

VII. Overview of Molecular Structure

1. Born-Oppenheimer approximation

As for atoms, all information about a molecule is contained in the wavefunction Ψ , which is the solution of the time-independent Schrödinger equation:

$$H\Psi(\vec{x}, \vec{r}) = E\Psi(\vec{x}, \vec{r}) \quad (7.1)$$

where \vec{x} stands collectively for the spatial and spin coordinates of the n electrons in the molecule, and \vec{r} denotes collectively the positions of all N nuclei in the molecule. In the non-relativistic limit, the total Hamiltonian for the molecule is

$$H = T_N + T_e + V_{Ne} + V_{ee} + V_{NN} \quad (7.2)$$

$$\equiv T_N + H^{el}$$

$$\text{where } T_N = -\sum_{\alpha} \frac{1}{2} M_{\alpha} \nabla_{\alpha}^2, \quad T_e = -\sum_i \frac{1}{2} \nabla_i^2 \quad (7.3-4)$$

$$V_{Ne} = -\sum_{\alpha, i} \frac{Z_{\alpha}}{|R_{\alpha} - r_i|}, \quad V_{ee} = \sum_{i>j} \frac{1}{|r_i - r_j|}, \quad V_{NN} = \sum_{\alpha>\beta} \frac{Z_{\alpha} Z_{\beta}}{|R_{\alpha} - R_{\beta}|} \quad (7.5-7)$$

Atomic units have been used, in which $\hbar = m_e = e = 1$.

T_N and T_e are the summed kinetic energy operators of the nuclei α with mass M_{α} and the electrons i with mass m_e , respectively, and V_{Ne} , V_{ee} and V_{NN} denote the summed Coulomb interaction energies between the nuclei and the electrons, between the electrons themselves, and between the nuclei themselves, respectively. Equation (7.1) is a $(3n + 3N)$ -dimensional second order partial differential equation, which cannot be readily solved.

Because the masses of the nuclei are much larger than that of the electrons, the nuclei move slowly compared with the electrons. It is usually (but not always!) a very good approximation to assume that the electronic energies (that is, the energies due to the motions of the electrons) can be determined accurately with the nuclei help fixed at each possible set of nuclear positions. In other words, it is assumed that the electrons adjust adiabatically to small or slow changes in the nuclear geometry. This approximation and its consequences were first examined by Born and Oppenheimer (1927, *Ann. Physik* **85**, 457), and has carried their names ever since.

In this approximation, the total wavefunction is separable

$$\Psi(\vec{x}, \vec{R}) = \Psi^{el}(\vec{x}; R) \Psi^{nuc}(\vec{R}) \quad (7.8)$$

into a nuclear part Ψ^{nuc} that depends only upon the nuclear coordinates \vec{R} , and an electronic part Ψ^{el} that depends on the electronic coordinates \vec{x} , but only parametrically on R . Ψ^{el} is the solution of the electronic eigenvalue equation

$$H^{el}\Psi^{el}(\vec{x}; R) = E^{el}(R)\Psi^{el}(\vec{x}; R) \quad (7.9)$$

where $E^{el}(R)$ is the potential energy surface, or, in the case of a diatomic molecule, the potential energy curve of the molecule in a particular electronic state. Substituting the Born-Oppenheimer wavefunction (7.8) into the Schrödinger equation, and using (7.9) gives:

$$\left[-\sum_{\alpha} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^2 + E^{el}(R) - E \right] \Psi^{nuc}(\vec{R}) = 0, \quad (7.10)$$

where we have made the assumption that

$$\begin{aligned}\nabla_{\alpha}^2 \Psi^{el} \Psi^{nuc} &= \Psi^{el} \nabla_{\alpha}^2 \Psi^{nuc} + 2 \nabla_{\alpha} \Psi^{el} \nabla_{\alpha} \Psi^{nuc} + \Psi^{nuc} \nabla_{\alpha}^2 \Psi^{el} \\ &\approx \Psi^{el} \nabla_{\alpha}^2 \Psi^{nuc}\end{aligned}\tag{7.11}$$

The neglect of the so-called “non-adiabatic” interactions ∇_{α} (the second and third terms in 7.11) is usually justified, except when the electronic wavefunction changes rapidly with the nuclear coordinates. This can happen, for example, in those regions where two states interfere with one another (at a surface- or curve-“crossing”). Equation (7.10) is an eigenvalue equation for the nuclear motion, where $E^{el}(R)$ acts as the potential in which the nuclei move. We will first discuss the methods for solving the *electronic* eigenvalue equation (7.9), and then illustrate the subsequent determination of the *nuclear* motion according to equation (7.10).

2. Calculation of electronic energies

As for atoms, the most general method to solve eq. (7.9) is the method of configuration interaction (CI), which is a straight-forward application of the Ritz linear variation method.

The electronic wave function is expanded linearly as

$$\Psi^{el}(\vec{x}_1, \dots, \vec{x}_n) = \sum_{k=1}^M c_k \Phi_k(\vec{x}_1, \dots, \vec{x}_n)\tag{7.12}$$

where Φ_k are the expansion functions, loosely referred to as configurations, and c_k the CI coefficients. If we substitute (7.12) into (7.9) and use the variational principle, which requires that the energy should be stationary with respect to variations in the wave function, we obtain the matrix eigenvalue equation

$$\hat{H}^{el} \vec{c} = E^{el} \vec{c},\tag{7.13}$$

where

$$(H^{el})_{kl} = \langle \Phi_k | H^{el} | \Phi_l \rangle,\tag{7.14}$$

and it has been assumed that the set of basis functions $\{\Phi_k\}$ is orthonormal. If this set were complete, which implies $k = 1, \dots, \infty$, the calculated eigenvalues would be exact. In practice, of course, a truncated set $\{\Phi_k\}$ is used, and the variational principle ensures that the resulting (lowest) eigenvalue is always an upper bound to the exact energy. The lowest k roots of eq. (7.13) form the energies of the lowest k electronic states of the molecule.

The functions Φ_k are usually constructed as linear combinations of products of one-electron functions $u_i(\vec{x})$, where the combinations are chosen to satisfy the spatial and spin symmetry conditions and the Pauli principle. As for atoms, one can write the functions Φ_k in terms of Slater determinants:

$$\Phi_k(\vec{x}_1, \dots, \vec{x}_n) = A \Xi_k(\vec{r}_1, \dots, \vec{r}_n) \Theta_k(s_1, \dots, s_n)\tag{7.15}$$

where A is the antisymmetrization operator and Ξ_k is a product of n spatial orbitals $u_i(\vec{r})$:

$$\Xi_k(\vec{r}_1, \dots, \vec{r}_n) = u_A(\vec{r}_1) u_B(\vec{r}_2), \dots, u_X(\vec{r}_n).\tag{7.16}$$

Θ_k is an n -electron eigenfunction of the total spin operators S^2 and S_z , and is generally a linear combination of products of n one-electron spin functions α and β (see e.g. the case of two electrons discussed on p. 33).

