Chapter 10

From molecules to solids

In the previous section, we studied the quantum mechanics of multi-electron – the subject of atomic physics. In this section, we will begin to explore how these concepts get translated into systems with many atoms, from simple molecular structures to the solid state. As with atomic physics, the subjects of molecular and solid state physics represent fields in their own right and it would fanciful to imagine that we could do more than touch on the basic principles. Nevertheless, in establishing the foundations of these subjects, we will see two things: firstly, by organising the heirarchy of approximation schemes, much be can be understood about the seemingly complex quantum dynamics of many-particle systems. Secondly, we will find that constraints imposed by symmetries (such as translation) allow a simple phenomenology to emerge from complex solid state systems. We begin our discussion with the molecular system.

A molecule consists of electrons moving in the complicated potential set up by all the constituent electric charges. Even in classical mechanics, it would be extremely difficult to solve the equations of motion of the internal molecular degrees of freedom. Fortunately, for most purposes, we can treat the motion of the electrons and nuclei separately, due to their very different masses. As the forces on a nucleus are similar in magnitude to those that act on an electron, so the electrons and nuclei must have comparable momenta. Therefore the nuclei are typically moving much more slowly than the electrons. In studying the motion of the electrons, we can therefore treat the nuclei as being "nailed down" in fixed positions. Conversely, in studying the nuclear motion (vibrations and rotations of the molecule) we can assume, as a first approximation, that the electrons adjust instantly to changes in the *molecular conformation* defined by the positions of the nuclei. This picture forms the basis of the **Born-Oppenheimer approximation**.

In quantum mechanics, the wavefunction of a molecule, $\Psi(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$, is a function of the positions of all the electrons and nuclei, and the Hamiltonian has the form

$$\hat{H} = \sum_{n} \frac{\hat{\mathbf{p}}_{n}^{2}}{2m_{e}} + \sum_{N} \frac{\hat{\mathbf{p}}_{N}^{2}}{2m_{N}} + V(\{\mathbf{r}_{n}\}, \{\mathbf{R}_{N}\}),$$

where, as usual, the momentum operators, $\hat{\mathbf{p}}_n$ and $\hat{\mathbf{p}}_N$, act only on the corresponding coordinates. Here we have labelled electrons by lower case letters $n = 1, 2, \cdots$ to distinguish them from nuclei which are denoted by capitals, $N = a, b, \cdots$. The statement that the electrons and nuclei have comparable momenta translates into the fact that $\nabla_n^2 \Psi$ and $\nabla_N^2 \Psi$ will be comparable. Therefore the second term in the Hamiltonian above, the sum over nuclear

J. Robert Oppenheimer 1904-1967

An American theoretical physicist best known for his role as the scientific director of the Manhattan Project: the World War II effort to develop



the first nuclear weapons at los Alamos National Laboratory In reference to the Trinity test in New Mexico, where his Los Alamos team first tested the bomb, Oppenheimer famously recalled the Bhagavad Gita: "If the radiance of a thousand suns were to burst at once into the sky, that would be like the splendor of the mighty one." and "Now I am become Death, the destroyer of worlds." As a scientist, Oppenheimer is remembered most for being the chief founder of the American school of theoretical physics while at the University of California, Berkeley. As director of the Institute for Advanced Study he held Einstein's old position of Senior Professor of Theoretical Physics. Oppenheimer's notable achievements in physics include the Born-Oppenheimer approximation, work on electron-positron theory, the Oppenheimer-Phillips process, quantum tunneling, special relativity, quantum mechanics, quantum field theory, black holes, and cosmic rays.

kinetic energies, can be neglected as a first approximation when we solve for the dependence of Ψ on the electron position vectors $\{\mathbf{r}_n\}$.

In the Born-Oppenheimer approximation, the time-independent Schrödinger equation for the electronic motion is therefore given by

$$\left[-\sum_{n} \frac{\hbar^2 \nabla_n^2}{2m_e} + V(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}) \right] \psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}) = E_k(\{\mathbf{R}_N\}) \psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}),$$

where the eigenfunctions ψ_k , with $k = 0, 1, 2, \cdots$, describe the electronic ground state and excited states with the nuclei nailed down at positions $\mathbf{R}_a, \mathbf{R}_b, \ldots$; E_k are the corresponding energy levels. Notice that the nuclear positions appear as parameters in ψ_k and E_k . As the molecular conformation is varied by changing $\mathbf{R}_a, \mathbf{R}_b, \ldots$, the ground state energy E_0 follows a curve called the molecular potential energy curve and the minimum of this curve defines the equilibrium conformation of the molecule. We shall discuss later how the molecular potential energy curve can be used to predict the vibrational and rotational energy levels of the molecule when we go beyond the approximation that the nuclei are nailed down.

10.1 The H_2^+ ion

The simplest system that exhibits molecular properties is the hydrogen ion H_2^+ , which consists of two protons with positions $\mathbf{R}_a, \mathbf{R}_b$ and one electron at **r**. With the potential energy

$$V(\mathbf{r}, \mathbf{R}_a, \mathbf{R}_b) = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|\mathbf{R}_a - \mathbf{R}_b|} - \frac{1}{|\mathbf{r} - \mathbf{R}_a|} - \frac{1}{|\mathbf{r} - \mathbf{R}_b|} \right)$$

the Schrödinger equation takes the form,

$$\left[-\frac{\hbar^2 \nabla_r^2}{2m_e} + V(\mathbf{r}, \mathbf{R}_a, \mathbf{R}_b)\right] \psi(\mathbf{r}; \mathbf{R}_a, \mathbf{R}_b) = E\psi(\mathbf{r}; \mathbf{R}_a, \mathbf{R}_b) \,.$$

Although this equation can actually be solved exactly using elliptical polar coordinates, it will be more instructive for our purposes to seek an approximate method of solution. Since there is no obvious parameter in which to develop a perturbative expansion, we will instead follow a variational route to explore the low energy states of system.

