

Notes on:
Molecular Physics

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1. Introduction

1.1 Textbooks

There are a number of textbooks to be recommended for those who wish to study molecular spectroscopy; the best ones are:

1) The series of books by Gerhard Herzberg

Molecular Spectra and Molecular Structure

I. Spectra of Diatomic Molecules

II. Infrared and Raman Spectroscopy of Polyatomic Molecules

III. Electronic Spectra of Polyatomic Molecules

2) Peter F. Bernath

Spectra of Atoms and Molecules

3) Philip R. Bunker and Per Jensen

Molecular Symmetry and Spectroscopy, 2nd edition

4) Hélène Lefebvre-Brion and Robert W. Field

Perturbations in the Spectra of Diatomic Molecules

A recent very good book is that of:

5) John Brown and Alan Carrington

Rotational Spectroscopy of Diatomic Molecules

1.2 Some general remarks on the spectra of molecules

Molecules are different from atoms:

- Apart from electronic transitions, always associated with the spectra of atoms, also purely vibrational or rotational transitions can occur. These transitions are related to radiation by multipole moments, similar to the case of atoms. While in atoms a redistribution of the electronic charge occurs in a molecule the transition can occur through a permanent dipole moment related to the charges of the nuclei.

- Superimposed on the spectral lines related to electronic transitions, there is always a rovibrational structure, that makes the molecular spectra much richer. In the case of polyatomics three different moments of inertia give rise to rotational spectra, in diatomics only a single rotational component. Each molecule has $3n-6$ vibrational degrees of freedom where n is the number of atoms.

- Atoms can ionize and ionization continua are continuous quantum states that need to be considered. In molecules, in addition, there are continuum states associated with the dissociation of the molecule. Bound states can couple, through some interaction, to the continua as a result of which they (pre)-dissociate.

1.3 Some examples of Molecular Spectra

The first spectrum is that of iodine vapour. It shows resolved vibrational bands, recorded by the classical photographic technique, in the so-called $B^3\Pi_{0u}^+ - X^1\Sigma_g^+$ system observed in absorption; the light features signify intense absorption. The discrete lines are the resolved vibrations in the excited state going over to the dissociative continuum at point C. Leftward of point C the spectrum looks like a continuum but this is an effect of the poor resolution. This spectrum demonstrates that indeed absorption is possible (in this case strong) to the continuum quantum state.

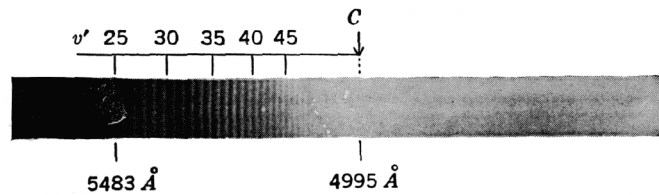
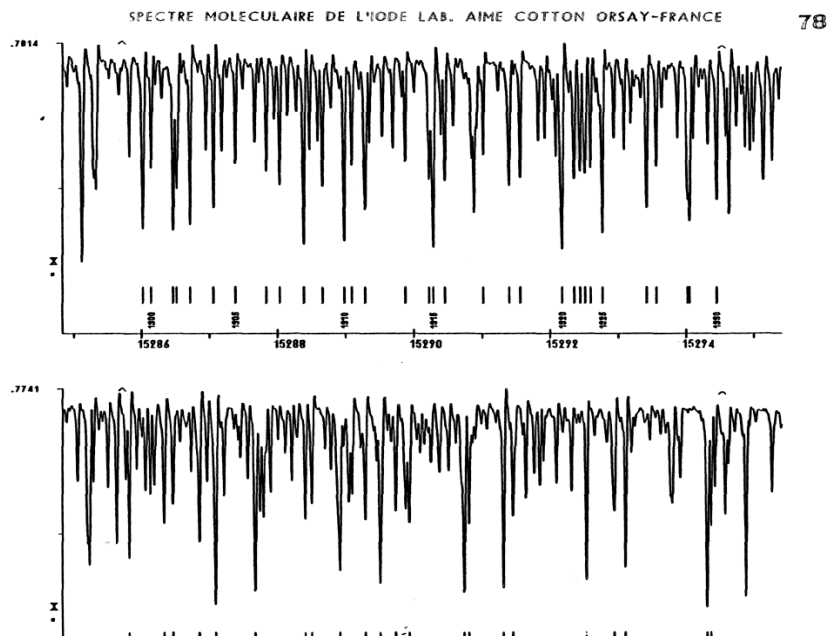
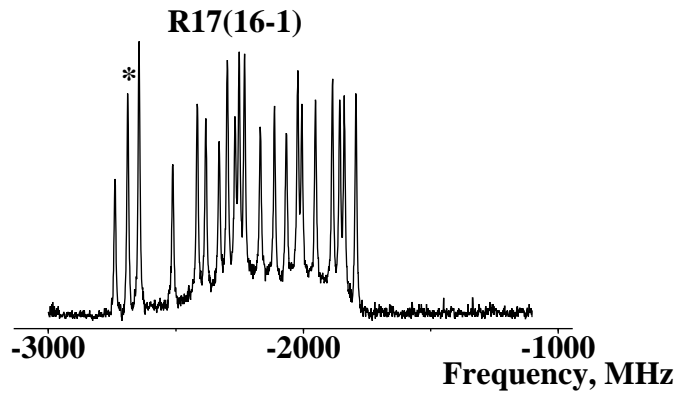


Fig. 15. Absorption Spectrum of I_2 Vapor. The arrow denoted by C indicates the position of the convergence limit of the bands, where a continuous absorption joins on.

Later the absorption spectrum was reinvestigated by Fourier-transform spectroscopy resulting in the important iodine-atlas covering the range 500-800 nm. There is several lines in each cm^{-1} interval and the numbers are well-documented and often used as a reference for wavelength calibration. Note that the resolution is determined by two effects: (1) Doppler broadening and (2) unresolved hyperfine structure. The figure shows only a small part of the iodine atlas of Gerstenkorn and Luc.



The hyperfine structure can be resolved when Doppler-free laser spectroscopic techniques are invoked. The following spectrum is recorded with saturation spectroscopy. A single rotational line of a certain band is shown to consist of 21 hyperfine components. These are related to the angular momentum of the two $I=5/2$ nuclei in the I_2 molecule.



Usually molecular spectra appear as regular progressions of lines. In the vibrational bands of diatomic molecules the rotational lines are in first order at equal separation. If a quantum state is perturbed that may be clearly visible in the spectrum. This is demonstrated in the spectra of two bands of the SiO molecule in the $H^1\Sigma^+ - X^1\Sigma^+$ system. The upper spectrum pertains to the (0,0) band and is unperturbed; the lower one of the (1,0) band clearly shown perturbation of the rotational structure.

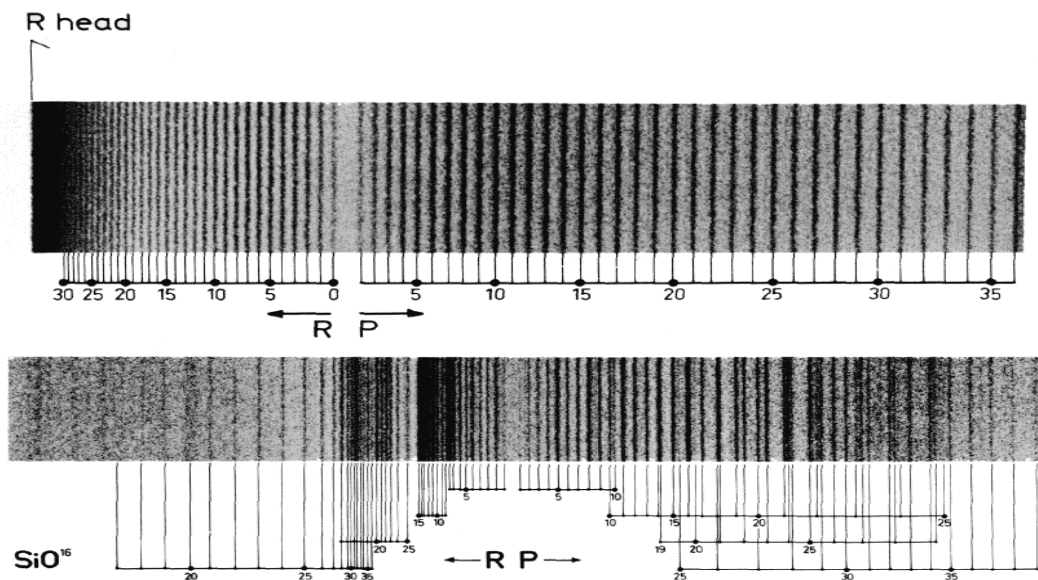


Fig. 1.1 A comparison of the SiO $H^1\Sigma^+ - X^1\Sigma^+$ 0,0 (top) and 1,0 (bottom) bands. The 0,0 band at 1435 Å is perturbation-free, but perturbations in the $v=1$ level of the $H^1\Sigma^+$ state cause the 1,0 band at 1413 Å to be shattered. (Courtesy I. Renhorn.)

2. Energy levels in molecules; the quantum structure

2.1. The Born-Oppenheimer approximation

The Hamiltonian for a system of nuclei and electrons can be written as:

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 + V(\vec{R}, \vec{r})$$

where the summation i refers to the electrons and A to the nuclei. The first term on the right corresponds to the kinetic energy of the electrons, the second term to the kinetic energy of the nuclei and the third term to the Coulomb energy, due to the electrostatic attraction and repulsion between the electrons and nuclei. The potential energy term is equal to:

$$V(\vec{R}, \vec{r}) = -\sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |R_A - R_B|} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

The negative terms represent attraction, while the positive terms represent Coulomb-repulsion. Note that a treatment with this Hamiltonian gives a non-relativistic description of the molecule, in which also all spin-effects have been ignored.

Now assume that the wave function of the entire molecular system is separable and can be written as:

$$\Psi_{mol}(\vec{r}_i, \vec{R}_A) = \psi_{el}(\vec{r}_i; \vec{R}) \chi_{nuc}(\vec{R})$$

where ψ_{el} represents the electronic wave function and χ_{nuc} the wave function of the nuclear motion. In this description it is assumed that the electronic wave function can be calculated for a particular nuclear distance R . Then:

$$\begin{aligned} \nabla_i^2 \psi_{el} \chi_{nuc} &= \chi_{nuc} \nabla_i^2 \psi_{el} \\ \nabla_A^2 \psi_{el} \chi_{nuc} &= \psi_{el} \nabla_A^2 \chi_{nuc} + 2(\nabla_A \psi_{el})(\nabla_A \chi_{nuc}) + \chi_{nuc} \nabla_A^2 \psi_{el} \end{aligned}$$

The Born-Oppenheimer approximation now entails that the derivative of the electronic wave function with respect to the nuclear coordinates is small, so $\nabla_A \psi_{el}$ is negligibly small. In words this means that the nuclei can be considered stationary, and the electrons adapt their positions instantaneously to the potential field of the nuclei. The justification for this originates in the fact that the mass of the electrons is several thousand times smaller than the mass of the nuclei. Indeed the BO-approximation is the least appropriate for the light H_2 -molecule.

If we insert the separable wave function in the wave equation:

$$H\Psi = E\Psi$$

then it follows:

$$\begin{aligned}
H\Psi_{mol} &= \chi_{nuc} \left\{ -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} \right\} \psi_{el} + \\
&+ \psi_{el} \left\{ \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |R_A - R_B|} - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 \right\} \chi_{nuc} = E_{total} \Psi_{mol}
\end{aligned}$$

The wave equation for the electronic part can be written separately and solved:

$$\left\{ -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} \right\} \psi_{el}(\vec{r}_i; \vec{R}) = E_{el}(\vec{R}) \psi_{el}(\vec{r}_i; \vec{R})$$

for each value of \vec{R} . The resulting electronic energy can then be inserted in the wave equation describing the nuclear motion:

$$\left\{ -\sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |R_A - R_B|} \right\} \chi_{nuc}(\vec{R}) + E_{el}(\vec{R}) \chi_{nuc}(\vec{R}) = E_{total} \chi_{nuc}(\vec{R})$$

We have now in a certain sense two separate problems related to two wave equations. The first relates to the electronic part, where the goal is to find the electronic wave function $\psi_{el}(\vec{r}_i; \vec{R})$ and an energy $E_{el}(\vec{R})$. This energy is related to the electronic structure of the molecule analogously to that of atoms. Note that here we deal with an (infinite) series of energy levels, a ground state and excited states, dependent on the configurations of all electrons. By searching the eigen values of the electronic wave equation for each value of R we find a function for the electronic energy, rather than a single value.

Solution of the nuclear part then gives the eigen functions $\chi_{nuc}(\vec{R})$ and eigen energies:

$$E_{nuc} = E_{total} - E_{el}(\vec{R}) = E_{vib} + E_{rot}$$

In the BO-approximation the nuclei are treated as being infinitely heavy. As a consequence the possible isotopic species (HCl and DCl) have the same potential in the BO-picture. Also all couplings between electronic and rotational motion is neglected (e.g. Λ -doubling).

2.2. Potential energy curves

The electrostatic repulsion between the positively charged nuclei:

$$V_N(\vec{R}) = \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |R_A - R_B|}$$

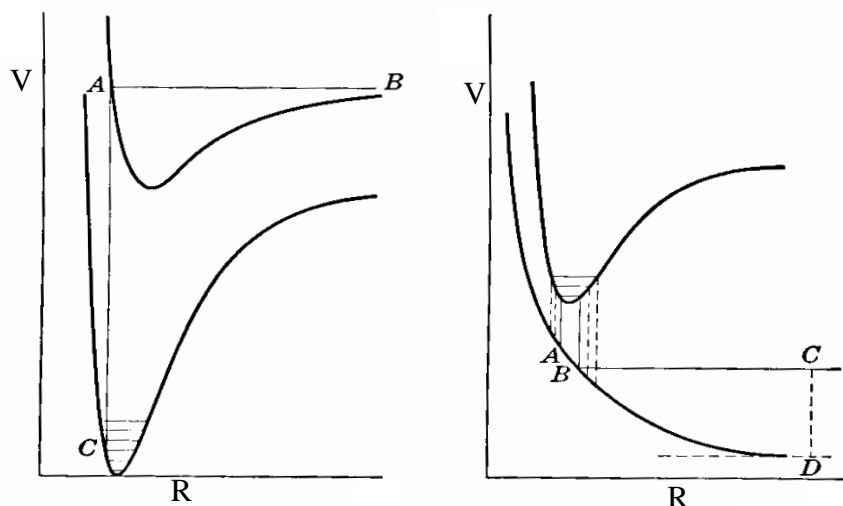
is a function of the internuclear distance(s) just as the electronic energy. These two terms can be taken together in a single function representing the potential energy of the nuclear motion:

$$V(\vec{R}) = V_{nuc}(\vec{R}) + E_{el}(\vec{R})$$

In the case of a diatom the vector-character can be removed; there is only a single internuclear distance between two atomic nuclei.

In the figure below a few potential energy curves are displayed, for ground and excited states. Note that:

- at small internuclear separation the energy is always large, due to the dominant role of the nuclear repulsion
- it is not always so that the electronic ground state corresponds to a bound state
- electronically excited states can be bound.



Electronic transitions can take place, just as in the atom, if the electronic configuration in the molecule changes. In that case there is a transition from one potential energy curve in the molecule to another potential energy curve. Such a transition is accompanied by absorption or emission of radiation; it does not make a difference whether or not the state is bound. The binding (chemical binding) refers to the motion of the nuclei.

2.3. Rotational motion in a diatomic molecule

Starting point is the wave equation for the nuclear motion in the Born-Oppenheimer approximation:

$$\left[-\frac{\hbar^2}{2\mu} \Delta_{\vec{R}} + V(\vec{R}) \right] \chi_{nuc}(\vec{R}) = E \chi_{nuc}(\vec{R})$$

where, just as in the case of the hydrogen atom the problem is transferred to one of a reduced mass. Note that μ represents now the reduced mass of the nuclear motion:

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

Before searching for solutions it is interesting to consider the similarity between this wave equation and that of the hydrogen atom. If a $1/R$ potential is inserted then the solutions (eigenvalues and eigenfunctions) of the hydrogen atom would follow. Only the wave function $\chi_{nuc}(\vec{R})$ has a different meaning: it represents the motion of the nuclei in a diatomic mole-

cule. In general we do not know the precise form of the potential function $V(R)$ and also it is not infinitely deep as in the hydrogen atom.

Analogously to the treatment of the hydrogen atom we can proceed by writing the Laplacian in spherical coordinates:

$$\Delta_{\vec{R}} = \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{R^2 \sin \theta} \frac{\partial^2}{\partial \phi^2}$$

Now a vector-operator \vec{N} can be defined with the properties of an angular momentum:

$$\begin{aligned} N_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) = i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \\ N_y &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) = i\hbar \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\ N_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = i\hbar \frac{\partial}{\partial \phi} \end{aligned}$$

The Laplacian can then be written as:

$$\Delta_{\vec{R}} = \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) - \frac{\vec{N}^2}{\hbar^2 R^2}$$

The Hamiltonian can then be reduced to:

$$\left[-\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} \vec{N}^2 + V(R) \right] \chi_{nuc}(\vec{R}) = E \chi_{nuc}(\vec{R})$$

Because this potential is only a function of internuclear separation R , the only operator with angular dependence is the angular momentum N^2 , analogously to L^2 in the hydrogen atom. The angular dependent part can again be separated and we know the solutions:

$$\begin{aligned} \vec{N}^2 |N, M\rangle &= \hbar^2 N(N+1) |N, M\rangle \quad \text{with} \quad N = 0, 1, 2, 3, \text{ etc} \\ N_z |N, M\rangle &= \hbar M |N, M\rangle \quad \text{with} \quad M = -N, -N+1, \dots, N \end{aligned}$$

The eigenfunctions for the separated angular part are thus represented by the well-known spherical harmonics:

$$|N, M\rangle = Y_{NM}(\theta, \phi)$$

and the wave function for the molecular Hamiltonian:

$$\chi_{nuc}(\vec{R}) = \mathfrak{R}(R) Y_{NM}(\theta, \phi)$$

Inserting this function gives us an equation for the radial part:

$$\left[-\frac{\hbar^2}{2\mu R^2} \frac{d}{dR} \left(R^2 \frac{d}{dR} \right) + N(N+1) + V(R) \right] \mathfrak{R}(R) = E_{vN} \mathfrak{R}(R)$$

Now the wave equation has no partial derivatives, only one variable R is left.

2.4. The rigid rotor

Now assume that the molecule consists of two atoms rigidly connected to each other. That means that the internuclear separation remains constant, e.g. at a value R_e . Since the zero point of a potential energy can be arbitrarily chosen we choose $V(R_e)=0$. The wave equation reduces to:

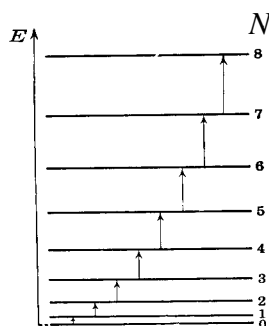
$$\left[\frac{1}{2\mu R_e^2} \vec{N}^2 \right] \chi_{nuc}(\vec{R}_e) = E_{rot} \chi_{nuc}(\vec{R}_e)$$

The eigenvalues follow immediately:

$$E_N = \frac{\hbar^2}{2\mu R_e^2} N(N+1) = BN(N+1)$$

where B is defined as the *rotational constant*. Hence a ladder of rotational energy levels appears in a diatom. Note that the separation between the levels is not constant, but increases with the rotational quantum number N .

For an HCl molecule the internuclear separation is $R_e=0.129$ nm; this follows from the analysis of energy levels. Deduce that the rotational constants 10.34 cm^{-1} .



This analysis gives also the isotopic scaling for the rotational levels of an isotope:

$$B \propto \frac{1}{\mu}$$

2.5 The elastic rotor; centrifugal distortion

In an elastic rotor R is no longer constant but increases with increasing amount of rotation as a result of centrifugal forces. This effect is known as *centrifugal distortion*. An estimate of this effect can be obtained from a simple classical picture. As the molecule stretches the

centrifugal force F_c is, at some new equilibrium distance R_e' , balanced by the elastic binding force F_e , which is harmonic. The centripetal and elastic forces are:

$$F_c = \mu\omega^2 R_e' \cong \frac{N^2}{\mu R_e'^3} \quad F_e = k(R_e' - R_e)$$

By equating $F_c = F_e$ and by assuming $R_e' \approx R_e$ it follows:

$$R_e' - R_e = \frac{N^2}{\mu k R_e^3}$$

The expression for the rotational energy including the centrifugal effect is obtained from:

$$E = \frac{N^2}{2\mu R_e'^2} + \frac{1}{2}(R_e' - R_e)$$

Now use R_e' for the above equations and expanding the first term of the energy expression it follows:

$$E = \frac{N^2}{2\mu R_e^2} \left(1 + \frac{N^2}{\mu k R_e^4}\right)^{-2} + \frac{1}{2} \frac{N^4}{\mu^2 k R_e^6} \cong \frac{N^2}{2\mu R_e^2} - \frac{N^4}{2\mu^2 k R_e^6} +$$

The quantum mechanical Hamiltonian is obtained by replacing N by the quantum mechanical operator \hat{N} . It is clear that the spherical harmonics $Y_{NM}(\Omega)$ are also solutions of that Hamiltonian. the result for the rotational energy can be expressed as:

$$E_N = BN(N+1) - DN^2(N+1)^2$$

where:

$$D = \frac{4B_e^3}{\omega_e^2}$$

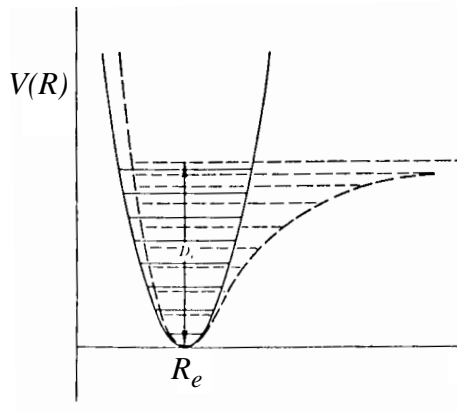
is the centrifugal distortion constant. This constant is quite small, e.g. $5.32 \times 10^{-4} \text{ cm}^{-1}$ in HCl, but its effect can be quite large for high rotational angular momentum states (N^4 dependence). Selection rules for the elastic rotor are the same as for the rigid rotor (see later).

2.6. Vibrational motion in a non-rotating diatomic molecule

If we set the angular momentum N equal to 0 in the Schrödinger equation for the radial part and introduce a function $Q(R)$ with $\mathfrak{R}(R) = Q(R)/R$ than a somewhat simpler expression results:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) \right] Q(R) = E_{vib} Q(R)$$

This equation cannot be solved straightforwardly because the exact shape of the potential $V(R)$ is not known. For bound states of a molecule the potential function can be approximated with a quadratic function. Particularly near the bottom of the potential well that approximation is valid (see figure).



Near the minimum $R=R_e$ a Taylor-expansion can be made, where we use $\rho = R - R_e$:

$$V(R) = V(R_e) + \left. \frac{dV}{dR} \right]_{R_e} \rho + \left. \frac{1}{2} \frac{d^2 V}{dR^2} \right]_{R_e} \rho^2 +$$

and:

$$V(R_e) = 0 \quad \left. \frac{dV}{dR} \right]_{R_e} = 0 \quad \left. \frac{d^2 V}{dR^2} \right]_{R_e} = k$$

Here again the zero for the potential energy can be chosen at R_e . The first derivative is 0 at the minimum and k is the spring constant of the vibrational motion. The wave equation reduces to the known problem of the 1-dimensional quantum mechanical harmonic oscillator:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{d\rho^2} + \frac{1}{2} k \rho^2 \right] Q(\rho) = E_{vib} Q(\rho)$$

The solutions for the eigenfunctions are known:

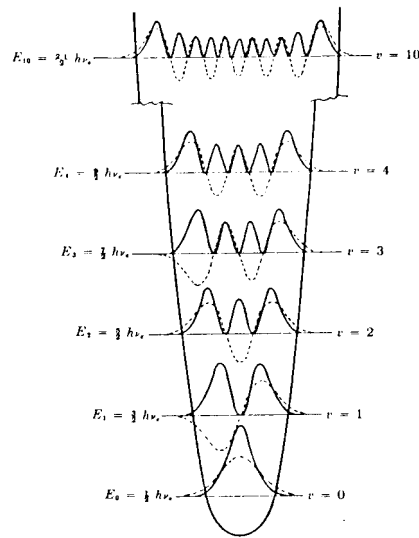
$$Q_v(\rho) = \frac{2^{-v/2} \alpha^{1/4}}{\sqrt{v! \pi^{1/4}}} \exp\left[-\frac{1}{2} \alpha \rho^2\right] H_v(\sqrt{\alpha} \rho) \quad \text{with} \quad \alpha = \frac{\mu \omega_e}{\hbar} \quad \omega_e = \sqrt{\frac{k}{\mu}}$$

where H_v are the Hermite polynomials; the energy eigenvalues are:

$$E_{vib} = \hbar \omega_e \left(v + \frac{1}{2} \right)$$

with the quantum number v that runs over values $v=0,1,2,3$.

