ON THE QUANTUM MECHANICAL PROBLEM OF A PARTICLE IN TWO POTENTIAL MINIMA

by

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ABSTRACT

The problem of a particle in two adjacent one-dimensional rectangular potential "boxes" is an exactly soluble representative of a class of two-minima problems of considerable physical interest which have not been solved exactly. It therefore affords a valuable opportunity for a critical examination of the extent of applicability of perturbation theory methods to such problems. An exact implicit solution of the problem is obtained, and is reduced to explicit approximate form in two important special cases. These approximations are reproduced by perturbation theory methods, and their ranges of validity are demonstrated by comparison with the exact solution. The application of the model to a physical system is demonstrated by using the identical two-box problem as a basis for calculation of some constants of the ammonia molecule.

ACKNOWLEDGEMENT

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TABLE OF CONTENTS

LIST OF PLATES

ON THE QUANTUM MECHANICAL PROBLEM OF A PARTICLE IN TWO POTENTIAL MINIMA

I. INTRODUCTION

The problem of a particle in two potential minima is of extensive interest in theoretical physics since it provides a model for many physical systems. The simple one-dimensional case in which the minima are rectangular in shape serves as a prototype by which we may understand many phenomena connected with metallic conduction[1], van der Waals forces[2], the stability of hydrogen-like ions[2], and the vibration spectra of certain polyatomic molecules[3]. For this reason many authors, including those mentioned in the footnotes, have discussed the model with a view to its physical significance.

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[1] M.F. Manning and M.E. Bell, Rev.Mod.Phys. 12, 215 (1940).

[2] S. Dushman, "Elements of Quantum Mechanics", (Wiley), pp. 214-218, and references given there. Dushman's approximation to the energy splitting is incorrect (compare his equation (3) with our equation (26a) for $c=a$ and $\lambda=1$), since he fails to consider the phase shift of the eigenfunction.

[3] See Part V below, where the present model is applied to the ammonia inversion spectrum.

It is felt, however, that none of the published discussions have taken full advantage of the possibilities of the problem in illustrating many mathematical methods which are constantly used in quantum mechanics. On the one hand, the problem is one of few non-trivial examples which may be solved by exact methods. On the other hand the solution may be carried out, with certain significant limitations, by means of perturbation theory. The complete knowledge obtained by the direct solution may then be employed to illustrate the nature of the perturbation theoretical results[1]. The pedagogic utility of the discussion is enhanced by the necessity of using wave-functions of the continuum, and of dealing with a type of perturbation theory that is not generally discussed in the literature.

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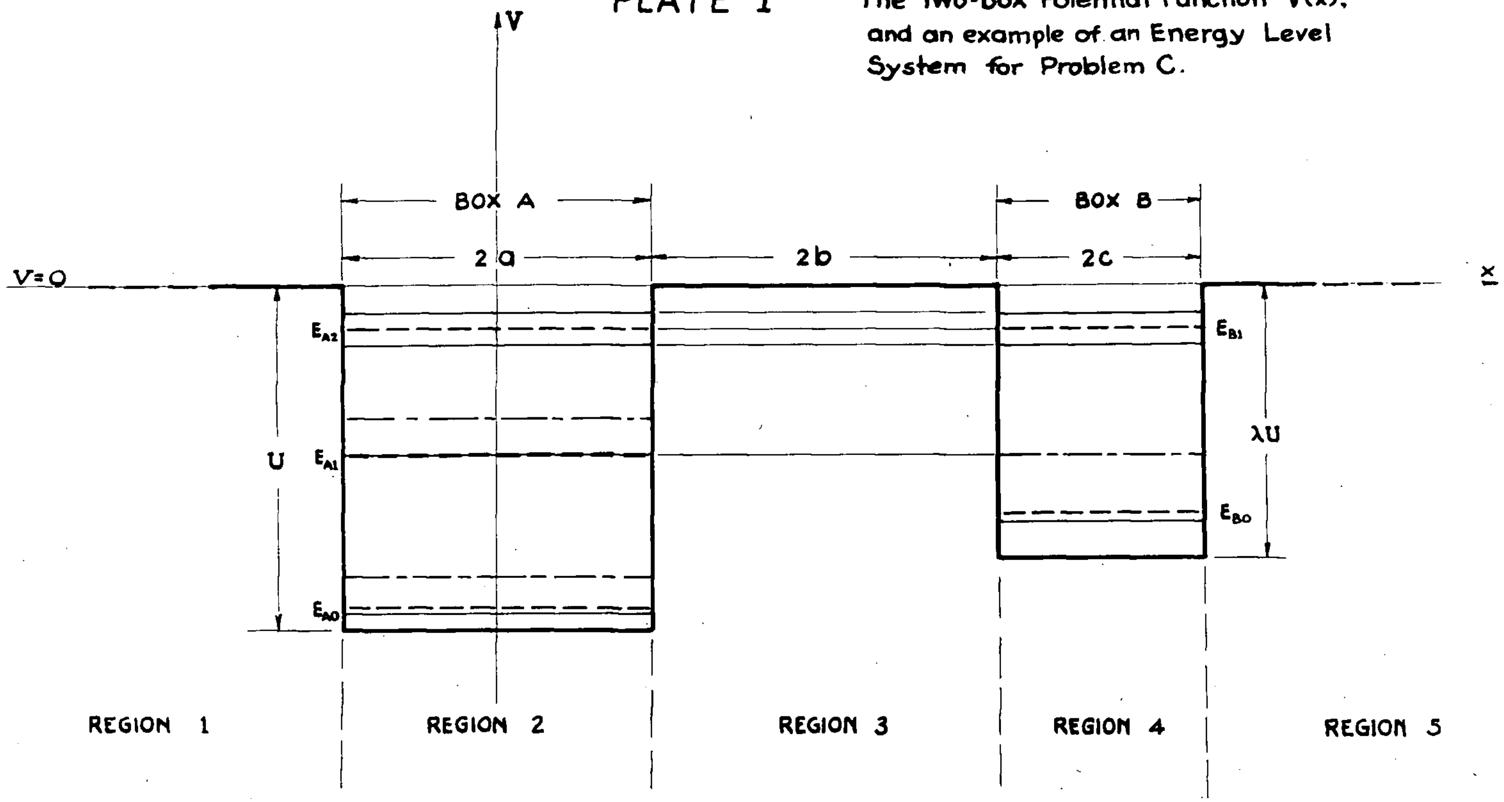
[1] P.M. Morse and E.C.G. Stückelberg, Helv.Phys.Acta, 4, 337, (1931), make this kind of illustration using a model for ammonia. However, they consider a less general case, and their model is more complicated.

PLATE I The Two-box Potential Function $V(x)$, and an example of an Energy Level System for Problem C.



Legend: - - - - - The levels of problems A and B are drawn in the appropriate BOX
—·—·— The $E_{\infty,n}$ of problems A and B are drawn in the appropriate BOX
———— The levels of problem C according to equations (23) and (24)

II. DIRECT SOLUTION

1. FORMULATION OF THE PROBLEM

We consider the problem of the one-dimensional motion of a particle of mass μ subject to a potential $V(x)$ shown in Plate I, and seek its bound energy levels together with the corresponding eigenfunctions. $V(x)$ vanishes outside two potential "boxes" A and B ($V(x)=0$ in regions 1, 3, and 5) and has the constant values $-U$ and $-\lambda U$ inside boxes A and B respectively ($V(x)=-U$ in region 2, $V(x)=-\lambda U$ in region 4).

We shall first solve the general problem in implicit form and then consider the explicit solutions of the following special cases:

Problem A, in which the width of box B is zero ($c=0$) or the depth of box B is zero ($\lambda=0$) and only box A is present.

Problem B, in which the width of box A is zero, and only box B is present.

Problem C, in which the distance $2b$ between the boxes is large.

Problem D, in which box B is much shallower than box A (λ is small compared to unity).

2. SOLUTION OF THE PROBLEM IN IMPLICIT FORM

The eigenfunctions $\varphi(x)$ satisfy the equation

$$d^2\varphi/dx^2 + K[E - V(x)]\varphi = 0, \tag{1}$$

which is the Schrödinger equation multiplied by

$$-K = -8\pi^2\mu/h^2. \tag{2}$$

If φ_i is the expression for a bound state ($E < 0$) eigenfunction in the ith region, the solutions of equation (1) are

$$\begin{aligned} \varphi_i &= A_i \cos\alpha_i(x + \delta_i) && \text{for } i = 2, 4; \\ \varphi_i &= A_i e^{\beta x} + B_i e^{-\beta x} && \text{for } i = 1, 3, 5; \end{aligned} \tag{3}$$

where

$$\alpha_2 = \sqrt{K(E+U)} = \alpha \qquad > 0 \text{ for } E > -U, \tag{4a}$$

$$\alpha_4 = \sqrt{K(E+\lambda U)} = \alpha', \tag{4b}$$

$$\beta = \sqrt{-KE} \qquad > 0 \text{ for } E < 0; \tag{4c}$$

so that

$$\alpha^2 + \beta^2 = KU, \quad \alpha'^2 + \beta^2 = \lambda K U. \tag{5}$$

The A_i, B_i, and δ_i are constants to be determined together with a condition for eigenvalues by the boundary conditions at infinity (where φ must not be infinite) and at the boundaries of the boxes (where φ and its first derivative φ' must be continuous). The conditions at infinity require that B_1 and A_5 shall vanish, so that equations (3) may be rewritten with some changes in the constants as

$$\varphi_1 = A\cos\alpha(a-\delta)\,e^{\beta(x+a)} \tag{6a}$$

$$\varphi_2 = A\cos\alpha(x+\delta) \tag{6b}$$

$$\varphi_3 \begin{cases} = \dfrac{A\cos\alpha(a+\delta)}{1+\gamma_A}\left[e^{-\beta(x-a)} + \gamma_A e^{\beta(x-a)}\right] & (6c) \\[2ex] = \dfrac{B\cos\alpha'(c+\delta')}{1+\gamma_B}\left[e^{\beta(x-a-2b)} + \gamma_B e^{-\beta(x-a-2b)}\right] & (6d) \end{cases}$$

$$\varphi_4 = B\cos\alpha'(x-a-2b-c-\delta') \tag{6e}$$

$$\varphi_5 = B\cos\alpha'(c-\delta')\,e^{-\beta(x-a-2b-2c)} \tag{6f}$$

where the first three and the last three expressions make up functions which are continuous at the boundaries of boxes A and B respectively. The two forms of φ_3 have been chosen to emphasize the symmetrical way in which the two boxes occur in the problem.