If the electron is close to one of the protons, one would expect the other proton to have a small influence on its dynamics, and that the wavefunction in this region would be close to that of a hydrogen atomic orbital. Therefore, in seeking the ground state of the H_2^+ ion, we may take a trial wavefunction that is a linear combination of the ground state (1s) wavefunctions centred on the two protons,

$$\psi(\mathbf{r};\mathbf{R}_a,\mathbf{R}_b) = \alpha\psi_a(\mathbf{r};\mathbf{R}_a) + \beta\psi_b(\mathbf{r};\mathbf{R}_b),$$

where $\psi_{a,b} = (\pi a_0^3)^{-1/2} \exp[-|\mathbf{r} - \mathbf{R}_{a,b}|/a_0]$, represents the corresponding hydrogenic wavefunction with a_0 the atomic Bohr radius. In this case, the coefficients α and β can be taken as real. The variational expression to be minimized in order to estimate the ground state energy is given by

$$\langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\alpha^2 H_{aa} + \beta^2 H_{bb} + 2\alpha\beta H_{ab}}{\alpha^2 + \beta^2 + 2\alpha\beta S}$$



where $H_{aa} = \langle \psi_a | \hat{H} | \psi_a \rangle = H_{bb} = \langle \psi_b | \hat{H} | \psi_b \rangle$, and $H_{ab} = \langle \psi_a | \hat{H} | \psi_b \rangle = \langle \psi_b | \hat{H} | \psi_a \rangle$. Note that the matrix elements $H_{aa} = H_{bb}$ because \hat{H} is symmetric with respect to \mathbf{R}_a and \mathbf{R}_b . Moreover, since ψ_a and ψ_b are not orthogonal we have to introduce the **overlap integral**, $S = \langle \psi_a | \psi_b \rangle$, which measures the overlap between the two atomic wavefunctions. In fact we can simplify this expression further, because the potential is symmetric about the mid-point between the two protons. The wavefunction must therefore be either symmetric or antisymmetric, $\alpha = \pm \beta$, and hence,

$$E_0 \le \langle E \rangle = \frac{H_{aa} \pm H_{ab}}{1 \pm S}$$

The matrix elements in this expression can be evaluated in closed form, though the calculation is rather tedious. $^{\rm 1}$

We have, therefore, found two possible wavefunctions for the H_2^+ ion,

$$\psi_g = \frac{\psi_a + \psi_b}{\sqrt{2(1+S)}}, \qquad \psi_u = \frac{\psi_a - \psi_b}{\sqrt{2(1-S)}}$$

with energies $E_g = \frac{H_{aa}+H_{ab}}{1+S}$, $E_u = \frac{H_{aa}-H_{ab}}{1-S}$. The subscript g refers to the term gerade (German for even) used in molecular physics to denote a state that is even under the operation of inverting the electronic wavefunction through the centre of symmetry of the molecule, without changing the positions of the nuclei. Such an inversion changes $\mathbf{r} \to \mathbf{R}_a + \mathbf{R}_b - \mathbf{r}$, which interchanges ψ_a and ψ_b . Note that this is not the same as parity inversion, which would also affect the nuclear coordinates. The ungerade (odd) state is denoted by subscript u. Note that ψ_g and ψ_u are orthogonal, even though ψ_a and ψ_b are not. In fact, ψ_g and ψ_u are just the orthonormal states that diagonalize the Hamiltonian, if we limit ourselves to linear combinations of ψ_a and ψ_b . In chemistry, ψ_g and ψ_u are called **molecular orbitals** and the assumption that they are linear combinations of atomic stationary states is called the **linear combination** of atomic orbitals (LCAO) approximation.

The state ψ_g has the lower energy, while ψ_u represents an excited state of the molecular ion. Physically, the reason for this is that, in the ψ_g state, the two atomic wavefunctions interfere constructively in the region between the protons, giving an enhanced electron density in the region where the electron is attracted strongly by both protons, which serves to screen the two protons from each other. Conversely, in ψ_u we have destructive interference in the region between the protons. If we plot E_g and E_u as functions of the nuclear separation $R = |\mathbf{R}_a - \mathbf{R}_b|$, the results are as shown in the figure right. For both curves, we have plotted E + Ry since -Ry is the ground state energy of the hydrogen *atom*. The curve of $E_g + \text{Ry}$ in the LCAO approximation has a minimum value of -1.8eV at $R = R_0 = 130\text{pm}$, which is the predicted equilibrium nuclear separation. The predicted energy required to dissociate the molecular ion into a hydrogen atom and a free proton is thus 1.8eV. The curve of $E_u + \text{Ry}$ does not have a minimum, suggesting that the odd wavefunction ψ_u does not correspond to a bound molecular state.



Molecular potential energy curves for H_2^+ ion.

$$S = \left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right) e^{-R/a_0}, \qquad H_{aa} = -\operatorname{Ry} + \frac{e^2}{4\pi\epsilon_0 R} \left(1 + \frac{R}{a_0}\right) e^{-2R/a_0}$$
$$H_{ab} = \frac{e^2}{4\pi\epsilon_0 a_0} \left(1 + \frac{R}{a_0}\right) e^{-R/a_0} + S\left(-\operatorname{Ry} + \frac{e^2}{4\pi\epsilon_0 R}\right),$$

where $R = |\mathbf{R}_a - \mathbf{R}_b|$ and Ry is the Rydberg constant, the binding energy of the Hydrogen atom in its ground state.

¹We simply quote the results here:

As the variational method provides an upper limit on the ground state energy, it is no surprise that the true molecular potential energy curve (shown dotted) lies below the LCAO one. The true values of the equilibrium separation and dissociation energy are 106pm and 2.8eV respectively. Clearly the LCAO wavefunction ψ_g is not a very accurate approximation to the true ground state. We could improve it by introducing further variational parameters or additional atomic orbitals. For example, when R becomes very small the true wavefunction should approach that of a He⁺ ion; we could include such a term in the trial function. We could also include an **effective charge parameter** in ψ_a and ψ_b , which is equivalent to replacing the Bohr radius a_0 by a free parameter.

Although not very reliable quantitatively, the LCAO wavefunction ψ_g does however exhibit a number of important features of the true ground state: (i) it is even (g) with respect to inversion of the electron wavefunction; (ii) there is constructive interference which leads to an enhanced probability of finding the electron in the region between the two nuclei. These features will be important when we come to discuss **bonding**. Since the odd *u*-states are orthogonal to the even *g*-states, and the true ground state is a *g*-state, the curve of E_u actually represents an upper limit on the energy of the lowest *u*-state. Thus the fact that the curve has no minimum does not really prove that there are no bound *u*-states; but this does turn out to be the case. The LCAO wavefunction ψ_u shows the characteristic feature of an **anti-bonding** state: there is destructive interference in the region between the two nuclei, so that the electron is actually forced out of the region of overlap of the two atomic wavefunctions.

