APPENDIX G: DOUBLE-WELL POTENTIAL: SYMMETRY AND TUNNELLING

Consider a model double-well potential

$$V(x) = E_0 \left(Cx^4 - x^2 \right) \tag{1}$$

This potential is plotted in Fig. 1 for the following choice of parameters: $E_0 = 2 \times 10^{-4}$ hartree and $C = 0.045$.

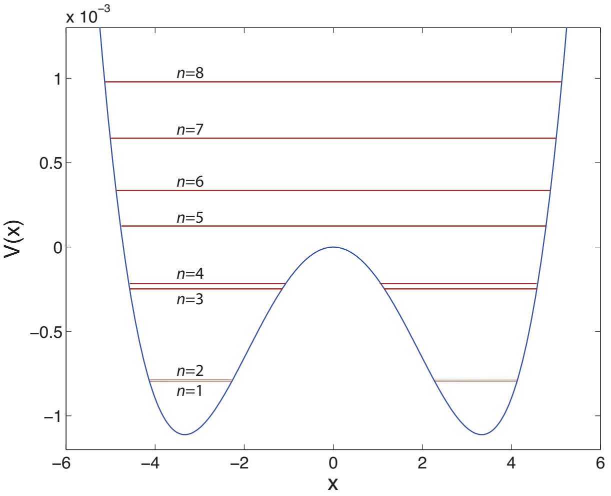

FIG. 1. Model double well potential with distance in a_0 and energy in hartree. The positions of the eight lowest levels is shown, for a mass of 1 atomic mass unit (1837 atomic units). The two lowest levels lie too close together to be fully resolved here.

I. ENERGY LOWER THAN THE BARRIER HEIGHT

When the barrier is high compared to the energy of the particle, then there are two degenerate states, corresponding to the particle being localized in one or the other of the wells. Because a quantum particle can tunnel through the barrier, and the potential is symmetric with respect to inversion ($x \to -x$), the proper wavefunctions are the positive and negative linear combinations of the wavefunctions corresponding to the two separate wells. If we designate these by ψ_l and ψ_r for the left- and right-hand wells, respectively, then the proper linear combinations are

$$\psi_{\pm} = N_{\pm} \left(\psi_l \pm \psi_r \right)$$

.

If we define an inversion operator P which transforms x into $-x$, then

$$P\psi_l = \psi_r$$

$$P\psi_r = \psi_l$$

and

$$P\psi_\pm = \pm\psi_\pm$$

The ± states are thus eigenfunctions of the inversion operator (sometimes called the parity operator). The wavefunction of the "-" states must vanish at the origin (because the functions are antisymmetric). For the "+" states, the derivative of the wavefunction must vanish at the origin. (A simple example would be the trigonometric functions $\sin x$ and $\cos x$.) Because the antisymmetric states must vanish at $x = 0$ the curvature (the second-derivative) of the wavefunction in these states will be slightly greater than the curvature of the corresponding symmetric wavefunction. Because the Schrodinger equation equates the second derivative to the square of the wavevector, and, hence, to the energy, a greater curvature corresponds to a higher energy. Consequently, in a double-well problem the antisymmetric state will have a slightly higher energy than the corresponding symmetric state.

For the potential shown in Fig. 1, and with a mass of 1 atomic mass unit [1] we can use the DVR method (described in Chapter 1 of the Chem 691 notes) to obtain the energies (Table I) and the wavefunctions (Fig. 2).

II. ENERGY HIGHER THAN THE BARRIER HEIGHT

Once the energy becomes larger than the barrier height, then the zeroth-order model is no longer a set of degenerate states corresponding to the left and right-hand wells but, rather, the set of quartic oscillator states which are eigenfunctions of the potential

$$V(x) = E_0 C x^4$$

TABLE I. Lowest energies (hartree) for a particle of mass 1 u in the double-well potential of Fig. 1.

n	parity	energy
1	$+$	-7.9500×10^{-4}
2	$-$	-7.9440×10^{-4}
3	$+$	-2.4814×10^{-4}
4	$-$	-2.1583×10^{-4}
5	$+$	1.2477×10^{-4}
6	$-$	3.3568×10^{-4}
7	$+$	6.4518×10^{-4}
8	$-$	9.7908×10^{-4}
9	$+$	1.3456×10^{-3}
10	$-$	1.7387×10^{-3}

