

Solutions

Chapter 2

2.1 In a diatomic molecule, there exists an interatomic distance r_0 at which the potential energies of the ionic and the covalent bonding types are equal, i. e. at which the potential curves intersect:

$$P_i(r_0) = P_n(r_0) . \quad (1)$$

At shorter distances, the ionic molecule is more stable. For $r \gg \varrho$, the exponential term for the repulsion in the two given potential functions can be neglected, so that in the case of the ionic molecule, essentially only the Coulomb interaction remains:

$$P_i(r) = -\frac{e^2}{4\pi \varepsilon_0 r} + I_E . \quad (2)$$

With the simplification $C = 0$, it follows that $P_n(r) = 0$, and thus from (1) and (2) we obtain the determining equation for the distance r_0 :

$$-\frac{e^2}{4\pi \varepsilon_0 r} + I_E = 0 , \quad (3)$$

$$r_0 = \frac{e^2}{4\pi \varepsilon_0 I_E} . \quad (4)$$

With $I_E = 1.42 \text{ eV}$, one finds

$$r_0 = 1.01 \cdot 10^{-9} \text{ m} .$$

2.2 In order to obtain the best possible resolution in the transmission electron microscope, i. e. the smallest possible value of d_p , one chooses an electron beam intensity (dose I) which approaches the threshold for damage of the molecules, ($I = N_{\text{cr}}$). Furthermore, the necessary signal/noise ratio S/N is minimised. If these two factors have been optimised, the remaining possibility is to increase the contrast C_n by stacking many monolayers upon each other. C_n is proportional to the square root of the number n of layers, so that with the contrast $C_1 = C$ for a single monolayer, we find:

$$C_n = \sqrt{n} C . \quad (1)$$

The theoretical point resolution can be calculated using the formula of Freyer:

$$d_p = \frac{S/N}{\sqrt{n} C \sqrt{f I}}, \quad (2)$$

where f is the electron yield factor (0.25). At the required resolution of $d_p = 1 \text{ \AA}$, this yields the number n of monolayers which will generate the necessary contrast:

$$n = \frac{(S/N)^2}{d_p^2 C^2 f I}. \quad (3)$$

With the given data for the microscope, one thus finds

$$n = 100$$

which in the case of hexadecachloro copper phthalocyanine corresponds to overall layer thicknesses of 340 to 380 \AA .

2.3 Due to the potential difference $U_d - U_s$ between the detector of the time-of-flight mass spectrometer and the substrate, which is at a distance d from the detector, an electric field E acts and accelerates the ionised molecules. If $q = n e$ is the charge of an n -fold ionised molecule and M is its molar mass, then for the acceleration a we find:

$$a = \frac{qE}{M} = \frac{q(U_d - U_s)}{M d} = \frac{n e (U_d - U_s)}{M d}. \quad (1)$$

The time T for the uniformly accelerated motion is given by

$$T = \sqrt{\frac{2d}{a}} \quad (2)$$

and therefore

$$T = \sqrt{\frac{2d^2 M}{n e (U_d - U_s)}}. \quad (3)$$

If we choose the time of the ionisation as the zero point of the time scale, then the apparatus registers a maximum at the time T (in the ideal case as a δ -function), which indicates the arrival of the large molecule. An accelerating voltage of $U_d - U_s = 2 \text{ kV}$, on the assumption that every molecule is only singly ionised ($n = 1$), yields

$$T = 5.1 \cdot 10^{-5} \text{ s}.$$

The time dependence of the current from the detector in fact exhibits a number of maxima for $t < T$, which are caused by solvent molecules as well as by fragments of the large molecules.

2.4 The number of C_{60} molecules which form a Langmuir film with a surface area A can be computed from the volume V of the solution with a molar particle concentration of c :

$$n = c V . \quad (1)$$

If the film consists of a single monomolecular layer, the average area A_M per molecule is found to be

$$A_M = \frac{A}{n} = \frac{A}{c V} . \quad (2)$$

With the experimental values given, this means that

$$A_M = 2.16 \cdot 10^{-19} \text{ m}^2 = 21.6 \text{ \AA}^2 .$$

The area of a C_{60} molecule defined by the van der Waals interaction is 78.5 \AA^2 . Considering that even for spherical closest packing, the space per molecule required is somewhat more than this area, one arrives at a value which is about four times greater per molecule than the available area A_M . This means that the film consists of four stacked monolayers of C_{60} molecules.

2.5 In the experimental method given, the osmotic pressure is compensated by the hydrostatic pressure p of a solution of density $\varrho = 0.867 \text{ g/cm}^3$ and height h :

$$p = \varrho g h . \quad (1)$$

In equilibrium, $\pi = p$, we thus have

$$\varrho g h = c N_A k T (1 + \alpha c) . \quad (2)$$

Calculating the mass concentration c' from the molar particle concentration c is carried out using the molecular mass M according to

$$c = \frac{n}{V} = \frac{c'}{M} \quad (3)$$

Inserting (3) into (2) leads to the equation

$$\frac{h}{c'} = \frac{N_A k T}{\varrho g M} + \frac{N_A k T \alpha}{\varrho g M^2} c' \quad (4)$$

$$\frac{h}{c'} = a + b c' . \quad (5)$$

Plotting h/c' against c' yields a straight line with a y-intercept of $a = 0.325 \text{ cm}^4/\text{mg}$ and a slope of $b = 0.202 \text{ cm}^7/\text{mg}^2$.

From a , using (4) and (5), we obtain the molecular mass M of the polymer:

$$M = 89606 \frac{\text{g}}{\text{mole}} .$$

The slope b yields the virial coefficient

$$\alpha = 5.57 \cdot 10^7 \text{ cm}^3/\text{mole}$$

and thus via $\alpha = \frac{1}{2} N_A v_p$ the occupied volume

$$v_p = 1.85 \cdot 10^{-16} \text{ cm}^3.$$

The volume occupied by a spherical molecule of radius r is a sphere with a radius $2r$ around the centre of the molecule, since the centre of every neighbouring molecule has to be at least at the distance $2r$ from the centre of the given molecule. It follows from this consideration that

$$v_p = \frac{4}{3} \pi (2r)^3 = \frac{32}{3} \pi r^3. \quad (6)$$

From this, we calculate a molecular radius of

$$r = 1.77 \cdot 10^{-6} \text{ cm} = 177 \text{ \AA}.$$

2.6 The specific heat C_V of a material at constant volume is defined as the derivative of its internal energy U with respect to the temperature:

$$C_V = \left(\frac{dU}{dT} \right)_{dV=0}. \quad (1)$$

Using the differential expression for the internal energy,

$$dU = T dS - p dV + \mu dN, \quad (2)$$

and $dN = 0$, we obtain from (1) and from the entropy S per degree of freedom,

$$S = \frac{1}{2} k \ln T \quad (3)$$

the specific heat per molecule and degree of freedom:

$$C_V = T \frac{\partial S}{\partial T} = \frac{k}{2}. \quad (4)$$

For a molecule with f degrees of freedom, we thus find

$$C_V = f \cdot \frac{k}{2}. \quad (5)$$

In analogy to the derivation of C_V from the internal energy U , one finds the specific heat C_P at constant pressure from the enthalpy $H = U + pV$. Per molecule we obtain

$$C_P = C_V + k. \quad (6)$$

In an ideal gas, the velocity of sound c_S is given by the equation

$$c_S = \sqrt{\frac{\gamma R T}{M}} \quad (7)$$

with $\gamma = C_P/C_V$ and $R = N_A k$. To compute c_S at a temperature T , we thus require in addition to the molecular mass M the value of the ratio γ , which from (5) and (6) follows directly from the number f^* of excited degrees of freedom of translation, rotation, and vibration:

$$C_V = \frac{k}{2} (f_T^* + f_R^* + f_S^*) . \quad (8)$$

If the temperature is too low to allow the population of the vibrational levels, i. e. $f^* = 0$, then from (5), (6) and (8) we obtain for γ the relation

$$\gamma = 1 + \frac{2}{f_T^* + f_R^*} . \quad (9)$$

a) In an *ideal diatomic gas*, three degrees of freedom of translation and two degrees of freedom of rotation are excited. We thus obtain $\gamma = \frac{7}{5}$ and therefore for the velocity of sound

$$c_S = \sqrt{\frac{7 R T}{5 M}} . \quad (10)$$

b) For an *ideal linear triatomic gas*, the same result holds, so that in this case, also,

$$c_S = \sqrt{\frac{7 R T}{5 M}} . \quad (11)$$

c) In an *ideal nonlinear triatomic gas*, the third degree of freedom of rotation can also be excited, so that $\gamma = \frac{4}{3}$ and

$$c_S = \sqrt{\frac{4 R T}{3 M}} . \quad (12)$$

According to the CRC Handbook of Chemistry and Physics, *air* is composed of 78.084% N_2 , 20.946% O_2 , 0.934% Ar, and 0.033% CO_2 . For an estimate of the velocity of sound in air, only the two main components N_2 and O_2 need be considered, since both are diatomic molecules, so that (10) can be used with the weighted mean of their molecular masses. With $M_{N_2} = 28.014$ g/mole and $M_{O_2} = 31.998$ g/mole, it follows that

$$\bar{M} = \frac{g(N_2) M_{N_2} + g(O_2) M_{O_2}}{g(N_2) + g(O_2)} = 28.857 \frac{\text{g}}{\text{mole}} \quad (13)$$

and, from (7) with $T = 298$ K,

$$c_{S, \text{Luft}} = 342.9 \frac{\text{m}}{\text{s}} .$$

(For comparison: the measured value is 346.7 m/s.)

Chapter 3

3.1 a) The electrostatic energy of the system of N independent rigid dipoles due to their interaction with the externally applied field E is given by

$$H = - \sum_{i=1}^N p E \cos \theta_i . \quad (1)$$

The distribution density of the angles θ between the dipoles and the direction of the field, using the notation $\beta = 1/kT$, is assumed to be given by

$$f(\theta) = \frac{1}{Z} e^{-\beta H(\theta)} \quad (2)$$

with the density of states (partition function)

$$Z = \int_{-1}^{+1} e^{-\beta H(\theta)} d^N(\cos \theta) . \quad (3)$$

The mean value \bar{P} of the macroscopic polarisation

$$P = \sum_{i=1}^N p \cos \theta_i \quad (4)$$

along the direction of the external field E can be found by using the distribution function f from (2); it is

$$\bar{P} = \int_{-1}^{+1} f(\theta) \left(\sum_{i=1}^N p \cos \theta_i \right) d^N(\cos \theta) . \quad (5)$$

With (1), (2) and (3) and employing the substitutions $u_i = \cos \theta_i$ and $x = \beta p E$, this becomes

$$\bar{P} = N p \int_{-1}^{+1} u e^{xu} du \left(\int_{-1}^{+1} e^{xu} du \right)^{-1} . \quad (6)$$

After integration, one obtains the expression

$$\bar{P} = N p \left[\coth x - \frac{1}{x} \right] = N p L(x) . \quad (7)$$

Writing \bar{P} as

$$\bar{P} = N p \overline{\cos \theta} , \quad (8)$$

we find from (7) the thermal average of the angle θ between the dipoles and the field direction:

$$\overline{\cos \theta} = \coth x - \frac{1}{x} = L(x) . \quad (9)$$

b) The orientation of a dipole precisely along the field direction corresponds to a thermal average of the angle θ between the dipole p and the field E of

$$\overline{\cos \theta} = L(x) = 1 ; \quad (10)$$

compare (9). With the limiting value

$$\lim_{x \rightarrow \infty} L(x) = 1 \quad (11)$$

this corresponds for $x = pE/kT$ and $T = 293$ K to

$$E \rightarrow \infty .$$

In order to orient the dipole precisely along the field direction, one would thus have to apply an infinitely strong electric field!

c) The function \coth can be expanded in a series according to

$$\coth(x) = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \frac{2x^5}{945} + \dots \quad \text{for } 0 < |x| < \pi . \quad (12)$$

For sufficiently small $|x|$, the series can be terminated after the first-order term in x , thereby simplifying the Langevin function $L(x)$ in (9) to

$$L(x) \rightarrow \frac{x}{3} . \quad (13)$$

If the orientation polarisation reaches 50% of its theoretical maximum value, then from (8) we find

$$\bar{P} = N p \overline{\cos \theta} = 0.5 N p \quad (14)$$

and thus with (9) and (13)

$$L(x) = \frac{x}{3} = 0.5 \quad \Rightarrow \quad x = \frac{3}{2} . \quad (15)$$

The simplification of $L(x)$ is a poor approximation and allows at most a qualitative estimate. The required electric field

$$E = \frac{x k T}{p} \quad (16)$$

for the given values of p and T is found to be

$$E = 9.8 \cdot 10^8 \text{ V/m} .$$

d) With $E = 10^7$ V/m and $T = 4.2$ K, one obtains

$$L(x) = 0.355$$

and thus an orientation of ca. 36%.

3.2 The water molecule represents an electric dipole ($p = 1.85 \text{ D} = 6.17 \cdot 10^{-30} \text{ Cm}$) with a negative partial charge on the O atom and a positive charge between the H atoms. In the presence of a (negative) anion, the molecule will therefore orient itself with its H atoms pointing towards the ion.

The molecule is considered in the following as a dipole of length d , consisting of a positive and a negative elementary charge. The electrostatic potential of a point charge q at a distance r is

$$\phi = \frac{q}{4\pi \varepsilon_0 r} \quad (1)$$

and produces a field

$$E = -\frac{d\phi}{dr} = \frac{q}{4\pi \varepsilon_0 r^2} . \quad (2)$$

The distance from the two point-like elementary charges $q = \pm e$ to the (also point-like) anion is $r \mp d/2$. At the position of the anion, the fields produced by the two point charges then superpose to give

$$E(r) = \frac{e}{4\pi \varepsilon_0 (r - d/2)^2} - \frac{e}{4\pi \varepsilon_0 (r + d/2)^2} \quad (3)$$

$$E(r) = \frac{p r}{2\pi \varepsilon_0 (r^2 - d^2/4)^2} \quad (4)$$

with $p = d r$. From the given dipole moment, one finds a dipole length of $d = 3.85 \cdot 10^{-11} \text{ m}$, so that $d^2/4$ can be neglected in comparison to r^2 :

$$E(r) = \frac{p}{2\pi \varepsilon_0 r^3} . \quad (5)$$

For the distances given, one finds the following field strengths at the position of the anion:

$$\begin{aligned} \text{a) at } r = 10^{-9} \text{ m :} & \quad E = 1.11 \cdot 10^8 \text{ V/m} \\ \text{b) at } r = 3 \cdot 10^{-10} \text{ m :} & \quad E = 4.11 \cdot 10^9 \text{ V/m} \\ \text{c) at } r = 3 \cdot 10^{-8} \text{ m :} & \quad E = 4.11 \cdot 10^3 \text{ V/m} \end{aligned}$$

3.3 a) From $\alpha/4\pi \varepsilon_0 = 10.3 \cdot 10^{-30} \text{ m}^3$, it follows that:

$$p_{\text{ind}} = 1.15 \cdot 10^{-33} \text{ Cm} = 3.4 \cdot 10^{-4} \text{ D} .$$

b) From the power density $P/A = W \cdot c$ and the energy density $W = \frac{1}{2} \varepsilon_0 E^2$, the electric field strength at the laser focus is found to be

$$E = 8.7 \cdot 10^9 \frac{\text{V}}{\text{m}}$$

and thus

$$p_{\text{ind}} = 2.98 \text{ D} .$$

3.4 The behaviour of a permanent magnetic moment μ_p in a magnetic field B can be described in precise analogue to the case of an electric dipole in a field E (cf. Problem 3.1). From the competition between the orientation in the external field and the thermal disorder at the temperature T , the average of the angle θ between μ_p and B takes on the value

$$\overline{\cos \theta} = L(x) = \coth x - \frac{1}{x} \quad (1)$$

with $x = \mu_p B / k T$. The macroscopic magnetisation along the field direction is then

$$M = N \mu_p \overline{\cos \theta}. \quad (2)$$

In the high-temperature approximation, we find

$$L(x) \rightarrow \frac{x}{3}, \quad (3)$$

so that for a required orientation of 1% at room temperature, we obtain

$$L(x) = \frac{\mu_p B}{3 k T} = 0.01. \quad (4)$$

With the given values, one derives the required magnetic field

$$B = 7.14 \text{ T}.$$

Only at low temperatures can one work with lower magnetic field strengths.

3.5 Making use of the polarisability volume $\alpha' = \alpha / 4\pi \epsilon_0$ instead of the polarisability α , the Debye equation (3.19) becomes

$$P_m = \frac{4\pi N_A \alpha'}{3} + \frac{N_A p_0^2}{9\epsilon_0 k T} \quad (1)$$

$$= a + b \frac{1}{T}. \quad (2)$$

Plotting P_m against $1/T$ thus yields a straight line with a y-intercept a and slope b . The temperature-dependent relative dielectric constant $\epsilon_r = \epsilon$ and therefore $P_m(T)$ are found from the measured values of the capacity C of a condenser (having C_0 without a dielectric) quoted in the problem by applying

$$\epsilon_r = \frac{C}{C_0}, \quad (3)$$

so that from (1), a plot of $P_m(T^{-1})$ is possible ($M = 152.23 \text{ g/cm}^3$). A straight-line fit yields the intercept $a = 82.63 \text{ cm}^3/\text{mole}$ and the slope $b = 10\,833 \text{ cm}^3 \text{ K/mole}$. From b , we can compute the dipole moment

$$p_0 = 4.45 \cdot 10^{-30} \text{ Cm} = 1.33 \text{ D}$$

and from a , the polarisability volume

$$\alpha' = 32.75 \cdot 10^{-30} \text{ m}^3.$$

3.6 At optical frequencies, the reorientation of the molecules can no longer follow the rapid changes in the applied field, so that the orientation polarisation becomes negligibly small. The Debye equation (cf. Problem 3.4) can then be simplified to the Clausius-Mosotti equation with $\varepsilon = n^2$:

$$P_m = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\varrho} = \frac{N_A \alpha}{3\varepsilon_0}. \quad (1)$$

Solving for α and using $\alpha' = \alpha/4\pi\varepsilon_0$, one obtains from the given index of refraction $n = 1.333$ with the molecular mass $M = 18.015$ g/mole and the density $\varrho = 0.9982$ g/cm³ the polarisability volume

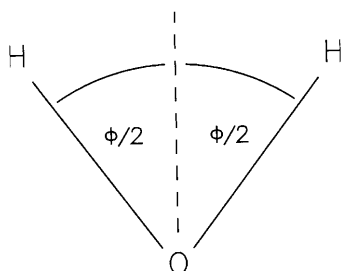
$$\alpha' = 1.47 \cdot 10^{-30} \text{ m}^3.$$

3.7 The dipole moment $p_{\text{H}_2\text{O}}$ of the water molecule can be treated as the vector sum of the dipole moments p_{OH} of two OH bonds. The dipole moments perpendicular to the plane of symmetry compensate each other, while the parallel components superpose constructively:

$$p_{\text{H}_2\text{O}} = 2 p_{\text{OH}} \cos \frac{\phi}{2}, \quad (1)$$

so that with $p_{\text{H}_2\text{O}} = 1.85$ D and $\phi = 104.25^\circ$, it follows that:

$$p_{\text{OH}} = 1.51 \text{ D}. \quad (2)$$



If the hydrogen peroxide molecule, $\text{H}-\text{O}-\text{O}-\text{H}$, is projected onto the plane of the page, its geometrical structure is similar to that of the water molecule, if a bonding angle of 90° is assumed for $\text{O}-\text{O}-\text{H}$. The $\text{O}-\text{O}$ bond is then perpendicular to the plane. Since it does not contribute to the dipole moment, the latter can be represented for this molecule also as $p_{\text{H}_2\text{O}_2}$ as the vector sum of the two moments of the p_{OH} bonds:

$$p_{\text{H}_2\text{O}_2} = 2 p_{\text{OH}} \cos \frac{\phi'}{2}, \quad (3)$$

where ϕ' is the angle between the two OH groups in the two-dimensional projection. With $p_{\text{H}_2\text{O}_2} = 2.13 \text{ D}$, we obtain

$$\phi' = 90.3^\circ.$$

3.8 The density of water vapour at a pressure of 1 bar is

$$\rho_{\text{Dampf}}(1 \text{ bar}) = \frac{18 \text{ g/mole}}{22.4 \text{ l/mole}} = 8.0 \cdot 10^{-4} \text{ g/cm}^3.$$

From $\varepsilon_{\text{fl}} = 1 + \chi_{\text{fl}} = 78.5$ for liquid water of density 1 g/cm^3 , one thus finds for water vapour at 1 bar

$$\chi_{\text{Dampf}}(1 \text{ bar}) = 77.5 \cdot 8.0 \cdot 10^{-4} = 6.2 \cdot 10^{-2}.$$

This means that at 50 mbar

$$\chi_{\text{Dampf}}(50 \text{ mbar}) = 3.1 \cdot 10^{-3}$$

and thus

$$\varepsilon_{\text{Dampf}}(50 \text{ mbar}) = 1 + 3.1 \cdot 10^{-3}$$

19% relative humidity at 40°C already exhibits the same effect on the value of ε as does dry air alone.

3.9 The Debye equation, (3.19), for the molar polarisability P_{m} makes the connexion between a macroscopically measurable quantity, the dielectric constant ε , and the microscopic quantities dipole moment p_0 and polarisability volume $\alpha' = \alpha/4\pi\varepsilon_0$ of chloroform.

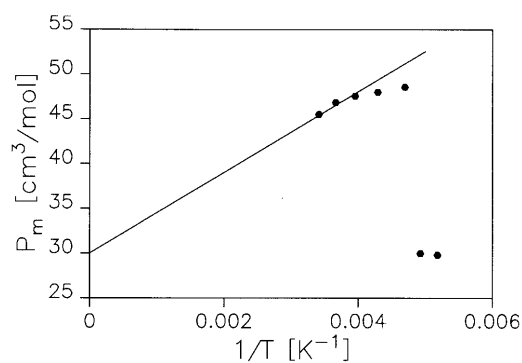


Fig. S.1. A graph of the molar polarisability P_{m} of CHCl_3 vs. the inverse temperature, $1/T$: data points and fitted line

If one plots P_m against $1/T$, then for temperatures above the melting point $T_S = -64^\circ\text{C}$ of chloroform, one obtains approximately a straight line with a y -intercept a and a slope b . Below T_S , the orientation polarisation is frozen in, so that its contribution to P_m (i.e. the term containing the permanent dipole moment p_0) vanishes. For $1/T > 1/T_S$, P_m is therefore practically independent of temperature and lies on a straight line parallel to the x -axis in the plot. For $T \rightarrow \infty$ the contribution from the orientation polarisation likewise vanishes, so that the y -intercept a in the plot should have the value of the constant ε for $1/T > 1/T_S$. For fitting the line to the data points in the plot, we thus use only the first three points and the required intercept on the y -axis.

From the slope $b = 4508.5 \text{ cm}^3 \text{ K/mole}$, we can compute the dipole moment of chloroform

$$p_0 = 2.87 \cdot 10^{-30} \text{ Cm} = 0.86 \text{ D}$$

and from the intercept $a = 30.0 \text{ cm}^3/\text{mole}$ its polarisability volume

$$\alpha' = 11.89 \cdot 10^{-30} \text{ m}^3.$$

3.10 From the Debye equation for the molar polarisability P_m

$$P_m = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\varrho} = \frac{N_A}{3\varepsilon_0} \left(\alpha + \frac{p_0^2}{3kT} \right) \quad (1)$$

with a given dipole moment p_0 and polarisability volume $\alpha' = \alpha/4\pi\varepsilon_0$ one can calculate the dielectric constant ε of chlorobenzene. To this end, we insert in (1)

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N_A \varrho}{3\varepsilon_0 M} \left(\alpha + \frac{p_0^2}{3kT} \right) \equiv x \quad (2)$$

and solve for ε :

$$\varepsilon = \frac{2x + 1}{1 - x}. \quad (3)$$

With the given data, we obtain $x = 0.801$ and thus

$$\varepsilon = 13.08.$$

3.11 The magnetic polarisability β is a microscopic quantity which relates the induced magnetic moment \mathbf{m} to the externally applied magnetic field \mathbf{B} :

$$\mathbf{m}_{\text{ind}} = \beta \mathbf{B} \quad (1)$$

(N : particle density). The moment \mathbf{m} can, on the other hand, also be expressed in terms of the macroscopic magnetic susceptibility:

$$\mathbf{m}_{\text{ind}} = \frac{1}{\mu_0 N} \mathbf{J} = \frac{\mu - 1}{\mu_0 N} \mathbf{B} = \frac{\kappa}{\mu_0 N} \mathbf{B} \quad (2)$$

(\mathbf{J} = macroscopic magnetisation). From this it follows that

$$\beta = \frac{\kappa}{\mu_0 N} . \quad (3)$$

In the classical ring-current model for the π electron system of benzene, one considers the six delocalised electrons to be forced onto a circular orbit by the Lorentz force in the field \mathbf{B} . The Lorentz force thus plays the role of a centripetal force:

$$m \boldsymbol{\omega} \times \mathbf{v} = q \mathbf{v} \times \mathbf{B} \quad (4)$$

($q = -e$ = electronic charge; m = electron mass; $\boldsymbol{\omega}$ = circular frequency; \mathbf{v} = orbital velocity). With $\omega = 2\pi/T$, we obtain the orbital period T :

$$T = \frac{2m\pi}{eB} . \quad (5)$$

The magnetic moment can be calculated classically according to

$$m_{\text{ind}} = I A , \quad (6)$$

where A is the area enclosed by the ring current I . For a ring current of radius r carried by n electrons, we thus have

$$m_{\text{ind}} = \frac{-ne}{T} \pi r^2 \quad (7)$$

and, with (5), we find

$$m_{\text{ind}} = \frac{ne^2 r^2 B}{2m} \quad (8)$$

(8) and (1) yield

$$\beta = \frac{ne^2 r^2}{2m} . \quad (9)$$

According to this model, the induced ring current gives rise to the anisotropy in the susceptibility and to the magnetic polarisability β . The expression found in (9) for β thus corresponds to the difference between the components perpendicular and parallel to the plane of the ring:

$$\beta = \beta_{\perp} - \beta_{\parallel} \quad (10)$$

so that the radius r of the ring current can be computed from (9) and the data given in the problem:

$$r^2 = \frac{2m}{ne^2 \mu_0} (\mu_0 \beta_{\perp} - \mu_0 \beta_{\parallel}) \quad (11)$$

and finally

$$r = 2.91 \cdot 10^{-11} \text{ m} .$$

This result shows that the diamagnetism of benzene is only approximately described by the ring-current model for the π electron system. The radius of the electronic orbits gives at best only the order of magnitude.

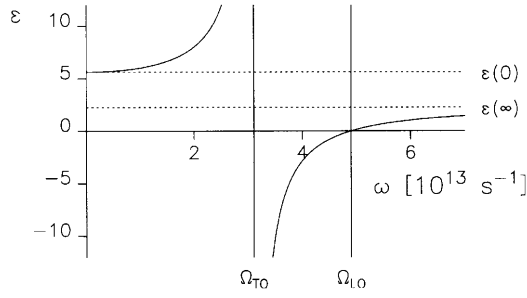


Fig. S.2. Dielectric function of the NaCl ionic crystal

3.12 The dielectric function of the NaCl crystal (Fig. S.2) is based on the model of a coupled photon-phonon field (polaritons). From the given values, one finds

$$\Omega_{LO} = 4.9 \cdot 10^{13} \text{ s}^{-1}$$

and then obtains the following frequency dependence for the dielectric constant ε :

An effect of the photon-phonon coupling is the formation of a frequency gap: for $\Omega_{TO} < \omega < \Omega_{LO}$, ε is negative and thus the wave vector $k = \omega \sqrt{\varepsilon(\omega)} / c$ is a purely imaginary quantity, so that in this frequency range, the wave is damped in a NaCl crystal as $e^{-|k|x}$. In the neighbourhood of Ω_{TO} , $|k|$ is large, the wave penetrates only a very short distance into the crystal, and it is completely reflected. For ω near Ω_{LO} , it is less strongly damped and can pass through a thin NaCl sheet (although attenuated). The transmitted rays are the so called residual radiation. More about this subject can be found in textbooks on solid-state physics.

Chapter 4

4.1 a) The time-independent Schrödinger equation in regions I, II, and III can be written in the following ways:

$$\text{I) } \quad \partial^2 \psi^{(1)} / \partial x^2 - \kappa^2 \psi^{(1)} = 0, \quad \kappa^2 = \frac{2m}{\hbar^2} (V_0 - E), \quad (1)$$

$$\text{II) } \quad \partial^2 \psi^{(2)} / \partial x^2 - k^2 \psi^{(2)} = 0, \quad k^2 = \frac{2m}{\hbar^2} E, \quad (2)$$

$$\text{III) } \quad \partial^2 \psi^{(3)} / \partial x^2 - \kappa^2 \psi^{(3)} = 0, \quad \kappa^2 = \frac{2m}{\hbar^2} (V_0 - E). \quad (3)$$

It follows from (1) and (3) that

$$k^2 + \kappa^2 = \frac{2m}{\hbar^2} V_0 = C. \quad (4)$$

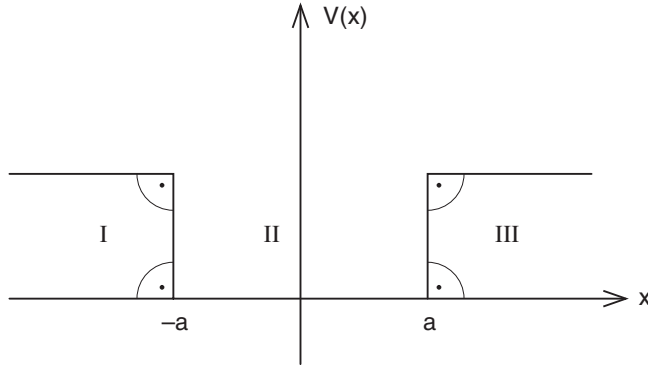


Fig. S.3. The “square-well” potential $V(x)$

b) Boundary conditions:

$$\lim_{x \rightarrow -\infty} \psi^{(1)}(x) = 0, \quad \text{therefore} \quad B^{(1)} = 0, \quad (5)$$

$$\lim_{x \rightarrow +\infty} \psi^{(3)}(x) = 0, \quad \text{therefore} \quad A^{(3)} = 0. \quad (6)$$

Continuity condition at the boundary:

$$\psi^{(1)}(-a) = \psi^{(2)}(-a)$$

yields

$$A^{(1)} e^{-\kappa a} = A^{(2)} e^{-ika} + B^{(2)} e^{ika}. \quad (7)$$

$$\partial \psi^{(1)}(-a)/\partial x = \partial \psi^{(2)}(-a)/\partial x$$

leading to

$$-\kappa A^{(1)} e^{-\kappa a} = -ik A^{(2)} e^{-ika} + ik B^{(2)} e^{ika}. \quad (8)$$

$$\psi^{(3)}(a) = \psi^{(2)}(a)$$

yields

$$B^{(3)} e^{-\kappa a} = A^{(2)} e^{ika} + B^{(2)} e^{-ika}. \quad (9)$$

$$\partial \psi^{(3)}(a)/\partial x = \partial \psi^{(2)}(a)/\partial x$$

and, finally,

$$-\kappa B^{(3)} e^{-\kappa a} = ik A^{(3)} e^{ika} - ik B^{(3)} e^{-ika}. \quad (10)$$

Here, $\partial \psi(\pm a)/\partial x$ means, more precisely, $\partial \psi(x)/\partial x|_{x=\pm a}$. It follows from (7) through (10) that

$$\left(1 \mp i \frac{k}{\kappa}\right) A^{(2)} e^{\mp ika} + \left(1 \pm i \frac{k}{\kappa}\right) B^{(2)} e^{\pm ika} = 0. \quad (11)$$

These are two homogeneous linear equations for $A^{(2)}, B^{(2)}$. The condition that they have a non-trivial solution is that the determinant of the coefficients vanishes, i. e.

$$\kappa^2 \sin(2ka) + 2k\kappa \cos(2ka) - k^2 \sin(2ka) = 0. \quad (12)$$

We find two types of solutions:

$$\alpha) \quad \text{symmetric,} \quad \kappa = k \tan(ka), \quad (13)$$

$$A^{(2)} = B^{(2)} = \frac{N}{2}; \quad A^{(1)} = B^{(3)} = N e^{\kappa a} \cos(ka), \quad (14)$$

and thus

$$\psi_s(x) = N \begin{cases} e^{\kappa(x+a)} \cos ka & (I) \\ \cos kx & (II) \\ e^{\kappa(-x+a)} \cos ka & (III) \end{cases}. \quad (15)$$

$$\beta) \quad \text{antisymmetric,} \quad \kappa = -k \cot(ka), \quad (16)$$

$$A^{(2)} = -B^{(2)} = \frac{N}{2}, \quad A^{(1)} = -B^{(3)} = -N e^{\kappa a} \sin(ka) \quad (17)$$

and thus

$$\psi_a(x) = N \begin{cases} -e^{\kappa(x+a)} \sin ka & (I) \\ \sin kx & (II) \\ e^{\kappa(-x+a)} \sin ka & (III) \end{cases}. \quad (18)$$

3) Normalisation:

$$\begin{aligned} 1 &\stackrel{!}{=} \int_{-\infty}^{+\infty} |\psi(x)|^2 dx = \int_{-\infty}^{-a} |\psi^{(1)}(x)|^2 dx \\ &\quad + \int_{-a}^{+a} |\psi^{(2)}(x)|^2 dx + \int_a^{\infty} |\psi^{(3)}(x)|^2 dx. \end{aligned} \quad (19)$$

The evaluation of the integrals is elementary. For the symmetric wavefunction, we find

$$N = \left\{ a + \frac{1}{a} \cos(ka) [\sin(ka) + \cos(ka)] \right\}^{-1/2}, \quad (20)$$

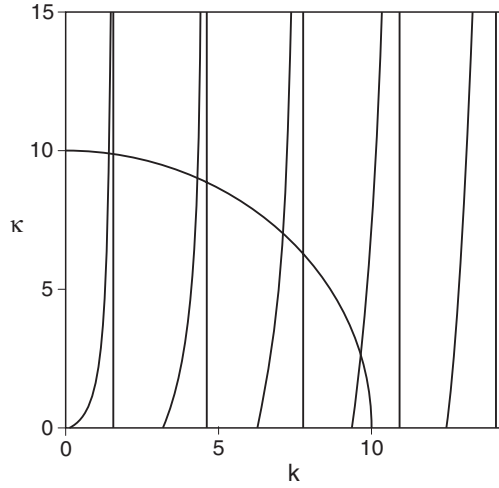


Fig. S.4. The graphical determination of the energy values for the symmetric bound states, $a = 1$, $C^2 = 10$. There are four energy values. (Note that the vertical lines are added only to guide the eye)

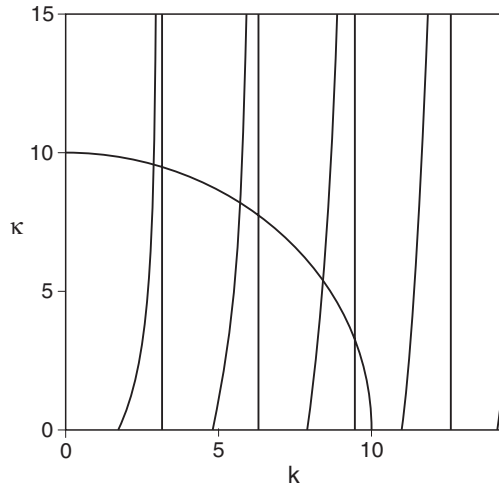


Fig. S.5. As in Fig. S.4, but for the antisymmetric bound states

and for the antisymmetric wavefunction,

$$N = \left\{ a + \frac{1}{a} \sin(ka) [\sin(ka) - \cos(ka)] \right\}^{-1/2}. \quad (21)$$

c) Graphical determination of the energy eigenvalues. For this purpose, we plot the curves (4), (13), i. e. (22) or (4), (16), i. e. (23) in the (k, κ) -plane and find the respective points of intersection of (22) and (23), Fig. S.4

$$\alpha) \quad \kappa = k \tan(ka), \quad \kappa^2 + k^2 = C^2. \quad (22)$$

For the example $a = 1$, $C^2 = 10$, we find four eigenvalues.

$$\beta) \quad \kappa = -k \cot(ka), \quad \kappa^2 + k^2 = C^2. \quad (23)$$

In the same example, we obtain three eigenvalues, cf. Fig. S.5.

In the symmetric case, α), there is at least one intercept, independently of a ; the ground state is symmetric.

d) The limiting case $V_0 \rightarrow \infty$:

For $V_0 \rightarrow \infty$, $C \rightarrow \infty$ also holds, and due to (1) and (3), we have also

$$\kappa \rightarrow \infty. \quad (24)$$

For finite values of k , we thus have $\alpha) \tan(ka) = \infty$, i. e.

$$k_n = \frac{2n-1}{2} \frac{\pi}{a}, \quad n \in \mathbb{N} \quad (25)$$

or

$$k_n = \frac{\pi n}{2a}, \quad n \text{ odd}, \quad (26)$$

$$\psi_s = \frac{1}{\sqrt{a}} \begin{cases} \cos k_n x & (II) \\ 0 & (I, III) \end{cases}. \quad (27)$$

$\beta) \cot(ka) = \infty$, i. e.

$$k_n = n \frac{\pi}{a}, \quad n \in \mathbb{N} \quad \text{or} \quad (28)$$

$$k_n = \frac{\pi n}{2a}, \quad n \text{ even}, \quad (29)$$

$$\psi_a = \frac{1}{\sqrt{a}} \begin{cases} \sin k_n x & (II) \\ 0 & (I, III) \end{cases}. \quad (30)$$

The energy values are:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{8ma^2} n^2, \quad n \in \mathbb{N}. \quad (31)$$

Matrix elements: the integrals are elementary.

$$x_{nm} = \int_{-a}^a x \psi_n \psi_m dx = 0 \quad (32)$$

for n and m even or n and m odd. This result also follows from symmetry considerations.

n odd, m even:

$$x_{nm} = (-1)^{\frac{n+m-1}{2}} \frac{16anm}{\pi^2(n^2 - m^2)^2}, \quad (33)$$

$$(x^2)_{nm} = 0 \quad (34)$$

for n even, m odd (or *vice versa*).

n, m odd, $n \neq m$:

$$(x^2)_{nm} = (-1)^{\frac{n-m}{2}} \frac{32a^2nm}{(n^2 - m^2)^2}, \quad (35)$$

n, m even, $n \neq m$:

$$(x^2)_{nm} = (-1)^{\frac{n-m}{2}} \frac{32a^2nm}{\pi^2(n^2 - m^2)^2}, \quad (36)$$

$n = m$:

$$(x^2)_{nn} = \frac{a^2}{3} - \frac{2a^2}{n^2\pi^2}. \quad (37)$$

Momentum matrix elements:

$$p_{nm} = \int_{-a}^a \psi_n \frac{\hbar}{i} \frac{d}{dx} \psi_m dx = 0 \quad (38)$$

for n and m even or n and m odd.

n odd, m even:

$$p_{nm} = \frac{\hbar}{ia} (-1)^{\frac{n+m-1}{2}} \frac{2nm}{n^2 - m^2} = p_{mn}^*. \quad (39)$$

e) Wave packet:

$$\psi(x, t) = \frac{1}{\sqrt{2}} [\psi_1(x)e^{-iE_1t/\hbar} + \psi_2(x)e^{-iE_2t/\hbar}], \quad (40)$$

where

$$E_2 - E_1 = 3\hbar\omega_0 \quad \text{with} \quad \omega_0 = \frac{\hbar^2\pi^2}{8ma^2}. \quad (41)$$

The integrals are elementary.

$$\langle x \rangle = \frac{32a}{9\pi^2} \cos(3\omega_0 t), \quad (42)$$

$$\langle x^2 \rangle = \frac{a^3}{3} - \frac{3a^2}{4\pi^2}, \quad (43)$$

$$\langle p \rangle = -\frac{4\hbar}{3a} \sin(3\omega_0 t). \quad (44)$$

Wave packet:

$$\psi(x, t) = \frac{1}{\sqrt{2}} \{ \psi_1(x)e^{-iE_1t/\hbar} + \psi_3(x)e^{-iE_3t/\hbar} \}, \quad (45)$$

where

$$E_3 - E_1 = 8\hbar\omega_0, \quad (46)$$

$$\langle x \rangle = \langle p \rangle = 0, \quad (47)$$

$$\langle x^2 \rangle = a^2 \left[\frac{1}{3} + \frac{8}{9\pi^2} - \frac{3}{2\pi^2} \cos(8\omega_0 t) \right]. \quad (48)$$

4.2 Ground-state wavefunction

$$\psi_{100} = 2a^{-3/2} e^{-r/a} \frac{1}{\sqrt{\pi}} \quad \text{with} \quad a \equiv a_0. \quad (1)$$

The definition of spherical polar coordinates:

$$x = r \cos \phi \sin \theta, \quad (2)$$

$$y = r \sin \phi \sin \theta, \quad (3)$$

$$z = r \cos \theta. \quad (4)$$

Expectation values in real space:

$$\begin{aligned} \langle \psi_{100} | x | \psi_{100} \rangle &= \langle \psi_{100} | y | \psi_{100} \rangle \\ &= \langle \psi_{100} | z | \psi_{100} \rangle = 0. \end{aligned} \quad (5)$$

This follows from symmetry considerations.

$$\langle x^2 \rangle = \langle \psi_{100} | x^2 | \psi_{100} \rangle, \quad (6)$$

$$= \frac{1}{\pi} a^{-3} \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi r^4 \cos^2 \phi \sin^3 \theta e^{-2r/a} \quad (7)$$

$$= \frac{1}{\pi} a^{-3} \int_0^\infty dr \int_0^\pi d\theta r^4 e^{-2r/a} \sin^3 \theta \pi \quad (8)$$

$$= a^{-3} \int_0^\infty dr r^4 e^{-2r/a} \cdot \frac{4}{3} \quad (9)$$

$$= a^2. \quad (10)$$

Correspondingly,

$$\langle y^2 \rangle = a^2 \quad (11)$$

and

$$\langle z^2 \rangle = a^2. \quad (12)$$

(11) and (12) also follow directly from (10) due to the spherical symmetry of (1).