▷ INFO. At this stage, it is helpful to introduce some notation to label the molecular orbitals. Although the wavefunctions $\psi_{g,u}$ that we have been discussing are formed in the LCAO approximation from linear combinations of atomic 1s $(n = 1, \ell = 0)$ states, with no orbital angular momentum, they do not themselves necessarily have zero orbital angular momentum. An $\ell = 0$ state must be proportional to Y_{00} , i.e., it must have no dependence on θ and ϕ , giving an isotropic probability distribution. But these states are certainly not isotropic: they have a 'dumbbell' shape, concentrated around the two protons. They do not have unique electronic orbital angular momentum because the operator $\hat{\mathbf{L}}^2$ for the electron does not commute with the Hamiltonian on account of the non-central terms $1/|\mathbf{r} - \mathbf{R}_a|$ and $1/|\mathbf{r} - \mathbf{R}_b|$ in the potential.

The only component of \mathbf{L} that does commute with these terms is L_z , provided we choose the z-axis parallel to the internuclear axis $\mathbf{R}_a - \mathbf{R}_b$. Therefore instead of classifying the states as s, p, d, \ldots orbitals according to whether $\ell = 0, 1, 2, \ldots$, we call them $\sigma, \pi, \delta, \ldots$ orbitals according to whether $\Lambda = 0, 1, 2, \ldots$, where $\Lambda \equiv |m_\ell|$. A subscript u or g denotes whether the state is even or odd under inversion; this notation can be applied to all *homonuclear* diatomic molecules, in which the potential is symmetric about the median plane of the molecule. Thus the ground state of the hydrogen molecular ion is σ_g and the corresponding odd state is σ_u^* , where the star signifies an antibonding orbital. In the LCAO approximation used above, these molecular orbitals are linear combinations of 1s atomic orbitals and so they can be written as $1s\sigma_g$ and $1s\sigma_u^*$. To get some insight into how this denotation applies, it is helpful to refer to the figures on the right.



Approximation	B.E./eV	R_0/pm
Experiment	4.75	74.1
MO fixed charge	2.70	85.2
MO variable charge	3.49	73.0
VB variable charge	3.78	74.6
Variable λ and charge	4.03	75.7
13 variable parameters	4.72	74.1

Table 10.1: Binding energy and equilibrium nuclear separation of the hydrogen molecule in various approximations.

10.2 The H_2 Molecule

We now turn to consider the hydrogen molecule. One might imagine that this would be a trivial extension of the H_2^+ ion, but in fact several new features arise when we consider this simple molecule. For two electrons with positions $\mathbf{r}_{1,2}$ and two protons at $\mathbf{R}_{a,b}$, in the Born-Oppenheimer approximation, the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m_e} \left(\nabla_{r_1}^2 + \nabla_{r_2}^2 \right) + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} \right] \,,$$

where $r_{1b} = |\mathbf{r}_1 - \mathbf{R}_b|$, etc. This is just the sum of two Hamiltonians for \mathbf{H}_2^+ ions, plus the additional term $\frac{e^2}{4\pi\epsilon_0}(\frac{1}{r_{12}} - \frac{1}{r_{ab}})$. It is plausible that the expectation values of $1/r_{12}$ and $1/r_{ab}$ will be comparable and therefore the extra term can be treated as a perturbation. Thus, as a first approximation we neglect it and assign each electron to one of the \mathbf{H}_2^+ molecular orbitals defined above. There are four ways of filling the two orbitals σ_g and σ_u^* , which we can represent by

$$\psi_q(\mathbf{r}_1)\psi_q(\mathbf{r}_2), \quad \psi_q(\mathbf{r}_1)\psi_u^*(\mathbf{r}_2), \quad \psi_u^*(\mathbf{r}_1)\psi_q(\mathbf{r}_2), \quad \psi_u^*(\mathbf{r}_1)\psi_u^*(\mathbf{r}_2).$$

Of these, we would expect the first to be the ground state.

However, at this stage, we have given no consideration to the constraints imposed by particle statistics. In fact, since the electrons are identical fermions, the wavefunction must be antisymmetric with respect to their interchange. Taking into account the spin degree of freedom, for both electrons to occupy the bonding σ_g molecular orbital, they must must have opposite spins and occupy the singlet spin state, $X_{0,0} = \frac{1}{\sqrt{2}}(\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2))$.

If we calculate the energy of the state $\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2)X_{0,0}$ as a function of the nuclear separation R, the minimum ground state energy occurs at $R_0 = 85$ pm and corresponds to a binding energy of 2.7eV. The true molecule is smaller and more tightly bound. Allowing for more variation in the atomic orbitals, in the form of a variable effective charge, gives an equilibrium value of R_0 much closer to experiment, but a binding energy that is still not high enough (see Table 10.2). The reason is that the σ_g^2 configuration alone is not a very good representation of the ground state. To understand why, consider the following.

If we multiply out the spatial part of the σ_g^2 wavefunction in the LCAO approximation, we see that it has a rather strange form,

$$\psi_{g}(\mathbf{r}_{1})\psi_{g}(\mathbf{r}_{2}) \propto \left[\psi_{a}(\mathbf{r}_{1})\psi_{b}(\mathbf{r}_{2}) + \psi_{b}(\mathbf{r}_{1})\psi_{a}(\mathbf{r}_{2})\right] + \left[\psi_{a}(\mathbf{r}_{1})\psi_{a}(\mathbf{r}_{2}) + \psi_{b}(\mathbf{r}_{1})\psi_{b}(\mathbf{r}_{2})\right].$$

The terms in the first square bracket correspond to the two electrons being shared between the two hydrogen atoms. This is the **covalent bonding** picture of the bound state. In the other square bracket, however, both electrons are assigned to the same atom, corresponding to **ionic bonding**. Since all the terms have equal coefficients, the ionic and covalent contributions are equal, which seems rather constraining, if not implausible. For example, it means that, when the two protons are pulled apart, the system is just as likely to be found to consist of an H^+ and an H^- ion as two neutral atoms.

If we go to the pure **valence bonding** (VB) approximation and drop the ionic part of the wavefunction altogether, we find that the predicted binding energy and nuclear separation are both improved (see Table 10.2). Including a small parameter λ for the amplitude of the ionic component, i.e., taking

$$\psi^{VB} \propto \left[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)\right] + \lambda\left[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_b(\mathbf{r}_2)\right],$$

we find that the variational method gives an optimal value of λ of about 1/6, meaning only about a 3% probability of finding the ionic configuration. Still, even with this refinement, the agreement with experiment is far from perfect. However, this doesn't that mean quantum mechanics is failing; by taking enough free parameters in the trial function an excellent result can be obtained, as shown in the Table.

