

Chemistry BC3253x:
Structure, Bonding, and Spectroscopy
 aka Quantum Chemistry

III. The Postulates of Quantum Mechanics

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- The state of a quantum mechanical system is fully specified by the function $\Psi(\mathbf{r}, t)$. $\Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\tau$ is the probability that the system is in the volume element $d\tau$ at time t . \mathbf{r} is a multi-dimensional position vector for all particles in the system.
 Consequence: Ψ must be *square-integrable*.
- For every classical observable there is a corresponding linear Hermitian quantum mechanical operator.
Definition: an operator \hat{A} is Hermitian if for well behaved functions f and g $\int f^* \hat{A} g d\tau = \int g \hat{A}^* f^* d\tau$
Theorems:
 - The eigenvalues of any Hermitian operator are real.
 - The eigenfunctions of any Hermitian operator form a complete orthogonal set.
- In any measurement of the observable associated with the operator A (or \hat{A}), the only values observed are the eigenvalues a of the equation $A\Psi = a\Psi$ where Ψ is the wavefunction for the system.
- The expectation value for the variable a associated with operator A for a system in the state is given by $\langle a \rangle = \int \Psi^*(x) A \Psi(x) d\tau$.
- The function $\Psi(\mathbf{r}, t)$ which describes the complete spatial and temporal system is the solution to the time-dependent Schrodinger equation: $H\Psi = i \hbar \partial\Psi/\partial t$
 If H is independent of t , then $\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) \exp(-iE_n t/\hbar)$
 where $\psi_n(\mathbf{r})$ is a solution of the time-independent Schrodinger equation $H\psi_n = E_n \psi_n$

Operators and the Uncertainty principle:

Theorem: Commuting Hermitian operators have simultaneous eigenfunctions

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Quantum Mechanics

Thus far: some formalism and some applications.

Now go back and reinforce and expand formalism before attacking the next solutions to the Schrodinger equation.

McQuarrie gives a formal development based on postulates.

We have already looked informally at some of these concepts and their implications for ψ , which depends on coordinates \mathbf{r}

note: \mathbf{r} is a vector that represents **all** the **spatial** coordinates.

However waves also oscillate in time: think of a vibrating string.

The sine wave in x describes its shape, but the amplitude oscillates.



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Postulate 1

The complete wavefunction depends on coordinates \mathbf{r} and time t . We write $\Psi(\mathbf{r}, t)$: *uppercase* Ψ when it includes the time variable; generally use *lowercase* ψ for $\psi(\mathbf{r})$, the spatial wavefunction.

- The state of a system is fully specified by the function $\Psi(\mathbf{r}, t)$. $\Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\tau$ is the probability that the system is in the volume element $d\tau$ at time t . Thus Ψ must be *square-integrable*.**

This is just a generalization of what we said already for $\psi(\mathbf{r})$.

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Hermitian Operators

An operator \hat{A} is **hermitian** if for well-behaved functions f and g

$$\int f^* \hat{A} g \, d\tau = \int g \hat{A}^* f^* \, d\tau$$

(well-behaved = continuous, single valued, and square integrable.)

Suppose $\hat{A} = a$ (multiply by real constant a). Is \hat{A} hermitian?

$$\int f^* \hat{A} g \, d\tau = \int f^* a g \, d\tau = a \int f^* g \, d\tau$$

$$\int g \hat{A}^* f^* \, d\tau = \int g a^* f^* \, d\tau = a^* \int g f^* \, d\tau \quad (a^* = a \text{ if } a \text{ is real})$$

but $f^*g = g f^*$, so yes, $\hat{A} = a$ is hermitian.

Suppose $\hat{A} = i a$ (multiply by constant $i a$). Is \hat{A} hermitian?

$$\int f^* \hat{A} g \, d\tau = \int f^* i a g \, d\tau = i a \int f^* g \, d\tau$$

$$\int g \hat{A}^* f^* \, d\tau = \int g (-i a^*) f^* \, d\tau = -i a^* \int g f^* \, d\tau$$

This $\hat{A} = i a$ is not hermitian.

