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On the Periodic Orbit Description of Tunneling in Symmetric and Asymmetric Double-Well Potentials

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Abstract

Semiclassical periodic orbit theory is applied to the double-well eigenvalue problem to show how this unified approach describes the quite different character of the level splitting (in the case of symmetric wells) and level shifts (in the asymmetric case) caused by tunneling.

I. Introduction

In molecular phenomena involving double-well potential functions (cf. Figure 1), level splitting and level shifts caused by tunneling through the barrier is well-known. Examples include inversion of the ammonia molecule, for which the double well is symmetric (cf. Figure 1a), and proton tunneling between DNA base pairs, for which the two wells are unsymmetrical (cf. Figure 1b). The purpose of this paper is to analyze this phenomenon in terms of semiclassical periodic orbit theory[1,2] and to point out the fundamental differences between the symmetrical and unsymmetrical cases. Since periodic orbit theory can also be applied to multi-dimensional systems, it is hoped that this analysis may be useful in suggesting how to approach the treatment of multi-dimensional double-well potential energy surfaces.

II. Semiclassical Eigenvalues via Periodic Orbit Theory.

The semiclassical eigenvalues of a potential well are described in an appealingly intuitive manner by their periodic orbits. One makes use of the following quantum mechanical relations:

$$g(E) \equiv \text{trace } (E-H)^{-1} = \sum_k (E-E_k)^{-1} \tag{1a}$$

$$= (i\hbar)^{-1} \int_0^\infty dt\ e^{iEt/\hbar} \int dx\ \langle x|e^{-iHt/\hbar}|x\rangle \quad . \tag{1b}$$

The eigenvalues $\{E_k\}$ are thus identified as the poles of the function $g(E)$, and the semiclassical approximation enters by invoking the usual semiclassical approximation to the propagator[3] (time evolution operator) in Eq. (1b). Further semiclassical approximations are that the integrals over t and x in Eq. (1b) are evaluated via the stationary phase approximation, and for one dimensional systems this gives[1,2,4] (using units such that $\hbar = 1$)

$$g(E) \propto \sum_{\substack{\text{periodic}\\ \text{orbits}}} e^{i(\Phi-\pi\ell/2)} \quad , \tag{2}$$

where $\Phi \equiv \Phi(E)$ is the action integral for a periodic trajectory with energy E,

$$\Phi(E) = \int dt\ p(t)\ \dot{x}(t) = \oint dx\ p(x,E) \quad ,$$

and ℓ is the number of classical turning points experienced by the trajectory. Uninteresting (for present purposes) proportionality constants are for simplicity omitted in Eq. (2). The sum is over all periodic orbits, i.e., trajectories that began and end with the same coordinate and momentum.

To see how Eq. (2) works, consider first a single potential well. A periodic trajectory is one that begins at some position x with momentum p and returns at some later time to this position with the same momentum. For a simple one dimensional potential well it is clear that there are an infinite number of such trajectories because the particle oscillates back and forth in the well forever. If $\phi(E)$ is the action integral for one pass across the well,

$$\phi(E) = \int_{x_<}^{x_>} dx\; p(x,E) = \int_{x_<}^{x_>} dx\,\sqrt{2\mu[E-V(x)]} \quad , \qquad (3)$$

where $x_<$ and $x_>$ are the classical turning points, then for a periodic orbit that makes k passes back and forth across the well one has

$$\Phi(E) = 2k\;\phi(E)$$

$$\ell = 2k \quad ,$$

so that in this case Eq. (2) gives

$$g(E) \propto \sum_{k=1}^{\infty} e^{i2k(\phi - \frac{\pi}{2})}$$

$$= \frac{e^{2i(\phi - \frac{\pi}{2})}}{1-e^{2i(\phi - \frac{\pi}{2})}} \quad . \qquad (4)$$

Eq. (4) shows that g(E) has poles at the values of E for which

$$e^{2i(\phi - \frac{\pi}{2})} = 1$$

or

$$\phi(E) - \frac{\pi}{2} = \pi n$$

or

$$\phi(E) = (n + \frac{1}{2})\pi \quad , \qquad (5)$$

where n is any integer. This is the well known WKB eigenvalue relation[5] for simple potential wells.

