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Applications of the WKB Approximation

A The Wilson–Sommerfeld Quantization Rules of the Pre-1925 Quantum Theory

To show how the WKB approximation is used, let us first derive the energies for a potential with one minimum, with a single left and a single right turning point. In region I, with $x < x_2$, the solution must be restricted to one with a decreasing exponential only. In region I,

$$u_I(x) = \frac{A}{\sqrt{|P(x)|}} e^{-\frac{1}{\hbar}\int_x^{x_2} d\xi |P(\xi)|}. \tag{1}$$

This relation will connect in region II, where $x > x_2$, onto the oscillatory solution

$$u_{II}(x) = \frac{2A}{\sqrt{P(x)}} \cos\left[\frac{1}{\hbar}\int_{x_2}^x d\xi\, P(\xi) - \frac{\pi}{4}\right]. \tag{2}$$

This formula can be rewritten as

$$u_{II}(x) = \frac{2A}{\sqrt{P(x)}} \cos\left[\left(\frac{1}{\hbar}\int_{x_2}^{x_1} d\xi\, P(\xi) - \frac{\pi}{2}\right) - \left(\frac{1}{\hbar}\int_x^{x_1} d\xi\, P(\xi) - \frac{\pi}{4}\right)\right]. \tag{3}$$

In region I', with $x > x_1$, we must again have a purely decreasing exponential solution

$$u_{I'}(x) = \frac{B}{\sqrt{|P(x)|}} e^{-\frac{1}{\hbar}\int_{x_1}^x d\xi |P(\xi)|}. \tag{4}$$

This relation will connect in region II, with $x < x_1$, onto

$$u_{II}(x) = \frac{2B}{\sqrt{P(x)}} \cos\left[\frac{1}{\hbar} \int_x^{x_1} d\xi\, P(\xi) - \frac{\pi}{4}\right].$$ (5)

Now, comparing the two expressions for $u_{II}(x)$, these match, if $|A| = |B|$, and if

$$\frac{1}{\hbar} \int_{x_2}^{x_1} d\xi\, P(\xi) - \frac{\pi}{2} = n\pi.$$ (6)

We can rewrite this as

$$\frac{1}{\pi} \int_{x_2}^{x_1} d\xi\, P(\xi) \equiv \frac{1}{2\pi} \oint d\xi\, P(\xi) = \hbar(n + \frac{1}{2}),$$ (7)

where $\oint$ is used to indicate the integral over one complete classical cycle of the classical orbit, starting at x_2, proceeding to x_1, and then back again to x_2. This quantity, using a generalized momentum, is known as the action variable, and usually denoted by J in classical mechanics. It is a function of the energy, E.

$$J(E) = \frac{1}{2\pi} \oint d\xi\, P(\xi) = \hbar(n + \frac{1}{2}).$$ (8)

This is the Wilson–Sommerfeld quantization rule, a generalization of the Planck quantization rule, which goes all the way back to the birth of the quantum theory.

For the simple 1-D harmonic oscillator, e.g., with $\mu = m$, and $V(x) = \frac{1}{2} m\omega_0^2 x^2$,

$$\begin{aligned}
J(E) &= \frac{1}{\pi} \int_{-x_0}^{+x_0} d\xi \sqrt{2m(E - \frac{1}{2} m\omega_0^2 \xi^2)} = \frac{1}{\pi} m\omega_0 \int_{-x_0}^{+x_0} d\xi \sqrt{(x_0^2 - \xi^2)} \\
&= \frac{1}{\pi} m\omega_0 x_0^2 \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} d\phi \cos^2\phi = \frac{1}{2} m\omega_0 x_0^2 = \frac{E}{\omega_0},
\end{aligned}$$ (9)

where we have used, $E = \frac{1}{2} m\omega_0^2 x_0^2$, in the first step, and have used the substitution, $\xi = x_0 \sin\phi$, in the integral. Thus, for the 1-D harmonic oscillator

$$J(E) = \frac{E}{\omega_0} = \hbar(n + \frac{1}{2}),$$ (10)

giving the exact quantum-mechanical result, $E = \hbar\omega_0(n + \frac{1}{2})$. For other simple problems, the integrals for $J(E)$ are a little more challenging but can be done in closed form. For the hydrogen atom, e.g., with $V(r) = -Ze^2/r + \hbar^2 l(l+1)/2\mu r^2$, leading to

$$J(E) = \frac{Ze^2 \sqrt{\mu}}{\sqrt{(-2E)}} - \hbar\sqrt{l(l+1)} = \hbar(n_r + \frac{1}{2}),$$ (11)

or

$$\frac{Ze^2 \sqrt{\mu}}{\sqrt{(-2E_{\text{WKB}})}} = \hbar(n_r + \frac{1}{2} + \sqrt{l(l+1)}).$$ (12)

This WKB result is to be compared with the exact quantum-mechanical result, which could be put in the form

$$\frac{Ze^2\sqrt{\mu}}{\sqrt{(-2E)}} = \hbar\left(n_r + \frac{1}{2} + \sqrt{(l + \tfrac{1}{2})^2}\right), \tag{13}$$

so the WKB expression for the energy, E, goes over to the exact result in the limit $(l^2 + l) \rightarrow (l + \tfrac{1}{2})^2 = (l^2 + l + \tfrac{1}{4})$, certainly valid in the limit of large quantum numbers, l, for which the classical orbit description begins to have some meaning.

Similarly, for the 3-D harmonic oscillator,

$$J(E) = \frac{E}{2\omega_0} - \frac{\hbar\sqrt{l(l+1)}}{2} = \hbar(n_r + \frac{1}{2}), \tag{14}$$

leads to

$$E_{\text{WKB}} = \hbar\omega_0(2n_r + 1 + \sqrt{l(l+1)}), \tag{15}$$

which again leads to the exact result

$$E = \hbar\omega_0(2n_r + l + \frac{3}{2}), \tag{16}$$

if, again, $l(l+1)$ is replaced by $(l + \tfrac{1}{2})^2$, valid for large values of l.

B   Application 2: The Two-Minimum Problem: The Inversion Splitting of the Levels of the Ammonia Molecule

In the vibrational spectrum of the ammonia molecule, NH_3, one degree of freedom exists, which corresponds to the motion of the N atom relative to the H_3 symmetrical triangle. This degree of freedom can be approximated by z, the distance of the N atom above (or below) the H_3 plane. The potential, $V(z)$, has the the symmetrical double minimum form shown in Fig. 37.1. Classically, the N atom would lie either above the H_3 plane and undergo a vertical oscillation about its upper equilibrium configuration at $z = +z_e$, or alternately it might lie below the H_3 plane and undergo an oscillation about its lower equilibrium configuration at $z = -z_e$. Quantum mechanically, of course, the N atom can tunnel from the upper minimum to the lower one, leading to a doubling of the vibrational energy levels, with one eigenfunction being an even function of z, the second an odd function of z. We have already seen the energy splitting, ΔE, is related to the frequency with which the N atom tunnels back and forth from one minimum to the other. The reduced mass for this degree of freedom is $3m_H m_N/(3m_H + m_N)$.

