On a model for rotational tunneling with a $C_6$-space-time symmetric analog

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Abstract
We analyze the simple model of a rigid rotor with $C_3$ symmetry and show that the use of parity simplifies considerably the calculation of its eigenvalues. We also consider a non-Hermitian space-time-symmetric counterpart that exhibits real eigenvalues and determine the exceptional point at which the antiunitary symmetry is broken.

1 Introduction
Rotational tunnelling takes place when groups of atoms in a molecule rotate, as an almost rigid structure, about a single bond. When the barriers between different nuclear configurations are sufficiently high some of the lowest states exhibit close energies and the transition between them can be investigated by

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suitable spectroscopies [1–3]. A typical example is provided by the methyl group (−CH$_3$).

Rotational symmetry is commonly studied by means of simple models based on effective Hamiltonians for properly chosen restricted rigid rotors [1–6]. In some cases a single rotor model provides an acceptable description of the experimental data but in others one has to resort to a set of coupled rotors. The Schrödinger equation for such models has been solved in more than one way [4–6].

In this paper we are interested in a well known algorithm for the solution of band matrices [7–10] that may be a convenient alternative approach to the iterative matrix inversion proposed several years ago [4]. Although today the diagonalization of a band matrix offers no difficulty we think that such alternative methods may still be of interest. In addition to the comparison of the methods for solving the eigenvalue equation we want to point out that the case of a small rotational barrier (or large quantum numbers) may lead to numerical errors due to almost degenerate rotational states.

In addition to what has just mentioned we will also discuss a space-time ($ST$) symmetric non-Hermitian version of the effective Hamiltonian for the restricted rotor that takes place when the barrier height is allowed to be purely imaginary. This kind of problems have been intensely studied in recent years (see [12] for an earlier review on the issue and also [13, 14] for closely related models).

In section 2 we discuss the problem of nearly degenerate energies by means of a simple rigid-rotor model with symmetry $C_3$. In section 3 we show how to go around such difficulty by means of symmetry arguments. In section 4 we consider the $ST$-symmetric non-Hermitian counterpart and determine the regions of exact and broken $ST$ symmetry. Finally, in section 5 we summarize the main results of the paper and draw conclusions.

2 Restricted-rotor model

For concreteness, in this paper we consider the rotation of a group of atoms hindered by a potential $V(\phi)$ with periodicity $V(\phi + 2\pi/3) = V(\phi)$. It is commonly
expanded in a Fourier series of the form

\[ V(\phi) = \sum_{j=0}^{\infty} V_{3j} \cos(3j\phi). \]  

(1)

For present discussion it is sufficient to consider just the leading term so that the hindered rotator is given by the effective Hamiltonian operator

\[ H = -B \frac{d^2}{d\phi^2} + V(\phi), \quad V(\phi) = V_3 \cos(3\phi), \]  

(2)

where the magnitude of the rotational constant \( B = \frac{\hbar^2}{2I} \) is determined by the moment of inertia \( I \) of the rotor. It is convenient to measure the energy \( E \) in units of \( B \) so that the dimensionless Schrödinger equation becomes

\[ H\psi = \epsilon\psi, \quad H = -\frac{d^2}{d\phi^2} + V(\phi), \quad V(\phi) = \lambda \cos(3\phi), \]

\[ \epsilon = \frac{E}{B}, \quad \lambda = \frac{V_3}{B}. \]  

(3)

Since the potential is periodic of period \( 2\pi/3 \) the eigenfunctions form basis for the irreducible representations \( A \) and \( E \) of the symmetry group \( C_3 \). Therefore, the Fourier expansions for the eigenfunctions are of the form

\[ \psi_s(\phi) = \sum_{j=-\infty}^{\infty} c_{j,s} f_{j,s}(\phi), \quad f_{j,s}(\phi) = \frac{1}{\sqrt{2\pi}} e^{i(3j\phi+s)}, \quad s = 0, \pm 1, \]  

(4)

where the subscripts \( s = 0 \) and \( s = \pm 1 \) correspond to the symmetry species \( A \) and \( E \), respectively. By means of the Fourier expansions (4) the Schrödinger equation (3) becomes a three-diagonal secular equation

\[ \lambda c_{m-1,s} + 2 \left[ \epsilon - (3m+s)^2 \right] c_{m,s} + \lambda c_{m+1,s} = 0, \quad m = 0, \pm 1, \pm 2, \ldots \]  

(5)

In practice we truncate the secular equation (5) and solve a matrix eigenvalue problem of dimension, say, \( 2N + 1 \). However, some time ago Häusler and Hülle [4] proposed an iterative method, based on matrix inversion, that avoids matrix diagonalization. Today, such diagonalization can be carried out most easily even in the most modest personal computer. Nonetheless, we want to point
out to an even simpler strategy proposed some time ago \cite{7-10} that consists in solving the secular equation (5) as a recurrence relation. The truncation of the secular equation just mentioned is equivalent to setting the boundary conditions \( c_{m,s} = 0 \) for \( |m| > N \) in the recurrence relation (5). Therefore, if we set \( c_{-N,s} = 1 \) we can calculate \( c_{j,s} \) for \( j = -N + 1, -N + 2, \ldots \) so that the roots of \( c_{N+1,s}(\epsilon) = 0 \) are exactly the roots of the characteristic polynomial of the secular matrix of dimension \( 2N + 1 \) that yield estimates of the energies of the problem.

