Quasi-exactly solvable double Morse potential and proton tunnelling in hydrogen bonded crystals by

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An overview

Starting from the concept of quasi-exactly solvable quantum systems, we present solutions to the Schrödinger equation with the double Morse potential, consisting of two back-to-back Morse functions. The resulting differential equation is found to be quasi-exactly solvable and closed form energies and wavefunctions are obtained using the Bethe ansatz method. The results obtained are used as prototype description for the of hydrogen-bonded crystals CrOOH and CrOOD.

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Outline

Part A: Quasi-exactly Solvable Quantum Systems

- Brief introduction to quasi-exactly solvable systems
- Characterizations of quasi-exactly solvable operators
- Exact polynomial solutions to quasi-exactly solvable models.

Part B: Proton Tunnelling in Hydrogen Bonded Crystals: Chromous Acids

- Some previous works and experimental results
- The double Morse potential
- Applications to tunnelling in chromous acids

Part C: Summary & Conclusions

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PART A *Quasi-exactly Solvable Quantum Systems*

Basic Definitions

Let \mathcal{E}_k and \mathcal{T}_k be two linear differential operators of order k which are defined on a given space \mathcal{H} and \mathcal{M}_n be a non-trivial finite-dimensional subspace of \mathcal{H} defined by

$$\mathcal{M}_n = \langle \phi_1, \dots, \phi_n \rangle, \qquad \phi_i \in \mathcal{H}$$
(1)

then

- Definition 1.1 T_k is said to be *quasi-exactly solvable* (QES) if it preserves the space M_n i.e T_kM_n ⊂ M_n. In other words, only a part of the spectrum is exactly obtainable.
- Definition 1.2 *E_k* is called *exactly-solvable*, if it preserves the complete flag of subspace *M*₁ ⊂ *M*₂ ⊂ *M*₃ ⊂ ... *M_n* ⊂ In other words, the spectrum is completely obtainable exactly.
- **Definition 1.3** We define a finite-dimensional polynomial space of order *n* by

$$\mathcal{P}_{n+1} = \langle 1, x, x^2, \dots, x^n \rangle, \qquad x \in \mathbb{R}.$$
 (2)

Lie-Algebraic QES Systems

These class of QES systems are characterized with the following results (where $D_x \equiv \frac{d}{dx}$):

Lemma 2.1.

Given that n > (k - 1) [or $n \le (k - 1)$], the operator $\mathcal{T}_k(x, D_x)$ is QES if it can be represented by a k-th degree [or n-th degree] polynomial of operators

$$J^{+} = x^{2}D_{x} - nx,$$

$$J^{0} = xD_{x} - \frac{n}{2},$$

$$J^{-} = D_{x},$$
(3)

which satisfy the sl₂ commutation relations $[J^{\pm}, J^0] = \mp J^{\pm}$ and $[J^+, J^-] = -2J^0$.

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Lie-Algebraic QES Systems

Remark 2.3 It is obvious therefore from Lemma 2.1 that among QES operators, there exist exactly-solvable operators: E_k(x, D_x) ⊂ T_k(x, D_x).

Moreover, the above results lead to the following important theorem

Theorem 2.4 [Turbiner, 1994]

Let n be a non-negative integer. The eigenvalue problem for a linear differential operator of k-th order in one variable

$$\mathcal{T}_k(x, D_x)\phi(x) = \epsilon\phi(x)$$
 (4)

where $\mathcal{T}_k(x, D_x)$ is symmetric, has (n + 1) linearly independent eigenfunctions in the form of a polynomial in variable x of order not higher than n, if and only if $\mathcal{T}_k(x, D_x)$ is QES. The problem has an infinite sequence of polynomial eigenfunctions, if and only if the operator is exactly-solvable.

Non Lie-algebraic QES Systems

It is important to note that not all QES systems are Lie-algebraic. We illustrate this phenomenon using a following Hamiltonian

The deformed sextic Hamiltonian

Consider the one dimensional Hamiltonian

$$H_s = -D_{xx} + V(x) \tag{5}$$

where

$$V(x) = A^{2}x^{6} + 2ABx^{4} + (B^{2} + (1 - 4n)A)x^{2} + 4\frac{x^{2} - 1}{(x^{2} + 1)^{2}}$$
(6)

is the deformed sextic potential, with

$$A = \frac{a}{n-a} \left(a - 1/2 \right)$$

$$B = \frac{a}{n-a} \left(3a - 2n + \frac{n}{2a} - 1 \right)$$

a being an arbitrary real parameter.

