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Helping Students Understand the Role of Symmetry in Chemistry Using the Particle-in-a-Box Model

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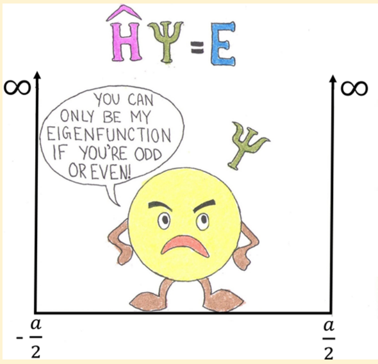
Ⓢ *Supporting Information*

ABSTRACT: In a course on chemical applications of symmetry and group theory, students learn to use several useful tools (like character tables, projection operators, and correlation tables), but in the process of learning the mathematical details, they often miss the conceptual big picture about "why" and "how" symmetry leads to the quite dramatic consequences that it does. This pedagogical gap is addressed in this paper by using one of the simplest chemical model systems, the particle in a box, along with a simple symmetry operator, parity, to get a clear understanding of the consequences of symmetry. The analysis of the particle-in-a-box model is extended by analogy to molecules, and connections are made to chemically important concepts like symmetry labels of molecular states, spectroscopic selection rules, and symmetry adapted linear combinations of orbitals.



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INTRODUCTION

Application of molecular symmetry and group theory is widespread in chemistry. It is used for classification of molecules, labeling molecular electronic states and vibrational normal modes, bringing about simplifications in the theory of chemical bonding, and explaining molecular spectra. Consequently, the study of the chemical applications of molecular symmetry is essential for a student majoring in chemistry. At the advanced undergraduate or graduate level, the typical group theory course in chemistry focuses on irreducible matrix representations of point groups and the use of character tables of these representations for determining symmetry characteristics of molecular wave functions, Hamiltonian matrix elements and spectroscopic selection rules.[1] One of us (Anirban Hazra) was the instructor for such a course (titled "Symmetry and Group Theory") given three times from 2011 onward at the Indian Institute of Science Education and Research (IISER) Pune, while the other author (Meghna A. Manae) was initially a student in the course and later assisted in teaching. The first time we taught this course, we sensed that the majority of students including those intending to specialize in physical chemistry found it difficult to take home the big picture about how symmetry simplifies chemistry. The students, for the most part, looked at the course as a "mathematical methods course" where one learns to apply techniques like using character tables and projection operators. We, however, wanted the course to be more intuitive and understanding based. The approach described in this paper is a result of our attempt to enable students to get a conceptual understanding of what is behind these techniques and why symmetry works. This proved to be very successful when we taught the course the second time onward, and we found strong student engagement with it in the classroom. We feel that this approach will be useful for instructors teaching symmetry concepts in advanced physical chemistry, spectroscopy and quantum chemistry courses to upper-division undergraduates and graduate students.

For students, the reason for missing the conceptual picture of how symmetry simplifies chemistry is largely related to the difficulty in visualizing complex and multidimensional molecular Hamiltonians, molecular wave functions, and symmetry operators that are central to the applications of symmetry in chemistry. Consider, for example, the following application taught in a group theory course: *An electronic transition in a molecule will be allowed if the direct product of the irreducible representations of the two electronic states involved in the transition is or contains the irreducible representation to which the coordinate x, y, or z belongs.* This result implies that only under specific symmetry conditions, the integrals

$$\int \psi_i^* x\, \psi_j\, \mathrm{d}\tau, \quad \int \psi_i^* y\, \psi_j\, \mathrm{d}\tau \ \text{or} \ \int \psi_i^* z\, \psi_j\, \mathrm{d}\tau$$

where ψ_i and ψ_j are the wave functions of the two electronic states (τ denotes all the coordinates on which these wave functions depend), can have nonzero values. It is hard for students to go beyond the techniques involved in determining irreducible representations and direct products, and get a feel for *why* this result is true and *how* it is connected to the symmetry of the molecule or the molecular Hamiltonian. Our

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goal, in this article, is to propose a way to address this difficulty. Our approach is to use a simple and familiar one-dimensional model Hamiltonian having only one nontrivial symmetry operation to discuss various group theoretical concepts, techniques and results (including the one described above). The simplification to a single dimension and single symmetry operation allows students to see through the mathematics, visualize the results, and get a conceptual understanding of the implications of symmetry in chemistry. We then extend these results by analogy to molecules, whereby students can make connections between the ideas in the simple model and real molecular applications of symmetry.

