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A quantum moat barrier, realized with a finite square well

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Abstract

The notion of a double well potential typically involves two regions of space separated by a repulsive potential barrier. The ground state is a wave function that is suppressed in the barrier region and localized in the two surrounding regions. We illustrate that an attractive potential well (a quantum moat) with a finite non-zero width also acts as a barrier, using a simple square well model. We also show how the pseudopotential method both explains the role of the well as a barrier, and greatly improves the efficiency of constructing wave functions for this system using matrix diagonalization. With this simplified model we provide an introduction to the ideas typically used to simplify calculations in solids, where in place of the double well potential, multiple potentials occur in a periodic array.

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I. INTRODUCTION

It is well known that a double well potential, i.e. one that defines two regions in space, separated by a barrier through which quantum tunneling is possible, leads to a splitting of otherwise degenerate energy levels. Starting with this well-established fact, in Ref. [1] we demonstrated two basic ideas for the simplified case of a δ -function potential separating the two regions. First, we showed that a quantum moat — an attractive potential well separating two regions — acts as a barrier for a particle not bound in that well, just like a positive barrier (wall) potential similarly acts as a barrier to define a double well potential. Second, we discussed the pseudopotential method [2, 3] that built on Herring's orthogonalized plane wave approach [4]. In fact this second idea allows one to make sense of the first, as it is otherwise not at all obvious why a moat or well requires a process similar to tunneling to allow a particle to move from one side to the other.

The purpose of this tutorial is to further explore these ideas, for the more realistic case where the moat or wall has a finite width. These two scenarios are depicted schematically in Fig. 1. The original problem addressed by Herring [4] was to describe the eigenstates

FIG. 1. A schematic of (a) the moat ($V_0 < 0$) and (b) the wall ($V_0 > 0$). Either potential divides the space into two regions. One of the goals of this tutorial is to illustrate that the potential on the left acts as a barrier between the two regions, similar to the one on the right, i.e. both systems can be described as double well potentials.

of an electron in a periodic array of atoms. A more accessible description to this problem

is a model with only two regions of space, representing a diatomic molecule instead of an infinite chain. As we shall see, even with this drastic simplification one can still appreciate the pseudopotential concept. The advantage of this model is that it is still exactly solvable, so when we use the pseudopotential to generate approximate solutions, we can monitor their accuracy by comparing them with the exact results. We begin with an examination of key features of the states of a moat barrier system and then proceed to connect these features with the pseudopotential method.

II. MOAT BARRIER SOLUTIONS

The potential for this system is given simply as

$$V(x) = \begin{cases} V_0, & (a-b)/2 < x < (a+b)/2 \\ 0, & 0 < x < (a-b)/2 \text{ or } (a+b)/2 < x < a \\ \infty, & \text{elsewhere,} \end{cases} \quad (1)$$

where V_0 defines the barrier, and can be positive (wall) or negative (moat). We are mostly interested in the behaviour of the positive-energy states of the wall and moat, as these are the states that allow freedom of movement to the left and right of the barrier region. In contrast, the case $V_0 < 0$ also admits negative-energy states; these particular states are bound within the moat and decay exponentially in the two outer regions. In addition, for the wall potential, we focus only on positive-energy states with energies $E \ll V_0$.

A. Comparing the Lowest Positive Energy States of the Potential Wall and Moat

The probability density of the ground state of a double well potential with a wall barrier ($V_0 > 0$) is nonzero in the two outer regions and suppressed in the central barrier region. Here we consider the case of a moat barrier ($V_0 < 0$) and demonstrate that its lowest positive-energy state has similar properties to that of the wall barrier.

We begin with the exact solution in a specific case, where $b/a = 0.3$ and $V_0/E_0 = 27.6$, where $E_0 \equiv \pi^2\hbar^2/(2mw^2)$ is the unit of energy, and $w \equiv (a-b)/2$ is the width of either region outside the barrier. In this case the lowest energy state has a positive energy, and its probability density is plotted in Fig. 2 (thick red curve). It has the tell-tale Schrödinger

cat-like shape, with equal probability density to the right and left of the barrier. Students can confirm that the first excited state has a similar probability density with only slightly higher energy. The first excited state has odd parity about the centre of the system, while the lowest energy state has even parity. We calculated these results in two ways, analytically, and numerically through matrix mechanics; brief descriptions of these calculations are provided in the Appendices. We refer students unfamiliar with numerical matrix mechanics to Refs. [5] and [6].

