Harmonic Oscillator (*1*)

After solving the electronic Schrödinger equation, one obtains, according to the Born-Oppenheimer approximation, an electronic potential on which the nuclei in a molecule move. Using this potential function, we can then solve the nuclear Schrödinger equation to obtain the wavefunctions describing molecular vibrations, rotations and translations. The problem is that the electronic Schrödinger equation is solved approximately and a properly analytic form for the electronic potential is not known. We are aware of the function's shape and we even know the value of this potential for any arrangement possible of the nuclei to almost the finest of accuracies. But a proper analytical function is not known, not even for the simple diatomic cases.

It is in principle possible to fit some calculated points of the electronic potential to a given functional form. Examples are polynomials (for the region around a stationary point), the Morse potential or the Lennard-Jones potential. Using these functional forms, solutions to the nuclear Schrödinger equation might then be sought. This is however only feasible for small molecules, which do not contain many atoms. For large molecules it becomes almost impossible to calculate enough points in all possible directions to accurately fit the potential energy surface on which the nuclei move and a different approximation has to be used. Furthermore, solving the resulting differential equation might prove to be an herculean task. A way out of this problem is to use the harmonic oscillator approximation. This assumes that at normal conditions and if the temperature is low enough, the molecular vibration is located mostly at the lowest vibrational levels for each oscillator and a parabolic potential might be used to good accuracy.

The Nuclear Equation for Polyatomics (*1, 2*)

In the current section we will derive the equations needed to determine molecular vibration. Instead of isolating vibrations from rotations and translations, we will solve the complete nuclear Schrödinger equation approximately. The effects of translation and rotation are discussed in the end of the section.

Let the atoms in the polyatomic molecule be described by the following set of cartesian coordinates:

$$\bar{r}_k = \bar{a}_k + \bar{d}_k \tag{1}$$

where $\bar{a}_k$ is the vector pointing to the equilibrium position of atom k and $\bar{d}_k$ is a vector describing displacements around the equilibrium position. Alternatively we can write these vectors as

$$\begin{bmatrix} r_{kx} \\ r_{ky} \\ r_{kz} \end{bmatrix} = \begin{bmatrix} a_{kx} \\ a_{ky} \\ a_{kz} \end{bmatrix} + \begin{bmatrix} d_{kx} \\ d_{ky} \\ d_{kz} \end{bmatrix} \tag{2}$$

We can furthermore define mass-weighted displacements as

$$\bar{q}_k = \sqrt{m_k} \bar{d}_k \tag{3}$$

The kinetic energy operator in the Schrödinger equation is rewritten in terms of second derivatives of $\bar{r}_k$. We wish however to express the kinetic energy operator (or in fact the Schrödinger equation) in terms of the mass-weighted vectorial base. For that, and taking the component over x as example,

$$\frac{\partial}{\partial x_k} = \frac{\partial a_{kx}}{\partial x_k}\frac{\partial}{\partial a_{kx}} + \frac{\partial d_{kx}}{\partial x_k}\frac{\partial}{\partial d_{kx}}$$

Since the vector $\bar{a}_k$ is just describing the equilibrium position of atom k, then it is a constant. Furthermore, from the change of coordinates we get

$$\frac{\partial}{\partial x_k} = \frac{\partial}{\partial d_{kx}} = \frac{\partial q_{kx}}{\partial d_{kx}}\frac{\partial}{\partial q_{kx}} = \sqrt{m_k}\frac{\partial}{\partial q_{kx}}$$

We can proceed similarly for the y and z components. Using the former result we can therefore rewrite the kinetic energy operator.

$$\hat{T} = -\frac{\hbar^2}{2m}\sum\nolimits_{k=1}^{N_n}\left(\frac{\partial^2}{\partial x_k^2} + \frac{\partial^2}{\partial y_k^2} + \frac{\partial^2}{\partial z_k^2}\right) = -\frac{\hbar^2}{2m}\sum\nolimits_{k=1}^{N_n} m\left(\frac{\partial^2}{\partial q_{kx}^2} + \frac{\partial^2}{\partial q_{ky}^2} + \frac{\partial^2}{\partial q_{kz}^2}\right)$$

$$\hat{T} = -\frac{\hbar^2}{2}\sum\nolimits_{k=1}^{N_n}\left(\frac{\partial^2}{\partial q_{kx}^2} + \frac{\partial^2}{\partial q_{ky}^2} + \frac{\partial^2}{\partial q_{kz}^2}\right) \tag{4}$$