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Postulate 2

2 For every classical observable there is a corresponding linear hermitian quantum mechanical operator.

Theorems:

A. The eigenvalues of any hermitian operator are real.

Observables are real: having hermitian operators guarantees that.

B. The eigenfunctions of any hermitian operator form a **complete orthogonal set**. (proof: McQuarrie, page 126)

A set of functions $G_k(\mathbf{r})$ is orthogonal if, when $i \neq j$,

$$\int G_i^*(\mathbf{r}) G_j(\mathbf{r}) \, d\tau = 0 \quad \text{integral over all values of coordinates.}$$

If $G_k(\mathbf{r})$ is square-integrable, then we can normalize it.

For normalized functions, $\int G_i^*(\mathbf{r}) G_i(\mathbf{r}) \, d\tau = 1$

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Complete orthonormal sets of functions

A set of functions $G_k(\mathbf{r})$ is **orthonormal** if $\int G_i^*(\mathbf{r}) G_j(\mathbf{r}) \, d\tau = \delta_{ij}$

Kroenicker delta: $\delta_{ij} = 1$ when $i = j$, $\delta_{ij} = 0$ when $i \neq j$

Why the *? Some functions are complex!

A set of functions $G_k(x)$ is **complete** if, for any $f(x)$, we can write

$$f(x) = \sum c_k G_k(x) \quad (\text{sum over } k). \quad c_k \text{ are expansion coefficients.}$$

How do we find c_k ? Make use of orthonormality!

1) Multiply by $G_j^*(x)$: $G_j^*(x) f(x) = \sum G_j^*(x) c_k G_k(x)$.

2) Integrate $\int G_j^*(x) f(x) \, dx = \sum \int G_j^*(x) c_k G_k(x) \, dx$.

3) But $\sum \int G_j^*(x) c_k G_k(x) \, dx = \sum c_k \delta_{jk}$

so the only term in the sum that remains is $k = j$, so

$$c_j = \int G_j^*(x) f(x) \, dx$$

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Complete orthonormal sets: Legendre Polynomials

Suppose we have a function in the interval $[-1, 1]$.

Fourier series uses sines and cosines as the orthogonal functions.

Legendre Polynomials are another convenient orthogonal set

Mathematicians have studied these extensively

Designated $P_n(x)$, $n = 0, 1, 2, \dots$

$$P_0(x) = 1, \quad P_1(x) = x, \quad P_2(x) = \frac{1}{2}(3x^2 - 1), \quad P_3(x) = \frac{1}{2}(5x^3 - 3x)$$

observe: n is the highest order in the polynomial

when n is even, P_n is even: $P_0(-x) = P_0(+x)$

when n is odd, P_n is odd: $P_1(-x) = -P_1(+x)$

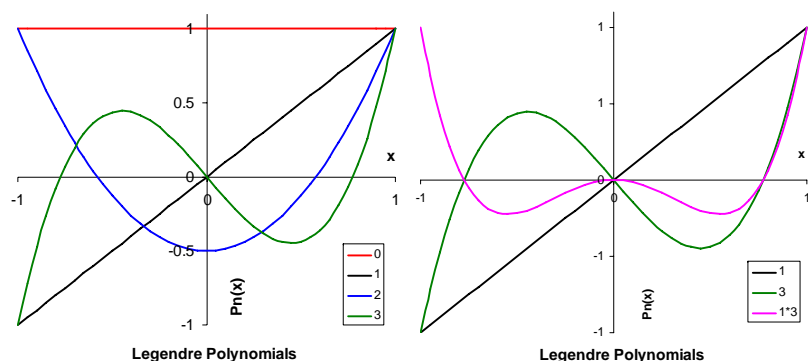
You can verify that they are orthonormal.