FIG. 2. The probability densities of the lowest positive-energy states for the wall barrier (thick red curve) and the moat potential (thin blue curve). The moat and wall both have a width $b/a = 0.3$ and are both centred in an infinite square well of width a . The moat has a depth of $V_0 = -27.6E_0$, and the wall has a height of $V_0 = +27.6E_0$, where $E_0 \equiv \pi^2\hbar^2/(2mw^2)$, and $w \equiv (a - b)/2$ is the width of each region on either side of the central wall/moat. Within the central wall/moat region, the states differ significantly: the wave function corresponding to the potential wall is almost completely suppressed while the wave function corresponding to the potential moat contains small oscillations. Outside the barrier region the two wave functions are very similar to one another.

A similar calculation is performed for $V_0/E_0 = -27.6$, i.e. for a moat with the same

absolute potential strength as the wall in the previous case. One finds five states with negative-energy solutions. These states are analogous to the core states in Herring's 1940 calculation [4]. Following his lead, we focus attention on the states that describe the conduction electrons — those electrons that would move from one side of the barrier to the other to provide conductivity in a metal consisting of an array of atoms. In our model these correspond to the positive-energy states.

The probability density of the first positive-energy state of the potential moat is given by the thin blue curve in Fig. 2. Note that, perhaps surprisingly for some, similarly to the case for the wall, it also has a characteristic Schrödinger cat-like shape and is largely excluded from the moat region. There are small oscillations in the moat region and a slightly reduced amplitude relative to the wall solution in the two outer regions, consistent with the fact that the probability density is conserved and equal to unity for both red and blue curves. Again, students should confirm that the state with the next highest energy has a similar probability density, and its wave function has opposite parity to the one in Fig. 2. Interestingly, for this particular moat barrier, the lowest positive-energy solution has odd parity while the next-highest energy solution has even parity, reversed from the case of the wall barrier. For a moat with an even number of negative-energy states, the situation reverts to the usual order.

B. Comparing the Lowest and Second-Lowest Positive Energy States of Each Potential

We have already mentioned that another tell-tale signature of double well potential states is the splitting of energy levels that occurs. The resulting two wave functions accurately approximate even and odd linear combinations of states confined to either side of the potential barrier, giving the two wave functions similar probability densities. For example, the first excited state for the potential wall used in Fig. 2 has a probability density (not shown) that is barely discernible from the one shown.

We want to see to what extent the moat potential exhibits the aforementioned behaviour, where successive energy states have similar probability densities. Therefore, to quantify the difference between the probability densities of the lowest positive-energy wave function ψ_1 and the next highest positive-energy wave function ψ_2 , we have defined [1] the dimensionless

figure of merit ΔA , given by

$$\Delta A \equiv \int_0^a dx \left| |\psi_1(x)|^2 - |\psi_2(x)|^2 \right|. \quad (2)$$

The more similar two probability densities are, the smaller ΔA becomes.

To illustrate what happens in the wall and moat case separately, we vary the potential strength $|V_0|$ in each case, and plot the results as a function of $|V_0|$ in Fig. 3, for four different widths, b/a : 0.20, 0.10, 0.05, and 0.02. Details for these calculations are available in Appendix A.

FIG. 3. (a) ΔA_{wall} and (b) ΔA_{moat} as a function of $v = \sqrt{|V_0|/E_0} [b/w]$. It is clear from figure (b) that something peculiar is occurring as v takes on integer values. This is just the condition that another of the quantum moat's (formerly) positive-energy states becomes a negative-energy state. It is therefore no surprise that when this is about to happen to the positive-energy state with the lowest energy, it will look very different from the positive-energy state with the second lowest energy, and ΔA_{moat} increases sharply. In the potential wall case (a) the measure of similarity goes quickly to zero. This shows the generic and expected behaviour for the even and odd positive-energy wave functions in a double well potential.

