Chapter 12. Electronic Spectroscopy

The atomic nuclei in a molecule are held together by the electrons. Otherwise, the nuclei alone would repel each other. Similar to atoms, we expect different electronic states of the molecule, depending on the orbitals in which the electrons are. The energy differences between these electronic states are of the same order as for atoms (1-20 eV), i.e., Visible and UV range.

§12.1   Electronic Energy and Total Energy of A Molecule

Neglecting spin and magnetic interactions, the total energy of the molecule consists of electron energy and nuclear energy:

$$E_{Total.Molecule} = E_{Total.Electrons} + E_{Total.Nuclei} \qquad (1)$$

where,

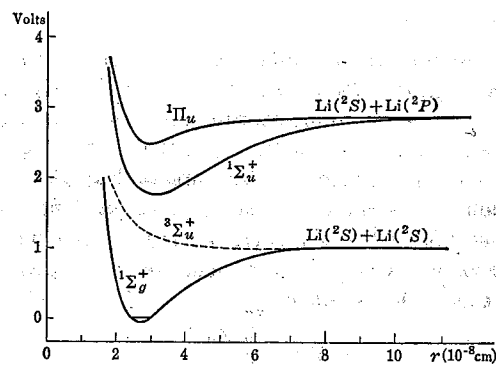$$E_{Total.Electrons} = E_{K, electrons} + V_{electrons} \qquad (2)$$

$$E_{Total.Nuclei} = E_{K, nuclei} + V_{nuclei} \qquad (3)$$

If we consider for a moment the electronic motions for fixed nuclei, it is clear that the electronic energy (potential + kinetic energy) will depend on the internuclear distance r. This dependence will be different for different electronic states. For example, if compare the interaction of two normal hydrogen atoms with the interaction of one normal and one highly excited hydrogen atom, the dependence will be different.

On account of the smallness of the mass of the electrons, compared to that of the nuclei, the electrons move much more rapidly than the nuclei; and therefore, the electronic energy, when the nuclei are no longer fixed, takes up the value corresponding to the momentary positions of the nuclei. Thus, in order to change the position of the nuclei, not only must work be done against the Coulomb repulsion of the nuclei, but also work must be supplied for the necessary change of electronic energy. In other words, the sum of electronic energy (potential + kinetic) and Coulomb potential of the nuclei acts as the potential energy under whose influence the nuclei carry out their vibrations.

Only if this potential energy, in its dependence on the internuclear distance, has a minimum is the electronic state in question a stable state of the molecule. If there is no minimum the electronic state is unstable, i.e., the two atoms repel each other for any value of the internuclear distance.

FIG. 68. Potential Curves of the Different Electronic States of the Li₂ Molecule [after Mulliken (514)]. The repulsive state with the broken potential curve has not been directly observed.

$^3\Sigma_u^+$ is unstable.

Others, $^1\Sigma_g^+$, $^1\Sigma_u^+$, $^1\Pi_u$, are stable.

As illustrated above, each different electronic state is
corresponding to one potential curve (diatomic molecule).

The curves represent the variation of the effective potential
energy of the nuclei (electronic energy + Coulomb potential
of the nuclei). Each electronic state is characterized by
a definite potential curve which may have a more or less
minimum (curve of attraction, stable molecular state) or
may have no minimum (curve of repulsion, unstable molecular
state).

Energy Eigenvalue Equation

Again, energy levels of molecule are determined
by the energy eigenvalue equation, i.e., Time-independent
Schrödinger equation:

$$\hat{H} |\psi\rangle = E |\psi\rangle \qquad (4)$$

where $\hat{H}$ is the Hamiltonian operator of the molecule.

$$\hat{H} = \hat{H}_{Kinetic} + \hat{H}_{potential}. \qquad (5)$$

Considering both electrons and nuclei, the Schrödinger equation

$$\sum_i \frac{\hat{\vec{P}}_i^2}{m_e} + \sum_k \frac{\hat{\vec{P}}_k^2}{M_k} + \frac{8\pi^2}{h^2} (E - \hat{V}) \psi = 0 \qquad (6)$$

where $\hat{\vec{P}}_i$ and $\hat{\vec{P}}_k$ are the momentum operators for electrons (with

mass me) and nuclei (with mass M_k), and $\hat{V}$ is the
potential energy operator in the molecule.

