

Generalisation of a property of Hamiltonians depending linearly upon a parameter: application to a model of inert gas matrix effect on vibrational spectra

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Abstract The property that the ground state eigenvalue of a Hamiltonian, depending linearly upon a parameter, is a concave function of this parameter is generalised. It is shown that the concavity or convexity of the n th eigenvalue depends upon the relative weights of the states below the n th state, with respect to those above it, in a weighted sum of transition energies. The result is illustrated on a model of matrix effect on gas phase molecular vibrational spectra. The model is applied to the 2,3-naphthylene molecule.

Keywords Concavity and convexity in chemistry · Molecular vibrational spectra · Inert gas matrix · Naphthylene

1 Introduction

The aim of this article is to generalize a concavity property, previously used in the context of electronic energy calculation [1], and to apply it to the context of vibrational calculations.

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Many molecules of astrophysical interest, such as polycyclic aromatic hydrocarbons (PAHs), have been the subject of infra-red studies in inert gas matrices [2]. However, in the interstellar medium these molecules can be considered as isolated to a very good approximation. So, the inert gas matrix effects have to be deconvoluted from the experimental spectra before a rigorous comparison with astrophysical spectra can be made.

This short communication presents a quartic oscillator effective Hamiltonian for modelling frequency shift by inert gas matrices. It is arguably the simplest model one can think of, and hence the one which is natural to start with. The model serves to illustrate a generalisation of the property that the ground state eigenvalue of a Hamiltonian depending linearly upon a parameter, is a concave function of this parameter.

The article is organised as follows: In the next section we state and prove a necessary and sufficient condition for the concavity or convexity of linearly parametrized Hamiltonian eigenvalues. Then, in Sect. 3, we describe a quartic oscillator model and the set of experimental data considered, to illustrate this theoretical result. In the last section, we discuss some numerical results for the 2,3-naphthylene molecule in connection with concavity and present the conclusions that can be drawn from our simple model.

2 Theorem

Let $H(Z)$ be a Hamiltonian acting on a Hilbert space, depending upon a set of parameters gathered in a vector Z (typically in \mathbb{N}^d , where \mathbb{N} is the set of natural integers, but, more generally, considered as an element of \mathbb{C}^d), such that for all real numbers, $\lambda \in [0, 1]$, it satisfies $H(\lambda Z_1 + (1 - \lambda)Z_2) = \lambda H(Z_1) + (1 - \lambda)H(Z_2)$. Let us assume that there is a domain, (i.e. an open and connected subset), \mathcal{D} , for the parameter Z such that the N lowest eigenvalues of $H(Z)$ do not cross over other eigenvalues and have their degeneracy order preserved, so that each of these eigenvalues can be followed unambiguously as a function of Z in this domain. Let us denote by $(E^i(Z))_{i \geq 0}$ the eigenvalues of $H(Z)$ in increasing order but repeated if degenerate, and by $(\phi^i(Z))_{i \geq 0}$ the associated eigenvectors forming an orthonormalized Hilbertian basis set. Let us consider the j th eigenvalue ($0 \leq j < N$), $E^j(Z)$. First, we suppose for simplicity that it is non degenerate.

Then, if, $\forall Z_1 < Z_2 < Z_3 \in \mathcal{D}$, the quantity:

$$S^j(Z_1, Z_2, Z_3) := \frac{Z_2 - Z_3}{Z_1 - Z_3} \sum_{i \geq 0} |\langle \phi^j(Z_2) | \phi^i(Z_1) \rangle|^2 (E^i(Z_1) - E^j(Z_1)) \\ + \frac{Z_1 - Z_2}{Z_1 - Z_3} \sum_{i \geq 0} |\langle \phi^j(Z_2) | \phi^i(Z_3) \rangle|^2 (E^i(Z_3) - E^j(Z_3)), \quad (1)$$

is positive, (respectively, negative, zero), then $E^j(Z)$ is a concave (respectively, convex, linear) function of Z .

