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Thermodynamic quantities and the motion of energy levels

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Abstract. From the eigenvalue equation $H_\lambda |\psi_n(\lambda)\rangle = E_n(\lambda) |\psi_n(\lambda)\rangle$ where $H_\lambda \equiv H_0 + \lambda V$ one can derive an autonomous system of first order differential equations for the eigenvalues $E_n(\lambda)$ and the matrix elements $V_{mn}(\lambda) := \langle \psi_m(\lambda)| V |\psi_n(\lambda)\rangle$ where λ is the independent variable. Thus one finds the 'motion' of the energy levels $E_n(\lambda)$. We discuss the dependence of the survival probability as well as some thermodynamic quantities (free energy, entropy, specific heat) on λ. This means we calculate the differential equations which these quantities obey. An application is given. Then we derive the equations of motion for the extended case $H_\lambda = H_0 + \lambda V_1 + \lambda^2 V_2$ and given an application to a supersymmetric Hamiltonian.

1. Introduction

Let $H_\lambda = H_0 + \lambda V$ be a Hamiltonian, where H_0 is the unperturbed Hamiltonian operator, V is the perturbation and λ is the real coupling parameter $(0 \leq \lambda < \infty)$. In the following it is assumed that the hermitean operators H_0 and V are time-independent. Furthermore, it is assumed that the spectrum of H_λ is discrete and bounded from below. If the Hamiltonian H_λ admits symmetries then the underlying Hilbert space is decomposed into invariant subspaces so that the eigenvalues are non-degenerate in these subspaces. It is assumed that there are no accidental degeneracies.

Recently Pechukas [1] and Yukawa [2, 3] discussed the 'motion' of energy levels $E_n(\lambda)$ where λ plays the rôle of the time. Let us assume that the eigenfunctions are real orthogonal. Using the orthogonality relation

$$\langle \psi_m(\lambda) \mid \psi_n(\lambda)\rangle = \delta_{mn}, \tag{1}$$

the completeness relation

$$I = \sum_{n \in I} |\psi_n(\lambda)\rangle \langle \psi_n(\lambda)|, \tag{2}$$

$$\left\langle \psi_n(\lambda) \,\middle|\, \frac{d\psi_n(\lambda)}{d\lambda} \right\rangle = 0 \tag{3}$$

and the assumptions described above, these authors derived the following

autonomous systems of first order ordinary differential equations

$$\frac{dE_n}{d\lambda} = p_n \tag{4a}$$

$$\frac{dp_n}{d\lambda} = 2 \sum_{m(\neq n)} \frac{V_{mn}V_{nm}}{E_n - E_m} \tag{4b}$$

$$\frac{dV_{mn}}{d\lambda} = \sum_{k(\neq m,n)} \left[V_{mk}V_{kn}\left(\frac{1}{E_m - E_k} + \frac{1}{E_n - E_k}\right)\right] - \frac{V_{mn}(p_m - p_n)}{E_m - E_n} \tag{4c}$$

where $p_n(\lambda) := \langle \psi_n(\lambda) | V | \psi_n(\lambda) \rangle$ and $V_{mn}(\lambda) := \langle \psi_m(\lambda) | V | \psi_n(\lambda) \rangle$ $(m \neq n)$.

Pechukas [1] and Yukawa [2, 3] discussed the dynamical system (1) in connection with quantum chaos (compare [4] and reference therein). Moreover, Yukawa [3] showed that the system (4) admits a Lax representation and is completely integrable. Consequently, no chaotic behaviour can be expected for system (4). Nakamura and Lakshmanan [5] gave the equations of motion for the eigenfunctions, namely

$$\frac{d|\psi_n\rangle}{d\lambda} = \sum_{m(\neq n)} \frac{V_{mn}}{E_n - E_m} |\psi_m\rangle \tag{5}$$

Steeb and van Tonder [6] discussed the connection with the perturbation theory and considered the extended case $H_\lambda = H_0 + \lambda_1 V_1 + \lambda_2 V_2$. Steeb and Louw [7] discussed energy dependent constants of motion for system (4). Let us mention that Aizu [8] described the parameter differentiation of quantum mechanical linear operators already 25 years ago. The results given above can be considered as a straightforward application. Furthermore we mention that the system given above is related to the generalized Calogero Moser system [5, 9].

