PERTURBATION STARTS AT 0.4000E 00 AND ENDS AT 0.5000E 00
THE PARTICLE MASS IS 0.1000E 01

UP	E1	E2	E3	E4
-0.1500E 03	-0.3776E 02	0.3658E 02	0.7090E 02	0.1484E 03
-0.1400E 03	-0.3344E 02	0.3673E 02	0.7175E 02	0.1489E 03
-0.1300E 03	-0.2927E 02	0.3689E 02	0.7264E 02	0.1495E 03
-0.1200E 03	-0.2526E 02	0.3706E 02	0.7359E 02	0.1500E 03
-0.1100E 03	-0.2140E 02	0.3722E 02	0.7458E 02	0.1506E 03
-0.1000E 03	-0.1771E 02	0.3740E 02	0.7563E 02	0.1512E 03
-0.9000E 02	-0.1419E 02	0.3757E 02	0.7674E 02	0.1518E 03
-0.8000E 02	-0.1083E 02	0.3776E 02	0.7789E 02	0.1524E 03
-0.7000E 02	-0.7650E 01	0.3795E 02	0.7910E 02	0.1530E 03
-0.6000E 02	-0.4640E 01	0.3815E 02	0.8036E 02	0.1537E 03
-0.5000E 02	-0.1803E 01	0.3835E 02	0.8167E 02	0.1543E 03
-0.4000E 02	0.8630E 00	0.3856E 02	0.8303E 02	0.1550E 03
-0.3000E 02	0.3359E 01	0.3878E 02	0.8443E 02	0.1557E 03
-0.2000E 02	0.5690E 01	0.3901E 02	0.8586E 02	0.1564E 03
-0.1000E 02	0.7858E 01	0.3924E 02	0.8733E 02	0.1572E 03
0.0000E 00	0.9870E 01	0.3940E 02	0.8883E 02	0.1579E 03
0.1000E 02	0.1173E 02	0.3973E 02	0.9034E 02	0.1587E 03
0.2000E 02	0.1345E 02	0.3998E 02	0.9187E 02	0.1595E 03
0.3000E 02	0.1503E 02	0.4024E 02	0.9340E 02	0.1603E 03
0.4000E 02	0.1648E 02	0.4050E 02	0.9493E 02	0.1611E 03
0.5000E 02	0.1782E 02	0.4077E 02	0.9645E 02	0.1620E 03
0.6000E 02	0.1904E 02	0.4105E 02	0.9795E 02	0.1628E 03
0.7000E 02	0.2015E 02	0.4132E 02	0.9944E 02	0.1637E 03
0.8000E 02	0.2117E 02	0.4160E 02	0.1009E 03	0.1646E 03
0.9000E 02	0.2210E 02	0.4188E 02	0.1023E 03	0.1655E 03
0.1000E 03	0.2296E 02	0.4216E 02	0.1037E 03	0.1664E 03
0.1100E 03	0.2373E 02	0.4245E 02	0.1051E 03	0.1673E 03
0.1200E 03	0.2444E 02	0.4273E 02	0.1064E 03	0.1683E 03
0.1300E 03	0.2509E 02	0.4300E 02	0.1077E 03	0.1692E 03
0.1400E 03	0.2568E 02	0.4328E 02	0.1089E 03	0.1701E 03
0.1500E 03	0.2623E 02	0.4355E 02	0.1101E 03	0.1711E 03

DO YOU WANT TO PLOT OUT THESE RESULTS AS AN APPROXIMATE GRAPH
ON THE TELETYPE. TYPE YES OR NO.