In what follows \( \epsilon_{0,s}(\lambda) < \epsilon_{1,s}(\lambda) < \epsilon_{2,s}(\lambda) < \ldots \) denote the energies of the hindered rotor. When \( \lambda = 0 \) the \( A \) states are \( \epsilon_{0,0}^{(0)} = 0, \epsilon_{2n-1,0}^{(0)} = \epsilon_{2n,0}^{(0)} = 9n^2, n = 1, 2, \ldots \). On the other hand, the \( E \) states are doubly degenerate for all \( \lambda \geq 0 \) and for \( \lambda = 0 \) satisfy \( (3n - 1)^2 = (-3n + 1)^2 \) which are obviously treated separately. In other words, the hindered potential splits the doubly degenerate \( A \) states while the \( E \) ones can be treated as nondegenerate with symmetry quantum numbers \( s = -1 \) (\( E_a \)) and \( s = 1 \) (\( E_b \)). For this reason the calculation of the latter eigenvalues is much simpler.

When \( \lambda \) is sufficiently small the eigenvalues \( \epsilon_{2n-1,0}(\lambda) \) and \( \epsilon_{2n,0}(\lambda) \) are quasi degenerate which may make their numerical calculation somewhat difficult. An example is given in Figure 1 that shows the characteristic polynomial \( P(\epsilon) \) for \( \lambda = 0.1 \) properly scaled to reduce its size. We clearly see that the splitting of the degenerate states is considerably smaller for \( n = 2 \) than for \( n = 1 \). In general, the magnitude of the splitting \( \epsilon_{2n,0}(\lambda) - \epsilon_{2n-1,0}(\lambda) \) decreases as \( n \) increases so that the problem also appears for greater values of \( \lambda \) if the quantum number is large enough. Some algorithms may fail to find the almost identical roots of \( P(\epsilon) \) if the accuracy of the calculation is insufficient. For \( \lambda = 0.1 \) the corresponding eigenvalues are \( \epsilon_{1,0} = 8.99990740760586, \epsilon_{2,0} = 9.00046293268167, \epsilon_{3,0} = 36.000370368357 \) and \( \epsilon_{4,0} = 36.000370373120 \).

The application of perturbation theory is most revealing. When \( \lambda \neq 0 \) the perturbation expansions for the first \( A \) eigenvalues are

\[
\epsilon_{0,0} = -\frac{1}{18} \lambda^2 + \frac{7}{23328} \lambda^4 - \frac{29}{8503056} \lambda^6 + \ldots,
\]
\[
\begin{align*}
\epsilon_{1,0} &= 9 - \frac{1}{108} \lambda^2 + \frac{5}{2519424} \lambda^4 - \frac{289}{293865615360} \lambda^6 + \ldots, \\
\epsilon_{2,0} &= 9 + \frac{5}{108} \lambda^2 - \frac{2519424}{763} \lambda^4 + \frac{293865615360}{1002401} \lambda^6 + \ldots, \\
\epsilon_{3,0} &= 36 + \frac{1}{270} \lambda^2 - \frac{317}{157464000} \lambda^4 + \frac{10044234900000}{5701} \lambda^6 + \ldots, \\
\epsilon_{4,0} &= 36 + \frac{1}{270} \lambda^2 + \frac{433}{157464000} \lambda^4 - \frac{10044234900000}{5861633} \lambda^6 + \ldots, \\
\epsilon_{5,0} &= 81 + \frac{1}{630} \lambda^2 + \frac{8001504000}{187} \lambda^4 - \frac{342986069260800000}{6743617} \lambda^6 + \ldots, \\
\epsilon_{6,0} &= 81 + \frac{1}{630} \lambda^2 + \frac{8001504000}{187} \lambda^4 + \frac{342986069260800000}{6743617} \lambda^6 + \ldots 
\end{align*}
\]

We appreciate that \(\epsilon_{2n,0}(\lambda) - \epsilon_{2n-1,0}(\lambda) = O(\lambda^{2n})\). We did not apply the standard perturbation theory for degenerate states because it is rather impractical in the present case; instead we obtained the perturbation expansions from the characteristic polynomial for sufficiently large values of \(N\).