First we describe the analytic perturbation of eigenvalues. Then we derive the dependence of the survivial probability and of thermodynamic quantities on λ. Then we give an application. Finally we derive the equations of motion for the eigenvalues of a supersymmetric Hamiltonian.

2. Analytic perturbation of eigenvalues

Let us consider the Hamiltonian

$$H_\lambda = H_0 + \lambda V_1 + \lambda^2 V_2 + \cdots + \lambda^n V_n. \tag{6}$$

We assume that the Hamiltonian (6) acts in a finite dimensional Hilbert space $\mathscr{H}$. More generally, we may suppose that a Hamiltonian is given, which is holomorphic in a given domain D_0 of the complex λ plane. The eigenvalues of H_λ satisfy the characteristic equation

$$\det(H_\lambda - E) = 0. \tag{7}$$

This is an algebraic equation in λ of degree dim $\mathscr{H}$, with coefficients which are

holomorphic in λ. It follows from function theory that the roots of equation (7) are (branches of) analytic functions of λ with only algebraic singularities. In other words, the eigenvalues of equation (7) for $\lambda \in D_0$ constitute one or several branches of one or several analytic functions that have only algebraic singularities in D_0.

3. Survival probability and thermodynamic quantities

It is obvious that the quantities which are derived from the energy spectrum also depend on λ. We discuss now the 'time evolution' of the quantities:

(i) survival probability

$$P(t, \lambda) = |\langle \psi(0) \mid \psi(t, \lambda)\rangle|^2, \tag{8}$$

where $|\psi(0)\rangle$ is the initial state,

(ii) the Helmholtz free energy

$$F(\beta, \lambda) = -\frac{1}{\beta} \ln \sum_{i=0}^{N-1} \exp(-\beta E_i(\lambda)), \tag{9}$$

(iii) the entropy

$$S(\beta, \lambda) = -\frac{\partial F(\beta, \lambda)}{\partial T}, \tag{10}$$

(iv) the specific heat

$$C = T \frac{\partial S(\beta, \lambda)}{\partial T}. \tag{11}$$

In this discussion we assume that we have a finite dimensional system, i.e., N energy levels.

Since

$$|\psi(t, \lambda)\rangle = \exp[-iH_\lambda t/\hbar]\, |\psi(0)\rangle, \tag{12}$$

we find

$$|\psi(t, \lambda)\rangle = \sum_{m=0}^{N-1} \alpha_m(\lambda) \exp[-iE_m(\lambda)t/\hbar]\, |\phi_m(\lambda)\rangle, \tag{13}$$

where we have used the expansion

$$|\psi(0)\rangle = \sum_{m=0}^{N-1} \alpha_m(\lambda)\, |\phi_m(\lambda)\rangle. \tag{14}$$

Consequently

$$P(t, \lambda) = \sum_{i,j=0}^{N-1} \alpha_i^2(\lambda)\alpha_j^2(\lambda) \cos[(E_i(\lambda) - E_j(\lambda))t/\hbar]. \tag{15}$$

We find the following equations for the 'evolution' of $P(t, \lambda)$ with respect to λ (t fixed)

$$\frac{dP}{d\lambda} = 4 \sum_{i,j=0}^{N-1} \alpha_i^2 \alpha_j \left[\sum_{k(\neq j)} \frac{\alpha_k V_{jk}}{E_j - E_k} \right] \cos[(E_i - E_j)t/\hbar]$$
$$- \frac{t}{\hbar} \sum_{i,j=0}^{N-1} \alpha_i^2 \alpha_j^2 \sin[(E_i - E_j)t/\hbar](p_i - p_j) \tag{16}$$

where

$$\frac{d\alpha_j}{d\lambda} = \sum_{k(\neq j)} \frac{\alpha_k V_{jk}}{E_j - E_k}. \tag{17}$$

Here we have used equation (5). These equations can be solved together with system (4) to give the λ-evolution of P.