YES

APPROXIMATE GRAPH OF THE ENERGIES OF THE GROUND STATE AND FIRST THREE
EXCITED STATES AS A FUNCTION OF THE PERTURBATION UP. UP IS PLOTTED ON
THE HORIZONTAL AXIS AND VARIES FROM $-0.1500E\ 03$ TO $0.1500E\ 03$
THE ENERGY IS PLOTTED ON THE VERTICAL AXIS AND VARIES FROM $0.1711E\ 03$
TO $-0.3778E\ 02$



DO YOU WANT TO RE-RUN THE PROGRAM WITH THE SAME VALUES FOR L1, L2, L3
AND MP BUT WITH DIFFERENT VALUES FOR THE PERTURBING POTENTIAL VP.
TYPE YES OR NO
NO

N	SIN(N*PI*L1/L3)	SIN(N*PI*L2/L3)
1	0.951056	1.000000
2	0.587786	0.000001
3	-0.587784	-1.000000
4	-0.951057	-0.000001
5	-0.000002	1.000000
6	0.951055	0.000004
7	0.587788	-1.000000
8	-0.587782	-0.000003
9	-0.951058	1.000000
10	-0.000004	0.000006
11	0.951055	-1.000000
12	0.587792	-0.000009
13	-0.587777	1.000000
14	-0.951059	0.000006

PROGRAM FINISHED

5. DISCUSSION

The unperturbed energies (in Rydbergs), for $V_p = 0$, are

$$E_n^{(0)} = \frac{n^2 \pi^2}{M_p L_3^2} \quad (29)$$

Equation (29), for the chosen parameters, gives $E_1^{(0)} = 9.87$, $E_2^{(0)} = 39.48$, $E_3^{(0)} = 88.83$, $E_4^{(0)} = 157.91$.

The first-order correction to the energy is given by equation (24). Thus, for the chosen parameters, the corrections to the first four levels are:

$n =$	1	2	3	4
$\frac{(\text{First-order correction})}{V_p} =$	0.194	0.024	0.150	0.077

The second-order correction to the energy of the n th level is given by equation (25), which can be evaluated using equation (26). For the example under discussion, values of I_{mn}/V_p are given in Table 1 while $E_{mn}^{(2)}/V_p^2$ values are given in Table 2. The ranges of n and m are restricted to $1 \leq n \leq 4$ and $1 \leq m \leq 10$.

Table 1. Values of I_{mn}/V_p

m	1	2	3	4	5	6	7	8	9	10
n										
1	—	0.059	-0.169	-0.107	0.126	0.136	-0.074	-0.141	0.023	0.125
2	0.059	—	-0.048	-0.043	0.028	0.052	-0.005	-0.050	-0.016	0.039
3	-0.169	-0.048	—	0.088	-0.117	-0.113	0.076	0.120	-0.036	-0.111
4	-0.107	-0.043	0.088	—	-0.053	-0.094	0.013	0.091	0.025	-0.072

Table 2. Values of $E_{mn}^{(2)}/V_p^2$

m	1	2	3	4	5	6	7	8	9	10	Total
n											
1	—	-1.19×10^{-4}	-3.63×10^{-4}	-7.79×10^{-5}	-6.72×10^{-5}	-5.34×10^{-5}	-1.15×10^{-5}	-3.21×10^{-5}	-6.93×10^{-7}	-1.61×10^{-5}	-7.40×10^{-4}
2	1.19×10^{-4}	—	-4.69×10^{-5}	-1.57×10^{-5}	-3.91×10^{-6}	-8.66×10^{-6}	-6.43×10^{-8}	-4.30×10^{-6}	-3.26×10^{-7}	-1.60×10^{-6}	$+3.74 \times 10^{-5}$
3	3.63×10^{-4}	4.69×10^{-5}	—	-1.12×10^{-4}	-8.66×10^{-5}	-4.77×10^{-5}	-1.45×10^{-5}	-2.66×10^{-5}	-1.71×10^{-6}	-1.37×10^{-5}	$+1.07 \times 10^{-4}$
4	7.79×10^{-5}	1.57×10^{-5}	1.12×10^{-4}	—	-3.21×10^{-5}	-4.43×10^{-5}	-4.97×10^{-7}	-1.76×10^{-5}	-9.58×10^{-7}	-6.27×10^{-6}	$+1.03 \times 10^{-4}$

