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Lecture Notes on

Molecular Spectroscopy

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Chapter 1

Introduction

1.1 One-electron Atoms

- A hydrogenic atom with nuclear charge Z is described by the HAMILTONIAN

$$H = -\frac{\hbar^2}{2\mu}\Delta - \frac{Ze^2}{4\pi\epsilon_0 r}, \quad (1.1)$$

where r is the distance between the electron and the nucleus and

$$\mu = \frac{m_N m_e}{m_N + m_e} \quad (1.2)$$

is the reduced mass of the pair nucleus-electron.

- Since $m_e \ll m_N$ the reduced mass μ is approximately the electron mass ($\mu \simeq m_e$).
- The LAPLACIAN operator Δ in spherical coordinates reads

$$\Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}. \quad (1.3)$$

1.1.1 Schrödinger Equation

- The time-independent SCHRÖDINGER equation

$$H\Psi(r, \theta, \phi) = E\Psi(r, \theta, \phi) \quad (1.4)$$

can be further separated by factoring the wavefunction

$$\Psi(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi) \quad (1.5)$$

where $Y_l^m(\theta, \phi)$ are the spherical harmonics and $R_{nl}(r)$ is the radial part. Moreover, the wavefunctions $\Psi(r, \theta, \phi)$ represent the one-electron atomic orbitals.

- Inserting (1.5) in (1.4) yields

$$\left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{2m_e r^2}{\hbar^2} \{E - V(r)\} - l(l+1) \right] R_{nl}(r) = 0 \quad (1.6)$$

$$\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + l(l+1) \right] Y_l^m(\theta, \phi) = 0. \quad (1.7)$$

- The spherical harmonics are described via the quantum numbers l and m_l .
- For the COULOMB potential $V(r) = -Ze^2/4\pi\epsilon_0 r$, the allowed orbital and magnetic quantum numbers are $l = 0, 1, \dots, n-1$ and $m = -l, -l+1, \dots, l$.
- The first few spherical harmonics are given

$$Y_0^0 = \sqrt{\frac{1}{4\pi}} \quad (1.8)$$

$$Y_1^0(\theta) = \sqrt{\frac{3}{4\pi}} \cos \theta \quad (1.9)$$

$$Y_1^{\pm 1}(\theta, \phi) = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}. \quad (1.10)$$

- The radial wavefunctions are given in terms of the quantum numbers n and l , and are expressed via the LAGUERRE *polynomials*.
- The first few radial wavefunctions are

$$R_{10}(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} \exp(-Zr/a_0) \quad (1.11)$$

$$R_{20}(r) = 2 \left(\frac{Z}{2a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) \exp(-Zr/2a_0) \quad (1.12)$$

$$R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \frac{Zr}{a_0} \exp(-Zr/2a_0) \quad (1.13)$$

where

$$a_0 = \frac{\hbar^2 4\pi\epsilon_0}{m_e e^2} = 0.529 \times 10^{-10} \text{m} = 0.529 \text{\AA} \quad (1.14)$$

is the BOHR *radius*.

- The associated energies with Ψ are given by

$$E_n = - \underbrace{\left(\frac{e^2}{4\pi\epsilon_0 a_0} \right)}_{=1 \text{ Hartree}} \frac{Z^2}{2n^2}, \quad n = 1, 2, 3, \dots \quad (1.15)$$

where the first term is the typical energy unit in atomic physics of 1 Hartree (27.2 eV).

- The transition frequency reads

$$\omega_{n',n} = (E_{n'} - E_n) / \hbar. \quad (1.16)$$

- The figures (1.1) and (1.2) show the radial wavefunctions and the radial distribution functions $r^2|R_{nl}(r)|^2$ of hydrogen atom ($Z = 1$).

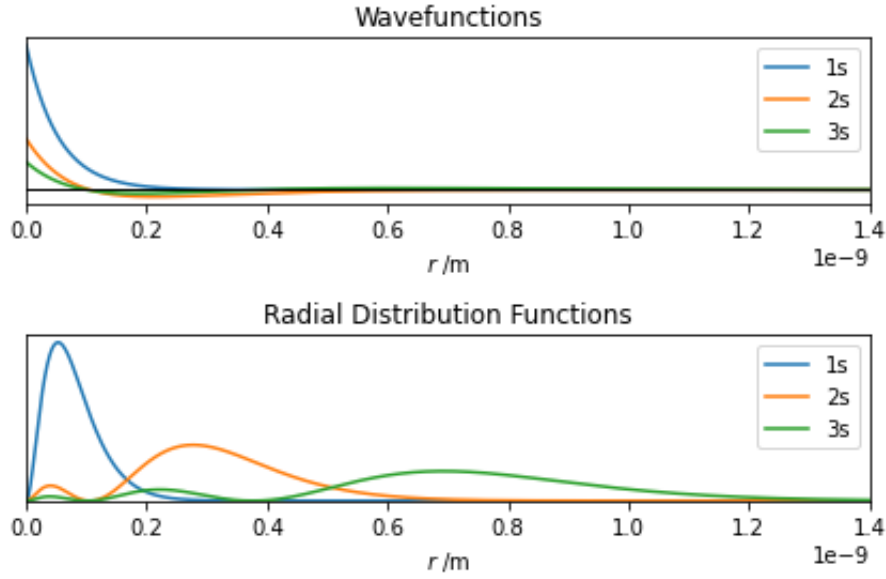


Fig. 1.1: Comparison between 1s, 2s and 3s orbitals.

- The figure (1.3) shows the comparison between 1s orbitals in H and He^+ .
- The figure (1.4) shows ($l = 3, m_l = 1$)-f-orbital.

1.2 Atomic Spectra

- Consider a transition from a state (n, l, m) to an other (n', l', m') . This transition is dipole allowed if

$$\mathbf{r}_{n,l,m;n',l',m'} \neq 0. \quad (1.17)$$

- The integrals over angular parts contain the spherical harmonics and can be evaluated separately, such that

$$\mathbf{r}_{n,l,m;n',l',m'} \propto \langle l', m' | \mathbf{r} | l, m \rangle \quad (1.18)$$

where $\langle \mathbf{r} | l, m \rangle = Y_l^m$ and $\langle l', m' | \mathbf{r} \rangle = (Y_{l'}^{m'})^*$.

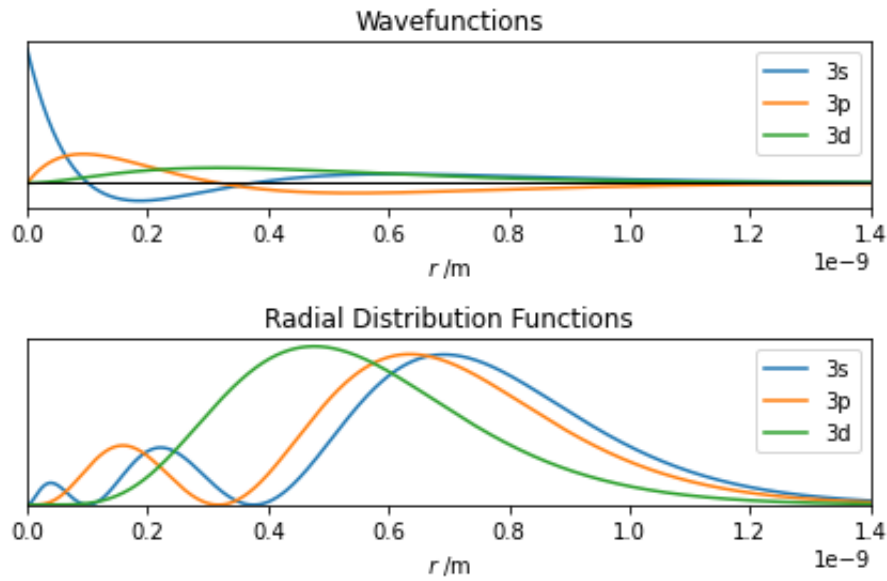
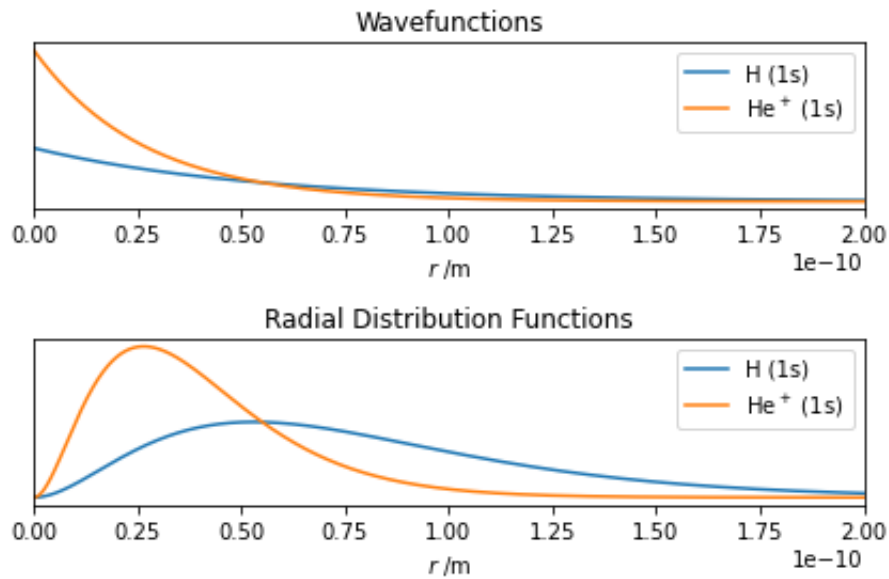


Fig. 1.2: Comparison between 3p, 3s and 3d orbitals.

Fig. 1.3: Comparison between 1s in H and He^+ .

- The spherical harmonics Y_l^m and $Y_l^{m'}$ are eigenstates of the operators $\vec{L}^2$ and L_z (because of the central potential)

$$L_z|l, m\rangle = \hbar m|l, m\rangle \quad (1.19)$$

$$\mathbf{L}^2|l, m\rangle = \hbar^2 l(l+1)|l, m\rangle. \quad (1.20)$$



Fig. 1.4: The $(l = 3, m_l = 1)$ -f-orbital.

1.2.1 Dipole Selection Rules

1.2.2 Δm selection rule

- Since

$$[L_z, z] = 0 \quad (1.21)$$

$$[L_z, x \pm iy] = \pm(x \pm iy)\hbar \quad (1.22)$$

we find

$$\langle l', m' | z | l, m \rangle (m' - m) = 0 \quad (1.23)$$

$$\langle l', m' | x + iy | l, m \rangle (m' - m - 1) = 0 \quad (1.24)$$

$$\langle l', m' | x - iy | l, m \rangle (m' - m + 1) = 0. \quad (1.25)$$

- Electric dipole transitions are only allowed (i.e. non zero matrix elements are possible) if $m' = m$ or $m' = m \pm 1$. Thus the change of the magnetic quantum number is

$$\boxed{\Delta m = 0, \pm 1.} \quad (1.26)$$

1.2.3 Δl selection rule

- Using the commutator

$$[\mathbf{L}^2, [\mathbf{L}^2, \mathbf{r}]] = 2\hbar^2(\mathbf{r}\mathbf{L}^2 + \mathbf{L}^2\mathbf{r}) \quad (1.27)$$

we obtain

$$\langle l', m' | \mathbf{r} | l, m \rangle (l + l') (l + l' + 2) \underbrace{[(l - l')^2 - 1]}_{(*)} = 0. \quad (1.28)$$

The factor $(*)$ is the important one for the selection rule and requires $l' = l \pm 1$, or

$$\boxed{\Delta l = \pm 1.} \quad (1.29)$$

1.2.4 Line Spectrum of Hydrogenic Atoms

- In the nonrelativistic case and for hydrogenic atoms, the eigenenergies of a given state only depends on its principal quantum number n , while l and m produce degenerate states.
- The photon energy of optical transition between levels n_A and n_B (with $n_A > n_B$) becomes

$$\hbar\omega_{BA} = 13.6 \text{ eV} \times Z^2 \left(\frac{1}{n_A^2} - \frac{1}{n_B^2} \right). \quad (1.30)$$

- The independent requirements

$$\Delta l = \pm 1, \quad \Delta m = 0, \pm 1$$

on the quantum numbers of the involved states for dipole-allowed processes considerably restrict the possible optical transitions.

- The figure (1.5) depicts the GROTRIAN diagram of the allowed transitions in hydrogen.

E Consider a system of two particles m_1 and m_2 interacting mutually via the potential $V(|\mathbf{r}_1 - \mathbf{r}_2|)$, where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ is the relative coordinate.

1. Starting from the classical expression of the HAMILTONIAN

$$H = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + V(|\mathbf{r}_1 - \mathbf{r}_2|),$$

prove that SCHRÖDINGER equation reads

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \left[-\frac{\hbar^2}{2m_1} \nabla_{r_1}^2 - \frac{\hbar^2}{2m_2} \nabla_{r_2}^2 + V(r) \right] \Psi(\mathbf{r}_1, \mathbf{r}_2, t).$$

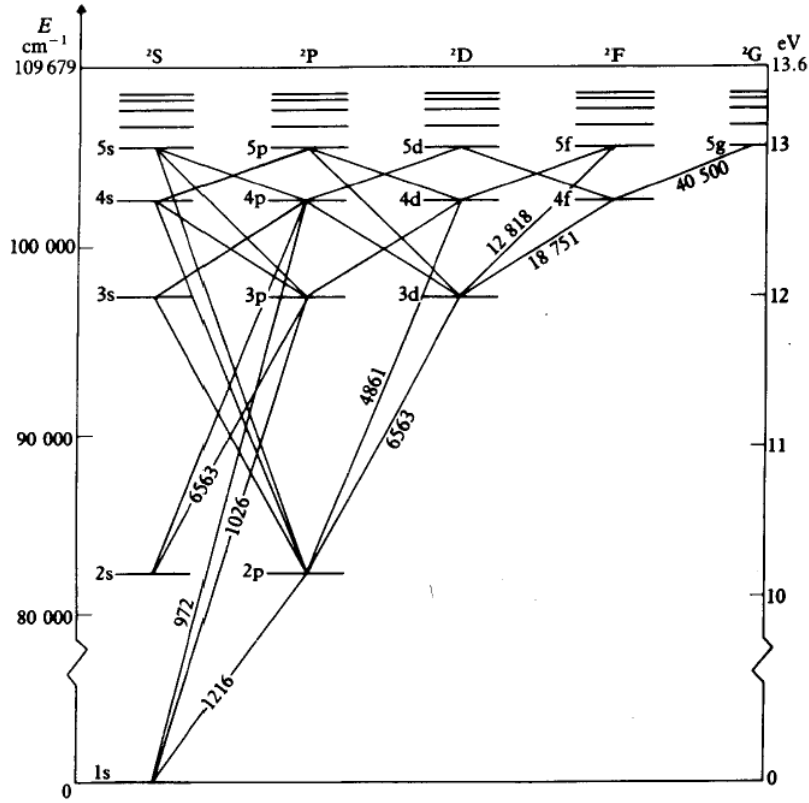


Fig. 1.5: GROTRIAN diagram for hydrogen atom. Numbers on the lines indicate wavelengths in Angström.

- Introducing the relative coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and the center of mass coordinate $\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}$, verify that

$$\frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu}, \quad (1.31)$$

where $\mathbf{P} = M\dot{\mathbf{R}}$ and $\mathbf{p} = \mu\dot{\mathbf{r}}$. Here $M = m_1 + m_2$ is the total mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass.

- Prove that it is possible to obtain equation (1.31) by introducing relative and total momenta $\mathbf{p} = \frac{m_2\mathbf{p}_1 - m_1\mathbf{p}_2}{m_1 + m_2}$, $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$, respectively.
- Taking into account that $\mathbf{P} = -i\hbar\nabla_{\mathbf{R}}$ and $\mathbf{p} = -i\hbar\nabla_{\mathbf{r}}$, check that SCHRÖDINGER equation becomes

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{R}, \mathbf{r}, t) = \left[-\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + V(r) \right] \Psi(\mathbf{R}, \mathbf{r}, t).$$

- By factoring the total wave function as

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \Phi(\mathbf{R})\psi(\mathbf{r}) \exp \left[-iE_{\text{tot}}t/\hbar \right],$$

check that $\Phi(\mathbf{R})$ and $\psi(\mathbf{r})$ are governed by the equations

$$\begin{aligned} -\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2\Phi(\mathbf{R}) &= E_{\text{CM}}\Phi(\mathbf{R}), \\ \left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(r)\right]\psi(\mathbf{r}) &= E\psi(\mathbf{r}), \end{aligned}$$

respectively, where $E_{\text{tot}} = E_{\text{CM}} + E$. Draw a conclusion from this exercise!

Chapter 2

Molecular Orbital Theory for H_2^+

- A molecule consists of atoms. The quantum mechanical treatment of isolated atoms leads to atomic orbitals centered at the origin of the coordinate system (i.e., where the atomic nucleus resides). It is now natural to compose the wavefunctions of electrons over distributed atomic nuclei, as they appear in molecules from atomic orbitals.

2.1 Molecular Hamiltonian and Born-Oppenheimer Approximation

- The HAMILTONIAN for point-like electrons ($N_{\text{el}}, \mathbf{r}_j, \mathbf{p}_j, m_e$) and nuclei ($N_{\text{nuc}}, Z_1, \dots, Z_{N_{\text{nuc}}}, \mathbf{R}_A, \mathbf{P}_A, M_A$) reads

$$H_{\text{mol}} = T_{\text{el}} + V_{\text{el-nuc}} + V_{\text{el-el}} + T_{\text{nuc}} + V_{\text{nuc-nuc}} \quad (2.1)$$

where

$$T_{\text{el}} = \sum_{j=1}^{N_{\text{el}}} \frac{\mathbf{p}_j^2}{2m_e} \quad (2.2)$$

$$T_{\text{nuc}} = \sum_{A=1}^{N_{\text{nuc}}} \frac{\mathbf{P}_A^2}{2M_A} \quad (2.3)$$

$$V_{\text{el-el}} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \quad (2.4)$$

$$V_{\text{nuc-nuc}} = \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |\mathbf{R}_A - \mathbf{R}_B|} \quad (2.5)$$

$$V_{\text{el-nuc}} = - \sum_{j \neq A} \frac{Z_A e^2}{4\pi\epsilon_0 |\mathbf{r}_j - \mathbf{R}_A|}. \quad (2.6)$$

- Seeking for solution of time-independent SCHRÖDINGER equation

$$H_{\text{mol}} \Psi_{\text{mol}}(\mathbf{r}, \mathbf{R}) = E \Psi_{\text{mol}}(\mathbf{r}, \mathbf{R}) \quad (2.7)$$

- Due to the mass difference $m_e/M_A < 10^{-3}$, it is reasonable to consider that electrons are much faster than nuclei. More precisely, nuclei can be considered fixed while electrons are moving. Therefore we neglect kinetic energy of nuclei in electronic problem. This is known as BORN-OPPENHEIMER approximation.
- The electronic HAMILTON operator is given by

$$H_{\text{el}}(\mathbf{R}) = T_{\text{el}} + V_{\text{el-el}} + V_{\text{el-nuc}}(\mathbf{R}) \quad (2.8)$$

where the dependence on positions of nuclei is parametric.

- Therefore, the electronic SCHRÖDINGER equation reads

$$H_{\text{el}}(\mathbf{R}) \Psi_{\text{el}}(\mathbf{r}, \mathbf{R}) = E(\mathbf{R}) \Psi_{\text{el}}(\mathbf{r}, \mathbf{R}) \quad (2.9)$$

where the electronic wavefunctions as well as eigenvalues carry parametric dependence on nuclear coordinates.

- In non-relativistic formulation spin is introduced as an additional degree of freedom which has two possible states α (spin-up) or β (spin-down). Further, we can introduce m_s as a kind of spin coordinate which can take the values $\pm 1/2$.

- α and β can be viewed as depending on spin-coordinate such that

$$\begin{aligned}\alpha(m_s) &\longrightarrow \alpha(1/2) = 1, \alpha(-1/2) = 0 \\ \beta(m_s) &\longrightarrow \beta(1/2) = 0, \beta(-1/2) = 1.\end{aligned}\tag{2.10}$$

- These state functions are orthogonal and normalized according to

$$\langle \alpha | \beta \rangle = 0 \tag{2.11}$$

$$\sum_{m_s=\pm 1/2} |\alpha(m_s)|^2 = |\alpha(1/2)|^2 + |\alpha(-1/2)|^2 = 1. \tag{2.12}$$

- The spatial and spin coordinates are comprised as follows

$$\{\mathbf{x}_i\} \equiv (\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad \mathbf{x} \equiv (\mathbf{r}, m_s). \tag{2.13}$$

2.2 Atomic Units

- In electronic structure theory it is common to use atomic units, which are best motivated by looking at the SCHRÖDINGER equation for the H-atom

$$\left(-\frac{\hbar^2}{2m_e} \Delta_r - \frac{e^2}{4\pi\epsilon_0 r} \right) |\psi\rangle = E |\psi\rangle. \tag{2.14}$$

- The energy eigenvalues are

$$E_n = -\left(\frac{e^2}{4\pi\epsilon_0 a_0} \right) \frac{1}{2n^2} = -\frac{E_h}{2n^2}. \tag{2.15}$$

- The characteristic energy is the HARTREE

$$1 E_h = \frac{e^2}{4\pi\epsilon_0 a_0} = 4.35975 \times 10^{-18} \text{ J} = 27.2114 \text{ eV} = 2.195 \times 10^5 \text{ cm}^{-1} (\times hc). \tag{2.16}$$

- The characteristic length is the BOHR radius

$$a_0 = \frac{\hbar^2 4\pi\epsilon_0}{m_e e^2} = 0.5292 \times 10^{-10} \text{ m} \tag{2.17}$$

- Scaling of lengths and energies: $r = \tilde{r} a_0$, $E = \tilde{E} E_h$, the SCHRÖDINGER equation in atomic units reads

$$\left(-\frac{1}{2} \tilde{\Delta}_r - \frac{1}{\tilde{r}} \right) |\psi\rangle = \tilde{E} |\psi\rangle. \tag{2.18}$$

E Consider the LENNARD-JONES interatomic potential for argon,

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (2.19)$$

where r is the interatomic distance, $\epsilon = 3.4 \text{ kJ} \cdot \text{mol}^{-1}$ is the depth of the potential well and $\sigma = 3.4 \text{ \AA}$ is the separation distance at which the potential is zero: $V(\sigma) = 0$. Figure (2.1) shows scaled plots of energy $V(r)$ and the force $F(r)$ with respect to r .

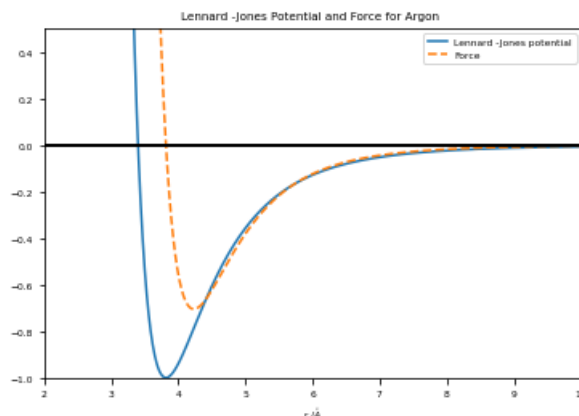


Fig. 2.1: LENNARD-JONES potential function $V(r)$ (in units of $\text{kJ} \cdot \text{mol}^{-1}$) and corresponding force function $F(r)$ between two argon atoms, which are related by $F(r) = -dV(r)/dr$. The plotted curves are for a LENNARD-JONES potential, Eq. (2.19), with parameters $\epsilon = 3.4 \text{ kJ} \cdot \text{mol}^{-1}$ and $\sigma = 3.4 \text{ \AA}$.

