Spectroscopic investigation of spin zero homonuclear and heteronuclear molecules

Nagalakshmi A. Rao
Department of Physics, Government Science College,
Bangalore-560001, Karnataka, India.
drnarao@gmail.com

B. A. Kagali
Department of Physics, Jnanabharathi Campus, Bangalore University,
Bangalore-560056, Karnataka, India.
bakagali@hotmail.com

In the present article, we introduce a model to investigate the energy spectrum of a relativistic rotor by considering the Klein-Gordon Hamiltonian. Rotational spectral lines are a signature of homonuclear and heteronuclear systems and play a key role in understanding diatomic molecules. We show that the energy-correction term arising due to unequal masses influences the line separation. Determining the rotational constant enables one to calculate the moment of inertia and bond length of the molecule.

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1 Introduction

The rigid rotator is a well-known problem in classical mechanics\(^1\) as also in quantum mechanics. The quantum theory of the band spectra of diatomic molecules began with the quantisation of angular momentum of the rigid rotator. Much of spectroscopic calculation relies on rigid rotator models. It is well-known that there exists a fundamental difference between atomic spectra and molecular spectra. While for atoms the line separation in a series decreases rapidly, for molecular spectra in the infrared, it is approximately a constant. Actually, for linear diatomic molecules, two additional modes of motion, namely rotation and vibration, not present in atoms, are possible. In literature, the energy spectrum of such a system is investigated non-relativistically. Presently, we propose to view the model in the relativistic framework.

After the classic application of relativistic wave equations to the atomic spectrum of hydrogen atom, there were several other applications of the relativistic wave equations to well-known problems of non-relativistic quantum mechanics. In the simplest from, one can cite the work of Sauter\(^2\), who treated the problem of a particle in an uniform field relativistically. Srinivasa Rao et.al.\(^3\), have dealt with the relativistic rigid rotator in an elegant way, treating the rotor as a dumb bell with equal masses. Following the prescription of Rao, we extend the treatment to a linear rotator with unequal masses. The foregoing discussion is applicable to any heteronuclear system, special case of which is the homonuclear species. Such studies, apart from being pedagogical in nature are potentially exciting and shed light on the spectra of diatomic molecules.

2 Klein-Gordon Rotor

In the simplest model of a rotator, we consider two atoms of masses \(m_1\) and \(m_2\) separated by distance \(r\).

The Klein-Gordon Hamiltonian for a system of two non-interacting particles may be written as

\[
H = c\sqrt{m_1^2c^2 + \vec{p}_1^2} + c\sqrt{m_2^2c^2 + \vec{p}_2^2}
\]

where \(\vec{p}_1\) and \(\vec{p}_2\) refer to the momenta of the two particles.

Introducing the centre of mass co-ordinate \(\vec{R}\) and the relative co-ordinate \(\vec{r}\), the two body problem may be reduced to an equivalent one-body problem. The relative co-ordinate, \(\vec{r}: (x, y, z)\) is expressed as

\[
\vec{r} = \vec{r}_1 - \vec{r}_2
\]
and the centre of mass co-ordinate \( \vec{R} : (X, Y, Z) \) is given by

\[
\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}.
\] (3)

It is straightforward to verify the following relations

\[
\frac{\partial}{\partial x_1} = \frac{m_1}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial x}
\] (4)

\[
\frac{\partial}{\partial x_2} = \frac{m_2}{M} \frac{\partial}{\partial X} - \frac{\partial}{\partial x}
\] (5)

where \( M = m_1 + m_2 \) is implied.

The eigenvalue equation, \( H \psi = W \psi \) may be written as

\[
\left\{ c \sqrt{m_1^2 c^2 - \hbar^2 \nabla_1^2} + c \sqrt{m_2^2 c^2 - \hbar^2 \nabla_2^2} - W \right\} \psi = 0
\] (6)

using \( \vec{p}_1 = -i \hbar \vec{\nabla}_1 \) and \( \vec{p}_2 = -i \hbar \vec{\nabla}_2 \) in Eqn.(1). Operating on the left by \( (H + W) \), we obtain,

\[
(W_1 + H_1) \psi = 0
\] (7)

with \( W_1 = c^2 (m_1^2 c^2 - \hbar^2 \nabla_1^2) + c^2 (m_2^2 c^2 - \hbar^2 \nabla_2^2) - W^2 \)

and \( H_1 = 2c^2 \sqrt{m_1^2 c^2 - \hbar^2 \nabla_1^2} \sqrt{m_2^2 c^2 - \hbar^2 \nabla_2^2} \).