The summations run over all N_n atoms in the molecule. Since we do not know *a priori* the analytical form for the electronic potential, we can directly express the potential as a MacLaurin series in terms of the new coordinate system:

$$E_{el}\left(\{\bar{q}_k\}\right) = E_{el}^0 + \sum\nolimits_{i=1}^{3N_n}\left(\frac{\partial E_{el}}{\partial q_i}\right)|_{q_i=0}\, q_i + \frac{1}{2}\sum\nolimits_{i,j=1}^{3N_n}\left(\frac{\partial^2 E_{el}}{\partial q_i \partial q_j}\right)|_{q_i,q_j=0}\, q_i q_j + \ldots$$

Assuming the displacements are not so large to take the molecule out of the equilibrium geometry, then the first derivatives of the potential zero out. Furthermore, since V_0 is simply a constant, which may actually be absorbed into the system's energy, then we obtain

$$E_{el}\left(\{\bar{q}_k\}\right) \approx \frac{1}{2}\sum\nolimits_{i,j=1}^{3N_n}\left(\frac{\partial^2 E_{el}}{\partial q_i \partial q_j}\right)|_{q_i,q_j=0} q_i q_j \tag{5}$$

The last expression is commonly known as the harmonic oscillator approximation.

The approximate total Hamiltonian for a polyatomic molecule written in mass-weighted coordinates is then

$$H = -\frac{\hbar^2}{2}\sum\nolimits_{k=1}^{N_n}\left(\frac{\partial^2}{\partial q_{kx}^2}+\frac{\partial^2}{\partial q_{ky}^2}+\frac{\partial^2}{\partial q_{kz}^2}\right)+\frac{1}{2}\sum\nolimits_{i,j=1}^{3N_n}\left(\frac{\partial^2 E_{el}}{\partial q_i \partial q_j}\right)|_{q_i,q_j=0} q_i q_j \tag{6}$$

Looking at this Hamiltonian, one easily sees that it is not separable due to the electronic potential energy term. The effort now goes into making this term also separable. For that it is more advantageous to go to a matrix formulation of the Hamiltonian operator.

In the mass-weighted basis, the momentum operator can be written as

$$\hat{p} = -i\hbar\left(\frac{\partial}{\partial q_{kx}}+\frac{\partial}{\partial q_{ky}}+\frac{\partial}{\partial q_{kz}}\right) = -i\hbar\bar{\nabla}$$

Using a vector definition for the momentum we can rewrite the kinetic energy operator in a matrix form:

$$\mathbf{T} = \frac{1}{2}\bar{p}^\top\bar{p} \tag{7}$$

where $\bar{p}^\top$ is the transposed vector. Similarly, we can put all the elements $\left(\frac{\partial^2 E_{el}}{\partial q_i \partial q_j}\right)|_{q_i,q_j=0}$ in a matrix $\mathbf{F}$ such that in the harmonic oscillator approximation

$$E_{el}\left(\{\bar{q}_k\}\right) = \frac{1}{2}\bar{q}^\top\mathbf{F}\bar{q} \tag{8}$$

Note that in this nomenclature we define the vectors $\bar{q}$ and $\bar{p}$ as the hyper-vector containing all the $\bar{q}_k$ and $\bar{p}_k$ one after the other, *i.e.*

$$\bar{q} = \begin{bmatrix} q_{1x} \\ q_{1y} \\ q_{1z} \\ q_{2x} \\ \ldots \\ q_{Nx} \\ q_{Ny} \\ q_{Nz} \end{bmatrix} \qquad \bar{p} = \begin{bmatrix} p_{1x} \\ p_{1y} \\ p_{1z} \\ p_{2x} \\ \ldots \\ p_{Nx} \\ p_{Ny} \\ p_{Nz} \end{bmatrix} \tag{9}$$

These vectors have therefore dimension $3N$. In matrix form the Hamiltonian is rewritten as

$$\mathbf{H} = \frac{1}{2}\bar{p}^\top \bar{p} + \frac{1}{2}\bar{q}^\top \mathbf{F}\bar{q} \tag{10}$$

One may then proceed to diagonalize the matrix $\mathbf{F}$, obtaining its eigenvectors $\mathbf{L}$ and the respective eigenvalues ($\mathbf{f}$).

