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Eulerian Angles

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I. SYNOPSIS

When studying polyatomic rotations, one needs a description of rotation which employs independent coördinates, hence this discussion.

II. THE EULERIAN ANGLES

There is no question that once we leave diatomic molecules, life gets difficult. Most chemistry concerns polyatomics, so sticking with diatomics is possibly excessively pedantic. Be that as it may, we need to discuss rotational aspects of polyatomic species.

To begin the study of polyatomic molecules we need to define rotations in three dimensions in a manner which is rigorous. We seek three *independent* angles, coordinates in a sense, which will suffice to allow us to write the Hamiltonian for the rotation in a clear, unambiguous, manner. Our Eulerian angles are not taken from Goldstein (which used to be the gold, no pun intended, standard in this field) [1] Instead, we now shift to a more current standard, which is exemplified by Zare [2] We need three angles, three rotations, which will unambiguously allow us to rotate a coordinate system from a starting to a final configuration. The order of operation will be prescribed, and remain inviolate. We start with the familiar polar angle from spherical polar coordinates, φ , which we take over completely as the first Euler angle. We rotate from the coordinate system $x_{space}, y_{space}, z_{space}$ to $\{x_N, y_N, z_N\}$ where z_N is collinear with z_{space} , since this first rotation is a rotation about the original z-axis. (The new y-axis is called the "line of nodes", hence the subscript 'N'.) Again, from spherical polar coordinates, we take the positive direction as $x \to y$.

Next, from the $\{x_N, y_N, z_N\}$ system, we rotate about the y_N -axis counterclockwise by an angle which we will call ϑ . This second rotation leads us from $\{x_N, y_N, z_N\}$ to $\{x_r, y_r, z_r\}$.

Finally, we rotate about the (new) z_u axis, again counterclockwise, to go from $\{x_r, y_r, z_r\}$ to $\{x_f, y_f, z_f\}$ where the subscript f stands for final. This last angle is called χ .

It is clear that we have for the first rotation

$$\begin{pmatrix} x_N \\ y_N \\ z_N \end{pmatrix} = \begin{pmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} x_{space} \\ y_{space} \\ z_{space} \end{pmatrix} \quad (2.1)$$

and for the second rotation about the newly created "y"

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FIG. 1: First Rotation in the Euler Scheme

axis, which is now called the line of nodes,

$$\begin{pmatrix} x_u \\ y_u \\ z_u \end{pmatrix} = \begin{pmatrix} \cos\vartheta & 0 & -\sin\vartheta \\ 0 & 1 & 0 \\ \sin\vartheta & 0 & \cos\vartheta \end{pmatrix} \otimes \begin{pmatrix} x_N \\ y_N \\ z_N \end{pmatrix}$$
(2.2)

and finally, once again about a z-axis, but this time the new one,

$$\begin{pmatrix} x_f \\ y_f \\ z_f \end{pmatrix} = \begin{pmatrix} \cos \chi & \sin \chi & 0 \\ -\sin \chi & \cos \chi & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} x_u \\ y_u \\ z_u \end{pmatrix}$$
(2.3)

The final coordinates are called the body coordinates, compared to the original set, which is referred to as the space coordinates (or lab coordinates).

The product of these three rotations, in the proper (invariable) order, will locate the body coordinates. Thus, the body coordinates are connected to the space coordinates through the transformation:



FIG. 2: Second Rotation in the Euler Scheme (showing the axis of rotation, \hat{n}_ϑ



FIG. 3: Third Rotation in the Euler Scheme (showing the axis of rotation, \hat{n}_{χ}

$$\begin{pmatrix} \cos\chi & \sin\chi & 0\\ -\sin\chi & \cos\chi & 0\\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} \cos\vartheta & 0 & \sin\vartheta\\ 0 & 1 & 0\\ -\sin\vartheta & 0 & \cos\vartheta \end{pmatrix} \otimes \begin{pmatrix} \cos\varphi & \sin\varphi & 0\\ -\sin\varphi & \cos\varphi & 0\\ 0 & 0 & 1 \end{pmatrix}$$
(2.4)