1. What is the meaning of the exponent 6 in the second term of this expression (i.e., why is the exponent necessarily chosen to be 6).
2. Calculate the separation distance $r = r_e$ when the energy is minimum (equilibrium) value, $V_{\min}$.
3. Calculate the ratio of $V_{\min}$ to the second term of the interaction potential at r_e .
4. Calculate the ratio of r_e to σ .
5. Calculate the ratio r_s to σ , where r_s is the separation where the magnitude of the force is maximum, $F_{\max}$.
6. Indicate the distances r_e , σ , and r_s on the curves.
7. Calculate the effective spring constant k of the bond for small displacement about the equilibrium position.

2.3 H_2^+ Molecule

- The simplest example is the H_2^+ molecule, consisting of two protons (A, B) and one electron e^- (see figure 2.2).

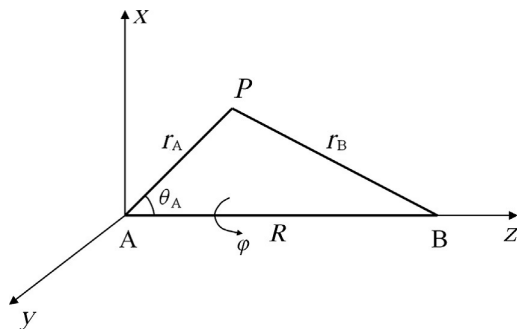


Fig. 2.2: H_2^+ molecule. The proton A is separated by the internuclear distance R from the proton B . The electron is located at P where r_A and r_B are distances with respect to proton A and B , respectively.

- The HAMILTONIAN reads

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}. \quad (2.20)$$

The first term here represents the electron's kinetic energy, the second and third its potential energy due to its attractive interactions with nuclei A and B and the final term is due to the repulsion of the nuclei (separated by the bond length, R).

- At first glance, it is surprising that this molecular ion is stable. (Why?)
- The corresponding electronic SCHRÖDINGER equation for a given internuclear distance R can be solved numerically, but here we are looking for an analytical method that captures the essential physics.

2.4 Linear Combination of Atomic Orbitals

- For the molecular wavefunction, we use the two linear combination of atomic orbitals (LCAO) approaches:

$$\Psi = c_A\psi_A + c_B\psi_B. \quad (2.21)$$

- One can now use these two approaches as variational approaches

$$E(R) = \frac{\int d^3r \Psi^* H \Psi}{\int d^3r |\Psi|^2} \quad (2.22)$$

and vary with respect to R . This allows one to find the internuclear distance that minimizes the total energy.

- Since hydrogen atoms are identical we seek for solutions fulfilling $|c_A| = |c_B|$, that is

$$\Psi_{\pm} = c_{\pm}(\psi_A \pm \psi_B), \quad (2.23)$$

where the normalized atomic ground state wavefunctions for the electron in atomic hydrogen (centered at the origin) ψ_A and ψ_B are given by

$$\psi_A = \frac{1}{\sqrt{\pi}} e^{-r_A}, \quad \psi_B = \frac{1}{\sqrt{\pi}} e^{-r_B}. \quad (2.24)$$

- The normalization condition for molecular wavefunctions, $\langle \Psi_{\pm} | \Psi_{\pm} \rangle = 1$, yields

$$\langle \Psi_{\pm} | \Psi_{\pm} \rangle = |c_{\pm}|^2 [\langle \psi_A | \psi_A \rangle + \langle \psi_B | \psi_B \rangle \pm \langle \psi_A | \psi_B \rangle \pm \langle \psi_B | \psi_A \rangle] = 1. \quad (2.25)$$

- Since $\langle \psi_A | \psi_A \rangle = \langle \psi_B | \psi_B \rangle = 1$ we obtain that

$$|c_{\pm}|^2 [2 \pm 2S] = 1 \implies c_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}}, \quad (2.26)$$

where

$$S = \langle \psi_A | \psi_B \rangle = \langle \psi_B | \psi_A \rangle \quad (2.27)$$

is called the *overlap* integral.

- We have to keep in mind that the functions ψ_A and ψ_B are not orthogonal, i.e. the integral

$$S = \int d^3r \psi_A^* \psi_B \quad (2.28)$$

is not equal to zero.

- We will calculate this integral and others similar to it using Sympy.

- Let us now calculate the expectation value of the energy $E_{\pm} = \langle \Psi_{\pm} | \hat{H} | \Psi_{\pm} \rangle$, i.e.

$$\begin{aligned} \frac{1}{|C_{\pm}|^2} E_{\pm} &= \langle \psi_A | \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) | \psi_A \rangle \\ &\quad + \langle \psi_B | \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) | \psi_B \rangle \\ &\quad \pm \langle \psi_A | \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) | \psi_B \rangle \\ &\quad \pm \langle \psi_B | \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) | \psi_A \rangle. \end{aligned} \quad (2.29)$$

- For an isolated hydrogen atom

$$\left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} \right) \psi_A = E_{1s} \psi_A, \quad (2.30)$$

$$\left(-\frac{1}{2} \nabla^2 - \frac{1}{r_B} \right) \psi_B = E_{1s} \psi_B, \quad (2.31)$$

where E_{1s} is the corresponding energy.

- Moreover

$$\langle \psi_A | \frac{1}{R} | \psi_A \rangle = \langle \psi_B | \frac{1}{R} | \psi_B \rangle = \frac{1}{R} \quad (2.32)$$

and

$$\langle \psi_A | \frac{1}{R} | \psi_B \rangle = \langle \psi_B | \frac{1}{R} | \psi_A \rangle = \frac{S}{R}. \quad (2.33)$$

- There are two other types of integrals

$$\langle \psi_A | \frac{1}{r_B} | \psi_A \rangle = \langle \psi_B | \frac{1}{r_A} | \psi_B \rangle \quad (2.34)$$

and

$$\langle \psi_A | \frac{1}{r_B} | \psi_B \rangle = \langle \psi_B | \frac{1}{r_A} | \psi_A \rangle. \quad (2.35)$$

- The integral (2.34) is the COULOMB potential felt by the orbital $\psi_A(\psi_B)$ due to nucleus $B(A)$.
- The *Coulomb* integral is defined as

$$J = -\langle \psi_A | \frac{1}{r_B} | \psi_A \rangle + \frac{1}{R}. \quad (2.36)$$

- The *Exchange* integral reads

$$K = -\langle \psi_A | \frac{1}{r_B} | \psi_B \rangle + \frac{S}{R}. \quad (2.37)$$

- Using these definitions, we obtain

$$\frac{1}{|C_{\pm}|^2} E_{\pm} = 2E_{1s} \pm 2SE_{1s} + 2J \pm 2K, \quad (2.38)$$

hence

$$E_{\pm} = E_{1s} + \frac{J \pm K}{1 \pm S}. \quad (2.39)$$

- The integrals S , J , and K cannot be evaluated in cartesian or spherical coordinates.

E The elliptical coordinates (λ, μ, φ) are defined as

$$\begin{cases} \lambda = \frac{r_A + r_B}{R} \\ \mu = \frac{r_A - r_B}{R} \\ \varphi = \arctan\left(\frac{y}{x}\right) \end{cases} \quad (2.40)$$

where $1 \leq \lambda < \infty$, $-1 \leq \mu \leq 1$, and φ is the azimuthal angle around the intermolecular axis, $0 \leq \varphi \leq 2\pi$. The two protons are sitting in the focal points (see figure 2.2).

1. Converting elliptical coordinates (λ, μ, φ) into the cartesian coordinates (x, y, z) through

$$\begin{cases} x = \frac{R}{2} \sqrt{(\lambda^2 - 1)(1 - \mu^2)} \cos \varphi \\ y = \frac{R}{2} \sqrt{(\lambda^2 - 1)(1 - \mu^2)} \sin \varphi \\ z = \frac{R}{2} \lambda \mu, \end{cases} \quad (2.41)$$

deduce that the volume element is

$$d^3r = \left(\frac{R}{2}\right)^3 (\lambda^2 - \mu^2) d\lambda d\mu d\varphi, \quad (2.42)$$

and the atomic orbital wavefunctions are

$$\psi_A = \frac{1}{\sqrt{\pi}} \exp\left[-\frac{R}{2}(\lambda + \mu)\right] \quad \text{and} \quad \psi_B = \frac{1}{\sqrt{\pi}} \exp\left[-\frac{R}{2}(\lambda - \mu)\right]. \quad (2.43)$$

2. Use SymPy to evaluate S , J , and K integrals.

The overlap integral is easier to handle in these coordinates

$$\begin{aligned}
S &= \langle \psi_A | \psi_B \rangle \\
&= \int d^3r \psi_A^* \psi_B \\
&= \frac{1}{\pi} \int_0^{2\pi} \int_{-1}^1 \int_1^\infty \exp \left[-\frac{R}{2}(\lambda + \mu) \right] \exp \left[-\frac{R}{2}(\lambda - \mu) \right] \frac{R^3}{8} (\lambda^2 - \mu^2) d\lambda d\mu d\phi \\
&= \frac{R^3}{4} \int_{-1}^1 \int_1^\infty e^{-\lambda R} (\lambda^2 - \mu^2) d\lambda d\mu \\
&= \left(\frac{R^2}{3} + R + 1 \right) e^{-R}.
\end{aligned} \tag{2.44}$$

Similarly, the COULOMB integral reads

$$\begin{aligned}
J &= -\frac{1}{\pi} \int_0^{2\pi} \int_{-1}^1 \int_1^\infty \frac{\exp[-R(\lambda + \mu)]}{\frac{R}{2}(\lambda - \mu)} \frac{R^3}{8} (\lambda^2 - \mu^2) d\lambda d\mu d\phi + \frac{1}{R} \\
&= -\frac{R^2}{2} \int_{-1}^1 \int_1^\infty e^{-(\lambda + \mu)R} (\lambda + \mu) d\lambda d\mu + \frac{1}{R} \\
&= \frac{(R + 1)e^{-2R}}{R}.
\end{aligned} \tag{2.45}$$

Moreover, the exchange integral is

$$\begin{aligned}
K &= -\frac{1}{\pi} \int_0^{2\pi} \int_{-1}^1 \int_1^\infty \exp \left[-\frac{R}{2}(\lambda + \mu) \right] \exp \left[-\frac{R}{2}(\lambda - \mu) \right] \\
&\quad \times \frac{R^3}{8} (\lambda^2 - \mu^2) d\lambda d\mu d\phi + \frac{S}{R} \\
&= -\frac{R^2}{2} \int_{-1}^1 \int_1^\infty e^{-\lambda R} (\lambda + \mu) d\lambda d\mu + \frac{S}{R} \\
&= -(R + 1)e^{-R} + \frac{S}{R}.
\end{aligned} \tag{2.46}$$

3. Use the results of integrals S , J and K to plot the potential energy curves $E_{\pm} = \frac{J \pm K}{1 \pm S}$, i.e., $E_{1s} = 0$, for the bonding and anti-bonding states of H_2^+ molecule, respectively, as a function of the internuclear distance R .

- The normalized molecular orbitals follow from symmetry arguments as

$$\Psi_+ = \sigma_g = [2(1 + S)]^{-1/2} (\psi_A + \psi_B) \quad \text{"symmetric"} \tag{2.47}$$

$$\Psi_- = \sigma_u = [2(1 - S)]^{-1/2} (\psi_A - \psi_B) \quad \text{"anti-symmetric"}. \tag{2.48}$$

where the index g stands for even (German: gerade) and u stands for odd (German: ungerade).

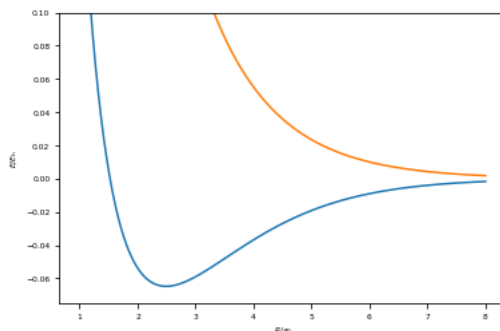


Fig. 2.3: Potential energy curve for bonding state (blue curve). Potential energy curve for anti-bonding state (orange curve).

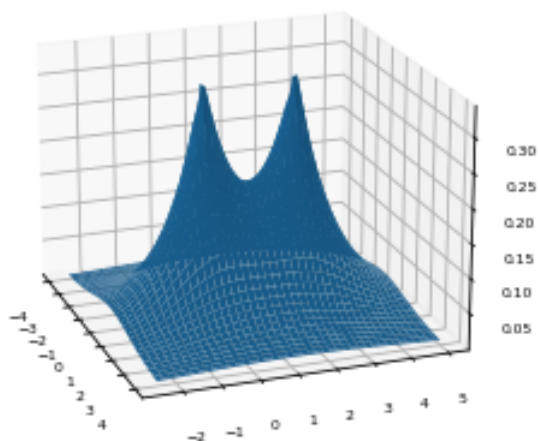


Fig. 2.4: The bonding molecular orbital wavefunction Ψ_+ .

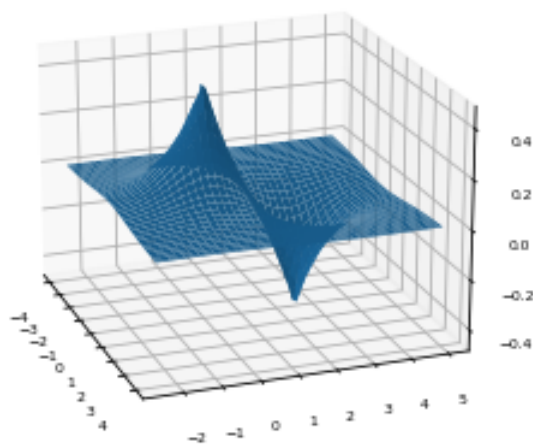


Fig. 2.5: The anti-bonding molecular orbital wavefunction Ψ_- .

Chapter 3

Many-electron Molecules

- We want to discuss the general properties of the electronic wavefunction within the BORN-OPPENHEIMER approximation (skip explicit reference to electronic quantities as well as parametric dependence on $\mathbf{R}$).
- The standard example for many-electron molecule: H_2 -like system in atomic units (skip tilde)

$$H \equiv H_{\text{el}} = \sum_{i=1}^2 h(\mathbf{r}_i) + \frac{1}{r_{12}}, \quad (3.1)$$

where $h(\mathbf{r}_i)$ is the single particle HAMILTONIAN

$$h(\mathbf{r}_i) = -\frac{1}{2}\Delta_i - \sum_A \frac{Z_A}{r_{iA}}. \quad (3.2)$$

- The HAMILTONIAN is symmetric, i.e.

$$H(\mathbf{x}_1, \mathbf{x}_2) = H(\mathbf{x}_2, \mathbf{x}_1). \quad (3.3)$$

3.1 Symmetry Postulate

- Since electrons are indistinguishable, any reasonable wavefunction should obey

$$|\Psi(\mathbf{x}_1, \mathbf{x}_2)|^2 = |\Psi(\mathbf{x}_2, \mathbf{x}_1)|^2 \quad (3.4)$$

which implies that

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = c\Psi(\mathbf{x}_2, \mathbf{x}_1) \quad (3.5)$$

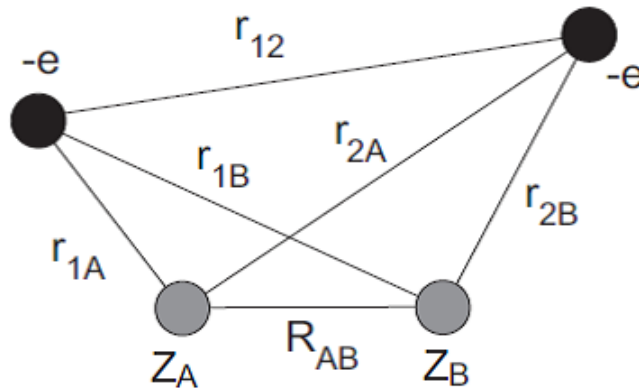


Fig. 3.1: Two-electron molecule.

with

$$|c|^2 = 1, \quad \text{i.e.} \quad c = e^{i\alpha} = \pm 1. \quad (3.6)$$

- **Symmetry postulate:** The wavefunction for a system of identical particles is either *symmetric* or *anti-symmetric* with respect to exchange of two particles.
- For electrons, the wavefunction is anti-symmetric, i.e.

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1) \quad (\text{PAULI principle}) \quad (3.7)$$

- The consequence of $\mathbf{x}_1 = \mathbf{x}_2$ yields

$$\Psi(\mathbf{x}_1, \mathbf{x}_1) = -\Psi(\mathbf{x}_1, \mathbf{x}_1) \quad \Rightarrow \quad \Psi(\mathbf{x}_1, \mathbf{x}_1) = 0, \quad (3.8)$$

hence PAULI repulsion.

3.1.1 Slater Determinant

- The electronic wavefunction is given in form of spin orbitals (SO)

$$\varphi(\mathbf{x}_i) = \psi(\mathbf{r}_i)g(m_{s_i}) \quad (3.9)$$

which is a *restricted* spin orbital since the spatial part is the same for α and β spin functions. This is good for closed shell systems.

- Let us construct the wavefunction for H_2 -like molecules which obeys PAULI principle.

- In the case no COULOMB repulsion ($1/r_{12} = 0$) the HAMILTONIAN describes two independent electrons in the field of the nuclei

$$H_0 = \sum_{i=1}^2 h(\mathbf{r}_i), \quad (3.10)$$

where the SCHRÖDINGER equation for single independent electron is

$$h(\mathbf{r}_i)\varphi_j(\mathbf{x}_i) = \epsilon_j\varphi_j(\mathbf{x}_i). \quad (3.11)$$

- The electronic wavefunction takes form of HARTREE product

$$\Psi(\{\mathbf{x}_i\}) = \varphi_j(\mathbf{x}_1)\varphi_k(\mathbf{x}_2). \quad (3.12)$$

E Suppose that the spin orbitals φ_j and φ_k are eigenfunctions of the one-electron operator h with eigenvalues ϵ_j and ϵ_k , respectively. Show that the two HARTREE products

$$\Psi^{12}(\{\mathbf{x}_i\}) = \varphi_j(\mathbf{x}_1)\varphi_k(\mathbf{x}_2), \quad \Psi^{21}(\{\mathbf{x}_i\}) = \varphi_j(\mathbf{x}_2)\varphi_k(\mathbf{x}_1)$$

and the SLATER determinant

$$\Psi(\{\mathbf{x}_i\}) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_j(\mathbf{x}_1) & \varphi_k(\mathbf{x}_1) \\ \varphi_j(\mathbf{x}_2) & \varphi_k(\mathbf{x}_2) \end{vmatrix}$$

are eigenfunctions of (3.10) with energy eigenvalue $E = \epsilon_j + \epsilon_k$.

- Let us now discuss the probability that one electron is in d^3r_1 and the other in d^3r_2 , i.e.

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2 &= \sum_{m_{s_1}} \sum_{m_{s_2}} |\Psi(\{\mathbf{x}_i\})|^2 d^3r_1 d^3r_2 \\ &= \sum_{m_{s_1}} \sum_{m_{s_2}} \varphi_j(\mathbf{x}_1) \varphi_j^*(\mathbf{x}_1) \varphi_k(\mathbf{x}_2) \varphi_k^*(\mathbf{x}_2) d^3r_1 d^3r_2 \\ &= \sum_{m_{s_1}} \sum_{m_{s_2}} \psi_j(\mathbf{r}_1) g(m_{s_1}) \psi_j^*(\mathbf{r}_1) g^*(m_{s_1}) \psi_k(\mathbf{r}_2) g(m_{s_2}) \psi_k^*(\mathbf{r}_2) g^*(m_{s_2}) d^3r_1 d^3r_2 \\ &= \underbrace{\sum_{m_{s_1}} |g(m_{s_1})|^2}_{=1} |\psi_j(\mathbf{r}_1)|^2 \underbrace{\sum_{m_{s_2}} |g(m_{s_2})|^2}_{=1} |\psi_k(\mathbf{r}_2)|^2 d^3r_1 d^3r_2 \\ &= |\psi_j(\mathbf{r}_1)|^2 |\psi_k(\mathbf{r}_2)|^2 d^3r_1 d^3r_2 \\ &= P(\mathbf{r}_1) P(\mathbf{r}_2) d^3r_1 d^3r_2 \end{aligned} \quad (3.13)$$

which is the case of independent distribution; in particular $P(\mathbf{r}_1, \mathbf{r}_1) \neq 0$ is possible what is not in accord with PAULI principle.

- An anti-symmetric wavefunction is obtained by superposition of two HARTREE products

$$\Psi(\{\mathbf{x}_i\}) = \frac{1}{\sqrt{2}} [\varphi_j(\mathbf{x}_1)\varphi_k(\mathbf{x}_2) - \varphi_k(\mathbf{x}_1)\varphi_j(\mathbf{x}_2)] . \quad (3.14)$$

- In 1929, SLATER pointed out that anti-symmetric wavefunction can be written in form of determinant

$$\Psi(\{\mathbf{x}_i\}) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_j(\mathbf{x}_1) & \varphi_k(\mathbf{x}_1) \\ \varphi_j(\mathbf{x}_2) & \varphi_k(\mathbf{x}_2) \end{vmatrix} \quad (3.15)$$

- All elements of a row involve the same electron, all elements of a column involve the same spin-orbital (leads naturally to PAULI principle).
- If any two rows of determinant are exchanged, sign of determinant changes.
- If any two columns of determinant are identical, determinant is zero.
- This has a consequence for probability $P(\mathbf{r}_1, \mathbf{r}_2)d^3r_1d^3r_2$:
 - case of two opposite spins

$$\varphi_1(\mathbf{x}_1) = \psi_1(\mathbf{r}_1)\alpha(m_{s_1}) \quad \text{and} \quad \varphi_2(\mathbf{x}_2) = \psi_2(\mathbf{r}_2)\beta(m_{s_2}). \quad (3.16)$$

Inserting (3.16) in (3.14) and integration of spin variables leads to

$$P(\mathbf{r}_1, \mathbf{r}_2)d^3r_1d^3r_2 = \frac{1}{2} (|\psi_1(\mathbf{r}_1)|^2|\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2|\psi_2(\mathbf{r}_1)|^2) d^3r_1d^3r_2 \quad (3.17)$$

which is just an average over the two possibilities to distribute the electrons over the two orbitals. Moreover, no correlation occurs. If both orbitals are the same we recover the HARTREE ansatz with restriction that both electrons have different spins.

- case of two equal spins

$$\varphi_1(\mathbf{x}_1) = \psi_1(\mathbf{r}_1)\alpha(m_{s_1}) \quad \text{and} \quad \varphi_2(\mathbf{x}_2) = \psi_2(\mathbf{r}_2)\alpha(m_{s_2}). \quad (3.18)$$

Inserting (3.18) in (3.14) and integration of spin variables leads to

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2)d^3r_1d^3r_2 &= \frac{1}{2} (|\psi_1(\mathbf{r}_1)|^2|\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2|\psi_2(\mathbf{r}_1)|^2 \\ &\quad + |\psi_1^*(\mathbf{r}_1)|\psi_2(\mathbf{r}_1)|\psi_2^*(\mathbf{r}_2)|\psi_1(\mathbf{r}_2) \\ &\quad - |\psi_1(\mathbf{r}_1)|\psi_2^*(\mathbf{r}_1)|\psi_2(\mathbf{r}_2)|\psi_1^*(\mathbf{r}_2)) d^3r_1d^3r_2. \end{aligned} \quad (3.19)$$

The extra terms lead to $P(\mathbf{r}_1, \mathbf{r}_1) = 0$, i.e. the wavefunction of two electrons with parallel spins is correlated (exchange correlation, FERMI hole).

