Internal Degrees of Freedom of Molecules

Adiabatic Theory of Molecule

For the internal dynamics of molecules it is of crucial importance that nuclei are much heavier than electrons. This leads to the adiabatic picture of the nuclei motion with respect to the motion of electrons. In the adiabatic picture, the coordinates of nuclei play the role of external parameters with respect to the state of the electronic sub-system, that is they play the same role as the adiabatic parameter $\lambda$ in our consideration of the adiabatic process. Here, however, we are dealing with more subtle situation where nuclei coordinates behave as external parameters with respect to the electrons only, not to each other. Mathematically, the adiabatic picture implies the following structure of the molecule wavefunction

$$\Psi(r, R) = \psi(R) \Phi_R(r),$$

where $r$ and $R$ stand for all the electron and nuclei coordinates, respectively. The function $\psi(R)$ is the wavefunction of nuclei. The function $\Phi_R(r)$ is the wavefunction of electrons at fixed positions of all nuclei. It obeys the Schrödinger equation

$$H^{(R)}_{el} \Phi = E^{(R)}_{el} \Phi.$$ (2)

Here $H^{(R)}_{el}$ is the electronic Hamiltonian in which the nuclei at fixed positions play the role of external potentials. Both the wavefunction $\psi$ and the eigenvalue $E_{el}$ thus depend on $R$. The nuclei motion is described by the effective Schrödinger equation

$$H^{(kin)}_{nuc} \psi + V_{eff} \psi = E \psi,$$ (3)

where $H^{(kin)}_{nuc}$ is the standard kinetic energy term and

$$V_{eff}(R) = V(R) + E^{(R)}_{el},$$ (4)

is the effective potential energy equal to the sum of bare potential energy, $V(R)$, (Coulomb repulsion between nuclei) and the electronic energy as a function of $R$. Note that it is entirely due to the attractive term $E^{(R)}_{el}$ that nuclei bind into a molecule.

The effective adiabatic potential $V_{eff}(R)$ is very rigid in the sense that the typical inter-nuclei separation turns out to be much smaller than its quantum uncertainty. Hence, the inter-nuclei separations are good quantum numbers characterizing the structure of the molecule. Consider some estimates proving this fact. First we estimate the electronic energy as

$$E^{(R)}_{el} \sim \frac{\hbar^2}{m_e R^2} \sim \frac{\hbar^2}{m_e a_B^2},$$ (5)

where $m_e$ is the electron mass and $a_B$ is the Bohr radius. Then we estimate the strength of the effective adiabatic potential $V_{eff}(R)$. To this end we replace it with a harmonic potential with respect to the relative coordinates of the nuclei. This is a quite accurate approximation because relative coordinates of nuclei do not change significantly with respect to their equilibrium values and we can expand $V_{eff}(R)$ in the Taylor series in the vicinity of the equilibrium configuration. The equivalent harmonic potential with respect to one of the relative coordinates, $R$, then reads

$$V_{eff}(R) = \text{const} - (k/2)(R - R_0)^2,$$ (6)

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where $R_0$ is the equilibrium position, and $k$ is the spring constant, which we estimate as

$$k \sim \frac{\partial^2 E_{\text{el}}^{(R)}}{\partial R^2} \sim \frac{E_{\text{el}}}{R_0^2} \sim \frac{E_{\text{el}}}{a_B^2}. \tag{7}$$

Given the spring constant, we readily estimate the frequency of the vibrations

$$\omega_{\text{vib}} \sim \sqrt{k/m_s} \tag{8}$$

($m_s$ is the typical nuclei mass) and the typical inter-level separation for the atomic vibrations

$$E_{\text{vib}} = \hbar \omega_{\text{vib}} \sim E_{\text{el}} \left(\frac{m_e}{m_s}\right)^{1/2}. \tag{9}$$

