

Chapter 1

Chemical bonding and the Tight Binding method

1.1 The H_2^+ problem and the covalent bonding

Let us begin by solving the simplest one electron molecule, i.e. H_2^+ . The Hamiltonian for this system for two protons located at R_1 and R_2 is:

$$H = \frac{p^2}{2m} - \frac{e^2}{|r - R_1|} - \frac{e^2}{|r - R_2|} + \frac{e^2}{|R_1 - R_2|}$$

The last term, the Coulomb repulsion between the two electrons is added but it is an irrelevant constant in the quantum mechanical problem. This problem can be solved by using the variational method. The simplest basis one could take is the 1s orbitals located at each of the protons: $\phi_i(r) = Ae^{-|r-R_i|/a_B}$. The ground state wavefunction of the molecule can be taken as the linear combination of the two 1s orbitals:

$$\psi(r) = a_1\phi_1(r) + a_2\phi_2(r)$$

The two basis functions are normalized, and the two coefficients a_1 and a_2 are to be found so that the energy $\langle \psi | H | \psi \rangle$ is minimized. This should be done, however, with the constraint of normalization of ψ by introducing a Lagrange multiplier. This method, as will be shown later, is equivalent to the Schroedinger equation written for ψ and projected on the two basis states:

For $i = 1, 2$ $\langle \phi_i | [H|\psi\rangle - E|\psi\rangle] = 0$ If one assumes the basis as orthonormal, i.e. neglect the overlap integral $S_{12} = \langle \phi_1 | \phi_2 \rangle \simeq 0$, one will finally end up with a 2 by 2 matrix to diagonalize:

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} = \begin{bmatrix} \varepsilon & t \\ t & \varepsilon \end{bmatrix} \text{ diagonalized} \implies \begin{bmatrix} \varepsilon + t & 0 \\ 0 & \varepsilon - t \end{bmatrix}$$

The diagonal elements $\varepsilon = H_{11} = H_{22}$ are usually called the **onsite energies** and they include the contribution of the neighboring atoms:

$$H_{11} = \langle \phi_1 | \frac{p^2}{2m} - \frac{e^2}{|r - R_1|} - \frac{e^2}{|r - R_2|} | \phi_1 \rangle = \varepsilon_0 - \langle \phi_1 | \frac{e^2}{|r - R_2|} | \phi_1 \rangle = \varepsilon$$

where ε_0 is the energy of the hydrogen atom ($\varepsilon_0 = -13.6 \text{ eV} = -0.5 \text{ a.u.}$). The physical meaning of the onsite energy H_{11} is the energy of an electron sitting in the orbital ϕ_1 in the presence of the other nuclei (here only the second proton). The Coulomb repulsion between the protons is a constant and omitted here; it will be included again when interested in the total energy of the molecule. The off-diagonal elements

$$H_{21} = H_{12} = \langle \phi_2 | \frac{p^2}{2m} - \frac{e^2}{|r - R_1|} - \frac{e^2}{|r - R_2|} | \phi_1 \rangle = t = \varepsilon_0 S_{12} - \langle \phi_2 | \frac{e^2}{|r - R_1|} | \phi_1 \rangle$$

are called the **hopping integrals** usually denoted by t . They couple the state ϕ_1 to the state ϕ_2 , and thus allow the electron to hop from one atom to one of its neighbors (here only proton number 2). It can also be interpreted as the hopping frequency, i.e. the frequency of the electron jumping from state ϕ_1 to state ϕ_2 . This can be shown by solving the time dependent problem above and show that the probability of the electron being on site 1 is an oscillatory function of time with frequency t/\hbar . The variation of the hopping integral and onsite energy versus distance is displayed in figure 1.1.

Had we not ignored the overlap integral, $S_{12} = S$, we would have to solve a *generalized eigenvalue problem*¹ of the following type:

$$\text{Det} \begin{bmatrix} \varepsilon - \lambda & t - \lambda S \\ t - \lambda S & \varepsilon - \lambda \end{bmatrix} = 0 \text{ diagonalized} \implies \begin{bmatrix} \frac{\varepsilon+t}{1+S} & 0 \\ 0 & \frac{\varepsilon-t}{1-S} \end{bmatrix}$$

¹It is called generalized because the eigenvalue λ is not only present on the diagonal but in the whole matrix. In general matrix eigenvalue equations of the type $\text{Det}(\mathcal{A} - \lambda\mathcal{B}) = 0$ are called generalized eigenvalue problems. The matrix \mathcal{A} needs to be hermitian, and \mathcal{B} must be positive definite.