We use the one-dimensional particle-in-a-box (PIB) model and perhaps the easiest to understand nontrivial symmetry operator—the one-dimensional parity operator—to analyze the role of symmetry. The PIB model, due to its simplicity, is routinely used while teaching quantum chemistry. Besides using this model to demonstrate the process of solving the Schrödinger equation and examining the resulting eigenvalues and eigenfunctions, this model has been invoked widely to explore various important concepts in quantum chemistry. It has been used to aid in the understanding of perturbation theory,[2] the phenomena of resonance stabilization, and the role of symmetry in degeneracy.[3] It has been used to clarify the concept of the variational principle and to introduce the projection operator.[4] The two-dimensional PIB has been employed to better understand the nature of multidimensional wave functions.[5] Our use of the PIB in the present paper to understand the role of symmetry in chemistry further testifies to the versatility of this model for teaching chemical concepts.

In the next section, we analyze the symmetry characteristics of the PIB model. Following that, we consider various different applications of symmetry; in each case, first for the PIB model and then for molecules. Finally, we discuss the response of students to the approach and present our conclusions.

■ SYMMETRY CHARACTERISTICS OF THE PARTICLE-IN-A-BOX MODEL

The one-dimensional PIB problem in an introductory quantum chemistry text is usually stated in the following way: Consider a particle of mass m which is confined to move along the x axis between $x = 0$ and $x = a$, i.e., the potential energy is zero in the range $0 \leq x \leq a$ and infinite everywhere else. Obtain the quantum mechanical stationary state wave functions and corresponding energies of the particle.

A slight change in the choice of the coordinate system, in particular the choice of origin $x = 0$, can make the symmetry in the Hamiltonian explicit. Although this leads to changes in the mathematical representation of the system, it does not affect its actual physical properties. It is therefore natural to make a choice of mathematical origin that allows the symmetry of the system to be most easily exploited. We take $x = 0$ as the center of the box, whereby the region of zero potential is defined between $-a/2 \leq x \leq a/2$ (see Figure 1), and we refer to this system as the particle-in-a-symmetric-box (PISB) model. The potential energy function $V(x)$ is now an even function.

$$V(-x) = V(x)$$

Like any other symmetry property, the symmetry of the potential energy function can be expressed mathematically by considering a transformation under which the function is invariant. In this case, the transformation is the one-dimensional parity operator $\hat{P}$ defined by its action on a general function $f(x)$ as

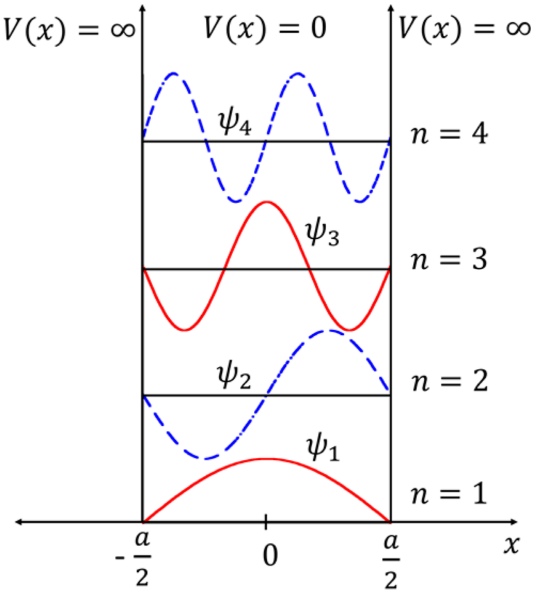

Figure 1. First four eigenstates of the PISB. The even eigenfunctions are shown with solid red lines states, while the odd eigenfunctions are shown with dashed blue lines.

