Week 11

PHY 402 Atomic and Molecular Physics
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4.6 Molecular ro-vibronic states

We now know how to calculate/ construct the molecular electronic energies/Born- Oppenheimer (BO) surfaces $E_q(\mathbf{R})$ from Eq. (4.2). Insertion into (4.6) then gives us the motional eigen states of the nuclei.

In BO-approximation (where we take only a single surface s in (4.6)) we have:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{R}} + E_s(\mathbf{R}) \right] F_s(\mathbf{R}) = E F_s(\mathbf{R}). \tag{4.22}$$

For a di-atomic molecule electronic energies can only depend on the distance between nuclei $|\mathbf{R}|$, not on the orientation of the inter-nuclear axis (direction of $\mathbf{R}$), hence $E_s(\mathbf{R}) = E_s(|\mathbf{R}|) \rightarrow$ mathematically (4.22) is a spherically symmetric Schrödinger equation (like e.g., Hydrogen).

Thus as for Hydrogen we can write the solution as a product of an angular part and a radial part (compare Eq. (1.35)), where the angles are defined in the sketch below.

$$F_s(\mathbf{R}) = \frac{\mathcal{F}_{\nu K}^s}{R} \mathscr{H}_{Km_K}(\theta, \varphi). \tag{4.23}$$
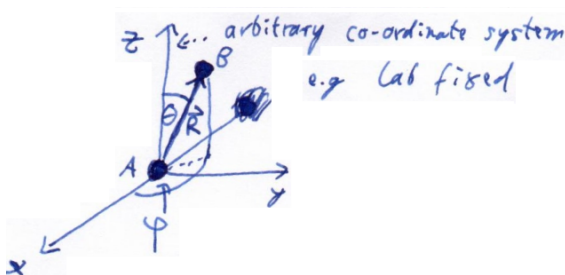
We know due to spherical symmetry that the angular part is given by spherical harmonics:

$$\mathscr{H}_{Km_K}(\theta, \varphi) = \overbrace{Y_{Km_K}(\theta, \varphi).}^{\text{Spherical harmonics}}$$

Now we insert ((4.23)) into ((4.22)) and use the 3D Laplacian, following all the same steps as for Hydrogen. We obtain again a Radial Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dR^2} - \underbrace{\frac{K(K+1)}{R^2}}_{*} \right) + \left(E_s(R) - \underbrace{E_{s,\nu,K}}_{=E \text{ earlier}} \right) \right] \mathcal{F}_{\nu K}^s(R) = 0. \tag{4.24}$$

- The electronic energies $E_s(R)$ take the role of the "potential energy" for the nuclei.

- If $K > 0$, the molecule is rotating about the center-point . $*$ represents the centrifugal force due to this.

- The detailed shape of $E_s(R)$ is calculated as discussed in section 4.3.

Let us consider the rough potential energy shape found in section 4.3:
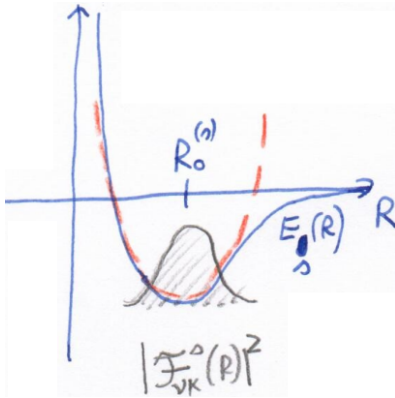
The binding BO-surfaces usually have one well-defined local minimum.

We can Taylor expand $E_s(R)$ around this minimum $R_0^{(s)}$, the expansion gives the red dashed line.

$$E_s(R) = E_s(R_0^{(s)}) + \frac{1}{2}k_s(R - R_0^{(s)})^2$$

where,

$$k_s = \frac{d^2 E_s(R)}{dR^2}\Big|_{R=R_0^{(s)}}.$$

(From now, write $R_0^{(s)} = R_0$.)

- Since usually it turns out that also $|\mathcal{F}_{\nu k}^s(R)|^2$ is non-zero only close to this minimum, we can write $+\frac{\hbar^2}{2\mu}\frac{K(kK+1)}{R^2} \rightarrow \frac{\hbar^2}{2\mu}\frac{K(K+1)}{R_0^2}$ in Eq. (4.24).

We call this quantity the

Rotational energy

$$E_{\text{rot}} = \frac{\hbar^2}{2\mu R_0^2}K(K+1) = \frac{\hbar^2}{2I}K(K+1), \tag{4.25}$$

where $I = \mu R_0^2$ is the <u>moment of inertia</u>.