E Consider the SLATER determinant of the triplet configuration which is formed by the spin orbitals (3.18).

- a) Show that this SLATER determinant indeed describes a triplet state, i.e. it corresponds to the eigenvalue $2\hbar^2$ of the spin operator $\mathbf{S}^2$ of the two electron system. Hint: $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$.
- b) Show that the two-electron density for real-valued spatial orbitals has the following form

$$P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} (|\psi_1(\mathbf{r}_1)|^2 |\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2 |\psi_2(\mathbf{r}_1)|^2) - \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \psi_1(\mathbf{r}_2).$$

S

- a) The case of triplet configuration corresponds to same spins, i.e.

$$\varphi_1(\mathbf{x}_1) = \psi_1(\mathbf{r}_1) \alpha(m_{s_1}) \quad \text{and} \quad \varphi_2(\mathbf{x}_2) = \psi_2(\mathbf{r}_2) \alpha(m_{s_2}),$$

hence the SLATER determinant reads

$$\begin{aligned} \Psi^T(\{\mathbf{x}_i\}) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\mathbf{r}_1) \alpha(m_{s_1}) & \psi_2(\mathbf{r}_1) \alpha(m_{s_1}) \\ \psi_1(\mathbf{r}_2) \alpha(m_{s_2}) & \psi_2(\mathbf{r}_2) \alpha(m_{s_2}) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} [\psi_1(\mathbf{r}_1) \alpha(m_{s_1}) \psi_2(\mathbf{r}_2) \alpha(m_{s_2}) - \psi_2(\mathbf{r}_1) \alpha(m_{s_1}) \psi_1(\mathbf{r}_2) \alpha(m_{s_2})]. \end{aligned}$$

The $\mathbf{S}^2$ operator can be written as

$$\begin{aligned} \mathbf{S}^2 &= (\mathbf{S}_1 + \mathbf{S}_2)^2 \\ &= \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2 \\ &= \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2S_{1x}S_{2x} + 2S_{1y}S_{2y} + 2S_{1z}S_{2z} \\ &= \mathbf{S}_1^2 + \mathbf{S}_2^2 + S_{1+}S_{2-} + S_{1-}S_{2+} + 2S_{1z}S_{2z}, \end{aligned} \tag{3.20}$$

where

$$\begin{aligned} \mathbf{S}_{i+} \alpha(m_{s_i}) &= 0 \\ \mathbf{S}_{i-} \alpha(m_{s_i}) &= \hbar \sqrt{(s_i + m_{s_i})(s_i - m_{s_i} + 1)} \beta(m_{s_i}) \\ \mathbf{S}_{i+} \beta(m_{s_i}) &= \hbar \sqrt{(s_i - m_{s_i})(s_i + m_{s_i} + 1)} \alpha(m_{s_i}) \\ \mathbf{S}_{i-} \beta(m_{s_i}) &= 0 \end{aligned}$$

with $i = 1, 2$ and

$$\begin{aligned}
\mathbf{S}_1^2 \alpha(m_{s_1}) &= \hbar^2 \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(m_{s_1}) = \frac{3}{4} \hbar^2 \alpha(m_{s_1}) \\
\mathbf{S}_2^2 \alpha(m_{s_2}) &= \hbar^2 \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(m_{s_2}) = \frac{3}{4} \hbar^2 \alpha(m_{s_2}) \\
S_{1+} S_{2-} \alpha(m_{s_1}) \alpha(m_{s_2}) &= S_{1-} S_{2+} \alpha(m_{s_1}) \alpha(m_{s_2}) = 0 \\
S_{1z} S_{2z} \alpha(m_{s_1}) \alpha(m_{s_2}) &= \left(\frac{\hbar}{2} \right) \left(\frac{\hbar}{2} \right) \alpha(m_{s_1}) \alpha(m_{s_2}) = \frac{\hbar^2}{4} \alpha(m_{s_1}) \alpha(m_{s_2}).
\end{aligned} \tag{3.21}$$

Finally we obtain

$$\mathbf{S}^2 \Psi^T = \left(\frac{3}{4} \hbar^2 + \frac{3}{4} \hbar^2 + \frac{\hbar^2}{4} + \frac{\hbar^2}{4} \right) \Psi^T = 2 \hbar^2 \Psi^T = \hbar^2 (1)(1+1) \Psi^T, \tag{3.22}$$

thus $S = 1$, i.e. triplet state.

- b) Let us now discuss the probability that one electron is in $d^3 r_1$ and the other in $d^3 r_2$, i.e.

$$\begin{aligned}
P(\mathbf{r}_1, \mathbf{r}_2) d^3 r_1 d^3 r_2 &= \sum_{m_{s_1}} \sum_{m_{s_2}} |\Psi^T(\{\mathbf{x}_i\})|^2 d^3 r_1 d^3 r_2 \\
&= \frac{1}{2} \sum_{m_{s_1}} \sum_{m_{s_2}} |\psi_1(\mathbf{r}_1) \alpha(m_{s_1}) \psi_2(\mathbf{r}_2) \alpha(m_{s_2}) \\
&\quad - \psi_2(\mathbf{r}_1) \alpha(m_{s_1}) \psi_1(\mathbf{r}_2) \alpha(m_{s_2})|^2 d^3 r_1 d^3 r_2 \\
&= \frac{1}{2} \sum_{m_{s_1}} \sum_{m_{s_2}} (\psi_1(\mathbf{r}_1) \alpha(m_{s_1}) \psi_2(\mathbf{r}_2) \alpha(m_{s_2}) \\
&\quad - \psi_2(\mathbf{r}_1) \alpha(m_{s_1}) \psi_1(\mathbf{r}_2) \alpha(m_{s_2})) \\
&\quad (\psi_1^*(\mathbf{r}_1) \alpha^*(m_{s_1}) \psi_2^*(\mathbf{r}_2) \alpha^*(m_{s_2}) \\
&\quad - \psi_2^*(\mathbf{r}_1) \alpha^*(m_{s_1}) \psi_1^*(\mathbf{r}_2) \alpha^*(m_{s_2})) d^3 r_1 d^3 r_2 \\
&= \frac{1}{2} \sum_{m_{s_1}} \sum_{m_{s_2}} (|\psi_1(\mathbf{r}_1)|^2 |\psi_2(\mathbf{r}_2)|^2 |\alpha(m_{s_1})|^2 |\alpha(m_{s_2})|^2 \\
&\quad + |\psi_2(\mathbf{r}_1)|^2 |\psi_1(\mathbf{r}_2)|^2 |\alpha(m_{s_1})|^2 |\alpha(m_{s_2})|^2 \\
&\quad - \psi_1(\mathbf{r}_1) |\alpha(m_{s_1})|^2 \psi_2^*(\mathbf{r}_1) \psi_2(\mathbf{r}_2) |\alpha(m_{s_2})|^2 \psi_1^*(\mathbf{r}_2) \\
&\quad - \psi_2(\mathbf{r}_1) |\alpha(m_{s_1})|^2 \psi_2^*(\mathbf{r}_1) \psi_1(\mathbf{r}_2) |\alpha(m_{s_2})|^2 \psi_1^*(\mathbf{r}_2)) d^3 r_1 d^3 r_2 \\
&= \frac{1}{2} (|\psi_1(\mathbf{r}_1)|^2 |\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2 |\psi_2(\mathbf{r}_1)|^2 \\
&\quad + \psi_1^*(\mathbf{r}_1) \psi_2(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) \psi_1(\mathbf{r}_2) \\
&\quad - \psi_1(\mathbf{r}_1) \psi_2^*(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \psi_1^*(\mathbf{r}_2)) d^3 r_1 d^3 r_2.
\end{aligned}$$

For real-valued spatial orbitals

$$P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}(|\psi_1(\mathbf{r}_1)|^2|\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2|\psi_2(\mathbf{r}_1)|^2) - \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_1(\mathbf{r}_2).$$

- In general, we use instead of an infinite set of spin-orbitals a finite one with K spatial orbitals and $2K$ spin orbitals over which the electrons are distributed.
- Let $i = 1, 2, \dots, K$ where

$$\varphi_{2i-1}(\mathbf{x}) = \psi_i(\mathbf{r})\alpha(m_s) \quad \varphi_{2i}(\mathbf{x}) = \psi_i(\mathbf{r})\beta(m_s) \quad (3.23)$$

- The SLATER determinant (SD) can be generalized to N electrons

$$\Psi(\{x_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_i(\mathbf{x}_1) & \varphi_j(\mathbf{x}_1) & \cdots & \varphi_k(\mathbf{x}_1) \\ \varphi_i(\mathbf{x}_2) & \varphi_j(\mathbf{x}_2) & \cdots & \varphi_k(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_i(\mathbf{x}_N) & \varphi_j(\mathbf{x}_N) & \cdots & \varphi_k(\mathbf{x}_N) \end{vmatrix}. \quad (3.24)$$

3.2 The Minimal Basis for H₂-Molecule

3.2.1 Ground State

- We introduce the simplest model where the HAMILTONIAN has the form

$$H = H_0 + \frac{1}{r_{12}}, \quad H_0 = h(\mathbf{r}_1) + h(\mathbf{r}_2). \quad (3.25)$$

- The H₂ molecule is composed of two H atoms, each described by a 1s atomic orbital

$$\varphi_i(\mathbf{r} - \mathbf{R}_i) = \frac{1}{\sqrt{\pi}} e^{-|\mathbf{r} - \mathbf{R}_i|}, \quad i = 1, 2 \quad (3.26)$$

- The two molecular orbitals (MOs) can be formed by linear superposition (LCAO MO) of these two atomic orbitals (AOs) linear superposition (LCAO MO)

$$\Psi_i(\mathbf{r}) = \sum_{\mu=1}^2 C_{\mu i} \varphi_{\mu}(\mathbf{r}). \quad (3.27)$$

- The normalized molecular orbitals follow from symmetry arguments as

$$\Psi_1 = \sigma_g = [2(1 + S_{12})]^{-1/2} (\varphi_1 + \varphi_2) \quad (3.28)$$

$$\Psi_2 = \sigma_u = [2(1 - S_{12})]^{-1/2} (\varphi_1 - \varphi_2) \quad (3.29)$$

$$\langle \Psi_1 | \Psi_2 \rangle = \delta_{12}. \quad (3.30)$$

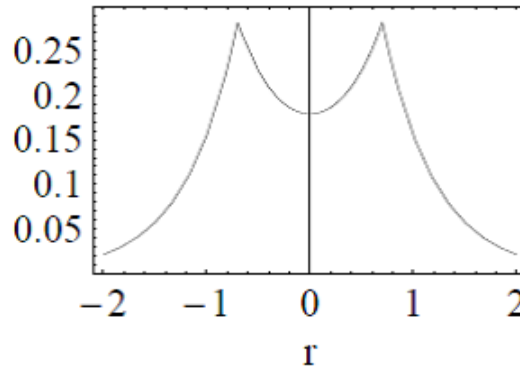


Fig. 3.2: The bonding molecular orbital probability density $|\Psi_1|^2$.

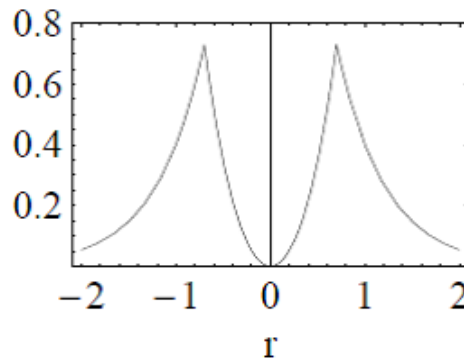


Fig. 3.3: The anti-bonding molecular orbital probability density $|\Psi_2|^2$.

- Since AOs are not normalized the overlap integral enters these MOs

$$S_{12} = \int d^3r \varphi_1^*(\mathbf{r}) \varphi_2(\mathbf{r}) = \left(1 + R_{AB} + \frac{R_{AB}^2}{3} \right) e^{-R_{AB}}. \quad (3.31)$$

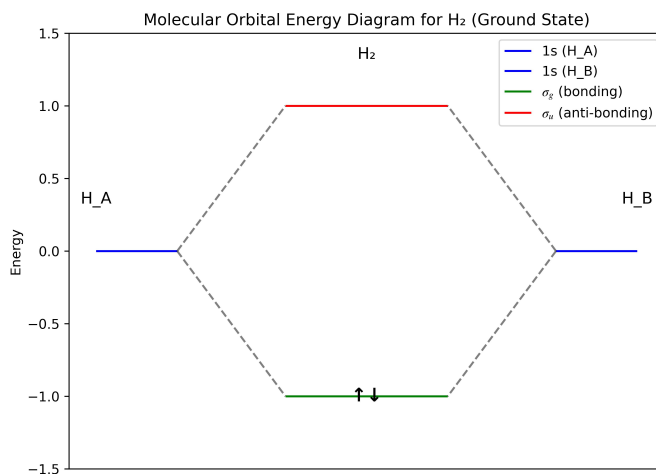
- There are four possible SOs

$$\varphi_1(\mathbf{x}) = \psi_1(\mathbf{r})\alpha(m_s) \quad \varphi_2(\mathbf{x}) = \psi_1(\mathbf{r})\beta(m_s) \quad (3.32)$$

$$\varphi_3(\mathbf{x}) = \psi_2(\mathbf{r})\alpha(m_s) \quad \varphi_4(\mathbf{x}) = \psi_2(\mathbf{r})\beta(m_s) \quad (3.33)$$

- It is to be expected that φ_1 and φ_2 have the same energy which is lower than that of the pair φ_3 and φ_4 .
- The single SD ground state is given by

$$|\Psi_0\rangle = |\varphi_1\varphi_2\rangle \rightarrow \Psi_0(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} (\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_1(\mathbf{x}_2)\varphi_2(\mathbf{x}_1)) \quad (3.34)$$



- **σ - and π - orbitals:** σ -orbital is a combination of two s- and p-orbitals aligned along the bond. σ -orbital extends along bond axis. π -orbital is a combination of two p-orbitals aligned perpendicular to the bond, has nodal plane containing the bond axis.

3.3 The energy of SD ground state

- Consider a general integral for the operator $O_{12} = O_{21}$

$$\langle \Psi_0 | O_{12} | \Psi_0 \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 [\varphi_1^*(\mathbf{x}_1) \varphi_1(\mathbf{x}_1) O_{12} \varphi_2^*(\mathbf{x}_2) \varphi_2(\mathbf{x}_2) - \varphi_1^*(\mathbf{x}_1) \varphi_2(\mathbf{x}_1) O_{12} \varphi_2^*(\mathbf{x}_2) \varphi_1(\mathbf{x}_2)] . \quad (3.35)$$

- The transition to spatial orbitals yields

$$\begin{aligned} \int d\mathbf{x}_1 d\mathbf{x}_2 \varphi_i^*(\mathbf{x}_1) \varphi_j(\mathbf{x}_1) O_{12} \varphi_k^*(\mathbf{x}_2) \varphi_l(\mathbf{x}_2) &= \int d^3r_1 d^3r_2 \psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1) O_{12} \psi_k^*(\mathbf{r}_2) \psi_l(\mathbf{r}_2) \\ &\times \sum_{m_{s_1}} g_i^*(m_{s_1}) g_j(m_{s_1}) \sum_{m_{s_2}} g_k^*(m_{s_2}) g_l(m_{s_2}) . \end{aligned} \quad (3.36)$$

- Due to orthogonality of spin functions the integral will be different from zero only if $g_i(m_{s_1}) = g_j(m_{s_1})$ and $g_k(m_{s_2}) = g_l(m_{s_2})$.
- For the present case only the first integral in the energy expression is non-zero.
- Consider **one-electron operators**

$$\begin{aligned} \langle \Psi_0 | h(\mathbf{r}_1) + h(\mathbf{r}_2) | \Psi_0 \rangle &= \int d^3r_1 \psi_1^*(\mathbf{r}_1) h(\mathbf{r}_1) \psi_1(\mathbf{r}_1) \\ &+ \int d^3r_2 \psi_1^*(\mathbf{r}_2) h(\mathbf{r}_2) \psi_1(\mathbf{r}_2) \equiv 2h_{11} . \end{aligned} \quad (3.37)$$

- The notation for **one-electron integrals** reads

$$h_{ij} = \int d^3r_1 \psi_i^*(\mathbf{r}_1) h(\mathbf{r}_1) \psi_j(\mathbf{r}_1) . \quad (3.38)$$

- Moreover, consider the **two-electron operator**: respective matrix element is called **Coulomb integral**

$$J_{ij} = \int d^3r_1 d^3r_2 |\psi_i(\mathbf{r}_1)|^2 \frac{1}{r_{12}} |\psi_j(\mathbf{r}_2)|^2 . \quad (3.39)$$

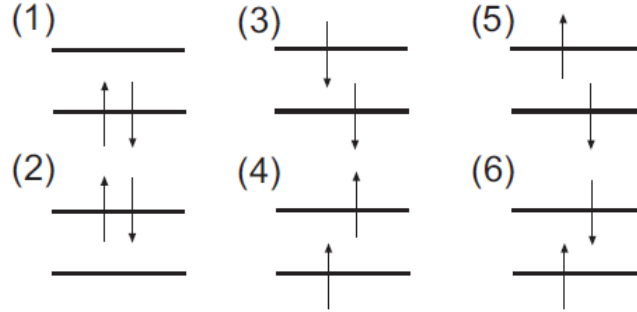
- Hence, the ground state energy of single determinant minimal basis set H_2 is

$$\boxed{E_0 = 2h_{11} + J_{11}} . \quad (3.40)$$

- We summarize the interpretation of single determinant ground state energy for H_2 as
 1. Each electron in a SO contributes the one-electron energy, here h_{11} which is energy in field of static nuclei plus kinetic energy.
 2. The pair of electrons with opposite spin in their spatial orbital contribute a two-electron energy, J_{11} which can be interpreted as the classical-like COULOMB interaction of the charge densities $|\psi_1(\mathbf{r}_1)|^2$ and $|\psi_1(\mathbf{r}_2)|^2$.

3.3.1 Excited Determinants

- So far we have discussed only one possibility for the distribution of the two electrons over the available 4 spin orbitals; in general for N electrons and $2K$ spin orbitals there are $(2K)!/(N!(2K-N)!)$ possibilities, i.e. 6 in the present case



- **Closed shell configurations:**

$$(1) \quad |\Psi_0\rangle = |\varphi_1\varphi_2\rangle$$

is a singlet state $((1\sigma_g)^2, |g^2\rangle)$; $E(g^2) = 2h_{11} + J_{11}$.

$$(2) \quad |\Psi_{11}^{2\bar{2}}\rangle = |\varphi_3\varphi_4\rangle$$

is a singlet state $((1\sigma_u)^2, |u^2\rangle)$; $E(u^2) = 2h_{22} + J_{22}$ (doubly excited determinant).

- **Open shell configurations:**

$$(3) \quad |\Psi_1^{\bar{2}}\rangle = |\varphi_2\varphi_4\rangle$$

$$(4) \quad |\Psi_{\bar{1}}^2\rangle = |\varphi_1\varphi_3\rangle$$

are triplet states $((1\sigma_g)^1, (1\sigma_u)^1)$ (singly excited determinant).

- The configurations (5) and (6) require special treatment since they correspond to $M_S = m_{s_1} + m_{s_2} = 0$, i.e. they are degenerate and not eigenfunctions of S^2 ; to find simultaneous eigenfunctions for S_z and S^2 one has to choose linear combinations of spin functions (so-called spin-adapted configuration which are important for describing dissociation into open shell fragments).

- **Energies of triplet states:**

- Consider the configuration (3)

$$E^{(3)} = \langle \varphi_2 \varphi_4 | H | \varphi_2 \varphi_4 \rangle$$

- The one-electron energies are $h_{11} + h_{22}$.
- The two-electron energies include the COULOMB integral J_{12} , but here also a second integral contributes which is of the type

$$K_{ij} = \int d^3r_1 d^3r_2 \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_1) \frac{1}{r_{12}} \psi_j(\mathbf{r}_2) \psi_i(\mathbf{r}_2) \quad (3.41)$$

is known as the **exchange integral** which is due to asymmetry of wavefunction, and has no classical counterpart.

- The energy of (3) reads

$$E^{(3)} = h_{11} + h_{22} + J_{12} - K_{12}.$$

- The second triplet state has an equal energy

$$E^{(4)} = E^{(3)}.$$

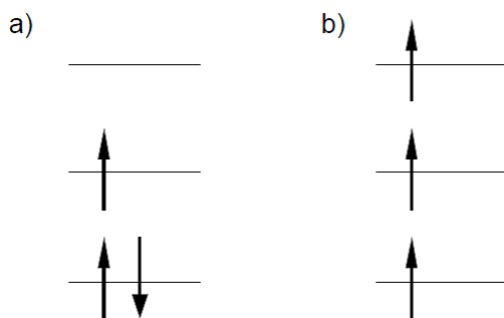
- The general rules for determination of energies of SDs are:

1. Each electron in spatial orbitals contributes h_{ii} independent on spin.
2. Each pair of electrons in spatial orbitals $\psi_i(\mathbf{r})$ and $\psi_j(\mathbf{r})$ contributes Coulomb energy J_{ij} independent on spin.
3. Each pair of electrons in spatial orbitals $\psi_i(\mathbf{r})$ and $\psi_j(\mathbf{r})$ having same spin contributes exchange energy $-K_{ij}$.

E Consider a three-electron system with three spatial orbitals. Determine the expectation value of the Hamiltonian

$$H = h(\vec{r}_1) + h(\vec{r}_2) + h(\vec{r}_3) + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}},$$

assuming a single SD wavefunction for the following configurations.



E The molecular orbitals MOs are filled with the electrons of the involved atoms in order of increasing energy, which in general is the following:

$$1s\sigma, 2s\sigma, 2p\sigma, 2p\pi, 3s\sigma, 3p\sigma, 3p\pi, 3d\sigma, 3d\pi, \dots$$

All MOs for homonuclear diatomic molecules have either σ or π and either g or u symmetry with respect to rotation about the molecular axes and inversion through the center of molecule, respectively. Note that σ_g and π_u are bonding MOs, whereas σ_u^* and π_g^* are antibonding MOs. Give the ground-state electron configurations of H_2^+ , H_2 , He_2^+ , He_2 , Li_2 , B_2 , C_2 , N_2 , O_2 and F_2 .

E The molecular orbital energy level diagram for heteronuclear diatomic molecules is similar to that for homonuclear ones except that the atomic orbitals on both atoms are no longer at the same energies. Moreover, since the heteronuclear diatomic molecule no longer has a center of symmetry the notation g/u is not applicable anymore. Give the ground-state electron configurations of LiH , CH , HF , CO , NO , PN , and XeF .

E Consider singly excited determinants with $M_S = 0$ for the minimal basis set H_2 molecule.

- Show that they are not simultaneous eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$.
- Create (anti)symmetric combinations (spin-adapted configurations) and show that they are eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$.