From this we learn that the vibrational levels in a molecule are equidistant and that there is a contribution from a zero point vibration. The averaged internuclear distance can be calculated for each vibrational quantum state with $|Q_v(\rho)|^2$. These expectation values are plotted in the figure. Note that at high vibrational quantum numbers the largest density is at the classical turning points of the oscillator.



The isotopic scaling for the vibrational constant is

$$\omega_e \propto \frac{1}{\sqrt{\mu}}$$

Note also that the zero point vibrational energy is different for the isotopes.

2.7. Anharmonicity in the vibrational motion

The anharmonic vibrator can be represented with a potential function:

$$V(\rho) = \frac{1}{2}k\rho^2 + k'\rho^3 + k''\rho^4$$

On the basis of energies and wave functions of the harmonic oscillator, that can be used as a first approximation, quantum mechanical perturbation theory can be applied to find energy levels for the anharmonic oscillator (with parameters k' and k''):

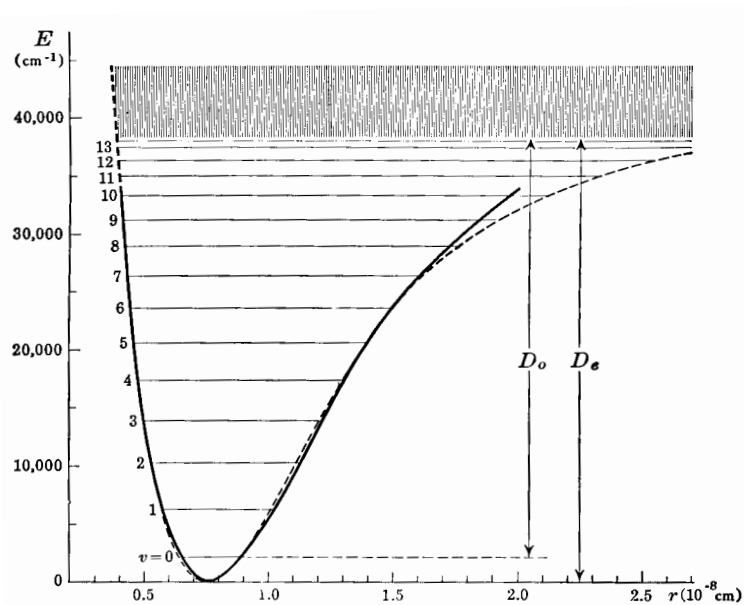
$$E_{vib} = \hbar\omega_e\left(v + \frac{1}{2}\right) - \frac{15}{4}\frac{k'^2}{\hbar\omega_e}\left(\frac{\hbar}{\mu\omega_e}\right)^3\left(v^2 + v + \frac{11}{30}\right) + O(k'')$$

In the usual spectroscopic practice an expansion is written (in cm^{-1}),

$$G(v) = \omega_e\left(v + \frac{1}{2}\right) - \omega_ex_e\left(v + \frac{1}{2}\right)^2 + \omega_ey_e\left(v + \frac{1}{2}\right)^3 + \omega_ez_e\left(v + \frac{1}{2}\right)^4 +$$

with ω_e , ω_ex_e , ω_ey_e and ω_ez_e to be considered as *spectroscopic constants*, that can be determined from experiment.

Note that for the anharmonic oscillator the separation between vibrational levels is no longer constant. In the figure below the potential and the vibrational levels for the H_2 -molecule are shown.



H_2 has 14 bound vibrational levels. The shaded area above the dissociation limit contains a continuum of states. The molecule can occupy this continuum state! For D_2 there are 17 bound vibrational states.

A potential energy function that often resembles the shape of bound electronic state potentials is the *Morse Potential* defined as:

$$V(R) = D_e [1 - e^{-a(R-R_e)}]^2$$

where the three parameters can be adjusted to the true potential for a certain molecule. One can verify that this potential is not so good at $r \rightarrow \infty$. By solving the Schrödinger equation with this potential one can derive the spectroscopic constants:

$$\omega_e = \frac{a}{2\pi} \sqrt{\frac{2D_e}{\mu}} \quad x_e = \frac{\hbar\omega_e}{4D_e} \quad \alpha_e = 6 \sqrt{\frac{x_e B_e^3}{\omega_e}} - 6 \frac{B_e^2}{\omega_e} \quad B_e = \frac{\hbar^2}{2\mu R_e^2}$$

The energies of the rovibrational levels then follow via the equation:

$$E_{vN} = \omega_e \left(v + \frac{1}{2}\right) - x_e \omega_e \left(v + \frac{1}{2}\right)^2 + B_e N(N+1) - D_e N^2(N+1)^2 - \alpha_e \left(v + \frac{1}{2}\right) N(N+1) +$$

Another procedure that is often used for representing the rovibrational energy levels within a certain electronic state of a molecule is that of Dunham, first proposed in 1932:

$$E_{vN} = \sum_{k,l} Y_{kl} \left(v + \frac{1}{2}\right)^k N^l (N+1)^l$$

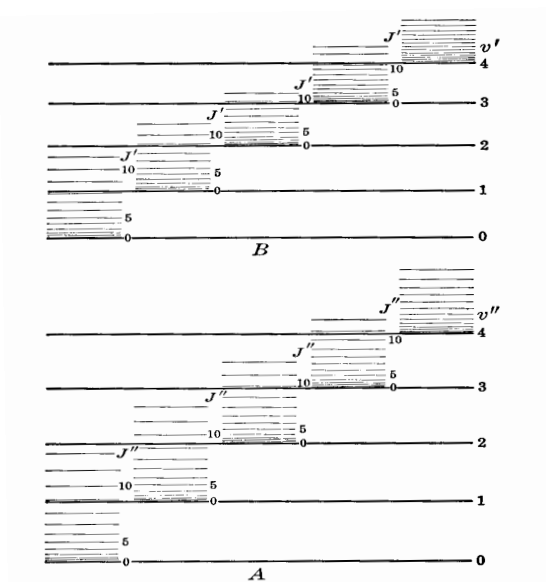
In this procedure the parameters Y_{kl} are fit to the experimentally determined energy levels; the parameters are to be considered a mathematical representation, rather than constants with

a physical meaning. nevertheless a relation can be established between the Y_{kl} and the molecular parameters B_e, D_e , etc. In approximation it holds:

$$Y_{10} \approx \omega_e \quad Y_{01} \approx B_e \quad Y_{20} \approx -\omega_e x_e \quad Y_{11} \approx \alpha_e \quad Y_{30} \approx \omega_e y_e$$

2.8. Energy levels in a diatomic molecule: electronic, vibrational and rotational

In a molecule there are electronic energy levels, just as in an atom, determined by the configuration of orbitals. Superimposed on that electronic structure there exists a structure of vibrational and rotational levels as depicted in the figure.



Transitions between levels can occur, e.g. via electric dipole transitions, accompanied by absorption or emission of photons. Just as in the case of atoms there exist selection rules that determine which transitions are allowed.

2.9. The RKR-procedure

The question is if there exists a procedure to derive a potential energy curve from the measurements on the energy levels for a certain electronic state. Such a procedure, which is the inverse of a Schrödinger equation does exist and is called the RKR-procedure, after Rydberg, Klein and Rees.

3. Transitions between quantum states

3.1. Radiative transitions in molecules

In a simple picture a molecule acts in the same way upon incident electromagnetic radiation as an atom. The multipole components of the electromagnetic field interacts with the charge distribution in the system. Again the most prominent effect is the electric dipole transition. In a molecule with transitions in the infrared and even far-infrared the electric dipole approximation is even more valid, since it depends on the inequality. The wavelength λ of the radiation is much longer than the size of the molecule d :

$$\frac{2\pi d}{\lambda} \ll 1$$

In the dipole approximation a dipole moment $\vec{\mu}$ interacts with the electric field vector:

$$H_{int} = \vec{\mu} \cdot \vec{E} = e\vec{r} \cdot \vec{E}$$

In a quantum mechanical description radiative transitions are treated with a "transition moment" M_{if} defined as:

$$M_{fi} = \langle \Psi_f | \vec{\mu} \cdot \vec{E} | \Psi_i \rangle$$

This matrix element is related to the strength of a transition through the Einstein coefficient for absorption is:

$$B_{fi}(\omega) = \frac{\pi e^2}{3\epsilon_0 \hbar^2} \left| \langle \Psi_f | \vec{\mu} \cdot \vec{E} | \Psi_i \rangle \right|^2$$

Very generally the Wigner-Eckart theorem can be used to make some predictions on allowed transitions and selection rules. The dipole operator is an \vec{r} -vector, so a tensor of rank 1. If the wave functions have somehow a dependence on a radial part and an angular part the theorem shows how to separate these parts:

$$\langle \gamma J M | r_q^{(1)} | \gamma' J' M' \rangle = (-1)^{J-M} \begin{bmatrix} J & 1 & J' \\ -M & q & M' \end{bmatrix} \langle \gamma J || r^{(1)} || \gamma' J' \rangle$$

In the description the tensor of rank 1 q can take the values 0, -1 and +1; this corresponds with x, y, and z directions of the vector. In all cases the Wigner-3j symbol has a value unequal to 0, if $\Delta J=0, -1$ and $+1$. This is a general selection rule following if J is an angular momentum:

$$\begin{aligned} \Delta J &= J' - J = -1, 0, 1 \\ J = J' &= 0 \quad \text{forbidden} \\ \Delta M &= M' - M = -1, 0, 1 \end{aligned}$$

The rule $\Delta M=0$ only holds for $q=0$, so if the polarisation is along the projection of the field axis.

3.1. Two kinds of dipole moments: atoms and molecules

In atoms there is no dipole moment. Nevertheless radiative transitions can occur via a transition dipole moment; this can be understood as a reorientation or relocation of electrons in the system as a result of a radiative transition. Molecules are different; they can have a permanent dipole moment as well. The dipole moment can be written as:

$$\vec{\mu} = \mu_e + \mu_N = - \sum_i e \vec{r}_i + \sum_A e Z_A \vec{R}_A$$

Where e and N refer to the electrons and the nuclei. In fact dipole moments can also be created by the motion of the nuclei, particularly through the vibrational motion, giving rise to:

$$\vec{\mu} = \vec{\mu}_0 + \left(\frac{d}{dR} \vec{\mu} \right)_{Re} \rho + \frac{1}{2} \left(\frac{d^2}{dR^2} \vec{\mu} \right) \rho^2 +$$

where the first term is the electronic transition dipole, similar to the one in atoms, the second is the permanent or rotating dipole moment and the third is the vibrating dipole moment.

3.2. The Franck-Condon principle

Here we investigate if there is a selection rule for vibrational quantum numbers in electronic transitions in a diatom. If we neglect rotation the wave function can be written as:

$$\Psi_{mol}(\vec{r}_i, \vec{R}_A) = \Psi_{el}(\vec{r}_i; \vec{R}) \Psi_{vib}(\vec{R})$$

The transition matrix element for an electronic dipole transition between states Ψ' and Ψ'' is:

$$\mu_{if} = \int \Psi' \mu \Psi'' d\tau$$

Note that on the left side within the integral there appears a complex conjugated function. The dipole moment contains an electronic part and a nuclear part (see above). Insertion yields:

$$\begin{aligned} \mu_{if} &= \int \Psi'_{el} \Psi'_{vib} (\mu_e + \mu_N) \Psi''_{el} \Psi''_{vib} d\vec{r} d\vec{R} = \\ &= \int \left(\int \Psi'_{el} \mu_e \Psi''_{el} d\vec{r} \right) \Psi'_{vib} \Psi''_{vib} d\vec{R} + \int \Psi'_{el} \Psi''_{el} d\vec{r} \int \Psi'_{vib} \mu_N \Psi''_{vib} d\vec{R} \end{aligned}$$

If two different electronic states Ψ'_{el} and Ψ''_{el} are concerned then the second term cancels, because electronic states are orthogonal. Note: it is the second term that gives rise to pure vibrational transitions (also pure rotational transitions) within an electronic state of the molecule. Here we are interested in electronic transitions. We write the electronic transition moment:

$$\overline{M_e(R)} = \int \Psi'_{el} \mu_e \Psi''_{el} d\vec{r}$$

In first approximation this can be considered independent of internuclear distance R . This is the Franck-Condon approximation, or the Franck-Condon principle. As a result the transition ma-

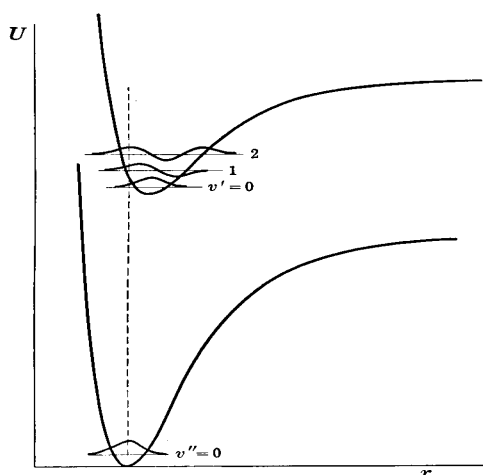
matrix element of an electronic transition is then:

$$\mu_{if} = \overline{M_e(R)} \int \psi'_{vib} \psi''_{vib} d\vec{R}$$

The intensity of a transition is proportional to the square of the transition matrix element, hence:

$$I \propto |\mu_{if}|^2 \propto |\langle v'|v'' \rangle|^2$$

So the Franck-Condon principle gives us a selection rule for vibrational quantum numbers in electronic transitions. The intensity is equal to the overlap integral of the vibrational wave function of ground and excited states. This overlap integral is called the Franck-Condon factor. It is not a strict selection rule forbidding transitions!



3.3. Vibrational transitions: infrared spectra

In the analysis of FC-factors the second term in the expression for the dipole matrix element was not further considered. This term:

$$\mu_{if} = \int \psi'_{el} \psi''_{el} d\vec{r} \int \psi'_{vib} \mu_N \psi''_{vib} d\vec{R}$$

reduces, in case of a single electronic state (the first integral equals 1 because of orthogonality) it can be written as:

$$\langle v' | \mu_{vib} | v'' \rangle = \langle v' | (a\rho + b\rho^2 + \dots) | v'' \rangle$$

where the first term represents the permanent dipole moment of the molecule. In higher order approximation in a vibrating molecule induced dipole moments play a role, but these are generally weaker.

An important consequence is that in a homonuclear molecule there exists no dipole moment, $\mu_{vib} = 0$, so there is *no* vibrational or infrared spectrum!

If we proceed with the approximation of a harmonic oscillator then we can use the known wave functions $Q_v(\rho)$ to calculate intensities in transitions between states with quantum numbers v_k and v_n :

$$\langle n|\rho|k\rangle = \int Q_n(\rho)\rho Q_k(\rho)d\rho = \sqrt{\frac{\hbar}{\mu\omega}} \left[\sqrt{\frac{n}{2}}\delta_{k,n-1} + \sqrt{\frac{n+1}{2}}\delta_{k,n+1} \right]$$

from which a selection rule follows for purely vibrational transitions:

$$\Delta v = v' - v = \pm 1$$

In case of an anharmonic oscillator, or in case of an induced dipole moment so-called overtone transitions occur. Then:

$$\Delta v = \pm 1, \pm 2, \text{ etc}$$

These overtone transitions are generally weaker by a factor of 100 than the fundamental infrared bands.

Note that vibrational transitions are not transitions involving a simple change of vibrational quantum number. In vibrational transitions the selection rules for the rotational or angular part must be satisfied (see below).

3.4. Rotational transitions

Induced by the permanent dipole moment radiative transitions can occur for which the electronic as well as the vibrational quantum numbers are not affected. The transition moment for a transition between states $|NM\rangle$ and $|N'M'\rangle$ can be written as:

$$M_{fi} = \langle \Psi_{N'M'} | \vec{\mu} \cdot \vec{E} | \Psi_{NM} \rangle$$

where the states represent wave functions:

$$|NM\rangle = \Psi_{NM}(\rho\theta\phi) = \psi_e R(\rho) Y_{NM}(\Omega)$$

The projection of the dipole moment onto the electric field vector (the quantization axis) can be written in vector form (in spherical coordinates) in the space-fixed coordinate frame:

$$\vec{\mu} = \mu_0 \begin{bmatrix} \sin\theta \cos\phi \\ \sin\theta \sin\phi \\ \cos\theta \end{bmatrix} \propto \mu_0 Y_{1m}$$

The fact that the vector can be expressed in terms of a simple spherical harmonic function Y_{1m}

allows for a simple calculation of the transition moment integral:

$$M_{fi} = \mu_0 \int_{\Omega} Y_{N'M'}^{\circ} \begin{bmatrix} \sin\theta \cos\phi \\ \sin\theta \sin\phi \\ \cos\theta \end{bmatrix} Y_{NM} d\Omega \propto \int_0^{2\pi} \int_0^{\pi} Y_{N'M'}^{\circ} Y_{1m} Y_{NM} d\Omega$$

$$= \sqrt{\frac{1}{4\pi}} (2N'+1) 3(2N+1) \begin{bmatrix} N' & 1 & N \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} N' & 1 & N \\ M' & m & M \end{bmatrix}$$

This gives only a non-zero result if:

$$\Delta N = N' - N = \pm 1$$

$$\Delta M = M' - M = 0, \pm 1$$

So rotational transitions have to obey these selection rules. The same holds for the vibrational transitions.

3.5. Rotation spectra

The energy expression for rotational energy levels, including centrifugal distortion, is:

$$F_v = B_v N(N+1) - D_v N^2(N+1)^2$$

Here we adopt the usual convention that ground state levels are denoted with N'' and excited state levels with N' . The subscript v refers to the vibrational quantum number of the state. Then we can express rotational transition between ground and excited states as:

$$\nu = F_v(N') - F_v(N'')$$

$$= (B_v N'(N'+1) - D_v N'^2(N'+1)^2) - [B_v N''(N''+1) - D_v N''^2(N''+1)^2]$$

Assume $N' = N'' + 1$ for absorption:

$$\nu_{abs} = B_v [(N''+1)(N''+2) - N''(N''+1)] - D_v [(N''+1)^2(N''+2)^2 - N''^2(N''+1)^2]$$

$$= 2B_v(N''+1) - 4D_v(N''+1)^3$$

If the centrifugal absorption is neglected and an equally spaced sequence of lines is found:

$$\nu_{abs}(N'') - \nu_{abs}(N''-1) = 2B_v$$

The centrifugal distortion causes the slight deviation from equally separated lines.

Note that in a pure rotation spectrum there are only absorbing transitions for which $\Delta N = N' - N'' = 1$, so in the R-branch (see below).

3.6. Rovibrational spectra

Now the *term values*, or the energies, are defined as:

$$T = G(v) + F_v(N)$$

$$F_v(N) = B_v N(N+1) - D_v N^2(N+1)^2$$

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2$$

For transitions $v'' \rightarrow v'$ one finds the transition energies:

$$\sigma(v' - v'') = F_{v'}(N') - F_{v''}(N'') + G(v') - G(v'')$$

Here $\sigma_0 = G(v') - G(v'')$ is the so-called *band origin*, the rotationless transition. Note that there is no line at this origin. So:

$$\sigma(v' - v'') = \sigma_0 + F_{v'}(N') - F_{v''}(N'')$$

Now the different *branches* of a transition can be defined. The R-branch relates to transition for which $\Delta N=1$. Note that this definition means that the rotational quantum number of the excited state is always higher by 1 quantum, irrespective of the fact that the transition can relate to absorption or emission. With neglect of the centrifugal distortion one finds the transitions in the R-branch:

$$\begin{aligned} \sigma_R &= \sigma_0 + B_{v'}(N+1)(N+2) - B_{v''}N(N+1) \\ &= \sigma_0 + 2B_{v'} + (3B_{v'} - B_{v''})N + (B_{v'} - B_{v''})N^2 \end{aligned}$$

Similarly transitions in the P-branch, defined as $\Delta N=-1$ transitions, can be calculated, again with neglect of centrifugal distortion:

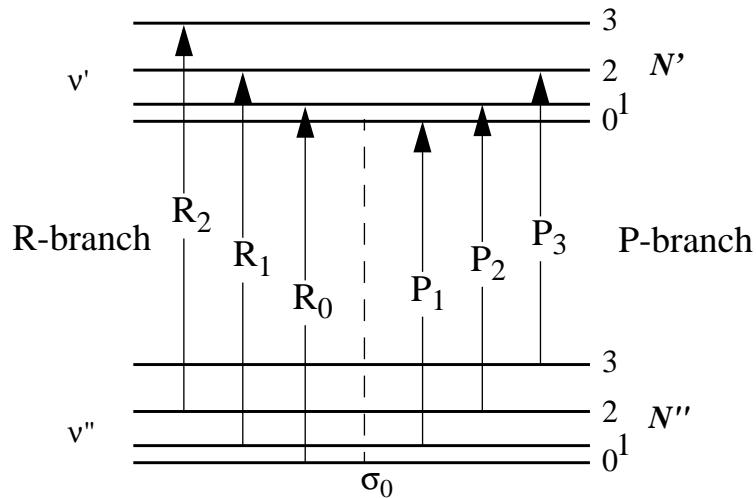
$$\sigma_P = \sigma_0 - (B_{v'} + B_{v''})N + (B_{v'} - B_{v''})N^2$$

Now the spacing between the lines is roughly $2B$; more precisely:

$$\begin{aligned} \sigma_R(N+1) - \sigma_R(N) &\sim 3B_{v'} - B_{v''} & so & < 2B_{v'} \\ \sigma_P(N+1) - \sigma_P(N) &\sim B_{v'} + B_{v''} & so & > 2B_{v'} \end{aligned}$$

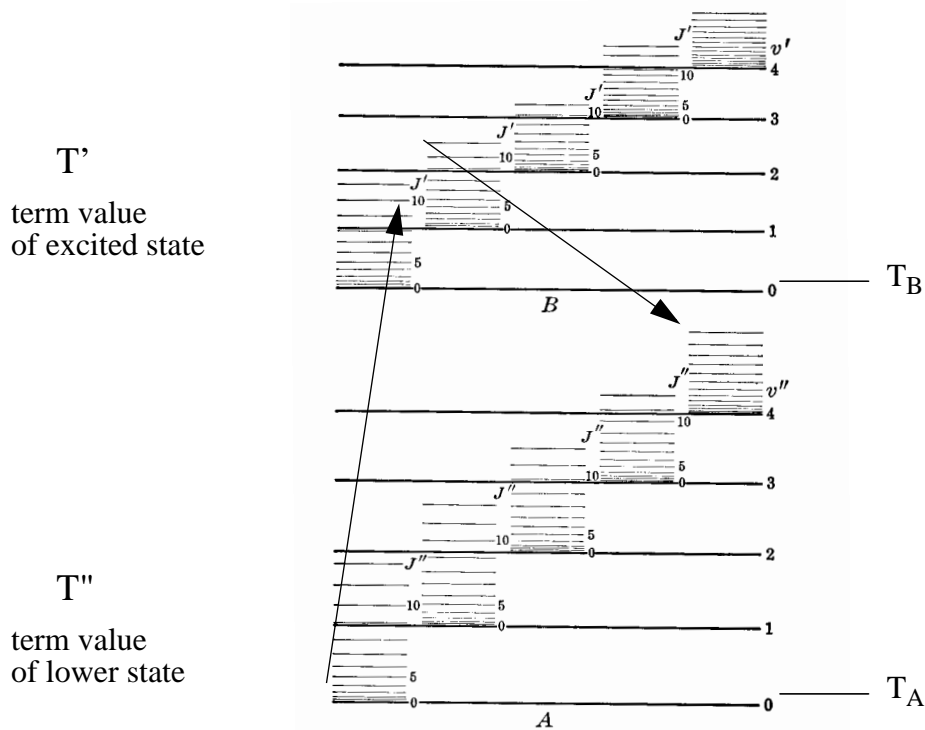
where the statement on the right holds if $B_{v'} < B_{v''}$. Hence the spacing in the P-branch is larger in the usual case that the rotational constant in the ground state is larger. There is a pile up of lines in the R-branch that can eventually lead to the formation of a *bandhead*, i.e. the point where a reversal occurs.