We can now rewrite Eq. (4.24) as <u>harmonic oscillator</u> TISE

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + \frac{1}{2}k_s(R - R_0)^2 - E_\nu\right]\mathcal{F}_\nu^s(R) = 0, \tag{4.26}$$

where, we used the definitions

Total energy The total energy of the molecular state $E_{s,\nu,k}$ can be decomposed into several contribution:

$$E_{s,\nu,K} = \overbrace{E_s(R_0)}^{\text{electronic energy}} + \overbrace{E_\nu}^{\text{vibrational energy}} + \overbrace{E_{\text{rot},K}}^{\text{rotational energy}} .\quad (4.27)$$

Here s : electronic state label

ν : vibrational quantum number

K : rotational quantum number

R_0 : equilibrium position.

Vibrational energy as usual

$$E_\nu = \hbar\omega_0\left(\nu + \frac{1}{2}\right) \qquad \nu = 0, 1, 2, ... \qquad (4.28)$$

where, $\omega_0 = \sqrt{k_s/\mu}$.

- There can be deviations from Eq. (4.28) due to an anharmonicity of $E_s(R)$ at larger vibrational quantum numbers ν, see sketch above.

- $\frac{\mathcal{F}_\nu^s(R)}{R}\mathcal{H}_{Km_K}(\theta, \varphi)$ is called a <u>ro-vibronic</u> state.

- Di-atomic molecules can also rotate around the inter nuclear axis ●—●↺: This is represented within the <u>electronic wavefunction</u> $\Phi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, ...)$ as <u>non-zero</u> Λ (see section 4.4).

- Rotations usually weakly couple to vibrations: Fast rotation increases centrifugal potential $\sim K(K+1)/R^2$ and can thus cause vibrations. This effect drops out if we can replace $R \to R_0$ in Eq. (4.24). If we include it, we have to keep the centrifugal term in Eq. (4.26) and thus also the vibrational part of the wave functions continues to depend on the rotational quantum number K: $\mathcal{F}_\nu^s(R) \to \mathcal{F}_{\nu K}^s(R)$.

Example for section 4.6: Energy-levels of diatomic molecules:
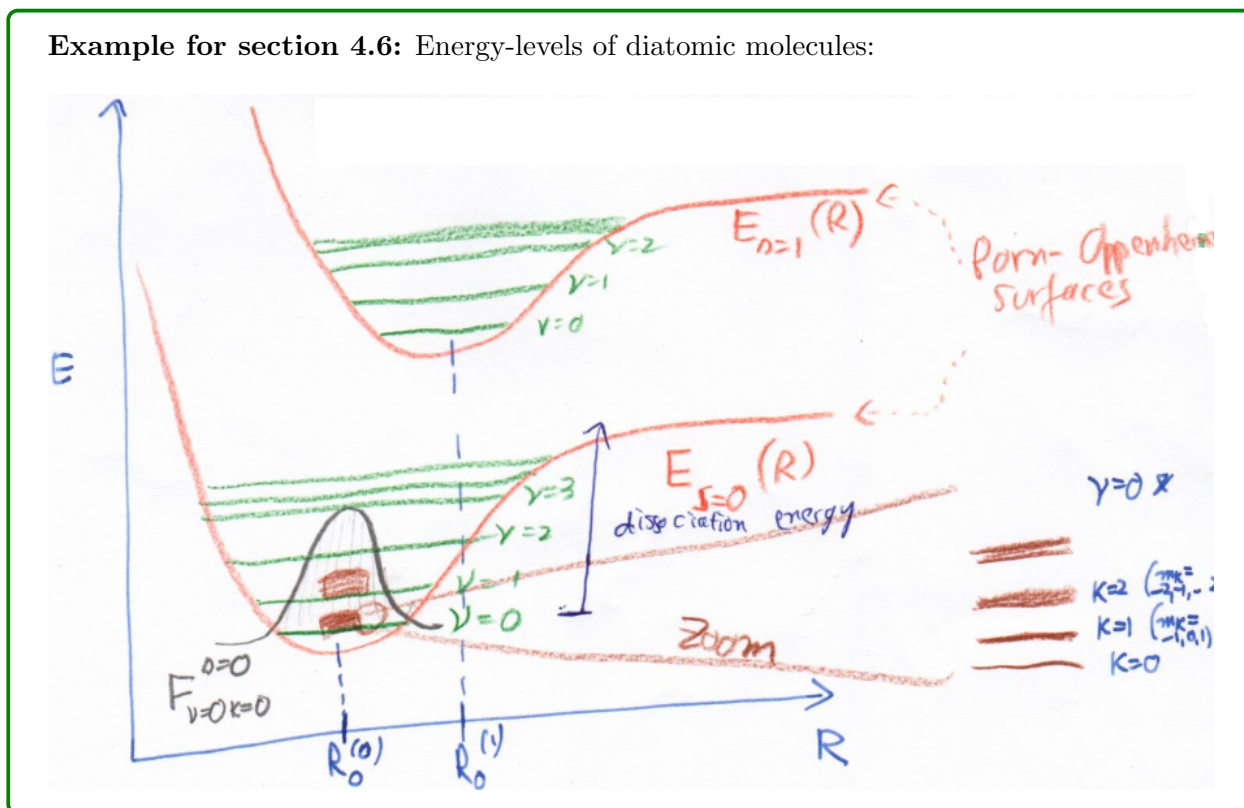
Now we know all the quantum numbers that should be allocated for molecular states (mainly focussing on di-atomic molecules for simplicity). Just as with atoms, it is frequently convenient to group all quantum numbers into one <u>collective index label</u> $a = \{s, \nu, K, m_K\}$. This thus includes the electronic state label s (see section 4.3), the vibrational quantum number ν, the rotational quantum number K and the z-component of rotational angular momentum (in the lab frame) m_K. Written as a wave function, the label a represents