Momentum expectation values:

$$\langle p_x \rangle = \langle p_y \rangle = \langle p_z \rangle = 0 \quad (13)$$

from symmetry considerations.

For the calculation of $\langle p_x^2 \rangle$, etc. we take

$$\frac{\partial}{\partial x} \psi_{100} = -\frac{1}{a} \frac{x}{r} \psi_{100}, \quad (14)$$

$$\frac{\partial^2}{\partial x^2} \psi_{100} = -\frac{1}{a} \left(\frac{1}{r} - \frac{x^2}{r^3} - \frac{x^2}{ar^2} \right) \psi_{100}, \quad (15)$$

$$\begin{aligned} \langle p_x^2 \rangle &= \langle \psi_{100} | p_x^2 | \psi_{100} \rangle \\ &= \frac{\hbar^2}{\pi a^4} \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi e^{-2r/a} r^2 \sin \theta \\ &\quad \times \left[\underbrace{\frac{1}{r}}_{(1)} - \underbrace{\frac{\cos^2 \phi \sin^2 \theta}{r}}_{(2)} - \underbrace{\frac{\cos^2 \phi \sin^2 \theta}{a}}_{(3)} \right] \end{aligned} \quad (16)$$

(1) yields

$$\frac{4\hbar^2}{a^4} \int_0^\infty e^{-2r/a} r dr = \frac{\hbar^2}{a^2}; \quad (17)$$

(2) yields

$$-\frac{\hbar^2}{a^4} \int_0^\infty dr e^{-2r/a} r \int_0^\pi \sin^3 \theta d\theta, \quad (18)$$

$$= -\frac{4\hbar^2}{3a^4} \int_0^\infty dr e^{-2r/a} r = -\frac{1}{3} \frac{\hbar^2}{a^2}; \quad (19)$$

and (3) yields

$$-\frac{\hbar^2}{a^4} \int_0^\infty dr e^{-2r/a} \frac{r^2}{a} \frac{4}{3} = -\frac{1}{3} \frac{\hbar^2}{a^2}. \quad (20)$$

All together, we find

$$\langle p_x^2 \rangle = \frac{\hbar^2}{a^2} \frac{1}{3}. \quad (21)$$

Owing to the spherical symmetry of the wavefunction (1), we find the corresponding result

$$\langle p_y^2 \rangle = \langle p_z^2 \rangle = \frac{\hbar^2}{a^2} \frac{1}{3}. \quad (22)$$

Because of the definition

$$\overline{\Delta p_x} = (\langle p_x^2 \rangle - \langle p_x \rangle^2)^{1/2} \quad (23)$$

and

$$\overline{\Delta x} = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}, \quad (24)$$

as well as (5, 10, 13, 21), it follows that

$$\overline{\Delta p_x} = \frac{1}{\sqrt{3}} \frac{\hbar}{a}, \quad \overline{\Delta x} = a \quad (25)$$

and we thus find for Heisenberg's uncertainty relation

$$\overline{\Delta x} \overline{\Delta p} = \frac{1}{\sqrt{3}} \hbar > \frac{\hbar}{2}. \quad (26)$$

The expectation value for the kinetic energy is

$$E_{\text{kin}} = \langle \psi_{100} | -\frac{\hbar^2}{2m} \Delta | \psi_{100} \rangle. \quad (27)$$

The Laplace operator in spherical polar coordinates is given by

$$\Delta = \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2}, \quad (28)$$

$$E_{\text{kin}} = \frac{\hbar^2}{2ma^2}. \quad (29)$$

$$E_{\text{pot}} = \langle \psi_{100} | -\frac{e^2}{4\pi\epsilon_0 r} | \psi_{100} \rangle = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{a}. \quad (30)$$

Expectation values for the angular momentum:

$$L^2 \psi_{klm} = l(l+1) \hbar^2 \psi_{klm}, \quad (31)$$

$$L_z \psi_{klm} = m \hbar \psi_{klm}. \quad (32)$$

From the commutation relations for the angular-momentum operators, it follows that

$$[L_z, L_{\pm}] = \pm \hbar L_{\pm}, \quad (33)$$

where

$$L_{\pm} = L_x \pm iL_y. \quad (34)$$

Applying (33), we write the equation

$$L_z L_+ |lm\rangle = L_+ (L_z + \hbar) |lm\rangle = (m+1)\hbar L_+ |lm\rangle. \quad (35)$$

Thus, $\psi_+ \equiv L_+ |lm\rangle$ is an eigenfunction of L_z (32) with the eigenvalue $\hbar(m+1)$ up to a normalisation factor, i. e.

$$\psi_+ \equiv L_+ |lm\rangle = N |lm+1\rangle. \quad (36)$$

In order to determine N , we set

$$\langle \psi_+ | \psi_+ \rangle \equiv \langle lm | L_- L_+ | lm \rangle = N^2 \langle lm+1 | lm+1 \rangle. \quad (37)$$

Using (34), we write

$$\begin{aligned} L_- L_+ &= L_x^2 + L_y^2 + iL_x L_y - iL_y L_x \\ &= L^2 - L_z^2 - L_z. \end{aligned} \quad (38)$$

With (31) and (32) and the normalisation of the wavefunctions, it follows from (37) that:

$$\hbar^2 (l^2 + l - m^2 - m) = N^2 \quad (39)$$

or

$$N = \sqrt{(l-m)(l+m+1)}\hbar \quad (40)$$

so that

$$L_+ |lm\rangle = \sqrt{(l-m)(l+m+1)}\hbar |lm+1\rangle \quad (41)$$

and, correspondingly,

$$L_- |lm\rangle = \sqrt{(l+m)(l-m+1)}\hbar |lm-1\rangle. \quad (42)$$

From (31), (32) and the normalisation of the wavefunctions, we have

$$\langle \psi_{klm} | L^2 | \psi_{klm} \rangle = l(l+1)\hbar^2, \quad (43)$$

$$\langle \psi_{klm} | L_z | \psi_{klm} \rangle = m\hbar. \quad (44)$$

With (41) and (42), we find

$$L_x = \frac{1}{2} (L_+ + L_-), \quad L_y = \frac{1}{2i} (L_+ - L_-) \quad (45)$$

and the orthogonality of the wavefunctions follows:

$$\langle \psi_{klm} | L_x | \psi_{klm} \rangle = \langle \psi_{klm} | L_y | \psi_{klm} \rangle = 0. \quad (46)$$

4.3 The trial solution is

$$\psi_{\pm} = c(\phi_a \pm \phi_b) \quad \text{with} \quad \int dV |\phi_a|^2 = \int dV |\phi_b|^2 = 1 \quad (1)$$

a) Normalisation:

$$\begin{aligned} \int |\psi_{\pm}|^2 dV &= c^2 \left(2 \pm 2 \int dV \phi_a^* \phi_b \right) \\ &= c^2 (2 \pm 2S) \stackrel{!}{=} 1, \quad \text{and thus} \\ c &= [2(1 \pm S)]^{-1/2}. \end{aligned} \quad (2)$$

b) Expectation value of the Hamiltonian:

$$E = \int dV \psi_{\pm}^* H \psi_{\pm}. \quad (3)$$

Insertion of (1) and (2) into (3):

$$E = \frac{2}{2(1 \pm S)} \int dV \phi_a^* \left[-\frac{\hbar^2}{2m} \Delta - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} \right] \phi_a \quad (4)$$

$$\pm \frac{2}{2(1 \pm S)} \int dV \phi_b^* \left(-\frac{\hbar^2}{2m} \Delta - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} \right) \phi_a. \quad (5)$$

The factors of 2 in (4) and (5) result from the fact that in E (3), there were originally two further integrals in which the indices a and b were exchanged relative to (4) and (5), but which otherwise were identical to (4) and (5) from symmetry considerations. Using the abbreviations E^0 , C , D , S as in the text, we find

$$E = \frac{1}{1 \pm S} [E^0 + C \pm (S \cdot E^0 + D)]. \quad (6)$$

This can be brought into the form

$$E = E^0 + \frac{C \pm D}{1 \pm S}. \quad (7)$$

c) with the trial solution

$$\psi = c_1 \phi_a + c_2 \phi_b \quad (8)$$

we obtain for the normalisation

$$\int dV \phi^* \phi = c_1^2 + c_2^2 + 2c_1 c_2 S \stackrel{!}{=} 1 \quad (9)$$

and thus

$$\psi = \frac{1}{\underbrace{\sqrt{c_1^2 + c_2^2 + 2c_1c_2S}}_{:=N}} (c_1\phi_a + c_2\phi_b) . \quad (10)$$

Then the energy expectation value is found to be

$$\tilde{E} = \int dV \psi^* H \psi = N^2 \{ (c_1^2 + c_2^2) [E^0 + C] + 2c_1c_2[SE^0 + D] \} , \quad (11)$$

$$\tilde{E} = E^0 + N^2 [(c_1^2 + c_2^2) C + 2c_1c_2D] . \quad (12)$$

Variation of \tilde{E} (12) with respect to c_1 :

$$\begin{aligned} \text{(i)} \quad \frac{\partial \tilde{E}}{\partial c_1} &= 2N^2(c_1C + c_2D) \\ &\quad - 2N^4(c_1 + c_2S)[(c_1^2 + c_2^2)C + 2c_1c_2D] \stackrel{!}{=} 0 , \end{aligned} \quad (13)$$

and with respect to c_2 :

$$\begin{aligned} \text{(ii)} \quad \frac{\partial \tilde{E}}{\partial c_2} &= 2N^2(c_2C + c_1D) \\ &\quad - 2N^4(c_2 + c_1S)[(c_1^2 + c_2^2)C + 2c_1c_2D] \stackrel{!}{=} 0 . \end{aligned} \quad (14)$$

We take

$$\frac{\text{(i)}c_2 - \text{(ii)}c_1}{2N^4} = 0 = (c_1^2 - c_2^2) S[(c_1^2 + c_2^2) C + 2c_1c_2D] \quad (15)$$

and thereby obtain

$$c_1^2 = c_2^2 \quad c_1 = \pm c_2 \quad (16)$$

in agreement with the original trial solution (1).

d) As in Fig. S.6, we have

$$r_{a/b} = \left(r^2 + \frac{1}{4}R^2 \mp rR \cos \theta \right)^{1/2} . \quad (17)$$

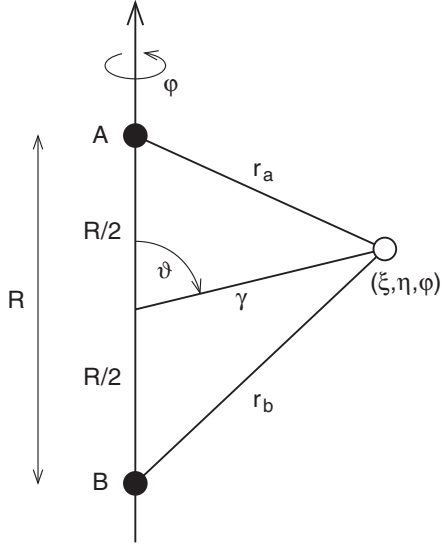
Prolate elliptical coordinates are defined by

$$\xi = \frac{r_a + r_b}{R} , \quad \eta = \frac{r_a - r_b}{R} . \quad (18)$$

To compute the volume element dV , which in spherical polar coordinates is given by

$$dV = r^2 \sin \theta dr d\theta d\phi , \quad (19)$$

Fig. S.6. The hydrogen molecule-ion



we write the determinant of the derivatives:

$$D = \left| \begin{array}{cc} \frac{\partial \xi}{\partial r} & \frac{\partial \xi}{\partial \theta} \\ \frac{\partial \eta}{\partial r} & \frac{\partial \eta}{\partial \theta} \end{array} \right|, \quad (20)$$

so that

$$d\xi d\eta = Ddrd\theta, \quad (21)$$

whereby, due to (17–19):

$$D = \frac{1}{R^2} \left| \begin{array}{l} \frac{1}{2r_a}(2r - R \cos \theta) + \frac{1}{2r_b}(2r + R \cos \theta); \left(\frac{1}{2r_a} - \frac{1}{2r_b} \right) + R \sin \theta \\ \frac{1}{2r_a}(2r - R \cos \theta) - \frac{1}{2r_b}(2r + R \cos \theta); \left(\frac{1}{2r_a} + \frac{1}{2r_b} \right) + R \sin \theta \end{array} \right|. \quad (22)$$

Calculation of D yields

$$D = \frac{2}{R} \frac{r^2 \sin \theta}{r_a r_b} \quad (23)$$

or, due to (18),

$$D = \frac{r^2 \sin \theta}{(R/2)^3 (\xi + \eta)(\xi - \eta)} . \quad (24)$$

The volume element dV (19), applying (21, 24), is given by

$$dV = \left(\frac{R}{2}\right)^3 (\xi^2 - \eta^2) d\xi d\eta d\phi, \quad (25)$$

where

$$\begin{aligned} 0 &\leq \phi < 2\pi, \\ -1 &\leq \eta < 1, \\ 1 &\leq \xi < \infty. \end{aligned} \quad (26)$$

As trial wavefunctions, it is advisable to choose

$$\phi(r; \alpha) = \frac{1}{\sqrt{\pi}} \left(\frac{\alpha}{a_0} \right)^{3/2} \exp \left(-\frac{\alpha r}{a_0} \right). \quad (27)$$

We first set $\beta = \alpha/a_0$.

Computation of the overlap integral S :

$$S = \int \phi_a \phi_b dV = \frac{\beta^3}{\pi} \int dV \exp [-\beta (r_a + r_b)] \quad (28)$$

or, in prolate elliptical coordinates,

$$S = \frac{\beta^3}{\pi} \left(\frac{R}{2} \right)^3 \int_0^{2\pi} d\phi \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi^2 - \eta^2) \exp (-\beta R \xi). \quad (29)$$

Integrating over $d\phi$ and $d\eta$ immediately yields

$$S = \frac{1}{4} (\beta R)^3 \int_1^\infty d\xi \left(2\xi^2 - \frac{2}{3} \right) \exp (-\beta R \xi). \quad (30)$$

Making use of the ancillary formulas from Problem 4.2, we can carry out the integration over ξ after combining terms,

$$S = \left[\frac{1}{3} \left(\frac{\alpha R}{a_0} \right)^2 + \frac{\alpha R}{a_0} + 1 \right] \exp \left(-\frac{\alpha R}{a_0} \right). \quad (31)$$

The Coulomb integral C :

$$\begin{aligned} C &= -\frac{e^2}{4\pi\epsilon_0} \int \phi_a \frac{1}{r_b} \phi_a dV \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{\beta^3}{\pi} \int dV \frac{1}{r_b} \exp (-2\beta r_a). \end{aligned} \quad (32)$$

Or, in prolate elliptical coordinates,

$$\begin{aligned} C &= -\frac{e^2 \beta^3}{4\pi^2 \epsilon_0} \left(\frac{R}{2} \right)^3 \int_0^{2\pi} d\phi \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi^2 - \eta^2) \\ &\quad \times \frac{2}{R(\xi - \eta)} \exp [-\beta R(\xi + \eta)]. \end{aligned} \quad (33)$$

Integration over ϕ and cancellation of $(\xi - \eta)$ yields:

$$C = -\frac{e^2 \beta^3 R^2}{8\pi\epsilon_0} \int_{-1}^{+1} d\eta \int_1^\infty d\xi (\xi + \eta) \exp[-\beta R(\xi + \eta)] . \quad (34)$$

Integration over η and introduction of a new variable $u = \xi + \eta$ gives:

$$C = -\frac{e^2 \beta^3 R^2}{8\pi\epsilon_0} \int_1^\infty d\xi \underbrace{\left(\frac{1}{\beta R} u + \frac{1}{(\beta R)^2} \right) \exp(-\beta R u)}_{=F(u)} \Bigg|_{u=\xi-1}^{u=\xi+1} \quad (35)$$

$$= -\frac{e^2 \beta^3 R^2}{8\pi\epsilon_0} \left[\int_2^\infty du F(u) + \int_0^\infty du F(u) \right] . \quad (36)$$

Evaluation of the integrals using the ancillary formulas of Problem 4.2 and combining terms, with $\beta = \alpha/a_0$, gives:

$$C = \frac{e^2}{4\pi\epsilon_0} \left\{ -\frac{1}{R} + \left(\frac{\alpha}{a_0} + \frac{1}{R} \right) \exp\left(-2\frac{\alpha R}{a_0}\right) \right\} . \quad (37)$$

The exchange integral D is:

$$\begin{aligned} D &= -\frac{e^2}{4\pi\epsilon_0} \int \phi_a \frac{1}{r_a} \phi_b dV \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{\beta^3}{\pi} \int dV \frac{1}{r_a} \exp[-\beta(r_a + r_b)] . \end{aligned} \quad (38)$$

Or, in prolate elliptical coordinates:

$$\begin{aligned} D &= -\frac{e^2}{4\pi^2\epsilon_0} \left(\frac{\beta R}{2} \right)^3 \int_0^{2\pi} d\phi \int_{-1}^{+1} d\eta \int_1^\infty d\xi \\ &\quad \times \frac{2}{R(\xi + \eta)} (\xi^2 - \eta^2) \exp(-\beta R\xi) . \end{aligned} \quad (39)$$

Integration over ϕ and cancellation of $(\xi + \eta)$ yields:

$$D = -\frac{e^2 \beta^3 R^2}{8\pi\epsilon_0} \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi - \eta) \exp(-\beta R\xi) . \quad (40)$$

Integration over η :

$$D = -\frac{e^2 \beta^3 R^2}{4\pi\epsilon_0} \int_1^\infty d\xi \xi \exp(-\beta R\xi) . \quad (41)$$

The final result is:

$$D = -\frac{e^2}{4\pi\epsilon_0} \frac{\alpha}{a_0} \left(1 + \frac{\alpha R}{a_0}\right) \exp(-\beta R) . \quad (42)$$

For the ground-state energy E^0 , we find:

$$E^0 = \int \phi_a \left[-\frac{\hbar^2}{2m} \Delta - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r_a} \right] \phi_a dV . \quad (43)$$

Evaluation in spherical polar coordinates: since the wavefunction does not depend on θ and ϕ , we use

$$\Delta = \Delta_r = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \quad (44)$$

and $dV = 4\pi r^2 dr$ on integrating only over r . Then

$$r^2 \Delta_r \phi_a \propto [-2r\beta + (\beta r)^2] \exp(-\beta r) . \quad (45)$$

For (43), it follows that

$$E^0 = \frac{\beta^3}{\pi} 4\pi \int_0^\infty dr \times \left\{ \left(-\frac{\hbar^2}{2m} \right) [-2\beta r + (\beta r)^2] - \frac{e^2}{4\pi\epsilon_0} r \right\} \exp(-2\beta r) , \quad (46)$$

and, after integrating,

$$E^0 = 4\beta^3 \left(\frac{\hbar^2}{2m} \frac{\beta}{4} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{4\beta^2} \right) . \quad (47)$$

Using $\beta = \alpha/a_0$ and the definition of the Bohr radius a_0 , we obtain

$$E^0 = \frac{e^2}{4\pi\epsilon_0} \frac{\alpha}{a_0} \left(\frac{\alpha}{2} - 1 \right) . \quad (48)$$

e) The total energy is given by:

$$E_{\text{mol}} = \frac{e^2}{4\pi\epsilon_0} \left[\frac{\alpha}{a_0} \left(\frac{\alpha}{2} - 1 \right) + \frac{-R^{-1} + (\alpha/a_0 + R^{-1})e^{-2\alpha R/a_0} \mp (\alpha/a_0)(1 + \alpha R/a_0)e^{-\alpha R/a_0}}{[(1/3)(\alpha R/a_0)^2 + \alpha R/a_0 + 1]e^{-\alpha R/a_0}} \right] + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} . \quad (49)$$

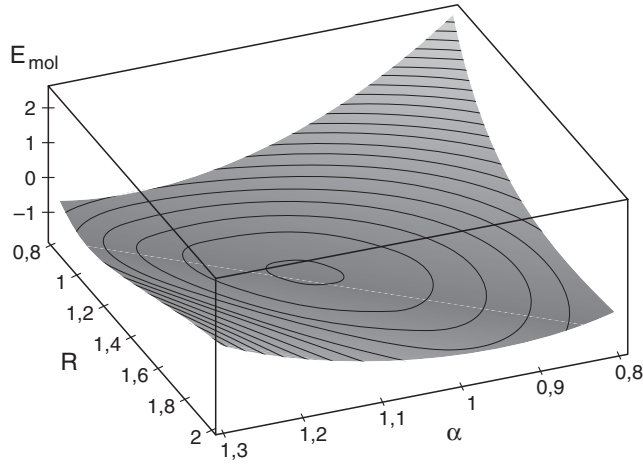


Fig. S.7. E_{mol} (49) as a function of α and R (in units of a_0) for the symmetric state

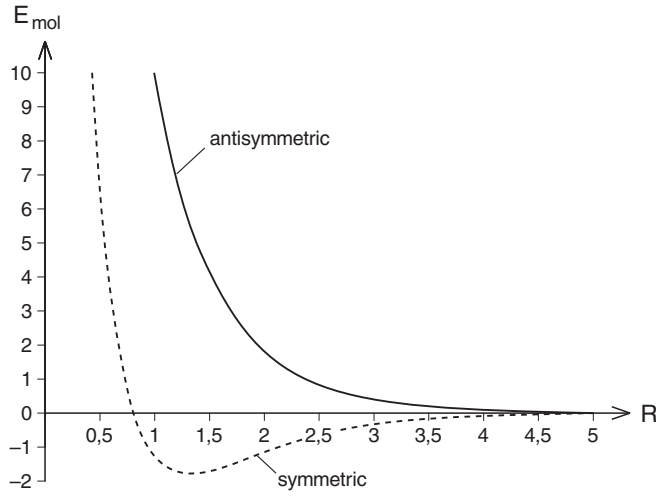


Fig. S.8. E_{mol} (49) for fixed $\alpha = 1$ as a function of R in units of a_0 for the symmetric and the antisymmetric states, resp.

The evaluation must now be carried out numerically, which can be easily done using a PC (cf. Figs. S.7–9).

f) Computation of the expectation values $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$.

In order to express x , y , z in prolate elliptical coordinate, we proceed as follows:

It follows from (18) that

$$\frac{R}{2}(\xi + \eta) = r_a, \quad \frac{R}{2}(\xi - \eta) = r_b \quad (50)$$

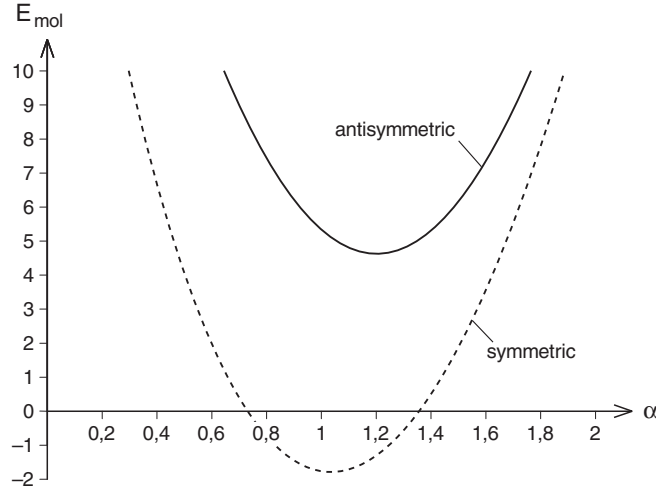


Fig. S.9. E_{mol} (49) for fixed $R = 1.36 a_0$ as a function of α for the symmetric and the antisymmetric states

and thus, using (17),

$$\frac{R^2}{4}(\xi \pm \eta)^2 = r^2 + \frac{1}{4}R^2 \mp rR \cos \theta. \quad (51)$$

From this, we find

$$\frac{R^2}{4}[(\xi + \eta)^2 + (\xi - \eta)^2] = 2r^2 + \frac{1}{2}R^2 \quad (52)$$

and

$$\frac{R^2}{4} \underbrace{[(\xi + \eta)^2 - (\xi - \eta)^2]}_{=4\xi\eta} = -2rR \cos \theta. \quad (53)$$

It follows from (53) that

$$-\frac{1}{2}R\xi\eta = r \cos \theta = z. \quad (54)$$

Due to (52), we have

$$\frac{R^2}{4}(\xi^2 + \eta^2 - 1) = r^2 = (x^2 + y^2 + z^2) \quad (55)$$

and, in addition, due to (54),

$$\frac{R^2}{4}(\xi^2 + \eta^2 - \xi^2\eta^2 - 1) = x^2 + y^2 \equiv r^2 \sin^2 \theta. \quad (56)$$

With $x = r \cos \theta \cos \phi$, $y = r \cos \theta \sin \phi$, it follows that

$$\frac{R}{2} (\xi^2 + \eta^2 - \xi^2 \eta^2 - 1)^{1/2} \cos \phi = x, \quad (57)$$

$$\frac{R}{2} \left(\underbrace{\xi^2 + \eta^2 - \xi^2 \eta^2 - 1}_{(\xi^2 - 1)(1 - \eta^2)} \right)^{1/2} \sin \phi = y. \quad (58)$$

We write

$$\langle \mathbf{x} \rangle = \int dV \mathbf{x} \psi^2. \quad (59)$$

Now, the wavefunction $\psi = N(\phi_a + \phi_b)$ as well as the expressions (54, 57, 58) for (x, y, z) and relation (25) for the volume element dV can be inserted into (59). Its evaluation is, as above, elementary and yields zero for all components. This can also be concluded directly from symmetry considerations, e. g. for $\langle x \rangle = \int dV x \psi^2$. Since $\psi(-x, y, z) = \psi(x, y, z)$, ψ^2 is also invariant with respect to $(x, y, z) \rightarrow (-x, y, z)$. On the other hand, the value of the integral must remain unchanged, from which it follows that $\langle x \rangle = -\langle x \rangle$ and thus $\langle x \rangle = 0$. The same reasoning also holds for $\langle \partial/\partial x \rangle$, $\langle \partial/\partial y \rangle$, and $\langle \partial/\partial z \rangle$, since e. g. in the transformation $(x, y, z) \rightarrow (-x, y, z)$, $\partial/\partial x \rightarrow -\partial/\partial x$ also holds.

In order to obtain a measure of the spatial extension of the wavefunction ψ , one must compute $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$. We illustrate this using as an example $\langle z^2 \rangle$, going immediately to prolate elliptical coordinates. With

$$\cosh X \equiv \frac{1}{2} (e^X + e^{-X}), \quad (60)$$

and inserting the expressions for z^2 , ψ , and dV , we obtain

$$\begin{aligned} \langle z^2 \rangle &= 2 \frac{\beta^3}{\pi} \left(\frac{R}{2} \right)^5 \int_0^{2\pi} d\phi \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi^2 - \eta^2) \xi^2 \eta^2 \\ &\quad \times [\cosh(\beta R \eta) \pm 1] \exp(-\beta R \xi). \end{aligned} \quad (61)$$

Due to (60), all the integrations can be carried out explicitly (first over ϕ , then over η , finally over ξ). With $\beta = \alpha/a_0$, the result is

$$\begin{aligned} \langle z^2 \rangle &= \left(\frac{a_0}{\alpha} \right)^2 \\ &\quad \left\{ \left[\frac{1}{30} \left(\frac{\alpha R}{a_0} \right)^4 + \frac{7}{30} \left(\frac{\alpha R}{a_0} \right)^3 + \frac{9}{10} \left(\frac{\alpha R}{a_0} \right)^2 + 2 \frac{\alpha R}{a_0} \right] \right. \\ &\quad \left. \times e^{-\alpha R/a_0} + \frac{1}{2} \frac{\alpha R}{a_0} + 2 \right\}. \end{aligned} \quad (62)$$

4.4 Conjecture:

$$\frac{\int \Psi^* H \Psi dV_1 \dots dV_n}{\int \Psi^* \Psi dV_1 \dots dV_n} \geq E_0. \quad (1)$$

Let E_0 be the smallest energy eigenvalue of the Schrödinger equation

$$H\Phi_0 = E_0\Phi_0 \quad (2)$$

and Φ_0 the corresponding eigenfunction, with Ψ the approximation for Φ_0 .

Since H is hermitian, the eigenfunctions Φ_j , $j = 0, 1, \dots$ can be chosen in such a way that they form a complete orthonormal basis, i. e.

$$\langle \Phi_i | \Phi_j \rangle = \delta_{ij}. \quad (3)$$

Every vector of the space of states can thus be expressed as a linear combination of the Φ_j :

$$\Psi = \sum_{j=0}^{\infty} a_j \Phi_j. \quad (4)$$

Inserting (4) into the left side of (1), we obtain using (3)

$$\sum_{j=0}^{\infty} a_j^2 E_j / \sum_{j=0}^{\infty} a_j^2 \quad (5)$$

and due to $E_j \geq E_0$

$$\sum_{j=0}^{\infty} a_j^2 E_j / \sum_{j=0}^{\infty} a_j^2 \geq E_0 \sum_{j=0}^{\infty} a_j^2 / \sum_{j=0}^{\infty} a_j^2 = E_0, \quad (6)$$

i. e. the inequality (1).

4.5 Let the Hamiltonian H of the Schrödinger equation

$$H\Psi = E\Psi \quad (1)$$

be given by

$$H = \sum_{i=1}^N H_i \quad (2)$$

with

$$H_i \phi_k^{(i)} = E_k^{(i)} \phi_k^{(i)} \quad (3)$$

and let

$$\left[H_i, \phi_k^{(j)} \right] = 0, \quad i \neq j. \quad (4)$$

We insert

$$\Psi_{k_1, k_2, \dots, k_N} = \prod_{j=1}^N \phi_{k_j}^{(j)}, \quad (5)$$

where k_1, \dots, k_N are a selection from the quantum numbers of (3), into (1) and obtain with (4)

$$\sum_{i=1}^N H_i \prod_{j=1}^N \phi_{k_j}^{(j)} = \sum_{i=1}^N \prod_{j=1}^{i-1} \phi_{k_j}^{(j)} \cdot \left(H_i \phi_{k_i}^{(i)} \right) \prod_{j=i+1}^N \phi_{k_j}^{(j)}, \quad (6)$$

which, due to (3), reduces to

$$\sum_{i=1}^N E_{k_i}^{(i)} \prod_{j=1}^N \phi_{k_j}^{(j)} = E \Psi \quad (7)$$

with

$$E = \sum_{i=1}^N E_{k_i}^{(i)}. \quad (8)$$

4.6 The functions

$$\Psi_1 = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \Psi_u \quad (1)$$

$$\Psi_2 = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \Psi_g \quad (2)$$

are given, where α and β are spin wavefunctions for spin \uparrow and spin \downarrow , resp. The arguments 1, 2 refer to particles 1, 2, and $\Psi_u(\Psi_g)$ is the even (odd) spatial wavefunction. We make use of the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (3)$$

where the connexion to the spin operator is given by:

$$\mathbf{S} = \frac{\hbar}{2} \boldsymbol{\sigma}. \quad (4)$$

For the components of the total spin, we find

$$S_i = S_{1i} + S_{2i}, \quad i = x, y, z, \quad (5)$$

where the indices 1, 2 refer to the two particles. Then

$$\begin{aligned} S^2 &= S_x^2 + S_y^2 + S_z^2 \\ &= S_1^2 + S_2^2 + 2S_{1z}S_{2z} + 2S_{1x}S_{2x} + 2S_{1y}S_{2y}. \end{aligned} \quad (6)$$

As usual, we define the ladder operators

$$S_{1\pm} = S_{1x} \pm iS_{1y}, \quad S_{2\pm} = S_{2x} \pm iS_{2y}, \quad (7)$$

whereby the following relations hold:

$$\begin{aligned} S_{1+}\alpha(1) &= 0, \quad S_{1+}\beta(1) = \hbar\alpha(1), \\ S_{1-}\alpha(1) &= \hbar\beta(1), \quad S_{1-}\beta(1) = 0, \end{aligned} \quad (8)$$

and correspondingly for $S_{2\pm}$. Then (6) can be cast in the form

$$S^2 = S_1^2 + S_2^2 + 2S_{1z}S_{2z} + S_{1+}S_{2-} + S_{1-}S_{2+}. \quad (9)$$

For the basis vectors

$$\alpha(1)\alpha(2), \quad \alpha(1)\beta(2), \quad \beta(1)\alpha(2), \quad \beta(1)\beta(2),$$

it follows using (8) and (3), i. e.

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1 \quad (10)$$

and owing to (4):

$$S^2\alpha(1)\alpha(2) = 2\hbar^2\alpha(1)\alpha(2) \quad (11)$$

$$S^2\alpha(1)\beta(2) = \hbar^2(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \quad (12)$$

$$S^2\beta(1)\alpha(2) = \hbar^2(\beta(1)\alpha(2) + \alpha(1)\beta(2)) \quad (13)$$

$$S^2\beta(1)\beta(2) = 2\hbar^2\beta(1)\beta(2). \quad (14)$$

From (11) and (12), $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$ are already eigenfunctions belonging to S^2 with the eigenvalue $2\hbar^2$. To determine the remaining eigenfunction, we add or subtract equations (12, 13) to or from one another, and obtain

$$S^2(\alpha(1)\beta(2) + \beta(1)\alpha(2)) = 2\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)], \quad (15)$$

i. e. the spin part of (1) is an eigenfunction of S^2 with the eigenvalue $2\hbar^2$. Correspondingly, we find

$$S^2(\alpha(1)\beta(2) - \beta(1)\alpha(2)) = 0, \quad (16)$$

i. e. the spin part of (2) is an eigenfunction of S^2 with the eigenvalue 0. Due to $S_z\alpha = \frac{\hbar}{2}\alpha$, $S_z\beta = -\frac{\hbar}{2}\beta$, we immediately obtain the result that $\alpha(1)\beta(2) \pm \alpha(2)\beta(1)$ are eigenfunction belonging to the z -component of the total spin, $S_z = S_{1z} + S_{2z}$, with the eigenvalue 0.

4.7 We make use of the atomic orbitals

$$\psi_{2s} = \frac{1}{\sqrt{4\pi}} R_{2,0}(r) = a^{-3/2} \frac{1}{\sqrt{2}} \left(1 - \frac{r}{2a}\right) e^{-r/(2a)} \frac{1}{\sqrt{4\pi}} \quad (1)$$

$$\psi_{2,1,1} = \sqrt{\frac{3}{8\pi}} R_{2,1}(r) \sin \theta e^{i\phi} \quad (2)$$

$$\psi_{2,1,0} = \sqrt{\frac{3}{4\pi}} R_{2,1}(r) \cos \theta \quad (3)$$

$$\psi_{2,1,-1} = \sqrt{\frac{3}{8\pi}} R_{2,1}(r) \sin \theta e^{-i\phi} \quad (4)$$

with

$$R_{2,1}(r) = a^{-3/2} \frac{1}{\sqrt{6}} \frac{r}{2a} e^{-r/(2a)}. \quad (5)$$

In order to identify them with wavefunctions of the p_x, p_y, p_z orbitals, we superpose the wavefunctions:

$$\psi_{2p_x} = \frac{1}{\sqrt{2}} (\psi_{2,1,1} + \psi_{2,1,-1}) = \sqrt{\frac{3}{4\pi}} \frac{x}{r} R_{2,1} \quad (6)$$

$$\psi_{2p_y} = \frac{1}{i} \frac{1}{\sqrt{2}} (\psi_{2,1,1} - \psi_{2,1,-1}) = \sqrt{\frac{3}{4\pi}} \frac{y}{r} R_{2,1}(r) \quad (7)$$

$$\psi_{2p_z} = \psi_{2,1,0} = \sqrt{\frac{3}{4\pi}} \frac{z}{r} R_{2,1}(r). \quad (8)$$

a) The points of maximum (charge) density

Both in the case of sp hybridisation and in the case of tetragonal sp^3 hybridisation (see part c of the problem), the wavefunctions can be written in the form

$$\psi = \left[\alpha(1 - \gamma r) + \gamma \sum_{i=1}^3 b_i x_i \right] e^{-\gamma r}, \quad (9)$$

where $x_1 = x, x_2 = y, x_3 = z$.

To find the maximum of $|\psi|^2$, we take:

$$\frac{\partial \psi_i}{\partial x_j} = \left\{ -\gamma \frac{x_j}{r} + \gamma b_j - \gamma \frac{x_j}{r} \left[\alpha(1 - \gamma r) + \gamma \sum_{i=1}^3 b_i x_i \right] \right\} e^{-\gamma r}. \quad (10)$$

From the requirement that $\partial |\psi|^2 / \partial x_j = 2\psi_i (\partial \psi_i / \partial x_j) = 0$, it follows that

$$\alpha(1 - \gamma r) + \gamma \sum_{i=1}^3 b_i x_i = 0 \quad (11)$$

or

$$x_j = 0 \quad (12)$$

or

$$x_j \left[1 + a(1 - \gamma r) + \gamma \sum_{i=1}^3 b_i x_i \right] = b_j r. \quad (13)$$

We specialise to the case of sp hybridisation, with

$$\psi_{\pm} = \psi_{2s} \pm \psi_{2p_x} \quad (14)$$

and thus in (9)

$$a = 1, \quad b_1 = \pm 1, \quad b_2 = b_3 = 0, \quad x_i = x, y, z. \quad (15)$$

We then find

$$x(2 - \gamma r \pm \gamma x) = \pm r \quad (16)$$

$$y(2 - \gamma r \pm \gamma x) = 0 \quad (17)$$

$$z(2 - \gamma r \pm \gamma x) = 0. \quad (18)$$

From this, it follows for the maxima of the charge density that

$$y = z = 0, \quad x = \mp \frac{3}{2\gamma}. \quad (19)$$

b) Centre of gravity of the charge distribution

Since in (9) ψ_{2s} and ψ_{2p_x} are normalised and orthogonal to one another, (9) is to be normalised by $1/\sqrt{2}$:

$$\bar{x}_{\pm} = \frac{1}{2} \langle \psi_{\pm} x \psi_{\pm} \rangle, \quad (20)$$

where $\langle \dots \rangle$ denotes the integration in spherical polar coordinates r, θ, ϕ , i. e.

$$\int_0^{\infty} r^2 dr \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi \psi_{\pm} x \psi_{\pm}. \quad (21)$$

The integrals can be evaluated in an elementary manner, and the result is

$$\bar{x}_+ = -\frac{27}{32}\pi a, \quad \bar{y}_+ = 0, \quad \bar{z}_+ = 0 \quad (22)$$

$$\bar{x}_- = \frac{27}{32}\pi a, \quad \bar{y}_- = 0, \quad \bar{z}_- = 0. \quad (23)$$

c) Maximum charge densities in the case of tetragonal hybridisation (sp^3). We make use of the result (13) from part (a) and obtain for

1) $a = 1, b_1 = b_2 = b_3 = 1$:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} [2 - \gamma r + \gamma(x + y + z)] = \begin{pmatrix} r \\ r \\ r \end{pmatrix}. \quad (24)$$

From this, it follows immediately that $x = y = z$ and then

$$x = -\frac{2 + \sqrt{3}}{(3 + \sqrt{3})\gamma}. \quad (25)$$

2) $a = 1, b_1 = 1, b_2 = b_3 = -1$: owing to (13), we have

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} [2 - \gamma r + \gamma(x - y - z)] = \begin{pmatrix} r \\ -r \\ -r \end{pmatrix}. \quad (26)$$

From this, it follows that $y = z = -x$ and

$$x = -\frac{2 + \sqrt{3}}{(3 + \sqrt{3})\gamma}. \quad (27)$$

3) $a = 1, b_1 = -1, b_2 = 1, b_3 = -1$: in analogy to 1) and 2), we obtain

$$x = \frac{2 + \sqrt{3}}{(3 + \sqrt{3})\gamma}, \quad x = z = -y. \quad (28)$$

4) $a = 1, b_1 = -1, b_2 = -1, b_3 = 1$:

$$x = \frac{2 + \sqrt{3}}{(3 + \sqrt{3})\gamma}, \quad x = y = -z. \quad (29)$$

Denoting x in (28) by x_0 , then the four coordinates of the maxima of the (charge) densities are given by:

$$x_0(-1, -1, -1); \quad x_0(-1, 1, 1); \quad x_0(1, -1, 1); \quad x_0(1, 1, -1), \quad (30)$$

which corresponds to the vertices of a tetrahedron with the edge length $x_0 2\sqrt{2}$.

d) With the wavefunctions (1–8), the superpositions corresponding to the hybridisation can be written immediately. In spherical polar coordinates, the integrals can be evaluated in elementary fashion, and they demonstrate the orthogonality of the wavefunctions.

Chapter 5

5.1 The electronic structure of polyenes (Fig. S.10)

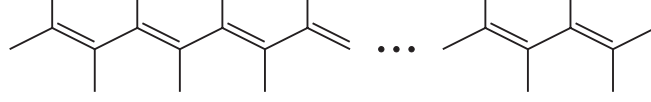


Fig. S.10. The π -electron system of the polyenes

Model for π -electrons: motion in a quantum wire. Equation of motion:

$$\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \phi(x) + (E - V_{ab}) \phi(x) = 0. \quad (1)$$

a) Boundary condition for simple connectivity (Fig. S.11, upper part):

$$\phi_{ba}(a) = \phi_{ab'}(a), \quad (2)$$

$$\phi'_{ba}(a) = \phi'_{ab'}(a). \quad (3)$$

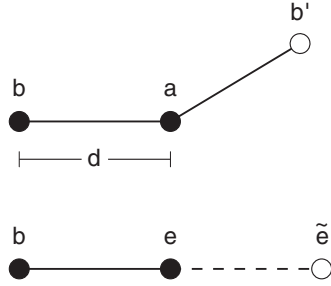


Fig. S.11.

b) Boundary condition at the end of the molecule (Fig. S.11, lower part): a π -electron can also be located with a certain probability outside the last atom e . (\tilde{e} is a fictitious atom or “empty cell” at which ϕ can decay to zero).

$$\phi_{be}(e) = \phi_{e\tilde{e}}(e), \quad (4)$$

$$\phi_{e\tilde{e}}(\tilde{e}) = 0, \quad (5)$$

$$\phi'_{be}(e) = \phi'_{e\tilde{e}}(e). \quad (6)$$

c) The butadiene molecule:

$$H_{\text{eff}} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

$$\text{with } V(x) = \begin{cases} 0 & \text{for } 0 \leq x \leq 5d \\ \infty & \text{otherwise} \end{cases}. \quad (7)$$

$$H_{\text{eff}}\phi(x) = E \quad (8)$$

$$\text{with } E = \frac{\hbar^2 k^2}{2m}, \quad (9)$$

$$k = n \frac{\pi}{5d}. \quad (10)$$

$$\phi(x) = \sqrt{\frac{2}{5d}} \sin kx \quad \text{with } 0 \leq x \leq 5d. \quad (11)$$

5.2 The complete solution can be found in 6.

Chapter 6

6.1 a) Symmetry operations:

1. Triangle

Rotation around the centroid by 120° , 240° ($\hat{=} -120^\circ$).