Because $V(-z) = V(z)$, we expect the one-dimensionalized wave functions, $u(z)$, to be either even or odd functions of z. Thus in the central exponential region, region I, with $-z_2 < z < +z_2$, we would expect $u(z)$ to be either a hyperbolic
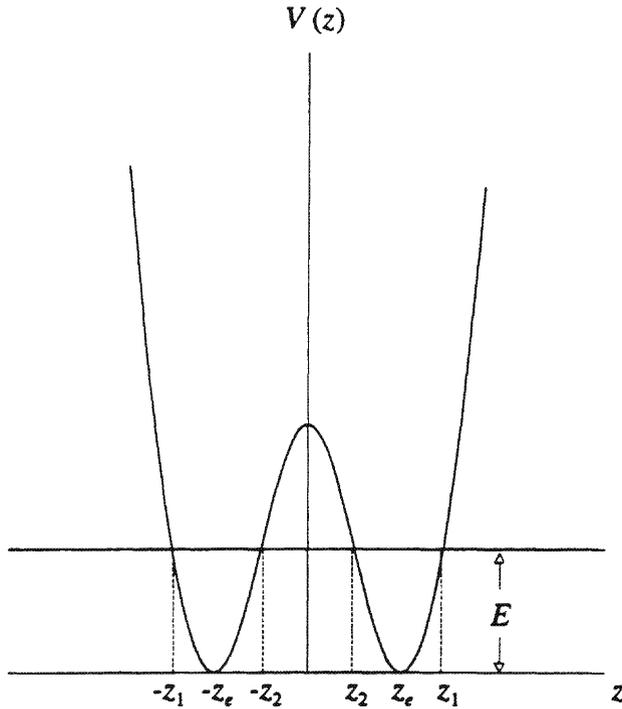
$$V(z)$$

FIGURE 37.1. The NH_3 inversion potential for the coordinate, z.

cosine or hyberbolic sine type function,

$$u_I(z) = \frac{A}{2\sqrt{|P(z)|}}\left[e^{+\frac{1}{\hbar}\int_0^z d\zeta |P(\zeta)|} \pm e^{-\frac{1}{\hbar}\int_0^z d\zeta |P(\zeta)|}\right]. \tag{17}$$

We will find it convenient to use

$$\int_0^{z_2} d\zeta \cdots = \int_0^z d\zeta \cdots + \int_z^{z_2} d\zeta \cdots \quad \text{to rewrite}$$

$$u_I(z) = \frac{A}{2\sqrt{|P(z)|}}\left[e^{\frac{1}{\hbar}\int_0^{z_2} d\zeta |P(\zeta)|}e^{-\frac{1}{\hbar}\int_z^{z_2} d\zeta |P(\zeta)|}\right.$$

$$\left.\pm e^{-\frac{1}{\hbar}\int_0^{z_2} d\zeta |P(\zeta)|}e^{+\frac{1}{\hbar}\int_z^{z_2} d\zeta |P(\zeta)|}\right]$$

$$= \frac{A}{2\sqrt{|P(z)|}}\left[\frac{1}{Q}e^{-\frac{1}{\hbar}\int_z^{z_2} d\zeta |P(\zeta)|} \pm Qe^{+\frac{1}{\hbar}\int_z^{z_2} d\zeta |P(\zeta)|}\right], \tag{18}$$

where we have named

$$Q \equiv e^{-\frac{1}{\hbar}\int_0^{z_2} d\zeta |P(\zeta)|}. \tag{19}$$

For energies, E, far below the maximum of the central potential hill this exponential quantity, $Q \ll 1$. Now the function u_I for the central exponential region is in a

form in which we can make the connection to region II, the upper oscillatory region of our potential. With the connection formulae for a left turning point, this would connect onto

$$
\begin{aligned}
u_{II}(z) &= \frac{A}{2\sqrt{P(z)}}\left(\frac{2}{Q}\cos\left[\frac{1}{\hbar}\int_{z_2}^{z}d\zeta\,P(\zeta)-\frac{\pi}{4}\right]\pm Q\cos\left[\frac{1}{\hbar}\int_{z_2}^{z}d\zeta\,P(\zeta)+\frac{\pi}{4}\right]\right)\\
&= \frac{A}{2\sqrt{P(z)}}\left(\frac{2}{Q}\cos\left[\frac{1}{\hbar}\int_{z_2}^{z}d\zeta\,P(\zeta)-\frac{\pi}{4}\right]\mp Q\sin\left[\frac{1}{\hbar}\int_{z_2}^{z}d\zeta\,P(\zeta)-\frac{\pi}{4}\right]\right)\\
&= \frac{AR}{2\sqrt{P(z)}}\cos\left[\left(\frac{1}{\hbar}\int_{z_2}^{z}d\zeta\,P(\zeta)-\frac{\pi}{4}\right)\pm\delta\right],
\end{aligned}
\tag{20}
$$

$$
\text{where}\qquad \tan\delta=\frac{Q^2}{2},\qquad\text{and}\qquad R=\sqrt{Q^2+\left(\frac{2}{Q}\right)^2}.
\tag{21}
$$

Also, $\tan\delta\approx\delta$, because we expect $Q^2\ll 1$. It will be convenient, for purposes of making the connection to the right exponential region, with $z>z_1$, to reexpress this WKB solution for the oscillatory region II as

$$
u_{II}(z)=\frac{AR}{2\sqrt{P(z)}}\cos\left(\left[\frac{1}{\hbar}\int_{z_2}^{z_1}d\zeta\,P(\zeta)-\frac{\pi}{2}\pm\delta\right]-\left[\frac{1}{\hbar}\int_{z}^{z_1}d\zeta\,P(\zeta)-\frac{\pi}{4}\right]\right).
\tag{22}
$$

Finally, in the exponential region I', with $z>z_1$, the solution must be an exponentially decreasing function as we penetrate further into the classically forbidden region,

$$
u_{I'}(z)=\frac{B}{\sqrt{|P(z)|}}e^{-\frac{1}{\hbar}\int_{z_1}^{z}d\zeta\,|P(\zeta)|}.
\tag{23}
$$

This solution connects onto an oscillatory solution in region II of the form

$$
u_{II}(z)=\frac{2B}{\sqrt{P(z)}}\cos\left[\frac{1}{\hbar}\int_{z}^{z_1}d\zeta\,P(\zeta)-\frac{\pi}{4}\right].
\tag{24}
$$

