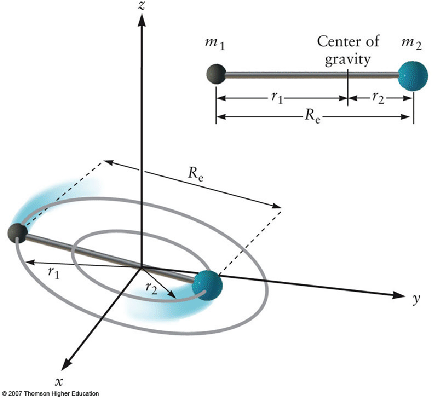
**Quantum Rotation in 3 Dimensions (Rigid Rotor)**

 A model of a rotating diatomic molecule is created as follows:

* Assume that two masses, *m*1 and *m*2, are connected to one another by a rigid rod of length *R*. System is called a rigid rotor.
* This system is allowed to freely rotate in 3D space about its center of mass. Since the distance between the masses is unvarying, we call this the rigid rotor model.
* Potential energy of this system is 0.
* is defined to be the reduced mass.
* is defined to be the moment of inertia.
* This system is best represented in spherical polar coordinates, with the radius *r=R* is fixed.

Derivation of the Wave Function

The wave function is stated (using the reduced mass ) in spherical coordinates with the Laplacian highlighted:

(1)

The following stipulations are applied to the potential energy:

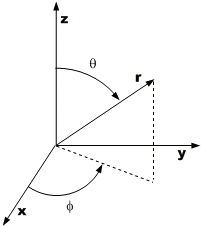
(2)

Therefore:

(3)

Expanding the Laplacian in terms of spherical coordinates and dropping the independent variables from yields:

(4)

Three things to note here:

* Recall that the derivation of the Laplacian in polar coordinates was quite tedious. The tedium is tenfold for the derivation of the Laplacian in spherical coordinates, so it is merely stated above without derivation. ☺
* In physics and chemistry, the definitions of the angles and have are switched with respect to the definitions you have learning in mathematics. measures the angle off of the positive z-axis, and is the counter clockwise angle measurement off of the positive x-axis. This distance from the origin is represented by *r* vice .☹
* Since the radius is constant (i.e. particles will not exist in a regime where the potential energy is infinite) we can let and which allows us to simplify the wave equation: ☺

(5)

Using the definition of the moment of inertia , this becomes:

(6)

Dividing both sides by yields:

(7)

Note:

(8)

Therefore:

(9)

and finally,

(10)

We now separate the variables, by letting let (or more simply written: This implies that:

(11)

Thus:

(12)

Dividing equation by yields

Multiply by :

Separating variables yields:

where M represents the eigenvalues. We now have two ordinary differential equations:

The solution to the first equation is familiar:

.

Recall the derivation from the particle in a ring problem. After applying boundary conditions (i.e. ) we noted that must be an integer. After normalization conditions are applied the solution is:

.

To solve the second equation we let :

which implies:

We use this to find:

Substituting this into:

Yields:

which simplifies to:

Let . This gives us:

which is known as the ***associate Legendre differential equation***. The equation has non-singulars solutions for only if is an integer and . The integers and are respectively referred to as the degree and order of the associate Legendre function. Note that so the singularity condition is met.

The derivation of a final solution is not discussed here and left open for exercise. The solutions to the general Legendre equation are called the ***associated Legendre functions*** . Some examples are given below:

|  |  |  |
| --- | --- | --- |
| **Associated Legendre Functions for** | | |
|  |  |  |
| 0 | 0 |  |
| 1 | 0 |  |
| 1 |  |
| 2 | 0 |  |
| 1 |  |
| 2 |  |
| 3 | 0 |  |
| 1 |  |
| 2 |  |
| 3 |  |
|  |  |  |

Recall that we had let . Back substituting, the above table is converted to the context of the rigid rotor problem:

|  |  |  |
| --- | --- | --- |
| **Associated Legendre Functions for** | | |
|  |  |  |
| 0 | 0 |  |
| 1 | 0 |  |
| 1 |  |
| 2 | 0 |  |
| 1 |  |
| 2 | ( |
| 3 | 0 |  |
| 1 |  |
| 2 |  |
| 3 |  |

We now have a solution for :

.

To find , a double integral is used to normalize :

.

Since and are independent in this expression, the double integral can be expressed as the product of two integrals:

=1.

We showed earlier that the second integral equals 1. Therefore:

We note here that the associate Legendre functions form an orthogonal set and that for the follow is true:

Since (thus we rewrite this expression as:

We can no conclude that:

,

Which implies that:

.

We now have a solution for the wave function:

.

Note that earlier we let:

And stated that must be an integer in order to find non-singular solutions to the Legendre function. Thus energy is quantized:

.

Each integer has values of associated with it that do not affect the energy levels. Thus each energy level has associated with it wave forms.

Example: Find the wave form associated with and :