To eliminate the square root operators in \( H_1 \), we operate on the left of Eqn.(7) by \( (W_1 - H_1) \) and obtain

\[
(W_1^2 - H_1^2) \psi = 0.
\] (8)

The operator equation of the above is

\[
\left\{ c^4 (m_1^2 c^2 - \hbar^2 \nabla_1^2) + c^4 (m_2^2 c^2 - \hbar^2 \nabla_2^2) - W^2 \right\}^2 - 4c^4 (m_1^2 c^2 - \hbar^2 \nabla_1^2)(m_2^2 c^2 - \hbar^2 \nabla_2^2) \psi = 0.
\] (9)

The above equation simplifies to

\[
\left[ c^4 (m_1^2 c^2 - \hbar^2 \nabla_1^2)^2 + c^4 (m_2^2 c^2 - \hbar^2 \nabla_2^2)^2 + W^4 - c^4 (m_1^2 c^2 - \hbar^2 \nabla_1^2)(m_2^2 c^2 - \hbar^2 \nabla_2^2)
\right.

\[ -2W^2 c^2 (m_1^2 c^2 - \hbar^2 \nabla_1^2) - 2W^2 c^2 (m_2^2 c^2 - \hbar^2 \nabla_2^2) \] \( \psi = 0. \) (10)

Noting that \( \vec{\nabla}_1 = -\vec{\nabla}_2 = \vec{\nabla} \) implies that \( \nabla_1^2 = \nabla_2^2 = \nabla^2. \)
Ignoring the translational motion of the system and holding the centre of mass at rest, Eqn.(10) reduces to

\[
\left[ W^4 + \left( m_1^4 c^8 + m_2^4 c^8 - 2 m_1^2 m_2^2 c^8 \right) - 2W^2 m_1^2 c^4 - 2W^2 m_2^2 c^4 + 4W^2 c^2 \right] \psi = 0. \tag{11}
\]

It may well be checked that in the case of equal masses, \( m_1 = m_2 = m_0 \), the above equation reduces to

\[
\nabla^2 \psi + \frac{(W^2 - 4m_0^2 c^4)}{4c^2 \hbar^2} \psi = 0, \tag{12}
\]

which is in agreement with the work of Rao et al.

The more general Eqn.(11) may be written in an elegant form as

\[
\left[ \nabla^2 + \frac{W^2 - 2(m_1^2 c^4 + m_2^2 c^4)}{4c^2 \hbar^2} + \frac{(m_1^2 c^4 - m_2^2 c^4)^2}{4W^2 c^2 \hbar^2} \right] \psi = 0 \tag{13}
\]

To test the validity of this equation, we consider various cases.

### 2.1 Single Particle Rotor

For a single particle of rest mass \( m_0 \), rotating about a fixed origin, Eqn.(6), with \( m_1 = m_0 \) and \( m_2 = 0 \), would yield,

\[
\nabla^2 \psi + \left( \frac{W^2 - m_0^2 c^4}{c^2 \hbar^2} \right) \psi = 0 \tag{14}
\]

Expressing \( \nabla^2 \) in spherical polar co-ordinates and noting that \( \frac{\partial R}{\partial r} = 0 \), we write

\[
\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \left( \frac{W^2 - \epsilon^2}{c^2 \hbar^2} \right) \psi = 0 \tag{15}
\]

where \( \epsilon = m_0 c^2 \).

With \( r = a \), \( I = m_0 a^2 \), the moment of inertia of the particle about an axis passing through the origin, the above equation may be written as

\[
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{I (W^2 - \epsilon^2)}{\epsilon \hbar^2} \psi = 0 \tag{16}
\]

Comparing this with the corresponding non-relativistic Schrödinger equation, we immediately obtain,

\[
\frac{I}{\hbar^2 \epsilon} (W^2 - \epsilon^2) = l(l + 1), \tag{17}
\]
where $l$ is an integer.

It follows from above that the energy eigenvalues are

$$ W = \epsilon \sqrt{1 + \frac{l(l+1)\hbar^2}{I\epsilon}} $$

(18)

**Non-relativistic limit**:

Taylor expansion of Eqn. (18) gives

$$ W \approx \epsilon \left(1 + \frac{1}{2} \frac{l(l+1)\hbar^2}{I\epsilon}\right) $$

(19)

Defining $W - \epsilon = E_{N\tau}$, we get the well-known expression for the energies

$$ E_{N\tau} = \frac{l(l+1)\hbar^2}{8\pi^2 I}, \text{ where } l = 0, 1, 2, ... $$

(20)

2.2 Homonuclear system

For a system of two particles of equal masses rotating about the centre of mass, $m_1 = m_2 = m_0$, $I = \mu a^2$ where the reduced mass $\mu = \frac{m_0}{2}$ and $\epsilon = 2m_0c^2$, the rest energy of the system, Eqn.(13) transforms into

$$ \nabla^2 \psi + \frac{(W^2 - \epsilon^2) m}{2\hbar^2 \epsilon} \psi = 0 $$

(21)

which is the appropriate Klein-Gordon equation of the system. As before the eigenenergies correspond to Eqn.(18).

