The Rigid Rotor (*1, 2*)

The main method to calculate the rotational component of the energy is called the rigid rotor. It can be solved analytically for many molecules with higher symmetry, but not for general asymmetric molecule. In that case one typically uses an approximate partition function derived from classical mechanics. Because the solution for the Schrödinger equation for molecular is dependent on the molecular shape, we begin by analysing the relatively simple case of a diatomic molecule and we will then generalise for other cases.

In the rigid rotor approximation, a molecule's moment of inertia is a constant for all rotational energy levels (*3*). This is typically a good approximation for small molecules. Larger molecules include internal rotations and the rigid rotor approximation eventually breaks. In those cases, rotational isomers (rotamers) are distinguished and treated as different species within the statistical mechanical treatment.

The Rigid Rotor for a Diatomic

The rigid rotor model for a diatomic molecule considers the molecule as being composed by two masses (the nuclei) rotating along a given axis. The molecule in the rigid rotor is stiff, meaning that it cannot be deformed by centrifugal forces: the bond distance is a constant. In this sense, the nature of the problem becomes equivalent to the description of a "particle on a sphere's surface" model. Because the there is no radial dependence on the system, the Schrödinger equation will describe a wavefunction with only angular components.

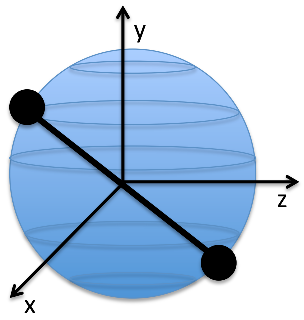

Figure 1: Particle on the surface of a sphere, a model to describe molecular rotation.

The number of rotation axes is the same as the number of dimensions considered. Therefore, for the three dimensional case the solution to the Schrödinger equation will have to describe three different modes of rotation. Because the molecular system has now a given shape and composition, the whole can no longer be considered as a point in space. The geometry has to be considered and a referential for the molecule must be chosen. This referential is placed at the centre of mass.

For the whole system the sphere equation is going to be valid,

$$x^2+y^2+z^2=r^2 \tag{1}$$

Since the two particles are free to move only around the sphere's surface, the potential energy zeroes on that surface. Anywhere else it will be infinite. This means that the system of equations for the rigid rotor resembles the particle in a box model, except for the difference in the symmetry of the problem. Because of the spherical symmetry, it is convenient to switch the mathematical description to polar spherical coordinates:

$$x=r sin\theta cos\phi \tag{2}$$

$$y=r sin\theta sin\phi \tag{3}$$

$$z=r cos\theta \tag{4}$$

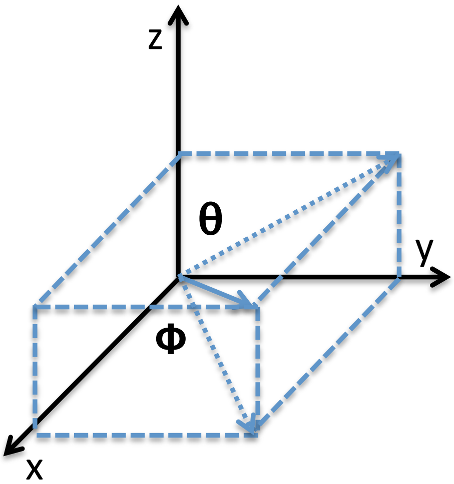

Figure 2: The spherical coordinate system.

In spherical coordinates we can write the kinetic energy operator as

$$\Delta=\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}=\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{5}$$

and the resulting Schrödinger equation has the form

$$-\frac{\hbar^2}{2m}\nabla^2\Psi=E\Psi \tag{6}$$

Because there is no radial dependence, $\frac{\partial}{\partial r}\Psi{=}0$ and the equation above simplifies to

$$-\frac{\hbar^2}{2m}\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}\Psi(\theta,\phi)-\frac{\hbar^2}{2m}\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Psi(\theta,\phi)=E\Psi(\theta,\phi) \tag{7}$$

$$\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}\Psi(\theta,\phi)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Psi(\theta,\phi)=-\frac{2mEr^2}{\hbar^2}\Psi(\theta,\phi)$$