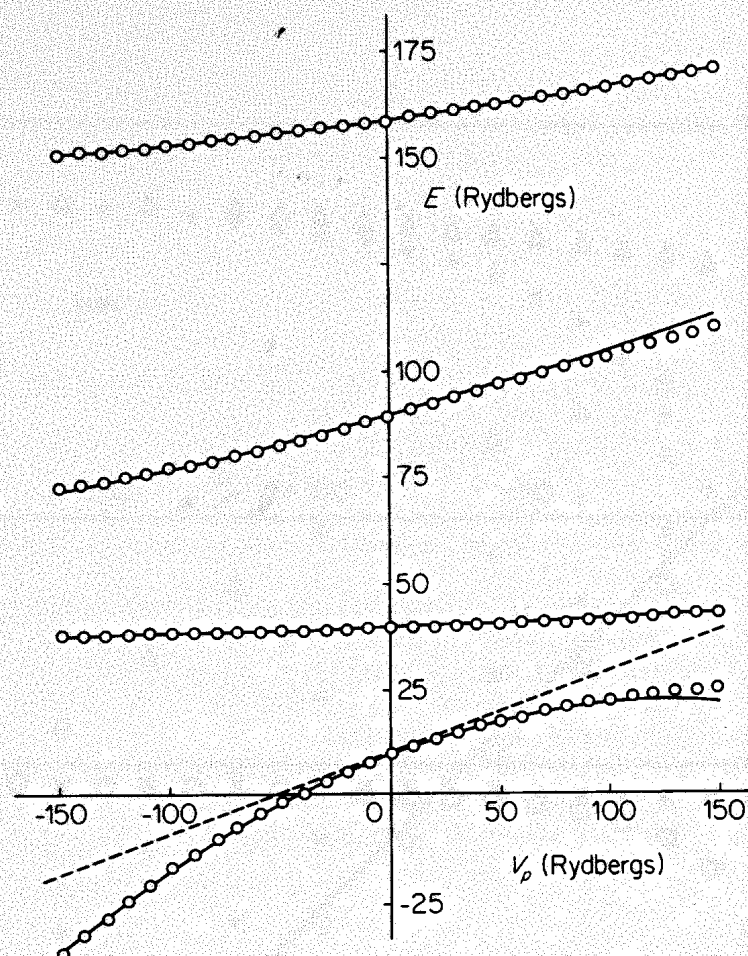


Figure 5. The results of the computer program (circles) for $L_1=0.4$, $L_2=0.5$, $L_3=1.0$, $M_p=1.0$ compared with the perturbation theory calculation. The solid curves are the results for first- plus second-order perturbation theory. The dashed line for the ground state shows the result for first-order perturbation theory alone

Figure 5 shows a comparison between the results of the computer program (the circles) and perturbation theory. The solid curves are the results for first- plus second-order perturbation theory corrections. The dashed line for the ground state shows the result for first-order perturbation theory alone. It can be seen that, even with the inclusion of the second-order correction, the results are starting to deviate from the (more accurate) computer results at the largest values of $|V_p|$. For these values of V_p the amount of admixture of other states into the unperturbed eigenstate is not small—which is the situation in which we would indeed expect second-order perturbation theory to break down.

Though they correspond to situations far outside the range of validity of perturbation theory the results for $V_p \gg E_n^0$ and $V_p \rightarrow -\infty$ are of some interest.

For $V_p \gg E_n^0$ the situation tends towards a pair of isolated infinite potential