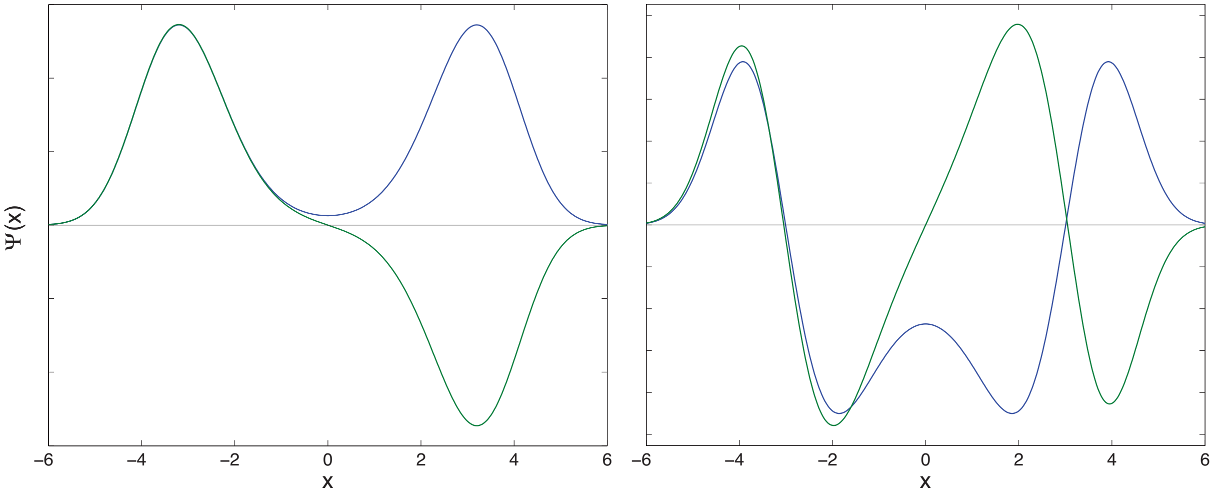

FIG. 2. Symmetric (blue) and antisymmetric (green) wavefunctions corresponding to the four lowest states of the potential shown in Fig. 1

perturbed by the negative harmonic potential $-E_0 x^2$.

III. TIME-DEPENDENT INTERPRETATION

For a Hamiltonian which is independent of time, the total time dependence of any wavefunction is

$$\psi_n(x,t) = \psi_n(x) e^{-i\omega_n t}$$

where the circular frequency $\omega_n = E_n/\hbar$. Let us now create a wavepacket which is the sum of the lowest two states

$$\begin{aligned}\Phi(x,t) &= 2^{-1/2}\left[\psi_1(x,t)+\psi_2(x,t)\right] = 2^{-1/2}\left[\psi_1(x)e^{-i\omega_1 t}+\psi_2(x)e^{-i\omega_2 t}\right] \\ &= 2^{-1/2}e^{-i\omega_1 t}\left[\psi_1(x)+e^{i\delta t}\psi_2(x)\right] \end{aligned} \tag{2}$$

where $\delta = \omega_1 - \omega_2 = (E_1 - E_2)/\hbar$. The probability of finding the particle at any position x at time t, $\mathcal{P}(x,t)$ is then

$$\mathcal{P}(x,t) = |\Phi(x,t)^*\Phi(x,t)|^2 = \frac{1}{2}\left[\psi_1(x)^2+\psi_2(x)^2+2\cos(\delta t)\psi_1(x)\psi_2(x)\right]$$

The system oscillates back and forth, starting with

$$\mathcal{P}(x,t=0) = \frac{1}{2}\left[\psi_1(x)+\psi_2(x)\right]^2$$

to

$$\mathcal{P}(x,t=\pi/2\delta) = \frac{1}{2}\left[\psi_1(x)^2+\psi_2(x)^2\right]$$

to

$$\mathcal{P}(x,t=\pi/\delta) = \frac{1}{2}\left[\psi_1(x)-\psi_2(x)\right]^2$$

and then back again.

