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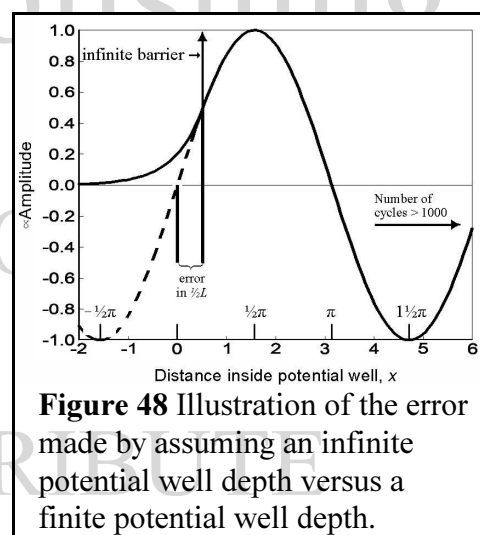
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A Particle in a Box with a Tooth - Perturbation Theory for adsorption on a surface with a molecule present.

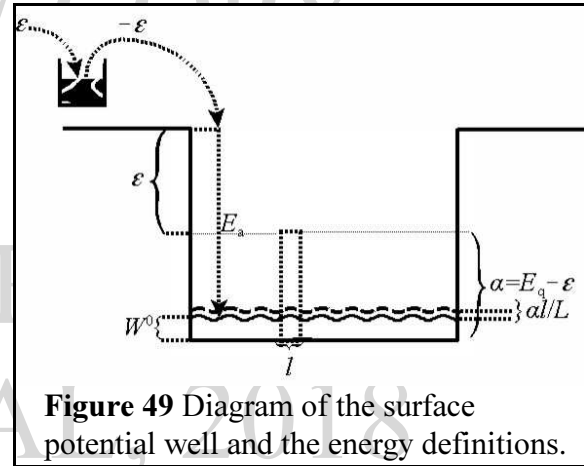
The quantum mechanical derivation needed for **Eq. (119)** will, for simplicity here, assume a 1 dimensional box of length  $L$ . Two Dimensions is an obvious extension. However, the 2 dimensional derivation simply doubles the indices and makes for confusion but does make the approximation even more valid since the consideration of **Eq. (126)** below is squared.

The following is a summary of the treatment that can be followed in a recommended textbook on Quantum Mechanics (for example[6].) This treatment assumes non-degenerate perturbation. The zero energy level is taken as the adsorbate on the bare surface, thus the energy,  $E_a$ , is to the top of the potential well. The energy,  $\epsilon$ , is a positive perturbation which is considerably smaller than  $E_a$ . There are two simplifying assumptions made in the following derivation. The first assumption is that the potential wall is very high. The second assumption is that the width of the well is extremely wide compared to an adsorbate molecule and the number of cycles for molecular wave.



The diagram in **Figure 48** illustrates the justification for the infinite wall assumption taking the place of the finite wall assumption. The error basically has to do with where the virtual sine wave crosses the zero amplitude. For a finite barrier the wave curves upward before  $x = 0$  and most of the wave may be simulated as a sine wave that goes to zero with  $x < 0$ . However, the difference is trivial compare to the overall wave that may exist, in this case, more than 1000 cycles.

In **Figure 49** is a diagram indicating the arrangement of the potential well with the reference state for the adsorbent being the bulk liquid state. A potential perturbation is shown that is energy of  $\varepsilon$  below the top of the potential well. This value is equal to the heat of vaporization of the pure liquid, which has been selected as the standard state. The overall depth of the well is  $E_q$ . The width of the perturbation is  $l$  as indicated by the dashed lines. The height from the bottom of the well, labeled  $\alpha$ , is equal to the energy of adsorption for the first molecule,  $E_q$ , minus  $\varepsilon$ . The increase in observed energy of adsorption for the next adsorbed molecule is labeled as  $\alpha l/L$ , as will be determined by the following derivation.