The problem has thus been reduced to finding suitable one-electron functions $u_i(\vec{r})$. Historically, two choices have been made.

(i) Atomic orbitals (AO's), which are one-electron hydrogenic functions centered at the nuclei. This method suffers from the fact that the AO's are non-orthogonal.

(ii) Molecular orbitals (MO's), which are delocalized functions over the whole molecule. The MO's are orthogonal, and are chosen such that *one* configuration Φ_1 is already a good approximation to Ψ^{el} ; that is, the goal is to choose the MO's such that expansion (7.12) becomes

$$\Psi^{el} \approx \sqrt{(0.99)} \Phi_1 + \sqrt{(0.01)} \Phi_2 + \dots \quad (7.17)$$

How does one find the appropriate MO's? Starting from an "ansatz" (a educated guess) for the form of the configuration function Φ_1 , the best MO's are expanded in a set of atomic orbitals

$$u_i(\vec{r}) = \sum_{\mu=1}^m \phi_{\mu}(\vec{r}_k) d_{\mu i} \quad , \quad (7.18)$$

where the function ϕ_{μ} is an atomic orbital centered at nucleus k . This is called the LCAO-MO (Linear Combination of Atomic Orbitals forming a MO) method.

Note that, as for atoms, in the Hartree-Fock equations, the electrons are treated as independent particles. Although energies and properties of molecules can be computed at this level of theory, in most cases it is necessary to carry the calculation on to the higher level of CI, where the Hartree-Fock solutions are used as starting points. One of the problems in molecular structure is that most aspects of chemistry are only concerned with small differences between large numbers. For example, the total binding energy of a molecule, or the excitation energy to the first excited electronic state, is usually less than 0.5% of the total energy.

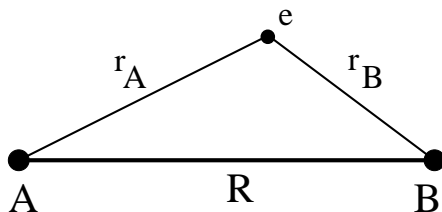
Let us consider two simple examples.

a) The H_2^+ ion

The simplest molecule, which is also of astrophysical interest, is the H_2^+ ion, which consists of two protons held together by one electron. The Hamiltonian is:

$$H^{el} = -\nabla^2/2 - 1/r_A - 1/r_B + 1/R \quad (7.19)$$

where $r_A = |\vec{r} - \vec{R}_A|$, $r_B = |\vec{r} - \vec{R}_B|$ and R is the internuclear distance $|\vec{R}_A - \vec{R}_B|$.



Although this system can be solved exactly (within the Born-Oppenheimer approximation), it is more instructive to obtain an approximate solution using the variational method.

If the electron is very close to A, the term $1/r_B$ is small, and the Hamiltonian reduces to that for the hydrogen atom, since $1/R$ is fixed (as a parameter). So we expect:

$$\phi^{el}(r) \approx \phi_A(r) \quad \text{for } r_A \ll r_B \quad (7.20)$$

with

$$\phi_A(r) = \sqrt{\frac{1}{\pi}} e^{-r_A} \quad (7.21)$$

a hydrogen 1s function centered on nucleus A. Similarly, we expect

$$\phi^{el}(r) \approx \phi_B(r) \quad \text{for } r_B \ll r_A \quad (7.22)$$

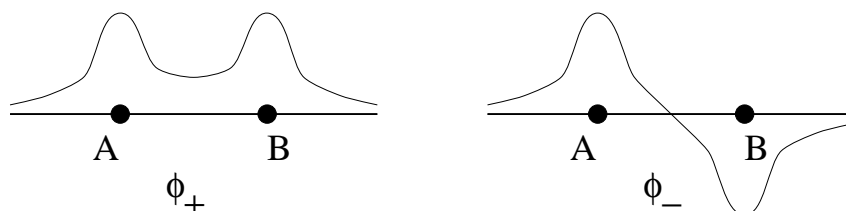
if the electron is close to nucleus B. Thus, we assume that the wave function in general can be written as a superposition of the hydrogen atomic wave functions:

$$\phi^{el}(r) = c_A \psi_A(r) + c_B \psi_B(r) . \quad (7.23)$$

This is the LCAO-MO approximation. Since the molecule has inversion symmetry, $c_A = \pm c_B$, so that we find two orbitals:

$$\phi_{\pm}^{el}(r) = c_{\pm}(\psi_A \pm \psi_B) . \quad (7.24)$$

The + and – combinations are called the bonding and antibonding orbitals, respectively.



The normalization constant c_{\pm} can be found by integrating ϕ_{\pm} over the whole space:

$$\frac{1}{c_{\pm}^2} = \int \phi_{\pm}^{el*} \phi_{\pm}^{el} d^3r = 2 \pm 2S(R) \quad (7.25)$$

where

$$S(R) = \int \psi_A \psi_B d^3r = (1+R+R^2/3)e^{-R} \quad (7.26)$$

is the “overlap integral.” The energies $E_{\pm}^{el}(R)$ can then be computed from:

$$\begin{aligned} E_{\pm}^{el}(R) &= \langle \phi_{\pm}^{el} | H^{el} | \phi_{\pm}^{el} \rangle \\ &= \frac{\langle \phi_A | H^{el} | \phi_A \rangle + \langle \phi_B | H^{el} | \phi_B \rangle \pm 2 \langle \phi_A | H^{el} | \phi_B \rangle}{2 \pm 2S(R)} . \end{aligned} \quad (7.27)$$

All integrals in (7.27) can be computed exactly for the hydrogen wave functions as functions of the H—H distance R . We can then plot the resulting potential energy curves E_{\pm}^{el} as functions of R (see Figure 7.1). The lower electronic state E_{-}^{el} is “bound”, whereas the upper state E_{+}^{el} has no minimum with respect to R , and is thus “unbound”.

Qualitatively, the LCAO-MO wave function gives the correct result, but quantitatively, it is quite poor. Table 7.1 compares the computed and experimental values for the equilibrium internuclear distance R_e and the dissociation energy D_e .