Figure 3 (a) compares the probability densities of the lowest even and odd wave functions for the potential wall. As expected, the two lowest states become more similar ($\Delta A_{\text{wall}} \rightarrow 0$) as the potential barrier height increases. Note that for sufficiently high barriers, the width of the barrier becomes immaterial.

For the potential moat, with results shown in Fig. 3 (b), there is a complication that, as the moat is made deeper, there exist discrete potentials at which a positive-energy state transitions into a negative-energy (i.e. bound in the moat) state. If we define a dimensionless value of the potential strength through $v \equiv \sqrt{|V_0|/E_0} (b/w)$ and increase it starting from $v = 0$, then at every odd (even) integer v , an odd (even) positive-energy state transitions into an odd (even) negative-energy state. This is an indication of resonance behaviour in the potential moat - notice that every integer value of v corresponds to perfect transmission in the standard equation for transmission across a well (see, for example, Eq. (2.172) as $E \rightarrow 0$ in Ref. 7).

Figure 3 (b) shows that ΔA_{moat} decreases provided we limit our focus to values of v near the half-integers. In other words, the two lowest positive-energy states generally become more similar as the moat strength increases, but only for ranges of potentials far from the transition potentials given by integer values of v . For example, in the case shown in Fig. 2, the values of b/a and $|V_0|/E_0$ correspond to approximately $v = 4.5$. The decrease of ΔA as a function of v is considerably slower for the moat than the wall; ΔA_{wall} decreases exponentially, while ΔA_{moat} , when evaluated at the half-integers, decreases proportionally to v^{-1} . The decrease in both cases happens more rapidly for smaller values of b/a .

To summarize this section it is clear that the moat has double-well characteristics similar to those of the wall, provided we focus on potential strengths for values of v well away from the positive-energy—negative-energy state transitions. Moats behave more like walls as the depth of the well, $|V_0|$ increases, and the analogy is closer for narrower moats.

III. THE PSEUDOPOTENTIAL METHOD

A deeper understanding of the effectiveness of a quantum moat as a barrier can be realized by recognizing the role of the negative-energy states as a pseudopotential. The essence of the pseudopotential method [2, 3, 8] is that the positive-energy states have to be orthogonal to these core states. To satisfy this orthogonality requirement, the positive-

energy wave functions are almost entirely excluded from the core region, and the parts of the wave function that still remain in the core region are small in amplitude and take on an oscillatory nature. For example, in our case with the moat, there is only one region, $-b/2 < x < b/2$, and so positive-energy wave functions will generally be excluded and oscillatory in this region (see the thin blue curve in Fig. 2).

From the point of view of a particle in a positive-energy state, the deeply bound (i.e. *core*) negative-energy states give rise to an effective repulsive potential. Hence, one can imagine a procedure for generating positive-energy states that omits these core states and replaces them instead with an effective pseudopotential. This is how a moat functions like a repulsive potential for particle transmission from one side to the other. The formal process for doing this is described in the following subsection.

A. The Orthogonalized Plane-Wave Method

The difficulty with constructing wave functions using a basis of ordinary plane waves [9] $\{|\phi_j\rangle\}$ is that a large number of Fourier components (i.e. the sine functions of our basis) is typically required to reproduce the rapid oscillations present in the core regions of a lattice. As a remedy, the orthogonalized plane-wave (OPW) method takes advantage of the orthogonality requirement of solutions to the time-independent Schrödinger equation by using a basis of modified plane waves, where the core state components are projected out from each plane wave basis state.

We use a new OPW basis $\{|\tilde{\phi}_j\rangle\}$ given by

$$|\tilde{\phi}_j\rangle = |\phi_j\rangle - \sum_B |\phi_B\rangle \langle \phi_B | \phi_j \rangle, \quad (3)$$

where $\{|\phi_j\rangle\}$ is the ordinary plane wave basis and the sum is over chosen core (negative-energy) states $\{|\phi_B\rangle\}$. The pseudopotential method is a realization of the OPW method, and allows one to formulate an effective potential using these negative-energy states; one also has the option to use only the more deeply bound negative-energy states, if one chooses to do so.