From Born-Oppenheimer approximation, we can separate the
electron motions from the nuclei motions:

$$\psi = \psi_e (\cdots) \, \psi_{vr} (\cdots)$$

This is because electrons move much faster than nuclei
($T_{electron} \sim 10^{-15} s$).

To a very good approximation, the total energy E of
the molecule is the sum of three components:

$$E = E_e + E_v + E_r$$

where $E_e = E_{e,k} + E_{e,p}$ —— the electron energy
(potential + kinetic)

E_v — vibrational energy

E_r — rotational energy.

The vibrations and rotations of the molecule in the different electronic states, are described by the model of the vibrating rotator, as we discussed in earlier lectures:

$$E_v = E(v) = hc\,\tilde{\nu}_e \left(v + \tfrac{1}{2}\right) - hc\,\tilde{\nu}_e\, x_e \left(v + \tfrac{1}{2}\right)^2 + \cdots$$

$$E_r = E_v(r) = hc\, B_v\, J(J+1) - hc\, D_v\, J^2(J+1)^2 + \cdots$$

The vibrational ($\tilde{\nu}_e$) and rotational (B_v, D_v) constants occuring in E_v and E_r have of course different values for the different electronic states of a molecule.
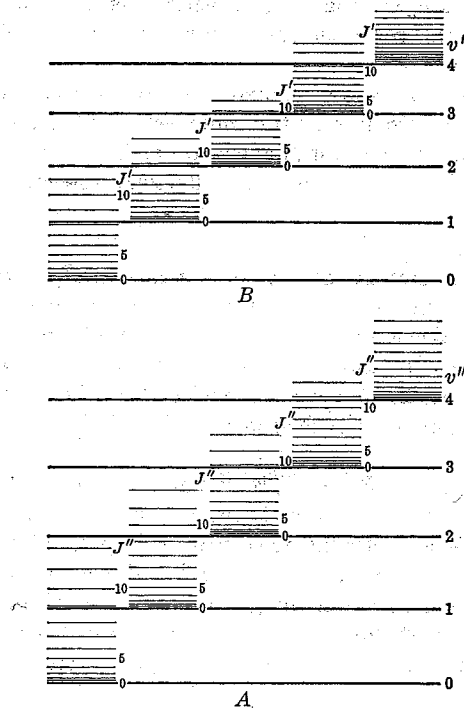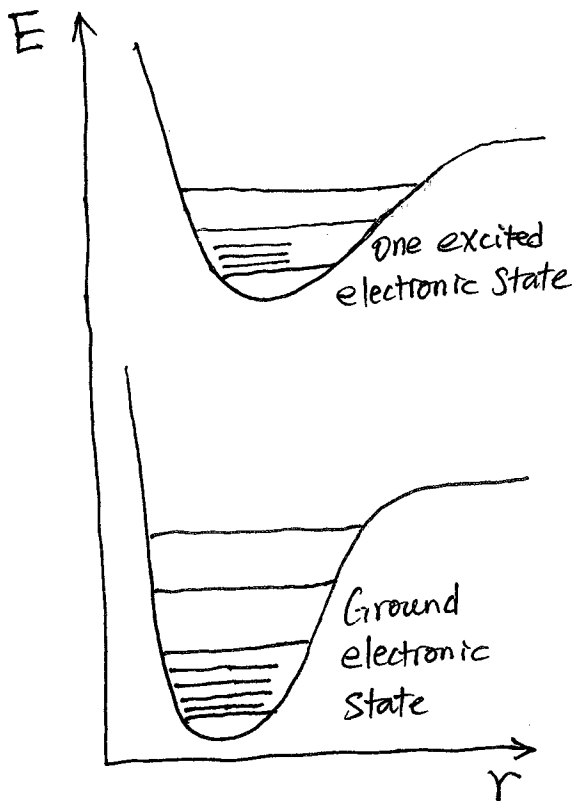

FIG. 69. Vibrational and Rotational Levels of Two Electronic States A and B of a Molecule (Schematic). Only the first few rotational and vibrational levels are drawn in each case.