An energy level diagram for rovibrational transitions is shown in the following figure. Where the spacing between lines is $2B$ the spacing between the R(0) and P(1) lines is $4B$. Hence there is a *band gap* at the origin.



3.7. Rovibronic spectra

If there are two different electronic states involved rovibronic transitions can occur, i.e. transitions where the electronic configuration, the vibrational as well as the rotational quantum numbers change. Transitions between a lower electronic state A and a higher excited state B as in the following scheme can take place:



Possible transitions between the lower and excited state have to obey the selection rules, including the Franck-Condon principle. Transitions can be calculated:

$$\begin{aligned} \nu &= T' - T'' \\ T' &= T_B - G'(v') + F'(N') \\ T'' &= T_A - G''(v'') + F''(N'') \end{aligned}$$

Again *R* and *P* branches can be defined in the same way as for vibrational transitions with transition energies:

$$\begin{aligned} \sigma_R &= \sigma_0 + 2B_{v'} + (3B_{v'} - B_{v''})N + (B_{v'} - B_{v''})N^2 \\ \sigma_P &= \sigma_0 - (B_{v'} + B_{v''})N + (B_{v'} - B_{v''})N^2 \end{aligned}$$

But now the constants have a slightly different meaning: σ_0 is the band origin including the electronic and vibrational energies, and the rotational constants $B_{v'}$ and $B_{v''}$ pertain to electronically excited and lower states. If now we substitute:

$$\begin{aligned} m &= N + 1 && \text{for } R\text{-branch} \\ m &= -N && \text{for } P\text{-branch} \end{aligned}$$

Then we obtain an equation that is fulfilled by the lines in the *R* branch as well as in the *P*-branch:

$$\sigma = \sigma_0 + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2$$

This is a quadratic function in m ; if we assume that $B' < B''$, as is usually the case, then:

$$\sigma = \sigma_0 + \alpha m - \beta m^2$$

a parabola results that represents the energy representations of *R* and *P* branches. Such a parabola is called a *Fortrat diagram* or a *Fortrat Parabola*. The figure shows one for a single rovibronic band in the CN radical at 388.3 nm.

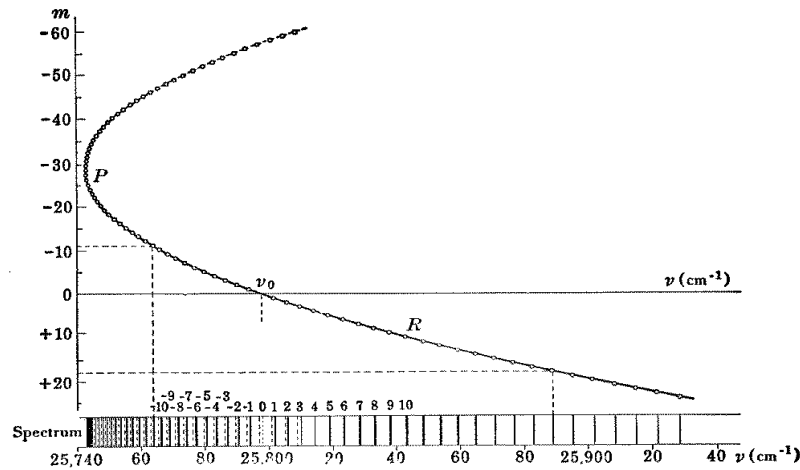


FIG. 24. Fortrat Parabola of the CN Band 3883 Å (see Fig. 18). The schematic spectrum below is drawn to the same scale as the Fortrat parabola above. The relation between curve and spectrum is indicated by broken lines for two points ($m = -11$ and $m = +18$). No line is observed at $m = 0$ (dotted line).

Note that there is no line for $m=0$; this implies that again there is a *band gap*. From such figures we can deduce that there always is a bandhead formation, either in the *R*-branch or in the *P*-branch. In the case of CN in the spectrum above the bandhead forms in the *P*-branch. The bandhead can easily be calculated, assuming that it is in the *P*-branch:

$$\frac{d\sigma_P}{dN} = -(B' + B'') + 2N(B' - B'') = 0$$

It follows that the bandhead is formed at:

$$N = \frac{B' + B''}{B' - B''}$$

3.8. Population distribution

If line intensities in bands are to be calculated the population distribution over quantum states has to be accounted for. From statistical thermodynamics a partition function follows for population of states at certain energies under the condition of thermodynamic equilibrium. In case of Maxwell-Boltzmann statistics the probability $P(v)$ of finding a molecule in quantum state with vibrational quantum number v is:

$$P(v) = \frac{e^{-(E(v))/(kT)}}{\sum_v e^{-(E(v'))/(kT)}}$$

When filling in the vibrational energy it follows:

$$P(v) = \frac{1}{N} e^{-\frac{\omega_e(v + \frac{1}{2})}{kT} - \frac{\omega_e x_e(v + \frac{3}{2})}{kT}}$$

where N is the Zustandssumme, and kT is expressed in cm^{-1} . As often in statistical physics (ergodic theorem) $P(v)$ can be interpreted as a probability or a distribution. As an example $P(v)$ is plotted as a function of v in the following figure.

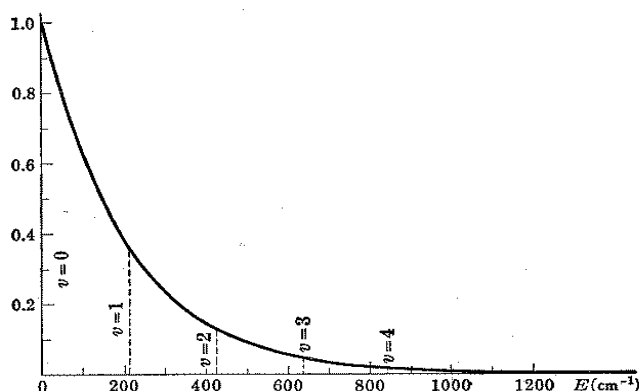


FIG. 58. Boltzmann Factor and Thermal Distribution of the Vibrational Levels. The curve gives the function $e^{-E/kT}$ for $T = 300^\circ \text{K}$. with E in cm^{-1} . The broken-line ordinates correspond to the vibrational levels of the I_2 molecule.

At each temperature the ratio of molecules in the first excited state over those in the ground

state can be calculated. $P(v=1)/P(v=0)$ is listed in the Table for several molecules for 300K and 1000K.

TABLE 14. RATIO OF THE NUMBER OF MOLECULES IN THE FIRST TO THAT IN THE ZEROth VIBRATIONAL LEVEL FOR 300° K. AND 1000° K.

| Gas | $\Delta G_{1/2}(\text{cm}^{-1})$ | $e^{-\Delta G_{1/2}hc/kT}$ | |
|-----------------|----------------------------------|----------------------------|-----------------------|
| | | For 300° K. | For 1000° K. |
| H ₂ | 4160.2 | 2.16×10^{-9} | 2.51×10^{-3} |
| HCl | 2885.9 | 9.77×10^{-7} | 1.57×10^{-2} |
| N ₂ | 2330.7 | 1.40×10^{-5} | 3.50×10^{-2} |
| CO | 2143.2 | 3.43×10^{-5} | 4.58×10^{-2} |
| O ₂ | 1556.4 | 5.74×10^{-4} | 1.07×10^{-1} |
| S ₂ | 721.6 | 3.14×10^{-2} | 3.54×10^{-1} |
| Cl ₂ | 556.9 | 6.92×10^{-2} | 4.49×10^{-1} |
| I ₂ | 213.2 | 3.60×10^{-1} | 7.36×10^{-1} |

In case of the distribution over rotational states the degeneracy of the rotational states needs to be considered. Every state $|J\rangle$ has $(2J+1)$ substates $|JM\rangle$. Hence the partition function becomes:

$$P(J) = \frac{(2J+1)e^{-E_{rot}/(kT)}}{\sum_{J'}(2J'+1)e^{-E_{rot}/(kT)}} = \frac{1}{N_{rot}}(2J+1)e^{-BJ(J+1)+DJ^2(J+1)^2}$$

In the figure the rotational population distribution of the HCl molecule is plotted. Note that it does not peak at $J=0$. The peak value is temperature dependent and can be found through setting:

$$\frac{d}{dJ}P(J) = 0$$

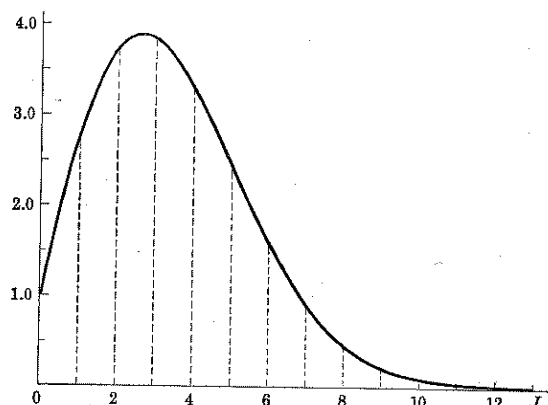


FIG. 59. Thermal Distribution of the Rotational Levels for $T = 300^\circ \text{K.}$ and $B = 10.44 \text{ cm}^{-1}$ (That is, for HCl in the Ground State). The curve represents the function $(2J+1)e^{-BJ(J+1)hc/kT}$ as a function of J . The broken-line ordinates give the relative populations of the corresponding rotational levels.

4. High vibrational levels in the WKB-approximation

4.1. The Wentzel Kramers Brillouin approximation

The Wentzel Kramers Brillouin (WKB) approximation is a tool to solve the one-dimensional Schrödinger equation. Both, wave functions and energy levels can be determined for a given potential. Before computers were in common use, this approximation belonged to the standard topics in basic quantum mechanic courses, but after the 1960's this approximation received less and less attention. Recently, however, the WKB approximation gained interest again, due to developments in the field of cold atoms. The WKB is wielded to determine the binding energy of the upper vibrational levels in diatomic molecules which is important for the value of the scattering length for s-wave collisions; an important parameter for experiments with cold atoms.

In molecular physics this approximation can aid in the investigation of vibrational levels close to a dissociation limit and can give tunneling rate constants in the case of, for instance, auto-ionization or pre-dissociation.

Besides this, the WKB approximation is widely applicable for a lot of quantum mechanical problems, provided a potential curve is known, and can help to interpret physical phenomena in some detail. Therefore, this approximation is presented in this chapter.

This and the following three paragraphs are based on the book: *Quantum Mechanics*, by E. Merzbacher (1964).

The derivation starts with the one-dimensional Schrödinger equation. The variable is chosen to be R rather than x , as this is the symbol for the internuclear distance in diatomic molecules.

$$\frac{d^2\Psi}{dR^2} + \frac{2\mu}{\hbar^2}[E - V]\Psi = 0$$

with μ as the reduced mass.

In the case that $V = \text{constant}$, the equation is easily solved and the solutions are

$$\Psi = e^{\pm ikR} \quad \text{for } E > V$$

$$\Psi = e^{\pm\kappa R} \quad \text{for } E < V$$

with

$$k = \left\{ \frac{2\mu}{\hbar^2}[E - V] \right\}^{1/2} \quad \kappa = \left\{ \frac{2\mu}{\hbar^2}[V - E] \right\}^{1/2}$$

In the following only k will be used, whether $E > V$ or $E < V$. In the latter case a purely positive imaginary number is assumed for k .

If $V = V(R)$ the solutions can be written in the form

$$\Psi(R) = e^{\pm iu(R)}$$

The problem is now to obtain the function $u(R)$. Substitute this wave function and also

$$k(R) = \left\{ \frac{2\mu}{\hbar^2}[E - V(R)] \right\}^{1/2}$$

in the Schrödinger equation to get

$$\left(\frac{du}{dR}\right)^2 = [k(R)]^2 + i\frac{d^2u}{dR^2}$$

In the case of $V(R) = V = \text{constant}$, $k(R) = k = \text{constant}$, the solution is

$$u(R) = kR$$

The second derivative (the first term) is then zero.

Omit the first term to obtain a zeroth order approximation

$$\left(\frac{du_0}{dR}\right)^2 = [k(R)]^2$$

which has the solution

$$u_0 = \pm \int k(R) dR + C_0$$

This solution will be starting point in an iteration procedure

$$\left(\frac{du_{n+1}}{dR}\right)^2 = [k(R)]^2 + i\frac{d^2u_n}{dR^2}$$

And u_1 will then become

$$u_1 = \pm \int \sqrt{k^2(R) \pm ik'(R)} dR + C_1$$

At this point one likes to stop the procedure. This is only valid, however, if $u_1 \cong u_0$, that is if the first order solution is almost the exact one. The condition $u_1 \cong u_0$ is fulfilled when

$$|k'| \ll |k^2|$$

If this is the case, the square root may be rewritten and u_1 becomes

$$\begin{aligned} u_1 &= \pm \int k(R) \left(1 \pm \frac{ik'(R)}{2k^2(R)}\right) dR + C_1 \\ &= \pm \int k(R) dR + \frac{i}{2} \log k(R) + C_1 \end{aligned}$$

Using this, the wave function Ψ can be determined.

$$\Psi \sim \exp[iu(R)] = \frac{1}{\sqrt{|k(R)|}} \exp[\pm i \int k(R) dR]$$

The constant of integration C_1 affects only the normalization of Ψ and will not be considered in the following.

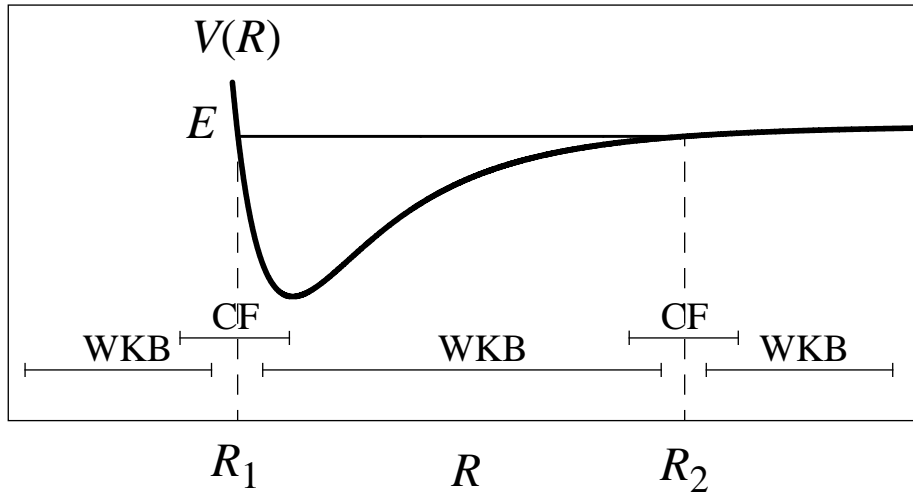
4.2. Breakdown of the approximation criterion

The criterion for the approximation was

$$|k'| \ll |k^2|$$

This breaks down when R is close to a classical turning point where $E = V$ and hence $k = 0$. The

strategy to find a solution for the whole range of R consists of two parts. First, find the WKB-solutions wherever the approximation is valid (i.e. far from the turning points). Second, find a wave function which is valid around the turning points and is also valid in a certain region where one can also use the WKB solutions. Now, we have solutions over the whole range, and all we have to do is to tie the different solutions together to find the total wave function. To do this, it is necessary to have a certain region where both, the WKB solution and the solution around the turning points, are valid. This is schematically depicted below. WKB stands for the regions where the approximation is valid and CF for the regions where the so-called ‘connection formulas’ have to be found. R_1 and R_2 are respectively the inner and outer turning point.



4.3. The connection formulas

To obtain the wave functions around the classical turning points the Schrödinger equation will be expressed in two new parameters. The equation will be reduced to a very simple one after the linearization of the potential around the turning points. The two new parameters, v and y are related to Ψ and R in the following way

$$v = \sqrt{|k|}\Psi$$

$$y = \int k dR$$

which implies

$$v = \exp[\pm iy]$$

The Schrödinger equation expressed in the new parameters will be

$$\frac{d^2 v}{dy^2} + \left[\frac{1}{4k^2} \left(\frac{dk}{dy} \right)^2 - \frac{1}{2k} \frac{d^2 k}{dy^2} + 1 \right] v = 0$$

Now, the potential is replaced by a straight line

$$V(R) - E \approx \alpha(R - R_t)$$

with R_t as one of the turning points. Note that V and E do not appear explicitly in the Schrödinger equation, but are hidden in k .

When this approximation is applied the Schrödinger equations takes on a simple form

$$\frac{d^2 v}{dy^2} + \left(1 + \frac{5}{36y^2}\right)v = 0$$

This equation gives the correct wave functions around the turning points and hopefully over such a range that it has some overlap with the ranges where the WKB solutions are valid to be able to connect the two solutions.

In the remaining of this paragraph it will be shown that it is possible to find a solution for this differential equation.

Suppose that the solution can be written in the form

$$v(y) = y^\lambda \int e^{yt} f(t) dt$$

with, $\lambda, f(t)$ and the path of integration not specified yet. After substitution the following must be valid

$$\int \left[\lambda(\lambda - 1) + 2\lambda yt + y^2 t^2 + y^2 + \frac{5}{36} \right] e^{yt} f(t) dt = 0$$

If it can be proven that this is equal to zero for all y , then the proposed solution is the right one. Choose λ such that the first term cancels the constant $5/36$, i.e. $\lambda = 1/6$ or $5/6$. The integral becomes

$$\int f(t) \left[2\lambda t + (1 + t^2) \frac{d}{dt} \right] e^{yt} dt = 0$$

Integration by parts gives two terms which should give zero when added, but if we can prove that both terms themselves are zero, this condition is automatically fulfilled. The two parts are

$$\int \left\{ 2\lambda t f(t) - \frac{d}{dt} (1 + t^2) f(t) \right\} e^{yt} dt = 0$$

$$\int \frac{d}{dt} [(1 + t^2) f(t) e^{yt}] dt = 0$$

The first one gives an expression for $f(t)$

$$2\lambda t f(t) = \frac{d}{dt}(1+t^2)f(t)$$

$$2\lambda t f(t) - 2t f(t) = (1+t^2) \frac{d}{dt} f(t)$$

$$(\lambda - 1) \int_0^t \frac{2t}{1+t^2} dt = \int_{f(0)}^{f(t)} \frac{1}{f(t)} df(t)$$

$$(\lambda - 1) \ln(1+t^2) = \ln\left(\frac{f(t)}{f(0)}\right)$$

$$f(t) = f(0)(1+t^2)^{\lambda-1}$$

This expression for $f(t)$ is inserted in the second equation. This leads to the integral

$$\int \frac{d}{dt} [(1+t^2)^\lambda e^{yt}] dt = 0$$

$$(1+t^2)^\lambda e^{yt} \Big|_{\text{lower limit}}^{\text{upper limit}} = 0$$

If the limits are chosen such that the function is zero, then of course also the difference is zero. This leads to the following solutions

$$t = +i$$

$$t = -i$$

$$t = +\infty \quad y < 0$$

$$t = -\infty \quad y > 0$$

With this choice of t , $f(t)$ and λ , we have found a non-trivial solution of the Schrödinger equation. This means that we now have an expression for the wave function around the turning points. All the wave functions in the different regions should be matched together. Doing so (some complex function theory is involved), it can be shown that the different parts of the WKB solution should be connected as follows:

Around the inner turning point ($R = R_1$)

$$+\frac{1}{\sqrt{|k|}} \exp\left(-\int_R^{R_1} |k| dR\right) \leftrightarrow \frac{2}{\sqrt{k}} \cos\left(\int_{R_1}^R k dR - \frac{1}{4}\pi\right)$$

$$-\frac{1}{\sqrt{|k|}} \exp\left(+\int_R^{R_1} |k| dR\right) \leftrightarrow \frac{2}{\sqrt{k}} \sin\left(\int_{R_1}^R k dR - \frac{1}{4}\pi\right)$$

Around the outer turning point ($R = R_2$)

$$\frac{2}{\sqrt{k}} \cos\left(\int_R^{R_2} k dR - \frac{1}{4}\pi\right) \leftrightarrow +\frac{1}{\sqrt{|k|}} \exp\left(-\int_{R_2}^R |k| dR\right)$$

$$\frac{2}{\sqrt{k}} \sin\left(\int_R^{R_2} k dR - \frac{1}{4}\pi\right) \leftrightarrow -\frac{1}{\sqrt{|k|}} \exp\left(+\int_{R_2}^R |k| dR\right)$$

These formulas are known as the connection formulas.

4.4. Bound states and the WKB approximation

In this paragraph, an expression will be derived to determine the energies of bound levels in a potential well. If the potential exhibits only one well, three regions can be distinguished: the classically allowed region (Region II) and twice a classically forbidden region (Regions I and III).

In Region I, the WKB wave function is

$$\Psi_I(R) = A \frac{1}{\sqrt{|k|}} \exp\left(-\int_R^{R_1} |k| dR\right) + B \frac{1}{\sqrt{|k|}} \exp\left(+\int_R^{R_1} |k| dR\right)$$

with A and B normalization constants.

Ψ_I must vanish rigorously when $R < R_1$ and thus $B = 0$. By applying the connection formulas

Ψ_{II} can be found

$$\Psi_{II}(R) = \frac{2}{\sqrt{k}} \cos\left(\int_{R_1}^R k dR - \frac{1}{4}\pi\right)$$

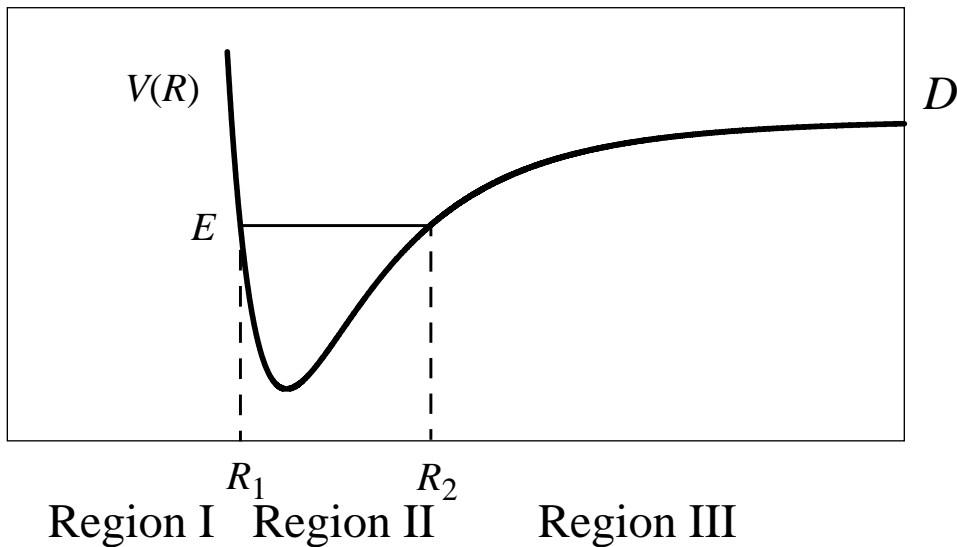
which can be rewritten into

$$\Psi_{II}(R) = -\frac{2}{\sqrt{k}} \cos\left(\int_{R_1}^{R_2} k dR\right) \sin\left(\int_R^{R_2} k dR - \frac{1}{4}\pi\right) + \frac{2}{\sqrt{k}} \sin\left(\int_{R_1}^{R_2} k dR\right) \cos\left(\int_R^{R_2} k dR - \frac{1}{4}\pi\right)$$

Only the second term gives rise to a decreasing exponential function in Region III (the wave function should vanish for large R) and therefore the first term should be equal to zero

$$\frac{2}{\sqrt{k}} \cos\left(\int_{R_1}^{R_2} k dR\right) \sin\left(\int_R^{R_2} k dR - \frac{1}{4}\pi\right) = 0$$

This term should be zero for every R , which means that the cosine should vanish or



$$\int_{R_1}^{R_2} k dR = \left(\nu + \frac{1}{2}\right)\pi$$

with ν a positive integer.

This leads to the formula known as the WKB-condition for bound levels in a potential well

$$v + \frac{1}{2} = \frac{(2\mu)^{1/2}}{\pi\hbar} \int_{R_1}^{R_2} [E(v) - V(R)]^{1/2} dR$$

All one needs for a calculation of the energy levels is the potential and a numerical procedure for the integral.