To create the pseudopotential, we first express a positive-energy state in terms of the OPW basis,

$$|\psi\rangle = \sum_j c_j |\tilde{\phi}_j\rangle \quad (4)$$

and substitute this into the Schrödinger equation

$$(\hat{H}_0 + \hat{V})|\psi\rangle = E|\psi\rangle, \quad (5)$$

where $\hat{H}_0$ is the kinetic energy term, $\hat{V}$ is the one-body potential of interest, and E is the energy of the positive-energy state. Taking the inner product with $\langle\tilde{\phi}_i|$, we get

$$\sum_j \langle\phi_i| \left[\hat{H}_0 + \hat{V} + \sum_B (E - E_B) |\phi_B\rangle \langle\phi_B| \right] |\phi_j\rangle c_j = E c_i, \quad (6)$$

where E_B is the energy of our selected negative-energy states. Equation (6) is the Schrödinger matrix equation with an effective potential, usually referred to as a pseudopotential $\hat{V}_{ps}$, which is a generalized version of Eq. (14) in Ref. [1],

$$\hat{V}_{ps} \equiv \hat{V} + \sum_B (E - E_B) |\phi_B\rangle \langle\phi_B|. \quad (7)$$

The pseudopotential method transforms the original Hamiltonian into a new type of pseudo-Hamiltonian. The solutions of Eq. (6) (the pseudo-solutions) typically lack the rapid oscillations found in the solutions to the original Hamiltonian, and thus require fewer Fourier components in their construction. Most often there is no need to transform back, as the pseudo-solutions are generally accurate in the region away from the core, which is the primary region of interest when studying many of a metal's properties. Also note that Eq. (7) has to be solved by iteration, as the pseudo-Hamiltonian depends on the energy eigenvalue E that we are determining.

The matrix elements of Eq. (6) consist of the sum of three components,

$$\langle\phi_i|\hat{H}_0|\phi_j\rangle, \quad \langle\phi_i|\hat{V}|\phi_j\rangle, \quad (8)$$

and

$$\sum_B (E - E_B) \langle\phi_i|\phi_B\rangle \langle\phi_B|\phi_j\rangle. \quad (9)$$

Because we know the energies and wave function forms for both the basis states and negative-energy states in this simplified model, every matrix element in the above three terms can be found analytically.

B. Approximation Using Free Atom Bound States

However, even with the formal pseudopotential method laid out as above, we face an additional, practical complication before we can apply it to atoms in a solid. Recall that the original motivation for studying the pseudopotential was to calculate the conduction states of a periodic array of atoms in a metal. Unfortunately, the bound states of atoms in a lattice are generally unknown. But because the deeply bound states of a free atom are nearly identical to the corresponding bound states of an atom in an array, the former can be used as approximations of the latter. As long as the energies and wave functions of the free atom bound states are reasonably similar to their counterparts in a lattice, then the conduction states should be accurately produced. For our model of the problem, this corresponds to using the negative-energy states of an isolated rectangular finite potential well of width b to approximate the negative-energy states of a rectangular potential moat embedded in an infinite square well. All three terms in Eq. (8) for this approximation are determined analytically in Appendix B.

As a practical guide to deciding which negative-energy states are sufficiently deeply bound to include in Eq. (9), we adopt the following criterion. We consider a negative-energy state ϕ_B of a single well in infinite space (corresponding to a free atom) centred at $x = a/2$ to be deeply bound if over 99% of its probability density is contained in $0 < x < a$, or in other words, if $\int_0^a dx |\phi_B(x)|^2 > 0.99$. This ensures that the analytic expressions that we adopt as approximations for the true bound states (see Appendix B) are reasonably accurate.