Reflection on each of the lines passing through the centroid and a vertex.

2. Square

Rotation around the centre point by 90° , 180° , 270° or in the reverse direction.

Reflection through a diagonal (2)

Reflection on each line passing through the centre point and the middle of each side (2).

3. Three collinear and equidistant points.

Reflection through the midpoint.

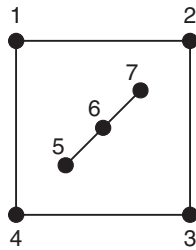
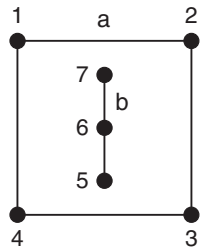


Fig. S.12. A straight line in a square. Case 1

Fig. S.13. Line in a square. Case 2

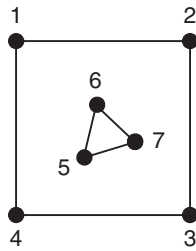
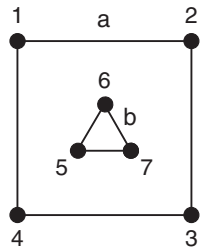


Fig. S.14. Triangle in a square. Case 3

Fig. S.15. Triangle in a square. Case 4

The orientations in which the number of symmetry operations is maximal: square and straight line; (Fig. S.12) (Fig. S.13)

Square and triangle: (Fig. S.14) (Fig. S.15)

b) When two symmetry operations are carried out in succession, the result again corresponds to a symmetry operation, as one can show by examining all the possible combinations. The inverse of a symmetry operation is clearly itself a symmetry operation. One can directly demonstrate the validity of the associative law by first taking $A \cdot B$ and then $(A \cdot B) \cdot C$, or first $B \cdot C$ and then $A \cdot (B \cdot C)$, noting that $(A \cdot B) \cdot C = A(B \cdot C)$, where A, B, C are symmetry operations. It is sufficient to examine a few examples.

The identification as a group can be carried out systematically, simply and in an elegant manner by considering that each symmetry operation can be represented by a permutation of the vertices and that the permutations form a group.

c) Interaction potentials

In Fig. S.12: the spacings are:

$$\begin{aligned} d_1^{(1)} &\equiv r_{12} = a, & d_2^{(1)} &\equiv r_{24} = \sqrt{2}a, & d_3^{(1)} &\equiv r_{56} = b, \\ d_4^{(1)} &\equiv r_{57} = 2b, & d_5^{(1)} &\equiv r_{16} = \frac{a}{\sqrt{2}}, \\ d_6^{(1)} &\equiv r_{45} = \sqrt{a^2 - 2ab + 2b^2}, \\ d_7^{(1)} &\equiv r_{15} = \sqrt{a^2 + 2ab + 2b^2}. \end{aligned}$$

If we write $V(d_k) = V(k)$, $k = 1, 2, \dots, 7$, then, taking the symmetries into account, we obtain

$$\begin{aligned} V^{(1)} &= 4V(1) + 2V(2) + 2V(3) + V(4) + 4V(5) \\ &\quad + 4V(6) + 4V(7). \end{aligned}$$

In the case that $V = r^2$, this reduces to

$$V^{(1)} = 14(a^2 + b^2).$$

In Fig. S.13:

$$\begin{aligned} d_1^{(2)} &\equiv r_{12} = a, & d_2^{(2)} &\equiv r_{24} = \sqrt{2}a, & d_3^{(2)} &\equiv r_{56} = b, \\ d_4^{(2)} &\equiv r_{57} = 2b, & d_5^{(2)} &\equiv r_{16} = \frac{a}{\sqrt{2}}, & d_6^{(2)} &\equiv r_{45} = \left| b - \frac{a}{\sqrt{2}} \right|, \\ d_7^{(2)} &\equiv r_{25} = b + \frac{a}{\sqrt{2}}, & d_8^{(2)} &\equiv r_{17} = \sqrt{\frac{a^2 + 2b^2}{2}}. \end{aligned}$$

$$\begin{aligned} V^{(2)} &= 4V(1) + 2V(2) + 2V(3) + V(4) + 4V(5) \\ &\quad + 2V(6) + 2V(7) + 4V(8). \end{aligned}$$

For the case $V = r^2$, this reduces to

$$V^{(2)} = 14(a^2 + b^2) .$$

In Fig. S.14:

$$d_1^{(3)} \equiv r_{12} = a, d_2^{(3)} \equiv r_{24} = \sqrt{2}a, d_3^{(3)} \equiv r_{56} = b ,$$

$$d_4^{(3)} \equiv r_{45} = \frac{1}{\sqrt{6}}\sqrt{3a^2 - (3 + \sqrt{3})ab + 2b^2} ,$$

$$d_5^{(3)} \equiv r_{46} = \frac{1}{\sqrt{6}}\sqrt{3a^2 + 2\sqrt{3}ab + 2b^2} ,$$

$$d_6^{(3)} \equiv r_{47} = \frac{1}{\sqrt{6}}\sqrt{3a^2 + (3 - \sqrt{3})ab + 2b^2} ,$$

$$d_7^{(3)} \equiv r_{16} = \frac{1}{\sqrt{6}}\sqrt{3a^2 - 2\sqrt{3}ab + 2b^2} ,$$

$$d_8^{(3)} \equiv r_{15} = \frac{1}{\sqrt{6}}\sqrt{3a^2 - (3 - \sqrt{3})ab + 2b^2} ,$$

$$d_9^{(3)} \equiv r_{17} = \frac{1}{\sqrt{6}}\sqrt{3a^2 + (3 + \sqrt{3})ab + 2b^2} .$$

$$V^{(3)} = 4V(1) + 2V(2) + 3V(3) + 2V(4) + 2V(5) \\ + 2V(6) + 2V(7) + 2V(8) + 2V(9) .$$

In the case $V = r^2$, this reduces to

$$V^{(3)} = 14\left(a^2 + \frac{b^2}{2}\right) .$$

In fig. S.15:

$$d_1^{(4)} \equiv r_{12} = a, d_2^{(4)} \equiv r_{24} = \sqrt{2}a, d_3^{(4)} \equiv r_{56} = b, d_4^{(4)}$$

$$\equiv r_{45} = \left| \frac{b}{\sqrt{3}} - \frac{a}{\sqrt{2}} \right| ,$$

$$d_5^{(4)} \equiv r_{46} = \sqrt{\frac{a^2}{2} + \frac{ab}{\sqrt{12}} \left(\sqrt{2 + \sqrt{3}} - \sqrt{2 - \sqrt{3}} \right) - \frac{b^2}{3}} ,$$

$$d_6^{(4)} \equiv r_{25} = \frac{b}{\sqrt{3}} + \frac{a}{\sqrt{2}} ,$$

$$d_7^{(4)} \equiv r_{26} = \sqrt{\frac{a^2}{2} + \frac{ab}{\sqrt{12}} \left(\sqrt{2 - \sqrt{3}} - \sqrt{2 + \sqrt{3}} \right) - \frac{b^2}{3}} ,$$

$$d_8^{(4)} \equiv r_{15} = \sqrt{\frac{a^2}{2} - \frac{b^2}{3}} ,$$

$$d_9^{(4)} \equiv r_{16} = \sqrt{\frac{a^2}{2} - \frac{ab}{\sqrt{12}} \left(\sqrt{2 - \sqrt{3}} + \sqrt{2 + \sqrt{3}} \right) - \frac{b^2}{3}},$$

$$d_{10}^{(4)} \equiv r_{17} = \sqrt{\frac{a^2}{2} + \frac{ab}{\sqrt{12}} \left(\sqrt{2 - \sqrt{3}} + \sqrt{2 + \sqrt{3}} \right) - \frac{b^2}{3}}.$$

$$V^{(4)} = 4V(1) + 2V(2) + 3V(3) + V(4) + 2V(5) \\ + V(6) + 2V(7) + 2V(8) + 2V(9) + 2V(10).$$

In the case that $V = r^2$, this reduces to

$$V^{(4)} = 14 \left(a^2 + \frac{b^2}{2} \right).$$

d) The numerical results can be found in Figs. S.16–S.19. From them, for example, it can be read out whether in the “square environment” the triangle can be stretched into a straight line.

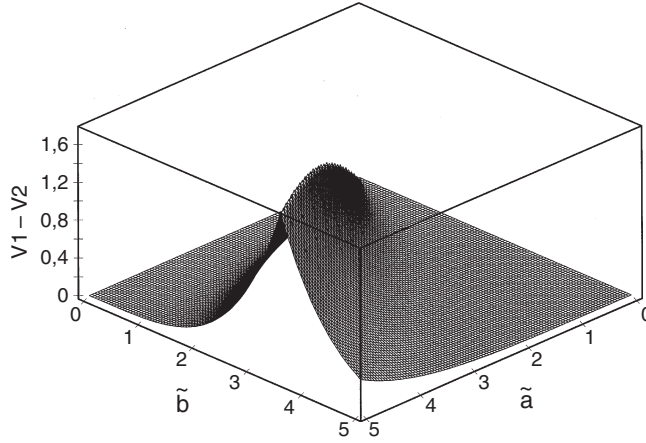


Fig. S.16. The potential difference $V1 - V2$, where $V1 = V^{(1)}$ with $V(r) = 1 - e^{(-r)}$

6.2 The orthogonality properties of group characters

If the group g is finite, then every representation $R \rightarrow U(R)$ is equivalent to a unitary representation, where $U(R)$ is thus a unitary matrix.

Proof: Take any positive definite Hermitian form, e. g. the unit form, apply all the transformations $U(R)$ to it and sum over R . In this manner, we obtain a positive definite Hermitian form H , which is invariant under every such transformation $U(R)$. Now choose the coordinate system in such a way that H assumes the unit form. Then $U(R)$, expressed in these coordinates, is unitary.

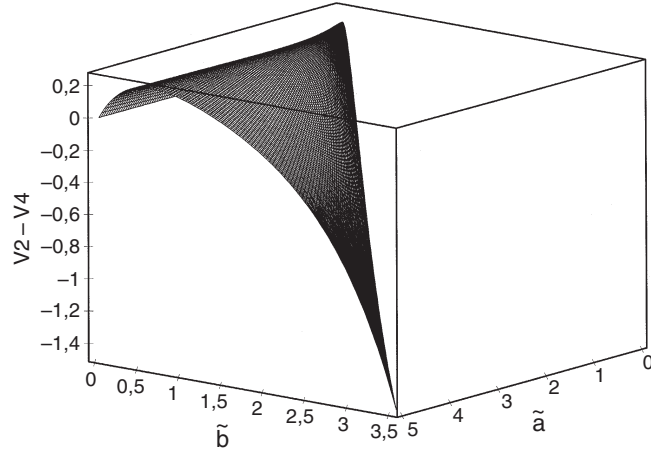


Fig. S.17. The potential difference $V2 - V4$

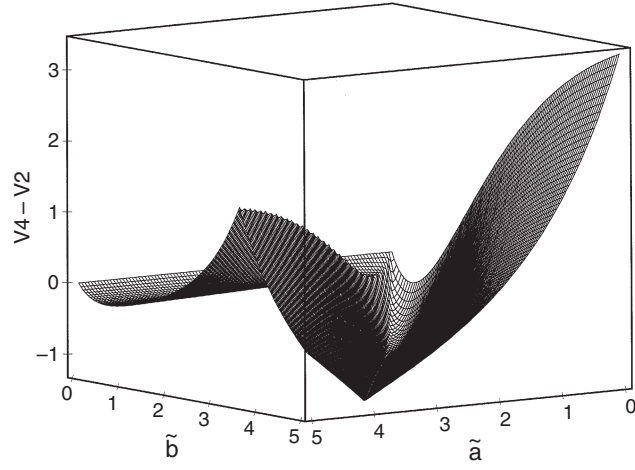


Fig. S.18. The potential difference $V4 - V2$

The same method of summation over the elements of the group is the basis of the orthogonality relations which we now discuss.

Let

$$R \rightarrow U(R) \quad g \text{ dimensional}, \quad (1)$$

$$R \rightarrow V(R) \quad g' \text{ dimensional} \quad (2)$$

be two inequivalent, irreducible representations of the finite group G . We express the matrices U, V in terms of their elements:

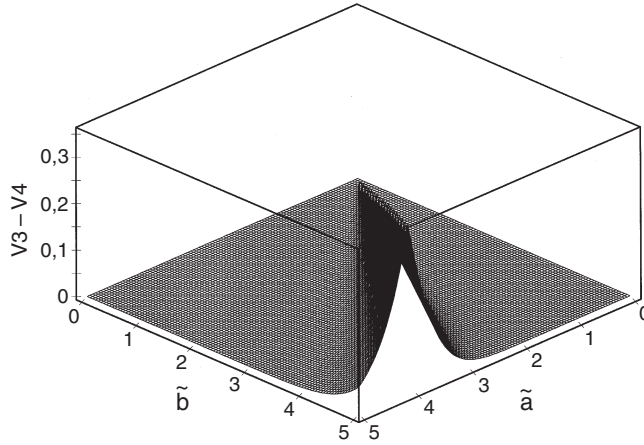


Fig. S.19. The potential difference $V3 - V4$

$$U(R) = (u_{ik}(R)), \quad (3)$$

$$V(R) = (v_{lm}(R)) \quad (4)$$

and write

$$V^{-1}(R) = (\hat{v}_{lm}(R)). \quad (5)$$

Let A be an arbitrary matrix with g rows and g' columns. We take

$$\sum_R U(R) A V^{-1}(R) = B, \quad (6)$$

where the sum runs over all the elements R of the group. Then B remains unchanged under the following transformation:

$$U(R_0) B V^{-1}(R_0) = B, \quad (7)$$

where R_0 is an arbitrary element of the group. For a unitary representation, the following relation naturally holds:

$$\hat{v}_{lm} = v_{ml}^*. \quad (8)$$

Proof:

$$U(R_0) U(R) = U(RR_0), \quad (9)$$

$$V^{-1}(R) V^{-1}(R_0) = V^{-1}(RR_0) \quad (10)$$

due to the properties of the representations. If the sum in (6) runs over all the elements R , so then so does $R' = RR_0$, with R_0 fixed. From I of the general theorem, it follows that the matrix $B = 0$, i. e.

$$\sum_R \sum_{kl} u_{ik}(R) a_{kl} \hat{v}_{lm}(R) = 0. \quad (11)$$

Since the a_{kl} are arbitrary, the following $g^2 \cdot g'^2$ equations result:

$$\sum_R u_{ik}(R) \hat{v}_{lm}(R) = 0 \quad (12)$$

or, for unitary transformations,

$$\sum_R u_{ik}(R) v_{ml}^*(R) = 0. \quad (13)$$

Using only one irreducible representation $R \rightarrow U(R)$, we find in a similar manner

$$U(R) A U^{-1}(R) = B, \quad (14)$$

i. e.

$$U(R) B = B U(R). \quad (15)$$

According to the theorem, B must be a multiple of the unit matrix, i. e.

$$\sum_R \sum_{kl} u_{ik}(R) a_{kl} \hat{u}_{lm}(R) = \alpha \delta_{im}, \quad (16)$$

where the constant α still depends on the matrix A . We set all the elements in the matrix A equal to zero except for one, $a_{kl} = 1$ for a *particular* pair of values k, l . It then follows that

$$\sum_R u_{ik}(R) \hat{u}_{lm}(R) = \alpha_{kl} \delta_{im}. \quad (17)$$

Since $(\hat{u}_{lm}(R))$ is the inverse matrix of $(u_{lm}(R))$, it holds that

$$\sum_{R,m} \hat{u}_{lm}(R) u_{mk}(R) = \delta_{lk}. \quad (18)$$

In (17), we set $m = i$ and sum over $m = 1, 2, \dots, g$, obtaining then for the left side of (17)

$$\sum_R \sum_m u_{mk}(R) \hat{u}_{lm}(R) \quad (19)$$

which, owing to (18), is

$$\sum_R \delta_{lk} \quad (20)$$

and, since the group has h elements, finally

$$h\delta_{lk} . \quad (21)$$

Setting $i = m$ in (17) and summing over the right-hand side with $m = 1, 2, \dots, g$, we obtain

$$g\alpha_{kl} . \quad (22)$$

Comparing the final results for both sides, we thus find

$$h\delta_{lj} = g\alpha_{kl} , \quad (23)$$

where then α_{kl} is determined by the order h of the group and the dimension g of the matrix representation. We thus obtain the first main result:

$$\frac{1}{h} \sum_R u_{ik}(R) \hat{u}_{lm}(R) = \begin{cases} \frac{1}{g} & \text{for } i = m, k = l \\ 0 & \text{otherwise} \end{cases} \quad (24)$$

for every irreducible representation $R \rightarrow U(R)$ and

$$\frac{1}{h} \sum_R u_{ik}(R) \hat{v}_{lm}(R) = 0 \quad (25)$$

for two arbitrary irreducible representations $R \rightarrow U(R)$ and $R \rightarrow V(R)$. In order to obtain the fundamental *orthogonality relations* of group characters, we set $i = k$ and $l = m$ and sum over i or l . We set

$$\sum_i u_{ii}(R) = \chi(R) \quad (26)$$

and

$$\sum_l \hat{u}_{ll}(R) = \hat{\chi}(R) \quad (27)$$

or

$$\sum_l \hat{v}_{ll}(R) = \hat{\chi}'(R) \quad (28)$$

and obtain

$$\frac{1}{h} \sum_R \chi(R) \hat{\chi}(R) = 1 . \quad (29)$$

For any two inequivalent irreducible representations, it holds correspondingly that

$$\frac{1}{h} \sum_R \chi(R) \hat{\chi}'(R) = 0 . \quad (30)$$

The expressions $\hat{\chi}(R)$ or $\hat{\chi}'(R)$ can be cast in a different form. If the representation matrices are unitary, it holds that $\hat{u}_{lm} = v_{ml}^*$ and $\hat{\chi} = \chi^*$ follows, where the asterisk denotes complex conjugate quantities. Furthermore, $U^{-1}(R) = U(R^{-1})$ and therefore

$$\hat{u}_{lm}(R) = u_{lm}(R^{-1}) . \quad (31)$$

It then also follows that

$$\hat{\chi}(R) = \chi(R^{-1}) . \quad (32)$$

If we distinguish the irreducible representations by indices i, j , then we can combine the Eqns. (29) and (30) into a single orthogonality relation, wherein we can write either

$$\frac{1}{h} \sum_R \chi_j(R^{-1}) \chi_i(R) = \delta_{ij} \quad (33)$$

due to (32), or, in the case of unitary representations,

$$\frac{1}{h} \sum_R \chi_j^*(R) \chi_i(R) = \delta_{ij} . \quad (34)$$

6.3 We apply $P_k = \sum_m |km\rangle \langle km|$ to $|v\rangle = \sum_l c_l |ln\rangle$. Due to the orthogonality relation (37) from problem 6.4, we find immediately

$$P_k |v\rangle = \sum_n c_{kn} |kn\rangle .$$

6.4 We show that

$$P_j = \frac{1}{h} \sum_R \hat{\chi}_j(R) R \quad (35)$$

is a projection operator, which projects the space of the basis vectors of the representation onto the subspace of the irreducible representation j with the character χ_j . Making use of Dirac's bra and ket notation, we denote the basis vectors by

$$|k, m\rangle , \quad (36)$$

where k refers to the subspace of the irreducible representation k , and m to the vector considered within this space. k thus distinguishes the blocks in Fig. 6.14. We first treat the case that all the blocks belong to different irreducible representations. We consider unitary representations and therefore can assume the orthonormalisation

$$\langle k, m | l, n \rangle = \delta_{kl} \delta_{mn} \quad (37)$$

and the representation of the identity I in the form

$$I = \sum_{k,m} |k, m\rangle \langle k, m| . \quad (38)$$

We now insert I (38) into (35) before and after R and obtain

$$\frac{1}{k} \sum_R \hat{\chi}_j(R) \sum_{k,m} |k, m\rangle \langle k, m| R \sum_{l,n} |l, n\rangle \langle l, n| . \quad (39)$$

Keeping the bra and ket notation in mind, we obtain in (39) the matrix element

$$\langle k, m| R |l, n\rangle = \delta_{kl} u_{m,n}^k(R) , \quad (40)$$

where the Kronecker delta δ_{kl} results from the zeroes outside the blocks in Fig. 6.14. Making use of the definition of the group character, $\hat{\chi}_j(R)$, we write

$$\hat{\chi}_j(R) = \sum_{\mu\nu} \delta_{\mu\nu} \hat{u}_{\mu\nu}^j(R) . \quad (41)$$

Employing (40) and (41), (39) can be brought into the form:

$$\sum_{\mu\nu} \sum_{k,m,n} \delta_{\mu\nu} \left\{ \frac{1}{h} \sum_R \hat{u}_{\mu\nu}^j(R) u_{m,n}^k \right\} |k, m\rangle \langle k, n| . \quad (42)$$

According to (24) and (25) (with $u \rightarrow u^j$, $v \rightarrow u^k$), the expression in brackets in (42) reduces to

$$\frac{1}{g} \delta_{\mu n} \delta_{\nu m} \delta_{jk} . \quad (43)$$

Using the Kronecker δ notation, we obtain successively

$$\sum_{\mu\nu} \delta_{\mu\nu} \sum_{m,n} \frac{1}{g} \delta_{\mu n} \delta_{\nu m} |j, m\rangle \langle j, n| , \quad (44)$$

$$\sum_{\mu} \sum_{m,n} \frac{1}{g} \delta_{\mu n} \delta_{\mu m} |j, m\rangle \langle j, n| , \quad (45)$$

$$\sum_{\mu} \sum_n \frac{1}{g} \delta_{\mu n} |j, \mu\rangle \langle j, n| \quad (46)$$

and thereby finally for (35)

$$P_j = \frac{1}{g} \sum_n |j, n\rangle \langle j, n| = \frac{1}{g} I_j . \quad (47)$$

Due to (37), P_j is clearly a projection operator onto the subspace j . Here, we use $\hat{\chi}_j(R)$, which is the same for equivalent representations. If several such representations occur in the representation of a group, then P_j projects onto the *sum* of the corresponding subspaces, i. e. the definition (35) now leads to

$$P_j = \frac{1}{g} \sum_{j,n} |j, n\rangle \langle n, j|, \quad (48)$$

where the sum j extends only over the representations which are equivalent to each other. The most important aspect of (48) is that subspaces with a particular, identical symmetry behaviour are sorted out.

The above proof is also interesting in the sense that we do not at all need to know the explicit form of $|j, n\rangle$, $|k, m\rangle$ or to determine it; only general properties enter the proof.

6.5 The result can be found in the text of 6.

Chapter 7

7.1 a) Let the solutions of the single-particle Schrödinger equation be known:

$$H(j)\chi_k(j) = E_k\chi_k(j), \quad (1)$$

where we can without loss of generality enumerate the quantum numbers by $k = 1, 2, \dots$. Since only N particles are present, it suffices to let k run up to N . The determinant $\det(\chi)$ is defined by

$$\det(\chi) = \sum_{P(k)} (-1)^P \chi_{k_1}(1) \chi_{k_2}(2) \dots \chi_{k_N}(N), \quad (2)$$

where the sum runs over all permutations k_1, k_2, \dots, k_N of $1, 2, \dots, N$. For an even permutation, $(-1)^P = 1$; otherwise $= -1$. Exchange of two indices (quantum numbers or particle index) reverses the sign of (2), so that the Pauli principle is fulfilled. Every term in the sum

$$\psi_k = \prod_{l=1}^N \chi_{k_l}(l) \quad (3)$$

in (2) obeys

$$\sum_{j=1}^N H(j)\psi_k = E\psi_k \quad \text{with} \quad E = \sum_{k=1}^N E_k, \quad (4)$$

since

$$\sum_{j=1}^N H(j) \prod_{l=1}^N \chi_{k_l}(l) = \sum_{j=1}^N \prod_{\substack{l=1 \\ l \neq j}}^N \chi_{k_l}(l) H(j) \chi_{k_j}(j) \quad (5)$$

and due to (1),

$$\sum_{j=1}^N \prod_{l=1}^N \chi_{kl}(l) E_{kj} = E \Psi_k. (6)$$

b) Inserting (2) and $\Omega = V(l, m)$ into

$$\overline{\Omega} = \frac{1}{N!} \left\langle \int \det(\chi^*) V(l, m) \det(\chi) dV_1 \dots dV_N \right\rangle \quad (7)$$

yields

$$\begin{aligned} \overline{\Omega} &= \frac{1}{N!} \\ &\times \left\langle \int \sum_{P(k)} \sum_{P'(k')} (-1)^{P+P'} \prod_{j,j'} \chi_{kj}^*(j) V(l, m) \chi_{k'j'}(j') dV_1 \dots dV_N \right\rangle. \end{aligned} \quad (8)$$

Due to

$$\left\langle \int \chi_j^* \chi_k dV \right\rangle = \delta_{jk} \quad (9)$$

the permutations $P(k)$, $P'(k')$ in (8) must be identical up to the factors in which j, j' are the same as l, m , i. e. where

$$k'_l = k_l \quad \text{and} \quad k'_m = k_m \quad (10)$$

or

$$k'_l = k_m \quad \text{and} \quad k'_m = k_l. \quad (11)$$

For (10), the permutations $P(k)$, $P'(k')$ are the same and $(-1)^{P+P'} = 1$, for (11) they differ by an odd permutation and $(-1)^{P+P'} = -1$. We thus find

$$\overline{V(l, m)} = \frac{1}{N!} (N-2)! \left[\sum_{k,k'} (V_{kk',kk'} - V_{kk',k'k}) \right] \quad (12)$$

with

$$V_{ij,kl} = \left\langle \iint \chi_i^*(1) \chi_j^*(2) V(1, 2) \chi_k(1) \chi_l(2) dV_1 dV_2 \right\rangle. \quad (13)$$

The factor $(N-2)!$ comes from the number of possible permutations in (8). Note that the indices on the variable within the integral play no role. For this reason, to obtain

$$\Omega = \frac{1}{2} \sum_{\substack{l,m \\ l \neq m}} V(l, m) \quad (14)$$

it is necessary only to count

$$\overline{\Omega} = \frac{1}{2} N(N-1) \overline{V(l, m)} = \frac{1}{2} \sum_{\substack{k \neq k' \\ k, k'}} (V_{kk', kk'} - V_{kk', k'k}) . \quad (15)$$

In an analogous but still more simple manner, the expectation value of $\Omega = \sum_j W(j)$ is found, where $W(j)$ is a single-particle operator, to be given by

$$\overline{\Omega} = \sum_k W_{kk} , \quad (16)$$

with

$$W_{kk} = \left\langle \int \chi_k^*(1) W(1) \chi_k(1) dV_1 \right\rangle . \quad (17)$$

7.2 We have

$$\overline{E} = \left\langle \int \Psi^* H \Psi dV_1 \dots dV_N \right\rangle \quad (18)$$

with

$$H = \sum_j H(j) + \frac{1}{2} \sum_{\substack{l,m \\ l \neq m}} V(l, m) . \quad (19)$$

From problem 7.1, we have

$$\overline{E} = \sum_k H_{kk} + \frac{1}{2} \sum_{\substack{k, k' \\ k \neq k'}} (V_{kk', kk'} - V_{kk', k'k}) \quad (20)$$

with

$$H_{kk} = \left\langle \int \chi_k^* H \chi_k dV \right\rangle , \quad (21)$$

and the definition (13). We separate the wavefunction χ_k into its spatial part ψ_q and its spin part s_m

$$\chi_k = \psi_q \cdot s_m \quad (22)$$

with

$$\langle s_m s_{m'} \rangle = \delta_{mm'} . \quad (23)$$

Since the electronic shell is closed, there are just as many spin- \uparrow as spin- \downarrow electrons, so that $\sum_k \rightarrow 2 \sum_q$, but in the case of $V_{kk'}, k'$, the spins of k and k' are the same:

$$\bar{E} = 2 \sum_q H_{q,q} + \sum_{\substack{qq' \\ q \neq q'}} (2V_{qq',qq'} - V_{qq',q'q}) , \quad (24)$$

where

$$V_{q_1 q_2, q_3 q_4} = \int \psi_{q_1}^*(1) \psi_{q_2}^*(2) V(1, 2) \psi_{q_3}(1) \psi_{q_4}(2) dV_1 dV_2 . \quad (25)$$

We vary \bar{E} (18) with the condition

$$\int |\psi_q|^2 dV = 1 \quad (26)$$

using the Lagrange parameter $2\varepsilon_q$, with respect to ψ_q^* :

$$\delta_{\psi_q^*} \left(\bar{E} - \sum_q 2\varepsilon_q \int |\psi_q|^2 dV \right) \stackrel{!}{=} 0 . \quad (27)$$

For the individual terms in (27) with (24), we obtain:

$$\text{A) } \delta_{\psi_q^*(1)} \left[2 \sum_{q'} \int \psi_{q'}^*(1) H(1) \psi_{q'}(1) dV_1 \right] = 2H(1) \psi_q(1) , \quad (28)$$

$$\begin{aligned} \text{B) } \delta_{\psi_q^*(1)} & \left[2 \sum_{\substack{q'q'' \\ q' \neq q''}} \iint \psi_{q'}^*(1) \psi_{q''}^*(2) V(1, 2) \psi_{q'}(1) \psi_{q''}(2) dV_1 dV_2 \right] \\ & = 4 \sum_{\substack{q' \\ q' \neq q}} \int dV_2 |\psi_{q'}(2)|^2 V(1, 2) \psi_q(1) \end{aligned} \quad (29)$$

$$\begin{aligned} \text{C) } \delta_{\psi_q^*(1)} & \left[- \sum_{\substack{q'q'' \\ q' \neq q''}} \iint \psi_{q'}^*(1) \psi_{q''}^*(2) V(1, 2) \psi_{q''}(1) \psi_{q'}(2) dV_1 dV_2 \right] \\ & = -2 \sum_{\substack{q' \\ q' \neq q}} \left[\int dV_2 \psi_{q'}^*(2) \psi_q(2) V(1, 2) \right] \psi_{q'}(1) \end{aligned} \quad (30)$$

$$D) \quad \delta\psi_q^*(1) \left(-2 \sum_{q'} \varepsilon_{q'} \int |\psi_{q'}|^2 dV \right) = -2\varepsilon_q \psi_q(1). \quad (31)$$

The Hartree-Fock equations are found from

$$\frac{1}{2}(A + B + C + D) = 0. \quad (32)$$

An iterative solution with a step denoted by i means that we can write (32) in the form

$$\begin{aligned} (H - \varepsilon_q) \psi_q^{i+1}(1) + 2 \left[\sum_{q' \neq q} \int |\psi_{q'}^i(2)|^2 V(1, 2) dV_2 \right] \psi_q^{i+1}(1) \\ - \sum_{q' \neq q} \left[\int \psi_{q'}^{i*}(2) \psi_q^i(2) V(1, 2) dV_2 \right] \psi_{q'}^{i+1}(1) = 0. \end{aligned} \quad (33)$$

If the $(i+1)$ -th step again leads to ψ_q^i , then clearly (33) is fulfilled for $\psi_q^{i+1} = \psi_q^i = \psi$.

7.3 We obtain ${}_{-1}^3\Psi_m^n$ with the aid of

$$a_{n\downarrow}^+ a_{m\uparrow} \Psi, \quad n \neq m, k. \quad (1)$$

With this, we find

$${}_{-1}^3\Psi_m^n = \prod_{k=1}^g a_{k\uparrow}^+ a_{k\downarrow}^+ \cdot a_{n\downarrow}^+ a_{m\downarrow}^+ \Phi_0. \quad (2)$$

To apply the spin raising operator

$$S_+ = \sum_j a_{j\uparrow}^+ a_{j\downarrow}, \quad (3)$$

we note that

$$a_{j\uparrow}^+ a_{j\downarrow} a_{k\uparrow}^+ a_{k\downarrow}^+ = a_{k\uparrow}^+ a_{k\downarrow}^+ a_{j\uparrow}^+ a_{j\downarrow} \quad \text{for } k \neq j \quad (4)$$

and

$$a_{k\uparrow}^+ a_{k\downarrow} a_{k\uparrow}^+ a_{k\downarrow}^+ = -a_{k\uparrow}^+ a_{k\uparrow}^+ a_{k\downarrow} a_{k\downarrow}^+ = 0, \quad (5)$$

as well as

$$\begin{aligned} a_{j\uparrow}^+ a_{j\downarrow} a_{n\downarrow}^+ a_{m\downarrow}^+ &= a_{j\uparrow}^+ \left(\delta_{jn} - a_{n\downarrow}^+ a_{j\downarrow} \right) a_{m\downarrow}^+ \\ &= a_{j\uparrow}^+ a_{m\downarrow}^+ \delta_{jn} - a_{j\uparrow}^+ a_{n\downarrow}^+ \left(\delta_{mj} - a_{m\downarrow}^+ a_{j\downarrow} \right). \end{aligned} \quad (6)$$

From (4–6) and $a\Phi_0 = 0$ (a is some annihilation operator), it follows almost immediately that

$$\begin{aligned} {}^3_0\Psi_m^n &= S_{+-} {}^3\Psi_m^n = \prod_{k=1}^g a_{k\uparrow}^+ a_{k\downarrow}^+ \cdot a_{n\uparrow}^+ a_{m\downarrow}^+ \Phi_0 \\ &\quad - \prod_{k=1}^g a_{k\uparrow}^+ a_{k\downarrow}^+ a_{m\uparrow}^+ a_{n\downarrow}^+ \Phi_0, \end{aligned} \quad (7)$$

i.e. up to an (unimportant) common sign, we obtain (7.35). In a corresponding manner, it follows that

$${}^3_1\Psi_m^n = S_{+0} {}^3\Psi_m^n = - \prod_{k=1}^g a_{k\uparrow}^+ a_{k\downarrow}^+ a_{m\uparrow}^+ \cdot a_{n\uparrow}^+ \Phi_0, \quad (8)$$

i.e. up to an unimportant sign, we obtain (7.36).

7.4 We choose from $k = 1, 2, \dots, \infty$ a selection of quantum numbers $k_1 < k_2 < \dots < k_N$. The possible wavefunctions are

$$\Psi_{k_1 k_2 \dots k_N} = a_{k_1}^+ a_{k_2}^+ \dots a_{k_N}^+ \Phi_0, \quad (1)$$

where for the vacuum state Φ_0 , we have

$$a_k \Phi_0 = 0 \quad (2)$$

for all $k = 1, 2, \dots, \infty$. The energies belonging to (1) are:

$$E = E_{k_1} + E_{k_2} + \dots + E_{k_N}. \quad (3)$$

7.5 To calculate

$$\langle \Psi_{k'_1} | \Omega | \Psi_{k_1} \rangle \quad (1)$$

with

$$\Psi_{k_j} = a_{k_j}^+ \Phi_0, \quad (2)$$

where Φ_0 is the vacuum state, we make use of the rule

$$\langle \Psi_k | = \langle a_k^+ \Phi_0 | = \langle \Phi_0 | a_k. \quad (3)$$

Using (2) and

$$\Omega = E_k a_k^+ a_k \quad (4)$$

we obtain with the aid of (3)

$$E_k \langle a_{k'_1}^+ \Phi_0 | a_k^+ a_k | a_{k_1}^+ \Phi_0 \rangle = E_k \langle \Phi_0 | a_{k'_1} a_k^+ a_k | a_{k_1}^+ \Phi_0 \rangle. \quad (5)$$

We apply the exchange relations

$$a_{k'} a_k^+ + a_k^+ a_{k'} = \delta_{kk'} , \quad (6)$$

and

$$a_k \Phi_0 = 0 \quad \text{for all } k , \quad (7)$$

obtaining

$$\begin{aligned} E_k \left\langle a_{k_1}^+ \Phi_0 \left| a_k^+ a_k \right| a_{k_1}^+ \Phi_0 \right\rangle &= E_k \left\langle \Phi_0 \left| a_{k_1} a_k^+ a_k \right| a_{k_1}^+ \Phi_0 \right\rangle \\ &= E_k \langle \Phi_0 | a_{k_1} a_k^+ \delta_{kk_1} | \Phi_0 \rangle \\ &= E_k \langle \Phi_0 | \Phi_0 \rangle \delta_{kk_1} , \end{aligned} \quad (8)$$

where

$$\langle \Phi_0 | \Phi_0 \rangle = 1 . \quad (9)$$

The final result for (1) with (2) and (4) is thus

$$\left\langle \Psi_{k_1'} \left| \Omega \right| \Psi_{k_1} \right\rangle = E_k \delta_{kk_1'} \delta_{kk_1} . \quad (10)$$

For the case that

$$\Omega = \sum_k E_k a_k^+ a_k \quad (11)$$

we must carry out the sum.

$$\left\langle \Psi_{k_1'} \left| \Omega \right| \Psi_{k_1} \right\rangle = \sum_k E_k \delta_{kk_1'} \delta_{kk_1} \quad (12)$$

$$= E_{k_1} \delta_{k_1 k_1'} . \quad (13)$$

Since on the right in

$$\Omega = a_{j_1'}^+ a_{j_2'}^+ V_{j_1' j_2'; j_1 j_2} a_{j_1} a_{j_2} \quad (14)$$

there are two annihilation operators, we have

$$\Omega | \Psi_{k_1} \rangle = 0 , \quad (15)$$

so that (1) vanishes for (14). The computation of (1) and later also of (9) with (4) or (14) can be carried out in a much more obvious and efficient manner if we interpret the effect of the annihilation operator a_k in (5) as follows: it can annihilate an electron in the state k only when it was previously created in the same state from the vacuum Φ_0 , i. e. we must have $k = k_1$ and it follows that

$$a_k a_k^+ \Phi_0 = \Phi_0 . \quad (16)$$

For $k \neq k_1$, on the other hand, we find

$$a_k a_{k_1}^+ \Phi_0 = 0. \quad (17)$$

Now applying the creation operator a_k to (16), we generate the new wavefunction $\Psi_k = a_k^+ \Phi_0$. The $\langle \rangle$ bracket in (5) can now be interpreted as

$$\langle a_{k_1}^+ \Phi_0 | a_k^+ \Phi_0 \rangle \equiv \langle \Psi_{k_1} | \Psi_k \rangle = \delta_{k_1 k}, \quad (18)$$

which, due to the orthogonality of the wavefunctions is just equal to the Kronecker delta, as given. The orthogonality can be readily demonstrated from (3), (6), and (7). Later, we shall explain the procedure for many-particle wavefunctions.