The differential equation above can be divided in two independent terms, one only dependent on θ, the other only dependent on ϕ. Therefore, the desired solutions for this Schrödinger equation will have the form

$$\Psi(\theta,\phi)=f(\theta)g(\phi) \tag{8}$$

Using this in 7,

$$\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}f(\theta)g(\phi)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}f(\theta)g(\phi)+\frac{2mEr^2}{\hbar^2}f(\theta)g(\phi)=0 \tag{9}$$

$$[sin\theta\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}+\frac{2mEr^2}{\hbar^2}sin^2\theta]f(\theta)g(\phi)=-\frac{\partial^2}{\partial\phi^2}f(\theta)g(\phi)$$

$$\frac{1}{f(\theta)}[sin\theta\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}+\frac{2mEr^2}{\hbar^2}sin^2\theta]f(\theta)=-\frac{1}{g(\phi)}\frac{\partial^2}{\partial\phi^2}f(\theta)g(\phi)$$

Since the left-hand-side of the above equation is only dependent on θ and the right-hand-side only dependent on ϕ, we can separate the Schrödinger equation into two independent differential equations: one for each variable.

The ϕ Equation

The direct consequence of the variable separability is that we can set both sides equal to a given constant. The resulting ϕ equation reads

$$\frac{1}{g(\phi)}\frac{d^2}{d\phi^2}f(\theta)g(\phi)=-n^2 \tag{10}$$

The solutions to this equation are just like the solutions for the particle in a box model, *i.e.*,

$$g(\phi)=A_n e^{in\phi} \tag{11}$$

with n a real number. According to the symmetry of the problem, the ϕ component of the wavefunction has to be periodic, with periods 2π. From this boundary condition we take that

$$e^{2in\pi}=1 \tag{12}$$

which is only valid if n is an integer. We arrive therefore to the quantization of the variable ϕ, requiring that $n = 0, \pm 1, \pm 2, ...$

From the normalization condition,

$$\int_{-\infty}^{+\infty} g^*(\phi)g(\phi)d\phi = \int_0^{2\pi} g^*(\phi)g(\phi)d\phi = 1 \tag{13}$$

we take that

$$A_n = (2\pi)^{-\frac{1}{2}} \tag{14}$$

and consequently

$$g_n(\phi) = \frac{1}{\sqrt{2\pi}} e^{in\phi} \tag{15}$$

where n is an integer number.

The θ Equation

Having solved the differential equation for ϕ, we can now focus on solving the left-hand-side of the Schrödinger equation, the θ equation:

$$\frac{1}{f(\theta)} sin\theta \frac{d}{d\theta} sin\theta \frac{d}{d\theta} f(\theta) + \frac{2mEr^2}{\hbar^2} sin^2\theta = n^2 \tag{16}$$

where, according to the ϕ equation, n is an integer. It then follows that

$$\frac{1}{f(\theta)} sin\theta cos\theta \frac{d}{d\theta} f(\theta) + \frac{1}{f(\theta)} sin^2\theta \frac{d^2}{d\theta^2} f(\theta) + \frac{2mEr^2}{\hbar^2} sin^2\theta = n^2 \tag{17}$$

Substituting $x = cos\theta$ we get

$$\frac{dx}{d\theta} = -sin\theta; \quad \frac{d^2x}{d\theta^2} = -cos\theta; \quad \frac{d}{d\theta} f(\theta) = -sin\theta \frac{d}{dx} f(x);$$

$$\frac{d^2}{d\theta^2} f(\theta) = \frac{d^2}{dx^2} f(x) sin^2\theta + \frac{d}{dx} f(x)(-cosx)$$

and consequently, the θ equation can be recast as

$$-\frac{(1-x^2)x}{f(x)} \frac{d}{dx} f(x) + \frac{(1-x^2)^2}{f(x)} \frac{d^2}{dx^2} f(x) - \frac{(1-x^2)x}{f(x)} \frac{d}{dx} f(x) + \frac{2mr^2E(1-x^2)}{\hbar^2} = n^2 \tag{18}$$

$$(1-x^2)\frac{d^2}{dx^2} f(x) - 2x \frac{d}{dx} f(x) + \left(\frac{2mEr^2}{\hbar^2} - \frac{n^2}{1-x^2}\right) f(x) = 0$$

