THE DOUBLE POTENTIAL WELL AND ITS APPLICATIONS.

We can use the square well as a simple schematic one-dimensional model to explain some of the most profound and far-reaching quantum mechanical phenomena in nature: covalent bonding and energy bands in solids. To motivate the model we begin by considering the H_2^+ molecular ion in three-dimensions: two protons, p_1 and p_2, interacting with a single electron e^-.
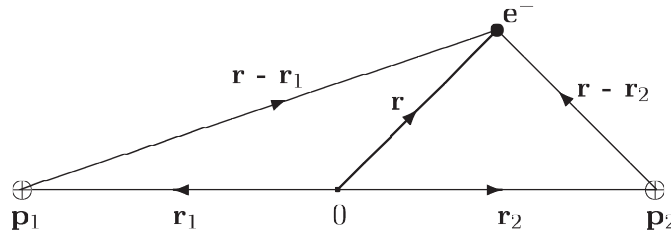

Figure 1: Coordinate system for H_2^+ ion. $R = r_1 - r_2$ is the vector separation of the protons, and its magnitude is $R = |r_1 - r_2|$.

For the system of 3 particles ($i = 1, 2, 3$) the full 3-dimensional Hamiltonian is

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r_1}|} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r_2}|} + \frac{e^2}{4\pi\epsilon_0 R}. \tag{1}$$

The summed terms are the kinetic energies of the three particles, the next two are the attractive potentials between the electron and the two protons, and the last represents the repulsive potential between the protons. When appropriate variable changes are made, when the centre-of-mass motion is taken out, and when the wave functions of the two protons are factored out (assuming the protons move slowly compared to the electron – this is the Born-Oppenheimer approximation) one eventually finds that the *electron* wave function ψ obeys a Schrödinger equation *with the same potential above*. Drawn in just 1-dimension the potential will look like this:
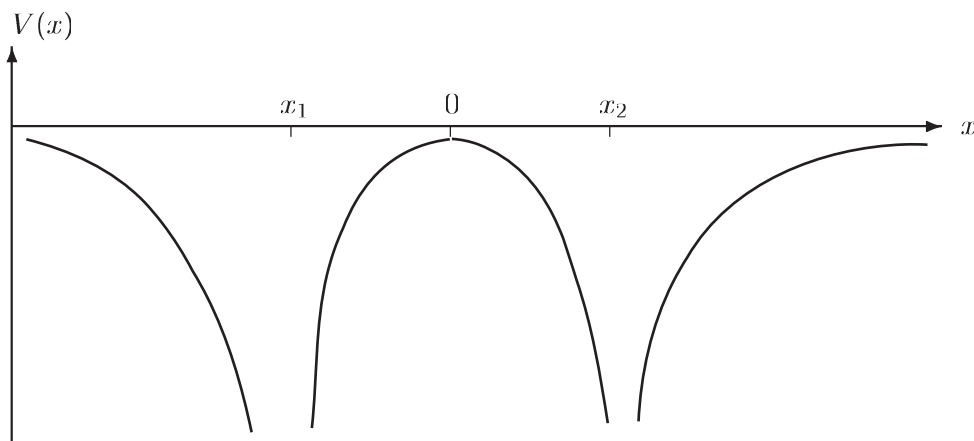

Figure 2: Realistic potential field for electron in H_2^+ ion.

This picture suggests that if the electron found itself bound to the left-hand proton in the energy level E_n then, to move over to the right-hand proton it would first have to surmount a potential barrier too high for its energy to allow, at least *classically*. The origin of this barrier is simply the attraction around each proton: to escape the coulomb attraction of the proton that has captured it the electron must do work in order to move over to the other proton. On the other hand quantum mechanically we know that tunnelling is possible and even *probable* if the barrier is not too thick and too high.

We now construct a very simple model of the above physics: a one-dimensional potential in which the electron moves, with the coulomb attraction of each proton being represented by two finite square wells centred at each proton and separated by a barrier. This barrier represents additional energy the electron must acquire to classically escape from the attraction of one proton and move over to the force field around the other proton.
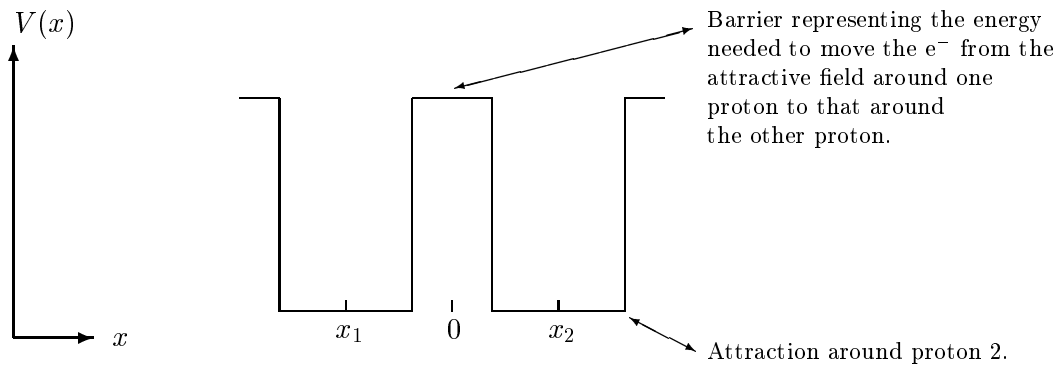

Figure 3: Idealised model potential field for electron in H_2^+ ion.

One crucial property of both the real problem and our model is the *symmetry of the potential*:

$$V(-x) = V(x) \tag{2}$$

Note that $x_1 = -x_2$. To solve the quantum mechanical problem we first imagine the two protons so far apart that there is no interaction between them. Then we expect the electron to be bound to one or the other proton, giving a wave function

$$
\begin{aligned}
\text{either} \quad \psi &= \psi_n(x - x_1) \equiv \psi_{(1)} \quad \text{for } e^- \text{ bound to proton 1,} \\
\text{or} \quad \psi &= \psi_n(x - x_2) \equiv \psi_{(2)} \quad \text{for } e^- \text{ bound to proton 2,}
\end{aligned}
\tag{3}
$$

