

Chem224 - Jeffrey Rinehart - Fall 2023

Week 0-1: # Applied Spectral Theory in Hilbert Space: A Quantum Chemistry Primer & Motivation for Symmetry and Group Theory in Spectroscopy

Objectives

1. Understand course objectives
2. Get to know each other and the interests of the class
3. Hilbert Spaces and Quantum Mechanics
4. Understand Dirac notation and its application in describing atomic orbitals
5. Understand the role of symmetry in quantum mechanics and spectroscopy

Section 1: Basics of Hilbert Spaces and Quantum Mechanics

1. Hilbert Spaces

Definition: A Hilbert space \mathcal{H} is a *complete* inner product space. That means it's a vector space equipped with an inner product $\langle \cdot, \cdot \rangle$ that is *complete* in the sense that every Cauchy sequence in \mathcal{H} converges to an element in \mathcal{H} .

- **Inner Product:** A function $\langle \cdot, \cdot \rangle : \mathcal{H} \times \mathcal{H} \rightarrow \mathbb{C}$ that satisfies certain properties like linearity, conjugate symmetry, and positive-definiteness.
- ***complete:** A space is complete* if every Cauchy sequence in the space has a limit that also resides within the space.

This means that a Hilbert space is one that defines distances between vectors using the projection of one vector onto another. For Example: the wavefunction of a molecule projected onto a basis vector composed of atomic orbitals is an inner product that would give the "distance" along each basis vector

A Familiar Hilbert Space: The Atomic Orbitals and Dirac Notation

Dirac Notation: The Basics

- **Ket:** A ket $|\psi\rangle$ represents a column vector (state vector) in a Hilbert space. It describes the state of a quantum system.

$$|\psi\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}$$

- **Bra:** A bra $\langle\phi|$ represents the conjugate transpose (Hermitian conjugate) of the corresponding ket. It's essentially a row vector.

$$\langle\phi| = (|\phi\rangle)^\dagger = (a_1^* \ a_2^* \ \cdots \ a_n^*)$$

- **Inner Product:** $\langle\phi|\psi\rangle$ gives a complex number. It's akin to the dot product in classical vector spaces but is way more general and powerful. Because it can essentially take the very complicated spaces of wavefunctions and linearize them - making any solution to the Schrödinger equation a vector in the Hilbert space (i.e a linear combination of some orthonormalized basis vectors)

- Matrix Form:

$$\langle\phi|\psi\rangle = \sum_{i=1}^n a_i^* b_i$$

- Integral form:

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$$\langle\phi|\psi\rangle = \int \phi^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r}$$

Here, $\phi^*(\mathbf{r})$ is the complex conjugate of the wave function $\phi(\mathbf{r})$, and $d\mathbf{r}$ is the volume element.

- **Outer Product**: \$ | \psi \rangle \langle \phi | \$ is a generalization of the cross product to any dimensionality. It expands the number of dimensions to define the total space of two or more vectors and creates a new Hilbert space.
 - translates operator language into matrix language (i.e. an abstract transformation into a representation of that transformation in a basis).

$$|\psi\rangle\langle\phi| = \begin{pmatrix} a_1 b_1^* & a_1 b_2^* & \cdots \\ a_2 b_1^* & a_2 b_2^* & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

Dirac Notation and Atomic Orbitals

- Atomic orbitals are solutions to the Schrödinger equation for electrons in atoms.

- Let's take the hydrogen atom as an example. The wavefunction $\psi_{n,l,m}(r, \theta, \phi)$ can be described as a ket $|n, l, m\rangle$.

Example: 1s Orbital

- 1s orbital corresponds to $n = 1, l = 0, m = 0$.
- In Dirac notation: $|1, 0, 0\rangle$.

Example: Overlap Integral

- The overlap integral between two orbitals ϕ_a and ϕ_b is:

$$\langle \phi_a | \phi_b \rangle = \int \phi_a^*(r, \theta, \phi) \phi_b(r, \theta, \phi) d\tau$$

- In Dirac notation, this is simply:

$$\langle a | b \rangle$$

- Don't worry - we never have to use the integral form of the inner product in practice! The matrix form allows us to transform and simplify $\langle a | b \rangle$ without ever having to calculate the integral itself!