Figure 3 shows the probability $\mathcal{P}(x,t)$ at $t = 0$, $\pi/2\delta$, and π/δ for the lowest state of the double-well potential of Fig. 1

Clearly, the time it takes the particle to tunnel from one of the wells to the other is

$$\tau_{tunnel} = \pi/\delta$$

. These are given in Table II. [2]

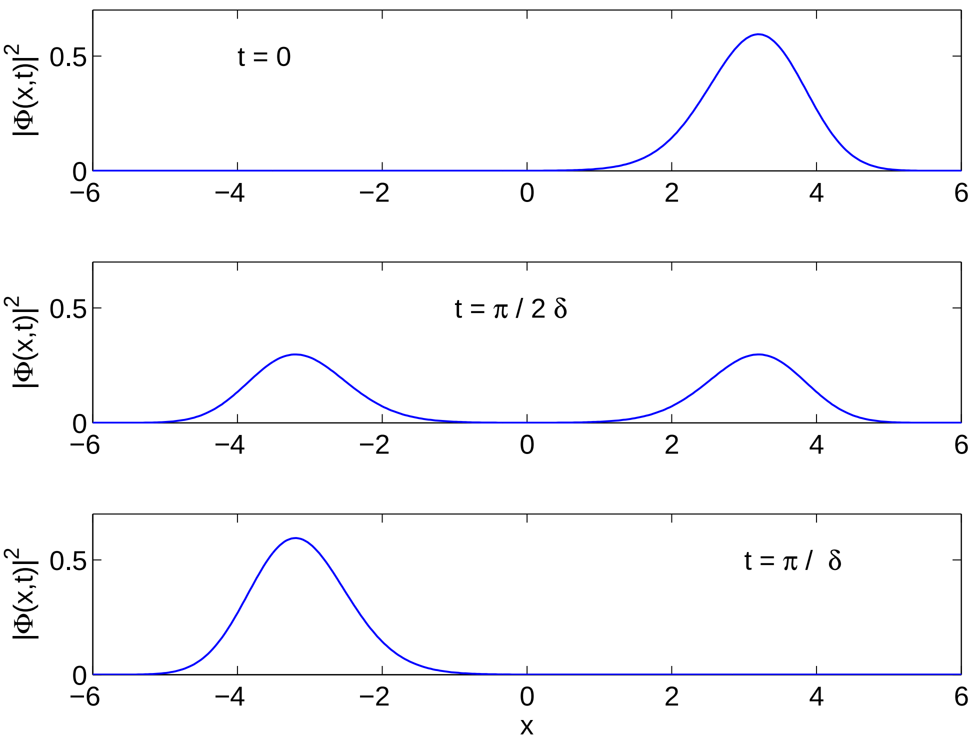

FIG. 3. Time-dependent evolution of a particle of mass $1u$ trapped in the lowest state of the double-well potential of Fig. 1.

TABLE II. Tunnelling time for a particle of mass $1u$ in the double-well potential of Fig. 1.

state	ΔE (hartree)	τ (atomic units)	τ (ps)
lowest	6.055×10^{-7}	5.188×10^{6}	125.4
second	3.231×10^{-5}	9.724×10^{4}	2.352

IV. PROBLEMS

Problem 1. For a classical particle in a harmonic well, the time it takes to go from one side of the well to the other and back (the period) is just $\tau = 2\pi/\omega$ where $\omega = \sqrt{k/m}$. Figure out the period of a classical particle of mass $1u$ in the left-hand well of the potential in Fig. 1 by fitting the left-hand well by a harmonic potential to determine k. Compare the period to the tunnelling times from Table II to obtain a semiclassical estimate of how many times the particle goes back and forth in a single well before tunnelling over to the other side By comparing these two times you can calculate the probability that the particle will tunnel.

Then, suppose you increase the mass of the particle to $2u$. Obtain, using the DVR procedure, the energies of the first two levels (n=1 and 2), determine the tunneling times, and the probability that the particle will tunnel.

Problem 2. Consider the simplistic double-well potential shown in Fig. 4. The potential is defined by Table III.

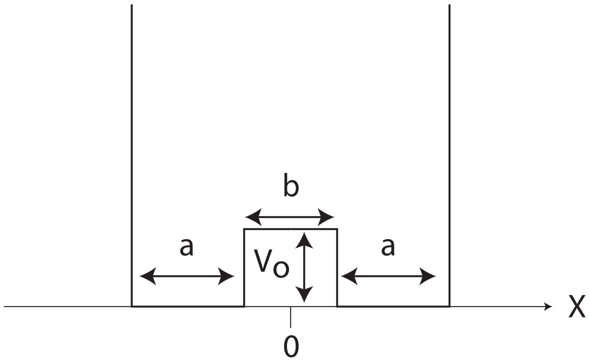

FIG. 4. Simplistic square double-well potential.

As in any square-well problem, in each region, the wavefunction is defined in regions which are classically allowed ($E > V$) by a linear combination of trigonometric functions or in regions which are classically forbidden ($E < V$) by a linear combination of hyperbolic functions. The symmetry of the problem allows us to chose, in the middle region, either the symmetric (cos or cosh) functions or the antisymmetric (sin or sinh) functions.

