# Chemistry 3P51 – Fall 2013
# Quantum Chemistry

Lecture No. 10
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## *Objectives*

- To introduce the concept of orthogonal and orthonormal functions.
- To introduce the concept of superposition of states.
- To introduce the concept of pure and mixed states.
- To show the probabilistic meaning of the expansion coefficients in a mixed state.

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## *Orthogonal and orthonormal functions*

- Functions $f_1(x)$ and $f_2(x)$ are said to be **orthogonal** to each other if

$$\int_{-\infty}^{+\infty} f_1^*(x) f_2(x)dx = \int_{-\infty}^{+\infty} f_2^*(x) f_1(x)dx = 0$$

- If $f_1(x)$ and $f_2(x)$ are **orthogonal and normalized**, they are said to be **orthonormal**.

- More than two functions can be **mutually orthonormal**

$$\int_{-\infty}^{+\infty} f_m^*(x) f_n(x)dx = \begin{cases} 1, & m = n \\ 0, & m \neq n \end{cases} \qquad m,n = 1,2,3,...$$

- The latter condition is usually written as:

$$\int_{-\infty}^{\infty} f_m^*(x) f_n(x)dx = \delta_{mn} = \begin{cases} 1, & m = n \\ 0, & m \neq n \end{cases}$$

where the symbol $\delta_{mn}$ is known as the **Kronecker delta**

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## *Orthogonality of eigenfunctions*

- Eigenfunctions of **any** operator representing an observable (particularly, eigenfunctions of any Hamiltonian) are **orthogonal**. If each eigenfunction is also normalized, together they form an **orthonormal set**, that is,

$$\int_{-\infty}^{\infty} f_m^*(x) f_n(x)dx = \delta_{mn}$$

- An example of this are the eigenfunctions for a particle in a 1D box. These eigenfunctions form and orthonormal set

$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)\,dx = \int_{-\infty}^{\infty} |\psi_n(x)|^2\,dx = 1$$

$$\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)\,dx = \frac{2}{L}\int_0^L \sin\frac{m\pi x}{L}\sin\frac{n\pi x}{L}\,dx$$

$$= \frac{2}{L}\int_0^L \frac{1}{2}\left[\cos\frac{(m-n)\pi x}{L} - \cos\frac{(m+n)\pi x}{L}\right]dx = 0, \quad m \neq n$$

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## *The principle of superposition of states*

Suppose we have solved the Schrödinger equation

$$\hat{H}\psi_n = E_n\psi_n$$

and obtained the eigenfunctions of the Hamiltonian,

$$\psi_1,\ \psi_2,\ \psi_3,\ \ldots$$

When the particle is in a state $\psi_n$, it has a definite energy $E_n$

**Superposition principle**: If the particle can be in eigenstates $\psi_1$, $\psi_2$, $\psi_3$, ..., then it can also be in a linear superposition of these states:

$$\varphi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \ldots = \sum_n c_n\psi_n$$

where $c_n$ are some constants, generally complex-valued.

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## *Pure and mixed states*

Wave functions that are eigenfunctions of the Hamiltonian are called **pure** states: $\psi_1$, $\psi_2$, $\psi_3$, ...

Wave functions that are *not* eigenfunctions of the Hamiltonian are called **mixed** states. It turns out that any mixed state $\varphi$ is a superposition (i.e., a linear combination) of pure states:

$$\varphi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \ldots = \sum_n c_n\psi_n$$

where $c_n$ are some coefficients.

**Note**: Every pure state can be *formally* treated as a superposition, e.g.,

$$\psi_2 = 0\cdot\psi_1 + 1\cdot\psi_2 + 0\cdot\psi_3 + 0\cdot\psi_4 + \ldots$$

Thus, *every* possible wave function of a particle can be written as a superposition of the eigefunctions of the corresponding Hamiltonian.

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## *Calculation of properties from wave-functions*

Given: A normalized wave function $\varphi$ describing the state of a particle and an operator $\hat{A}$ representing some physical property.

Is $\varphi$ an eigenfunction of $\hat{A}$ ?
$\hat{A}\varphi = a\varphi$ ?