We get a match with the earlier form for $u_{II}(z)$, if $|2B|=\frac{1}{2}|AR|$, and if

$$
\frac{1}{\hbar}\int_{z_2}^{z_1}d\zeta\,P(\zeta)-\frac{\pi}{2}\pm\delta=n\pi,
\tag{25}
$$

or

$$
\frac{1}{\pi}\int_{z_2}^{z_1}d\zeta\,P(\zeta)=\hbar(n+\tfrac{1}{2})\mp\frac{\delta\hbar}{\pi}.
\tag{26}
$$

The left-hand side gives the action integral $J(E)$ for the upper potential minimum at the energy E appropriate for the even (or odd) solution for the full problem. If the energy, E, is far below the central potential maximum, the potential in the vicinity of the potential minimum between $+z_2$ and $+z_1$ can be approximated by a parabola, with $J(E)=E/\omega_0$. With $E=E^{(0)}+\Delta E$, we get

$$
J(E)=J(E^{(0)})+\left(\frac{\partial J}{\partial E}\right)_0\Delta E+\cdots=\hbar(n+\tfrac{1}{2})+\frac{1}{\omega_0}\Delta E+\cdots.
\tag{27}
$$

Therefore, eq. (26) can be put in the form

$$J(E) = \hbar(n + \tfrac{1}{2}) + \frac{\Delta E}{\omega_0} = \hbar(n + \tfrac{1}{2}) \mp \frac{\delta \hbar}{\pi}. \tag{28}$$

With $\delta \approx \tan \delta = \tfrac{1}{2}Q^2$, this equation leads to

$$\Delta E = \mp \frac{\hbar \omega_0}{2\pi} Q^2, \tag{29}$$

where the upper (lower) signs refer to the even (odd) solutions. The even functions lie at lower energies. Finally,

$$Q^2 = e^{-2\frac{1}{\hbar}\int_0^{z_2} d\zeta |P(\zeta)|} = e^{-\frac{1}{\hbar}\int_{-z_2}^{+z_2} d\zeta |P(\zeta)|} \tag{30}$$

is a function of E. However, for energy levels far below the central potential maximum, the energy splitting is very small compared with $E_n^{(0)} = \hbar\omega_0(n + \tfrac{1}{2})$, so we can express the energy splitting of the nth vibrational state by

$$\Delta E_n = \Delta E_{\text{odd}} - \Delta E_{\text{even}} = \frac{\hbar\omega_0}{\pi} Q_n^2 = \frac{\hbar\omega_0}{\pi} e^{-\frac{1}{\hbar}\int_{-z_2}^{+z_2} d\zeta \sqrt{2\mu(V(\zeta)-E_n^{(0)})}}. \tag{31}$$

We have seen previously the exponential,

$$e^{-G}, \qquad \text{with} \qquad G = \frac{1}{\hbar}\int_{-z_2}^{+z_2} d\zeta \sqrt{2\mu(V(\zeta) - E_n^{(0)})}, \tag{32}$$

is related to the probability the N atom tunnel through the central potential maximum. In Chapter 6, we showed the frequency with which the N atom tunnels back and forth from one potential minimum to the other is given by

$$\nu_{\text{tunneling}} = \frac{\Delta E}{2\pi\hbar} = \frac{\nu_0}{\pi} e^{-G}. \tag{33}$$

The factor, ν_0, the oscillator frequency in a single well, gives the frequency with which the N atom hits the potential barrier. The probability the N atom tunnel through the barrier is thus given by e^{-G}/π. The factor e^{-G} is known as the Gamow factor, because Gamow first discussed the tunneling phenomenon in connection with α decay in a heavy nucleus (see also problem 8).

Problems

52. In certain quark models, a linear confinement potential is used for heavy quarks, such as the charmed or b quarks, for which nonrelativistic quantum theory is approximately valid. The one-dimensionalized radial wave equation for such a quark would be

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}(E - V_{\text{eff.}}(r))u(r) = 0,$$

with

$$V_{\text{eff.}}(r) = kr, \qquad \text{for } r \geq 0, \qquad k = \text{positive constant},$$

$$V_{\text{eff.}}(r) = \infty, \qquad \text{for } r < 0, \quad \text{so } u = 0 \text{ for } r \le 0.$$

Find the WKB approximation for the energy, E_n, as a function of $m, k, \hbar$. The boundary condition at $r = 0$ leads to a WKB solution near $r = 0$ of the form

$$u_{\text{WKB}}(r) = \frac{A}{\sqrt{P(r)}} \sin\left[\frac{1}{\hbar}\int_0^r dr' P(r')\right],$$

with $P(r) = \sqrt{2m(E - V_{\text{eff.}}(r))}$. (Note: $P(r)$ is finite at $r = 0$.)

53. Show that the WKB connection formulae can be converted to the form

$$u_I = \frac{A}{\sqrt{P(x)}} e^{\pm\frac{i}{\hbar}\int_x^{x_2} d\xi\, P(\xi)} \qquad \longleftrightarrow \qquad u_{II}$$

$$u_{II} = \frac{A}{\sqrt{|P(x)|}} \left(\frac{1}{2} e^{\pm i\frac{\pi}{4}} e^{-\frac{1}{\hbar}\int_{x_2}^{x} d\xi\, |P(\xi)|} + e^{\mp i\frac{\pi}{4}} e^{+\frac{1}{\hbar}\int_{x_2}^{x} d\xi\, |P(\xi)|}\right)$$

for the right/left running wave solutions $\quad \dfrac{A}{\sqrt{P(x)}} e^{\pm\frac{i}{\hbar}\int_x^{x_2} d\xi\, P(\xi)}$,

in region I, with a similar relation at the boundary $x = x_1$ (see Fig. P53).