2.3 Heteronuclear System

A more general case is a system of two non-interacting particles of unequal masses rotating about their centre of mass. The energy eigen-values are obtained by solving Eqn.(13).

Expressing $\nabla^2$ in spherical polar coordinates, as before and observing that it transforms to the \(\left(\frac{-L^2}{\hbar^2}\right)\) operator with eigenvalues $l(l+1)$, we write

$$ a^2 \frac{\{W^2 - 2(m_1^2c^4 + m_2^2c^4)\}}{4c^2\hbar^2} + \frac{a^2 (m_1^2c^4 - m_2^2c^4)^2}{4W^2c^2\hbar^2} = l(l+1) $$

(22)

Writing $\alpha = m_1^2c^2$, $\beta = m_2^2c^2$, it is obvious to check that the above equation may be written as

$$ a^2 W^4 - (A + B)W^2 + C = 0, $$

(23)
where

\[ A = 2a^2 (\alpha^2 + \beta^2) \]

\[ B = 4l (l + 1) c^2 \hbar^2 \]

\[ C = a^2 (\alpha^2 - \beta^2)^2 \]

Eqn.(23) is solved using Mathematica\(^4\). Obviously, from the solution of the above equation for equal masses one should recover the energies of the homonuclear system. Hence of the four solutions, two of them being zero and the other being negative, are rejected and the only admissible solution is

\[
W = \left[ (m_1 c^4 + m_2 c^4) + \frac{2l}{a^2} (l+1)c^2 \hbar^2 + \frac{2}{a^2} \sqrt{(m_1 c^4 + m_2 c^4)(m_2 c^4 a^2 + l(l+1)c^2 \hbar^2)} \right]^2 \tag{24}
\]

The eigenenergies of a heteronuclear rotor are explicitly obtained from the above equation

**Non-relativistic limit**

To arrive at the non-relativistic limit of Eqn.(24), we first square the expression and then use the Taylor expansion for the term within the square root. This leads to

\[
W^2 = \epsilon^2 \left[ 1 + \frac{4 l (l + 1) c^2 \hbar^2}{\epsilon^2} + \frac{2}{a^2} \frac{(m_1 c^2 - m_2 c^2)^2 l (l + 1) c^2 \hbar^2}{\epsilon^2 \{m_1 c^2 m_2 c^2 a^2 + l (l + 1) c^2 \hbar^2\}} \right] \tag{25}
\]

where \( \epsilon = m_1 c^2 + m_2 c^2 \) is the total rest energy of the system.

The relativistic correction is made evident by the binomial expansion of Eqn.(25) which gives

\[
W \approx \epsilon + \frac{2l (l + 1) c^2 \hbar^2}{a^2 \epsilon} + \frac{1}{2} \frac{(m_1 c^2 - m_2 c^2)^2 l (l + 1) c^2 \hbar^2}{\epsilon \{m_1 c^2 m_2 c^2 a^2 + l (l + 1) c^2 \hbar^2\}} \tag{26}
\]

While the first term corresponds to the rest energy of the system, the second refers to the NR term and the third gives first relativistic correction.

It is straightforward to check that

\[
E_{Nr} = \frac{2l (l + 1) \hbar^2}{I} \frac{\mu}{M} \tag{27}
\]

where \( \mu = \frac{m_1 m_2}{m_1 + m_2} \), \( I = \mu a^2 \) and \( M = m_1 + m_2 \) as before.

In the case of equal masses, we recover the well-known expression for the energies of the non-relativistic rigid rotator.
Relativistic Rotational Coefficient

In spectroscopic calculations, the rotational constant, $B$, is an important parameter, characteristic of the molecule. It is seen that the energy spectrum of a non-relativistic rigid rotator consists of a series of equidistant lines, the first one lying at $2B$ and the separation of successive lines also being $2B$.