(7)

The deformed sextic Hamiltonian

Introducing parameter $z = x^2$ along with the gauge transformation $T_s = \mu(z)^{-1} H_s \mu(z)$, where

$$\mu(z) = \frac{1}{z+1} \exp\left(-\frac{A}{4}z^2 - \frac{B}{2}z\right),$$
(8)

then H_s transforms to

$$T_s(z) = 4 (T_1 + T_2 - AT_3)$$
(9)

where

$$T_{1} = (z-1)D_{zz} + (az - a - 1)D_{z},$$

$$T_{2} = D_{zz} + 2\left(a - \frac{1}{1-z}\right)D_{z} - \frac{2a}{z-1},$$

$$T_{3} = (z-1)(z-1-n/a)D_{z} - n(z-1)$$
(10)

It is straightforward to realize that due to the rational term in $T_s(z)$, the operator does not belong to the class of Lie-algebraic potentials, however, it is QES because it leaves invariant the module

$$\mathcal{M}_n(z) = \langle 1 - a(z-1), (z-1)^2, (z-1)^3, \dots, (z-1)^n \rangle$$
(11)

Bethe Ansatz Method

If we consider a second order differential equation of the form

$$\left[P(t)\frac{d^2}{dt^2} + Q(t)\frac{d}{dt} + W(t)\right]S(t) = 0$$
(12)

where

$$P(t) = \sum_{k=0}^{4} p_k t^k, \qquad Q(t) = \sum_{k=0}^{3} q_k t^k, \qquad W(t) = \sum_{k=0}^{2} w_k t^k, \tag{13}$$

where p_k , q_k and w_k are constants, then we can summarize the main results in the following theorem

Theorem 3.1. [Zhang, 2012]

Given a pair of polynomials P(t) and Q(t), then the values of the coefficients w_k of the polynomial W(t) such that the differential equation (12) has degree *n* polynomial solution

$$S(t) = \prod_{i=1}^{n} (t - t_i)$$
 (14)

with distinct roots t_1, t_2, \ldots, t_n are given by

Bethe Ansatz Method

$$w_2 = -n(n-1)p_4 - nq_3,$$
 (15)

$$w_1 = -[2(n-1)p_4 + q_3] \sum_{i=1}^n t_i - n(n-1)p_3 - nq_2, \quad (16)$$

$$w_0 = -[q_3 + 2(n-1)p_4] \sum_{i=1}^n t_i^2 - 2p_4 \sum_{i$$

$$-\left[2(n-1)p_3+q_2\right]\sum_{i=1}t_i-n\left[(n-1)p_2+q_1\right],$$
(17)

where the roots t_1, t_2, \ldots, t_n satisfy the Bethe ansatz equations

$$\sum_{j\neq i}^{n} \frac{2}{t_i - t_j} + \frac{q_3 t_i^3 + q_2 t_i^2 + q_1 t_i + q_0}{p_4 t_i^4 + p_3 t_i^3 + p_2 t_i^2 + p_1 t_i + p_0} = 0, \qquad i = 1, 2, \dots, n$$
(18)

Equations (15)–(18) give all polynomials W(t) such that the differential equation (12) has degree *n* polynomial solutions (14).

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Corollary 3.2 (A Special Case)

Given that $q_3 = -2(n-1)p_4$, then the ODE (12) has (n+1) polynomial solutions S(t), because if we write Eq. (12) as

$$HS(t) = -w_0 S(t), \tag{19}$$

then we show that H is an element of the sl_2 enveloping algebra \mathcal{U}_{sl_2} ,

$$H = p_4 J^+ J^+ + p_3 J^+ J^0 + p_2 J^0 J^0 + p_1 J^0 J + p_0 J^- J^- + \left[\frac{1}{2}(3n-2)p_3 + q_2\right] J^+ + \left[(n-1)p_2 + q_1\right] J^0$$
(20)
$$+ \left(\frac{n}{2}p_1 + q_0\right) J^- + \frac{n}{2} \left[(n-1)p_2 - \frac{n}{2}p_2 + q_1\right].$$

Thus, any second order differential operators belonging to U_{sl_2} must have (n + 1) linearly independent polynomial solutions.