Use these connection formulae to calculate the transmission and reflection coefficients for a wave incident on a potential barrier of arbitrary but smooth shape, with incident energy, $E < V_{\text{max.}}$. In particular, show that the transmission coefficient, T, is given by

$$T = \frac{\text{Transm. Flux}}{\text{Inc.Flux}} = \left(\frac{4D}{D^2+4}\right)^2, \qquad \text{with } D = e^{-\frac{1}{\hbar}\int_{x_2}^{x_1} dx\sqrt{2m(V(x)-E)}}.$$

54. For the one-dimensionalized potential of the shape shown in Fig. P54, demonstrate for arbitrary energies in the continuum, $E > 0$, but $E < V_{\text{max.}}$, the solutions in general will satisfy $|u_{IV}|^2 \gg |u_{II}|^2$. Show also that for the special values of $E = E_n$, for which

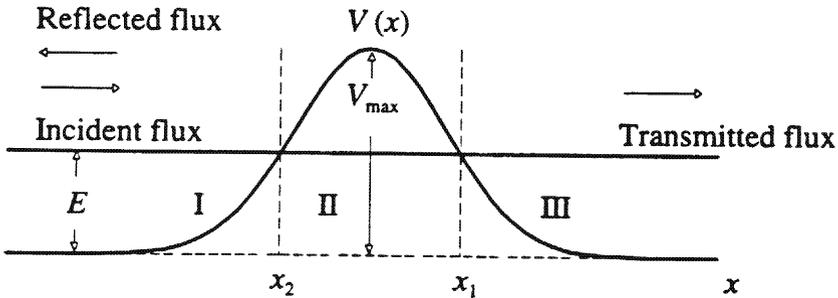$$\frac{1}{\pi}\int_{x_1}^{x_2} dx\sqrt{2\mu(E_n - V(x))} \approx \hbar(n + \tfrac{1}{2}),$$
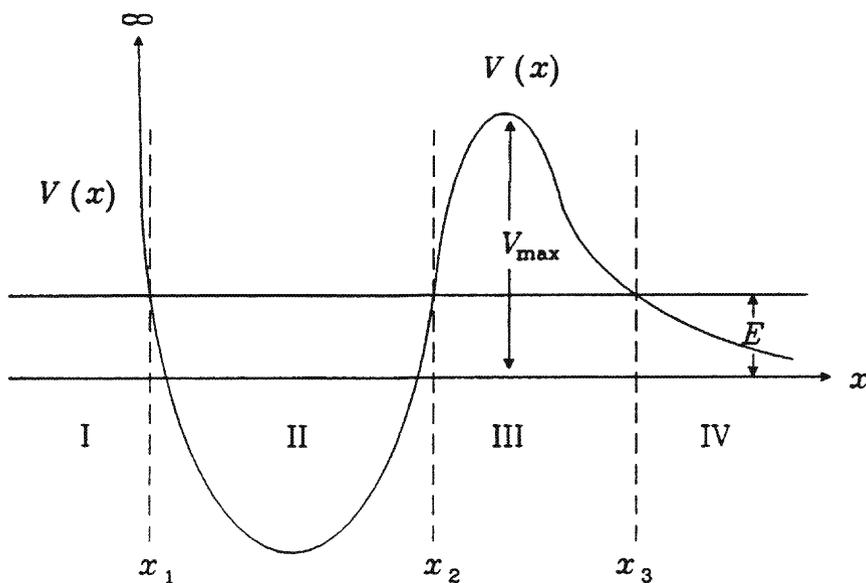

FIGURE P53.

FIGURE P54.

the situation is reversed, and for these energies, $|u_{II}|^2 \gg |u_{IV}|^2$. Estimate the width, ΔE, of these virtual bound or quasibound states (or resonances) in terms of ω_0, the approximate circular frequency in the well, and the penetrability factor

$$Q^2 = e^{-\frac{1}{\hbar} \int_{x_2}^{x_3} dx \sqrt{2\mu(V(x) - E_n)}}.$$

55. A symmetrical X_2Y_4 molecule, such as C_2H_4 (ethylene), has one degree of freedom, ϕ, which corresponds to a highly hindered internal rotation of one essentially rigid CH_2 unit relative to the other on the circle, as shown in Fig. 4.3 of Chapter 4. The wave equation separates approximately, so the hindered internal

rotation can be described by a one-degree-of-freedom Schrödinger equation,

$$-\frac{\hbar^2}{2I}\frac{d^2u}{d\phi^2} + V(\phi)u(\phi) = Eu(\phi),$$

with $I = I_1 I_2/(I_1 + I_2)$, $I_1 = I_2 = 2m_Y r_Y^2$, In Chapter 4, this problem was solved in a square well approximation. Now, we shall choose a more realistic potential that can be approximated by (see Fig. P55),

$$V(\phi) = V_0(1 - \cos 2\phi),$$

with minima at $\phi = 0$ and π and maxima at $\phi = \frac{\pi}{2}, \frac{3\pi}{2}, \ldots$. The constant, V_0, can be expected to be very large compared with the lowest allowed energy eigenvalues. In that case, the energy levels occur in closely spaced multiplets. The average position of a multiplet can be approximated by the quadratic approximation for $V(\phi)$, e. g. $V(\phi) \approx V_0 \frac{4\phi^2}{2}$ near the potential minimum at $\phi = 0$, so $E \approx E_n = \hbar\omega_0(n + \frac{1}{2})$, with $\omega_0 \approx \sqrt{(4V_0/I)}$. In particular, show how the splitting into multiplets depends on the energies, $\hbar\omega_0$, and the penetrability factors

$$Q = e^{-\frac{1}{\hbar}\int_{\frac{\pi}{2}}^{\Phi_2} d\phi' \sqrt{2I(V(\phi')-E)}}.$$

Use the fact that solutions of the form, $(A/\sqrt{|P|})\cosh(\ldots)$ in the classically forbidden region I (see Fig. P55), must connect onto solutions of the form, $\pm(A/\sqrt{|P|})\cosh(\ldots)$ in the region $\phi \rightarrow \phi + 2\pi$, i.e., region V in Fig. P55, whereas solutions of type $(A/\sqrt{|P|})\sinh(\ldots)$ in region I must connect onto solutions of the form $\pm(A/\sqrt{|P|})\sinh(\ldots)$ in region V, in order to preserve both probability density and probability density current.

Try to generalize your result for the energy splitting for the potentials

$$V(\phi) = V_0(1 - \cos N\phi), \qquad \text{with } N = 3, 4, \ldots.$$

For arbitrary N, show that the energy multiplets are made up of (N+1) levels, with (N-1) two-fold degenerate states and two nondegenerate states, now crowded into the same ΔE, viz.,

$$\Delta E = \frac{2\hbar\omega_0}{\pi} Q^2,$$

valid for $N = 2$.

For very large N, we have effectively bands of very finely spaced discrete allowed energy values, the Bloch bands of condensed matter physics.