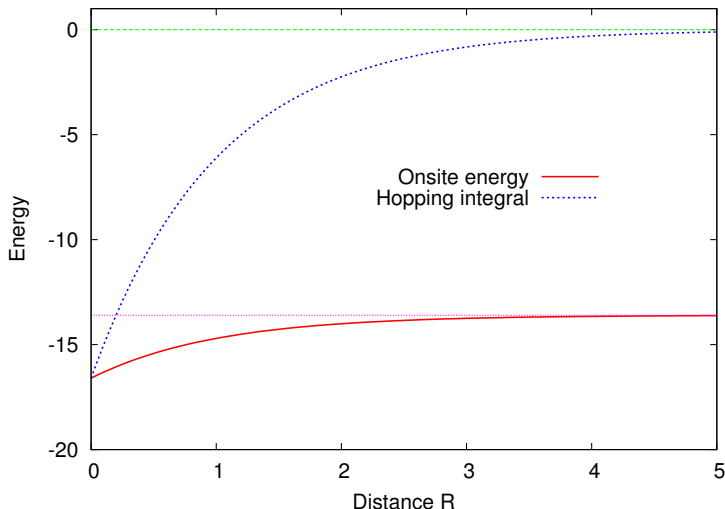


Figure 1.1: Change of hopping and onsite energies as a function of distance between the atoms.

Thus, we can see that the effect of including the overlap integral is to shift the ground state upwards. (Note that t is always negative so that the $+$ sign corresponds to the (ground) **bonding state**, and the $-$ sign is for the (excited) **anti-bonding state**.)

Due to symmetry, one can easily find that the ground state is $|\psi_+\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle + |\phi_2\rangle)$. It is called the bonding state since it is responsible for the bonding of the molecule: the charge density $|\psi_+|^2$ in the middle of the bond is non zero, whereas for the excited state, $|\psi_-\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle - |\phi_2\rangle)$ the charge density $|\psi_-|^2$ is zero at the center of the bond (see figure 1.2).

The binding energy of the molecule is the energy necessary to bring the the hydrogen atom and a proton from infinity to their actual position to form a molecule. It is therefore $E_{\text{Binding}} = \varepsilon + t + \frac{e^2}{|R_1 - R_2|} - (\varepsilon_0 + 0) \simeq t$. At larger distances, the difference $\varepsilon - \varepsilon_0$ cancels out the proton-proton repulsion and only the hopping term, which goes exponentially to zero, remains. At small distances, however, the difference $\varepsilon - \varepsilon_0$ remains finite whereas the proton-proton repulsion goes to infinity. This results in a repulsion between the protons at small distances and an attraction at larger distances. The plot of the total energy can be seen as the upper curve in figure 1.3 labeled by “2 atomic basis”. This figure shows the importance of the choice of the

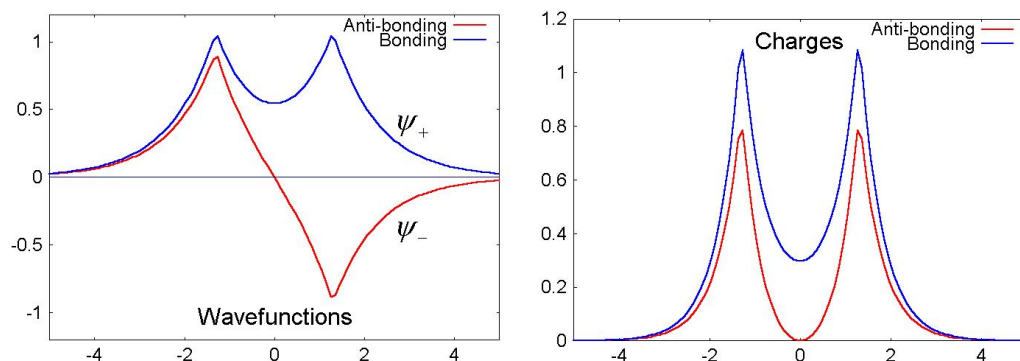


Figure 1.2: The wavefunctions (left) and charge distribution (right) for the bonding and antibonding states of the H_2^+ molecule. The protons are located at ± 1.3 a.u. corresponding to the maxima of the curves.