If we rewrite

$$\frac{2mr^2E}{\hbar^2} = j(j+1) \tag{19}$$

then the equation above becomes the associated Legendre differential equation, a well known problem in the mathematical and physical literature, which also has well-known and well established solutions. With the condition above we therefore restrict the rotational energy levels to be a function of the natural number j

$$E(j)=\frac{\hbar^2 j(j+1)}{2mr^2} \tag{20}$$

Note that due to the quadratic dependence on j, the energy is greater or equal to zero, and that because of the term $j+1$ the rotational energy of the system can never be zero. Note furthermore that this energy is independent of the quantum number n that we obtained by solving the ϕ equation. It follows from the differential equations that $n\leq j$, thus meaning that each energy level has degeneracy $2j+1$.

The solutions to this differential equation are the Legendre polynomials,

$$f(x,n,j)=(-1)^n\frac{(1-x^2)^{\frac{n}{2}}}{2^j j!}\frac{d^{n+j}}{dx^{n+j}}(x^2-1)^j \tag{21}$$

Doing the back substitution $(x\rightarrow\theta)$ and introducing a normalization constant,

$$A_n^j=(\frac{2j+1}{2}\frac{[j-|n|]!}{[j+|n|]!})^{\frac{1}{2}} \tag{22}$$

we write the function in θ as

$$f_n^j(x)=(-1)^n\frac{A_n^j sin^n\theta}{2^j j!}\frac{d^{n+j}}{d\theta^{n+j}}(cos^2\theta-1)^2 \tag{23}$$

Once more, the normalization constant can be obtained by integration of the square of the absolute value of $f_n^j(x)$ over the domain of θ.

Placing both equations together we obtain the rigid rotor wavefunction for a diatomic.

$$\Psi^{j,n}(\theta,\phi)=\sqrt{\frac{2j+1}{4\pi}\frac{(j-|n|)!}{(j+|n|)!}}\frac{(-1)^n sin^n\theta}{2^j j!}e^{in\phi}\frac{d^{n+j}}{d\theta^{n+j}}(cos^2\theta-1)^2 \tag{24}$$

The Rigid Rotor for Polyatomics

The rotational energy for a diatomic is a function of mr^2, which is the moment of inertia for a diatomic. To generalize the energy expression for other chemical systems we can start by writing that energy in terms of the inertia instead of in terms of the mass and the bond distance. However, direct substitution of mr^2 by the moment of inertia does not lead to a faithful representation of the rotational component of the energy and other

”corrections” should be considered. To begin with, the moment of inertia for polyatomics is not just a scalar, but rather a 3×3 matrix (there are three axes of rotation) (*4*):

$$I=\begin{bmatrix} \sum_i m_i(y_i^2+z_i^2) & -\sum_i m_i(x_iy_i) & -\sum_i m_i(x_iz_i) \\ -\sum_i m_i(x_iy_i) & \sum_i m_i(x_i^2+z_i^2) & -\sum_i m_i(y_iz_i) \\ -\sum_i m_i(x_iz_i) & -\sum_i m_i(y_iz_i) & \sum_i m_i(x_i^2+y_i^2) \end{bmatrix} \tag{25}$$

The first step towards the generalization to polyatomics begins by building this matrix and calculating its eigenvalues and eigenvectors. Using the eigenvalues, $I_a \leq I_b \leq I_c$, groups of symmetry with respect to the rotation can be distinguished, forming three different classes of molecules:

- Spherical tops, molecules with spherical symmetry and thus $I_a=I_b=I_c$. Examples are methane and C_{60}.
- Symmetric tops, molecules with two identical I_i:
  - Prolate tops, for which $I_a<I_b=I_c$. Examples are iodo-methane and other linear molecules.
  - Oblate tops, for which $I_a=I_b<I_c$. Examples are ammonia, benzene, BF_3.
- Asymmetric tops, for which $I_a<I_b<I_c$. Examples are water or formaldehyde.