Applying the condition that φ' shall be continuous at the boundaries of box A to the first three of equations (6) we obtain

$$\beta/\alpha = \tan\alpha(a-\delta) \tag{7a}$$

$$\beta/\alpha = \frac{1+\gamma_A}{1-\gamma_A}\tan\alpha(a+\delta) \tag{7b}$$

which determine δ and γ_A as functions of α and β, and consequently (in virtue of equations (4)) as implicit functions of E. Thus elimination of δ between equations (7a) and (7b) yields for γ_A :

$$\gamma_A = \frac{\beta^2-\alpha^2+2\alpha\beta\cot 2\alpha a}{KU} = \frac{(\beta-\alpha\tan\alpha a)(\beta+\alpha\cot\alpha a)}{KU}. \tag{8a}$$

Similarly we obtain from the last three of equations (6)

$$\beta/\alpha' = \tan\alpha'(c - \delta') \quad , \tag{7c}$$

$$\beta/\alpha' = \frac{1+\gamma_B}{1-\gamma_B}\tan\alpha'(c+\delta') \quad , \tag{7d}$$

$$\gamma_B = \frac{\beta^2 - \alpha'^2 + 2\alpha'\beta\cot 2\alpha' c}{\lambda\kappa v} = \frac{(\beta - \alpha'\tan\alpha' c)(\beta + \alpha'\cot\alpha' c)}{\lambda\kappa v} \quad . \tag{8b}$$

If we now insist that the two forms of ϕ_3 in equations (6c) and (6d) represent the same function we obtain the condition

$$\gamma_A\gamma_B = \bar{\epsilon}^2 \quad , \tag{9}$$

where

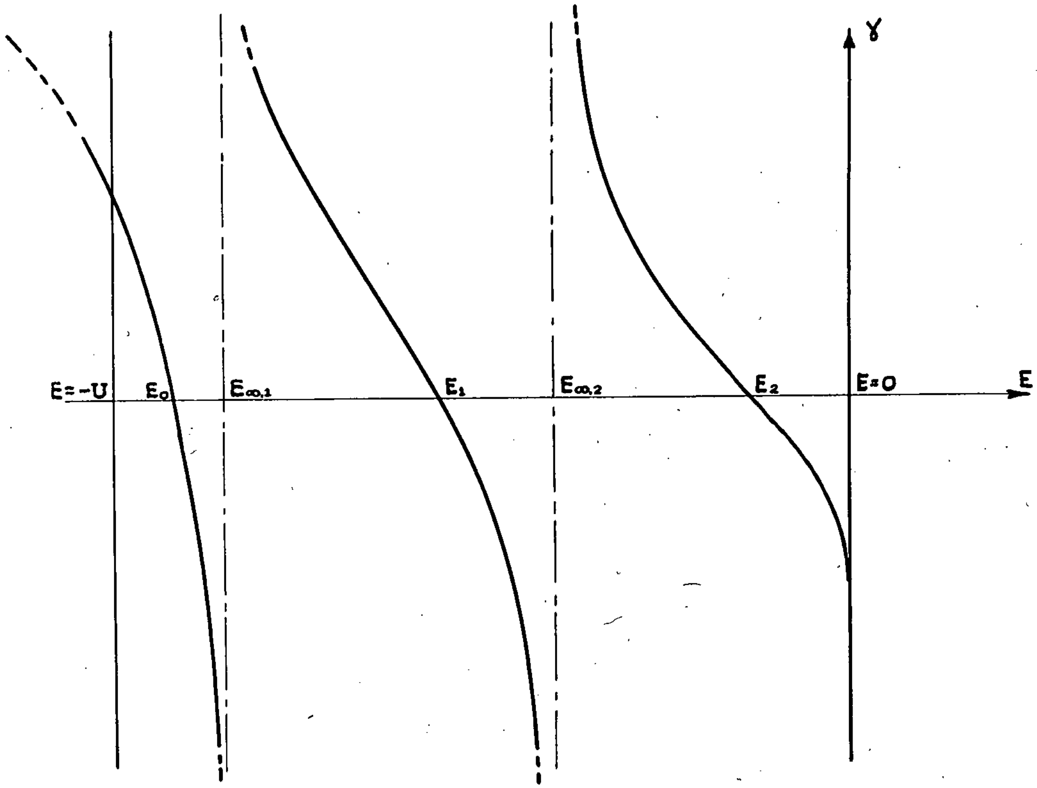
$$\bar{\epsilon} = e^{-2\beta b} \tag{10}$$

Equation (9) is clearly a condition for eigenvalues since in accordance with equations (4), (8), and (10) it is an implicit equation in E and the constants a , b , c , v , and λ of the potential energy function. If the values of E satisfying equation (9) for a particular set of values of the constants are found, say by numerical methods, then γ_A and γ_B may be found from equations (8), and δ and δ' may be found from equations (7). Thus the equations we have found give us complete information about both the eigenvalues and the eigenfunctions in implicit form.

3. PROBLEM A, THE SINGLE-BOX A CASE

If c or λ is zero and box A alone is present, it is clear that the eigenfunction in the whole region to

PLATE II   A rough sketch of γ_A as a Function of E for the case in which $4 < 32\mu a^2 U/h^2 < 9$



The Zeros of γ_A are the Single-box Levels
Notice that the slope γ_A' is Negative at each Zero

the right of box A may be represented by the function ϕ_3 of equation (6c). The condition that ϕ shall not be infinite at $x=+\infty$ now implies that

$$\gamma_A = 0 \qquad , \qquad (11)$$

which with equations (8a) and (4) is the condition for eigenvalues.

γ_A has been roughly sketched in Plate II as a function of E for the case in which U lies in the range $4 < 32\mu a^2 U/\hbar^2 < 9$. $\gamma_A(E)$ is real only for $E<0$ and is positive for all $E \leqq -U$, approaching $+\infty$ as $E \to -\infty$. In the region of bound energy levels ($-U < E < 0$) its zeros are separated by infinite discontinuities at the points[1]

$$E_{\infty,n} = n^2\hbar^2/32\mu a^2 \quad ; \quad n = 1, 2, 3, --- \quad . \qquad (12)$$

As E increases, the sign of γ_A changes from $-$ to $+$ at each $E_{\infty,n}$ and from $+$ to $-$ at each zero. The zeros, when placed in increasing order, are alternately zeros of the first and second factors of γ_A in equation (8a).

The eigenfunctions ϕ_A corresponding to the bound levels of problem A may be obtained by setting $\gamma_A = 0$ in equation (7b) and eliminating β by means of equation (7a):

$$\delta = l\pi/2\alpha \qquad , \qquad (13)^2$$

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[1]As $U \to \infty$, each zero approaches the $E_{\infty,n}$ which lies immediately above it. Thus the $E_{\infty,n}$ may be though of as the levels of an infinitely deep box with base at $-U$.

[2]In order to avoid extra notation we shall use the symbols α, β to denote either the functions of E defined in equations (4) or the special values of the functions corresponding to eigenvalues of E.

where ℓ is an even or odd integer according as the first or second factor of γ_A in equation (8a) vanishes. Substitution of equation (13) into equations (6) after setting $\gamma_A = 0$ in equation (6c) shows that the bound state eigenfunctions are alternately multiples of the even and odd functions

$$\begin{aligned} \varphi_{A1} &= \cos \alpha a \; e^{\beta(x+a)} \\ \varphi_{A2} &= \cos \alpha x \\ \varphi_{A3} &= \cos \alpha a \; e^{-\beta(x-a)} \end{aligned} \tag{14a}$$

and

$$\begin{aligned} \varphi_{A1} &= -\sin \alpha a \; e^{\beta(x+a)} \\ \varphi_{A2} &= \sin \alpha x \\ \varphi_{A3} &= \sin \alpha a \; e^{-\beta(x-a)} \end{aligned} \tag{14b}$$

according as the first or second factor of γ_A vanishes.

In both cases it may be shown that

$$\int_{-\infty}^{+\infty} \varphi_A^2 \, dx = a + 1/\beta \quad , \tag{15a}$$

which determines the normalizing factor. For later use we observe with the help of equation (8a) that for the even functions

$$\cos^2 \alpha a = \alpha^2/(\alpha^2+\beta^2) = \alpha^2/KU \quad , \tag{15b}$$

and for the odd functions

$$\sin^2 \alpha a = \alpha^2/(\alpha^2+\beta^2) = \alpha^2/KU \; . \tag{15c}$$

The eigenfunctions of problem A for the continuum of free energy states ($E > 0$) must also be found since we will require a complete set of eigenfunctions in applying perturbation theory. Setting

$$k = \sqrt{KE} \qquad > 0 \text{ for } E > 0, \tag{16}$$

we find that outside box A, φ no longer has the exponential form of expression (3) but that it has the oscillatory form $A\cos k(x+\delta)$. Thus the condition that φ shall be bounded at infinity is automatically fulfilled and we need impose only the four continuity conditions at the boundaries of the box. It is clear that equation (1) and the continuity conditions are satisfied for every $E > 0$ by the following linearly independent pair of functions φ_k^+ and φ_k^- of which the first is even and the second is odd:

$$\begin{aligned}
\varphi_{k1}^{\pm} &= \pm\frac{1}{\sqrt{\pi}}\cos k(x-\delta^{\pm}) \\
\varphi_{k2}^{+} &= \frac{1}{\sqrt{\pi}}\frac{\cos k(a+\delta^{+})}{\cos\alpha a}\cos\alpha x \\
\varphi_{k2}^{-} &= \frac{1}{\sqrt{\pi}}\frac{\cos k(a+\delta^{-})}{\sin\alpha a}\sin\alpha x \\
\varphi_{k3}^{\pm} &= \frac{1}{\sqrt{\pi}}\cos k(x+\delta^{\pm})
\end{aligned} \tag{17}$$,

where δ^+ and δ^- are determined by the equations

$$\begin{aligned}
k\tan k(a+\delta^{+}) &= \alpha\tan\alpha a \\
k\tan k(a+\delta^{-}) &= -\alpha\cot\alpha a
\end{aligned} \tag{18}$$,

and where α and k are defined in equations (4) and (16). Further, we obtain a complete set of eigenfunctions by including only the $\varphi_k^{\pm}$, since for given E , any three solutions of the second order differential equation (1) and the boundary conditions are linearly dependent.

The factor $1/\sqrt{\pi}$ in equations (17) has been chosen to make the $\varphi_k^{\pm}$ normalized to "delta-functions" (see Appendix A).

4. PROBLEM B, THE SINGLE-BOX B CASE

It is clear from the symmetrical way in which boxes A and B enter the problem that all the results derived in section 3 for problem A may be transformed into corresponding results for problem B by making the following substitutions:

$$\begin{aligned} a &\longrightarrow c \\ v &\longrightarrow \lambda v \\ \alpha &\longrightarrow \alpha' \\ x &\longrightarrow x-a-2b-c \\ \delta &\longrightarrow \delta' \\ \gamma_A &\longrightarrow \gamma_B \end{aligned},$$

and leaving all other quantities unchanged.

We shall denote by ϕ_B the bound-state eigenfunctions found in this way from equations (14).