Each potential curve corresponds to one electronic state.

✻   Energy Band and Spectrum Band.

Compared with atoms,   the   energy levels become

energy "bands" in molecules.

The spectral lines corresponding to the transitions between
atomic energy levels become spectral bands, corresponding
to transitions between molecular energy bands.

3P ——————————————

3S ——————————————

Na atom

B

A

589 nm
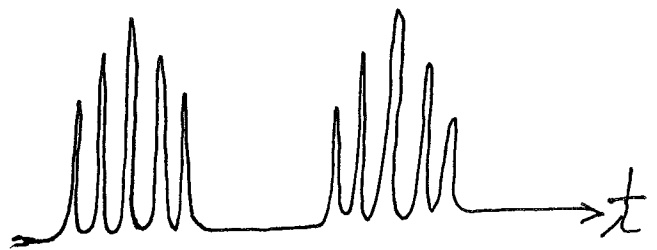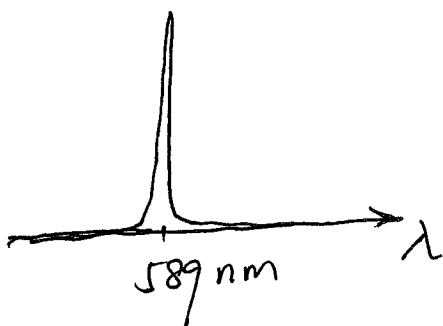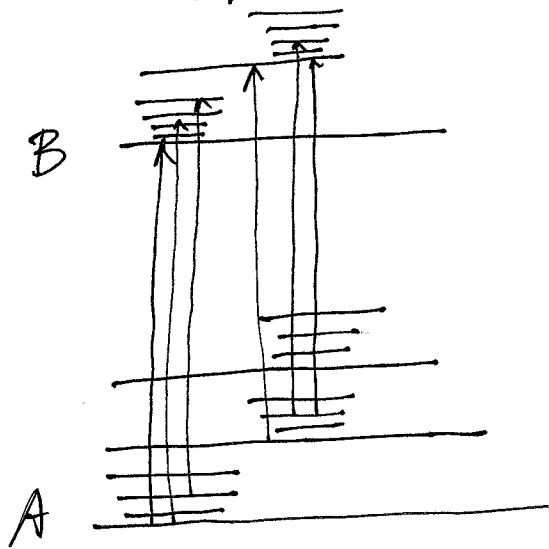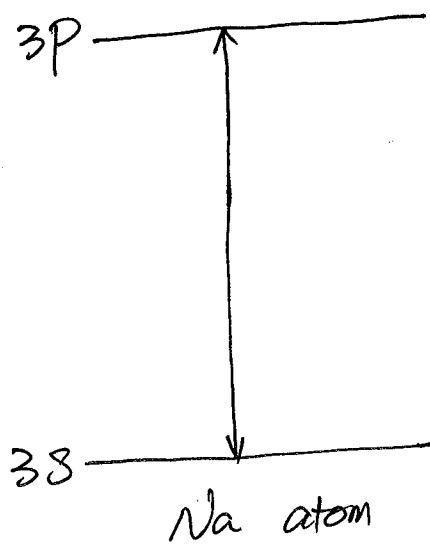
The energy band and spectral band of molecule owe to the
vibrational and rotational motions of the molecules.