To estimate the quantum mechanical uncertainty, $\Delta R$, of the coordinate $R$, we just need to recall the result for the ground-state uncertainty of the coordinate of the harmonic oscillator of the mass $m_s$ and the spring constant $k$. Using the relation between $\Delta R$ and $E_{\text{vib}}$,

$$\frac{\hbar^2}{m_s(\Delta R)^2} \sim E_{\text{vib}}, \tag{10}$$

we find

$$\left(\frac{\Delta R}{R}\right)^2 \sim \left(\frac{m_e}{m_s}\right)^{1/2} \ll 1. \tag{11}$$

Let us compare inter-level separations of vibrational and rotational degrees of freedom. For the typical inter-level separation of the rotational levels we have (only the kinetic part of the Hamiltonian is relevant for the rotations)

$$E_{\text{rot}} \sim \frac{\hbar^2}{m_s R^2} \sim E_{\text{vib}} \left(\frac{m_e}{m_s}\right)^{1/2} \sim E_{\text{el}} \frac{m_e}{m_s}. \tag{12}$$

We see that

$$E_{\text{rot}} \ll E_{\text{vib}} \ll E_{\text{el}}. \tag{13}$$

Finally, we establish the orders of magnitudes of realistic values. As is known, $E_{\text{el}} \sim (1 \div 10) \text{ eV}$, where

$$1 \text{ eV} = 1.16 \times 10^4 \text{ K}. \tag{14}$$

Note that for our purposes it is most convenient to measure inter-level separations in Kelvins, since this immediately yields the ranges of the temperatures when corresponding degrees of freedom get excited. So,

$$E_{\text{el}} \sim (10^4 \div 10^5) \text{ K}. \tag{15}$$

A reasonable estimate for the parameter $\sqrt{m_e/m_s}$ is $\sim 10^{-2}$ leads us to

$$E_{\text{vib}} \sim (10^2 \div 10^3) \text{ K}, \tag{16}$$

$$E_{\text{rot}} \sim (1 \div 10) \text{ K}. \tag{17}$$
Spherical Quantum Rotator

To a very good approximation, the rotational degrees of freedom of a molecule decouple from the other degrees of freedom, and thus can be treated as a separate subsystem—quantum rotator. Here we consider the simplest case of a spherical quantum rotator. This case corresponds to an axially symmetric molecule of (distinguishable) atoms and, in particular, to the case of a diatomic molecule of two non-identical atoms.

The eigenstates of the spherical rotator are labelled by two quantum numbers, the angular momentum, \( l = 0, 1, 2, \ldots \), and the projections of the angular momentum (onto some given axis), \( m_l = -l, \ldots, -1, 0, 1, \ldots, l \). For a given \( l \) there are \((2l + 1)\) different values of \( m_l \). The energy spectrum of the spherical rotator is

\[
E_l = \frac{\hbar^2 l(l + 1)}{2I},
\]

where the parameter \( I \) is called moment of inertia. For example, in the case of a rigid diatomic molecule

\[
I = \frac{m_1 m_2}{m_1 + m_2} R_0^2 \quad \text{(rigid diatomic molecule)},
\]

where \( m_1 \) and \( m_2 \) are the masses of the atoms, and \( R_0 \) is the separation between the two nuclei. Note that energies do not depend on \( m_l \), which means that each energy level is \( 2l + 1 \)-fold degenerate.

It is convenient to introduce the parameter

\[
\theta = \frac{\hbar^2}{2I},
\]

which characterizes typical energy scale associated with rotations at \( l \sim 1 \), and to write

\[
E_l = \theta l(l + 1).
\]

For the partition function we thus have

\[
Z = \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} e^{-\theta l(l+1)} = \sum_{l=0}^{\infty} (2l + 1) e^{-\theta l(l+1)}.
\]

There are two characteristic cases:

\[
T \gg \theta \quad \text{classical regime},
\]

and

\[
T \ll \theta \quad \text{ultra-quantum regime}.
\]

**Classical regime.** In the classical regime the smallness of the parameter \( \theta/T \) in Eq. (35) renders the discreteness of \( l \) irrelevant and we may replace the summation with integration. With the same accuracy, we do not distinguish between \((2l + 1)\) and \(2l\), and also between \( l(l + 1) \) and \( l^2 \) [because typical \( l \sim \sqrt{T/\theta} \gg 1\)].

\[
Z = \int_0^\infty \, dl \, 2l e^{-\theta l^2} = \int_0^\infty \, dx \, e^{-\theta x} = T/\theta.
\]

Then, by the standard thermodynamical procedure we find

\[
F = -T \ln(T/\theta),
\]
Ultra-quantum regime. In this regime the temperature is much smaller than the separation between the ground state and the first excited state. Hence, with the exponential accuracy in the parameter $\theta/T$ the molecule does not rotate—rotational degrees of freedom are frozen out.