5. PROBLEM C, IN WHICH THE TWO BOXES ARE FAR APART

We return now to the two-box problem and consider the case in which the distance $2b$ between the two boxes is large. For arbitrarily large b, $\bar{\epsilon}$ (see equation (10)) is correspondingly small. Hence the value of $\gamma_A\gamma_B$ is arbitrarily close to zero. It follows that every two-box level E is arbitrarily close to a level E_0 of problem A or B (a zero of γ_A or γ_B). Indeed, for sufficiently large b, every such E may be approximated by a solution of the equation

$$\left[\gamma_A(E_0)+(E-E_0)\gamma_A'(E_0)\right]\left[\gamma_B(E_0)+(E-E_0)\gamma_B'(E_0)\right]=\epsilon^2 , \quad (19)$$

where

$$\gamma_A' = \frac{d\gamma_A}{dE} \quad , \tag{20a}$$

$$\gamma_B' = \frac{d\gamma_B}{dE} \quad , \tag{20b}$$

$$\epsilon = \bar{\epsilon}(E_0) = e^{-2\sqrt{-KE_0}\, b} \quad . \tag{20c}$$

Two possible cases now present themselves. In the first case, which we shall call "non-degenerate", E_0 is a level of one single-box problem but not of the other. In the second case, which we shall call "degenerate", E_0 is a level of both single-box problems[1]. Since equation (9) is symmetric in γ_A and γ_B, we need only discuss those cases in which $E_0 = E_A$ is a level of problem A ($\gamma_A(E_A) = 0$).

In the non-degenerate case equation (19) becomes

$$E - E_A = \frac{2\epsilon^2/\gamma_A'}{\gamma_B^2 \pm \sqrt{\gamma_B^2 + 4\epsilon^2\gamma_B'/\gamma_A'}} \quad , \tag{21}$$

where the functions and derivatives are evaluated at $E = E_A$. The sign in the denominator must agree with the sign of γ_B in order that $\lim_{b\to\infty} E = E_A$. When b is so large that

$$\gamma_B^2 >> |4\epsilon^2\gamma_B'/\gamma_A'| \quad , \tag{22}$$

---

[1]In our special use of the word "degenerate" we refer to a case in which there is a simultaneous level of two different problems rather than one in which there is more than one linearly independent eigenfunction belonging to a single level of the same problem.

the approximation reduces to

$$E - E_A = \epsilon^2 / \gamma_A' \gamma_B \quad . \tag{23}$$[1]

In the degenerate case we merely set $\gamma_A = \gamma_B = 0$ in equation (19) and obtain

$$E - E_A = \pm \epsilon / \sqrt{\gamma_A' \gamma_B'} \tag{24}$$

The derivative $\gamma_A'(E_A)$ may be found by differentiating the expression (8a) using equations (4) and (5) and the fact that $\gamma_A(E_A) = 0$. The result is

$$\gamma_A'(E_A) = -K^2 U (1 + \beta a) / 2\alpha^2 \beta^2 \quad . \tag{25a}$$

Similarly for a level E_B of problem B,

$$\gamma_B'(E_B) = -K^2 \lambda U (1 + \beta c) / 2\alpha'^2 \beta^2 . \tag{25b}$$

The last two equations show that the derivatives γ_A' and γ_B' which appear in equations (23) and (24) are always negative. Hence the sign of $E - E_A$ in equation (23) is always opposite to that of $\gamma_B(E_A)$ and the right hand side of equation (24)

---

[1]Condition (22) ensures that E is much closer to E_A than to the nearest level E_B of problem B; i.e., there is no approximate degeneracy. Eliminating ϵ between equations (22) and (23), we have

$$|E - E_A| << |\gamma_B / 4\gamma_B'| \quad ,$$

so that even if E_B is so close to E_A that

$$\gamma_B(E_A) + (E_B - E_A)\gamma_B'(E_A) \approx \gamma_B(E_B) = 0 ,$$

and

$$\gamma_B / \gamma_B' \approx E_A - E_B \quad ,$$

we have

$$|E - E_A| << |E_B - E_A| / 4 \quad .$$

is always real.

Stated in words, equation (24) implies that any level which is common to both single-box problems (or to the two-box problem when the boxes are infinitely far apart) becomes split into two levels when the boxes are a large but finite distance apart. One of these levels lies above and the other lies below the original level, both by the same amount of order ϵ . On the other hand, equation (23) implies that each level which does not approach a level of problem B as $b \rightarrow \infty$, differs from the corresponding problem A level E_A only by an amount of order ϵ^2 , and lies above or below E_A in accordance with the following rule:

The level is "repelled" by the "closest" level of the other single-box problem, where we define the problem B level which is "closest" to E_A to be that level which is not separated from E_A by an $E_{\infty,n}$ of problem B (analagous to the $E_{\infty,n}$ of problem A given by equation (12)).

If the original level E_A lies "equally close" to two problem B levels (i.e., if it coincides with an $E_{\infty,n}$ of problem B), equation (23) shows that since $\gamma_B(E_{\infty,n}) = \infty$, the problem C level E coincides with E_A at least to terms of order ϵ^2 . Moreover, when we write the exact equation (9) in the form $\gamma_A = \bar{\epsilon}^2/\gamma_B$, it is clear that E coincides exactly with E_A , since $\gamma_A(E_A) = 0$.

The above results are illustrated by the sketched-in levels in Plate I, where the boxes should be farther apart than they are in the sketch. The lowest level lies below

E_{A0} since it is "repelled" by the higher level E_{B0}, and similarly the next lowest level lies below E_{B0} since it is "repelled" by E_{A1}. The third level coincides with E_{A1} since the latter coincides with $E_{\infty,1}$ of problem B. The highest levels lie above and below the coincident levels E_{A2} and E_{B1}.

Making use of equations (8) and (25) we rewrite equations (23) and (24) in explicit form in order to compare these results with those of perturbation theory. Thus for degenerate levels we have:

$$E - E_A = \pm \frac{2\epsilon\alpha\alpha'\beta^2}{K^2 U\sqrt{\lambda(1+\beta a)(1+\beta c)}} , \qquad (26a)$$

and for non-degenerate levels:

$$E - E_A = -\frac{2\epsilon^2\lambda\alpha^2\beta^2}{KU(1+\beta a)(\beta^2-\alpha^2+2\alpha'\beta\cot 2\alpha' c)} . \qquad (26b)$$

We shall now discuss the eigenfunctions of problem C. Again we need only discuss those cases in which the problem C level E lies close to a problem A level E_A. In these cases the values of S determined by equations (7a) and (7b) differ little from those given by expression (13), and the first three of equations (6) differ little from equations (14). Thus in the neighborhood of the box to which the unperturbed level belongs, the two-box eigenfunction differs little from the corresponding single-box eigenfunction.

To determine the nature of the perturbed eigenfunction near box B we find the ratio $|B/A|$ of the amplitudes of the oscillatory parts of the eigenfunctions inside the two boxes. First we equate expressions (6c) and (6d) at $x=a$ and eliminate ϵ by means of equation (9); then we simplify by means of equations (5), (7), and (8) to give:

$$|B/A| = \sqrt{\frac{\gamma_A}{\gamma_B}}\left|\frac{(1+\gamma_A)\cos\alpha(a+\delta)}{(1+\gamma_A)\cos\alpha'(c+\delta')}\right| = \sqrt{\frac{\gamma_A}{\lambda\gamma_B}}\left|\frac{\sin\alpha a}{\sin\alpha' c}\right| . \quad (27)$$

In the non-degenerate case we may use equation (9) to give

$$\gamma_A \approx \epsilon^2/\gamma_B$$

so that

$$|B/A| \approx \frac{\epsilon}{\sqrt{\lambda}|\gamma_B|}\left|\frac{\sin\alpha a}{\sin\alpha' c}\right| , \quad (28)$$

which shows that the ratio of amplitudes of the eigenfunction in the regions of boxes B and A is of order ϵ and hence the chance of finding the particle near box B is of order ϵ^2 compared to the chance of finding it near box A.

In our solution of problem C by perturbation theory, we shall take the problem A eigenfunction ϕ_A to be the unperturbed eigenfunction corresponding to the perturbed eigenfunction ϕ belonging to the problem C level E . It is clear from equations (14) and (28) that both ϕ and ϕ_A are of order ϵ near box B. Thus the difference $\phi-\phi_A$ between the perturbed and unperturbed wave-function is of the same order of size as the unperturbed wave-function itself; a fact which will be very troublesome in our application of perturbation theory.

In the degenerate case we obtain with the help of equation (24):

$$\gamma_A \approx (E-E_A)\gamma_A'(E_A) \approx \pm\epsilon\sqrt{\gamma_A'/\gamma_B'} . \quad (29a)$$

and similarly:

$$\gamma_B \approx \pm \epsilon \sqrt{\gamma_B'/\gamma_A'} \quad . \tag{29b}$$

Further, since expressions (8) are almost zero, we obtain with the help of equations (5):

$$|\sin 2\alpha a| \approx 2\alpha\beta/\kappa V , \quad |\sin 2\alpha' C| \approx 2\alpha'\beta/\kappa\lambda V \tag{30}$$

Substituting equations (29) and (30) into equation (27) and then substituting (25) into the result, we obtain finally:

$$|B/A| \approx \sqrt{\frac{1+\beta a}{1+\beta c}} \quad , \tag{31}$$

which directly shows that in the degenerate case the ratio of amplitudes of the problem C eigenfunction in the regions of the two boxes is of order unity, irrespectively of how far apart the boxes are or of how small the function becomes in the region between the boxes.

It is clear from previous arguments that if φ_A and φ_B are the problem A and problem B eigenfunctions (given by equations (14) and their analogues for problem B) which belong to E_A , the eigenfunctions φ belonging to the two problem C levels which are close to E_A must both be approximated by constant multiples of φ_A and φ_B near the appropriate boxes. Thus equation (31) tells us that apart from an arbitrary multiplicative constant, each φ must approximate the normalized single-box eigenfunctions near the corresponding boxes:

$$\varphi \approx \varphi_A \big/ \sqrt{a + 1/\beta} \qquad \text{near box A,} \tag{32a}$$

and

$$\varphi \approx \varphi_B \big/ \sqrt{c + 1/\beta} \qquad \text{near box B.} \tag{32b}$$

But since ϕ_A and ϕ_B are of order ϵ near their opposite boxes, it is clear from these equations that ϕ may be approximated everywhere by the sum or difference of the normalized ϕ_A and ϕ_B :

$$\phi \approx \phi_A/\sqrt{a+1/\beta} \pm \phi_B/\sqrt{c+1/\beta} \quad . \tag{32c}$$

Finally the ratio P_A/P_B of the probability of finding the particle near box A to that of finding it near box B may be approximated by means of equations (15a), (32a), and (32b). We find:

$$\frac{P_A}{P_B} \approx \left(\frac{\int_{-\infty}^{+\infty} \phi_A^2 dx}{a+1/\beta}\right) \Bigg/ \left(\frac{\int_{-\infty}^{+\infty} \phi_B^2 dx}{c+1/\beta}\right) = 1 \quad . \tag{33}$$

6. PROBLEM D, IN WHICH ONE BOX IS SHALLOW

In problem D, where we suppose that λ is small (box B is shallow) and b is arbitrary, we obtain an explicit approximate expression for the eigenvalues by considering the fact that equation (9) defines E as a many-valued function of λ . It is clear that for every level E_A of problem A, there is a branch of this function which approaches E_A as $\lambda \to 0$. But each of these branches may be expanded in a series of the form

$$E = E_A + \lambda\left(\frac{dE}{d\lambda}\right)_{\substack{\lambda=0\\E=E_A}} + \frac{\lambda^2}{2}\left(\frac{d^2E}{d\lambda^2}\right)_{\substack{\lambda=0\\E=E_A}} + \cdots , \tag{34}$$

which implies that $E - E_A$ may be determined to any order of accuracy in λ , provided λ is sufficiently small. The range of application of these series will be discussed later (see Part IV).

