Notes on: Molecular Physics

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1. Energy levels in molecules; the quantum structure

1.1. The Born-Oppenheimer approximation

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

$$H = -\frac{{''}^2}{2m} \sum_{i} \nabla_i^2 - \sum_{A} \frac{{''}^2}{2M_A} \nabla_A^2 + V(\vec{R}, \vec{r})$$

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:

$$V(\vec{R},\vec{r}) = -\sum_{A,i} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 |R_A - R_B|} + \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

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:

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

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 H₂-molecule.

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

$$H\Psi = E\Psi$$

then it follows:

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

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

$$\left\{-\frac{^{"2}}{2m}\sum_{i}\nabla_{i}^{2}+\sum_{i>j}\frac{e^{2}}{4\pi\varepsilon_{0}r_{ij}}-\sum_{A,i}\frac{Z_{A}e^{2}}{4\pi\varepsilon_{0}r_{Ai}}\right\}\psi_{el}(\vec{r}_{i};\vec{R}) = E_{el}(\vec{R})\psi_{el}(\vec{r}_{i};\vec{R})$$

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

$$\left\{-\sum_{A}\frac{\pi^{2}}{2M_{A}}\nabla_{A}^{2}+\sum_{A>B}\frac{Z_{A}Z_{B}e^{2}}{4\pi\varepsilon_{0}[R_{A}-R_{B}]}\right\}\chi_{nuc}(\vec{R})+E_{el}(\vec{R})\chi_{nuc}(\vec{R})=E_{total}\chi_{nuc}(\vec{R})$$

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 <u>function</u> 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).

1.2. 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 thee dominant role of the nuclear repulsion

- it is not always so that de 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 form 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.

1.3. Rotational motion in a diatomic molecule

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

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

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 molecule. 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:

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

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

$$N_{x} = -i'' \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) = i'' \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right)$$
$$N_{y} = -i'' \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) = i'' \left((-\cos \phi) \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right)$$
$$N_{z} = -i'' \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = i'' \frac{\partial}{\partial \phi}$$

The Laplacian can then be written as:

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

The Hamiltonian can then be reduced to:

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

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:

$$\vec{N}^{2}|N,M\rangle = "^{2}N(N+1)|N,M\rangle \quad with \quad N = 0, 1, 2, 3, etc$$
$$N_{z}|N,M\rangle = "M|N,M\rangle \quad with \quad M = -N, -N+1, N$$

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:

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

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

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

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

1.4. 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:

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

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:

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

1.5 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:

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

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:

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

The quantum mechanical Hamiltonian is obtained by replacing N by the quantum mechanical operator 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).

1.6. 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 $\Re(R) = Q(R)/R$ than a somewhat simpler expression results:

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

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 $\rho = R - R_e$:

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

and:

$$V(R_e) = 0 \qquad \frac{dV}{dR}\Big]_{R_e} = 0 \qquad \frac{d^2V}{dR^2}\Big]_{R_e} = k$$

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:

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

The solutions for the eigenfunctions are known:

$$Q_{\nu}(\rho) = \frac{2^{-\nu/2} \alpha^{1/4}}{\sqrt{\nu!} \pi^{1/4}} \exp\left[\frac{1}{2} \alpha \rho^{2}\right] H_{\nu}(\sqrt{\alpha} \rho) \qquad \text{with} \qquad \alpha = \frac{\mu \omega_{e}}{"} \qquad \omega_{e} = \sqrt{\frac{k}{\mu}}$$

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

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

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 form 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.

1.7. 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 "):

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

In the usual spectroscopic practice an expansion is written (in cm⁻¹),

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \omega_e z_e \left(v + \frac{1}{2} \right)^4 + \frac{1}{2} \left(v + \frac{1}{2} \right)^4 + \frac{1$$

with ω_e , $\omega_e x_e$, $\omega_e y_e$ and $\omega_e z_e$ 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:

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

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

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

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:

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

1.8. 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.

1.9. The RKR-procedure

The question is if there exists a procedure to derive a potential energy curve form 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.

2. Transitions between quantum states

2.1. 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*:

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

In the dipole approximation a dipole moment μ 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:

$$B_{fi}(\omega) = \frac{\pi e^2}{3\varepsilon_0} \left| \langle \Psi_f | \overrightarrow{\mu} \cdot \overrightarrow{E} | \Psi_i \rangle \right|^2$$

Very generally the Wigner-Eckart theorem can be used to make some predictions on allowed transitions and selection rules. The dipole operator is an $\dot{\vec{r}}$ -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:

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

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:

$$\Delta J = J' - J = -1, 0, 1$$

$$J = J' = 0 \qquad forbidden$$

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

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

2.1. 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:

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

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.