To see a concrete example consider the situation where the wells are high enough to allow us to approximate the wave functions by those of the infinite square well. For the even parity states, $n = 1, 3, 5 \ldots$, these would be

$$
\begin{aligned}
\psi_{(1)} &= \sqrt{\frac{2}{L}} \cos \frac{n\pi}{L}(x - x_1) \qquad 0 \le (x - x_1) \le L \\
&= 0 \;\; \text{elsewhere}
\end{aligned}
\tag{4}
$$

$$
\begin{aligned}
\psi_{(2)} &= \sqrt{\frac{2}{L}} \cos \frac{n\pi}{L}(x - x_2) \qquad 0 \le (x - x_2) \le L \\
&= 0 \;\; \text{elsewhere}
\end{aligned}
\tag{5}
$$

At first sight it may therefore appear likely that when the protons are slowly moved closer the electron continues orbiting around the proton it first chose, giving two possible wave functions $\psi = \psi_{(1)}$ or $\psi_{(2)}$; this is the 'classical' intuition. Indeed the classical prediction is that the electron

will bind to one proton, so that the other proton sees a neutral system, feels little attraction and simply drifts off – the molecule is unstable and should not be found in any laboratory. This was a great mystery before the advent of quantum mechanics because experimentally it was known a stable H_2^+ molecule exists in nature with a binding energy of 2.65 eV. How does quantum mechanics explain this?

The secret lies in the quantum mechanical theorem we have already proved: *if the potential is mirror-symmetric, $V(-x) = V(x)$ then the wave function has a definite symmetry under $x \to -x$;* ψ is either symmetric (parity +1) or antisymmetric (parity −1). A glance at the diagram of the potential shows that a mirror reflection about the origin, $x \to -x$ is *equivalent* to interchanging the two protons, $x_1 \leftrightarrow x_2$. Neither of the wave functions $\psi_{(1)}$ or $\psi_{(2)}$ has this symmetry on its own - they have definite symmetry about *different* points: $\psi_{(1)}$ about $x = x_1$ and $\psi_{(2)}$ about $x = x_2$; neither about $x = 0$. But the following linear combinations *do* have definite symmetry about $x = 0$:

$$\begin{aligned} \psi_s &= \psi_n(x - x_1) + \psi_n(x - x_2) \equiv \psi_{(1)} + \psi_{(2)} \quad \text{is symmetrical about} \quad x = 0; \\ \psi_a &= \psi_n(x - x_1) - \psi_n(x - x_2) \equiv \psi_{(1)} - \psi_{(2)} \quad \text{is antisymmetrical about} \; x = 0. \end{aligned} \quad (6)$$

This suggests that a *general* way to solve the problem is to postulate an approximate wave function which is a linear combination of eigenstates, ψ_n, of each square well alone

$$\psi(x, x_1, x_2) = c_1 \psi_n(x - x_1) + c_2 \psi_n(x - x_2) \equiv c_1 \psi_{(1)} + c_2 \psi_{(2)}, \quad (7)$$

where c_1 and c_2 are constants to be determined from the TISE for the double-well potential. (Here we chose the ground states $n = 1$ since we are searching for the H_2^+ ground state.). Because of the symmetry of the potential we expect the two possibilities $c_1 = \pm c_2$ to emerge in the solution. Note that the two wave functions in this linear combination are not orthogonal because they correspond to the same function evaluated at different points. Practitioners of molecular quantum mechanics call this approximation technique LCAO – Linear Combination of Atomic Orbitals. A better version of the approximation includes a sum over all the states of the single well ($\sum_n$).

This assumption, that somehow the electron is 'shared' between the two protons, is completely at variance with classical physics where the electron, once it binds to one of the protons, will continue to orbit around it leaving the other proton to wander off because it is not attracted to the neutral H-atom. In pictures the contrast looks like this:
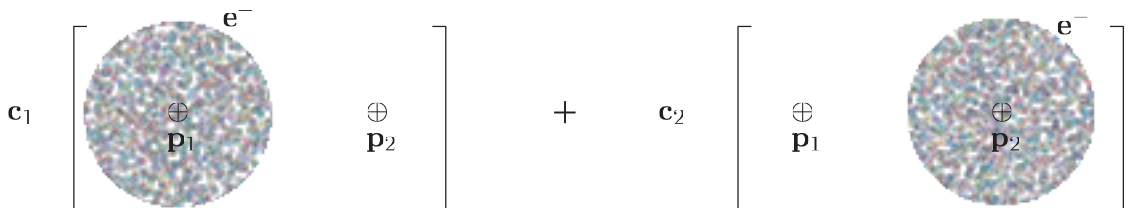
CLASSICAL:
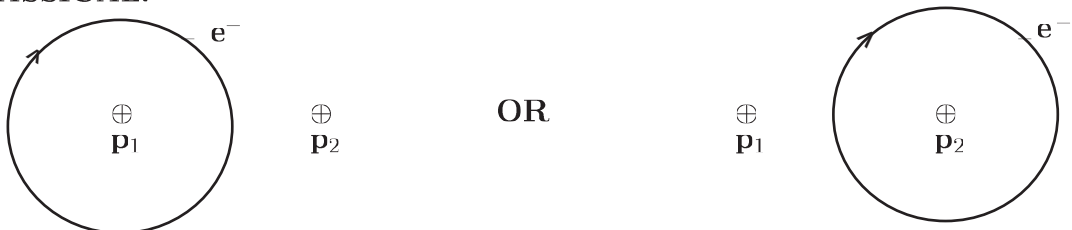
QUANTUM:

Figure 4: Classical and schematic quantum mechanical pictures of H_2^+ ion.

(1) The Formal Argument.

The TISE for the problem is

$$\hat{H}\psi = E\psi \tag{8}$$

and our ansatz is

$$\psi = c_1\psi_{(1)} + c_2\psi_{(2)} \tag{9}$$

giving

$$c_1\hat{H}\psi_{(1)} + c_2\hat{H}\psi_{(2)} = c_1 E\psi_{(1)} + c_2 E\psi_{(2)} \tag{10}$$

Multiplying this equation respectively by the normalised, but not orthogonal, $\psi_{(1)}^*$ and $\psi_{(2)}^*$ and integrating with respect to x in each case gives

$$c_1 H_{11} + c_2 H_{12} = c_1 E + c_2 E K_{12} \tag{11}$$

$$c_1 H_{21} + c_2 H_{22} = c_1 E K_{21} + c_2 E \tag{12}$$

where

$$H_{ij} = \int_{-\infty}^{+\infty} \psi_{(i)}^* \hat{H}\psi_{(j)} dx = \int_{-\infty}^{+\infty} \psi_n^*(x - x_i)\hat{H}\psi_n(x - x_j)dx \tag{13}$$

$$K_{ij} = \int_{-\infty}^{+\infty} \psi_{(i)}^* \psi_{(j)} dx = \int_{-\infty}^{+\infty} \psi_n^*(x - x_i)\psi_n(x - x_j)dx \tag{14}$$