The coefficients of λ and λ^2 in the above expansion have been determined from equation (9) by partial differentiation (see Appendix B) in order to compare the direct result of equation (34) with that of perturbation theory. They are:

$$E_1 = \left(\frac{dE}{d\lambda}\right)_{\substack{\lambda=0\\ E=E_A}} = \epsilon^2\alpha^2\left(e^{-4\beta c}-1\right)/2K(1+\beta a) \tag{35a}$$

and

$$E_2 = \frac{1}{2}\left(\frac{d^2E}{d\lambda^2}\right)_{\substack{E=E_A\\ \lambda=0}} = \epsilon^2\alpha^2 U\left[(1+4\beta c)e^{-4\beta c}-1\right]/4\beta^2(1+\beta a) \tag{35b}$$
$$+ E_1^2\left[\left(\frac{d\epsilon^2}{dE}\right)/\epsilon^2 - \gamma_B'/\gamma_B - \gamma_A''/2\gamma_A'\right]_{\substack{E=E_A\\ \lambda=0}}$$

where E_1 denotes expression (35a), the primes denote differentiation with respect to E, and all the functions are evaluated at $E = E_A$.

III. PERTURBATION THEORY SOLUTION

1. STANDARD PERTURBATION THEORY TREATMENT OF PROBLEM D

In solving problem D we shall make use of the results of the usual kind of perturbation theory which is found in most books on quantum mechanics[1]. In order to apply the standard theory, the perturbation of the Hamiltonian operator must be expressible as a power series in some parameter such that the perturbation vanishes when the parameter is zero.

Let $V_A(x)$ and $V_B(x)$ be the potential functions of problems A and B respectively:

$$V_A(x) = \begin{cases} -U & \text{for } |x| < a \\ 0 & \text{for } |x| > a \end{cases}, \tag{36a}$$

$$V_B(x) = \lambda \overline{V}_B(x) \tag{36b}$$

where

$$\overline{V}_B(x) = \begin{cases} -U & \text{for } |x-a-2b-c| < c \\ 0 & \text{for } |x-a-2b-c| > c \end{cases}. \tag{36c}$$

---

[1] Although most texts do not consider the case in which the unperturbed problem has a continuous spectrum, their discussions may easily be generalized with the help of equations (81) and (82) of Appendix A, to give the results stated in equations (43)-(45).

Application of the theory to our problem is simplified by the fact that the bound states are not degenerate, that all the eigenfunctions considered are real, and that the perturbation operator is simply proportional to the expansion parameter (see equation (36b)).

Let $H_A(x)$, $H_B(x)$, and $H(x)$ be the Hamiltonian operators of problems A, B, and D respectively:

$$H_A = -\frac{1}{K}\frac{d^2}{dx^2} + V_A \quad , \tag{37a}$$

$$H_B = -\frac{1}{K}\frac{d^2}{dx^2} + V_B \quad , \tag{37b}$$

$$H = -\frac{1}{K}\frac{d^2}{dx^2} + V_A + V_B \quad , \tag{37c}$$

so that clearly

$$H = H_A + V_B \quad . \tag{38}$$

In view of equations (38) and (36b) and the fact that λ is small for problem D, it is clear that we may take problem A as the unperturbed problem, V_B as the perturbing operator, and λ as the expansion parameter. Accordingly, we suppose that if box B is sufficiently shallow (λ is sufficiently small), there is a normalized bound-state eigenfunction φ of problem C corresponding to each normalized bound-state eigenfunction

$$\varphi_0 = \varphi_A / \sqrt{a + 1/\beta} \tag{39}$$

of problem A belonging to the eigenvalue $E_0 = E_A$, such that φ and the eigenvalue E to which it belongs are expressible as power series in λ of the form

$$\varphi = \varphi_0 + \lambda\varphi_1 + \lambda^2\varphi_2 + - - - \quad , \tag{40}$$

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + - - - \quad . \tag{41}$$

We find the coefficients of these series from standard perturbation theory, expressed in terms of "matrix elements" of the form

$$\bar{V}_{pq} = \int_{-\infty}^{+\infty} \varphi_p \varphi_q \bar{V}_a \, dx = -U \int_{a+2b}^{a+2b+2c} \varphi_p \varphi_q \, dx \; ; \; p,q = \beta, \beta', \overset{+}{k}, \text{or } \overset{-}{k} . \quad (42)$$

Thus,

$$E_1 = \bar{V}_{\beta\beta} \quad , \quad (43)$$

$$\varphi_1 = \sum_{\beta'} \frac{\bar{V}_{\beta\beta'} \varphi_{\beta'}}{E_\beta - E_{\beta'}} + \int_0^\infty \frac{\bar{V}_{\beta\overset{+}{k}} \varphi_{\overset{+}{k}} + \bar{V}_{\beta\overset{-}{k}} \varphi_{\overset{-}{k}}}{E_\beta - E_k} \, dk \quad , \quad (44)$$

$$E_2 = \sum_{\beta'} \frac{\bar{V}_{\beta\beta'}^2}{E_\beta - E_{\beta'}} + \int_0^\infty \frac{\bar{V}_{\beta\overset{+}{k}}^2 + \bar{V}_{\beta\overset{-}{k}}^2}{E_\beta - E_k} \, dk \quad , \quad (45)$$

where the summations are over all the bound states of the unperturbed problem whose eigenvalues $E_{\beta'}$ differ from E_β .

The values of E_1 and E_2 are calculated in Appendix C. The calculation of E_1 is a straightforward integration. In calculating E_2 , the range of integration in equation (45) is first extended from $-\infty$ to $+\infty$, and then contour integration is employed. Investigation of the poles of the integrand shows that there are terms from the integral which exactly cancel out the terms of the summation, and the balance of the integral involves only the constants α and β of the level E_β . Thus it is shown that the results of perturbation theory agree exactly with the directly obtained results of equations (35).

2. SPECIAL PERTURBATION THEORY TREATMENT OF PROBLEM C

When the distance $2b$ between the boxes is infinite, $V(x)$ reduces to $V_A(x)$ for all finite x , and problem C reduces to problem A. If, however, we had initially chosen the origin of the x coordinate at the centre of box B, the two-box problem would have reduced to problem B when $b = \infty$. Accordingly we assume that as $b \to \infty$, every eigenvalue E approaches an eigenvalue E_0 of problem A or B. Further, if E_0 is a "non-degenerate" single-box level, say of problem A, we assume that the normalized eigenfunction φ belonging to E has the form

$$\varphi(x,b) \cong \varphi_\beta(x) + \psi(x,b) \quad , \tag{46}$$

where φ_β is the normalized problem A eigenfunction belonging to $E_0 = E_\beta$, and $\psi(x,b)$ is a function whose maximum numerical value approaches zero as $b \to \infty$ (i.e., ψ approaches zero uniformly in x as $b \to \infty$). On the other hand, if E_0 is a "degenerate" single-box level, we assume that

$$\varphi(x,b) \cong A\varphi_A(x) + B\varphi_B(x,b) + \psi(x,b) \quad , \tag{47}$$

where $A\varphi_A + B\varphi_B$ is a linear combination of the problem A and problem B eigenfunctions belonging to E_0, and ψ approaches zero uniformly as $b \to \infty$.

We may now use perturbation theory to solve problem C approximately if we assume that for every single-box eigenvalue $E_0 = E_\beta$ (say of problem A), there is an eigenvalue E of problem C which is expressible as a power series in the parameter ϵ (defined in equation (20)) of the form

$$E = E_\beta + \epsilon E_1 + \epsilon^2 E_2 + \cdots \quad . \tag{48}$$

If E_0 is a "non-degenerate" level we may substitute equations (46) and (48) into the Schrödinger equation for problem C to obtain:

$$(H_A + V_B)(\varphi_0 + \psi) \equiv (E_0 + \epsilon E_1 + \epsilon^2 E_2 + \cdots)(\varphi_0 + \psi), \qquad (49)$$

in which we may regard V_B as a perturbing operator, ψ as the perturbation of the wavefunction, and $(\epsilon E_1 + \epsilon^2 E_2 + \cdots)$ as the perturbation of the energy level.

In this problem, however, we cannot employ standard perturbation theory, for although the perturbing operator $V_B(x,\epsilon)$ vanishes when the expansion parameter $\epsilon = 0$, it is not expressible as a power series in ϵ. Moreover, the function ψ need not be expressible as a power series in ϵ. We need only assume that the function

$$\bar{\psi} = \psi/\epsilon \qquad (50)$$

is bounded as $\epsilon \longrightarrow 0$.