### 3 Parity

In order to solve the problem posed by the quasi-degenerate \(A\) states we take into account that the potential is parity invariant: \(V(-\phi) = V(\phi)\). If \(P\) denotes the parity operator then \(P\psi_s(\phi) = \psi_s(-\phi) = \psi_{-s}(\phi)\) transforms states \(E_a\) into \(E_b\) but the \(A\) states remain as such. This fact allows us to separate the latter states into even and odd ones:

\[
\begin{align*}
\psi_{A_+}(\phi) &= c_0 \frac{1}{\sqrt{2\pi}} + \sum_{j=1}^{\infty} c_j \frac{1}{\sqrt{\pi}} \cos(3j\phi), \\
\psi_{A_-}(\phi) &= \sum_{j=1}^{\infty} c_j \frac{1}{\sqrt{\pi}} \sin(3j\phi).
\end{align*}
\]

In this way we have a secular equation

\[
\begin{align*}
\epsilon c_0 + \frac{\lambda}{\sqrt{2}} c_1 &= 0, \\
\frac{\lambda}{\sqrt{2}} c_0 + (\epsilon - 9) c_1 + \frac{\lambda}{2} c_2 &= 0, \\
\frac{\lambda}{2} c_{n-1} + (\epsilon - 9n^2) c_n + \frac{\lambda}{2} c_{n+1} &= 0, \quad n = 2, 3, \ldots
\end{align*}
\]

5
for the $A_+$ states and another one

$$\frac{\lambda}{2}c_{n-1} + (\epsilon - 9n^2)c_n + \frac{\lambda}{2}c_{n+1} = 0, \quad n = 2, 3, \ldots ,$$

(9)

for the $A_-$ states. This analysis based on parity is similar to using the symmetry point group $C_{3v}$ where the states labelled here as $A_+$ and $A_-$ belong to the symmetry species $A_1$ and $A_2$, respectively, and the effect of the parity operator is produced by one of the reflection planes $\sigma_v$.

In this way, the recurrence relations (or the corresponding tri-diagonal matrices) do not exhibit close roots for any value of $\lambda$ and the calculation is considerably simpler. If we choose $c_j = 0$ for $j < 0$ and $c_0 = 1$ we can calculate $c_j$ for all $j > 0$ and obtain the $A_+$ eigenvalues from the termination condition $c_N(\epsilon) = 0$ for sufficiently large $N$. Exactly in the same way with $c_j = 0$ for $j < 1$ and $c_1 = 1$ we obtain the $A_-$ energies of the restricted rotor. The perturbation expansions for the first eigenvalues suggest that $\epsilon_{2n-1,0}$ is $A_+$ while $\epsilon_{2n,0}$ is $A_-.

For large values of $\lambda$ the eigenvalues behave asymptotically as

$$\epsilon_v = -\lambda + 3\sqrt{\frac{\lambda}{2}(2v + 1)} + O(1).$$

(10)

Figure 2 shows the lowest eigenvalues for states of symmetry $A$ and $E$ calculated with the expressions indicated above.

4 Space-time symmetry

The unitary operator $U = C_6$ that produces a rotation by an angle of $2\pi/6$ leads to the transformation $UV(\phi)U^{-1} = V(\phi + \pi/3) = -V(\phi)$ and $UH(\lambda)U^{-1} = H(-\lambda)$. From its application to the eigenvalue equation $H(\lambda)\psi_n = \epsilon_n(\lambda)\psi_n$, $UH(\lambda)U^{-1}\psi_n = H(-\lambda)U\psi_n = \epsilon_n(\lambda)U\psi_n$, we conclude that $\epsilon_n(\lambda)$ is also an eigenvalue $\epsilon_m(-\lambda)$ of $H(-\lambda)$. Since $\psi_n$ and $U\psi_n$ belong to the same symmetry species ($A_+, A_-, E_a, E_b$) and $\lim_{\lambda \to 0} \epsilon_m(-\lambda) = \lim_{\lambda \to 0} \epsilon_n(\lambda)$ then we conclude that $m = n$ and $\epsilon_n(-\lambda) = \epsilon_n(\lambda)$ which explains why the perturbation expansions for the eigenvalues of $H(\lambda)$ have only even powers of $\lambda$:

$$\epsilon_n(\lambda) = \sum_{j=0}^{\infty} \epsilon_n^{(2j)}\lambda^{2j}.$$
This result suggests that \( \epsilon_n(i g) \) is real for \( g \) real, at least for sufficiently small values of \( |g| \). This conclusion is consistent with the fact that \( H(i g) \) is \( S T \) symmetric \(^{16, 17} \) with respect to the transformation given by the antiunitary operator \(^{18} U T \) as follows from \( U T H(i g) T U^{-1} = H(i g) \), where \( T \) is the time-reversal operator \( T H T^* = H^\ast \) and the asterisk denotes complex conjugation.