**Yes**

The particle has a definite value of property $A$, which is equal to the eigenvalue $a$. Repeated measurements of this property will yield the same result: $a$.

**No**

The particle does not have a definite value of property $A$. Repeated measurements of this property will yield different eigenvalues $a_n$. The average of these will be

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



## *Proof of the formula for the average value of a property*

As explained above, every wave function $\varphi$ describing the particle can be thought of as a superposition of states

$$\varphi = \sum_n c_n \psi_n, \tag{1}$$

where $\psi_n$ are normalized eigenfunctions of some operator $\hat{A}$ with eigenvalues $a_n$. Consider the integral

$$I_1 = \int_{-\infty}^{\infty} \varphi^* \varphi \, dx \tag{2}$$

Let us plug Eq. (1) into Eq. (2):

Kronecker delta

$$I_1 = \int_{-\infty}^{\infty} \left( \sum_m c_m \psi_m \right)^* \left( \sum_n c_n \psi_n \right) dx$$

$$= \sum_m \sum_n c_m^* c_n \int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx = \sum_m \sum_n c_m^* c_n \delta_{mn} = \sum_n c_n^* c_n = \sum_n |c_n|^2$$

## *Proof of the formula for the average value of a property*

The condensed notation used on the previous slide means the following:

$$I_1 = \int_{-\infty}^{\infty} (c_1\psi_1 + c_2\psi_2 + \ldots)^* (c_1\psi_1 + c_2\psi_2 + \ldots)\, dx$$

$$= c_1^* c_1 \underbrace{\int_{-\infty}^{\infty} \psi_1^* \psi_1\, dx}_{=1} + c_1^* c_2 \cancelto{0}{\int_{-\infty}^{\infty} \psi_1^* \psi_2\, dx} + c_1^* c_3 \cancelto{0}{\int_{-\infty}^{\infty} \psi_1^* \psi_3\, dx} + \ldots$$

$$+ c_2^* c_1 \cancelto{0}{\int_{-\infty}^{\infty} \psi_2^* \psi_1\, dx} + c_2^* c_2 \underbrace{\int_{-\infty}^{\infty} \psi_2^* \psi_2\, dx}_{=1} + c_3^* c_2 \cancelto{0}{\int_{-\infty}^{\infty} \psi_3^* \psi_2\, dx} + \ldots$$

$$+ \ldots$$

$$= c_1^* c_1 + c_2^* c_2 + \ldots = \sum_n |c_n|^2$$



## *Proof of the formula for the average value of a property*

Now consider the integral

$$I_2 = \int_{-\infty}^{\infty} \varphi^* \hat{A} \varphi\, dx$$

We have

$$I_2 = \int_{-\infty}^{\infty} \varphi^* \hat{A} \varphi\, dx = \int_{-\infty}^{\infty} \left( \sum_m c_m \psi_m \right)^* \hat{A} \left( \sum_n c_n \psi_n \right) dx = \sum_m \sum_n c_m^* c_n \int_{-\infty}^{\infty} \psi_m^* \hat{A} \psi_n\, dx$$

The integrals appearing here are:

$$\int_{-\infty}^{\infty} \psi_m^* \hat{A} \psi_n\, dx = \int_{-\infty}^{\infty} \psi_m^* a_n \psi_n\, dx = a_n \int_{-\infty}^{\infty} \psi_m^* \psi_n\, dx = a_n \delta_{mn}$$

Therefore,

$$I_2 = \sum_m \sum_n c_m^* c_n a_n \delta_{mn} = \sum_n c_n^* c_n a_n = \sum_n |c_n|^2 a_n$$

## *Proof of the formula for the average value of a property*

Finally, consider the ratio

$$\frac{I_2}{I_1} = \frac{\int_{-\infty}^{\infty} \varphi^* \hat{A} \varphi\, dx}{\int_{-\infty}^{\infty} \varphi^* \varphi\, dx} = \frac{\sum_n |c_n|^2 a_n}{\sum_n |c_n|^2} = \langle a \rangle$$