Summary

Dirac notation provides a clean, mathematical framework for using quantum mechanical principles on complex systems. This will be very important to spectroscopy and with a general understanding of the rules you can easily figure out the rules of any measurement or even make up new ones!

Operators in Dirac Notation

- Adjoint Property and Self-Adjoint Operators** The adjoint of an operator \hat{A} is another operator \hat{A}^\dagger defined in such a way that for every pair of vectors $|u\rangle$ and $|v\rangle$ in the Hilbert space, the following relation holds:

$$\langle u | \hat{A} | v \rangle = \langle v | \hat{A}^\dagger | u \rangle^*$$

Here, the * denotes complex conjugation.

- conjugate transpose of an operator
- In Dirac notation, \hat{A}^\dagger acts on bras just like \hat{A} acts on kets.

Hermitian Operators

If an operator is Hermitian it means that $\hat{A} = \hat{A}^\dagger$. This is common for operators that correspond to observable quantities.

$$A = A^\dagger \quad \text{and} \quad \langle \psi | A | \phi \rangle = \langle \phi | A | \psi \rangle^*$$

- **Symbols:**

- A : An operator acting on states in Hilbert space
- A^\dagger : The adjoint (Hermitian conjugate) of A
- $\langle \psi | A | \phi \rangle$ and $\langle \phi | A | \psi \rangle^*$: Inner products involving A

- **Why is it important?**

Self-adjoint operators are crucial because they correspond to physical observables. Their eigenvalues are always real.

3. Eigenvalues and Eigenvectors

- **Mathematical formulation:** $A|\psi\rangle = \lambda|\psi\rangle$ $A|\psi\rangle = \lambda|\psi\rangle$

- **Symbols:**

- A : The operator
- $|\psi\rangle$: Eigenvector corresponding to eigenvalue λ
- λ : Eigenvalue

- **Why are they important?**

Eigenvalues and eigenvectors give us the possible outcomes and states, respectively, for measurements of the associated observable.

Example of Spectral Decomposition

Hilbert Space and Atomic Orbitals

In quantum mechanics, the state of a system is described by a vector in a Hilbert space. For atomic orbitals, the relevant Hilbert space is the space of square-integrable functions. Let's choose a simple basis for our Hilbert space, consisting of atomic orbitals:

$$\text{Basis} = \{|2s\rangle, |2p_x\rangle, |2p_y\rangle, |2p_z\rangle\}$$

2. Spectral Decomposition

A useful property of Hilbert spaces that we can use is the spectral decomposition.

The spectral decomposition of an operator \hat{A} is given by:

$$\hat{A} = \sum_i \lambda_i |u_i\rangle \langle u_i|$$

Where λ_i are the eigenvalues and $|u_i\rangle$ are the corresponding eigenvectors.

For example, if we're considering the Hamiltonian operator \hat{H} , the eigenvalues λ_i would be the energies E_i , and the $|u_i\rangle$ would be the eigenstates corresponding to these energies.

3. Outer Products and Operators

In the operator formalism of quantum mechanics, an outer product $|a\rangle\langle b|$ is an operator that acts on the vectors in the Hilbert space. The matrix representation of this operator depends on the basis chosen.

For instance, consider an operator coupling $2s$ and $2p_x$ orbitals:

$$\hat{J}_{s-px} = |2s\rangle\langle 2p_x| + |2p_x\rangle\langle 2s|$$

Its matrix form in the given basis would be:

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

4. Symmetry and Operators

An operator commutes with a symmetry operation if the system is invariant under that symmetry. For inversion symmetry:

$$[\hat{I}, \hat{J}_{s-px}] = 0$$

In our example, inversion symmetry restricts J to be zero, as $2s$ and $2p_x$ behave differently under inversion.

5. Coupling Constant

Adding a coupling constant J to \hat{J}_{s-px} :

$$\hat{J}_{s-px} = J(|2s\rangle\langle 2p_x| + |2p_x\rangle\langle 2s|)$$

The matrix form becomes:

$$\begin{pmatrix} 0 & J & 0 & 0 \\ J & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

Here, J controls the strength of the coupling between $2s$ and $2p_x$.