Eqn.(26) may be written as

$$W_{KG} = \epsilon + l(l+1)hc \left[ \frac{h}{4\pi^2 Ic} \frac{2\mu}{M} \left\{ 1 + \frac{(m_1 - m_2)^2 a^2}{4(m_1 m_2 c^2 a^2 + l(l+1)\hbar^2)} \right\} \right]$$  \hspace{1cm} (28)

Apparently, the second term within the brackets may rightly be called the ‘energy correction term’ resulting due to unequal masses. This term highlights the effect of going from homonuclear to heteronuclear species.

The above equation may be put in a compact form as

$$W_{KG} = \epsilon + l(l+1)hc B_{Rel}$$  \hspace{1cm} (29)

where

$$B_{Rel} = \frac{h}{4\pi^2 Ic} \frac{2\mu}{M} \left\{ 1 + \frac{(m_1 - m_2)^2 a^2}{4(m_1 m_2 c^2 a^2 + l(l+1)\hbar^2)} \right\}$$  \hspace{1cm} (30)

$B_{Rel}$ may be called the $l$-dependent Relativistic Rotational Coefficient. In the case of equal masses,

$$B_{Rel} = \frac{h}{8\pi^2 Ic} ,$$  \hspace{1cm} (31)

which is in agreement with the well-known rotational constant, $B$ of non-relativistic theory. Thus Eqn. (31) for homonuclear molecules is only a special case of the more general equation (Eqn.30) applicable to heteronuclear molecules.

Energy Spectrum

Starting from Eqn.(25) and carrying out the Taylor expansion up to the first order, one can readily obtain

$$W_{KG} = \epsilon + l(l+1)hcB_{Rel} - \frac{l^2 (l+1)^2 \hbar^2 c^2 B_{Rel}^2}{2\epsilon}$$  \hspace{1cm} (32)

which may be written as

$$W_l = \epsilon + l(l+1)hc(B + B_l) - \frac{l^2 (l+1)^2 \hbar^2 c^2}{2\epsilon} (B + B_l)^2$$  \hspace{1cm} (33)

where
\[ B = \frac{\hbar}{4\pi^2 Ic} \frac{2\mu}{M} \]  

(34)

and

\[ B_l = B \frac{(m_1 c^2 - m_2 c^2)^2 a^2}{4 (m_1 c^2 m_2 c^2 a^2 + l (l + 1) c^2 \hbar^2)}. \]  

(35)

Essentially, for a rotor having unequal masses, each level is shifted differently. The rotational constant is trivially modified and \( B_l \) may be interpreted as the relativistic correction term to the rotational constant, for a given transition.

Eqn.(33) may also be written as

\[ W_l = W_0 + \frac{l^2 (l + 1)^2 h^2 c^2}{2\epsilon} \left( B_l^2 + 2BB_l \right) \]  

(36)

where

\[ W_0 = \epsilon + \frac{l (l + 1) hc B}{2} - \frac{l^2 (l + 1)^2 h^2 c^2 B^2}{2\epsilon} \]  

(37)

It is interesting to note that for equal masses, \( B_l = 0 \) and \( W_l = W_0 \), the empirical formula obtained by Rao et.al.

Introducing the wave number, \( \tilde{\nu}_l = \frac{W_{l+1} - W_l}{hc} \), we obtain for the transition \( l + 1 \to l \),

\[ \tilde{\nu}_l = T_1 + T_2 + T_3 + T_4 + T_5 \]  

(38)

where

\[ T_1 = 2 (l + 1) B \]
\[ T_2 = -\frac{2hc}{\epsilon} B^2 (l + 1)^3 \]
\[ T_3 = (l + 1) \{(l + 2) B_{l+1} - lB_l\} \]
\[ T_4 = -\frac{(l+1)^2 hc}{2\epsilon} \left\{ (l + 2)^2 B_{l+1}^2 - l^2 B_l^2 \right\} \]
\[ T_5 = -\frac{(l+1)^2 hc}{2\epsilon} 2B \left\{ (l + 2)^2 B_{l+1} - l^2 B_l \right\} \]

A more rigorous calculation shows that the terms \( T_3, T_4 \) and \( T_5 \) are mass-dependent and are explicitly given by

\[ T_3 = \frac{B (l + 1) m_1 c^2 m_2 c^2 \left(m_1 c^2 - m_2 c^2\right)^2 a^4}{2 \left(m_1 c^2 m_2 c^2 a^2 + (l + 1) (l + 2) c^2 \hbar^2\right) \left(m_1 c^2 m_2 c^2 a^2 + l (l + 1) c^2 \hbar^2\right)} \]  