Eq. (2) can also be applied to the double-well potentials sketched in Figure 1, but to include the effects of tunneling it is necessary to include complex-valued periodic trajectories[6] as well as the real ones. Consider a trajectory beginning in potential well 1 in Figure 1. In addition to the term in Eq. (4) from the real-valued trajectories that oscillate back and forth in well 1, there are complex-valued trajectories that tunnel through the barrier; Figure 2 depicts the simplest such trajectory, for which the contribution to g(E) is

$$e^{i\phi_1} e^{-\theta} e^{2i\phi_2} e^{-i\frac{\pi}{2}} e^{-\theta} e^{i\phi_1} e^{-i\frac{\pi}{2}} = -e^{-2\theta} e^{2i\phi_1} e^{2i\phi_2} \quad , \qquad (6)$$

where ϕ_1 and ϕ_2 are the phase integrals across wells 1 and 2, and where the various factors are indicated sequentially: the particle begins at the left hand turning point, travels across well 1, tunnels through the barrier, tunnels across well 2 and back, tunnels back through the barrier, and returns to its starting point; there are two turning points for this periodic trajectory. θ is the imaginary action integral (the barrier penetration integral) for one pass through the barrier:

$$\theta = \int_{x_2}^{x_3} dx \sqrt{2\mu[V(x)-E]} \quad . \tag{7}$$

It is easy to see how to incorporate all trajectories of the above type, i.e., those that tunnel through the barrier and back only once. For a trajectory that makes k_1 extra passes back and forth across well 1 before it tunnels, then tunnels and makes k_2 extra passes back and forth across well 2 before it tunnels back through the barrier, and then makes k_3 extra passes back and forth across well 1 before terminating at its origin, the contribution to $g(E)$ is

$$e^{i[\phi_1+2k_1(\phi_1-\frac{\pi}{2})]}\, e^{-\theta}\, e^{i[2\phi_2-\frac{\pi}{2}+2k_2(\phi_2-\frac{\pi}{2})]}\, e^{-\theta}\, e^{i[\phi_1-\frac{\pi}{2}+2k_3(\phi_1-\frac{\pi}{2})]}$$

$$= -e^{-2\theta}\, e^{2i(\phi_1-\frac{\pi}{2})}\, e^{2i(\phi_2-\frac{\pi}{2})}\, e^{2ik_1(\phi_1-\frac{\pi}{2})}\, e^{2ik_2(\phi_2-\frac{\pi}{2})}\, e^{2ik_3(\phi_1-\frac{\pi}{2})} \quad . \tag{8}$$

The total contribution of such trajectories is obtained by summing over k_1, k_2, and k_3,

$$\sum_{k_1=0}^{\infty} \sum_{k_2=0}^{\infty} \sum_{k_3=0}^{\infty} \quad ,$$

which when added to the contribution of the real trajectories finally gives

$$g(E) \propto \frac{e^{2\pi i n_1}}{1-e^{2\pi i n_1}} - \frac{e^{-2\theta}\, e^{2\pi i n_1}\, e^{2\pi i n_2}}{(1-e^{2\pi i n_1})^2\,(1-e^{2\pi i n_2})} \quad , \tag{9}$$

where

$$n_1 \equiv n_1(E) = [\phi_1(E) - \frac{\pi}{2}]/\pi \tag{10a}$$

$$n_2 \equiv n_2(E) = [\phi_2(E) - \frac{\pi}{2}]/\pi \quad . \tag{10b}$$

Eq. (9) is the final expression from which the results of interest are obtained below.

Symmetric (Degenerate) Case.