4.5. Levels close to the dissociation limit

This paragraph is based on an article by Robert J. Leroy and Richard Bernstein (*JCP* 52, 3869-3879 (1970)). In this article energy levels are investigated close to a dissociation limit. An expression is derived for the dependence of the binding energy as a function of the vibrational quantum number. Experimentally it usually becomes harder to probe the higher levels in a potential and with this formula the highest levels can be predicted on the basis of lower ones. Also an estimation of the value of the dissociation limit can be given.

The starting point is the WKB-condition for bound levels as was derived in the previous paragraph

$$v + \frac{1}{2} = \frac{(2\mu)^{1/2}}{\pi\hbar} \int_{R_1}^{R_2} [E(v) - V(R)]^{1/2} dR$$

Differentiating this expression with respect to $E(v)$ gives

$$\frac{dv}{dE(v)} = \frac{(\mu/2)^{1/2}}{\pi\hbar} \int_{R_1}^{R_2} [E(v) - V(R)]^{-1/2} dR$$

The outer part of a molecular potential close to the dissociation limit can be described by

$$V(R) = D - \frac{C_n}{R^n}$$

with C_n a constant and n is related to the dominant electrostatic interaction between the two atoms (for instance $n = 1$ in the case of ions and $n = 6$ in the case of a van der Waals interaction). D is the dissociation limit. Insert this potential in the formula and also change the variable of integration to $x = R_2/R$

$$\frac{dv}{dE} = \frac{(\mu/2)^{1/2}}{\pi\hbar} \frac{C_n^{1/n}}{[D - E]^{1/2 + 1/n}} \int_1^{R_2/R_1} x^{-2} (x^n - 1)^{-1/2} dx$$

This integral is known if the upper limit is ∞ i.e. if $R_1 = 0$. On the next page it is shown that this is a valid approximation. The integral of the lower figure is finite though the value of the function itself goes to infinity at the turning points. The surface beneath the function at the right-hand side in the lower figure, is bigger than at the left-hand side and this difference will increase when one gets closer to the dissociation limit. The error made by using the approximate potential becomes smaller close to the limit. And the error made by taking 0 as lower limit in stead of R_1 is also negligible. This means that the integral derived above may be evaluated between 1 and ∞ .

With those limits, the integral is analytically solvable (see for instance I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products*, Academic Press Inc., New York, 1965,

Sec. 3.251, p. 295)

$$\int_1^{\infty} x^{\mu-1} (x^p - 1)^{\nu-1} dx = \frac{1}{p} \beta\left(1 - \nu - \frac{\mu}{p}, \nu\right)$$

with in our case $\mu = -1$, $p = n$ and $\nu = 1/2$, this becomes

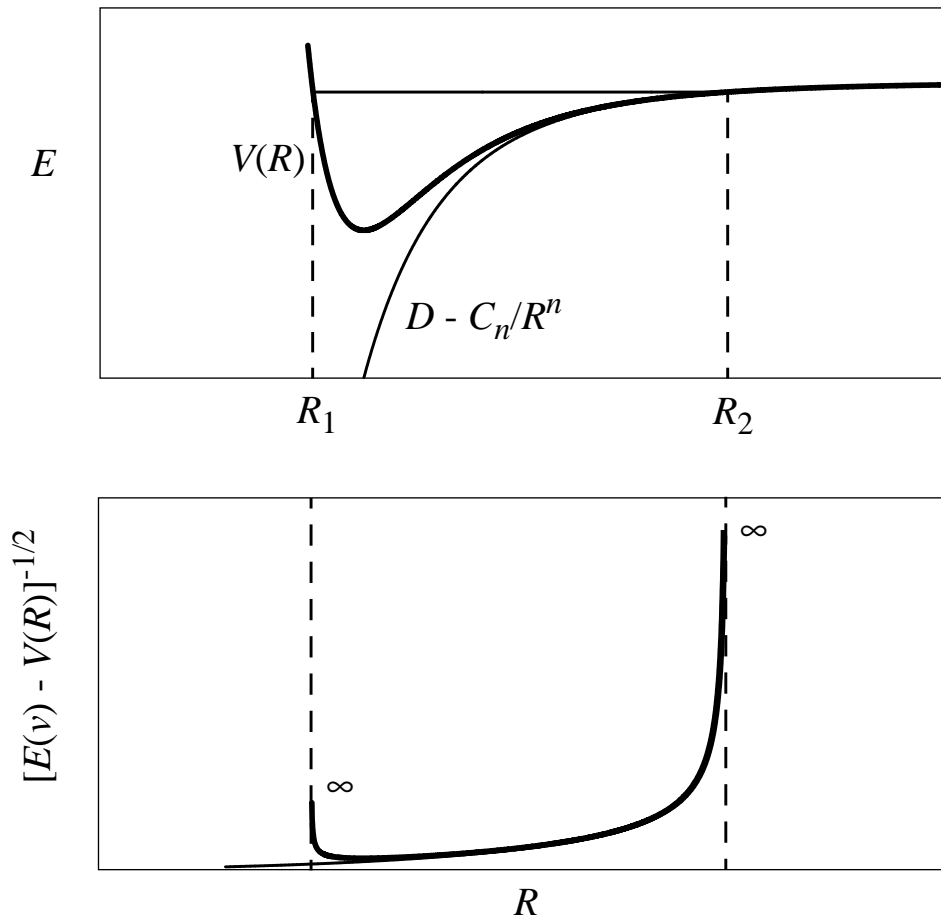
$$\int_1^{\infty} x^{-2} (x^n - 1)^{-1/2} dx = \frac{1}{n} \beta\left(\frac{1}{2} + \frac{1}{n}, \frac{1}{2}\right)$$

The β -function is defined as follows

$$\beta(p, q) = \frac{\Gamma(p)\Gamma(q)}{\Gamma(p+q)}$$

and the Γ -function

$$\Gamma(z) = \int_0^{\infty} e^{-t} t^{z-1} dt$$



Using those definitions and $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$ results in the following equation

$$\begin{aligned}\frac{dE}{dv} &= \hbar\left(\frac{2\pi}{\mu}\right)^{1/2} \frac{\Gamma(1+1/n)}{\Gamma(1/2+1/n)} \frac{n}{C_n^{1/n}} [D-E]^{\frac{n+2}{2n}} \\ &= K_n [D-E]^{\frac{n+2}{2n}}\end{aligned}$$

with K_n a constant depending on both C_n and μ , the reduced mass. Rearrange the terms and integrate from the dissociation limit D to $E(v)$

$$\begin{aligned}\frac{1}{K_n} \int_D^{E(v)} [D-E(v)]^{\frac{-2-n}{2n}} dE(v) &= \int_{v_D}^v dv \\ -\frac{1}{K_n} \frac{2n}{n-2} [D-E(v)]^{\frac{n-2}{2n}} &= v - v_D\end{aligned}$$

Put $E(v)$ to one side

$$E(v) = D - \left[(v_D - v) \frac{n-2}{2n} K_n \right]^{\frac{2n}{n-2}}$$

with v_D the ‘effective’ vibrational quantum number at the dissociation limit. It indicates how close the highest level is to the dissociation limit. If for instance $v_D = 13.01$ then $v = 13$ is just bound. If, however, $v_D = 12.99$ then $v = 13$ is just not bound in the potential. The denominator of the exponent becomes 0 for $n = 2$, and the expression is only valid for $n > 2$. In the case $n = 1$, the Schrödinger equation can be solved analytically and for $n = 2$, a different expression can be found (described in the same article, but not treated here).

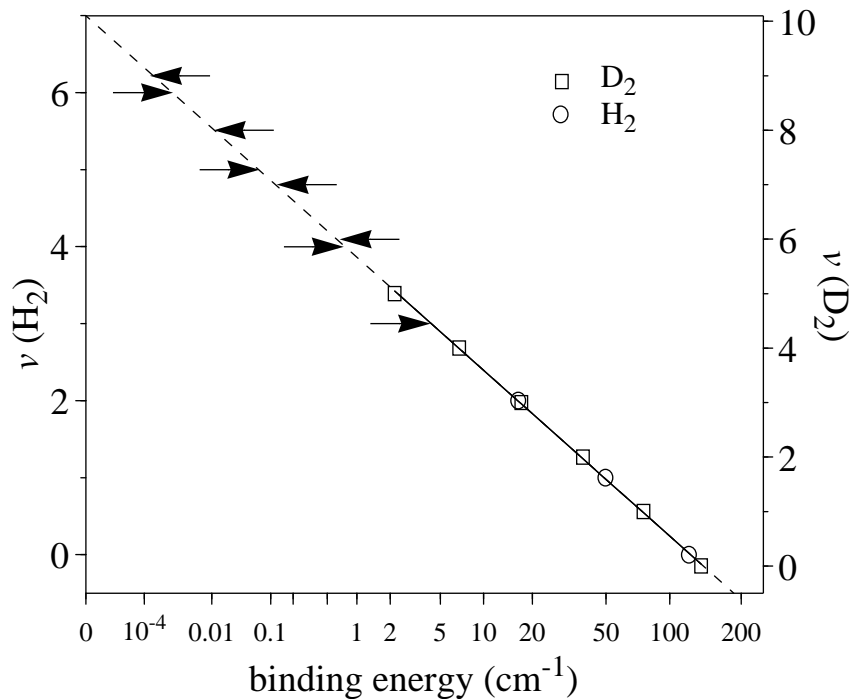
The formula can be rewritten in terms of the binding energy ϵ

$$v = v_D - a_n \epsilon_v^{\frac{n-2}{2n}}$$

with a_n a constant.

An application of this formula is shown in the next figure. Without going into too much detail, an electronic state in H_2 with a long range dependence of R^{-3} , was populated in a multi photon laser experiment. Both the binding energy and the vibrational quantum number were known and using the formula, a prediction could be made for the higher vibronic levels (indicated with arrows). If the dissociation limit was not known, then also the binding energy would have been unknown. In that case, the expression could be used in a fitting routine to

determine the value of the dissociation limit D .



For the so-called I potential in H_2 $n = 3$ and $C_3 = 0.554929$ atomic units. This number is isotope independent, but a_3 is not. For H_2 $a_3 = 3.2343 \text{ cm}^{1/6}$ and for D_2 $a_3 = 4.5722 \text{ cm}^{1/6}$. Plotting the vibrational quantum number vs. $\epsilon^{1/6}$, a straight line is to be expected.

Finally, a list is presented with the interpretation of the different n -values

- $n = 1$ 2 charged atoms (Coulomb)
- $n = 2$ 1 charged atom and 1 atom with a permanent dipole moment
- $n = 3$ 2 atoms with permanent dipole moments
- $n = 3$ identical uncharged atoms in electronic states whose total angular momenta differ by one (i.e. $\Delta L = 1$)
- $n = 4$ 1 charged atom and one neutral atom
- $n = 4$ 1 atom with a permanent dipole moment and 1 atom with a permanent quadrupole moment
- $n = 5$ 2 atoms with permanent quadrupole moments
- $n = 6$ induced dipole - induced dipole interaction

The last R dependence is also known as the van der Waals interaction and this term will always be present.

4.6. The harmonic oscillator

The WKB approximation gives the right energy levels in the case of a harmonic oscillator. This remarkable result will be derived below.

The energy levels of a potential $V(R) = \frac{1}{2}cR^2$ can be found in any elementary book on quan-

tum mechanics

$$E(\nu) = \hbar \sqrt{\frac{c}{\mu}} \left(\nu + \frac{1}{2} \right)$$

Start with the WKB condition for bound levels

$$\nu + \frac{1}{2} = \frac{(2\mu)^{1/2}}{\pi\hbar} \int_{R_1}^{R_2} \left[E(\nu) - \frac{1}{2}cR^2 \right]^{1/2} dR$$

with R_1 and R_2 the two turning points. For a certain energy $E(\nu)$, the turning points are

$$R_2 = -R_1 = \sqrt{\frac{2E}{c}}$$

The equation becomes

$$\begin{aligned} \nu + \frac{1}{2} &= \frac{(2\mu)^{1/2}}{\pi\hbar} \int_{R_1}^{R_2} \left[E(\nu) - \frac{1}{2}cR^2 \right]^{1/2} dR \\ &= \frac{(c\mu)^{1/2}}{\pi\hbar} \int_{R_1}^{R_2} \left[\frac{E(\nu)}{c} - R^2 \right]^{1/2} dR \end{aligned}$$

By applying the following standard integral

$$\int \sqrt{(a^2 - x^2)} dx = \frac{1}{2} \left[x \sqrt{(a^2 - x^2)} + a^2 \operatorname{asin} \frac{x}{|a|} \right]$$

the condition becomes

$$\nu + \frac{1}{2} = \frac{(c\mu)^{1/2}}{\hbar} \frac{E(\nu)}{c}$$

which can be rearranged into the first formula of this paragraph

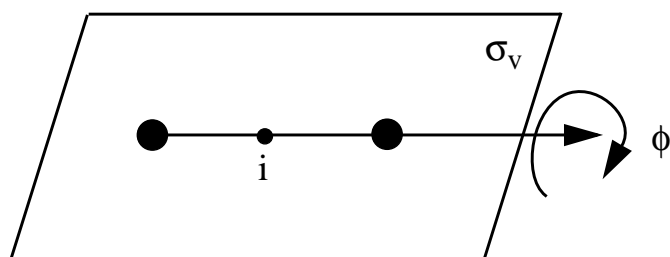
$$E(\nu) = \hbar \sqrt{\frac{c}{\mu}} \left(\nu + \frac{1}{2} \right)$$

Note however, that the corresponding wave functions Ψ are not exactly the same as the analytical solutions. In the analytical case the solutions are Hermite polynomial functions, but in the WKB case, the functions are somewhat different.

5. Electronic states

5.1. Symmetry operations

Symmetry plays an important role in molecular spectroscopy. Quantum states of the molecular Hamiltonian are classified with quantum numbers that relate to symmetries of the problem; the invariance of the Hamiltonian under a symmetry operation of the molecule in its body fixed frame is connected to a quantum number. For a diatomic molecule the symmetries are:



The Hamiltonian H_0 :

$$H_0 = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + V(\vec{r}_i, R)$$

is invariant under the symmetry operations:

- R_ϕ rotation over every angle ϕ about the molecular axis
- σ_v reflection in a molecular plane containing the molecular axis
- i inversion in the molecular centre

These operators not only leave the molecular Hamiltonian invariant, they are also commuting observables. In the language of quantum mechanics this means that these operators can generate a set of simultaneous eigenfunctions of the system.

Note that the operator i only applies in a diatomic molecule with inversion symmetry, i.e. a homonuclear molecule. These operators form *groups*, for a homonuclear molecules the $D_{\infty h}$, for the heteronuclear molecules the $C_{\infty v}$ point group.

5.2. Classification of states

The electronic states of the molecules are classified according to the eigenvalues under the symmetry operations.

The reflection operator σ_v (later we will see that this operator is connected to the concept of parity for a molecular eigen state) acts has two eigenvalues:

$$\sigma_v \psi_e = \pm \psi_e \quad \text{eigenvalues} \quad +, -$$

The operator R_ϕ is connected to another constant of the motion, $L_{\vec{z}}$. Assume that in a molecule the electronic angular momenta are coupled to a resulting vector $\vec{L} = \sum_i \vec{l}_i$. In an atom \vec{L} is a

constant of the motion, since there is overall rotational symmetry. Here is the distinct difference between atoms and molecules; the overall rotational symmetry is broken. In a diatom there is only axial symmetry around the internuclear axis of the molecule. Hence only L_z is a constant of the motion. The eigen value equation is:

$$L_z \psi_e = \frac{\hbar}{i} \frac{\partial \psi_e}{\partial \phi} = \Lambda \hbar \psi_e \quad \text{eigenvalues} \quad \Lambda = 0, \pm 1, \pm 2, \pm 3,$$

In the nomenclature of diatomic molecules the electronic states are called:

| | | |
|----------|-----|------------------------|
| Σ | for | $\Lambda = 0$ |
| Π | for | $\Lambda = \pm 1$ |
| Δ | for | $\Lambda = \pm 2$ |
| Φ | for | $\Lambda = \pm 3$ etc. |

The energy of the molecule depends on Λ^2 ; states with Λ and $-\Lambda$ are degenerate.

For the inversion operator there are two eigenvalues:

$$i\psi_e = \pm \psi_e \quad \text{eigenvalues} \quad g, u$$

The g (gerade) and u (ungerade) symbols are chosen for a distinction with the eigenvalues of the σ_v operator.

Hence we find simultaneous eigenvalues, under the three symmetry operations, resulting in possible quantum states:

| | Homonuclear | Heteronuclear |
|---------------|---|---------------------|
| $\Lambda = 0$ | $\Sigma_g^+ \Sigma_u^+ \Sigma_g^- \Sigma_u^-$ | $\Sigma^+ \Sigma^-$ |
| $\Lambda = 1$ | $\Pi_g^+ \Pi_u^+ \Pi_g^- \Pi_u^-$ | $\Pi^+ \Pi^-$ |
| $\Lambda = 2$ | $\Delta_g^+ \Delta_u^+ \Delta_g^- \Delta_u^-$ | $\Delta^+ \Delta^-$ |
| etc | | |

Remarks.

- There is a double degeneracy under the σ_v operator for states $\Lambda \neq 0$. Therefore the +/- signs are usually omitted for $\Lambda \neq 0$.
- There is no degeneracy under the i operator for u and g states. So u and g states have different energies.

The electron spins are added in the molecule in the same way as in atoms: $\vec{S} = \sum \vec{s}_i$. In the classification of states the multiplicity $(2S+1)$ due the electron spin is given in the same way as in atoms. Hence we identify states as:

$^1\Sigma_g^+$ for the ground state of the H_2 molecule

$^3\Sigma_g^-$ for the ground state of the O_2 molecule

$^2\Pi_{3/2}$ for the ground state of the OH molecule; here spin-orbit coupling is included (see later)

Additional identifiers usually chosen are the symbols X, A, B, C, ..., a, b, c, ... These just relate

to a way of sorting the states. The electronic ground state is referred to with X. The excited states of the same multiplicity get A, B, C, etc, whereas a, b, c are reserved for electronic states of different multiplicity. For historical reasons for some molecules the symbols X, A, B, C, ..., a, b, c, ... are used differently, e.g. in the case of the N₂ molecule.

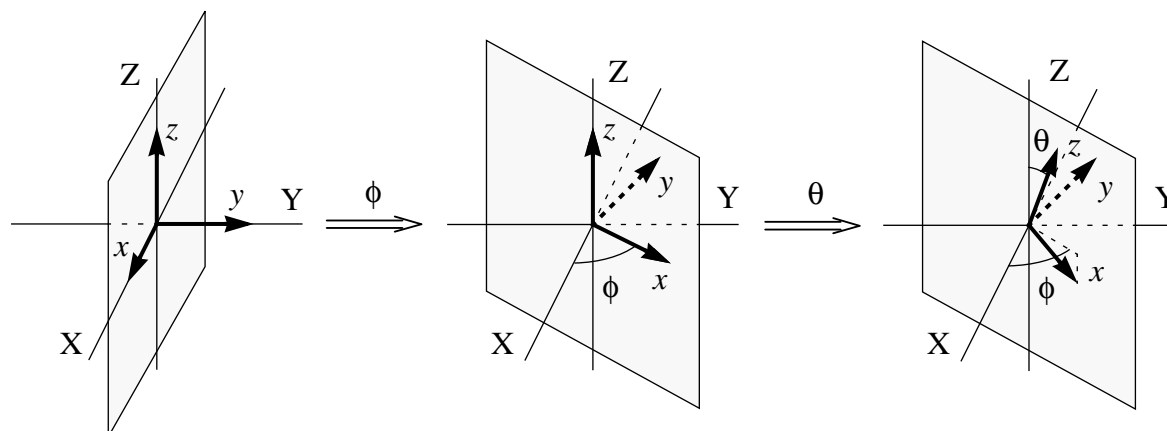
5.3. Interchange of identical nuclei; the operator P

In molecular physics usually two different frames of reference are chosen that should not be confused. As the origins of the *body fixed frame* and the *space fixed frame* the centre of gravity of the molecule is chosen. The coordinates in the space fixed frame are denoted with capitals (X, Y, Z) and those in the body fixed frame with (x, y, z). By making use of Euler-angles the two reference frames can be transformed into one another. The z -axis is by definition the line connecting nucleus 1 with nucleus 2 and this defines the Euler-angles θ and ϕ . By definition $\chi = 0$ and this ties the x - and y -axis (see figure). For an Euler-transformation with $\chi = 0$:

$$x = X \cos \theta \cos \phi + Y \cos \theta \sin \phi - Z \sin \theta$$

$$y = -X \sin \phi + Y \cos \phi$$

$$z = X \sin \theta \cos \phi + Y \sin \theta \sin \phi + Z \cos \theta$$



Euler-transformation with $\chi = 0$. First (x, y, z) rotated around the z -axis over angle ϕ . Then the x - and y -axis stay in the XY -plane. Subsequently (x, y, z) is rotated around the y -axis over angle θ . The y -axis stays in the XY -plane by doing so. The grey plane in the drawing is the xz -plane.

If R is the separation between the nuclei, then R, θ and ϕ can be expressed in the positions of the nuclei in the space fixed frame (see also figure below):

$$\theta = \arccos \left(\frac{Z_1}{\sqrt{X_1^2 + Y_1^2 + Z_1^2}} \right)$$

$$\phi = \arccos \left(\frac{X_1}{\sqrt{X_1^2 + Y_1^2}} \right) \quad \text{and} \quad R = 2\sqrt{X_1^2 + Y_1^2 + Z_1^2}$$

Where (X_1, Y_1, Z_1) is the position of nucleus 1 in the space fixed frame.

If the operator interchanging the two nuclei is called P then:

$$\begin{aligned}
 P(X_1, Y_1, Z_1, X_2, Y_2, Z_2) &= (X_2, Y_2, Z_2, X_1, Y_1, Z_1) \\
 &= (-X_1, -Y_1, -Z_1, -X_2, -Y_2, -Z_2)
 \end{aligned}$$

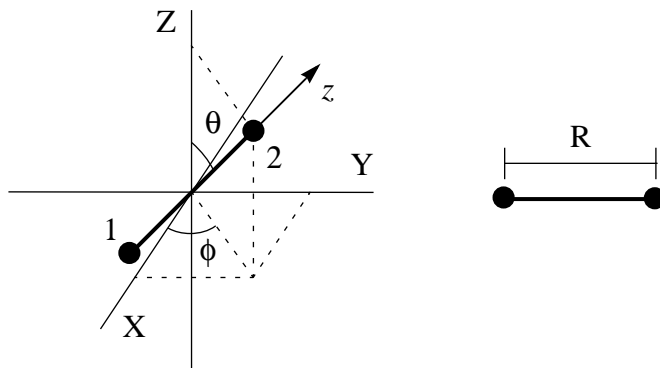


Fig: Under the inversion-operation P not only the angles θ and ϕ change, but also the z -axis.