Caution: For $N = 2$, all solutions are either symmetric or antisymmetric with respect to reflections in the plane $\phi = 3\pi/N = 3\pi/2$, in region III of Fig. P55, if they are made to have either symmetry, or antisymmetry with respect to reflections in the plane $\phi = \pi/N = \pi/2$, in region I of Fig. P55. For $N \geq 3$, symmetries in regions near $\phi = 3\pi/N, 5\pi/N, \ldots$ may not be simple for the doubly degenerate states. For such doubly degenerate states, a linear combination of symmetric and antisymmetric (or even and odd) functions may also be acceptable solutions even if the solutions are made symmetric or antisymmetric with respect to reflections in the plane $\phi = \pi/N$.
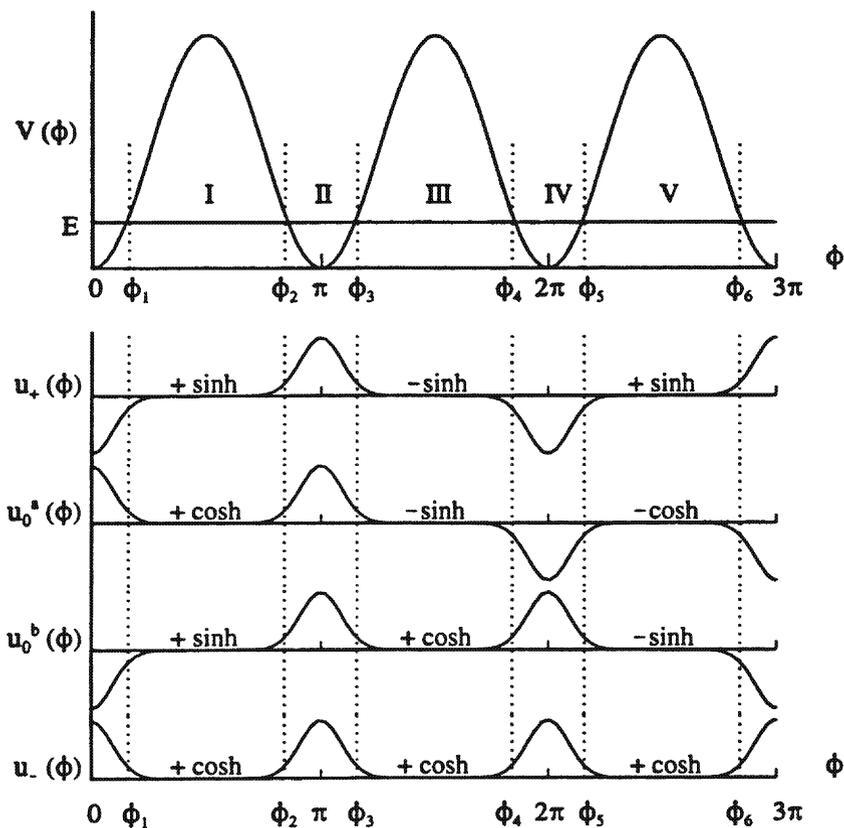
FIGURE P55. The hindering potential $V(\phi)$ for the X_2Y_4 molecule and the four eigenfunctions $u_-(\phi)$ (lowest E) $u_0^{(a)}(\phi)$, $u_0^{(b)}(\phi)$ (degenerate doublet) and $u_+(\phi)$ (highest E) for the $n = 0$ quartet.

Solution for Problem 55

The Case $N = 2$: We will start the process of finding the allowed solutions by assuming the solutions in the first classically forbidden region, near $\phi = \frac{\pi}{2}$ (region I of Fig. P55), must be either an even or an odd function of $(\phi - \frac{\pi}{2})$. Thus, in region I,

$$u_I(\phi) = \frac{A}{\sqrt{|P(\phi)|}} \cosh \frac{1}{\hbar}\left(\int_{\frac{\pi}{2}}^{\phi} d\phi' |P(\phi')|\right) \qquad \text{for even } u_I,$$

$$u_I(\phi) = \frac{A}{\sqrt{|P(\phi)|}} \sinh \frac{1}{\hbar}\left(\int_{\frac{\pi}{2}}^{\phi} d\phi' |P(\phi')|\right) \qquad \text{for odd } u_I. \qquad (1)$$

We shall continue these WKB solutions to region V, near $\phi = \frac{\pi}{2} + 2\pi$, where we will require $u_V = \pm u_I$; i.e., even functions must end up as even functions, odd functions must end up as odd functions, so the probability density and probability density current are single-valued functions in the 3-D space. Let us, however, start with exponential functions in region I:

$$u_I^{(+)} = \frac{1}{\sqrt{|P|}} e^{+\frac{1}{\hbar}\int_{\frac{\pi}{2}}^{\phi} d\phi' |P(\phi')|} = \frac{1}{Q}\frac{1}{\sqrt{|P|}} e^{-\frac{1}{\hbar}\int_{\phi}^{\phi_2} d\phi' |P(\phi')|},$$

$$u_I^{(-)} = \frac{1}{\sqrt{|P|}} e^{-\frac{1}{\hbar}\int_{\frac{\pi}{2}}^{\phi} d\phi' |P(\phi')|} = Q\frac{1}{\sqrt{|P|}} e^{+\frac{1}{\hbar}\int_{\phi}^{\phi_2} d\phi' |P(\phi')|}, \tag{2}$$

where ϕ_2 gives the right boundary of the classically forbidden region I, and where we have used

$$\int_{\frac{\pi}{2}}^{\phi} d\phi' |P(\phi')| = \int_{\frac{\pi}{2}}^{\phi_2} d\phi' |P(\phi')| - \int_{\phi}^{\phi_2} d\phi' |P(\phi')|,$$

and where Q is defined through

$$Q = e^{-\frac{1}{\hbar}\int_{\frac{\pi}{2}}^{\phi_2} d\phi' |P(\phi')|}.$$

We shall now use the WKB connection formulae to connect these solutions to the oscillatory solutions, valid in region II for $\phi_2 < \phi < \phi_3$:

$$u_I^{(+)} \rightarrow \frac{2}{Q}\frac{1}{\sqrt{P(\phi)}} \cos\left(\frac{1}{\hbar}\int_{\phi_2}^{\phi} d\phi' P(\phi') - \frac{\pi}{4}\right),$$

$$u_I^{(-)} \rightarrow \frac{Q}{\sqrt{P(\phi)}} \cos\left(\frac{1}{\hbar}\int_{\phi_2}^{\phi} d\phi' P(\phi') + \frac{\pi}{4}\right). \tag{3}$$

In the cosine functions, we shall now use

$$\frac{1}{\hbar}\int_{\phi_2}^{\phi} d\phi' P(\phi') = \frac{1}{\hbar}\int_{\phi_2}^{\phi_3} d\phi' P(\phi') - \frac{1}{\hbar}\int_{\phi}^{\phi_3} d\phi' P(\phi'),$$

and relate the integral over the complete oscillatory region to the action variable, $J(E)$, with $E = E^{(0)} + \Delta E$, where $E^{(0)}$ is the solution for a single oscillatory well of approximately parabolic shape, with $E^{(0)} = \hbar\omega_0(n + \frac{1}{2})$, and ΔE is the shift in this energy level caused by the presence of the potential hills. With $\Delta E \ll E^{(0)}$, we then have

$$\frac{1}{\hbar}\int_{\phi_2}^{\phi_3} d\phi' P(\phi') = \frac{\pi}{\hbar}\Big(J(E)\Big)$$

$$= \frac{\pi}{\hbar}\left(J(E^{(0)}) + \left(\frac{\partial J}{\partial E}\right)_{E^{(0)}}\Delta E\right) = \frac{\pi}{\hbar}\left(\hbar(n + \frac{1}{2}) + \frac{1}{\omega_0}\Delta E\right).$$