Sometimes symmetry helps: if j is odd and k is even,

then $P_j(x) P_k(x)$ is odd, so $\int P_j(x) P_k(x) \, dx = 0$.

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Complete orthonormal sets: Legendre Polynomials



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Using complete orthonormal sets

You have already used implicitly the concept of expanding in a complete orthonormal set. When you draw hybrid sp^2 orbitals or σ molecular orbitals, you describe new functions (orbitals) starting with (s, p, d, etc.).

These (s, p, d) orbitals, eigenfunctions for \hat{H} for the hydrogen atom, are used to construct wavefunctions for many other systems, with different \hat{H} 's.

Since the Hamiltonian operator \hat{H} is hermitian,

its eigenfunctions form a complete orthonormal set.

For a given \hat{H} , call this set $\{\phi_n(\mathbf{x})\}$ $\hat{H} \phi_n(\mathbf{x}) = E_n \phi_n(\mathbf{x})$.

Now suppose we want to find the $\psi(\mathbf{x})$ for a **different \hat{H}**

$$\psi(\mathbf{x}) = \sum c_k \phi_k(\mathbf{x}) \quad \text{where, as seen before } c_k = \int \phi_k^*(\mathbf{x}) \psi(\mathbf{x}) d\mathbf{x}.$$

So $\psi(\mathbf{x})$ may be a hybrid orbital, or a molecular orbital, written in terms of combinations of s', p's, etc.

We will see how this works later.

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Postulates 3 and 4

- In any measurement of the observable associated with the operator A , the only values observed are the eigenvalues a of the equation $A\Psi = a\Psi$ where Ψ is the wavefunction for the system.
- The **expectation value** for the variable a associated with operator A for a system in the state $\psi(\mathbf{x})$ is given by

$$\langle a \rangle = \int \psi^*(\mathbf{x}) A \psi(\mathbf{x}) d\mathbf{x}$$

Suppose we have a system in a state $\psi_n(\mathbf{x})$ which is an eigenfunction of the operator H , i.e. $H\psi_n(\mathbf{x}) = E_n \psi_n(\mathbf{x})$.

What is $\langle E \rangle$?

$$\begin{aligned} \langle E \rangle &= \int \psi_n^*(\mathbf{x}) H \psi_n(\mathbf{x}) d\mathbf{x} = \int \psi_n^*(\mathbf{x}) E_n \psi_n(\mathbf{x}) d\mathbf{x} \\ &= E_n \int \psi_n^*(\mathbf{x}) \psi_n(\mathbf{x}) d\mathbf{x} = E_n \end{aligned}$$

Since system is in an eigenstate, the energy is exactly E_n

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Expectation values

Suppose we have a system in a normalized state $\Phi(\mathbf{x})$ which is NOT an eigenfunction of the operator H . What is $\langle E \rangle$?

We still have $H\psi_n(\mathbf{x}) = E_n \psi_n(\mathbf{x})$. $\Phi(\mathbf{x}) = \sum c_k \psi_k(\mathbf{x})$

If $\Phi(\mathbf{x})$ is normalized, then

$$\begin{aligned} 1 &= \int \Phi^*(\mathbf{x}) \Phi(\mathbf{x}) d\mathbf{x} = \int \sum_j c_j^* \psi_j^*(\mathbf{x}) \sum_k c_k \psi_k(\mathbf{x}) d\mathbf{x} \\ &= \sum_j \sum_k c_j^* c_k \int \psi_j^*(\mathbf{x}) \psi_k(\mathbf{x}) d\mathbf{x} = \sum_j \sum_k c_j^* c_k \delta_{jk} = \sum_k c_k^* c_k \\ &\quad c_k^* c_k \text{ is the probability } P_k \text{ that the system is in state } k. \end{aligned}$$

