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An undergraduate-oriented comment about inverting spectral data to determine the interatomic potential

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An elementary, analytically soluble example of a pair of isospectral potentials is discussed. This example was developed in response to an inquiry by an undergraduate student who was intrigued by the widely used (but not often discussed in undergraduate courses) Rydberg–Klein–Rees (RKR) procedure for inverting rovibrational data to determine potential functions of diatomic molecules, which is based on the semiclassical (WKB) approximation. The pair of potentials discussed provide a clear elementary example of the insufficiency of the energy level spectrum to determine the potential, even in a case in which the bound states form a complete set. © 2020 American Association of Physics Teachers.

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I. INTRODUCTION

For nearly fifty years, I started each of my courses preaching about the benefits of self-study ahead of class, referring to the introduction of book printing by Gutenberg as the point in history when the role of the professor should have transformed from a knowledge provider to guide in an adventurous intellectual pursuit. For the majority of my students, these sermons remained futile.

The recent abrupt need to switch to remote teaching/learning allowed a radical transformation of my teacher–student mode of interaction, remotely teaching an elective undergraduate Molecular Spectroscopy course offered to second- and third-year Materials Science and Engineering students who had completed a one-semester quantum chemistry course at the Guangdong–Technion Israel Institute of Technology in Shantou, Guangdong, China. Rather than mimicking traditional lecturing via live (“zoom”) or video-recorded classes, the students were offered a (closed) website (“moodle”) where they could find reading materials, references to appropriate chapters in their course textbook,¹ and exercises, along with a detailed learning guide accompanying each chapter. The students were promised credit for “good” questions and comments, and I made an effort to respond promptly (synchronizing my day with China time—six hours ahead of Israel), loading crudely edited questions and responses on the course website. Indeed, a steady flow of enquiries required my attention, providing me with feedback that I have never before benefitted from about the students’ progress and their difficulties.

II. INVERTING SPECTRAL DATA: INSUFFICIENCY OF THE VIBRATIONAL SPECTRUM

The Rydberg–Klein–Rees (RKR) procedure for inverting vibration-rotation data to obtain the potential energy function of a diatomic molecule is briefly discussed in the textbook used in the course mentioned above¹ (p. 216). The non-uniqueness of the inversion of vibrational-only data into a potential function intrigued the curiosity of one of the

students (see acknowledgements). I quickly offered an appropriate source,² supplemented by an elementary introduction to the WKB (semiclassical) approximation, which the RKR procedure is based on. The purpose of the present comment is to illustrate that, in a particularly simple context, vibrational energy levels are not sufficient to determine the potential. In more fancy language, to illustrate the existence of isospectral potentials (e.g., Ref. 3).

We will only consider potentials, $V(x)$, $-\infty < x < \infty$, with a single minimum at some x_e , i.e., such that $V(x)$ is monotonically decreasing over $-\infty < x < x_e$ and monotonically increasing over $x_e < x < \infty$. For energies that satisfy $E \geq V(x_e)$, we will refer to the two roots of the equation $V(x) = E$ as the left- and right classical turning points, x_ℓ and x_r . If $\lim_{x \rightarrow \pm\infty} V(x) = V_{\pm\infty} < \infty$, then we define $x_\ell = -\infty$ for $E \geq V_{-\infty}$ and $x_r = \infty$ for $E \geq V_{\infty}$.

The period of oscillation of a particle with mass m and energy E in the potential $V(x)$ is given by⁵

$$T = \sqrt{2m} \int_{x_\ell}^{x_r} \frac{dx}{\sqrt{E - V(x)}}.$$

A somewhat similar expression,

$$\frac{\sqrt{2m}}{h} \int_{x_\ell}^{x_r} \sqrt{E - V(x)} dx,$$

appears in the semiclassical (Bohr–Sommerfeld, Einstein–Brillouin–Keller) quantization conditions.