We have used the fact that $K_{11} = K_{22} = 1$ which follows from the normalisation of the single-well energy eigenstates ψ_n after changing the variable of integration to $x - x_1$ or $x - x_2$ respectively. K_{12} and K_{21} are non-vanishing because the wave functions are evaluated at separate points

$$K_{12} = \int_{-\infty}^{+\infty} \psi_n^*(x - x_1)\psi_n(x - x_2)dx \tag{15}$$

and if the wells are close enough the two wave functions in the integrand overlap due to them tunnelling into and through the classically forbidden (repulsive) region. For the ground state, $n = 1$:
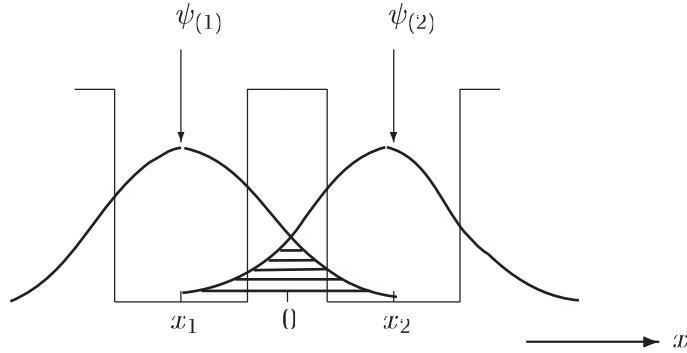

Figure 5: Region of overlap contributing non-zero values to integrals K_{12} & K_{21}.

Inspection of the above expression for K_{12} and the fact that the bound-state wave functions are real shows that the expression is symmetric under $x_1 \leftrightarrow x_2$, so that

$$K_{12} = K_{21} \tag{16}$$

Also, since $\hat{H}$ is a Hermitian operator (see later in the course for this; but the proof is simple: just integrate the kinetic energy term $\partial^2/\partial x^2$ twice by parts to get $\hat{H}$ to act on the first wave function in the integral) and the ψ_n are real we can show that

$$H_{12} = H_{21} \tag{17}$$

4

Those interested or sceptical should study the Appendix for detailed proofs. Finally, the reality of the ψ_n, the fact that they have definite parity, and that $\hat{H}$ is even in $x \to -x$ and symmetric under $x_1 \leftrightarrow x_2$ implies

$$H_{11} = H_{22} \tag{18}$$

It is this latter condition which is crucial in eventually leading to the expected symmetric and antisymmetric wave functions.

Our equations therefore simplify to

$$
\begin{aligned}
c_1(H_{11} - E) + c_2(H_{12} - EK_{12}) &= 0 \tag{19} \\
c_1(H_{12} - EK_{12}) + c_2(H_{11} - E) &= 0 \tag{20}
\end{aligned}
$$

These simultaneous *homogeneous* equations in c_1 and c_2 only have consistent solutions if

$$
\left|
\begin{array}{cc}
H_{11} - E & H_{12} - EK_{12} \\
H_{12} - EK_{12} & H_{11} - E
\end{array}
\right| = 0 \tag{21}
$$

$$\text{ie.} \quad (H_{11} - E)^2 = (H_{12} - EK_{12})^2 \tag{22}$$

giving the two possibilities

$$H_{11} - E = \pm(H_{12} - EK_{12}) \tag{23}$$

Substituting each possibility into the original equations and solving for c_1, c_2 gives the two solutions, one symmetric and the other antisymmetric, just as we expect from the theorem:

$$
\begin{aligned}
\textbf{Antisymmetric} \quad & c_1 = -c_2 \ \text{ giving} \quad E = E_a \ = \ \frac{H_{11} - H_{12}}{1 - K_{12}}; \\
\textbf{Symmetric} \quad & c_1 = +c_2 \ \text{ giving} \quad E = E_s \ = \ \frac{H_{11} + H_{12}}{1 + K_{12}}.
\end{aligned} \tag{24}
$$

Thus, starting with a *single* energy $E_{n=1}$ for the electron in either well (when the wells are separated a large distance) we arrived at *two distinct* energies with their corresponding wave functions when the wells are close enough:

$$
\begin{aligned}
\textbf{Antisymmetric:} \quad & \psi_a = c_{1a}(\psi_{(1)} - \psi_{(2)}) \qquad E_a \ = \ \frac{H_{11} - H_{12}}{1 - K_{12}} \\
\textbf{Symmetric:} \quad & \psi_s = c_{1s}(\psi_{(1)} + \psi_{(2)}) \qquad E_s \ = \ \frac{H_{11} + H_{12}}{1 + K_{12}}
\end{aligned} \tag{25}
$$

where c_{1a} and c_{1s} are chosen to normalise ψ_a and ψ_s. In the jargon of quantum mechanics, the *degeneracy* in energy when the wells are far apart (ie. when both possible states $\psi = \psi_{(1)}$ and $\psi = \psi_{(2)}$ have the same energy $E_{n=1}$ – the level is doubly degenerate) is *lifted* when the wells come close enough for tunnelling to occur; the result is that the degenerate energies become two separated energy levels at E_s and E_a:
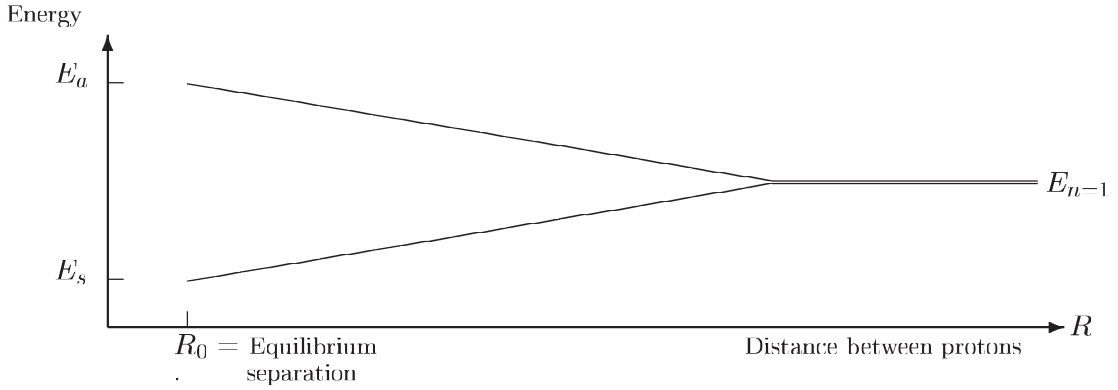
Figure 6: Lifting the degeneracy in the H_2^+ ion. This is a greatly simplified version of Fig. 12

Which of the energies E_a' or E_s' is smallest depends on the actual numerical values of H_{11}, H_{12} and K_{12}. A detailed discussion of these integrals reveals that $E_s < E_a$; for the ground state we shall give a simple physical argument to establish this in the following section.