Rewriting the identity (49) with the help of

$$H_A \varphi_0 \equiv E_0 \varphi_0 \quad ,$$

we find that

$$(\epsilon E_1 + \epsilon^2 E_2 + \cdots)(\varphi_0 + \psi) \equiv (H_A - E_0)\psi + V_B(\varphi_0 + \psi). \quad (51)$$

Multiplying both sides of this identity by φ_0, integrating over all x, and dividing by ϵ, we obtain the identity in ϵ:

$$(E_1 + \epsilon E_2 + \cdots)\int_{-\infty}^{+\infty} \varphi_0(\varphi_0 + \psi)\,dx \equiv \epsilon^{-1}\int_{-\infty}^{+\infty} \varphi_0 V_B(\varphi_0 + \psi)\,dx \;. \qquad (52a)$$

Since φ_0 and ψ are of order ϵ (or less) near box B (see equations (14) and (50)), and E_1 is independent of ϵ, we find on taking limits as $\epsilon \longrightarrow 0$ that the first order correction E_1 vanishes:

$$E_1 = 0 \quad . \tag{52b}$$

In order to determine E_2, we set $E_1 = 0$ in equation (52a) and divide again by ϵ. We find that as $\epsilon \longrightarrow 0$,

$$\epsilon^{-2} \int_{-\infty}^{+\infty} V_\beta \varphi_\beta (\varphi_\beta + \Psi) \longrightarrow E_2 \quad . \tag{53}$$

Now $\bar{\Psi}$ may be expressed in terms of the unperturbed eigenfunctions in the form (see Appendix A):

$$\bar{\Psi} = \sum_{\text{all } \beta'} q_{\beta'} \varphi_{\beta'} + \int_0^\infty (q_{\bar{k}}^+ \varphi_{\bar{k}}^+ + q_{\bar{k}}^- \varphi_{\bar{k}}^-) \, dk \quad . \tag{54}$$

Thus we find on substitution of equations (50) and (54) into equation (53), that in a notation similar to that of equation (42) above:

$$\epsilon^{-2} V_{\beta\beta} + \epsilon^{-1} \int_0^\infty (q_{\bar{k}}^+ V_{\bar{k}\beta}^+ + q_{\bar{k}}^- V_{\bar{k}\beta}^-) \, dk \longrightarrow E_2 , \tag{55}$$

where a vanishing term of the form $\epsilon^{-1} \sum q_{\beta'} V_{\beta'\beta}$ has been neglected.

In order to obtain an explicit expression for E_2, we would have to find explicit expressions for the $q_{\bar{k}}^{\pm}$. We attempt to find the asymptotic values of the $q_{\bar{k}}^{\pm}$ by substituting equation (54) into equation (51), setting $E_1 = 0$, multiplying by $\varphi_{\bar{k}}^{\pm}$, integrating over all x, dividing by ϵ, and using equation (81) of Appendix A. We find then, that

$$(E_\beta - E_k) q_{\bar{k}}^{\pm} \longrightarrow \epsilon^{-1} V_{\bar{k}\beta}^{\pm} + \int_0^\infty (q_{\bar{k}'}^+ V_{\bar{k}'\bar{k}}^{+\pm} + q_{\bar{k}'}^- V_{\bar{k}'\bar{k}}^{-\pm}) \, dk' \quad . \tag{57}$$

Thus the $q_k^\pm$ approach the solutions of a pair of simultaneous integral equations, which we have been unable to solve exactly.

We may check the validity of our result by finding the first two coefficients of the expansions of the $q_k^\pm$ in powers of λ :

$$q_k^\pm = q_{k0}^\pm + \lambda q_{k1}^\pm + \lambda^2 q_{k2}^\pm + --- . \tag{58}$$

Substituting equations (58) and (36b) into the relationship (57), and equating the first two powers of λ on either side, we obtain in the notation of equation (42):

$$q_{k0}^\pm \longrightarrow 0 , \tag{59a}$$

$$(E_\rho - E_k) q_{k1}^\pm \longrightarrow \epsilon^{-1} \overline{V}_{k\rho}^\pm . \tag{59b}$$

Equations (36b), (55), (58) and (59) now tell us that to the second order in λ :

$$E_z \approx \lambda \overline{V}_{\rho\rho} + \lambda^2 \lim_{\epsilon \to 0} \int_0^\infty \frac{(\overline{V}_{k\rho}^+/\epsilon)^2 + (\overline{V}_{k\rho}^-/\epsilon)^2}{E_\rho - E_k} dk . \tag{60}$$

Comparing this result with equations given in Appendix C, we find our result to be in agreement with that of the last section.

In the special but important case that E_0 is a degenerate single-box level, we are rewarded with greater success. Substituting equations (47) and (48) into the Schrödinger equation for problem C, we find:

$$H(A\phi_A + B\phi_B + \psi) \equiv (E_0 + \epsilon E_1 + ---)(A\phi_A + B\phi_B + \psi) . \tag{61}$$

Substituting $H_A + V_B$ for H , multiplying by ϕ_A , integrating over all x , dividing by ϵ , and taking limits as

$\epsilon \longrightarrow 0$, we obtain:

$$B\,\epsilon^{-1}\int_{-\infty}^{+\infty}\varphi_A\varphi_B V_B\,dx - A\,E_1\int_{-\infty}^{+\infty}\varphi_A^2\,dx = 0 \quad . \tag{62a}$$

Similarly, using $H_B + V_A$ for H, and multiplying by φ_B, we obtain:

$$A\,\epsilon^{-1}\int_{-\infty}^{+\infty}\varphi_A\varphi_B V_A\,dx - B\,E_1\int_{-\infty}^{+\infty}\varphi_B^2\,dx = 0 \quad . \tag{62b}$$

But from equations (14), (15b), (15c) and their analogues for problem B, we find that

$$\int_{-\infty}^{+\infty}\varphi_A\varphi_B V_A\,dx = \int_{-\infty}^{+\infty}\varphi_A\varphi_B V_B\,dx = \pm 2\alpha\alpha'\beta\epsilon/K U\sqrt{\lambda} \quad . \tag{63}$$

Accordingly, with equation (15a) and its analogue, the condition for simultaneous solutions of equations (62) takes the form

$$\begin{vmatrix} -(a+1/\beta)E_1 \,, & \pm 2\alpha\alpha'\beta/K^2U\sqrt{\lambda} \\ \pm 2\alpha\alpha'\beta/K^2U\sqrt{\lambda}\,, & -(c+1/\beta)E_1 \end{vmatrix} = 0 \quad , \tag{62}$$

which yields two possible solutions for E_1 :

$$E_1 = \pm\frac{2\alpha\alpha'\beta^2}{K^2U\sqrt{\lambda}\,(1+\beta a)(1+\beta c)} \quad . \tag{65}$$

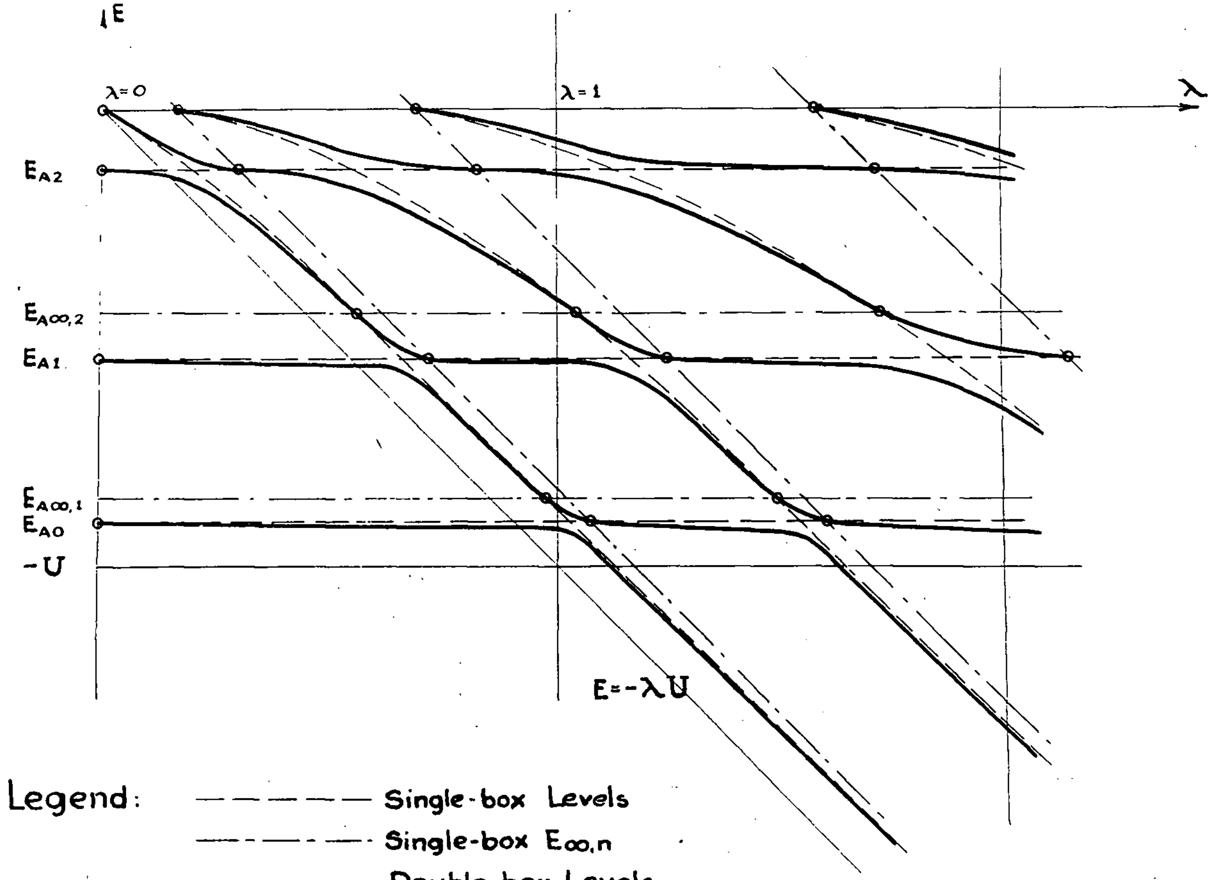
This result agrees exactly with equation (26a).

Finally we obtain from equations (62), (63), and (65), the ratio

$$\left|\frac{B}{A}\right| = \sqrt{\frac{1+\beta a}{1+\beta c}} \quad . \tag{67}$$

which agrees with equation (31). It is clear that we could also derive equation (33) from our perturbation theory results, using the same arguments as before.