Or in R, θ and ϕ :

$$P(R, \theta, \phi) = (R, \pi - \theta, \phi + \pi)$$

Because the z -axis by definition runs from nucleus 1 to 2, it will be turned around. From the equations it follows that the y -axis also turns around. If the i^{th} electron has a position (x_i, y_i, z_i) , then the positions of all particles of the molecule represented by $(R, \theta, \phi; x_i, y_i, z_i)$ and so:

$$P(R, \theta, \phi; x_i, y_i, z_i) = (R, \pi - \theta, \phi + \pi; x_i, -y_i, -z_i)$$

The inversion-operator in the space-fixed frame I^{SF} , is then defined as:

$$I^{SF}(X, Y, Z) = (-X, -Y, -Z)$$

It can be deduced that:

$$I^{SF}(R, \theta, \phi; x_i, y_i, z_i) = (R, \pi - \theta, \phi + \pi; -x_i, y_i, z_i)$$

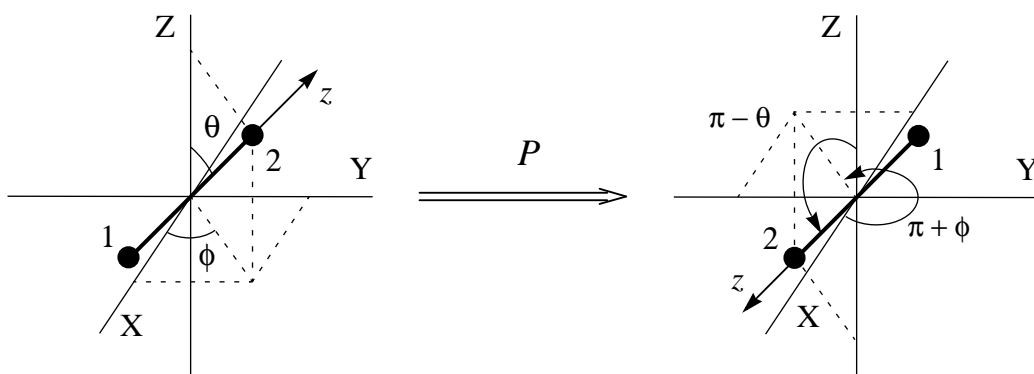


Fig: Under the interchange operator P not only the angles θ and ϕ change, but also the z -axis. For the inversion-operator in the body-fixed frame I^{BF} , it holds that:

$$i^{BF}(R, \theta, \phi; x_i, y_i, z_i) = (R, \theta, \phi; -x_i, -y_i, -z_i)$$

By combining the last two equations it follows:

$$i^{BF} I^{SF}(R, \theta, \phi; x_i, y_i, z_i) = (R, \pi - \theta, \phi + \pi; x_i, -y_i, -z_i)$$

Hence the important relationship for the inversion operators is proven:

$$P = i^{BF} I^{SF}$$

5.4. The parity operator

Parity is defined as the inversion in a space-fixed frame, denoted by the operator I^{SF} . We wish to prove here that this operator I^{SF} is equivalent to a reflection through a plane containing the nuclear axis (z -axis). For this plane we take xz , but the same proof would hold for any plane containing the z -axis. One can write:

$$\sigma_v(xz)(R, \theta, \phi; x_i, y_i, z_i) = (R, \theta, \phi; x_i, -y_i, z_i)$$

with $\sigma_v(xz)$ a reflection through the xz -plane. A rotation of 180° around the axis perpendicular to the chosen plane (so the y -axis), gives in the body-fixed frame:

$$R_{180}(y)(x, y, z) = (-x, y, -z)$$

with $R_{180}(y)$ the rotation-operator around the y -axis. In some textbooks $R_{180}(y)$ is written as $C_2(y)$. The nuclei exchange position:

$$R_{180}(y)(R, \theta, \phi) = (R, \pi - \theta, \phi + \pi)$$

and the xyz -frame then rotates. The total rotation is:

$$R_{180}(y)(R, \theta, \phi; x_i, y_i, z_i) = (R, \pi - \theta, \phi + \pi; -x_i, -y_i, z_i)$$

By combining equations one gets:

$$\sigma_v(xz)R_{180}(y)(R, \theta, \phi; x_i, y_i, z_i) = (R, \pi - \theta, \phi + \pi; -x_i, y_i, z_i)$$

This is the prove that:

$$I^{SF} = \sigma_v(xz)R_{180}(y)$$

or in general:

$$I^{SF} = \sigma_v R_{180}$$

where the axis of R_{180} must be perpendicular to the plane of σ_v . In isotropic space the state of a molecule is independent of the orientation; hence a molecule can undergo an arbitrary rotation without change of state. Hence it is proven that σ_v signifies the parity operation:

$$I^{SF} = \sigma_v$$

5.5 Parity of molecular wave functions; total (+/-) parity

Parity plays an important role in molecular physics, particularly in determining the selection rules for allowed transitions in the system. Quantum mechanics dictates that all quantum states have a definite parity (+) or (-). As discussed above parity is connected to the operator I_{SF} defined in the space-fixed frame, but most molecular properties are calculated in the body-fixed

frame. Hence we usually refer to σ_v as the parity operator. The total wave function of a molecular system can be written:

$$\Psi_{mol} = \Psi_{el}\Psi_{vib}\Psi_{rot}$$

and hence the parity operator should be applied to all products.

In diatomic molecules the vibrational wave function is only dependent on the parameter R , the internuclear separation and therefore:

$$\sigma_v \Psi_{vib} = + \Psi_{vib}$$

Note that this is not generally the case for polyatomic molecules.

The rotational wave functions can be expressed as regular Y_{JM} functions for which the parity is:

$$\sigma_v Y_{JM} = (-1)^J Y_{JM}$$

where J is the rotational angular momentum, previously defined as N . More generally $|\Omega JM\rangle$ wave functions can be used, in similarity to symmetric top wave functions $|JKM\rangle$, in which J is the angular momentum and Ω is the projection onto the molecular axis in the body-fixed frame, while M is the projection in the body-fixed frame. In fact Ω is also the total electronic angular momentum. The effect of the parity operator is:

$$\sigma_v |\Omega JM\rangle = (-1)^{J-\Omega} |-\Omega, J, M\rangle$$

where J takes the role of the total angular momentum.

So in general the wave functions for rotational motion are somewhat more complicated than the spherical harmonics $Y_{NM}(\theta, \phi)$, which are the proper eigen functions for a molecule in a $^1\Sigma$ state. The situation is different when \vec{L} and/or \vec{S} are different from zero. Then \vec{J} is not perpendicular to the molecular axis. It can be shown that the wave functions are:

$$|\Omega JM\rangle = (-1)^{M-\Omega} \sqrt{\frac{2J+1}{8\pi^2}} D_{M\Omega}^{(J)}(\alpha\beta\gamma)$$

where D stands for the Wigner D -functions. The phase factor depends on the choice of the phase convention; the above equation is in accordance with the Condon-Shortly convention. Note that other conventions are in use in the literature.

This is related to the effect of the parity operator on the spin part of the electronic wave function:

$$\sigma_v |S\Sigma\rangle = (-1)^{S-\Sigma} |S, -\Sigma\rangle$$

Note that here Σ has the meaning of the projection of the spin S onto the molecular axis; that is a completely different meaning of Σ than for the states in case $\Lambda=0$. For the orbital angular momentum of the electrons:

$$\sigma_v |\Lambda\rangle = \pm(-1)^\Lambda |-\Lambda\rangle$$

So remember for $\Lambda=0$ states there are indeed two solutions:

$$\sigma_v |\Sigma^\pm\rangle = \pm |\Sigma^\pm\rangle$$

because the states Σ^+ and Σ^- are entirely different states with different energies. The effect of the parity operator on the total wave function is then:

$$\begin{aligned} \sigma_v(\Psi_{el}\Psi_{vib}\Psi_{rot}) &= \sigma_v(|n\Lambda\Sigma\Omega\rangle|v\rangle|\Omega JM\rangle) \\ &= (-1)^{J-2\Sigma+S+\sigma} |n, -\Lambda, S, -\Sigma\rangle|v\rangle|-\Omega, J, M\rangle \end{aligned}$$

where $\sigma=0$ for all states except for Σ^- states, for which $\sigma=1$.

Since the σ_v operation changes the signs of Λ , Σ , and Ω the true parity eigenfunctions are linear combinations of the basis functions, namely:

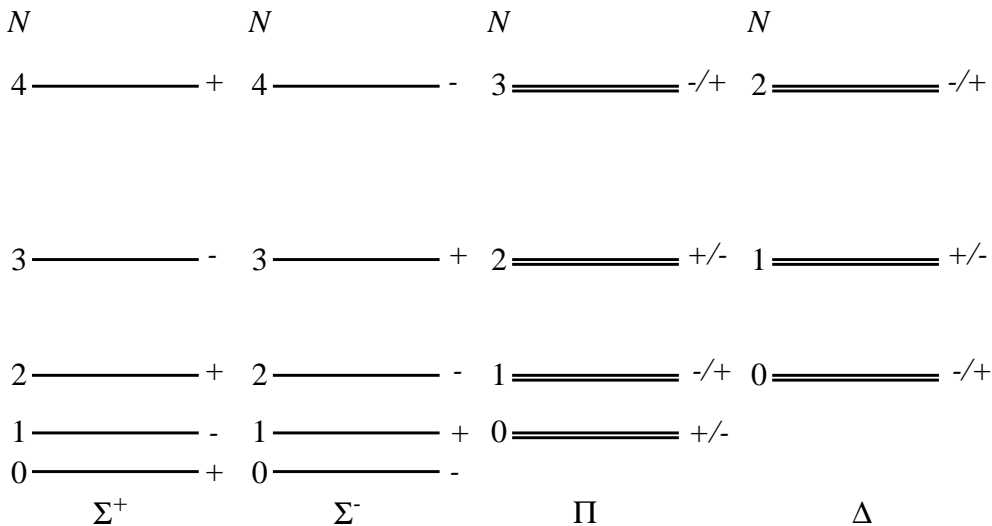
$$|^{2S+1}\Lambda_\Omega^\pm\rangle = \frac{|^{2S+1}\Lambda_\Omega\rangle \pm (-1)^{J-2\Sigma+S+\sigma} |^{2S+1}\Lambda_{-\Omega}\rangle}{\sqrt{2}}$$

for which the parity operator acts as:

$$\sigma_v |^{2S+1}\Lambda_\Omega^\pm\rangle = \pm |^{2S+1}\Lambda_\Omega^\pm\rangle$$

These symmetrized wave functions can be used to derive the selection rules in electric dipole transitions.

With these equations the parity of the various levels in a diatom can be deduced. In a Σ^- state the parity is $(-)^{N+I}$, with N the pure rotation. For a Σ^+ state the parity is $(-)^N$. States with $\Lambda>0$ are double degenerate and both positive and negative rotational levels occur for each value of N . Note that we have jumped back from the angular momentum J (which includes Ω) to N which refers to pure rotation.



The lowest energy levels in the Π and Δ states are purposely depicted higher. Those are the levels for which the pure rotational angular momentum is $N=0$. Note that in a state of Π electronic symmetry there is 1 quantum of angular momentum in the electrons; hence the lowest quantum state is $J=1$. In a Δ state $J=2$ is the lowest state.

5.6 Rotationless parity (e/f)

Because of the J -dependent phase factor the total parity changes sign for each J -level in a rotational ladder. Therefore another parity concept was established where this alternation is divided out. (e) and (f) parity is defined in the following way (for integer values of J):

$$\begin{aligned}\sigma_v \psi &= +(-1)^J \psi & \text{for } e \\ \sigma_v \psi &= -(-1)^J \psi & \text{for } f\end{aligned}$$

For half-integer values of J the following definitions are used:

$$\begin{aligned}\sigma_v \psi &= +(-1)^{J-1/2} \psi & \text{for } e \\ \sigma_v \psi &= -(-1)^{J-1/2} \psi & \text{for } f\end{aligned}$$

It can be verified that all levels in a Σ^+ state have (e) parity. Similarly, all levels in a Σ^- state have (f) parity. For Π states all levels occur in e/f pairs with opposing parity.

The use of e/f suppresses the phase factor in the definition of the parity eigenfunctions. Now it is found, for example in the evaluation of symmetrized basis functions for ${}^2\Pi$ states:

$$\begin{aligned}|{}^2\Pi_{3/2}, e/f\rangle &= \frac{|{}^2\Pi_{3/2}\rangle \pm |{}^2\Pi_{-3/2}\rangle}{\sqrt{2}} \\ |{}^2\Pi_{1/2}, e/f\rangle &= \frac{|{}^2\Pi_{1/2}\rangle \pm |{}^2\Pi_{-1/2}\rangle}{\sqrt{2}} \\ |{}^2\Sigma_{1/2}^+, e/f\rangle &= \frac{|{}^2\Sigma_{1/2}^+\rangle \pm |{}^2\Sigma_{-1/2}^+\rangle}{\sqrt{2}} \\ |{}^2\Sigma_{1/2}^-, e/f\rangle &= \frac{|{}^2\Sigma_{1/2}^-\rangle \pm |{}^2\Sigma_{-1/2}^-\rangle}{\sqrt{2}}\end{aligned}$$

5.7 g/u and s/a symmetries in homonuclear molecules

For homonuclear molecules the point group $D_{\infty h}$ contains the inversion operation i defined in the body-fixed frame. The operation i leaves the vibrational, rotational and electron spin parts of the wave function unchanged; it only acts on the electronic part of the wave function. The important point to realize is that the transition dipole moment operator $\vec{\mu}$ is of u -parity and hence the selection rules for electric dipole transitions are $g \leftrightarrow u$.

In the above the interchange operator P was defined and it was proven that:

$$P = i^{BF} I^{SF} = i^{BF} \sigma_v$$

States which remain unchanged under the P operator are called *symmetric* (s), while those changing sign are called *anti-symmetric* (a). Under the operation I_{SF} or σ_v the levels get their (+/-) symmetry, while the operation i_{BF} introduces the g/u symmetry. Thus it follows when the electronic state is:

| | | | |
|----------|---|---|---------------------------|
| gerade | → | + | levels are symmetric |
| | | - | levels are anti-symmetric |
| ungerade | → | + | levels are anti-symmetric |
| | | - | levels are symmetric |

This gives the following ordering:

| | | | | | | | | | | | | |
|-----|---|-------|--------------|---|-------|--------------|---|-------|--------------|---|-------|--------------|
| N | | | | | | | | | | | | |
| 4 | + | ----- | s | - | ----- | a | + | ----- | a | - | ----- | s |
| 3 | - | ----- | a | + | ----- | s | - | ----- | s | + | ----- | a |
| 2 | + | ----- | s | - | ----- | a | + | ----- | a | - | ----- | s |
| 1 | - | ----- | a | + | ----- | s | - | ----- | s | + | ----- | a |
| 0 | + | ----- | s | - | ----- | a | + | ----- | a | - | ----- | s |
| | | | Σ_g^+ | | | Σ_g^- | | | Σ_u^+ | | | Σ_u^- |

For $\Lambda > 0$ states the Π_g^- states are ordered as Σ_g^- , etc.

5.8 The effect of nuclear spin

The magnetic moment of the nuclei interact with the other angular momenta in the molecular system. When all the angular momenta due to rotation, electronic orbital and spin angular momentum are added to \vec{J} then the spin of the nucleus \vec{I} can be added:

$$\vec{F} = \vec{J} + \vec{I}$$

If both nuclei have a spin they can both be added following the rules for addition of angular momenta.

$$\vec{F} = \vec{J} + \vec{I}_1 + \vec{I}_2$$

The additions of angular momenta play a role in heteronuclear as well as homonuclear molecules. Of course the degeneracy of the levels should be taken into account: $(2I_1+1)(2I_2+1)$.

In a homonuclear molecule the symmetry of the nuclear spin wave functions play a role. For diatomic homonuclear molecules we must distinguish between nuclei with:

- *integral spin*, which obey the *Bose-Einstein* statistics
- *half-integral spin* which obey the *Fermi-Dirac* statistics

The symmetrization postulate of quantum mechanics tells us that all wave functions are either

unchanged or change sign under permutation of two particles. The total wave function Ψ must be symmetric for integral spin particles, anti-symmetric for half-integral spin particles. This gives rise to symmetry restrictions that can be viewed in various ways; the textbooks give also various arguments, starting from different perspectives. One view is to start from the interchange operator P , consider electronic states with g-symmetry (under i_{BF}) and +-symmetry (under σ_v) and neglect the vibrational part (always a positive parity in diatomics). Then the rotational parts of the wave function and the nuclear spin wave functions remain. The product of the exchange properties of these wave functions should follow the proper statistics. For the rotational levels (here we restrict ourselves to pure rotation; in case of angular momentum coupling between electronic and rotational motion it also applies) the parity is $(-)^N$. Hence it follows:

| | | | |
|-----------|----------|---------|------------------------------------|
| FD-nuclei | even N | require | Ψ_{nuc} anti-symmetric |
| | odd N | require | Ψ_{nuc} symmetric |
| BE-nuclei | even N | require | Ψ_{nuc} symmetric |
| | odd N | require | Ψ_{nuc} anti-symmetric |

If the symmetry of the wave function is considered then the rules change for -parity states and for u -states. One can derive:

| | | | |
|-----------|----------|---------|------------------------------------|
| FD-nuclei | s levels | require | Ψ_{nuc} anti-symmetric |
| | a levels | require | Ψ_{nuc} symmetric |
| BE-nuclei | s levels | require | Ψ_{nuc} symmetric |
| | a levels | require | Ψ_{nuc} anti-symmetric |

The nuclear spin weight is $(2I+1)^2$ where I is the spin. Of the $(2I+1)^2$ possible states:

$$\begin{array}{ll} (2I+1)(I+1) & \text{are symmetric} \\ (2I+1)I & \text{are anti-symmetric} \end{array}$$

5.9 Para and ortho hydrogen

In the hydrogen molecule with two spin $I_H=1/2$ the total nuclear spin is:

$$\vec{I}_{\text{tot}} = \vec{I}_H + \vec{I}_H = 0, 1$$

There exist $(2I+1)^2=4$ possible quantum states of which 3 are symmetric and one anti-sym-

metric under interchange of the two particles (note that α means spin up, β spin down):

$$I = 1 \quad \begin{array}{c} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{array}$$

and:

$$I = 0 \quad \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Note that the three states for $I=1$ have $M_I=+1, -1$ and 0 .

For the hydrogen nuclei FD-statistics applies, hence the symmetric wave function ψ_{nuc} couples with a levels and in the electronic ground state, of $^1\Sigma_g^+$ symmetry, with the odd N levels. This form of hydrogen is called *ortho-hydrogen*; the other is *para-hydrogen*. There is a 3:1 ratio of levels in ortho vs para. It is not easy for the molecule to undergo a transition from ortho to para; in electromagnetic transitions this does not occur, since the electric dipole does not affect the ordering of nuclear spins.

5.10 Missing levels in the oxygen molecule

The nuclear spin of ^{16}O nuclei is $I=0$. As a consequence the nuclear spin wave function can be left out of the problem, or in other words, it should be considered as having positive symmetry. The electronic ground state of O_2 has a $^3\Sigma_g^-$ symmetry, hence has a negative parity for the electronic wave function. ^{16}O nuclei follow Bose-Einstein statistics, so the total wave function must be symmetric under the interchange operator. The symmetric states (s symmetry, see the figure for Σ^- states) are the ones with odd N quantum numbers for pure rotation. These s-states combine with symmetric nuclear spin wave functions, the (a)-states would combine with anti-symmetric nuclear spin wave functions, *but these do not exist*. As a consequence the (a) states, or the states with even rotational angular momentum do not exist.

The energy levels of the oxygen molecule in its ground state are depicted in the figure.

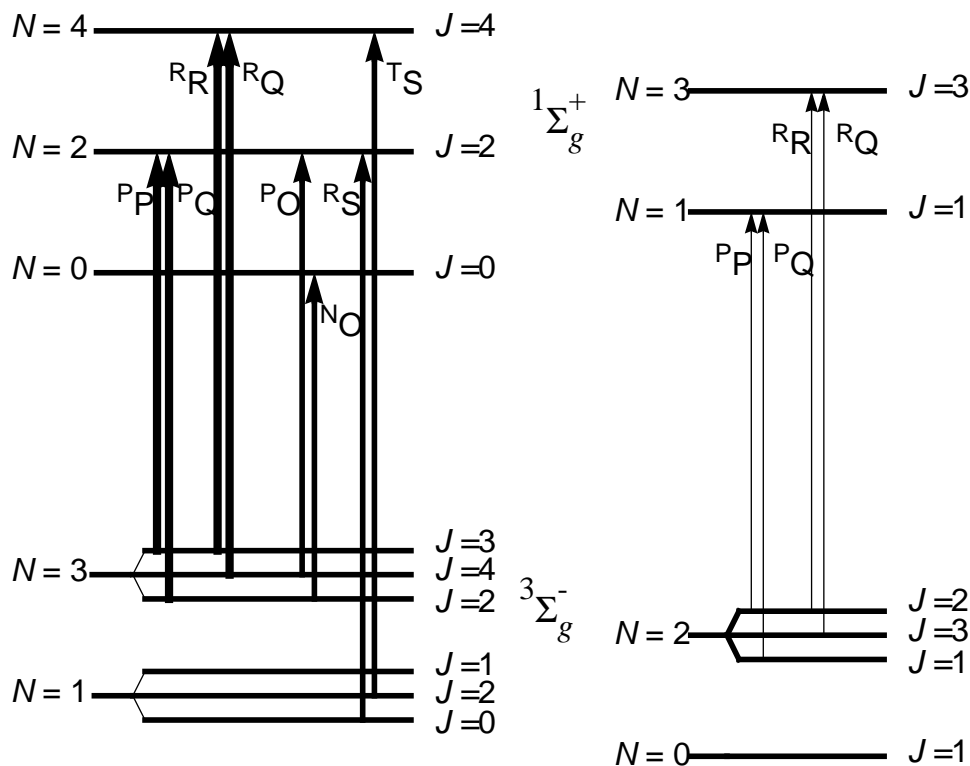


Figure: The allowed and forbidden states and transitions in the $^{16}\text{O}_2$ molecule.

Note that this analysis only holds for the $^{16}\text{O}_2$ molecule, and for the $^{18}\text{O}_2$ molecule, because the ^{18}O nucleus also has $I=0$. The heteronuclear species (isotopomers) $^{16}\text{O}^{18}\text{O}$, $^{16}\text{O}^{17}\text{O}$ and $^{17}\text{O}^{18}\text{O}$ do not follow this peculiar behaviour since the additional inversion symmetry is lifted. In the $^{17}\text{O}_2$ isotopomer the situation is also different, because the nuclear spin is $I=5/2$. This gives rise to an intensity alternation (which one?), but not to a disappearing of lines. So for all isotopomers except $^{16}\text{O}_2$ and $^{18}\text{O}_2$ the level scheme depicted on the right is appropriate.

In the figure the rotational levels of the electronic ground state ($^3\Sigma_g^-$) are split into three components as a result of the triplet structure. The electron spins of the two paired outer electrons lign up to a triplet giving molecular oxygen a paramagnetic character. The interaction between the resulting spin vector \vec{S} and the rotational angular momentum \vec{N} , $\vec{J} = \vec{N} + \vec{S}$ causes a lifting of the degeneracy and a splitting into three components, wherever possible (not for $N=0$ obviously).

In the electronically excited state of $^1\Sigma_g^+$ symmetry, the situation is similar. Because the electronic parity is positive here the odd N -levels are missing; also there is no triplet splitting, since we deal with a singlet state.

The transitions depicted in the figure are also anomalous. Since both the ground and excited states are of g -symmetry electric dipole transitions are not allowed. A second reason is that $^1\Sigma_g^+ - ^3\Sigma_g^-$ transitions are not allowed for electric dipole. The thick lines are the allowed but very weak magnetic dipole transitions, while the thinner lines refer to the branches of the

electric quadrupole transitions (again weaker by a factor 10^6). The fact that the transition is between a triplet state and a singlet state is also a reason for its weakness.

5.11 The 3:1 ratio in N_2

Herzberg measured, in the 1930s, a spectrum (the Raman spectrum in the electronic ground state of $^1\Sigma_g^+$ symmetry) for the nitrogen molecule and observed a 3:1 ratio between lines. This phenomenon could only be explained by assuming that the nitrogen (^{14}N) nucleus has a nuclear spin of $I=1$. In those days nuclei were considered to be built from protons and electrons; the neutron was not yet observed, postulated however. The ^{14}N nucleus was considered to be built from 14 protons and 7 electrons giving rise to a charge of 7+ and a mass of 14 amu. But 21 particles of half-integer spin should build a nucleus of total half-integer spin and should therefore obey Fermi-Dirac statistics. This paradox gave support to the neutron hypothesis.

6. Open Shell Molecules

6.1 Introduction

In our discussion of rotational energies we have assumed (tacitly) that \vec{N} was the only angular momentum. This assumption is very good for $^1\Sigma$ in which all electronic spins are paired off and the orbital angular momentum, although in principle not necessarily zero, manifests itself only in second order. The situation is drastically different in states other than $^1\Sigma$ in which both \vec{L} and \vec{S} can be effectively different from zero. On the other hand in the discussion of electronic energies the molecule was considered as non-rotating $\vec{N} = 0$. In actual molecules all these angular momenta may be present and coupled in a complicated way by gyroscopic and magnetic forces. Individual angular momenta then lose their identity and only certain sums resulting from effective couplings are constants of motion which can be determined from the observed spectra.