The wavefunction (7.23) can be improved by adding other atomic orbitals (for example 2s or 2p functions) to the expansion, and by varying the exponent of the hydrogenic functions (7.21).

b) The H_2 molecule

The next simplest molecule is H_2 . This molecule cannot be solved analytically. As a first approximation, let us use the two molecular orbitals ϕ_{\pm}^{el} for the H_2^+ molecule as a starting point, and form an H_2 wavefunction from these. In the ground state of H_2 , both electrons will be in the

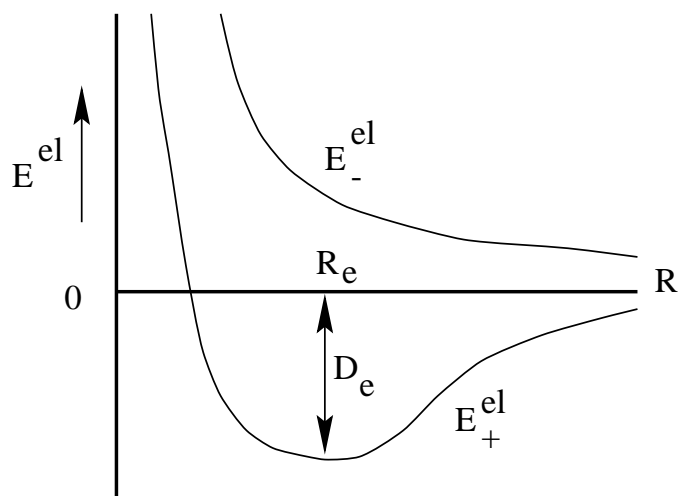


Figure 7.1– The bound and unbound potential energy curves of the H_2^+ ion.

Table 7.1– Energetics of the H_2^+ ion

Property	Calc.	Expt.
$R_e(\text{\AA})$	1.3	1.03
$D_e(\text{eV})$	1.76	2.8

energetically more favorable orbital ϕ_+^{el} . Because of the Pauli principle, the two electrons must then be paired as a singlet:

$$\Phi_1 = \sqrt{\frac{1}{2}} \phi_+(1)\phi_+(2)\{\alpha_1\beta_2 - \beta_1\alpha_2\} , \quad (7.28)$$

with ϕ_+ given by (7.24). This wavefunction works well near R_e , but it fails terribly at large R , where it partly represents an H^- and an H^+ ion pair rather than two ground-state H atoms. This can be seen by expanding (7.28) into the atomic orbitals ϕ_A and ϕ_B :

$$\begin{aligned} \Phi_1 &= \frac{(\phi_A + \phi_B)_1 (\phi_A + \phi_B)_2}{(2 + 2S)^{1/2} (2 + 2S)^{1/2}} = \frac{1}{2 + 2S} \{\phi_A\phi_A + \phi_A\phi_B + \phi_B\phi_A + \phi_B\phi_B\} \\ &= \frac{1}{2 + 2S} \{(\phi_B\phi_A + \phi_A\phi_B) + (\phi_A\phi_A + \phi_B\phi_B)\}. \end{aligned} \quad (7.29)$$

This problem can be remedied by adding a second configuration made up of the ϕ_- combination:

$$\Phi_2 = \sqrt{\frac{1}{2}} \phi_-(1)\phi_-(2)\{\alpha_1\beta_2 - \beta_1\alpha_2\} \quad (7.30)$$

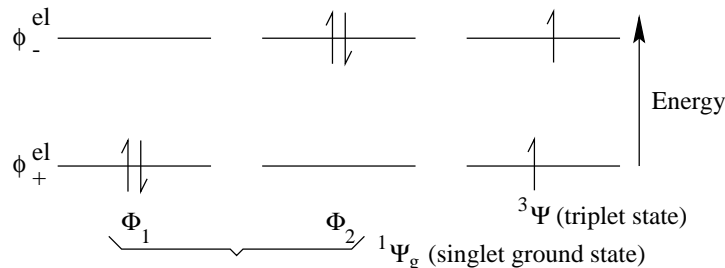
so that the CI wavefunction becomes

$${}^1\Psi_g^{el} = c_1\Phi_1 + c_2\Phi_2 \quad (7.31)$$

and the coefficients c_i can be obtained by diagonalizing the 2×2 interaction matrix.

As for H_2^+ , this level of treatment gives a correct qualitative description of the ground state of H_2 , but to obtain good quantitative agreement, it is necessary to include many more functions

in the LCAO-MO function (7.23). The singlet ground state of H_2 is bound and has a dissociation energy of $4.75eV$. One can also construct a “triplet” H_2 state by putting one electron in the ϕ_+ orbital and one in the ϕ_- orbital. The resulting potential curve is “repulsive” or unbound, that is, it has the same general shape as the E_-^{el} potential of H_2^+ . Note that these potential curves are the same for the isotopes HD, D_2 , etc... under the Born-Oppenheimer approximation.



Note that for atoms, it was argued that electrons with aligned spins (large total spin) lie lowest in energy (Hund’s rule 1). Now we find for H_2 that it is the singlet state that binds, while the triplet state does not. This paradox is explained by the fact that for molecules, it is the electron density *between* the nuclei that leads to binding, and this effect *outweighs* the lower $e - e$ repulsion energy in the high spin states.

Another point of interest involves the large R behavior of the internuclear potential. In a second-order perturbation expansion, it is found that two H-atoms attract each other with a R^{-6} van der Waals potential. Thus, even the triplet state eventually becomes attractive at very large R , but with very shallow well depth that results in no bound states – although weak bonds are found in other molecules. Note also that not all pairs of atoms can form bound molecular states; for example, two ground state He atoms cannot form a bound electronic state.

3. Nuclear motion

Once the electronic potential energy surfaces have been computed the motion of the nuclei can be determined by solving eq. (7.10). Consider for simplicity the case of a diatomic molecule.

If we transform to the center-of-mass coordinates and define the internuclear coordinate $\vec{R} = \vec{R}_1 - \vec{R}_2$, the nuclear kinetic energy term reduces to a term containing the center-of-mass motion, which is not of interest (being a constant), and a term describing the relative motion. This last term can be separated further into a part governing the radial motion along $R = |\vec{R}|$, and a part containing the angular coordinates, described by the nuclear angular momentum operator J (compare, for example, (1.3)-(1.7) for atoms):

$$T_N = -\frac{1}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{J^2}{2\mu R^2}, \quad (7.32)$$

where $\mu = M_1 M_2 / (M_1 + M_2)$ is the reduced nuclear mass. If we write

$$\Psi^{nuc}(\vec{R}) = Y_{JM}(\hat{R}) F(R) / R \quad (7.33)$$

where \hat{R} denotes the angular part of \vec{R} and use

$$J^2 Y_{JM}(\hat{R}) = J(J+1) Y_{JM}(\hat{R}) \quad (7.34)$$

we obtain

$$\left\{ -\frac{1}{2\mu} \frac{d^2}{dR^2} + E^{el}(R) + \frac{J(J+1)}{2\mu R^2} - E \right\} F(R) = 0. \quad (7.35)$$

a) Vibration

If the electronic state is bound, that is, stable with respect to dissociation, it has a minimum $-D_e$ at a certain distance R_e . The potential can then be expanded in powers of $(R - R_e)$ about R_e (writing $V = E^{el}$):

$$V(R) = V(R_e) + \left(\frac{dV}{dR}\right)_{R_e} (R - R_e) + \frac{1}{2} \left(\frac{d^2V}{dR^2}\right)_{R_e} (R - R_e)^2 + \dots \quad (7.36)$$