Consider first the symmetric double-well (Figure 1a) so that

$$n_1(E) = n_2(E) \equiv n(E) \quad , \tag{11}$$

and Eq. (9) becomes

$$g(E) \propto \frac{e^{2\pi in}}{1-e^{2\pi in}} - e^{-2\theta} \frac{(e^{2\pi in})^2}{(1-e^{2\pi in})^3} \quad . \tag{12}$$

The unperturbed (and thus unsplit) eigenvalues are determined by

$$n(E) = \text{integer},$$

and let E be close to such an eigenvalue, E_0 say. Then

$$n(E) \simeq n(E_0) + n'(E_0)\ (E-E_0) + \ldots \quad , \tag{13}$$

where

$$n(E_0) = \text{integer} \quad ,$$

so that

$$e^{2\pi i n(E)} \simeq e^{2\pi i n(E_0)} e^{2\pi i n'(E_0)(E-E_0)}$$

$$\simeq 1 + 2\pi i n'(E_0)(E-E_0) \quad ,$$

or

$$1 - e^{2\pi i n(E)} \simeq -2\pi i n'(E_0)(E-E_0) \quad . \tag{14}$$

Discarding multiplicative factors, Eq. (12) then becomes

$$g(E) \propto \frac{1}{E-E_0} + \frac{e^{-2\theta}}{[2\pi n'(E_0)]^2 (E-E_0)^3} \quad . \tag{15}$$

The semiclassical expression in Eq. (15) is to be compared with the quantum mechanical expression, Eq. (1a), including only the two energy levels $E_0 - \frac{\Delta E}{2}$ and $E_0 + \frac{\Delta E}{2}$, where ΔE is the splitting; i.e., for E close to E_0 one has

$$g_{QM}(E) \simeq \frac{1}{E-E_0 + \frac{\Delta E}{2}} + \frac{1}{E-E_0 + \frac{\Delta E}{2}} \quad ;$$

expanding this to lowest order in ΔE gives

$$g_{QM}(E) \simeq 2\left[\frac{1}{E-E_0} + \frac{(\Delta E/2)^2}{(E-E_0)^3}\right] \quad . \tag{16}$$

Comparising Eqs. (15) and (16) identifies the semiclassical expression for the level splitting as follows:

$$\frac{\Delta E}{2} = \frac{e^{-\theta}}{2\pi n'(E_0)} \quad . \tag{17}$$

This result, which is also obtained by conventional WKB methods[7], is valid only for small splittings because periodic orbits were included that involved only one tunneling back and forth across the well, and also because the above expressions have been evaluated only to lowest order in ΔE.

Asymmetric (Non-Degenerate) Case.

Here $n_1(E) \neq n_2(E)$ and we consider the shift in one of the unperturbed eigenvalues, E_1 say, of well 1 that is caused by the tunneling. Thus let E be near E_1, where

$$n_1(E_1) = \text{integer} \quad ,$$

so that

$$e^{2\pi i n_1(E)} \simeq e^{2\pi i n_1(E_1)} e^{2\pi i n_1'(E_1)(E-E_1)}$$

$$\simeq 1 + 2\pi i n_1'(E_1)(E-E_1) \quad ,$$

or

$$1-e^{2\pi i n_1(E)} \simeq -2\pi i n_1'(E)(E-E_1) \quad .$$

Eq. (9) then gives (dropping multiplicative factors)

$$g(E) \propto \frac{1}{E-E_1} - \frac{e^{-2\theta}\, e^{2\pi i n_2(E_1)}}{[-2\pi i n_1'(E_1)][1-e^{2\pi i n_2(E_1)}](E-E_1)^2} \quad . \tag{18}$$

If E_2 is the eigenvalue of well 2--i.e.,

$$n_2(E_2) = \text{integer}$$

--that is closest to E_1, then

$$e^{2\pi i n_2(E_1)} \simeq e^{2\pi i n_2(E_2)} e^{2\pi i n_2'(E_2)(E_1-E_2)}$$

$$\simeq 1 + 2\pi i n_2'(E_2)(E_1-E_2) \quad ,$$

or

$$1 - e^{2\pi i n_2(E_1)} \simeq -2\pi i n_2'(E_2)(E_1-E_2) \quad ,$$

so that Eq. (18) becomes

$$g(E) \propto \frac{1}{E-E_1} - \frac{e^{-2\theta}}{(E-E_1)^2[2\pi i n_1'(E_1)][2\pi i n_2'(E_2)](E_1-E_2)} \quad . \tag{19}$$