§12.2 . Quantum Numbers for Molecular Spectroscopy

	Atomic Spectroscopy	Molecular Spectroscopy
Electronic Orbital Angular Momentum	l for single electron L for many electrons coupled M_L : projection of $\vec{\hat{L}}$ along z $l = 0, 1, 2, 3, \cdots$ $\quad s, p, d, f$ $L = 0, 1, 2, 3, \cdots$ $\quad S, P, D, F$ $M_L = L, L-1, \cdots, -L$	l for single electron L for many electrons (bad) M_L : projection along internuclear axis (good quantum number) $\lambda = |m_l| = 0, 1, 2, \cdots, l$ $\Lambda = |M_L| = 0, 1, 2, \cdots, L$ $\lambda = 0, 1, 2, 3$ $\quad \sigma, \pi, \delta, \varphi$ $\Lambda = 0, 1, 2, 3$ $\quad \Sigma, \Pi, \Delta, \Phi$
Electronic Spin Angular Momentum	s for single electron ($S = \frac{1}{2}$) S for many electrons coupled M_S : projection of $\vec{\hat{S}}$ along z $M_S = S, S-1, \cdots, -S$	s for single electron ($S = \frac{1}{2}$) S for many electrons (good quantum number) $\Sigma = M_S = S, S-1, \cdots, -S$ projection of $\vec{\hat{S}}$ in internuclear axis
Total Angular Momentum of electrons	$\vec{\hat{j}} = \vec{\hat{l}} + \vec{\hat{s}}$ for single electron $\vec{\hat{J}} = \vec{\hat{L}} + \vec{\hat{S}}$ for many electrons coupled M_J : projection of $\vec{\hat{J}}$ along z-axis $M_J = J, J-1, \cdots, -J$ $J = L+S, L+S-1, \cdots, |L-S|$ $\left(\text{For } jj \text{ coupling,} \atop \vec{\hat{J}} = \vec{\hat{j}}_1 + \vec{\hat{j}}_2 + \cdots + \vec{\hat{j}}_i \right)$	$\Omega = \Lambda + \Sigma$ (algebraic sum) The projection of the total angular momentum of electrons about the internuclear axis.

|	Atomic Spectroscopy	Molecular Spectroscopy
Angular momentum of nuclear rotation	N/A	$\hat{\vec{R}}$ or $\hat{\vec{N}}$
Total Angular momentum of Molecule (excluding nuclear spins)	$\hat{\vec{J}}$ in atom has the same role as $\hat{\vec{J}}$ in molecule, but just there is no $\hat{\vec{R}}$ in atom (or $\hat{\vec{R}} \equiv 0$) $\therefore \hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$ or $\hat{\vec{J}} = \sum_i \hat{\vec{j_i}}$.	$\hat{\vec{J}}$: the sum of electron spin, electronic orbital angular momentum, and angular momentum of nuclear rotation. $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}} + \hat{\vec{R}}$ Some case $= \hat{\vec{\Omega}} + \hat{\vec{R}}$ At least, four different coupling cases between Λ, Σ, and $\hat{\vec{R}}/\hat{\vec{N}}$.
Nuclear Spin	I (only one nucleus) $M_I = I, I-1, \cdots, -I$	I for single nucleus $\hat{\vec{T}} = \sum_K \hat{\vec{I_K}}$ for many nuclei coupled For diatomic molecule, $T = I_1 + I_2, I_1 + I_2 - 1, \cdots, |I_1 - I_2|$
Total Angular momentum of Atom or Molecule	$\hat{\vec{F}} = \hat{\vec{J}} + \hat{\vec{I}}$ $F = J+I, J+I-1, \cdots, |J-I|$ M_F: Projection along z	$\hat{\vec{F}} = \hat{\vec{J}} + \hat{\vec{T}}$ $F = J+T, J+T-1, \cdots, |J-T|$.