For the thermodynamic quantities, free energy, entropy and specific heat we find the equations of motion (β fixed)

$$\frac{dF}{d\lambda} = \langle V \rangle, \tag{18}$$

$$\frac{d\tilde{S}}{d\lambda} = \beta^2(\langle H \rangle \langle V \rangle - \langle HV \rangle) \tag{19}$$

and

$$\frac{d\tilde{C}}{d\lambda} = \beta^2(1 + \beta\langle H \rangle)(\langle HV \rangle - \langle H \rangle \langle V \rangle) + \beta^3(\langle H^2 \rangle \langle V \rangle - \langle H^2 V \rangle) \tag{20}$$

where, taking

$$Z := \sum_{i=0}^{N-1} \exp(-\beta E_i), \tag{21}$$

we have put

$$\langle H \rangle := \frac{1}{Z} \sum_{i=0}^{N-1} E_i \exp(-\beta E_i) \tag{22}$$

$$\langle V \rangle := \frac{1}{Z} \sum_{i=0}^{N-1} p_i \exp(-\beta E_i) \tag{23}$$

$$\langle HV \rangle := \frac{1}{Z} \sum_{i=0}^{N-1} E_i p_i \exp(-\beta E_i) \tag{24}$$

$$\langle H^2 \rangle := \frac{1}{Z} \sum_{i=0}^{N-1} E_i^2 \exp(-\beta E_i) \tag{25}$$

$$\langle H^2 V \rangle := \frac{1}{Z} \sum_{i=0}^{N-1} E_i^2 p_i \exp(-\beta E_i) \tag{26}$$

and $\tilde{S} \equiv S/k$ and $\tilde{C} \equiv Ck$. Equations (18) through (20), together with system (1), form an autonomous system of (nonlinear) first order ordinary differential equations.

4. Example

First we notice that if we have a finite dimensional system with N energy levels then the number of differential equations n is given by

$$n = N + N + N(N-1)/2 \equiv N(3/2 + N/2). \tag{27}$$

In our first example the scaled Hamiltonian operator is given by the matrix representation

$$H_\lambda = \begin{pmatrix} 1 & \lambda & 0 & 0 \\ \lambda & 2 & 2\lambda & 0 \\ 0 & 2\lambda & 3 & \lambda \\ 0 & 0 & \lambda & 4 \end{pmatrix}. \tag{28}$$

This Hamiltonian operator admits no symmetry. We put $H_0 = \mathrm{diag}\,(1, 2, 3, 4)$ where diag (. . .) denotes that H_0 is a diagonal matrix. Obviously the eigenvalues of H_0 are given by $E_0 = 1$, $E_1 = 2$, $E_2 = 3$, $E_3 = 4$. The eigenfunctions are the standard basis in $\mathscr{R}^4$, namely $|\psi_0(0)\rangle = (1, 0, 0, 0)^T, \ldots, |\psi_3(0)\rangle = (0, 0, 0, 1)^T$ (T denotes transpose). In order to solve the dynamical system (4) where $N = 4$ we have to determine the initial conditions. Since

$$V = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 2 & 0 \\ 0 & 2 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \tag{29}$$

it is obvious that $p_0(0) = p_1(0) = p_2(0) = p_3(0) = 0$ and $V_{10}(0) = 1$, $V_{20}(0) = 0$, $V_{21}(0) = 2$, $V_{30}(0) = 0$, $V_{31}(0) = 0$, $V_{32}(0) = 1$. The number of differential equations is $n = 14$. Integrating the dynamical system (4) with these initial data we find that $E_0(\lambda)$ and $E_1(\lambda)$ become smaller with increasing λ and $E_2(\lambda)$ and $E_3(\lambda)$ become larger with increasing λ. This is called level repulsion. No level crossings occur. Notice, however, that for large λ only the interacting part plays a rôle. The Hamiltonian $H_\lambda = H_0 + \lambda V$ has the asymptotic form λV, so that in this region eigenvalues are proportional to λ, i.e., they dissipate in 'time'. This is not level repulsion and should be distinguished from genuine repulsion.