The quantum mechanical approximation to g(E), taking into account only the energy level $E_1 + \Delta E$, i.e., for E near E_1, is

$$g_{QM}(E) \simeq \frac{1}{E-E_1-\Delta E} \quad ,$$

which, expanded to lowest order in ΔE, is

$$g_{QM}(E) \simeq \frac{1}{E-E_1} + \frac{\Delta E}{(E-E_1)^2} \quad . \tag{20}$$

Comparing Eqs. (19) and (20) leads to the semiclassical expression for the level shift,

$$\Delta E = \frac{e^{-2\theta}}{[2\pi n_1'(E_1)][2\pi n_2'(E_2)](E_1-E_2)} \quad . \tag{21}$$

III. Discussion.

Equations (17) and (21) give the semiclassical results for the splitting of degenerate levels and shift in non-degenerate levels, respectively, caused by tunneling between the wells. Considering $e^{-\theta} << 1$, the most interesting and obvious difference between the symmetric and asymmetric cases is that the perturbation of the levels in the symmetric is much greater than that in the asymmetric case, as has been noted before.[7a] The symmetry of the two wells allows the particle to "hop" from one well to the other much faster than it would ordinarily be able to tunnel.

Another interesting comparison to the quantum mechanical situation is possible by considering the quantum mechanical energy levels to come from a 2 x 2 matrix H_{ij},

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} , \tag{21}$$

with $H_{11} = E_1$ and $H_{22} = E_2$ being the unperturbed levels. In the degenerate case $E_1 = E_2 \equiv E_0$ and the eigenvalues of the matrix are

$$E = E_0 \pm H_{12} , \tag{22}$$

so that

$$\frac{\Delta E}{2} = H_{12} ;$$

comparing with the semiclassical expression, Eq. (17), identifies the "exchange interaction" H_{12} as

$$H_{12} = \frac{\hbar\omega}{2\pi} e^{-\theta} \quad , \tag{23}$$

where $\hbar\omega = 1/n'(E_0)$. For the asymmetric case, $E_1 \neq E_2$, the eigenvalue close to E_1 is given to lowest order in H_{12} by second order perturbation theory

$$E = E_1 + \frac{H_{12}^{\ 2}}{E_1 - E_2} \quad , \tag{24a}$$

i.e.,

$$\Delta E = \frac{H_{12}^{\ 2}}{E_1 - E_2} \quad , \tag{24b}$$

and comparing this to the semiclassical expression, Eq. (21), leads to the identification

$$H_{12} = \sqrt{\frac{\hbar\omega_1}{2\pi} \, \frac{\hbar\omega_2}{2\pi}} \, e^{-\theta} \quad , \tag{25}$$

where $\hbar\omega_1 = 1/n_1'(E_1)$, $\hbar\omega_2 = 1/n_2'(E_2)$. In both cases, therefore, one obtains essentially the same identification, Eqs. (23) and (25), for the semiclassical approximation to the exchange interaction.

Another interesting comparison is to the level <u>width</u> of a metastable state in a potential as sketched in Figure 3. The width Γ of the level is given semiclassically by[7a,7c]

$$\Gamma = \frac{e^{-2\theta}}{2\pi n'(E)} \quad , \tag{26}$$

where $\pi n(E) = \phi(E)$ is the action integral over the bound well. The level width is thus seen to be much more closely related to the asymmetric, non-degenerate energy level shift than it is to the level splitting in the symmetric, degenerate case.

