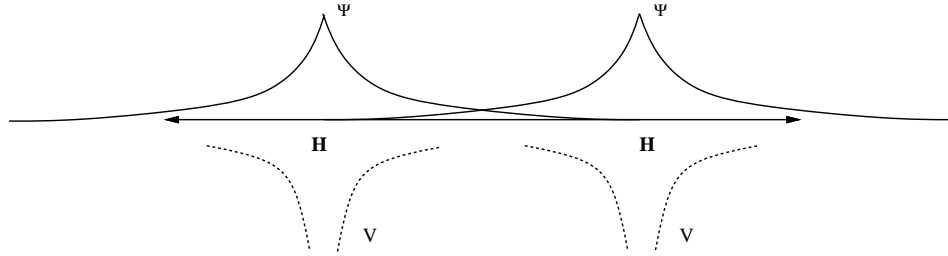


## Physics 2: Chemical Bonding and ‘Tight Binding’

To get a feeling for the meaning of parameters in a ‘band theory’, it is useful to think about the Hydrogen molecule,  $H_2^+$ :



where we have depicted the two potentials and the associated wavefunctions for each of the two Hydrogen atoms in the *absence* of the other.

The basic idea is to use  $\Psi_1$ , the wavefunction for the first Hydrogen, and  $\Psi_2$ , the wavefunction for the second Hydrogen, to try to find the wavefunction in the presence of *both* Hydrogens. We set:

$$\begin{aligned}\hat{H}_1 &= \frac{|\hat{\mathbf{p}}|^2}{2m} + V(\mathbf{r} - \mathbf{R}_1) \\ \hat{H}_2 &= \frac{|\hat{\mathbf{p}}|^2}{2m} + V(\mathbf{r} - \mathbf{R}_2) \\ \hat{H} &= \frac{|\hat{\mathbf{p}}|^2}{2m} + V(\mathbf{r} - \mathbf{R}_1) + V(\mathbf{r} - \mathbf{R}_2)\end{aligned}$$

for the first, second and both Hydrogen atoms respectively. Now the original wavefunctions are supposed to be the solutions to their relevant atoms:

$$\begin{aligned}\hat{H}_1 \Psi_1 &= e_1 \Psi_1 \\ \hat{H}_2 \Psi_2 &= e_2 \Psi_2\end{aligned}$$

where  $e_1$  and  $e_2$  are the energies for the electron to sit on the two atoms.

The idea here is to make use of the two dimensional space made from  $\Psi_1$  and  $\Psi_2$  to solve the problem. The Hamiltonian matrix is:

$$H_{ij} = \int_V d^3\mathbf{r} \Psi_i^\dagger \hat{H} \Psi_j$$

which needs to be diagonalised to find the energies. (Unfortunately, the current wavefunctions are *not* orthogonal, and this causes some complications that we will simply ignore.) Now:

$$\begin{aligned}H_{11} &= e_1 + \int_V d^3\mathbf{r} \Psi_1^\dagger V(\mathbf{r} - \mathbf{R}_2) \Psi_1 \\ H_{12} &= \int_V d^3\mathbf{r} \Psi_1^\dagger V(\mathbf{r} - \mathbf{R}_1) \Psi_2 \\ H_{21} &= \int_V d^3\mathbf{r} \Psi_2^\dagger V(\mathbf{r} - \mathbf{R}_2) \Psi_1 \\ H_{22} &= e_2 + \int_V d^3\mathbf{r} \Psi_2^\dagger V(\mathbf{r} - \mathbf{R}_1) \Psi_2\end{aligned}$$

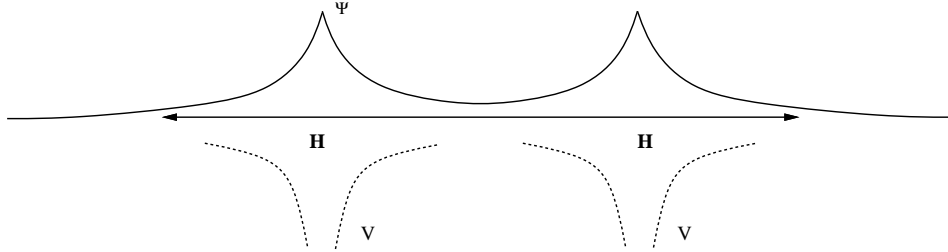
where we have assumed that the two wavefunctions are orthogonal (such a basis, known as Wannier orbitals, does in fact exist). The problem is then greatly simplified by ignoring the corrections to the diagonal elements, which are usually small, and in terms of:

$$t = - \int_V d^3\mathbf{r} \Psi_1^\dagger V(\mathbf{r} - \mathbf{R}_1) \Psi_2 = - \int_V d^3\mathbf{r} \Psi_2^\dagger V(\mathbf{r} - \mathbf{R}_2) \Psi_1$$

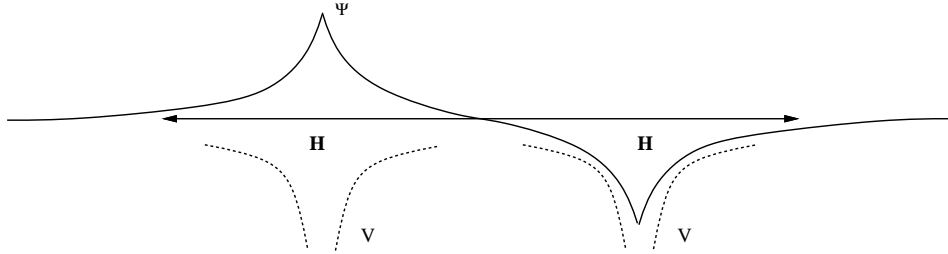
the so-called ‘hopping matrix-element’, we find a  $2 \times 2$  matrix:

$$H = \begin{bmatrix} e & -t \\ -t & e \end{bmatrix}$$

which can be diagonalised to form the bonding combination  $\frac{1}{\sqrt{2}}(\Psi_1 + \Psi_2)$ :



at energy  $E = e - t$  and the anti-bonding combination  $\frac{1}{\sqrt{2}}(\Psi_1 - \Psi_2)$ :



at energy  $E = e + t$ .

When there are many atoms in the system, the tight-binding approximation involves giving each atom an energy  $e_i$  and each nearby pair of atoms a hopping matrix-element  $t_{ij}$ .

In periodic crystals, chemical bonding does *not* correspond to either gaining or losing  $t$ , but is more sophisticated. In fact there is a spatially dependent phase:

$$e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_{j'})}$$

the so-called Bloch phase, which measures the ‘fraction’ of the bond energy,  $t_{jj'}$ , that an electron gains from the bond between the  $j$ ’th and  $j'$ ’th atoms. If there is an atom at both  $\pm(\mathbf{R}_j - \mathbf{R}_{j'})$ , then the contribution is:

$$\cos \mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_{j'})$$

and ranges between bonding and anti-bonding.