Here we mention the classic theorem of von Neumann and Wigner [10]. This theorem shows that real symmetric matrices (respectively Hermitian matrices) with a multiple eigenvalue form a real algebraic variety of codimension 2 (respectively 3) in the space of all real symmetric matrices (respectively all hermitian matrices). This implies the famous 'non-crossing rule' which asserts that a 'generic' one parameter family of real symmetric matrices (or two-parameter family of Hermitian matrices) contains no matrix with a multiple eigenvalue. Lax [11] showed that in a three dimensional vector space of $n \times n$ symmetric matrices the eigenvalues must cross if $n = 2 \pmod 4$, i.e., the vector space must contain a non-zero matrix with a multiple eigenvalue.

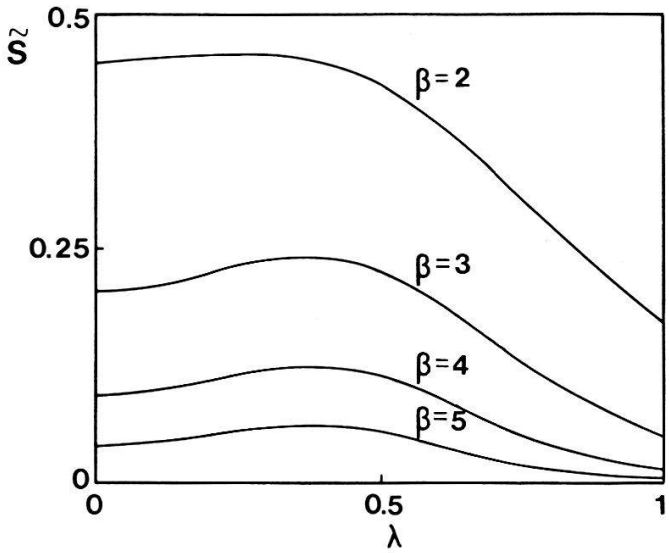

Figure 1
Entropy as a function of λ for various β's.

Notice further that the constants of motion are given by

$$\sum_{m=0}^{3} E_0(\lambda) = 10 \tag{30a}$$

$$\sum_{m<n}^{3} E_m(\lambda)E_n(\lambda) + 6\lambda^2 = 35 \tag{30b}$$

$$\sum_{n<m<k}^{3} E_k(\lambda)E_m(\lambda)E_n(\lambda) + 30\lambda^2 = 50 \tag{30c}$$

$$E_0(\lambda)E_1(\lambda)E_2(\lambda)E_3(\lambda) + 30\lambda^2 - \lambda^4 = 24. \tag{30d}$$

where $10 = \mathrm{Tr}\, H$ (Tr denotes the trace). The technique to find these constants of motion is described by Steeb and Louw [7].

In particular we are interested in the case where the entropy $S(\beta, \lambda)$ takes the maximal value as a function of λ. Figure 1 shows the dependence of the entropy on λ for various β's. For small temperatures (large β) we expect from the definition of $S(\beta, \lambda)$ that only the lowest energy eigenvalues will play a significant role in the behaviour of S. In fact we find that S attains a maximum where $E_1 - E_2$ is smallest (see discussion below for a two level system). For large temperatures (small β) the higher energy levels also become important and the behaviour of S becomes more difficult to analyze.

5. Two level system

Let us consider a two level system where the energy eigenvalues $E_0(\lambda)$ and $E_1(\lambda)$ depend on a real parameter λ. We assume that $E_0(\lambda) < E_1(\lambda)$ for $\lambda = 0$.