The following definitions and facts are provided:

- (1) The classical periods of oscillation in a one-dimensional harmonic (parabolic) potential do not depend on the energy (or amplitude) of the oscillation. Potentials that satisfy this property are referred to as isochronous.
- (2) Two potentials, $V^{(1)}(x)$ and $V^{(2)}(x)$, which have the same periods of oscillation at all energies, are referred to as isoperiodic.
- (3) Two potentials that have the same distance between the right and the left classical turning points $x_\ell(E) - x_r(E)$,

at all energies, are referred to as shear equivalent. Shear equivalent potentials are isoperiodic.^{4,5}

- (4) Potentials that are shear-equivalent to a parabola are isochronous.^{6,7} A much broader view of isochronous systems was offered by Calogero.⁸
- (5) A potential, which is continuous with continuous first and second derivatives (a C^2 potential), is isochronous if and only if it is shear-equivalent to a parabola.^{9,10} However, singular isochronous potentials have been reported.¹¹
- (6) Shear-equivalent potentials have equal Bohr–Sommerfeld phase integrals, $\oint p dx$, at all energies. It follows that such potentials have the same EBK (or lowest order WKB) spectra, except in limiting cases in which the Maslow index has to be modified, as illustrated below.
- (7) Shear equivalent potentials need not share a common quantum spectrum.¹²

In the RKR procedure (which is based on the semiclassical quantization), the vibrational spectrum provides the distances between the left- and right “classical turning points” (R_ℓ and R_r , respectively) at the energies of the available vibrations. This is not enough to construct the potential. The task of determining the potential is completed by examining the rotational levels associated with each vibrational level. They provide a distinct moment of inertia at each vibrational level, from which a “bond-length” is derived, which is (naively) assumed to be equal to $R_\ell + R_r/2$.

III. A PAIR OF ISOSPECTRAL POTENTIALS

Let us now consider the two potentials,

$$V^{(1)}(x) = \left(\frac{m\omega^2}{2}\right)x^2 \quad \text{for } -\infty < x < \infty$$

and

$$V^{(2)}(x) = \begin{cases} \infty & \text{for } -\infty < x < 0 \\ \left(\frac{m\left(\frac{\omega}{2}\right)^2}{2}\right)x^2 & \text{for } 0 \leq x < \infty. \end{cases}$$

For any energy $E > 0$, the classical turning points are easily calculated: for the first potential, we find $-x_\ell = x_r = 1/\omega\sqrt{2E/m}$, and for the second potential, $x_\ell = 0$ and $x_r = 2/\omega\sqrt{2E/m}$. Hence, the distance between the left- and right classical turning points is the same for both potentials. What this implies is that classically they have the same period at all energies (well, in this—harmonic—case, the period does not depend on the energy). Moreover, the semiclassical quantization, at the Bohr–Sommerfeld level,

$$\oint p dx = \oint \sqrt{2m(E - V(x))} dx = hn,$$

yields the same spectrum, $E_n = \hbar\omega n$. However, the Einstein–Brillouin–Keller (EBK)¹³ quantization condition

$$\oint p dx = \oint \sqrt{2m(E - V(x))} dx = h\left(n + \frac{\mu}{4} + \frac{b}{2}\right),$$

where μ is the number of classical turning points and b is the number of hard walls,¹⁴ yields $E = \hbar\omega\left(n + \frac{1}{2}\right)$ for the symmetric harmonic oscillator ($\mu = 2$; $b = 0$), but $E_n = \hbar\omega\left(n + \frac{3}{4}\right)$ for the half oscillator ($\mu = 1$; $b = 1$): these two potentials, the symmetric oscillator and the half-oscillator, are classically “isochronous” and hence semiclassically “isospectral.”

What about quantum mechanics?

The first potential is a simple harmonic oscillator, and so the energy is given by

$$E_n^{(1)} = \hbar\omega\left(n + \frac{1}{2}\right);$$

the average value of x is zero, at all n , and the matrix elements of the electric dipole transitions are

$$\langle \psi_{n+1}^{(1)} | \hat{x} | \psi_n^{(1)} \rangle = \frac{a}{\sqrt{2}} \sqrt{n+1},$$

where $a = \sqrt{\hbar/m\omega}$. We note in passing that the right classical turning point at the energy $E = \hbar\omega\left(n + \frac{1}{2}\right)$ is $x_r = a\sqrt{2n+1}$, which is about twice the electric dipole matrix element calculated above.