Furthermore, for each eigenvalue of the inertia matrix auxiliary energy constants can be defined

$$A=\frac{\hbar^2}{2I_a} \geq B=\frac{\hbar^2}{2I_b} \geq C=\frac{\hbar^2}{2I_c} \tag{26}$$

Using these constants, after solving the Schrödinger equation the following energies can be obtained for the different kind of systems:

- Spherical tops: Since $I_a=I_b=I_c$, then also $A=B=C$ and

  $$E(j)=Bj(j+1) \tag{27}$$

- Prolate tops:

  $$E(j)=Bj(j+1)+(A-B)k^2 \tag{28}$$

  with $k=0, \pm 1, \pm 2, ..., \pm j$. Therefore, additionally to the degeneracies caused by the quantum number n we require an extra two-fold degeneracy due to k.

- Oblate tops: Similarly to prolate tops,

  $$E(j){=}Bj(j+1){+}(C-B)k^2 \tag{29}$$

  with the same conditions on k and the respective consequences. Special cases are linear molecules with symmetry $C_{\infty v}$ and $D_{\infty h}$, for which $I_a{=}0$ thus $A{=}\infty$ and only the case $k{=}0$ exists.

- Asymmetric tops: As already mentioned, there is not yet a known analytical form of the rotational energy for this case.

Partition Functions and their Derivatives

As the above treatment showed, molecular rotations are not dependent on the shape or size of the system. These are molecular properties and only depend on the atomic composition and structure. This is reflected in the energies of rigid rotors, which depend on quantum numbers, constants and the moment of inertia of the molecule. All the energies show furthermore a general structure, which we will use to derive all the partition functions and the respective derivatives. Particular cases are considered later.

$$q_{rot}{=}\sum\nolimits_j g_j e^{-\frac{\varepsilon_j}{k_B T}}{=}\sum\nolimits_j g_j e^{-\frac{A(j)}{T}} \tag{30}$$

The logarithm of the partition function can be calculated directly. Furthermore, since there is no dependence on the size or shape of the container, all derivatives with respect to the volume zero out:

$$\frac{\partial}{\partial V} log(q_{rot}){=}0 \tag{31}$$

$$\frac{\partial}{\partial log(V)} log(q_{rot}){=}0 \tag{32}$$

As such, we only require the calculation of the temperature derivatives. We can use an approach similar to what was done for the molecular translations, noticing that now we have no dependence on the molecular volume. In that case, the identical results can be immediately obtained and

$$\frac{\partial}{\partial T} log(q_{rot}){=}\frac{1}{T^2}\frac{\sum_j g_j A(j) e^{-\frac{A(j)}{T}}}{\sum_j g_j e^{\frac{A(j)}{T}}} \tag{33}$$

$$\frac{\partial^2}{\partial T^2} log(q_{rot}){=}-\frac{2}{T^3}\frac{\sum_j g_j A(j) e^{-\frac{A(j)}{T}}}{\sum_j g_j e^{\frac{A(j)}{T}}}{+}\frac{1}{T^4}\frac{\sum_j g_j A^2(j) e^{-\frac{A(j)}{T}}}{\sum_j g_j e^{-\frac{A(j)}{T}}}{-}\frac{1}{T^4}(\frac{\sum_j g_j A(j) e^{-\frac{A(j)}{T}}}{\sum_j g_j e^{-\frac{A(j)}{T}}})^2 \tag{34}$$

Table 1: The values of $A(j)$ for different symmetries in the rigid rotor model.

Case	$A(j)$	Comment
Atom	0	So that q_{rot}=1
Diatomic	$\frac{\hbar^2 j(j+1)}{2k_B I}$	$I{=}\mu r^2{=}\frac{m_1 m_2}{m_1+m_2}r^2$
Spherical Top	$\frac{\hbar^2 j(j+1)}{2k_B I}$	I is 3-fold degenerate
		eigenvalue of inertia matrix
Prolate Top	$\frac{\hbar^2 j(j+1)}{2k_B I_b} + \frac{\hbar^2 k^2}{2k_B}(\frac{I_b - I_a}{I_b I_a})$	—
Oblate Top	$\frac{\hbar^2 j(j+1)}{2k_B I_b} + \frac{\hbar^2 k^2}{2k_B}(\frac{I_b - I_c}{I_b I_c})$	—
Asymmetrical Top	—	No analytical expression for the energy

$$\frac{\partial}{\partial log(T)} log(q_{rot}){=}\frac{1}{T}\frac{\sum_j g_j A(j) e^{-\frac{A(j)}{T}}}{\sum_j g_j e^{\frac{A(j)}{T}}} \tag{35}$$