 \triangleright INFO. As mentioned above, there are four possible ways of putting two electrons into the $1s\sigma_g$ and $1s\sigma_u^*$ molecular orbitals. From these four two-electron states we can make three states that are symmetric under interchange of the positions of the electrons, all of which need to be combined with the antisymmetric spin state $X_{0,0}$,

In addition we can make a triplet of states from an antisymmetric spatial wavefunction and the symmetric triplet spin states X_{1,m_S} ($m_S = 0, \pm 1$),

$${}^{3}\Sigma_{u} : X_{1,m_{S}}[\sigma_{g}(\mathbf{r}_{1})\sigma_{u}^{*}(\mathbf{r}_{2}) - \sigma_{u}^{*}(\mathbf{r}_{1})\sigma_{g}(\mathbf{r}_{2})]/\sqrt{2}$$
 .

We have introduced to the left of these equations a new notation, called the **molecular term**, to describe the overall quantum numbers of the molecule, all of which must be good quantum numbers because they correspond to operators which commute with the molecular Hamiltonian. It derives from a historic spectroscopic notation used in atomic physics. The term is written ${}^{2S+1}\Lambda_{u/g}$. The prefix 2S + 1 denotes the multiplicity of the total spin state of the electrons, hence 1 for a singlet and 3 for a triplet state. The central greek capital letter represents the magnitude of the total \hat{L}_z quantum number, $\Lambda = 0, 1, 2...$ being represented by $\Sigma, \Pi, \Delta...$ In the case of the molecular orbitals above based on the 1s atomic orbitals, all the wavefunctions clearly have zero orbital angular momentum about the internuclear axis and hence they are all Σ states. The g or u suffix means even or odd under inversion, and is only meaningful for homonuclear molecules. Notice that since $(\pm 1)^2 = +1$ we get a g-state by combining two g or two u-states, and a u-state by combining a g and a u-state.

In terms of the molecular orbital approach, the VB approximation implies that the ground state is not simply the σ_g^2 configuration but rather a mixture of the two ${}^{1}\Sigma_g$ states,

$$\psi^{VB} \propto (1+\lambda)(1+S)\sigma_q(\mathbf{r}_1)\sigma_q(\mathbf{r}_2) - (1-\lambda)(1-S)\sigma_u^*(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_2).$$

Thus there is **configuration mixing** in the hydrogen molecule. The two states can mix because they have the same overall quantum numbers. At large nuclear separations the energy eigenstates are clearly separated into those that are almost a pair of neutral atoms and those consisting of an H⁺ and an H⁻ ion. In the case of the *u*-states, we can see by expanding the spatial wave functions that ${}^{3}\Sigma_{u}$ is of the former type and ${}^{1}\Sigma_{u}$ of the latter. Since these configurations have different resultant



Molecular potential energy and configuration mixing in H_2 .

electron spins they do not mix significantly (just like singlet and triplet states of atomic helium). Also the u- and g-states are prevented from mixing by their different inversion symmetry. However, the two ${}^{1}\Sigma_{g}$ configurations have the same electron spin and symmetry and can mix to give the above covalent-bonded ground state and an orthogonal excited state that is more ionic.

10.3 From molecules to solids

With these basic principles in hand, we could go on to discuss the orbital and electronic structure of more complicated molecules. In doing so, we would sink deeper into the realm of quantum chemistry. Instead, we will use these simple ideas of molecular bonding to develop a surprisingly versatile and faithful description of the ordered solid state. With *ca.* 10^{23} nuclei and electrons now involved such an enterprise seems foolhardy. However, we will see that, by exploiting symmetries, we can capture many of the basic principles of the solid state.

Let us then consider the electronic structure of an ordered crystalline array of equivalent atoms. (The consideration of more complicated periodic structures would not present conceptual challenges, but would bring unnecessary complications to the discussion.) Once again, we can draw upon the Born-Oppenheimer approximation and focus solely on the motion of electrons around an otherwise ordered array of nuclei. Even then, we are confronted with a many-particle Hamiltonian of apparantly great complexity,

$$\hat{H} = -\sum_n \frac{\hbar^2 \nabla_n^2}{2m_e} - \sum_{n,N} \frac{e^2}{4\pi\epsilon_0} \frac{Ze^2}{r_{nN}} + \sum_{m,n} \frac{e^2}{4\pi\epsilon_0} \frac{e^2}{r_{mn}}$$

Here the second term represents the interaction of the electrons with the consituent nuclei, and the third term involves the electron-electron interaction. In a physical system, we would have to take into account the influence of further relativistic corrections which would introducte additional spin-orbit couplings.

To address the properties of such a complex interacting system, we will have to draw upon many of the insights developed previously. To begin, it is helpful to partition the electrons into those which are bound to the core and those which are able to escape the potential of the individual atomic nuclei and propagate "freely" through the lattice. The electrons which are tightly bound to the nuclei screen the nuclear charge leading to a modified nuclear potential, $V_{\text{eff}}(\mathbf{r})$. Focussing on those electrons which are free, the effective Hamiltonian can be written as, $\hat{H} \simeq \sum_n \hat{H}_n + \sum_{m,n} \frac{e^2}{4\pi\epsilon_0} \frac{e^2}{r_{mn}}$, where

$$\hat{H}_n = -\frac{\hbar^2 \nabla_n^2}{2m_e} + V_{\text{eff}}(\mathbf{r}_n)$$

represents the single-particle Hamiltonian experienced by each of the electrons – i.e. \hat{H}_n describes the motion of an electron moving in a periodic lattice potential, $V_{\text{eff}}(\mathbf{r}) = V_{\text{eff}}(\mathbf{r} + \mathbf{R})$ with \mathbf{R} belonging to the set of periodic lattice vectors.

Despite engineering this approximation, we are still confronted by a challenging many-particle problem. Firstly, the problem remains coupled through the electron-electron Coulomb interaction. Secondly, the electrons move in a periodic potential. However, if we assume that the electrons remain mobile – the jargon is **itinerant**, free to propagate through the lattice, they screen each other and diminish the effect of the Coulomb interaction. Therefore, we can proceed by neglecting the Coulomb interaction altogether, when the Hamiltonian is said to be free. Of course, we still have to contend with the constraints placed by Pauli exclusion and wavefunction antisymmetry. But we are now in the realm of the molecular orbital theory, and can proceed analogously using the variational LCAO approach.