2.2. 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:

$$\mu_{if} = \int \Psi'_{el} \Psi'_{vib} (\mu_e + \mu_N) \Psi''_{el} \Psi''_{vib} d\vec{r} d\vec{R} =$$
$$= \int (\int \Psi'_{el} \mu_e \Psi''_{el} d\vec{r}) \Psi'_{vib} \Psi''_{vib} d\vec{R} + \int \Psi'_{el} \Psi''_{el} d\vec{r} \int \Psi'_{vib} \mu_N \Psi''_{vib} d\vec{R}$$

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:

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

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 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:

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

So the Franck-Condon principle gives us 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 Frank-Condon factor. It is not a strict selection rule forbidding transitions!



2.3. 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:

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

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} :

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

form 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:

$$\Delta v = \pm 1, \pm 2, etc$$

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).

2.4. 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_{lm} allows for a simple calculation of the transition moment integral:

$$M_{fi} = \mu_0 \int_{\Omega} Y_{N'M'}^{\circ} \left[\begin{array}{c} \sin\theta\cos\phi\\ \sin\theta\sin\phi\\ \cos\theta \end{array} \right] Y_{NM} d\Omega \propto \int_{0}^{2\pi} \int_{0}^{\pi} Y_{N'M'}^{\circ} Y_{1m} Y_{NM} d\Omega$$
$$= \sqrt{\frac{1}{4\pi} (2N'+1)3(2N+1)} \left[\begin{array}{c} N' \ 1 \ N\\ 0 \ 0 \ 0 \end{array} \right] \left[\begin{array}{c} N' \ 1 \ N\\ M' \ m \ M \end{array} \right]$$

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.

2.5. 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:

$$v = F_{v}(N') - F_{v}(N')$$
$$= (B_{v}N'(N'+1) - D_{v}N'^{2}(N'+1)^{2} - [B_{v}N'(N'+1) - D_{v}N'^{2}(N'+1)^{2}])$$

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

$$v_{abs} = B_{v}[(N''+1)(N''+2) - N''(N''+1)] - D_{v}[(N''+1)^{2}(N''+2)^{2} - N''^{2}(N''+1)^{2}]$$
$$= 2B_{v}(N''+1) - 4D_{v}(N''+1)^{3}$$

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

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

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).

2.6. Rovibrational spectra

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

$$T = G(\mathbf{v}) + F_{\mathbf{v}}(N)$$
$$F_{\mathbf{v}}(N) = B_{\mathbf{v}}N(N+1) - D_{\mathbf{v}}N^{2}(N+1)^{2}$$
$$G(\mathbf{v}) = \omega_{e}\left(\mathbf{v} + \frac{1}{2}\right) - \omega_{e}x_{e}\left(\mathbf{v} + \frac{1}{2}\right)^{2}$$

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

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

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:

$$\sigma_{R} = \sigma_{0} + B_{v}'(N+1)(N+2) - B_{v}''N(N+1)$$
$$= \sigma_{0} + 2B_{v}' + (3B_{v}' - B_{v}'')N + (B_{v}' - B_{v}'')N^{2}$$

Similarly transitions in the P-branch, defined as ΔN =-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 2*B*; more precisely:

$$\sigma_R(N+1) - \sigma_R(N) \sim 3B_v' - B_v'' \qquad so \qquad < 2B_v'$$

$$\sigma_P(N+1) - \sigma_P(N) \sim B_v' + B_v'' \qquad so \qquad > 2B_v'$$

where the statement on the right holds if $B_{\nu'} < B_{\nu''}$. 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.

$$v = T' - T''$$

$$T' = T_B - G'(v') + F'(N')$$

$$T'' = T_A - G''(v'') + F''(N'')$$

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

$$\sigma_{R} = \sigma_{0} + 2B_{v}' + (3B_{v}' - B_{v}'')N + (B_{v}' - B_{v}'')N^{2}$$

$$\sigma_{P} = \sigma_{0} - (B_{v}' + B_{v}'')N + (B_{v}' - B_{v}'')N^{2}$$

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:

$$m = N+1$$
 for $R-branch$
 $m = -N$ for $P-branch$

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:

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

2.7 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:

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

When filling in the vibrational energy it follows:

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

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 $T = 300^{\circ}$ K, with E in cm⁻¹. The broken-line ordinates correspond to the vibrational levels of the I₂ 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.