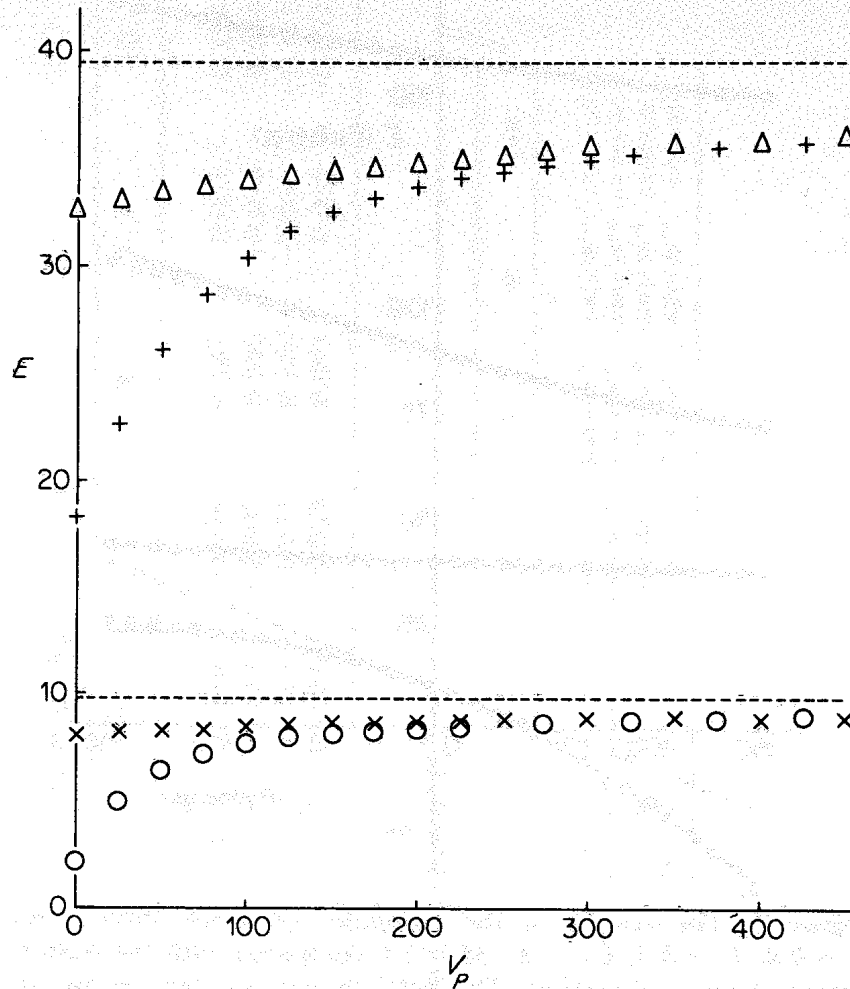


Figure 6. The energy levels for $V_p \gg E_n^0$. $L_1 = 1.0$, $L_2 = 1.2$, $L_3 = 2.2$, $M_p = 1.0$. The dashed lines indicate the ground state and first excited state energies for the particle in an infinite potential well of width $L_1 = L_3 - L_2$.

wells, of width L_1 and $L_3 - L_2$. It will be found for this case that the energies tend towards the (constant) values for the infinite potential wells with these widths. Furthermore, if $L_1 = L_3 - L_2$ these levels are degenerate. This kind of situation is shown in Figure 6.

For $V_p \rightarrow -\infty$ the situation tends towards an infinite potential well of width $L_2 - L_1$ with the zero of energy shifted to V_p . Hence

$$E_n \rightarrow V_p + \frac{n^2 \pi^2}{M_p (L_2 - L_1)^2}.$$

An example of this behaviour is shown in Figure 7.