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We take these composite rotation matrix multiplications in order, i.e., first the φ rotation, then the ϑ rotation yielding

$$\begin{pmatrix} \cos\vartheta & 0 & -\sin\vartheta \\ 0 & 1 & 0 \\ \sin\vartheta & 0 & \cos\vartheta \end{pmatrix} \otimes \begin{pmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
(2.5)

which yields

$$\begin{pmatrix} \cos\vartheta\cos\varphi & \cos\vartheta\sin\varphi & -\sin\vartheta \\ -\sin\varphi & \cos\varphi & 0 \\ \sin\vartheta\cos\varphi & \sin\vartheta\sin\varphi & \cos\vartheta \end{pmatrix}$$

and finally, including the χ rotation, we have

$$\begin{pmatrix} \cos\chi & \sin\chi & 0 \\ -\sin\chi & \cos\chi & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} \cos\vartheta\cos\varphi & \cos\vartheta\sin\varphi & -\sin\vartheta \\ -\sin\varphi & \cos\varphi & 0 \\ \sin\vartheta\cos\varphi & \sin\vartheta\sin\varphi & \cos\vartheta \end{pmatrix}$$

We finally arrive at the overall transformation

 $\begin{pmatrix} \cos\chi\cos\vartheta\cos\varphi - \sin\varphi\sin\chi & \cos\chi\cos\vartheta\sin\varphi + \cos\varphi\sin\chi & -\cos\chi\sin\vartheta \\ -\sin\chi\cos\vartheta\cos\varphi - \sin\varphi\cos\chi & -\sin\chi\cos\vartheta\sin\varphi + \cos\varphi\cos\chi & \sin\chi\sin\vartheta \\ \sin\vartheta\cos\varphi & \sin\vartheta\sin\varphi & \cos\vartheta \end{pmatrix}$ (2.6)

The angle φ is the exact same angle as that used in spherical polar coördinates, i.e., is familiar. ϑ measures the tilt down from the original z-axis, and is also familiar from spherical polar coördinates. The new angle, χ , is uncommon.

III.

We have derived the transformation which takes the space coördinates into the body coördinates, i.e.,

$$\vec{x}_{body} = \Phi_{space \rightarrow body} \vec{x}_{space}$$

where Φ is a 3x3 matrix (above). $\Phi(\varphi, \vartheta, \chi)$ is a function of the three Euler angles. As noted above, this overall transformation is a compound of three different rotations, $R(\varphi), R(\vartheta), R(\chi)$, in reverse order, i.e.,

$$\Phi = R(\chi) \otimes R(\vartheta) \otimes R(\varphi)$$

As usual, these are written from right to left, i.e., we do $R(\varphi)$ first, then $R(\vartheta)$, and finally $R(\chi)$.

There must be an inverse transformation which takes the body coördinates back into the space coördinates, i.e., Φ^{-1} . This must have the form

$$\Phi^{-1} = R^{-1}(\varphi) \otimes R^{-1}(\vartheta) \otimes R^{-1}(\chi)$$

As with all rotations in three dimensions, the result of doing and then undoing must be the unit operation, i.e., no operation at all. Thus

$$\Phi^{-1} \otimes \Phi = 1$$

IV. INFINITESIMAL ROTATIONS IN QM

Consider a system described by a set of eigenfunctions $|i\rangle$, such that

$$|i\rangle' = U_{op}|i\rangle$$

where $|i\rangle'$ is a new set of basis functions. We then have

$$\langle i|i\rangle' = \langle i|U_{op}^{\dagger}U_{op}|i\rangle$$

where the superscript dagger implies transpose complex conjugate. This last equation is the same as the radius preserving rotation in space, the lengths and angles between the unprimed and the primed system are maintained during the linear transformation U_{op} , if $U_{op}^{\dagger} = U_{op}^{-1} = I$. The matrix representative of an operator will change

The matrix representative of an operator will change upon this kind of transformation. Consider the operator Q_{op} so that