In particular, we can building a trial wavefunction by combining orbital states of the single ion, $V_{\text{ion}}(\mathbf{r})$, where $V_{\text{eff}}(\mathbf{r}) = \sum_{\mathbf{R}} V_{\text{ion}}(\mathbf{r} - \mathbf{R})$. As with the hydrogen molecule, the Hamiltonian for the individual nuclei, $\hat{H}_0 = \frac{\hbar^2 \nabla^2}{2m_e} + V_{\text{ion}}(\mathbf{r})$ are associated with a set of atomic orbitals, ψ_q , characterized by a set of quantum numbers, q. In the **atomic limit**, when the atoms are far-separated, these will mirror the simple hydrogenic states. To find the variational ground state of the system, we can then build a trial state from a linear combination of these atomic orbitals. Taking only the lowest orbital, q = 0, into account we have,

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} \alpha_{\mathbf{R}} \psi(\mathbf{r} - \mathbf{R}) \,,$$

where, as before, $\alpha_{\mathbf{R}}$ represent the set of variational coefficients, one for each site (and, in principle, each atomic orbital if we had taken more than one!).

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Once again, we can construct the variational state energy,

$$E = \frac{\langle \psi | \hat{H}_0 | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\sum_{\mathbf{R}, \mathbf{R}'} \alpha_{\mathbf{R}}^* H_{\mathbf{R}\mathbf{R}'} \alpha_{\mathbf{R}'}}{\sum_{\mathbf{R}, \mathbf{R}'} \alpha_{\mathbf{R}}^* S_{\mathbf{R}\mathbf{R}'} \alpha_{\mathbf{R}'}}$$

where, as before, $H_{\mathbf{R}\mathbf{R}'} = \int d^d r \psi^*(\mathbf{r} - \mathbf{R}) \hat{H}_0 \psi(\mathbf{r} - \mathbf{R}')$ denote the matrix elements of the orbital wavefunction on the Hamiltonian and $S_{\mathbf{R}\mathbf{R}'} = \int d^d r \psi^*(\mathbf{r} - \mathbf{R}) \psi(\mathbf{r} - \mathbf{R}')$ represent the overlap integrals. Then, varying the energy with respect to $\alpha^*_{\mathbf{R}}$, we find that the coefficients obey the **secular equation** (exercise)

$$\sum_{\mathbf{R}'} \left[H_{\mathbf{R}\mathbf{R}'} - ES_{\mathbf{R}\mathbf{R}'} \right] \alpha_{\mathbf{R}'} = 0 \,.$$

Note that, if the basis functions were orthogonal, this would just be an eigenvalue equation.

 \triangleright EXERCISE. To develop this idea, let us first see how the method relates to back to the problem of H₂⁺: In this case, the secular equation translates to the 2 × 2 matrix equation,

$$\left(\begin{array}{cc} H_{aa}-E & H_{ab}-ES \\ H_{ab}-ES & H_{aa}-ES \end{array}\right)\boldsymbol{\alpha}=0\,,$$

where the notation and symmetries of matrix elements follow from section 10.1. As a result, we find that the states α divide into even and odd states as expected.

Now let us consider a one-dimensional periodic lattice system. If we assume that the atoms are well-separated, it is evident that both the overlap integrals and matrix elements will decay exponentially fast with orbital separation. The dominant contribution to the energy will then derive from matrix elements coupling only neighbouring states. In this case, the secular equation separates into the coupled sequence of equations,

$$(\varepsilon - E)\alpha_n - (t + ES)(\alpha_{n+1} + \alpha_{n-1}) = 0,$$

for each n, where $H_{nn} = \varepsilon$ denotes the atomic orbital energy, $H_{n,n+1} = H_{n+1,n} = -t$ is the matrix element between neighbouring states, $S_{n,n} = 1$

and $S_{n+1,n} = S_{n+1,n} = S$. All other matrix elements are exponentially small. Here we consider a system with N lattice sites and impose the periodic boundary condition, $\alpha_{n+N} = \alpha_n$. The periodicity of the secular equation suggests a solution of the from $\alpha_n = \frac{1}{\sqrt{N}}e^{ikna}$, where $k = 2\pi m/Na$ denote a discrete set of N reciprocal lattice vectors with m integer lying in the range $-N/2 < m \leq N/2$. Substitution confirms that this is a solution with energies (exercise),

$$E_k = \frac{\varepsilon - 2t\cos(ka)}{1 + S\cos(ka)} \,.$$

The reciprocal lattice vector k parameterizes a **band** of states.

Then, according to the LCAO approximation, for a single electron, distributed throughout the system, the lowest energy state is predicted to be the uniform state $\alpha_n = \frac{1}{\sqrt{N}}$ with the energy $E_0 = \frac{\varepsilon - 2t}{1+S}$. (Here we have assumed that the matrix element, t is positive – in the atomic limit, consider why this is a sound assumption.) However, if we suppose that each atom contributes a non-zero fraction of electrons to the system, we must consider the influence of Pauli exclusion and particle statistics.

Since the electrons are fermions, each state k can host two electrons in a total spin singlet configuration. The lowest energy state is then obtained by adding electron pairs sequentially into states of increasing k until all electrons are accounted for. If the maximum k value, known as the Fermi wavevector, k_F , lies within the band of states, elementary excitations of the electrons cost vanishingly small energy leading to **metallic** behaviour. On the other hand, if the system is stoichiometric, with each atom contributing an integer number of electrons, the Fermi wavevector may lie at a **band gap** between two different band of states. In this case, the system has a gap to excitations and the material forms a **band insulator**.

▷ EXERCISE. Consider how the calculation above can be extended to a twodimensional square lattice system. What would be the corresponding band dispersion?

 \triangleright EXERCISE. In the one-dimensional system, extend the calculation to compute the electron band structure for a periodic lattice with two atomic orbitals on each site, one with *s*-wave symmetry, and another with *p*-wave. In particular, consider how the dispersion would change with the orientation of the *p* state relative to the chain direction.

 \triangleright INFO. To add flesh to these ideas, let us then consider a simple, but prominent problem from the realm of quantum condensed matter physics. In recent years, there has been great interest in the properties of **graphene**, a single layer of graphite. Remarkably, high quality single crystals of graphene can be obtained by running graphite – a pencil! – over an adhesive layer. The resulting electron states of the single layer compound have been of enormous interest to physicists. To understand why, let us implement the LCAO technology to explore the valence electron structure of graphene.

Graphene forms a periodic two-dimensional honeycomb lattice structure with two atoms per each unit cell. With an electron configuration $1s^2 2s^2 2p^2$, the two 1s electrons are bound tightly to the nucleus. The remaining 2s electrons **hybridize** with one of the p orbitals to form three sp^2 hydridized orbitals. These three orbitals form the basis of a strong covalent bond of σ orbitals that constitute the honeycomb lattice. The remaining electron, which occupies the out-of-plane p_z orbital, is then



One dimensional band structure for E_k for S = 0.3, t = 1 and $\varepsilon = 0$. Here we have shown schematically a band-filling with $k_F a = \pi/2$.