$$\mathbf{L}^\top \mathbf{F}\mathbf{L} = \mathbf{f} \tag{11}$$

Since the matrix of eigenvectors forms a unitary transformation, the following relations are true:

$$\mathbf{L}^\top \mathbf{L} = \mathbf{L}\mathbf{L}^\top = (\mathbf{L}^\top)^{-1}(\mathbf{L})^{-1} = (\mathbf{L})^{-1}(\mathbf{L}^\top)^{-1} = \mathbf{I} \tag{12}$$

where $\mathbf{I}$ is the identity matrix. Using yet another change of variables, we can write

$$\bar{q} = \mathbf{L}\bar{Q} \qquad \bar{q}^\top = \bar{Q}^\top \mathbf{L}^\top \tag{13}$$

$$\bar{p} = (\mathbf{L}^\top)^{-1}\bar{P} \qquad \bar{p}^\top = \bar{P}^\top (\mathbf{L})^{-1} \tag{14}$$

then

$$\mathbf{H} = \frac{1}{2}\bar{p}^\top \bar{p} + \frac{1}{2}\bar{q}^\top \mathbf{F}\bar{q} = \frac{1}{2}\bar{P}^\top (\mathbf{L})^{-1}(\mathbf{L}^\top)^{-1}\bar{P} + \frac{1}{2}\bar{Q}^\top \mathbf{L}^\top \mathbf{F}\mathbf{L}\bar{Q} = \frac{1}{2}\bar{P}^\top \bar{P} + \frac{1}{2}\bar{Q}^\top \mathbf{f}\bar{Q}$$

going now back to the explicit non-matrix notation,

$$H = \frac{1}{2}\sum_{i=1}^{3N_n} P_i^2 + \frac{1}{2}\sum_{i=1}^{3N_n} f_i Q_i^2 = \frac{1}{2}\sum_{i=1}^{3N_n}\left(P_i^2 + f_i Q_i^2\right) = \sum_{i=1}^{3N_n} H_i$$

which means that we found a form and a vectorial basis in which the nuclear Schrödinger equation becomes separable under the harmonic oscillator approximation. In the previous equation the f_i represent the eigenvalues of $\mathbf{F}$. The characteristic vibrational frequencies in this basis are

$$\omega_i = \sqrt{f_i} \tag{15}$$

The sign of the eigenvalues determines what the structure actually represents (*1*). If all eigenvalues are positive, then the structure corresponds to a stationary point in the Potential Energy Surface (PES) that minimizes energy. If there is however one negative eigenvalue, then the structure minimizes the energy in all but one direction. These saddle points are associated to transition states. More than two imaginary vibrational frequencies have no application/meaning in chemistry.

We note now that if we put all the nuclear masses in a diagonal matrix **M** then we can go directly from the displacement base to the $\bar{Q}$ base by making

$$\bar{Q} = \mathbf{L}^{\top}\mathbf{M}^{\frac{1}{2}}\bar{d} = \mathbf{W}^{-1}\bar{d} \tag{16}$$

$$\bar{d} = \mathbf{W}\bar{Q} \tag{17}$$

$$\bar{p}_d = \left(\mathbf{W}^{\top}\right)^{-1}\bar{P} \tag{18}$$

Here $\bar{p}_d$ is the momentum in the displacement base. Note that the full transformation matrix **W** is no longer a unitary transformation. We may furthermore diagonalize directly the matrix **E** of elements $\left(\frac{\partial^2 V}{\partial d_i \partial d_j}\right)|_{d_i,d_j=0}$. This can be converted to **F** using

$$\mathbf{E} = \mathbf{M}^{\frac{1}{2}}\mathbf{F}\mathbf{M}^{\frac{1}{2}} \tag{19}$$

or

$$\mathbf{F} = \mathbf{M}^{-\frac{1}{2}}\mathbf{E}\mathbf{M}^{-\frac{1}{2}} \tag{20}$$

This is quite a useful procedure because one usually calculates the Hessian of the electronic potential in the displacement base. The only thing left to do is to calculate energies and wavefunctions for the harmonic oscillator. This can be done directly in the $\bar{Q}$ space:

$$H_i = \frac{1}{2}P_i^2 + \frac{1}{2}f_i Q_i^2 = -\frac{1}{2}\hbar^2\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}f_i Q_i^2$$

Putting a wavefunction in place, we assemble the secular equation

$$H_i\psi^{nuc} = -\frac{1}{2}\hbar^2\frac{\partial^2}{\partial Q_i^2}\psi^{nuc} + \frac{1}{2}f_i Q_i^2\psi^{nuc} = E^{nuc}\psi^{nuc}$$