(39)
\[ T_3 = \frac{B^2 \hbar c (l+1)^2(l+2)m_1 c^2 m_2 c^2 (m_1 c^2 - m_2 c^2)^2 a^6 \left(m_1 c^2 m_2 c^2 a^2 - 2l (l+1)c^2 \hbar^2\right)\left(m_1 c^2 m_2 c^2 a^2 + l (l+1)c^2 \hbar^2\right)^2}{16 \varepsilon \left(m_1 c^2 m_2 c^2 a^2 + (l+1) (l+2) c^2 \hbar^2\right)^2 \left(m_1 c^2 m_2 c^2 a^2 + l (l+1)c^2 \hbar^2\right)} \]  

\[ T_5 = \frac{B^2 \hbar c (l+2)^2 (m_1 c^2 - m_2 c^2)^2 a^2 \left[2l (l+1) c^2 \hbar^2 + (l+2) m_1 c^2 m_2 c^2 a^2\right]}{2 \varepsilon \left(m_1 c^2 m_2 c^2 a^2 + (l+1) (l+2) c^2 \hbar^2\right)\left(m_1 c^2 m_2 c^2 a^2 + l (l+1)c^2 \hbar^2\right)} \]  

It is straightforward to check that \( T_3, T_4 \) and \( T_5 \) vanish when the masses are equal. While the first two terms of Eqn.(38) correspond to the usual expression for the wave number of the spectral line, the last three terms arising mainly due to unequal masses do contribute to the small relativistic correction in the wave number.

Thus the application of relativistic quantum mechanics to the investigation of the spectra of heteronuclear linear diatomic molecules using the KG equation entails great mathematical complexities in all.

**First Rotational Line**

In the spirit of non-relativistic approximation, we retain \( T_1 \) and \( T_3 \) and neglect all other terms in higher powers of \( B \), to obtain

\[ \bar{\nu}_2 = 2 (l+1) B + (l+1) \{(l+2) B_{l+1} - l B_l\}. \]  

The first rotational line occurs at \( l = 0 \), leading to

\[ \bar{\nu}_0 = 2B + 2B_1. \]  

It is trivial to check that

\[ \bar{\nu}_0 = \frac{B}{2} \left[ \frac{M^2 c^2 a^2 + 8 \hbar^2}{\mu M c^2 a^2 + 2 \hbar^2} \right] \]  

where \( m_1 m_2 = \mu M \) is implied. In units of Compton wavelength expressing \( \tilde{a} = \frac{a}{\hbar/Mc} \) and \( \tilde{a}_0 = \frac{a}{\hbar/\mu c} \), we obtain

\[ \bar{\nu}_0 = \frac{B}{2} \left[ \tilde{a}^2 + 8 \tilde{a} \tilde{a}_0 + 2 \right]. \]  

For equal masses, \( \bar{\nu}_0 = 2B \), by virtue of Eqn.(42). It is thus seen that the allowed transitions for homonuclear diatomic molecules are regularly spaced at an interval of \( 2B \). However, for a heteronuclear KG rotor, the lines are no longer exactly equidistant. Apparently, the measurement and identification of one of the spectral lines allows us to calculate the moment of inertia and then the bondlength of the molecule.
3 Results and Discussion

A rigid rotator approximates a diatomic molecule when vibrational motion is ignored. In literature, the energy spectrum of a rigid rotator is investigated non-relativistically using the Schrodinger equation. In the present article, we have introduced the notion of the ‘relativistic rotator’ and obtained the eigen energies relativistically. To investigate the energy spectrum of spin zero homonuclear and heteronuclear systems, we solve the Klein-Gordon equation in the centre of mass frame. Step by step elimination of the square root of an operator results in the fourth order equation in $W$, from which the eigen-energies are extracted. This novel approach can be extended to spin half systems, as well.

Apparently, it is seen that the eigenenergies of heteronuclear systems reduce to those of homonuclear species when $m_1 = m_2$, and have an appropriate non-relativistic limit. It is seen that the level spacing which is equidistant for a non-relativistic rotator is not so for a relativistic rotor. Interestingly, the first rotational line of a non-relativistic rotator and that of a Klein-Gordon rotor occurs at $2B$. While it is known that the pure rotation spectrum of a diatomic molecule consists of equispaced lines, that of a relativistic rotator is not so.

It has been established that the rotational constant of homonuclear and heteronuclear diatomic molecules depend on the electronegativity of the constituent atoms\(^6\). Relativistic studies, apart from having immense pedagogical value are also of practical use in the light of ever increasing accuracies of modern experimental methods.

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