3.4 Hybridization

- Hybrid orbitals are often constructed from the linear combination of atomic orbitals with similar energy.
- Hybrid orbitals are chosen in a way that the overlap between bond partners is large as possible.
- If only s and p orbitals are considered, the result is called *sp-hybridization*.
- In the case of ground-state carbon atom $(1s)^2(2s)^2(2p_x)(2p_y)$ two unpaired electrons in p_x and p_y orbitals. If, for example, two hydrogen atoms would bond to the carbon atom, a maximum overlap occurs in x and y directions producing bond angle of 90° . As both p_x and p_y orbitals are occupied by one electron, only the p_z is available for hybridization.
- Since the difference in energy between 2s and 2p states is not very large (~ 4 eV), the energy needed to promote the 2s electron is overcompensated by the gain in bonding energy making them practically degenerate in energy (this is the case of time-independent perturbation theory in the presence of degeneracy).
- In *sp¹-hybridization* two additional bonds for carbon atom in the $\pm z$ -direction. The residual two 2p-orbitals (p_x and p_y) lead to two π -bonds.
- The two possible (orthogonal) sp_z hybrid atomic orbitals are

$$\phi_1(s, p_z) = c_1\phi(s) + c_2\phi(p_z) \quad (3.42)$$

$$\phi_2(s, p_z) = c_3\phi(s) + c_4\phi(p_z). \quad (3.43)$$

- Since ϕ_1 and ϕ_2 are orthonormal, i.e.

$$\int |\phi_i|^2 dV = 1, \quad \int \phi_1^* \phi_2 dV = 0 \quad (3.44)$$

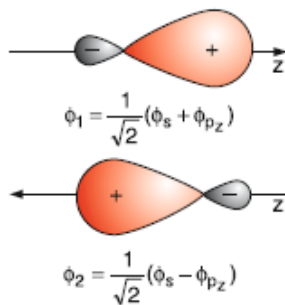
we obtain

$$c_1 = c_2 = c_3 = \frac{1}{\sqrt{2}}; \quad c_4 = -\frac{1}{\sqrt{2}}, \quad (3.45)$$

so the two hybrid atomic orbitals are

$$\phi_1 = \frac{1}{\sqrt{2}}[\phi(s) + \phi(p_z)] \quad (3.46)$$

$$\phi_2 = \frac{1}{\sqrt{2}}[\phi(s) - \phi(p_z)]. \quad (3.47)$$



- Substituting the atomic hydrogen wavefunctions for $\phi(s)$ and $\phi(p_z)$ yields the normalized angular part of hybrid orbitals to be

$$\phi_{1,2}(\theta) = \frac{1}{2\sqrt{\pi}} [1 \pm \sqrt{3} \cos \theta], \quad (3.48)$$

where θ is the angle with respect to z-axis. Therefore

- $|\phi_1|^2$ is maximum at $\theta = 0^\circ$, and
- $|\phi_2|^2$ is maximum at $\theta = 180^\circ$.
- Examples of sp^1 -hybridization are CO_2 "Carbon dioxide" and C_2H_2 "Acetylene", two double bonds in CO_2 and one triple bond in C_2H_2 : the residual two 2p-orbitals (p_x and p_y) lead to two π -orbitals.
- In some cases, s and p electrons assume a charge distribution given as linear combination of an s-orbital and two p-orbitals (sp^2 -hybridization):

$$\phi_1(sp^2) = \frac{1}{\sqrt{3}}\phi(s) + \sqrt{\frac{2}{3}}\phi(p_x) \quad (3.49)$$

$$\phi_2(sp^2) = \frac{1}{\sqrt{3}}\phi(s) - \frac{1}{\sqrt{6}}\phi(p_x) + \frac{1}{\sqrt{2}}\phi(p_y) \quad (3.50)$$

$$\phi_3(sp^2) = \frac{1}{\sqrt{3}}\phi(s) - \frac{1}{\sqrt{6}}\phi(p_x) - \frac{1}{\sqrt{2}}\phi(p_y), \quad (3.51)$$

and the angular parts read

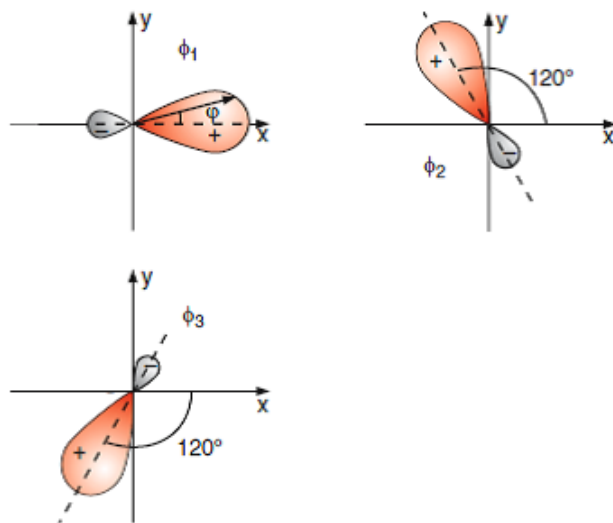
$$\phi_1(\varphi) = \frac{1}{2\sqrt{\pi}} \left[\sqrt{\frac{1}{3}} + \sqrt{2} \cos \varphi \right] \quad (3.52)$$

$$\phi_2(\varphi) = \frac{1}{2\sqrt{\pi}} \left[\sqrt{\frac{1}{3}} - \frac{1}{\sqrt{2}} \cos \varphi + \sqrt{\frac{3}{2}} \sin \varphi \right]$$

$$, \phi_3(\varphi) = \frac{1}{2\sqrt{\pi}} \left[\sqrt{\frac{1}{3}} - \frac{1}{\sqrt{2}} \cos \varphi - \sqrt{\frac{3}{2}} \sin \varphi \right],$$

where φ is the angle towards x-axis.

- Three maxima are occurring at $\varphi = 0^\circ$ for ϕ_1 , $\varphi = 120^\circ$ for ϕ_2 , and $\varphi = 240^\circ$ for ϕ_3 .



- *sp²-hybridization*: two p-orbitals (p_x and p_y) are combined with 2s-orbital resulting in three hybrid orbitals. The residual p-orbital is responsible for π -bond.
- Examples of *sp²-hybridization* are C_2H_4 "Ethylene", C_6H_6 "Benzene", and CH_2O "Formaldehyde".
- In some cases, for example methane molecule, CH_4 , the atomic orbitals of carbon are described via *sp³-hybridization* where all three 2p-orbitals are combined with 2s-orbital resulting in four hybrid orbitals.
- The orthonormal hybrid functions are

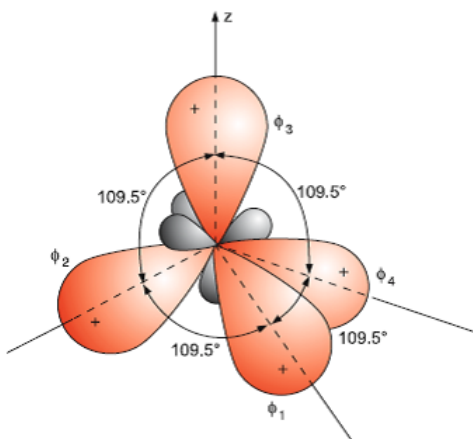
$$\phi_1(sp^3) = \frac{1}{2}\phi(s) + \frac{\sqrt{3}}{2}\phi(p_z) \quad (3.53)$$

$$\phi_2(sp^3) = \frac{1}{2}\phi(s) + \sqrt{\frac{2}{3}}\phi(p_x) + \frac{1}{2\sqrt{3}}\phi(p_z) \quad (3.54)$$

$$\phi_3(sp^3) = \frac{1}{2}\phi(s) - \frac{1}{\sqrt{6}}\phi(p_x) + \frac{1}{\sqrt{2}}\phi(p_y) - \frac{1}{2\sqrt{3}}\phi(p_z), \quad (3.55)$$

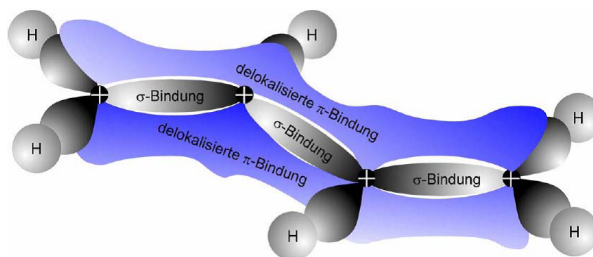
$$\phi_4(sp^3) = \frac{1}{2}\phi(s) - \frac{1}{\sqrt{6}}\phi(p_x) - \frac{1}{\sqrt{2}}\phi(p_y) - \frac{1}{2\sqrt{3}}\phi(p_z). \quad (3.56)$$

$$(3.57)$$



3.5 Delocalized π -orbitals

- In case of butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$), the delocalized four π -orbitals arise due to the overlap of four p-orbitals of the sp^2 -hybridized carbon atoms extending over the molecular backbone. Butadiene has two double bonds, each contributing two π -orbitals formed by the overlap of p-orbitals on adjacent carbon atoms. However, because the double bonds are separated by a single bond (σ -bond), the p-electrons are not confined to just the two double bonds but are delocalized over the entire four carbon π -system.
- This delocalization occurs through the overlap of the p-orbitals on all four carbon atoms, forming a conjugated π -system. The result is a set of four molecular orbitals that span the molecule, with the π -electrons distributed across these orbitals rather than being localized between specific carbon pairs. This delocalization lowers the overall energy of the molecule. The lowest-energy molecular orbital, for example, has all four p-orbitals in phase, allowing the π -electrons to be spread over the entire carbon framework.

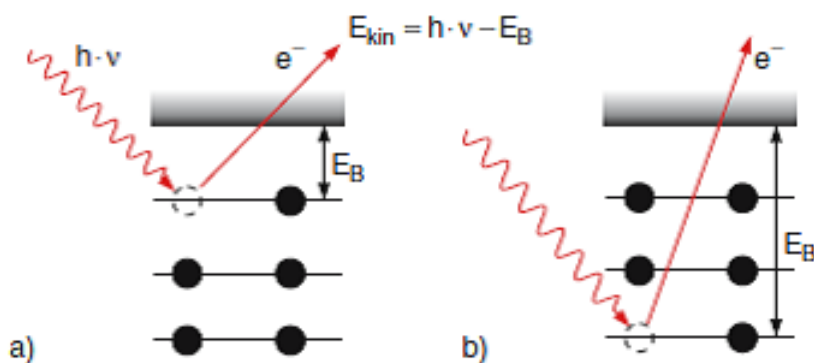


- p-orbitals can combine to delocalized π -systems which are often forming the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) and then responsible for the optical properties.

3.6 Koopmans' Theorem

- KOOPMANS' theorem states that the ionization energy of a molecule is equal to the orbital energy of the ejected electron.
- Let the binding energy of electron $E_B = \varepsilon_q$ where ε_q is the orbital energy obtained, for example, from self-consistent HARTREE-FOCK calculations (see next section).
- This approximation does not account for
 1. Reorganization energy of electrons in the resulting ion.
 2. Difference of correlation energy between neutral molecule and ion.
- One of the main applications of KOOPMANS' theorem is the photoelectron spectroscopy. The figure below shows the photoionisation (a) of an electron in the valence shell (b) of an inner shell electron with X-rays (frequency ν) of a molecule. The electron is ejected with kinetic energy

$$E_{\text{kin}} = h\nu - E_B. \quad (3.58)$$



- E** Consider a photoelectron spectroscopy experiment with water as sample. What kind of radiation should be used and why? The figure below shows the formation of molecular orbitals by linear combination of atomic orbitals. Calculate the kinetic energy of an electron emitted from the highest occupied molecular orbital HOMO if the beam energy is 5 keV.

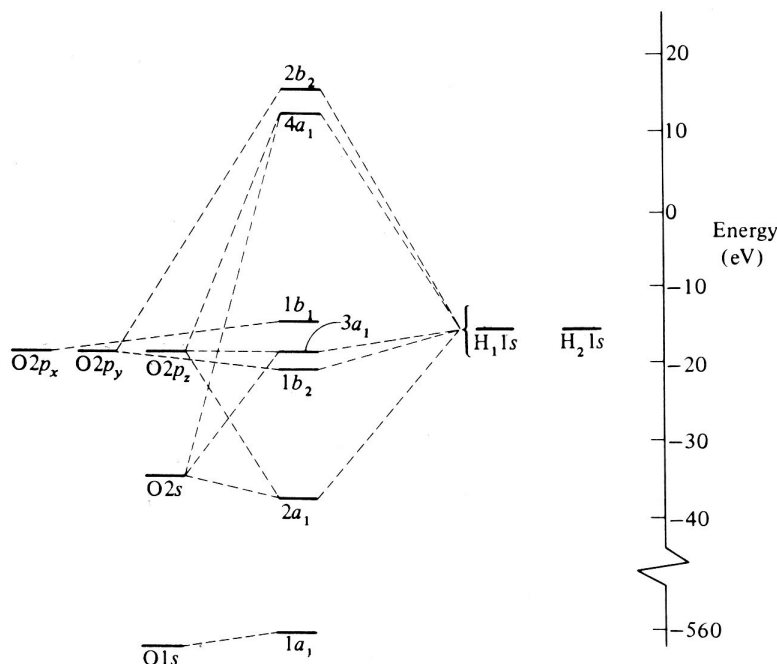
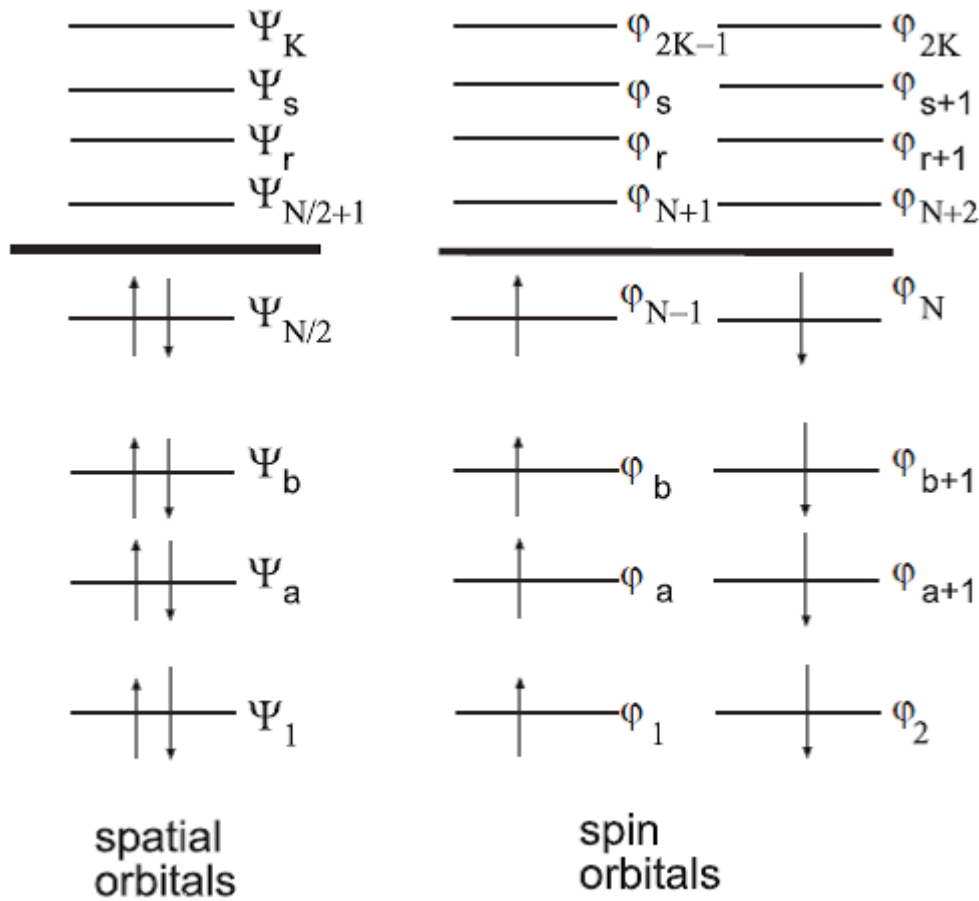


Fig. 3.4: Orbital energies of H₂O with minimal basis set.

3.7 Hartee-Fock Equations

- HARTREE FOCK (HF) theory is the essential method used in most quantum chemical calculations.
- It is based on single determinant description of wave function with spin orbitals being determined by a variational procedure.
- Consider given $2K$ spin orbitals and N electrons to build single determinant (HARTREE FOCK) ground state.
- The N orbitals filled (label $a; b$) reads

$$|\Psi_0\rangle = |\varphi_1 \dots \varphi_a \varphi_b \dots \varphi_N\rangle, \quad (3.59)$$



and the remaining orbitals "*virtual orbitals*" are empty (label $s; r$).

- Assume restricted description (closed shell) where spin orbitals have identical spatial part

$$\varphi_i(\mathbf{x}) \rightarrow \psi_j(\mathbf{r})\alpha(m_s) \quad \text{or} \quad \psi_j(\mathbf{r})\beta(m_s).$$

- The ground state energy to be optimized with respect to a single determinant wave function is given by

$$\begin{aligned}
 E_0[\{\varphi_a\}] &= \langle \Psi_0 | H | \Psi_0 \rangle \\
 &= 2 \sum_a^{N/2} h_{aa} + \sum_{ab}^{N/2} (2J_{ab} - K_{ab}).
 \end{aligned} \tag{3.60}$$

- The form of the spin orbitals is optimized by a variational procedure subject to the constraint that they are orthonormal

$$\varphi_a = \varphi_a + \delta\varphi_a, \quad \langle \varphi_a | \varphi_b \rangle - \delta_{ab} = 0. \tag{3.61}$$

- The Lagrangian multiplier method

$$\mathcal{L}[\{\varphi_a\}] = E_0[\{\varphi_a\}] - \sum_{ab} \varepsilon_{ab} (\langle \varphi_a | \varphi_b \rangle - \delta_{ab}) \Rightarrow \delta \mathcal{L} = 0 \quad (3.62)$$

gives an equation which determines the spatial orbitals is given by

$$f(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = \varepsilon_i\psi_i(\mathbf{r}_1). \quad (3.63)$$

- The FOCK operator

$$f(\mathbf{r}_1) = h(\mathbf{r}_1) + \sum_b^{N/2} [2J_b(\mathbf{r}_1) - K_b(\mathbf{r}_1)] \equiv h(\mathbf{r}_1) + v^{\text{HF}}(\mathbf{r}_1) \quad (3.64)$$

is an effective one-electron operator where

- $h(\mathbf{r}_1)$ is the **core operator**,
- $v^{\text{HF}}(\mathbf{r}_1)$ is **HF potential operator**,
- the factor 2 for COULOMB operator comes from summation over spin up and down orbitals,
- there is no such factor for the exchange operator since it concerns orbitals with parallel spins only.
- The COULOMB operator

$$J_b(\mathbf{r}_1) = \int d^3r_2 |\psi_b(\mathbf{r}_2)|^2 \frac{1}{r_{12}} \quad (3.65)$$

is a local operator since

$$J_b(\mathbf{r}_1)\psi_a(\mathbf{r}_1) = \left[\int d^3r_2 |\psi_b(\mathbf{r}_2)|^2 \frac{1}{r_{12}} \right] \psi_a(\mathbf{r}_1). \quad (3.66)$$

It provides an effective one-electron potential acting on given electron due to all other electrons (J_b contribution from electron in ψ_b), and the expectation value leads to *Coulomb* integral

$$\langle \psi_a | J_b(\mathbf{r}_1) | \psi_a \rangle = J_{ab}. \quad (3.67)$$

- The EXCHANGE operator

$$K_b(\mathbf{r}_1)\psi_a(\mathbf{r}_1) = \left[\int d^3r_2 \psi_b^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_a(\mathbf{r}_2) \right] \psi_b(\mathbf{r}_1) \quad (3.68)$$

is a nonlocal operator coming from antisymmetrization of wave function and the expectation value leads to *exchange* integral

$$\langle \psi_a | K_b(\mathbf{r}_1) | \psi_a \rangle = K_{ab}. \quad (3.69)$$

- **Note:** HF equation depends via the FOCK operator on its own solutions (non-linear pseudo eigenvalue equation).

E The bond order $b = 1/2(n - n^*)$, where n is the number of electrons in bonding orbitals and n^* of electrons in antibonding orbitals, is a measure for the net bonding in diatomic molecules.

- a) Determine the bond order for B_2 , C_2 , N_2 , O_2 and Ne_2 .
- b) What do we learn about chemical bonding in these examples?

E The ionization potential $I_p = E_{N-1} - E_N$ is the energy difference between a molecule with N electrons and the one with $(N - 1)$ electrons, i.e. where one electron is removed from some orbital with energy ϵ_c .

- a) Show that, if the energy relaxation of the spatial orbitals is neglected, the ionization potential reads

$$I_p = -\epsilon_c.$$

- b) What follows for the electron affinity $EA = E_N - E_{N+1}$ if an electron is added to the virtual orbital with energy ϵ_r ?

E Assume that the ground state SLATER-determinant $|\Psi\rangle$ of an N -electron molecule has been calculated from HARTREE-FOCK's method. Proof BRILLOUIN's theorem, which states that the matrix element of the Hamiltonian $\hat{H}$ between the ground state and a single excited determinant $|\Psi_a^r\rangle$ (i.e. one where an occupied spin orbital a is replaced by virtual orbital r) reads

$$\langle \Psi | \hat{H} | \Psi_a^r \rangle = 0.$$

Chapter 4

Molecular Transitions

- Spectroscopy is powerful tool to probe the microscopic world of atoms and molecules.
- The spectrum of absorption or emission consists of peaks, each of which is associated with a transition between two energy levels of the system

$$h\nu = |E_2 - E_1|. \quad (4.1)$$

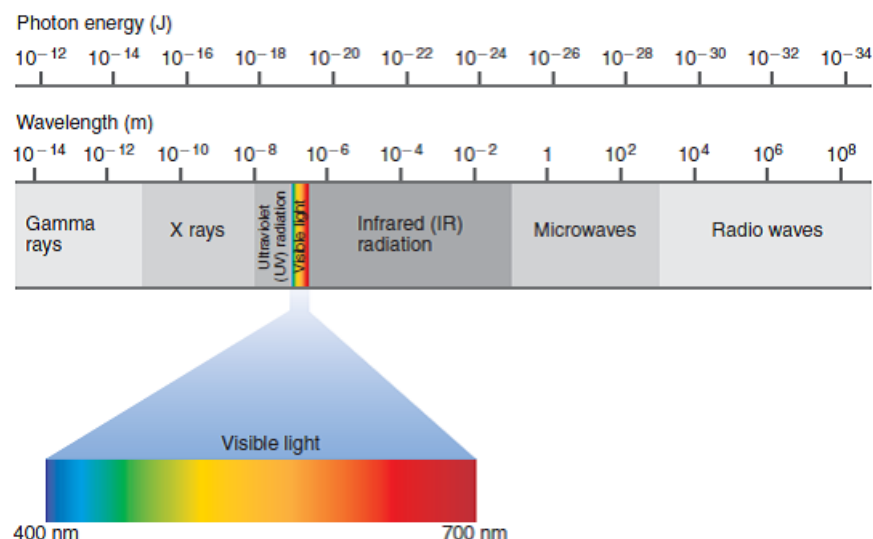
- Spectroscopists commonly use the unit of cm^{-1} for the quantity wave number $\tilde{\nu} = 1/\lambda$ instead of the wavelength λ or frequency ν . the relationship between ν and $\tilde{\nu}$ is given by $\nu = c\tilde{\nu}$, where c is the speed of light. Hence

$$|E_2 - E_1| = hc\tilde{\nu}. \quad (4.2)$$

Spec. Range	λ (m)	ν (Hz)	$\tilde{\nu}$ (cm^{-1})	Energy (J)	Spec.
Radio	> 0.1	$< 3 \times 10^9$	> 0.1	$< 2 \times 10^{-24}$	NMR
Microwave	$0.001 - 0.1$	$3 \times 10^9 - 3 \times 10^{11}$	$0.1 - 10$	$2 \times 10^{-24} - 2 \times 10^{-22}$	Rot.
Infrared	$7 \times 10^{-7} - 10^{-3}$	$3 \times 10^{11} - 4 \times 10^{14}$	$10 - 10^4$	$2 \times 10^{-22} - 3 \times 10^{-19}$	Vib.
Visible	$4 \times 10^{-7} - 7 \times 10^{-7}$	$4 \times 10^{14} - 7 \times 10^{14}$	$10^4 - 3 \times 10^4$	$3 \times 10^{-19} - 5 \times 10^{-19}$	Elec.
UV	$10^{-8} - 4 \times 10^{-7}$	$7 \times 10^{14} - 3 \times 10^{16}$	$3 \times 10^4 - 10^6$	$5 \times 10^{-19} - 2 \times 10^{-17}$	Elec.