Atomically resolved STM image of graphene sheet at 77K.



Figure 10.1: Left: dispersion relation of graphene $E_{\mathbf{k}}$ obtained with the LCAO approximation. Notice that near the centre of the band, the dispersion becomes point-like. Around these points, the dispersion takes form of a linear (Dirac) cone. Right: band structure of a sample of multilayer epitaxial graphene. Linear bands emerge from the K-points in the band structure. Three "cones" can be seen from three layers of graphene in the MEG sample.

capable of forming an itinerant band of electron states. It is this band which we now address.

Once again, let us suppose that the wavefunction of this band involves the basis of single p_z orbital states localized to each lattice site,

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} \left[\alpha_{\mathbf{R}} \psi_1(\mathbf{r} - \mathbf{R}) + \beta_{\mathbf{R}} \psi_2(\mathbf{r} - \mathbf{R}) \right] \,.$$

Here the p_z orbital wavefunction ψ_1 is centred on one of the atoms in the unit cell, and ψ_2 is centred on the other. Once again, taking into account matrix elements involving only nearest neighbours, the trial wavefunction translates to the secular equation,

$$\begin{aligned} (\varepsilon - E)\alpha_{\mathbf{R}} - (t + ES)(\beta_{\mathbf{R}} + \beta_{\mathbf{R}-\mathbf{a}_1} + \beta_{\mathbf{R}-\mathbf{a}_2}) &= 0\\ (\varepsilon - E)\beta_{\mathbf{R}} - (t + ES)(\alpha_{\mathbf{R}} + \alpha_{\mathbf{R}+\mathbf{a}_1} + \alpha_{\mathbf{R}+\mathbf{a}_2}) &= 0\,, \end{aligned}$$

where the lattice vectors $\mathbf{a}_1 = (\sqrt{3}/2, 1/2)a$ and $\mathbf{a}_2 = (\sqrt{3}/2, -1/2)a$, with *a* the lattice spacing, are shown in the figure to the right. Note that the off-diagonal matrix elements involve only couplings between atoms on different sublattices. Once again, we can make the ansatz that the solutions are of the form of plane waves with $\alpha_{\mathbf{R}} = \frac{\alpha_{\mathbf{k}}}{\sqrt{N}}e^{i\mathbf{k}\cdot\mathbf{R}}$ and $\beta_{\mathbf{R}} = \frac{\beta_{\mathbf{k}}}{\sqrt{N}}e^{i\mathbf{k}\cdot\mathbf{R}}$. Notice that, in this case, we must allow for different relative weights, $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$. Substituting, we find that this ansatz is consistent if

$$(\varepsilon - E)\alpha_{\mathbf{k}} - (t + ES)f_{\mathbf{k}}\beta_{\mathbf{k}} = 0$$

$$(\varepsilon - E)\beta_{\mathbf{k}} - (t + ES)f_{\mathbf{k}}^*\alpha_{\mathbf{k}} = 0$$

where $f_{\mathbf{k}} = 1 + 2e^{-i\sqrt{3}k_x a/2} \cos(k_y a/2)$. Although this equation can be solved straightforwardly, it takes a particularly simple form when the overlap integral between neighbouring sites, S, is neglected. In this case, one obtains,

$$E_{\mathbf{k}} = \varepsilon \pm |f_{\mathbf{k}}|t$$
.

The corresponding band structure is shown right as a function of \mathbf{k} . In particular, one may note that, at the band centre, the dispersion relation for the electrons becomes point-like (see Fig. 10.3).

In the half-filled system, where each carbon atom contributes a single electron to the band, the Fermi level lies precisely at the centre of the band where the dispersion, $E_{\mathbf{k}}$ is point like. Doping electrons into (or removing electrons from) the system results in (two copies) of a linear dispersion, $E_{\mathbf{k}} \simeq c|\mathbf{k}|$, where is c is a constant (velocity). Such a linear dispersion relation is the hallmark of a relativistic particle (cf. a photon). Of course, in this case, the electrons are not moving at relativistic velocities. But their properties will mirror the behaviour of relativistic particles. And herein lies the interest that these materials have drawn.



Finally, let us comment on the influence of the electron-electron interaction effects that were neglected in our treatment above. In principle, we could adopt a Hartree or Hartree-Fock scheme to address the effects of electron interaction in a perturbative manner. Indeed, such a programme would lead to interaction corrections which would modify the electronic band structure derived above. It is a surprising yet robust feature of Fermi systems that the properties of the non-interacting ground state wavefunction remain qualitatively correct over an unreasonably wide range of interaction strengths.² This *rigidity* can be ascribed to the contraints implied on the nodal structure of the wavefunction imposed by particle statistics. However, in some cases, the manifestations of electron interactions translate to striking modifications in the experimental behaviour leading to effects such as interaction-driven electron localization – the Mott transition, local moment and itinerant magnetism, quantum Hall fluids, and superconductivity. Such phases, which by their nature, lie outside any perturbative scheme built around the non-interacting ground state, form the field of quantum condensed matter and solid state physics.

With this detour, we now return to the simple molecular system, and consider the question of excitations and transitions.

10.4 Molecular spectra

In the atomic system, our consideration of radiative transitions was limited to the problem of electronic transitions between states. In the molecular system, the internal structure allows for transitions involving **rotational** and **vibrational excitations** of the consituent nuclei. As with atoms, **electronic transitions** are typically of order eV, and so corresponds to wavelengths in or near the optical region. However, it is unlikely that an electronic transition will occur without inducing motion of the nuclei as well, because the equilibrium distances between the nuclei will be different in the initial and final electron states. The typical energies of rotational states of molecules are much smaller than those of electronic excited states, of order $\hbar^2/2I$, where I is the molecular moment of inertia. Substituting typical values for the interatomic spacing and atomic masses, one finds that rotational energies are $\mathcal{O}(10^{-4}\text{eV})$, corresponding to the far infra-red or microwave regions. Typical energies for vibrational excitations of molecules are $\mathcal{O}(10^{-1}\text{eV})$ (see section 10.4.2 below), corresponding to the infra-red waveband.

All of these types of transitions can occur **radiatively**, i.e. through the emission or absorption of a photon of the appropriate frequency $\nu = \Delta E/h$.³ As in the case of atoms, the most probable radiative transitions are usually **electric dipole** transitions. In an electric dipole transition, the photon carries one unit of angular momentum and negative parity, so there will be the usual selection rule for the change in the total angular momentum quantum number of the molecule:

$$\Delta J = 0, \pm 1, \qquad \text{but not } 0 \to 0,$$

accompanied by a change in the parity of the molecular state (which may impose further restrictions on ΔJ).