Complete molecular state: e.g., $\Psi_a = \Phi_s(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \underbrace{\dfrac{\mathcal{F}_\nu^s(R)}{R} \mathscr{H}_{K m_K}(\theta, \varphi)}_{=F_s(\mathbf{R})}$.

4.7 Molecular spectra

- Now we can describe all molecular states, we again ask how transitions between such states can occur through interactions with electromagnetic radiation, and thus which shape molecular spectra will take.

- For the same arguments as used in section 3 for the case of atoms, transitions between different molecular states $(a = \{s, \nu, K, m_K\})$ are governed by the

Molecular dipole-moment operator:

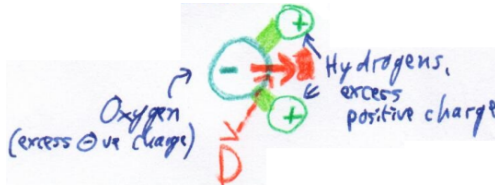$$\hat{\mathbf{D}} = e\Big(\sum_i Z_i \mathbf{R}_i - \sum_j \mathbf{r}_j \Big) \qquad (4.29)$$

where, $\mathbf{R}_i$: positions of nuclei

$\mathbf{r}_i$: positions of electrons.

Unlike the case for atoms, where always $\langle \phi_n | (-e\mathbf{r}) | \phi_n \rangle = 0$, molecules can have a

permanent electric dipole-moment

$$\mathbf{D}_{aa} = \langle \psi_a | \hat{\mathbf{D}} | \psi_a \rangle \neq 0. \qquad (4.30)$$

Example: Water molecule, H_2O:

Dipole-moment of water:

$|\mathbf{D}| = 1.85\,D$ (D = Debye)
1 Debye $\approx 0.2\,e\text{Å}$

It will also be useful to consider the dipole-moment in electronic state s for a specific fixed nuclear configuration[5] $\mathbf{R}$:

$$\hat{\mathbf{D}}_s(\mathbf{R}) = \langle \Phi_s | \hat{\mathbf{D}} | \Phi_s \rangle = \underbrace{\int d^{3N}\mathbf{r}_i\, \Phi_s^*(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, ...)\hat{\mathbf{D}}\,\Phi_s(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, ...)}_{\text{still depends on } \mathbf{R}}. \qquad (4.31)$$

For the same reasons as in atoms, transitions between molecular states due to absorption or emission of elm-radiation (which give rise to spectra) are governed by transition matrix elements:

$$\mathbf{D}_{ba}(\mathbf{R}) = \langle \psi_b | \hat{\mathbf{D}} | \psi_a \rangle. \qquad (4.32)$$

However, a major difference to atoms, is that for molecules we can differentiate a large number of different types of internal transitions.

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[5]In contrast, Eq. (4.30) contains an average over all possible nuclear configurations.

4.7.1 Rotational transitions

Consider a transition <u>without</u> change of electronic or vibrational state, i.e. from a state with label $a = \{s, \nu, K, m_K\}$ to a state with label $b = \{s, \nu, K', m'_K\}$. Assume $\nu = 0$, i.e., vibrational ground state.