Quantum Harmonic Oscillator

In this section we will drop the superscript *nuc* from the wavefunction for convenience. Furthermore, as previously noted, the f_i are related to vibrational frequencies according to 15. We will furthermore use that relation and express the harmonic oscillator in terms of the vibrational frequency, which we generically denote ω. The first step to solving the above differential equation consists in rendering the equation dimensionless to simplify the treatment. By dividing everything by $\hbar\omega$

$$\left[-\frac{\hbar}{2\omega}\frac{\partial^2}{\partial x^2}+\frac{1}{2}\frac{\omega}{\hbar}x^2\right]\psi(x)=\frac{E}{\hbar\omega}\psi(x)=\epsilon\psi(x)$$

and then by making the change of variable $y=\sqrt{\frac{\omega}{\hbar}}x$

$$\left[-\frac{\hbar}{2\omega}\left(\sqrt{\frac{\omega}{\hbar}}\right)^2\frac{\partial^2}{\partial y^2}+\frac{1}{2}y^2\right]\psi(y)=\left[-\frac{1}{2}\frac{\partial^2}{\partial y^2}+\frac{1}{2}y^2\right]\psi(y)=\epsilon\psi(y)$$

which finally yields

$$\frac{\partial^2}{\partial y^2}\psi(y)+\left(2\epsilon-y^2\right)\psi(y)=0 \tag{21}$$

This is the simplest form we have for the differential equation.

To solve the differential equation we need several steps. The first one is to determine the asymptotic behaviour of the solution. This is either for low energy states or whenever y is too large. In this case, $(2\epsilon-y^2)\approx -y^2$, which yields the following differential equation

$$\frac{\partial^2}{\partial y^2}\psi(y)=y^2\psi(y) \tag{22}$$

that is solved by a Gaussian function of the form $\psi(y)=Ae^{-\frac{\alpha y^2}{2}}$. Plugging this trial solution in the differential equation yields

$$\frac{1}{\psi(y)}\frac{\partial^2}{\partial y^2}\psi(y)=-\alpha\left(1-\alpha y^2\right)=y^2$$

Since y is very large, then the solution is given approximately by $\alpha=\pm1$ and the general solution to the differential equation is

$$\psi(y)=\phi_{01}e^{-\frac{y^2}{2}}+\phi_{02}e^{\frac{y^2}{2}}$$

Of the two parts of the solution, only one is "well-behaved", meaning that only one is possible to normalize. As $y\rightarrow\pm\infty$, the second exponential will diverge. This term shall therefore be discarded from the solution since it is not physically meaningful. In going from the limiting behavior back to the general solution we assume that ϕ_{01} is a function of y. The trial solution to the quantum harmonic oscillator is a function of the form

$$\psi(y)=\phi(y)e^{-\frac{y^2}{2}} \tag{23}$$

We can now insert this function in the full differential equation to get

$$\frac{\partial^2}{\partial y^2}\phi(y)e^{-\frac{y^2}{2}} + \left(2\epsilon - y^2\right)\phi(y)e^{-\frac{y^2}{2}} = 0 \Leftrightarrow$$

$$e^{-\frac{y^2}{2}}\left[\frac{\partial^2}{\partial y^2}\phi(y) - 2y\frac{\partial}{\partial y}\phi(y) + \left(y^2 - 1\right)\phi(y)\right] + \left(2\epsilon - y^2\right)\phi(y)e^{-\frac{y^2}{2}} = 0$$

and we finally obtain

$$\frac{\partial^2}{\partial y^2}\phi(y) - 2y\frac{\partial}{\partial y}\phi(y) + (2\epsilon - 1)\phi(y) = 0 \tag{24}$$

Since we do not know *a priori* how to solve this differential equation, we can try to obtain a series-like solution, *i.e.*,

$$\phi(y) = \sum\nolimits_{n=0}^{\infty} C_n y^n$$

Inserting the Ansatz for $\phi(y)$ in the differential equation results in

$$\sum\nolimits_{n=2}^{\infty} n(n-1)C_n y^{n-2} - 2y\sum\nolimits_{n=1}^{\infty} nC_n y^{n-1} + (2\epsilon - 1)\sum\nolimits_{n=0}^{\infty} C_n y^n = 0 \Leftrightarrow$$

$$\sum\nolimits_{n=0}^{\infty} (n+2)(n+1)C_{n+2} y^n - 2\sum\nolimits_{n=0}^{\infty} nC_n y^n + (2\epsilon - 1)\sum\nolimits_{n=0}^{\infty} C_n y^n = 0 \Leftrightarrow$$

$$\sum\nolimits_{n=0}^{\infty} \left[(n+2)(n+1)C_{n+2} + (2\epsilon - 2n - 1)C_n\right] y^2 = 0$$

Since the former equation must be valid for any power of y and for any value of y, then it follows that the series above defined must have coefficients such that

$$C_{n+2} = \frac{2n + 1 - 2\epsilon}{(n+2)(n+1)}C_n \tag{25}$$

For the resulting wavefunction to be physically meaningful it is then necessary that the resulting power series either converges or truncates.