Gas	$\Delta G_{\frac{1}{2}}({ m cm}^{-1})$	$e^{-\Delta G_{\frac{1}{2}hc}/kT}$		
		For 300° K.	For 1000° K	
H_2	4160.2	2.16×10^{-9}	$2.51 imes10^{-3}$	
HCl	2885.9	$9.77 imes10^{-7}$	1.57×10^{-2}	
N ₂	2330.7	1.40×10^{-5}	$3.50 imes 10^{-2}$	
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	$3.14 imes10^{-2}$	$3.54 imes 10^{-1}$	
Cl_2	556.9	$6.92 imes10^{-2}$	4.49×10^{-1}	
I ₂	213.2	$3.60 imes 10^{-1}$	7.36×10^{-1}	

Table 14. ratio of the number of molecules in the first to that in the zeroth vibrational level for 300° K. and 1000° K.

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 $T = 300^{\circ}$ K. and B = 10.44 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.



2.8 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:

3. Electronic states

3.1 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 :

$$H_0 = -\frac{{"}^2}{2m} \sum_{i} \nabla_i^2 + V(\dot{r}_i, R)$$

is invariant under the symmetry operations:

 $- R_{\phi}$ rotation over every angle ϕ about the molecular axis $- \sigma_v$ reflection in a molecular plane containing the molecular axis

- *i* in version 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.

3.2. 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:

 $\sigma_v \psi_e = \pm \psi_e$ eigenvalues +,-

The operator R_{ϕ} is connected to another constant of the motion, L_{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:

$$L_{z}\psi_{e} = \frac{\partial \psi_{e}}{\partial \phi} = \Lambda''\psi_{e} \qquad eigenvalues \qquad \Lambda = 0, \pm 1, \pm 2, \pm 3,$$

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

$$\begin{split} \Sigma & \text{for} & \Lambda = 0 \\ \Pi & \text{for} & \Lambda = \pm 1 \\ \Delta & \text{for} & \Lambda = \pm 2 \\ \Phi & \text{for} & \Lambda = \pm 3 \quad \text{, etc.} \end{split}$$

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

For the inversion operator there are two eigenvalues:

$$i\psi_e = \pm \psi_e$$
 eigenvalues 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:

Heteronuclear

$\Lambda = 0$	$\Sigma_{g}^{+}\Sigma_{\mu}^{+}\Sigma_{g}^{-}\Sigma_{\mu}^{-}$	$\Sigma^+ \Sigma^-$
$\Lambda = 1$	$\Pi_{g}^{+} \Pi_{u}^{+} \Pi_{g}^{-} \Pi_{u}^{-}$	$\Pi^+ \Pi^-$
$\Lambda = 2$	$\Delta_{g}^{\circ} \Delta_{u}^{+} \Delta_{g}^{\circ} \Delta_{u}^{-}$	$\Delta^+ \Delta^-$
etc	6 6	

Homonuclear

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: $\dot{S} = \sum \dot{s}_i$. 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 H₂ molecule

 ${}^{3}\Sigma_{g}^{-}$ for the ground state of the O₂ 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.

3.3. 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 nucleaus 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:

$$P(X_1, Y_1, Z_1, X_2, Y_2, Z_2) = (X_2, Y_2, Z_2, X_1, Y_1, Z_1)$$

= $(-X_1, -Y_1, -Z_1, -X_2, -Y_2, -Z_2)$
Z



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 posititions 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 en ϕ change, but also the *z*-as. 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:

$$\int F^{T}(R, \theta, \phi; x_{i}, y_{i}, z_{i}) = (R, \pi - \theta, \phi + \pi; x_{i}, -y_{i}, -z_{i})$$

Hence the important relationship for the inversion operators is proven:

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

3.4. 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_{ν} . 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_{ν} signifies the parity operation:

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

3.5 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 Σ 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:

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

where *D* stands for the Wigner *D*-functions. The phase factor depends on the choice of the phase convention; the above equation is in accordnace 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 Λ =0. For the orbital angular momentum of the electrons:

$$\sigma_{\nu}|\Lambda\rangle = \pm (-1)^{\Lambda}|-\Lambda\rangle$$

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:

$$\sigma_{v}(\psi_{el}\psi_{vib}\psi_{rot}) = \sigma_{v}(|n\Lambda\Sigma\Omega\rangle|v\rangle|\Omega JM\rangle)$$
$$= (-1)^{J-2\Sigma+S+\sigma}|n, -\Lambda, S, -\Sigma\rangle|v\rangle|-\Omega, J, M\rangle$$

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:

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

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 $(-)^{N+1}$, 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.