We investigate

$$\langle \Psi_{k_1 k_2} | \Omega | \Psi_{k_1 k_2} \rangle \quad (19)$$

for

$$\Psi_{k_1 k_2} = a_{k_1}^+ a_{k_2}^+ \Phi_0 \quad (20)$$

and (4), and initially obtain

$$\langle a_{k_1}^+ a_{k_2}^+ \Phi_0 | E_k a_k^+ a_k | a_{k_1}^+ a_{k_2}^+ \Phi_0 \rangle; \quad (21)$$

we then apply the rule

$$\langle a_{k_1}^+ a_{k_2}^+ \Phi_0 | = \langle \Phi_0 | a_{k_2}' a_{k_1}'. \quad (22)$$

We obtain from (21)

$$E_k \langle \Phi_0 | a_{k_2}' a_{k_1}' a_k^+ a_k | a_{k_1}^+ a_{k_2}^+ \Phi_0 \rangle. \quad (23)$$

Using (6), we transfer all the annihilation operators to the right-hand side and apply (7):

$$\begin{aligned} & E_k \langle \Phi_0 | a_{k_2}' a_{k_1}' a_k^+ a_k | a_{k_1}^+ a_{k_2}^+ \Phi_0 \rangle \\ &= E_k \langle \Phi_0 | a_{k_2}' a_{k_1}' a_k^+ (\delta_{kk_1} - a_{k_1}^+ a_k) a_{k_2}^+ \Phi_0 \rangle \\ &= E_k \langle \Phi_0 | a_{k_2}' a_{k_1}' a_k^+ a_{k_2}^+ | \Phi_0 \rangle \delta_{kk_1} \\ &\quad - E_k \langle \Phi_0 | a_{k_2}' a_{k_1}' a_k^+ a_{k_1}^+ \Phi_0 \rangle \delta_{kk_2}. \end{aligned} \quad (24)$$

Application of the exchange relations can now be continued. The final result is:

$$\begin{aligned}
E_k \left\langle \Phi_0 \left| a_{k'_2} a_{k'_1} a_k^+ a_k \right| a_{k_1}^+ a_{k_2}^+ \Phi_0 \right\rangle \\
= E_k (\delta_{kk_1} \delta_{kk'_1} \delta_{k_2 k'_2} - \delta_{kk_1} \delta_{k'_1 k_2} \delta_{kk'_2} \\
- \delta_{kk_2} \delta_{kk'_1} \delta_{k_1 k'_2} + \delta_{kk_2} \delta_{kk'_2} \delta_{k'_1 k_1}) .
\end{aligned} \tag{25}$$

For \sum_k (13), we find

$$(E_{k_1} + E_{k_2}) \delta_{k_1 k'_1} \delta_{k_2 k'_2} - (E_{k_1} + E_{k_2}) \delta_{k_1 k'_2} \delta_{k_2 k'_1} . \tag{26}$$

The evaluation of (23) and of the following expression (27) can be carried out much more efficiently (see below). We finally treat

$$\left\langle \Psi_{k'_1 k'_2} \left| a_{j'_1}^+ a_{j'_2}^+ V_{j'_1 j'_2; j_1 j_2} a_{j_1} a_{j_2} \right| \Psi_{k_1 k_2} \right\rangle , \tag{27}$$

which can be cast in the form

$$V_{j'_1 j'_2; j_1 j_2} \langle \Phi_0 | a_{k'_2} a_{k'_1} a_{j'_1}^+ a_{j'_2}^+ a_{j_1} a_{j_2} a_{k_1}^+ a_{k_2}^+ | \Phi_0 \rangle . \tag{28}$$

Making use of the exchange relations, we transfer all the annihilation operators to the right-hand side. The somewhat lengthy but elementary computation yields:

$$\begin{aligned}
\left\langle \Psi_{k'_1 k'_2} \left| a_{j'_1}^+ a_{j'_2}^+ V_{j'_1 j'_2; j_1 j_2} a_{j_1} a_{j_2} \right| \Psi_{k_1 k_2} \right\rangle \\
= V_{j'_1 j'_2; j_1 j_2} (\delta_{k'_1 j'_1} \delta_{k'_2 j'_2} - \delta_{j'_1 k'_2} \delta_{j'_2 k'_1}) (\delta_{k_1 j_2} \delta_{k_2 j_1} - \delta_{k_2 j_2} \delta_{k_1 j_1}) .
\end{aligned} \tag{29}$$

Finally, we introduce the more elegant method for calculating the matrix elements of many-body functions, which we will explain using the (4) as an example. The many-body functions have the form

$$\Psi_{k_1 k_2 \dots k_N} = a_{k_1}^+ a_{k_2}^+ \dots a_{k_N}^+ \Phi_0 , \tag{30}$$

where all the k 's are different, since otherwise, due to $a_k^+ a_k^+ = 0$, $\Psi_{k_1 \dots k_N}$ would vanish. Furthermore, due to $a_k^+ a_{k'}^+ = -a_{k'}^+ a_k^+$, we can bring the indices (quantum numbers) into a particular ordering which we are free to determine, e.g. $k_1 < k_2 < \dots < k_N$. We consider

$$\begin{aligned}
\left\langle \Psi_{k'_1 \dots k'_N} \left| a_k^+ a_k \right| \Psi_{k_1 \dots k_N} \right\rangle \\
= \left\langle a_{k'_1}^+ \dots a_{k'_N}^+ \Phi_0 \left| a_k^+ a_k a_{k_1}^+ a_{k_2}^+ \dots a_{k_N}^+ \Phi_0 \right. \right\rangle .
\end{aligned} \tag{31}$$

Applying a_k to the right, we remember that only an electron already in the state k can be annihilated. We thus have $k = k_j$ for some $j = 1, \dots, N$. Otherwise, we obtain zero. To carry out the “annihilation”, we have to bring a_k into the j -th position in $a_{k_1}^+ \dots a_{k_N}^+$, i.e. a_k must be exchanged $(j-1)$ times with $a_{k_l}^+, l < j$. Due to (6) with $k \neq k'$, this yields a factor of $(-1)^{j-1}$. We then transfer the creation operator a_k^+ in (31) to the now empty position. This again yields a factor of $(-1)^{j-1}$. All together,

we thus have

$$a_k^+ a_k \Psi_{k_1 \dots k_N} = \Psi_{k_1 \dots k_N} \quad \text{if } k = k_j, j = 1, \dots, N, \quad (32)$$

$$\text{otherwise} = 0. \quad (33)$$

In the case (32), the orthogonality relation

$$\langle \Psi_{k'_1 k'_2 \dots k'_N} | \Psi_{k_1 k_2 \dots k_N} \rangle = \delta_{k_1 k'_1} \dots \delta_{k_N k'_N} \quad (34)$$

therefore is all that remains of (31). It can readily be proved with the aid of (6) and (7). The procedure can be applied in an analogous way to

$$\Omega = a_{k'}^+ a_k \quad (35)$$

and to (27) with the corresponding functions (30).

7.6 Instead of the indices i, j, k, l in (7.55), we introduce double indices k, s , where $k = 1, 2, \dots$ refers to the quantum number(s) of the spatial part of the electronic wavefunctions and $s = 1/2, -1/2$ to the spin quantum numbers, which we can denote more simply by \uparrow, \downarrow . The wavefunction ${}_{-1}^3\Psi_m^n$ (7.33) in 2nd quantisation is then given by

$${}_{-1}^3\Psi_m^n = \prod_{k=1}^g a_{k\uparrow}^+ a_{k\downarrow}^+ \cdot a_{m\downarrow}^+ a_{n\downarrow}^+ \Phi_0. \quad (1)$$

To evaluate (7.37), we must compute the expectation value of (7.55) with the corresponding new indices with respect to (1). For the computation of the expectation values, we can use the fact that the annihilation operators $a_{k'\downarrow}^+$ or $a_{k'\uparrow}^+$ act in (1) where $k' = k$ and the spins are the same. Here, however, we must keep in mind the sign change due to the exchange operations. The final result is given in (7.37).

Chapter 8

8.1 According to Heisenberg's uncertainty relations, the lifetime $\tau = \Delta t$ and the energy uncertainty ΔE of a state is given by

$$\Delta E \cdot \Delta t \approx h. \quad (1)$$

Since the ground state has an infinite lifetime, its energy is precisely defined. The lifetime broadening of a transition line is thus due only to the energy width, i. e. the uncertainty, of the excited state:

$$\Delta \bar{\nu} = \frac{\Delta E}{h c} = \frac{1}{c \cdot \Delta t}. \quad (2)$$

For the energy uncertainties of the two excited states a and b and the linewidths of their transitions to the ground state, we thus have

- a) $\Delta t = 10 \text{ s} : \Delta E = 6.6 \cdot 10^{-35} \text{ J}$
 $\bar{\nu} = 3.3 \cdot 10^{-12} \text{ cm}^{-1}$
 b) $\Delta t = 1 \text{ ns} : \Delta E = 6.6 \cdot 10^{-25} \text{ J}$
 $\bar{\nu} = 3.3 \cdot 10^{-2} \text{ cm}^{-1}$.

8.2 The thermal population ratio N_2/N_1 of two states with the energies E_1 and E_2 is given in equilibrium by the Boltzmann distribution

$$\frac{N_2}{N_1} = e^{-\Delta E/kT} \quad (1)$$

($\Delta E = E_2 - E_1$; $k = 1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$: Boltzmann's constant; T : temperature; the differing statistical weights of the states have been neglected here). For a given number $N = N_1 + N_2$ of molecules in an ensemble, we then find for the thermal population of state 2:

$$N_2 = \frac{N}{1 + N_1/N_2} = \frac{N}{1 + e^{\Delta E/kT}}. \quad (2)$$

With the value given, $N = 10^5$, one obtains for $\Delta E = 20.15 \text{ cm}^{-1}$:

- a) $T = 29 \text{ K} : N_2 = 2.69 \cdot 10^4$
 b) $T = 290 \text{ K} : N_2 = 4.75 \cdot 10^4$
 c) $T = 2900 \text{ K} : N_2 = 4.97 \cdot 10^4$

and for $\Delta E = 20\,150 \text{ cm}^{-1}$:

- a) $T = 29 \text{ K} : N_2 = 0$
 b) $T = 290 \text{ K} : N_2 = 0$
 c) $T = 2900 \text{ K} : N_2 = 5$

While neighbouring rotational terms are already nearly equally populated at room temperature, electronically excited states are hardly populated thermally even at high temperatures.

Chapter 9

9.1 Only molecules with permanent electric dipole moments exhibit a pure microwave rotational spectrum: H_2O , H_2O_2 , CH_3Cl , CH_2Cl_2 , NH_3 , NH_4Cl , HCl , HBr . For molecules such as CH_4 and CS_2 , rotational spectra become observable only when IR-active vibrations are excited.

9.2 a) The spectral position $\bar{\nu}$ of the transition between the rotational levels J and $J + 1$ is (from (9.15)) given by

$$\bar{\nu}_{J \rightarrow J+1} = F(J+1) - F(J) = 2B(J+1). \quad (1)$$

The spectral spacing $\Delta\bar{\nu}$ between each two neighbouring lines is, in this simplified model, independent of J :

$$\Delta\bar{\nu} = \bar{\nu}_{J+1 \rightarrow J+2} - \bar{\nu}_{J \rightarrow J+1} = 2B. \quad (2)$$

With the given value $\Delta\bar{\nu} = 0.71433 \text{ cm}^{-1}$, one finds for the rotational constant of $^{79}\text{Br}^{19}\text{F}$:

$$B = 0.357 \text{ cm}^{-1}$$

and for the moment of inertia

$$\Theta = 7.84 \cdot 10^{-46} \text{ kg m}^2.$$

The moment of inertia of a diatomic molecule with the atomic masses m_1 and m_2 and the bond length (i. e. the internuclear distance) R can be calculated from

$$\Theta = m_1 R_1^2 + m_2 R_2^2 = m_r R^2 \quad (3)$$

where

$$m_r = \frac{m_1 m_2}{m_1 + m_2} \quad (4)$$

denotes the reduced mass in the centre-of-mass system. With (3) and (4), one obtains from Θ the bond lengths

$$R = 1.76 \cdot 10^{-10} \text{ m} = 1.76 \text{ \AA}.$$

The position of the transition $J = 9 \rightarrow (J + 1) = 10$ can be computed from (1); the result is

$$\bar{\nu}_{9 \rightarrow 10} = 7.14 \text{ cm}^{-1}.$$

The transition moment between two rotational levels of a linear molecule depends to a good approximation only on the electric dipole moment of the molecule and can therefore be considered to be constant for all purely rotational transitions. The intensity of a line in a pure rotational spectrum can thus be explained in terms of the population N_J of the absorbing state alone; it in turn is given by the degeneracy factor g_J of the level and its thermal population at the temperature T (Boltzmann distribution):

$$\frac{N_J}{N_0} = \frac{g_J}{g_0} e^{-(E_J - E_0)/kT} \quad (5)$$

and thus, due to $g_J = 2J + 1$,

$$N_J = N_0 (2J + 1) e^{-hcB J(J+1)/kT}. \quad (6)$$

From the derivative of this function with respect to J , the most strongly populated state J_{\max} is found to be given by the value of

$$J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \quad (7)$$

rounded to an integer.

It then follows for $^{79}\text{Br}^{19}\text{F}$ at $T = 298 \text{ K}$ that $J = 16.53$ and thus

$$J_{\max} = 17.$$

The most intense transition is therefore observed for $J = 17 \rightarrow J = 18$.

b) Classical mechanics gives for the energy of a rigid rotor

$$E = \frac{1}{2} \Theta \omega^2 = 2\pi^2 \Theta \nu^2, \quad (8)$$

where ν is the rotational frequency of the molecule. Setting this expression equal to the quantum-mechanically calculated energy of the state, $E = hcB J(J + 1)$, we find

$$\nu = \frac{h}{4\pi^2 \Theta} \sqrt{J(J + 1)} = 2cB \sqrt{J(J + 1)}. \quad (9)$$

From this, one obtains

$$J = 0: \quad \nu = 0$$

$$J = 1: \quad \nu = 3.0 \cdot 10^{10} \text{ s}^{-1}$$

$$J = 10: \quad \nu = 2.2 \cdot 10^{11} \text{ s}^{-1}.$$

9.3 From the atomic masses

$$m_1 \text{H} = 1.673 \cdot 10^{-27} \text{ kg}$$

$$m_2 \text{D} = 3.344 \cdot 10^{-27} \text{ kg}$$

$$m_{35} \text{Cl} = 58.06 \cdot 10^{-27} \text{ kg}$$

$$m_{37} \text{Cl} = 61.38 \cdot 10^{-27} \text{ kg}$$

one can compute the reduced masses of the diatomic molecules, finding

$$m_r(^1\text{H}^{35}\text{Cl}) = 1.626 \cdot 10^{-27} \text{ kg}$$

$$m_r(^1\text{H}^{37}\text{Cl}) = 1.629 \cdot 10^{-27} \text{ kg}$$

$$m_r(^2\text{D}^{35}\text{Cl}) = 3.162 \cdot 10^{-27} \text{ kg}.$$

From the formula for the rotational constant,

$$B = \frac{h}{8\pi^2 c \Theta} = \frac{h}{8\pi^2 c m_r R^2} \quad (1)$$

and under the assumption that the bond length is the same for different isotopes, it follows that

$$\frac{B_1}{B_2} = \frac{m_{r,2}}{m_{r,1}} \quad (2)$$

and thus with $B_1 \text{H}^{35}\text{Cl} = 10.5909 \text{ cm}^{-1}$:

$$B_1 \text{H}^{37}\text{Cl} = 10.5714 \text{ cm}^{-1} \quad \text{and} \quad B_2 \text{D}^{35}\text{Cl} = 5.446 \text{ cm}^{-1}.$$

9.4 The energy of a transition line $J \rightarrow J + 1$ in a pure rotational spectrum is given in terms of the rotational constant B by

$$\bar{\nu} = 2B(J + 1) \quad (1)$$

With $B = 10.6 \text{ cm}^{-1}$, one obtains

$$\begin{aligned} \text{for } \bar{\nu}_1 &= 106.0 \text{ cm}^{-1}: J_1 = 4 \\ \text{for } \bar{\nu}_2 &= 233.2 \text{ cm}^{-1}: J_2 = 10. \end{aligned}$$

Under the assumption of a constant transition moment, the line intensity is proportional to the population $N(J)$ of the absorbing rotational level J . According to (9.16), it depends on the degeneracy factor $(2J + 1)$ and on the thermal population from the Boltzmann factor:

$$N_J = N_0 (2J + 1) e^{-hcB J(J+1)/kT}. \quad (2)$$

The transitions J_1 and J_2 have the same intensity for $N_{J_1} = N_{J_2}$ and therefore for

$$N_0 (2J_1 + 1) e^{-hcB J_1(J_1+1)/kT} = N_0 (2J_2 + 1) e^{-hcB J_2(J_2+1)/kT}. \quad (3)$$

With the values computed above for J_1 and J_2 , this condition is met at a temperature of

$$T = \frac{90 hcB}{k \ln \frac{7}{3}}. \quad (4)$$

From this, one computes

$$T = 1620.8 \text{ K}.$$

9.5 The spectral position of a line in a purely rotational spectrum of a rigid rotor can be calculated from (9.15):

$$\bar{\nu}_{J \rightarrow J+1} = F(J + 1) - F(J) = 2B(J + 1). \quad (1)$$

From this, a constant spacing of $\Delta\bar{\nu}$ between any two neighbouring lines is found:

$$\Delta\bar{\nu} = 2B = \text{const.} \quad (2)$$

Since the centrifugal stretching constant D is in general several orders of magnitude smaller than the rotational constant B , this first approximation is sufficient to associate the transitions $\bar{\nu}_{J \rightarrow J+1}$ with the corresponding levels J . The lines given in the problem

$$J_1 \rightarrow J_2: \quad \bar{\nu}_1 = F(J_2) - F(J_1) = 84.544 \text{ cm}^{-1}$$

$$J_2 \rightarrow J_3: \quad \bar{\nu}_2 = F(J_3) - F(J_2) = 101.355 \text{ cm}^{-1}$$

$$J_3 \rightarrow J_4: \quad \bar{\nu}_3 = F(J_4) - F(J_3) = 118.112 \text{ cm}^{-1}$$

have a spacing of $2B \approx 16.8 \text{ cm}^{-1}$, which, together with (1), permits the following identification:

$$J_1 = 4; \quad J_2 = 5; \quad J_3 = 6; \quad J_4 = 7.$$

The model of a rigid rotor is greatly simplified. On replacing it by a nonrigid rotor, one takes the effect of centrifugal stretching into account and thus obtains for the energy (in cm^{-1}) of a pure rotational state of quantum number J

$$F(J) = B J(J+1) - D J^2(J+1)^2, \quad (3)$$

where D is the centrifugal stretching constant; for a diatomic molecule, we have

$$D = \frac{\hbar^3}{4\pi k \Theta^2 R_e^2 c} \quad (4)$$

(Θ : moment of inertia of the molecule; R_e : equilibrium internuclear distance without rotation; k : force constant of the elastic valence oscillation along the internuclear axis). The line belonging to the transition $J \rightarrow J+1$ has the energy

$$\bar{\nu}_{J \rightarrow J+1} = F(J+1) - F(J) = 2B(J+1) - 4D(J+1)^3. \quad (5)$$

Inserting the corresponding J values for the first two transitions given, $\bar{\nu}_1$ and $\bar{\nu}_2$, we obtain the system of linear equations

$$J_1 = 4 \rightarrow J_2 = 5: \quad \bar{\nu}_1 = 10B - 500D \quad (6)$$

$$J_2 = 5 \rightarrow J_3 = 6: \quad \bar{\nu}_2 = 12B - 864D \quad (7)$$

and thus

$$D = \frac{6\bar{\nu}_1 - 5\bar{\nu}_2}{1320} \quad \text{and} \quad B = \frac{1}{10}\bar{\nu}_1 + 50D. \quad (8)$$

Inserting the numerical values yields

$$D = 3.70 \cdot 10^{-4} \text{ cm}^{-1} \quad \text{and} \quad B = 8.47 \text{ cm}^{-1}.$$

The resulting exact value of B agrees sufficiently well with the value used above, so that the correspondence of the J values to the lines is confirmed. Making use of the well-known formula for the rotational constant,

$$B = \frac{h}{8\pi^2 c m_r R_e^2} \quad (9)$$

and inserting the atomic masses $m_{1\text{H}} = 1.673 \cdot 10^{-27} \text{ kg}$ and $m_{79\text{Br}} = 131.03 \cdot 10^{-27} \text{ kg}$ as well as

$$m_r = \frac{m_{1\text{H}} m_{79\text{Br}}}{m_{1\text{H}} + m_{79\text{Br}}}, \quad (10)$$

the equilibrium distance between the nuclei and thus the average bond length of the molecule at rest can be found:

$$R_e = 1.41 \cdot 10^{-10} \text{ m} = 1.41 \text{ \AA}.$$

The model of the nonrigid diatomic rotor is based on the assumption of an elastic coupling of the nuclei with the force constant k . The resulting harmonic oscillation along the bond axis has the fundamental frequency

$$\omega = \sqrt{\frac{k}{m_r}}. \quad (11)$$

Solving this equation for k and inserting into (4), and making use of (9) with some elementary rearrangements, we find for the oscillation frequency

$$\omega = 4\pi c \sqrt{\frac{B^3}{D}}. \quad (12)$$

With the values of D and B obtained above, this yields

$$\omega = 4.83 \cdot 10^{14} \text{ s}^{-1} \quad \hat{=} \quad \bar{\nu} = 2564 \text{ cm}^{-1}.$$

9.6 The moment of inertia Θ of the hydrogen cyanide or Prussic acid molecule $\text{H}-\text{C}\equiv\text{N}$ in its centre-of-mass system is

$$\Theta = m_{\text{C}} R_{\text{C}}^2 + m_{\text{N}} R_{\text{N}}^2 + m_{\text{H}} R_{\text{H}}^2. \quad (1)$$

Here, m_{C} , m_{N} and m_{H} are the relative atomic masses of carbon, nitrogen and hydrogen, and R_{C} , R_{N} , R_{H} are the distances of each of the atoms from the centre of mass.

In the centre-of-mass system, we have

$$m_{\text{N}} R_{\text{N}} = m_{\text{C}} R_{\text{C}} + m_{\text{H}} R_{\text{H}} \quad (2)$$

so that, with

$$R_{\text{CN}} = R_{\text{C}} + R_{\text{N}} \quad (3)$$

and

$$R_{CH} = R_H - R_C \quad (4)$$

we have three equations at our disposal with which the distances in the centre-of-mass system in (1) can be eliminated. With the total molecular mass

$$M = m_C + m_N + m_H, \quad (5)$$

equation (1) for the moment of inertia can be rearranged to give

$$\Theta = m_N R_{CN}^2 + m_H R_{CH}^2 - \frac{1}{M} (m_N R_{CN} - m_H R_{CH})^2. \quad (6)$$

Inserting the values given, we obtain

$$\Theta = 1.885 \cdot 10^{-46} \text{ kg m}^2$$

and from this, using

$$B = \frac{h}{8\pi^2 c \Theta}$$

we arrive at the rotational constant

$$B = 1.485 \text{ cm}^{-1}.$$

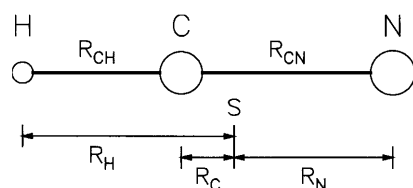


Fig. S.20. A linear triatomic molecule HCN: bond lengths and distances from the atoms to the centre of mass S

9.7 The rotational energy of a generalised three-dimensional body transformed to the principal axis system with the remaining diagonal elements Θ_{xx} , Θ_{yy} and Θ_{zz} of the moment of inertia tensor and the components L_x , L_y and L_z of angular momentum L is given by

$$E = \frac{L_x^2}{2 \Theta_{xx}} + \frac{L_y^2}{2 \Theta_{yy}} + \frac{L_z^2}{2 \Theta_{zz}}. \quad (1)$$

The ammonia molecule, NH_3 , is a symmetric top with an axis of rotation which in the following is taken to be the z axis of the coordinate system. Then the following relation holds:

$$\Theta_{zz} \equiv \Theta_{\parallel} . \quad (2)$$

Owing to the symmetry of NH_3 , the two remaining principal components of the moment of inertia are equal; the associated principal axes are perpendicular to the rotational axis:

$$\Theta_{xx} = \Theta_{yy} \equiv \Theta_{\perp} . \quad (3)$$

Inserting this in (1) and making use of $L^2 = L_x^2 + L_y^2 + L_z^2$, we obtain

$$E = \frac{L_x^2 + L_y^2}{2\Theta_{\perp}} + \frac{L_z^2}{2\Theta_{\parallel}} \quad (4)$$

$$= \frac{L^2}{2\Theta_{\perp}} + L_z^2 \left(\frac{1}{2\Theta_{\parallel}} - \frac{1}{2\Theta_{\perp}} \right) . \quad (5)$$

In addition to the quantisation of the total angular momentum L of the molecule according to

$$L^2 = \hbar^2 J(J+1) , \quad (6)$$

in a symmetric-top molecule there exists a quantisation of the component L_z of the angular momentum along the rotational axis, since the symmetry of the charge distribution makes one direction in space unique:

$$L_z = \hbar K \quad \text{with} \quad K = 0, \pm 1, \pm 2, \dots, \pm J . \quad (7)$$

Then we obtain from (5)

$$E = \frac{\hbar^2}{2\Theta_{\perp}} J(J+1) + \left(\frac{\hbar^2}{2\Theta_{\parallel}} - \frac{\hbar^2}{2\Theta_{\perp}} \right) K^2 \quad (8)$$

and finally

$$F(J, K) = \frac{E}{hc} = B J(J+1) + C K^2 \quad (9)$$

with the rotational constants

$$B = \frac{h}{8\pi^2 c \Theta_{\perp}} \quad \text{and} \quad C = \frac{h}{8\pi^2 c} \left(\frac{1}{\Theta_{\parallel}} - \frac{1}{\Theta_{\perp}} \right) . \quad (10)$$

From the data and formulas given, we can compute the two principal elements of the moment of inertia tensor of the symmetric-top molecule, obtaining

$$\Theta_{\perp} = 2.86 \cdot 10^{-47} \text{ kg m}^2$$

$$\Theta_{\parallel} = 4.38 \cdot 10^{-47} \text{ kg m}^2$$

and from this,

$$B = 9.78 \text{ cm}^{-1}$$

$$C = -3.39 \text{ cm}^{-1}.$$

Due to $\Theta_{\parallel} > \Theta_{\perp}$, we require $C < 0$, so that in the case of NH_3 we are dealing with a “cushion-shaped” molecule. The rotational spectrum of the molecule is obtained from (9) taking the selection rules

$$\Delta J = \pm 1, \quad \Delta K = 0 \quad (11)$$

into account, so that we find for the transition energies:

$$\bar{\nu}_{J \rightarrow J+1} = F(J+1, K) - F(J, K) = 2B(J+1). \quad (12)$$

9.8 As derived in problem 9.5 (Eq. 12), the frequency of the valence oscillation of a diatomic molecule is determined from the rotational constant B and the centrifugal stretching constant D according to the relation

$$\omega = 4\pi c \sqrt{\frac{B^3}{D}}. \quad (1)$$

With the values given, we find

$$\omega = 5.64 \cdot 10^{14} \text{ s}^{-1} \triangleq \bar{\nu} = 2995 \text{ cm}^{-1}.$$

The experimental value is $\bar{\nu} = 2991 \text{ cm}^{-1}$. The discrepancy results from the use of an insufficiently precise model as the basis of the calculation: the diatomic molecule is treated as a harmonic oscillator by approximating the bond as an elastic spring and applying the linear force relation (Hooke’s Law), $F = -k(R - R_e)$. Making use of an anharmonic oscillator potential for the bond leads to an improvement of the calculated values.

9.9 The reduced mass of $^{12}\text{C}^{16}\text{O}$ is $1.139 \cdot 10^{-26} \text{ kg}$, and the bond length is $112.82 \cdot 10^{-12} \text{ m}$. From these values, we can compute the rotational constant

$$B = \frac{h}{8\pi^2 c \Theta} = \frac{h}{8\pi^2 c m_r R^2}, \quad (1)$$

obtaining

$$B = 1.931 \text{ cm}^{-1}.$$

The transition frequencies in the microwave rotational spectrum are given by

$$\bar{\nu}_{J \rightarrow J+1} = 2B(J+1). \quad (2)$$

For the first four lines, one obtains from this formula the microwave frequencies:

$$\bar{\nu}_{0 \rightarrow 1} = 2B = 3.862 \text{ cm}^{-1} \hat{=} 115.86 \text{ GHz}$$

$$\bar{\nu}_{1 \rightarrow 2} = 4B = 7.724 \text{ cm}^{-1} \hat{=} 231.72 \text{ GHz}$$

$$\bar{\nu}_{2 \rightarrow 3} = 6B = 11.586 \text{ cm}^{-1} \hat{=} 347.58 \text{ GHz} \quad \text{and}$$

$$\bar{\nu}_{3 \rightarrow 4} = 8B = 15.448 \text{ cm}^{-1} \hat{=} 463.44 \text{ GHz}.$$

An analogous calculation leads for the isotopes $^{13}\text{C}^{16}\text{O}$ to $m'_t = 1.191 \cdot 10^{-26} \text{ kg}$ and $B' = 1.847 \text{ cm}^{-1}$, and thus to

$$\bar{\nu}'_{0 \rightarrow 1} = 3.694 \text{ cm}^{-1} \hat{=} 110.82 \text{ GHz},$$

In order to obtain a spectral separation of the two lines belonging to the $0 \rightarrow 1$ transitions, one would need a resolution defined by

$$A = \frac{\bar{\nu}}{\Delta\bar{\nu}} = \frac{\bar{\nu}_{0 \rightarrow 1}}{\bar{\nu}_{0 \rightarrow 1} - \bar{\nu}'_{0 \rightarrow 1}}. \quad (3)$$

With $\Delta\bar{\nu} = 0.168 \text{ cm}^{-1}$ or $\Delta\nu = 5.04 \text{ GHz}$, this corresponds to a resolution of $A = 23.0$.

9.10 The vector of total angular momentum L of a molecule has $2J+1$ orientational components with respect to a particular direction in space. Without an external electric field, the $2J+1$ states are energetically degenerate. For a molecule with a permanent electric dipole moment, this degeneracy is lifted in an electric field E by the Stark effect, since the different spatial orientations of the angular momentum relative to the direction of the field correspond to different energy shifts ΔE :

$$\Delta E_J = \frac{p^2 E^2}{B} f(J, M^2) \quad (1)$$

with $M = 0, \pm 1, \pm 2, \dots, \pm J$ (p : electric dipole moment). For $M \neq 0$, a twofold degeneracy remains, and therefore each rotational level J exhibits $(J+1)$ -fold splitting:

$$J = 2: \quad 3\text{-fold splitting} \quad (M = 0, \pm 1, \pm 2)$$

$$J = 3: \quad 4\text{-fold splitting} \quad (M = 0, \pm 1, \pm 2, \pm 3).$$

As a result of the selection rules $\Delta J = \pm 1$ and $\Delta M = 0$, each line in the rotational spectrum thus shows a $(J+1)$ -fold splitting. Then e.g. the transition $J = 2 \rightarrow (J+1) = 3$ leads to three spectral lines:

$$J = 2, M = 0 \rightarrow J = 3, M = 0$$

$$J = 2, M = \pm 1 \rightarrow J = 3, M = \pm 1$$

$$J = 2, M = \pm 2 \rightarrow J = 3, M = \pm 2.$$

The number of lines into which a transition is split in an E -field gives a unique method of identifying the J values in the rotational spectrum.

9.11 Setting the classical energy of a rigid rotor

$$E_{\text{rot, klass}} = \frac{1}{2} \Theta \omega^2 \quad (1)$$

equal to the term calculated quantum mechanically:

$$E_{\text{rot, QM}} = hcB J(J+1) = \frac{\hbar^2}{2\Theta} J(J+1), \quad (2)$$

one obtains the dependence of the circular frequency ω (which is defined only classically) on the rotational quantum number J (which is defined only quantum mechanically):

$$\omega(J) = \frac{\hbar}{\Theta} \sqrt{J(J+1)}. \quad (3)$$

Projected onto a plane, the rotating dipole moment can be identified within the framework of classical electrodynamics as a moment which oscillates harmonically at the frequency ω . It radiates electromagnetic waves whose frequency (in cm^{-1}) corresponds to the rotational frequency of the rotor:

$$\bar{\nu}_{\text{klass}} = \frac{\omega(J)}{2\pi c} = \frac{\hbar}{2\pi c \Theta} \sqrt{J(J+1)}. \quad (4)$$

In contrast, the quantum-mechanical result for the frequency of a (very improbable) radiative transition from $J \rightarrow J-1$ is

$$\bar{\nu}_{\text{QM}} = 2B J = \frac{\hbar}{2\pi c \Theta} J. \quad (5)$$

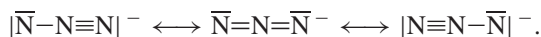
The ratio of the two frequencies is

$$\frac{\bar{\nu}_{\text{QM}}}{\bar{\nu}_{\text{klass}}} = \sqrt{\frac{J}{J+1}}. \quad (6)$$

In the classical limit $J \rightarrow \infty$, the two theories yield the same result.

Chapter 10

10.1 All molecules whose dipole moment changes during oscillation also absorb radiation in the infrared spectral region (vibrational absorption spectra). In the case of symmetric molecules, in particular bending vibrations and asymmetric stretching vibrations are important, since the symmetric stretch vibrations are IR inactive. Thus of the molecules given, all exhibit IR absorption with the exception of H_2 and N_2 . In the case of the linear azide ion, N_3^- , the bending vibration is IR active, as can be seen from the mesomeric representation:



10.2 The total number of all the thermodynamic degrees of freedom of an N-atomic molecule is $f = 3N$. The balance for translation, rotation, and vibration is as follows:

Total number of degrees of freedom: $f = 3N$

Number of translational degrees of freedom: $f_T = 3$

Number of rotational degrees of freedom: $f_R = \begin{cases} 2 & \text{for a linear molecule} \\ 3 & \text{otherwise} \end{cases}$

Number of vibrational degrees of freedom: $f_V = \begin{cases} 3N - 5 & \text{for a linear molecule} \\ 3N - 6 & \text{otherwise} \end{cases}$.

From this it follows that the number of vibrational degrees of freedom f_V for

- a) HBr (linear) : $f_V = 1$
- b) OCS (linear) : $f_V = 4$
- c) SO₂ (nonlinear) : $f_V = 3$
- d) H—O—O—H (nonlinear) : $f_V = 6$
- e) H—C≡C—H (linear) : $f_V = 7$
- f) C₆H₆ : $f_V = 30$.

10.3 A quantum-mechanical calculation yields for the energy terms G_v of a harmonic oscillator

$$G_v = \frac{1}{hc} \hbar \omega \left(v + \frac{1}{2} \right) = \bar{\nu}_e \left(v + \frac{1}{2} \right) \quad \text{with} \quad \bar{\nu}_e = \frac{\omega}{2\pi c}. \quad (1)$$

The vibrational frequency of the harmonic oscillator is

$$\omega = \sqrt{\frac{k}{m_r}}, \quad (2)$$

so that for a transition between neighbouring states v and $v + 1$, it follows that:

$$\bar{\nu}_{v \rightarrow v+1} = G_{v+1} - G_v = \bar{\nu}_e = \frac{\omega}{2\pi c}. \quad (3)$$

With (2), one therefore obtains the wavenumber of a photon which can stimulate transitions between neighbouring levels:

$$\bar{\nu}_{v \rightarrow v+1} = \frac{1}{2\pi c} \sqrt{\frac{k}{m_r}} \quad (4)$$

as well as the wavelength of the photon:

$$\lambda = \frac{1}{\bar{\nu}_{v \rightarrow v+1}}. \quad (5)$$

From the given values, $k = 855 \text{ N/m}$ and $m_r = m_{\text{Proton}} = 1.6726 \cdot 10^{-27} \text{ kg}$, one obtains

$$\bar{\nu}_{v \rightarrow v+1} = 3795.6 \text{ cm}^{-1} \quad \text{and} \quad \lambda = 2.60 \text{ m}. \quad (6)$$

10.4 Since the energy levels of an harmonic oscillator obey the equation

$$E_v = \hbar\omega \left(v + \frac{1}{2} \right) \quad \text{with} \quad v = 0, 1, 2, \dots, \quad (1)$$

the minimum excitation energy E_{\min} is given by

$$E_{\min} = \hbar\omega = \hbar \sqrt{\frac{k}{m_r}}, \quad (2)$$

where for the vibrational frequency, the relation

$$\omega = \sqrt{\frac{k}{m_r}} \quad (3)$$

(m_r : reduced mass) is employed.

a) For the limiting case of small displacements, the equation of motion of a frictionless pendulum in a gravitational field can be used as the equation of motion of the harmonic oscillator. The force constant k corresponds in this case to

$$k = \frac{mg}{l} \quad (4)$$

with $m = m_r$: pendulum mass; $g = 9.81 \text{ m/s}^2$: acceleration of gravity; $l = 1 \text{ m}$: length of the pendulum. Then the oscillation frequency is

$$\omega = \sqrt{\frac{k}{m_r}} = \sqrt{\frac{g}{l}} \quad (5)$$

so that it follows from (2) that:

$$E_{\min} = 3.3 \cdot 10^{-34} \text{ J} = 2.1 \cdot 10^{-15} \text{ eV} = 1.7 \cdot 10^{-11} \text{ cm}^{-1}.$$

b) At the oscillation frequency $\nu = 5 \text{ Hz}$ and $\omega = 2\pi\nu$, one finds for the movement of a mechanical clock the minimum excitation energy

$$E_{\min} = 3.3 \cdot 10^{-33} \text{ J} = 2.1 \cdot 10^{-14} \text{ eV} = 1.7 \cdot 10^{-10} \text{ cm}^{-1}.$$

c) Correspondingly, for the quartz oscillator of a clock with $\nu = 33 \text{ kHz}$

$$E_{\min} = 2.2 \cdot 10^{-29} \text{ J} = 1.4 \cdot 10^{-10} \text{ eV} = 1.1 \cdot 10^{-6} \text{ cm}^{-1}.$$

d) The minimum excitation energy of the valence oscillation of O_2 with a force constant of $k = 1177 \text{ N/m}$ and $m_r = 13.28 \cdot 10^{-27} \text{ kg}$ is given by

$$E_{\min} = 3.1 \cdot 10^{-20} \text{ J} = 0.2 \text{ eV} = 1580 \text{ cm}^{-1}.$$

It can be seen that in the cases (a) to (c), the minimum excitation energies are so small that one can assume a practically continuous energy spectrum. In the oxygen molecule in (d), the effect of quantisation is, in contrast, clearly observable, and the system can no longer be described classically.

10.5 Treating the $N \equiv O$ molecule as an anharmonic oscillator, we find the vibronic energy levels to be given by

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

and with

$$\omega_e = 2\pi c \bar{\nu}_e, \quad (2)$$

the vibrational energy terms are:

$$G_v = \frac{E_v}{hc} = \bar{\nu}_e \left(v + \frac{1}{2} \right) - x_e \bar{\nu}_e \left(v + \frac{1}{2} \right)^2. \quad (3)$$

The transition energies $\bar{\nu}_{0 \rightarrow v}$ from the ground state ($v = 0$) to an excited vibrational level ($v > 0$) are found from this to be

$$\bar{\nu}_{0 \rightarrow v} = G_v - G_0 = \bar{\nu}_e v [1 - x_e(v + 1)]. \quad (4)$$

Then for the fundamental frequency (transition from $v = 0 \rightarrow v = 1$), we find

$$\bar{\nu}_{0 \rightarrow 1} = \bar{\nu}_e (1 - 2x_e), \quad (5)$$

and for the first harmonic (transition from $v = 0 \rightarrow v = 2$)

$$\bar{\nu}_{0 \rightarrow 2} = 2 \bar{\nu}_e (1 - 3x_e). \quad (6)$$

Equations (5) and (6) form a linear system of two equations for two unknowns ($\bar{\nu}_e$, x_e). From them, we obtain the vibrational constant

$$\bar{\nu}_e = 3\bar{\nu}_{0 \rightarrow 1} - \bar{\nu}_{0 \rightarrow 2} \quad (7)$$

and the anharmonicity constant

$$x_e = \frac{2\bar{\nu}_{0 \rightarrow 1} - \bar{\nu}_{0 \rightarrow 2}}{6\bar{\nu}_{0 \rightarrow 1} - 2\bar{\nu}_{0 \rightarrow 2}}. \quad (8)$$

With the given values for the central frequencies of the rotational-vibrational transitions ($\Delta J = 0$), one obtains

$$\bar{\nu}_e = 1903.98 \text{ cm}^{-1} \quad \text{and} \quad x_e = 0.007332.$$

In the vibronic ground state, $v = 0$, the anharmonic oscillator has according to (3) the zero-point energy

$$G_0 = \frac{1}{2} \bar{\nu}_e \left(1 - \frac{x_e}{2} \right) \quad (9)$$

or

$$G_0 = 948.5 \text{ cm}^{-1}.$$

Treating the molecule approximately as an harmonic oscillator with the reduced mass

$$m_r = \frac{m_{^{14}\text{N}} \cdot m_{^{16}\text{O}}}{m_{^{14}\text{N}} + m_{^{16}\text{O}}}, \quad (10)$$

one assumes a linear force law and computes the force constant k from

$$k = m_r \omega_e^2. \quad (11)$$

The energy levels of the harmonic oscillator are

$$E_v = \hbar \omega_e \left(v + \frac{1}{2} \right), \quad (12)$$

so that in going from the harmonic (12) to the anharmonic oscillator (1), we must make the substitution

$$\omega_e \longrightarrow \omega_e \left[1 - x_e \left(v + \frac{1}{2} \right) \right]. \quad (13)$$

The constant vibrational frequency ω_e of the harmonic oscillator thus becomes a frequency ν that depends on the vibrational quantum number. In the anharmonic oscillator, the equilibrium vibrational frequency defined in (1) and used in (11), ω_e , thus corresponds to the frequency of an infinitesimally small oscillation about the equilibrium internuclear distance in the hypothetical state $v = -\frac{1}{2}$.

With $\omega_e = 3.59 \cdot 10^{14} \text{ s}^{-1}$ and $m_r = 1.24 \cdot 10^{-27} \text{ kg}$, one finds for the force constant

$$k = 1594.9 \frac{\text{kg}}{\text{s}^2}.$$

Treating the vibrational quantum number v as a continuous variable, the expression (3) for the vibrational terms G_v can be differentiated with respect to v :

$$G(v) = \bar{\nu}_e \left(v + \frac{1}{2} \right) - x_e \bar{\nu}_e \left(v + \frac{1}{2} \right)^2 \quad (14)$$

$$\frac{dG(v)}{dv} = \bar{\nu}_e - 2x_e \bar{\nu}_e \left(v + \frac{1}{2} \right). \quad (15)$$

From this, we can find at the frequency

$$v_{\max} = \frac{1}{2x_e} - \frac{1}{2} = 67.69 \approx 68 \quad (16)$$

the maximum of the function $G(v)$:

$$G(v_{\max}) = 64\,919 \text{ cm}^{-1}.$$

This maximum vibrational energy can be considered as the lower limit of the energy continuum, so that after subtracting the zero-point energy, the dissociation energy D_0 of the molecule is found to be:

$$D_0 = G(v_{\max}) - G_0 \quad (17)$$

or

$$D_0 = 63\,970 \text{ cm}^{-1} = 7.93 \text{ eV} = 765.3 \frac{\text{kJ}}{\text{mole}}.$$

This is not an especially good estimate. Its deviation from the experimental value $D_0 = 5.91 \text{ eV}$ is due in particular to the neglect of terms of higher order in $(v + \frac{1}{2})$ in the expression for the energies. The cubic, quadratic and higher terms are important especially for large values of v ; in the approximation used, we have namely $G(v) \rightarrow -\infty$ for $v \rightarrow \infty$.

10.6 The given data permit a calculation only in the harmonic oscillator approximation. For the energy terms, we thus find the expression

$$G_v = \bar{\nu}_e \left(v + \frac{1}{2} \right), \quad (1)$$

and thus we have for the zero-point energy of the molecule

$$G_0 = \frac{1}{2} \bar{\nu}_e. \quad (2)$$

Under the assumption that the molecule is in its vibrational ground state $v = 0$ both before and immediately after the reaction, the energy difference ΔE between the reactants and the products is due solely to their different zero-point energies:



$$\Delta E = G_{0,\text{HCl}} + G_{0,\text{D}_2} - (G_{0,\text{DCI}} + G_{0,\text{HD}}). \quad (4)$$

With the given values for the $\bar{\nu}_e$ of the individual molecules, we obtain

$$\Delta E = 129 \text{ cm}^{-1} = 1.54 \frac{\text{kJ}}{\text{mole}}.$$

In the reaction of one mole each of reactant molecules, an energy of 1.54 kJ is thus set free – the reaction is exothermic.