$$\hat{P}f(x) = f(-x)$$

The invariance of the potential energy of the PISB under the operation of parity is then expressed as

$$\hat{P}V(x) = V(x)$$

As a consequence, the Hamiltonian commutes with the parity operator (see Proof 1 in the Supporting Information), i.e.,

$$[\hat{H}, \hat{P}] = \hat{H}\hat{P} - \hat{P}\hat{H} = 0$$

This, considered along with the theorems that commuting operators have a common set of eigenfunctions, and one-dimensional bound state Hamiltonians have nondegenerate eigenfunctions,[6] leads to the result that all the eigenfunctions of the Hamiltonian are eigenfunctions of the parity operator. It can be shown easily that the eigenvalues of the parity operator can only be unity or negative unity and that all the eigenfunctions of the parity operator are either even or odd functions [see Proof 2 in the Supporting Information].

It is very important for the student to fully comprehend the significance of this result: Even before solving for the eigenfunctions of the PISB, one can say based on the symmetry of the Hamiltonian that the eigenfunctions will be either even or odd functions. In other words, *the symmetry of the Hamiltonian is reflected in its eigenfunctions*. All the applications of symmetry in chemistry are due to this central result. In the next section, we will discuss in detail the consequences of this result in the context of chemical applications.

■ IMPLICATIONS OF SYMMETRY IN CHEMISTRY

For a molecule belonging to a particular symmetry point group, by definition, operating on the molecule with a symmetry operation from the point group will yield an equivalent structure of the molecule. Just like in the PISB, the molecular Hamiltonian can be shown to commute with the symmetry operations in the point group (see, e.g., ref 1c). Analogous to the PISB, even before solving the molecular Schrödinger equation which is a rather hard problem, one can say something about the symmetry properties of the molecular eigenfunctions. In particular, one can show that every eigenfunction forms a basis for some irreducible representation of the point group to which the molecule belongs [see Proof 3 in the Supporting Information]. This symmetry property of the eigenfunctions is a multidimensional extension of the concept of even and odd functions, and leads to all the other implications of symmetry described in the following subsections.

Symmetry Labels of the States

In the case of the PISB, all the eigenstates are either even or odd, and this property can be used to label the states as shown in Figure 2a. Analogously, because each electronic state in a molecule is a basis for some irreducible representation of the point group of the molecule, the label associated with the irreducible representation (the corresponding Mulliken symbol) can be used to label the state. For instance, in the case of water which has C_{2v} symmetry, the electronic states are labeled using symbols A_1, A_2, B_1, and B_2 as shown in Figure 2b.[7]

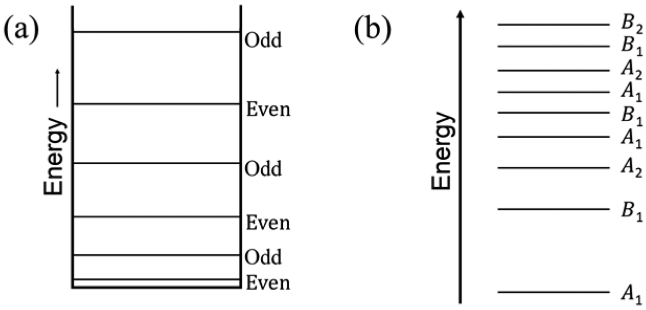

Figure 2. (a) Labeling of translational energy eigenstates (not to scale) for the PISB; (b) labeling of electronic energy eigenstates (not to scale) for the water molecule.