At $R = R_e$, the first derivative vanishes, and up to quadratic terms:

$$V(R) \simeq -D_e + \frac{1}{2}k(R - R_e)^2 \quad (7.37)$$

with $k = (d^2V/dR^2)_{R_e}$. Thus, if rotation is neglected ($J = 0$), the radial equation (7.35) becomes that for the “harmonic oscillator”. The solution to eq. (7.35) can in that case be written as

$$E = -D_e + E^{vib} \quad (7.38)$$

$$E^{vib} = \omega_e(v + 1/2) \quad (7.39)$$

$$\omega_e = (k/\mu)^{1/2} . \quad (7.40)$$

Thus, in the harmonic oscillator approximation, the vibrational levels are equidistant. As Figure 7.2 shows, this is a good approximation for the lowest few vibrational levels, but the higher levels will lie much closer together due to “anharmonicities” in the potential curve. The harmonic oscillator wave functions can be written in terms of Hermite polynomials. Some characteristic wave functions are illustrated in Figure 7.3. Note that the quantum number v of the wave function is the same as the number of nodes.

Eq. (7.35) can also be solved analytically for the case that the potential $V = E^{el}$ is parameterized by a “Morse” potential:

$$V = D_e \left[1 - e^{-\beta(R-R_e)}\right]^2 \quad (7.41)$$

which is a much better approximation to the true potential than the harmonic oscillator. The vibrational energies are denoted as “term values” $G(v)$ in cm^{-1} ; for the Morse potential:

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2, \quad (7.42)$$

where

$$\omega_e = \beta \left[\frac{D_e \hbar}{\pi c \mu} \right]^{1/2}, \quad (7.43)$$

$$\omega_e x_e = \hbar \beta^2 / 4\pi c \mu, \quad (7.44)$$

and $\omega_e x_e$ is called the anharmonicity constant. The vibrational quantum number v can take the values 0, 1, 2, ... Note that the lowest vibrational state of this system still lies above the energy of the potential minimum; that is, there is a “zero-point vibrational energy” for $v=0$:

$$G(0) = \omega_e/2 - \omega_e x_e/4 . \quad (7.45)$$

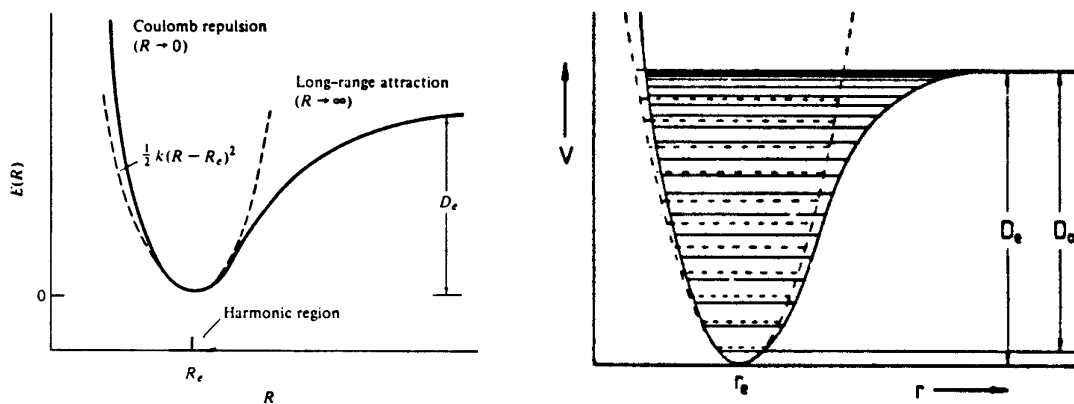


Figure 7.2– a) Harmonic approximation to the molecular potential curve $E^{el}(R)$ of a diatomic molecule, b) Energy levels of a harmonic oscillator (dashed lines), compared with those for an anharmonic potential (solid line).

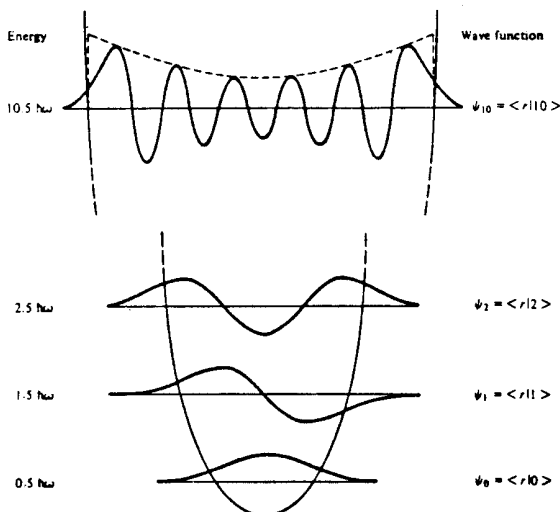


Figure 7.3– Energy levels and corresponding wavefunctions for a harmonic oscillator potential. Note that the quantum number and the number of wavefunction nodes are the same. The time-averaged classical position of the oscillator in a high vibrational level is shown by the dashed curve.

b) Rotation

If we assume that the nuclei are fixed at the equilibrium geometry R_e , the angular part of eg. (7.10), using (7.32), reduces to the equation for a “rigid rotor”:

$$\left\{ \frac{J^2}{2\mu R_e^2} - E^{rot} \right\} Y_{JM}(\hat{R}) = 0. \quad (7.46)$$

Thus:

$$J^2 Y_{JM}(\hat{R}) = 2\mu R_e^2 E^{rot} Y_{JM}(\hat{R}) = J(J+1) Y_{JM}(\hat{R}). \quad (7.47)$$

The rotational energy can be written as

$$E^{rot} = \frac{\hbar^2 J(J+1)}{2I} = \frac{\hbar^2}{2\mu R_e^2} J(J+1) = B_e J(J+1) \quad (7.48)$$