basis in the total energy calculation of the system. Above, we chose the simplest possible basis functions, namely the eigenstates of the hydrogen atom : $\exp(-r/a_B)$. The denominator a_B , however, can be chosen as a variational parameter. The second curve from the bottom with + signs, which is the best one just above the exact value, was calculated by optimizing the a_B parameter at every distance $R = R_1 - R_2$. This results, as one can see, in the correct inter particle spacing; and more importantly, it also gives the correct curvature of this total energy curve. The curvature, or the second derivative at the equilibrium distance is just the spring constant, in a harmonic approximation, of the H-H bond. And here, we see that in order to obtain the correct spring constant, or equivalently the vibrational frequency, it is very important to optimize the basis functions at every bond length[?]. This is the simplest example of a **covalent bond** where the charge is equally shared between the two atoms.

1.1.1 Mulliken population analysis

Within the atomic basis, the number of electrons on each atom can be found from the coefficients of the expansion of the eigenfunctions on the basis states. In this case, the basis was not really orthogonal. If we call the integral $\langle \phi_1 | \phi_2 \rangle = S$ the **overlap integral**, then the normalization of the bonding state implies: $a_1^2 + a_2^2 + 2a_1a_2S = 1$. The first term can be interpreted as

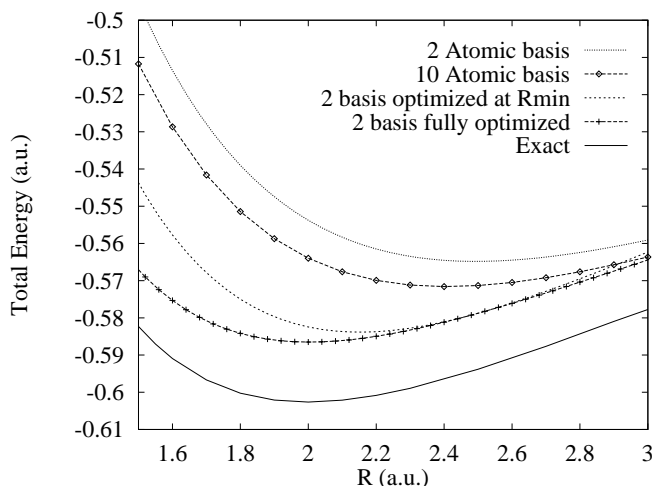


Figure 1.3: The total energies of H_2^+ molecule obtained with several choices of basis functions. Optimizing the basis at every distance (fully optimized: dashed line with + sign) yields the correct bond length ($R = 2$ a.u.) and vibrational frequency when compared to the exact result (lowest solid curve).

the probability, or the fraction of the bonding electron on atom 1, the second term is the probability, or the fraction of the bonding electron on atom 2, and the last term is the probability, or the fraction of the electron on the bond 1-2. Here, by symmetry, we find $a_1 = a_2 = 1/\sqrt{2 + 2S}$. Note that even though this definition is intuitive, the number of electrons on the bond, using this definition, is not necessarily a positive number, and therefore one must be careful about its real meaning. Note also that the obtained results also depend on the chosen basis and the overlap between them. Last, one could also define the fraction of the bonding electron on atom 1 to be $|\langle \phi_1 | \psi_+ \rangle|^2 = |a_1 + a_2 S|^2$. But note that in this case the sum of the fractions on atoms 1 and 2 is not equal to 1 if the basis is non-orthogonal.