The presence of the various angular momenta introduces a number of new phenomena and problems:

- (1) coupling schemes,
- (2) interactions which may not only shift but also split electronic energy levels,
- (3) breakdown of certain rules and approximations.

| ANGULAR MOMENTA | DEFINITION | QUANTUM NUMBER |
|--------------------|-------------------------------|-----------------------------|
| Electronic orbital | $\vec{L} = \sum \vec{l}_i$ | L |
| SF projection | L_Z | M_L |
| BF projection | L_z | Λ |
| Electronic spin | $\vec{S} = \sum \vec{s}_i$ | S |
| SF projection | S_Z | M_S |
| BF projection | S_z | Σ |
| Rotational | \vec{R} | R |
| SF projection | R_Z | M |
| BF projection | R_z | - |
| Total orbital | $\vec{N} = \vec{R} + \vec{L}$ | N |
| BF projection | N_z | Λ |
| Total molecular | $\vec{J} = \vec{N} + \vec{S}$ | J |
| SF projection | J_Z | M_J |
| BF projection | J | $\Omega = \Lambda + \Sigma$ |
| Total electronic | $\vec{J} = \sum \vec{j}_i$ | - |
| BF projection | - | Ω |

In the table all the angular momenta are collected which appear in calculations of molecular energies, with their projections in SF-Z axis and the BF-z axis (the molecular axis), and associated

quantum numbers. The coupling of \vec{l}_i 's to \vec{L} and \vec{s}_i 's to \vec{S} corresponds to the atomic Russell-Saunders coupling, while the coupling to $\vec{J}_a (j_i = l_i + s_i)$ represents an analogon of jj-coupling. We have disregarded the possibility of a vibrational angular momentum. Various possible ways of coupling the angular momenta introduced by Hund in 1926 (known as Hund's cases) are discussed in the following section.

The new interactions which have to be considered in the presence of unpaired electronic spin and non-zero orbital momenta are:

spin-spin,

spin-orbit (and also spin other orbit),

spin-rotation.

The microscopic hamiltonian for the spin-spin (H_{ss}) and spin-orbit (H_{sor}) interaction is:

$$H_{ss} = \left(\frac{\mu_0}{4\pi}\right) g_e^2 \mu_B^2 \sum_{j>i} \frac{[(\vec{s}_i \cdot \vec{s}_j) r_{ij}^2 - 3(\vec{r}_{ij} \cdot \vec{s}_i)(\vec{r}_{ij} \cdot \vec{s}_j)]}{r_{ij}^5}$$

and:

$$H_{sor} = \left(\frac{\mu_0}{4\pi}\right) 2mg_e \mu_B^2 \sum_{\alpha, j} \left(\frac{Z_\alpha}{r_{j\alpha}^3}\right) \left([\vec{r}_{j\alpha} \times \left(\frac{1}{2}\vec{v}_j - \vec{v}_\alpha\right)] \cdot \vec{s}_j \right) -$$

$$-\left(\frac{\mu_0}{4\pi}\right) 2mg_e \mu_B^2 \sum_{j \neq i} \left(\frac{1}{r_{ij}^3}\right) \left[\vec{r}_{ij} \times \left(\frac{1}{2}\vec{v}_j - \vec{v}_i\right) \cdot \vec{s}_j \right]$$

In these expressions g_e is the electronic g factor, μ_B the Bohr magneton, $\vec{r}_{\mu\kappa} = \vec{r}_\mu - \vec{r}_\kappa$ ($\vec{r}_{\mu\kappa} = |\vec{r}_{\mu\kappa}|$) and \vec{v}_μ stands for the velocity of the particle μ .

Actually this expression, first derived by Van Vleck (1951), is a sum:

$$H_{sor} = H_{so} + H_{sr}$$

where

$$H_{so} = \left(\frac{\mu_0}{4\pi}\right) 2mg_e \mu_B^2 \left\{ \sum_{\alpha, j} \left(\frac{Z_\alpha}{r_{j\alpha}^3}\right) \left([\vec{r}_{j\alpha} \times \frac{1}{2}\vec{v}_j] \cdot \vec{s}_j \right) - \sum_{j \neq i} \left(\frac{1}{r_{ij}^3}\right) \left([\vec{r}_{ji} \times \left(\frac{1}{2}\vec{v}_j - \vec{v}_i\right)] \cdot \vec{s}_j \right) \right\}$$

$$H_{sr} = -\left(\frac{\mu_0}{4\pi}\right) 2mg_e \mu_B^2 \sum_{\alpha, j} \left(\frac{Z_\alpha}{r_{j\alpha}^3}\right) ([\vec{r}_{j\alpha} \times \vec{v}_\alpha] \cdot \vec{s}_j)$$

The hamiltonian H_{so} is the most general form of the fine structure interaction. It contains the usual spin-orbit interaction, the spin-other-orbit interaction and the cross terms between the various \vec{r}'_s , \vec{v}'_s and \vec{s}'_s . The most common forms of H_{so} are:

$$H_{so}' = \sum_{j, \alpha} \zeta_j(\vec{r}_j) (\vec{l}_{j\alpha} \cdot \vec{s}_j) \quad or \quad H_{so}'' = A(\vec{L} \cdot \vec{S})$$

The last form of H_{so} can only be used when \vec{L} and \vec{S} are well (or almost well) defined. In elementary text books this form is written as:

$$H_{so}'' = A\Lambda\Sigma$$

This expression can only be used for the diagonal contribution of H_{so} and only when Λ and Σ are good (or almost good) quantum numbers. In this expression A is the spin-orbit coupling

constant ($A > 0$ for normal and $A < 0$ for inverted fine structure) and $\vec{l}_{j\alpha}$ is the orbital angular momentum of the j -th electron with respect to the α nucleus. The spin rotation hamiltonian is usually written in the form:

$$H_{sr} = \gamma(\vec{R} \cdot \vec{S})$$

(often with \vec{N} replacing \vec{R} and λ replacing γ).

6.2 Hund's Coupling Cases

Case (a)

This case occurs when

(1) all l 's are coupled to \vec{L} and all s_i 's to \vec{S} ,

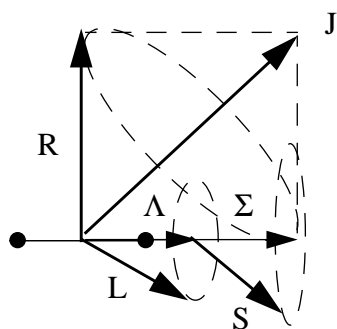
(2) the coupling \vec{L} of and \vec{S} to the axial internuclear field (sometimes called the $\vec{L} \cdot \vec{A}$ and $\vec{S} \cdot \vec{A}$ coupling, respectively) is much stronger than the spin-orbit ($\vec{L} \cdot \vec{S}$) or any other possible coupling (e.g. $\vec{R} \cdot \vec{L}$) i.e.:

$$\begin{aligned} \vec{L} \cdot \vec{A} \gg \vec{L} \cdot \vec{S} & \quad \text{and} \quad \vec{L} \cdot \vec{A} \gg \vec{R} \cdot \vec{L} \\ \vec{S} \cdot \vec{A} \gg \vec{L} \cdot \vec{S} & \quad \text{and} \quad \vec{S} \cdot \vec{A} \gg \vec{N} \cdot \vec{S} \end{aligned}$$

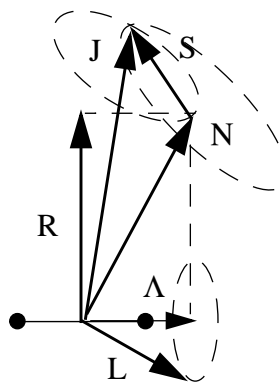
A gyroscopic diagram of this coupling is shown in the figure below. Both \vec{L} and \vec{S} precess independently about the internuclear axis and only their components (Λ and Σ , respectively) and their sum:

$$\Omega = \Lambda + \Sigma$$

are constants of motion. This sum, written as a vector $\vec{\Omega}$ couples with \vec{R} to a total molecular angular momentum:



Hunds case (a)



Hunds case (b)

Its quantum number can take the values:

$$J = \Omega, \Omega + 1, \Omega + 2, \dots$$

Consequently, the levels with $J < \Omega$ cannot occur. Hund's case (a) is quite common in the ground state of $^1\Sigma$ molecules, especially the light ones.

Case (b)

In this case \vec{L} is still coupled to internuclear axis but \vec{S} is decoupled from it, more or less. Put

differently, \vec{S} is coupled more strongly to $\vec{N} = \vec{R} + \vec{\Lambda}$ than to \vec{A} , i.e.

$$\vec{L} \cdot \vec{A} \gg \vec{L} \cdot \vec{S} \quad \text{and} \quad \vec{L} \cdot \vec{A} \gg \vec{R} \cdot \vec{L}$$

$$\vec{N} \cdot \vec{S} \gg \vec{S} \cdot \vec{A}$$

The couplings of the various angular momenta and their precessions are shown in the figure. Explicitly the couplings are:

$$\vec{R} + \vec{\Lambda} = \vec{N}$$

$$\vec{N} + \vec{S} = \vec{J}$$

The quantum numbers J and N can take the values:

$$J = N + S, N + S - 1, \dots, |N - S|$$

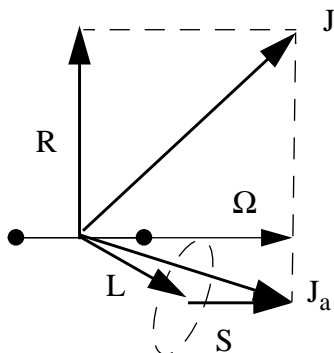
$$N = \Lambda, \Lambda + 1, \Lambda + 2, \Lambda + 3, \dots$$

Precession of \vec{S} around \vec{N} is slow compared to rotation because the interaction which couples these vectors ($\gamma \vec{N} \cdot \vec{S}$) is relatively weak. The case (b) coupling is especially important when $\Lambda = 0$ but $S \neq 0$ (CN, H_2^+ , HgH, NH, O_2, \dots), but can also occur for other electronic states, particularly when there are relatively few electrons.

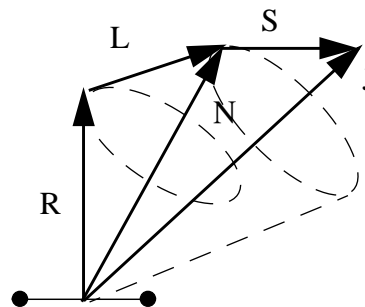
Case (c)

The coupling diagram for this case is shown in the figure below. It occurs when the spin-orbit coupling is much stronger than the coupling to the internuclear axis:

$$\vec{L} \cdot \vec{S} \gg \vec{L} \cdot \vec{A} \quad \text{and} \quad \vec{L} \cdot \vec{S} \gg \vec{S} \cdot \vec{A}$$



Hund's case (c)



Hund's case (d)

This is usually the case in heavy molecules, like Br_2 , I_2 . The coupling which produces \vec{J}_a may be of Russel-Saunders or of jj type:

$$\vec{J}_a = \vec{L} + \vec{S} \quad \vec{J}_a = \sum \vec{j}_i \quad (\vec{j}_i = \vec{l}_i + \vec{s}_i)$$

Case (d)

In cases (a) and (b) the $\vec{L} \cdot \vec{A}$ coupling is assumed to be strong. However, in some excited states of H_2 , He_2 and other molecules, the electronic orbit is so large that this coupling becomes too weak. The gyroscopic effects uncouple \vec{L} from the internuclear axis. The coupling diagram ap-

propriate for this situation, shown in the figure above, corresponds to the coupling scheme:

$$\vec{R} + \vec{L} = \vec{N}$$

$$\vec{N} + \vec{S} = \vec{J}$$

When $S = 0$ we expect a splitting of a level into $2L + 1$ components characterized by:

$$N = R + L, R + L - 1, \dots, \dots, |R - L|$$

Splitting between the J components when $S > 0$ is determined by the $\vec{N} \cdot \vec{S}$ interaction which is usually very weak.

The Hund's coupling schemes are idealizations, at their best actual molecules can only approach them. Nevertheless, they are useful as a classification and as an indication of the "best" basis for calculations of molecular energies.

6.3 Calculation of rotational energies

6.3.1 Case (a)

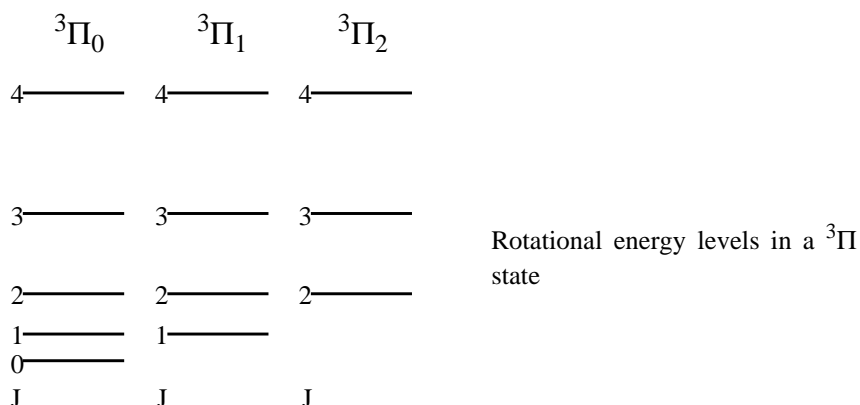
An expression for the rotational energy can in this case be obtained from the "pure" rotational hamiltonian

$$H_r = B\vec{R}^2 = B(\vec{J}^2 - \vec{\Omega}^2)$$

assuming a simple "rotational" basis set of $|J\Omega M\rangle$ corresponding to eigenvalues of \vec{J}^2 , J_z and J_z . The result for the energy, or rotational term value, is:

$$F_v(J) = B[J(J+1) - \Omega^2] = BJ(J+1)$$

In the second line the term $-B\Omega^2$ is disregarded because it is a constant in a given electronic state. Rotational levels of a $^3\Pi$ multiplet are shown schematically in the figure. The lowest levels in this figure correspond to $J = \Omega$. For a $^2\Pi$ state, apart from $J = 1/2$, each value of J occurs for each of the two multiplet components which have $\Omega = 3/2, 1/2$.

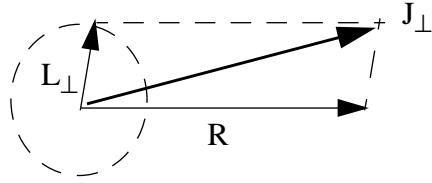


The question is, how good is the expression for the rotational energy. First of all we note that R is NOT a good quantum number. Its value is fixed by the condition:

$$R^2 = J(J+1) - \Omega^2$$

Strictly speaking the only good quantum numbers for a rotating molecule are J , M_J and Ω . Then \vec{R} should be considered more properly as the perpendicular component of \vec{J} (i.e. $J_{\perp}; \Omega = J_{\parallel}$). But this J_{\perp} does not result from nuclear rotation alone, but has also a contri-

tribution from the rapidly precessing perpendicular component



L_{\perp} of \vec{L} . The “pure” nuclear rotation couples with L_{\perp} to produce J_{\perp} . The operator \vec{R} of the pure rotational angular momentum and the rotational hamiltonian are:

$$\vec{R} = J_{\perp} - L_{\perp}$$

$$H_r = B\vec{R}^2 = (J_{\perp} - L_{\perp})^2 = J_{\perp}^2 + L_{\perp}^2 - 2(J_{\perp} \cdot L_{\perp})$$

Hence:

$$F_v(J) = B_v[J(J+1) - \Omega^2] + B_v\langle L_{\perp}^2 \rangle - 2B_v\langle J_{\perp} \cdot L_{\perp} \rangle$$

The last term in this expression may be approximated by:

$$-2B_v\langle \vec{R} \cdot L_{\perp} \rangle$$

The term $B_v(\langle L_{\perp}^2 \rangle - \Omega^2)$ has a constant value in a given electronic state and can be removed as a part of electronic energy. The rotational energy can then be written as:

$$F_v(J) = B_v[J(J+1)] + f_v(\Omega, J)$$

$f_v(\Omega, J)$ represents contribution of the last term of in the equation. As will be shown later this term is responsible for the Λ -doubling.

Spin orbit coupling $A \Lambda \Sigma$ splits the electronic state into $2S + 1$ multiplet components that have different values of Ω and $f_v(\Omega, J)$.

6.3.2 Case (b)

In the pure case (b) with $\vec{S} = 0$ an expression for the rotational energy $F_v(N)$ follow from:

$$\vec{R}^2 = \vec{N}^2 - \Lambda^2$$

i.e.

$$F_v(N) = B_v[N(N+1) - \Lambda^2]$$

which reduces to $F_v(N) = B_v[N(N+1)]$ because $B_v\Lambda^2$ is independent of the rotational quantum number (R or N).

A (somewhat) better approach is analogous to that followed in case (a). By writing:

$$\vec{R} = N_{\perp} - L_{\perp}$$

we get:

$$\begin{aligned} H_r &= B_v\vec{R}^2 = B_v(N_{\perp}^2 + L_{\perp}^2 - 2N_{\perp}L_{\perp}) \\ &= B_v(\vec{N}^2 - N_{\parallel}^2 + L_{\perp}^2 - 2(N_{\perp} \cdot L_{\perp})) \end{aligned}$$

i.e.:

$$F_v(N) = B_v[N(N+1) - \Lambda^2 + \langle L_{\perp}^2 \rangle] + f_v(\Lambda, N)$$

The last term represents a coupling between electronic and rotational motion, in fact the same

as above. If this coupling is neglected and the terms $-2B_v(\Lambda^- - \langle L_{\perp}^- \rangle)$ are included in the ro-vibrational energy, then $F_v(N)$ reduces to:

$$F_v(N) = B_v N(N+1)$$

The treatments followed above neglect not only other electronic couplings, but also for the Hund's case (b) essential $\vec{N} \cdot \vec{S}$ coupling to obtain \vec{J} . This coupling can, in good approximation, be written as:

$$H_{SN} = \gamma(\vec{S} \cdot \vec{N})$$

with γ as the spin-rotation constant. It can be interpreted as an interaction of the spin magnetic moment with the magnetic field produced by molecular rotation. This field can be produced by:

- (1) simple rotation of the nuclear frame and
- (2) by excitation of electrons to states with non-zero angular momentum.

The second effect is generally the most important one, depending on the separation between the electronic states. We consider now two examples of case (b) coupling assuming a basis set of $|NSJM\rangle$.

- (1) $^2\Sigma$ states

For these states the spin-rotation interaction is the only one contributing to the rotational energy.

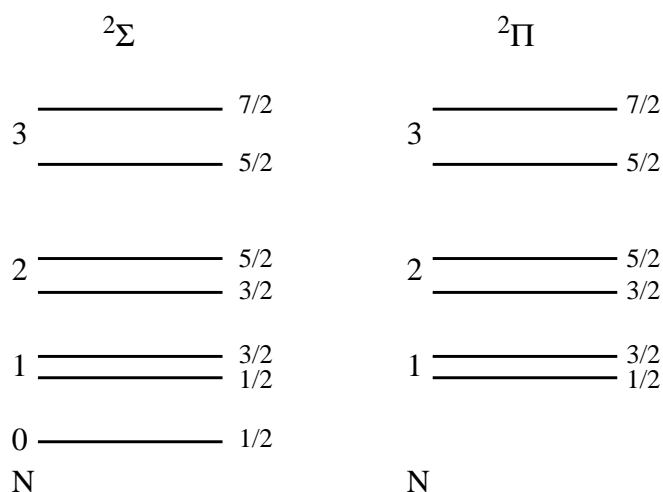
$$H_{SN} \rangle = \frac{1}{2}[J(J+1) - S(S+1) - N(N+1)] = \frac{1}{2}\gamma \begin{cases} N & \text{for } J = N + 1/2 \\ -(N+1) & \text{for } J = N - 1/2 \end{cases}$$

i.e.

$$F_v(N) = \begin{cases} B_v N(N+1) + \frac{1}{2}\gamma N & \text{for } J = N + 1/2 \\ B_v N(N+1) - \frac{1}{2}\gamma(N+1) & \text{for } J = N - 1/2 \end{cases}$$

Energy levels for $^2\Sigma$ and a $^2\Pi$ states are shown schematically in the figure. States for $J = N + 1/2$ and $J = N - 1/2$ are often designated as F_1 and F_2 following Herzberg. The spin rotation splitting in the figure is greatly exaggerated. Each value of J occurs in association with two possible values of N (e.g. $J = 3/2$ from $N = 1$ and $N = 2$).

It should be noted that in the $^2\Sigma$ state a spin-orbit type interaction $\sum \vec{S} \cdot \vec{l}_i$ (see $^3\Sigma$ states) may contribute significantly to γ . The splitting of a $^2\Sigma$ state due to the spin-rotation interaction is known as p-doubling.



2) ${}^3\Sigma$ states

The best known example of this state and coupling is O_2 in its ground state. Since there are two unpaired electronic spins the following interactions have to be considered:

(1) spin-rotation, (2) spin-spin, (3) polarization, or induced spin-orbit

Spin-rotation interaction is, in principle, the same as in the case of ${}^2\Sigma$ states. The contribution is given by above, which for a ${}^3\Sigma$ state ($S = 1$) yields a triplet (this splitting is sometimes called ρ -tripling):

$$\langle H_{SN} \rangle = \begin{cases} \gamma N & \text{for } J = N + 1 \\ -\gamma & \text{for } J = N \\ -\gamma(N + 1) & \text{for } J = N - 1 \end{cases}$$

It was shown by Kramers (1939) that in the case of two parallel spins this interaction, when averaged over the molecular rotation, is equivalent to:

$$H_{ss} = \lambda(3 \cos^2 \chi - 1) = \lambda(3S_z^2 - \vec{S}^2)$$

where χ is the angle between \vec{S} and the molecular axis. So the spin-spin interaction is equivalent to $\vec{S} \cdot \vec{A}$. Calculation of the spin-spin contribution is rather straightforward if use can be made of angular momentum techniques. The result is:

$$\langle H_{ss} \rangle = \langle NSJ | H_{ss} | NSJ \rangle = -\lambda \left[\frac{3X(X + 1) - 4S(S + 1)N(N + 1)}{2(2N - 1)(2N + 3)} \right]$$

where:

$$X = J(J + 1) - S(S + 1) - N(N + 1)$$

and λ is the spin-spin coupling constant. For $S=1$ we obtain from this expression:

$$\langle H_{ss} \rangle = \begin{cases} \frac{\lambda N}{2N + 3} & \text{for } J = N + 1 \\ \lambda & \text{for } J = N \\ \lambda \frac{N + 1}{2N - 1} & \text{for } J = N - 1 \end{cases}$$

The polarization effect involves excitation of electrons to states with non-zero orbital momentum l_i ; this momentum (or momenta) interact then with \vec{S} via a spin-orbit type coupling $\sum \vec{S} \cdot \vec{l}_i$. Hebb (1936) considered a coupling of the type $\vec{S} \cdot \vec{L}_\perp$. Another possible mechanism is a magnetic spin excitation of orbital angular momentum. This excitation is especially important

when there is a low lying Π state. Both mechanisms involve perturbation of the ground state by a Π state. Effective hamiltonians in both mechanisms have the same angular dependence as the spin-spin interactions and, except for a different coupling constant, give the same contribution to the energy. The effects of spin-spin and of the other interaction cannot be separated from observed spectra. In the following we assume that λ contains all the effects. The constant λ can be large; for O_2 .

$$\lambda = 39\,667 \text{ MHz} \quad \gamma = -252.7 \text{ MHz} \quad B = 43\,102 \text{ MHz}$$

The resulting rotational energies are:

$$F_v(N) = B_v N(N+1) + \gamma(N+1) - 3\lambda \frac{N+1}{2N+3}$$

$$F_v(N) = B_v N(N+1)$$

$$F_v(N) = B_v N(N+1) - \gamma N - 3\lambda \frac{N}{2N-1}$$

6.3.3 Case (c) and (d)

Case (c) occurs quite often in heavy diatomic molecules, (d) is however quite rare. The latter case requires a weak coupling of \vec{L} to the internuclear axis and a strong $\vec{N} \cdot \vec{S}$ (or $\vec{R} \cdot \vec{S}$) coupling, conditions which are difficult to fulfil, simultaneously.

If we disregard all the weaker effects the rotational energy in case (c) is given by the same expression as in case (a):

$$F_v(J) = B_v J(J+1)$$

Similar arguments yield for case (d):

$$F_v(R) = B_v R(R+1)$$

When spin-orbit interaction is large the LS manifold may appear as a set of distinct energy levels. In case (d) the manifold may contain $(2L+1)(2S+1)$ levels because N can take values from $R+L$ to $R-L$, except when $R < L$. Splitting between the L sublevels may be large but between the J components when $S > 0$ is normally negligible because the $\vec{N} \cdot \vec{S}$ coupling is usually very weak.