Compare this to

$$\langle x \rangle = \frac{\sum_i w_i x_i}{\sum_j w_j}$$

If the wave function $\varphi$ is normalized, then

$$I_1 = \int_{-\infty}^{\infty} \varphi^* \varphi\, dx = \sum_n |c_n|^2 = 1$$

In that case, the average value of property $a$ (represented by $\hat{A}$) is

$$\boxed{\langle a \rangle = \int_{-\infty}^{\infty} \varphi^* \hat{A} \varphi\, dx = \sum_n |c_n|^2 a_n}$$

Compare this to

$$\langle x \rangle = \sum_i p_i x_i$$

The probability that a measurement of property $a$ will yield the value $a_n$ is

$$P(a_n) = |c_n|^2$$



## *Example of mixed states*

Example. A particle in a 1D box of length $L$ is in the state

$$\varphi = \frac{\sqrt{5}}{3}\psi_1 + \frac{2}{3}\psi_2,$$

where $\psi_1$ and $\psi_2$ are normalized eigenfunctions of $\hat{H}$ with the eigenvalues $E_1$ and $E_2$.
What are the probabilities that a measurement of energy will produce the values $E_1$ and $E_2$? What is the average energy?

Solution. $P(E_1) = |c_1|^2 = \frac{5}{9}, \quad P(E_2) = |c_2|^2 = \frac{4}{9}$

Check: $|c_1|^2 + |c_2|^2 = \frac{5}{9} + \frac{4}{9} = \frac{9}{9} = 1$

Since

$$E_n = n^2 \varepsilon_0, \quad \text{where} \quad \varepsilon_0 = \frac{h^2}{8mL^2}$$

we have

$$\langle E \rangle = |c_1|^2 E_1 + |c_2|^2 E_2 = \frac{5}{9}(\varepsilon_0) + \frac{4}{9}(2^2 \varepsilon_0) = \frac{21}{9}\varepsilon_0$$

## Calculation of expansion coefficients

Suppose that a normalized wave function $\varphi$ is a superposition of normalized eigenfunctions $\psi_n$:

$$\varphi = \sum_n c_n \psi_n$$

To determine the expansion coefficients $c_n$ we multiply both sides by $\psi_m^*$ and integrate to obtain

$$\int_{-\infty}^{\infty} \psi_m^* \varphi \, dx = \int_{-\infty}^{\infty} \psi_m^* \left( \sum_n c_n \psi_n \right) dx = \sum_n c_n \int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx = \sum_n c_n \delta_{mn} = c_m$$

where we have used the fact that $\delta_{mn} = 0$ for every term in the sum except for the one term in which $m=n$. Thus,

$$\boxed{c_n = \int_{-\infty}^{\infty} \psi_n^* \varphi \, dx}$$

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## Example showing the probabilistic meaning of coefficients

Example. Suppose the particle in a box is in the state

$$\varphi(x) = \left( \frac{30}{L^5} \right)^{1/2} x(L-x), \qquad 0 \le x \le L$$

Calculate the probability that a measurement of the energy of the particle will yield the ground-state eigenvalue

$$E_1 = \varepsilon_0 \equiv \frac{h^2}{8mL^2}$$

Solution. We have

$$P(E_1) = |c_1|^2,$$

where the coefficient $c_1$ is given by

$$c_1 = \int_{-\infty}^{\infty} \psi_1^*(x) \varphi(x) \, dx = \left( \frac{2}{L} \right)^{1/2} \left( \frac{30}{L^5} \right)^{1/2} \int_0^L x(L-x) \sin \frac{\pi x}{L} \, dx$$

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## *Example showing the probabilistic meaning of coefficients*

From the table of standard integrals,

$$\int x \sin ax \, dx = \frac{1}{a^2} \sin ax - \frac{x}{a} \cos ax$$

$$\int x^2 \sin ax \, dx = \frac{2}{a^3} \cos ax + \frac{2x}{a^2} \sin ax - \frac{x^2}{a} \cos ax$$

Evaluation of all necessary integrals gives

$$c_1 = \frac{8\sqrt{15}}{\pi^3} = 0.999277...$$

The final answer:

$$P(E_1) = |c_1|^2 = \frac{960}{\pi^6} = 0.998555...$$

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