4.1 Selection of Linear Effects Applied in Spectroscopy

- Linear optical processes produce a signal proportional to the intensity of the incident light field, I_{in} . Examples include:



- Absorption: Attenuation of light due to energy uptake by the medium.
- Luminescence: Emission of light (e.g., fluorescence, phosphorescence) following absorption or other excitation processes.
- Elastic scattering: Incoherent scattering, including:
 - * RAYLEIGH scattering: By bound charges, primarily electrons (e^-).
 - * THOMSON scattering: By free electrons (e^-).
 - * MIE scattering: By particles with sizes comparable to the wavelength, λ .
- Inelastic scattering: Incoherent scattering, including:
 - * RAMAN scattering: By molecules, resulting in energy shifts.
 - * COMPTON scattering: By electrons (e^-), with energy loss.
- These processes span spectral ranges from radio frequencies to X-rays.

4.2 Dipole Transitions

4.2.1 Interaction with Electromagnetic Radiation

- The superposition of quantum eigenstates can generate an oscillating dipole moment, enabling interaction with the electromagnetic field of a wave.

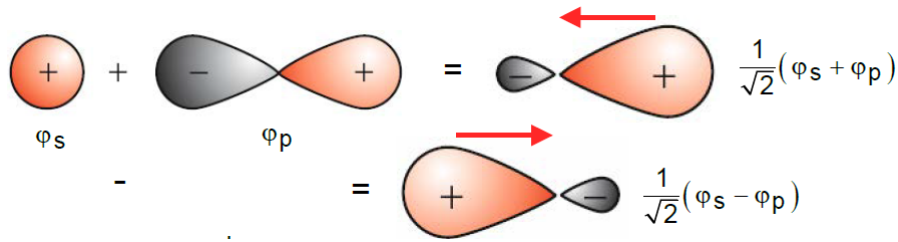
- **Example:** Consider a quantum system in a superposition of an s-wave and a p-wave state, described by the time-dependent wave function:

$$\psi(t) = \frac{1}{\sqrt{2}} \left[\varphi_s e^{-iE_s t/\hbar} + \varphi_p e^{-iE_p t/\hbar} \right], \quad (4.3)$$

where φ_s and φ_p are the stationary s- and p-wave functions, and E_s and E_p are their corresponding energies. The system evolves periodically with a time period $T = h/(E_p - E_s)$. At times $t = 0, 0.5T, 1T, 1.5T, 2T, 2.5T, 3T, \dots$, the wave function alternates between the symmetric and antisymmetric combinations:

$$\frac{1}{\sqrt{2}} [\varphi_s + \varphi_p] \quad \text{and} \quad \frac{1}{\sqrt{2}} [\varphi_s - \varphi_p].$$

This oscillation results in a time-dependent dipole moment, as the superposition switches between these two states every half-period.



4.2.2 Electric Transition Dipole

- Most relevant are electric dipole transitions. The transition dipole moment reads

$$\vec{d} = \langle \text{initial state} | q\vec{r} | \text{final state} \rangle \quad (4.4)$$

where q is the charge, often one electron $\vec{r}$ is its spatial coordinate.

- The signal is proportional to $|\vec{d}|^2$.
- Other transitions are possible but 1000 times weaker are magnetic dipole or electric quadrupole transitions.

4.2.3 Einstein Coefficients

- The basic principles involving photons are induced absorption, spontaneous emission, and stimulated emission.

- Assume an idealized material with two nondegenerate energy levels, 1 and 2, having populations N_1 and N_2 , respectively. Moreover, let us consider that the total number of atoms in these two levels is constant

$$N_1 + N_2 = N. \quad (4.5)$$

- We can distinguish three forms of interaction between light and atoms (introduced in 1917 by A. EINSTEIN):

a) **Spontaneous Emission, Fluorescence**

An excited atom emits a photon spontaneously (or induced via vacuum fluctuations) when the electron in the upper energy level E_2 jumps to the lower energy level E_1 . The rate dN_2^{sp}/dt describing the depopulation of E_2 reads

$$\frac{dN_2^{\text{sp}}}{dt} = -A_{21}N_2, \quad A_{21} = \frac{1}{\tau_{\text{sp}}} \quad (4.6)$$

where A_{21} is EINSTEIN coefficient for spontaneous emission and τ_{sp} being the lifetime for spontaneous radiation in the upper energy level. The emitted photons are not coherent and the radiation is isotropic.

b) **Stimulated Emission**

An incoming photon induces an excited atom to emit another one. The radiation is not isotropic (the emitted photons have the same direction and with the same phase). The corresponding rate equation reads

$$\frac{dN_2^{\text{st}}}{dt} = -B_{21}N_2\rho(\nu), \quad (4.7)$$

where B_{21} is EINSTEIN coefficient for the stimulated emission and $\rho(\nu)$ is the spectral energy density.

c) **Induced Absorption**

An incoming photon is absorbed by an electron in the lower energy level E_1 , and subsequently the electron jumps into the upper energy level E_2 :

$$\frac{dN_1^{\text{abs}}}{dt} = -B_{12}N_1\rho(\nu), \quad (4.8)$$

where B_{12} is EINSTEIN coefficient for absorption.

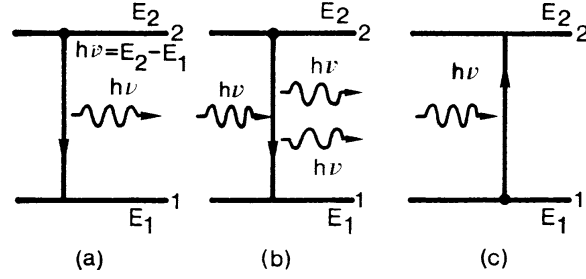


Fig. 4.1: Schematic illustration of the three processes: (a) spontaneous emission; (b) stimulated emission; (c) absorption.

- With A_{21} , B_{21} and B_{12} EINSTEIN was able to derive PLANCK's law for black-body radiation.
- Combining the three processes, the change of upper- and lower-level populations can be written as

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} = B_{21}N_2\rho(\nu) - B_{12}N_1\rho(\nu) + A_{21}N_2. \quad (4.9)$$

- The relation

$$\frac{dN_2}{dt} = -\frac{dN_1}{dt} \quad (4.10)$$

can be easily derived from Eq.(4.5).

- Assumption: atoms are in thermal equilibrium with a reservoir of temperature T require equal numbers of "upward" and "downward" transitions such that

$$\frac{dN_2}{dt} = \frac{dN_1}{dt} = 0, \quad (4.11)$$

and the population N_1 and N_2 are given by the BOLTZMANN distribution $N_1 \sim e^{-E_1/k_B T}$, $N_2 \sim e^{-E_2/k_B T}$ where $k_B = 1.38 \times 10^{-23} \text{J.K}^{-1}$ is the BOLTZMANN constant. Hence

$$\frac{N_2}{N_1} = e^{-\frac{(E_2-E_1)}{k_B T}} = e^{-\frac{h\nu}{k_B T}} \quad (4.12)$$

where $E_2 - E_1 = h\nu$ is the photon energy.

- Equation (4.12) implies that $N_1 > N_2$, thus more absorption than stimulated emission.
- For high intense light, the spontaneous emission is negligible and, therefore, both levels are equally populated, i.e., $N_1 \approx N_2$.

- Equation (4.11) yields

$$B_{21}N_2\rho(\nu) - B_{12}N_1\rho(\nu) + A_{21}N_2 = 0,$$

so that

$$\frac{N_2}{N_1} = \frac{B_{12}\rho(\nu)}{B_{21}\rho(\nu) + A_{21}}. \quad (4.13)$$

Comparison Eq. (4.13) and (4.12) gives

$$\rho(\nu) = \frac{A_{21}}{B_{21}} \frac{1}{\left(\frac{B_{12}}{B_{21}}e^{\frac{h\nu}{k_B T}} - 1\right)} \quad (4.14)$$

[E] What is the relation between coefficients A_{21} , B_{21} and B_{12} ?

[S] Following EINSTEIN approach for $T \rightarrow \infty \leadsto \rho(\nu) \rightarrow \infty$:
Since $A_{21} < \infty$,

$$\begin{aligned} \lim_{T \rightarrow \infty} \rho(\nu) &= \lim_{T \rightarrow \infty} \frac{A_{21}}{B_{12}e^{\frac{h\nu}{k_B T}} - B_{21}} = \infty \\ &\Rightarrow \lim_{T \rightarrow \infty} \underbrace{(B_{12}e^{\frac{h\nu}{k_B T}} - B_{21})}_{=1} = 0 \\ &\Rightarrow \boxed{B_{12} = B_{21}} \end{aligned} \quad (4.15)$$

Hence

$$\rho(\nu) = \frac{A_{21}}{B_{21}(e^{\frac{h\nu}{k_B T}} - 1)} \quad (4.16)$$

- Now we compare with the experimental results of RAYLEIGH-JEANS at low frequencies ($\nu \rightarrow 0$)

$$\rho^{\text{RJ}}(\nu) = \frac{8\pi\nu^2}{c^3} k_B T \quad (4.17)$$

Taylor expansion around $\nu \rightarrow 0$:

$$e^{\frac{h\nu}{k_B T}} = \sum_{\nu=0}^{\infty} \left(\frac{h\nu}{k_B T}\right)^{\nu} \frac{1}{\nu!} \approx 1 + \frac{h\nu}{k_B T} \quad (4.18)$$

thus

$$\lim_{\nu \rightarrow 0} \rho(\nu) = \frac{A_{21}}{B_{21}(1 + \frac{h\nu}{k_B T} - 1)} = \frac{A_{21}}{B_{21} \frac{h\nu}{k_B T}} = \frac{A_{21}}{B_{21}} \frac{k_B T}{h\nu}. \quad (4.19)$$

Comparing Eq.(4.17) with (4.19) yields

$$\begin{aligned}\frac{A_{21}}{B_{21}} \frac{k_B T}{h\nu} &\stackrel{!}{=} \frac{8\pi\nu^2}{c^3} k_B T \\ \Rightarrow \frac{A_{21}}{B_{21}} &= \frac{8\pi h\nu^3}{c^3}.\end{aligned}\quad (4.20)$$

$$\boxed{\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{k_B T}} - 1}}. \quad (4.21)$$

which is PLANCK's law of black-body radiation.

- **Note:** The speed of light c is here the value in the medium $c = c_0/n$, where c_0 is the speed of light in vacuum and n is the index of refraction.
- EINSTEIN derivation was a strong indication that the concept of quanta with $E = h\nu$ is correct.
- PLANCK's law is universal since it is independent of the atoms that take part and the particular energy levels. The only condition is that the body is able to absorb photons of all frequencies.
- **Example:** Consider black-body radiation for a sphere filled with gas, in thermal equilibrium $T = 1000^\circ\text{C}$. The ratio of spontaneous to stimulated emission is

1. For visible light, $\frac{A_{21}}{B_{21}} = 10^{10}$.
2. For radio frequencies, $\frac{A_{21}}{B_{21}} = 10^8$.

E Write the rate equations for a degenerate two-level system (degeneracies g_1, g_2). Assume thermal equilibrium for the radiation field and upper- and lower-level populations, then derive the following relations for the EINSTEIN coefficients:

$$\frac{g_1}{g_2} B_{12} = B_{21} = B, \quad (4.22)$$

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3}, \quad (4.23)$$

$$\frac{A}{B\rho(\nu)} = \exp[h\nu/k_B T] - 1. \quad (4.24)$$

- The EINSTEIN coefficient for stimulated emission is related to transition dipole moment as

$$\boxed{B_{21} = \frac{2\pi^2}{3\epsilon_0 h^2} |\vec{d}_{21}|^2}. \quad (4.25)$$

- Plugging (4.25) into (4.20) yields the EINSTEIN coefficient for spontaneous emission

$$A_{21} = \frac{16\pi^3\nu_{21}^3}{3\epsilon_0hc^3}|\vec{d}_{21}|^2. \quad (4.26)$$

4.3 Rotational Spectroscopy

- The total wavefunction of a molecule is expressed as a product of distinct contributions:

$$\Psi_{\text{tot}} = \Psi_{\text{internal}} \cdot \Psi_{\text{rot}}(\theta, \varphi, \psi) \cdot \Psi_{\text{trans}}(\mathbf{R}_{\text{CM}}) \quad (4.27)$$

This product form holds when the degrees of freedom are uncoupled and no external forces act, i.e., for free motion.

- Ψ_{internal} : Describes intramolecular structure and dynamics, including electronic states and vibrational modes.
- Ψ_{rot} : Represents the molecule's spatial orientation and rotational motion.
- Ψ_{trans} : Governs translational motion of the center of mass, described by a wavepacket.

4.3.1 Rotation of Molecules

- In general, the orientation of a molecule in space is described by three EULER angles (θ, Ψ, ϕ) .
- In the case of diatomic molecules the rotation around bond axis (Ψ) is not associated with a moment of inertia (assuming point masses m_1 and m_2 for the nuclei) and rotational energy.
- The time-independent SCHRÖDINGER equation $\hat{H}\Psi_{\text{rot}} = E_{\text{rot}}\Psi_{\text{rot}}$ where the HAMILTONIAN operator is

$$H = -\frac{\hbar^2}{2\mu}\Delta = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \quad (4.28)$$

Here $I = \mu r_0^2$ is the molecule's moment of inertia in terms of its reduced mass, $\mu = m_1 m_2 / (m_1 + m_2)$, and the bond length r_0 .

- The same as the hydrogen atom where the wavefunctions Ψ_{rot} are the spherical harmonic functions $Y_J^{M_J}(\theta, \phi)$.

- The rotational energies is therefore

$$E(J) = \frac{\hbar^2}{2I}J(J+1) \quad (4.29)$$

and are $(2J+1)$ -fold degenerate, corresponding to the values $M_J = -J, -J+1, \dots, J-1, J$.

- Spectroscopists often use the unit of wavenumber cm^{-1} to express the energy where $1\text{cm}^{-1} = J/hc$, with $c = 3 \times 10^{10} \text{cm} \cdot \text{s}^{-1}$. Hence

$$F(J) = \frac{E(J)}{hc} = BJ(J+1), \quad B = \frac{\hbar^2}{2Ihc} = \frac{h}{8\pi^2cI} \quad (4.30)$$

where $B = \hbar^2/2Ihc = h/8\pi^2cI$ is the molecule rotational constant (in cm^{-1}).

- Rotational energies are very low compared to thermal energy $k_B T$. At room temperature this corresponds to 25meV or 200cm^{-1} .
- For typical diatomic molecules, such as N_2 has a rotational constant of about 2cm^{-1} .

4.3.2 Rigid Rotor Transitions

- A rotating molecule can emit or absorb a photon when making a transition between energy levels.
- The corresponding selection rules can be derived from non vanishing transition dipole integral

$$\mathbf{d} = \int_V \Psi_f^* \hat{\mathbf{d}} \Psi_i dV \quad (4.31)$$

where $\hat{\mathbf{d}}$ is the electric dipole moment operator.

- The radial part always gives a contribution which is not relevant for selection rules. Therefore we consider solely the angular part

$$\mathbf{d} = \int_V (Y_{J'}^{M_{J'}})^* \hat{\mathbf{d}} Y_{J''}^{M_{J''}} \sin \theta d\theta d\phi. \quad (4.32)$$

- The integral (4.32) is zero unless $\Delta J = J' - J''$ and $\Delta M_J = M_{J'} - M_{J''}$ fulfill the following conditions

$$\Delta J = \pm 1, \quad \Delta M_J = 0, \pm 1.$$

- The population probability for a rotational level reads

$$P(J) = N(2J+1)e^{-\frac{\hbar^2 J(J+1)}{2Ik_B T}}. \quad (4.33)$$

4.3.3 Centrifugal Distortion

- When a non-rigid (real) molecule rotates, its nuclei are affected by centrifugal forces which become stronger with increasing rotation.
- The molecule's moment of inertia become stronger. Therefore, the effective rotational constant B decreases.
- The size of this effect is related to the atomic masses, the bond length, and the bond force constant k . Thus, the energetic separation between rotational transitions is reduced due to the additional term in the energy formula for the rotation energy levels

$$F(J) = BJ(J+1) - D[J(J+1)]^2 \quad (4.34)$$

where D is rotational constant that is smaller than B

$$D = \frac{h^3}{32\pi^4\mu^2kr^6}. \quad (4.35)$$

- A more accurate formula for rotational wavenumbers is

$$\tilde{\nu} = F(J+1) - F(J) = 2B(J+1) - 4D(J+1)^3. \quad (4.36)$$

4.3.4 Polyatomic Molecules

- A linear polyatomic molecule, such as HCN and C_2H_2 can be treated similarly as above: it has a unique rotational constant B that depends on the moment of inertia

$$I = \sum_i m_i r_i^2 \quad (4.37)$$

where r_i is the distance from the atom i from the center of the mass and m_i is the atomic mass.

- For a linear and diatomic molecules, there is only one rotational axis, for example, the axis perpendicular to intermolecular axis passing through the center of mass.
- In the case of nonlinear polyatomic molecules, we can identify three principal rotational axes associated with the principal moments of inertia, labeled as $I_a \leq I_b \leq I_c$ which corresponds to the three *rotational constants*,

$$A = \frac{h}{8\pi^2cI_a}, \quad B = \frac{h}{8\pi^2cI_b}, \quad C = \frac{h}{8\pi^2cI_c}. \quad (4.38)$$

- It is useful to classify polyatomic molecules based on the values of I_a , I_b , and I_c :
 - $I_a = I_b = I_c$: spherical top (e.g., CH_4 , SF_6);
 - $I_a = I_b < I_c$: oblate symmetric top (e.g., BF_3 , NH_3 , C_6H_6);
 - $I_a < I_b = I_c$: prolate symmetric top (e.g., CH_3Cl , CH_3CN);
 - $I_a < I_b < I_c$: asymmetric top (e.g., H_2O , $\text{C}_6\text{H}_5\text{OH}$);

E The moment of inertia of a molecule, considered as a rigid collection of point masses, m_i , can be represented by the tensor

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} \end{pmatrix},$$

where

$$\begin{aligned} I_{xx} &= \sum_i m_i(y_i^2 + z_i^2), & I_{yy} &= \sum_i m_i(x_i^2 + z_i^2), & I_{zz} &= \sum_i m_i(x_i^2 + y_i^2), \\ I_{xy} &= -\sum_i m_i x_i y_i, & I_{yz} &= -\sum_i m_i y_i z_i, & I_{xz} &= -\sum_i m_i x_i z_i. \end{aligned}$$

The atomic positions, (x_i, y_i, z_i) , are measured relative to the molecular center of mass in an arbitrary coordinate frame. There exists a transformation of the coordinate frame such that this matrix is diagonal: the axes of this transformed frame are called the *principal* axes and the diagonal inertia matrix elements, $I_a \leq I_b \leq I_c$, are the *principal moments of inertia*. It is with respect to these axes that the molecular moments of inertia are usually reported. Furthermore, in spectroscopy, it is conventional to define the rotational constants given in (4.38), which are reported in wavenumber units (cm^{-1}).

1. The file `CHCl3.dat` contains the positions of the atoms in the molecule CHCl_3 in XYZ format. Determine the rotational constants for this molecule and

```
# CHCl3
# Columns are: atom mass (atomic units), x, y, z (Angstroms)
12      0.0000    0.0000    0.4563    # C
1.0079   0.0000    0.0000    1.5353    # H
34.9689   0.0000    1.6845   -0.0838    # Cl
34.9689   1.4588   -0.8423   -0.0838    # Cl
34.9689  -1.4588   -0.8423   -0.0838    # Cl
```

classify it as a spherical, oblate, prolate, or asymmetric top.

2. Repeat this exercise for hydrogen peroxide using the file `H2O2.dat`

```
# H2O2
# Columns are: atom mass (atomic units), x, y, z (Angstroms)
15.9994  0.0000  0.7375  -0.0528  # O
15.9994  0.0000  -0.7375  -0.0528  # O
1.0079   0.8190  0.8170   0.4220  # H
1.0079  -0.8190  -0.8170   0.4220  # H
```

4.3.5 Symmetric Top Molecules

- The HAMILTON operator for the rotational energy of a non-linear polyatomic molecules is

$$H_{\text{rot}} = \frac{\mathbf{J}_a^2}{2I_a} + \frac{\mathbf{J}_b^2}{2I_b} + \frac{\mathbf{J}_c^2}{2I_c} \quad (4.39)$$

where the total rotational angular momentum operator $\mathbf{J}^2 = \mathbf{J}_a^2 + \mathbf{J}_b^2 + \mathbf{J}_c^2$.

- For a symmetric top, two of I_a , I_b , and I_c are equal, the Hamiltonian (4.39) can be written as follows:

$$\begin{aligned} H_{\text{rot}} &= \frac{\mathbf{J}_a^2}{2I_a} + \frac{1}{2I_b}(\mathbf{J}_b^2 + \mathbf{J}_c^2), \quad (\text{prolate tops, } I_b = I_c) \\ &= \frac{\mathbf{J}_a^2}{2I_a} + \frac{1}{2I_b}(\mathbf{J}^2 - \mathbf{J}_a^2) \\ &= \frac{\mathbf{J}^2}{2I_a} + \mathbf{J}_a^2 \left(\frac{1}{2I_a} - \frac{1}{2I_b} \right), \end{aligned} \quad (4.40)$$

$$\begin{aligned} H_{\text{rot}} &= \frac{1}{2I_b}(\mathbf{J}_a^2 + \mathbf{J}_b^2) + \frac{\mathbf{J}_c^2}{2I_c}, \quad (\text{oblate tops, } I_a = I_b) \\ &= \frac{1}{2I_b}(\mathbf{J}^2 - \mathbf{J}_c^2) + \frac{\mathbf{J}_c^2}{2I_c} \\ &= \frac{\mathbf{J}^2}{2I_b} + \mathbf{J}_c^2 \left(\frac{1}{2I_c} - \frac{1}{2I_b} \right). \end{aligned} \quad (4.41)$$

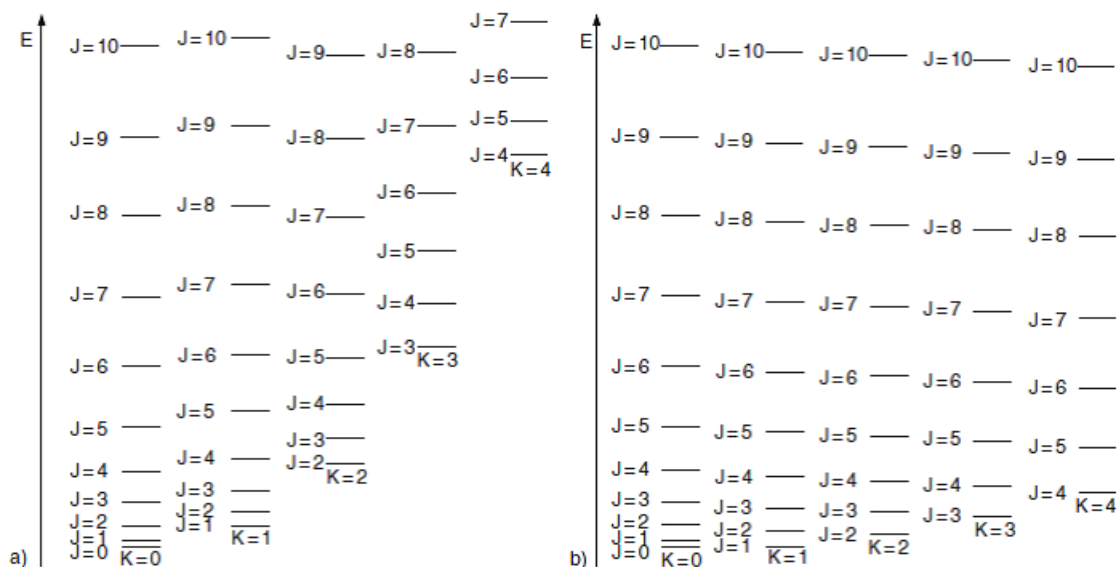
- In a prolate symmetric rotator molecule, such methyl iodide, $\mathbf{J}$ need not be perpendicular to the a -axis. Considering the $\mathbf{J}_a$ operator to represent the rotation of the molecule around the z -axis, $\mathbf{J}_a$ can take only the values $\hbar K$, where K is a second rotational quantum number, the corresponding energy levels are therefore

$$F(J, K) = BJ(J+1) + (A-B)K^2. \quad (4.42)$$

- Similarly, for oblate tops the energy levels are

$$F(J, K) = BJ(J+1) + (C-B)K^2. \quad (4.43)$$

- In general, $\hbar K$ is the projection of $\mathbf{J}$ onto the symmetry axis of the symmetric top. K takes the values $(2J + 1) - J \leq K \leq +J$. Each state (J, K) is also $(2J + 1)$ -fold degenerate.
- Since J cannot be smaller than K , each rotational term ladder starts with a J value $J_{\min} = K$. For prolate symmetric tops the energies for a given J increase with increasing K (see case (a) in the figure below). For oblate symmetric tops the energies for a given J decrease with increasing K (see case (b) in the figure below).