Projection Operator

Symmetry adapted linear combinations (SALC) of orbitals, which are used as a basis to get approximate solutions of the Schrödinger equation, are obtained using projection operators. To better understand projection operators, we construct them for the symmetry operations of the PISB and use them for obtaining even or odd functions from general one-dimensional functions, and then extend the idea to molecules. The symmetry operations of the PISB, namely the identity operation $\hat{E}$ and parity $\hat{P}$ form a group. The character table for this group is

	$\hat{E}$	$\hat{P}$
Even	1	1
Odd	1	-1

and the two projection operators $\hat{P}_+$ and $\hat{P}_-$ can be constructed as

$$\hat{P}_\pm = \frac{1}{2}[\hat{E} \pm \hat{P}]$$

To see the effect of the projection operators, we expand any well behaved one variable function as a linear combination of eigenfunctions of the PISB (which are sine and cosine functions) as these form a complete basis of the space of one-dimensional functions. This expansion can alternatively be thought of as a Fourier series expansion. By grouping even and odd functions together in the expansion, a general function $f(x)$ can always be written as a sum of some even function $f_{\text{even}}(x)$ and some odd function $f_{\text{odd}}(x)$

$$f(x) = f_{\text{even}}(x) + f_{\text{odd}}(x)$$

The projection operator $\hat{P}_+$ operates on $f(x)$ and projects out the even part of the function as shown below.

$$\begin{aligned}\hat{P}_+ f(x) &= \frac{1}{2}(\hat{E} + \hat{P})f(x) = \frac{1}{2}\hat{E}[f_{\text{even}}(x) + f_{\text{odd}}(x)] \\ &\quad + \frac{1}{2}\hat{P}[f_{\text{even}}(x) + f_{\text{odd}}(x)] \\ &= \frac{1}{2}[f_{\text{even}}(x) + f_{\text{odd}}(x)] + \frac{1}{2}[f_{\text{even}}(x) - f_{\text{odd}}(x)] = f_{\text{even}}(x)\end{aligned}$$

Similarly, $\hat{P}_-$ operating on $f(x)$ projects out the odd part of the function. Thus, the projection operators give symmetry adapted functions.

Analogously, the projection operators in molecules give functions which are the basis of some irreducible representation of the point group of the molecule. The projection operator in the case of molecules, $\hat{P}^j$, to obtain functions which form the basis for irreducible representation j, is defined as (see, e.g., ref 1a),

$$\hat{P}^j = \frac{l_j}{h}\sum_R \chi(R)^j \hat{R}$$

where l_j is the dimension of the irreducible representation, h is the order of the group, $\hat{R}$ is a symmetry operator in the group, $\chi(R)^j$ is the character of the matrix corresponding to operator $\hat{R}$ in the jth irreducible representation and the summation is over all the symmetry operations in the group. It is easily seen that the operators $\hat{P}_\pm$ for the symmetry group of the PISB are special cases of this general formula.

Hamiltonian Matrix Elements

One of the most important applications of quantum chemistry is the calculation of energy by solving the Schrödinger equation. While exact solutions are possible for one-electron systems like the hydrogen atom, in the case of molecules, only approximate solutions can be obtained. Approximate approaches, like perturbation theory and the variational method, involve the calculation of Hamiltonian matrix elements

$$H_{ij} = \int \phi_i \, \hat{H} \, \phi_j \, \mathrm{d}\tau$$

where ϕ_k are wave functions, not necessarily eigenfunctions of the Hamiltonian. The wave functions ϕ_k are often taken to be SALCs using the projection operator technique discussed earlier. In that case, just based on the symmetry properties of ϕ_k, we can say whether the matrix element is zero or not.

For the PISB, if we take ϕ_j to be a symmetry adapted function, i.e., it is either even or odd, it follows that $\hat{H}\phi_j$ has the same parity as ϕ_j. So the Hamiltonian matrix element can be nonzero only if ϕ_i and ϕ_j have the same parity [see Proof 4 in the Supporting Information]. By knowing that certain integrals are zero just based on symmetry, we can save considerable amount of time that would potentially be used to evaluate these integrals.