Proof By linearity we have,

$$H(Z_2) = \frac{Z_2 - Z_3}{Z_1 - Z_3} H(Z_1) + \frac{Z_1 - Z_2}{Z_1 - Z_3} H(Z_3). \tag{2}$$

Taking the expectation value over $\phi^j(Z_2)$ and inserting the closure relationships given by the Hilbert basis sets $(\phi^i(Z_1))_{i \geq 0}$ and $(\phi^i(Z_3))_{i \geq 0}$ we obtain,

$$E^j(Z_2) = \frac{Z_2 - Z_3}{Z_1 - Z_3} \sum_{i \geq 0} |\langle \phi^j(Z_2) | \phi^i(Z_1) \rangle|^2 E^i(Z_1) + \frac{Z_1 - Z_2}{Z_1 - Z_3} \sum_{i \geq 0} |\langle \phi^j(Z_2) | \phi^i(Z_3) \rangle|^2 E^i(Z_3). \tag{3}$$

Adding and subtracting $E^j(Z_1)$, (respectively, $E^j(Z_3)$), to the $E^i(Z_1)$'s, (respectively, the $E^i(Z_3)$'s), and using the fact that $\sum_{i \geq 0} |\langle \phi^j(Z') | \phi^i(Z) \rangle|^2 = 1$, we arrive at,

$$E^j(Z_2) = S^j(Z_1, Z_2, Z_3) + cE^j(Z_1) + (1 - c)E^j(Z_3), \tag{4}$$

where we have set, $c := \frac{Z_2 - Z_3}{Z_1 - Z_3}$.

So, if $\forall Z_1 < Z_3 \in \mathcal{D}$, $\forall c \in [0, 1]$, $S^j(Z_1, cZ_1 + (1 - c)Z_3, Z_3) \geq 0$, then,

$$E^j(cZ_1 + (1 - c)Z_3) \geq cE^j(Z_1) + (1 - c)E^j(Z_3), \tag{5}$$

and $E^j(Z)$ is concave. In the same way, if $\forall Z_1 < Z_3 \in \mathcal{D}$, $\forall c \in [0, 1]$, $S^j(Z_1, cZ_1 + (1 - c)Z_3, Z_3) \leq 0$, (resp. = 0), then $E^j(Z)$ is convex, (resp. linear).

Remarks: In the sums over i in the expression of $S^j(Z_1, Z_2, Z_3)$ as a convex combination, the term for $i = j$ is zero, all the terms for $i < j$ are negative and all those for $i > j$ are positive. So the sign of $S^j(Z_1, Z_2, Z_3)$ depends upon the relative importance of the states below the j th state with respect to those above it, in the sum of transition energies with respect to level E^j , weighted by the transition probabilities from state $\phi^j(Z_2)$. In particular, for $j = 0$ there is no state below, thus we have necessarily, $S^j(Z_1, Z_2, Z_3) \geq 0$, that is to say, the ground state eigenvalue is always a concave function. This is the result used in [1].

The generalisation to the case where $E^j(Z)$ is degenerate, is straightforward. The same proof is valid for any normalized vector of the degenerate eigenspace. It implies that $S^j(Z_1, Z_2, Z_3)$ is invariant under a unitary transformation of $\phi^j(Z_2)$ in the degenerate eigenspace. This, in turn, implies that transition probabilities, $|\langle \phi^j(Z) | \phi^i(Z') \rangle|^2$, such that $E^i(Z')$ has a lower degeneracy order than $E^j(Z)$, are zero.

Also, the derivation of the proof follows through the same steps in the case of Z -dependent Hilbert spaces, $\mathcal{H}(Z)$, provided that, for all $Z, Z' \in \mathcal{D}$ the states of interest, $(\phi^j(Z'))_{0 \leq j < N}$, belong to $\mathcal{H}(Z)$, so that $\sum_{i \geq 0} |\langle \phi^j(Z') | \phi^i(Z) \rangle|^2 = \|\phi^j(Z')\|^2 = 1$.

A condition that is sufficient but not necessary, for concavity, (resp. convexity, linearity) of $E^j(Z)$, is that, for all $Z, Z' \in \mathcal{D}$, $\sum_{i \geq 0} |\langle \phi^j(Z') | \phi^i(Z) \rangle|^2 (E^i(Z) - E^j(Z))$ be positive, (resp. negative, zero).