Examples of Molecular Quantum numbers
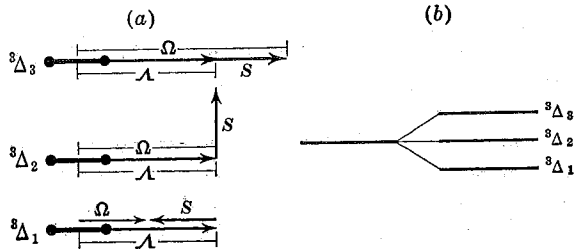
FIG. 96. (a) Vector Diagrams and (b) Energy Level Diagram for a $^3\Delta$ State ($\Lambda = 2$, $S = 1$). In (a) the approximate magnitude $S(h/2\pi)$ [rather than $\sqrt{S(S+1)}(h/2\pi)$] is used. In (b), to the left the term is drawn without taking the interaction of Λ and S into account; to the right, taking account of it.
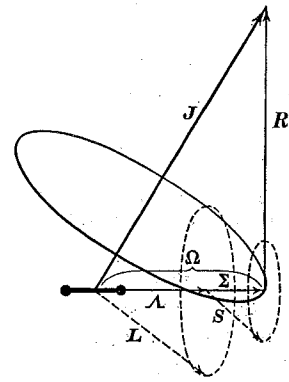

FIG. 97. Vector Diagram for Hund's Case (a). The nutation of the figure axis is indicated by the solid-line ellipse; the much more rapid precessions of L and S about the line joining the nuclei are indicated by the broken-line ellipses.

orbital   spin

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

$$\Lambda = 0, 1, 2, 3$$
$$\Sigma, \Pi, \Delta, \Phi$$

$$2S+1 \longrightarrow multiplicity$$

$$\Lambda = 2 \Rightarrow \Delta$$

$$S = 1 \Rightarrow \Sigma = 1, 0, -1$$

$$\left.\right\} \Rightarrow \quad ^3\Delta_3, \ ^3\Delta_2, \ ^3\Delta_1$$

$$\therefore \ \Omega = \Lambda + \Sigma = 3, 2, 1$$

$$^{2S+1}\Lambda_{(\Lambda+\Sigma)}$$

The electronic energy of a multiplet term

$$T_e = T_0 + A\,\Lambda\,\Sigma$$

a constant for given multiplet   orbital   spin

① internal magnetic field H_i produced by electron orbital motion ~~with~~ causes the procession of $\overset{\Lambda}{S}$ about the internuclear axis.

$$H_i \propto \Lambda.$$

② The magnetic moment of spin in the internuclear direction $\mu_i \propto \Sigma$

For singlet ($S=0$), $\Omega = \Lambda$, e.g. $^1\Pi_1$

For doublet ($S=\frac{1}{2}$), $\Omega = \Lambda \pm \frac{1}{2}$, e.g. $^2\Pi_{1/2}, \ ^2\Pi_{3/2}$

For triplet ($S=1$), $\Omega = \Lambda$ and $\Lambda \pm 1$,

e.g., $^3\Pi_0, \ ^3\Pi_1, \ ^3\Pi_2$

For quartet ($S=\frac{3}{2}$), $\Lambda + \Sigma = \Lambda + \frac{3}{2}, \ \Lambda + \frac{1}{2}, \ \Lambda - \frac{1}{2}, \ \Lambda - \frac{3}{2}$

for $\Lambda = 1$, $\Lambda + \Sigma = \frac{5}{2}, \ \frac{3}{2}, \ \frac{1}{2}, \ -\frac{1}{2}$. $\Omega = \frac{5}{2}, \frac{3}{2}, \frac{1}{2} = |\Lambda + \Sigma|$

But actually 4 different energy levels: $^4\Pi_{5/2}, \ ^4\Pi_{3/2}, \ ^4\Pi_{1/2}, \ ^4\Pi_{-1/2}$.

## Symmetry Properties of the Electronic Eigenfunctions

For the classification of molecular electronic states, in addition to the quantum numbers introduced above, the symmetry properties of the electronic eigenfunctions are of great importance. These symmetry properties depend on the symmetry properties of the field in which the electrons move.