PLATE III — The Eigenvalues of Problem C as a function of λ

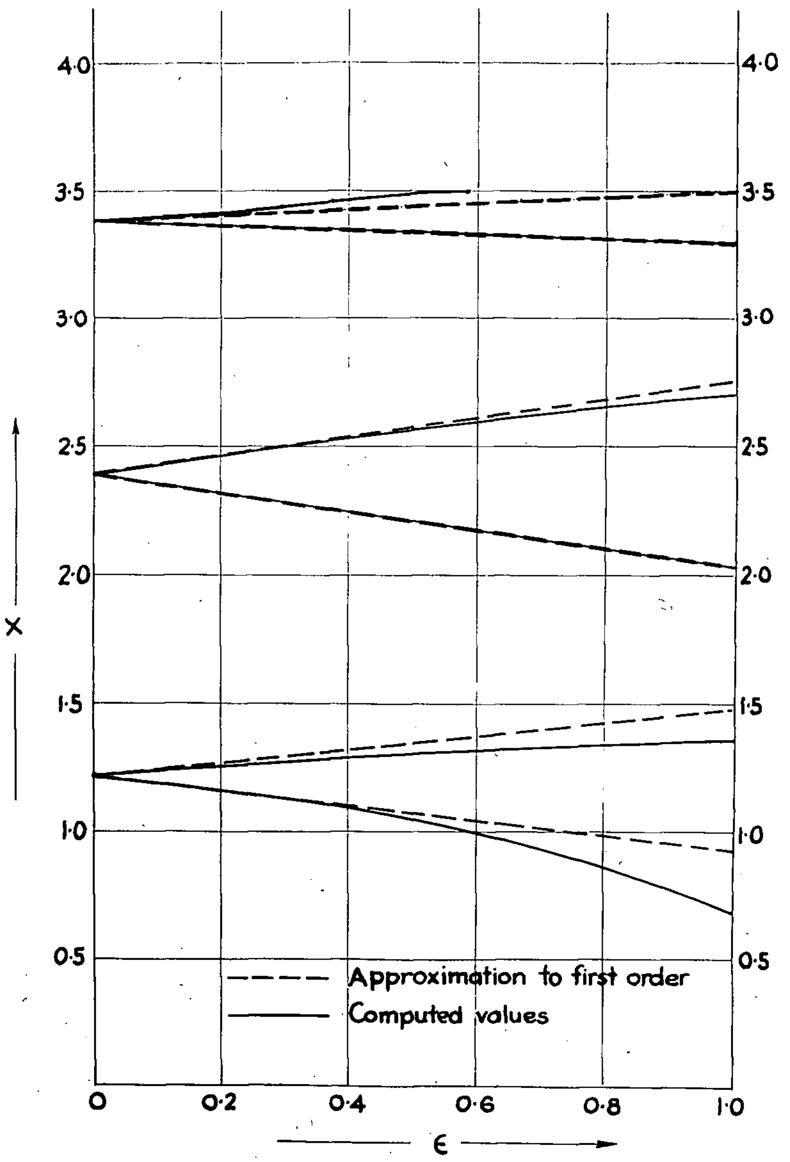


IV. DISCUSSION

The directly obtained results for the eigenvalues of the two-box problem are illustrated in Plates III and IV. Plate III is a sketch of the eigenvalues ϵ as a many-valued function of λ for the case in which problem A has three levels ϵ_{A0} , ϵ_{A1} , and ϵ_{A2} , and box B is slightly narrower than box A. The horizontal dashed lines represent the problem A eigenvalues, while the sloping dashed lines represent the problem B eigenvalues. Similarly the dot-dashed lines represent the infinities $\epsilon_{\infty,n}$ of γ_A and γ_B . The heavy lines represent the two-box levels themselves. In accordance with equation (9), it is clear that if b is not infinite ($\bar{\epsilon}$ is not zero), γ_A is zero if and only if γ_B is infinite, and vice versa. Accordingly the heavy curves must cross the discontinuous curves at the encircled points, which mark the intersections of the single-box levels with the $\epsilon_{\infty,n}$, and can cross the discontinuous curves only at these points.

The approximate results obtained by both direct and perturbation theory methods for problem C, in which b is large, are illustrated by the fact that in this case the heavy curves closely follow the dashed curves. In accordance with equations (23) and (24), and equations (52b) and

PLATE IV $X = \alpha a$ as a function of ϵ for the case in which $a\sqrt{KU} = 3{\cdot}5$, showing the approximations to the first order in ϵ.



(65), the heavy curves lie farther (at distances of order ϵ) from the nearest dashed curves near the points of intersection of two dashed curves (the points where "degenerate" single-box levels occur), than at other points (where the distances from the dashed curves are of order ϵ^2).

The approximate results obtained by the two methods for problem D, in which λ is small, are illustrated by the behaviour of the three curves which follow E_{A0} , E_{A1} , and E_{A2} before their first turning points. It is clear that when b is large, the curves turn so sharply that the series (34) and (41) cannot be expected to be valid beyond the first turning point of each curve, and certainly the approximations given by the first two terms of the series will not be valid beyond these points. Further, since the coefficients of the series depend upon b , and the curves must pass through the encircled points regardless of the value of b , it is clear that the series can never be valid beyond the first encircled point of each curve, and that the approximations to the second order in λ can never be trusted beyond the first turning points.

Plate IV shows the behaviour of the levels of a two-box problem in which both boxes are identical ($\lambda = 1$ and $c = a$), as functions of ϵ , and thereby illustrates the results of equations (26a) and (65). In order to show numerical results, the dimensionless constant $\sqrt{a^2 KU}$ is given the value $3 \cdot 5$, and the dimensionless quantity $x = \alpha a = \sqrt{a^2 K(E+U)}$ is used instead of E .

The continuous curves represent the exact values of x. In accordance with equations (4), (9), and (20c), each continuous curve has an equation of the form

$$\left|\frac{x^2 - y^2 - 2xy\cot 2x}{12\cdot 25}\right|^{\frac{y_0}{y}} = \epsilon \quad , \tag{68a}$$

where

$$y = \beta a = \sqrt{12\cdot 25 - x^2} \quad , \tag{68b}$$

and y_0 is the value of y at one of the single-box levels (where $\epsilon = 0$).

The dashed curves represent the approximations to the exact curves in accordance with equations (26a) and (65), and the approximation

$$\Delta\alpha \approx \frac{K\Delta\dot{E}}{2\alpha} \quad , \tag{69}$$

obtained from equation (4a).

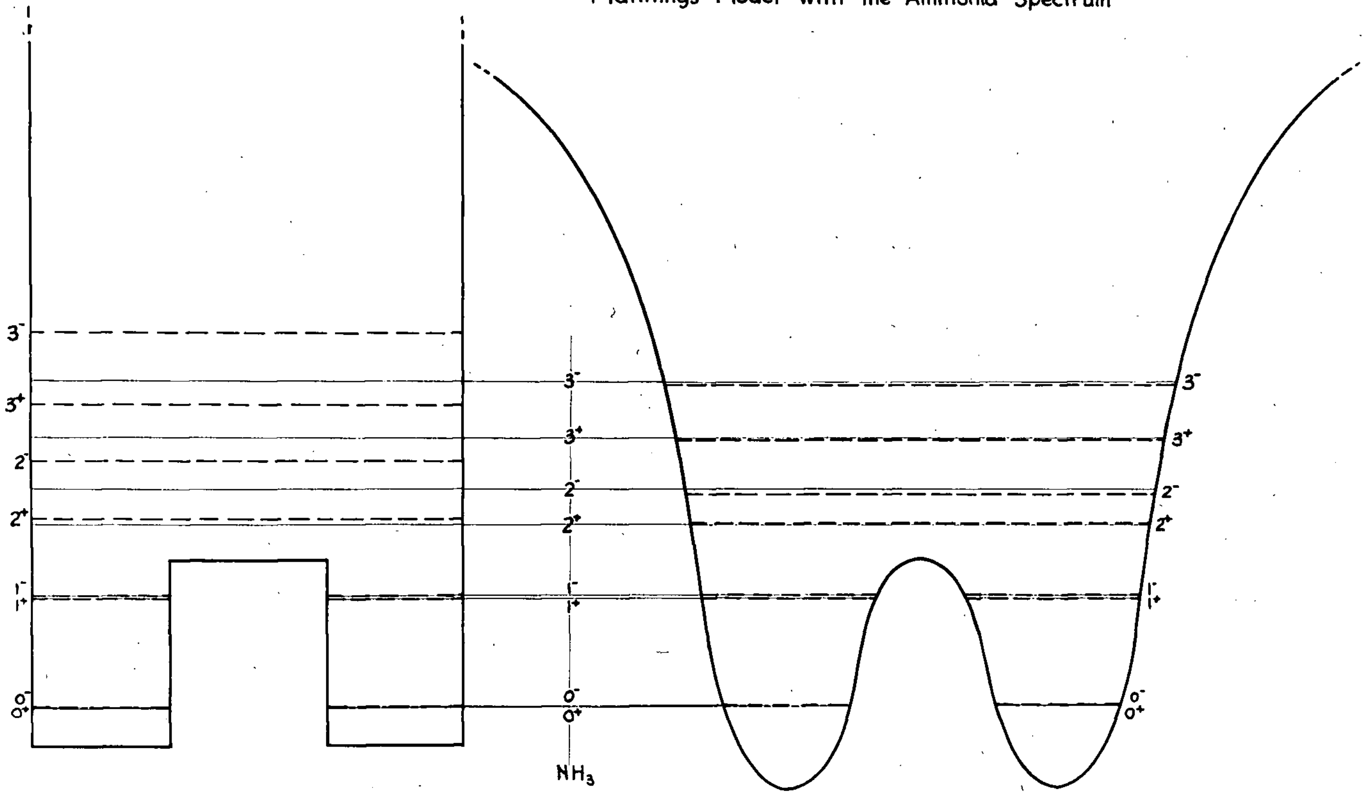
The range of applicability of the approximation for the lower levels is surprisingly large. For the lowest level, for instance, the approximation is valid from $\epsilon = 0$ to $\epsilon \approx 0\cdot 4$. The value of y_0 for this curve is $\approx 3\cdot 3$, and hence we find from equation (20c), that the value of b/a for the point of departure is

$$b/a = -\frac{\log \epsilon}{2y_0} \approx 0\cdot 14 \quad ; \tag{70}$$

that is, the approximation is valid for values of b between infinity and $0\cdot 14a$!

PLATE V

Comparison of the Square Well Model and Manning's Model with the Ammonia Spectrum



V. APPLICATION OF THE MODEL TO THE AMMONIA INVERSION SPECTRUM

In order to illustrate the value of the two-box problem as a prototype model for a physical system, we shall use it to calculate some of the constants of the ammonia molecule. Many authors[1] have pointed out that the motion of the NH_3 molecule which contributes to the inversion spectrum is that in which the nitrogen atom moves back and forth through the triangle formed by the three hydrogen atoms. There is an equilibrium position for the nitrogen atom on either side of the triangle, and a potential barrier with a maximum in the plane of the triangle which the nitrogen atom must traverse.

It has been shown[2] that although the molecule is three dimensional, the method of normal coordinates may be used, and hence the levels of the inversion spectrum closely approximate the levels of a one-dimensional two-minimum problem. Many authors have used this fact to estimate some constants of the ammonia molecule. Manning[3], for instance, assumed a potential function similar to that shown on the right-hand side of Plate V, and by assuming a reduced mass

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[1] G. Herzberg, "Infrared and Raman Spectra", (Van Nostrand), pp. 221 to 224, and references given there.

[2] N. Rosen and P.M. Morse, Phys.Rev.42, 210, (1932).

[3] M.F. Manning, Jour.of Chem.Phys. 3, 136, (1935).

$\mu = 4.60 \times 10^{-24}$ gm, and fitting the lowest three levels of his model to those found from the ammonia spectrum, he determined the "equilibrium height of the NH_3 pyramid" (half the separation of the minima), the height of the "potential hump" between the minima, and the asymptotic value of the potential function at large distances from the minima. He then calculated some of the higher levels and found them to be in good agreement with those of ammonia.