(2) The simple Physical Argument.

We now repeat the above discussion in a more informal form. Misapplying our classical intuition to the quantum mechanical problem we have already guessed that there are two possibilities for the electron wave function: either the electron is localised around the left proton or around the right one. This is shown in Fig.4 or, in terms of wave functions:
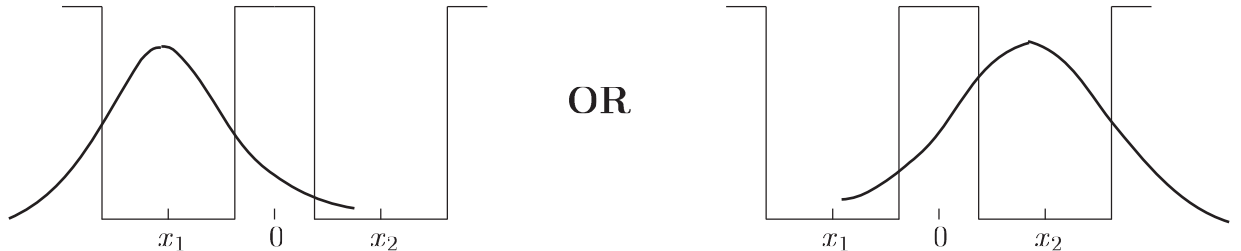

Figure 7: Electron wave function in H_2^+ ion from 'classical' reasoning.

Quantum mechanically neither of these is any good because we have already argued that the symmetry of the potential (eq.2) requires the 2-well wave function to be either symmetric or antisymmetric; instead we are driven to take the definite parity combinations in eq.6 to be our starting point for a possible ground state ($n = 1$). We can see qualititively how quantum mechanics leads to a dramatic physical difference in these two states. First note that *physically ψ_n and $-\psi_n$* represent the same wave function because they only differ by a constant phase ($e^{i\pi} = -1$) which cancels out in all physical quantities (ie. in expectation values). However, once we have a physical situation where *two* or more wave functions are superimposed, their phase *difference* has physical consequences because of interference - this is the superposition principle. Thus, keeping in mind the demands of the symmetric potential, there are two candidates for the ground state ψ which are physically the same *when the wells are far apart*:
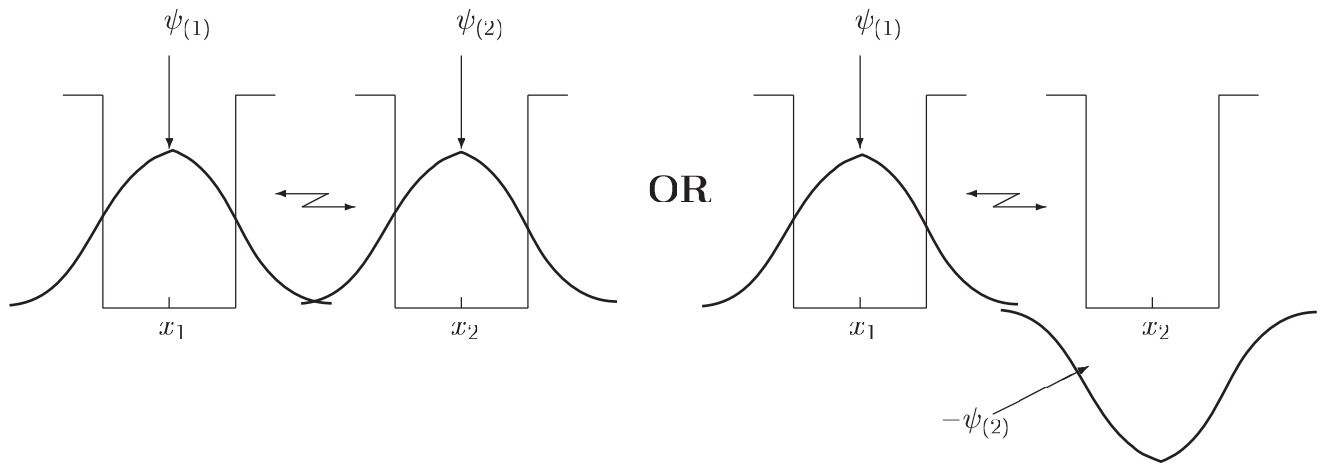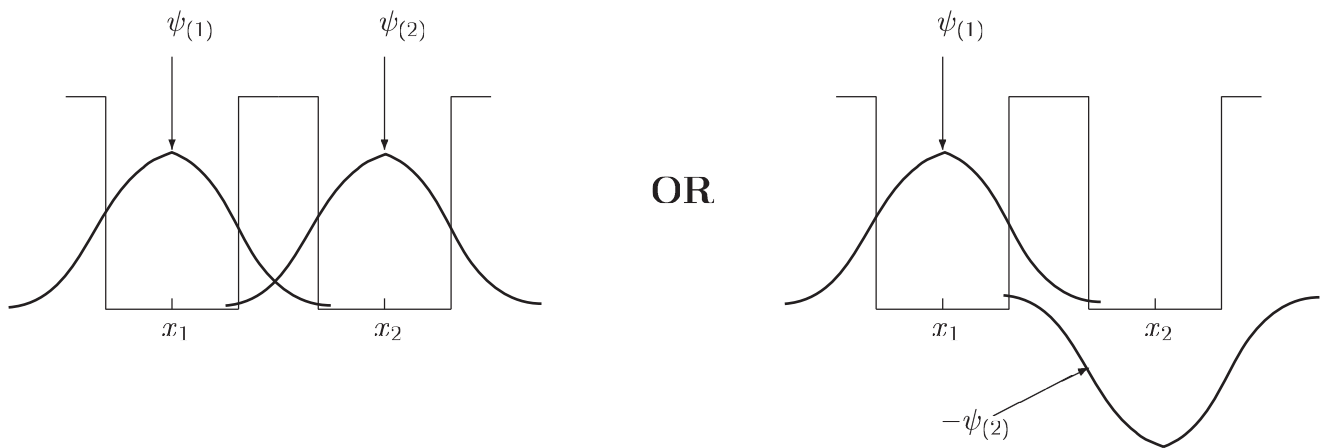
6

Figure 8: Definite parity electron wave functions for protons far apart.