In a diatomic molecule, any plane through the internuclear axis is a plane of symmetry. For both homonuclear and heteronuclear diatomic molecules, if the electronic eigenfunction of a state remains unchanged, we say it's symmetric, and designate it as "+" on the right-upper corner, e.g., Σ^+; if the electronic eigenfunction changes sign when reflected at any plane passing through both nuclei, we say it's antisymmetric, and designate it as "−", e.g., Σ^-.

$$\psi(z) = \pm \psi(-z)$$
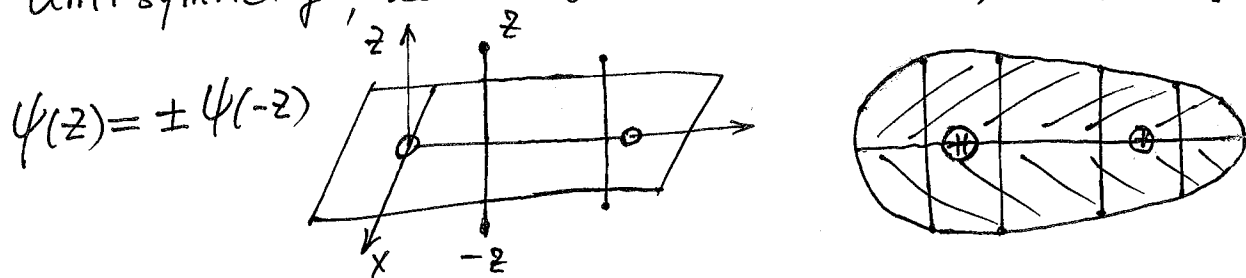
If the two nuclei in the molecule have the same charge, for example, $O^{16}O^{16}$, or $O^{16}O^{18}$, the field in which the electrons move has a center of symmetry (in addition to the symmetry axis). In other words, the field remains unaltered by a reflection of the nuclei at this center of symmetry (midpoint of the

internuclear axis). In consequence of this center symmetry, the electronic eigenfunctions remain either unchanged or only change sign when reflected at the center. In the first case, the electronic state is called an even state, and designated by "g" in right-lower corner, e.g., Σ_g. In the second case, the electronic state is called an odd state, expressed as "u", e.g., Σ_u.

$$\psi(x,y,z) = \pm \psi(-x,-y,-z)$$
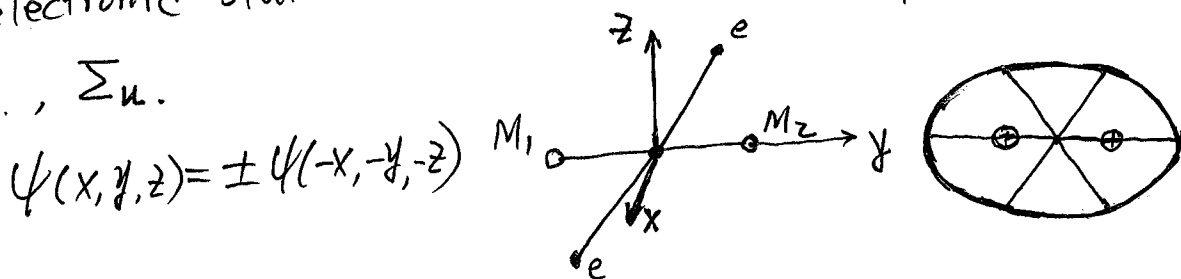
plane symmetry : (for both homonuclear and heteronuclear)

$$+ \quad - \quad \text{symmetry}$$

$$- \quad - \quad \text{antisymmetry}$$

Center symmetry (for homonuclear but on the count of charge)

$$g \quad - \quad \text{symmetry (even state)}$$

$$u \quad - \quad \text{antisymmetry (odd state)}$$

*. From Electronic Configurations to Electronic States

In atomic spectroscopy, e.g., Na, the electronic configuration for the ground state is $1s^2 2s^2 2p^6 3s^1$ ← number of electrons on this orbital.