$$\begin{aligned} \langle E \rangle &= \int \Phi^*(\mathbf{x}) H \Phi(\mathbf{x}) d\mathbf{x} = \int \sum_j c_j^* \psi_j^*(\mathbf{x}) H \sum_k c_k \psi_k(\mathbf{x}) d\mathbf{x} \\ &= \sum_j \sum_k c_j^* c_k \int \psi_j^*(\mathbf{x}) H \psi_k(\mathbf{x}) d\mathbf{x} = \sum_j \sum_k c_j^* c_k \int \psi_j^*(\mathbf{x}) E_k \psi_k(\mathbf{x}) d\mathbf{x} \\ &= \sum_j \sum_k c_j^* c_k E_k \int \psi_j^*(\mathbf{x}) \psi_k(\mathbf{x}) d\mathbf{x} = \sum_j \sum_k c_j^* c_k E_k \delta_{jk} \\ \langle E \rangle &= \sum_k c_k^* c_k E_k = \sum_k P_k E_k \end{aligned}$$

The expectation value is a weighted average of the eigenvalues.

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Expectation values

Conclusion: if a system is described by an eigenfunction of H , then the system has the exact energy corresponding to that state.

But if a system is described by some function that is not an eigenfunction, then this is not a pure state, but a **superposition**.

According to postulate 3, any *single* measurement of E will give a single eigenvalue E_k , but if we make a number of measurements, we will see a distribution of energies whose average (expectation) value depends on the particular function.

(Most real observations are of necessity averages.)

Superposition states are not stationary states: they evolve in time.

Eigenfunctions, which have exact energies, are **stationary states**.

This is all consistent with the Heisenberg uncertainty principle

$$\Delta E \Delta t > \hbar/4\pi$$

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Schrödinger's Cat

Famous thought experiment of Schrödinger (1935)

Put a cat in a box along with a radioactive atom and some sealed poison gas. If the atom decays, the emitted particle will break the seal and kill the cat. The half-life of the atom is such that it has a 50% chance of decay in some time interval Δt .

Is the cat alive or dead?

Schrödinger said it is both:

in a superposition state.



Read the web to see much more lengthy discussions on this.



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Postulate 5: Time Dependent Schrödinger Equation

5. The function $\Psi(\mathbf{r}, t)$ which describes the complete spatial and temporal system is the solution to the time-dependent Schrödinger equation: $H\Psi = i\hbar \partial\Psi/\partial t = (-\hbar/i) \partial\Psi/\partial t$

What is the solution $\Psi(\mathbf{r}, t)$?

We can find a general solution when H is independent of t

Hypothesis: If $\Psi(\mathbf{r}, t)$ is separable, $\Psi_n(\mathbf{r}, t) = \psi_k(\mathbf{r}) T(t)$

Substitute: $H \psi_k(\mathbf{r}) T(t) = i\hbar \partial\{\psi_k(\mathbf{r}) T(t)\}/\partial t$

RHS: $i\hbar \partial\{\psi_k(\mathbf{r}) T(t)\}/\partial t = \psi_k(\mathbf{r}) i\hbar \partial T(t)/\partial t$

LHS: since H is independent of t , $H \psi_k(\mathbf{r}) T(t) = T(t) H \psi_k(\mathbf{r})$

So $T(t) H \psi_k(\mathbf{r}) = \psi_k(\mathbf{r}) i\hbar \partial T(t)/\partial t$

Divide both sides by $\psi_k(\mathbf{r}) T(t)$:

$$H \psi_k(\mathbf{r}) / \psi_k(\mathbf{r}) = i\hbar \partial T(t)/\partial t / T(t)$$

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Postulate 5: Time Dependent Schrödinger Equation

$$H \psi_k(\mathbf{r}) / \psi_k(\mathbf{r}) = i\hbar \partial T(t)/\partial t / T(t)$$

The LHS depends only on \mathbf{r} , the RHS on t . The only way this equation can be correct for all \mathbf{r} and t is if both sides are equal to the same constant. For now, call it c .