In our calculations we first assume a two-box potential function of the type discussed above, in which both boxes are identical. Then, by using the same reduced mass and making the same fit as Manning, we determine the constants, a, b, and U. Our numerical method is first to use graphical methods to determine the values of $X = \alpha a$ and $Y = \beta a$ for the two lowest levels of the single-box problem for various values of $M = a^2 K U$. Then, assuming the approximation (26a) to be valid, we notice that if ΔE is the splitting of one of these levels when the boxes are a distance $2b$ apart, then

$$\epsilon = \frac{(\Delta E/2) K^2 U (1 + \beta a)}{2 \alpha^2 \beta^2}, \qquad (71)$$

or

$$\epsilon = \frac{\alpha^2 K \Delta E (1 + Y)}{4 X^2 Y^2}. \qquad (72)$$

But if X_0 and X_1 are the values of X for the first two single-box levels, we have

$$X_1^2 - X_0^2 = a^2 K (E_1 - E_0), \qquad (73)$$

and hence

$$\epsilon = \frac{\Delta E}{E_1 - E_0} \cdot \frac{M(x_1^2 - x_0^2)(1+y)}{4x^2y^2} \qquad (74)$$

Thus, by using the ratios $\Delta E/(E_1 - E_0)$ as found from the lowest two ammonia levels, we calculate ϵ for each level, and then find the two corresponding values of

$$\frac{b}{a} = -\frac{\log \epsilon}{2y} \qquad (75)$$

By trying different M's and interpolating, we find one for which the two ratios b/a are equal. Finally, using this M and the assumed μ, we calculate a, b, and U.

We find that our value for the "equilibrium height of the NH_3 pyramid" ($a+b$) agrees very well with Manning's, and that our value for the height of the "potential hump" agrees fairly well; but we find no higher bound-levels. Therefore we next assume a potential function, as shown on the left-hand side of Plate V. After finding the necessary equations for this problem, and making numerical calculations similar to those of the last paragraph, we go on to calculate higher levels.

The results of our calculations are shown in the following table and are illustrated in Plate V.

Levels
(cm^{-1})

	Manning	Square Well	NH_3
0^+ 0^-	0 0.83	0 0.83	0 0.66
1^+ 1^-	935 961	936 961	932.4 968.1
2^+ 2^-	1610 1870	1640 2170	1597.5 1910
3^+ 3^-	2360 2840	2650 3290	2380 2861

Shapes of Potential Functions

	Manning	Square Wells	Square Wells With Infinite Sides
Widths of Boxes (2a)	-	0.28 Å	0.36 Å
Separation of Boxes (2b)	-	0.44 Å	0.41 Å
Equilibrium Height of Pyramid	0.37 Å	0.36 Å	0.38 Å
Height of Potential Hump	2071 cm^{-1}	1640 cm^{-1}	1650 cm^{-1}
$V(\infty)$	45100 cm^{-1}	1640 cm^{-1}	∞

APPENDIX A. NORMALIZATION OF THE EIGENFUNCTIONS OF THE CONTINUUM

It is well known that we may choose normalized problem A eigenfunctions φ_β and $\varphi_k^\pm$ (equations (14), (15) and (17)) such that a large class of functions $f(x)$ may be expressed in the form

$$f(x) = \sum_\beta g_\beta \varphi_\beta(x) + \int_0^\infty (g_k^+ \varphi_k^+(x) + g_k^- \varphi_k^-(x))\,dk\,, \quad (76)^1$$

where the g_β and $g_k^\pm$ are functions of β and k given by:

$$g_\beta = \int_{-\infty}^{+\infty} f(x)\varphi_\beta(x)\,dx \qquad , \qquad (77a)$$

$$g_k^\pm = \int_{-\infty}^{+\infty} f(x)\varphi_k^\pm(x)\,dx \qquad . \qquad (77b)$$

Conversely, if arbitrary functions g_β and $g_k^\pm$ are chosen to define a function $f(x)$ by means of equation (76), then equations (77) necessarily hold. Substituting equation (76) into equation (77b), we obtain for arbitrary g_β , g_k^+ , and g_k^- ,

$$g_k^\pm = \int_{-\infty}^{+\infty} \varphi_k^\pm \left\{ \sum_\beta \varphi_\beta g_\beta + \int_0^\infty (g_{k'}^+ \varphi_{k'}^+ + g_{k'}^- \varphi_{k'}^-)dk' \right\} dx \,. \quad (78)$$

But since $\varphi_\beta \varphi_k^\pm$ vanishes at $x = \pm\infty$, we know from the orthogonality theorem for eigenfunctions that

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[1]For example, E.C. Kemble, "Fundamental Principles of Quantum Mechanics", Ch. VI, where the integration is carried out over E rather than k .

$$\int_{-\infty}^{+\infty} \varphi_k^{\pm} \varphi_b \, dx = 0 \quad , \tag{79}$$

and hence equation (78) may be written

$$q_k^{\pm} = \int_{-\infty}^{+\infty} \varphi_k^{\pm} \int_0^{\infty} (q_{k'}^{\pm} \varphi_{k'}^{\pm} + q_{k'}^{\mp} \varphi_{k'}^{\mp}) \, dk' \, dx \quad . \tag{80}$$

Further, since φ_k^{+} and φ_k^{-} are respectively even and odd functions of x, it follows that for arbitrary $g(k')$,

$$\int_{-\infty}^{+\infty} \varphi_k^{\pm} \int_0^{\infty} \varphi_{k'}^{\mp} g(k') \, dk' \, dx = 0 \tag{81}$$

Therefore, since the $q_k^{\pm}$ are arbitrary functions, equation (80) implies that

$$\int_{-\infty}^{+\infty} \varphi_k^{\pm} \int_0^{\infty} \varphi_{k'}^{\pm} g(k') \, dk' \, dx = g(k) \quad , \tag{82}$$

which in turn implies that in the symbolism of delta-functions,

$$\int_{-\infty}^{+\infty} \varphi_k^{\pm} \varphi_{k'}^{\pm} \, dx = \delta(k - k') \quad . \tag{83}$$

Knowing that equation (82) holds for suitably normalized $\varphi_k^{\pm}$, we may start with unnormalized functions, say

$$\varphi_k^{\pm} = \cos k(x + \delta^{\pm}) \qquad \text{for} \qquad x > a \tag{84}$$

and derive the normalizing factors as follows:

Choose a particular $k > 0$, and a number Δ such that $0 < \Delta < k$. Let $f(k')$ be defined by the equations

$$f(k') = \begin{cases} 0 & \text{for} \quad |k' - k| > \Delta \\ 1 & \text{for} \quad |k' - k| < \Delta \end{cases} \tag{85}$$

Then, if $C_k^{\pm}$ is the normalizing factor for $\varphi_k^{\pm}$, we find on substituting $f(k)$ for $g(k)$ and $C_k^{\pm} \varphi_k^{\pm}$ for $\varphi_k^{\pm}$ in equation (82) and dropping the $\pm$ signs,

$$\int_{-\infty}^{+\infty} c_k \varphi_k \int_{k-\Delta}^{k+\Delta} c_{k'} \varphi_{k'}\, dk'\, dx = 1 \quad . \tag{86}$$

Thus since

$$I(x,\Delta) = c_k \varphi_k \int_{k-\Delta}^{k+\Delta} c_{k'} \varphi_{k'}\, dk' \tag{87}$$

is an even function of x , equation (86) implies that

$$2\int_0^{\infty} I(x,\Delta)\, dx \equiv 1 \tag{88}$$

for all $\Delta > 0$, and consequently,

$$2L = 2\lim_{\Delta\to 0}\int_0^{\infty} I\, dx = 1 \quad . \tag{89}$$

But we shall show that

$$L = \pi c_k^2/2 \tag{90}$$

and hence that

$$c_k = \pm 1/\sqrt{\pi} \quad . \tag{91}$$

To prove equation (90) we notice that for every real number ξ ,

$$\lim_{\Delta\to 0}\int_0^{\xi} I(x,\Delta)\, dx = 0 \tag{92}$$

since I approaches zero and the path of integration is of finite length. Hence equation (89) implies that

$$L = \lim_{\Delta\to 0}\int_{\xi}^{\infty} I\, dx \quad . \tag{93}$$

Now we choose ξ in such a way that

$$\cos k(\xi+\delta) = 0 , \tag{94a}$$

$$\sin k(\xi+\delta) = 1 \quad . \tag{94b}$$

Substituting equation (84) into equation (86), changing the variable of integration to $y = x - \xi$, and expanding the trigonometric functions with the help of equations (94), we find that

$$J = \int_{\xi}^{\infty} I\,dx = \int_{0}^{\infty} C_k \sin ky \int_{k-\Delta}^{k+\Delta} [p(k')\sin k'y + q(k')\cos k'y]\,dk'\,dy, \tag{95}$$

where

$$p(k') = C_{k'} \sin k'(\xi + \delta) , \tag{96a}$$

$$q(k') = C_{k'} \cos k'(\xi + \delta) . \tag{96b}$$

Integrating by parts in equation (95) and using the formulae

$$\int_0^{\infty} \frac{\sin ax \sin bx}{x}\,dx = \frac{1}{2} \log \frac{a+b}{a-b} \quad \text{for } 0 < b < a , \tag{97a}$$

and

$$\int_0^{\infty} \frac{\sin ax \cos bx}{x}\,dx = \begin{cases} 0 & \text{for } 0 < a < b \\ \frac{\pi}{2} & \text{for } 0 < b < a \end{cases} , \tag{97b}$$

we obtain

$$\begin{aligned} J = {} & \frac{\pi}{2} C_k\, p(k-\Delta) - \frac{C_k}{2}\left[q(k+\Delta) \log \frac{2k+\Delta}{\Delta} - q(k-\Delta) \log 2\frac{k-\Delta}{\Delta} \right] \\ & + \int_0^{\infty} C_k \sin ky \int_{k-\Delta}^{k+\Delta} \left[\frac{\cos k'y}{y} \frac{dp}{dk'} + \frac{\sin k'y}{y} \frac{dq}{dk'} \right] dk'\,dy . \end{aligned} \tag{98}$$

But in accordance with equations (94) and (97), we find that the first term approaches $\pi C_k^2/2$ as $\Delta \to 0$, and the second term vanishes since $q(k+\Delta)$ and $q(k-\Delta)$ must be of order Δ . Finally, we find that we may interchange the order of integration in the last term, since $\int_0^a \log x\,dx$ exists. Hence the last term vanishes also, and

$$L = \lim_{\Delta \to 0} J = \pi C_k^2/2 . \tag{99}$$

APPENDIX B. DERIVATION OF EQUATIONS (35a) AND (35b)