In the limit of very large n we see that the quotient between coefficients tends to

$$\frac{C_{n+2}}{C_n} = \frac{2n + 1 - 2\epsilon}{(n+2)(n+1)} \approx \frac{2n}{n^2} = \frac{2}{n}$$

This relates every other coefficient and the same expression is valid for both even and odd coefficients, then we conclude that the ratio between consecutive coefficients tends to

$$\frac{C_{n+1}}{C_n} = \frac{1}{n}$$

in the limit of large n. Because the numerator has a $-\epsilon$ contribution, then for not-large-enough-n the ratio between consecutive coefficients is larger than $\frac{1}{n}$:

$$\frac{C_{n+1}}{C_n} \geq \frac{1}{n}$$

By applying the recursive relation we can rewrite $C_n \geq \frac{C_0}{n!}$, where C_0 is the constant associated with the first coefficient. Plugging this result in the series, we obtain

$$\sum\nolimits_{n=0}^{\infty} C_n y^n \geq \sum\nolimits_{n=0}^{\infty} C_0 \frac{y^n}{n!} = C_0 e^y$$

Even though we did not prove that the series is convergent (nor divergent), we know now that if we do not truncate the series for $\phi(y)$, the function will converge to a value that cannot be normalized and is not well behaved. We therefore conclude that we must truncate the series at some point. This is achieved by zeroing the denominator at some order n

$$2n + 1 - 2\epsilon = 0 \Leftrightarrow \epsilon = n + \frac{1}{2}$$

which yields the eigenenergies allowed for the quantum harmonic oscillator:

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) \tag{26}$$

Even though we do not have yet expressions for all coefficients, we know from the mathematical literature that $\phi(y)$ are Hermite polynomials. These can be calculated using the recursion formulae,

$$H_n(y) = e^{\frac{y^2}{2}} \left(y - \frac{d}{dy} \right)^n e^{-\frac{y^2}{2}} = (-1)^n e^y \frac{d^n}{dy^n} e^{-y} \tag{27}$$

The general solution for the quantum harmonic oscillator is then

$$\psi_n(x) = A_n H_n \left(\sqrt{\frac{\omega}{\hbar}} x \right) e^{-\frac{\omega}{2\hbar} x^2}$$

where A_n is a normalization constant, which can be determined from the orthonormalization condition:

$$\int_{-\infty}^{+\infty} \psi_n^*(x) \psi_m(x) dx = \int_{-\infty}^{+\infty} A_n H_n \left(\sqrt{\frac{\omega}{\hbar}} x \right) e^{-\frac{\omega}{2\hbar} x^2} A_m H_m \left(\sqrt{\frac{\omega}{\hbar}} x \right) e^{-\frac{\omega}{2\hbar} x^2} dx$$

Changing again to the y variable we reach

$$A_n A_m \sqrt{\frac{\hbar}{\omega}} \int_{-\infty}^{+\infty} H_n(y) e^{-\frac{y^2}{2}} H_m(y) e^{-\frac{y^2}{2}} dx = A_n A_m \sqrt{\frac{\hbar}{\omega}} \delta_{nm} 2^n n! \sqrt{\pi}$$

from which

$$A_n = \sqrt[4]{\frac{\omega}{\pi\hbar}} \sqrt{\frac{1}{2^n n!}} \tag{28}$$

and

$$\psi_n(x) = \sqrt[4]{\frac{\omega}{\pi\hbar}} \sqrt{\frac{1}{2^n n!}} H_n \left(\sqrt{\frac{\omega}{\hbar}} x \right) e^{-\frac{\omega}{2\hbar} x^2} \tag{29}$$

Translations and Rotations (*2*)

In the previous sections we solved the full nuclear Schrödinger equation. Within the approximation used, the general force acting on the atoms in some direction is given by

$$\frac{\partial}{\partial d_i} E_{el}\left(\{\bar{d}_k\}\right) = \sum_{j=1}^{3N_n} \left(\frac{\partial^2 E_{el}}{\partial d_i \partial d_j}\right) |_{d_i, d_j = 0} d_j$$

where we express the electronic potential surface in cartesian displacements. If all atoms feel a force in the same direction, then $d_j = \delta$ and we get

$$\frac{\partial}{\partial d_i} E_{el}\left(\{\bar{d}_k\}\right) = \delta \sum_{j=1}^{3N_n} \left(\frac{\partial^2 E_{el}}{\partial d_i \partial d_j}\right) |_{d_i, d_j = 0}$$