Substituting this equation into eq. (3), we have

$$u_I^{(+)} \rightarrow \frac{2}{Q}\frac{1}{\sqrt{P(\phi)}} \cos\left(\frac{1}{\hbar}\int_{\phi}^{\phi_3} d\phi' P(\phi') - \frac{\pi}{4} - n\pi - \frac{\pi\Delta E}{\hbar\omega_0}\right),$$

$$u_{\mathrm{I}}^{(-)} \to Q \frac{1}{\sqrt{P(\phi)}} \cos\left(\frac{1}{\hbar}\int_\phi^{\phi_3} d\phi' P(\phi') + \frac{\pi}{4} - (n+1)\pi - \frac{\pi\,\Delta E}{\hbar\omega_0}\right). \quad (4)$$

Now, expanding in the small quantity, $(\pi\,\Delta E)/(\hbar\omega_0)$, we have

$$u_{\mathrm{I}}^{(+)} \to \frac{2}{Q}\frac{1}{\sqrt{P(\phi)}}(-1)^n\left[\cos\left(\frac{1}{\hbar}\int_\phi^{\phi_3} d\phi' P(\phi') - \frac{\pi}{4}\right)\right.$$
$$\left. - \frac{\pi\,\Delta E}{\hbar\omega_0}\cos\left(\frac{1}{\hbar}\int_\phi^{\phi_3} d\phi' P(\phi') + \frac{\pi}{4}\right)\right],$$

$$u_{\mathrm{I}}^{(-)} \to Q\frac{1}{\sqrt{P(\phi)}}(-1)^{(n+1)}\left[\cos\left(\frac{1}{\hbar}\int_\phi^{\phi_3} d\phi' P(\phi') + \frac{\pi}{4}\right)\right.$$
$$\left. + \frac{\pi\,\Delta E}{\hbar\omega_0}\cos\left(\frac{1}{\hbar}\int_\phi^{\phi_3} d\phi' P(\phi') - \frac{\pi}{4}\right)\right]. \quad (5)$$

We now use the WKB connection formulae to connect the oscillatory solutions for $\phi < \phi_3$ onto the exponential solutions for $\phi > \phi_3$, valid in region III, to obtain

$$u_{\mathrm{I}}^{(+)} \to \frac{1}{Q}\frac{(-1)^n}{\sqrt{|P(\phi)|}}\left[e^{-\frac{1}{\hbar}\int_{\phi_3}^\phi d\phi'|P(\phi')|} - 2\frac{\pi\,\Delta E}{\hbar\omega_0}e^{+\frac{1}{\hbar}\int_{\phi_3}^\phi d\phi'|P(\phi')|}\right],$$

$$u_{\mathrm{I}}^{(-)} \to -Q\frac{(-1)^n}{\sqrt{|P(\phi)|}}\left[e^{+\frac{1}{\hbar}\int_{\phi_3}^\phi d\phi'|P(\phi')|} + \frac{1}{2}\frac{\pi\,\Delta E}{\hbar\omega_0}e^{-\frac{1}{\hbar}\int_{\phi_3}^\phi d\phi'|P(\phi')|}\right]. \quad (6)$$

Now using

$$e^{-\frac{1}{\hbar}\int_{\phi_3}^\phi d\phi'|P(\phi')|} = e^{-\frac{1}{\hbar}\int_{\phi_3}^{\frac{3\pi}{2}} d\phi'|P(\phi')|}e^{-\frac{1}{\hbar}\int_{\frac{3\pi}{2}}^\phi d\phi'|P(\phi')|} = Qe^{-\frac{1}{\hbar}\int_{\frac{3\pi}{2}}^\phi d\phi'|P(\phi')|},$$

we get

$$u_{\mathrm{I}}^{(+)} \to \frac{(-1)^n}{\sqrt{|P(\phi)|}}\left[e^{-\frac{1}{\hbar}\int_{\frac{3\pi}{2}}^\phi d\phi'|P(\phi')|} - \frac{2}{Q^2}\frac{\pi\,\Delta E}{\hbar\omega_0}e^{+\frac{1}{\hbar}\int_{\frac{3\pi}{2}}^\phi d\phi'|P(\phi')|}\right],$$

$$u_{\mathrm{I}}^{(-)} \to \frac{(-1)^n}{\sqrt{|P(\phi)|}}\left[-e^{+\frac{1}{\hbar}\int_{\frac{3\pi}{2}}^\phi d\phi'|P(\phi')|} - \frac{Q^2}{2}\frac{\pi\,\Delta E}{\hbar\omega_0}e^{-\frac{1}{\hbar}\int_{\frac{3\pi}{2}}^\phi d\phi'|P(\phi')|}\right]. \quad (7)$$

For levels far below the potential barriers, we expect the penetration factor, Q^2, to be such that $Q^2 \ll 1$. Also, the energy shift caused by barrier penetration should be proportional to Q^2. The quantity $\frac{\Delta E}{\hbar\omega_0}Q^2$ can thus be expected to be completely negligible, so the negative exponential in the last expression can be neglected. If we now name

$$\frac{1}{\sqrt{|P(\phi)|}}e^{\pm\int_{\frac{3\pi}{2}}^\phi d\phi'|P(\phi')|} = u_{\mathrm{III}}^{(\pm)},$$

and introduce the shorthand notation

$$\beta \equiv \frac{\pi\,\Delta E}{\hbar\omega_0 Q^2},$$

the above equations give us the connection formulae

$$u_{\mathrm{I}}^{(+)} \to (-1)^n \left[u_{\mathrm{III}}^{(-)} - 2\beta u_{\mathrm{III}}^{(+)} \right],$$
$$u_{\mathrm{I}}^{(-)} \to (-1)^n \left[-u_{\mathrm{III}}^{(+)} \right]. \tag{8}$$