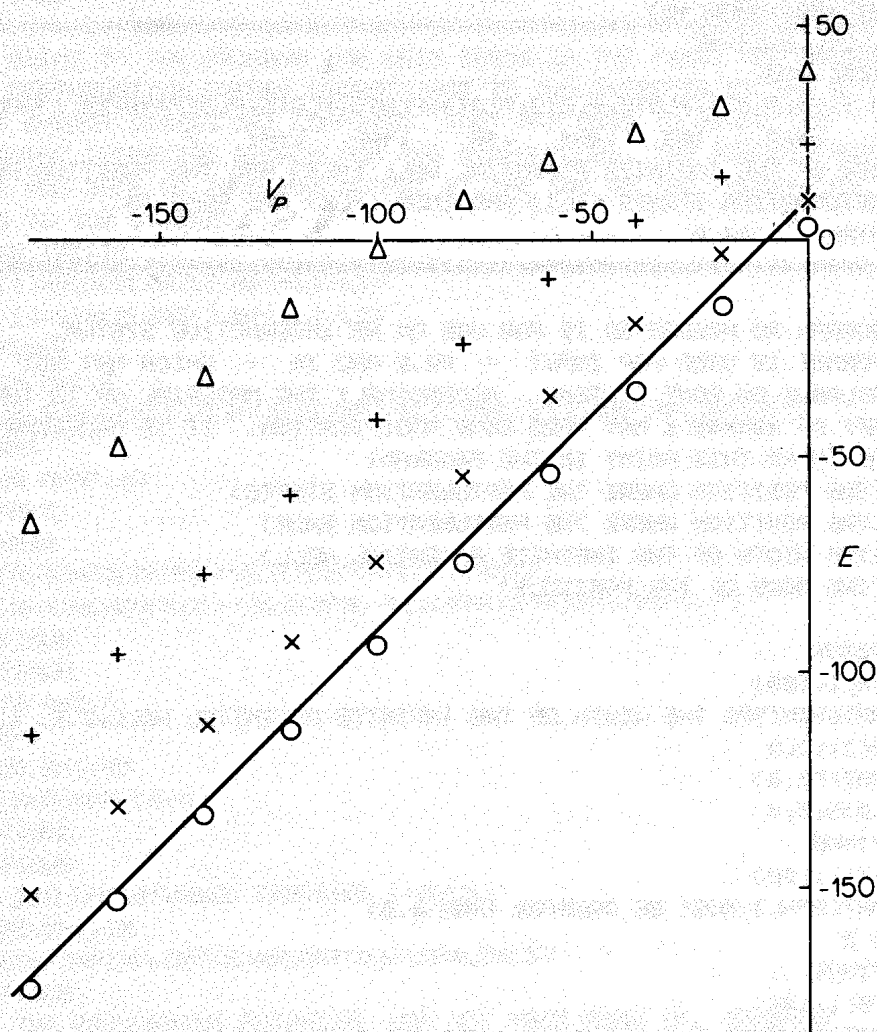


Figure 7. The energy levels for $V_p \rightarrow -\infty$ and $L_1 = 0.5$, $L_2 = 1.5$, $L_3 = 2.0$, $M_p = 1.0$. The straight line corresponds to $E = V_p + \pi^2 / M_p(L_2 - L_1)^2$ and it can be seen that the ground state energy tends asymptotically to this value for $V_p \rightarrow -\infty$.

MAIN PROGRAM

C THIS PROGRAM USES AN ITERATIVE TECHNIQUE TO FIND THE GROUND STATE AND
 C FIRST THREE EXCITED STATES OF A PARTICLE IN AN INFINITE POTENTIAL
 C WELL WITH AN ADDITIONAL PERTURBING POTENTIAL IN PART OF
 C THE WELL.

COMMON L1,L2,L3,UP,MP,N,PI

DIMENSION SL1(15),SL2(15),HDV(5,10),EUK(10),EC2(5),EP(5),E(51,4),

1 PLOT(120),NAME(40)

REAL L1,L2,L3,MP

LOGICAL BOOL

DATA Y,YN,PLOT1,PLOT2,PLOT3,PLOT4,PLOT5,PLOT6,PLOT7/4HYES,4HNO,

1 4H1,4H2,4H3,4H4,4H,4H-,4H! /

C THE WIDTH OF THE INFINITE POTENTIAL WELL (=L3) AND THE POSITION WHERE
 C THE PERTURBATION STARTS (=L1) AND ENDS (=L2) ARE READ IN.