6.4. Intermediate Cases

6.4.1 Background

The calculation of rotational energies in the preceding section are not very accurate for a number of reasons. First of all, molecules never comply to pure Hund's coupling cases. In a molecule \vec{S} can be coupled to $\vec{\Lambda}$ or to the molecular axis in low rotational states, but as the rotational frequency increases and becomes larger than the precession frequency of \vec{S} about $\vec{\Lambda}$, \vec{S} decouples from $\vec{\Lambda}$ and couples to \vec{N} instead. We then get a transition from case (a) to case (b), also known as *spin-uncoupling*. Many molecules, e.g. OH belong to an INTERMEDIATE CASE. Similar *L-uncoupling* occurs when rotation becomes much faster than precession of \vec{L} about the molecular axis. We then get a transition from case (b) to case (d), which is rather uncommon.

Another reason lies in energies involved in the various couplings. In case (a) \vec{S} is strongly coupled to $\vec{\Lambda}$ and states differing Σ (because e.g. of spin-orbit coupling) have large energy differences. In case (b) \vec{S} is weakly coupled to \vec{N} , and states differing in orientation of \vec{S} (i.e. in J) show only a small energy difference. Consequently an effect which is considered as relatively

small in one case is not necessarily so in another. A practical consequence of this is that off-diagonal contributions of some interactions generally cannot be disregarded a priori. In this situation energies are solutions of (often large) secular equations.

6.4.2. Hamiltonians and representations

It should be obvious by now that electronic effects upon rotational energies have to be taken into account right from the beginning. We shall consider explicitly only the rotational energies in a certain electronic state, the various smaller effects will be included in a later stage. The molecular hamiltonian can, in this approximation be written as a sum:

$$H = H_{ev} + H_r$$

H_{ev} is the vib-electronic hamiltonian of a non-rotating molecule and H_r is the rotational hamiltonian. When z is the molecular axis H_r can be written as:

$$H_r = B(R_x^2 + R_y^2) = B[(J_x - L_x - S_x)^2 + (J_y - L_y - S_y)^2]$$

For calculations an equivalent hamiltonian is:

$$H_r = B(\vec{J}^2 - J_z^2) + B(\vec{L}^2 - L_z^2) + B(\vec{S}^2 - S_z^2) + B(L_+ S_- + L_- S_+) - \\ - B(J_+ L_- + J_- L_+) - B(J_+ S_- + J_- S_+)$$

It is seen from this expression that $\langle H_r \rangle$ equals $BJ(J+1)$ when both \vec{L} and \vec{S} can be ignored {(case (a) and (c)}, $BN(N+1)$ when \vec{L} can but \vec{S} cannot be ignored, and $BR(R+1)$ when none of them can be ignored {case (d)}.

When spin-orbit interaction is considered explicitly H_{ev} can be written as:

$$H_{ev} = H_{ev}^0 + A(\vec{L} \cdot \vec{S}) = H_{ev}^0 + \sum_i \zeta(\vec{r}_i)(\vec{l}_i \cdot \vec{s}_i)$$

The simplest basis functions for the calculation are:

$$|ev, r\rangle = |ev\rangle|r\rangle$$

where $|r\rangle$ is the rotational and $|ev\rangle$ the electronic wave function. Both have to be specified formally as far as possible. To this end we have to look which quantum numbers are good or bad. Quantum numbers which MUST be good in non-rotating molecule and degeneracies of the states in question are:

| | | |
|----------|--------------------------------------|---------------------|
| case (a) | Ω ($\Omega=\Lambda+\Sigma$) | 2 or 1 |
| case (b) | same | $2(2S+1)$ or $2S+1$ |
| case (c) | Ω | 2 or 1 |
| case (d) | L, Λ, S, Σ | $(2L+1)(2S+1)$ |

When the spin-orbit interaction is large Ω is a good quantum number and $|\Omega\rangle$ is a good basis because the operator associated with Ω satisfies:

$$(L_z + S_z)|\Omega\rangle = \Omega|\Omega\rangle$$

However, on this basis Λ or Σ is NOT a good quantum number. When the spin-orbit interaction is small Λ , S and Σ are almost good quantum numbers and $|\Lambda S \Sigma\rangle$ is the best basis we can choose. Finally, when both spin-orbit and the axis interaction are not strong (e.g. electrons in Rydberg orbitals) Λ , S , Σ and L are almost good and $|\Lambda S \Sigma\rangle$ is a good basis. This basis may correspond to case (d) when energies $E(^{2S+1}L)$ of the multiplets are less than the rotational separation BJ ; we have case (d) when all $E(^{2S+1}L) \gg BJ$, case (b) is between (a) and (d).

In the following we shall adopt the $|\Lambda S \Sigma\rangle$ basis for the non-rotating molecule. But it should be kept in mind that these are not exact eigenfunctions of the hamiltonian because spin-orbit

mixes states with different Λ , S and Σ . In calculations it is often more convenient to assume that $|\Lambda S \Sigma\rangle$ are the exact eigenfunctions but the quantum numbers Λ , S and Σ are not perfectly good, i.e.

$$\begin{aligned} L_z |\Lambda S \Sigma\rangle &= \Lambda |\Lambda S \Sigma\rangle + |\delta_\Lambda\rangle \\ S_z |\Lambda S \Sigma\rangle &= \Sigma |\Lambda S \Sigma\rangle + |\delta_\Sigma\rangle \end{aligned}$$

$|\delta_\Lambda\rangle$ and $|\delta_\Sigma\rangle$ are small functions which may be considered as due to mixing effects. The rotational functions $|r\rangle$ can be specified as $|\Omega J M\rangle$ when J and M is the quantum number associated with \vec{J} and J_z , respectively. In the absence of external fields J and M are perfect quantum numbers but Ω is NOT a quantum number for rotation because it is not an eigenvalue of a rotational operator. It enters in the problem because of the presence of operator $L_z + S_z$. In the rotational function $|\Omega J M\rangle \equiv |\Omega J\rangle$, Ω should be considered as a parameter. The basis set for a rotating molecule is chosen to be

$$|ev, r\rangle = |\Lambda S \Sigma, \Omega J\rangle = |\Lambda S \Sigma\rangle |\Omega J\rangle$$

It is seen from the expression for H_r that the operators \vec{L} and \vec{S} contribute to matrix elements via products $J_x L_x, J_y L_y, J_x S_x$ and $J_y S_y$. Selection rules for matrix elements of L_x, L_y and S_x, S_y are:

$$\Delta\Lambda = \pm 1 \quad \Delta\Sigma = \pm 1$$

Matrix elements of the relevant operators can be obtained from well known expressions, for example:

$$\begin{aligned} \langle S \Sigma | \vec{S}^2 | S \Sigma \rangle &= S(S+1) \\ \langle S \Sigma | S_z | S \Sigma \rangle &= \Sigma \end{aligned}$$

$$\langle S(\Sigma \pm 1) | S_\pm | S \Sigma \rangle = \sqrt{(S \pm \Sigma)(S \pm \Sigma + 1)}$$

For the \vec{L} operator replace S by L , Σ by Λ and $|S \Sigma\rangle$ by $|L \Lambda\rangle$, but for the \vec{J} operator \vec{S}_\pm should be replaced by \vec{J}_\mp .

There are complications in actual calculations (1) because some quantum numbers may not be good or only approximately good and (2) because some of the quantum numbers may not be defined at all, e.g. L . In the latter case some of the expressions cannot be used and these matrix elements have to be represented by parameters.

6.4.3 ${}^2\Pi$ State

For this state $\Lambda = \pm 1, S = 1/2, \Sigma = \pm 1/2$. The basis set $|\Lambda S \Sigma, \Omega J\rangle$ comprises four functions:

$$\begin{aligned} |1\rangle &= |1, \frac{1}{2}, \frac{1}{2}, \frac{3}{2}, J\rangle & |3\rangle &= |-1, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, J\rangle \\ |2\rangle &= |1, \frac{1}{2}, -\frac{1}{2}, \frac{1(3)}{2}, J\rangle & |4\rangle &= |-1, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, J\rangle \end{aligned}$$

Diagonal matrix elements of H_{ev} are:

$$\begin{aligned} \langle 1 | H_{ev} | 1 \rangle &= \langle 3 | H_{ev} | 3 \rangle = E + \frac{1}{2}A \\ \langle 2 | H_{ev} | 2 \rangle &= \langle 4 | H_{ev} | 4 \rangle = E - \frac{1}{2}A \end{aligned}$$

The matrix of these elements corresponds to two degenerate states with $\Omega = \pm 3/2, \pm 1/2$. In the representation chosen the matrix elements of $B(\vec{J}^2 - J_z^2), B(\vec{S}^2 - S_z^2)$ and

$B(L_+ - L_-) = BL_{\perp}^2$ are all diagonal. The (off-diagonal) matrix elements of:

$$B(L_+ S_- + L_- S_+) - B(J_+ L_- + J_- L_+)$$

are all zero (these operators do not contribute on the diagonal). The reason is that the basis set contains only functions with $\Lambda = \pm 1$ and the operators L_{\pm} cannot produce non-zero matrix elements corresponding to $\Delta\Lambda = \pm 1$. So the only off-diagonal contribution comes from the operator:

$$-B(J_+ S_- + J_- S_+)$$

whose matrix elements can be obtained from the general expressions. The final form of the energy matrix with the present approximation is given in the table (see below).

Eigenvalue of this matrix are most easily obtained by subtracting 1/2 trace from each 2 x 2 matrix. The resulting eigenvalues are:

$$E_{\Pi} = E + B\langle L_{\perp}^2 \rangle + B[(J + 1/2)^2 - 1] \pm \frac{1}{2} \sqrt{A(A - 4B) + 4B^2(J + 1/2)^2}$$

This expression, with $E + B\langle L_{\perp}^2 \rangle$ ignored, was first derived by Hill and Van Vleck (1932) and is known as the Hill-Van Vleck expression for Π states. It represents energy of two doubly degenerate levels.

| | 1> | 2> | 3> | 4> |
|----|---|---|---|---|
| 1> | $B[J(J+1)-7/4+\langle L_{\perp}^2 \rangle + A/2]$ | $-B[(J-1/2)(J+3/2)]^{1/2}$ | 0 | 0 |
| 2> | $-B[(J-1/2)(J+3/2)]^{1/2}$ | $B[J(J+1)+1/4+\langle L_{\perp}^2 \rangle - A/2]$ | 0 | 0 |
| 3> | 0 | 0 | $B[J(J+1)-7/4+\langle L_{\perp}^2 \rangle + A/2]$ | $-B[(J-1/2)(J+3/2)]^{1/2}$ |
| 4> | 0 | 0 | $-B[(J-1/2)(J+3/2)]^{1/2}$ | $B[J(J+1)+1/4+\langle L_{\perp}^2 \rangle - A/2]$ |

When $J=1/2$ the functions |1> and |3> do not exist in both matrices.

The hamiltonian matrix factors then into two identical 1x1 matrices. The result is a doubly degenerate level with energy:

$$E_{\Pi_{1/2}} = E - \frac{1}{2}A + B\langle L_{\perp}^2 \rangle + B\left[J(J + 1) + \frac{1}{4}\right]$$

From the general expression E_{Π} the limiting (a) and (b) case can be obtained by expanding the square root.

Case (a)

$$sqrt = |A| \left\{ 1 - 2\frac{B}{A} + \frac{1}{2} \left(\frac{4B^2}{A^2} \right) [(J + 1/2)^2 - 1] \right\}$$

with $|A|$ replaced by A and keeping only terms of order B/A we obtain:

Apart from $\frac{1}{2}B = B\langle S_{\perp}^2 \rangle$ this expression agrees with $B[J(J + 1) - \Omega^2]$.

Case (b)

$$E_{\Pi_{3/2}} = \frac{1}{2}A + B\left[J(J+1) - \frac{7}{4}\right]$$

$$E_{\Pi_{1/2}} = -\frac{1}{2}A + B\left[J(J+1) + \frac{1}{4}\right]$$

For a pure Hund's case (b) $A = 0$. With this value of A we obtain

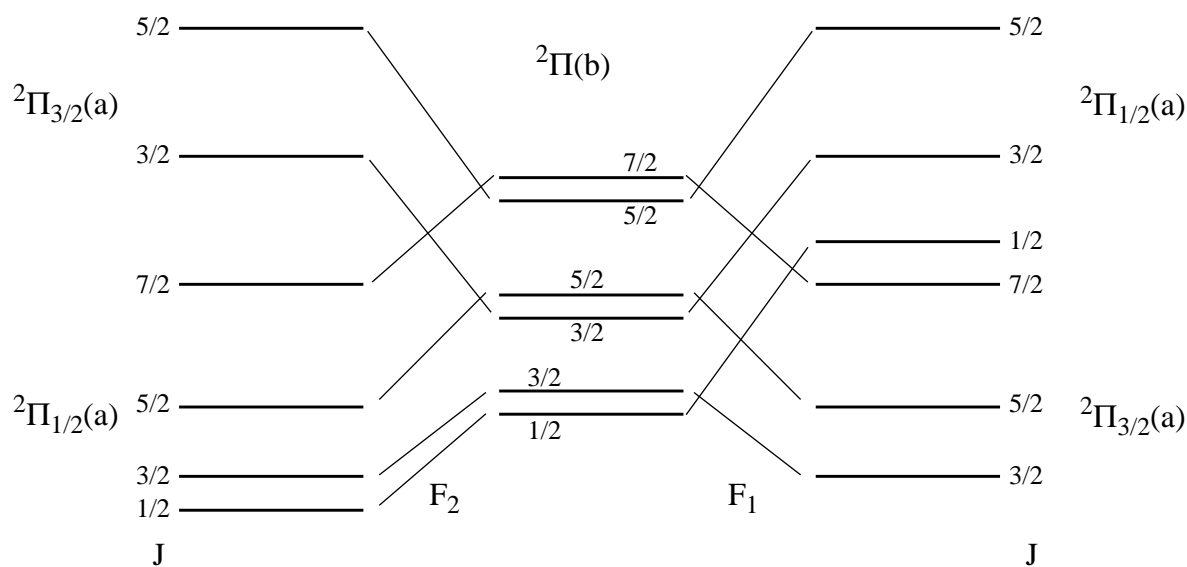
$$E = \begin{cases} B[(J+1/2)(J+3/2) - 1] \\ B[(J-1/2)(J+1/2) - 1] \end{cases}$$

These expressions are consistent with $BN(N+1)$ for $N = J \pm 1/2$.

The basis set consisting of functions $|\Lambda SNJ\rangle$ is also quite convenient to handle ${}^2\Pi$ states in intermediate coupling. This set corresponds to case (b), while the one we have used is clearly an (a) set. It is also interesting to note that molecular energies follow approximately case (b), not only when $BJ \gg |A\Lambda|$ but also when $A/B = 4$. This quantity is a measure of the coupling to the internuclear axis. Generally $A(A-4B)$ has the same value for $A/B = x$ and just $A/B = 4-x$. When $x > 4$ there are two possible values of A (one positive and one negative) which give terms with the same separations. This corresponds to regular ($A > 0$) and inverted ($A < 0$) doublets.

In the figure is shown a correlation diagram between case (b) and case (a) both for regular and inverted fine structure.

Light molecules (large B , small A) approach case (b) already at low J -values, heavier molecules are closer to case (a). OH radical is a good example of this situation.



6.5 Λ -doubling

6.5.1 Qualitative Features

As has been shown electronic energy depends on Λ^2 . Consequently all states with $|\Lambda| > 0$ are doubly degenerate. Similarly, in case of electronic multiplets, the energy depends only on Ω^2 and so the states with $\pm\Omega$ are also doubly degenerate. The Ω -degeneracy, for example in ${}^2\Sigma$, ${}^3\Sigma$ states can be lifted by spin-rotation and spin-spin interaction. It was discovered already in the 1930's that also states with $\Omega = 0$ were split into doublets. The origin of this splitting, for example in ${}^1\Pi$ and ${}^3\Pi_0$, must obviously be a lifting of the Λ -degeneracy in these states. The splitting was consequently called Λ -doubling.

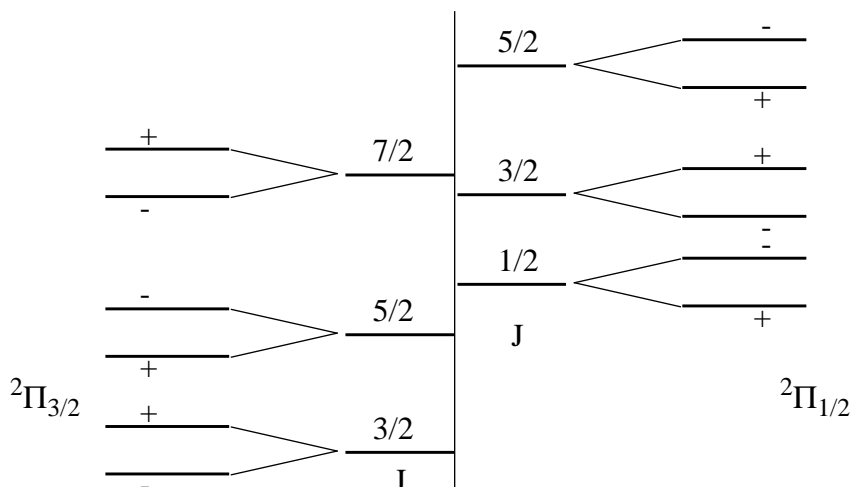
Interactions responsible for Λ -doubling must be capable to reverse not only Ω (e.g. from ${}^2\Sigma_{1/2} \rightarrow {}^2\Sigma_{-1/2}$ or ${}^2\Pi_{1/2} \rightarrow {}^2\Pi_{-1/2}$) but also Λ to $-\Lambda$. The interaction must involve operators L_x and L_y because only these follow the selection rule $\Delta\Lambda = \pm 1$ and so can reverse Λ in one or more steps. An obvious candidate is interaction between molecular rotation and electronic orbital motion. It may be seen as an incipient decoupling of \vec{L} from the molecular axis and hence a transition from case (a) or (b) to case (d). In the vector model possible interactions are contained in $f_v(\Omega, J)$ or $f_v(\Lambda, N)$ i.e. of the type $B\vec{N} \cdot \vec{L}$ or $B\vec{J} \cdot \vec{L}$. However, these effects may also be seen as a partial breakdown of the Born-Oppenheimer approximation. As a consequence of this breakdown electrons follow, with a considerable amount of slippage, the nuclear motion. The coupling operator is of the type $B\vec{R} \cdot \vec{L}$.

From a quantum mechanical point of view Λ -doubling may also be seen as a result of perturbation of the state in question by other states. Since this perturbation must change Λ the perturbing state must have different values of Λ (so Σ or Δ state in case of Λ -doubling of a Π -state), but the same multiplicity. Although a perturbing state may lie more than 10^4 cm^{-1} away from the state in question it may produce strong, easily measurable, effects. For example in OH the Λ -splitting is:

| | | |
|---------|----|------------------------|
| 1.6 GHz | in | ${}^2\Pi_{3/2}, J=3/2$ |
| 6.0 GHz | in | ${}^2\Pi_{3/2}, J=5/2$ |
| 4.7 GHz | in | ${}^2\Pi_{1/2}, J=1/2$ |

although the perturbing ${}^2\Sigma_{1/2}$ state is 32000 cm^{-1} away. Generally the splitting is greatest for smallest Ω , and in Δ states much smaller than in Π states. A (very) essential point in the perturbation approach to Λ -doubling is that the effect arises from the difference in the interaction between (+) and (-) parity rovibrational sublevels of the interacting electronic states, for example Π and Σ . Consequently the two components of a Λ -doublet have different symmetries, one (+), the other (-). The (+) state can have lower or higher energy than the (-) state, both cases occur. Lambda splitting in a ${}^2\Pi$ is shown schematically in the figure below with the correct parity of the Λ -doublets (case of OH).

Although electron interaction may be regarded as the main agent of Λ -doubling spin-orbit interaction cannot be neglected in states with $\Lambda > 0$. In these states the latter interaction is much stronger than Λ -doubling and may have a profound perturbing effect.



The Λ -splittings in Π can be described by simple empirical expressions:

| | | |
|---------------|---------|--------------------------|
| $^1\Pi$ | | $qJ(J+1)$ |
| $^2\Pi$ | case(b) | $qN(N+1)$ |
| $^2\Pi_{1/2}$ | case(a) | $a(J+1/2)$ |
| $^2\Pi_{3/2}$ | case(a) | $b(J-1/2)(J+1/2)(J+3/2)$ |
| $^3\Pi$ | case(b) | $qN(N+1)$ |

In the so-called pure precession approximation (introduced by Van Vleck) rough values of the constants are ($\Delta(\Pi, \Sigma)$ is the separation between the Π and a perturbing Σ state):

$$q = 2B_v^2 \frac{L(L+1)}{\Delta(\Pi\Sigma)} = \frac{4B_v^2}{\Delta(\Pi\Sigma)}$$

$$a = \frac{4AB_v}{\Delta(\Pi\Sigma)}$$

$$b = \frac{8B_v^3}{A\Delta(\Pi\Sigma)}$$

In the following section we shall discuss Λ -doubling in a $^2\Pi$ state in some detail and derive a more complete expression for a and b ; the limiting case (b) will yield the value for the Λ -coupling constant q .

Since the two Λ -doublets have opposite symmetries electric dipole (E1) transitions are possible between them. The transitions produce well known Λ -doubling spectra in microwave and EBR spectroscopy. Microwave spectra of interstellar OH radical originate from these transitions.

6.5.2. Λ -doubling in $^2\Pi$ states

Lambda-doubling in these states is most common and best known. Celebrated examples are OH, CH, NO. These states are split by spin-orbit interaction into $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ multiplets. The next higher electronic states are $^2\Sigma$, and these may be regarded as the only perturbers. In essence, Λ -doubling in $^2\Pi$ states arises because interaction between even parity $^2\Pi$ states with, for example $^2\Sigma$ states is slightly different from the interaction between odd parity $^2\Pi$ and

$^2\Sigma$ states.

Since in the spin-doublet states spin-orbit interactions cannot be disregarded, a fairly complete hamiltonian for a $^2\Pi$ state which can show all the relevant effects, is:

$$\begin{aligned} H &= H_r + H_{so} = B\vec{R}^2 + A(\vec{L} \cdot \vec{S}) \\ &= B[(J_x - L_x - S_x)^2 + (J_y - L_y - S_y)^2] + AL_zS_z + A(L_xS_x + L_yS_y) \\ &= B(\vec{J}^2 - L_z^2) + \vec{S}^2 + AL_zS_z - 2B(\vec{J} \cdot \vec{S}) + B(L_x^2 + L_y^2) + \\ &\quad + (2B + A)(L_xS_x + L_yS_y) - 2B(J_xL_x + J_yL_y) \end{aligned}$$

(z is the molecular axis). With this hamiltonian a case (a) basis set $|\Lambda\Sigma, \Omega J\rangle$ is the obvious choice. Operators which connect states with different Λ are L_x and L_y . When only these operators are present the selection rules for matrix elements are:

$$\Delta\Lambda = \pm 1 \quad \Delta\Sigma = 0$$

Similarly different Σ states are connected by S_x and S_y and the selection rules with only these operators are:

$$\Delta\Lambda = 0 \quad \Delta\Sigma = \pm 1$$

In the matrix elements S_z and L_z do not change the states. Obviously three such operators are needed to change $^2\Pi_{\pm 3/2}$ into $^2\Pi_{\mp 3/2}$. These operators change also $\Lambda \rightarrow -\Lambda$ and $\Sigma \rightarrow -\Sigma$, as required for Λ -doubling. Consequently we expect that Λ -splitting in a $^2\Pi_{3/2}$ state should be proportional to B^3J^3 if this splitting is determined only by a gyroscopic interaction. But the reasoning followed above applies also to $^2\Pi_{1/2}$ states; we need three $\Delta\Lambda$ and $\Delta\Sigma$ operators to change both Λ and Σ . However, it is known from experiments that Λ -doubling in $^2\Pi_{1/2}$ states is larger than in $^2\Pi_{3/2}$ states and that it is proportional to B_v , and so must be generated by a single operator. This is possible thanks to the spin-orbit interaction of the perpendicular components of \vec{L} and \vec{S} ($L_xS_x + L_yS_y$). Matrix elements of these operators with $\Delta\Sigma = +1$ and $\Delta\Lambda = -2$ connect the states with $\Sigma = -1/2$, $\Lambda = +1$ and $\Sigma = 1/2$, $\Lambda = -1$ in a single $\Delta\Omega = -1$ transition. It is interesting to note that three $\Delta\Omega = \pm 1$ matrix element can reverse the signs not only of Ω but also of Λ and Σ for a $^2\Pi_{3/2}$ state.