 $\langle i|Q_{op}|j \rangle \rightarrow Q_{i,j}$

$$< i |U_{op}^{\dagger}U_{op}Q_{op}U_{op}^{\dagger}U_{op}|j> = < i |U_{op}Q_{op}U_{op}^{\dagger}|j>' = Q_{i,j}'$$

This means that the operator has been transformed, i.e.,

$$Q_{op}' = U_{op}Q_{op}U_{op}^{\dagger} = Q_{op}' = U_{op}Q_{op}U_{op}^{-1}$$

If the transformation U_{op} (a unitary transformation) can be written as

$$U_{op} = I_{op} + i\epsilon R_{op}$$

where R_{op} is going to be an infinitesimal rotation operator, then two such transformations, compounded, would have the form

$$U_{op}^2 = \left(I_{op} + i\frac{\epsilon}{2}R_{op}\right)^2$$

i.e., if we did each of these for $\epsilon/2$ the net would be as if we did the original for ϵ , i.e.,

$$U_{op}^2 = \left(I_{op} + \imath \frac{\epsilon}{2} R_{op}\right)^2 = U_{op}$$

If we did this over and over again, using smaller and smaller increments then we would eventually have

$$U_{op} = \lim_{n \to \infty} \left(I_{op} + i \frac{\epsilon}{n} R_{op} \right)^n \tag{4.1}$$

This is a fancy way of writing

$$U_{op} = e^{(i\epsilon R_{op})} \tag{4.2}$$

which can be verified by taking the Taylor expansion of this exponential form (Equation 4.2) and identifying each term as being present in the product's expansion (Equation 4.1).

V. FINITE VS. INFINITESIMAL ROTATIONS

One can now associate a vector with a finite rotation represented by an orthogonal (radius preserving) transformation. The direction would be the axis of rotation, and the magnitude would be the angle of rotation, or something related to it. But, since the rotations, in three dimensions, were not commutative, i.e., $Rot_1 \otimes Rot_2 \neq Rot_2 \otimes Rot_1$, neither Rot_1 nor Rot_2 can be "true" vectors. On the other hand, for infinitesimal rotations, this association of a rotation with a vector is perfectly plausible.

VI.

Consider the finite rotation about the z-axis

$$R_z = \begin{pmatrix} \cos\varphi & \sin\varphi & 0\\ -\sin\varphi & \cos\varphi & 0\\ 0 & 0 & 1 \end{pmatrix}$$

when φ is infinitesimal, i.e., close to zero. Then the cosine is approximately 1, and if the infinitesimal angle is $\delta\varphi$ then one has

$$R_z = \begin{pmatrix} 1 & \delta\varphi & 0\\ -\delta\varphi & 1 & 0\\ 0 & 0 & 1 \end{pmatrix}$$

Consider $R_z(\varphi)$ as rotating about the z-axis from φ_0 to $\varphi_0 + \varphi$ i.e., which means that the effect of the rotation would be to substitute the value at $\varphi_0 - \varphi$ for the new value φ_{new} , i.e.,

$$R_z(\varphi)|\varphi_0\rangle = |\varphi_{new}\rangle = |\varphi_0 - \varphi\rangle$$

in the space coördinate system. Then

$$|\varphi_{new}\rangle = |\varphi_0\rangle + \left(\frac{\partial|\varphi\rangle}{\partial\varphi}\right)_{\varphi=\varphi_0}\varphi + \cdots$$



FIG. 4: R(g) \to ? Here, we have that Rg($\varphi)$ picks up an "earlier" or "older" value of g

which could be written as

$$|\varphi_{new}\rangle = \left(1 - \frac{\varphi}{n}\frac{\partial}{\partial\varphi}\right)^n$$

 \mathbf{SO}

$$\varphi_0 - \varphi \rangle = |\varphi_{new}\rangle = \left(e^{-\varphi \frac{\partial}{\partial \varphi}}\right)|\varphi_0\rangle$$

and we then write

$$R_z(\varphi) = e^{-\varphi \frac{\partial}{\partial \varphi}}$$

and remember that $\mathcal{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$ and we choose a reduced coördinate scheme where $\hbar = 1$:

$$R_z(\varphi) = e^{-\imath \varphi \mathcal{L}_z}$$

VII.