Detailed proofs can be found in Zhang (2012). Also, the above method can be easily generalized to differential equations with higher degree polynomials P(t), Q(t) and W(t), provided that deg $W(t) < \deg Q(t)$, see for example Agboola and Zhang (2012), Agboola (2012).

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PART B

Proton Tunnelling in Hydrogen Bonded Crystals: Chromous Acids

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Some previous works

- Using infra-red data spectroscopy, Snyder and Ibers (1962), concluded that the O-H-O bond in HCrO₂ (chromous acid) is symmetric, whereas the O-D-O bond in DCrO₂ (deuteriated chromous acid) is asymmetric. And also suggested the use of a double minimum potential with high barrier for CrOOD and one with a very low barrier for CrOOH for the spectrum description of the chromous acid.
- Hamilton and Ibers (1963) used neutron diffraction study to further proved the asymmetric nature of O–D–O bond in polycrystalline DCrO₂.
- Christensen, Hansen and Lehmann (1976) who performed more extensive neutron diffraction on CrOOH and CrOOD and concluded that at room temperature, the O-D-O bonds are non centrosymmetric, while the O-H-O bond at room temperature is extensively short.
- With the help of X-ray diffraction, Douglass (1957) determined the crystal structure of CrOOH and found that the structure is best refined in the space group $R\bar{3}m$ (Trigonal).

Some previous works

- Lawrence and Robertson (1981), used the one-dimensional double Morse potential to analyse the I.R. spectra of both CrOOH and CrOOD. They pointed out the advantages of the double Morse potential for the description of the O-H-O bond CrOOH and then used the WKB approximation to solve the corresponding differential equation.
- Using the incoherent inelastic neutron scattering, Tomkinson *et al* (1985) obtained a broad band centred at ~ 2050cm⁻¹, which they assigned to the $|1\rangle \rightarrow |2\rangle$ transition. They showed that the assignment of 1650cm⁻¹ for this transition is too low and has a poor agreement with experiments.

Motivation

• The descriptions of the O–H–O bond in this chromous acids remain problems of interest because most often, the absorption bands associated directly with the hydrogen bond are obscured through their interaction with other vibrational modes of the system being studied. As a result, there is yet no complete satisfactory explanation for some experimentally observed results.

The Double Morse Well



Figure : Pictorial representation of O-H-O bond in chromous acids

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Proton Tunnelling in Hydrogen Bonded Crystals

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The Double Morse Potential

The double Morse potential is a combination of two back-to-back Morse functions and its of the form

$$V(x) = D\left[\frac{A^2}{2}\cosh(2\alpha x) - 2A\cosh(\alpha x)\right], \qquad A = 2e^{-\alpha(R-r_0)}$$
(21)

where D, α , r_0 are the usual Morse parameters and 2R is the oxygen-oxygen separation across the hydrogen bond, and x represents the displacement of the proton or deuteron from the centre of the hydrogen bond.

- **Remark 4.1** It is important to note that the parameters D and α should not be too closely identified with those of the diatomic molecule, as D is not to be interpreted as a dissociation energy in the present context. For each case, the parameters of potential (21) are estimated by fitting the model into the experimental data available.
- Remark 4.2The potential V(x) has two minima if and only if A < 2. This minima are located at $x = x_{\pm} = \alpha^{-1} \ln(\zeta)$, $\zeta = \frac{1 \pm \sqrt{1 A^2}}{A}$. Since $\ln(\zeta) \ge 0$, then there exist a critical value of R_c determined by the equation $R_c = \alpha^{-1} \ln 2 + r_0$

The Double Morse Potential



Figure : The double Morse function

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Proton Tunnelling in Hydrogen Bonded Crystals