3 A model for inert gas matrix effect

At the simplest level of theory, the fundamental vibrational frequencies of a molecule can be obtained from a set of independent harmonic oscillator Hamiltonians,

$$H_i^0 = \frac{1}{2} P_i^2 + \frac{1}{2} \omega_i^2 Q_i^2, \quad (6)$$

in mass-weighted normal coordinates, Q_i , with conjugate moments, P_i .

Let us assume that, a matrix made of a rare gas with atomic number Z , affects the vibrational levels according to a quartic perturbation of the form, $(a_i Z + b_i) Q^4$, where a_i and b_i are real numbers dependent *a priori* upon vibration i . The vibrational energy levels of the molecule in the matrix will be the eigenvalues of the quartic anharmonic oscillator Hamiltonian,

$$H_i(Z) = \frac{1}{2} P_i^2 + \frac{1}{2} \omega_i^2 Q_i^2 + (a_i Z + b_i) Q^4. \quad (7)$$

As argued in the introduction, it is arguably the simplest empirical model one can think of. However, the determination of the spectrum of such a Hamiltonian is a very difficult mathematical problem. For instance, the usual perturbation series diverge unless sophisticated renormalization schemes are employed, in particular, when the quartic force constant becomes large with respect to the quadratic one [3]. Moreover, when the quartic force constant is less than zero, the spectrum is not bounded from below, so that the use of variational methods can be problematic.

So, to avoid these problems, we place our model in finite dimensional Hilbert spaces, spanned by a finite number of the low lying harmonic oscillator eigenfunctions which have a negligible weight in the unbounded regions of the potential, if any, (i.e. on the other side of the barriers isolating the potential well, when $(a_i Z + b_i) < 0$). However, we assume that the number of harmonic oscillator (HO) basis functions is large enough so that: $\sum_{i \geq 0} |\langle \phi^j(Z) | \phi^i(Z') \rangle|^2 = 1$, holds to numerical accuracy for the states of interest in our study (i.e. the two lowest eigenstates). This insures that the theorem of Sect. 2 is relevant to our numerical model (see remark for the case of Z -dependent Hilbert spaces).

For each vibrational mode, the model has three free parameters, (ω_i, a_i, b_i) . So, to apply the model to a concrete case, three experimental and/or theoretical data are required to fix the values of these parameters. We have chosen to apply the model to the case of 2,3-naphthylene, because it is a molecule for which there exist experimental wave numbers for four different vibrational modes with three different rare gas matrices, namely neon, argon and krypton [4], as well as scaled, harmonic theoretical calculations [5].

We have considered that the theoretical numbers are “exact” for the no matrix case at the harmonic level of approximation, that is to say, that the empirical scaling factors employed by the authors take care of the finite basis set and electronic correlation corrections to the quadratic force constants. So, we have taken the ω_i ’s from the theoretical wave numbers [5]. The a_i , b_i ’s have been fitted to reproduce the experimental, fundamental transition wave numbers for neon and krypton matrices. The experimental numbers for argon seems somewhat less accurate, (less significant digits tabulated in [4]), and will only be used for comparison with the numbers interpolated from our model.

4 Results and conclusions

The results of vibrational calculations with the effective Hamiltonians described in the previous section are displayed in Table 1. The eigenproblems for each effective Hamiltonian were solved in basis sets of 60 HO functions with the code CONVIV [6].

The quartic constants $k_i := a_i Z + b_i$ were interpolated for argon, $Z = 18$, and extrapolated for $Z = 0$. The relevant Z values for the model are those of rare gases, $Z = 2$ for helium, $Z = 10$ for neon, $Z = 18$ for argon, $Z = 36$ for krypton, $Z = 54$ for xenon ... Within our model, the case $Z = 0$ has the natural interpretation of the anharmonicity corrected no-matrix case. The b_i coefficients give an effective anharmonicity quartic constant for the no-matrix case. However, the importance of some real matrix effects could very well decrease with gases of heavier atoms, then the anharmonic no-matrix values would rather be found at large Z . So, the proposed, effective Hamiltonian should be considered primarily as a “quick inspection” model. It serves us to illustrate the concavity property which gives lower energy bounds for interpolated Z -values and upper energy bounds for extrapolated Z -values.