It should be clear from these remarks that a correct picture of Λ -doubling cannot be obtained by taking only e.g. the $\vec{J} \cdot \vec{L}$ interaction, instead the complete hamiltonian should be considered in a secular matrix equation.

To start with we consider the two degenerate $^2\Pi$ states and a single (also degenerate) $^2\Sigma$ state perturbing the $^2\Pi$ states. So we have a basis set of six $|\Lambda\Sigma, \Omega J\rangle \equiv |\Lambda\Sigma\Omega\rangle$ states:

$$\begin{aligned} |0, \frac{1}{2}, \frac{1}{2}\rangle &= |^2\Sigma_{1/2}\rangle & |0, -\frac{1}{2}, -\frac{1}{2}\rangle &= |^2\Sigma_{-1/2}\rangle & |1, -\frac{1}{2}, \frac{1}{2}\rangle &= |^2\Pi_{1/2}\rangle \\ |-1, \frac{1}{2}, -\frac{1}{2}\rangle &= |^2\Pi_{-1/2}\rangle & |1, \frac{1}{2}, \frac{1}{2}\rangle &= |^2\Pi_{3/2}\rangle & |-1, -\frac{1}{2}, -\frac{3(1)}{2}\rangle &= |^2\Pi_{-3/2}\rangle \end{aligned}$$

In this basis the non-zero matrix elements of the hamiltonian are:

$$\langle {}^2\Sigma_{1/2}|H|^2\Sigma_{1/2}\rangle = \langle {}^2\Sigma_{-1/2}|H|^2\Sigma_{-1/2}\rangle \equiv \alpha = B_\Sigma \left[J(J+1) + \frac{1}{4} \right] + E$$

$$\langle {}^2\Pi_{1/2}|H|^2\Pi_{1/2}\rangle = \langle {}^2\Pi_{-1/2}|H|^2\Pi_{-1/2}\rangle \equiv \beta = B_\Pi \left[J(J+1) + \frac{1}{4} \right] - \frac{1}{2}A_\Pi$$

$$\langle {}^2\Pi_{3/2}|H|^2\Pi_{3/2}\rangle = \langle {}^2\Pi_{-3/2}|H|^2\Pi_{-3/2}\rangle \equiv \gamma = B_\Pi \left[J(J+1) - \frac{7}{4} \right] + \frac{1}{2}A_\Pi$$

$$\langle {}^2\Sigma_{1/2}|H|^2\Sigma_{-1/2}\rangle = \langle {}^2\Sigma_{-1/2}|H|^2\Sigma_{1/2}\rangle \equiv \delta = B_\Sigma \left(J + \frac{1}{2} \right)$$

$$\langle {}^2\Pi_{3/2}|H|^2\Pi_{1/2}\rangle = \langle {}^2\Pi_{-3/2}|H|^2\Pi_{-1/2}\rangle \equiv \varepsilon = B_\Pi \sqrt{\left(J - \frac{1}{2} \right) \left(J + \frac{3}{2} \right)}$$

$$\langle {}^2\Pi_{1/2}|H|^2\Sigma_{-1/2}\rangle = \langle {}^2\Pi_{-1/2}|H|^2\Sigma_{1/2}\rangle^\circ \equiv \zeta = \langle \Pi | 2BL_y | \Sigma \rangle \left(J + \frac{1}{2} \right)$$

$$\langle {}^2\Pi_{3/2}|H|^2\Sigma_{1/2}\rangle = \langle {}^2\Pi_{-3/2}|H|^2\Sigma_{-1/2}\rangle^\circ \equiv \eta = \langle \Pi | 2BL_y | \Sigma \rangle \sqrt{\left(J - \frac{1}{2} \right) \left(J + \frac{3}{2} \right)}$$

$$\langle {}^2\Pi_{1/2}|H|^2\Sigma_{1/2}\rangle = \langle {}^2\Pi_{-1/2}|H|^2\Sigma_{-1/2}\rangle^\circ \equiv \theta = \langle \Pi | 2BL_y + AL_y | \Sigma \rangle$$

Energy of the Π state is assumed to be zero and so $E = h\nu(\Pi, \Sigma)$ and the subscript Π or Σ is introduced to indicate that B and A can be different in the two states.

The diagonal matrix elements α , β , γ follow from the first four terms of H with $-2(\vec{J} \cdot \vec{S}) \equiv -2\Sigma\Omega$. The “purely spin” matrix elements δ and ε follow from the $J_x S_x + J_y S_y$ part of $-2(\vec{J} \cdot \vec{S})$ using the following phase conventions:

$$\pm i \langle \Sigma | S_x | \Sigma \pm 1 \rangle = \langle \Sigma | S_y | \Sigma \pm 1 \rangle = \frac{1}{2} \sqrt{S(S+1) - \Sigma(\Sigma \pm 1)}$$

$$\pm i \langle \Omega | J_x | \Omega \pm 1 \rangle = -\langle \Sigma \Omega | J_y | \Omega \pm 1 \rangle = \frac{1}{2} \sqrt{J(J+1) - \Omega(\Omega \pm 1)}$$

The “purely orbital” matrix elements ζ and η follow from the last term, with:

$$\pm i \langle \Lambda | L_x | \Lambda \pm 1 \rangle = \langle \Lambda | L_y | \Lambda \pm 1 \rangle$$

Since L is not defined matrix elements of L_y (and L_x) have to be considered as parameters. The matrix elements θ follow from the last but one term. The term $B(L_x^2 + L_y^2)$ yields a small contribution independent of J and is left out:

$$\begin{array}{c}
|{}^2\Sigma_{1/2}\rangle \quad |{}^2\Sigma_{-1/2}\rangle \quad |{}^2\Pi_{1/2}\rangle \quad |{}^2\Pi_{-1/2}\rangle \quad |{}^2\Pi_{3/2}\rangle \quad |{}^2\Pi_{-3/2}\rangle \\
\begin{array}{c}
|{}^2\Sigma_{1/2}\rangle \\
|{}^2\Sigma_{-1/2}\rangle \\
|{}^2\Pi_{1/2}\rangle \\
|{}^2\Pi_{-1/2}\rangle \\
|{}^2\Pi_{3/2}\rangle \\
|{}^2\Pi_{-3/2}\rangle
\end{array}
\begin{array}{|c}
\hline
\alpha \quad \delta \quad \theta \quad \zeta \quad \eta \quad 0 \\
\delta \quad \alpha \quad \zeta \quad \theta \quad 0 \quad \eta \\
\theta \quad \zeta \quad \beta \quad 0 \quad \varepsilon \quad 0 \\
\zeta \quad \theta \quad 0 \quad \beta \quad 0 \quad \varepsilon \\
\eta \quad 0 \quad \varepsilon \quad 0 \quad \gamma \quad 0 \\
0 \quad \eta \quad 0 \quad \varepsilon \quad 0 \quad \gamma \\
\hline
\end{array}
\end{array}$$

With these matrix elements the hamiltonian matrix has the form given in the matrix. This matrix can be reduced to two 3 x 3 matrices by using a symmetrized basis:

$$\frac{1}{\sqrt{2}}[|{}^2\Lambda_{\Omega}\rangle \pm |{}^2\Lambda_{-\Omega}\rangle] \equiv |\Lambda_{\Omega\pm}\rangle$$

These functions have definite positive-negative (or Kronig's even-odd) parity.

Matrix elements of the hamiltonian on the basis $|\Lambda_{\Omega\pm}\rangle$ can easily be obtained from the expressions; for symmetric Σ^+ states the equations are valid without any changes, for antisymmetric Σ^- states the matrix elements indicated by an asterisk get a negative sign. All matrix elements between states of different parity are zero. This follows from invariance of the hamiltonian under the inversion operation.

The resulting matrices yield two cubic secular equations (one for + and one for the - sign) which cannot be solved exactly. Dousmanis et al (1955) used a perturbation expansion of the roots (similar to perturbation expansion in quantum mechanics) and obtained rather lengthy and complicated expressions from which the desired Λ -splitting can be obtained. These formulae have to be used when high accuracy is desired. Below we shall consider three special cases.

$$\begin{array}{c}
|{}^2\Sigma_{1/2\pm}\rangle \quad |{}^2\Pi_{1/2}\rangle \quad |{}^2\Pi_{3/2}\rangle \\
\begin{array}{c}
|{}^2\Sigma_{1/2\pm}\rangle \\
|{}^2\Pi_{1/2}\rangle \\
|{}^2\Pi_{3/2}\rangle
\end{array}
\begin{array}{|c}
\hline
\alpha \pm \delta \quad \theta \pm \zeta \quad \eta \\
\theta^* \pm \zeta^* \quad \beta \quad \varepsilon \\
\eta^* \quad \varepsilon^* \quad \gamma \\
\hline
\end{array}
\end{array}$$

Case (1): Effect of the $^2\Sigma$ states negligible

In this case the matrix elements η , ζ and θ are zero and the hamiltonian matrix reduces to:

$$\begin{bmatrix} \alpha + \delta & 0 & 0 \\ 0 & \beta & \varepsilon \\ 0 & \varepsilon^* & \gamma \end{bmatrix}$$

The resulting secular equation can be readily solved for the energies of the two states, ($^2\Pi_{1/2}$, $^2\Pi_{3/2}$) and perturbed wavefunctions. The results for the energies are:

$$E_{\pm} = \frac{1}{2}(\alpha + \beta) \pm B_{\Pi} \sqrt{4\left(J + \frac{1}{2}\right)^2 + \frac{A_{\Pi}}{B_{\Pi}}\left(\frac{A_{\Pi}}{B_{\Pi}} - 4\right)}$$

This result shows that in the extreme case (b) the Λ -splitting originates from the small difference between the interactions of the positive and negative states.

Case (2): $A=0$

This represents an extreme case (b). With $A=0$ the matrix elements are:

$$\begin{aligned} \kappa_{+} &= \alpha + \delta = E + B_{\Sigma}(J + 1/2)(J + 3/2) \\ \kappa_{-} &= \alpha - \delta = E + B_{\Sigma}(J - 1/2)(J + 1/2) \\ \mu_{+} &= \Theta + \zeta = (J + 3/2)\langle \Pi | 2BL_y | \Sigma \rangle \\ \mu_{-} &= \Theta - \zeta = -(J - 1/2)\langle \Pi | 2BL_y | \Sigma \rangle \\ \beta &= B_{\Pi}[J(J + 1) + 1/4] = B_{\Pi}(J + 1/2)^2 \\ \gamma &= B_{\Pi}[J(J + 1) - 7/4] = B_{\Pi}[(J + 1/2)^2 - 2] \\ \varepsilon &= B_{\Pi}\sqrt{(J - 1/2)(J + 3/2)} \\ \eta &= \sqrt{(J - 1/2)(J + 3/2)}\langle \Pi | 2BL_y | \Sigma \rangle \end{aligned}$$

With these matrix elements the two cubic secular equations (one with κ_{+} and μ_{+} , the other with κ_{-} and μ_{-} both factor into a product of a linear and a quadratic equation. These can be solved to:

$$\begin{aligned} E_{\Pi+} &\cong B_{\Pi}[(J + 1/2)(J + 3/2) - 1] - 8(J + 1/2)(J + 3/2) \frac{|\langle \Pi | BL_y | \Sigma \rangle_{+}|^2}{\Delta(\Pi, \Sigma)} \\ E_{\Pi-} &\cong B_{\Pi}[(J - 1/2)(J + 1/2) - 1] - 8(J - 1/2)(J + 1/2) \frac{|\langle \Pi | BL_y | \Sigma \rangle_{-}|^2}{\Delta(\Pi, \Sigma)} \end{aligned}$$

Herein $\Delta(\Pi, \Sigma) = E$ is the energy separation between the Π and Σ states and the subscript (+) and (-) indicates a symmetric and an antisymmetric state, respectively. However, when $A = 0$ as we have assumed, the two Π states coalesce in energy. This implies that we should replace $J + 1/2$ and $J - 1/2$ by N . The Λ -splitting is then obtained by subtracting

the difference between E_{Π^+} and E_{Π^-} . The result can be written in the form

$$\Delta v_{\Lambda} = (C_1 - C_2)N(N + 1)$$

where

$$C_1 = 2 \frac{|\langle \Pi | BL_y | \Sigma \rangle_+|^2}{\Delta(\Pi, \Sigma)} \quad C_2 = 2 \frac{|\langle \Pi | BL_y | \Sigma \rangle_-|^2}{\Delta(\Pi, \Sigma)}$$

This result shows that in the extreme case (b) the Λ -splitting originates from the small difference between the interactions of the positive and negative states.

Case (3): $\kappa - W = -\Delta(\Pi, \Sigma)$

Usually the energy difference $\Delta(\Pi, \Sigma)$ between the Π and Σ states is much larger than the Λ -splitting (in OH $\Delta(\Pi, \Sigma) = 32\,683 \text{ cm}^{-1}$, Λ -splitting $0.05 - 1 \text{ cm}^{-1}$). In this case $\kappa - W$ can be assumed to be a constant $\{ \equiv -\Delta(\Pi, \Sigma) \}$. The secular equation reduces then to one of second order:

$$W^2 - W \left[\beta + \gamma + \frac{1}{\Delta} (\mu_{\pm} \mu_{\pm}^{\circ} + \eta \eta^{\circ}) \right] + \left[\beta \gamma - \varepsilon \varepsilon^{\circ} + \frac{1}{\Delta} (\mu_{\pm} \mu_{\pm}^{\circ} \gamma + \eta \eta^{\circ} \beta - \mu_{\pm} \varepsilon \eta^{\circ} - \mu_{\pm}^{\circ} \varepsilon^{\circ} \eta) \right] = 0$$

which can be solved. If we disregard terms of order Λ^{-n} with $n > 1$ the result is:

$$2W = \beta + \gamma \pm B_{\Pi} X + \frac{1}{\Delta} (\mu_{\pm} \mu_{\pm}^{\circ} + \eta \eta^{\circ}) \pm \frac{1}{B_{\Pi} X} [(\beta - \gamma)(\mu_{\pm} \mu_{\pm}^{\circ} - \eta \eta^{\circ}) + 2\mu_{\pm} \varepsilon \eta^{\circ} + 2\mu_{\pm}^{\circ} \varepsilon^{\circ} \eta]$$

where again:

$$X = \sqrt{4(J + 1/2)^2 + Y(Y - 4)} \quad Y = A_{\Pi}/B_{\Pi}$$

The two signs correspond to the two components of the spin-doublet: for $A > 0$ (normal doublet) the (+) sign corresponds to $\Pi_{3/2}$, the (-) sign to $\Pi_{1/2}$, for $A < 0$ (inverted doublet) the correspondence is reversed.

The Λ -splitting is obtained by subtracting the expression with only μ_{-} from that with only μ_{+} :

$$\Delta v_{\Lambda} = \frac{1}{2\Delta} \left\{ (\mu_{+} \mu_{+}^{\circ} - \mu_{-} \mu_{-}^{\circ}) \left(1 \pm \frac{\beta - \gamma}{B_{\Pi} X} \right) + \Phi \right\}$$

$$\Phi = \frac{2}{B_{\Pi} X} (\mu_{+} \varepsilon \eta^{\circ} + \mu_{+}^{\circ} \varepsilon^{\circ} \eta - \mu_{-} \varepsilon \eta^{\circ} - \mu_{-}^{\circ} \varepsilon^{\circ} \eta)$$

After filling in some of the constants:

$$\Delta v_{\Lambda} = \frac{1}{\Delta} \left(J + \frac{1}{2} \right) \left\{ \left(1 \pm \left(\frac{2}{X} \mp \frac{Y}{X} \right) \right) [\langle \Pi | 2BL_y + AL_y | \Sigma \rangle \langle \Pi | 2BL_y | \Sigma \rangle^{\circ} + cc] \pm \Phi_2 \right\}$$

$$\Phi_2 = \frac{4}{X} \left(J - \frac{1}{2} \right) \left(J + \frac{3}{2} \right) | \langle \Pi | 2BL_y | \Sigma \rangle |^2$$

The upper signs are appropriate for the upper spin-component, the lower signs for the lower component. From the last expression only the real part should be taken.

Even in the present approximation the theory needs some extension. All the relevant matrix elements should be replaced by a sum over the vibrational (v, v') levels of a given electronic level and over electronic levels of proper symmetry. In a more complete theory also interaction between Π and Δ levels should be included. Following Mulliken (1931) term-energies and Λ -splitting of ${}^2\Pi$ levels are usually written in terms of the following (Λ -)constants:

$$q = C_1 - C_2$$

$$p = a_1 - a_2$$

where:

$$C_1 = 8\Sigma(v', {}^2\Sigma_+) \frac{|\langle \Pi | 2BL_y | \Sigma \rangle|^2}{\Delta(\Pi, \Sigma)}$$

$$C_2 = 8\Sigma(v', {}^2\Sigma_-) \frac{|\langle \Pi | 2BL_y | \Sigma \rangle|^2}{\Delta(\Pi, \Sigma)}$$

$$a_1 = 8\Sigma(v', {}^2\Sigma_+) \frac{\text{Re}[\langle \Pi | AL_y | \Sigma^+ \rangle \langle \Sigma^+ | BL_y | \Pi \rangle]}{\Delta(\Pi, \Sigma^+)}$$

$$a_2 = 8\Sigma(v', {}^2\Sigma_-) \frac{\text{Re}[\langle \Pi | AL_y | \Sigma^- \rangle \langle \Sigma^- | BL_y | \Pi \rangle]}{\Delta(\Pi, \Sigma^-)}$$

(Σ_{\pm} indicates rovibrational and electronic Σ states with positive and negative parity). With these constants the expression for the term energy is:

$$\begin{aligned} T(J) = & T_0 + B_v \left[\left(J + \frac{1}{2} \right)^2 - 1 \pm \frac{1}{2} X \right] + \frac{1}{2} \left[o + \frac{1}{2} p^\circ + q^\circ \left(J + \frac{1}{2} \right)^2 \right] + \\ & \pm \frac{1}{2X} \left[(2 - Y) \left(o + \frac{1}{2} p^\circ + q^\circ \right) + (p^\circ + 2q^\circ) \left(J - \frac{1}{2} \right) \left(J + \frac{3}{2} \right) \right] + \\ & + [\pm] \frac{1}{2} \left(J + \frac{1}{2} \right) \left\{ \left[\pm 1 + \frac{1}{X} (2 - Y) \right] \left(\frac{1}{2} p + q \right) + \frac{1}{2X} q \left(J - \frac{1}{2} \right) \left(J + \frac{3}{2} \right) \right\} \end{aligned}$$

where:

$$p^\circ = a_1 + a_2 \quad q^\circ = C_1 + C_2 \quad o = \Sigma(v', {}^2\Sigma) |\langle \Pi \rangle | AL_y | \Sigma \rangle|^2 / \Lambda(\Pi, \Sigma)$$

The bracketed signs $[\pm]$ refer to the symmetric (+) and antisymmetric (-) Λ -levels. The unbracketed signs refer to the two components of the spin doublet.

Although the expression looks rather complicated, the one derived from it for the Λ -splitting is simple:

$$\Delta v_\Lambda = \left(J + \frac{1}{2} \right) \left[\left(\frac{1}{2} p + q \right) \left(\pm 1 + \frac{2}{X} - \frac{Y}{X} \right) + \frac{2q}{X} \left(J - \frac{1}{2} \right) \left(J + \frac{3}{2} \right) \right]$$

(\pm refers to components of the spin-doublet).

Limiting Case (b)

In the extreme case (b) $A = 0$ and $Y = 0$ we obtain:

$$\Delta v_{\Lambda} = \pm q N(N+1)$$

with the (+) sign for $N = J + 1/2$ and the (-) sign for $N = J - 1/2$. In the simplest case of a Σ^+ state the Λ -doubling constant is:

$$q = 8 \frac{|\langle \Pi | B L_y | \Sigma \rangle|^2}{\Delta(\Pi, \Sigma)}$$

The matrix elements appearing are difficult to evaluate, usually they are obtained from a fit of observed spectra. A rough estimate can be obtained from the so-called PURE PRECESSION approximation. It is assumed (Van Vleck 1929) that:

- (1) vibrational excitation in the Σ states is small so that $B \equiv B_v$ is a constant,
- (2) moment of inertia is independent of Ω (good approximation only for electrons in Rydberg-type orbits),
- (3) angular momentum \vec{L} of constant value precesses such that both the Π and the Σ state result from projection of this \vec{L} .

In this approximation the matrix element the result for q is:

$$q = \frac{2B_v^2 L(L+1)}{\Delta(\Pi, \Sigma)}$$

Often it is assumed that \vec{L} is that of a single electron ($L \rightarrow 1$).

Limiting case (a)

For this case ($Y \rightarrow \pm\infty$) we use the approximation

$$\frac{1}{X} \cong \frac{1}{|Y|} \left[1 + \frac{2}{Y} - \frac{2}{Y^2} \left(J + \frac{1}{2} \right)^2 \right]$$

By substituting this expression we obtain in Y^0 order for the splitting of the ${}^2\Pi_{1/2}$ state (with the lower signs in the equation for Δv_{Λ}):

$$\Delta v_{\Lambda}^{1/2} = \pm a \left(J + \frac{1}{2} \right)$$

with:

$$a = \frac{2}{\Delta(\Pi, \Sigma)} \{ \langle \Pi | 2BL_y + AL_y | \Sigma \rangle \langle \Pi | 2BL_y | \Sigma \rangle^{\circ} + cc \}$$

herein the (+) sign corresponds to $A > 0$ and the (-) sign to $A < 0$. If the general equation is used the result for Δv_{Λ} is:

$$\Delta v_{\Lambda}^{1/2} = \pm (p + 2q) \left(J + \frac{1}{2} \right)$$

The upper signs in yield zero in Y^0 order. If we neglect the J -independent terms in the expansion we obtain for the splitting of the ${}^2\Pi_{3/2}$ state in Y^{-1} order:

$$\Delta v_{\Lambda}^{3/2} = b \left(J - \frac{1}{2} \right) \left(J + \frac{1}{2} \right) \left(J + \frac{3}{2} \right)$$

where

$$b = \frac{4}{Y\Delta(\Pi, \Sigma)} |\langle \Pi | 2BL_y | \Sigma \rangle|^2 = \frac{16B(4)}{A\Delta(\Pi, \Sigma)} |\langle \Pi | BL_y | \Sigma \rangle|^2$$

$$= \frac{16B(4)}{\Delta(\Pi, \Sigma)\Delta(\Pi_{1/2}, \Pi_{3/2})} |\langle \Pi | BL_y | \Sigma \rangle|^2$$

(with the approximation $E(^2\Pi_{1/2}) - E(^2\Pi_{3/2}) = A$). The expression yields to order Y^{-2} :

$$\Delta v_\Lambda^{\frac{3}{2}} = \pm \left(\frac{p}{Y^2} + \frac{2q}{Y} \right) \left(J - \frac{1}{2} \right) \left(J + \frac{1}{2} \right) \left(J + \frac{3}{2} \right)$$

with the (+) sign for corresponds to $A > 0$ and the (-) sign to $A < 0$.

These results agree with the expressions proposed in the introduction and we have the expected B dependence ($\sim B^3$ for $^2\Pi_{3/2} \sim B$ for $^2\Pi_{1/2}$). However, the accuracy is limited by the approximation $\kappa - W = \text{constant}$, neglect of coupling between Π and Δ states, neglect of the spin-rotation, etc. However, the J -dependence derived is confirmed by experiments. From the results for the limiting cases it is possible to draw a correlation diagram between the Λ -split levels of a $^2\Pi$ multiplet for case (a) and (b) coupling. Such a diagram is shown in the figure below. The basis rule for this diagram is that levels of a given symmetry “combine” only with levels of the same symmetry; the spin-splitting, of course, disappears in case $A = 0$ and the two spin-doublet components correlate with a single N -level. We see that the Λ -levels for each J -value except $J = 1/2$ of the $\Pi_{1/2}$ multiplets (both normal and inverted) cross. So there are values of Y such that the Λ -splitting disappears for these levels. Transitions are allowed between Λ -sublevels of different parity both of different and the same ro-vibrational levels. The latter type of transitions, also known as Λ -transitions, are well known from interstellar OH and CH radicals and from laboratory spectra of NO.