10.7 The force constant k of a molecular bond can be calculated on the model of an harmonic oscillator from

$$k = m_r \omega^2 = 4\pi^2 c^2 m_r \bar{\nu}^2. \quad (1)$$

Here, m_r is the reduced mass of the molecule and $\bar{\nu}$ is the frequency of the fundamental oscillation. For the hydrogen halides, the following table can be written:

	$^1\text{H}^{19}\text{F}$	$^1\text{H}^{35}\text{Cl}$	$^1\text{H}^{81}\text{Br}$	$^1\text{H}^{127}\text{I}$
$\bar{\nu}/\text{cm}^{-1}$	4141.3	2988.9	2649.7	2309.5
$m_r/10^{-27} \text{ kg}$	1.598	1.624	1.653	1.661
$k/\text{N/m}$	968.0	515.7	411.7	314.4

10.8 The iodine molecule is treated as an anharmonic oscillator, so that the vibronic energy terms are given by

$$G_v = \bar{\nu}_e \left(v + \frac{1}{2} \right) - x_e \bar{\nu}_e \left(v + \frac{1}{2} \right)^2. \quad (1)$$

From this, we find the spacing $\bar{\nu}_{0 \rightarrow 1}$ of the first two vibrational levels

$$\bar{\nu}_{0 \rightarrow 1} = \bar{\nu}_e (1 - 2x_e) \quad (2)$$

and with the given values for the vibrational constant $\bar{\nu}_e$ and the anharmonicity constant x_e

$$\bar{\nu}_{0 \rightarrow 1} = 213.71 \text{ cm}^{-1}.$$

The intensity of the vibrational transitions with $\Delta v = 1$ is proportional to the population N_v of the absorbing state v , since the excited states are nearly unpopulated at low temperatures. From the Boltzmann distribution, we then find for the ratio of the intensities $I_{0 \rightarrow 1}$ of the fundamental vibrational band and $I_{1 \rightarrow 2}$ of the “hot band” at $T = 300 \text{ K}$:

$$\frac{I_{1 \rightarrow 2}}{I_{0 \rightarrow 1}} = \frac{N_1}{N_0} = e^{-hc\bar{\nu}_{0 \rightarrow 1}/kT} \quad (3)$$

(more precisely, this holds for every pair of equivalent rotational-vibrational transitions), and thus

$$\frac{I_{1 \rightarrow 2}}{I_{0 \rightarrow 1}} = 0.359.$$

10.9 The diatomic functional groups which contribute are treated as a first approximation as harmonic oscillators. Their vibrational frequency is then

$$\omega = 2\pi c \bar{\nu} = \sqrt{\frac{k}{m_r}}. \quad (1)$$

As an additional approximation, we assume that on exchange of two isotopes, e. g. $H \leftrightarrow D$, or two atoms which are similar in their bonding properties and have the same electron configurations in their outer shells, e. g. $O \leftrightarrow S$, the bond strength remains unchanged. While the reduced mass m_r thus is different after the exchange, the force constant k remains the same. The relation between the wavenumber $\bar{\nu}$ of the oscillation and the reduced mass m_r of the functional groups for the same force constant is then according to (1)

$$\bar{\nu} \propto \frac{1}{\sqrt{m_r}}. \quad (2)$$

The frequency of the O–D stretching vibration can be estimated from the value for the O–H vibration:

$$\bar{\nu}_{O-D} \approx \bar{\nu}_{O-H} \sqrt{\frac{m_{r,OH}}{m_{r,OD}}} \quad (3)$$

and with $\bar{\nu}_{O-H} = 3600 \text{ cm}^{-1}$:

$$\bar{\nu}_{O-D} \approx 2620 \text{ cm}^{-1}.$$

Since the force constant of the C–S group is comparable at most with that of the C–O single bond, but not with that of the C=S double bond (different bonding character), they can be estimated as:

$$\bar{\nu}_{C-S} \approx \bar{\nu}_{C-O} \sqrt{\frac{m_{r,CO}}{m_{r,CS}}} \quad (4)$$

and with $\bar{\nu}_{C-O} = 1150 \text{ cm}^{-1}$:

$$\bar{\nu}_{C-S} \approx 1020 \text{ cm}^{-1}.$$

10.10 The problem can be solved only in the harmonic-oscillator approximation with the given data.

a) The energy levels G_v of the harmonic oscillator are

$$G_v = \bar{\nu}_e \left(v + \frac{1}{2} \right). \quad (1)$$

The vibrational constant $\bar{\nu}_e$ corresponds here to the energy of the fundamental oscillation of the harmonic oscillator and can be computed from the force constant k and the reduced mass $m_r = 1.6266 \cdot 10^{-27}$ kg of the HCl molecule from

$$\bar{\nu}_e = \frac{\omega_e}{2\pi c} = \frac{1}{2\pi c} \sqrt{\frac{k}{m_r}}, \quad (2)$$

leading to

$$\bar{\nu}_e = 2991.3 \text{ cm}^{-1}.$$

For $v = 0$, the zero-point energy is found to be

$$G_0 = \frac{1}{2} \bar{\nu}_e \quad (3)$$

or

$$G_0 = 1495.7 \text{ cm}^{-1}.$$

b) To calculate the rotational-vibrational spectrum, we need the rotational constant B . It can be determined from the equilibrium bond length R_e and the reduced mass m_r according to

$$B = \frac{h}{8\pi^2 c m_r R_e^2}, \quad (4)$$

leading to the result

$$B = 10.59 \text{ cm}^{-1}.$$

c) Without taking centrifugal stretching and vibrational stretching into account, the energy terms of the states with vibrational quantum number v and rotational quantum number J are given by

$$G(v, J) = \bar{\nu}_e \left(v + \frac{1}{2} \right) + B J(J+1). \quad (5)$$

The lines of the rotational-vibrational spectrum are found from the transition energies between the states (v'', J'') and (v', J') , with the convention $v' > v''$, to be

$$\bar{\nu}(v', v''; J', J'') = G(v', J') - G(v'', J'') \quad (6)$$

$$= \bar{\nu}_e (v' - v'') + B [J'(J'+1) - J''(J''+1)]. \quad (7)$$

For the fundamental oscillation, $v' = 1$ and $v'' = 0$, so that Eq. (7) can be simplified to

$$\bar{\nu}(J', J'') = \bar{\nu}_e + B [J'(J'+1) - J''(J''+1)]. \quad (8)$$

From this we obtain

$$\begin{aligned} \text{for the } P \text{ branch} \quad (J' = J'' - 1): \bar{\nu}(J'') &= \bar{\nu}_e - 2B J'' \\ \text{for the } R \text{ branch} \quad (J' = J'' + 1): \bar{\nu}(J'') &= \bar{\nu}_e + 2B (J'' + 1) . \end{aligned}$$

Finally, one computes from these expressions the innermost three lines of the P and R branches:

$$\begin{aligned} P_{(1)} : J'' = 1 &\Rightarrow \bar{\nu} = 2970.12 \text{ cm}^{-1} \\ P_{(2)} : J'' = 2 &\Rightarrow \bar{\nu} = 2948.94 \text{ cm}^{-1} \\ P_{(3)} : J'' = 3 &\Rightarrow \bar{\nu} = 2927.76 \text{ cm}^{-1} \\ R_{(0)} : J'' = 0 &\Rightarrow \bar{\nu} = 3012.48 \text{ cm}^{-1} \\ R_{(1)} : J'' = 1 &\Rightarrow \bar{\nu} = 3033.66 \text{ cm}^{-1} \\ R_{(2)} : J'' = 2 &\Rightarrow \bar{\nu} = 3054.84 \text{ cm}^{-1} . \end{aligned}$$

d) Two qualitative differences are found between the spectrum calculated in (c) and the experimentally-determined spectrum.

On the one hand, chlorine is found in nature as an isotopic mixture of ^{35}Cl and ^{37}Cl in the ratio 3:1. Due to the different reduced masses of the two isotopically different HCl molecules, one observes two spectra which are shifted relative to each other and exhibit an intensity ratio of 3:1.

Secondly, another difference is due to vibrational stretching. It leads to a loss of validity of the Born-Oppenheimer approximation, since the internuclear distance now depends on the vibrational state. The rotational constants $B_{v'}$ and $B_{v''}$ are then different, and the transition energies from (7) are

$$\begin{aligned} \bar{\nu}(v', v''; J', J'') &= \bar{\nu}_e (v' - v'') + B_{v'} J' (J' + 1) \\ &\quad - B_{v''} J'' (J'' + 1) . \end{aligned} \quad (9)$$

For the P branch, ($J' = J'' - 1$) follows from a simple rearrangement

$$\begin{aligned} \bar{\nu}_P &= \bar{\nu}_e (v' - v'') - 2B_{v''} (J' + 1) \\ &\quad - (B_{v''} - B_{v'}) J' (J' + 1) . \end{aligned} \quad (10)$$

Since the internuclear distance is greater in the higher state v' than in the state with v'' , and therefore $B_{v''} > B_{v'}$, the lines of the P branch shift further apart with increasing J' (i. e. in the direction towards the outside of the vibrational band).

For the R branch ($J' = J'' + 1$), from (9) we find

$$\begin{aligned} \bar{\nu}_R &= \bar{\nu}_e (v' - v'') + 2B_{v''} (J'' + 1) \\ &\quad - (B_{v''} - B_{v'}) (J'' + 1)(J'' + 2) . \end{aligned} \quad (11)$$

Since $B_{v''} > B_{v'}$, the lines in the R branch move closer together with increasing J'' , until they finally reverse along the wavenumber axis and shift towards the centre of the band. The R branch thus exhibits a sharp edge.

10.11 The selection rules for the rotational-vibrational transition $(v'', J'', M'') \rightarrow (v', J', M'_J)$ with $M_J = -J, \dots, +J$ are given by

$$\Delta v = 0, \pm 1, \pm 2, \dots$$

$$\Delta J = \pm 1$$

$$\text{and } \Delta M_J = 0, \pm 1.$$

In the *P* branch, ($J' = J'' - 1$), the degree of degeneracy of the absorbing state is $2J'' + 1$, since the $M_{J''}$ values run from $-J''$ to $+J''$. In contrast, in the state J' , the quantum number $M_{J'}$ can take on only values from $-(J'' - 1)$ to $(J'' - 1)$. For $\Delta M_J = -1, 0$ or $+1$ there are thus exactly $2J'' - 1$ subtransitions, so that all together, $6J'' - 3 = 6J' + 3$ subtransitions are possible.

In the *R* branch, ($J' = J'' + 1$), $M_{J'}$ can take on values from $-(J'' + 1)$ to $(J'' + 1)$, and there are in each case $2J'' + 1$ subtransitions for $\Delta M_J = -1, 0, +1$. All together, one thus obtains $6J'' + 3$ subtransitions.

With the definition $J = \min(J', J'')$, for both branches there are $3 \cdot (2J + 1)$ subtransitions with $\Delta M_J = 0, \pm 1$. If each subtransition makes the same contribution to the line intensity, the latter is proportional to the product of the number of subtransitions times the thermal population of the absorbing state. The ratio of a line intensity to that of the first line of the *R*-branch is then given by

$$\begin{aligned} \frac{I_{v'', J'' \rightarrow v', J'}}{I_{v'', 0 \rightarrow v', 1}} &= \frac{3(2J + 1)}{3} e^{-\frac{hc}{kT} B_{v''} [J''(J''+1)-0]} \\ &= (2J + 1) e^{-\frac{hc}{kT} B_{v''} J''(J''+1)}. \end{aligned}$$

10.12 As derived in problem (10.10d), the positions of the lines in the *R* branch ($J' = J'' + 1$) of the rotational-vibrational spectrum of a diatomic molecule such as HCl are found from

$$\begin{aligned} \bar{\nu}_R &= \bar{\nu}_e(v' - v'') + 2B_{v''}(J'' + 1) \\ &\quad - (B_{v''} - B_{v'}) (J'' + 1)(J'' + 2). \end{aligned} \quad (1)$$

With increasing J'' , the lines move closer together, until finally at J_K a direction reversal along the wavenumber axis occurs. J_K is the level which forms the band edge of the *R* branch.

The spacing between two neighbouring lines in the *R* branch with $J'' = J_K$ and $J'' = J_K + 1$ is

$$\Delta \bar{\nu}_R = \dots = 2B_{v''} - 2(B_{v''} - B_{v'})(J_K + 2). \quad (2)$$

At the band edge, $\Delta \bar{\nu}_R$ becomes negative, so that with $B_{v''} > B_{v'}$, the value of the rotational quantum number J_K can be calculated:

$$J_K > \frac{B_{v''}}{B_{v''} - B_{v'}} - 2. \quad (3)$$

From $B_{v''} = B_0$ and $B_{v'} = B_1$, one finds

$$J_K > 32.46 \Rightarrow J_K = 33.$$

Beyond $J_K + 1 = 34$, the line of the R branch move again towards the centre of the band. The line corresponding to J_K forms the band edge. From (1), it follows for the fundamental vibrational band that

$$\begin{aligned} \bar{\nu}_R(J_K) &= \bar{\nu}(1, 0) + 2B_0(J_K + 1) \\ &\quad - (B_0 - B_1)(J_K + 1)(J_K + 2) \end{aligned} \quad (4)$$

and, with the given value of $\bar{\nu}(1, 0)$, the band edge is at

$$\bar{\nu}_R(J_K) = 3235.25 \text{ cm}^{-1}.$$

(For comparison: $\bar{\nu}_R(J_K - 1) = 3234.97 \text{ cm}^{-1}$ and $\bar{\nu}_R(J_K + 1) = 3234.92 \text{ cm}^{-1}$.)

10.13 If we wish to describe a diatomic molecule using the model of an anharmonic oscillator, the Morse potential is often used:

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

(R : internuclear distance; R_e : equilibrium internuclear distance or equilibrium bond length). It reproduces an approximately parabolic potential curve in the neighbourhood of the equilibrium internuclear distance, and takes the effect of nuclear repulsion for small R and the transition to a continuum for large R into account.

The prefactor D_e determines the gap between the equilibrium potential and the edge of the continuum and can be determined from the anharmonicity constant

$$x_e = \frac{\hbar\omega_e}{4D_e}, \quad (2)$$

yielding

$$D_e = \frac{hc\bar{\nu}_e^2}{4x_e\bar{\nu}_e}. \quad (3)$$

With the given values for $\bar{\nu}_e$ and $x_e\bar{\nu}_e$, one obtains

$$D_e = 15\,505 \text{ cm}^{-1}.$$

The parameter a is related to D_e and the reduced mass m_r of the molecule via

$$a = \omega_e \sqrt{\frac{m_r}{2D_e}} = 2\pi c\bar{\nu}_e \sqrt{\frac{m_r}{2D_e}}. \quad (4)$$

Using the atomic masses $M_H = 1.008 \text{ g/mole}$ and $M_{Rb} = 85.47 \text{ g/mole}$, one finds $m_r = 1.654 \cdot 10^{-27} \text{ kg}$ and thus

$$a = 9.144 \cdot 10^7 \text{ cm}^{-1}.$$

The rotational constant B at the equilibrium distance R_e is found from

$$B = \frac{h}{8\pi^2 c m_r R_e^2} \quad (5)$$

with the given values to be

$$B = 3.02 \text{ cm}^{-1}$$

and the rotational constant $B(R)$, which depends on the internuclear distance, is

$$B(R) = \frac{R_e^2}{R^2} B. \quad (6)$$

As a result, the rotational energy (in cm^{-1}) is given by

$$E_{\text{rot}}(R) = B(R) J(J+1) = B R_e^2 J(J+1) \cdot \frac{1}{R^2}. \quad (7)$$

The effective potential of the rotating anharmonic oscillator RbH is finally obtained as the sum of a pure Morse potential and the rotational energy:

$$V_{\text{eff}}(R) = V(R) + E_{\text{rot}}(R). \quad (8)$$

As the rotational quantum number J increases, the bond is weakened, until it finally becomes unstable. This phenomenon is based upon the fact that with decreasing internuclear distance, the rotational energy increases, while for $R > R_e$, the potential (Morse) energy decreases. Beyond a certain value of J , the effective potential based on the sum of these two energies no longer has a minimum; cf. Fig. S.21.

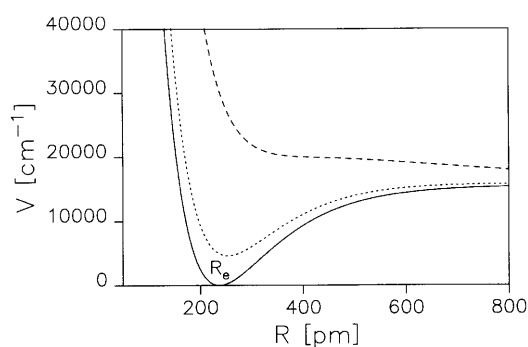


Fig. S.21. A graph of the (effective) potential of the anharmonic oscillator RbH vs. internuclear distance --- $J = 100$ $J = 40$ — $J = 0$

10.14 a) The positions of the vibrational levels of the anharmonic oscillator $^1\text{H}^{35}\text{Cl}$ are described by

$$G_v = \bar{\nu}_e \left(v + \frac{1}{2} \right) - x_e \bar{\nu}_e \left(v + \frac{1}{2} \right)^2. \quad (1)$$

From this we find the transition energies (selection rule $\Delta v = 1$) to be

$$\bar{\nu}_{v \rightarrow v+1} = G_{v+1} - G_v = \bar{\nu}_e [1 - 2x_e (v + 1)]. \quad (2)$$

A numerical fit of the function $G(v)$ to the given energy values yields as fit parameters the vibrational constant $\bar{\nu}_e$ and the anharmonicity constant x_e , Figs. S.22 and S.23.

The function G_v computed in this way shows clearly that with increasing vibrational quantum number v , the spacing between neighbouring levels becomes smaller.

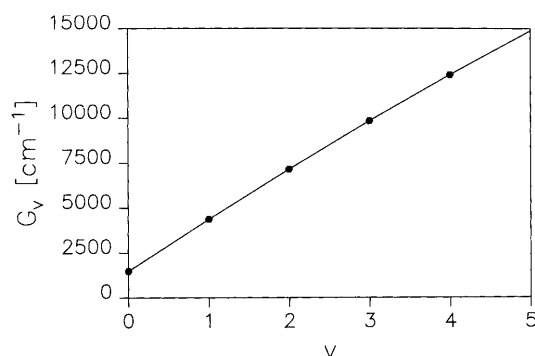


Fig. S.22. A graph of the energy values G_v : measured points and fit curve (fit parameters: vibrational constant $\bar{\nu}_e = 2989.74 \text{ cm}^{-1}$; anharmonicity constant $x_e = 0.0174$)

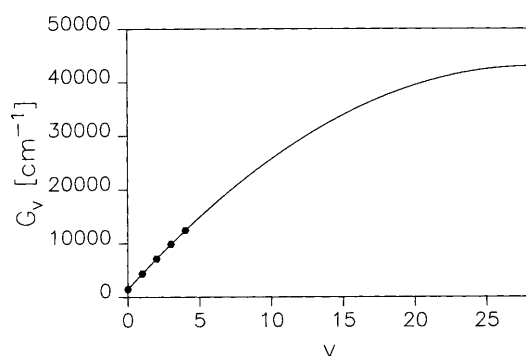


Fig. S.23. Extrapolation of the fitted function G_v out to its maximum

The values for $\bar{\nu}_e$ and x_e can just as well be obtained from a plot of the data for $\bar{\nu}_{v \rightarrow v+1}$ with a straight-line fit. A purely algebraic solution of the over-determined system of equations is also readily possible.

The anharmonicity constant x_e is related to the distance D_e between the energy minimum of the Morse potential and the edge of the continuum as well as the vibrational constant $\bar{\nu}_e$ through

$$x_e = \frac{\hbar\omega_e}{4D_e} = \frac{hc\bar{\nu}_e}{4D_e} . \quad (3)$$

From this, the dissociation energy D_0 can be computed by subtracting the zero-point energy of the oscillator, G_0 from D_e :

$$D_0 = D_e - hc G_0 = \frac{hc\bar{\nu}_e}{4x_e} - hc G_0 ; \quad (4)$$

with the values obtained above, we find

$$D_0 = 8.239 \cdot 10^{-19} \text{ J} = 5.14 \text{ eV} = 41\,474 \text{ cm}^{-1} .$$

b) Since the Morse potential curves of isotopic molecules are to a first approximation identical, the values of the potential minimum D_e , the equilibrium internuclear distance R_e , and the force constant k associated with the potential parameter a are the same for the bond in the deuterated molecule $^2\text{D}^{35}\text{Cl}$ as those for $^1\text{H}^{35}\text{Cl}$. The reduced masses of the two isotopic molecules are however different (in the following, HCl will be denoted by the index 1, and DCl by the index 2):

$$\begin{aligned} m_{r,1}\text{H}^{35}\text{Cl} &= 1.6266 \cdot 10^{-27} \text{ kg} \equiv m_1 \\ m_{r,2}\text{D}^{35}\text{Cl} &= 3.1623 \cdot 10^{-27} \text{ kg} \equiv m_2 . \end{aligned}$$

Due to the identical force constants, one finds

$$k = m_1\omega_{e,1}^2 = m_2\omega_{e,2}^2 . \quad (5)$$

From this, we obtain the ratio of the vibrational constants:

$$\frac{\bar{\nu}_{e,2}}{\bar{\nu}_{e,1}} = \frac{\omega_{e,2}}{\omega_{e,1}} = \sqrt{\frac{m_1}{m_2}} \equiv \gamma , \quad (6)$$

and with

$$\gamma = 0.7172$$

the vibrational constant $\bar{\nu}_{e,2}$ for DCl:

$$\bar{\nu}_{e,2} = 2144.23 \text{ cm}^{-1} .$$

The heavy isotope thus vibrates more slowly than the light one. The anharmonicity constant is obtained from (3) with $D_{e,2} = D_{e,1}$, so that

$$\frac{x_{e,2}}{x_{e,1}} = \frac{\omega_{e,2}}{\omega_{e,1}} = \gamma \quad (7)$$

and thus for DCl

$$x_{e,2} = 0.0125 .$$

The heavy isotope remains closer to its equilibrium position during the vibration, it does not move as far onto the flat portion of the Morse potential as the light isotope; so it thus experiences less anharmonicity.

The rotational constants B are inversely proportional to the moments of inertia and, due to the identical equilibrium internuclear distance, also to the reduced masses of the isotopic molecules:

$$\frac{B_2}{B_1} = \frac{m_1}{m_2} = \gamma^2 . \quad (8)$$

Using the value of B_1 given for HCl, we obtain B_2 for DCl:

$$B_2 = 5.45 \text{ cm}^{-1} .$$

The rotational structure of the heavier molecule is thus more finely spaced than that of the light molecule.

c) From (1), for $v = 0$ we can derive the zero-point energy $G_{0,2}$ of the anharmonic oscillator DCl:

$$G_{0,2} = \frac{1}{2} \bar{\nu}_{e,2} \left(1 - \frac{1}{2} x_{e,2} \right) . \quad (9)$$

Making use of the values calculated in part (b), we find

$$G_{0,2} = 1065.41 \text{ cm}^{-1}$$

and thus at constant D_e the dissociation energy $D_{0,2}$ of DCl:

$$\begin{aligned} D_{0,2} &= D_e - G_{0,2} \\ D_{0,2} &= 8.32 \cdot 10^{-19} \text{ J} = 5.19 \text{ eV} = 41\,891 \text{ cm}^{-1} . \end{aligned} \quad (10)$$

The difference of the dissociation energies of the two isotopic molecules can be used for their laser photochemical separation. An isotopic mixture HCl/DCl is excited by intense laser light at ca. $41\,700 \text{ cm}^{-1} \hat{=} 240 \text{ nm}$; this is possible e. g. with a frequency-doubled dye laser. Since the energy of the photons lies between the dissociation energies of the two isotopes, it is sufficient to break the HCl bonds while the DCl molecule remains stable. With additional separation procedures one can then sort out the remaining DCl molecules.

10.15 The SO_2 molecule exhibits three normal modes of vibration, which are similar to those of the water molecule. Since in both cases the dipole moment of the molecule undergoes a change, all of the vibrational modes are IR active. In the symmetrical vibrational mode $\bar{\nu}_1$, only the bond lengths change to first approximation, while the bond angle Θ remains constant. In contrast, in the $\bar{\nu}_2$ mode, mainly the normal coordinate Θ varies, while the bond lengths change only a little. In polyatomic molecules, vibrations can change the symmetry of the electronic wavefunction. The electronic transition dipole moments thus contain coupled electronic/vibronic matrix elements, and a large value of the vibronic overlap integral leads to intense lines. In the case of SO_2 , the overlap of the “bending oscillation” $\bar{\nu}_2$ with the geometric variation between the ground and the excited state is greatest (the bond angle Θ changes and the bond lengths remain constant). The 0–0 transition is thus followed by an intense vibrational series with line spacing $\bar{\nu}_2$. Although the other vibrational modes are also IR active, they are observed with much lower intensities.

Chapter 11

11.1 Angular momentum and the Born-Oppenheimer Approximation

We consider a triatomic molecule:

$$H = - \sum_j \frac{\hbar^2}{2m_j} \Delta_j + V(\mathbf{R}_{31}, \mathbf{R}_{32}); \quad \mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j. \quad (1)$$

Let V be invariant with respect to common rotations of the \mathbf{R}_{ij} .

Total angular momentum:

$$\mathbf{L} = \sum_i \mathbf{L}_i = \sum \text{nuclear angular momenta}. \quad (2)$$

Total momentum:

$$\mathbf{P} = \sum_i \mathbf{P}_i = \sum \text{momenta of the nuclei} \quad (3)$$

with

$$\mathbf{L}_i = \mathbf{R}_i \times \mathbf{P}_i \quad (4)$$

and

$$H = \sum_i \frac{\mathbf{P}_i^2}{2m_i} + V = H_0 + V. \quad (5)$$

Consider the commutation relation:

$$[H_0, \mathbf{L}] = \sum_{ij} \frac{1}{2m_i} [\mathbf{P}_i^2, \mathbf{L}_j]. \quad (6)$$

For $i = j$ and considering the example of L_z , we find (without index)

$$\left[\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right), \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \right] f(x, y, z) = 0. \quad (7)$$

For $i \neq j$, the following results hold:

$$[P_i, L_j] = P_i L_j - L_j P_i = 0 \quad \text{due to different nuclei.} \quad (8)$$

$$[H_0, L] = 0. \quad (9)$$

Consider

$$[V, L]. \quad (10)$$

Due to rotational invariance, V commutes with the rotation operators $D(\alpha, \beta, \gamma) = D_z(\alpha)D_y(\beta)D_x(\gamma)$, where

$$D(\phi) = e^{-\frac{i}{\hbar} L_z \alpha} \cdot e^{-\frac{i}{\hbar} L_y \beta} \cdot e^{-\frac{i}{\hbar} L_x \gamma}. \quad (11)$$

Treating α, β, γ as infinitesimal quantities, we find also that

$$[V, L] = 0, \quad (12)$$

as one can show through a series expansion of (11).

Chapter 12

12.1 Since the H_2 molecule has no permanent electric dipole moment, the pure rotational spectrum cannot be observed as a microwave absorption spectrum. Instead, one employs Raman spectroscopy.

The condition for Raman activity of this molecule is a change in its polarisability on rotation. Since the length of each principal axis i of the polarisability ellipsoid is proportional to $1/\sqrt{\alpha_i}$ (α_i : polarisability in the direction i), its sections perpendicular to the molecular axis are circular. The section in the plane containing the molecular axis is, in contrast, for non-spherically-symmetric molecules always a non-degenerate ellipse. Upon rotation of the molecule about an axis which is not the molecular symmetry axis, the polarisability in the plane of polarisation of the exciting light thus changes, so that the pure rotational spectrum can be observed by applying Raman spectroscopy.

The rotational states of the molecule are given in first approximation by

$$F_J = B J(J+1). \quad (1)$$

In the Raman spectrum, the selection rule for optical transitions is $\Delta J = \pm 2$; the distance of the lines from the band origin is therefore:

$$\bar{\nu}_J = \bar{\nu}_{J \rightarrow J+2} = B(4J+6) \quad (2)$$

and the spacing of two neighbouring rotational Raman lines is:

$$\Delta \bar{\nu} = \bar{\nu}_{J+1} - \bar{\nu}_J = 4B. \quad (3)$$

The rotational constant

$$B = \frac{h}{8\pi^2 c \Theta} = \frac{h}{8\pi^2 c m_r R_e^2} \quad (4)$$

can be calculated using the atomic mass $m_H = 1.673 \cdot 10^{-27}$ kg, the reduced mass $m_r = \frac{1}{2} m_H$, and the equilibrium bond length $R_e = 0.7414$ Å; the result is

$$B = 60.829 \text{ cm}^{-1}.$$

From (3), we find the spacing of neighbouring spectral lines:

$$\Delta \bar{\nu} = 243.3 \text{ cm}^{-1}.$$

12.2 Every molecule whose polarisability ellipsoid is non-spherical in the ground state (i.e. not spherical tops) exhibits a pure rotational Raman spectrum, since its polarisability in the plane of polarisation of the exciting light changes when it rotates.

Except for the molecules CH_4 and SF_6 , which each have spherical symmetry, all the molecules listed exhibit a pure rotational Raman spectrum.

12.3 If the electric dipole moment of a molecule changes on oscillation, then it is IR active. A mode of oscillation is, on the other hand, Raman active, if the oscillation produces a periodic change of the polarisability.

Molecules with a centre of inversion exhibit a complementary IR activity and Raman activity of their oscillation modes: an oscillation is either IR active or Raman active.

We thus observe the following behaviour:

N_2 :	only Raman active.
C_2H_4 :	planar structure with a centre of inversion: Raman and IR complementarity.
CH_3OH :	no centre of inversion, dipole moment and polarisability change, thus both Raman and IR activity.
HD :	only different isotopes, behaves like a homonuclear, diatomic molecule: only Raman activity.
CCl_4 :	tetrahedral structure, no centre of inversion: Raman active; asymmetric bending and stretch vibrations are also IR active.
CS_2 :	linear, centre of inversion: Raman and IR complementarity.
SO_2 :	bent, no centre of inversion: both Raman and IR.
NH_3 :	pyramidal: both Raman and IR activity.
BeCl_2 :	exists in the gas phase at $T > 750^\circ\text{C}$ as a linear molecule with a centre of inversion: Raman and IR complementarity.
CH_3COCH_3 :	no centre of inversion: both Raman and IR activity.
$(\text{CO})_5\text{Re}-\text{Re}(\text{CO})_5$:	centre of inversion: Raman and IR complementarity.

12.4 The ammonia molecule, NH_3 , is a symmetric top, whose symmetry axis passes through the N atom. The two principal moments of inertia perpendicular and parallel to the axis of symmetry have the values

$$\Theta_{\perp} = 2.86 \cdot 10^{-47} \text{ kg m}^2 \quad \text{and} \quad \Theta_{\parallel} = 4.38 \cdot 10^{-47} \text{ kg m}^2.$$

The rotational constants B and C can be calculated from these values:

$$B = \frac{h}{8\pi^2 c \Theta_{\perp}} \quad \text{and} \quad C = \frac{h}{8\pi^2 c} \left(\frac{1}{\Theta_{\parallel}} - \frac{1}{\Theta_{\perp}} \right), \quad (1)$$

leading to $B = 9.78 \text{ cm}^{-1}$ and $C = -3.39 \text{ cm}^{-1}$. The positions of the rotational levels are given by

$$F(J, K) = B J(J+1) + C K^2$$

with $K = 0, \pm 1, \pm 2, \dots, \pm J$. (2)

Here, the quantum number J denotes the total angular momentum of the molecule, while K refers to rotation around the axis of symmetry:

$$|L_{\parallel}| = \hbar K. \quad (3)$$

The rotation around the symmetry axis is not Raman active, since the polarisability of the molecule remains unchanged during this rotation. The first selection rule for Raman transitions in symmetric-top molecules follows from this:

$$\Delta K = 0. \quad (4)$$

For a change in the quantum number J of the total angular momentum, in contrast, we find

$$\Delta J = 0, \pm 1, \pm 2 \quad \text{for} \quad K \neq 0, \quad (5)$$

$$\Delta J = \pm 2 \quad \text{for} \quad K = 0. \quad (6)$$

In the special case of the symmetric top, we thus observe that for all rotational states with $J \neq 0$, Raman transitions with $\Delta J = \pm 1$ are allowed. The Raman spectrum consists of a superposition of the two subspectra with $\Delta J = \pm 1$ (P and R branches) and $\Delta J = \pm 2$ (O and S branches).

If J' and J'' are the rotational levels of the molecule before and after the Raman scattering process, with $\Delta J = J'' - J'$, then we find from (2), taking the selection rules (4–6) into account, the pure rotational Raman shift $\Delta \bar{\nu} = F_{J'} - F_{J''}$ of the scattered light relative to the primary light for the Stokes lines:

S branch:

$$\Delta J = +2 \Rightarrow \Delta \bar{\nu} = -B(4J' + 6) \quad (J' = 0, 1, 2, \dots)$$

R branch:

$$\Delta J = +1 \Rightarrow \Delta \bar{\nu} = -2B(J' + 1) \quad (J' = 1, 2, 3, \dots)$$

Anti-Stokes- lines:

O branch:

$$\Delta J = -2 \Rightarrow \Delta \bar{\nu} = B(4J' - 2) \quad (J' = 2, 3, 4, \dots)$$

P branch:

$$\Delta J = -1 \Rightarrow \Delta \bar{\nu} = 2B J' \quad (J' = 2, 3, 4, \dots).$$

The wavelength of the primary light (N₂-Laser) lies at $336.732 \text{ nm} \hat{=} 29\,697.2 \text{ cm}^{-1}$. For the innermost Raman lines, we obtain the following positions:

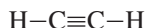
$J' =$		0	1	2	3
Stokes:	<i>S</i> branch	29 638.5 cm^{-1}	29 599.4 cm^{-1}	29 560.3 cm^{-1}	29 521.2 cm^{-1}
		337.39 nm	337.84 nm	338.29 nm	338.73 nm
	<i>R</i> branch		29 658.1 cm^{-1}	29 638.5 cm^{-1}	29 619.0 cm^{-1}
Anti-Stokes:	<i>O</i> branch		337.17 nm	337.39 nm	337.62 nm
				29 755.9 cm^{-1}	29 795.0 cm^{-1}
	<i>P</i> branch			336.06 nm	335.62 nm
				29 736.3 cm^{-1}	29 755.9 cm^{-1}
				336.28 nm	336.06 nm

See also Fig. S.24.

12.5 a) IR and Raman lines do not occur together, they are complementary (cf. problem 12.3). From this we can conclude that the molecule A₂B₂ has a centre of inversion. Since an IR line with PR structure is observed, it must also be a linear molecule. The general structure formula is thus



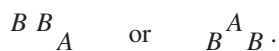
The number of normal vibrations is $f = 3N - 5 = 7$, where however twice two bending vibrations are degenerate; there remain five non-equivalent vibrations. Since the two most energetic modes lie in the range of the C–H stretching vibration, the given frequencies can be associated to the normal vibrations of the molecule



as follows:

1) 3374 cm^{-1}	$\longleftrightarrow \longleftrightarrow$	Raman active	symmetric stretching vibration C–H
2) 3287 cm^{-1}	$\longleftrightarrow \rightarrow \leftarrow$	IR active (PR)	asymmetric stretching vibration C–H
3) 1973 cm^{-1}	$\leftarrow \leftarrow \rightarrow \rightarrow$	Raman active	symmetric stretching vibration C≡C
4) 729 cm^{-1}	$\uparrow \downarrow \uparrow$	IR active (PQR)	bending vibration
5) 612 cm^{-1}	$\uparrow \downarrow \uparrow \downarrow$	Raman active	bending vibration
		(weak)	

b) Since one of the vibrations is both IR and also Raman active, the molecule AB₂ cannot have a centre of inversion. Owing to the complex structure of the infrared bands, it must be a bent molecule:



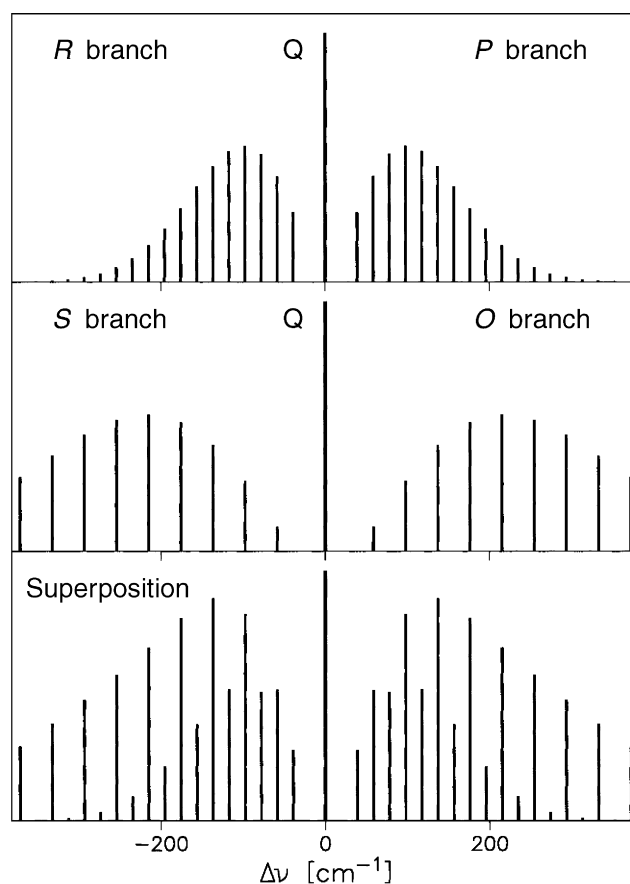
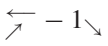




Fig. S.24. Rotational Raman spectrum of the symmetric-top molecule NH_3 : superposition of the two series with $\Delta J = \pm 1$ (above: *R* and *P* branch) and $\Delta J = \pm 2$ (centre: *S* and *O* branch). below: superposed spectrum; every second line of the *R* and *P* branches falls together with a line of the *S* and *O* branches. This causes the alternating line intensities

Both structures lead to three vibrational modes. From data on the polarisation of Raman lines, one obtains information about whether the vibrational mode is symmetric or asymmetric: in the case of a symmetric molecule, a symmetric vibration leads to an isotropic deformation of the polarisability ellipsoid, so that polarised primary light remains polarised after Raman scattering. Asymmetrical vibrations produce an anisotropic deformation of the polarisability ellipsoid with the result that the molecules are arbitrarily oriented and lead to a depolarisation of the scattered light.

The two most energetic vibrations lie in the range of the O–H stretching vibration, so that the observed modes can be attributed to the molecule



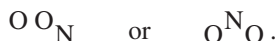
- | | | | | |
|----|------------------------|---|---------------------------------|---------------------------------|
| 1) | 3756 cm^{-1} |  | IR active | asymmetric stretching vibration |
| 2) | 3652 cm^{-1} |  | IR and Raman active (polarised) | symmetric stretching vibration |
| 3) | 1595 cm^{-1} |  | IR active | bending vibration |

The frequencies of the bending vibrations are in general lower than those of the stretching vibrations; also even if they are in principle Raman active, the intensity of the lines is often so weak that they are not observed.

12.6 Since both molecules have vibrational modes which are both IR and also Raman active (i. e. the IR and Raman active modes are not complementary), neither N_2O nor NO_2 can have a centre of inversion symmetry. Due to the PR structure of its IR bands, N_2O must be linear. The only remaining possible structure is thus



In contrast, the complex rotational structure of the IR bands of NO_2 indicate that this molecule is not linear. On the basis of the available information, we can give two possible molecular structures:



12.7 In *diatomic homonuclear molecules*, the nuclear spin I of the two identical nuclei A and B ($I = I_A = I_B$) has an influence on the molecular statistics, i. e. on the probability that a particular molecular state will occur. Under the assumption of decoupled partial motions, the *total wavefunction* of the molecule can be written in terms of a product state:

$$\Psi(\mathbf{r}_A, \sigma_A, \mathbf{r}_B, \sigma_B, \mathbf{r}_i, \sigma_i) \quad (1)$$

$$= \Psi^{\text{KS}}(\sigma_A, \sigma_B) \Psi^{\text{ES}}(\sigma_i) \Psi^{\text{el}}(R, \mathbf{r}_i) R^{-1} \Psi^{\text{vib}}(R) \Psi^{\text{rot}}(\theta, \phi)$$

$$= \Psi^{\text{KS}}(\sigma_A, \sigma_B) \Psi^{\text{R}}(\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_i, \sigma_i) \quad (2)$$

with $\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_i$: coordinates of the nuclei A and B and of the electrons i in the centre-of-mass system;

R : internuclear distance;

Ψ^{KS} : nuclear spin state;

Ψ^{ES} : electronic spin state;

Ψ^{el} : solution of the Schrödinger equation for the two-centre problem with fixed nuclei (Born-Oppenheimer approximation);

Ψ^{vib} : state of the harmonic oscillator;

Ψ^{rot} : state of the rigid rotor.

Upon *exchange of the identical nuclei A and B*, Ψ^{KS} is multiplied by a factor $(-1)^\kappa$, and the “remainder wavefunction” Ψ^{R} by a factor $(-1)^\varrho$. The parity of the total wavefunction, i. e. its behaviour under exchange of the nuclei, $A \leftrightarrow B$, can be mathematically described by

$$\Psi(\mathbf{r}_B, \sigma_B, \mathbf{r}_A, \sigma_A, \mathbf{r}_i, \sigma_i) = (-1)^{\kappa+\varrho} \Psi(\mathbf{r}_A, \sigma_A, \mathbf{r}_B, \sigma_B, \mathbf{r}_i, \sigma_i). \quad (3)$$

Since the parity of the wavefunction is independent of internal interactions (couplings), it can be determined from the product state (1) [if coupling is present: series expansion of the wavefunction in terms of product states with the same $(-1)^{\kappa+\varrho}$].

The behaviour of Ψ with respect to *inversion* of the spatial vectors of all the particles is described by the parity $(-1)^P$ (upper index of the term symbol: + for $P = 0$ or – for $P = 1$). Because spins are axial vectors, they are unaffected by spatial inversion, so that the spin wavefunctions Ψ^{KS} and Ψ^{ES} have positive parity. While the vibrational wavefunction $R^{-1} \Psi^{\text{vib}}$ depends only on the magnitude R of the internuclear distance and therefore remains unchanged upon inversion, the rotational function Ψ^{rot} in the state J is multiplied by $(-1)^J$. Finally, one imagines the inversion for the electronic eigenfunction Ψ^{el} to consist of two symmetry operations which are carried out one after the other: the first operation, a rotation of the molecule by 180° about an axis perpendicular to the molecular symmetry axis which passes through the centre of gravity, leaves Ψ^{el} unchanged; the following reflection through a plane perpendicular to the axis of rotation and containing the nuclei changes the relative coordinates and causes a modification of Ψ^{el} by a factor of $(-1)^s$.