**Figure 49** Diagram of the surface potential well and the energy definitions.

Starting with the unperturbed equation with various states  $n$ :

$$\hat{H}^0 \psi_n^0 = W_n^0 \psi_n^0 \quad (122)$$

Where  $\hat{H}$  is the Hamiltonian operator,  $\psi$  are the wave functions and  $W$  are the energy eigenvalues.

The unperturbed eigenfunctions, individually labeled with integer  $n$ , are:

$$\psi_n^0 = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (123)$$

Where  $L$  is the length of the potential box and  $x$  is the position within the box ( $0 \leq x \leq L$ ). The energy eigenvalues for the unperturbed system are:

$$W_n^0 = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (124)$$

(This is the off-set from the bottom of the well to the first ground state. Energies will be referenced against  $E_a$  and not  $E_q$ .) A perturbation of  $\varepsilon > 0$  is introduced with a width of  $l$  which changes  $\hat{H}^0$  to  $\hat{H}^0 + \hat{H}'$  and  $W^0$  to  $W^0 + W'$ . This leads to the use of the original wave functions in combinations to yield<sup>28</sup> an  $n$  by  $n$  matrix of corrections,  $\mathbf{H}'_{mn}$ . This matrix used to correct the original equation. (It is assumed that there are no degeneracies):

$$\mathbf{H}'_{mn} = \int \psi_m^{0*} \hat{H}' \psi_n^0 ds \quad (125)$$

Since

<sup>28</sup> The original wave functions were  $\psi_n^0$  where  $n$  is enough wave functions either for practical purposes or the energy of the next function would be the free particle. The corrected wave function due to the perturbation for the  $m$ th level is then:  $\psi_m = a_1 \psi_1^0 + a_2 \psi_2^0 + \dots + (-1) \psi_m^0 + \dots + a_m \psi_m^0$ . The index, however, was discontinued at the  $n$ th level, so  $m$  then runs from 1 to  $n$ , thus creating an  $n \times n$  matrix of equations.

$$l < 1 \times 10^{-6} L \quad \therefore \quad \alpha l \lll E_q L \quad (126)$$

then the first order correction ( $a_n = 1$  and  $a_{m \neq n} \ll a_n$ ) should be an extremely good estimate of the overall perturbation energy. The first order approximation is obtained in the following fashion. For each original  $n$  there is now a  $\psi$  that is modified in the perturbed system; call it  $\psi'_n$ . These  $\psi'_n$  consist of linear combinations of the original  $\psi_n^0$ s. The perturbed system to the first order yields then:

$$(\hat{H}^0 + \hat{H}')\psi'_n = (W^0 + W'_n)\psi'_n \quad (127)$$

and rearranged:

$$\hat{H}^0\psi'_n - W_n^0\psi'_n = (W'_n - \hat{H}')\psi'_n \quad (128)$$

Using the linear combinations of  $\psi_n^0$ s for each  $\psi'_n$  and **Eq. 122** for each  $j$ :

$$\hat{H}^0\psi'_n = \hat{H}^0 \sum_j a_j \psi_j^0 = \sum_j a_j W_j^0 \psi_j^0 \quad \text{also} \quad W_n^0\psi'_n = W_n^0 \sum_j a_j \psi_j^0 \quad (129)$$

$$\sum_j a_j W_j^0 \psi_j^0 - W_n^0 \sum_j a_j \psi_j^0 = (W'_n - \hat{H}')\psi'_n \quad (130)$$

$$\sum_j a_j (W_j^0 - W_n^0) \psi_j^0 = (W'_n - \hat{H}')\psi'_n \quad (131)$$

Multiplying both side by the complex conjugates,  $\psi_n^{0*}$ s:

$$\psi_n^{0*} \sum_j a_j (W_j^0 - W_n^0) \psi_j^0 = \psi_n^{0*} (W'_n - \hat{H}')\psi'_n \quad (132)$$

and then integrating over all space, the values of the integrals are either 1 or 0, depending upon the values of  $j$  and  $n$  except for the integral with  $\hat{H}'$ .