1) $H \psi_k(\mathbf{r}) / \psi_k(\mathbf{r}) = c$, so $H \psi_k(\mathbf{r}) = c \psi_k(\mathbf{r})$

If $c = E_k$ this is the **spatial** Schrödinger equation!

The separation constant is its eigenvalue E_k . $H \psi_k(\mathbf{r}) = E_k \psi_k(\mathbf{r})$

2) $i\hbar \partial T(t)/\partial t / T(t) = E_k$ so $\partial T(t) / \partial t = (-iE_k/\hbar) T(t)$

What function has this behavior? $T(t) = \exp(-iE_k t/\hbar)$

Thus if H is independent of T , $\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) \exp(-iE_n t/\hbar)$

where $\psi_n(\mathbf{r})$ is a solution of the time-independent

Schrödinger equation $H \psi_n = E_n \psi_n$

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Postulate 5: Time Dependent Schrödinger Equation

Summary: when H is independent of t :

- 1) The time independent (spatial) Schrödinger equation is a consequence of the time dependent one!
- 2) The energy E in the phase $e^{-iE_n t/\hbar}$ of the time-dependent wave function is the eigenfunction of the time-independent part:

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) \exp(-iE_n t/\hbar)$$

For most applications in this course, we will focus on the **spatial functions** from the time-independent Schrödinger equation

$$H \psi_n(\mathbf{r}) = E_n \psi_n(\mathbf{r})$$

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Time Dependent Wave Function

When H is independent of t , the time-dependent wavefunction is

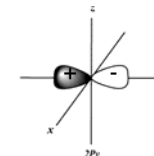
$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) \exp(-iE_n t/\hbar)$$

where $H\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r})$

$E = h\nu = \hbar\omega$, so $\omega_n = E_n/\hbar$, so $\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) \exp(-i\omega_n t)$

The function oscillates sinusoidally

in time with frequency ω_n .



Note that

$$\begin{aligned} \Psi_n^*(\mathbf{r}, t) \Psi_n(\mathbf{r}, t) d\tau &= \psi_n^*(\mathbf{r}) \exp(+i\omega_n t) \psi_n(\mathbf{r}) \exp(-i\omega_n t) d\tau \\ &= \psi_n^*(\mathbf{r}) \psi_n(\mathbf{r}) d\tau \end{aligned}$$

The spatial wavefunction alone describes the probability.

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Simultaneous Eigenfunctions

Consider operators \hat{A} and \hat{C} .

A function $f(x)$ is a **simultaneous eigenfunction** of these operators if $\hat{A}f = af$ and $\hat{C}f = cf$

Theorem (asserted but not proven here):

Commuting Hermitian operators have simultaneous eigenfunctions.

It is also true that if two operators do not commute, they do not have simultaneous eigenfunctions.

While all of this is very abstract, a remarkable fact is that we can make all sorts of statements about the as-yet-unknown wavefunctions for a system simply by looking at some properties of the operators!

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Commuting operators and Simultaneous Eigenfunctions

Some operators **commute with the hamiltonian** \hat{H} .

For example, the operator for the angular momentum along the z axis, \hat{J}_z , (or L_z) commutes with \hat{H} : $[\hat{H}, \hat{J}_z] = \hat{H} \hat{J}_z - \hat{J}_z \hat{H} = 0$

Thus any eigenfunction of \hat{H} is also an eigenfunction of \hat{J}_z

A system described by that function has a single value for E and J_z .

But other operators **do not commute with \hat{H}** , e.g. \hat{J}_x !

So in the quantum world, a molecule in a given state

(an eigenfunction of \hat{H}) has a well-defined J_z , but not J_x .

The **Heisenberg uncertainty principle** is related to commutators:

x , the operator for position x , and p_x , the operator for momentum,

do not commute: $[x, p_x] = -i\hbar$. From this it can be shown that

$\Delta x \Delta p_x > \hbar/4\pi$ (but we won't go through the details.)

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