3.6 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):

$$\sigma_{v} \Psi = + (-1)^{J} \Psi \quad for \quad e$$

$$\sigma_{v} \Psi = -(-1)^{J} \Psi \quad for \quad f$$

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

$$\sigma_{v} \Psi = + (-1)^{J-1/2} \Psi \quad for \quad e$$

$$\sigma_{v} \Psi = -(-1)^{J-1/2} \Psi \quad for \quad f$$

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:

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

3.7 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 μ 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	\rightarrow	+	levels are symmetric
		-	levels are anti-symmetric
ungerade	\rightarrow	+	levels are anti-symmetric
		-	levels are symmetric

This gives the following ordering:



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

3.8 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 \hat{J} then the spin of the nucleus \hat{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 odd N	require require	ψ_{nuc} anti-symmetric 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 a levels	require require	ψ_{nuc} anti-symmetric 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:

(2I+1)(I+1)	are symmetric
(2I+1)I	are anti-symmetric

3.9 Para and ortho hydrogen

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

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

There exist $(2I+1)^2=4$ possible quantum states of which 3 are symmetric and one anti-symmetric under interchange of the two particles (note that α means spin up, β spin down):

$$I = 1 \qquad \begin{aligned} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{aligned}$$

and:

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

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.

3.10 Missing levels in the oxygen molecule

The nuclear spin of ¹⁶O 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 a having positive symmetry. The electronic ground state of O₂ has a ${}^{3}\Sigma_{g}$ symmetry, hence has a negative parity for the electronic wave function. ¹⁶O 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 ${}^{16}O_2$ molecule.

Note that this analysis only holds for the ${}^{16}O_2$ molecule, and for the ${}^{18}O_2$ molecule, because the ${}^{18}O$ nucleus also has I=0. The heteronuclear species (isotopomers) ${}^{16}O^{18}O$, ${}^{16}O^{17}O$ and ${}^{17}O^{18}O$ do not follow this peculiar behaviour since the additional inversion symmetry is lifted. In the ${}^{17}O_2$ 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 ${}^{16}O_2$ and ${}^{18}O_2$ 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 com-

ponent 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 10⁶). The fact that the transition is between a triplet state and a singlet state is also a reason for its weakness.

3.11 The 3:1 ratio in N₂

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=I. 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 form 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.

4. Open Shell Molecules

4.1 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		Λ
Electronic spin	$\vec{S} = \sum \vec{s}_i$	S
SF projection	S _Z	M_S
BF projection	S _z	Σ
Rotational	Ř	R
SF projection	R _Z	М
BF projection	R _z	-
Total orbital	$\vec{N} = \vec{R} + \vec{L}$	Ν
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	$\dot{J} = \sum \vec{j_i}$	-
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}_i and \vec{s}_i 's to \vec{S} corresponds to the atomic Russel-Saunders coupling, while the coupling to $\vec{J}_a(j_i = l_i + \vec{s}_i)$ 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:

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

and:

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

In these expressions g_e is the electronic g factor, μ_{β} 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

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

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 $\tilde{r}'s$, $\tilde{v}'s$ and $\tilde{s}'s$. The most common forms of H_{so} are:

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

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 $\tilde{l}_{j\alpha}$ 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).

4.2 Hund's Coupling Cases

Case (a)

This case occurs when \rightarrow

(1) all \vec{l} 's are coupled to \vec{L} and all \vec{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.q. $\vec{R} \cdot \vec{L}$) i.e.:

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

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 Ω couples with \vec{R} to a total molecular angular momentum:



Hunds case (a)

Hunds case (b)

It's 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.

$$\vec{L} \cdot \vec{A} \gg \vec{L} \cdot \vec{S} \qquad and \qquad \vec{L} \cdot \vec{A} \gg \vec{R} \cdot \vec{L}$$
$$\vec{N} \cdot \vec{S} > \vec{S} \cdot \vec{A}$$

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:

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

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

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, H₂⁺, HgH, NH, O₂,...), 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:





This is usually the case in heavy molecules, like Br₂, I₂. The coupling which produces \dot{J}_a may be of Russel-Saunders or of jj type:

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

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 H₂, He₂ 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:

$$N = R + L, R + L - 1, ..., |R - L|$$

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.

4.3 Calculation of rotational energies

4.3.1 Case (a)

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

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

assuming a simple "rotational" basis set of $|J\Omega M\rangle$ corresponding to eigenvalues of $\overset{3}{J}^{2}$, 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 contribution 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:

 \overrightarrow{P} - I I

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

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 $B_{\nu}(\langle L_{\perp}^2 \rangle - \Omega^2)$ 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:

$$F_{v}(J) = B_{v}[J(J+1)] + f_{v}(\Omega, J)$$

 $f_{\nu}(\Omega, J)$ 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 $f_{\nu}(\Omega, J)$.