We can now iterate this procedure to connect the $u_{\mathrm{III}}^{(\pm)}$ onto the corresponding $u_{\mathrm{V}}^{(\pm)}$ in region V, where the original ϕ has been incremented by 2π. This equation yields

$$u_{\mathrm{I}}^{(+)} \to (-1)^{2n} \left[-u_{\mathrm{V}}^{(+)} - 2\beta \left(u_{\mathrm{V}}^{(-)} - 2\beta u_{\mathrm{V}}^{(+)} \right) \right] = [(4\beta^2 - 1)u_{\mathrm{V}}^{(+)} - 2\beta u_{\mathrm{V}}^{(-)}],$$
$$u_{\mathrm{I}}^{(-)} \to (-1)^{2n} \left[-u_{\mathrm{V}}^{(-)} + 2\beta u_{\mathrm{V}}^{(+)} \right] \qquad = \qquad [2\beta u_{\mathrm{V}}^{(+)} - u_{\mathrm{V}}^{(-)}]. \tag{9}$$

Combining these formulae to make even or odd functions of ϕ in region I, these even or odd functions in region I would connect to a linear combination of even and odd functions in region V, where ϕ has been incremented by 2π:

$$\frac{1}{\sqrt{|P(\phi)|}} \cosh\left(\frac{1}{\hbar} \int_{\frac{\pi}{2}}^{\phi} d\phi' |P(\phi')| \right) = \tfrac{1}{2}\left(u_{\mathrm{I}}^{(+)} + u_{\mathrm{I}}^{(-)} \right)$$
$$\to \tfrac{1}{2}\left[(2\beta^2 - 1)(u_{\mathrm{V}}^{(+)} + u_{\mathrm{V}}^{(-)}) + 2\beta(1 + \beta)(u_{\mathrm{V}}^{(+)} - u_{\mathrm{V}}^{(-)}) \right]$$
$$= \frac{1}{\sqrt{|P(\phi)|}} \left[(2\beta^2 - 1) \cosh\left(\frac{1}{\hbar} \int_{\frac{5\pi}{2}}^{\phi} d\phi' |P(\phi')| \right) \right.$$
$$\left. + 2\beta(1 + \beta) \sinh\left(\frac{1}{\hbar} \int_{\frac{5\pi}{2}}^{\phi} d\phi' |P(\phi')| \right) \right], \tag{10}$$

and

$$\frac{1}{\sqrt{|P(\phi)|}} \sinh\left(\frac{1}{\hbar} \int_{\frac{\pi}{2}}^{\phi} d\phi' |P(\phi')| \right) = \tfrac{1}{2}\left(u_{\mathrm{I}}^{(+)} - u_{\mathrm{I}}^{(-)} \right)$$
$$\to \tfrac{1}{2}\left[2\beta(\beta - 1)(u_{\mathrm{V}}^{(+)} + u_{\mathrm{V}}^{(-)}) + (2\beta^2 - 1)(u_{\mathrm{V}}^{(+)} - u_{\mathrm{V}}^{(-)}) \right]$$
$$= \frac{1}{\sqrt{|P(\phi)|}} \left[2\beta(\beta - 1) \cosh\left(\frac{1}{\hbar} \int_{\frac{5\pi}{2}}^{\phi} d\phi' |P(\phi')| \right) \right.$$
$$\left. + (2\beta^2 - 1) \sinh\left(\frac{1}{\hbar} \int_{\frac{5\pi}{2}}^{\phi} d\phi' |P(\phi')| \right) \right]. \tag{11}$$

Thus, we see from eq. (10) $u_{\mathrm{even}}(\phi) \to \pm u_{\mathrm{even}}(\phi + 2\pi)$ only if $\beta = -1$, or if $\beta = 0$. From eq. (11), $u_{\mathrm{odd}}(\phi) \to \pm u_{\mathrm{odd}}(\phi + 2\pi)$ only if $\beta = +1$, or if $\beta = 0$. The potential $V_0(1 - \cos 2\phi)$ thus splits the zeroth-order energies $E^{(0)} = \hbar\omega_0(n + \tfrac{1}{2})$ into three closely spaced levels, one of them with $\Delta E = 0$, being doubly degenerate. The four values of ΔE are

$$\Delta E = -Q^2 \frac{\hbar\omega_0}{\pi} \qquad \text{with} \quad u_{\mathrm{even}}(\phi) \to +u_{\mathrm{even}}(\phi + 2\pi),$$
$$\Delta E = 0 \qquad \text{with} \quad u_{\mathrm{even}}(\phi) \to -u_{\mathrm{even}}(\phi + 2\pi),$$
$$\Delta E = 0 \qquad \text{with} \quad u_{\mathrm{odd}}(\phi) \to -u_{\mathrm{odd}}(\phi + 2\pi),$$

$$\Delta E = +Q^2 \frac{\hbar \omega_0}{\pi} \qquad \text{with} \quad u_{\text{odd}}(\phi) \to +u_{\text{odd}}(\phi + 2\pi). \tag{12}$$

The four eigenfunctions for the case $n = 0$ are shown qualitatively in Fig. P55. The four eigenfunctions are also either even or odd functions of $(\phi - \frac{3\pi}{2})$; i.e., they are even or odd with respect to reflections in the plane $\phi = \frac{3\pi}{2}$, where the potential again has a maximum. In particular, the eigenfunction u_- of the nondegenerate level, with $\Delta E = -Q^2 \hbar \omega_0/\pi$, is even with respect to reflections in planes through any potential maximum, and the eigenfunction u_+ of the nondegenerate level, with $\Delta E = +Q^2 \hbar \omega_0/\pi$, is odd with respect to reflections in planes through any potential maximum. Conversely, the eigenfunctions u_0 for the doubly degenerate level, with $\Delta E = 0$, are alternately even and odd functions when reflected in planes through successive potential maxima. Because any linear combination of the two eigenfunctions u_0 is again an eigenfunction with the same eigenvalue, we would, however, have to exercise care in using the symmetry with respect to reflections in successive planes of symmetry of the potential.

The case for $V(\phi) = V_0(1 - \cos N\phi)$,   arbitrary N:

In this case, the maxima of the potentials will be centered about the angles

$$\frac{\pi}{N}, \left(\frac{\pi}{N} + \frac{2\pi}{N}\right), \left(\frac{\pi}{N} + 2\frac{2\pi}{N}\right), \dots, \left(\frac{\pi}{N} + k\frac{2\pi}{N}\right), \dots, \left(\frac{\pi}{N} + N\frac{2\pi}{N}\right)$$

$$= \left(\frac{\pi}{N} + 2\pi\right)$$

Let us rename these regions with the index k, starting with $k = 0$ for the starting hill and ending with $k = N$, for which we have incremented ϕ by 2π. Eqs. (8) and (9) can now be put in the form

$$u_{0,\text{even}} \to (-1)^n \left[-\beta u_{1,\text{even}} - (1 + \beta)u_{1,\text{odd}} \right],$$
$$u_{0,\text{odd}} \to (-1)^n \left[-\beta u_{1,\text{odd}} + (1 - \beta)u_{1,\text{even}} \right]. \tag{13}$$

$$u_{0,\text{even}} \to (-1)^{2n} \left[(2\beta^2 - 1)u_{2,\text{even}} + 2\beta(1 + \beta)u_{2,\text{odd}} \right],$$
$$u_{0,\text{odd}} \to (-1)^{2n} \left[(2\beta^2 - 1)u_{2,\text{odd}} - 2\beta(1 - \beta)u_{2,\text{even}} \right]. \tag{14}$$