$$\sum_j a_j (W_j^0 - W_n^0) \int \psi_n^{0*} \psi_j^0 d\tau = W'_n \int \psi_n^{0*} \psi_n^0 d\tau - \int \psi_n^{0*} \hat{H}' \psi_n^0 d\tau \quad (133)$$

$$\int \psi_n^{0*} \psi_j^0 d\tau = 0, n \neq j, \quad \& \quad \int \psi_n^{0*} \psi_n^0 d\tau = 1 \quad (134)$$

$$0 = \sum_n a_n (W_n^0 - W_n^0) = W'_n - \int \psi_n^{0*} \hat{H}' \psi_n^0 d\tau \quad (135)$$

or:

$$W'_n = \int \psi_n^{0*} \hat{H}' \psi_n^0 d\tau \quad (136)$$

Thus, for the first order approximation, only the matrix elements  $H'_{nn}$  are used to make the calculation. This is almost always justified for even fairly large perturbations. It certainly should be justified in this case since the perturbation is less than a millionth of the overall well as indicated by **Eq. (126)**. The diagonal matrix  $H'_{nn}$  should yield all of the  $W'_n$  values required for this calculation.

Concentrating on the  $n$ th  $\psi$  and using the real part of the  $\psi_n$ s, and noting from the arrangement illustrated in **Figure 49** that  $\hat{H}' = \alpha$  between distance  $x - 1/2l$  and  $x + 1/2l$ , where  $x$  is an arbitrary position at  $(0 + 1/2l) \leq y \leq (L - 1/2l)$  ( the  $1/2l$ ,  $\lll L$  and can be ignored also), then:

$$W_n' = \alpha \int_{x-\frac{1}{2}l}^{x+\frac{1}{2}l} \psi_n^{0*} \psi_n^0 d\tau \quad (137)$$

Using **Eq. 123** This yields the perturbation on the original energies of:

$$W_n = \int_0^L \psi_n^{0*} \hat{H}^0 \psi_n^0 d\tau + \alpha \int_{x-\frac{1}{2}l}^{x+\frac{1}{2}l} \psi_n^{0*} \psi_n^0 d\tau \quad (138)$$

Now for a little transformation. The first integral as given by **Eq. (138)** is the starting  $W^0$ s. The second integral yields:

$$\frac{2}{L} \int_{x-\frac{1}{2}l}^{x+\frac{1}{2}l} \sin^2 \left( \frac{n\pi\tau}{L} \right) d\tau = \frac{1}{L} \left( \tau - \frac{L}{n\pi} \sin \left( \frac{n\pi\tau}{L} \right) \cos \left( \frac{n\pi\tau}{L} \right) \right)_{\tau=x-\frac{1}{2}l}^{\tau=x+\frac{1}{2}l} \quad (139)$$

But what is  $n$ ?  $n$  is the original  $n$  for the solution to the entire potential well, but between  $\tau = x - \frac{1}{2}l$  and  $\tau = x + \frac{1}{2}l$  there will be only  $\sim 6$  to  $\sim 30$  wave nodes according to the deBroglie wave equation. Therefore, expressing this within the perturbation the following change in the integer may be made:

$$n = \frac{kL}{l} \quad 6 \lesssim k \lesssim 30 \quad (140)$$

Substituting  $kL/l$  for  $n$  into **Eq. (139)**, evaluating the integral, substituting into **Eq. (138)** and using the trigonometric relationship for sine-cosine, the following is obtained:

$$W_n = W_n^0 + \frac{\alpha}{L} \left( l - \frac{l}{k\pi} \left[ \sin \left( \frac{2k\pi x + l}{l} \right) - \sin \left( \frac{2k\pi x - l}{l} \right) \right] \right) \quad (141)$$

or using the minima and maxima of the sine terms:

$$W_n = W_n^0 + \frac{\alpha l}{L} \left( 1 \pm \frac{1}{k\pi} \right) \cong W_n^0 + \frac{\alpha l}{L} \quad (142)$$

Recognizing that the convention for the  $W$ s are from the bottom of the potential well as opposed to the top referenced against the vapor pressure potential, and The  $\pm 1/k\pi$  is small compared to 1 and the exact value depends upon the position  $x$  and the *number* of nodes, whether an even integer, an odd integer or somewhere in between.