- The selection rules

$$\Delta J = \pm 1, \quad \Delta K = 0 \quad (4.44)$$

include $\Delta K = 0$ results in the expression for the transition frequencies or wavenumbers

$$\begin{aligned} \nu(\text{or } \tilde{\nu}) &= F(J+1, K) - F(J, K) \\ &= 2B(J+1) \end{aligned} \quad (4.45)$$

means that the rotation around the symmetry axis does not change the electric dipole, i.e. the transition between the rotational states is not induced by interaction with light.

- The requirement that the molecule must have a permanent dipole moment applies to symmetric rotors also.

E In the NO molecule the distance between nitrogen (^{14}N) and the oxygen (^{16}O) atom is 0.115 nm.

- Calculate the moment of inertia of the molecule.
- What is the frequency of the transition from the $J = 2$ to $J = 3$ level?

E The phosphine molecule, PH_3 , is an oblate symmetric top with rotational constants, $A = B = 4.524\text{ cm}^{-1}$ and $C = 3.919\text{ cm}^{-1}$.

- a) The file `PH3-spec.txt`, available at <https://scipython.com/chem/cal/>, provides a low-pressure, high-resolution spectrum of phosphine in the region $\tilde{\nu} = 0 - 200\text{ cm}^{-1}$.
- Make a plot, similar to Figure 4.2, of the expected rotational absorption spectrum of PH_3 .
 - Does it resemble that of a diatomic molecule?

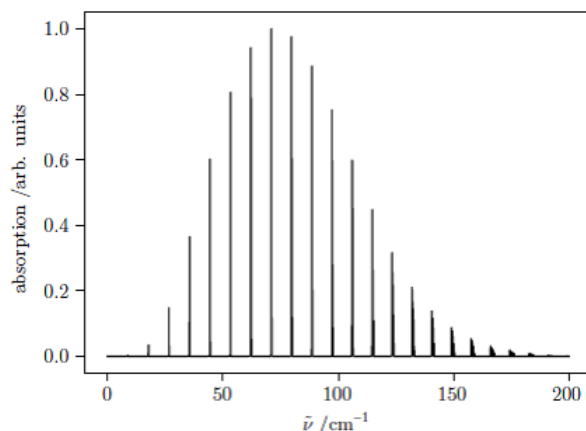


Fig. 4.2: Rotational spectrum of PH_3 .

- b) For larger J some more structure is apparent, therefore, zoom in on the region between $140 - 160\text{ cm}^{-1}$ and label the group of lines by their $J + 1 \leftarrow J$.
- What is the reason behind this structure?
- c) When centrifugal distortion is taken into account in phosphine molecule, the rotational energy levels become

$$\tilde{\nu} = 2B(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}K^2(J + 1).$$

- How many lines do you expect for the $J = 17 \leftarrow 16$ transition?

- Use the above expression for $\tilde{\nu}$ to fit the observed $J = 17 \leftarrow 16$ transition wavenumbers, which can be read in from the file `PH3-lines.txt`. What are the values of fitted parameters B , D_J and D_{JK} ?

4.4 Born-Oppenheimer Separation

- Neglecting spin the molecular SCHRÖDINGER equation reads

$$H_{\text{mol}}\Psi(r;R) = E\Psi(r;R). \quad (4.46)$$

- Born-Oppenheimer idea (1927)
 - $m_{\text{el}}/M_n < 10^{-3}$: nuclei move much slower than electrons. The motion of the electrons and of the nuclei occur on different timescales and can be treated separately.
 - For electrons the world changes slowly.
 - Electrons see a "frozen" potential due to the nuclei. Only the position of the nuclei and not their speed is relevant for the electronic wavefunction.
 - Nuclei can be considered as fixed and electrons are always in a stationary state (only adiabatic changes possible).
- Let us define an electronic Hamiltonian with parametric dependence on nuclear coordinates as

$$\begin{aligned} H_{\text{el}}(R) &= T_{\text{el}} + V_{\text{el-nuc}} + V_{\text{el-el}} \\ H_{\text{el}}(R)\psi_a(r;R) &= E_a(R)\psi_a(r;R). \end{aligned} \quad (4.47)$$

- Assuming that adiabatic electronic wave functions $\psi_a(r;R) = \langle r, R | \psi_a \rangle$ define a complete basis in the electronic HILBERT space.
- This allows to expand the total molecular wave function as

$$\Psi(r;R) = \sum_a \chi_a(R)\psi_a(r;R). \quad (4.48)$$

Hence

$$\begin{aligned}
 H_{\text{mol}}\Psi(r;R) &= (H_{\text{el}}(R) + T_{\text{nuc}} + V_{\text{nuc-nuc}}) \sum_a \chi_a(R) \psi_a(r;R) \\
 &= \sum_a [E_a(R) + V_{\text{nuc-nuc}}] \chi_a(R) \psi_a(r;R) \\
 &\quad + \sum_a T_{\text{nuc}} \chi_a(R) \psi_a(r;R) \\
 &= E \sum_a \chi_a(R) \psi_a(r;R).
 \end{aligned} \tag{4.49}$$

- Multiplying of Eq. (4.49) by $\psi_b^*(r, R)$ from the left and integration over all electronic coordinates yields

$$\begin{aligned}
 \int dr \psi_b^*(r;R) H_{\text{mol}} \Psi(r;R) &= [E_b(R) + V_{\text{nuc-nuc}}] \chi_b(R) \\
 &\quad + \sum_a \int dr \psi_b^*(r;R) T_{\text{nuc}} \psi_a(r;R) \chi_a(R) \\
 &= E \chi_b(R).
 \end{aligned} \tag{4.50}$$

- Since the electronic wave functions depend on the nuclear coordinates and $P_n = -i\hbar \nabla_n$ we have

$$\begin{aligned}
 T_{\text{nuc}} \psi_a(r;R) \chi_a(R) &= \sum_n \frac{1}{2M_n} \left\{ [P_n^2 \psi_a(r;R)] \chi_a(R) \right. \\
 &\quad + 2[P_n \psi_a(r;R)] P_n \chi_a(R) \\
 &\quad \left. + \psi_a(r;R) P_n^2 \chi_a(R) \right\}.
 \end{aligned} \tag{4.51}$$

- The last term represents kinetic energy operator acting on $\chi_a(R)$. The remaining terms can be combined into the so-called *nonadiabaticity* operator (change of electronic wave function)

$$\begin{aligned}
 \Theta_{ab} &= \int dr \psi_a^*(r;R) T_{\text{nuc}} \psi_b(r;R) \\
 &\quad + \sum_n \frac{1}{M_n} \left[\int dr \psi_a^*(r;R) P_n \psi_b(r;R) \right] P_n.
 \end{aligned} \tag{4.52}$$

- Thus, we obtain an equation for expansion coefficients $\chi_a(R)$ that reads

$$\boxed{(T_{\text{nuc}} + E_a(R) + V_{\text{nuc-nuc}} + \Theta_{aa} - E) \chi_a(R) = - \sum_{b \neq a} \Theta_{ab} \chi_b(R).} \tag{4.53}$$

- The later is an exact stationary SCHRÖDINGER equation for the nuclear wave function $\chi_a(R)$.
- The solution to Eq.(4.53) requires the knowledge of electronic spectrum for all configurations of nuclei during their motion.
- The nonadiabaticity operator accounts for finite kinetic energy of nuclei and triggers transitions between individual adiabatic electronic states.
- Introducing an effective potential if the electronic system is in its adiabatic state $|\psi_a\rangle$:

$$U_a(R) = E_a(R) + V_{\text{nuc-nuc}}(R) + \Theta_{aa}. \quad (4.54)$$

- The formal solution to Eq.(4.53) is $\chi_{aM}(R) = \langle R|\chi_{aM}\rangle$. The index M denotes the (set of) vibrational quantum numbers related to the total electronic spectrum.
- The molecular wave function is

$$\Psi_M(r; R) = \sum_a \chi_{aM}(R) \psi_a(r; R). \quad (4.55)$$

- **Born-Oppenheimer Approximation:** $\Theta_{ab} = 0$.
- **Adiabatic Approximation:** $\Theta_{a \neq b} = 0$.
- The nuclear SCHRÖDINGER equation reads

$$H_a(R)\chi_a(R) = (T_{\text{nuc}} + U_a(R))\chi_a(R) = E\chi_a(R), \quad (4.56)$$

where electronic state specific solutions are labeled by M .

- The adiabatic molecular wave function in BORN-OPPENHEIMER approximation is

$$\Psi_{aM}^{(\text{adia})}(r; R) = \chi_{aM}(R) \psi_a(r; R). \quad (4.57)$$

E Given the following ansatz for the total molecular wave function

$$\Psi(r; R) = \sum_i \chi_i(R) \psi_i(r; R) \quad (4.58)$$

where $\psi_i(r; R)$ is the adiabatic electronic wave function and $\chi_i(R)$ the nuclear wave function for electronic state i .

- Show that the matrix elements of the nuclear kinetic energy operator

$$\int dr \psi_j^*(r; R) \hat{T}_{\text{nuc}} \psi_i(r; R)$$

are given by the nonadiabaticity operator (M_n mass of n -th nucleus)

$$\begin{aligned} \hat{\Theta}_{ij} &= \int dr \psi_i^*(r; R) \hat{T}_{\text{nuc}} \psi_j(r; R) \\ &+ \sum_n \frac{1}{M_n} \left[\int dr \psi_i^*(r; R) \hat{P}_n \psi_j(r; R) \right] \hat{P}_n. \end{aligned} \quad (4.59)$$

4.4.1 Potential Energy Surfaces

- Consider adiabatic Born–Oppenheimer PES ($\Theta_{ab} = 0$) for a particular electronic state

$$U_a(R) = E_a(R) + V_{\text{nuc-nuc}}(R). \quad (4.60)$$

- This is function of all the $3N_{\text{nuc}}$ nuclear coordinates R (remember the notation $R = (R_1, \dots, R_{3N_{\text{nuc}}})$).
- In total $3N_{\text{nuc}} - 6$ intramolecular coordinates are necessary to completely specify the internal energy of the molecule ($3N_{\text{nuc}} - 5$ for linear molecules).
- The gradient of the potential reads

$$\nabla U_a(R) = \{\partial U_a(R)/\partial R_1, \dots, \partial U_a(R)/\partial R_{3N_{\text{nuc}}}\}. \quad (4.61)$$

- The stationary points $R^{(a)}$ are obtained as follows

$$\nabla U_a(R)|_{R=R^{(a)}} = 0, \quad (4.62)$$

- The nature of stationary point is determined from $3N_{\text{nuc}} \times 3N_{\text{nuc}}$ force constant matrix (Hessian)

$$\kappa_{mn}^{(a)} = \frac{\partial^2 U_a(R)}{\partial R_m \partial R_n} \quad (m, n = 1, \dots, 3N_{\text{nuc}}). \quad (4.63)$$

- For more than two coordinates in fact potential energy hypersurface.
- In many cases the discussion can be restricted to one important coordinate. This defines the potential energy curves.

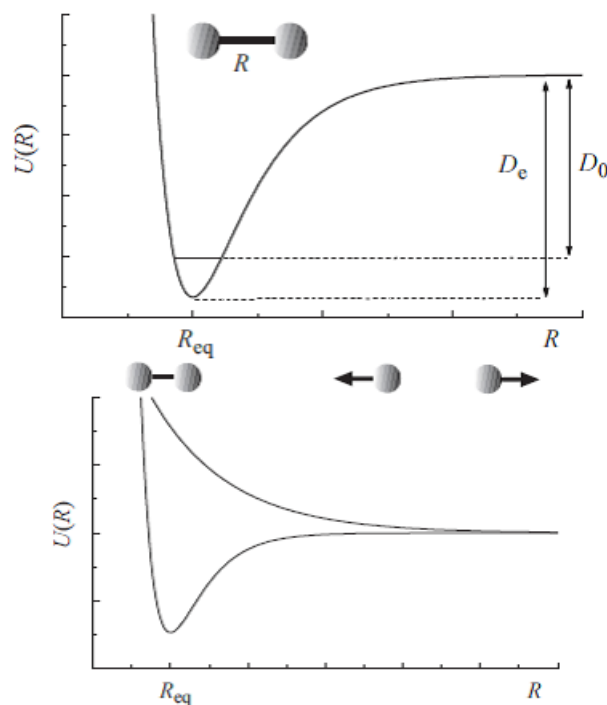


Fig. 4.3: Schematic view of a typical potential energy curve of a diatomic molecule. Here, R_{eq} denotes the equilibrium bond length and $D_0(D_e)$ the dissociation energy which does (does not) take into account the quantum mechanical zero-point energy. Lower panel: case with unbound excited state.

4.5 Molecular Vibrations

- The main approximations for potential energy curves are:
 1. Parabolic Potential: comprises constant and quadratic term, simplest approximation near minima, leading terms of TAYLOR expansion, harmonic oscillator.
 2. MORSE potential: accounts for anharmonicities, qualitatively correct also for large displacements, analytically solvable.

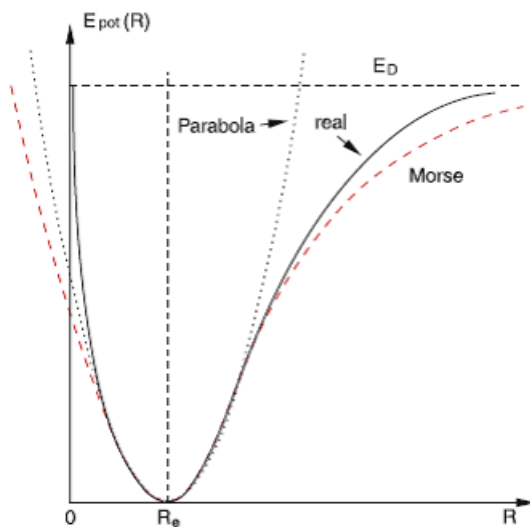


Fig. 4.4: Comparison of parabolic and Morse potentials with the real (experimental) potential.

4.5.1 The Harmonic Oscillator

- The simplest model used for describing vibrations in diatomic molecules is one-dimensional harmonic oscillator. The potential energy reads

$$U(x) = \frac{1}{2}kx^2 \quad (4.64)$$

where $x = R - R_e$ is the equilibrium distance, R is the instantaneous interatomic separation, R_e is the equilibrium bond length and k being the bond force constant.

- The harmonic oscillator Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \quad (4.65)$$

where μ is the reduced mass of the two atoms.

- This models any real potential in the vicinity of its equilibrium point.
- Solving the time-independent SCHRÖDINGER equation, $\hat{H}\psi = E\psi$, yields the energies

$$E_v = \hbar\omega_0 \left(v + \frac{1}{2} \right), \quad v = 0, 1, 2, \dots \quad (4.66)$$

with vibrational angular frequency $\omega_0 = \sqrt{k/\mu}$, and the wavefunctions

$$\psi_v(q) = N_v H_v(q) e^{-q^2/2}, \quad q = (\mu k / \hbar^2)^{1/4} x \quad (4.67)$$

where $N_v = (\sqrt{\pi}2^v v!)^{-1/2}$ is a normalization constant and $H_v(q)$ is the HERMITE polynomials of the order v , defined as

$$H_v(q) = (-1)^v e^{q^2} \frac{d^v}{dq^v} \left(e^{-q^2} \right). \quad (4.68)$$

- Here we list the first few HERMITE polynomials

$$\begin{aligned} H_0(q) &= 1 \\ H_1(q) &= 2q \\ H_2(q) &= 4q^2 - 2 \\ H_3(q) &= 8q^3 - 12q \\ H_4(q) &= 16q^4 - 48q^2 + 12 \end{aligned}$$

- The HERMITE polynomials fulfill the recurrence relation

$$H_{v+1}(q) = 2qH_v(q) - 2vH_{v-1}(q), \quad (4.69)$$

hence given the first two polynomials, $H_0 = 1$ and $H_1 = 2q$, all other terms can be obtained.

- In spectroscopy, the terms values $G(v) = E_v/(hc)$ are used instead of the energy eigenvalues. The equation (4.66) becomes

$$G(v) = \omega_e \left(v + \frac{1}{2} \right), \quad \omega_e = \omega_0/(2\pi c). \quad (4.70)$$

- An important feature is that the lowest level $v = 0$ is not at the zero of energy. According to Eq.(4.70) the energy of $v = 0$ is $\omega_e/2$, known as the *zero-point energy*. The vibrational energy levels can never be less than the zero-point energy, even when the sample is cooled down to 0 K. This is due to Heisenberg's uncertainty principle.

4.5.2 The Anharmonic Oscillator

- For larger vibrational quantum numbers v , the vibrational states of a real molecule converge with frequencies differs significantly from the constant frequency ω_0 of the harmonic oscillator.
- The true interatomic potential is not a parabola since real diatomic molecules dissociate at high excitation.

- An appreciable model for real molecule is the *Morse potential*

$$U(x) = D_e[1 - e^{-ax}]^2, \quad (4.71)$$

where D_e is the molecule's dissociation energy (measured from the bottom of the potential), the parameter $a = \sqrt{k_e/2D_e}$ and $k_e = (d^2U/dx^2)|_{x=0}$ is the bond force constant at the bottom of the potential well.

- The SCHRÖDINGER equation for MORSE potential can be solved exactly, and the corresponding energies are

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2, \quad (4.72)$$

where

$$\omega_e = \frac{a}{2\pi c} \sqrt{\frac{2D_e}{\mu}} \quad \text{and} \quad \omega_e x_e = \frac{\omega_e^2}{4D_e} \quad (4.73)$$

are the equilibrium harmonic frequency and the anharmonicity constant, respectively.

E The binding potential of a diatomic molecule is well described by a MORSE potential (4.71). The vibrational spectrum of the CO molecule shows a fundamental band at 2143 cm^{-1} and the first overtone band at 4260 cm^{-1} . The observed bands can be used to estimate the parameters ω_e and $\omega_e x_e$:

$$\begin{aligned} \tilde{\nu}_{v=0 \rightarrow 1} &= \omega_e - 2\omega_e x_e = 2143 \text{ cm}^{-1}, \\ \tilde{\nu}_{v=0 \rightarrow 2} &= 2\omega_e - 6\omega_e x_e = 4260 \text{ cm}^{-1}. \end{aligned}$$

- Use this information to infer the MORSE parameters, D_e and a .
- Deduce the value of bond strength which is the energy required to dissociate the molecule from its ground state ($v = 0$, with energy $G(0) = \omega_e/2 - \omega_e x_e/4$).
- The vibrational energy levels converge with increasing quantum number v . Calculate the highest energy level, $v_{\max}$ from the condition

$$\left. \frac{dG(v)}{dv} \right|_{v=v_{\max}} = 0.$$

- Calculate the classical turning points $x_{\pm}$ from matching the above formula for $U(x)$ to an arbitrary energy level E_v .

- Make a plot for the potential energy curve and energy levels as horizontal lines between the classical turning points by creating a suitable array of bond displacements, $x = R - R_e$ and using the MORSE oscillator formula for $U(x)$.
- The rotational constants for CO molecule are 1.9314 cm^{-1} and 1.6116 cm^{-1} in the ground and in the first excited vibrational state, respectively. By how much does the internuclear distance change as a result of vibrational excitation?

E Consider the RbH molecule. Its reduced mass can be very well approximated by the mass of the hydrogen atom (why?). The binding potential is well described by a MORSE potential

$$U(R) = D_e[1 - e^{-a(R-R_e)}]^2 \quad (4.74)$$

with $R_e = 236.7 \text{ pm}$, the dissociation energy $D_e = 1.922 \text{ eV}$, and $a = 0.009162 \text{ pm}^{-1}$.

- Calculate the force constant, k , and the rotational constants B and D , which account for the centrifugal distortion up to first order.
- Calculate the rotational transition energies for $J = 0 \rightarrow 1$, $5 \rightarrow 6$, and $10 \rightarrow 11$.
- Sketch the effective potential for $J = 0, 40, 80, 100$.

4.6 Vibrational Spectroscopy

4.6.1 Electromagnetic Vibrational Transitions

- Electromagnetic radiation with resonant frequency can be radiated or absorbed by transitions between vibrational levels.
- The electric dipole moment of the molecule varies periodically with the frequency of the vibration.
- Only vibrations which change the dipole moment are infrared active. Frequently vibrations are infrared inactive due to symmetry reasons, e.g. symmetric stretch vibration CO_2 .
- The vibrational spectra are located in the infrared spectral region. Furthermore,

- the energies of molecular vibrations are ranged, roughly, from 100 cm^{-1} to 4000 cm^{-1} and
- the wavelength region varies from $100\text{ }\mu\text{m}$ to $3\text{ }\mu\text{m}$.
- The selection rule for harmonic oscillator $\Delta v = 1$.
- For most diatomic molecules, the energy gap, $G(1) - G(0)$ in Eq.(4.72), between the $v = 0$ ground state and the $v = 1$ first excited state is of the order of 1000 cm^{-1} . The ratio of the populations of these states is

$$\frac{n_1}{n_0} = \exp\left(-\frac{\Delta E}{k_B T}\right) = \exp\left(-\frac{[G(1) - G(0)]hc}{k_B T}\right), \quad (4.75)$$

which is less than 1% at room temperature, i.e. most of the molecules are in the $v = 0$ ground state.