Forces on atoms should not change if we move all atoms in the same direction by the same displacement. Therefore

$$\delta \sum_{j=1}^{3N_n} \left(\frac{\partial^2 E_{el}}{\partial d_i \partial d_j}\right) |_{d_i, d_j = 0} = 0$$

Since we took any possible displacement, which is not necessarily zero, then we conclude that the summation term must zero out. If we now split the indices in atoms and unit vectors from the referential we finally reach

$$\sum_{l=1}^{N_n} \sum_{\beta=1}^{2} \left(\frac{\partial^2 E_{el}}{\partial d_{k,\alpha} \partial d_{l,\beta}}\right) |_{d_{k,\alpha}, d_{l,\beta} = 0} = 0 \tag{30}$$

where k and l refer to atoms and α and β refer to the axes of the referential (x, y and z). From the equation above one gets nine invariance conditions, of which only six (five in linear molecules) are unique. In the first set of 3 conditions, *i.e.* for $\alpha = \beta$, we obtain the invariance to translations, which can be proved to yield exactly three zero eigenvalues in the matrix $\mathbf{F}$. The respective eigenvectors describe the position of the center of mass moving in a given direction. The other set of 3 (2) conditions, *i.e.* for $\alpha \neq \beta$, gives the invariance to rotations, which also gives rise to three (two) approximately zero eigenvalues (rotations and vibrations are not always separable, *c.f.* below). The respective eigenvectors describe rotations of the center of mass along the principal axes. The $3N_n - 6(5)$ non-zero eigenvalues left correspond to molecular vibration. Consequently, we do not need to worry about translational and rotational motion when solving the vibrational Schrödinger. External motion of the nuclei separates from internal degrees of freedom. The decoupling between rotations and vibrations is however not always strictly verified, as there might be Coriolis coupling that contaminates vibrational motion with some rotational character. However, such coupling can most of the times be neglected for equilibrium geometries. This is indeed a test that can be used to determine how close (far) an optimized geometry is from an equilibrium structure (*1*).

Since the electronic potential function is invariant to translational and rotational motion, then it is a function of $3N_n - 6(5)$ internal coordinates/variables. The electronic potential E^{elec} defines then a hypersurface in an $3N_n - 6(5)$-dimensional space. This hypersurface is known as PES.

Zero Point Vibrational Energy (ZPVE)

From the eigenvalues of the quantum harmonic oscillator one verifies that even for the zeroth vibrational level there is energy associated with molecular vibration (*1*). Therefore, even at zero Kelvin the vibrational energy is not zero and a vibrational contribution has to be added to electronic energies for an accurate calculation of total molecular energies. This is the ZPVE. The ZPVE can be calculated by summing the vibrational frequencies when the vibrational quantum number is zero, thus yielding

$$E_{ZPVE} = \frac{1}{2}\sum\nolimits_{i=1}^{3N_n-6} h\omega_i \tag{31}$$

Note that for linear molecules the index i runs over $3N_n - 5$ vibrational modes.

ZPVE are sensible to isotopic abundance. Most programs calculate all energies using directly the natural abundance of isotopes or even just the most abundant one. This assumes that the change in energies with respect to mass is strictly linear, which is not true for vibrational energies and the respective frequencies.

Partition Function for Harmonic Oscillator

In polyatomics, and assuming the harmonic oscillator approximation, normal vibrational modes can be treated independently. This is a direct consequence of the separability of the Hamiltonian. The total vibrational partition function of a molecule is written as

$$q^{vib} = \prod\nolimits_i q_i^{vib} \tag{32}$$

where i runs over the $3N_n - 5$ (linear) or $3N_n - 6$ (non-linear) normal modes (*3*). If a vibrational mode is described by an imaginary vibrational frequency (like in a transition state), this mode should be skipped in accordance to transition state theory (*4, 5*). If anharmonicity is to be considered, the separability of normal modes is no longer applicable. This is however for the "high temperature" case (the concept of high temperature is dependent on the depth of the potential, or on the absolute value of the vibrational frequency).

With the harmonic oscillator approximation,

$$q^{vib} = \prod_i \sum_{v=0}^{\infty} e^{-\frac{\hbar\omega_i\left(v+\frac{1}{2}\right)}{k_BT}} = \prod_i e^{-\frac{\hbar\omega_i}{2k_BT}} \sum_{v=0}^{\infty} e^{-\frac{\hbar\omega_i v}{k_BT}} \tag{33}$$

Note that the ω_i are given in equation 15 as a function of the matrix $\mathbf{F}$ eigenvalues.