The one-dimensional Schrödinger equation for a proton (deuteron) of mass μ , constrained by the potential (21) is given by

$$\psi''(x) + \frac{2\mu}{\hbar^2} \left[E - D\left(\frac{A^2}{2}\cosh(2\alpha x) - 2A\cosh(\alpha x)\right) \right] \psi(x) = 0, \qquad -\infty < x < \infty$$
(22)

where *E* is the energy and $\psi(x)$ is the wavefunction which satisfies the boundary conditions $\psi(\pm \infty) = 0$. Extracting the appropriate asymptotic behaviour by making the transformation of the form

$$\psi(z) = e^{-Ax\sqrt{\gamma}}\phi(z), \qquad z = \cosh \alpha x,$$
(23)

we obtain

$$(z^{2}-1)\phi''(z) + z\phi'(z) + \left[-2A\sqrt{\gamma}z^{2} + z + 2A\sqrt{\gamma}\right]\phi'(z) + Az\left(2\gamma - \sqrt{\gamma}\right)\phi(z)$$
$$= \left(\frac{\gamma A^{2}}{2} - \xi\right)\phi(z), \qquad (24)$$

where

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• **Comment 4.3** We shall hereafter refer to γ as the quantum effect parameter, which will be henceforth treated as an adjustable parameter, due to the ambiguity in determining the values D and α .

In what follows, we show that (24) is quasi-exactly solvable, i.e has polynomial solutions of degree $n \ge 0$, which we write in the form

$$\phi(z) = \prod_{i=1}^{n} (z - z_i), \qquad \phi(z) \equiv 1 \text{ for } n = 0,$$
 (26)

where $\{z_i\}$ are the roots of the polynomials to be determined. To solve equation (24), we apply the functional Bethe ansatz method presented in section 2. Substituting (26) into (24), we obtain

$$(z^{2}-1)\sum_{i=1}^{n}\frac{1}{z-z_{i}}\sum_{j\neq i}^{n}\frac{2}{z_{i}-z_{j}} + \left[-2A\sqrt{\gamma}z^{2}+z+2A\sqrt{\gamma}\right]\sum_{i=1}^{n}\frac{1}{z-z_{i}} + A\sqrt{\gamma}z\left(2\sqrt{\gamma}-1\right)$$
(27)
$$=\left(\frac{\gamma A^{2}}{2}-\xi\right)$$

The right hand side of this equation is a constant, while the left hand side is a meromorphic function with simple poles $z = z_i$ and singularity at $z = \infty$. For this equation to be valid, the left hand side must also be a constant. Thus by Liouville's theorem, we demand that the coefficients of the powers of u as well as the residues at the simple poles of the left hand side be zero. This demand yields the constraint

$$\sqrt{\gamma} = \left(n + \frac{1}{2}\right),$$
 (28)

from which the number of bound states can be obtain, depending on the parameters of the crystals. For instance, by fitting the parameters of the model with experimental data, Matsushita and Matsubara (1982), obtained the value of $\gamma^{-1} = 0.01$ for KDP based crystals, thus (by the concept of quasi-exact solvability) it is possible to find exact energy levels and corresponding wavefunctions for the first n + 1 = 11 states for such crystals.

4. Proton Tunnelling in Chromous Acids

Bound states of Double Morse Potential

Furthermore, the exact energy eigenvalues are also obtained as

$$\xi_n = 2A\sqrt{\gamma} \sum_{i=1}^n z_i + \frac{\gamma A^2}{2} - n^2,$$
 (29)

with the corresponding wavefunction

$$\psi_n(z) = e^{-Az\sqrt{\gamma}} \prod_{i=1}^n (z - z_i), \qquad z = \cosh \alpha x, \tag{30}$$

where the roots $\{z_i\}$ are determined by the Bethe ansatz equations of the form

$$\sum_{j\neq i}^{n} \frac{2}{z_i - z_j} = \frac{2A\sqrt{\gamma}z_i^2 - z_i - 2A\sqrt{\gamma}}{z_i^2 - 1}.$$
(31)

• **Comment 4.4** One way to understand the quasi-exact solvability of the present model is to demonstrate that equation (24) has a hidden sl₂ symmetry. This can be shown by expressing the Hamiltonian as a combination of generators of Lie algebra.