Let $\psi = \psi(x, y, z)$, and let $R_z(\delta \alpha)$ mean that $\psi(x, y, z)$ becomes $\psi(x + y\delta\alpha, y - x\delta\alpha, z)$ which is the meaning of rotating about the z-axis be $\delta \alpha$. Expanding $\psi(x + y\delta\alpha, y - x\delta\alpha, z)$ in a Taylor series, we have

$$\psi(x,y,z)|_{after \ rotation} = \psi(x+y\delta\alpha, y-x\delta\alpha, z) = \psi(x,y,z) + y\frac{\partial\psi(x,y,z)}{\partial x}\delta\alpha - x\frac{\partial\psi(x,y,z)}{\partial y}\delta\alpha + \cdots$$

$$\frac{\delta\psi(x,y,z)}{\delta\alpha} = +y\frac{\partial\psi(x,y,z)}{\partial x} - x\frac{\partial\psi(x,y,z)}{\partial y}$$

(remember,

$$\psi(x+y\delta\alpha,y-x\delta\alpha,z) = \left[\mathbf{1}+\delta\alpha\left(y\frac{\partial}{\partial x}-x\frac{\partial}{\partial y}\right)\right]\psi(x,y,z)+\cdots$$

this alternate interpretation).

$$\psi(x+y\delta\alpha,y-x\delta\alpha,z) = \left[\mathbf{1} - \delta\alpha\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right]\psi(x,y,z)$$

Since

$$\mathcal{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

we would have

$$\frac{\partial}{\partial \alpha} = \frac{\mathcal{L}}{\imath}$$

For an infinitesimal rotation, we have (again, having $\hbar = 1$)

$$R_z = \mathbf{1} + \frac{\mathcal{L}_z}{\imath} \delta \alpha$$

and if $\alpha = n\left(\frac{\alpha}{n}\right)$ then and $\delta \alpha = \frac{\alpha}{n}$ then in the limit, n goes to infinity we have

$$R_z = \left(\mathbf{1} + \frac{\mathcal{L}_z}{\imath} \frac{\alpha}{n}\right)^n$$

which is

$$e^{\alpha \frac{\mathcal{L}_z}{\imath}} = e^{-\imath \alpha \mathcal{L}_z}$$

If we use an axis other than the z-axis, then we need to define a vector whose direction is that axis. Call that vector \hat{n} , then for a general rotation

$$R_n(\alpha) = e^{-i\alpha \vec{L} \cdot \hat{n}}$$

VIII. ANOTHER DERIVATION OF RESULT $\frac{\partial}{\partial \alpha} = \frac{\mathcal{L}}{\imath}$

From the polar coördinate definitions, we have

$$\left(1 + \frac{\sin^2 \varphi}{\cos^2 \varphi}\right) d\varphi = \frac{dy}{x} - \frac{y}{x^2} dx$$

or

and

$$\left(\frac{1}{\cos^2\varphi}\right)d\varphi = \frac{dy}{x} - \frac{y}{x^2}dx$$

which leads to

$$\left(\frac{\partial\varphi}{\partial y}\right)_x = \cos\varphi \tag{8.1}$$

$$\left(\frac{\partial\varphi}{\partial x}\right)_y = -\sin\varphi \tag{8.2}$$

$$x\frac{\partial}{\partial y} = \cos^2\varphi\frac{\partial}{\partial\varphi}$$

and

$$y\frac{\partial}{\partial x} = -\sin^2\varphi\frac{\partial}{\partial\varphi}$$

which leads to

$$\vec{L}\cdot \hat{k} = -\imath \frac{\partial}{\partial \varphi}$$

in our case, and in general

$$\vec{L}\cdot\hat{n}=-\imath\frac{\partial}{\partial\alpha}$$

where \hat{n} is the unit axis around which the rotation is taking place. If the system is invariant under this rotation about this axis, then the component of angular momentum \mathcal{L}_n is a constant of the motion.