But as the wells (protons) move nearer the separate wave functions $\psi_{(1)}$ and $\psi_{(2)}$ begin to overlap, and their superposition leads to the symmetric and antisymmetric wave functions ψ_s and ψ_a being quite different:
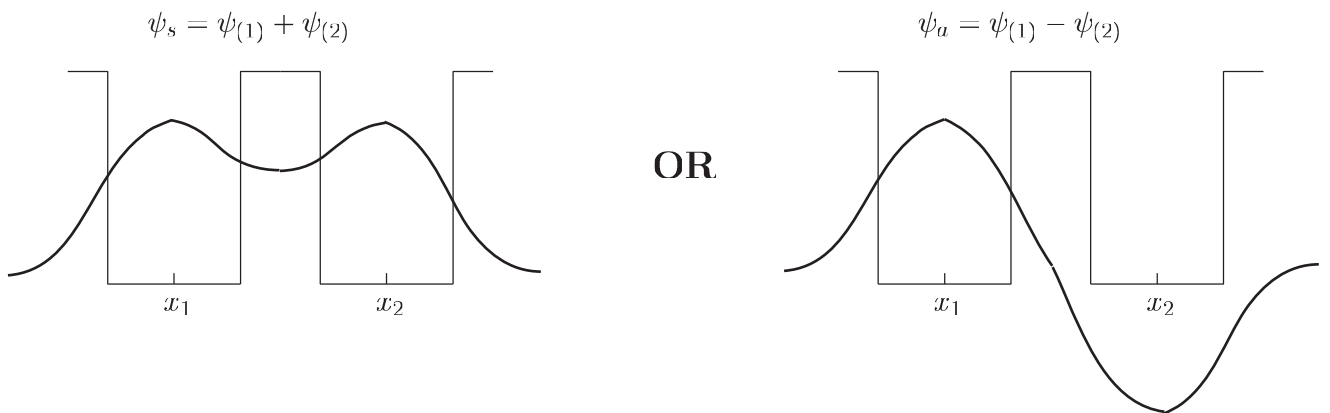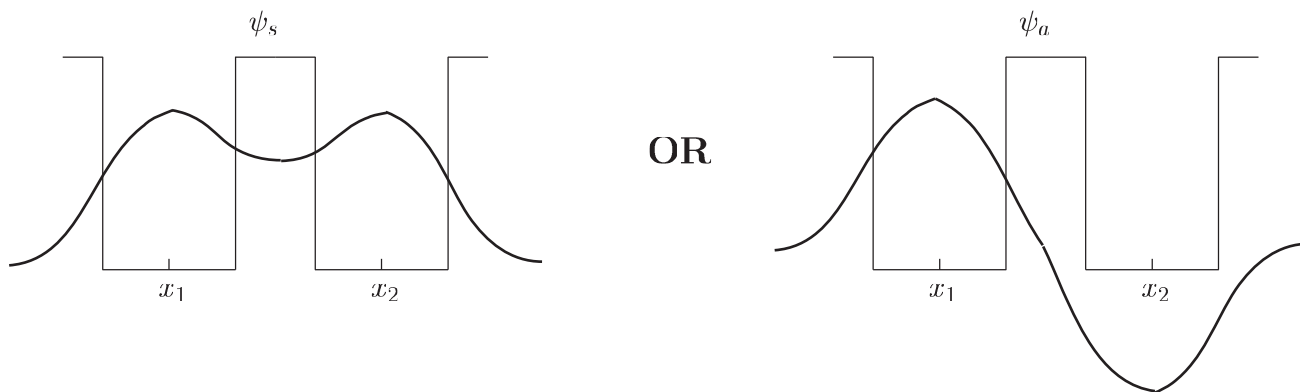

Superposition gives:

Figure 9: Definite parity electron wave functions for H$_2^+$ ion.

The second part of the argument is to show, for the ground state ($n = 1$), that $E_s < E_a$; it is here that the dramatic difference in symmetric and antisymmetric wave functions comes into play. Let's look at the symmetric and antisymmetric electron wave functions using the Born interpretation: $|\psi(x)|^2$ represents the probability density; but since the electron is electrically charged it also represents the density of negative electric charge $-e|\psi(x)|^2 \propto |\psi(x)|^2$.

Wave functions:

Probability densities:

Here the e^- has a significant probability of being found mid-way between the two protons.

Here the e^- *avoids* the region between the protons and is most likely to be found around either one of them. This is closest to, but not quite, the classical picture.
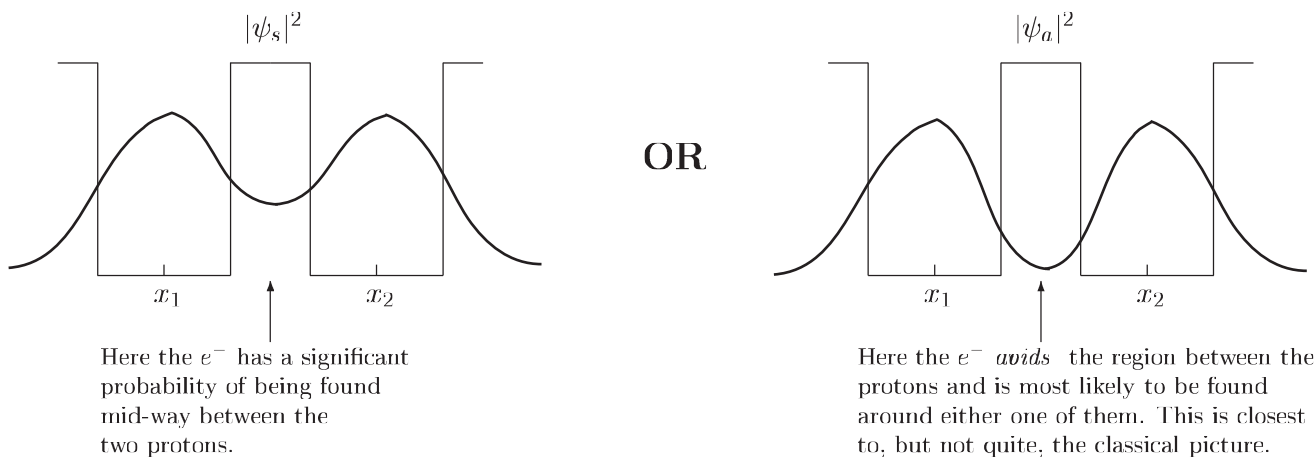
Figure 10: Electron wave functions and -ve charge densities for H_2^+ ion.