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Thus, if we write Eq. (24) in the form

$$\mathcal{H}\phi(z) = \mathcal{E}\phi(z) \tag{32}$$

where \mathcal{H} and \mathcal{E} are given by

$$\mathcal{H} = (z^2 - 1) \frac{d^2}{dz^2} + \left[-2A\sqrt{\gamma}z^2 + z + 2A\sqrt{\gamma}\right] \frac{d}{dz} + A\sqrt{\gamma}z \left(2\sqrt{\gamma} - 1\right),$$
$$\mathcal{E} = \left(\frac{\gamma A^2}{2} - \xi\right),$$
(33)

then it can easily be shown that if equation (28) holds, with n being a non-negative integer, the differential operator \mathcal{H} is an element of the enveloping algebra of the sl₂ algebra

$$\mathcal{H} = J^0 J^0 - J^- J^- - 2A\sqrt{\gamma} J^+ + nJ^0 + 2A\sqrt{\gamma} J^- + \frac{n^2}{4}.$$
 (34)

Moreover, equations (28)-(31) give the exact closed form solutions of the present model. For instance, one can obtain the exact energies and wavefunctions for some eigenstates as follows:

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Bound states of Double Morse Potential

• When n = 0, equations (29) and (30) give

$$\xi_0 = \frac{\gamma A^2}{2} \quad \Rightarrow \quad E_0 = \frac{\hbar^2 \alpha^2 A^2 \gamma}{4\mu}$$

$$\psi_0(z) \sim e^{-Az\sqrt{\gamma}}, \qquad z = \cosh(\alpha x). \tag{35}$$

respectively. This wave function has no nodes and so the state described by it is the ground state of the system.

• When n = 1, we have the first excited state solutions

$$\xi_{1} = 2\sqrt{\gamma}Az_{1} + \gamma A^{2}/2 - 1 \quad \Rightarrow \quad E_{1} = \frac{\hbar^{2}\alpha^{2}}{2\mu} \left(2\sqrt{\gamma}Az_{1} + \gamma A^{2}/2 - 1\right)$$
$$\psi_{1}(z) \sim (z - z_{1})e^{-Az\sqrt{\gamma}}, \qquad z = \cosh(\alpha x), \tag{36}$$

provided z_1 satisfies the equation

$$2A\sqrt{\gamma}z_1^2 - z_1 - 2A\sqrt{\gamma} = 0 \qquad \Rightarrow \qquad z_1 = \frac{1}{4A\sqrt{\gamma}} \left(1 \pm \sqrt{1 + 16A^2\gamma}\right). \tag{37}$$

• Similarly, when n = 2 we have the second excited state solution, given by

$$\xi_{2} = 2A\sqrt{\gamma}(z_{1}+z_{2}) + \gamma A^{2}/2 - 4 \Rightarrow$$

$$E_{2} = \frac{\hbar^{2}\alpha^{2}}{2\mu} \left[2A\sqrt{\gamma}(z_{1}+z_{2}) + \gamma A^{2}/2 - 4 \right]$$

$$\psi_{2}(z) \sim (z-z_{1})(z-z_{2})e^{-Az\sqrt{\gamma}}, \qquad z = \cosh(\alpha x), \qquad (38)$$

provided z_1, z_2 satisfy the equations

$$\frac{2}{z_1 - z_2} = \frac{A\sqrt{\gamma}z_1^2 - z_1 - A\sqrt{\gamma}}{z_1^2 - 1}$$
$$\frac{2}{z_2 - z_1} = \frac{A\sqrt{\gamma}z_2^2 - z_2 - A\sqrt{\gamma}}{z_2^2 - 1}.$$
(39)

(a) < ((a) <

Applications to Chromous Acids

In this section, we use the results of the previous section to discuss the proton tunnelling in and CrOOH and CrOOD. For both cases, using the energy bands obtained from experimental analyses, we obtain the values of the potential parameters, which are then used in the calculation of the spectrums. We also assume, as an initial hypothesis, that the assignments of Lawrence and Robertson (1981) (which are based on Synder and Ibers' (1962) results) for the CrOOD spectrum is correct. Thus, we have the following assignments $(8.07 \text{ cm}^{-1} = 1 \text{ meV})$

$$\omega_{12} \equiv E_2 - E_1 = 199.98 \ meV$$

$$\omega_{03} \equiv E_3 - E_0 = 238.42 \ meV$$

$$\omega_{01} \equiv E_1 - E_0 = 0.87 \ meV.$$
(40)

The first two assignments were obtained experimentally by Synder and Ibers (1962), while the last assignment was obtained Lawrence and Robertson (1980), using the first two assignment. The relevant hydrogen bond lengths obtained by Hamilton and Iber (1961) for CrOOH and CrOOD which are given as 2.492Å and 2.552Å respectively.