The analogy in the case of molecules is that, if ϕ_i and ϕ_j are symmetry adapted functions, the Hamiltonian matrix element can be nonzero only if ϕ_i and ϕ_j form a basis for the *same* irreducible representation whereby the integrand transforms as the totally symmetric representation of the group. The Hamiltonian matrix is block diagonal according to the symmetries of the basis functions as shown in Figure 3. In the case of PISB, there are two blocks, and in the case of molecules, the number of blocks is equal to the number of irreducible representations of the symmetry group of the molecule.

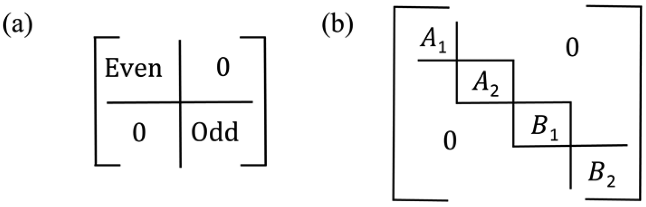

Figure 3. (a and b) Panels diagrammatically explain the diagonalization of the Hamiltonian written in a basis of SALC functions for the PISB and water molecule, respectively.

Notice that, in the previous two paragraphs we say “can be nonzero” rather than “will be nonzero” because while the integral will certainly be zero if ϕ_i and ϕ_j have different symmetries, the integral needs to be evaluated explicitly if ϕ_i and ϕ_j have the same symmetry. The point is that the integral of an even function taken over symmetric limits is not zero because of symmetry reasons, but for instance, as shown in Figure 4 can have a zero integral because of its specific definition. Incidentally, the function in Figure 4 is constructed by taking the product of the ground and second excited state eigenfunctions of the PISB which are both even; their orthogonality makes the integral zero.

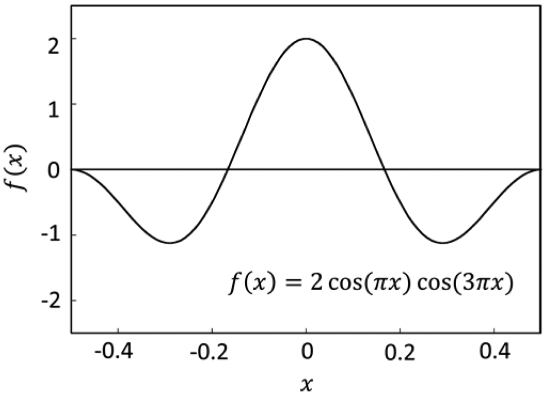

Figure 4. Given function is an example of an even function whose integral over symmetric limits goes to zero.

Spectroscopic Selection Rules

In the case of the PISB, consider the following integral:

$$\int_{-a/2}^{a/2} \psi_i^* x\, \psi_j \, d\tau$$

where ψs are the eigenfunctions of the PISB which are either odd or even functions. Knowing that x is an odd function, we can say that this integral can have a nonzero value only if ψ_i and ψ_j are of opposite parity. If x were replaced by x^2 (an even function) in the above integral, the value of the integral can be nonzero only if ψ_i and ψ_j are of the same parity.

We can now apply this logic to spectroscopic selection rules of molecules, which dictate whether a particular transition will be allowed or not depending on the value of the integral

$$\int_{\text{all space}} \psi_i^* \hat{O}\, \psi_j \, d\tau$$

where $\hat{O}$ is the dipole moment operator in the case of absorption and emission spectroscopy, and an element of the polarizability tensor in the case of Raman spectroscopy. When symmetry operations of the point group are applied, the dipole moment operator transforms like the coordinates x, y, and z, while the elements of the polarizability tensor transform like the binary products of the coordinates x^2, y^2, z^2, xy, xz, and yz. The above integral can be nonzero when the direct product of the irreducible representations corresponding to the two states and $\hat{O}$ (which can be looked up from the character table) is the totally symmetric irreducible representation, or is a reducible representation that when reduced contains the totally symmetric irreducible representation.

Variational Calculation of the Wave Function

The variational theorem states that the expectation value of energy obtained with any given trial function will always be greater than or equal to the exact ground state energy of the system. This is the basis of the variational method in quantum chemistry. Although this method is usually applied to calculate the approximate ground state energy, it can be used equally effectively to calculate certain specific excited state energies by a clever use of symmetry.