We can easily take into account the main exponential correction. To this end we keep the second term in the series (35), neglecting the rest of the terms [which are exponentially smaller]. We have

$$Z = 1 + 3e^{-2(\theta/T)},$$

and then find

$$F = -T \ln \left[ 1 + 3e^{-2(\theta/T)} \right] \approx -3T e^{-2(\theta/T)},$$

$$S = [3 + 6(\theta/T)] e^{-2(\theta/T)},$$

$$E = 6\theta e^{-2(\theta/T)},$$

$$C = 12(\theta/T)^2 e^{-2(\theta/T)}.$$

Gas of Molecules

The statistics of internal degrees of freedom of molecules is decoupled from the statistics of the translational degrees of freedom, simply because the translational motion—the motion of the center of mass of a molecule—is dynamically independent from the internal motions. Hence, for a dilute (= non-interacting) gas of molecules the partition function factorizes into the product of the partition functions of translational and internal motions:

$$Z(V,T) = Z_{\text{tr}}(V,T) Z_{\text{int}}(T).$$

Note that $Z_{\text{int}}$ is $V$-independent. Correspondingly, we have

$$F(V,T) = F_{\text{tr}}(V,T) + F_{\text{int}}(T),$$

and see that the equation of state for the gas of molecules is the same as for the mono-atomic gas, since $F_{\text{int}}(T)$ is $V$-independent and thus cannot change the expression for the pressure:

$$P = -\left( \frac{\partial F}{\partial V} \right)_T = -\left( \frac{\partial F_{\text{tr}}}{\partial V} \right)_T = NT/V.$$

Similarly, for the entropy we have

$$S(V,T) = S_{\text{tr}}(V,T) + S_{\text{int}}(T),$$
and from the fact that \( S_{\text{int}} \) depends only on \( T \) conclude that for any heat capacity \( C_\xi \) [\( \xi \) is either \( V \), or \( P \), or any other fixed quantity] we get
\[
C_\xi = C_\xi^{(\text{tr})} + C_\xi^{(\text{int})},
\]
where
\[
C_\xi^{(\text{int})} = T \frac{dS_{\text{int}}}{dT}.
\]
The contribution of the internal degrees of freedom to \( C_\xi \) is one and the same for any \( \xi \).

**Classical limits for internal motions.** The vibrational degrees of freedom are just harmonic oscillators. Hence, we conclude that each vibrational degree contributes at \( T \gg E_{\text{vib}} \) the amount \( T = (T/2 + T/2) \) to the energy and, correspondingly, \( 1 = (1/2 + 1/2) \) to the heat capacity (recall that each half comes independently from kinetic and potential energies). So, if \( \nu_{\text{vib}} \) is the total number of vibrational degrees of freedom, we have
\[
E_{\text{vib}} = \nu_{\text{vib}} T \quad (T \gg E_{\text{vib}}),
\]
\[
c_{\text{vib}} = \nu_{\text{vib}} \quad (T \gg E_{\text{vib}}).
\]
(Here we use a small letter \( c \) to emphasize that we are dealing with the heat capacity of a single molecule rather than that of the whole gas.)