- The fundamental vibrational band, corresponding to the transition $v = 0 \rightarrow 1$, occurs at the following wavenumber

$$\tilde{\nu}_{v=0 \rightarrow 1} = G(1) - G(0) = \omega_e - 2\omega_e x_e \quad (4.76)$$

- The *overtone bands*, for which ($\Delta v > 1$) are observed at wavenumbers

$$\tilde{\nu}_{v=0 \rightarrow v} = G(v) - G(0) = \omega_e v - \omega_e x_e v(v+1). \quad (4.77)$$

- The overtone intensity is about a factor 10 weaker than the fundamental ones.

4.6.2 Normal Modes

- The geometry of molecule with N atoms can be described by $3N - 6$ internal coordinates (linear molecule by $3N - 5$), which characterize the positions of the nuclei relative to each other, e.g. H_2O has 3 internal coordinates and 4 for CO_2 molecule.
- In molecules exist complex vibrational motions, to which many atoms contribute.
- The restoring forces are to first order linear with the displacements.
- These vibrations can be decomposed in *normal modes* which behave like one dimensional harmonic oscillators.
- This is analogous to *eigenmodes* (resonant vibrations) of coupled oscillators and of macroscopic objects.

4.6.2.1 Harmonic Approximation and Normal Mode Analysis

- Let us focus on the nuclear dynamics in vicinity of stationary point $R^{(a)}$ where $U_a(R)$ has a minimum. For small deviations, $\Delta R_n^{(a)} = R_n^{(a)} - R^{(a)}$, ($n = 1, \dots, 3N_{\text{nuc}}$) we perform Taylor expansion.
- The Hamiltonian for the nuclear degrees of freedom in the adiabatic approximation reads

$$\begin{aligned}
 H_a &= U_a(R^{(a)}) + \sum_{n=1}^{3N_{\text{nuc}}} \frac{P_n^2}{2M_n} + \sum_{m,n=1}^{3N_{\text{nuc}}} \frac{1}{2} \kappa_{mn}^{(a)} \Delta R_m^{(a)} \Delta R_n^{(a)} + \dots \\
 &= U_a(R^{(a)}) + \frac{1}{2} \begin{bmatrix} P_1 & P_2 & \dots & P_{3N_{\text{nuc}}} \end{bmatrix} \begin{bmatrix} \frac{1}{M_1} & 0 & \dots & 0 \\ 0 & \frac{1}{M_2} & & \\ \vdots & & \ddots & \\ 0 & & & \frac{1}{M_{3N_{\text{nuc}}}} \end{bmatrix} \begin{bmatrix} P_1 \\ P_2 \\ \vdots \\ P_{3N_{\text{nuc}}} \end{bmatrix} + \\
 &\quad \frac{1}{2} \begin{bmatrix} \Delta R_1^{(a)} & \Delta R_2^{(a)} & \dots & \Delta R_{3N_{\text{nuc}}}^{(a)} \end{bmatrix} \begin{bmatrix} \kappa_{11}^{(a)} & \kappa_{21}^{(a)} & \dots & \kappa_{3N_{\text{nuc}}1}^{(a)} \\ \kappa_{12}^{(a)} & \kappa_{22}^{(a)} & & \\ \vdots & & \ddots & \\ \kappa_{13N_{\text{nuc}}}^{(a)} & & & \kappa_{3N_{\text{nuc}}3N_{\text{nuc}}}^{(a)} \end{bmatrix} \begin{bmatrix} \Delta R_1^{(a)} \\ \Delta R_2^{(a)} \\ \vdots \\ \Delta R_{3N_{\text{nuc}}}^{(a)} \end{bmatrix} + \dots
 \end{aligned} \tag{4.78}$$

where we neglect all higher order terms beyond the quadratic term.

- Introducing linear transformation to mass-weighted normal mode coordinates $q_{a,\xi}$

$$\Delta R_n^{(a)} = \sum_{\xi} M_n^{-1/2} A_{n\xi}^{(a)} q_{a,\xi}, \tag{4.79}$$

to diagonalize the potential energy part since the kinetic energy operator is diagonal due to the Cartesian property of the displacements. Hence we obtain

$$H_a = U_a(q_{a,\xi} = 0) + H_a^{(mn)} \tag{4.80}$$

where

$$H_a^{(mn)} = \frac{1}{2} \sum_{\xi} (p_{\xi}^2 + \omega_{a,\xi}^2 q_{a,\xi}^2). \tag{4.81}$$

- Here $\omega_{a,\xi}$ being the normal mode frequencies where $\omega_{a,\xi}^2$ are the nonzero eigenvalues of the Hessian matrix $\kappa_{mn}^{(a)}$.

- The corresponding energy eigenvalues are

$$E_{aN} = \sum_{\xi} \hbar \omega_{a,\xi} (N_{\xi} + \frac{1}{2}) \quad N_{\xi} = 0, 1, 2, \dots \quad (4.82)$$

with $N = N_1, N_2, \dots$

- The nuclear motion (4.81) can be understood as a superposition of independent harmonic vibrations where the oscillations of the individual atoms have all the same frequency $\omega_{a,\xi}$, but different amplitudes determined by their masses (cf. Eq. (4.79)).
- Using product ansatz for multidimensional wave function

$$\chi_{aN}^{(\text{adia})}(q) = \prod_{\xi} \chi_{aN_{\xi}}^{(\text{adia})}(q_{a,\xi}) \quad (4.83)$$

yields

$$H_a^{(mn)} \chi_{aN}^{(\text{adia})}(q) = E_{aN} \chi_{aN}^{(\text{adia})}(q), \quad (4.84)$$

where

$$\chi_{aN_{\xi}}^{(\text{adia})}(q_{a,\xi}) = \frac{\sqrt{\lambda_{a,\xi}}}{\sqrt{\sqrt{\pi} 2^{N_{\xi}} N_{\xi}!}} \exp\left(-\frac{1}{2} \lambda_{a,\xi}^2 q_{a,\xi}^2\right) H_{N_{\xi}}(\lambda_{a,\xi} q_{a,\xi}), \quad (4.85)$$

with $\lambda_{a,\xi}^2 = \omega_{a,\xi} / \hbar$ ($H_{N_{\xi}}$ are HERMITE polynomials).

- In the case of two electronic states (ground state g and excited state e), $a = g/e$, we expand the potential $U_e(R)$ into a TAYLOR series in the vicinity of the stationary point $R^{(e)}$:

$$U_e(R) = U_e(R^{(e)}) + \sum_{m,n=1}^{3N_{\text{nuc}}} \frac{1}{2} \kappa_{mn}^{(e)} \Delta R_m^{(e)} \Delta R_n^{(e)}. \quad (4.86)$$

- Assuming that both states have same normal modes $q_{\xi} = q_{g,\xi}$ we can write

$$\Delta R_n^{(e)} = R_n - R_n^{(g)} - (R_n^{(e)} - R_n^{(g)}) = \sum_{\xi} M_n^{-1/2} A_{n\xi}^{(g)} (q_{\xi} - q_{\xi}^{(e)}). \quad (4.87)$$

- In general, the shifted-oscillator Hamiltonian for a state ϕ_a reads

$$H_a = U_a(q_{\xi} = q_{\xi}^{(a)}) + \frac{1}{2} \sum_{\xi} \left(p_{\xi}^2 + \omega_{a,\xi}^2 (q_{\xi} - q_{\xi}^{(a)})^2 \right), \quad (4.88)$$

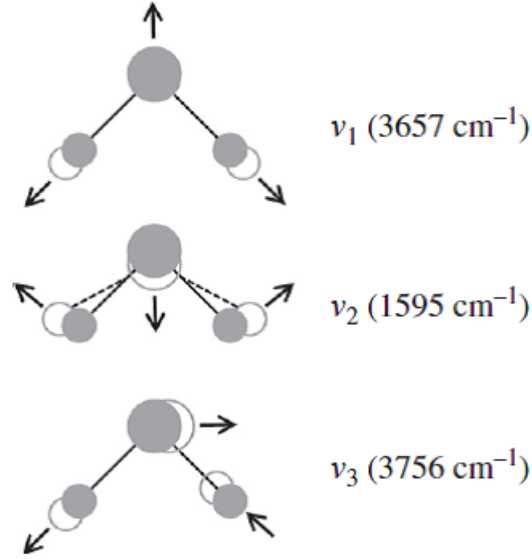


Fig. 4.5: Displacement vectors for the three normal modes of water. The different amplitudes are determined by the atomic masses (cf. Eq. (4.79)).

and the corresponding wave functions are

$$\chi_{aN_\xi}(q_\xi) = \frac{\sqrt{\lambda_{a,\xi}}}{\sqrt{\sqrt{\pi} 2^{N_\xi} N_\xi!}} \exp\left(-\frac{1}{2}\lambda_{a,\xi}^2(q_\xi - q_\xi^{(a)})^2\right) H_{N_\xi}(\lambda_{a,\xi}(q_\xi - q_\xi^{(a)})). \quad (4.89)$$

E Anharmonic coupling can lead to transitions between eigenstates of different harmonic oscillators corresponding, for instance, to bond stretching and bending vibrations. Consider such a two-mode case that can be described by the oscillator Hamiltonian

$$H(Q_1, Q_2) = \sum_{\xi=1,2} \frac{\hbar\omega_\xi}{4} (P_\xi^2 + Q_\xi^2),$$

expressed in dimensionless coordinates (q_ξ/p_ξ are original mass-weighted oscillator coordinates/momenta)

$$Q_\xi = q_\xi \sqrt{\frac{2\omega_\xi}{\hbar}}, \quad P_\xi = p_\xi \sqrt{\frac{2}{\hbar\omega_\xi}}.$$

The eigenstates of this uncoupled Hamiltonian can be written as $|N_1; N_2\rangle \equiv |N_1\rangle \otimes |N_2\rangle$. In second order of perturbation theory with respect to some anhar-

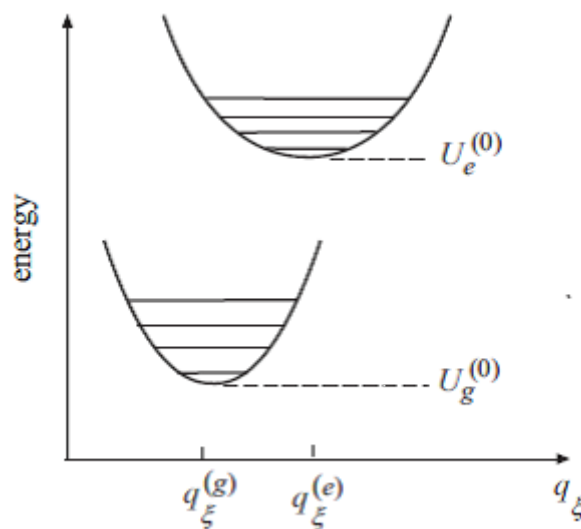


Fig. 4.6: Shifted harmonic oscillator potential surfaces for two electronic states which are described by the same normal coordinate q_ξ .

monic coupling operator V , transition rates between uncoupled states are given by the Golden rule

$$k_{N_1, N_2 \rightarrow M_1, M_2} = \frac{2\pi}{\hbar} |\langle N_1; N_2 | V | M_1; M_2 \rangle|^2 \delta(E_{N_1, N_2} - E_{M_1, M_2}).$$

Calculate matrix elements, $\langle N_1; N_2 | V | M_1; M_2 \rangle$, for the anharmonic coupling of the form

$$V(Q_1, Q_2) = cQ_1Q_2^2$$

specified to $|N_1 = 0; N_2 = 1\rangle$ and $|M_1 = 0, 1, 2; M_2 = 1\rangle$. Discuss the consequences for the transition rate between these states.

Hint: Introduce oscillator creation and annihilation operators!

4.7 Vibration–Rotation Transitions

- For real molecules, rotational states have energy levels that are much closer together than vibrational states (see Figure (4.7)). Within transitions between vibrational states, the rotational quantum number J can either increase or decrease resulting an increase in the molecule's energy. These transitions can correspond to the absorption of infrared light.

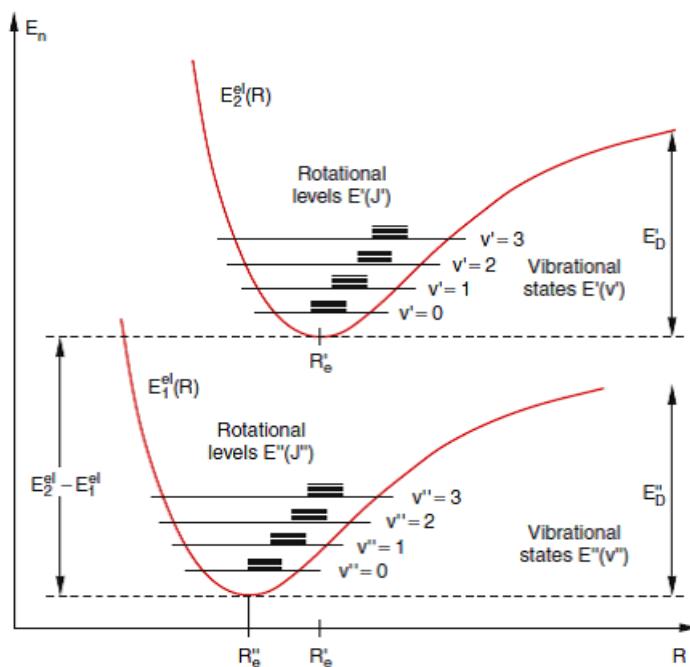


Fig. 4.7: Rotational and vibrational levels in two different electronic states of a diatomic molecule.

- Under the harmonic oscillator and rigid rotor approximations, the energies of the allowed vibration-rotation transitions for a diatomic molecule can be described via the following expressions:

$$\begin{aligned}
 E_{v+1,J+1} - E_{v,J} &= \left[\hbar\omega_0 \left(v + \frac{3}{2} \right) + B(J+1)(J+2) \right] \\
 &\quad - \left[\hbar\omega_0 \left(v + \frac{1}{2} \right) + BJ(J+1) \right] \\
 &= \hbar\omega_0 + 2B(J+1) \quad (J \longrightarrow J+1, \text{ "R-branch"})
 \end{aligned}$$

$$\begin{aligned}
 E_{v+1,J-1} - E_{v,J} &= \left[\hbar\omega_0 \left(v + \frac{3}{2} \right) + B(J-1)J \right] \\
 &\quad - \left[\hbar\omega_0 \left(v + \frac{1}{2} \right) + BJ(J+1) \right] \\
 &= \hbar\omega_0 - 2BJ \quad (J \longrightarrow J-1, \text{ "P-branch"})
 \end{aligned}$$

- The vibration-rotation absorption spectrum of a linear molecule is characterized by two sets of lines: a P-branch at lower energy and a R-branch at higher energy.

- These absorption lines correspond to different initial values of the rotational quantum number J : $P(J)$ and $R(J)$. The first line of the P-branch corresponds to $J = 1$ (as $\Delta J = -1$ and J cannot be negative) and occurs at $\hbar\omega_0 - 2B$. The first line of the R-branch corresponds to $J = 0$ and occurs at $\hbar\omega_0 + 2B$.
- The presence of a gap between $P(1)$ and $R(0)$ (where the "Q-branch", corresponding to $\Delta J = 0$ is not allowed, i.e. there is no transition at the pure vibrational frequency $\hbar\omega_0$) suggests to find the maximum spacing between the peaks: The lines with lower wavenumbers are $P(1), P(2), P(3) \dots$; those at higher wavenumbers $R(0), R(1), R(2) \dots$.
- The relative intensities of the different lines with different J values are determined by their thermal populations, as discussed for pure rotational spectroscopy. Figure (4.8) depicts an example of a calculated diatomic vibration-rotation absorption spectrum. Nonlinear molecules also exhibit a transition at energy $\hbar\omega_0$ with $\Delta J = 0$, namely "Q-branch" is shown in Figure (4.9).

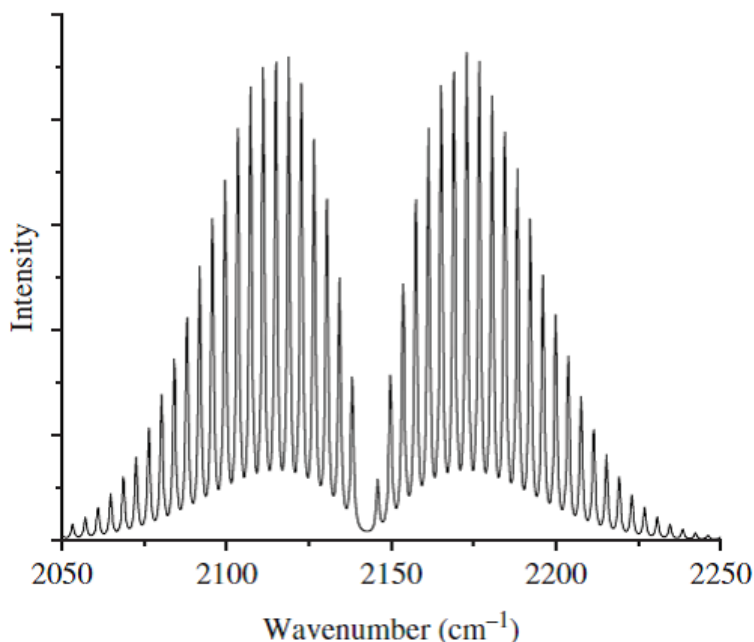


Fig. 4.8: Vibration-rotation spectrum for a rigid rotor/harmonic oscillator model of the CO molecule at 298 K. $B = 1.93 \text{ cm}^{-1}$ and $\omega_0 = 2143 \text{ cm}^{-1}$.

E The high-resolution infrared absorption spectrum of a typical diatomic molecule exhibits signals caused by transitions between its energy levels, namely rotational and vibrational states. In real molecules, the vibrational motion is described

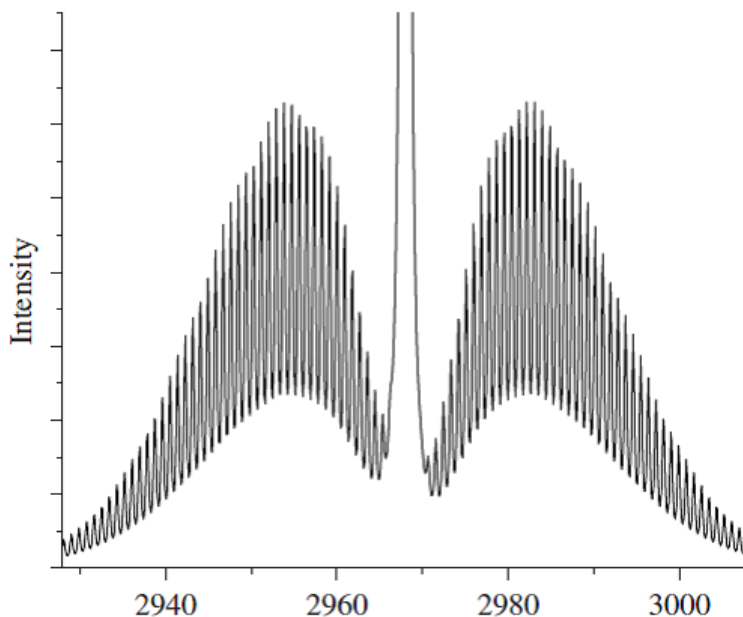


Fig. 4.9: Vibration–rotation spectrum for a rigid rotor/harmonic oscillator model of the CH_3Cl molecule at 298 K. $B = 0.44 \text{ cm}^{-1}$ and $\omega_0 = 2968 \text{ cm}^{-1}$.

via anharmonic oscillators. The bands match a change in the vibrational quantum number ($\Delta v = 0, 1, 2, \dots$). In addition, they can be observed with sufficient sensitivity, where the fundamental band ($v = 0 \rightarrow v = 1$) is expected to be significantly the strongest. Each band comprises individual transition lines that involve a change in the rotational quantum number, $\Delta J = \pm 1$ (for a closed-shell diatomic molecule). The group of lines with $\Delta J = -1$ is known as the P-branch, while those with $\Delta J = +1$ define the R-branch. The files, `C0-v01.txt` and `C0-v02.txt`, which can be downloaded from <https://scipython.com/chem/cas/>, contain the infrared absorption spectrum of carbon monoxide CO, measured in the region of the fundamental ($v = 0 \rightarrow v = 1$) and first overtone ($v = 0 \rightarrow v = 2$) bands, respectively.

1. Using Python make a plot for the fundamental infrared absorption band of carbon monoxide and identify the rovibrational peaks in the P- and R-branches.
2. Using the data in the file `C0-v02.txt`, identify the number of peaks for the first overtone band.
3. By fitting the spectrum, provide an estimation for the spectroscopic parameters $\omega_e, \omega_e x_e, B, \alpha_e$ and D given in the following expression for the

rovibrational energy levels

$$E(v, J) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \left[B - \alpha_e \left(v + \frac{1}{2} \right) \right] J(J+1) - D[J(J+1)]^2.$$

4. Use the fitted parameters to predict the locations of lines that are not observed in the measured spectrum.
5. Plot the residuals for all of the fitted lines on a scatter plot.

4.8 Electronic Spectroscopy

- Electronic absorption bands are usually in the visible and ultraviolet ranges.
- Each electronic state has its own potential energy surface.
- Each electronic band contains many lines. They correspond to electronic transitions with different rotational and vibrational levels (see Fig.4.10).

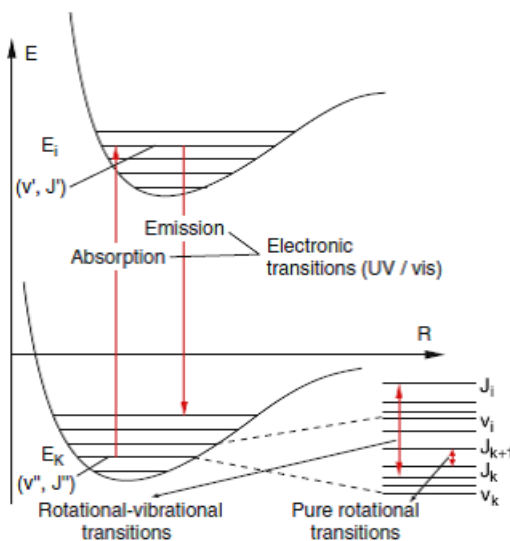


Fig. 4.10: Schematic representation of the structure of molecular transitions.

4.8.1 Spectroscopic Notation for Diatomic Molecules

- In molecules, the total orbital angular momentum of electrons is not conserved due to the coupling with the motion of nuclei. However, diatomic molecules

have an axial symmetry w.r.t the axis joining both nuclei which implies that the projection of electrons' total orbital momentum onto the molecular axis is conserved. Hence, molecular term symbols are classified according to the absolute value of this projection, Λ .

1. For diatomic molecules, we have

$$\begin{array}{ll} \Lambda = 0 & \longrightarrow \Sigma \\ \Lambda = 1 & \longrightarrow \Pi \\ \Lambda = 2 & \longrightarrow \Delta \\ \Lambda = 3 & \longrightarrow \Phi \\ \vdots & \vdots \end{array}$$

2. An additional subscript $+$ or $-$ is added to Σ terms only, depending whether the molecular wavefunction changes sign under reflection through a plane passing through the molecular axis. Molecular states that change sign after reflection are denoted with $-$ and those which do not are labeled with $+$.
3. The total spin of the electrons is denoted as an additional degree of degeneracy, $2S + 1$, to the spectroscopic notation for electronic terms

$$^{2S+1}\Lambda^{\pm}.$$

4. The total electronic angular momentum (spin plus orbital, the equivalent for J for atoms), denoted as Ω , is included as a subscript in spectroscopic notation:

$$^{2S+1}\Lambda_{\Omega}^{\pm}.$$

5. In the case of homonuclear molecules or dimers, the symmetry about the center of mass has to be taken into account. If we perform a transformation inverting the position of electrons w.r.t the center of mass ($\vec{r} \longrightarrow -\vec{r}$), the square of the electronic wavefunction should be invariant. The wavefunctions that do not change sign under this transformation are called *gerade* (g) and those do change sign are labeled as *ungerade* (u). These German words mean *even* and *odd*, respectively. This completes the overall spectroscopic notation to be

$$^{2S+1}\Lambda_{\Omega,g/u}^{\pm}.$$

4.8.2 Franck-Condon Factors

- A vibronic transition is transition from one specific vibrational level of an electronic state to a specific vibrational level of another electronic state.