1.2 Ionic bonding

If in the previous problem, the two atoms A and B were not identical, then the onsite energies would be different. Hoppings, however will remain equal,

or at the most, complex conjugate to each other, due to the hermiticity of the Hamiltonian. Assume again that the basis is orthonormal and there is no overlap: $S = 0$. The Hamiltonian matrix will have the following form

$$\begin{bmatrix} \varepsilon_A & t \\ t & \varepsilon_B \end{bmatrix} \text{ diagonalized} \implies \begin{bmatrix} E_+ & 0 \\ 0 & E_- \end{bmatrix}$$

and its eigenvalues are defined by:

$$E_{\pm} = \bar{E} \pm \sqrt{\Delta E^2 + |t|^2} \quad (1.1)$$

where $\bar{E} = (\varepsilon_A + \varepsilon_B)/2$, and $\Delta E = (\varepsilon_A - \varepsilon_B)/2$. We see that the eigenvalues are split from the position of the average onsite energy, and the splitting is nearly $|t|$ for a small difference in onsite, or half the difference between the onsite for very different elements or small hoppings. The former limit is called a **covalent** bonding, and the latter, and **ionic** bonding.

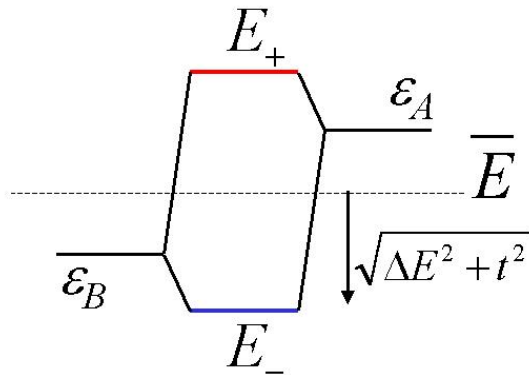


Figure 1.4: The energy diagram of a diatomic molecule.

1.2.1 Eigenvector analysis and charge distribution

The distribution of electrons on different atoms or the bonds can be obtained from the eigenstates of the system. To avoid complications, we assume in the

first place that there is no overlap. The eigenvectors of the above matrix can be put as the column vectors of a unitary matrix which is in fact the matrix taking us from the atomic basis to the eigenvectors basis: $H = U^\dagger H_{\text{Diagonal}} U$ and we have

$$U = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \quad (1.2)$$

where $\tan 2\theta = t/\Delta E = 1/x$ (assuming $\varepsilon_A > \varepsilon_B$, $\Delta E > 0$ and $x < 0$). For an electron in the ground state E_- , the probability of finding the electron on atom A is $p_A = \dots$, and the probability of it being on atom B is $p_B = 1 - p_A = \dots$. We see that in the limit of large x , $p_B \simeq 1$ and $p_A \simeq 0$, the ground state electron is almost on atom B : this is the ionic limit where there is a large charge transfer to the atom with highest electronegativity. The lower the atomic energy level of an atom, the higher the probability of it attracting an electron and thus, the higher its electronegativity.

$x = 0$ or $t \gg \Delta E$ is called the covalent limit where the electron is equally shared between the two atoms $p_A = p_B = 1/2$. The same calculations can be performed for a non orthogonal basis $\langle \phi_A | \phi_B \rangle = S_{AB} \neq 0$. The conclusions are qualitatively the same. The effect of having an overlap is to displace the energy levels to a slightly higher value.

You can see that for He_2 the result is the same except that there are 4 electrons and therefore both bonding and antibonding levels are filled and there is very little binding if any, so that He stays in the atomic state and not molecular at least at non zero temperatures. Strictly at zero temperature, however, one expects to have binding of two He atoms due to longer range Van der Waals interactions.

1.3 The general case: LCAO method

The general problem of a many atom-many orbital molecule can be solved by using the same variational method:

$$\psi(r) = \sum_i a_i \phi_i(r)$$

Minimizing the energy along with the normalization constraint leads to the following set of equations:

$$\frac{\partial}{\partial a_l^*} \sum_{i,j} (a_i^* a_j \langle \phi_i | H | \phi_j \rangle - E a_i^* a_j \langle \phi_i | \phi_j \rangle) = 0$$

This is nothing but a **generalized eigenvalue problem** completely equivalent to projecting the Schrodinger equation on the basis ϕ_i . We finally have to solve the following generalized eigenvalue equation for E :

$$\det(H_{ij} - ES_{ij}) = 0$$

where H_{ij} are the matrix elements of the Hamiltonian operator in the basis defined by ϕ_i and S_{ij} is the **overlap matrix**. This variational method used to find the eigenvalues and eigenstates of a given Hamiltonian by choosing a **localized basis set** is called the **LCAO** or Linear Combination of Atomic Orbitals method, also called **Tight Binding** by most physicists.