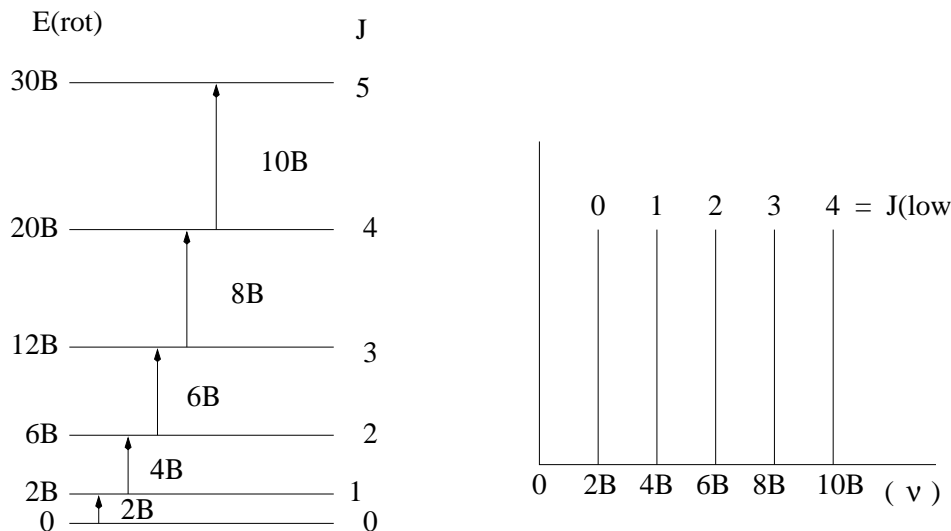


Figure 7.4– Energy levels of a rigid diatomic rotor and corresponding absorption spectrum.

where $I = \mu R_E^2$ is the “moment of inertia” of a rotating dumbbell, and $B_e = 1/2\mu R_E^2$ is the “rotational constant”. J can take the values $0, 1, 2, \dots$, and M can take the values $J, J-1, \dots, -J$. Thus, each rotational level J is $(2J+1)$ -fold degenerate. By convention, E^{rot} is denoted as the rotational term value $F(J)$ in cm^{-1} :

$$F(J) = B_e J(J+1) \quad (7.49)$$

Note that the energy difference between two adjacent rotational levels is $2B_e(J+1)$, that is, the energy difference increases with J , as Figure 7.4 shows. This energy difference is usually much less than ω_e , the energy difference between two vibrational levels.

In reality, molecules are not truly rigid, and so the rotational and vibrational motions interact, or “couple.” The energies of such vibration-rotation states of the molecule are readily obtained by solving the one-dimensional differential equation (7.35) numerically for $J \neq 0$. The result can no longer be written as the sum of a harmonic oscillator vibrational energy and a rigid rotor rotational energy, but will in general be of the form

$$E = E_{min}^{el} + \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \dots \\ + B_v J(J+1) - D_v J^2(J+1)^2 + \dots \quad (7.50)$$

where the rotational energies are affected by centrifugal distortions:

$$F(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \dots \quad (7.51)$$

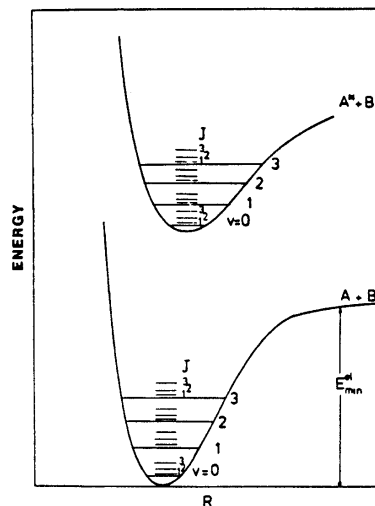
The rotation constants B_v, D_v, \dots are indicated explicitly for a particular vibrational state, because the moment of inertia is expected to change with vibration:

$$B_v = B_e - \alpha_e(v+1/2) + \dots \quad (7.52a)$$

$$D_v = D_e + \beta_e(v+1/2) + \dots \quad (7.52b)$$

Note: D_e in eq. (7.52b) should not be confused with the dissociation energy D_e ! Experimentally determined energies are usually fitted to the form (7.50) and given in terms of the constants $\omega_e, \omega_e x_e, \dots, B_e, \alpha_e, D_e, \beta_e, \dots$ etc.

Figure 7.5– Energy level diagram for two different electronic states of a diatomic molecule AB. The quantum numbers v indicate the vibrational energy levels, the quantum numbers J the rotational energy levels (where the spacing between the latter has been exaggerated for clarity).



In summary, the energy levels of a molecule can be written as:

$$E = E^{el} + E^{vib} + E^{rot} \quad (7.53)$$

with the contributions in the approximate ratios:

$$E^{el} : E^{vib} : E^{rot} = 1 : \left(\frac{m_e}{M}\right)^{1/2} : \frac{m_e}{M} \quad (7.54)$$

Thus, the energy difference between levels belonging to two different electronic states is much larger than the difference between two vibrational states within the same electronic state, which, in turn, is much larger than the difference between two rotational levels within the same electronic and vibrational state. This last energy difference is typically 10^{-3} eV, or a few cm^{-1} , so that “pure rotation” transitions lie in the “millimeter” and sub-millimeter part of the spectrum. The energy spacing between two adjacent vibrational levels is typically 0.1-0.3 eV, or $500\text{-}3000 \text{ cm}^{-1}$, so that “vibration-rotation” transitions occur at *infrared* wavelengths. Finally, the energy difference between two electronic states is, as for atoms, typically a few eV, so that *electronic* transitions occur at *visible* and *ultraviolet* wavelengths.

4. Nomenclature

a) Labelling

For historical reasons, electronic states are often given letter designations to label them roughly in order of energy or discovery. For diatomics, the ground state is denoted with the letter X. The letters A, B, C, D, ... are reserved for the lowest excited electronic states of the *same* spin multiplicity as X, usually in order of increasing energy. Sometimes additional states, for example, E', F', ... have to be inserted into the sequence (after later discoveries or new interpretations). The letters a, b, c, d, ... denote the lowest excited states of *different* spin multiplicity from the ground state. For polyatomic molecules, the convention is the same, expect that all letters have a *tilde* superposed, for example, \tilde{X} , \tilde{A} , \tilde{b} , ... because the un-accented letters are needed to add symmetry labels to the electronic states.

In one or two instances, all of the states of a molecule have been re-labelled to correct for a previous major classification error. A notable example of astrophysical interest is C_2 , which for many decades was thought to have a $^3\Pi_u$ ground state. Ballik and Ramsay (1963, *Ap. J.* **137**, 61,

84) proved that the lowest ${}^1\Sigma_g^+$ state lies $\approx 600\text{cm}^{-1}$ below the lowest ${}^3\Pi_u$ state and is actually the ground state of the molecule. In 1969, Herzberg *et al.*, (*Can. J. Phys.* **47**, 2735) discovered some new excited states of C_2 and proposed that the whole system be re-labelled before new states should be designated. Thus, in the old literature, the ground state was denoted $\text{X } {}^3\Pi_u$, whereas the correct notation is $\text{X } {}^1\Sigma_g^+$ and a ${}^3\Pi_u$.