For our three dimensional problem, in Euler angles, we have

$$\vec{L} \cdot \hat{n_{\varphi}} = -\imath \frac{\partial}{\partial \varphi}$$

 \mathbf{SO}

$$egin{aligned} ec{L} \cdot \hat{n_{artheta}} &= -\imath rac{\partial}{\partial artheta} \ ec{L} \cdot \hat{n_{\chi}} &= -\imath rac{\partial}{\partial \chi} \end{aligned}$$

IX. EULER ANGLE REPRESENTATION

The Euler Angle rotations can be represented as

$$R(\varphi,\vartheta,\chi) = e^{-i\chi \vec{L}\cdot\hat{n}_{\chi}} e^{-i\vartheta \vec{L}\cdot\hat{n}_{\vartheta}} e^{-i\varphi \vec{L}\cdot\hat{n}_{\vartheta}}$$

where this form has been chosen to represent the rotation of the physical system, rather than the coördinate system. This rotation is equivalent to first a rotation of χ about the original z-axis, then a rotation of ϑ about the new Y-axis, and then finally a rotation of φ about the new z-axis.

We are using the Euler angle representation which employs three unit vectors \hat{n}_{φ} , \hat{n}_{ϑ} and \hat{n}_{χ} associated with the three Euler angles. We need to express these in terms of the Cartesian unit vectors in the space system, \hat{i}, \hat{j} , and \hat{k} . We know that

$$\hat{n}_{\varphi} = \hat{k}$$

since the first rotation is about the original (space) z-axis. This means that

$$-\imath \frac{\partial}{\partial \varphi} = \mathcal{L}_z$$

The new y-axis after the first (φ) rotation, is $-\sin \varphi \hat{i} + \cos \varphi \hat{j}$, as seen in Figure IX. Thus



FIG. 5: The φ rotation changes the axis of rotation for the second (ϑ) rotation.

$\hat{n}_{\vartheta} = -\sin\varphi \hat{i} + \cos\varphi \hat{j}$

After the first (φ) rotation, the x-axis is transformed into $\cos \varphi \hat{i} + \sin \varphi \hat{j}$ which is now itself rotated in the second (ϑ) rotation into $\sin \vartheta \left(\cos \varphi \hat{i} + \sin \varphi \hat{j}\right)$ so



$$\hat{n}_{\chi} = \sin\vartheta \left(\cos\varphi \hat{i} + \sin\varphi \hat{j}\right) + \hat{k}\cos\vartheta$$

which means that

$$-\imath \frac{\partial}{\partial \varphi} = \mathcal{L}_z \quad (9.1)$$
$$-\imath \frac{\partial}{\partial \vartheta} = -\sin \varphi \mathcal{L}_x + \cos \varphi \mathcal{L}_y \quad (9.2)$$
$$-\imath \frac{\partial}{\partial \chi} = \sin \vartheta \cos \varphi \mathcal{L}_x + \sin \vartheta \sin \varphi \mathcal{L}_y + \cos \vartheta \mathcal{L}_z \quad (9.3)$$

From these equations, we can solve for the components of angular momentum directly, i.e.,

$$\mathcal{L}_z = -\imath \frac{\partial}{\partial \varphi}$$

multiplying Equation 9.2 through by $\sin \varphi$ we get

$$-i\sin\varphi\frac{\partial}{\partial\vartheta} = -\sin^2\varphi\mathcal{L}_x + \sin\varphi\cos\varphi\mathcal{L}_y$$

multiplying Equation 9.3 through by $-\cos\varphi$ we obtain

$$+\imath \frac{\cos\varphi}{\sin\vartheta} \frac{\partial}{\partial\chi} = -\cos^2\varphi \mathcal{L}_x - \cos\varphi \sin\varphi \mathcal{L}_y + \cos\varphi \cot\vartheta \mathcal{L}_z$$

and adding, yields

$$-\imath \sin \varphi \frac{\partial}{\partial \vartheta} + \imath \frac{\cos \varphi}{\sin \vartheta} \frac{\partial}{\partial \chi} = -\mathcal{L}_x + \imath \cos \varphi \cot \vartheta \frac{\partial}{\partial \varphi}$$