The partition function as above written is a product of geometrical series', which for finite temperatures converges to

$$q^{vib} = \prod_i \frac{e^{-\frac{\hbar\omega_i}{2k_BT}}}{1 - e^{-\frac{\hbar\omega_i}{k_BT}}} \tag{34}$$

For temperatures approaching the absolute zero, this partition function also approaches the value of zero, which means that its natural logarithm will tend to $-\infty$. Because of this, entropy, Gibbs energy and the Helmoltz energy will all tend to $-\infty$, a behavior not in agreement with the third law of thermodynamics. This is however the natural behaviour for the harmonic oscillator at low temperatures. To heal this problem we can consider that the ground state of each vibrational level has zero energy and therefore we can shift the partition function by multiplying it by $e^{\frac{\hbar\omega_i}{2k_BT}}$. Note that this is feasible because the partition function measures the accessibility of states to a system. Therefore, energy differences and not absolute energy values are the most important factor in this calculation. In this case, a new vibrational partition function is obtained, which attends the third law of thermodynamics.

$$q^{vib} = \prod_i \frac{1}{1 - e^{-\frac{\hbar\omega_i}{k_BT}}} \tag{35}$$

We will however consider the full model for now and later on consider ways of correcting for anharmonic effects. From the full partition function we can then derive

$$log\left(q^{vib}\right) = -\sum_i \frac{\hbar\omega_i}{2k_BT} - \sum_i log\left(1 - e^{-\frac{\hbar\omega_i}{k_BT}}\right) \tag{36}$$

Defining the characteristic vibrational temperature for the vibrational mode i as

$$\theta_i = \frac{\hbar\omega_i}{k_B} \tag{37}$$

then

$$log\left(q^{vib}\right) = -\sum\nolimits_i \frac{\theta_i}{2T} - \sum\nolimits_i log\left(1 - e^{-\frac{\theta_i}{T}}\right) \tag{38}$$

From here on we can calculate the derivatives of the partition function. Since we deal with internal motion, the derivative with respect to the system's volume is zero. Temperature derivatives are given by

$$\frac{\partial}{\partial T} log\left(q^{vib}\right) = \frac{1}{2}\sum \frac{\theta_i}{T^2} + \sum \frac{\theta_i}{T^2}\frac{1}{e^{\frac{\theta_i}{T}} - 1} \tag{39}$$

$$\frac{\partial^2}{\partial^2 T} log\left(q^{vib}\right) = -\sum \frac{\theta_i}{T^3} + \sum\nolimits_i \theta_i \left[\frac{\theta_i e^{\frac{\theta_i}{T}} - 2Te^{\frac{\theta_i}{T}} + 2T}{T^4\left(e^{\frac{\theta_i}{T}} - 1\right)^2}\right] \tag{40}$$

With these, we have everything needed to calculate the vibrational contribution to thermodynamic functions.

Limitations Harmonic Oscillator

The main limitation of the harmonic oscillator is that it allows no breaking of chemical bonds. Instead, bonds can be indefinitely stretched and they will never break. This is naturally unphysical (*1*). The consequence is that for an harmonic oscillator all energy levels are equally spaced. In a real oscillator, the energy between different vibrational quantum levels decreases with quantum number. Furthermore, contrary to the harmonic oscillator, a real oscillator has a finite number of energy levels. A consequence of the two limitations is that vibrational frequencies calculated using the harmonic oscillator approximation are always larger than the real vibrational frequencies. This difference can be as large as 3% just from the harmonic oscillator approximation. In order to calculate realistic vibrational frequencies from first principles one must scale calculated frequencies by a method and basis set specific factor. The literature has many publications on recommended scaling factors that can be used (see for instance (*6*)).

Low Vibrational Frequencies

The degree of (an)harmonicity of a given vibrational mode depends on the depth of the potential well associated with the vibrational mode. The lower the vibrational frequency, the shallower the potential well becomes, and anharmonicity effects get stronger. For the low-frequency vibrations, the harmonic oscillator approximation is no longer appropriate. Not only is the model inadequate, it blows up the calculation of internal energies and entropies: the former becomes infinitely negative and the latter infinitely positive.

$$S_{HO} = R\left[\frac{h\omega}{k_BT\left(e^{h\omega/k_BT}-1\right)} - log\left(1-e^{-h\omega/k_BT}\right)\right] \tag{41}$$

Note that the same does not apply to enthalpies. If we write down the enthalpy for a single mode of a harmonic oscillator

$$H_{HO} = k_B\theta\left(\frac{1}{2}+\frac{1}{e^{\theta/T}-1}\right)$$

and MacLaurin-expand the expression we see that

$$H_{HO}{\approx}k_B\left(T+\frac{\theta^2}{12T}+...\right)$$

which in the limit of $\theta = 0$ falls to the value of k_BT.