In transitions, it is the convention to *always* list the upper state first, irrespective of whether absorption or emission is considered. For example, in C_2 a transition is denoted as $\text{A } {}^1\Pi_u\text{-X } {}^1\Sigma_g^+$, where in emission $\text{A}\rightarrow\text{X}$. Note that this is the reverse of the usual convention in atomic spectroscopy, where the lower state is listed first (although we haven't followed this convention strictly throughout these notes!). Also, sometimes in the literature on microwave spectra of molecules one sees the lower state listed first.

b. Diatomic molecules

In general, the nomenclature of electronic states is based upon the symmetry properties of a molecule. For example, atoms have *spherical* symmetry, and the total angular momentum L is a good quantum number, so that we can classify the states by the value of L : $L = 0, 1, 2, 3, \dots$ are denoted as S, P, D, F, ... states. Diatomic molecules have cylindrical symmetry, which means that L is no longer a good quantum number; only the component Λ of orbital angular momentum along the internuclear axis is defined, where Λ can be 0, 1, 2, 3, As for atoms, Λ is vector sum of the angular momenta $\vec{\lambda}_i$ of the individual electrons in the molecule $\vec{\Lambda} = \sum_i \vec{\lambda}_i$. All electronic states with $\Lambda > 0$ are doubly degenerate. Classically, this degeneracy can be thought of as being due to electrons orbiting clockwise or anti-clockwise around the internuclear axis, the energy being the same in both cases. If $\Lambda = 0$, there is no orbiting motion, and no degeneracy.

In analogy with the notation for atoms, the states are designated by their value of Λ : $\Lambda = 0, 1, 2, \dots$ correspond to $\Sigma, \Pi, \Delta, \dots$ states, the Greek equivalents of S, P, D, ... used for atoms. One also distinguishes Σ^+ and Σ^- states, depending on whether the electronic wave function is symmetric (+) or antisymmetric (-) with respect to reflection across any plane containing the internuclear axis. For $\Lambda > 0$, one component will have + symmetry, and the other - symmetry, but the symbolism Π^\pm, Δ^\pm is not often used.

If the diatomic molecule has two identical nuclei, such as $\text{H}_2, \text{C}_2, \dots$ subscripts u and g must be added to distinguish functions that are "gerade" or "ungerade" upon inversion through the center of the molecule. Just as for atoms, the total spin S of the electrons in a particular electronic state is indicated by the multiplicity $2S + 1$ as a superscript. Thus, the ground state of the H_2 molecule is denoted as $\text{X } {}^1\Sigma_g^+$.

c) Polyatomic molecules; some elementary symmetry considerations

Molecular symmetry is the unifying thread throughout spectroscopy and molecular structure theory. It makes it possible to classify states, and, more importantly, to determine selection rules without having to do any sophisticated calculations. The application of symmetry arguments to atoms and molecules has its origin in group theory developed by mathematicians, and it is for this reason that the subject is often presented in a rigorous mathematical formulation. However, it is possible to progress quite a long way in understanding molecular symmetry without any such mathematical knowledge, and only some simple arguments will be used below. Other simplified treatments of molecular symmetry and group theory are given by Holas, Ch. 4, Steinfeld Ch. 6, F. A. Cotton, "Chemical Applications of Group Theory" (1963), and M. Tinkham, "Group Theory and Quantum Mechanics" (1964). The latter book contains a more mathematical discussion.

The great utility of group theory lies in its abstractness. Provided any set of elements A, B, C, D, \dots obeys the following four conditions, they form a group:

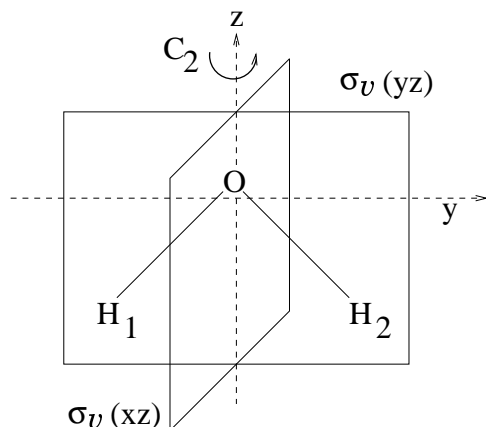


Figure 7.6– An illustration of the various symmetry elements belonging to the C_{2v} group, with water as an illustrative case.

- (1) *Closure*. If A and B are any two members of the group, then their product $A * B$ must also be a member of the group.
- (2) *Associativity*. The rule of combination must be such that the associative law holds. That is, if A , B , and C are any three elements of the group, then $(A * B) * C = A * (B * C)$.
- (3) *Identity*. The group must contain a single element I such that for any element A of the group, $A * I = I * A = A$. I is called the *identity element*.
- (4) *Inverse*. Each element A of the group must have an inverse A^{-1} that is also a member of the group. By the term inverse we mean that $A * A^{-1} = A^{-1} * A = I$, where I is the identity element.

Each molecule has a number of so-called “symmetry elements,” which together comprise the point group to which the molecule belongs (Point groups are so named because of the fact that the symmetry operations in the groups leave at least one point in space unchanged. Space groups leave lines, planes, or polyhedra unchanged, and so are very useful in the crystallographic study of solids.). For molecules, the symmetry operations (in addition to the identity operation) that must be considered include rotation about an axis, reflection about a plane, inversion through a point, or a combination of these operations.

In what follows we’ll take as an example the H_2O molecule. The symmetry elements leave the molecule in an indistinguishable orientation from that before the operation was carried out. This does not mean that the molecule has the exact same orientation, simply that the pattern of equivalent atoms is the same. As Figure 7.6 shows, water has the following symmetry elements:

- (i) the “identity” element I : the symmetry operation I consists of doing nothing to the molecule, so that it may seem too trivial to be of importance. However, it is a necessary element required by the rules of group theory. All molecules have the identity element of symmetry.
- (ii) a “two-fold axis of symmetry” C_2 : rotation of the molecule by $2\pi/n$ radians, with $n=2$, about the z -axis produces a configuration which is indistinguishable from the initial one.
- (iii) a “symmetry plane” $\sigma_v(xz)$ perpendicular to the plane of the molecule, that is, reflection through the plane to an equal distance on the opposite side produces a configuration indistinguishable from the initial one. The subscript ‘ v ’ stands for vertical and implies that the plane is vertical with respect to the highest-fold axis, which is C_2 in this case.
- (iv) a symmetry plane $\sigma_v(yz)$ in the plane of the molecule. Any planar molecule has at least one plane of symmetry.