PI=ATAN(1.0)*4.0

C

C THE PROGRAM AS PRESENTED IS FOR USE ON AN INTERACTIVE SYSTEM.
 C FREE FORMAT IS USED FOR INPUT - F0.0 AND I0 - WHICH MAY NOT
 C BE AVAILABLE ON SOME SYSTEMS. ACCORDINGLY THE MATERIAL UP TO THE
 C NEXT SET OF *****S MAY NEED SOME MODIFICATION. IT IS NECESSARY
 C TO READ IN AT THIS POINT IN THE PROGRAM:

C L1 (THE POSITION WHERE THE PERTURBATION STARTS)

C L2 (THE POSITION WHERE THE PERTURBATION ENDS)

C L3 (THE WIDTH OF THE INFINITE POTENTIAL WELL)

C MP (THE MASS OF THE PARTICLE)

C

2 CONTINUE

WRITE(1,100)

100 FORMAT(53HTYPE THE WIDTH OF THE INFINITE POTENTIAL WELL,I.E. L3)

READ(1,1)L3

1 FORMAT(F0.0)

IF(L3)3,3,4

3 CONTINUE

WRITE(1,102)

102 FORMAT(27HL3 MUST BE GREATER THAN 0.0)

GOTO 2

4 CONTINUE

WRITE(1,106)

106 FORMAT(55HTYPE THE POSITION WHERE THE PERTURBATION STARTS I.E. L1)

READ(1,1)L1

IF(L1.GE.0.0.AND.L1.LT.L3)GOTO 6

WRITE(1,108)

108 FORMAT(30HL1 MUST LIE BETWEEN 0.0 AND L3)

GOTO 4

6 CONTINUE

WRITE(1,110)

110 FORMAT(53HTYPE THE POSITION WHERE THE PERTURBATION ENDS I.E. L2)

READ(1,1)L2

IF(L2.GT.L1.AND.L2.LE.L3)GOTO 8

WRITE(1,112)

112 FORMAT(29HL2 MUST LIE BETWEEN L1 AND L3)

GOTO 6

8 CONTINUE

C NEXT THE MASS OF THE PARTICLE (=MP) IS INPUT.

WRITE(1,114)

114 FORMAT(37HTYPE THE MASS OF THE PARTICLE I.E. MP)

MAIN PROGRAM

```

      READ(1,1)MP
      IF(MP)9,9,10
      9 CONTINUE
      WRITE(1,116)
      116 FORMAT(49HTHE MASS OF THE PARTICLE MUST BE GREATER THAN 0.0)
      GOTO 8
      10 CONTINUE
C=====
C AT THIS POINT IN THE PROGRAM THE MAIN TERMS IN THE FIRST AND SECOND
C ORDER PERTURBATION THEORY CORRECTIONS TO THE ENERGIES OF THE 5
C LOWEST ENERGY STATES ARE COMPUTED. THEY ARE USED TO GUIDE THE
C SUBSEQUENT ITERATIVE SEARCH FOR THE EIGENVALUES. THE RESULTS ARE
C STORED AND SOME OF THEM ARE OUTPUT AT THE END OF THE PROGRAM AS
C AN AID TO THE STUDENT.
      DO 12 I=1,15
      SL1(I)=SIN(FLOAT(I)*PI*L1/L3)
      SL2(I)=SIN(FLOAT(I)*PI*L2/L3)
      12 CONTINUE
      DO 14 N=1,5
      HDU(N,N)=(L2-L1)/L3-(SL2(2*N)-SL1(2*N))/(2.0*PI*FLOAT(N))
      NP=N+1
      DO 16 M=NP,10
      MMN=M-N
      MPN=M+N
      HDU(N,M)=(SL2(MMN)-SL1(MMN))/FLOAT(MMN)
      HDU(N,M)=(HDU(N,M)-(SL2(MPN)-SL1(MPN))/FLOAT(MPN))/PI
      16 CONTINUE
      14 CONTINUE
      DO 18 N=2,5
      NM=N-1
      DO 20 M=1,NM
      HDU(N,M)=HDU(M,N)
      20 CONTINUE
      18 CONTINUE
C COMPUTE THE UNPERTURBED ENERGIES (=EU(N))
      DO 22 N=1,10
      EU(N)=PI*PI*FLOAT(N)*FLOAT(N)/(MP*L3*L3)
      22 CONTINUE
C AS YET THE PERTURBING POTENTIAL HAS NOT BEEN READ IN. HOWEVER,
C WE WISH TO BE ABLE TO EXPRESS THE ENERGY, UP TO SECOND ORDER, AS:
C 
$$E = EU(N) + UP*HDU(N,N) + UP*UP*EC2(N)$$
 . THUS.
      DO 24 N=1,5
      EC2(N)=0.0
      DO 26 M=1,10
      IF(M-N)25,26,25
      25 CONTINUE
      EC2(N)=EC2(N)+(HDU(N,M)*HDU(N,M))/(EU(N)-EU(M))
      26 CONTINUE
      24 CONTINUE
      28 CONTINUE
C THE VALUES OF THE PERTURBATION (=UP) ARE READ IN
C=====
C
C FURTHER INPUT IS REQUIRED HERE
C UP1 (THE LOWEST VALUE OF THE PERTURBING POTENTIAL UP)
C DUP (THE AMOUNT BY WHICH THE PERTURBING POTENTIAL IS TO BE INCREASED)