The A and B coefficients are obtained by requiring that the wavefunction and its first derivative be continuous at the boundary between regions III and IV (or between regions II and III), namely (in the case where $E < V_o$ and the wavefunction is symmetric)

$$\cosh(\kappa b/2) = A\cos(kb/2) + B\sin(kb/2)$$

TABLE III. Square double-well potential of Fig. 4.

region	x	$V(x)$	$\psi(x)$
I	$x \leq -a - b/2$	∞	0
II [a]	$-a - b/2 < x < -b/2$	0	$A\cos(kx) + B\sin(kx)$
III [b]	$-b/2 < x < b/2$	V_o	$\cosh(\kappa x)$ (symmetric) or $\sinh(\kappa x)$ (antisymmetric)
			$\cos(k_{\text{III}}x)$ (symmetric) or $\sin(k_{\text{III}}x)$ (antisymmetric)
IV [a]	$b/2 < x < a + b/2$	0	$A\cos(kx) + B\sin(kx)$
V	$x \geq a + b/2$	∞	0

[a] Here $k = \sqrt{2mE}$.

[b] Here, one needs to distinguish whether $E < V_o$ (first line), in which case $\kappa = \sqrt{2m(V_o - E)}$, or $E > V_o$ (second line), in which case $k_{\text{III}} = \sqrt{2m(E - V_o)}$

and

$$\kappa\sinh(\kappa b/2) = k\left[-A\sin(kb/2) + B\cos(kb/2)\right]$$

These are two linear equations in two unknowns (A and B). In matrix notation we have

$$\mathbf{C}\mathbf{a} = \mathbf{b}$$

where

$$\mathbf{C} = \begin{bmatrix} \cos(kb/2) & \sin(kb/2) \\ -k\sin(kb/2) & k\cos(kb/2) \end{bmatrix}$$

$$\mathbf{a} = \begin{bmatrix} A \\ B \end{bmatrix}$$

and

$$\mathbf{b} = \begin{bmatrix} \cosh(\kappa b/2) \\ \kappa\sinh(kb/2) \end{bmatrix}$$

In Matlab, these (or any set of) linear equations can be solved using the backslash operator, namely `a = C\b`.

The wavefunction must vanish at the outer edges of regions II and IV, namely

$$\psi_{\mathrm{IV}}(x = a + b/2) = A\cos[k(a + b/2)] + B\sin[k(a + b/2)] = 0$$

In general this will occur only for discrete values of the energy. In other words, the roots of the function $\psi_{\mathrm{III}}(x; E)$ as a function of E will define the allowed energies.

I have put on the course website (in the Matlab files) a Matlab function script `double_well.m` which returns $\psi_{\mathrm{III}}(x = a + b/2; E)$. Note that this function script has only E as an argument. You must supply the values of a, b, the mass, and V_o through a `global` statement, as well as a parameter `flags` which is $+1$ if you are choosing a symmetric state or -1 if you are choosing an antisymmetric state. Thus, in your calling script you need the statement

```
global flags a b mass Vo
```

For the parameters $V_o = 0.0015$, $a = 3.05$, $b = 2.4$, and mass=1837

a. Plot, on a single plot, the square double-well potential defined by these parameters as well as the potential of Fig. 1. In making this plot, shift the potential[Eq. (1)] of Fig. 1 up so that the minimum of this potential lies at $V = 0$.

b. You can determine the energies of the square double-well potential by looking for the energies for which $\psi(x = a + b/2) = 0$ Use the Matlab command

```
ezplot('double_well',E0,E1)
```

to plot the value of $\psi(x = a + b/2)$ as a function of energy over the range $0 \le E \le 0.007$. Then, to determine the exact quantum level energies, execute the command

```
fzero('double_well',E)
```

where `E` is a guess of the energy, which you can obtain from your plot of $\psi(x = a + b/2)$ as a function of E.

Determine the splitting between the lowest two levels of the double square well with positive inversion symmetry. Compare this with the comparable splitting for the potential of Eq. (1), which you can get from the numbers in Table I. Also, calculate the splitting between the positive and negative parity states for the two lowest pairs of levels and also compare these to the values for the potential of Eq. (1).

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[1] The symbol for the atomic mass unit (or Dalton) is u.

[2] The easiest way to calculate these is to do everything in atomic units, so that τ is just π/δ. Then, use the known conversion from atomic units of time into seconds.