Having the temperature derivatives, the only thing left to do is to define $A(j)$ for all the specific cases, which simply requires getting the respective energies from the section . Table 1 summarises the values of $A(j)$:

The Classical Limit of a Rigid Rotor

For most cases, the eigenvalues of the inertia matrix are large enough for the rotational energy to become a quasi-continuum on the rotational quantum number. It is thus not only important but also convenient to calculate the classical limit for the rotational partition function, as it too can significantly reduce the computational costs of a calculation. The classical limit for rotations under the rigid rotor approximation is valid whenever molecules have less light atoms (*5*). Furthermore, with the classical limit we can use an estimate for asymmetric molecules, an important result to ensure the applicability of the model for any molecule, thus also to obtain thermodynamic quantities. As table 1 shows, diatomics and spherical tops show the same energy expression, while symmetrical tops (prolate and oblate) show similar expressions that can be generalized identically. We will thus couple those cases two-by-two and then present the case of asymmetric tops.

The classical limits for partition functions is obtained by transformation of a summation over quantum numbers into the respective integral. For diatomics and spherical tops we obtain

$$q_{rot}{=}\int_0^{+\infty} g_j e^{-\frac{A(j)}{T}} dj{=}\int_0^{+\infty} (2j+1) e^{-\frac{\hbar^2 j(j+1)}{2k_B I T}} dj \tag{36}$$

$$=\frac{2k_BITe^{-\frac{\hbar^2}{2k_BIT}}}{\hbar^2}\simeq\frac{2k_BIT}{\hbar^2}$$

Note that the last approximation is valid whenever we expect the exponent in the exponential function to be very small. The derivatives we require are also easily obtained:

$$\frac{\partial}{\partial T}log(q_{rot})=\frac{1}{T} \tag{37}$$

$$\frac{\partial^2}{\partial T^2}log(q_{rot})=-\frac{1}{T^2} \tag{38}$$

$$\frac{\partial}{\partial log(T)}log(q_{rot})=1 \tag{39}$$

$$\frac{\partial}{\partial V}log(q_{rot})=0 \tag{40}$$

$$\frac{\partial}{\partial log(V)}log(q_{rot})=0 \tag{41}$$

For the symmetrical tops we have a slightly more complicated situation since we must transform summations over two quantum numbers (thus also a double integral) and we also need to account for the 2-fold-k-degeneracy. Furthermore, the variable of integration k is dependent on the variable of integration j, since $k = 0, \pm 1, \pm 2, ..., \pm j$. We therefore start by assuming that quantum numbers are independent from one another, which yields

$$q_{rot}\simeq\int_0^{+\infty}\int_0^{+\infty}g_je^{-\frac{A(j)}{T}}djdk=2\int_0^{+\infty}2(2j+1)e^{-\frac{\hbar^2j(j+1)}{2k_BI_bT}}e^{-\frac{\hbar^2k^2}{2k_BT}(\frac{|I_b-I_x|}{I_bI_x})}djdk \tag{42}$$

with $x = a$ for prolate tops and $x = c$ for oblate tops. Solving this integral gives

$$q_{rot}\simeq(\frac{2k_BI_bT}{\hbar^2})^{\frac{3}{2}}(\frac{\pi I_x}{|I_b-I_x|})^{\frac{1}{2}} \tag{43}$$

The derivatives we are interested in are once more easily obtained:

$$\frac{\partial}{\partial T}log(q_{rot})=\frac{3}{2T} \tag{44}$$

$$\frac{\partial^2}{\partial T^2}log(q_{rot})=-\frac{3}{2T^2} \tag{45}$$

$$\frac{\partial}{\partial log(T)}log(q_{rot})=\frac{3}{2} \tag{46}$$

$$\frac{\partial}{\partial V}log(q_{rot})=0 \tag{47}$$

$$\frac{\partial}{\partial log(V)}log(q_{rot})=0 \tag{48}$$

Table 2: Values for σ as given in (*3*).