Consider a particle in a symmetric one-dimensional potential (not necessarily a PISB potential) whose states we want to obtain variationally. As proved earlier in the paper, the eigenfunctions of such a system where $V(-x) = V(x)$ will be either even or odd functions. Consider the variational trial function to be expanded as a linear combination of the PISB eigenfunctions (which form a complete basis) where the coefficients of expansion are the variational parameters. Now suppose, in the linear expansion we choose only *even* PISB eigenfunctions, then the variational procedure would give an upper bound to the lowest-energy even eigenstate of the system. Similarly, in the expansion if we choose only *odd* PISB eigenfunctions, the variational procedure would give an upper bound to the lowest-energy odd eigenstate. By restricting the variational flexibility of the trial function using symmetry, we can get the energy of not only the ground state, but an excited state which happens to be the lowest-energy state of parity opposite to the ground state.

In the case of molecules, consider the example of water which belongs to the C_{2v} point group. Since there are four irreducible representations for this group, a trial function can be chosen such that it is only composed of functions that form the basis for one of the irreducible representations (this can be done using projection operators). Then, the variational method can be used to obtain the energy of not just the ground state (A_1 symmetry), but the lowest energy state corresponding to all the other irreducible representations (A_2, B_1, and B_2), which will yield three excited state energies. The ordering of the excited state energies cannot be determined by symmetry considerations and can be obtained only after performing the actual variational calculation. Similarly for different spin multiplicities (noting that the molecular Hamiltonian commutes with the spin angular momentum operator), the variational method can be used to obtain the lowest energy state of each multiplicity like singlet, triplet, quartet and so on.

STUDENT RESPONSE

As mentioned in the Introduction, of the three times we taught the course Symmetry and Group Theory, we used the approach described in the paper the second and third times. This approach was introduced toward the later part of the course by which time the students had already seen several group theory concepts. After the ideas in the paper were discussed, students collectively expressed that the concepts they had learned until then were concretized, and they could get a physical feel for the role of symmetry in chemistry. To get some more systematic information on learning outcomes, we organized an interactive session with a group of 47 students where we specifically discussed this approach and then requested written feedback about its effectiveness. The details of this assessment procedure, including the description of the student group, the feedback form, our analysis and a few verbatim quotes of the students are given in the Supporting Information. We were happy to note that a large fraction of students grasped the central idea that the symmetry of the molecule is reflected in the Hamiltonian, which in turn is reflected in the symmetry of the wave function leading to all the different chemical consequences. They expressed that the session helped them go beyond the mathematics and get a conceptual feel for the various implications that symmetry has in chemistry.

CONCLUSIONS

Understanding the implications of symmetry on a molecule may seem daunting to students due to the multidimensional nature of the molecular Hamiltonian and wave functions which are hard to visualize. Utilizing the PIB, more specifically the symmetric box in one dimension, we have proposed an effective way to understand and explain the simplifications that symmetry brings about in chemistry. The PISB serves as a bridge between the abstract concepts in group theory and their application to molecules. Using analogy as a pedagogical technique, we discuss group theoretical concepts for the simple PISB model and then extrapolate to molecules. This helps to get conceptual understanding and also affords a broad consolidated view of the various different results discussed in a group theory course. Moreover, it aids in verifying intuition about any new chemical implication of symmetry that one encounters. When we taught symmetry concepts using this approach, we found clear student engagement with it because of its relative simplicity. On the basis of our positive experience in using this method while teaching, we feel that the PISB model will be a very effective tool for other instructors wanting to communicate the conceptual basis of the applications of symmetry in chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00856.

> Proofs for various theorems stated in the manuscript, a homework assignment that instructors can use, a detailed description of our evaluation of student learning, a sample feedback questionnaire, and verbatim quotes from some feedback questionnaires (PDF)

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Notes

The authors declare no competing financial interest.

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