As a final point, the probability P for tunneling through a potential barrier is[5]

$$P = e^{-2\theta} \quad ,$$

whether the barrier is symmetric or asymmetric. (This quantity appears commonly, for example, in considering quantum effects to reaction rate constants.) There have been attempts to determine P by distorting the barrier problem into a double-well problem, as indicating in Figure 4, and then identifying P by

$$P \propto \Delta E \quad ,$$

where ΔE is the splitting (in the symmetric well case) or level shift (in the asymmetric case). From the discussion above it is clear that this identification is correct only in the asymmetric case; i.e., the rate of tunneling through a barrier, even a symmetric one, is much slower than the rate of hopping back and forth in a symmetric double-well potential.

In concluding, we note that there is considerable interest now in trying to extend semiclassical eigenvalue methods to multi-dimensional systems, and much progress has been made recently for multi-dimensional potential energy surfaces that possess a single well.[8-10] It is hoped that this periodic orbit picture of dealing with double-well potentials may be of use in extending multi-dimensional periodic orbit methods to treat multi-dimensional double-well potential energy surfaces.

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Figure Captions

1. Sketch of a symmetric (a) and asymmetric (b) double-well potential function.
2. The simplest complex-valued periodic trajectory that tunnels from well 1 to well 2 and back.
3. A potential function giving rise to metastable levels (or equivalently scattering resonances).
4. Sketch of a typical potential barrier, indicating (via broken lines) how it can be distorted into a double-well potential.