The parity of the overall state under spatial inversion is thus

$$(-1)^P = (-1)^{J+s}. \quad (4)$$

Since the indices + and – of the term symbol refer to the rotational ground state $J = 0$, we have:

$$(-1)^s = +1 \iff s = 0 \quad \text{for } +, \quad (5)$$

$$(-1)^s = -1 \iff s = 1 \quad \text{for } -. \quad (6)$$

In order to understand the behaviour of the “remainder wavefunction” Ψ^{R} [without nuclear spins, cf. (1),(2)] under *exchange of the nuclear positions*, we likewise decompose this operation into two sequential symmetry operations: first, Ψ^{R} is multiplied by $(-1)^P$ on inversion of all the particles. Under the following inversion of the electrons alone, an additional factor of $(-1)^\pi$ occurs; it is denoted in the term symbol by the lower index g (for $\pi = 0$) or u (for $\pi = 1$). The two individual operations together amount to an exchange of the nuclei, while the electrons remain unaffected. The parity of Ψ^{R} under nuclear exchange is thus, taking account of (4), given by

$$(-1)^\varrho = (-1)^{P+\pi} = (-1)^{J+s+\pi}. \quad (7)$$

Finally, we need to investigate the behaviour of the *nuclear spin wavefunction* Ψ^{KS} under exchange of the identical nuclei *A* and *B* with nuclear spins $I_A = I_B = I$ and magnetic nuclear spin quantum numbers $M_I = -I, \dots, I$. The total nuclear spin of the molecule is found by vector addition of the two individual spins and can take on the values

$$I_{\text{ges}} = 2I, 2I - 1, \dots, 0. \quad (8)$$

From a quantum-mechanical analysis (cf. problem 12.8), we obtain the symmetric and antisymmetric states with positive or negative parity, $(-1)^K$:

for integral *I*:

$$\begin{aligned} I_{\text{ges}} = 2I, 2I - 2, \dots, 0 & \quad \text{symmetric} \\ I_{\text{ges}} = 2I - 1, 2I - 3, \dots, 1 & \quad \text{antisymmetric} \end{aligned}$$

for half-integral *I*:

$$\begin{aligned} I_{\text{ges}} = 2I, 2I - 2, \dots, 1 & \quad \text{symmetric} \\ I_{\text{ges}} = 2I - 1, 2I - 3, \dots, 0 & \quad \text{antisymmetric.} \end{aligned}$$

Each state I_{ges} is $(2I_{\text{ges}}+1)$ -fold degenerate; from this fact, one derives the *ratio of the statistical weights of the antisymmetric to the symmetric nuclear spin states* (cf. problem 12.10):

$$\frac{g_a}{g_s} = \frac{I}{I + 1}. \quad (9)$$

a) nuclear spin $I = 0$

Because nuclei with integer spins are Bosons, the total wavefunction Ψ must be symmetric under exchange of the nuclei, i. e. with (3) and (7):

$$(-1)^{K+Q} = (-1)^{K+J+s+\pi} \stackrel{!}{=} +1. \quad (10)$$

Only the symmetric nuclear spin state $I_{\text{ges}} = 0$ exists, so that

$$(-1)^K = +1. \quad (11)$$

From (10) and (11), it follows that:

$$(-1)^Q = (-1)^{J+s+\pi} \stackrel{!}{=} +1. \quad (12)$$

Now with (5) and (6) we have the result

– for even electronic terms (index g):

$$\pi = 0 \implies (-1)^{J+s} \stackrel{!}{=} +1$$

$$\implies \text{for terms with positive parity (index +): } s = 0 \implies (-1)^J \stackrel{!}{=} +1$$

only rotational states with even *J* exist.

example: $^1\Sigma_g^+, ^1\Pi_g^+$

\implies for terms with negative parity (index –):

$$s = 1 \implies (-1)^J \stackrel{!}{=} -1$$

only rotational states with odd *J* exist.

example: $^1\Sigma_g^-, ^3\Sigma_g^-, ^1\Pi_g^-$

- for odd electronic terms (index u):
 $\pi = 1 \implies (-1)^{J+s} \stackrel{!}{=} -1$
 \implies for terms with positive parity (index +):
 $s = 0 \implies (-1)^J \stackrel{!}{=} -1$
 only rotational states with odd J exist.
 example: $^1\Sigma_u^+, ^1\Pi_u^+$
 \implies for terms with negative parity (index -):
 $s = 1 \implies (-1)^J \stackrel{!}{=} +1$
 only rotational states with even J exist.
 example: $^1\Sigma_u^-, ^1\Pi_u^-$.

For terms with $\Lambda > 0$ (Π terms), there are in each case two states with + and - parity and the same J which are degenerate; thus, all the J values occur.

b) nuclear spin $I = 1$

The nuclei are again Bosons, so that here also, the total wavefunction must be symmetric:

$$(-1)^{\kappa+e} = (-1)^{\kappa+J+s+\pi} \stackrel{!}{=} +1. \quad (13)$$

We now must distinguish between symmetric and antisymmetric nuclear spin states:

- $I_{\text{ges}} = 2, 0$: Ψ^{KS} symmetric, $(-1)^\kappa = +1 \implies (-1)^e \stackrel{!}{=} +1$ [cf. (12)].
 degree of degeneracy: $5 + 1 = 6$.
- $I_{\text{ges}} = 1$: Ψ^{KS} antisymmetric, $(-1)^\kappa = -1 \implies (-1)^e \stackrel{!}{=} -1$
 degree of degeneracy: 3.

The ratio of the statistical weights of the antisymmetric to the symmetric nuclear spin states is, as can be expected from (9), given by

$$\frac{g_a}{g_s} = \frac{1}{2}. \quad (14)$$

For the individual electronic terms, the result is just as in (a); however, the population ratios between rotational states with even and odd J are not 1:0 or 0:1 (allowed/forbidden states), but instead 2:1 or 1:2. The states which can exclusively exist in (a) are here doubly populated in comparison to the states which are missing in (a).

12.8 The space of angular momenta $\varepsilon(j_1, j_2)$ is spanned by two angular momenta j_1 and j_2 . The states $|J, M\rangle$ are eigenvectors of the operators J^2 and J_z :

$$J^2 |J, M\rangle = J(J+1) \hbar^2 |J, M\rangle \quad (1)$$

$$J_z |J, M\rangle = M \hbar^2 |J, M\rangle \quad (2)$$

and in addition, like all the vectors in the space $\varepsilon(j_1, j_2)$, they are eigenvectors of J_1^2 and J_2^2 with the eigenvalues $j_1(j_1 + 1)\hbar^2$ and $j_2(j_2 + 1)\hbar^2$.

The angular-momentum space $\varepsilon(j_1, j_2)$ can be represented as the direct sum of invariant subspaces $\varepsilon(J)$:

$$\varepsilon(j_1, j_2) = \varepsilon(j_1 + j_2) \oplus \varepsilon(j_1 + j_2 - 1) \oplus \dots \oplus \varepsilon(|j_1 - j_2|) \quad (3)$$

The vectors $|J, M\rangle$, which span the subspaces, will be determined in general in the following.

The subspace $\varepsilon(J = j_1 + j_2)$

The ket vector $|j_1, j_2; m_1 = j_1, m_2 = j_2\rangle$ is the only eigenvector belonging to the eigenvalue $M = j_1 + j_2$ and, since J^2 and J_z commute, it is also an eigenvector of J^2 with the eigenvalue $J = j_1 + j_2$. With a suitable choice of the phase factor, we then have

$$|J = j_1 + j_2, M = j_1 + j_2\rangle = |j_1, j_2; m_1 = j_1, m_2 = j_2\rangle. \quad (4)$$

In order to find the remaining vectors $|J, M\rangle$ of the subspace $\varepsilon(j_1, j_2)$, we make use of the “ladder operator” J_- with

$$J_- |J, M\rangle = \hbar \sqrt{J(J+1) - M(M-1)} |J, M-1\rangle. \quad (5)$$

Application to the vector (4) yields

$$J_- |j_1 + j_2, j_1 + j_2\rangle = \hbar \sqrt{2(j_1 + j_2)} |j_1 + j_2, j_1 + j_2 - 1\rangle. \quad (6)$$

Due to $J_- = J_{1-} + J_{2-}$, it follows with (4) that

$$\begin{aligned} & |j_1 + j_2, j_1 + j_2 - 1\rangle \\ &= \frac{1}{\hbar \sqrt{2(j_1 + j_2)}} J_- |j_1 + j_2, j_1 + j_2\rangle \end{aligned} \quad (7)$$

$$= \frac{1}{\hbar \sqrt{2(j_1 + j_2)}} (J_{1-} + J_{2-}) |j_1, j_2; j_1, j_2\rangle \quad (8)$$

$$\begin{aligned} &= \frac{1}{\hbar \sqrt{2(j_1 + j_2)}} \left[\hbar \sqrt{2j_1} |j_1, j_2; j_1 - 1, j_2\rangle \right. \\ &\quad \left. + \hbar \sqrt{2j_2} |j_1, j_2; j_1, j_2 - 1\rangle \right] \end{aligned} \quad (9)$$

and thus

$$\begin{aligned} |j_1 + j_2, j_1 + j_2 - 1\rangle &= \sqrt{\frac{j_1}{j_1 + j_2}} |j_1, j_2; j_1 - 1, j_2\rangle \\ &+ \sqrt{\frac{j_2}{j_1 + j_2}} |j_1, j_2; j_1, j_2 - 1\rangle. \end{aligned} \quad (10)$$

This vector, which is already normalised, is a linear combination of the two basis vectors of $\varepsilon(j_1, j_2)$ which belong to $M = j_1 + j_2 - 1$. By repeated application of the operator J_- , we obtain the vectors of the subspace up to

$$|J = j_1 + j_2, M = -(j_1 + j_2)\rangle = |j_1, j_2; -j_1, -j_2\rangle. \quad (11)$$

In this way, all the $2(j_1 + j_2) + 1$ basis vectors $|J, M\rangle$ of the subspace $\varepsilon(j_1 + j_2)$ can be found.

The remaining subspaces $\varepsilon(J)$

In the subspace $\varepsilon(j_1 + j_2 - 1)$, $M = j_1 + j_2 - 1$ is the largest eigenvalue of J_z , and the associated eigenvector is $|J = j_1 + j_2 - 1, M = j_1 + j_2 - 1\rangle$. It can be expanded in terms of the basis vectors of $\varepsilon(j_1, j_2)$ with the eigenvalue $M = j_1 + j_2 - 1$:

$$\begin{aligned} |j_1 + j_2 - 1, j_1 + j_2 - 1\rangle &= \alpha |j_1, j_2; j_1, j_2 - 1\rangle \\ &+ \beta |j_1, j_2; j_1 - 1, j_2\rangle. \end{aligned} \quad (12)$$

The normalisation of this vector is determined by the condition

$$|\alpha|^2 + |\beta|^2 = 1. \quad (13)$$

From its orthogonality to the vector $|j_1 + j_2, j_1 + j_2 - 1\rangle$, which belongs to the subspace $\varepsilon(j_1 + j_2)$, it also follows with (10) that

$$\alpha \sqrt{\frac{j_2}{j_1 + j_2}} + \beta \sqrt{\frac{j_1}{j_1 + j_2}} = 0. \quad (14)$$

With a suitable choice of the phase factors, we obtain from (13) and (14) the relations

$$\begin{aligned} |j_1 + j_2 - 1, j_1 + j_2 - 1\rangle &= \sqrt{\frac{j_1}{j_1 + j_2}} |j_1, j_2; j_1, j_2 - 1\rangle \\ &- \sqrt{\frac{j_2}{j_1 + j_2}} |j_1, j_2; j_1 - 1, j_2\rangle. \end{aligned} \quad (15)$$

By repeated application of the operator J_- , one finds the $2(j_1 + j_2 - 1) + 1$ basis vectors which span the subspace $\varepsilon(j_1 + j_2 - 1)$.

Applying a corresponding procedure, one can finally generate all the basis vectors of all the subspaces. The eigenstates $|j_1, j_2; m_1, m_2\rangle$ of the operators $\mathbf{J}_1^2, \mathbf{J}_2^2, J_{1z}$ and J_{2z} are transformed thereby into eigenstates $|J, M\rangle$ of $\mathbf{J}_1^2, \mathbf{J}_2^2, \mathbf{J}^2$ and J_z . The coefficients which occur in the series expansion of the new basis vectors in terms of the old ones are called ‘‘Clebsch-Gordan coefficients’’.

a) The above formalism, developed for the general case, will now be applied to the special case of two nuclear spins $j_1 = I_A = 1$ and $j_2 = I_B = 1$. The total nuclear spin $I = I_A + I_B$ of the molecule can take on the values

$$I = 2, 1, 0. \quad (16)$$

The angular-momentum space $\varepsilon(1, 1)$ is thus decomposed into the subspaces $\varepsilon(I = 2)$, $\varepsilon(I = 1)$, and $\varepsilon(I = 0)$ with dimensions 5, 3 and 1.

The subspace $\varepsilon(I = 2)$

According to (4), the vector $|J = 2, M = 2\rangle$ can be written as

$$|2, 2\rangle = |1, 1; 1, 1\rangle. \quad (17)$$

Application of the ladder operator J_- leads –analogously to (10)– to

$$|2, 1\rangle = \frac{1}{\sqrt{2}} [|1, 1; 1, 0\rangle + |1, 1; 0, 1\rangle]. \quad (18)$$

Furthermore, one finds

$$|2, 0\rangle = \frac{1}{\sqrt{6}} [|1, 1; 1, -1\rangle + 2 |1, 1; 0, 0\rangle + |1, 1; -1, 1\rangle] \quad (19)$$

$$|2, -1\rangle = \frac{1}{\sqrt{2}} [|1, 1; 0, -1\rangle + |1, 1; -1, 0\rangle] \quad (20)$$

$$|2, -2\rangle = |1, 1; -1, -1\rangle \quad (21)$$

The subspace $\varepsilon(I = 1)$

The general result (15) now corresponds to

$$|1, 1\rangle = \frac{1}{\sqrt{2}} [|1, 1; 1, 0\rangle - |1, 1; 0, 1\rangle] \quad (22)$$

and therefore

$$|1, 0\rangle = \frac{1}{\sqrt{2}} [|1, 1; -1, 1\rangle - |1, 1; 1, -1\rangle], \quad (23)$$

$$|1, -1\rangle = \frac{1}{\sqrt{2}} [|1, 1; 0, -1\rangle - |1, 1; -1, 0\rangle]. \quad (24)$$

It is notable that the vector $|0, 1\rangle$ contains no contribution from the components $|1, 1; 0, 0\rangle$. The corresponding Clebsch-Gordan coefficient is 0.

The subspace $\varepsilon(I = 0)$

The choice of suitable real phase factors leads to the basis vector of the one-dimensional subspace:

$$|0, 0\rangle = \frac{1}{\sqrt{3}} [|1, 1; 1, -1\rangle - |1, 1; 0, 0\rangle + |1, 1; -1, 1\rangle]. \quad (25)$$

b) One can derive from the results of (a) the fact that the states belonging to $I = 2$ and $I = 0$, $|J, M\rangle$, are symmetric on nuclear exchange, while the states belonging to $I = 1$ change their sign on nuclear exchange, and are thus antisymmetric.

12.9 The (unstable) isotope ^{19}F is a Fermion due to its nuclear spin of $1/2$; the total wavefunction of the molecule $^{19}\text{F}_2$ is thus antisymmetric under nuclear exchange. With the notation from problem 12.7, this yields

$$(-1)^{\kappa+J+s+\pi} \stackrel{!}{=} -1. \quad (1)$$

The electronic term for the ground state is even ($\pi = 0$) and has positive parity ($s = 0$). From this, one can conclude that

$$(-1)^{\kappa+J} \stackrel{!}{=} -1. \quad (2)$$

The maximum total spin I which can result from vector addition of the two nuclear spins $I_A = I_B = \frac{1}{2}$ is $I = 1$ (ortho fluorine). The three degenerate states with $M = 0, \pm 1$ are symmetric ($\kappa = 0$), so that due to (2), only rotational states of odd quantum number J can occur.

In contrast, the state belonging to a total spin of $I = 0$ (para fluorine) is antisymmetric ($\kappa = 1$), and its rotational states have even values of J .

The statistical weights of the two types of molecule behave as

$$\frac{g_{\text{Para}}}{g_{\text{Ortho}}} = \frac{g_a}{g_s} = \frac{1}{3}. \quad (3)$$

12.10 In order to derive the ratio of the statistical weights of the antisymmetric and the symmetric states of a diatomic homonuclear molecule in general, we need to investigate the following cases for the nuclear spins $I_A = I_B = I$ and the total spin I_{ges} :

- integer I :
 - symmetric states:
 - $I_{\text{ges}} = 2I, 2I - 2, \dots, 0$ ($I + 1$ states)
 - degree of degeneracy in each case $2I_{\text{ges}} + 1$
 - overall abundance:

$$g_s = (2 \cdot 2I + 1) + [2 \cdot (2I - 2) + 1] + \dots + 1 \quad (1)$$

$$= 4 \sum_{n=0}^I n + I + 1 \quad (2)$$

$$= (I + 1)(2I + 1); \quad (3)$$

- antisymmetric states:
 - $I_{\text{ges}} = 2I - 1, 2I - 3, \dots, 1$ (I states)
 - degree of degeneracy in each case $2I_{\text{ges}} + 1$
 - overall abundance:

$$g_a = [2 \cdot (2I - 1) + 1] + [2 \cdot (2I - 3) + 1] + \dots + (2 \cdot 1 + 1) \quad (4)$$

$$= 4 \sum_{n=0}^{I-1} n + 3I \quad (5)$$

$$= I(2I + 1). \quad (6)$$

For integer values of I , one thus obtains the ratio

$$\frac{g_a}{g_s} = \frac{I(2I + 1)}{(I + 1)(2I + 1)} = \frac{I}{I + 1}.$$

• half-integer I :

– symmetric states:

$$I_{\text{ges}} = 2I, 2I - 2, \dots, 1 \quad (I + \frac{1}{2} \text{ states})$$

degree of degeneracy in each case $2I_{\text{ges}} + 1$

overall abundance:

$$g_s = (2 \cdot 2I + 1) + [2 \cdot (2I - 2) + 1] + \dots + (2 \cdot 1 + 1) \quad (7)$$

$$= 4 \sum_{n=\frac{1}{2}}^I n + I + \frac{5}{2} \quad (8)$$

$$= (I + 1)(2I + 1); \quad (9)$$

– antisymmetric states:

$$I_{\text{ges}} = 2I - 1, 2I - 3, \dots, 0 \quad (I + \frac{1}{2} \text{ states})$$

degree of degeneracy in each case $2I_{\text{ges}} + 1$

overall abundance:

$$g_a = [2 \cdot (2I - 1) + 1] + [2 \cdot (2I - 3) + 1] + \dots + 1 \quad (10)$$

$$= 4 \sum_{n=0}^{I-\frac{1}{2}} n + I + \frac{1}{2} \quad (11)$$

$$= I(2I + 1). \quad (12)$$

For half-integral I also, the ratio is given by

$$\frac{g_a}{g_s} = \frac{I(2I + 1)}{(I + 1)(2I + 1)} = \frac{I}{I + 1}. \quad (13)$$

Chapter 13

13.1 The information contained in the term symbols of the form $^{2S+1}\Lambda_{(g,u)\Omega}^{\pm}$ is collected in the table below. There, we find for a diatomic molecule

- Λ , the z -component of the total angular momentum of all the electrons in the molecule (the z direction is the direction of the molecular symmetry axis);
- S , the total spin of the shell electrons ($2S + 1$: multiplicity; z -component: Σ);
- $\Omega = |\Lambda + \Sigma|$, the total angular momentum of the electronic shell in the z direction;
- σ , the symmetry of the electronic wavefunction on reflection in a plane containing the nuclei;
- P , the parity of the electronic wavefunction of a homonuclear molecule (with identical nuclear charges and therefore an inversion-symmetric nuclear field), i. e. the symmetry on inversion of all the particles (gerade/ungerade \equiv even/odd) (see the table below).

13.2 From the data given, one can extract the following information about the states of the separated atoms A and B :

- A : $1s \Rightarrow L_A = 0$; $m_{L,A} = 0$;
 $S_A = \frac{1}{2}$; $m_{S,A} = \pm\frac{1}{2}$;
 B : $1s^2 2s^2 2p$; $1s^2$ and $2s^2$ are closed shells with $S = L = 0$
 $\Rightarrow L_B = 1$; $m_{L,B} = 0, \pm 1$;
 $S_B = \frac{1}{2}$; $m_{S,A} = \pm\frac{1}{2}$.

Since AB is a heteronuclear molecule, the possible exclusion of terms due to the Pauli principle need not be considered. For the molecule AB we thus find:

- $AB: m_L = 0, \pm 1 \Rightarrow \Lambda = 0, 1$
 \Rightarrow one Σ and one Π term; $S = 0, 1 \Rightarrow \Sigma = 0, \pm 1$.

From this we find the possible terms

- $\Lambda = 0$: $^1\Sigma_0^+$, $^1\Sigma_0^-$, $^3\Sigma_0^+$, $^3\Sigma_0^-$, $^3\Sigma_1^+$, $^3\Sigma_1^-$
 $\Lambda = 1$: $^1\Pi_1$, $^3\Pi_0$, $^3\Pi_1$, $^3\Pi_2$.

	Λ	S	Ω	Σ	σ	P	Remark
$^1\Sigma^+$	0	0	0	0	+		$^1\Sigma^+$ and $^1\Sigma^-$ not degenerate!
$^1\Sigma_u^+$	0	0	0	0	+	u	identical nuclear charges; molecular orbitals ug
$^3\Phi_3$	3	1	3	0			$^3\Phi_3^+$ and $^3\Phi_3^-$ degenerate
$^3\Phi_3^-$	3	1	3	0	–		
$^3\Phi_{g3}^-$	3	1	3	0	–	g	identical nuclear charges; molecular orbitals gg or uu

13.3 a) The electron configuration of a diatomic homonuclear molecule can be found by successively filling the orbitals of the known term scheme (cf. Fig. 13.4), taking into account the Pauli principle and Hund's rules. For the oxygen molecules under discussion here, one then obtains

$$\begin{aligned} \text{O}_2^+ &: (\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p) \\ \text{O}_2 &: (\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p)^2 \\ \text{O}_2^- &: (\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p)^3 \\ \text{O}_2^{2-} &: (\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p)^4 \end{aligned}$$

b) From the electron configurations in (a), the term symbols $^{2S+1}\Lambda_{(g,u)}^\pm$ of the ground states can be derived. The problem can be simplified by remembering that closed electronic shells have neither orbital angular momentum nor spin. For computing the total orbital angular momentum $\Lambda = L_z$ and spin S of the electronic shells therefore only the outermost unfilled shell needs to be considered.

The homonuclear diatomic molecules have a nuclear field with inversion symmetry, so that the electron terms exhibit an even/odd symmetry; with an even number of electrons in u orbitals, one has a g term, with an odd number, a u term.

$$\begin{aligned} \text{O}_2^+ &: \Lambda = 1; S = \frac{1}{2} \implies {}^2\Pi_g \\ \text{O}_2 &: \Lambda = 0; S = 0 \implies {}^1\Sigma_g^+ \\ &\quad \Lambda = 0; S = 1 \implies {}^3\Sigma_g^- \\ &\quad \Lambda = 2; S = 0 \implies {}^1\Delta_g \\ &\quad \Lambda = 2; S = 2 \text{ Pauli forbidden} \\ &\quad \text{according to Hund's rule, the state of highest multiplicity lies energetically} \\ &\quad \text{lowest; the ground state is thus } {}^3\Sigma_g^- \\ \text{O}_2^- &: \Lambda = 1; S = \frac{1}{2} \implies {}^2\Pi_g \text{ } (\pi^3 \text{ behaves like } \pi^1) \\ \text{O}_2^{2-} &: \text{all shells are closed, therefore no orbital angular momentum or spin; com-} \\ &\quad \text{pletely symmetric state} \implies {}^1\Sigma_g^+ \end{aligned}$$

c) The energetically lowest allowed transition of O_2 changes the electronic configuration of the molecule according to

$$\begin{aligned} &(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p)^2 \\ \longrightarrow &\dots (\pi_u 2p)^3 (\sigma_g 2p)^2 (\pi_g^* 2p)^3 \end{aligned}$$

and its terms according to

$${}^3\Sigma_g^- \longrightarrow {}^3\Sigma_u^-.$$

Here, we have taken the selection rules for radiative transitions, namely $\Delta\Lambda = 0, \pm 1$, $\Delta S = 0$ and in particular also $g \leftrightarrow u$ into account. We are thus dealing with a $\pi \rightarrow \pi^*$ transition.

13.4 From the term symbol $^3\Pi_u$, one can conclude that we are dealing with $S + 1$ (triplet state) and $\Lambda = 1$. In order to yield an H atom in its ground state upon dissociation, an electron must occupy the molecular orbital ($1s\sigma_g$); due to $\Lambda = 1$, the other orbital must then be a π state. Since the molecular state is stable in comparison to the dissociation products, we can assume that both electrons occupy bonding orbitals. The odd electron term requires finally one g and one u state for the participating electrons.

The energetically lowest electronic configuration which fulfills the conditions listed above is then

$$(1s\sigma_g)(2p\pi_u).$$

Chapter 14

14.1 a) For the position G_v of the vibronic levels above the minimum of the potential curve of the given electronic state, the following approximate formula holds:

$$G_v = \bar{\nu}_e \left(v + \frac{1}{2} \right) - x_e \bar{\nu}_e \left(v + \frac{1}{2} \right)^2. \quad (1)$$

The spacing between two neighbouring vibrational levels v and $v + 1$ is then

$$\Delta \bar{\nu}_v = G_{v+1} - G_v = \bar{\nu}_e [1 - 2x_e (v + 1)]. \quad (2)$$

The point of convergence of the limiting continuum is at the vibrational level v_C at which the difference to the level $v_C + 1$ becomes negative or zero:

$$\Delta \bar{\nu}_{v_C} \stackrel{!}{=} 0. \quad (3)$$

With (2), this yields the relation between the position of the point of convergence v_C and the anharmonicity constant x_e :

$$v_C = \frac{1}{2x_e} - 1. \quad (4)$$

From this relation, we can compute the points of convergence of the limiting continuum and thus the number of vibrational levels up to the particular dissociation limit, namely v_C'' for the ground state and v_C' for the excited state, with the result

$$v_C'' = 70 \quad \text{and} \quad v_C' = 54.$$

The dissociation energy D_0 of an electronic state is the difference between the energy G_{v_C} at the point of convergence and the zero-point energy G_0 :

$$D_0 = G_{v_C} - G_0. \quad (5)$$

One calculates D_0'' for the ground state and D_0' for the excited state:

$$D_0'' = 56\,896\text{ cm}^{-1} = 1.13 \cdot 10^{-18}\text{ J} = 680.6 \frac{\text{kJ}}{\text{mole}} = 7.1\text{ eV},$$

$$D_0' = 47\,755\text{ cm}^{-1} = 9.49 \cdot 10^{-19}\text{ J} = 571.3 \frac{\text{kJ}}{\text{mole}} = 5.9\text{ eV}.$$

b) The dissociation energies of the ground state and of the electronically excited state can also be found from spectroscopic data. To this end, we require knowledge of

- the energy $hc\bar{\nu}_{00}$ of the 0–0 transition line (from the $v = 0$ level of the ground state into the same level of the excited state),
- the energy $\bar{\nu}_C$ of the point of convergence (distance of the dissociation limit of the excited state from the $v = 0$ level of the ground state; the absorption begins at the latter)
- and the sum of the excitation energies E_{At} of the atomic dissociation products of the electronically excited state (the difference between the continuum edges of the ground state and the excited state).

We then find for the dissociation energy D_0'' of the ground state:

$$D_0'' = hc\bar{\nu}_C - E_{\text{At}}$$

$$\Rightarrow D_0'' = 28\,923\text{ cm}^{-1} = 5.75 \cdot 10^{-19}\text{ J}$$

$$= 346.0 \frac{\text{kJ}}{\text{mole}} = 3.6\text{ eV}$$

and for the dissociation energy D_0' of the excited state

$$D_0' = hc\bar{\nu}_C - hc\bar{\nu}_{00}$$

$$\Rightarrow D_0' = 19\,853\text{ cm}^{-1} = 3.94 \cdot 10^{-19}\text{ J}$$

$$= 237.5 \frac{\text{kJ}}{\text{mole}} = 2.5\text{ eV}.$$

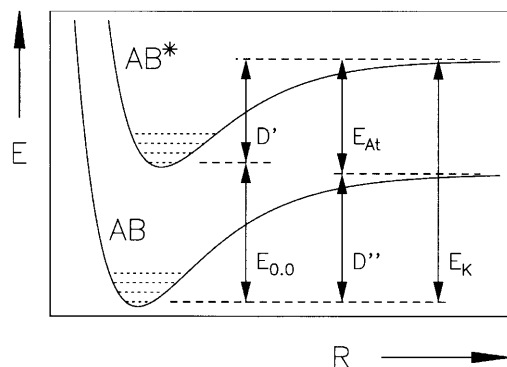


Fig. S.25. Visualisation of the calculation of the dissociation energies (explained in the text)

The discrepancy between the results in (a) and in (b) is due to the linear extrapolation according to (2) which is employed in (a): the linear relation between $\Delta\bar{\nu}_v$ and v is extrapolated to v_C with $\Delta\bar{\nu}_{v_C} = 0$. This approximation however becomes worse and worse as the vibrational quantum number v increases, since for large values of v in the calculation of the level energies from (1), terms of third and fourth order in v become significant. This results in a value of v_C calculated from (3) which is larger than the true value and thus an overestimate of the number of vibrational levels below the point of convergence.

14.2 The energy spacings $\Delta\bar{\nu}_v$ between neighbouring vibrational levels v and $v+1$ are, according to Eq. (2) in problem 14.1, given by

$$\Delta\bar{\nu}_v = G_{v+1} - G_v = \bar{\nu}_e [1 - 2x_e(v+1)]. \quad (1)$$

In the plot of $\Delta E \triangleq \Delta\bar{\nu}_v$ against v , one however finds a strong deviation from the linear behaviour for large values of the quantum number v , so that the linear extrapolation from small v to the point of convergence v_C with $\Delta\bar{\nu}_{v_C} = 0$, the so called Birge-Sponer extrapolation, no longer seems reasonable. The function $\Delta\bar{\nu}_v(v)$ decreases faster than the extrapolation line; cf. Fig. S.26. The reason for this is the increasing contribution of the terms of third and fourth order in the equation for the energetic positions of the vibronic levels for increasing v :

$$\begin{aligned} G_v = \bar{\nu}_e \left(v + \frac{1}{2} \right) - x_e \bar{\nu}_e \left(v + \frac{1}{2} \right)^2 + y_e \bar{\nu}_e \left(v + \frac{1}{2} \right)^3 \\ - z_e \bar{\nu}_e \left(v + \frac{1}{2} \right)^4 + \dots \end{aligned} \quad (2)$$

Extrapolation of $\Delta\bar{\nu}_v(v)$ using a power series of third or fourth order thus leads to a better result for v_C than the linear Birge-Sponer extrapolation.

The dissociation energy D is obtained as the area under the function $\Delta\bar{\nu}_v(v)$, i. e. the integral

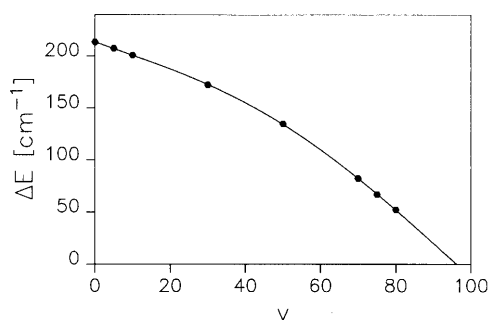


Fig. S.26. A Birge-Sponer plot for determining the point of convergence of the limiting continuum of I_2 (extrapolation to $\Delta E = 0$: $v_C = 97$)

$$D = \int_0^{v_C} \Delta \bar{\nu}_v(v) dv. \quad (3)$$

Applying this procedure with the given data to the molecule I_2 leads to the point of convergence $v_C = 97$ and the dissociation energy

$$D = 12\,293 \text{ cm}^{-1} = 2.44 \cdot 10^{-19} \text{ J} = 147.1 \frac{\text{kJ}}{\text{mole}} = 1.5 \text{ eV}.$$

14.3 a) The given data for the energetic positions of the vibronic levels of the electronically-excited state of O_2 can be evaluated in terms of a Birge-Sponer plot, cf. Fig. S.27. From the nonlinear extrapolation of the function $\Delta \bar{\nu}_v(v)$ out to the point of convergence of the limiting continuum v_C with $\Delta \bar{\nu}_{v_C} = 0$, one obtains $v_C = 18$ and, from the area under the curve, the dissociation energy D'_0 of the excited state

$$D'_0 = 6897 \text{ cm}^{-1} = 1.37 \cdot 10^{-19} \text{ J} = 82.5 \frac{\text{kJ}}{\text{mole}} = 0.86 \text{ eV}.$$

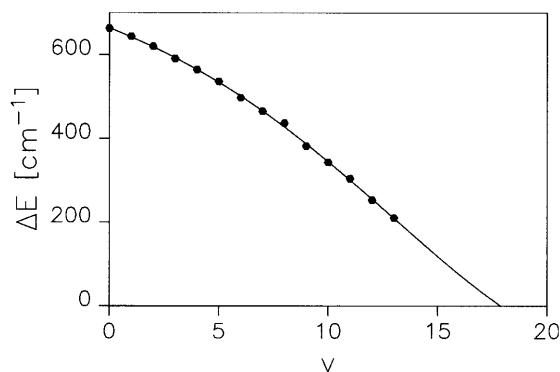


Fig. S.27. A Birge-Sponer plot for determining the point of convergence of the limiting continuum of O_2 (Extrapolation to $\Delta E = 0$: $v_C = 18$)

b) From the energy $\bar{\nu}_{00}$ of the 0–0 transition, the dissociation energy D'_0 of the excited state, and the total excitation energy E_{At} of the atomic dissociation products, we can calculate the dissociation energy D''_0 of the ground state:

$$\begin{aligned} D''_0 &= hc \bar{\nu}_{00} + D'_0 - E_{At} \\ &= (50\,062.6 + 6897 - 15875) \text{ cm}^{-1} \\ \Rightarrow D''_0 &= 41\,085 \text{ cm}^{-1} = 8.16 \cdot 10^{-19} \text{ J} \\ &= 491.5 \frac{\text{kJ}}{\text{mole}} = 5.1 \text{ eV}. \end{aligned}$$

14.4 a) The data given for the oscillation frequency $\bar{\nu}_e''$ of the CO molecule in its ground state and the band intervals $\bar{\nu}_e'$ of the vibrational states in the electronically excited state permit us –within the harmonic-oscillator model– to calculate the force constants k'' and k' of the molecular bonding in the ground state and in the excited state:

$$k = m_r \omega_e^2 = m_r 4\pi^2 c^2 \bar{\nu}_e^2 \quad (1)$$

and, with the reduced mass $m_r = 1.14 \cdot 10^{-26}$ kg

$$k'' = 1855.5 \frac{\text{kg}}{\text{s}^2},$$

$$k' = 885.0 \frac{\text{kg}}{\text{s}^2}.$$

Relative to the ground state, the bonding in the excited state is thus weaker.

The relation between the rotational constants B'' in the ground state and B' in the excited state as well as the equilibrium bond lengths R_e'' and R_e' in the rigid-rotor approximation is given by

$$B = \frac{h}{8\pi^2 c \Theta} = \frac{h}{8\pi^2 c m_r R_e^2}. \quad (2)$$

Due to $B' < B''$, we therefore find $R_e' > R_e''$, i.e. the average internuclear distance is larger in the excited state than in the ground state. Calculation with the given data yields

$$R_e'' = 1.13 \text{ \AA},$$

$$R_e' = 1.24 \text{ \AA}.$$

For radiative electronic transitions between different rotational levels, the selection rule $\Delta J = 0, \pm 1$ applies. In a diatomic molecule, the angular momentum of the electronic shells Ω and the angular momentum N of the rotational motion of the whole molecule are coupled to the total angular momentum J :

$$J = N + \Omega. \quad (3)$$

If we are dealing with a Π electron term, then $\Omega = 1$, and the state $J = 0$ does not exist. The origins of the branches of the rotational bands thus permit us to draw conclusions about the terms which contribute to the electronic transition. In the present case, the band origins are $P(2)$, $Q(1)$, and $R(0)$, i.e.:

$$P \text{ branch } (J' = J'' - 1) : \text{ first line } 2 \rightarrow 1,$$

$$Q \text{ branch } (J' = J'') : \text{ first line } 1 \rightarrow 1,$$

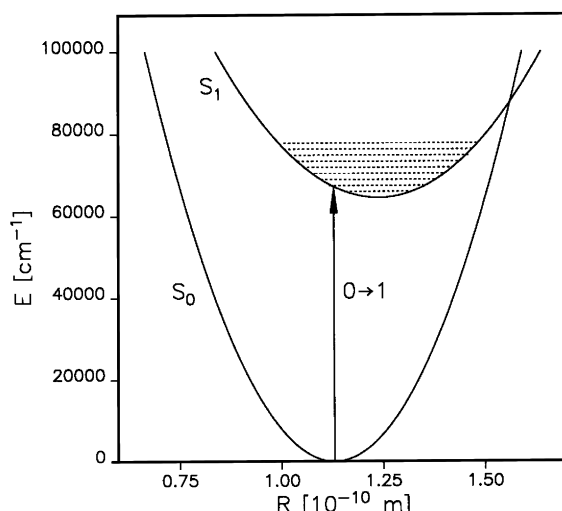
$$R \text{ branch } (J' = J'' + 1) : \text{ first line } 0 \rightarrow 1.$$

This means that the rotational level $J' = 0$ is lacking in the excited state, while it exists in the excited state. We can therefore assume that we are dealing with a transition of the type ${}^1\Sigma \longrightarrow {}^1\Pi$.

b) With the information obtained in part (a), a simplified term scheme can be sketched, if one retains the harmonic-oscillator approximation and thus draws parabolic potential curves $U(R)$:

$$U(r) = \frac{k}{2} (R - R_e)^2. \quad (4)$$

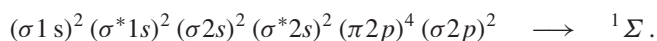
This term scheme contains the ground state and the excited electronic state including its vibronic levels. According to the Frank-Condon principle, only vertical transitions are allowed, since in the adiabatic approximation the internuclear distance remains constant during the transition.



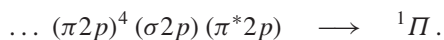
The absorption begins in the $J'' = 0$ level of the ground state for which the probability density at the equilibrium internuclear distance R_e'' is greatest. The transition ends at the “turning point” of the $J' = 1$ level of the excited state. Since the greatest probability density of this state lies in the neighbourhood of the turning point, the overlap integral of the wavefunctions in the ground state and the excited state is maximal for the 0–1 transition. For this transition, we can thus expect the highest intensity.

The equilibrium internuclear distance R_e' in the excited state is further away from R_e'' than the turning point of the vibronic levels $J' = 2, 3, \dots$. The intensity of the 0–0 transition should therefore be less than that of the first three or four lines of the vibrational series.

c) The molecule CO is isoelectronic with N_2 , in its ground state it thus has the same electron configuration:



Since we are dealing here with a heteronuclear molecule, no g/u symmetry occurs. On excitation, an electron from the bonding σ state is raised into the non-bonding π state. This determines the configuration of the excited state:



This verifies the assumption derived in (a) for the term symbols of the two states.

14.5 The continuous or diffuse spectra of polyatomic molecules in the short wavelength region, $\lambda < 200$ nm (VUV) have several causes:

- owing to the numerous possibilities of absorption by different chromophore groups, several band systems overlap;
- the energy is not sufficient to excite the molecule into the dissociation continuum, whereby large molecules often have flatter potential curves than smaller ones and are thus less stable;
- in the region of the excitation spectra considered, there is an intersection of the potential curves of several different electronic terms and thus a tendency to predissociation, which causes a shorter lifetime and therefore a greater linewidth in the excited states.

14.6 The molecular orbital which is delocalised over the whole polyene can be modeled in terms of a potential well of length $L = 10$ Å with infinitely high walls. The energy of an electron in this potential well is then quantised according to

$$E_n = \frac{n^2 h^2}{8 m_e L^2} \quad \text{with } n = 1, 2, 3, \dots \quad (1)$$

(m_e : electron mass). The spacings between neighbouring energy levels become greater as n increases. Each state which is associated with the quantum number n is described by the wavefunction ψ_n :

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \quad (2)$$

The minimum excitation energy of the electron which is in the ground state $n = 1$ is, from (1)

$$\Delta E_{\min} = E_2 - E_1 = 3 \frac{h^2}{8 m_e L^2}, \quad (3)$$

and, with the given data,

$$E_{\min} = 1.83 \cdot 10^{-19} \text{ J} = 1.14 \text{ eV} = 9098 \text{ cm}^{-1}.$$

The minimum excitation energy of the electron lies in the near infrared.

The probability density is given by the squared magnitude of the wavefunction ψ . The occupation probability $W_{0 \leq x \leq l}$ of the particle in the state n in the range 0 to l is calculated by integration:

$$W_{0 \leq x \leq l} = \int_0^l \psi_n \psi_n^* dx = \frac{2}{L} \int_0^l \sin\left(\frac{n\pi x}{L}\right)^2 dx \quad (4)$$

$$= \frac{l}{L} - \frac{1}{2n\pi} \sin\left(\frac{2n\pi l}{L}\right). \quad (5)$$

With $n = 1$ and $l = \frac{L}{5}$, we obtain from this

$$W_{0 \leq x \leq l} = 0.05.$$

The electron thus can be found with a probability of 5% at a distance of 0 to 2 Å from the edge of the potential well.