▷ INFO. In a gas or a liquid, transitions can also be produced by collisions

²The feature is embodied in the theory of the electron liquid known as **Landau's Fermi** liquid theory.

³Spectroscopists always quote wavenumbers $\tilde{\nu} = \nu/c$ instead of frequencies, and measure them in cm⁻¹.

between molecules. The appropriate energy change can be provided by excitation or de-excitation of the other molecule, or as part of the kinetic energy of the collision. Such **non-radiative transitions** do not have to obey the selection rules above. Thus, for example, a molecule in a **metastable** state, i.e. one that cannot return to the ground state via an allowed radiative transition, can be de-excited by a collision. In the absence of any incident radiation or other non-thermal sources of excitation, collisions will bring about a thermal distribution of molecular energy levels, with the number of molecules in state *i* being given by $n_i \propto g_i \exp\left[-\frac{E_i}{k_{\rm B}T}\right]$, where g_i is the degeneracy and E_i the energy. At room temperature, $k_{\rm B}T \sim 2 \times 10^{-2} \, {\rm eV}$, so typically many rotational states of molecules are excited, but not electronic or vibrational.

To study the motion of nuclei in the Born-Oppenheimer Approximation and the associated types of transitions more formally, we must go back to the molecular Schrödinger equation considered above. Having found the electronic eigenfunctions, ψ_k , in the Born-Oppenheimer approximation, we can use the completeness property of these functions to express the full stationary state wavefunction of the molecule as

$$\Psi(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}) = \sum_k \phi_k(\{\mathbf{R}_N\})\psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}),$$

where ϕ_k represents the nuclear part of the wavefunction. Substituting this expression into the full time-independent Schrödinger equation, we obtain

$$\left[-\sum_{n=1,2,\dots} \frac{\hbar^2 \nabla_n^2}{2m_e} - \sum_{N=a,b,\dots} \frac{\hbar^2 \nabla_N^2}{2m_N} + V(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}) \right] \Psi(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$$

= $E\Psi(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$.

Using the electronic energy levels E_k , we have

$$\sum_{k} \left[-\sum_{N=a,b,\dots} \frac{\hbar^2}{2m_N} \nabla_N^2 + E_k(\{\mathbf{R}_N\}) \right] \phi_k \psi_k = E \sum_k \phi_k \psi_k \,.$$

Now another important aspect of the Born-Oppenheimer approximation comes into play: the dependence of $\psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$, the electronic part of the wavefunction, on the nuclear coordinates $\{\mathbf{R}_N\}$ is weak compared with that of the nuclear part $\phi_k(\{\mathbf{R}_N\})$. We shall verify this explicitly in section 10.4.2 below. Therefore we can write $\nabla_N^2 \phi_k \psi_k \simeq \psi_k \nabla_N^2 \phi_k$, to a good approximation. Using the orthogonality of the ψ_k s, we can now pick out the k = 0 term, for example, by multiplying by ψ_0^* and integrating over all electron positions, to obtain

$$\left[-\sum_{N=a,b,\dots}\frac{\hbar^2}{2m_N}\nabla_N^2 + E_0(\{\mathbf{R}_N\})\right]\phi_0 = E\phi_0.$$

Thus the nuclear part of the wavefunction, ϕ_0 , satisfies a Schrödinger equation in which the full potential $V({\mathbf{r}_n}, {\mathbf{R}_N})$ is replaced by the molecular potential energy curve $E_0({\mathbf{R}_N})$, which we derived earlier in the approximation that the nuclei were nailed down at positions ${\mathbf{R}_N}$. The replacement of the full potential by $E_0({\mathbf{R}_N})$ in the nuclear Schrödinger equation corresponds physically to assuming that the electrons react instantly to changes in the molecular conformation.

10.4.1 Molecular rotation

In general, the Schrödinger equation for the nuclear motion has many solutions, which give the various molecular energy levels for a given electronic configuration. Here, for simplicity, we focus on diatomic molecules which capture the main features of the general phenomenology. In this case, $E_0(\mathbf{R}_1, \mathbf{R}_2) = E_0(R)$ where $R = |\mathbf{R}_1 - \mathbf{R}_2|$ and the usual separation of variables can be performed. One equation describes the translational motion of the overall centre of mass, and leads to a continuum of possible energies for a free molecule, or the usual energies of a particle in a box if it is confined. The equation for the relative coordinate, $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$, is given by

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{R}}^2 + E_0(R)\right]\phi_0 = E\phi_0\,,$$

where μ is the reduced mass of the two atoms. In this case, $E_0(R)$ acts as a central potential, and the usual separation into angular and radial equations can be carried out.

The simplest solutions are the purely rotational states, in which the whole molecule rotates around its centre of mass. The solutions will be the spherical harmonic functions Y_{J,m_J} . Conventionally the quantum numbers are labelled J and m_J (m_J taking values $J, J - 1, \dots, -J$), and the corresponding energy is given by

$$E_J = \frac{\hbar^2}{2I} J(J+1) \,,$$

where $I = \mu R_0^2$ is the moment of inertia of the molecule about an axis through the centre of mass orthogonal to the bond, and R_0 is the equilibrium bond length.

As mentioned earlier, the typical energies of rotational states of molecules are much smaller than those of electronic excited states. Since molecular dimensions are determined by the electronic wavefunction, their scale is set by the Bohr radius a_0 . Thus moments of inertia are of order $m_N a_0^2$ and the scale of rotational energies is $\hbar^2/m_N a_0^2$. For the electronic states, the uncertainty relation implies momenta of order \hbar/a_0 and hence electron energies around $\hbar^2/m_e a_0^2$, a factor of $m_N/m_e \sim 10^4$ greater.