- Separating of the wavefunction Ψ of a molecular state in an electronic contribution ψ and a nuclear wavefunction χ yields

$$\Psi_i(r, R) = \psi_i(r, R)\chi_i(R).$$

- The transition matrix element between initial and final states reads

$$\begin{aligned} M_{if} &= \int \Psi_f^*(r, R) e\vec{r} \Psi_i(r, R) dr dR \\ &= \int \psi_f^*(r, R) \chi_f^*(R) e\vec{r} \psi_i(r, R) \chi_i(R) dr dR \\ &\simeq \int \psi_f^*(r, R_e) e\vec{r} \psi_i(r, R_e) dr \int \chi_f^*(R) \chi_i(R) dR, \end{aligned} \tag{4.90}$$

where the variation of the electronic wavefunction ψ with the nuclear coordinate R is neglected and the electronic wavefunction is taken at the nuclear coordinate R_e at the equilibrium structure.

- Rewriting the square of transition matrix element as

$$M_{if}^2 = |\vec{d}_{if}|^2 \text{FC}_{if},$$

with

$$\vec{d}_{if} = \int \psi_f^*(r, R_e) e\vec{r} \psi_i(r, R_e) dr$$

being the electronic transition dipole and

$$\text{FC}_{if} = \left| \int \chi_f^*(R) \chi_i(R) dR \right|^2 \tag{4.91}$$

is the so-called the *Franck-Condon factor*.

- The FRANCK-CONDON factor reflects the overlap of the two nuclear wavefunctions.
- The CONDON approximation states that the nuclear coordinates are frozen during the fast electronic transition. The transition is *vertical*, e.g. in a potential energy diagram, as the nuclear coordinates do not change during the transition.
- The FRANCK-CONDON factor characterizes the overlap between vibrational eigenfunctions of lower and upper electronic state.

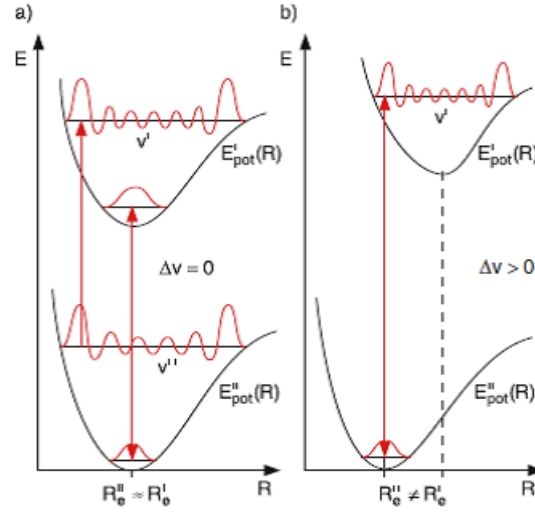


Fig. 4.11: Illustration of the Franck-Condon principle for vertical transitions with $\Delta v = 0$ and $\Delta v > 0$ in case of potential curves with $R''_e = R'_e$ (no shift) and $R''_e \neq R'_e$ (shifted potentials). With increasing shift of potentials higher Δv are possible.

E Calculate the FRANCK-CONDON overlap integrals $\langle \chi_i(R) | \chi_j(R) \rangle$ of the $0 \rightarrow 0$, $0 \rightarrow 1$ and $0 \rightarrow 2$ transitions for a shifted harmonic oscillator model in dependence of the HUANG-RHYS factor S . What is the ratio of the first two transitions for $S = 1$?

- Consider a FRANCK-CONDON progression in which the second peak is half as strong as the first peak. How large is the dimensionless shift between the potential in the ground and the electronically excited state? Assume that both potentials are harmonic and have the same curvature.

4.8.3 Absorption

- Let us consider the process of light absorption within BORN-OPPENHEIMER approximation where total Hamiltonian is time-dependent

$$H(t) = H_{\text{mol}} - d\mathcal{E}(t). \quad (4.92)$$

- For an electronic two state system the time-dependent SCHRÖDINGER equation reads

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} |\chi_g\rangle \\ |\chi_e\rangle \end{pmatrix} = \begin{pmatrix} T + U_g - \mathcal{E}(t)d_{gg} & -d_{ge}\mathcal{E}(t) \\ -d_{eg}\mathcal{E}(t) & T + U_e - \mathcal{E}(t)d_{ee} \end{pmatrix} \begin{pmatrix} |\chi_g\rangle \\ |\chi_e\rangle \end{pmatrix}. \quad (4.93)$$

In the following, we will consider the case of vanishing dipole moments ($d_{gg} = d_{ee} = 0$, e.g., homonuclear diatomics).

- The absorption of light from the electronic ground state to the electronic excited state is discussed in context of BEER's law which states that the intensity of the electric field inside a medium decays exponentially as a function of the distance travelled, i.e.

$$I(x) = I(x=0) \exp(-\alpha x), \quad (4.94)$$

where α is the absorption coefficient.

- The derivation starts from sample volume V with N_{mol} molecules and a surface area A onto which light with frequency ω hits (assuming incidence perpendicular to the surface along x only).
- The electric field is assumed to be monochromatic and directed along the dipole moment vector

$$\mathcal{E}(t) = \mathcal{E}_0(e^{i\omega t} + e^{-i\omega t}) \quad (4.95)$$

- The change of radiation field energy in time interval dt due to absorption in the interval dx is

$$dE = -\frac{N_{\text{mol}} A dx}{V} \hbar \Omega k_{\text{abs}} dt. \quad (4.96)$$

Here $\frac{N_{\text{mol}} A dx}{V}$ is the fraction of the molecules in the considered volume element, k_{abs} is the mean energy absorbed by one molecule within dt . Moreover, k_{abs} is the respective absorption rate constant which is according to the Golden Rule (at zero temperature)

$$k_{\text{abs}} = \frac{2\pi}{\hbar} \mathcal{E}_0^2 \sum_{MN} f(E_{g,M}) |\langle \chi_{e,N} | d_{eg} | \chi_{g,M} \rangle|^2 \delta(\hbar\omega - \hbar\omega_{eg} - (E_{e,N} - E_{g,M})), \quad (4.97)$$

where $\chi_{a,N}$ and $E_{a,N}$ are the nuclear eigenstate and its energy, respectively, for the electronic state a and the vibrational state N , and $\hbar\omega_{eg}$ is the bare electronic energy gap.

- The thermal population of initial states reads

$$f(E_{g,M}) = \exp\{-E_{g,M}/k_B T\} \sum_{M'} \exp\{-E_{g,M'}/k_B T\}. \quad (4.98)$$

- Let us calculate the change of field energy density $du = dE/Adx$ ($n_{\text{mol}} = N_{\text{mol}}/V$ is the number density)

$$\frac{du}{dt} = -n_{\text{mol}} \hbar \omega k_{\text{abs}} = \frac{dI}{dx} \quad (4.99)$$

where the last equality expresses the continuity equation.

- For monochromatic field the intensity after cycle averaging is given by

$$I = \langle |S| \rangle_{\text{cycle}} = \frac{c}{2\pi} \mathcal{E}_0^2 \quad (4.100)$$

- Thus we have an expression for BEER's law

$$\frac{dI}{dx} = -n_{\text{mol}} \hbar \omega k_{\text{abs}} \frac{2\pi}{c \mathcal{E}_0^2} I \quad (4.101)$$

- Combining everything with Eq.(4.94) gives the absorption coefficient

$$\alpha(\omega) = \frac{4\pi^2 \omega n_{\text{mol}}}{c} \sum_{MN} f(E_{g,M}) |\langle \chi_{e,N} | d_{eg} | \chi_{g,M} \rangle|^2 \delta(\hbar\omega - \hbar\omega_{eg} - (E_{e,N} - E_{g,M})). \quad (4.102)$$

- The matrix $\langle \chi_{e,N} | d_{eg} | \chi_{g,M} \rangle$ can simplified to $d_{eg} \langle \chi_{e,N} | \chi_{g,M} \rangle$ in accordance with Condon approximation, which assumes that the transition dipole matrix elements do not depend on the nuclear coordinate.
- Eq. (4.102) tells us that the absorption coefficient is determined by the square of the so-called FRANCK-CONDON factor, provided that the incoming photon is in resonance with a transition.

$$\alpha(\omega) = \frac{4\pi^2 \omega n_{\text{mol}}}{3c} |d_{eg}|^2 \mathcal{D}_{\text{abs}}(\omega - \omega_{eg}), \quad (4.103)$$

with

$$\mathcal{D}_{\text{abs}}(\omega) = \sum_{MN} f(E_{g,M}) |\langle \chi_{e,N} | \chi_{g,M} \rangle|^2 \delta(\hbar\omega - (E_{e,N} - E_{g,M})) \quad (4.104)$$

is the *lineshape function*.

- For the case of single harmonic vibrational coordinate having the same frequency in ground and excited state an analytical solution is available.
- Introducing the FOURIER representation of the Delta function, the lineshape function can be written as

$$\mathcal{D}_{\text{abs}}(\omega) = \frac{1}{2\pi\hbar} \sum_{MN} \int dt f(E_{g,M}) |\langle \chi_{e,N} | \chi_{g,M} \rangle|^2 e^{i(\omega - (E_{e,N} - E_{g,M})/\hbar)t}. \quad (4.105)$$

E Prove that the lineshape function reads

$$\begin{aligned} \mathcal{D}_{\text{abs}}(\omega) &= \frac{1}{\hbar} e^{-\Delta g^2(1+2n(\omega_{\text{vib}}))} \sum_{M,N=0} \frac{1}{M!} [\Delta g^2(1+n(\omega_{\text{vib}}))]^M \\ &\times \frac{1}{N!} [\Delta g^2(n(\omega_{\text{vib}}))]^N \delta(\omega - (N-M)\omega_{\text{vib}}), \end{aligned} \quad (4.106)$$

with

$$\Delta g = \sqrt{\frac{2\omega_{\text{vib}}}{\hbar}} (q^{(\text{g})} - q^{(\text{e})}) \quad (4.107)$$

is the dimensionless shift of potentials and

$$n(\omega_{\text{vib}}) = \frac{1}{\exp\{\omega_{\text{vib}}/k_{\text{B}}T\} - 1} \quad (4.108)$$

is the BOSE-EINSTEIN distribution.

- The absorption coefficient becomes a collection of sharp lines corresponding to transitions at frequencies $(N-M)\omega_{\text{vib}}$ (vibrational progression).
- The zero-temperature case ($\omega_{\text{vib}} = 0$) is

$$\mathcal{D}_{\text{abs}}(\omega)|_{T=0} = \frac{e^{-\Delta g^2}}{\hbar} \sum_{M=0} \frac{\Delta g^{2M}}{M!} \delta(\omega - M\omega_{\text{vib}}), \quad (4.109)$$

which is a sequence of sharp lines at frequencies $\omega_{\text{eg}} + M\omega_{\text{vib}}$ with weighting factors

$$w_M = e^{-\Delta g^2} \sum_{M=0} \frac{\Delta g^{2M}}{M!} \quad (4.110)$$

that follow from a so-called POISSON distribution.

- The maximal at $M \approx \Delta g$ or, in terms of energies, at $M\omega_{\text{vib}} \approx \hbar\omega_{\text{vib}}\Delta g^2$.
- The vibrational quantum number at which the absorption reaches its maximum is given by the difference $U_{\text{e}}(q = q^{(\text{g})}) - U_{\text{e}}(q = q^{(\text{e})}) = \hbar\omega_{\text{vib}}\Delta g^2$ (vertical transition) where Δg^2 defines the HUANG-RHYS factor.
- The emission spectrum is along the same lines, where the difference between absorption and emission maxima is STOKES *shift*.

$$S = 2\hbar\omega_{\text{vib}}\Delta g^2. \quad (4.111)$$

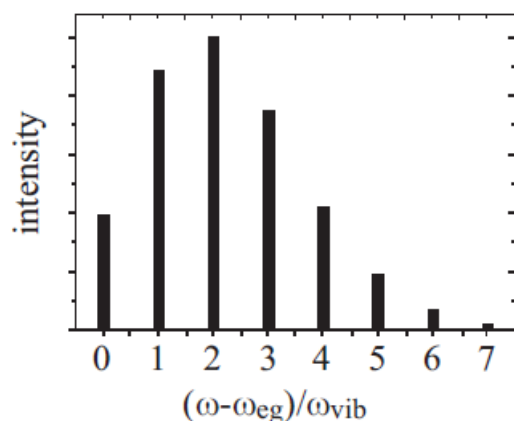


Fig. 4.12: Stick spectrum of the absorption for $\Delta g = 1.5$.

4.8.4 Fluorescence

- Fluorescence is a spontaneous emission by a dipole allowed transition from an electronically excited state to the ground state (singlet states), typically $S_1 \rightarrow S_0$.
- It is often assumed that the absorption spectrum corresponding to the lowest-energy electronic transition of a molecule and the fluorescence spectrum arising from emission from that same state should be mirror images of one another.
- *Strickler-Berg symmetry*: fluorescence spectrum is roughly mirror symmetric to the first electronic absorption band $S_0 \rightarrow S_1$.
- Mirror image symmetry in absorption and fluorescence requires that the same pair of electronic states be involved, e.g. there is no internal conversion process preceding emission.
- The potential energy surfaces for both states must have the same vibrational frequencies (i.e. same curvature), although they may be displaced.
- The fluorescence must be long-lived enough that there is time to establish a Boltzmann population of excited-state vibrational levels prior to emission, just as absorption originated from a Boltzmann population of ground-state vibrational levels.
- Vibrational relaxation in upper electronic state and $FC_{0,v'}$ and $FC_{v'',0}$ of absorption and emission are equal, hence mirror symmetry with respect to $v' = 0 \leftrightarrow v'' = 0$ transition.

- Stokes shift defined as shift of the 00-transition is due to low energy vibrations and the relaxation process.

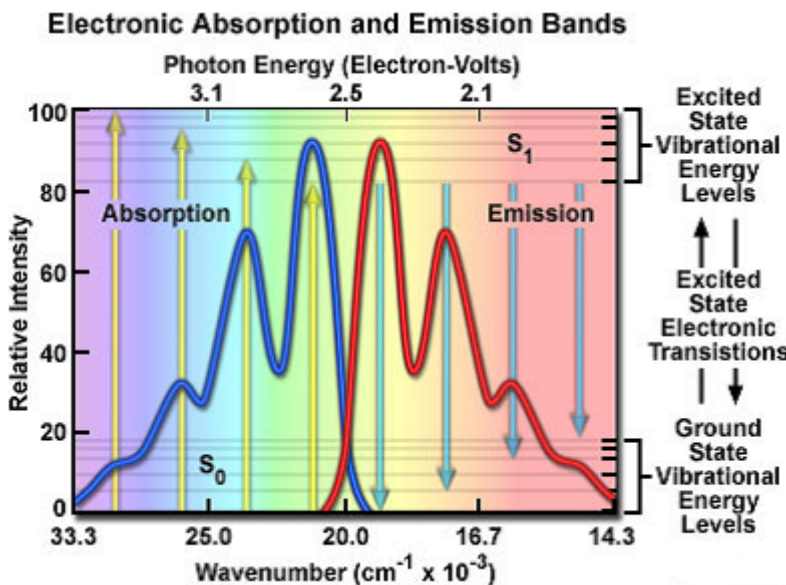


Fig. 4.13: Illustration of the absorption and fluorescence bands expected if internal conversion is fast relative to fluorescence. The relative intensities of individual transitions within the absorption and fluorescence bands are determined by the Franck-Condon principle.

4.9 Raman Spectroscopy

- To discuss the classical picture of light scattering with molecules, suppose an electric field $\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega t)$ induces a dipole moment $\mathbf{d}_{\text{ind}}(t)$ in a molecule

$$\mathbf{d}_{\text{ind}}(t) = \epsilon_0 \alpha \mathbf{E}(t). \quad (4.112)$$

- The proportionality constant α is the *electronic polarizability* of the molecule – how much can the electric field disturb the electron density of the molecule from its equilibrium?
- The electronic polarizability of the molecule can change when the atomic nuclei move (due to molecular oscillations).

- Expand α into TAYLOR series around equilibrium geometry along all normal oscillation modes q

$$\alpha = \alpha_0 + \sum_{q=1}^N \left[\left(\frac{\partial \alpha}{\partial q} \right)_{q_0} q + \frac{1}{2} \left(\frac{\partial^2 \alpha}{\partial q \partial q'} \right)_{q_0 q'_0} q q' + \dots \right] \quad (4.113)$$

- Each normal mode can oscillate with its characteristic frequency ω_q : $q = q_0 \cos \omega_q t$
- If we consider only one normal mode as an example, we find for the dipole moment

$$\mathbf{d}_{\text{ind}}(t) = \left[\alpha_0 + \left(\frac{\partial \alpha}{\partial q} \right)_{q_0} q_0 \cos(\omega_q t) \right] \mathbf{E}_0 \cos(\omega_0 t) \quad (4.114)$$

- This can also be written as

$$\begin{aligned} \mathbf{d}_{\text{ind}}(t) = & \alpha_0 \mathbf{E}_0 \cos(\omega_0 t) + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q} \right)_{q_0} q_0 \mathbf{E}_0 \cos((\omega_0 - \omega_q)t) \\ & + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q} \right)_{q_0} q_0 \mathbf{E}_0 \cos((\omega_0 + \omega_q)t) \end{aligned} \quad (4.115)$$

- The oscillation at the frequency ω_0 corresponds to elastically scattered light (RAYLEIGH scattering).
- The oscillation at reduced frequency $(\omega_0 - \omega_q)$ corresponds to inelastically scattered (Stokes) light, the frequency change corresponds to the molecular vibration frequency.
- The oscillation at increased frequency $(\omega_0 + \omega_q)$ corresponds to inelastically scattered (Anti-Stokes) light.
- Both Stokes and Anti-Stokes scattering only occur for $\left(\frac{\partial \alpha}{\partial q} \right)_{q_0} \neq 0$.
- This gives a **selection rule** for RAMAN-active molecular vibrations: the polarizability of the molecule needs to change due to the oscillation.
- Instead of inelastic scattering of *visible* light, molecular vibrations can directly *absorb infrared* light.
- The selection rule for infrared absorption for molecules is that the *molecular dipole moment* needs to change during the oscillation.

- Very often, specific molecular vibrations (or phonons in solid state) are either RAMAN-active or infrared-active. Both spectroscopy methods can be combined to yield a more complete picture.
- We calculate the intensity of the inelastically scattered light based on the classical picture focusing on the Stokes side

$$\mathbf{d}_{\text{Stokes}}(t) \propto \frac{1}{2} \left(\frac{\partial \alpha}{\partial q} \right)_{q_0} q_0 \mathbf{E}_0 \cos((\omega_0 - \omega_q)t). \quad (4.116)$$

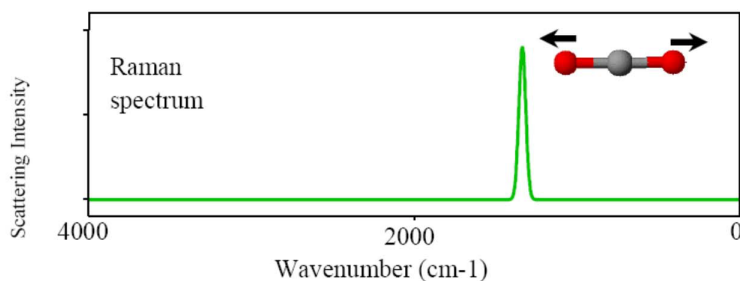
- The total power P emitted by a Hertzian dipole is given by

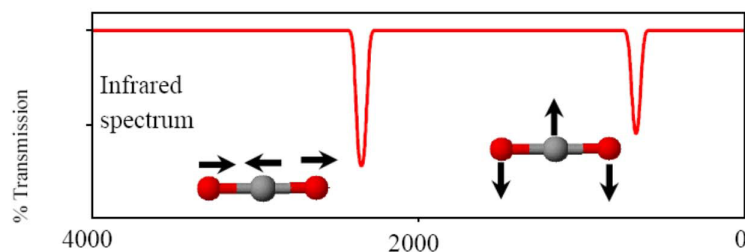
$$P = \frac{|\ddot{\mathbf{d}}_{\text{Stokes}}(t)|^2}{6\pi\epsilon_0 c^3} = \frac{q_0^2}{12\pi\epsilon_0 c^3} \left(\frac{\partial \alpha}{\partial q} \right)_{q_0}^2 (\omega_0 - \omega_q)^4 E_0^2. \quad (4.117)$$

Thus, the Stokes intensity is proportional to

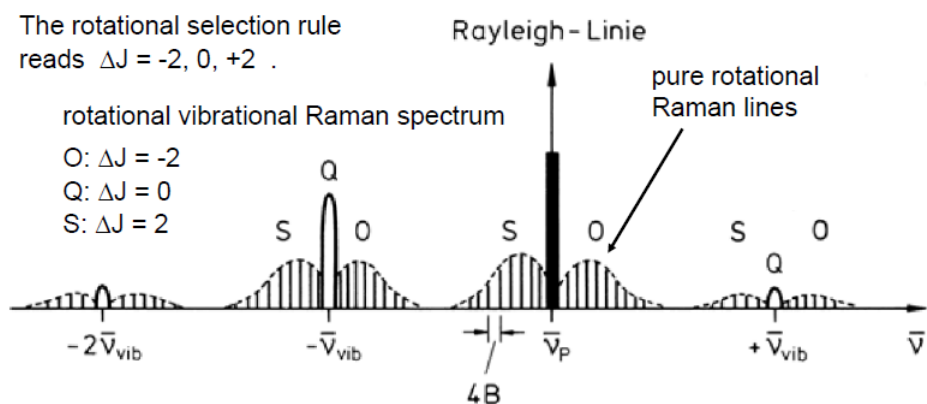
$$I_{\text{Stokes}} \propto \left(\frac{\partial \alpha}{\partial q} \right)_{q_0}^2 (\omega_0 - \omega_q)^4 E_0^2 \quad (4.118)$$

- The Stokes intensity is proportional to incident laser power E_0^2 . Additionally, it increases with the fourth power of the excitation frequency $I_{\text{Stokes}} \propto \omega_0^4$.
- Short-wavelength excitation yields larger RAMAN signals – without sample-induced effects, going from 800 nm to 400 nm excitation yields a factor of 16.
- If a molecule exhibits symmetry, totally symmetric modes are IR inactive but RAMAN active (and optically active) while antisymmetric modes behave the other way round. If the symmetry is not perfectly fulfilled all modes show up in all spectra but the intensities are small for symmetry forbidden bands.
- As an example, we present schematically IR and RAMAN spectrum of CO₂





- The RAMAN effect is of very general nature. In principle it can occur whenever a quantized excitation is possible. The scattered light contains then frequency components which are shifted by the excitation quantum to lower (Stokes) or to higher (anti-Stokes) energies. In the second case the higher level of the quantized excitation has to be populated prior to the scattering event.
- For molecules in the gas phase this applies to pure rotational excitations but also to rotational levels of vibrational excitations.



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