```

MAIN PROGRAM

```

C      NUP (THE REQUIRED NUMBER OF VALUES OF THE PERTURBING POTENTIAL)
C      NOTE THAT NUP IS AN INTEGER VARIABLE - THE OTHERS ARE REAL
C
      WRITE(1,118)
118  FORMAT(52HTYPE THE LOWEST VALUE OF THE PERTURBING POTENTIAL UP)
      READ(1,1)UP1
      30 CONTINUE
      WRITE(1,120)
120  FORMAT(52HTYPE THE REQUIRED NUMBER OF VALUES OF THE PERTURBING ,
1 9HPOTENTIAL)
      READ(1,29)NUP
      29 FORMAT(I0)
      IF(NUP.GT.0.AND.NUP.LT.52)GOTO 32
      WRITE(1,122)
122  FORMAT(53HTHE REQUIRED NUMBER MUST BE POSITIVE AND LESS THAN 52)
      GOTO 30
      32 CONTINUE
      WRITE(1,124)
124  FORMAT(55HTYPE THE AMOUNT BY WHICH THE PERTURBING POTENTIAL IS TO ,
1 12HBE INCREASED)
      READ(1,1)DUP
      WRITE(1,208)
      WRITE(1,208)
C*****
      WRITE(1,200)
200  FORMAT(1H ,45HRESULTS OF COMPUTER PROGRAM TO CALCULATE THE ,
1 20HENERGY OF A PARTICLE)
      WRITE(1,202)L3
202  FORMAT(1H ,49HIN A PERTURBED INFINITE POTENTIAL WELL. THE WELL ,
1 9HWIDTH IS ,E11.4)
      WRITE(1,204)L1,L2
204  FORMAT(1H ,27HTHE PERTURBATION STARTS AT ,E11.4,13H AND ENDS AT ,
1 E11.4)
      WRITE(1,206)MP
206  FORMAT(1H ,15X,21HTHE PARTICLE MASS IS ,E11.4)
C SET OUT THE HEADING FOR THE RESULTS
      WRITE(1,208)
208  FORMAT(1H )
      WRITE(1,210)
210  FORMAT(1H ,6X,2HUP,12X,2HE1,12X,2HE2,12X,2HE3,12X,2HE4)
      WRITE(1,208)
      DO 34 I=1,NUP
      UP=UP1+FLOAT(I-1)*DUP
C COMPUTE THE ENERGY OF THE 5 LOWEST STATES USING 2ND ORDER PERTURBATION
      DO 36 N=1,5
      EP(N)=EU(N)+UP*HDX(N,N)+UP*UP*EC2(N)
      36 CONTINUE
C SORT THE EP(N) IN CASE THE PERTURBATION HAS PRODUCED A CROSS OVER
C OF THE LEVELS
      39 CONTINUE
      DO 37 N=1,4
      IF(EP(N).LT.EP(N+1))GOTO 37
      EPN=EP(N+1)
      EPNP=EP(N)
      EP(N)=EPN
      EP(N+1)=EPNP

```