Chapter 15

15.1 a) For the transmission T of a weakly absorbing homogeneous (i. e. stirred) sample, in the first approximation, the Lambert-Beers law applies:

$$T = \frac{I}{I_0} = e^{-\alpha cd} \quad (1)$$

(I_0 : intensity of the incident light; I : intensity of the transmitted light; α : absorption coefficient; c : molar concentration of the sample; d : thickness of the sample).

With the extinction coefficient (decadic absorption coefficient) $\varepsilon = \alpha \log e$, this relation becomes

$$T = \frac{I}{I_0} = 10^{-\varepsilon cd}. \quad (2)$$

From the definition of the optical density

$$\text{OD} = \log \frac{I_0}{I} = \varepsilon cd, \quad (3)$$

we find the relation between the optical density and the transmission:

$$\text{OD} = -\log T, \quad (4)$$

and, with the given value $T = 16\% = 0.16$ for $\lambda = 256 \text{ nm}$,

$$\text{OD}(256) = 0.796.$$

From (3) we obtain the extinction coefficient

$$\varepsilon = \frac{\text{OD}}{cx} \quad (5)$$

and finally

$$\varepsilon(256) = 159.2 \frac{\text{l}}{\text{mole cm}}.$$

For a sample thickness of 0.1 cm, we calculate using (2) that the transmission is

$$T = 83\% .$$

b) The integral A giving the area under an inhomogeneously broadened absorption band of Gaussian profile

$$g(\bar{\nu}) = e^{-a\bar{\nu}^2} \quad (6)$$

can be evaluated simply using

$$A = \int_{-\infty}^{\infty} e^{-a\bar{\nu}^2} d\bar{\nu} = \sqrt{\frac{\pi}{a}} . \quad (7)$$

The full width at half maximum, (FWHM) $\Delta\bar{\nu}$ of the Gaussian curve is

$$\Delta\bar{\nu} = 2\sqrt{\frac{\ln 2}{a}} . \quad (8)$$

Approximating the line shape as a rectangle with the same height as the Gaussian $g_{\max} = 1$ and the width $\Delta\bar{\nu}$, we obtain for the area

$$A = 1 \cdot 2\sqrt{\frac{\ln 2}{a}} . \quad (9)$$

An equivalent approximation is to treat the area as an equilateral triangle of height g_{\max} and base width $2\Delta\bar{\nu}$. The areas determined from (7) and (9) differ by a factor

$$\frac{\sqrt{\pi}}{2\sqrt{\ln 2}} \approx 1.06 . \quad (10)$$

Calculation of the integral absorption from the linewidth $\Delta\bar{\nu}$ using the rectangle approximation (9) is thus a sufficiently good approximation.

The definition of the integral absorption used for the computation of the oscillator strength is

$$A = \int \varepsilon(\nu) d\nu . \quad (11)$$

In changing the variable from ν to $\bar{\nu}$, we must still take a factor of c (velocity of light) into account:

$$A = c \int \varepsilon(\bar{\nu}) d\bar{\nu} , \quad (12)$$

so that the approximation (9) becomes

$$A = c \varepsilon_{\max} \Delta\bar{\nu} . \quad (13)$$

With the data given in the problem, one finds the integral absorption of the band to be

$$A = 1.91 \cdot 10^{16} \frac{1}{\text{mole cm s}} = 1.91 \cdot 10^{16} \frac{\text{cm}^2}{\text{mmole s}}.$$

The oscillator strength f of the transition is found from the value of A thus calculated by applying the simple relation

$$f = 1.44 \cdot 10^{-19} \cdot A \quad (14)$$

with A in units of $(\text{cm}^2/\text{mmole s})$. This leads to

$$f = 2.75 \cdot 10^{-3}.$$

One thus obtains $f \ll 1$; the transition is in fact forbidden.

15.2 From the density $\varrho = 1 \text{ g/cm}^3$ and the molecular mass $M = 18 \text{ g/mole}$, we can calculate the approximate molarity c of seawater to be

$$c = \frac{\varrho}{M} = 55.6 \frac{\text{mole}}{\text{l}}. \quad (1)$$

From (3) and (4) from problem 15.1, for a given extinction coefficient ε , we find the relation between the layer thickness d and the transmission T to be

$$d = \frac{-\log T}{\varepsilon c}. \quad (2)$$

Using the given transmissions T , we then obtain the following water depths d :

for $T = 50\%$: $d = 873 \text{ cm}$,

for $T = 10\%$: $d = 290.1 \text{ cm}$.

15.3 In a one-dimensional potential well of length L with infinitely high walls, we find the energy eigenvalues E_n and eigenfunctions ψ_n from problem 14.6. The strength of an electrical dipole transition from the initial state ψ_n into the final state ψ_m depends on the value of the transition dipole moment Θ_{mn} , i. e. on the transition matrix element of the dipole operator $e\mathbf{r}$, which is a measure of the change in the dipole moment during the transition:

$$\Theta_{mn} = \int \psi_m^* e\mathbf{r} \psi_n dV \quad (1)$$

or, in the one-dimensional case,

$$\Theta_{mn} = \int_0^L \psi_m^* ex \psi_n dx. \quad (2)$$

With the wavefunctions ψ_n , we find

$$\Theta_{mn} = \frac{2e}{L} \int_0^L \sin\left(\frac{m\pi x}{L}\right) x \sin\left(\frac{n\pi x}{L}\right) dx. \quad (3)$$

Applying the trigonometric addition theorems, we obtain

$$\begin{aligned} \Theta_{mn} &= \frac{eL}{\pi^2 (m-n)^2} \{\cos[(m-n)\pi] - 1\} \\ &\quad - \frac{eL}{\pi^2 (m+n)^2} \{\cos[(m+n)\pi] - 1\} \end{aligned} \quad (4)$$

and thus for the two special cases

$$\text{a) } n \rightarrow m = n+1 : \Theta_{mn} = \frac{2eL}{\pi^2} \left(\frac{1}{(2n+1)^2} - 1 \right), \quad (5)$$

$$\text{b) } n \rightarrow m = n+2 : \Theta_{mn} = 0. \quad (6)$$

The oscillator strength f of the electronic transition $n \rightarrow m$ at the frequency ν is given by

$$f = \frac{8\pi^2 m_e \nu}{3 h e^2} |\Theta_{mn}|^2 \quad (7)$$

and with (5) and (6)

$$\text{a) } n \rightarrow m = n+1 : f_a = \frac{32 m_e \nu L^2}{3\pi^2 h} \left(\frac{1}{(2n+1)^2} - 1 \right)^2 \quad (8)$$

$$\text{b) } n \rightarrow m = n+2 : f_b = 0. \quad (9)$$

From the bond energies E_n , we determine the transition frequencies ν :

$$\text{a) } n \rightarrow m = n+1 : \Delta E_a = h\nu = \frac{h^2}{8m_e L^2} (2n+1), \quad (10)$$

$$\text{b) } n \rightarrow m = n+2 : \Delta E_b = h\nu = \frac{h^2}{2m_e L^2} (n+1). \quad (11)$$

Inserting into (8) and (9), this gives finally the oscillator strengths of the two transitions

$$\text{a) } n \rightarrow m = n+1 : f_a = \frac{64}{3\pi^2} \cdot \frac{n^2 (n+1)^2}{(2n+1)^3}, \quad (12)$$

$$\text{b) } n \rightarrow m = n+2 : f_b = 0. \quad (13)$$

In β carotene, the conjugated π electron system of the polyene chain can be modeled as a potential well. It consists of eleven double and ten single bonds and extends over 22 C atoms, i. e. each wavefunction in the potential well is delocalised

over 22 C atoms. With an average bond length of $R = 140$ pm, the length L of the potential well is then

$$L = 22 R = 3.08 \cdot 10^{-9} \text{ m} . \quad (14)$$

The levels in the potential well are to be filled with the 22 delocalised π electrons from the eleven double bonds from the lowest upwards, so that up to $n = 11$, all the levels are occupied with two electrons, each with antiparallel spins. The excitation of the molecule thus starts from the state $n = 11$. According to (10) and (11), we can now calculate the excitation energies:

$$\begin{aligned} \text{a) } n \rightarrow m = n + 1 : \Delta E_a &= \frac{h^2}{8m_e L^2} \cdot 23 \\ &= 1,46 \cdot 10^{-19} \text{ J} \hat{=} 7353 \text{ cm}^{-1} , \end{aligned} \quad (15)$$

$$\begin{aligned} \text{b) } n \rightarrow m = n + 2 : \Delta E_b &= \frac{h^2}{2m_e L^2} \cdot 12 \\ &= 3.05 \cdot 10^{-19} \text{ J} \hat{=} 15\,346 \text{ cm}^{-1} . \end{aligned} \quad (16)$$

These results correctly describe the order of magnitude of the measured transition energies. Finally, using (12), the oscillator strength of the transition $11 \rightarrow 12$ can be determined:

$$f_a = 3.1$$

The oscillator strength gives the ratio between the actual intensity of the transition and that of an ideal harmonic oscillator. This follows from its definition: for an electron which is harmonically oscillating in three dimensions, we find $f = 1$; in the one-dimensional case, we have $f = \frac{1}{3}$. The above calculated value of $f = 3.1$ can thus not be particularly precise. To be sure, we should not expect it to be, since we are comparing two essentially different models (potential well and harmonic oscillator).

15.4 a) On cooling of the H_2 gas, the populations of the excited rotational and vibronic states is reduced. The ratio of the population numbers N_1 of the first excited state of energy E_1 and N_0 in the ground state is, for a given temperature T , given by:

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-E_1/kT} \quad (1)$$

(g_1, g_0 : degree of degeneracy of the excited and the ground states; k : Boltzmann's constant). As a *first criterion* for the freezing out of the rotational and vibronic degrees of freedom, we can apply the condition

$$\text{1st criterion: } E_1 \stackrel{!}{=} kT . \quad (2)$$

The population of the first excited state is then (neglecting the different degrees of degeneracy)

$$N_1 = \frac{1}{e} \cdot N_0 \approx 0.37 \cdot N_0. \quad (3)$$

Freezing out of the vibrational degree of freedom thus occurs at the temperature

$$T_{S,1} = \frac{hc \bar{\nu}_{0 \rightarrow 1}}{k}, \quad (4)$$

where $\bar{\nu}_{0 \rightarrow 1} = 4159.2 \text{ cm}^{-1}$ is the wavenumber of the first vibrational transition of hydrogen in its ground state:

$$T_{S,1} = 5987 \text{ K}.$$

With the rotational constant $B = 60.8 \text{ cm}^{-1}$ of the H_2 ground state, the temperature for freezing out of the rotational degrees of freedom follows:

$$T_{R,1} = \frac{hcB J(J+1)}{k} = \frac{2hcB}{k} \quad (5)$$

with $J = 1$ for the first excited rotational level and thus

$$T_{R,1} = 175 \text{ K}.$$

As the *second criterion* for freezing out of the rotational and vibrational degrees of freedom, we now require that the population of the corresponding first excited state decrease to 1% of the population of the ground state:

$$\text{2nd criterion: } \frac{N_1}{N_0} \stackrel{!}{=} 1\% = 0.01. \quad (6)$$

For the vibrational states, the two degrees of degeneracy are $g_1 = g_0 = 1$, so that with (1), we find

$$T_{S,2} = \frac{hc \bar{\nu}_{0 \rightarrow 1}}{k \ln 100}. \quad (7)$$

At a temperature $T_{S,2}$, the $n = 1$ vibrational state is practically unoccupied:

$$T_{S,2} = 1300 \text{ K}.$$

The degree of degeneracy of the rotational states of quantum number J are $g_J = 2J + 1$. With $g_0 = 1$ and $g_1 = 3$, one finds from (1) the temperature for freezing out of the rotational degrees of freedom:

$$T_{R,2} = \frac{2hcB}{k \ln 300} \quad (8)$$

and therefore for H_2

$$T_{R,2} = 30.7 \text{ K}.$$

b) For HCl, we use $B = 10.39 \text{ cm}^{-1}$ and $\bar{\nu}_{0 \rightarrow 1} = 2885.6 \text{ cm}^{-1}$. From (4), (5), (7), and (8) we can then compute the temperatures at which, according to the above criteria, the rotational and vibrational degrees of freedom of HCl gas freeze out:

$$T_{S,1} = 4154 \text{ K},$$

$$T_{S,2} = 902 \text{ K},$$

$$T_{R,1} = 29.9 \text{ K},$$

$$T_{R,2} = 5.2 \text{ K}.$$

c) Hydrogen gas can be cooled with liquid helium in a cryostat, since it does not yet condense at the calculated temperatures.

In contrast, HCl is already solid at the temperatures which are necessary to freeze out the rotational degrees of freedom ($T_F = 158.3 \text{ K}$). The effective temperature for rotation and vibration can however be reduced to the required value in a jet (supersonic beam).

15.5 The relativistic red shift of the light emitted by the star if it is moving away from the terrestrial observer at the velocity v_F , is given by

$$\frac{\lambda_{v_F}}{\lambda_0} = \sqrt{\frac{c + v_F}{c - v_F}}. \quad (1)$$

Here, λ_{v_F} and λ_0 are the wavelengths of the light with and without the Doppler shift, and c is the velocity of light in vacuum. From this, we obtain the proper velocity of the star:

$$v_F = c \cdot \frac{\lambda_{v_F}^2 - \lambda_0^2}{\lambda_{v_F}^2 + \lambda_0^2}, \quad (2)$$

and, inserting the values given in the problem text,

$$v_F = 2.3 \cdot 10^7 \frac{\text{m}}{\text{s}}.$$

To compute the inhomogeneous linewidth due to the Doppler effect, we consider the velocity distribution of the $^{48}\text{Ti}^{8+}$ ions in the rest system of the star. This velocity distribution has a Gaussian profile

$$N = N_0 e^{-\frac{m}{2kT} v^2}, \quad (3)$$

where N and N_0 are the numbers of ions which are moving with the velocities v or 0 relative to the observer, and m is the mass of the ions. The full width at half maximum (FWHM), Δv , of the velocity distribution is

$$\Delta v = 2 \sqrt{\frac{2kT \ln 2}{m}}. \quad (4)$$

Since the velocity v of the ions is much smaller than the velocity of light c , the Doppler-shifted frequency ν_v of a moving atom can be determined non-relativistically from the unshifted frequency ν_0 of an ion at rest:

$$\nu_v = \nu_0 \left(1 - \frac{v}{c}\right). \quad (5)$$

For the wavelength shift of the moving source relative to that of the source at rest, we find from this the relation

$$\delta\lambda = \lambda_0 \frac{v}{c}. \quad (6)$$

The Doppler shift of the radiation emitted by the moving ions is proportional to their velocity. We thus find from the Gaussian distribution of the velocities a Gaussian absorption profile which, owing to (4) and (6), has a linewidth (FWHM) of

$$\Delta\lambda = \frac{\lambda_0}{c} \Delta v = \frac{2\lambda_0}{c} \sqrt{\frac{2kT \ln 2}{m}}. \quad (7)$$

For a given width $\Delta\lambda$ of the spectral line, one can extract the temperature:

$$T = \left(\frac{c \Delta\lambda}{2\lambda_0}\right)^2 \frac{m}{2k \ln 2}. \quad (8)$$

With $\Delta\lambda = 0.618 \text{ \AA}$, we calculate the surface temperature of the star to be

$$T = 8.4 \cdot 10^5 \text{ K}.$$

15.6 The energy uncertainty ΔE of a state with the lifetime τ is given by the uncertainty relation

$$\Delta E \cdot \tau \approx \hbar. \quad (1)$$

Since the ground state has an infinitely long lifetime, its energy is arbitrarily sharp. The lifetime broadening of an absorption line from the ground state into an excited state is therefore determined only by the uncertainty of the excited state; it is inversely proportional to its lifetime.

a) Due to the depopulation of the S_2 state through rapid radiationless processes (internal conversion, vibrational relaxation), its lifetime is of the order of 10^{-12} s , while that of the S_1 state lies near 10^{-8} s . Since the S_1 state is thus sharper than the S_2 state, the $S_0 - S_1$ absorption line is narrower than the $S_0 - S_2$ line.

b) Radiative transitions from the triplet state T_1 into the ground state S_0 are forbidden, so that the T_1 state is metastable and exhibits a long lifetime $\tau = 10^{-8} - 10^2 \text{ s}$. The $S_0 - T_1$ line is thus in general very narrow.

15.7 The CO molecule is isoelectronic with N_2 ; its electron configuration in the neutral ground state is

$$(1s\sigma)^2 (1s\sigma^*)^2 (2s\sigma)^2 (2s\sigma^*)^2 (2p\pi)^4 (2p\sigma)^2.$$

The three observable bands in the photoelectron spectrum belong to electrons from the three energetically highest occupied molecular orbitals, since these have the lowest binding or ionisation energies E_{ion} . The binding energy can to a first approximation be determined from the difference of the energy of the ionising He-lamp radiation ($E_{\text{He}} = 58.4 \text{ nm} = 21.21 \text{ eV}$) and the kinetic energy E_{kin} of the photoelectrons; cf. Fig. S.28:

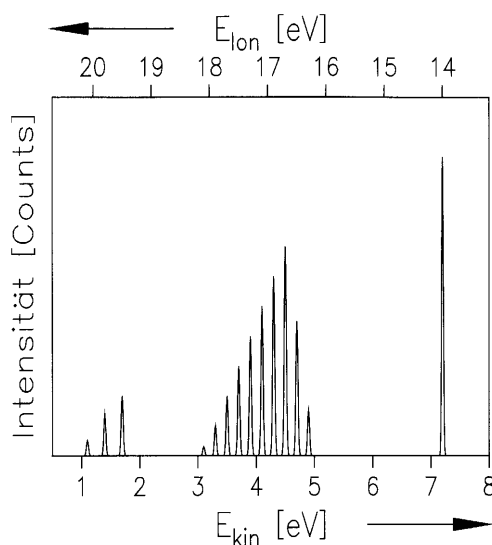


Fig. S.28. The photoelectron spectrum of CO after excitation at 21.21 eV. For problem 15.7

$$E_{\text{ion}} = E_{\text{He}} - E_{\text{kin}}.$$

E_{kin}/eV	E_{ion}/eV	Molecular orbital	Vibrational constant $\bar{\nu}_e/\text{cm}^{-1}$
7.2	14.0	$2p\sigma$	
4.9	16.3	$2p\pi$	1610
1.7	19.5	$2s\sigma^*$	2420

The $\bar{\nu}_e$ values calculated from the vibronic maxima of the bands correspond approximately to the vibrational constants in the corresponding excited states of CO^+ . For the ground state of neutral CO, one finds $\bar{\nu}_e = 2143 \text{ cm}^{-1}$. Removing a $2p\pi$ electron weakens the bond, so that the vibrational frequency decreases. $2p\pi$ can thus be identified as a bonding orbital, $2s\sigma^*$ in contrast as an antibonding orbital.

15.8 From the spacings of the vibronic maxima in the 9 eV band of the photoelectron spectrum of H₂O, the vibrational constant $\bar{\nu}_e$ of the corresponding molecular orbital can be determined:

$$\Delta E = 0.41 \text{ eV} \implies \bar{\nu}_e = 3306 \text{ cm}^{-1}.$$

This value is comparable with the vibrational constant $\bar{\nu}_1 = 3657 \text{ cm}^{-1}$ of the symmetric stretching vibration of neutral H₂O. For the 7 eV band, one calculates a value according to

$$\Delta E = 0.125 \text{ eV} \implies \bar{\nu}_e = 1008 \text{ cm}^{-1},$$

which is more strongly shifted compared to $\bar{\nu}_2 = 1595 \text{ cm}^{-1}$ for the bending vibration. This suggests that the 7 eV electron originates from a more strongly bonding orbital, since its excitation has a stronger effect on the vibrational behaviour of the molecule.

Chapter 18

18.1 a) The nuclear spin can be treated as a classical angular momentum \mathbf{I} . It corresponds to a magnetic moment $\boldsymbol{\mu}$:

$$\boldsymbol{\mu} = \gamma \mathbf{I}, \quad (1)$$

where we have introduced as proportionality constant the gyromagnetic ratio γ . In a constant external magnetic field \mathbf{B} , a torque therefore acts on the spin and it is equal to the rate of change of the angular momentum:

$$\frac{d}{dt} \mathbf{I} = \boldsymbol{\mu} \times \mathbf{B}. \quad (2)$$

Together with (1), this yields the equation of motion of the magnetic moments:

$$\frac{d}{dt} \boldsymbol{\mu} = \boldsymbol{\mu} \times (\gamma \mathbf{B}) \quad (3)$$

as well as that of the nuclear spins:

$$\frac{d}{dt} \mathbf{I} = \mathbf{I} \times (\gamma \mathbf{B}). \quad (4)$$

In order to solve this equation of motion, one introduces a rotating coordinate system with the unit vectors $\mathbf{i}, \mathbf{j}, \mathbf{k}$, which rotates in the laboratory (rest) system according to

$$\frac{d}{dt} \mathbf{i} = \boldsymbol{\Omega} \times \mathbf{i} \quad (5)$$

at the frequency Ω . The total differential (3) thus becomes

$$\frac{\partial}{\partial t} \boldsymbol{\mu} + \boldsymbol{\Omega} \times \boldsymbol{\mu} = \boldsymbol{\mu} \times \gamma \mathbf{B}. \quad (6)$$

The second term in the sum on the left side describes the rotation of the coordinate system, while the first term gives the rate of change of $\boldsymbol{\mu}$ in the rotating system:

$$\frac{\partial}{\partial t} \boldsymbol{\mu} = \boldsymbol{\mu} \times (\gamma \mathbf{B} + \boldsymbol{\Omega}). \quad (7)$$

In the rest system of $\boldsymbol{\mu}$, its time derivative is zero, so that we find from Eq. (7) for the Larmor frequency Ω_L with which the rest system and thus the vector $\boldsymbol{\mu}$ in the laboratory system rotates:

$$\Omega_L = -\gamma \mathbf{B}. \quad (8)$$

Thus in a static magnetic field, $\boldsymbol{\mu}$ and –from (1)– also the nuclear spins \mathbf{I} carry out a precessional motion around the direction of the field at the frequency Ω_L .

b) The gyromagnetic ratio γ for a particular nucleus can be computed from the corresponding nuclear g -factor g_I (5.58569 for ^1H), the nuclear magneton $\mu_N = 0.505 \cdot 10^{-26} \text{ A m}^2$, and Planck's constant \hbar according to

$$\gamma = \frac{g_I \mu_N}{\hbar}. \quad (9)$$

For the Larmor frequency $\nu_L = \frac{1}{2\pi} \Omega_L$ it follows using (8) that

$$\nu_L = \frac{g_I \mu_N}{h} B, \quad (10)$$

and, with the given value for the Earth's magnetic field B ,

$$\nu_L = 553.4 \text{ Hz}.$$

18.2 a) Inserting the fixed magnetic field $B = 2.166 \text{ T}$ into expression (10) from problem 18.1 for the Larmor frequency of a proton, one finds

$$\nu_L = 9.22 \cdot 10^7 \text{ Hz} = 92.2 \text{ MHz}.$$

This is, however, the frequency of the radio station SDR 3, which broadcasts from the Stuttgart Television Tower at high power. The student is worried that therefore his measurements will be disturbed by the radio signals (or that reception of SDR3 in the laboratory will be disturbed by the NMR apparatus).

b) Solving Eq. (10) from problem 18.1 for the magnetic field B , we find

$$B = \frac{h\nu}{\mu_N g_I}. \quad (1)$$

With the g -factor $g_I = 5.58569$ for protons, ^1H , and the given frequency ν , we calculate the field strength

$$B_{\text{H}} = 0.71 \text{ T}.$$

On the other hand, with $g_I = 1.40482$ for ^{13}C , we obtain

$$B_{\text{C}} = 2.83 \text{ T}.$$

18.3 Denoting the resonance magnetic field for the standard, TMS, as B_{T} and the resonance magnetic field for the sample substance as B_{S} , the chemical shift δ obeys the equation

$$\delta = 10^6 \frac{B_{\text{T}} - B_{\text{S}}}{B_{\text{T}}}. \quad (1)$$

There is thus a linear relationship between δ and the field B_{S} , so that the calculation of the centre of gravity of the lines of a multiplet can be carried out equally well on the B axis or on the δ axis:

$$\langle B \rangle = \frac{1}{2} (B'_{\text{S}} + B''_{\text{S}}) \quad (2)$$

$$\text{or } \langle \delta \rangle = \frac{1}{2} (\delta' + \delta'') \quad (3)$$

(for a doublet of lines). The chemical shift of the nuclei A and B is defined as the centre of gravity of the doublets, since in the special case of weak coupling $J \ll \delta$, the splitting due to the dipole-dipole interaction is symmetric around the position of the unsplit line:

$$\delta_A = 5.75 \text{ ppm} \quad \text{and} \quad \delta_B = 1.05 \text{ ppm}$$

(the assignment of the nuclei A and B is arbitrary). The doublet splitting of the two lines is caused by the dipole-dipole coupling between two nuclei with spins $\frac{1}{2}$ and the coupling constant J_{AB} . It corresponds to the line spacing in the two doublets:

$$J_{AB} = 0.1 \text{ ppm}.$$

Since from Eq. (10) in problem 18.1, the resonance frequency

$$\nu = \frac{g_I \mu_{\text{N}}}{h} B \quad (4)$$

is proportional to the resonance field, the chemical shift can be expressed in terms of a frequency using (1):

$$\delta = 10^6 \frac{\nu_{\text{T}} - \nu_{\text{S}}}{\nu_{\text{T}}}. \quad (5)$$

The coupling constant, i. e. the line spacing in the doublet, is then

$$J_{AB} = \Delta\nu_S = (-) 10^{-6} \nu_T \Delta\delta, \quad (6)$$

and with $\nu_T = 100 \text{ MHz}$ and $\Delta\delta = 0.1$,

$$J_{AB} = 10 \text{ Hz}.$$

18.4 An electronegative neighbour atom withdraws electrons from the vicinity of a spin and thereby reduces the magnetic shielding of the electrons at the nuclei. Resonance then occurs at a lower B field, so that the chemical shift δ increases.

From the quantitative values of the electronegativities EN of the neighbouring atoms, $X = \text{O, N, C}$,

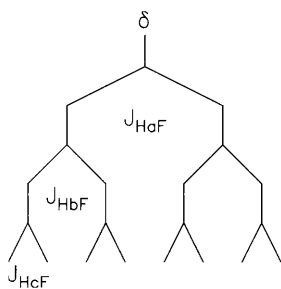
$$\text{EN}_\text{O} > \text{EN}_\text{N} > \text{EN}_\text{C},$$

it follows for the chemical shifts of the methyl protons that

$$\delta(\text{O}-\text{CH}_3) > \delta(\text{N}-\text{CH}_3) > \delta(\text{C}-\text{CH}_3),$$

or, more precisely: $\delta(\text{O}-\text{CH}_3) \approx 3.3 \text{ ppm}$, $\delta(\text{N}-\text{CH}_3) \approx 2.3 \text{ ppm}$ and $\delta(\text{C}-\text{CH}_3) \approx 0.9 \text{ ppm}$.

18.5 For the NMR spectrum of the fluorine nucleus, the coupling constants J_{HH} between the protons are irrelevant when, as in the present case, the chemical shifts δ of the three inequivalent protons are very different: $\Delta\delta \gg J_{\text{H}_i\text{H}_j}$ (the protons are so to speak “very inequivalent”). The dipole-dipole interaction of the F nucleus with the proton H_a then causes a doublet splitting of the F resonance line with a line spacing of $J_{\text{H}_a\text{F}}$; the interaction with H_b gives rise to an additional splitting of both lines into pairs with a spacing of $J_{\text{H}_b\text{F}}$; and finally, the interaction with H_c causes a splitting of each line into two new lines at a spacing of $J_{\text{H}_c\text{F}}$. The final result is a splitting into $2^3 = 8$ lines of equal intensity.



H_a	H_b	H_c	$\Delta\nu$ relative to the centre of the octet
↑	↑	↑	$\frac{1}{2}(85 + 50 + 20) \text{ Hz} = 77.5 \text{ Hz}$
↑	↑	↓	$\frac{1}{2}(85 + 50 - 20) \text{ Hz} = 57.5 \text{ Hz}$
↑	↓	↑	$\frac{1}{2}(85 - 50 + 20) \text{ Hz} = 27.5 \text{ Hz}$
↑	↓	↓	$\frac{1}{2}(85 - 50 - 20) \text{ Hz} = 7.5 \text{ Hz}$
↓	↑	↑	$\frac{1}{2}(-85 + 50 + 20) \text{ Hz} = -7.5 \text{ Hz}$
↓	↑	↓	$\frac{1}{2}(-85 + 50 - 20) \text{ Hz} = -27.5 \text{ Hz}$
↓	↓	↑	$\frac{1}{2}(-85 - 50 + 20) \text{ Hz} = -57.5 \text{ Hz}$
↓	↓	↓	$\frac{1}{2}(-85 - 50 - 20) \text{ Hz} = -77.5 \text{ Hz}$

18.6 In 1,1,2 trichloroethane, $\text{CH}_2^a\text{Cl}-\text{CH}^b\text{Cl}_2$, there are two types a and b of inequivalent protons. Since the H^b is in the immediate neighbourhood of two electronegative chlorine atoms, its chemical shift is larger than that of the two H^a , whose C atom is substituted with only one Cl. Due to the dipole-dipole interaction with H^b , the lines of the two H^a protons split into two lines with a spacing of $J_{H^aH^b}$ and equal intensity; the H^b resonance, in contrast, splits into three lines due to the coupling with the two H^a , with a line spacing of $J_{H^aH^b}$ and relative intensities in the ratio 1:2:1. The integrated intensity ratio of the resonance signals of H^a (two protons) to H^b (one proton) is 2:1.

In the measured spectrum, one observes a doublet at $\delta = 3.95 \text{ ppm}$ (H^a) and a triplet at $\delta = 5.77 \text{ ppm}$ (H^b). The line splitting is in each case $J_{H^aH^b} = 6.0 \text{ Hz}$. Furthermore, one observes a smaller solvent peak at $\delta = 7.28 \text{ ppm}$, which is caused by CHCl_3 impurities in the CDCl_3 solvent.

18.7 In the spectrum of $\text{H}_3^a\text{C}-\text{CH}_2^b-\text{CH}_2^c-\text{NO}_2$, the assignment of the signals to the inequivalent proton species can be carried out noting the inductive effect of the electron-attracting NO_2 group: because of the lowest electron density and nuclear shielding at the positions of the H^c protons, their resonance occurs at the lowest B field, so that their chemical shift has the largest value:

$$\delta_c = 4.38 \text{ ppm}.$$

Taking into account the long-distance effects on the two other groups of protons, one finds

$$\delta_b = 2.07 \text{ ppm} \quad \text{and} \quad \delta_a = 1.03 \text{ ppm}.$$

Through the dipole-dipole interaction with the two H^b , the H^c line splits into a triplet. Since there is no measurable additional splitting due to interactions with the H^a , one concludes that the coupling constant J_{ac} is negligible:

$$J_{ac} \approx 0.$$

The same result can be derived from the threefold splitting of the H^a signal. It is valid only within the precision of the measurement, i.e. the resolution of the spectrometer.

For the H^b line, due to the interactions with three protons of type H^a and two protons of type H^c , one would expect a $4 \cdot 3 = 12$ -fold splitting. From the multiplicity of 6, however, it can be concluded that there is an interaction with five (for this interaction) equivalent protons ($5 + 1 = 6$ -fold splitting) and thus an equally strong coupling of H^b to H^a and H^c :

$$J_{ba} = J_{bc}.$$

In fact, small deviations from a simple sextet pattern are observed, since $J_{ba} = J_{bc}$ is not precisely fulfilled.

18.8 a) In the molecule $\text{CH}_3^a\text{CH}^b\text{O}$, there are two types a and b of inequivalent protons. Taking the inductive effect of the electronegative oxygen atom in the aldehyde group into account, one sees that for the chemical shifts of the two protons,

$$\delta_b > \delta_a.$$

The precise numerical values can be taken from part b):

$$\delta_a = 2.20 \text{ ppm} \quad \text{and} \quad \delta_b = 9.80 \text{ ppm}.$$

The ratio of the integrated intensities of the signals of three nuclei of type H^a to that from one nucleus of type H^b is approximately 3:1.

The H^a line splits into a doublet of equally intense lines with a spacing of $J = 2.9 \text{ Hz}$; the H^b resonance, in contrast, splits into a quartet with the same line spacing and the relative intensity ratios 1:3:3:1.

b) The chemical shift δ is computed from the resonance-field strengths B_T for the frequency standard TMS and B_S for the sample, according to the formula

$$\delta = 10^6 \cdot \frac{B_T - B_S}{B_T}. \quad (1)$$

The linear relationship between δ and B_S allows us to extract the difference ΔB_S of the magnetic resonance field strengths directly from the difference $\Delta\delta$ between the chemical shifts of two types of protons. Since for the standard, the chemical shift is defined to be $\delta_T = 0$, it corresponds to an external B_0 field at a value of B_T , so that it follows from (1) that:

$$\Delta B_S = (-) 10^{-6} B_T \Delta\delta. \quad (2)$$

With $\Delta\delta = 7.6 \text{ ppm}$, one obtains

$$\text{for } B_0 = 1.5 \text{ T: } \Delta B_S = 1.14 \cdot 10^{-5} \text{ T},$$

$$\text{for } B_0 = 7.0 \text{ T: } \Delta B_S = 5.32 \cdot 10^{-5} \text{ T}.$$

The differences ΔB_P of the resonance field strengths correspond to the differences between the local magnetic fields in the different regions of the molecule.

18.9 To predict the NMR spectrum of incompletely deuterated acetone, $\text{CD}_3\text{COCD}_2\text{H}$, we need merely take into account the coupling of the proton to the two deuterium nuclei of the CD_2H group. Since the spin of the deuterium nuclei is $I = 1$, it has three possible orientations relative to the direction of the external magnetic field: $m_I = -1, 0, 1$. The nine possible combinations for two spins are then

$$\begin{aligned} &(+1, +1); (+1, 0); (+1, -1); (0, +1); \\ &(0, 0); (0, -1); (-1, +1); (-1, 0); (-1, -1). \end{aligned}$$

From the coupling of the proton spin to the two deuterium spins, we thus find a multiplet consisting of five equidistant lines (pentet; the line spacing is J_{HD}) with the relative line intensities 1:2:3:2:1, as one can see from the number of possible combinations for the total (combined) spin of the two D nuclei ($m_{I_{\text{ges}}} = -2, -1, 0, 1, 2$).

18.10 Due to diffusion, rotation, or other processes, the magnetic environment of a spin is constantly changing, e. g. due to changes in its distance and angle to a neighbouring dipole. In the model, this is simulated by superposing a statistically fluctuating field onto the constant external magnetic field B_0 , which takes on the values $+B_i$ and $-B_i$. The shift of the precession frequency of the spin relative to the frequency ω_0 in the B_0 field alone is then given by

$$\Delta\omega_0 = \pm \gamma B_i. \quad (1)$$

If τ is the average time during which the magnetic environment remains constant, then it follows for the average phase shift $\delta\phi$ which the precessing spin undergoes between two successive field jumps, relative to a spin in the field B_0 , that

$$\delta\phi = \pm \tau \gamma B_i \quad (2)$$

with $\delta\phi \ll 1$. The time-dependent change of the phase angle ϕ can be compared with a “random walk”, in which a drunken man staggers alternately forward and backward along a straight path; cf. Fig. S.29. The average distance L which he will move after n steps of length s , expressed as the mean squared distance, is

$$\langle L^2 \rangle = n s^2. \quad (3)$$

Applied to the model of a spin in a fluctuating B field, this means that

$$\langle \phi^2 \rangle = n (\delta\phi)^2 = n \tau^2 \gamma^2 B_i^2. \quad (4)$$

Here, $\langle \phi^2 \rangle$ is the mean squared phase shift relative to a spin in the constant B_0 field. The spin contributes to the resonance signal approximately so long as its phase shift is less than a value of 1 rad. The number n of steps required to reach this limit is found from (4) to be

$$n = \frac{1}{\tau^2 \gamma^2 B_i^2}. \quad (5)$$

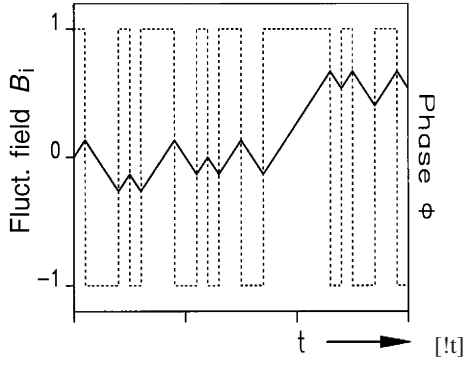


Fig. S.29. The phase φ of a spin in a fluctuating magnetic field (\cdots magnetic field $B_0 \pm B_i$, — Phase shift φ relative to spins in only the B_0 field)

The time required for n fluctuations of an average length τ , i. e. the time for a sufficient phase loss of a spin relative to the spin in only the B_0 field, is denoted as the transverse relaxation time T_2 in Bloch's theory of magnetic resonance:

$$T_2 = n \tau = \frac{1}{\tau \gamma^2 B_i^2}. \quad (6)$$

In contrast, in a rigid lattice, in which merely the unchanging magnetic environments B_0 and $B_0 \pm B_i$ are present, the result is

$$T_2' = \frac{1}{\gamma B_i}. \quad (7)$$

The linewidth in the case of rapid fluctuations with the characteristic time τ follows from (6):

$$\Delta\omega = \frac{1}{T_2} = \tau \gamma^2 B_i^2. \quad (8)$$

With (7) and (8), we obtain an expression for the line narrowing caused by fluctuations relative to the width $\Delta\omega_0$ in a rigid lattice :

$$\Delta\omega = (\Delta\omega_0)^2 \cdot \tau. \quad (9)$$

The requirement $\delta\phi \ll 1$ means that $\Delta\omega_0 \cdot \tau \ll 1$, so that

$$\Delta\omega \ll \Delta\omega_0. \quad (10)$$

Motional narrowing thus becomes more and more effective the shorter the mean fluctuation time τ .

18.11 In liquids, the fluctuations of the local magnetic field at the location of a spin are often much more rapid than in a solid, in which neither diffusion nor rotation of the molecules are effective. According to Eq. (6) from problem 18.10, the transverse relaxation time T_2 depends on the mean fluctuation time τ and the strength B_1 of the field fluctuations:

$$T_2 = n \tau = \frac{1}{\tau \gamma^2 B_1^2}.$$

It is therefore longer in liquids ($T_2 \approx 10^{-4} - 10$ s) than in solids ($T_2 \approx 10^{-4}$ s). The shorter lifetime of the phase-coherent spin states in solids leads –due to the uncertainty relation– to broader NMR lines (T_2 : phase-loss time).

18.12 a) At a lower exchange frequency, one finds two distinct resonance signals, which are separated by $\Delta\nu = 39$ Hz. The two lines begin to merge when their widths $\Delta\omega_L$, determined by the lifetimes, correspond to their separation on the frequency axis. A single line is accordingly observed when

$$\Delta\omega_L > 2\pi \Delta\nu. \quad (1)$$

The linewidth $\Delta\omega_L$ is coupled to the lifetime τ of the states (i. e. of the magnetic environments):

$$\Delta\omega_L = \frac{1}{\tau}. \quad (2)$$

From (1) and (2), we obtain

$$\tau < \frac{1}{2\pi \Delta\nu}, \quad (3)$$

and thus for the exchange frequency $\nu_A = \frac{1}{\tau}$ between the different environments:

$$\nu_A = \frac{1}{\tau} > 2\pi \Delta\nu. \quad (4)$$

With the given value for $\Delta\nu$, one obtains

$$\nu_A = 245 \text{ Hz}.$$

b) The cyclohexane ring occurs in three different conformations, of which two are termed “chair” forms and the third a “boat” form. On inversion between the two chair conformations and the boat conformation, the methyl substituent jumps between an axial and an equatorial position and thus between different magnetic environments. The protons of the methyl group exhibit different chemical shifts, depending on their position, so that one observes two groups of NMR lines at low temperatures. On raising the sample temperature, one increases the inversion frequency, until according to (a), line broadening and merging and finally, at high frequencies, exchange narrowing occurs (compare problem 18.10).

18.13 a) For the manipulation of an individual experiment, the maximum time available is the time up to complete loss of phase coherence, i. e. the transverse relaxation time T_2 :

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{2T_1}.$$

Here, T_2' is composed of the inhomogeneous contributions (e. g. due to different B fields at the locations of different nuclei) and the homogeneous contributions due to spin-spin interactions. T_1 denotes the longitudinal or spin-lattice relaxation time.

b) The pulse sequence $\frac{\pi}{2} - \tau - \pi - \tau$ is used in the spin-echo method to switch off the inhomogeneous contributions to the phase-loss time T_2 (local variations in the B field, chemical shifts, etc.). Irradiation at a second radiofrequency leads to frequent and rapid flipping of the spins of those nuclear species which are in resonance at this second frequency. In this way, the anisotropic dipole-dipole interaction with these nuclei is switched off.

18.14 Instead of carrying out numerous individual measurements with different τ as in the spin-echo technique, one can also follow the decrease of the echo height in a single experiment by applying the method of Carr and Purcell; here, several π pulses are applied at times $\tau, 3\tau, 5\tau, \dots$ and thus echoes are obtained at times of $2\tau, 4\tau, 6\tau, \dots$; cf. Fig. S.30. The pulse sequence has the following form:

$$\frac{\pi}{2} - \tau - \pi - \tau - \text{Echo} - \tau - \pi - \tau - \text{Echo} - \tau - \pi - \dots$$

The nuclear magnetisation is first rotated into the $x - y$ -plane, then it decreases due to loss of phase coherence of the spins ("spreading out" of spin directions); and then, following inversion of the spins around the y axis by the π pulse, it again increases up to the echo. Thereafter, the spins again spread out in the reverse sense, and the process is repeated.