1.4 Other types of bonding in materials

Covalent and ionic bonding are present in semiconductors mostly. The strength of these bonds is of the order of a few eV per bond. Electrons are mostly localized on atoms and bonds between them.

1.4.1 Metallic bonding

Other types of bonding exist as well. The most important of them being the metallic bonding where the electronic cloud is delocalized and fills out all the space. This cloud is of course formed of only the valence electrons of the metallic atoms. The electronic charge density is almost uniform and screening is very efficient in this case. The total potential (electron-ion + electron-electron) is therefore weak or almost constant and the plane wave (free particle) description can be reasonable to leading order. Metallic bonding exists in alkaline atoms (first column of the periodic table) such as Sodium (Na) or Potassium (K) which have an extended 3s or 4s state hybridizing with its nearest atoms. It also exists in transition metals such as Fe, Ni, Cu, Ag, Au, etc... These elements have a partially filled localized 3d or 4d state in addition to their extended 4s or 5s state which serves to fillup the space. The bandwidth of the s states is quite large of the order of tens of eV due to the large overlap of these states yielding a large value for the hopping integral. The bandwidth, as will be shown in the exercises, is proportional to the hopping integrals.

Metallic bonding is also present in the p-elements such as Al which has a partially (half-)filled 3p shell. Most metallic compounds have a close-packed

structure such as FCC, BCC or HCP, whereas semiconductors or insulators have a lower coordination number and void spaces where the electron density is almost zero.

The strength of metallic bond is also of the order of a few eV.

1.4.2 Van der Waals bonding

A weaker type of bond is called Van der Waals (VdW). It is due to the attraction between induced dipoles. In the case of a molecule formed of two atoms which have a zero permanent dipole moment each, the fluctuations of the instantaneous dipole moments create fields which interact with the dipole of the other atom: $E_{\text{VanderWaals}} \propto -\vec{p}_1 \cdot \vec{E}_2$ but the dipole moment of atom 1 is itself induced by the field due to atom 2: $\vec{p}_1 = \alpha \vec{E}_2$, \vec{E}_2 being the field created by atom 2 at the position of atom 1, is proportional to the inverse of the cubed distance between the two atoms: $E_2 = \beta p_2 / R_{12}^3$, so that the instantaneous interaction energy becomes $E_{\text{VanderWaals}} = -\frac{1}{2} \alpha \cdot E_2^2 = -\frac{1}{2} \alpha \beta^2 p_2^2 / R_{12}^6$. Although the dipole moment has zero average, the average of its square is not zero, and this leads to an induced dipole interaction inversely proportional to the 6th power of the distance between the atoms. For two chains, or an atom and a plane, the VdW interaction becomes inversely proportional to the 4th power of the distance; and for two planes, it becomes inversely proportional to the 2nd power of the distance. It is therefore a long-ranged interaction although weak, and is often modeled with a 6-12 Lennard-Jones type of function. The strength of this interaction is typically of the order of or less than 0.1 eV and it is mostly present between atoms or molecules with filled shells (rare gas elements) so that no chemical (covalent or ionic) bond can be formed between them. Other typical examples are VdW interaction between two rare gas atoms, two fullerenes, two carbon nanotubes or two graphene layers.

In the Lennard-Jones potential, the short-range repulsive part (which is empirically proposed to be of the form $1/r^{12}$) is due to the overlap of the electronic clouds of the two species. This overlap causes the levels to be shifted up in the energy, and when they are filled up, the resulting total energy becomes very large, strongly increasing with overlap and thus decreasing with interatomic distance. Another way of looking at this is the increase in the electronic kinetic energy as atoms come closer to each other. In this case, the volume per electron becomes smaller, and due to this confinement, the kinetic energy, which is like $\hbar^2/2ma^2$, where a is the size of the confinement,

increases drastically. As a result, electronic energy levels will be shifted upwards.