Applications to Chromous Acids

Solving the system ω_{12} and ω_{01} for r_0 ranging from 0.9Å to 1.0Å and with $\hbar = 1$, that is, we seek solutions to the non-linear system of equations

$$\frac{\alpha^2}{2\mu} \left[2A\sqrt{\gamma} \left(z_1 + z_2 - \frac{1}{4A\sqrt{\gamma}} \left(1 + \sqrt{1 + 16A^2\gamma} \right) \right) - 3 \right] = 199.98 \ \text{meV}$$
$$\frac{\alpha^2}{2\mu} \left[\frac{1}{4A\sqrt{\gamma}} \left(1 + \sqrt{1 + 16A^2\gamma} \right) - 1 \right] = 0.87 \ \text{meV}$$
(41)

where

$$A=2e^{-\alpha(R-r_0)}, \quad \gamma=\frac{2\mu D}{\alpha^2},$$

 z_1 and z_2 are obtained from the Bethe ansatz equations (39).

• **Remark 4.5** In order to make our solutions as analytic as possible, we used the solve function of the Maple symbolic computational software.

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r ₀ (Å)	α (Å ⁻¹)	<i>D</i> (eV)	<i>z</i> 1	<i>z</i> ₂	
0.90	0.51967906	0.000324526	52.34232396	-0.094541541	
	0.40006160	0.000299285	45.80461389	7.965432749	
0.92	0.5196790582	0.000317849	52.34232396	-0.094541541	
	0.4000615994	0.000294534	45.80461389	7.965432749	
0.94	0.5196790582	0.000311310	52.34232396	-0.094541541	
	0.4000615994	0.000289858	45.80461389	7.965432749	
0.96	0.5196790582	0.000304906	52.34232396	-0.094541541	
	0.4000615994	0.000285257	45.80461389	7.965432749	
0.98	0.5196790582	0.000298633	52.34232396	-0.094541541	
	0.4000615994	0.000280728	45.80461389	7.965432749	
1.00	0.5196790582	0.000292489	52.34232396	-0.094541541	
	0.4000615994	0.000276271	45.80461389	7.965432749	

Potential Well Parameter for CrOOD

Table : CrOOD well parameters and Bethe ansatz roots for various assumed r_0 with $2R_D = 2.552$ Å.

Applications to Chromous Acids

• **Remark 4.6** The Bethe ansatz roots are equally important in our computation, as the energy spectrum is directly depending on the values of the roots, thus in cases of multiple roots, effort has been made to carefully select the roots which give consistent results with the experimental data.

As a check, we use the obtained values to compute the assignment ω_{03} and we obtained:

- For $\alpha = 0.4000615994 \text{\AA}^{-1}$, $\omega_{03} = 0.27592 \text{ eV}$ (with roots $z_1 = 80.22028218$, $z_2 = 0.1691047166$, $z_3 = 26.67422118$),
- For $\alpha = 0.5196790582\text{Å}^{-1}$, $\omega_{03} = 0.46710 \text{ eV}$ (with roots $z_1 = -0.1311967046$, $z_2 = 104.7172731$, $z_3 = 34.85447411$).

Although these values are larger than the observed value of 0.23842 eV. For the case $\alpha = 0.4000615994 \text{Å}^{-1}$, the calculated value is consistent with the observed value with about 14% error, which is likely due of the approximation in the Lawrence and Robertson's assignment of ω_{01} .

(a) < ((a) <

ω_{ij}	$E_j - E_i \pmod{1}$	<i>z</i> ₁	<i>z</i> ₂	<i>z</i> 3
ω_{01}	0.89996			
	$\sim 7 { m cm}^{-1}$	9.4627526		
ω_{12}	0.31832688	9.4627526		
	$\sim 2567 \mathrm{cm}^{-1}$	63.964291	11.051377	
ω_{03}	0.5539746			
000	\sim 4468cm $^{-1}$	112.20949	37.355160	-0.1227278
was	0.2347502	63.964291	11.051377	
25	$\sim 1893 { m cm}^{-1}$	112.20949	37.355160	-0.1227278
ωορ	0.2669873			
02	$\sim 2574 { m cm}^{-1}$	63.964291	11.051377	
ω_{13}	0.5530771	9.4627526		
10	\sim 4460cm $^{-1}$	112.20949	37.355160	-0.1227278

Transition Frequencies for CrOOH

Table : CrOOH transition frequencies with the corresponding Bethe ansatz roots with values $r_0 = 1.16\text{\AA}$, $2R_H = 2.492\text{\AA}$, $\alpha = 0.4000615994\text{\AA}^{-1}$ and D = 0.2430737783 meV.