Notice that **Eq. (142)** is the starting point for the  $\chi$  theory derivation. This can be seen by making the association  $\alpha = E_q - \varepsilon$  and recognizing that the third molecule sees both of the previous molecules as perturbations<sup>29</sup>:

$$W_{n,1} = \alpha \quad \text{and} \quad \alpha = E_q - \varepsilon \quad (143)$$

$$W_{n',2} = \alpha + \alpha \frac{l}{L} = \alpha \left( 1 + \frac{l}{L} \right) \quad (144)$$

**Table 25** Error expected from the QM treatment to derive the  $\chi$  equation.

| Nodes across the adsorbate molecule | maximum error $\pm 1/k\pi$ |
|-------------------------------------|----------------------------|
| 6                                   | 5.3 %                      |
| 8                                   | 3.9 %                      |
| 10                                  | 3.2 %                      |
| 15                                  | 2.1 %                      |
| 20                                  | 1.6 %                      |

<sup>29</sup> Since the 2<sup>nd</sup> (and the first) adsorbed molecule are also probability waves, the base level in the box includes them both as part of the box. Classically speaking, there is a probability that

$$W_{n'',3} = \alpha \left(1 + \frac{l}{L}\right) + \alpha \left(1 + \frac{l}{L}\right) \frac{l}{L} = \alpha \left(1 + \frac{l}{L}\right)^2 \quad (145)$$

The primes in this equation indicate a slightly different quantum numbers. For each of the molecules added, however, there is an additional energy of  $\varepsilon$  that needs to be added since the accounting for the definition of  $\alpha$  begins with release of  $\varepsilon$ . This adds a term of  $N\varepsilon$  at the end of this series (3 $\varepsilon$  for the third equation.) By extension to 2D, that this continues with larger numbers of adsorbate molecules to yield **Eq. (121)**.

The primary problem is variation in  $l$  and how that effects the precision. In the **Table 25** are some maximum errors that could be seen from differences in  $l$ . The adsorbate N<sub>2</sub> has a thermal deBroglie wave length of about 12 nodes<sup>30</sup> per molecule diameter, so the maximum error from this effect for a particular molecule is given as 1.6 %. Since the molecules move around, this value varies between +1.6 % and -1.6 % depending upon  $x$ . With enough particles it would seem reasonable that the error averages out. Thus, by chance, the error should be insignificant.

An important point to keep in mind is that the quantity  $al/L$  is an area (in 3D a volume), and the specifics of the term  $al$ , whether  $\alpha$  is small or  $l$  is small, does not matter for the perturbation except for the maximum error, and a large  $\alpha$  and a small  $l$  yields the highest error, since non-degeneracy was assumed, then if the preadsorbed molecules are expressed as a wave, the effective  $l$  becomes larger and  $\alpha$  must become small for the term to remain a constant.

Another point to notice is that the surface free of any adsorbate molecules is given by:

$$\left(1 - \frac{l}{L}\right)^N \quad \text{or for 3D:} \quad \left(1 - \frac{a}{A_s}\right)^N \quad (146)$$

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<sup>30</sup> The thermal deBroglie wave length is given by the equation  $\lambda = \frac{h}{\sqrt{2\pi mkT}}$  where  $h$  is Plank's constant,  $k$  = Boltzmann's,  $m$  is the mass of the molecule and  $T$  is temperature in kelvins. Assuming 77.2 K and Nitrogen radius or either 0.23 nm by IUPAC convention or 0.155 nm as van der Waal, the wave length,  $\lambda$ , calculates to be 0.038 nm. This yield the ratio of diameter to wave length of 12.2 and 8.2 respectively.

<sup>31</sup> OK, for the sceptics and critics:  $e := \lim_{n \rightarrow \infty} (1 + 1/n)^n$  thus, substituting  $-A/a=n$ , raising both sides to the  $N^{\text{th}}$  power to match **Eq. (121)** and noticing  $a/A$  is extremely small (typically  $< 10^{-4}$  for an error of 0.02%) and  $\theta = NA/a$  then one ends up with this equation.