Now the partition function $Z(\lambda)$ is given by

$$Z(\lambda) = \exp(-\beta E_0(\lambda)) + \exp(-\beta E_1(\lambda)) \tag{31}$$

Then for the Helmholtz free energy we find

$$F(\lambda) = E_0(\lambda) - \frac{1}{\beta} \ln [1 + \exp(-\beta \Delta E(\lambda))] \tag{32}$$

where

$$\Delta E(\lambda) = E_1(\lambda) - E_0(\lambda). \tag{33}$$

The entropy is given by equation (8). It follows that

$$\frac{S(\lambda)}{k} = \ln [1 + \exp(-\beta \Delta E(\lambda))] + \frac{\beta \Delta E(\lambda)}{1 + \exp(\beta \Delta(\lambda))} \tag{34}$$

We are interested in finding the maximum of $S(\lambda)$ as a function of λ. From $dS(\lambda)/d\lambda = 0$ and equation (34) we obtain

$$\frac{\beta^2 \Delta E(\lambda) \exp(\beta \Delta E(\lambda))}{1 + \exp(\beta \Delta(\lambda))} \frac{d(\Delta E(\lambda))}{d\lambda} = 0 \tag{35}$$

Let us first discuss the limiting case $T = 0$ and $T \to \infty$. For $T = 0$ we know that $S(T = 0, \lambda)/k = 0$ if $E_0(\lambda) \neq E_1(\lambda)$ and $S(T = 0, \lambda)/k = \ln 2$ if $E_0(\lambda) = E_1(\lambda)$. For $T \to \infty$ $(\beta \to 0)$ we know that $S(T \to \infty)/k = \ln 2$. Therefore equation (35) is satisfied identically in the limiting cases.

If $T > 0$ and $\beta > 0$ then the condition (35) for the extremum of $S(\lambda)$ becomes

$$\frac{d(\Delta E(\lambda))}{d\lambda} = 0. \tag{36}$$

The second derivative of S with respect to λ at any point where the condition (36) is satisfied is given by

$$\frac{d^2 S(\lambda)}{d\lambda^2} = \frac{\beta^2 \Delta E(\lambda) \exp(\beta \Delta E(\lambda))}{[1 + \exp(\beta \Delta E(\lambda))]^2} \frac{d^2 \Delta E(\lambda)}{d\lambda^2} \tag{37}$$

When $\Delta E(\lambda)$ attains a minimum, $S(\lambda)$ will attain a maximum, as long as $\Delta E(\lambda)$ remains positive.

6. Supersymmetric Hamiltonian

In some applications we also find different coupling within the interaction. For example, let

$$Q := (b - \lambda(b + b^\dagger)^2) c^\dagger \tag{38}$$

be the generator of a supersymmetric Hamiltonian [12], where b and c are boson

and fermion annihilation operators. Then the Hamiltonian is given by

$$H_\lambda = \{Q, Q^\dagger\} \tag{39}$$

where the braces denotes an anticommutator bracket. The Hamiltonian can be written as $H_\lambda = H_0 + V$ where

$$H_0 = c^\dagger c + b^\dagger b \tag{40}$$

and

$$V = -4\lambda c^\dagger c a + 2\lambda a - \lambda a^3 + \lambda^2 a^4, \tag{41}$$

where $a \equiv b^\dagger + b$.