A simple example of the improvement in efficiency is presented in Fig. 4, where the analytic solution can be well-approximated using the pseudopotential method with a far smaller matrix ($N = 10$) compared to that required in an ordinary plane-wave expansion ($N \approx 100$, not shown). The converged solution in Fig. 4 clearly shows that the probability density has peaks in the two regions outside of the moat region, with essentially zero amplitude in the moat region itself. This signature characteristic of a double well potential makes it clear that the notion of a moat as a quantum barrier applies just as well for a finite-width potential as it did for the δ -function potential [1].

FIG. 4. The analytic solution (red squares) for the lowest even positive-energy wave function of a moat of width $b/a = 0.10$ and a potential strength of $V_0/E_0 = -405$. The ordinary sine-wave expansion (green triangles) and the pseudopotential method using approximate negative-energy states (blue circles) both approximate this wave function using a matrix of size of $N = 10$. The ordinary method does a poor job (it can of course be improved with an increased matrix size), while the pseudopotential method is very accurate with a small matrix representation.

IV. PEDAGOGICAL FEATURES

The result of Fig 4 illustrates several things: (i) first, it is a demonstration of the physical principles behind the pseudopotential, which explains how a moat behaves like a repulsive potential for states not bound within the moat, (ii) it shows that calculations can be done much more efficiently with orthogonalized plane waves (orthogonalized sine-waves in our case), and (iii) it shows that the use of approximate wave functions for the negative-energy

states (see Appendix B), works very well in this instance. A good exercise for students is to use exact wave functions for the negative-energy states $\{|\phi_B\rangle\}$ — then the agreement with the analytical result will be of order machine precision, whereas the pseudopotential calculations shown in Fig. 4 have some small error (invisible on this scale) greater than machine precision. We refer students unfamiliar with the required matrix mechanics to Ref. [5].

We also end with a message of what this is *not*: it is tempting to apply classical thinking to intuit why the bound wave functions act like a wall in the pseudopotential method. For example, one might assume that the reason the moat acts like a wall is because the positive-energy particles cannot occupy the same positions as the negative-energy particles trapped in the moat's centre. Or, if the particles are charged, like electrons, then one might assume that the conduction electrons are electrically repelled by the collection of bound electrons in the moat. Both these arguments are incorrect. We emphasize that the positive-energy wave functions of the moat potential will still behave as if the moat were a wall even if none of the moat's bound states are actually occupied, or if the potential were the result of something other than charged particles. In other words, the arguments presented in this paper depend on neither Coulomb repulsion nor the Pauli Exclusion Principle. They depend only on the requirement that the eigenstates of the time-independent Schrödinger equation are orthonormal to each other.

V. SUMMARY

In this paper we have examined the cases of double well potentials in which the potential barrier was either a negative potential moat or a positive potential wall. Solving the time-independent Schrödinger equation for both these systems showed that the lowest positive-energy states in both potentials are very similar in appearance except when, in the case of the moat potential, a positive-energy state is on the verge of becoming a negative-energy state. We have also shown how to apply the pseudopotential method to find the positive-energy states, and that this method is more efficient than the original plane wave expansion method. Most importantly, the use of a pseudopotential explains why an attractive quantum moat potential behaves like a positive barrier from the point of view of a positive-energy state. This exercise generalizes the result of Ref. [1] to potential moats with non-zero width.

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Appendix A: Analytic Solutions of Wave Functions

In the following sections of the Appendix, we describe the solutions and energies of finite square potential walls and moats surrounded by an infinite square well spanning $0 < x < a$. We refer to Region I as $0 < x < w$, Region II as $w < x < w + b$, and Region III as $w + b < x < a$, where b is the width of the central barrier region and $w = (a - b)/2$.

For subsection (III) we consider negative-energy states of the finite potential well system that extend over all values of x . Then, Regions I, II and III refer to the ranges $-\infty < x < w$, $w < x < w + b$, and $w + b < x < \infty$, respectively.