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The CrOOH Spectral Well



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PART C Summary & Conclusions

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5. Summary and Conclusion

Summary

- We have discussed the concept of quasi-exactly solvable systems in quantum mechanics and the classifications of QES operators have also been described.
- Exact closed-form polynomial solutions to double Morse potential has been obtained in terms of the roots of the algebraic Bethe ansatz equations.
- The solutions obtained has been applied as a prototype description for the O–H–O bond in chromous acids.

Conclusions

We compare our results with previous results of Snyder and Iber (1962) and Tomkinson *et al* (1984)

	LR ^{HI}	LR ^{CHL}	TTHEG ^{exp}	Present
D (eV)	1.44	3.69		0.000243
α (Å ⁻¹)	4.53	3.23		0.40
r ₀ (Å)	0.958	0.948	1.16	1.16
ω_{01} (cm ⁻¹)	214	519		\sim 7
$\omega_{12} (\mathrm{cm}^{-1})$	1621	1542	~ 2050	\sim 2567
$\omega_{12} (\mathrm{cm}^{-1})$			${\sim}2516$	~ 2574
$\omega_{03}~(\mathrm{cm}^{-1})$	3264	3833		\sim 4468

Conclusions

- Despite the low values of parameter α and D, the transition frequencies obtained for the O–H–O bond is in agreement with experimental observations.
- Tomkinson *et al* (1984) experimentally observed a broad band of $\sim 2050 \text{cm}^{-1}$ which they assigned to the transition ω_{12} and the claimed that the band 1650cm^{-1} assigned by Lawrence and Robertson (1980) is to low to give a consistent explanation of the CrOOH spectrum. Our result also confirms the validity of thier claim with the assignment of $\sim 2267 \text{cm}^{-1}$.
- An overtone of \sim 2516cm⁻¹ was also observed by Tomkinson *et al*, this we confirm with our calculation of \sim 2574cm⁻¹.
- Unlike previous theoretical studies, one advantage of the present approach is that, using an approximation $1/r^2 \approx \alpha^2 / \sinh^2(\alpha r)$ for the centrifugal barrier , one can further investigation of the effect of the angular momentum on the transition frequencies.
- It would be interesting to generalize the results of the present work to studying the phase transition of potassium dihydroden phosphate (KDP) based crystals and the inversion spectrum in ammonia isotopomers. Research along this path is under way.
- Moreover, by obtaining solutions to the system ω_{12} and ω_{03} , it may be possible to improve the calculated transition frequencies. Nonetheless, we hope that the findings in the present Contribution will further elucidate the spectral properties of hydrogen bonded crystals.

Some References

Relevant Published Works

- D. Agboola and Y.-Z. Zhang, J. Math. Phys. 53, 042101 (2012).
- D. Agboola, J. Math. Phys. 53, 052302 (2012).
- D. Agboola and Y.-Z. Zhang, Mod. Phys. Lett. A 27, 1250112 (2012).
- D. Agboola and Y.-Z. Zhang, Ann. Phys. (NY) 327, 2275 (2012).
- D. Agboola and and Y.-Z. Zhang, Ann. Phys. (NY), *in press* (2012).

Similar Works in Preparation

- Symmetric double-Morse model: Application to the inversion spectrum in ammonia and its C_{3v} isotopomers.
- Exact spectral properties of KDP crystals: A quasi-exact solvablility approach.

Other Relevant References

- Y.-Z. Zhang, J. Phys. A: Math. Theor. 45, 065206 (2012).
- R. G. Snyder and J. A. Ibers, J. Chem. Phys. 36, 1356 (1962).
- W.C. Hamilton and J. A. Iber, Acta crystallogr. 16, 1209 (1961).
- M. C. Lawrence and G. N. Robertson, Molec. Phys. 43, 193 (1981).

Thank You.

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