The a_i coefficients, which can be deduced from the slope of the quartic constants of Table 1, give the strength of the matrix dependency. Unlike the b_i coefficients which are found with both signs according to the vibration, the a_i ’s are all negative. Consequently, the higher the atomic weight, the lower the energy levels and the smaller the fundamental transition frequencies in agreement with the experimental data. The total quartic constants resulting from the intrinsic anharmonicity of the molecule and the matrix effect are found negative for out-of-plane vibrations and positive for bending vibrations for all rare gases.

The upper and lower energy bounds given by the theorem of Sect. 2, applied to the “quick inspection” model of Sect. 3, are so close to the actual energy values that, one can conclude that the energy levels depend essentially linearly upon Z , the curvature of the eigenvalues of the Hamiltonian as functions of Z being negligible. This is because line shift effects are found to be small when experimental wave numbers are compared to the theoretical ones or compared between themselves. Consequently, the quartic force constants are confined to a small range of values for which non linear effects hardly show up. The first excited state eigenvalues are further away from the energy bounds than the ground state eigenvalues.

Table 1 Interpolation and extrapolation of matrix effects on the vibrations of 2,3-Naphthylene

	Harm	Z=0	Ne	Ar	Kr
<i>C-C-C bending 1</i>					
Quartic constant	0	$5.96 \cdot 10^{-11}$	$5.34 \cdot 10^{-11}$	$4.84 \cdot 10^{-11}$	$3.73 \cdot 10^{-11}$
ZPE	219.0	221.4(019)	221.2	220.9(615)	220.5
Bound from concavity		221.4(040)		220.9(606)	
First level	657.0	668.8(472)	667.7	666.6(979)	664.5
Bound from concavity		668.8(633)		666.6(913)	
Transition	438.0	447.4	446.5	445.7 (444)	444
<i>C-C-C bending 2</i>					
Quartic constant	0	$2.27 \cdot 10^{-10}$	$2.18 \cdot 10^{-10}$	$2.11 \cdot 10^{-10}$	$1.94 \cdot 10^{-10}$
ZPE	300.0	304.8(252)	304.6	304.4(837)	304.1
Bound from concavity		304.8(261)		304.4(833)	
First level	900.0	923.6(643)	922.8	922.0(168)	920.4
Bound from concavity		923.6(709)		922.0(141)	
Transition	600.0	618.8	618.1	617.5 (618)	616.2
<i>C-C-C out-of-plane</i>					
Quartic constant	0	$+0.56 \cdot 10^{-11}$	$-0.69 \cdot 10^{-11}$	$-1.69 \cdot 10^{-11}$	$-3.94 \cdot 10^{-11}$
ZPE	369.5	369.5(817)	369.4	369.2(545)	368.9
Bound from concavity		369.5(824)		369.2(542)	
First level	1108.5	1108.9(082)	1108.0	1107.2(712)	1105.6
Bound from concavity		1108.9(142)		1107.2(689)	
Transition	739.0	739.3	738.6	738.0 (738)	736.7
<i>C-H out-of-plane</i>					
Quartic constant	0	$-1.79 \cdot 10^{-10}$	$-1.95 \cdot 10^{-10}$	$-2.08 \cdot 10^{-10}$	$-2.36 \cdot 10^{-10}$
ZPE	421.5	419.4(776)	419.3	419.1(530)	418.8
Bound from concavity		419.4(782)		419.1(527)	
First level	1264.5	1254.3(205)	1253.4	1252.6(737)	1251.0
Bound from concavity		1254.3(261)		1252.6(714)	
Transition	843.0	834.8	834.1	833.5 (833)	832.2

The “Harm” column shows the values corresponding to the harmonic Hamiltonians. Below the “ZPE” (zero point energy) and “first level” rows, we show the upper bounds for “Z=0” and lower bounds for Ar assuming that the eigenvalues are concave functions of the atomic number Z, which is always true for the ground state for the class of Hamiltonians considered, and seems also true for the first excited state as can be checked *a posteriori*. The digits after the first decimal place are in parentheses. In the “Transition” row, we show in parentheses the experimental, fundamental frequency for Ar. All wave numbers are in cm^{-1} . Quartic constants are in atomic units

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