That was easy! But what about the second potential?

Well, semiclassically, it ought to be isospectral. For the harmonic oscillator, the semiclassical treatment yields the same spectrum of equidistant levels as the solution of the Schrodinger equation (except that in the semiclassical treatment, the energy is given in the form of $\hbar\omega n$ —the form originally postulated by Planck—rather than $\hbar\omega\left(n + \frac{1}{2}\right)$, unless we invoke the Maslow correction). So one might guess that the same would hold true for $V^{(2)}(x)$.

Let us first consider the potential

$$V^{(3)}(x) = \left(\frac{m\left(\frac{\omega}{2}\right)^2}{2}\right)x^2 \quad \text{for } -\infty < x < \infty.$$

This is a simple harmonic potential, with $E_n^{(3)} = \hbar\omega/2\left(n + \frac{1}{2}\right)$, $n = 0, 1, 2, \dots$. For $x \geq 0$, we note that $V^{(3)}(x)$ coincides with $V^{(2)}(x)$. Moreover, the odd numbered solutions for $V^{(3)}(x)$, i.e., $\psi_1^{(3)}(x), \psi_3^{(3)}(x), \psi_5^{(3)}(x), \dots$, are odd functions of x , and so they vanish at $x=0$. So defining

$$\psi_n^{(2)}(x) = \begin{cases} 0 & \text{for } x < 0 \\ \sqrt{2}\psi_{2n+1}^{(3)}(x) & \text{for } x \geq 0, \end{cases}$$

we obtain the solutions of the Schrodinger equation for the potential $V^{(2)}(x)$, with the eigenvalues

$$E_n^{(2)} = E_{2n+1}^{(3)} = \hbar\frac{\omega}{2}\left((2n+1) + \frac{1}{2}\right) = \hbar\omega\left(n + \frac{3}{4}\right).$$

The prefactor $\sqrt{2}$ was inserted in front of the wave function to maintain normalization after half the range was cut out. The argument for the half-oscillator ($V^{(2)}$) spectrum was presented by Gol’dman *et al.*¹⁵

So $V^{(2)}(x)$, just like $V^{(1)}(x)$, has a spectrum of equidistant levels, separated by $\hbar\omega$. To make these two potentials fully isospectral, we need to pull $V^{(2)}(x)$ down by $\hbar\omega/4$, but this

does not affect the wavefunctions or anything that depends on them.

We can distinguish between $V^{(1)}(x)$ and $V^{(2)}(x)$ by noting that while the former corresponds to $\langle \psi_n^{(1)} | x | \psi_n^{(1)} \rangle = 0$, for all n , the latter yields

$$\left\{ \frac{1}{n+2} \frac{\sqrt{\pi}}{a} \langle \psi_n^{(2)}(x) | x | \psi_n^{(2)}(x) \rangle; n = 0, 1, 2, \dots \right\} \\ = \{1, 1, 0.9375, 0.875, 0.8203, 0.7734, \dots\} \rightarrow_{n \rightarrow \infty} 0,$$

where a is larger by the factor $\sqrt{2}$ than that for the $V^{(1)}$ wave function. Clearly, the average value of x grows (sublinearly) with n , and so we can expect the rotational spectrum to exhibit an increasing moment of inertia, i.e., smaller spacings between rotational levels.

Finally, we examine the electric dipole transition matrix elements

$$\left\{ \frac{1}{\sqrt{n+1}} \frac{\sqrt{\pi}}{a} \langle \psi_n^{(2)}(x) | x | \psi_{n+1}^{(2)}(x) \rangle; n = 0, 1, 2, \dots \right\} \\ = \{0.8165, 0.7906, 0.7795, 0.7734, 0.7695, \dots\} \\ \rightarrow_{n \rightarrow \infty} 0.75.$$

We note (without attempting an interpretation) that these electric dipole matrix elements rise with n somewhat more slowly than those for the symmetric harmonic potential, $V^{(1)}$.

IV. CONCLUSION

The comparison between the harmonic oscillator and the half-oscillator spectra provides an elementary illustration of isospectrality. Examination of the diagonal and the off-diagonal dipole matrix elements suggests that the vibration-rotation spectra as well as the vibrational transition probabilities can be used to distinguish between such isospectral potentials.