A molecule with these 4 particular symmetry elements is said to have C_{2v} symmetry. A useful device for thinking about groups is what is called the multiplication table, which tabulates the products of various pairs of elements within the group. Clearly, the elements of the multiplication table must also be elements in the group. For the C_{2v} group, the multiplication table shown below.

$$\begin{array}{l} \hat{I} \\ \hat{C}_2 \\ \hat{\sigma}_v(xz) \\ \hat{\sigma}_v(yz) \end{array} \begin{pmatrix} \hat{I} & \hat{C}_2 & \hat{\sigma}_v(xz) & \hat{\sigma}_v(yz) \\ \hat{I} & \hat{C}_2 & \hat{\sigma}_v(xz) & \hat{\sigma}_v(yz) \\ \hat{C}_2 & \hat{I} & \hat{\sigma}_v(yz) & \hat{\sigma}_v(xz) \\ \hat{\sigma}_v(xz) & \hat{\sigma}_v(yz) & \hat{I} & \hat{C}_2 \\ \hat{\sigma}_v(yz) & \hat{\sigma}_v(xz) & \hat{C}_2 & \hat{I} \end{pmatrix}$$

In constructing group multiplication tables, it is helpful to remember that in each row or column of the table each element of the group appears only once. You'll notice that certain products in the multiplication table above block-diagonalize into like symmetry elements. These elements are said to be *conjugate*, that is for elements P and Q there is another element X of the group such that $P = X^{-1}QX$. Each group of mutually conjugate elements is called a *class*. For the C_{2v} group each element is in its own class, for the C_{3v} group the C_3 and C_3^2 elements form a class, as do the three vertical reflection planes.

From these tables and a consideration of how the symmetry elements affect various coordinate systems, it is possible to come up with a variety of matrices that multiply in the same way as the symmetry elements do. Any set of non-null square matrices that multiply in the same way as the elements of a group is said to form a *representation* of that group, and the order of the matrices is called the *dimension* of the representation. Not all representations are created equal, that is, some are more useful than others. If the matrices of a representation can be converted by the same similarity transformation into the same block diagonal form, the representation is said to be *reducible*, otherwise the representation is said to be *irreducible*. In spectroscopy, we'll be concerned nearly exclusively with the *irreducible* representations of point groups.

In particular, we'll just state here (for more information consult the books noted above) that in fact the full matrices are often not needed – their traces alone can provide sufficient information. If, in a certain representation, the matrix $\mathbf{D}(\hat{R})$ corresponds to the symmetry operation \hat{R} , then the trace of $\mathbf{D}(\hat{R})$ is called the *character* of \hat{R} for that representation. Tabulations of the characters of the various representations for a group are called, not surprisingly, character tables, and a wide variety of them are presented in the back of most spectroscopy texts. By construction, the classes are listed on the horizontal header of the table, while the irreducible representations are listed on the vertical header to the left. For these irreducible representations and character tables, there are five important theorems that are useful in considering the connection between group theory and molecular structure:

- (1) The number of non-equivalent irreducible representations of a group is equal to the number of classes in that group.
- (2) The sum of the squares of the dimensions of all the non-equivalent irreducible representations of a group is equal to the order of the group.
- (3) The sum of the squares of the absolute values of the characters in any irreducible representation is equal to the order of the group.
- (4) The characters of two non-equivalent irreducible representations i and j satisfy

$$\sum_{\hat{R}} \chi_i^*(\hat{R})\chi_j(\hat{R}) = 0 \quad (11.1)$$

where $\chi_i(\hat{R})$ and $\chi_j(\hat{R})$ are the characters of the symmetry operation \hat{R} in the representations i and j , and where the sum runs over the h symmetry operations of the group.

(5) If the characters for some particular representation i satisfy

$$\sum_{\hat{R}} |\chi_i(\hat{R})|^2 = h \quad (11.2)$$

then i is irreducible.

Theorem (4) implies that two non-equivalent irreducible representations cannot have the same set of characters, while (3) and (4) can be combined into the so-called Great Orthogonality Theorem:

$$\sum_{\hat{R}} \chi_i^*(\hat{R}) \chi_j(\hat{R}) = h \delta_{ij} \quad (11.3)$$

which is very useful in putting together character tables. For the C_{2v} group, which is of order 4, there are four symmetry elements and so each of the four irreducible representations must be nondegenerate. For the C_{3v} group, appropriate for symmetric tops like ammonia or acetonitrile, the number of symmetry elements is six (the identity, \hat{C}_3 , \hat{C}_3^2 , and three $\hat{\sigma}_v$ elements). It turns out in this case that there are three irreducible representations, and so

$$l_1^2 + l_2^2 + l_3^2 = 6 \quad (11.4)$$

The only set of three integers which satisfies (11.4) is 1,1,2, and so the C_{3v} group must have two non-degenerate and one doubly degenerate irreducible representations. For the C_{2v} group, the character table is as follows:

Table 7.2– Different “symmetry types” in the character table of the C_{2v} group

I	C_2	σ_{xz}	σ_{yz}	Label	
+	+	+	+	A_1	z
+	+	–	–	A_2	
+	–	+	–	B_1	x
+	–	–	+	B_2	y

One can show that for a molecule with C_{2v} symmetry, only 4 different “types of symmetry” exist, which are listed in Table 7.2. The table shows how a function of a certain symmetry type, also called a ‘representation’, behaves under each of the symmetry operations. They are either unchanged (+) or they change sign (–). The different irreducible representations, or symmetry types, are given labels: A_1 , A_2 , B_1 , and B_2 in this case. Functions which are symmetric with respect to the principle symmetry axis C_n are denoted with the letter A, whereas those that are antisymmetric with respect to C_n are denoted with the letter B. The subscripts 1 or 2 then follow from the behavior under the other elements $\sigma_v(xz)$ and $\sigma_v(yz)$. A_1 is called the “totally symmetric” representation, must always be present, and is always listed first in character tables. As they should be, the character sets for each of the representations are orthogonal to each other. Also listed in Table 7.2 are the symmetry types of the (x, y, z) coordinates (or translation operators). We’ll find these to be quite useful in the consideration of selection rules in just a bit.

For groups with irreducible representations that are degenerate, the letter E refers to those that are two dimensional, while three, four, and five dimensional irreducible representations are labelled

T, G, H . If a molecule has a center of symmetry (is in CO_2 or SF_6 , for example, a subscript g (for *gerade*) or u (for *ungerade*) is added according to whether the character is symmetric or antisymmetric under inversion. By convention, the identity operator is always listed first in the header row of the character table, and the number within the first column of the character table itself provides you with the dimensionality of the irreducible representation.