(I) MOAT: POSITIVE-ENERGY STATES

For the positive-energy states of the quantum moat, we define $k \equiv \sqrt{2mE/\hbar^2}$ and $q \equiv \sqrt{2m(E - V_0)/\hbar^2}$. The even-state wave function is

$$\Psi_{m,e}(x) = \begin{cases} A_e \sin(kx), & \text{I} \\ A_e L_e \cos q(x - \frac{a}{2}), & \text{II} \\ -A_e \sin k(x - a), & \text{III} \end{cases} \quad (\text{A1})$$

where straightforward matching at the boundaries requires that k and q satisfy

$$\tan(kw) = \frac{k}{q} \cot(qb/2), \quad (\text{A2})$$

and the even-parity amplitude is given by

$$|A_e|^2 = \frac{1}{w} \left[1 - \frac{\sin(2kw)}{2kw} + \frac{bL_e^2}{2w} \left[1 + \frac{\sin(qb)}{qb} \right] \right]^{-1}, \quad (\text{A3})$$

with $L_e = \sin(kw)/\cos(qb/2)$.

The odd-state wave function is

$$\Psi_{m,o}(x) = \begin{cases} A_o \sin(kx), & \text{I} \\ A_o L_o \sin q(x - \frac{a}{2}), & \text{II} \\ A_o \sin k(x - a). & \text{III} \end{cases} \quad (\text{A4})$$

where k and q satisfy

$$\tan(kw) = -\frac{k}{q} \tan(qb/2), \quad (\text{A5})$$

and the odd-parity amplitude is given by

$$|A_o|^2 = \frac{1}{w} \left[1 - \frac{\sin(2kw)}{2kw} + \frac{bL_o^2}{2w} \left[1 - \frac{\sin(qb)}{qb} \right] \right]^{-1}, \quad (\text{A6})$$

with $L_o = -\sin(kw)/\sin(qb/2)$.

To find the energies and amplitudes of the positive-energy states of the moat, define $z^2 = |E|/E_0$ and $z_0^2 = |V_0|/E_0$, substitute $kw = z$, $qw = \sqrt{z_0^2 + z^2}$, and $qb = (b/w)\sqrt{z_0^2 + z^2}$ into Eqs. (A2, A5), and solve each numerically for z .

(II) WALL: POSITIVE-ENERGY STATES

For the positive-energy states of the quantum wall, we define $q \equiv \sqrt{2mE/\hbar^2}$ and $\kappa \equiv \sqrt{2m(V_0 - E)/\hbar^2}$. The even-state wave function is

$$\Psi_{w,e}(x) = \begin{cases} A_e \sin(qx), & \text{I} \\ A_e L_e \cosh \kappa(x - \frac{a}{2}), & \text{II} \\ -A_e \sin q(x - a). & \text{III}, \end{cases} \quad (\text{A7})$$

where q and κ satisfy

$$\tan(qw) = -\frac{q}{\kappa} \coth(\kappa b/2), \quad (\text{A8})$$

and the even-parity amplitude is given by

$$|A_e|^2 = \frac{1}{w} \left[1 - \frac{\sin(2qw)}{2qw} + \frac{bL_e^2}{2w} \left[\frac{\sinh(\kappa b)}{\kappa b} + 1 \right] \right]^{-1}, \quad (\text{A9})$$

with $L_e = \sin(qw)/\cosh(\kappa b/2)$.

The odd wave function is

$$\Psi_{w,o}(x) = \begin{cases} A_o \sin(qx), & \text{I} \\ A_o L_o \sinh \kappa(x - \frac{a}{2}), & \text{II} \\ A_o \sin q(x - a). & \text{III} \end{cases} \quad (\text{A10})$$

where q and κ satisfy

$$\tan(qw) = -\frac{q}{\kappa} \tanh(\kappa b/2), \quad (\text{A11})$$

and the odd-parity amplitude is given by

$$|A_o|^2 = \frac{1}{w} \left[1 - \frac{\sin(2qw)}{2qw} + \frac{bL_o^2}{2w} \left[\frac{\sinh(\kappa b)}{\kappa b} - 1 \right] \right]^{-1}, \quad (\text{A12})$$

with $L_o = -\sin(qw)/\sinh(\kappa b/2)$.