The binding energy of VdW potentials is a fraction of 0.1 eV.

1.4.3 Hydrogen bonding

Yet a fifth type of bonding can exist between two atoms separated by a proton. It is thus called the hydrogen bond. It exists in many organic molecules: it is responsible for the stability of DNA by keeping the two strands bound together. It is also responsible for the stability of ice where a single hydrogen attached to an oxygen atom is also attracted by another oxygen belonging to another water molecule. It is, however, not only electrostatic in origin. The proton sees actually a double well, and thus has the capability of hopping from one oxygen to the other and keep them together just like the electron in the H_2^+ molecule was hopping from one proton to the other and kept the system bound together due to its hopping integral. Only the charges are inversed in this case and the proton is 2000 times heavier than the electron. So one expects its hopping integral to be much smaller due to a strongly reduced kinetic energy. The strength of the hydrogen bond is indeed weak, of the order of a few tenths of an eV.

1.5 Total energy and Cohesion in the one electron picture

The **binding**, in the case of molecules, or the **cohesive** energy, in the case of solids of a system is defined as minus the difference between its total energy, and the sum of the energies of its constituents or atoms. It tells us therefore how much energy is gained in bringing these atoms together to form a molecule or solid, and is positive by construction. This is, for large enough systems, an extensive quantity (proportional to the number of atoms forming the system). One usually uses the binding or cohesive energy per atom to describe how strong the bonding in a given system is. For comparison of stabilities between two molecules, however, one uses the total (binding or cohesive) energy itself. Typical cohesive energies for different systems are given in the table 1.1 below.

As we saw in the case of the H_2^+ molecule, the negative hopping integral t was responsible for the bonding between the two protons. Except for the

System	Si	GaAs	Al	NaCl	Ne	Ice
Structure	Diamond	FCC	FCC	FCC	FCC	Hex (for O)
Bonding	covalent	polar	metallic	ionic	VdW	hydrogen
$\mathcal{E}_{\text{cohesive}}/\mathcal{N}$ (eV)	4.64	6.7	3.34	8.18	0.02	0.58

Table 1.1: Cohesive energies for several structures with different types of bonding. In cases where a pair of atom is involved in the unit cell, \mathcal{N} refers to the number of pairs. A distinction was made between polar and ionic to emphasize that in polar bonds charge transfer is partial, whereas it can be near one for ionic bonds as in salts.

Van der Waals interaction, other types of bonding can be described in similar terms, and in all of them, the cohesion comes from the hopping term which is always negative and dominant at large distances. When atoms are squeezed together, however, the overlap between the electronic clouds takes over. As we saw, the overlap matrix raised the bonding state to higher energies. Due to Pauli principle, we have to fill up each state by two electrons at the most, so that when all the filled levels are moved up in energy, their sum which forms the total energy is much increased. This, as explained before is the reason for the short-range repulsive part of the pair interaction between atoms.

An important term in the one electron Hamiltonian which we did not discuss is the Coulomb repulsion between the electrons. This term is large in magnitude and should be added to the electron-ion interaction which has the opposite sign. When considering the hopping integral, we also include this term in the one electron Hamiltonian. Neglecting quantum effects such as exchange and correlation for the moment, the hopping integral is defined as

$$t_{12} = \langle \phi_2 | H | \phi_1 \rangle = \langle \phi_2 | \frac{p^2}{2m} + \int dr \frac{\rho(r')}{|r - r'|} - \sum_i \frac{Z_i e^2}{|r - R_i|} | \phi_1 \rangle$$

and within the two-center approximation, one usually drops the contribution of atoms other than 1 and 2, and the electrons localized on them. The total energy of a molecule is obtained by diagonalizing its Hamiltonian and filling up each of the states (from the bottom) by two opposite-spin electrons. The sum of the energies of the filled states gives the one-electron contribution to the total energy. It is also called the **band energy**. This energy must be corrected since it includes twice the Coulomb repulsion between the electrons. Therefore from it, one must subtract the Coulomb repulsion between the electrons, and if included, the exchange and correlation interaction between

the electrons which are also Coulombic in nature. For more details on these terms, please refer to the chapters on the Hartree-Fock and the Density Functional Theory.