In the *symmetric* case the negative electronic charge distribution is significant half way between the protons, which are therefore *both* attracted towards this region, and hence towards each other – a net attractive force binding the protons to each other. This is the *covalent* binding which forms the basis of much chemistry, epecially the overwhelmingly important carbon chemistry, the key to molecular biology. This 'exchange' force is a purely quantum mechanical phenomenon because it relies on the tunnelling of both wave functions $\psi_{(1)}$ and $\psi_{(2)}$ into the classically forbidden region between the wells.

In the *antisymmetric* case the electron avoids the region half way between the protons and is to be found almost exclusively around either one or the other proton. Thus each proton and its accompanying negative charge cloud - with a net positive charge - 'sees' an equal positive charge from the other proton and *its* negative cloud: the protons and their negative cloud experience

a net repulsion, so the force cannot bind the protons together and the state is unstable. Fig. 11 on the following page depicts the negative charge distributions in these two cases.

Expressed in terms of energies, the above argument implies that the symmetric state has a *lower* energy than when the two wells are far apart (when it is $E_{n=1}$, the ground state energy of one electron bound in one well), while the antisymmetric state has a higher energy. For the actual H_2^+ ion the energy can be plotted as a function of the distance $R = |\mathbf{r}_1 - \mathbf{r}_2|$ between the protons (notice that H_{ij}, K_{ij} only depend on x_1 and x_2, not x which is integrated out):
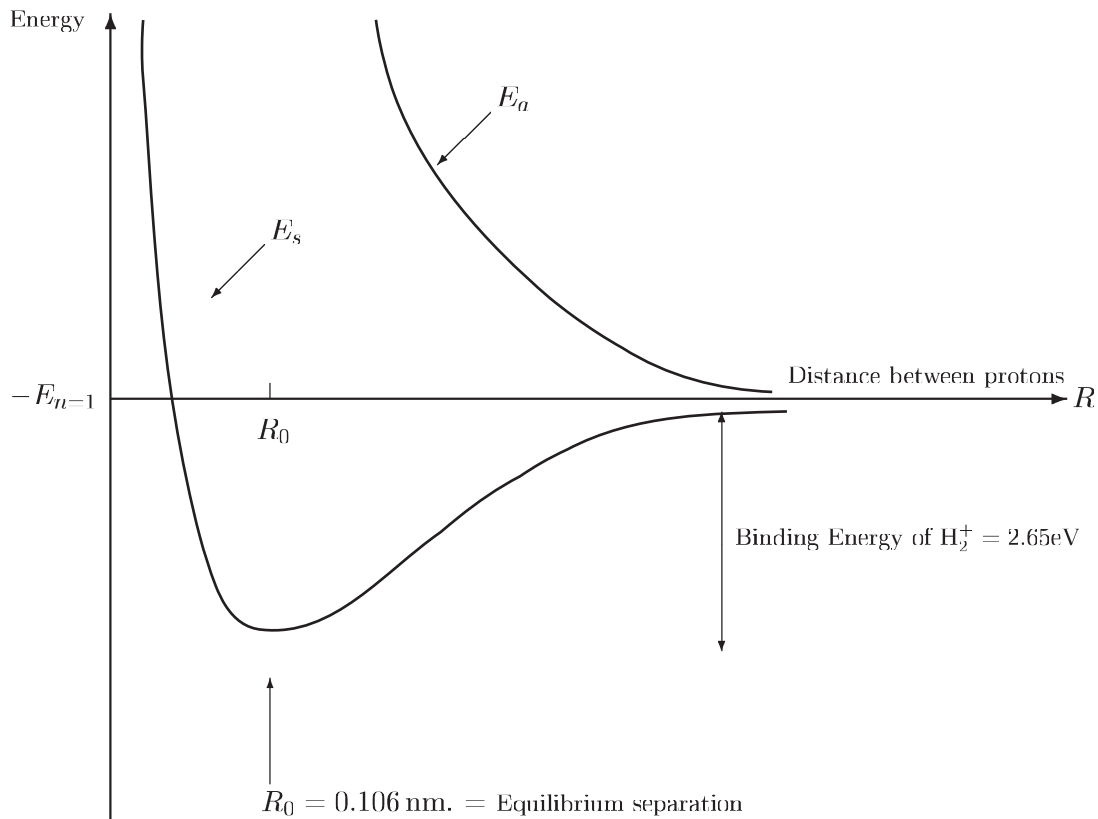

Figure 12: Electron energy versus inter-proton separation for H_2^+ ion.

Both curves asymptote to $E_{n=1}$ because,
as $R = |x_1 - x_2| \to \infty$, both $H_{12} \to 0$ and $K_{12} \to 0$, but $H_{11} \to E_{n=1}$.

To emphasise the contrast with classical physics imagine placing the electron initially in one well around proton 1: the state at $t = 0$ is therefore $\psi = \psi_{n=1}(x - x_1)$. Then one can show that the probability of finding the electron in the ground state about the proton 2 at a later time t is

$$P_{1 \to 2}(t) \propto \sin^2 \frac{(E_a - E_s)}{\hbar} t \;=\; \sin^2 \omega t \tag{26}$$

which shows that in the H_2^+ ion the electron can be pictured as tunnelling back-and-forth between the two protons with frequency $\omega = (E_a - E_s)/\hbar$. It is this *exchange* which produces the attractive *exchange force* or *covalent bonding* in the symmetric state. The resulting charge distribution, with the electron spending a significant fraction of its time in the classically forbidden region half-way between the protons, enables us to understand how the attractive force is produced.

Figure 11: Negative charge density ($\propto |\psi|^2$) produced by the electron
.   in the H_2^+ molecular ion.

SYMMETRIC STATE

Region of significant negative charge density

ANTISYMMETRIC STATE

Region of negative charge depletion

THE AMMONIA (NH$_3$) MASER.