The author's "hidden agenda" is to illustrate that the transition to remote teaching/learning imposed by the Covid-19 pandemic can possibly revolutionize the professor's role from an information provider to a guide in an intellectual pursuit. This requires an intensively involved teaching style that university administrators who look for cheaper mass-teaching technologies will not be happy with, as well as curious and committed students.

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APPENDIX: GENERATING FUNCTIONS FOR HARMONIC OSCILLATOR MATRIX ELEMENTS

This appendix is presented as an opportunity to introduce a somewhat richer application of generating function ideas than are usually offered to undergraduates.

The various matrix elements reported above were calculated by explicit integration (over $0 \leq x < \infty$) of appropriate expressions in terms of harmonic oscillator wave functions.

However, the well-known generating functions for the Hermite polynomials,

$$\exp(\zeta^2 - (s - \zeta)^2) = \sum_{n=0}^{\infty} \frac{s^n}{n!} H_n(\zeta),$$

can be applied as follows:

$$\exp(-\zeta^2) \exp(\zeta^2 - (s - \zeta)^2) \exp(\zeta^2 - (t - \zeta)^2) \\ = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \frac{s^{n_1} t^{n_2}}{n_1! n_2!} \exp(-\zeta^2) H_{n_1}(\zeta) H_{n_2}(\zeta).$$

Integrating over ζ from 0 to ∞ , we obtain

$$\frac{\sqrt{\pi}}{2} \exp(2st)(1 + \operatorname{erf}(s+t)) \\ = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \frac{s^{n_1} t^{n_2}}{n_1! n_2!} \int_0^{\infty} \exp(-\zeta^2) H_{n_1}(\zeta) H_{n_2}(\zeta) d\zeta,$$

providing a generating function for

$$\int_0^{\infty} \exp(-\zeta^2) H_{n_1}(\zeta) H_{n_2}(\zeta) d\zeta,$$

which, for odd valued $n_1 = n_2$, provides the factor required for normalization.

The old-fashioned application of such generating functions involved somewhat tedious expansion of the generating function $\sqrt{\pi}/2 \exp(2st)(1 + \operatorname{erf}(s+t))$, a task that a symbolic programming platform such as maple readily performs. We note that the expansion contains no terms with $n_1 \neq n_2$ when they are both odd (since they correspond to distinct eigenfunctions of the "half-oscillator" Hamiltonian), but it does contain spurious terms with either n_1 or n_2 or both being even.

In fact, the normalization can be easily adapted from that of the harmonic oscillator wave functions by multiplying by $\sqrt{2}$ to create a factor of 2 in the integrals that range over $x \geq 0$ only. Thus, the normalized eigenfunctions of the half-oscillator are

$$\psi_n(\xi) = \sqrt{\frac{2}{2^{2n+1}(2n+1)!\sqrt{\pi}}} \exp\left(-\frac{\xi^2}{2}\right) H_{2n+1}(\xi); \\ 0 \leq \xi < \infty.$$

To eliminate the spurious terms, we consider the generating function for the odd Hermite polynomials,

$$(\exp(\zeta^2 - (s - \zeta)^2) - \exp(\zeta^2 - (s + \zeta)^2))/2 \\ = \sum_{n=0}^{\infty} \frac{s^{2n+1}}{(2n+1)!} H_{2n+1}(\zeta).$$

The left-hand side can be simplified into $\exp(-s^2) \sinh(2s\zeta)$. Hence,

$$\exp(-s^2 - t^2) \int_0^{\infty} \exp(-\zeta^2) \sinh(2s\zeta) \sinh(2t\zeta) d\zeta \\ = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \frac{s^{2n_1+1} t^{2n_2+1}}{(2n_1+1)!(2n_2+1)!} \\ \times \int_0^{\infty} \exp(-\zeta^2) H_{2n_1+1}(\zeta) H_{2n_2+1}(\zeta) d\zeta. \quad (\text{A1})$$

The left-hand side is equal to

$$\frac{\sqrt{\pi}}{2} \sinh(2st) = \frac{\sqrt{\pi}}{2} \sum_{n=0}^{\infty} \frac{(2st)^{2n+1}}{(2n+1)!}. \quad (\text{A2})$$

Equating the right-hand side of Eq. (A1) to that of Eq. (A2), we obtain

$$\int_0^{\infty} \exp(-\zeta^2) H_{2n_1+1}(\zeta) H_{2n_2+1}(\zeta) d\zeta = \delta_{n_1, n_2} \frac{\sqrt{\pi}}{2} 2^{2n_1+1} (2n_1+1)!,$$

which reproduces the result presented above, with no spurious terms.

