Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 11
Sep 27th, 2013

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Objectives

- To introduce the concept of commutator of operators.
- To discuss the physical implications on observables represented by commuting operators.
- To introduce the concept of spread in measurements and its role in the Heisenberg's uncertainty principle.
- To introduce the concept of Hermitian operator and its need to represent observables of a system.

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Commutation of operators

In general, operator multiplication is not commutative, that is,

$$(\hat{A}\hat{B})f \neq (\hat{B}\hat{A})f$$

> **Definition:** The commutator of two operators is an operator defined by
>
> $$[\hat{A},\hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

Two operators are said to commute if their commutator is zero:

$$[\hat{A},\hat{B}] = 0$$

Clearly, $[\hat{A},\hat{B}] = -[\hat{B},\hat{A}]$. Hence, if $[\hat{A},\hat{B}] = 0$, then $[\hat{B},\hat{A}] = 0$

CAUTION: When evaluating a commutator, always let operators act on a trial function to avoid getting an incorrect result.

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Important theorem on commutative operators

> *Theorem.* If two operators commute, then they share the same set of eigenfunctions.

Proof. Let $[\hat{A},\hat{B}] = 0$ and let $\hat{A}\psi_n = a_n\psi_n$, $\hat{B}\varphi_n = b_n\varphi_n$ $\quad(*)$

We want to show that $\psi_n = \varphi_n$ for every n.

Because the operators commute, we have

$$[\hat{A},\hat{B}]\psi_n = \hat{A}\hat{B}\psi_n - \hat{B}\hat{A}\psi_n = \hat{A}(\hat{B}\psi_n) - a_n(\hat{B}\psi_n) = 0$$

so $\quad \hat{A}(\hat{B}\psi_n) = a_n(\hat{B}\psi_n)$

This means that $\hat{B}\psi_n$ is an eigenfunction of $\hat{A}$ with the eigenvalue a. But according to $(*)$, the eigenfunction of $\hat{A}$ with the eigenvalue a is ψ_n. Therefore, it must be that

$$\hat{B}\psi_n = (\text{const})\psi_n$$

Comparing this with $\hat{B}\varphi_n = b_n\varphi_n$
we see that the functions ψ_n and φ_n must be the same. QED.

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Physical significance of theorem about commuting operators

- If two operators commute, then each eigenfunction of one operator is simultaneously an eigenfunction of the other. Thus, if the system is in one of these eigenstates, then the two physical properties represented by these operators **simultaneously** have definite eigenvalues.

- The result stated above has an important implication:

If two operators $\hat{A}$ and $\hat{B}$ commute, then the properties represented by these operators **can** be measured simultaneously to arbitrary precision, i.e., the observables a and b have definite values.

If two operators $\hat{A}$ and $\hat{B}$ do not commute, then the properties a and b **cannot** be measured simultaneously to arbitrary precision.

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The spread in measurements

The spread in measurements is characterized by:

variance:	$\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2$
standard deviation ("uncertainty"):	$\sigma_a = \sqrt{\sigma_a^2}$

If a wave function ψ of a particle is an eigenfunction of $\hat{A}$, then

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi^* (\hat{A}\psi)\, dx = \int_{-\infty}^{\infty} \psi^* (a\psi)\, dx = a\int_{-\infty}^{\infty} \psi^* \psi\, dx = a$$

$$\langle a^2 \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A}^2 \psi\, dx = \int_{-\infty}^{\infty} \psi^* \hat{A}(\hat{A}\psi)\, dx = a\left(\int_{-\infty}^{\infty} \psi^* \hat{A}\psi\, dx\right) = a^2$$

so the variance is zero: $\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2 = a^2 - a^2 = 0$

If ψ is *not* an eigenfunction of $\hat{A}$, then $\sigma_a^2 > 0$

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Operators that represent observables are Hermitian

- Operators and eigenfunctions may be complex-valued. However, eigenvalues of quantum-mechanical operators must be real because they represent measurable values of physical properties.

To see what this restriction implies, let us multiply the equation

$$\hat{A}\psi = a\psi$$

by ψ* from the left and integrate. This gives

$$\int \psi^* \hat{A}\psi \, dx = \int \psi^* a\psi \, dx = a\int \psi^* \psi \, dx = a$$

Now let us take the complex conjugate of the original equation,

$$\hat{A}^* \psi^* = a^* \psi^*$$

multiply it by ψ from the left and integrate to get

$$\int \psi \hat{A}^* \psi^* dx = \int \psi a^* \psi^* dx = a^* \int \psi \psi^* dx = a^*$$

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Operators that represent observables are Hermitian

If we want the eigenvalue a to be real, we must have

$$a = a^*$$

Thus, a quantum-mechanical operator must be such that

$$\int \psi^* \hat{A}\psi \, dx = \int \psi \hat{A}^* \psi^* dx \qquad (*)$$

for <u>any</u> wave function ψ.

Not every operator satisfies Eq. ($*$). A linear operator that satisfies this equation is called **Hermitian.**

The mathematical requirement that the operator $\hat{A}$ be Hermitian is equivalent to the physical requirement that the eigenvalues (and hence average values) of $\hat{A}$ be real.

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Heisenberg's uncertainty principle

- Statement: The position and linear momentum of a particle cannot simultaneously have definite values. For any state of a particle, the product of uncertainties in the position and linear momentum is

$$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2}}$$

- In the above expression

  σ_x is the standard deviation of position meassurements

  σ_p is the standard deviation of position meassurements

- In practice, the uncertainty principle is a non-negligible effect only on a macroscopic scale because Planck's constant is very small.

Appendix: The commutator of two operators is crucial in the uncertainty principle

- ***Theorem***. If a system is described by the wave-function ψ and the operators $\hat{A}$ and $\hat{B}$ represent two observable quantities, then

$$\sigma_A^2 \sigma_B^2 \geq \frac{1}{4}\left\{\int_{-\infty}^{+\infty} \psi^*(x)\left[\hat{A},\hat{B}\right]\psi(x)\,dx\right\}^2$$

- ***Corollary***. If the operators $\hat{A}$ and $\hat{B}$ do not commute, then their corresponding observable quantities do not have simultaneously definite values. This is the most general formulation of the **uncertainty principle** for a pair of physical quantities represented by operators $\hat{A}$ and $\hat{B}$