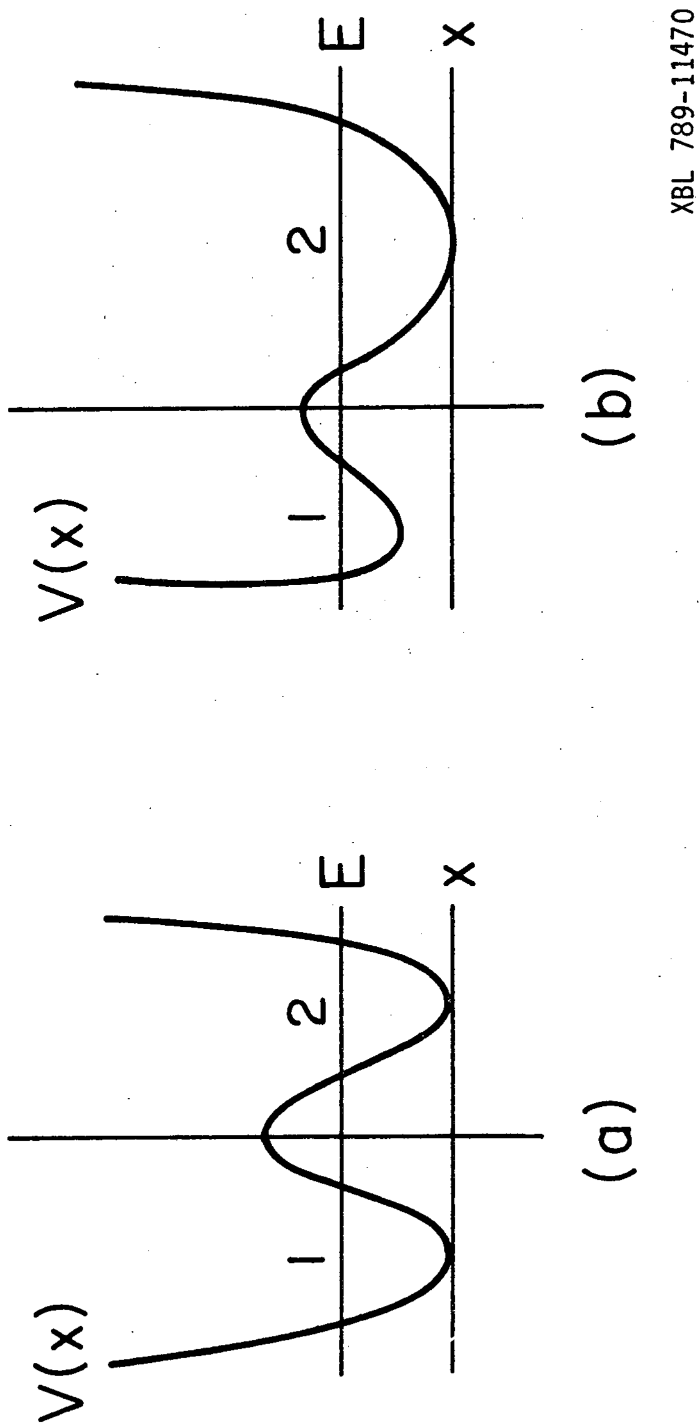

Figure 1

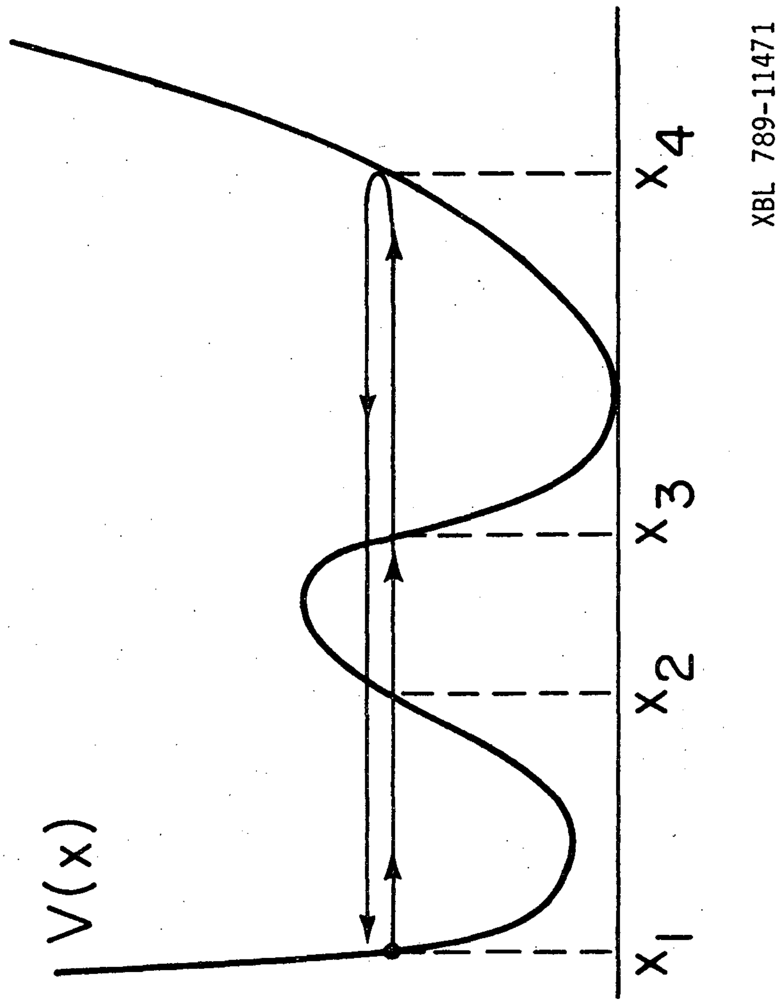

Figure 2

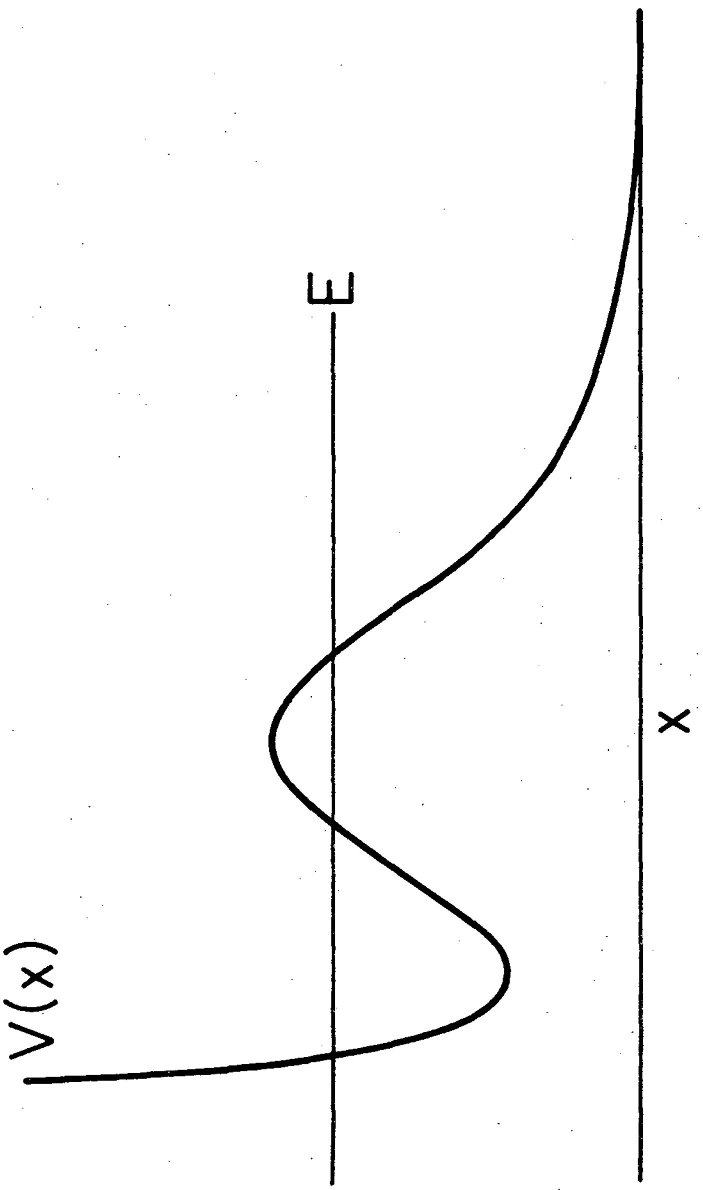

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Figure 3