As a slight modification, we note that multiplication of both sides of Eq. (A1) by ζ before integrating with respect to ζ yields

$$\begin{aligned} & \exp(-s^2 - t^2) \int_0^{\infty} \exp(-\zeta^2) \sinh(2s\zeta) \sinh(2t\zeta) \zeta d\zeta \\ &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \frac{s^{2n_1+1} t^{2n_2+1}}{(2n_1+1)!(2n_2+1)!} \\ & \quad \times \int_0^{\infty} \exp(-\zeta^2) H_{2n_1+1}(\zeta) H_{2n_2+1}(\zeta) \zeta d\zeta. \end{aligned} \quad (\text{A3})$$

The left-hand side yields

$$\frac{\sqrt{\pi}}{4} ((s+t)\exp(2st)\text{erf}(s+t) - (s-t)\exp(-2st)\text{erf}(s-t)).$$

Writing this expression as a double power series in s and t is a bit messy, but easily carried out on Maple (or a similar

platform). The low index results agree with those presented above for both the diagonal and the off-diagonal matrix elements.

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¹J. L. McHale, *Molecular Spectroscopy*, 2nd ed. (CRC Press, Boca Raton, FL, 2017).

²F. Castaño, J. de Juan, and E. Martínez, "The calculation of potential energy curves of diatomic molecules: The RKR method," *J. Chem. Educ.* **60**, 91–93 (1983).

³J. Katriel and A. Rosenhouse, "Classical limit of the Korteweg-de Vries hierarchy of isospectral transformations," *Phys. Rev. D* **32**, 884–890 (1985).

⁴N. H. Abel, "Auflösung einer mechanischen Aufgabe," *J. Reine Angew. Math.* **1**, 153–157 (1826).

⁵L. D. Landau and E. M. Lifchitz, *Mechanics*, 3rd ed., translated by J. B. Sykes and J. S. Bell (Pergamon, New York, 1976).

⁶E. T. Osypowski and M. G. Olsson, "Isynchronous motion in classical mechanics," *Am. J. Phys.* **55**, 720–725 (1987).

⁷C. Antón and J. L. Brun, "Isochronous oscillations: Potentials derived from a parabola by shearing," *Am. J. Phys.* **76**, 537–540 (2008).

⁸F. Calogero, *Isochronous Systems* (Oxford U. P., Oxford, 2008).

⁹S. Bolotin and R. S. MacKay, in *Localization and Energy Transfer in Nonlinear Systems*, edited by L. Vázquez, R. S. MacKay, and M. P. Zorzano (World Scientific, New Jersey, 2003), pp. 217–224.

¹⁰D. J. Cross, "Every isochronous potential is shear-equivalent to a harmonic potential," *Am. J. Phys.* **86**, 198–200 (2018).

¹¹M. Urabe, "Potential forces which yield periodic motions of a fixed period," *J. Math. Mech.* **10**, 569–578 (1961).

¹²J. Dorignac, "On the quantum spectrum of isochronous potentials," *J. Phys. A* **38**, 6183–6210 (2005).

¹³J. B. Keller, "Corrected Bohr-Sommerfeld quantum conditions for nonseparable systems," *Ann. Phys.* **4**, 180–188 (1958).

¹⁴M. Brack and R. K. Bhaduri, *Semiclassical Physics* (CRC Press, Boca Raton, FL, 2018).

¹⁵I. I. Gol'dman, V. D. Krivchenkov, V. I. Kogan, and V. M. Galitskii, *Problems in Quantum Mechanics* (Infosearch, London, 1960), pp. 8–62.