For simplicity assume di-atomic molecule, but not necessarily a homonuclear one, e.g. CO (this has a permanent dipole moment of $0.122\,D$). Also move to a ket notation for the total state

$$\psi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \Phi_s(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\frac{\mathcal{F}^s_\nu(R)}{R}\mathscr{H}_{K m_K}(\theta, \varphi)$$

$$\downarrow$$

$$|\psi_a\rangle = |s\nu K m_K\rangle = \underbrace{|s\rangle}_{\text{electrons}} \otimes \underbrace{|\nu K m_K\rangle}_{\text{nuclei}}.$$

We now see

$$\mathbf{D}_{ba} = \langle\psi_b|\hat{\mathbf{D}}|\psi_a\rangle = \langle\nu K' m'_K| \underbrace{\langle s|\hat{\mathbf{D}}|s\rangle}_{= \mathbf{D}_s(\mathbf{R})} |\nu K m_K\rangle$$

$$\text{using Eq. (4.31)}$$

$$= \int d\Omega\, \mathscr{H}^*_{K' m'_K}(\theta, \varphi)\underbrace{\left(\int_0^\infty dR\, |\mathcal{F}^s_{\nu=0}(R)|^2 \mathbf{D}_s(R)\right)}_{\approx \mathbf{D}_s(\mathbf{R}_0)\text{ dipole moment}}\mathscr{H}_{K m_K}(\theta, \varphi). \qquad (4.33)$$

$$\text{at equilibrium configuration}$$

The approximation in the last line is actually exact if the vibrational wave-packet $|\mathcal{F}^s_{\nu=0}(R)|^2 = \delta(R - R_0)$. If, instead, the vibrational wave-packet is just a very narrow Gaussian, it still is a very good approximation.

Now we directly see the

> **Rule for purely rotational transitions:** $\Rightarrow$ only molecules with permanent dipole moment at $\mathbf{R}_0$ can have <u>purely rotational transition</u>.

The remaining integration in Eq. (4.33) over $d\Omega$ gives (as for Hydrogen atom)

> **Rotational selection rules:**
>
> (for $\Lambda = 0$ states) $\qquad \Delta K = K' - K = \pm 1 \qquad \Delta m_K = m'_K - m_K = 0, \pm 1.$ (4.34)

- Photo absorption implies angular momentum change by ± 1 through angular momentum conservation.
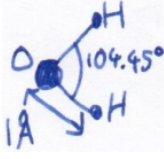
From Eq. (4.25), we find that photon energies matching a <u>rotational transition</u> are

$$\Delta E = E_{\text{rot}}(K+1) - E_{\text{rot}}(K) = \underbrace{\frac{\hbar^2}{\mu R_0^2}(K+1)}_{\text{di-atomic case}} = \underbrace{\frac{\hbar^2}{2I}(K+1)}_{\text{more generally valid}} . \qquad (4.35)$$

Example: Microwave-Oven:

These operate typically at a frequency $\sim \nu_M = 2.4\,\text{GHz} \to \lambda = 12\,\text{cm}$

Consider a water-molecule: As seen in the preceding example, it has $|\mathbf{D}_{aa}| \neq 0$ and can thus undergo purely rotational transitions.

$I \approx 2 \times 10^{-47}\,\text{kg m}^2$ and $\Delta E = \underbrace{\frac{\hbar^2}{2I}}_{E_0}(K+1) \overset{!}{=} h\nu$. This

gives $\nu = \frac{E_0}{\hbar} = 420\,\text{GHz}$ or $\lambda = \frac{\hbar c}{E_0} = 0.7$ mm.

Since rotations are the lowest energy excitations, the micro-wave frequency ν_M is closest to some rotational resonances and the oven hence excites rotations.

Q: Why is the oven not designed to operate precisely on the rotation resonance?

4.7.2 Ro-vibrational transitions

Next consider the slightly more general transition

$$a = \{s, \underline{\nu}, K, m_K\} \to b = \{s, \underline{\nu}', K', m_K'\}, \qquad \nu \neq \nu', \qquad (4.36)$$

where in addition to the rotational state also the vibrational state is allowed to change.

As before we can write

$$\mathbf{D}_{ba} = \langle \psi_b | \mathbf{D} | \psi_a \rangle = \langle \nu' K' m_K' | \mathbf{D}_s(\mathbf{R}) | \nu K m_K \rangle.$$

Let us expand the dipole-moment around the equilibrium position

$$\mathbf{D}_s(\mathbf{R}) \approx \mathbf{D}_s(\mathbf{R}_0) + \underline{\underline{\boldsymbol{\nabla} D_s(\mathbf{R}_0)}} \cdot (\mathbf{R} - \mathbf{R}_0) + ..., \qquad (4.37)$$

where $\underline{\underline{\boldsymbol{\nabla} D_s(\mathbf{R})}}$ denotes the Jacobian matrix of the vector field $\mathbf{D}_s(\mathbf{R})$, defined via $[\underline{\underline{\boldsymbol{\nabla} D_s(\mathbf{R}_0)}}]_{ij} = \partial D_{s,i}/\partial R_j|_{\mathbf{R}=\mathbf{R}_0}$.