Let us find the **total** contribution to the energy of all the internal degrees of freedom in the classical limit. The total number of degrees of freedom is \( 3\nu \), where \( \nu \) is the total number of nuclei. As we remember, in the classical statistics the kinetic and potential energies are statistically independent. Moreover, the total kinetic energy is always equal to \( (3/2)\nu T \). In our case, the potential energy consists only of \( \nu_{\text{vib}} \) harmonic potentials (in terms of relative distances), each of these potentials contributing \( T/2 \) to the energy [\( 1/2 \) to the heat capacity]. Subtracting \( (3/2)T \) associated with the translational motion of the molecule, we arrive at the energy and heat capacity of the internal degrees of freedom:
\[
E_{\text{int}} = \frac{3(\nu - 1)}{2} T + \frac{\nu_{\text{vib}}}{2} T \quad (T \gg E_{\text{vib}}, E_{\text{rot}}),
\]
\[
c_{\text{int}} = \frac{3(\nu - 1)}{2} + \frac{\nu_{\text{vib}}}{2} \quad (T \gg E_{\text{vib}}, E_{\text{rot}}).
\]
The number \( \nu_{\text{vib}} \) can be related to \( \nu \) by subtracting from \( 3\nu \) [the total number of degrees of freedom] the 3 translational degrees and the rotational degrees. In a general case, there are 3 rotational degrees of freedom (3 independent angles), while in the axially symmetric case there are only 2 rotational degrees, since the rotation around the symmetry axis does not change the configuration of particles and thus is not a degree of freedom. We thus have
\[
\nu_{\text{vib}} = \begin{cases} 
3\nu - 5 & \text{(axial symmetry)}, \\
3\nu - 6 & \text{(no axial symmetry)}. 
\end{cases}
\]

In the temperature regime \( E_{\text{rot}} \ll T \ll E_{\text{vib}} \) the vibrational degrees of freedom are still frozen out, while the rotational degrees of freedom are already in their classical limit. Hence, it is reasonable to separate in the equations (43) and (44) vibrational contributions from the rotational ones, so that we could use their classical limits independently. Subtracting (41) and (42) from (43) and (44), respectively, and taking into account (45), we get
\[
E_{\text{rot}} = \begin{cases}
T & \text{(axial symmetry)}, \\
(3/2)T & \text{(no axial symmetry)}.
\end{cases} \quad (T \gg E_{\text{rot}}),
\]
\[ c_{\text{rot}} = \begin{cases} 
1 & \text{(axial symmetry)} \\
3/2 & \text{(no axial symmetry)} 
\end{cases} \quad (T \gg E_{\text{rot}}). \quad (47) \]

The results for the axially symmetric case are already known to us from the classical limit of the spherical quantum rotator.

The fact that in the classical limit the heat capacity of internal degrees of freedom is just a constant number has a simple implication in terms of entropy, and, correspondingly adiabats. Indeed, if \( C^{(\text{int})} = N c_{\text{int}} \) is just a temperature-independent number then

\[
S_{\text{int}} = N c_{\text{int}} \ln T + \text{const} = N \ln T^{c_{\text{int}}} + \text{const}. \quad (48)
\]

This means that the exponents of the adiabats will get an extra term equal to the heat capacity of the internal degrees of freedom with the elegant final results in terms of the total (translational plus internal) heat capacities per molecule:

\[
V T^{c_{\text{V}}} = V_0 T_0^{c_{\text{V}}} \quad (T, V) - \text{adiabat}, \quad (49)
\]

\[
\frac{T^{c_{\text{P}}}}{P} = \frac{T_0^{c_{\text{P}}}}{P_0} \quad (T, P) - \text{adiabat}. \quad (50)
\]

**Problem 33.** Typical vibrational frequency of the \( \text{H}_2 \) molecule is \( \sim 6000 \text{ K} \). Typical rotational level separation for \( \text{H}_2 \) is less than \( 100 \text{ K} \). Estimate \( C_V \) and \( C_P \) per molecule for the \( \text{H}_2 \) gas at room temperature. [Note that I use a convenient Stat. Mech. jargon: First, I measure energy in Kelvins, which causes no problem since Kelvins are unambiguously related to Joules by the Boltzmann constant. Secondly, I also use Kelvins for measuring frequencies which basically means that I do not distinguish between \( \omega \) and \( \hbar \omega \). Hence, when I say that the frequency \( \omega = 6000 \text{ K} \), I actually mean that \( \hbar \omega = 6000 \text{ K} = 6000 \text{ KB J}. \)]