$\begin{pmatrix} n - \text{principal } q.n. \\ l - \text{electron orbital } q.n. \end{pmatrix}$ $n, l \quad n \, l \quad n \, l \quad n \, l$

In molecular spectroscopy, we have similar electronic configuration, but with molecular symbols.

For example, O_2 ground state : (open-shell)

$$1\sigma_g^2 \; 1\sigma_u^2 \; 2\sigma_g^2 \; 2\sigma_u^2 \; 3\sigma_g^2 \; 1\pi_u^4 \; 1\pi_g^2$$

Again, the principle govern the electronic configuration is the Pauli Exclusion Principle — no two electrons can have all the same quantum numbers.

Molecule has similar electronic configurations as atoms, but 1, 2, 3 in the molecular electronic configuration, its definition is different from atoms. It comes as it appears for the first time or 2nd or 3rd time. (See Fig 7.1 in Brown's book). (Counting from bottom)

Only consider the open-shell configuration, $1\pi_g^2$

Each electron occupies π orbital: $\lambda_1 = \pm 1$, $\lambda_2 = \pm 1$

$$\therefore \Lambda = |\lambda_1 + \lambda_2| = |M_L| = |2, 0, 0, -2|$$

$$= 2, 0,$$

Atoms

$l_1 = 1$
$l_2 = 1$

$\therefore \vec{L} = \vec{l_1} + \vec{l_2}$

$\Rightarrow L = l_1 + l_2, \; l_1 + l_2 - 1, \cdots, |l_1 - l_2|$

$= 2, 1, 0,$

For $\Lambda = 0$, $\Rightarrow$ Σ state.

$S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$ $\Rightarrow$ $S = 1, 0$

The ground state of O_2 is $^3\Sigma_g^-$.
Electronic state

Electronic Configuration of H_2: $1\sigma_g^2$

$\lambda_1 = 0$, $\lambda_2 = 0$ $\Rightarrow \Lambda = 0$ $\Rightarrow$ Σ state

$S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$ $\Rightarrow S = 0, 1$ $\Rightarrow$ ground $S = 0$ $\Rightarrow 2S+1 = 1$

$\Rightarrow$ Ground state of H_2: $^1\Sigma_g^+$

N_2: $1\sigma_g^2 \, 1\sigma_u^2 \, 2\sigma_g^2 \, 2\sigma_u^2 \, 3\sigma_g^2 \, 1\pi_u^4$

$\lambda_1 = \pm 1$, $\lambda_2 = \pm 1$, $\lambda_3 = \pm 1$, $\lambda_4 = 1$

$\Rightarrow \Lambda = 0$ for ground state

$S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$, $S_3 = \frac{1}{2}$, $S_4 = \frac{1}{2}$

$\Rightarrow S = 0$ for ground state

$\therefore$ Ground state electronic state is $^1\Sigma_g^+$

§12.3. Selection Rules for electronic Spectroscopy:

The quantum numbers and symmetry properties affect the spectra of diatomic molecules through the selection rules. ~~that~~ Conversely, if these selection rules are known, the quantum numbers and symmetry properties of the various energy levels of a molecule may be determined from the observed band spectra.

The selection rules are obtained by evaluating the matrix elements of the electric dipole moment. We must distinguish between selection rules that hold quite generally, independent of the coupling case, and those that hold only for a definite coupling case.

General Selection rules :

$$\Delta J = 0, \pm 1, \quad \text{but} \quad J=0 \not\leftrightarrow J=0$$

$$\text{Parity}: \quad + \longleftrightarrow -, \quad + \not\leftrightarrow +, \quad - \not\leftrightarrow -$$

(In homonuclear case, $g \longleftrightarrow u$, $g \not\leftrightarrow g$, $u \not\leftrightarrow u$)

Selection rules holding for case (a)

$$\Delta \Lambda = 0, \pm 1$$

$$\Sigma^+ \longleftrightarrow \Sigma^+, \quad \Sigma^- \longleftrightarrow \Sigma^-$$

$$\Delta S = 0 \quad (\text{not strict})$$

$$\Delta v = \text{any value}.$$