Iterating this once more, we have the connection into the next hill

$$u_{0,\text{even}} \to (-1)^{3n} \left[\beta(3 - 4\beta^2)u_{3,\text{even}} - (1 + \beta)(4\beta^2 - 1)u_{3,\text{odd}} \right],$$
$$u_{0,\text{odd}} \to (-1)^{3n} \left[\beta(3 - 4\beta^2)u_{3,\text{odd}} + (1 - \beta)(4\beta^2 - 1)u_{3,\text{even}} \right]. \tag{15}$$

Before iterating this into the kth hill, it will be convenient to change the notation, and rename $\beta \equiv \cos\alpha$. With this notation, the above relations and the continued iteration process give

$$u_{0,\text{even}} \to (-1)^n \left[-\cos\alpha \ u_{1,\text{even}} - (1 + \cos\alpha)u_{1,\text{odd}} \right],$$
$$u_{0,\text{odd}} \to (-1)^n \left[-\cos\alpha \ u_{1,\text{odd}} + (1 - \cos\alpha)u_{1,\text{even}} \right],$$

$$u_{0,\text{even}} \rightarrow (-1)^{2n}\left[\cos(2\alpha) \ u_{2,\text{even}} + (1 + \cos\alpha)\frac{\sin(2\alpha)}{\sin\alpha}u_{2,\text{odd}}\right],$$

$$u_{0,\text{odd}} \rightarrow (-1)^{2n}\left[\cos(2\alpha) \ u_{2,\text{odd}} - (1 - \cos\alpha)\frac{\sin(2\alpha)}{\sin\alpha}u_{2,\text{even}}\right],$$

$$u_{0,\text{even}} \rightarrow (-1)^{3n}\left[-\cos(3\alpha) \ u_{3,\text{even}} - (1 + \cos\alpha)\frac{\sin(3\alpha)}{\sin\alpha}u_{3,\text{odd}}\right],$$

$$u_{0,\text{odd}} \rightarrow (-1)^{3n}\left[-\cos(3\alpha) \ u_{3,\text{odd}} + (1 - \cos\alpha)\frac{(\sin 3\alpha)}{\sin\alpha}u_{3,\text{even}}\right],$$

$$\cdots\cdots\cdots$$

$$u_{0,\text{even}} \rightarrow (-1)^{k(n+1)}\left[\cos(k\alpha) \ u_{k,\text{even}} + (1 + \cos\alpha)\frac{\sin(k\alpha)}{\sin\alpha}u_{k,\text{odd}}\right],$$

$$u_{0,\text{odd}} \rightarrow (-1)^{k(n+1)}\left[\cos(k\alpha) \ u_{k,\text{odd}} - (1 - \cos\alpha)\frac{(\sin k\alpha)}{\sin\alpha}u_{k,\text{even}}\right],$$

$$\cdots\cdots\cdots$$

$$u_{0,\text{even}} \rightarrow (-1)^{N(n+1)}\left[\cos(N\alpha) \ u_{N,\text{even}} + (1 + \cos\alpha)\frac{\sin(N\alpha)}{\sin\alpha}u_{N,\text{odd}}\right],$$

$$u_{0,\text{odd}} \rightarrow (-1)^{N(n+1)}\left[\cos(N\alpha) \ u_{N,\text{odd}} - (1 - \cos\alpha)\frac{\sin(N\alpha)}{\sin\alpha}u_{N,\text{even}}\right], \quad (16)$$

where the last iteration must give

$$u_{N,\text{even}} = u_{\text{even}}(\phi + 2\pi) = \pm u_{0,\text{even}}(\phi),$$

or

$$u_{N,\text{odd}} = u_{\text{odd}}(\phi + 2\pi) = \pm u_{0,\text{odd}}(\phi).$$

A single (nondegenerate) even solution exists if $\cos\alpha = -1$, and a single (nondegenerate) odd solution if $\cos\alpha = +1$. In addition, both an even and an odd solution exists if

$$\sin N\alpha = 0, \qquad \cos N\alpha = \pm 1, \qquad\qquad \text{or}$$

$$\alpha = \frac{\ell\pi}{N}, \qquad \ell = 1, 2, \ldots, (N - 1).$$

Recalling $\cos\alpha = (\pi\,\Delta E)/Q^2\hbar\omega_0)$, the final spectrum of allowed energies is

$$\Delta E = -Q^2\frac{\hbar\omega_0}{\pi}, \qquad\qquad \text{with nondegenerate even eigenfunction,}$$

$$\Delta E = +Q^2\frac{\hbar\omega_0}{\pi}, \qquad\qquad \text{with nondegenerate odd eigenfunction,}$$

$$\Delta E = Q^2\frac{\hbar\omega_0}{\pi}\cos\frac{\ell\pi}{N}, \qquad \text{with } \ell = 1, 2, \ldots, (N - 1), \text{ all doubly degenerate.}$$

For $N = 3$, which might apply to the X_2Y_6 molecule, each zeroth-order energy, $E_n^{(0)}$, is split into four levels with

$$(\Delta E)_n = +Q_n^2\frac{\hbar\omega_0}{\pi}, \quad +\tfrac{1}{2}Q_n^2\frac{\hbar\omega_0}{\pi}, \quad -\tfrac{1}{2}Q_n^2\frac{\hbar\omega_0}{\pi}; \quad -Q_n^2\frac{\hbar\omega_0}{\pi}.$$

The penetration factor, Q_n^2, may of course be so small for the ground state, $n = 0$, the splitting may be unobservable (e.g., in C_2H_6).

The case of very large N is of relevance in solid-state physics, where periodic boundary conditions are used. If we have a crystalline lattice with N repeat units, we assume the $(N + 1)^{\text{th}}$ unit is identical with the first. If N is very large, the spacing of our multiplet of $2 + (N - 1) = (N + 1)$ sublevels can effectively be replaced by a band of continuum states of width $2Q_n^2\hbar\omega_0/\pi$. The penetration factor Q_n^2 is a sensitive function of $E_n^{(0)}$. For $n = 0$, far below the top of the potential barriers, we may have $Q_0^2 \ll 1$, leading to a narrow band. For $n > 0$, Q_n^2 may grow dramatically with n, leading to ever wider bands as the top of the potential barriers is approached.