The equations of motion for the Hamiltonian

$$H_\lambda = H_0 + \lambda V_1 + \lambda^2 V_2 \tag{42}$$

can be derived taking into account the assumptions described above. We find

$$\frac{dE_n}{d\lambda} = p_n + \lambda q_n \tag{43a}$$

$$\frac{dp_a}{d\lambda} = 2 \sum_{m(\neq n)} \frac{V_{1nm}(V_{1mn} + 2V_{2mn})}{E_n - E_m} \tag{43b}$$

$$\frac{dq_n}{d\lambda} = 2 \sum_{m(\neq n)} \frac{V_{2nm}(V_{1mn} + 2\lambda V_{2mn})}{E_n - E_m} \tag{43c}$$

$$\frac{dV_{1mn}}{d\lambda} = \sum_{k(\neq m,n)} \frac{(V_{1mk} + 2\lambda V_{2mk})V_{1kn}}{E_m - E_k} + \sum_{k(\neq m,n)} \frac{(V_{1kn} + 2\lambda V_{2kn})V_{1mk}}{E_n - E_k} + \frac{(V_{1mn} + 2\lambda V_{2mn})(p_n - p_m)}{E_m - E_n} \tag{43d}$$

$$\frac{dV_{2mn}}{d\lambda} = \sum_{k(\neq m,n)} \frac{(V_{1mk} + 2\lambda V_{2mk})V_{2kn}}{E_m - E_k} + \sum_{k(\neq m,n)} \frac{(V_{1kn} + 2\lambda V_{2kn})V_{2mk}}{E_n - E_k} + \frac{(V_{1mn} + 2\lambda V_{2mn})(q_n - q_m)}{E_m - E_n} \tag{43e}$$

where $p_n(\lambda) := \langle \psi_n(\lambda| V_1 |\psi_n(\lambda)\rangle$ and $q_n(\lambda) := \langle \psi_n(\lambda)| V_2 |\psi_n(\lambda)\rangle$.

Equations (43a) through (43e) cannot be applied to the Hamiltonian (39) since energy levels are degenerate. A basis of the underlying Hilbert space is given by

$$\{|m\rangle\, |0\rangle; |m\rangle c^\dagger |0\rangle; m = 0, 1, 2, \ldots\} \tag{44}$$

where

$$|m\rangle := (m!)^{-1/2}(b^\dagger)^m\, |0\rangle. \tag{45}$$

The matrix representation of the unperturbed Hamiltonian H_0 is given by $H_0 = \mathrm{diag}\,(0, 1, 1, 2, 2, \ldots)$. In order to apply equations (43a) through (43d) we have to decompose the Hilbert space owing to the symmetries. In the present

case we find the invariant subspaces $S_1 = \{|m\rangle\ |0\rangle\}$ and $S_2 = \{|m\rangle c^\dagger\ |0\rangle\}$. For the subspace with basis S_1 the matrix representation of H_0 is given by $H_0 = \mathrm{diag}\,(0, 1, 2, \ldots)$ and for the subspace with the basis S_2 we find $H_0 = \mathrm{diag}\,(1, 2, 3, \ldots)$. In these subspaces we can apply equations (43a) through (43d). We have calculated the 'λ evolution' of 100 energy levels of the infinite matrix and taken into account the lowest 10 levels. For the range $0 \leq \lambda \leq 0.5$ no level crossings occur in both subspaces.

7. Conclusions

Pechukas [1] and Yukawa [2, 3] have shown that the eigenvalues $E_n(\lambda)$ and the matrix elements $V_{mn}(\lambda)$ for the Hamiltonian $H_\lambda = H_0 + \lambda V$ can be written as an autonomous system of ordering differential equations (1) which admits a lax representation. Nakamura and Lakshmanan [5] found the time-evolution for the eigenfunctions $|\psi_m(\lambda)\rangle$. We have shown that the 'time-evolution' of other quantities can also be written as ordinary differential equations and can therefore be included into system (4). Furthermore we have derived the equations of motion for the extended case $H_\lambda = H_0 + \lambda V_1 + \lambda^2 V_2$ and applied to a supersymmetric Hamiltonian. The system of ordinary differential equations for the 'time-evolution' of the eigenvalues and matrix elements has the advantage that for all Hamiltonian operators of the form $H_\lambda = H_0 + \lambda V$ with nondegenerate eigenvalues we have the same equations of motion (4). Only the initial values must be changed for different systems. The disadvantage is that the number of equations increases very rapidly with increasing number of energy levels N.

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