4.3.2 Case (b)

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

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

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:

$$H_{r} = B_{v} \vec{R}^{2} = B_{v} (N_{\perp}^{2} + L_{\perp}^{2} - 2N_{\perp}L_{\perp})$$

= $B_{v} (\vec{N}^{2} - N_{\parallel}^{2} + L_{\perp}^{2} - 2(N_{\perp} \cdot L_{\perp}))$

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 $-2B_{\nu}(\Lambda^2 - \langle L_{\perp}^2 \rangle)$ are included in the ro-vibrational energy, then $F_{\nu}(N)$ reduces to:

$$F_{\nu}(N) = B_{\nu}N(N+1)$$

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.

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

i.e.

$$F_{v}(N) = \begin{bmatrix} B_{v}N(N+1) + \frac{1}{2}\gamma N & for & J = N+1/2 \\ \\ B_{v}N(N+1) - \frac{1}{2}\gamma(N+1) & for & J = N-1/2 \end{bmatrix}$$

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 F₁ and F₂ 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).

ation 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 <u>p-doubling</u>.



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 <u> ρ -tripling</u>):

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

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:

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

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:

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

The polarization effect involves excitation of electrons to states with non-zero orbital momentum l_{i} ; this momentum (or momenta) interact then with \hat{S} via a spin-orbit type coupling $\sum \hat{S} \cdot l_i$. Hebb (1936) considered a coupling of the type $\hat{S} \cdot L_{\perp}$. 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 O₂.

 $\lambda = 39\ 667\ \text{MHz}\quad \gamma = -252.7\ \text{MHz}\quad B = 43\ 102\ \text{MHz}$ 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 $N \cdot S$ coupling is usually very weak.

4.4. Intermediate Cases

4.4.1 Background

The calculation of rotational energies in the preceeding 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 \hat{S} can be coupled to Λ or to the molecular axis in low rotational states, but as the rotational frequency increases and becomes larger than the precession frequency of \hat{S} about Λ , \hat{S} decouples from Λ and couples to \hat{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 \hat{L} about the molecular axis. We then get a transition from 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{A} 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 offdiagonal contributions of some interactions generally cannot be disregarded a priori. In this situation energies are solutions of (often large) secular equations.

4.4.2. 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:

$$H_{ev} = H_{ev}^{0} + A(\vec{L} \cdot \vec{S}) = H_{ev}^{0} + \sum_{i} \varsigma(\vec{r}_{i})(\vec{l}_{i} \cdot \vec{s}_{i})$$

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)	$\Omega (\Omega = \Lambda + \Sigma)$	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 then 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.

$$L_{z}|\Lambda S\Sigma\rangle = \Lambda|\Lambda S\Sigma\rangle + |\delta_{\Lambda}\rangle$$
$$S_{z}|\Lambda S\Sigma\rangle = \Sigma|\Lambda S\Sigma\rangle + |\delta_{\Sigma}\rangle$$

 $|\delta_{\Lambda}\rangle$ 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 $|\Omega JM\rangle$ when J and M is the quantum number associated with \tilde{J}^2 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 $|\Omega JM\rangle \equiv \Omega J\rangle$, 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:

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

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

$$\langle S\Sigma | \vec{S}^2 | S\Sigma \rangle = S(S+1)$$

$$\langle S\Sigma | S_z | S\Sigma \rangle = \Sigma$$

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

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.

4.4.3 ²Π 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:

$$|1\rangle = |1, \frac{1}{2}, \frac{1}{2}, \frac{3}{2}, J\rangle \qquad |3\rangle = |-1, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, J\rangle$$
$$|2\rangle = |1, \frac{1}{2}, -\frac{1}{2}, \frac{1(3)}{2}, J\rangle \qquad |4\rangle = |-1, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, J\rangle$$

Diagonal matrix elements of $H_{\rho\nu}$ are:

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

1

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 $B(J^2 - J_z^2), B(S^2 - S_z^2)$ and $B(\vec{L}^2 - L_z^2) = BL_{\perp}^2$ 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:

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

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 ² Π states. It represents energy of two doubly degenerate levels.

	1>	2>		3>	4>
1>	$B[J(J+1)-7/4+] +A/2$	-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+ <l_ -A/2</l_ 	_ ² >]	0	0
3>	0	0	B[J(J+	1)-7/4+ <l_2>] +A/2</l_2>	-B[(J-1/2)(J+3/2)] ^{1/2}
4>	0	0	-B[(J-	1/2)(J+3/2)] ^{1/2}	$B[J(J+1)+1/4+]$ -A/2

When J=1/2 the functions $|1\rangle$ and $|3\rangle$ 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)

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

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

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

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. his 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.