To find the energies and amplitudes of the positive-energy states of the wall, define $z^2 = |E|/E_0$ and $z_0^2 = |V_0|/E_0$, substitute $qw = z$, $\kappa w = \sqrt{z_0^2 - z^2}$, and $\kappa b = (b/w)\sqrt{z_0^2 - z^2}$ into Eqs. (A8, A11), and solve each numerically for z .

(III) SOLUTIONS OF THE FINITE POTENTIAL WELL IN FREE SPACE

We *could* solve for the negative-energy states of a finite potential moat contained within an infinite square well. This procedure would give exact results, but this exercise would be contrary to the philosophy behind the pseudopotential method. Instead, we solve for the bound states of the finite potential well in free space, with a potential given by

$$V(x) = \begin{cases} V_0, & -b/2 < x < b/2 \\ 0, & \text{elsewhere.} \end{cases} \quad (\text{A13})$$

We define $q \equiv \sqrt{2m(E_B - V_0)/\hbar^2}$ and $\kappa \equiv \sqrt{-2mE_B/\hbar^2}$; then the even-parity wave function is ($x' \equiv x - a/2$)

$$\psi_{B,e}(x') = \begin{cases} A_e \exp(\kappa(x' + b/2)), & \text{I} \\ A_e \frac{\cos(qx')}{\cos(qb/2)}, & \text{II} \\ A_e \exp(-\kappa(x' - b/2)), & \text{III} \end{cases} \quad (\text{A14})$$

where κ and q satisfy

$$\kappa = q \tan(qb/2), \quad (\text{A15})$$

and the even-parity amplitude is given by

$$|A_e|^2 = \frac{2}{b} \left[\frac{2}{\kappa b} + \frac{1 + \sin(qb)/(qb)}{\cos^2(qb/2)} \right]^{-1}. \quad (\text{A16})$$

The odd-parity wave function is

$$\psi_{B,o}(x') = \begin{cases} A_o \exp(\kappa(x' + b/2)), & \text{I} \\ -A_o \frac{\sin(qx')}{\sin(qb/2)}, & \text{II} \\ -A_o \exp(-\kappa(x' - b/2)). & \text{III} \end{cases} \quad (\text{A17})$$

where κ and q satisfy

$$\kappa = -q \cot(qb/2), \quad (\text{A18})$$

and the odd-parity amplitude is given by

$$|A_o|^2 = \frac{2}{b} \left[\frac{2}{\kappa b} + \frac{1 - \sin(qb)/(qb)}{\sin^2(qb/2)} \right]^{-1}. \quad (\text{A19})$$

If we define $\tilde{z} \equiv qb/2$, and $\tilde{z}_0 = (b/2)\sqrt{-2mV_0/\hbar^2}$, then $\kappa b/2 \equiv \sqrt{\tilde{z}_0^2 - \tilde{z}^2}$, and one can readily solve (graphically and iteratively) Eqs. (A15, A18) for $\tilde{z}$ and therefore E_B .

Appendix B: Matrix Elements of the Pseudopotential Method

Every element in the matrix of the pseudo-Hamiltonian is given by the sum of the three terms

$$\langle \phi_m | \hat{H}_0 | \phi_n \rangle, \quad \langle \phi_m | \hat{V} | \phi_n \rangle, \quad (\text{B1})$$

and

$$\sum_B (E - E_B) \langle \phi_m | \phi_B \rangle \langle \phi_B | \phi_n \rangle. \quad (\text{B2})$$

Defining $E_n^{(0)} = n^2 \pi^2 \hbar^2 / (2ma^2)$ to be the energy of the n^{th} state, $\langle x | \phi_n \rangle = A_n \sin(n\pi x/a)$, where $A_n = \sqrt{2/a}$, of the infinite square well, the first term in Eq. (B1) is simply given by

$$\langle \phi_m | \hat{H}_0 | \phi_n \rangle = E_n^{(0)} \delta_{mn}. \quad (\text{B3})$$