Given the abstractness of group theory, why do we care? Consider, for a moment, the electronic and vibrational wave functions of a molecule. Using the Born-Oppenheimer approximation, we know that they must satisfy the Schrödinger equation, or $\hat{H}\psi_{j,v} = E_v\psi_{j,v}$, where \hat{H} , $\psi_{j,v}$, and E_v are either the electronic or vibrational Hamiltonian, wave functions, and energies. The subscript v labels the energy levels and the subscript j distinguishes the wave functions belonging to each level E_v . Thus, if the v th level is n -fold degenerate, $j = 1, 2, \dots, n$. If \hat{O}_R is an operator corresponding to one of the symmetry operations in the point group of a molecule, it can be shown that

$$[\hat{O}_R, \hat{H}] = 0$$

The proof of this is straightforward, but tedious, and so we omit it here. Clearly the potential terms do not change if the molecular framework is altered into one which is undistinguishable from the original, but the kinetic energy operator is also unchanged and so the commutation relation holds (for a full discussion of these points, pp. 117-123 of *Molecular Symmetry* by D.S. Schonland (Van Norstrand, Princeton, 1965) is a good place to start). Thus, we are free to choose our wavefunctions such that they are eigenfunctions not only of the total energy but also of the symmetry operations within the point group. This has two critical implications:

- (1) The wave functions of each electronic or vibrational level of a molecule transform according to an irreducible representation of the molecular point group, and
- (2) The degree of degeneracy of an energy level, barring “accidental degeneracies,” is equal to the dimension of the irreducible representation to which its wavefunction belongs.

Thus, even without solving the Schrödinger equation, we *know* the possible degeneracies at the very start! Every vibrational level of a C_{2v} molecule must be non-degenerate, E levels are doubly degenerate, T levels are triply degenerate, etc. Given the behavior we know must exist under the individual symmetry operations of the group, we also know a great deal about the quantitative behavior of the wavefunctions (number of nodes, symmetry, and so forth). As a simple example, let’s again consider the water molecule, and how its molecular orbitals are assembled.

First we examine the symmetry properties of some atomic orbitals attached to the nuclei, for example, the 1s, 2s, and 2p function on O. What happens to each of these functions if the symmetry operations are applied? Clearly, the 1s and 2s orbitals remain unchanged, as does the 2p_z orbital. However, under some symmetry operations, the 2p_x and 2p_y orbitals are transformed into themselves, but under others, they end up as “-” themselves (c.f. Table 7.3).

Now consider the hydrogen 1s orbitals. Under C_2 and $\sigma_v(xz)$, the 1s orbital on atom #1 is transformed into the 1s orbital on atom #2 and *vice versa*. Thus, the individual 1s orbitals do not have a definite symmetry type, since they do not transform into + or - themselves. However, the $1s(\text{H}_1) + 1s(\text{H}_2)$ and $1s(\text{H}_1) - 1s(\text{H}_2)$ combinations do have a definite character.

The total wavefunction of the H_2O molecule is built up as the product of a number of one electron orbitals, such as those listed in Table 7.3, each with a definite symmetry type. Thus, the total wave function has a definite symmetry type, and this type can be used as the “label” each electronic state. For example, the ground state wave function of H_2O is totally symmetric, so that the state can be labelled as $\tilde{X}^1\text{A}_1$; the first excited electronic state is the $\tilde{A}^1\text{B}_1$ state.

Having classified the electronic states of H_2O as definite symmetry types within C_{2v} symmetry, we can then use the very powerful theorems of group theory to immediately say whether a certain

Table 7.3– Atomic Orbital Symmetries in Water

Function	I	C ₂	σ_{xz}	σ_{yz}	Label
1s(O)	+	+	+	+	A ₁
2s(O)	+	+	+	+	A ₁
2p _z (O)	+	+	+	+	A ₁
2p _x (O)	+	–	+	–	B ₁
2p _y (O)	+	–	–	+	B ₂
1s(H ₁)	+	1s(H ₂)	1s(H ₂)	+	?
1s(H ₂)	+	1s(H ₁)	1s(H ₁)	+	?
1s(H ₁) + 1s(H ₂)	+	+	+	+	A ₁
1s(H ₁) – 1s(H ₂)	+	–	–	+	B ₂

transition will be, for example, electric dipole allowed or not, without any calculations! The physical reasoning is exactly the same as for the case of the parity selection rule in atoms: the integrand has to be a totally symmetric function, because otherwise integration over the whole coordinate space will give zero. In group-theoretical language: the product of the symmetry types of the wave functions involved and that of the dipole operator must be A₁.

For example, in the case of H₂O, we have to figure out whether the integrand in

$$\langle \tilde{A}^1 B_1 | \vec{d} | \tilde{X}^1 A_1 \rangle = \int \Psi_A^* \vec{d} \Psi_X d^3x \quad (7.55)$$

is totally symmetric. One can show that the electric dipole operator $\vec{d}=(x,y,z)$ also has definite symmetry. Just as the 2p-functions, the x-component transforms according to B₁, the y-component according to B₂, and the z-component according to A₁ symmetry. (These are noted in the last column of Table 7.2). We can then use simple multiplication rules for the symmetry types to find the overall symmetry of the integrand of (7.55):

$$A \times A = A; \quad A \times B = B; \quad B \times B = A; \quad 1 \times 1 = 1; \quad 1 \times 2 = 2; \quad 2 \times 2 = 1. \quad (7.56)$$

Thus, for the z-component of the dipole operator we obtain:

$$B_1 \times A_1 \times A_1 = B_1 \times A_1 = B_1 \neq A_1, \quad (7.57)$$

so that the $\tilde{A}^1 B_1 - \tilde{X}^1 A_1$ transition cannot occur by the z-component of the electric dipole moment operator. For the other components, we find

$$\text{x – component : } B_1 \times B_1 \times A_1 = A_1 \times A_1 = A_1 \quad \dots \quad \text{yes!} \quad (7.58)$$

$$\text{y – component : } B_1 \times B_2 \times A_1 = A_2 \times A_1 = A_2 \neq A_1. \quad (7.59)$$

Thus, the $\tilde{A}^1 B_1 - \tilde{X}^1 A_1$ transition is x-polarized and electric dipole allowed.

One can show that there are only a handful of possible symmetry groups to which molecules can belong; C_{2v} is certainly one of the most common ones. for each symmetry group, one can label the electronic states according to their symmetry types or representations. “Character” tables of the possible representations, and their behavior under the symmetry operations of a certain group, are given in the back of the textbooks mentioned above.