or

$$\mathcal{L}_x = +i\sin\varphi \frac{\partial}{\partial\vartheta} - i\cos\varphi \left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\chi} - \cot\vartheta \frac{\partial}{\partial\varphi}\right)$$

or, in "final" form

$$\mathcal{L}_x = \imath \left(\sin \varphi \frac{\partial}{\partial \vartheta} - \cos \varphi \left(\frac{1}{\sin \vartheta} \frac{\partial}{\partial \chi} - \cot \vartheta \frac{\partial}{\partial \varphi} \right) \right)$$

From Equation 9.2 we now obtain

or

$$-\cos\varphi\mathcal{L}_{y} - i\frac{\partial}{\partial\vartheta} = -\sin\varphi\left(+i\sin\varphi\frac{\partial}{\partial\vartheta} - i\cos\varphi\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\chi} - \cot\vartheta\frac{\partial}{\partial\varphi}\right)\right)$$
$$-\mathcal{L}_{y} = i\frac{1}{\cos\varphi}\frac{\partial}{\partial\vartheta} - \frac{\sin\varphi}{\cos\varphi}i\sin\varphi\frac{\partial}{\partial\vartheta} + \sin\varphi i\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\chi} - \cot\vartheta\frac{\partial}{\partial\varphi}\right)$$

which is

$$\mathcal{L}_{y} = -i\left(\cos\varphi\frac{\partial}{\partial\vartheta} + \sin\varphi\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\chi} - \cot\vartheta\frac{\partial}{\partial\varphi}\right)\right)$$

or, in "final" form

$$\mathcal{L}_y = -i\cos\varphi\frac{\partial}{\partial\vartheta} - \sin\varphi i\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\chi} - \cot\vartheta\frac{\partial}{\partial\varphi}\right)$$

X. THE HAMILTONIAN

Now we need to obtain

$$\vec{\mathcal{L}} \equiv \hat{i}\mathcal{L}_x + \hat{j}\mathcal{L}_y + \hat{k}\mathcal{L}_z$$

which will be used to form the Hamiltonian, presumably by forming

$$-rac{\hbar^2}{2I_x}\mathcal{L}_x^2-rac{\hbar^2}{2I_y}\mathcal{L}_y^2-rac{\hbar^2}{2I_z}\mathcal{L}_z^2$$

but it is not clear what the relation is between the I_x , I_y , and I_z on the one hand, and the I_A , I_B , and I_C values from the principal axis transformation on the other hand.

We quote the final Schrödinger Equation for symmetric tops as [3]

$$\frac{1}{\sin\vartheta}\frac{\partial\left(\sin\vartheta\frac{\partial\psi}{\partial\vartheta}\right)}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2\psi}{\partial\varphi^2} + \left(\cot^2\vartheta + \frac{C}{B}\right)\frac{\partial^2\psi}{\partial\chi^2} - 2\frac{\cot\vartheta}{\sin\vartheta}\frac{\partial^2\psi}{\partial\chi\partial\varphi} + \frac{W}{hB}\psi = 0$$

Here, ϑ and φ " are equivalent to the usual polar angles between an axis fixed space and some axis fixed in the molecule, and χ is the angle of rotation around the axis fixed in the molecule. For a symmetric top, this chosen axis is naturally the molecular or symmetry axis. C is the rotational constant for the symmetry axis and B is $\frac{\hbar^2}{2I_B}$ for the axis perpendicular to the symmetry axis". We note that this result is not derived in Townes and Schawlow, but referenced back to Kemble [4] where it is also not derived.

- H. Goldstein, Classical Mechanics, Addison-Wesley Pub. Co., Inc. Reading, Massachusetts, 1959, page107
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- [3] C. H., Townes and A. L. Schalow, "MicroWave Spec-

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[4] E. C. Kemble, "The Fundamental Principles of Quantum Mechanics", McGraw-Hill Book Co., New York, 1937