The second term is similar to the first but the potential is nonzero only between $x = w$ and $x = w + b$; we obtain

$$V_0 \int_w^{w+b} A_n \sin(n\pi x/a) A_m \sin(m\pi x/a) dx = \quad (B4)$$

$$\begin{cases} \left. \frac{V_0}{2\pi n} \left[\frac{2\pi n}{a} x - \sin\left(\frac{2\pi n}{a} x\right) \right] \right|_w^{w+b}, & m = n \\ \left. \frac{V_0}{\pi} \left[\frac{\sin((m-n)\pi x/a)}{m-n} - \frac{\sin((m+n)\pi x/a)}{m+n} \right] \right|_w^{w+b}, & m \neq n. \end{cases} \quad (B5)$$

The third term, Eq. (B2), is the most complicated. The energy of each core state is given by $E_B = -\hbar^2 \kappa^2 / 2m$, as κ is defined in Appendix A(III). The integrals given by $\langle \phi_m | \phi_B \rangle$ and $\langle \phi_B | \phi_n \rangle$ have four outcomes that depend on the orientations (even or odd) of the basis and core states involved. If the core state is even and the basis state is odd, or vice-versa, then the inner product is simply 0. If the basis and core states are both even or both odd, the integrals are more complicated.

Define the definite integrals R_I , $R_{II,e}$, and $R_{II,o}$. The first is the piecewise integral over the regions where $V = 0$, and due to symmetry, R_I is the same for Regions I and III, for both even and odd core states. The second and third integrals are piecewise integrals over the centre moat region for the even and odd core states, respectively. For the integral R_I , A_{eo} should be replaced by A_e when the core state is even and A_o when the core state is odd, as given in Appendix A(III). Recall that in all these cases, the core and basis states have the same orientation. Note that the solutions for the finite potential well were derived for a well of width b centred at $x = 0$. To align the finite potential well with the moat, use $x' = x - a/2$. We obtain

$$\begin{aligned}
R_I &= \int_0^w dx A_{eo} \exp(\kappa(x-w)) A_n \sin(n\pi x/a) \\
&= A_{eo} \sqrt{2a} \frac{[\kappa a \sin(n\pi w/a) - n\pi \cos(n\pi w/a) + \exp(-\kappa w)n\pi]}{(\kappa a)^2 + (n\pi)^2} \\
R_{II,e} &= \int_w^{w+b} dx \frac{A_e}{\cos(qb/2)} \cos(q(x-a/2)) A_n \sin(n\pi x/a) \\
&= -\frac{A_e}{\cos(qb/2)} \sqrt{\frac{a}{2}} \left[\frac{\cos(qa/2 - (n\pi/a + q)x)}{n\pi + qa} + \frac{\cos(qa/2 + (n\pi/a - q)x)}{n\pi - qa} \right] \Bigg|_w^{w+b} \\
R_{II,o} &= \int_w^{w+b} dx \frac{A_o}{\sin(qb/2)} \sin(q(x-a/2)) A_n \sin(n\pi x/a) \\
&= \frac{A_o}{\sin(qb/2)} \sqrt{\frac{a}{2}} \left[\frac{\sin(qa/2 - (n\pi/a + q)x)}{n\pi + qa} + \frac{\sin(qa/2 + (n\pi/a - q)x)}{n\pi - qa} \right] \Bigg|_w^{w+b}
\end{aligned}$$

Then the value of the integral $\langle \phi_B | \phi_n \rangle$ is given by

$$\langle \phi_B | \phi_n \rangle = \begin{cases} 0, & \text{One is even, the other is odd} \\ 2R_I + R_{II,e}, & \text{Basis and core states are both even} \\ 2R_I + R_{II,o}, & \text{Basis and core states are both odd.} \end{cases} \quad (B6)$$

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- [9] We will continue to use the terms “plane wave” basis and “plane wave” states, but in our problem we are imbedding the potential of interest (a repulsive or attractive square well) in an infinite square well, so, we use the linear combination of plane waves which are the suitably normalized $\sin(j\pi x/a)$, $j = 1, 2, 3, \dots$, where “a” is the width of the infinite square well.

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