Insertion into Eq. (4.33) (however with allowing $\nu' \neq \nu$ in the ket) gives

$$\mathbf{D}_{ba} = \int d\Omega\, \mathscr{H}^*_{K' m_K'}(\theta, \varphi) \left(\int_0^\infty dR\, \mathcal{F}^{s*}_{\nu'}(R) \left[\underbrace{\mathbf{D}_s(R_0)}_{\substack{= \delta_{\nu'\nu} \text{ since} \\ \mathcal{F}_{\nu'}, \mathcal{F}_\nu \text{ are orthonormal} \\ (= 0 \text{ here), since we want } \nu \neq \nu'}} + \underbrace{\boldsymbol{\nabla} D_s(\mathbf{R}_0) \cdot (\mathbf{R} - \mathbf{R}_0)}_{\substack{\text{If } \mathbf{D}_s \text{ \underline{constant},} \\ \text{(independent of } \mathbf{R}) \text{ this} \\ \text{and all h.o.t. vanish.}}} \right] \mathcal{F}^s_\nu(R) \right) \mathscr{H}_{K m_K}(\theta, \varphi)$$

$$(4.38)$$

From the two statements below (4.38) we can infer the

> **Rule for rotational-vibrational transitions:** $\Rightarrow$ only molecules where the dipole-moment changes as a function of $\mathbf{R}$ (= as "a function of vibrations") can have purely ro-vibrational transitions (without electronic state change, which means: $s = s'$).

If $\frac{\partial}{\partial R}\mathbf{D}_s(R)$ is non-zero, integration over R and angles gives

> **Ro-vibrational selection rules** (valid for harmonic vibrations only)
>
> (For $\Lambda = 0$ states) $\qquad \Delta\nu = \nu' - \nu = \pm 1 \qquad \Delta K = \pm 1 \qquad \Delta m_K = 0, \pm 1.$ (4.39)

- To see the rule $\Delta\nu = \pm 1$, use oscillator states for $\mathcal{F}_\nu(R)$ and the recursion relation

$$2x\, H_\nu(x) = 2\nu\, H_{\nu-1}(x) + H_{\nu+1}(x) \qquad \text{for Hermite polynomials } H_\nu(x). \qquad (4.40)$$

- We still need a change of rotational state $\Delta K = \pm 1$ for angular momentum conservation (vibration does not directly affect angular momentum).

- Deviations from the rules (4.39) happen due to

  - higher than linear terms of $(R - R_0)$ in Eq. (4.38).
  - anharmonicity (deviations from an oscillator potential) of $E_s(R)$, see comment below Eq. (4.28).

These deviations then weakly allow $\Delta\nu = \pm 2$, $\Delta\nu = 3$, etc.

> All up, <u>photon energies</u> matching <u>ro-vibrational transitions</u> are:
>
> $$\Delta E = \underbrace{\hbar\omega_0}_{\text{see Eq. (4.28)}} + \begin{cases} +\frac{\hbar^2}{2I}(K+1) & \Delta K = +1 \quad \text{R-branch} \\ -\frac{\hbar^2}{2I}K & \Delta K = -1 \quad \text{P-branch} \end{cases}$$

Example: Greenhouse effect:

Earth likes to shed excess energy through IR radiation around $\lambda \simeq 4 - 100\,\mu$m.

Atmosphere is mostly O_2, N_2. For N_2: $\lambda = c/\nu_0 = 6\mu$m, O_2: $\lambda = c/\nu_0 = 3\mu$m. (dangerously close)

These would scatter IR radiation and thus retain heat, but cannot, since $\mathbf{D}_{ss}(\mathbf{R}) = 0$ for a <u>homonuclear molecule</u> due to <u>symmetry</u>, regardless of nuclear separation $\mathbf{R}$.

However: CO_2 or CH_4 can have $\underline{\underline{\boldsymbol{\nabla} D_s(\mathbf{R}_0)}} \neq 0$ (even though also for them $D_s(\mathbf{R}_0) = 0$).
$\implies$ these are <u>green house gases</u> that scatter IR radiation.

(No net dipole in equilibrium, but becomes non-zero under vibration.)