The antiunitary symmetry tells us that the eigenvalues are either real or appear as pairs of complex conjugate numbers. If the antiunitary symmetry is exact \( (A \psi = a \psi) \) then the eigenvalues are real, otherwise we say that it is broken. In the present case we know, from the analysis based on perturbation theory, that this symmetry is exact for sufficiently small values of \( |g| \).

A straightforward calculation, like the one in the preceding section, confirms that the perturbation series for the \( E \) states also have only even powers of \( \lambda \)

\[
\begin{align*}
\epsilon_{0,\pm 1} &= 1 - \frac{1}{10} \lambda^2 + \frac{83}{32000} \lambda^4 - \frac{4581}{3080000} \lambda^6 + \ldots, \\
\epsilon_{1,\pm 1} &= 4 + \frac{1}{14} \lambda^2 - \frac{143}{5480} \lambda^4 + \frac{2601}{1747920} \lambda^6 + \ldots, \\
\epsilon_{2,\pm 1} &= 16 + \frac{1}{110} \lambda^2 + \frac{383}{3726800} \lambda^4 - \frac{72621}{958253450000} \lambda^6 + \ldots, \\
\epsilon_{3,\pm 1} &= 25 + \frac{1}{182} \lambda^2 + \frac{385828352}{305329233764} \lambda^4 + \frac{144549}{303529233764} \lambda^6 + \ldots, \\
\epsilon_{4,\pm 1} &= 49 + \frac{1}{374} \lambda^2 + \frac{1043}{8370179840} \lambda^4 + \frac{90081}{336001341687040} \lambda^6 + \ldots.
\end{align*}
\]

In this case the interaction potential does not break the two-fold degeneracy.

Since \( \langle \cos(3\phi) \psi | \cos(3\phi) \psi \rangle \leq \langle \psi | \psi \rangle \) for all \( \psi \) the series \(^{11} \) has a finite radius of convergence \(^{19} \) and \( \epsilon_n(i g) \) will be real in the region of analyticity. More precisely, a given eigenvalue \( \epsilon(i g) \) is real for all \( |g| < |g_e| \) where \( g_e \) is an exceptional point where two eigenvalues coalesce as shown in Figure 3 for the two lowest eigenvalues of symmetry \( E \) and \( A \). For \( |g| > |g_e| \) the coalescing eigenvalues become a pair of complex conjugate numbers. There are simple and efficient numerical methods for the calculation of the exceptional points for quantum mechanical models similar to this one \(^{20} \); for the first two \( E \) and \( A \) states shown in Figure 3 we obtained \( |g_{e1}| = 2.9356105095073260590 \), \( \epsilon(g_{e1}) = 2.6226454301444952679 \) and \( |g_{e2}| = 6.6094587620331389653 \), \( \epsilon(g_{e2}) = 4.6995725311868146666 \), respectively. Figure 4 shows that the exceptional points
increase with the quantum number which leads to the conclusion that the $ST$ symmetry is exact for all $|g| < |g_{e1}|$.

Some time ago Bender and Kalveks [13] and Fernández and Garcia [14] discussed other space-time-symmetric hindered rotors with somewhat different symmetries and calculated several exceptional points. In particular, the latter authors estimated the trend of the location of the exceptional points in terms of the quantum numbers of the coalescing states.

5 Conclusions

We have shown that the use of parity considerably simplifies the calculation of the eigenvalues with eigenfunctions of symmetry $A$ of the restricted rigid rotor with $C_3$ symmetry. This strategy is particularly useful in the case of small barriers or large quantum numbers. We are aware that this situation is not commonly encountered in most physical applications of the model [1–6] but we think that it is worth taking into account the difficulties that it may rise.

We have also shown that this simple model exhibits a non-Hermitian $ST$-symmetric counterpart with real eigenvalues for sufficiently small $|\lambda| = |g|$ and obtained the exceptional point $g_e$ that determines the phase transition between exact and broken $ST$ symmetry. In this way we added another member to the family of similar problems intensely investigated in the last years [12] (and references therein).

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Figure 1: Scaled characteristic polynomial $P(\epsilon)$ for $\lambda = 0.1$
Figure 2: Lowest eigenvalues $\epsilon(\lambda) + \lambda$ of symmetry $E$ (upper panel) and $A$ (lower panel)
Figure 3: First two eigenvalues $\epsilon(ig)$ of symmetry $E$ (upper panel) and $A$ (lower panel)
Figure 4: Lowest eigenvalues $\epsilon(ig)$ of symmetry $E$ (upper panel) and $A$ (lower panel)