Vibrational modes with low frequencies are typically associated with internal rotations of molecular groups, which may take place in a hindered fashion, if there is a high energy energy barrier to be overcome, or simply freely. The degree of hindered- to free-rotor of a given internal rotation is solely determined by the associated vibrational frequency. Because of the low values of the associated frequency, these modes are quickly affected by anharmonicity effects, but they also reach quicker the classical behaviour. Whenever the temperature is high enough, Pitzer suggested to simply treat internal degrees of freedom simply as being classical. The harmonic oscillator model should be replaced by the free-rotor and contribution of one such vibrational mode to the internal energy is then given (*7–10*)

$$U_{free-rotor} = \frac{1}{2}RT \tag{42}$$

while for entropies we get instead

$$S_{free-rotor} = R\left[\frac{1}{2}+log\left(\frac{\sqrt{8\pi^3 I_{int}k_BT}}{\sigma_{int}h}\right)\right] \tag{43}$$

Here, I_{int} and σ_{int} are reduced inertias and symmetry numbers for the internal rotation. In his work, Pitzer also considered a more accurate treatment for a hindered rotor.

Perhaps the most common example is the rotation along the $C-C$ bond of a methyl group in ethane. It is well known that the staggered structure of ethane corresponds to a minimum in the potential surface, since it minimizes the repulsion between the hydrogen atoms. On the other hand, the eclipsed structure maximizes the repulsion between hydrogen atoms. This structure corresponds to a saddle point for the internal rotation in the molecule. Other cases with low-vibrational frequencies are the van der Waals complexes describing two weakly interacting molecules. Because of the weak interaction, the potential is highly anharmonic and the associated vibrational motion acquires such behaviour. Other consequences are that many local minima may exist, instead of a single equilibrium structure. The barriers between these minima are consequently also low and complex tunnel effects may occur (*2*).

Internal rotations might also cause problems in geometry optimizations, which end in a false stationary point. The internal rotations have typically an activation barrier associated with them, which is periodic over the rotation angle, and the optimizer falls then to the transition structure instead of the actual minimum. To solve this problem in typical geometry optimizations, one may add a fraction of the vibrational perturbation to the actual geometry and reoptimize the structure with tighter convergence criteria.

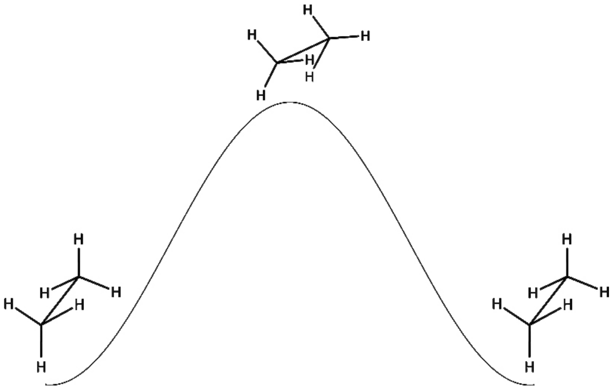

Figure 1: Sketch of ethane's potential surface for the rotation of one methyl group. Marvin 19.27, 2019 was used for drawing chemical structures, ChemAxon (http://www.chemaxon.com)". The picture was furthermore modified to include the shape of the potential.

The Grimme Correction for Free-Rotation

Grimme proposed a simple and black-box like correction for ideal gas entropies (*11*), which consists on an interpolation between the free-rotor and harmonic oscillator partition functions. For that one starts by defining a moment of inertia for a free-rotor with the same frequency as the vibrational mode

$$\mu = \frac{h}{8\pi^2\omega} \tag{44}$$

which we restrict to reasonable values using

$$\mu^{'} = \frac{\mu B_{avg}}{\mu + B_{avg}} \tag{45}$$

These modified moments of inertia are defined for every vibrational mode in the molecule. In the equation above, B_{avg} is an average molecular moment of inertia, which we calculate as the geometric mean of the eigenvalues of the inertia matrix. By using a weight function

$$w(\omega) = \frac{1}{1 + \left(\frac{\omega_0}{\omega}\right)^a} \tag{46}$$

the interpolation between models is done via

$$S_{vib} = w(\omega)S_{HO} + [1 - w(\omega)]S_{free-rotor} \tag{47}$$

Recommended values for $a = 4$ and ω_0 should be between 50 and $150cm^{-1}$. We set $\omega_0 = 75cm^{-1}$.

For consistency we calculated all the thermodynamic functions for the free-rotor, which we then used to interpolate in the same manner as entropy.

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