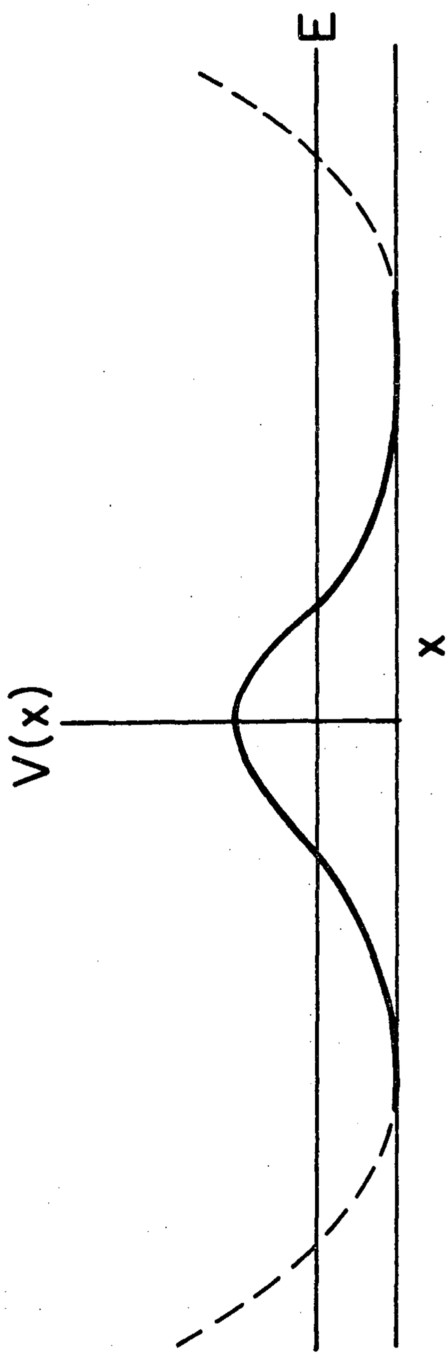

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Figure 4

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