From equation (9), we have

$$E' = \frac{dE}{d\lambda} = -\frac{\partial}{\partial\lambda}(\gamma_A\gamma_B - \bar{\epsilon}^2)\Big/\frac{\partial}{\partial E}(\gamma_A\gamma_B - \bar{\epsilon}^2) , \qquad (100)$$

which with equations (4), (8), (9), and (20) becomes ,

$$E' = \bar{\epsilon}^2\left(\frac{\gamma_B}{\lambda} - \frac{\partial\alpha'}{\partial\lambda}\frac{\partial\gamma_B}{\partial\alpha'}\right)\Big/\left(\bar{\epsilon}^2\gamma_B' + \gamma_B^2\gamma_A' - \gamma_B\frac{\partial\bar{\epsilon}^2}{\partial E}\right) . \qquad (101)$$

Hence for $\lambda = 0$ and $E = E_A$,

$$E_1 = \left(\bar{\epsilon}^2/\lambda\gamma_B\gamma_A'\right)_{\substack{\lambda=0\\ E=E_A}} \qquad (102)$$

Setting $E = E_A$ and $\alpha' = i\beta$ (c.f. equations (4b) and (4c)) in equation (8b) we obtain

$$(\lambda\gamma_B)_{\lambda=0} = 4\beta^2/\kappa\upsilon(1-e^{-4\beta c}) . \qquad (103)$$

Hence with equations (20a) and (25a) we obtain equation (35a):

$$E_1 = \epsilon^2\alpha^2(e^{-4\beta c}-1)/2K(1+\beta a) . \qquad (104)$$

To obtain E_2 we differentiate equation (101):

$$E'' = \frac{d^2E}{d\lambda^2} = \left(\frac{\partial E'}{\partial\lambda}\right)_{\alpha'} + \left(\frac{\partial\alpha'}{\partial\lambda}\right)\left(\frac{\partial E'}{\partial\alpha'}\right) + E'\left(\frac{\partial E'}{\partial E}\right) . \qquad (105)$$

For $\lambda = 0$ we find

$$\left(\frac{\partial E'}{\partial\lambda}\right)_{\alpha'} = \bar{\epsilon}^2\left(\gamma_B\frac{d\bar{\epsilon}^2}{dE} - \bar{\epsilon}^2\gamma_B' - \frac{\partial\alpha'}{\partial\lambda}\frac{\partial\gamma_B}{\partial\alpha'}\gamma_A'\right)\Big/\lambda^2\gamma_B^3\gamma_A'^2 , \qquad (106)$$

$$\left(\frac{\partial E'}{\partial\alpha'}\right)_{\lambda} = -\bar{\epsilon}^2\frac{\partial\gamma_B}{\partial\alpha'}\Big/\lambda\gamma_B^2\gamma_A' , \qquad (107)$$

and

$$\frac{\partial E'}{\partial E} = \frac{\partial \bar{\epsilon}^2}{\partial E} / \lambda \gamma_B \gamma_A' - \bar{\epsilon}^2 (\gamma_A' \gamma_B' + \gamma_B \gamma_A'') / \lambda \gamma_B^2 \gamma_A'^2 , \quad (108)$$

where all the expressions are to be evaluated at $E = E_A$ and $\lambda = 0$. Substituting into equation (105) we find with the help of equation (102) that

$$(E'')_{\substack{\lambda=0\\E=E_A}} = 2E_2 = \Big\{ -2E_1 \left(\frac{\partial \gamma_B}{\partial \alpha'} \frac{\partial \alpha'}{\partial \lambda} / \gamma_B \right) + E_1^2 \left[2 \left(\frac{\partial \bar{\epsilon}^2}{\partial E} / \bar{\epsilon}^2 - \gamma_B' / \gamma_B \right) - \gamma_A'' / \gamma_A \right] \Big\}_{\substack{\lambda=0\\E=E_A}} . \quad (109)$$

Finally, we find $\frac{\partial \alpha'}{\partial \lambda}$ from equation (4b) and $\frac{\partial \gamma_B}{\partial \alpha'}$ from equation (8b), set $\alpha' = \lambda \beta$, and use equations (35a) and (109) to obtain equation (35b).

APPENDIX C. CALCULATION OF THE COEFFICIENTS E_1 AND E_2 BY MEANS OF EQUATIONS (43) AND (45)

We find E_1 from equations (14), (15), and (42):

$$E_1 = \bar{V}_{\beta\beta} = -\left[U\alpha^2/KU(a+1/\beta)\right]\int_{a+2b}^{a+2b+2c} e^{-2\beta(x-a)}\,dx \quad (110)$$

On evaluating the integral, we find that equation (110) agrees exactly with equation (35a).

To find E_2 , we first use equations (14), (15), and (42) to calculate the matrix elements

$$\bar{V}_{\beta\beta'} = \pm\left[U\alpha\alpha'/KU\sqrt{(a+1/\beta)(a+1/\beta')}\right]\int_{a+2b}^{a+2b+2c} e^{-(\beta+\beta')(x-a)}\,dx\,, \quad (111)^1$$

from which we obtain

$$\bar{V}^2_{\beta\beta'} = \epsilon\epsilon'\alpha\alpha'\beta\beta'\left[e^{2(\beta+\beta')}-1\right]/K^2(\beta+\beta')^2(1+\beta a)(1+\beta' a)\,. \quad (112)$$

Similarly we use equations (14), (15), (17), and (42) to find the matrix elements

$$\bar{V}_{\beta k^{\pm}} = \pm\left[U\alpha/\sqrt{\pi KU(a+1/\beta)}\right]\int_{a+2b}^{a+2b+2c} e^{\beta(x-a)}\cos k(x+\delta^{\pm})\,dx\,. \quad (113)$$

Writing the cosine function in exponential form, and using the equation

$$E_\beta - E_k = -(k+i\beta)(k-i\beta)/K\,, \quad (114)$$

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[1]In this equation α' represents the value of $\alpha(\epsilon)$ for $\epsilon = E_{\beta'}$.

we obtain

$$\bar{V}^{2}_{\beta k^{\pm}}/(E_\beta - E_k) = N\,(T_1 + T_2 + T_3 + T_4^{\pm} + T_5^{\pm}) , \tag{115}$$

where

$$N = \epsilon^2 \alpha^2 \beta\, U / 4\pi\,(1+\beta a) , \tag{116}$$

$$T_1(k) = 2e^{2(ik-\beta)c} / (k+i\beta)^2 (k-i\beta)^2 , \tag{117}$$

$$T_2(k) = T_1(-k) , \tag{118}$$

$$T_3(k) = (1 - e^{-4\beta c}) / (k+i\beta)^2 (k-i\beta)^2 , \tag{119}$$

$$T_4^{\pm}(k) = e^{2ik(a+2b+\delta^{\pm})} \left[e^{2c(ik-\beta)} - 1 \right]^2 / (k+i\beta)^2 (k-i\beta)^2 , \tag{120}$$

and

$$T_5^{\pm}(k) = T_4^{\pm}(-k) . \tag{121}$$

From equations (118) and (121), and the fact that T_3 is an even function of k, the integral in equation (45) takes the form

$$I = N \int_{-\infty}^{+\infty} (2T_1 + T_3 + T_4^{+} + T_4^{-})\, dk . \tag{122}$$

We now evaluate the integral in the last equation by means of contour integration. Choosing the contour which runs along the real axis from $-R$ to $+R$ (where $R > 0$) and then around the semi-circle in the upper half-plane from $+R$ to $-R$, we find that the integral around the semi-circle approaches zero as $R \to \infty$. Hence

$$I = 2\pi i N \text{ (Sum of residues of the integrand at its poles in the upper half-plane.)} \tag{123}$$

T_1 and T_3 have poles at $k = i\beta$ only. The residue of $2T_1$ is

$$R_1 = 4\frac{d}{dk}\left[e^{2(ik-\beta)c}/(k+i\beta)^2\right]_{k=i\beta} = (2\beta c+1)e^{-4\beta c}/i\beta^3 \qquad (124)$$

while that of T_3 is

$$R_3 = 2(1-e^{-4\beta c})\left[\frac{d}{dk}(k+i\beta)^{-2}\right]_{k=i\beta} = (1-e^{-4\beta c})/i\beta^3 \qquad (125)$$

Adding R_1 and R_3 and multiplying by $2\pi i N$, we find that the contribution of T_1 and T_3 to I is exactly equal to the first term of equation (35b).

In order to evaluate the residues of T_4^+ and T_4^-, we find from equations (18) that

$$e^{2ik(a+\delta^\pm)} = \frac{(k+\alpha)e^{2i\alpha a} \pm (k-\alpha)}{(k-\alpha)e^{2i\alpha a} \pm (k+\alpha)} \qquad (126)$$

and hence that

$$e^{2ik(a+\delta^+)} + e^{2ik(a+\delta^-)} = -2kv/(k^2+\alpha^2+2ik\alpha\cot 2\alpha a) = 2/\gamma_a(E_k) \qquad (127)$$

Equation (127) tells us that $T_4^+ + T_4^-$ has a pole corresponding to each level $E_{\beta'}$ (i.e., for $k = i\beta'$) as well as to E_β ($k = i\beta$). The residue at $k = i\beta'$ is

$$R_4(i\beta') = \left\{e^{2ikb}\left[e^{(2ik-\beta)c}-1\right]^2/(k+i\beta)^3(k-i\beta)\gamma_a'(E_k)\frac{dE_k}{dk}\right\}_{k=i\beta'} . \qquad (128)$$

Evaluating this residue with the help of equations (4) and (25a), we find that in accordance with equation (112),

$$2\pi i N R_4(i\beta') = -V^2_{\beta\beta'}/(E_\beta - E_{\beta'}) \qquad (129)$$

Thus every term of equation (45) which arises from a discrete level $E_{\beta'}$ is cancelled by an equal and opposite term which arises from the continuum levels.

Finally we evaluate the residue of $T_4^+ + T_4^-$ at $k = i\beta$:

$$R_4'(i\beta) = -\tfrac{1}{2}\left[\left(\frac{d^2 f}{dk^2}\right)\Big/\left(\frac{df}{dk}\right)^2\right]_{k=i\beta} , \tag{130}$$

where

$$f(k) = (k + i\beta)^3\, \gamma_A e^{-2ikb} / 2\left[e^{2(ik-\beta)c} - 1\right]^2 \tag{131}$$

Using the equation

$$\frac{d^2\gamma_A}{dk^2} = \gamma_A''\left(\frac{dE_k}{dk}\right)^2 + \gamma_A'\left(\frac{d^2E_k}{dk^2}\right) , \tag{132}$$

we obtain with the help of equations (4):

$$R_4(i\beta) = \epsilon^2\left(e^{-4\beta c} - 1\right)^2\Big\{2Kb/\beta - \gamma_A''/2\gamma_A' + K\left[1 + 2\beta c e^{-4\beta c}/(e^{-4\beta c} - 1)\right]/\beta^2\Big\}\Big/ 8\beta^3(1+\beta a)\gamma_A' \tag{133}$$

But on substituting $k = i\beta$ in equation (133) we find with the help of equation (35a) that $2\pi i N R_4(i\beta)$ is exactly the second term in equation (35b).

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