The decrease of the echo height is due here (besides longitudinal relaxation) only to homogeneous relaxation, caused by spin-spin interactions, so that the relaxation time $T_{2, \text{hom}}$ can be simply determined. The echo height decreases according to

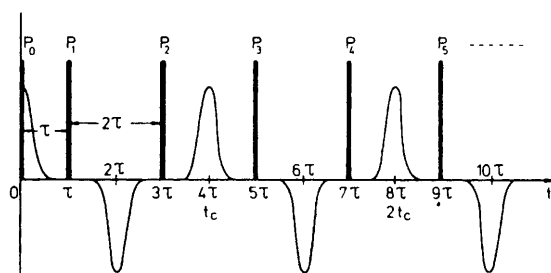


Fig. S.30. Pulse sequence and echoes in the Carr-Purcell method. After M. Mehring: *Principles of High Resolution NMR in Solids*; Chap. 3 (Springer, Berlin, Heidelberg 1983)

$$M_{xy}(t) = M_{xy}(0) \cdot e^{-1/T_2, \text{hom}}$$

with $t = n \cdot 2\tau$.

18.15 We write the Schrödinger equation

$$i\hbar\dot{\psi} = H\psi \quad (1)$$

in the form

$$\dot{\psi} = -\frac{i}{\hbar}H\psi. \quad (2)$$

Its formal solution is

$$\psi = e^{-\frac{i}{\hbar}Ht}\psi(0). \quad (3)$$

Inserting (3) into

$$\int \psi^* D \psi dx, \quad (4)$$

where D is an arbitrary operator, we obtain

$$= \int \left[e^{\frac{i}{\hbar}Ht}\psi^*(0) \right] D e^{-\frac{i}{\hbar}Ht}\psi(0) dx. \quad (5)$$

Since H is an hermitian operator, we have

$$\int (H\psi^*) \phi dx = \int \psi^* H\phi dx, \quad (6)$$

and likewise

$$\int (H^n \psi^*) \phi dx = \int \psi^* H^n \phi dx. \quad (7)$$

Making use of (7) and

$$e^{\frac{i}{\hbar}Ht} = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} H^n, \quad (8)$$

we obtain from (5)

$$\int \psi^*(0) \underbrace{e^{\frac{i}{\hbar}Ht} D e^{-\frac{i}{\hbar}Ht}}_{D_H(t)} \psi(0) dx. \quad (9)$$

Using the bra and ket notation, we can write with (4) and (9)

$$\langle \psi(t) | D | \psi(t) \rangle = \langle \psi(0) | D_H(t) | \psi(0) \rangle, \quad (10)$$

where

$$D_H = e^{\frac{i}{\hbar} H t} D e^{-\frac{i}{\hbar} H t} . \quad (11)$$

Differentiating both sides of (11) with respect to time, we find

$$\dot{D}_H(t) = \frac{i}{\hbar} H \underbrace{e^{\frac{i}{\hbar} H t} D e^{-\frac{i}{\hbar} H t}}_{D_H} - \frac{i}{\hbar} \underbrace{e^{\frac{i}{\hbar} H t} D e^{-\frac{i}{\hbar} H t} H}_{D_H} , \quad (12)$$

$$= \frac{i}{\hbar} (H D_H - D_H H) , \quad (13)$$

or, finally, using the commutator notation,

$$\dot{D}_H = \frac{i}{\hbar} [H, D_H] . \quad (14)$$

18.16 We represent the spin function as a superposition

$$|\phi\rangle = a |\uparrow\rangle + b |\downarrow\rangle , \quad (15)$$

whereby

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} , \quad |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} . \quad (16)$$

In units of \hbar , the operator for the x component of the angular momentum is

$$I_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} . \quad (17)$$

We compute its expectation value:

$$\langle\phi| I_x |\phi\rangle = (a^* \langle\uparrow| + b^* \langle\downarrow|) I_x (a |\uparrow\rangle + b |\downarrow\rangle) , \quad (18)$$

where the following relations hold

$$\langle\uparrow| I_x |\uparrow\rangle = 0 , \quad (19)$$

$$\langle\downarrow| I_x |\downarrow\rangle = 0 , \quad (20)$$

$$\langle\downarrow| I_x |\uparrow\rangle = \frac{1}{2} , \quad (21)$$

$$\langle\uparrow| I_x |\downarrow\rangle = \frac{1}{2} . \quad (22)$$

With (19–22), we find for (18)

$$\frac{1}{2} (a^* b + b^* a) . \quad (23)$$

If we set $a = ce^{i\phi/2}$ and $b = ce^{-i\phi/2}$ in this expression, we find for the expectation value of the x component:

$$\frac{1}{2} |c|^2 (e^{-i\phi} + e^{i\phi}) = |c|^2 \cos \phi, \quad (24)$$

and correspondingly for the y component:

$$\langle \phi | I_y | \phi \rangle = -|c|^2 \sin \phi \quad (25)$$

as well as

$$\langle \phi | I_z | \phi \rangle = 0. \quad (26)$$

The expectation value of the spin vector thus undergoes a coherent rotational motion.

18.17 We begin with the usual commutation relations,

$$I_x I_y - I_y I_x = iI_z, \quad I_y I_z - I_z I_y = iI_x, \quad I_z I_x - I_x I_z = iI_y \quad (27)$$

and Heisenberg's equation of motion

$$\dot{I}_{kx} = \frac{i}{\hbar} [H, I_{kx}]. \quad (28)$$

Taking

$$H = \hbar J I_{kz} I_{lz}, \quad l \neq k \quad (29)$$

and (27), we obtain

$$\begin{aligned} \dot{I}_{kx} &= i2J [I_{kz} I_{lz}, I_{kx}] \\ &= i2J I_{lz} \underbrace{[I_{kz}, I_{kx}]}_{iI_{ky}} \end{aligned} \quad (30)$$

and thus

$$\dot{I}_{kx} = -2J I_{lz} I_{ky}. \quad (31)$$

Since this equation is not closed, we set up another Heisenberg equation

$$\begin{aligned} (I_{ky} I_{lz})' &= i2J [I_{kz} I_{lz}, I_{ky} I_{lz}] \\ &= i2J \underbrace{I_{lz}^2}_{\frac{1}{4}} \underbrace{[I_{kz}, I_{ky}]}_{-iI_{kx}}, \end{aligned} \quad (32)$$

obtaining

$$(I_{ky} I_{lz})' = \frac{1}{2} J I_{kx}. \quad (33)$$

From (31) and (33), we find by standard methods the result

$$\ddot{I}_{kx} = -J^2 I_{kx} . \quad (34)$$

Its solution is

$$I_{kx}(t) = a \cos Jt + b \sin Jt , \quad (35)$$

where

$$a = I_{kx}(0) \quad (36)$$

and, due to

$$\dot{I}_{kx}(0) = Jb = -2J (I_{Iz} I_{ky})_{t=0} , \quad (37)$$

b is found to be given by

$$b = -2 (I_{Iz} I_{ky})_{t=0} . \quad (38)$$

The solution we are seeking is therefore

$$I_{kx}(t) = I_{kx}(0) \cos Jt - 2 (I_{Iz} I_{ky})_{t=0} \sin Jt . \quad (39)$$

The solution for $I_{ky} I_{Iz} = I_{Iz} I_{ky}$ follows immediately from (31) and (39).

18.18 We write

$$\begin{aligned} \langle \psi | I_{\pm}(0) | \psi \rangle &= (\alpha^* \langle \uparrow | + \beta^* \langle \downarrow |) [I_x(0) \pm i I_y(0)] \\ &\quad \times (\alpha |\uparrow\rangle + \beta |\downarrow\rangle) . \end{aligned} \quad (40)$$

On multiplying through, we obtain expressions of the form $\alpha^* \alpha \langle \uparrow | I_x | \uparrow \rangle$ etc. These can be evaluated with the aid of (19–22) and corresponding relations for I_y . We find for (40)

$$e^{i\Omega t} \langle I_+ \rangle = e^{i\Omega t} \alpha^* \beta \quad (41)$$

and

$$e^{-i\Omega t} \langle I_- \rangle = e^{-i\Omega t} \alpha \beta^* . \quad (42)$$

We set

$$\alpha^* \beta = |\alpha| |\beta| e^{-i\phi} \quad (43)$$

and obtain

$$\langle I_x(t) \rangle = \frac{1}{2} [I_+(t) + I_-(t)] = |\alpha| |\beta| \cos(\Omega t - \phi) \quad (44)$$

and

$$\langle I_y(t) \rangle = \frac{1}{2i} [I_+(t) - I_-(t)] = |\alpha| |\beta| \sin(\Omega t - \phi) , \quad (45)$$

from which we can see the precessional motion directly.

18.19 The magnetic moment of the proton is

$$\boldsymbol{\mu} = \frac{e}{m_0} \mathbf{s}, \quad (46)$$

and its energy in a magnetic field:

$$V_s = -\boldsymbol{\mu} \cdot \mathbf{B}. \quad (47)$$

The following relations hold:

$$\mathbf{B} = \text{rot } \mathbf{A} = \frac{1}{\omega_\lambda} N_\lambda b_\lambda \mathbf{i} (\mathbf{k}_\lambda \times \mathbf{e}_\lambda) e^{ik_\lambda r} + \text{c.c.} \quad (48)$$

with

$$N_\lambda = \sqrt{\frac{\hbar \omega_\lambda}{2\varepsilon_0 V}}. \quad (49)$$

In the usual experimental arrangement (see also problem 18.20), the spin is subjected to a constant field \mathbf{B} along the z direction and an oscillating field perpendicular to it (48). Correspondingly, we choose $\mathbf{k}_\lambda = (0, 0, k_z)$ and $\mathbf{e}_\lambda = (0, e_y, 0)$.

We then obtain

$$V_s = \frac{e}{m_0} \frac{1}{\omega_\lambda} \sqrt{\frac{\hbar \omega_\lambda}{2\varepsilon_0 V}} i k_\lambda e^{ik_\lambda z} s_x b_\lambda + \text{h.c.} \quad (50)$$

Setting $s_x = \frac{1}{2}(s_+ + s_-)$ and $s = \hbar \mathbf{I}$, we find

$$V_s = \frac{e}{2m_0} \cdot \sqrt{\frac{\hbar}{2\varepsilon_0 \omega_\lambda V}} k_\lambda \mathbf{i} e^{ik_\lambda z} \hbar (I_+ + I_-) b_\lambda + \text{h.c.} \quad (51)$$

From this result, we can immediately read off the coupling constant that we are seeking. We arrive at the “rotating-wave” approximation by investigating the motion of the operators in the Heisenberg representation (without interactions between \mathbf{I} and \mathbf{B} (48)). Then $b_\lambda \sim e^{-i\omega_\lambda t}$, $I_\pm \sim e^{i\Omega t}$ is found. In the neighbourhood of resonance, $\Omega \approx \omega_\lambda$, the terms $I_+ b_\lambda$, $I_- b_\lambda^+$ vary slowly, while the terms $I_+ b^+ \sim e^{i\Omega t + i\omega_\lambda t}$ and $I_- b$ oscillate rapidly and make practically no contribution to the interaction energy. They can therefore be neglected in (51).

18.20 We start with

$$\dot{b}^+ = \frac{i}{\hbar} [H, b^+]. \quad (1)$$

Due to the commutation relations

$$[b, b^+] = 1, \quad [b^+, I_x] = [b^+, I_y] = [b^+, I_z] = 0, \quad (2)$$

it follows that

$$\dot{b}^+ = i\omega b^+ - gI_+ . \quad (3)$$

A precessing spin is described by:

$$\langle I_+(t) \rangle = \langle I_+(0) \rangle e^{i\Omega t} . \quad (4)$$

The equation of motion with damping is:

$$\dot{b}^+ = i\omega b^+ - \kappa b^+ - g \langle I_+(0) \rangle e^{i\Omega t} . \quad (5)$$

It has the *solution*:

$$b^+(t) = -g \langle I_+(0) \rangle e^{i\Omega t} (i\Omega - i\omega + \kappa)^{-1} . \quad (6)$$

Chapter 19

19.1 The dipole-dipole interaction between an electron spin and the nuclear spins leads to a hyperfine splitting of the ESR lines. The number of lines is given by the number $2I + 1$ of different possible orientations of the nuclear spin I relative to the direction of the electronic spin. The spins of the participating nuclei are $I = 0$ for ^{12}C ; $I = \frac{1}{2}$ for ^{13}C , ^1H and ^{19}F ; $I = 1$ for ^2D ; and $I = \frac{3}{2}$ for ^{35}Cl and ^{37}Cl .

$[^{12}\text{CF}_2\text{H}]^\bullet$	6 lines	(2-fold splitting by H, 3-fold by F_2 with $I_{\text{ges}}, \text{F}_2 = 1$);
$[^{13}\text{CF}_2\text{H}]^\bullet$	12 lines	(additional 2-fold splitting by ^{13}C);
$[^{12}\text{CF}_2\text{D}]^\bullet$	9 lines	(3-fold splitting by D, 3-fold by F_2);
$[^{12}\text{CClH}_2]^\bullet$	12 lines	(4-fold splitting by Cl, 3-fold by H_2).

19.2 a) The hyperfine structure of the naphthalene radical is determined by the interaction of its electronic spin with two groups α and β , each having four equivalent protons. The coupling constants are a_α and a_β .

For the orientations of the four equivalent α proton spins, $I = \frac{1}{2}$, relative to the electronic spin, there are five possibilities ($M_I = 0, \pm 1, \pm 2$), so that the ESR signal splits into five lines with a spacing of a_α and with relative intensities of 1:4:6:4:1 (Pascal's triangle!). Due to the interaction with the four β proton spins, each of these five lines again splits into five lines with a spacing of a_β and with relative intensities of 1:4:6:4:1. Thus, five groups of five lines each are observed, whereby the intensity ratios and spacings of the group maxima are determined by the α interaction (1:4:6:4:1; a_α).

The 25 lines can thus be associated with the orientations (M_α, M_β) of the total spins I_α and I_β of the two groups of equivalent protons. With increasing B field, i. e. for the lines of the given spectrum going from left to right, one obtains

$(-2, -2)(-2, -1)(-2, 0)(-1, -2)(-2, 1)(-1, -1)$
 $(-2, 2)(-1, 0)(0, -2)(-1, 1)(0, -1)(-1, 2)(0, 0)$
 $(1, -2)(0, 1)(1, -1)(0, 2)(1, 0)(2, -2)(1, 1)(2, -1)$
 $(1, 2)(2, 0)(2, 1)(2, 2).$

b) In agreement with the notation of the H locations in the problem text (structural formula), in 1-iodo naphthalene, the iodine substituent is located at an α position. The interaction of the electronic spin with the remaining three α proton spins and the four β spins then leads to a splitting into 20 lines which can be grouped into four pentets. The intensity ratio of the group maxima is 1:3:3:1, and their spacing is a_α .

In 2-iodo naphthalene, on the other hand, the iodine atom replaces a β proton, so that a splitting into five quartets and thus likewise a total of 20 lines is observed. The intensity ratios of the group maxima are 1:4:6:4:1, and their spacing is again a_α .

The interaction with the spin of the ^{127}I nucleus (nuclear spin $\frac{5}{2}$) was neglected in the above considerations. It would further split each of the lines into six sublines.

c) The substitution of one hydrogen by a methyl group leads in analogy to (b) to a splitting of the ESR signal in each case into 20 lines. In addition, the interactions with the three methyl protons produces a further quartet splitting of each line with the intensity ratio (1:3:3:1) – the hyperfine structure thus includes all together 80 lines.

19.3 a) In the $[\text{NH}_2]^\bullet$ radical, the dipole-dipole interaction of the electronic spin with the spin of the nitrogen nucleus ^{14}N ($I = 1$) leads to a splitting of the signal into three lines of equal intensity, with a spacing of $a_\text{N} = 1.03$ mT. The coupling with the two proton spins $I = \frac{1}{2}$ splits each of the three lines into a triplet (line spacing $a_\text{H} = 0.35$ mT, intensity ratio 1:2:1).

b) The ESR spectrum of the azide radical $[\text{N}_3]^\bullet$ exhibits a hyperfine structure with seven lines, which is caused by the spin-spin interaction of the free electron with the total spin of the three nitrogen nuclei. The lines of the septet have the relative intensities 1:3:6:7:6:3:1; cf. Figs. S.31 and S.32.

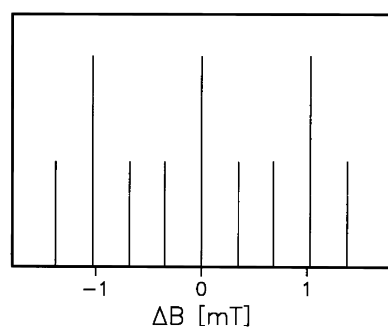


Fig. S.31. Hyperfine structure in the ESR spectrum of the $[\text{N}_3]^\bullet$ radical. One observes nine lines, which can be grouped into three triplets

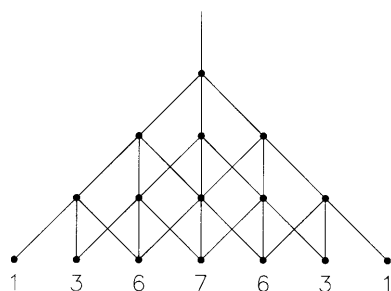


Fig. S.32. Since the nuclear spin is $I = 1$, the relative line intensities cannot be obtained using Pascal's triangle. Instead, one uses the "family-tree method" (counting the various possibilities for going from the tip to a particular end point)

19.4 a) From the hyperfine-structure coupling constants a_α and a_β of naphthalene, using the McConnell equation one can calculate the spin density at the C atoms α and β ; cf. Fig. S.33:

$$\begin{aligned} a_\alpha &= (-) 0.495 \text{ mT} \quad \Rightarrow \quad \varrho_\alpha = 0.22 \\ a_\beta &= (-) 0.186 \text{ mT} \quad \Rightarrow \quad \varrho_\beta = 0.08. \end{aligned}$$

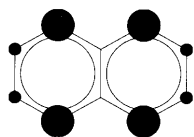
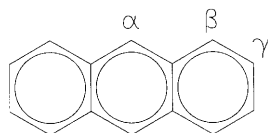


Fig. S.33. The spin-density distribution in the naphthalene radical anion. The free electron spends 22% of its time at each of the α -C atoms, 8% at each of the β -C atoms

The π electron is localised to the extent of 88% at the four α -C atoms. The normalisation condition $\sum \varrho_i = 1$ is not well fulfilled; instead, one obtains $\sum \varrho_i = 1.2$. The McConnell equation is merely a rough approximation. No information can be obtained about the occupation probability at the two central C atoms (which have no C-H bonds).



b) The assignment of the given values for the spin density, ϱ_i , to the inequivalent C positions in anthracene (see above) can be carried out by means of a comparison with naphthalene. The spin density ϱ , and with it the coupling strength a , decrease on going from the centre of the molecule outwards, and we find

$$\varrho_\alpha = 0.193, \quad \varrho_\beta = 0.097, \quad \varrho_\gamma = 0.048.$$

The normalisation condition is well fulfilled, $\sum \varrho_i = 0.966$. Applying the McConnell equation, one can obtain the hyperfine-structure coupling constants for

the interaction of the electronic spin with the proton spins, starting from the spin densities:

$$a_\alpha = Q \varrho_\alpha = (-) 0.434 \text{ mT},$$

$$a_\beta = Q \varrho_\beta = (-) 0.218 \text{ mT},$$

$$a_\gamma = Q \varrho_\gamma = (-) 0.108 \text{ mT}.$$

The interaction of the electronic spin with the three types of protons leads to the following splittings (number of lines, relative intensity ratios, and line spacings):

$$H_\alpha : 3 \text{ lines, } 1:2:1, a_\alpha,$$

$$H_\beta : 5 \text{ lines, } 1:4:6:4:1, a_\beta,$$

$$H_\gamma : 5 \text{ lines, } 1:4:6:4:1, a_\gamma.$$

One thus expects a hyperfine-structure splitting of the ESR signal of anthracene into 75 lines.

19.5 The resonance frequency ν of an electron in a magnetic field of strength B is given by the relation

$$\nu = \frac{g \mu_B}{h} B \quad (1)$$

($\mu_B = 9.274 \cdot 10^{-24} \text{ Am}^2$: Bohr magneton). From it, with the given values for the frequency and the B field, we can compute the g -factor of the electron:

$$g = \frac{h\nu}{\mu_B B}. \quad (2)$$

Since the hyperfine-structure splitting of the signal is symmetric around the centre of gravity of the lines, we take as the B field the average value of the two line positions ($B = 303.32 \text{ mT}$). From this, we obtain

$$g = 2.0022$$

for an electron in atomic hydrogen. The strength of the dipole-dipole interaction is independent of the applied B field, so that we find the coupling constant directly from the spacing of the two hyperfine-structure lines:

$$a = \Delta B = 50.70 \text{ mT}.$$

19.6 In the CH_3 radical, the hyperfine structure of the ESR lines is due to the interactions of the free electron spin with the three equivalent protons of nuclear spin $I = \frac{1}{2}$. One observes a quartet, for which the relative line intensities of 1:3:3:1 can be derived using Pascal's triangle. In the triply-deuterated CD_3 radical, an interaction with three equivalent D nuclear spins of $I = 1$ occurs. The line intensities in the resulting septet are determined by the family-tree method described in problem 19.3 b) to be 1:3:6:7:6:3:1.

19.7 The six protons in the benzene molecule are chemically and magnetically equivalent. This has two consequences: on the one hand, spin diffusion takes place between the nuclei, i. e. there is a rapid exchange of their spin orientations. Any differences in the interactions of the electron with the individual nuclear spins is averaged out, so that one must treat the equivalent protons all together, i. e. as a total spin. This picture also enters into the description of the dipole-dipole interaction for the elucidation of the fine structure of NMR spectra.

On the other hand, the free electron of the benzene radical anions is localised to the extent of $\frac{1}{6}$ on each of the equivalent C atoms, so that its spin couples equally strongly to each of the six protons. It is therefore irrelevant how the spin orientations which contribute to a given total spin are distributed among the individual protons.

The rotation of the molecule as a whole has no influence at all upon these two intramolecular effects. It therefore causes no wiping out of the hyperfine structure owing to exchange phenomena.

In order to calculate the hypothetical exchange narrowing of the ESR signal, we first briefly ignore the counterarguments given. The hyperfine-structure coupling constant for the interaction of the free electron spin with the proton spins in benzene is $a = 0.375$ mT. The hyperfine structure of the ESR signals vanishes when the lifetime broadening ν_L of the individual lines becomes as large as the spacing $\Delta\nu_{\text{Hfs}}$ of two neighbouring lines. The lifetime τ of a spin state is obtained from Heisenberg's uncertainty relation according to:

$$\Delta E \cdot \tau \equiv h \Delta\nu \cdot \tau = \hbar, \quad (1)$$

and from it, the lifetime broadening of a hyperfine-structure line:

$$\nu_L = \Delta\nu = \frac{\hbar}{h \tau} = \frac{1}{2\pi \tau}. \quad (2)$$

In the case of a benzene molecule rotating about its sixfold symmetry axis, the lifetime of a particular spin state is limited by the rotational frequency ν_R . The rotation leads to a rapid exchange of the nuclear spin positions at an exchange frequency of

$$\nu_A = \frac{1}{\tau} = 6 \nu_R. \quad (3)$$

It follows from this that

$$\nu_L = \frac{6\nu_R}{2\pi}, \quad (4)$$

and with

$$\nu_L = \Delta\nu_{\text{Hfs}} = \frac{g \mu_B}{h} a, \quad (5)$$

one finally obtains the rotational frequency at which, according to this model, the hyperfine structure should be averaged out:

$$\nu_R = \frac{\pi g \mu_B}{3h} a. \quad (6)$$

With the value given for a , we calculate

$$\nu_R = 1.10 \cdot 10^7 \text{ Hz}.$$

The rotational frequency corresponds classically to a rotational energy of

$$E_R = \frac{1}{2} \Theta_{\parallel} (2\pi \nu_R)^2 = 7.1 \cdot 10^{-30} \text{ J} \hat{=} 3.6 \cdot 10^{-7} \text{ cm}^{-1}.$$

The rotational energy levels of the symmetric-top molecule are given by

$$F(J, K) = B J(J+1) + C K^2, \quad (7)$$

with $K = -J \dots +J$ and the rotational constants

$$B = \frac{h}{8\pi^2 c \Theta_{\perp}} = 0.19 \text{ cm}^{-1} \quad \text{and} \\ C = \frac{h}{8\pi^2 c} \left(\frac{1}{\Theta_{\parallel}} - \frac{1}{\Theta_{\perp}} \right) = -0.10 \text{ cm}^{-1}.$$

This shows that for benzene in the gas phase, even at the lowest temperatures, the thermal population of the rotational excitation states would be sufficient to average out the hyperfine structure. In measurements in the gas phase, however, the hyperfine structure is indeed observed. The assumption that the rotation of the benzene molecule leads to an exchange narrowing of the ESR signal must therefore be incorrect.

19.8 Excitons are delocalised excitation states which can move due to the interactions between neighbouring molecules in a crystal. Since the nitrogen nuclear spins are not uniquely oriented, the different dipole-dipole interactions between the electronic spin and the nuclear spins are spatially averaged out, as long as the hopping rate of the triplet excitons, and with it the exchange frequency between different environments of the electronic spins, is high enough. There is thus a motional narrowing of the lines which are broadened by the hyperfine structure.

If one dopes NaNO_2 crystals with 1% of KNO_2 , then the guest molecules act as traps for the triplet excitons. Since the triplet excitation state is localised on the KNO_2 molecules, one can now observe the hyperfine structure.

19.9 The fine-structure constant D of pyrazine represents a quantum-mechanical expectation value and implies an integration over the distance to the electron, r_{12} , and its component z_{12} , over all of space. To carry this out, knowledge of the exact triplet wavefunction ${}^3\Psi$ is required. In the SI unit system and with the correct units for D , we have

$$hc D = \frac{\mu_0}{4\pi} \frac{3}{4} g_e^2 \mu_B^2 \int {}^3\Psi^* \left(\frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5} \right) {}^3\Psi dV_1 dV_2. \quad (1)$$

One can, however, determine an averaged distance r of the two electrons which are localised in the triplet state, if they are treated as localised point dipoles. We thus require

$$r_{12} = r \stackrel{!}{=} \text{const}. \quad (2)$$

Since pyrazine has an essentially planar molecular structure, the z -component of the distance r can be neglected ($z_{12} \approx 0$), and we obtain

$$hc D = \frac{\mu_0}{4\pi} \frac{3}{4} g_e^2 \mu_B^2 \frac{1}{r^3} \int {}^3\Psi^* {}^3\Psi dV_1 dV_2. \quad (3)$$

Owing to the normalisation condition for the wavefunction, the integral has a value of 1. In the point-dipole model, one thus obtains for the average distance r of the two triplet electronic spins:

$$r = \left(\frac{3\mu_0 g_e^2 \mu_B^2}{16\pi D hc} \right)^{\frac{1}{3}}. \quad (4)$$

In the present case, we can calculate

$$r = 1.63 \text{ \AA}.$$

19.10

$$D = \frac{3}{4} \frac{1}{\hbar^2} g_e^2 \mu_B^2 \int {}^3\Psi^* \left(\frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5} \right) {}^3\Psi dV_1 dV_2 \quad (1)$$

$$E = \frac{3}{4} \frac{1}{\hbar^2} g_e^2 \mu_B^2 \int {}^3\Psi^* \left(\frac{y_{12}^2 - x_{12}^2}{r_{12}^5} \right) {}^3\Psi dV_1 dV_2. \quad (2)$$

19.11 Proceed as described in the text.

19.12 a) The size of the molecules and thus the extent of their π electron system increases in the series

$$\text{benzene} < \text{naphthalene} < \text{anthracene} < \text{tetracene}. \quad (1)$$

Since, owing to the planarity of the molecules, the z component of the distance r_{12} of the triplet electrons can be neglected, the fine-structure parameter D is directly correlated with r_{12} and thereby with the molecular size:

$$D \propto \frac{1}{r_{12}^3}. \quad (2)$$

Here, r_{12} can already be understood as the averaged distance. The larger the molecule, the larger r_{12} , and the smaller the fine-structure constant D . We thus find that

$$D_{\text{benzene}} > D_{\text{naphthalene}} > D_{\text{anthracene}} > D_{\text{tetracene}}. \quad (3)$$

The experimental values are 0.15, 0.10, 0.07, and 0.06 cm^{-1} .

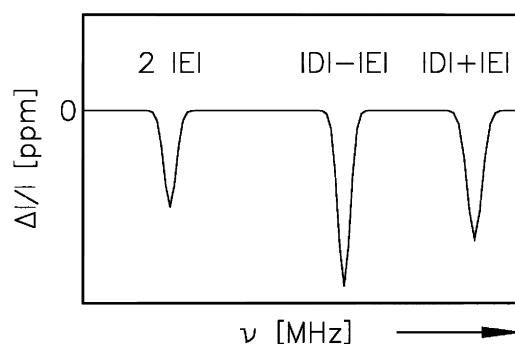


Fig. S.34. A schematic ADMR spectrum

The fine-structure parameter E , in contrast, contains the expectation value of the difference $y_{12}^2 - x_{12}^2$ of the components of the distance of the electrons in the molecular plane. Since the longer molecular axis is denoted as x , for all molecules we find $E \leq 0$. In particular, in the rotationally-symmetric benzene molecule, it follows that $E = 0$. The magnitude of E increases with the x dimension of the molecules:

$$|E|_{\text{benzene}} < |E|_{\text{naphthalene}} < |E|_{\text{anthracene}} < |E|_{\text{tetracene}}. \quad (4)$$

The experimental values for these energies are 0, -0.013 , -0.015 , and -0.030 cm^{-1} .

b) Corresponding to the results in (a), one attributes a D value of 0.15 cm^{-1} to benzene, while tetracene has the other extreme value of 0.06 cm^{-1} . With the aid of Eq. (4) from problem 19.9, one can calculate from this the averaged electron distances in the two molecules to be

$$r_{\text{benzene}} = 2.05 \text{ \AA} \quad \text{and} \quad r_{\text{tetracene}} = 2.79 \text{ \AA}.$$

19.13 a) in the case that irradiation with microwaves causes a redistribution of a slowly-decaying sublevel into a rapidly-decaying sublevel of the triplet state, the overall population of the triplet state decreases, while that of the singlet ground state increases. The transmission of the sample, which is determined by the ground-state population, therefore decreases in an ADMR experiment:

$$\Delta I < 0. \quad (1)$$

The ADMR spectrum yields the transmitted intensity I at a fixed optical frequency as a function of the wavelength of the applied microwave radiation. One thus observes three signals, when the microwave frequency corresponds to one of the transition frequencies between the triplet sublevels 0, $D - E$ and $D + E$:

$$\nu_{\text{signal}} = 2E, D - E, D + E. \quad (2)$$

b) The transmission of a sample is given by the Lambert-Beers law according to:

$$I = I_0 \cdot 10^{-\varepsilon S_0 c d} \quad \text{with} \quad (3)$$

I : transmitted intensity;
 I_0 : irradiation intensity;
 ε : extinction coefficient;
 d : optical path length;
 c : sample concentration;
 S_0 : fraction of the molecules in the S_0 state.

Irradiation with microwaves leads to a change in the ground-state population by ΔS_0 ; the transmitted light intensity thus becomes

$$I' = I_0 \cdot 10^{-\varepsilon (S_0 + \Delta S_0) c d}. \quad (4)$$

For the relative change in transmission, it follows that

$$\frac{\Delta I}{I} = \frac{I' - I}{I} = 10^{-\varepsilon \Delta S_0 c d} - 1 = e^{-\varepsilon \ln 10 \Delta S_0 c d} - 1. \quad (5)$$

This expression can be expanded up to the first-order term in the case of low optical densities

$$\text{OD} = \varepsilon c d, \quad (6)$$

leading to the result:

$$\frac{\Delta I}{I} = -\varepsilon \ln 10 \Delta S_0 c d, \quad (7)$$

or finally,

$$\frac{\Delta I}{I} = -\Delta S_0 \text{OD} \ln 10. \quad (8)$$

Here, OD is the optical density (absorption) of the sample without microwave irradiation.

c) With the values given for *Rb. sphaeroides* GA, one can compute the change in the ground-state population, finding

$$\Delta S_0 = +7.6 \cdot 10^{-4}.$$

The fraction of molecules in the S_0 ground state, relative to the overall number of molecules, thus increases by 0.076%. This shows that ADMR is an extremely sensitive method of measurement, which however also requires a correspondingly sensitive detection apparatus.

Chapter 20

20.1 a) The interaction energy E_{WW} between the two dipoles μ_{D} and μ_{A} at a distance of $\mathbf{r} = \mathbf{r}_{\text{A}} - \mathbf{r}_{\text{D}}$ is

$$\begin{aligned} E_{\text{WW}} &= \text{const} \cdot \frac{(\mu_{\text{D}} \cdot \mu_{\text{A}}) r^2 - 3 (\mathbf{r} \cdot \mu_{\text{D}}) (\mathbf{r} \cdot \mu_{\text{A}})}{r^5} \\ &= \text{const} \cdot \kappa \frac{\mu_{\text{D}} \mu_{\text{A}}}{r^3} \end{aligned} \quad (1)$$

with

$$\kappa = \cos \phi_{\text{DA}} - 3 \cos \phi_{\text{D}} \cos \phi_{\text{A}} \quad (2)$$

(ϕ_{DA} is the angle between the dipole orientations; ϕ_{D} , ϕ_{A} is the angle between the dipoles and the vector connecting them). The transfer rate k_{ET} is proportional to the square of the interaction energy:

$$k_{\text{ET}} \propto E_{\text{WW}}^2 \propto \kappa^2 \frac{\mu_{\text{D}}^2 \mu_{\text{A}}^2}{r^6}. \quad (3)$$

If one identifies μ_{D}^2 and μ_{A}^2 with the oscillator strengths of the transitions of the donor and the acceptor, then one finally arrives at a qualitative relation:

$$k_{\text{ET}} \propto \kappa^2 \frac{1}{r^6} \int f_{\text{D}}(\overline{\nu}) \varepsilon_{\text{A}}(\overline{\nu}), \quad (4)$$

which contains the overlap integral of the donor fluorescence and the acceptor absorption, the orientation factor κ^2 , and the distance term $1/r^6$. (In contrast, for the exchange interaction, an exponential distance dependence is obtained.)

b) Inserting the data into the formula given in the problem text, we can calculate the Förster radius of fluorescein, obtaining

$$r_0 = 50.2 \text{ \AA}$$

c) At low concentrations, $c \ll c_0$, the yield ϕ for Förster transfer is proportional to the probability that an acceptor molecule is located at a distance $r \leq r_0$ from the donor and is therefore within the volume $\frac{4\pi}{3} r_0^3$ around the position of the donor. It is thus proportional to the concentration c of the molecules:

$$\phi \propto c \quad \text{for } c \ll c_0. \quad (5)$$

For the case of high concentrations, $c \gg c_0$, near each excited molecule there are several acceptor molecules within the critical radius r_0 . The yield ϕ is then proportional to the rate k_{ET} of energy transfer to the next neighbours and thus to the square of the concentration:

$$\phi \propto k_{\text{ET}} \propto \frac{1}{r^6} \propto c^2 \quad \text{for } c \gg c_0. \quad (6)$$

20.2 The distance dependence of the energy transfer rate k_{ET} is given by

$$k_{\text{ET}} \propto \frac{1}{r^6}, \quad (1)$$

so that for the (critical) Förster radius and an arbitrary distance r_1 , we can write the relation

$$k_0 r_0^6 = k_1 r_1^6 \iff r_0 = \left(\frac{k_1}{k_0} \right)^{\frac{1}{6}} r_1. \quad (2)$$

In the case of twelve chain links, we find for the chain length and thus the distance r_1 between the donor and the acceptor:

$$r_1 = 46.1 \text{ Å},$$

and from it, using (2), the Förster radius

$$r_0 = 37.7 \text{ Å}.$$

This corresponds to a chain with ca. $n = 9$ links.

20.3 a) With the techniques of Second Harmonic Generation (SHG) and ellipsometry, one measures different physical properties of the system consisting of the substrate and the overlayer.

The non-linear optical process of frequency doubling (SHG) takes place on the gold surface. The decrease in SHG intensity during layer formation is due to a change in the electronic structure of the surface and is thus a measure of the coverage with sulphur atoms.

In contrast, ellipsometry, i. e. the polarisation-dependent measurement of the reflection coefficient of the interface, is sensitive to structural changes in the layer itself. From the longer time for layer formation measured with this technique, one can derive the fact that following the relatively rapid process of chemisorption, a slower process of reorientation and restructuring of the molecules occurs, until finally all of the alkyl chains are stretched and oriented parallel to each other.

b) The parallel orientation of the alkyl chains is stabilised by lateral intermolecular van der Waals forces. These increase with increasing length of the molecules. In the solution, the molecules are often bent (cis-conformations) and are nearly spherical in overall shape. The loss of entropy on stretching out the molecules is compensated by the energy gain from their chemisorption and orientation.

c) The depth of the holes (2.5 Å) just corresponds to the lattice constant of the substrate [Au(111) surface] and can thus be identified as a defect in the uppermost atomic layer of the gold substrate. The cause of this is corrosion of the surface, i. e. removal of gold atoms into the solution. There, they react with the alkane-thiols to give gold-thiolate compounds.

Chapter 22

22.1 One can, at least theoretically, make use of the entire inhomogeneous linewidth Γ for photochemical hole-burning. The width of the hole corresponds to twice the homogeneous linewidth, which is due only to the lifetime limit:

$$\gamma_{\text{hole}} = 2 \gamma_h = \frac{2}{2\pi \tau}. \quad (1)$$

With $\Gamma = 700 \text{ cm}^{-1}$ and $\gamma_{\text{hole}} = 0.55 \text{ cm}^{-1}$, we calculate the maximum number n_{max} of the holes to be burned to be

$$n_{\text{max}} = \frac{\Gamma}{\gamma_{\text{hole}}} = 1273. \quad (2)$$

The information density D of the optical data-storage medium can thus be increased by a factor of the order of 10^3 :

$$D = 10^8 \frac{\text{bits}}{\text{cm}^2} \cdot n_{\text{max}} \approx 10^{11} \frac{\text{bits}}{\text{cm}^2}. \quad (3)$$

We mention a few of the many practical problems which crop up in trying to construct this type of optical storage medium:

- Cooling of the material to a low temperature, (4 K).
- Tuning of the laser to the individual address bits, both spatially and in its frequency.
- The velocity of the photochemical reactions limits the writing speed.
- A satisfactory signal/noise ratio for reading requires a minimum readout time.
- Laser systems for the required wavelength range (diffraction limit λ^2 !) are very impractical. A fourth dimension could be included by making use of an holographic storage scheme.

22.2 a) Organic materials which are to be employed as data-storage media must fulfill at least the following criteria:

- Thermal and chemical stability. There should be no thermally-induced reactions even during longer storage periods, since they would erase the stored information. Likewise, the material in the form used must be completely chemically inert and must not for example be oxidised by oxygen from the air.
- Lack of material and chemical fatigue. The photochemical reaction must be completely reversible, i. e. there must be no side or decomposition reactions. After a cycle of forward and backward reactions, exactly the original number of molecules must be present in the initial state. If the yield of a side reaction, which removes molecules from the cycle, is only 0.1%, then the number of photoactive molecules is reduced to 37% of its original value after 1000 cycles.

- Sensitivity in the wavelength range of semiconductor lasers (700–800 nm). In order to design miniaturised devices, in particular the irradiation apparatus must be small. This requirement is satisfied by semiconductor lasers.
- High velocities of the photochemical reactions, in order to allow short times for writing and erasing operations.
- Destruction-free readout of the information. On reading the data bits, i. e. essentially registering an absorption spectrum, which may consist of only one point, the back reaction is always also induced. Thus the readout process erases a portion of the stored information. There are various suggestions for the solution of this problem (two-photon processes, switching the photochromism on and off by protonation of the molecules, etc.).

b) In the course of the photoreaction $A \rightarrow B$, a portion of the A molecules is converted into the form B . The absorption spectrum of the mixture represents at every point in time an additive superposition of the spectra of both of the pure species. At a certain wavenumber $\bar{\nu}$, the time-dependent optical density OD of the sample is given by

$$\text{OD}(t) = \varepsilon_A(\bar{\nu}) c_A(t) d + \varepsilon_B(\bar{\nu}) c_B(t) d. \quad (1)$$

Here, $\varepsilon_A(\bar{\nu})$ and $\varepsilon_B(\bar{\nu})$ are the extinction coefficients of the two species at the wavenumber $\bar{\nu}$, and $c_A(t)$ and $c_B(t)$ are their concentrations, depending on the total irradiation time; d is the optical path length. If only two forms, A and B , are involved in the reaction, then due to conservation of the overall number of both molecules, we have

$$c_0 = c_A(t) + c_B(t) \quad \Longleftrightarrow \quad c_B(t) = c_0 - c_A(t), \quad (2)$$

where c_0 is the initial concentration of the starting material. >From (1), it follows that

$$\text{OD}(t) = [\varepsilon_A(\bar{\nu}) - \varepsilon_B(\bar{\nu})] c_A(t) d + \varepsilon_B(\bar{\nu}) c_0 d. \quad (3)$$

At the wavenumbers $\bar{\nu}$ at which the two absorption spectra of the pure species overlap, i. e. for $\varepsilon_A(\bar{\nu}) = \varepsilon_B(\bar{\nu})$, OD(t) remains constant in time:

$$\text{OD}(t) = \text{const}(t) = \varepsilon_B(\bar{\nu}) c_0 d \quad \text{for} \quad \varepsilon_A(\bar{\nu}) = \varepsilon_B(\bar{\nu}). \quad (4)$$

At these wavenumbers $\bar{\nu}$, all the spectra thus overlap – isosbestic points exist.

If only two species with differing absorption behaviour take part in the photoreaction, then the existence of isosbestic points is certain. >From the fact that none are present in the case shown, one must conclude that in the course of the photoreaction, still (at least) a third form is generated. If its spectrum differs from that of the other two forms, then one will not observe any isosbestic points.

In the case of the fulgides, an undesirable side reaction in the form of a rotation of the aromatic rings around the exocyclic double bond occurs. It can, however, be suppressed by a suitable substitution of the molecule, so that the fulgide becomes truly bistable.

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