To bring about a radiative rotational transition, an emitted or absorbed photon must interact with the electric dipole moment of the molecule. Since the initial and final electronic states are the same, this state needs to have a permanent electric dipole moment. Thus we can have purely rotational radiative transitions in **heteronuclear** diatomic molecules like HCl and CO, which have permanent dipole moments, but not in **homonuclear** ones like H_2 and O_2 .⁴

The usual electric dipole selection rules apply; $\Delta J = \pm 1$, 0 with a parity change. In a rotational state with angular momentum quantum numbers Jand m_J , the nuclear wavefunction $\phi(\{\mathbf{r}_N\})$ is proportional to the spherical harmonic Y_{Jm_J} , which has parity $(-1)^J$. (For simplicity, we consider only molecular states in which the electronic wavefunction has zero angular momentum and even parity, such as the diatomic ${}^1\Sigma_g$ states.) Then the fact

⁴However, we can produce purely rotational transitions in all types of molecules by the process of Raman scattering, in which a photon is effectively absorbed and then reemitted by a molecule, since the virtual intermediate state can have a dipole moment.

that the parity must change in a radiative transition excludes the possibility $\Delta J = 0$. Therefore the possible energy changes in emission $(J + 1 \rightarrow J; J = 0, 1, 2 \cdots)$ are given by:

$$\Delta E = \frac{\hbar^2}{2I} \left[(J+1)(J+2) - J(J+1) \right] = \frac{\hbar^2}{I} (J+1) \,.$$

In fact, the rate for spontaneous emission between rotational states is very small, because of the small energy release (varying as ω^3), and so rotational transitions are more conveniently studied by **absorption** spectroscopy. The same formula for the energies of transition clearly applies to the $J \rightarrow (J+1)$ absorption case. Therefore the spectrum is expected to consist of equally spaced lines, separated by energy \hbar^2/I . Observation of this spacing can be used to determine the moment of inertia and hence the bond length of the molecule. Strictly speaking the spacing isn't quite uniform, because the radial Schrödinger equation acquires a centrifugal potential term $\hbar^2 J(J+1)/2\mu R^2$ which means that the equilibrium separation slightly increases with J and consequently the moment of inertia increases and the line spacing decreases.

 \triangleright EXERCISE. Use perturbation theory to estimate the strength of the effect of the centrifugal term.

 \triangleright INFO. The intensities of rotational spectral lines show some interesting features. Although the transition matrix element depends on the quantum numbers, the dominant factor is usually the population of the initial state. As mentioned earlier, non-radiative transitions due to molecular collisions bring about a thermal distribution,

$$n_J \propto g_J \exp[-E_J/k_{\rm B}T] \propto (2J+1) \exp[-\hbar^2 J(J+1)/2Ik_{\rm B}T]$$
.

This increases with J up to some value, which depends on the temperature, and then decreases. Thus successive spectral lines increase and then decrease in intensity.

10.4.2 Vibrational transitions

Another important type of molecular motion is vibration, in which the nuclei oscillate around their equilibrium positions. For a diatomic molecule, we can Taylor expand the molecular potential $E_0(R)$ around the equilibrium nuclear separation R_0 to obtain

$$E_0(R) = E_0(R_0) + \frac{1}{2}(R - R_0)^2 \partial_R^2 E_0|_{R_0} + \dots$$

Keeping only the two terms shown on the right-hand side, we have the potential for a simple harmonic oscillator with classical frequency $\omega = ((1/\mu)\partial_R^2 E_0|_{R_0})^{1/2}$ where μ is the reduced mass. Thus we expect the energy levels including nuclear vibration to be given by

$$E = E_0(R_0) + (n+1/2)\hbar\omega, \qquad n = 0, 1, 2, \dots$$

The excitation energies of molecular vibrational states are typically larger than those of rotational states by a factor of about $\sqrt{m_N/m_e}$ and smaller than electronic excitation energies by a factor of about $\sqrt{m_e/m_N}$. As we discussed earlier, $E_0(R_0)$ will be of the same order of magnitude as atomic energies, i.e. of the order of $\hbar^2/m_e a_0^2$ where a_0 is the Bohr radius. Thus, on dimensional grounds, $\partial_R^2 E_0|_{R_0}$ will be of order $\hbar^2/m_e a_0^4$, and $\hbar\omega \sim \hbar^2/\sqrt{m_e m_N} a_0^2$. Therefore the vibrational energy is smaller than the electronic by a factor of order $\sqrt{m_e/m_N}$. This puts vibrational spectra in the wavelength region around 10μ m, which is in the infra-red.

We can now check explicitly that the Born-Oppenheimer approximation is valid for nuclear vibrational states, as follows. The mean square nuclear vibrational momentum is of order $m_N \hbar \omega \sim \sqrt{m_N/m_e} (\hbar/a_0)^2$, which means that $\nabla_N^2 \phi_k \sim \sqrt{m_N/m_e} \phi_k/a_0^2$, where ϕ_k is the nuclear part of the wavefunction. On the other hand $\nabla_N^2 \psi_k \sim \psi_k/a_0^2$, where ψ_k is the electronic part. Thus $\phi_k \nabla_N^2 \psi_k$ is smaller than $\psi_k \nabla_N^2 \phi_k$ by a factor of $\sqrt{m_e/m_N}$, and it is legitimate to neglect the former.

For vibrational transitions we have the selection rule (exercise)

$$\Delta n = \pm 1$$
.

This implies only a single energy in the spectrum,

$$\Delta E = (E_{n+1} - E_n) = \hbar \omega \,,$$

corresponding to the classical frequency of oscillation. In practice the Taylor expansion around $R = R_0$ has non-negligible terms of higher than second order and the harmonic oscillator approximation is not very reliable: there is **anharmonicity**. The flattening of the molecular potential energy curve at larger separations has the effect of bringing the energy levels closer together. Thus transitions at larger n have lower energies than that given above. Also, since the true stationary state wavefunctions are not precisely harmonic oscillator eigenfunctions, our selection rule is not exactly valid, and transitions with $|\Delta n| > 1$ become possible.

▷ INFO. Vibrational modes for polyatomic molecules can be quite complicated. If there are N atoms, in general there are 3N - 6 normal modes (3N coordinates, less 3 to define the overall position of the centre of mass, and less 3 to define the overall orientation of the molecule) or 3N - 5 in the case of a diatomic molecule. Thus, in the simple case of the linear CO₂ molecule, there are four modes, two with the atoms remaining collinear (one with the two O atoms moving in antiphase with the C stationary, and one with the O atoms moving in phase in the opposite direction to the C atom) and two degenerate orthogonal bending modes. In the following chapter, we will turn to consider the vibrational motion of periodic lattice systems where, once again, a degree of simplicity is restored!



Figure 10.2: Generally vibrational transitions occur in conjunction with rotational transitions. Consequently, it is possible to observe both rotational and vibrational transitions in the vibrational spectrum. The top figure shows an energy level diagram demonstrating some of the transitions involved in the IR vibration-rotation spectrum of a linear molecule: P branch (where $\Delta J = 1$), Q branch (not always allowed, $\Delta J = 0$) and R branch $(\Delta J = +1)$. The lower figure shows the vibration-rotation spectrum of HCl. The left hand branch of the spectrum represents the P branch and the right the R. The Q branch is not allowed. The splitting of the lines is associated with the two isotopes 35 Cl and 37 Cl.