In the ammonia molecule the three hydrogen atoms form the base of a pyramid whose apex is the nitrogen atom. The hydrogen atoms form an equilateral triangle whose symmetry axis passes through the nitrogen atom, so that its distance from the plane of the triangle plays the role of the one-dimensional variable x. If the nitrogen atom is in the plane of the hydrogen atoms they repel it; the nitrogen atom is therefore classically trapped a distance x above or below the hydrogen atoms in a double potential well $V(x) = V(-x)$ with a repulsive barrier at the location of the hydrogen triangle, $x = 0$. This corresponds precisely to the one-dimensional model discussed above, with the two single-well wave functions $\psi_{(1)}$ and $\psi_{(2)}$ corresponding to the two possible configurations of the ammonia molecule:
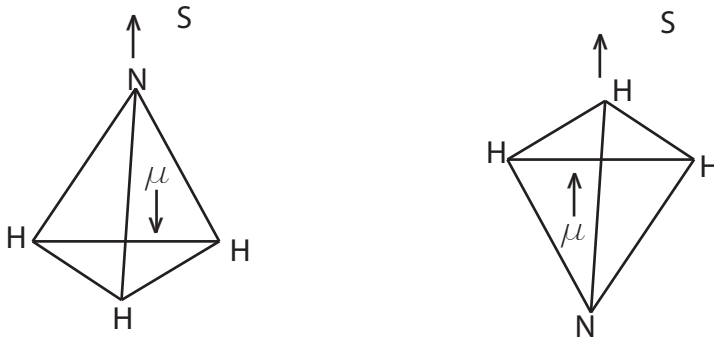
(The vectors shown are the spin **S** of the molecule and its electric dipole moment μ whose relative directions differ for the two states. This is important, but will not concern us here.)
Thus we find again that the two-fold degeneracy of the molecule is lifted by quantum mechanical tunnelling between the two states depicted, leading to two separate levels differing in energy by

$$E_a - E_s = h\nu \sim 1\,\text{eV} \tag{27}$$

corresponding to a frequency $\nu = 24,000\,\text{MHz} = 24\,\text{GHz}$, or a wavelenth of 12.5 mm which is in the microwave range. Excitation to and from the higher level can be caused by exposing the gas to microwave radiation, forming the basis of the MASER – Microwave Amplification by Stimulated Emission of Radiation. This seminal device, invented by Townes in 1954, the forerunner of the LASER, involves two processes. First, the interaction of the electric dipole moment of a beam of ammonia molecules with an electrostatic field makes it possible to separate out a beam of molecules in the antisymmetric state; this creates a highly enhanced population in the upper energy level E_a – a population inversion. The beam, passed through a resonant cavity is then exposed to electromagnetic radiation at the resonant frequency 24 GHz, which 'stimulates' a rapid de-excitation of the molecules down to the ground state level E_s, thereby emitting 24 GHz radiation *in phase* with the incident radiation. This dramatic increase in the intensity of the incident radiation field is the coherent amplification process.

Masers are important in astrophysics of the interstellar medium where high fluxes of photons can induce a population inversion, particularly in the densest star forming regions. Two examples of observed masing molecules are water, H_2O and cyanogen, CN. The cosmic microwave background radiation, CMBR, 'officially' discovered by Penzias and Wilson in 1965, was actually first detected by McKellar in 1941 when he discovered CN molecules in the interstellar medium which had suffered a population inversion. Although he correctly inferred that a radiation field at a temperature of 2.3 K could have caused this, neither he nor anyone else realised that this radiation was actually the CMBR.

**RESONANCE STABILISATION OF BENZENE, C_6H_6**

The valency 4 carbon atom gives this well-loved organic molecule a highly pleasing regular hexagonal structure:
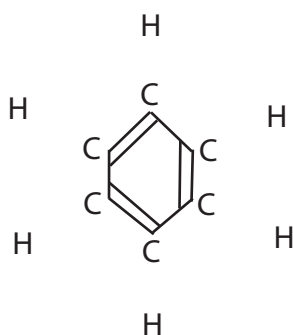
where the 4 bonds of each carbon atom are shown as lines. Benzene displays a stronger binding than expected on the basis of this picture because there actually exist two possible configurations of the double bonds:
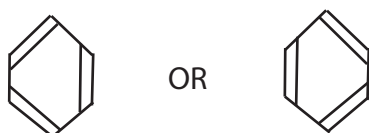

each of which alone has the same energy, $E_{n=1}$ – the ground state is doubly degenerate. But now we know that the true benzene wave function should be a linear combination of the two states depicted above, leading to $H_{12} \neq 0$ and $K_{12} \neq 0$, as for the double-well. The degeneracy is therefore lifted, with two distinct levels, the lowest being less than $E_{n=1}$, making the molecule more stable. Physically one can think of the system as jumping back-and-forth between the two states, leading to the title of this section and to the Chemists' notation:
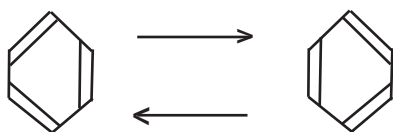
ENERGY BANDS & GAPS IN SOLIDS.