Group	C_1,C_i,C_s,$C_{\infty v}$	C_n,C_{nv},C_{nh},C_{nv}	$D_{\infty h}$	D_n,D_{nh},D_{nd}	T,T_d	S_n	O_h	I_h
σ	1	n	2	$2n$	12	$\frac{n}{2}$	24	60

As noted above, using quantum mechanics we have no access to the partition function of asymmetric tops. This keeps us from calculating the contribution from the rotational energy to the whole partition function, at least in some cases. A very important result from classical rigid rotor valid as an approximation to polyatomic molecules is the partition function

$$q_{rot}=\frac{\sqrt{\pi}}{\sigma}(\frac{2k_BT}{\hbar^2})^{\frac{3}{2}}(I_aI_bI_c)^{\frac{1}{2}} \tag{49}$$

This partition function is dependent on the three eigenvalues of the molecular inertia and also on a parameter σ, the (external) symmetry number, which is a measure of the molecular symmetry. σ describes the number of unique symmetry actions that leave the molecule unchanged, even though the atoms change their position. The symmetry number reflects the symmetry of the nuclear wavefunction with respect to a given rotation and it ensures that equation 49 is not overcounting the number of accessible states whenever symmetry is present. It is because of this parameter that the partition function 49 is valid for any molecular system in general, as it corrects for the symmetry upon rotation of the molecule.

In our program we used the values for σ as given in (*3*). Using this partition function we can calculate the remaining derivatives.

$$\frac{\partial}{\partial T}log(q_{rot})=\frac{3}{2T} \tag{50}$$

$$\frac{\partial^2}{\partial T^2}log(q_{rot})=-\frac{3}{2T^2} \tag{51}$$

$$\frac{\partial}{\partial log(T)}log(q_{rot})=\frac{3}{2} \tag{52}$$

$$\frac{\partial}{\partial V}log(q_{rot})=0 \tag{53}$$

$$\frac{\partial}{\partial log(V)}log(q_{rot})=0 \tag{54}$$

Note that, in terms of derivatives, the symmetrical tops and the general expression yield the same results.

As referred in the beginning of this section, the classical limit of the rotational partition function has smaller errors for molecules with heavier atoms. The two main sources of errors in this approximation arise whenever the molecules are too light or for low enough temperatures. For the practical purposes we are interested in, very light molecules refer to diatomics with a hydrogen atom (*5*).

Beyond the Rigid Rotor

The main approximation of the rigid rotor model is that, despite the rotational movement, the centrifugal energy acting on a molecule is always too low to deform the system. This is however, not always verifiable. To compensate for this deficiency, a non-rigid rotor model has to be considered.

Much like the rigid rotor, the non-rigid variant of the model has no general analytical solution for all types of molecules. The energies of non-rigid rotors however, are obtained by adding a correction to the energies of the respective rigid rotor model.

By looking at the expression for the inertia matrix, increased bond lengths are associated to higher inertia moments, thus also larger rotational deformation. Since the rotational energy is directly proportional to the constant B, which itself is proportional to the inverse of the inertia I, the real rotational energy has to be smaller than the energy calculated by the rigid rotor model. Assuming that the deformation of the molecular system is simply a small correction to the results previously obtained, we can build the real rotational energy as a Maclaurin series on $j(j+1)$, thus

$$E_{rot}{=}Bj(j+1){-}Dj^2(j+1)^2{+}... \tag{55}$$

Such an expression for the energy can be obtained by considering a force that keeps the molecule from breaking apart due to the centrifugal force. These terms are to be added as contributions to the potential energy in the Hamiltonian.

The Maclaurin series 55 can be truncated on the quadratic term with very high accuracy. Spectroscopy or vibrational corrections to the rotational energy can be used to calculate D (non-rigidness contributions arise whenever the decoupling of rotations and vibrations is not strong enough). In the first case, *e.g.*, D is calculated from the difference between consecutive peaks in rotational spectra.

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