Imagine an H_3^{++} ion with 3 protons and only one electron modelled as a triple-well problem. The wave function, reflecting the symmetry of the potential, will therefore involve a linear combination of three single-well eigenstates: $\psi = c_1\psi_{(1)} + c_2\psi_{(2)} + c_3\psi_{(3)}$. A repeat of the procedure given earlier now leads to 3 homogeneous equations for the three c's on equating to zero the determinant of the 3×3 matrix of coefficients, leading to a cubic equation for the energies, giving three distinct energy levels and three distinct wave functions. The triply degenerate ground state energy splits into three: Alternatively, just draw the 3 possible wave functions.
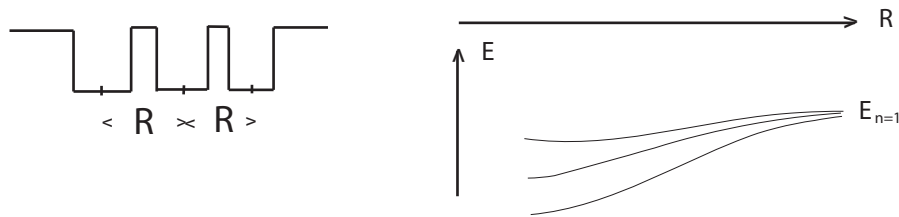
The pattern is set: for N identical wells we expect the N-fold degenerate ground state energy to split into N levels. An ideal solid is a regular array of atomic ions, each presenting an attractive well to an electron confined to the crystal lattice, but with repulsive barriers between the wells. Modelled as before, we therefore expect a macroscopic solid with $N \sim 10^{23}$ atomic wells to generate 10^{23} levels from the 10^{23}-fold degenerate single-well level. This will happen, as for all the cases considered above, for each level $E_{n=1}, E_{n=2}, E_{n=3}, E_{n=4}, \ldots$ of the single well:
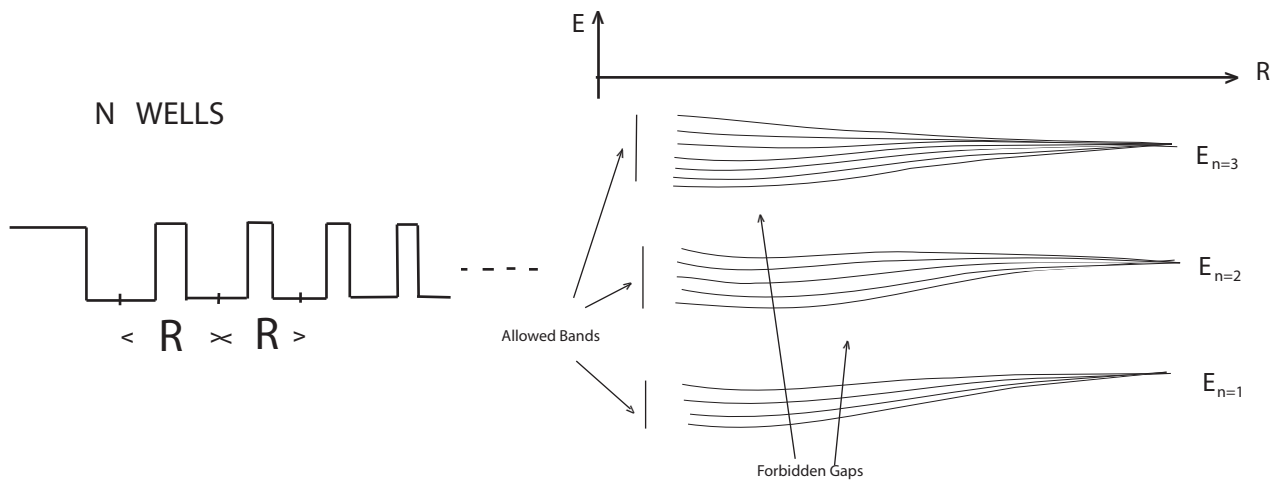
With so many atoms in the lattice the split lines, although discrete, are so close that they make up sets of essentially continuous *bands* of allowed energies separated by *forbidden bands*. Thus we see that the band structure of solids arises from quantum mechanical tunnelling through the barriers between ions, while the forbidden gaps arise from quantisation of energies resulting from localisation in potential wells (remember that the quantised energies $E_{n-1}, E_{n-2}, E_{n-3}, \ldots$ come from solving the single-well problem and it is their separation that produces the gaps in the diagram above). The scientific, technological, economic and sociological implications of these properties have been, and will continue to be, far-reaching and profound!

APPENDIX: Proof that $H_{12} = H_{21}$ and $H_{11} = H_{22}$.

The Hamiltonian is of course Hermitian, and using the fact that the bound-state wave functions are *real*,

$$H_{12} = \int \psi_n(x - x_1)\, \hat{H}\, \psi_n(x - x_2)\, dx \;\; \text{by definition.} \tag{28}$$

$$= \int \{\hat{H}\, \psi_n(x - x_1)\}\, \psi_n(x - x_2) \;\; \text{since } \hat{H} \text{ is Hermitian.} \tag{29}$$

$$= H_{21} \tag{30}$$

The Hamiltonian for our model double square well has the form:

$$\hat{H}(x, x_1, x_2) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(|x - x_1|) + V(|x - x_2|) \tag{31}$$

where $V(x)$ is the single finite square well potential

$$\begin{aligned} V(|x - x_i|) &= -V_0 \quad \text{for} \quad |x - x_i| < L/2 \\ &= 0 \quad\;\; \text{for} \quad |x - x_i| > L/2 \end{aligned} \tag{32}$$

To check that the double-well potential drawn in the text is indeed $V_D = V(|x-x_1|) + V(|x-x_2|)$ just draw it following the definition above, keeping in mind that we have placed the origin symmetrically between the wells so that $x_1 = -x_2$ with x_1 negative. Just as for the more realistic potential in 3-dimensions, the double-well potential $V_D = V(|x - x_1|) + V(|x - x_2|)$ has the following two symmetries:

$$\begin{aligned} V_D(x, x_1, x_2) &= V_D(x, x_2, x_1) \quad \text{ie. } 1 \leftrightarrow 2 \text{ symmetric.} \tag{33} \\ &= V_D(-x, -x_1, -x_2) \quad \text{ie. mirror-symmetric about the origin.} \tag{34} \end{aligned}$$

The first is obvious; the second follows by just looking at the drawing of the double-well potential. Formally it follows from the following manipulations:

$$\begin{aligned} V_D(-x, -x_1, -x_2) &= V(|-x + x_1|) + V(|-x + x_2|) \tag{35} \\ &= V(|x - x_1|) + V(|x - x_2|) \text{ using the properties of } |\;| \tag{36} \\ &= V_D(x, x_1, x_2) \tag{37} \end{aligned}$$

Now since $\partial^2/\partial x^2$ is symmetrical under $x \to -x$ and does not depend on x_1 or x_2, $\hat{H}$ also has the above symmetries. Hence,

$$H_{11} = \int \psi_n(x - x_1)\, \hat{H}(x, x_1, x_2)\, \psi_n(x - x_1)\, dx \;\; \text{by definition} \tag{38}$$

$$= \int \psi_n(x - x_1)\, \hat{H}(x, x_2, x_1)\, \psi_n(x - x_1)\, dx \;\; \text{using the 1st. symmetry of } \hat{H} \tag{39}$$

$$= \int \psi_n(x + x_2)\, \hat{H}(x, -x_1, -x_2)\, \psi_n(x + x_2)\, dx \;\; \text{using } x_1 = -x_2 \tag{40}$$

$$= \int \psi_n(-y + x_2)\, \hat{H}(-y, -x_1, -x_2)\, \psi_n(-y + x_2)\, dy \;\; \text{using } y = -x,\, dx = -dy \tag{41}$$

$$= \int \psi_n(-y + x_2)\, \hat{H}(y, x_1, x_2)\, \psi_n(-y + x_2)\, dy \;\; \text{using the 2nd. symmetry of } \hat{H} \tag{42}$$

$$= \int \psi_n(y - x_2)\, \hat{H}(y, x_1, x_2)\, \psi_n(y - x_2)\, dy \;\; \text{since the wf's have } same \text{ parity} \tag{43}$$

$$= H_{22} \tag{44}$$

The last step involves no sign change because, although the wave function may have negative parity, it gets squared because the integrand contains the product of two wave functions with the same energy (E_n) and therefore the same parity.