2 Molecular Structure and Intramolecular Electron Delocalization

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2.1 A Primer on Quantum Mechanics

Description of Quantum-Mechanical Systems

- wave-particle duality implies that electromagnetic irradiation can display particle nature while particles like electrons can display the characteristics of waves.

- all information on the quantum state of a quantum system at any time t can be described mathematically by a complex function $\psi(r, t)$, called wavefunction

- $\psi(r, t)$ can be regarded as a probability amplitude that defines the probability of the possible results of measurements made on the quantum system

Dirac Notation

- Dirac ("bra-ket") notation treats wavefunctions as state vectors and utilizes bras and kets
  - ket $|\phi\rangle$ denotes a state vector, that is, an element of an abstract complex vector space, the state space V, and represents a state of a quantum system
  - bra $\langle f|$ denotes a linear functional $f: V \to \mathbb{C}$ that maps each vector $|\phi\rangle$ in the vector space V to a complex number in the complex plane $\mathbb{C}$, as given by the scalar product $(\langle f|, |\phi\rangle)$, denoted most often $\langle f|\phi\rangle$
  - letting the linear functional $\langle f|$ act on a vector $|v\rangle$ is denoted as $\langle f|v\rangle \in \mathbb{C}$ that has the form of a matrix multiplication of the row vector $\langle f|$ with the column vector $|v\rangle$
- advantages to understanding wavefunctions as elements of an abstract vector space:
  - Bra-ket notation accomplishes simpler formulations of wavefunctions
  - linear algebra can be used to manipulate and understand state vectors corresponding to wavefunctions

State Space

- the ensemble of all wavefunctions, or quantum states, in which a quantum system can be found, forms an abstract complex vector space, the state space V

- V is a Hilbert space, i.e., a complex vector space equipped with a scalar product (inner product, projection product), that is a map $V \times V \to \mathbb{C}$ defined as

$$(\psi_1, \psi_2) = \int_{-\infty}^{\infty} \psi_1^*(r,t)\psi_2(r,t)dr$$

- state spaces can be of finite dimension or infinite dimension; in the latter case, state spaces can also be discrete or continuous.
  - The spin state space of an electron in a magnetic field is of dimension 2, constituted of the state up and the state down.
  - The orbital state space of an electron in an infinite potential is infinite and discrete.
  - The position state space of an electron in space is infinite and continuous.

Properties of the Scalar Product

Inversion and Linearity

- $\langle \psi | \phi \rangle = \langle \phi | \psi \rangle^*$
- linearity on the right: $\langle \psi | \lambda_1 \phi_1 + \lambda_2 \phi_2 \rangle = \lambda_1 \langle \psi | \phi_1 \rangle + \lambda_2 \langle \psi | \phi_2 \rangle$ where $(\lambda_1, \lambda_2) \in \mathbb{C}^2$
- semi-linearity on the left: $\langle \lambda_1 \psi_1 + \lambda_2 \psi_2 | \phi \rangle = \lambda_1^* \langle \psi_1 | \phi \rangle + \lambda_2^* \langle \psi_2 | \phi \rangle$ where $(\lambda_1, \lambda_2) \in \mathbb{C}^2$

Normalization

- $\langle \phi | \phi \rangle \in \mathbb{R}^+$. $\sqrt{\langle \phi | \phi \rangle}$ also noted $||\phi||$ is called the norm of $|\phi\rangle$
- a state $|\phi\rangle$ is said to be normalised if $||\phi|| = 1$

Orthogonality

- $\langle \phi | \phi \rangle = 0 \Leftrightarrow |\phi\rangle = 0$
- two states $|\phi\rangle$ and $|\psi\rangle$ are said to be orthogonal if $\langle \psi | \phi \rangle = 0$

Observables and Expectation Values

- any observable Ω, that is, a mesurable physical property of a quantum system, can be represented by a corresponding operator $\hat{\Omega}$, a mathematical operation that can be performed on the wave function ψ respectively the corresponding state vector $|\psi\rangle$

- to obtain more information on an observable $\hat{\Omega}$ of a defined quantum system, the following associated equation, called Eigenvalue equation, needs to be solved:

$$\hat{\Omega}\ |\psi\rangle = \omega|\psi\rangle$$

  - wavefunctions ψ that fulfill the Eigenvalue equation are called Eigenfunctions (allowed states)
  - Eigenvalue ω is a constant that to the value of the observable Ω

- expectation value can be calculated as

$$\langle\Omega\rangle = \int \Psi^* \hat{\Omega} \Psi \, d\tau = \omega$$

because if Ψ is an Eigenfunction, then $\int \Psi^* \omega \Psi \, d\tau = \omega \int \Psi^* \Psi \, d\tau = \omega$

Hermitian Conjugate Operators and Hermiticity

- for any linear operator $\hat{\Omega}$, the conjugate operator (adjoint) $\hat{\Omega}^{\dagger}$ is defined as:

$$\langle \Psi_i | \hat{\Omega}\Psi_j \rangle = \int \Psi_i^* \hat{\Omega}\Psi_j d\tau = \int \Psi_j (\hat{\Omega}^{\dagger}\Psi_i)^* d\tau = \langle \hat{\Omega}^{\dagger}\Psi_i | \Psi_j \rangle$$

- Hermiticity: quantum-mechanical operators $\hat{\Omega}$ that are identical to their own adjoint are said to be Hermitian operators.

$$\hat{\Omega} = \hat{\Omega}^{\dagger}$$

- **any quantum-mechanical operator $\hat{\Omega}$ corresponding to a physical observable Ω can be shown to be a Hermitian operator.**

Consequences of Hermiticity

- Hermiticity has important implications (by its definition):
  - all Eigenvalues, the values of the observables, are always real, that is, $\omega = \omega^*$
  - the set of all Eigenfunctions $\Psi(r, t)$ is complete
  - the ensemble of the Eigenfunctions form an orthonormal basis of the state, that is, they are orthogonal (hence, linearly independent) and normalized

$$\langle \Psi_i | \Psi_j \rangle = \int \Psi_i^* \Psi_j d\tau = 0 \quad \text{for} \quad i \neq j \quad \text{and} \quad \langle \Psi_i | \Psi_i \rangle = \int \Psi_i^* \Psi_i d\tau = 1$$

- any state vector can be formed from a combination of basis states with complex coefficients:

$$|\phi\rangle = \sum_v c_i |\psi_i\rangle \quad \text{with} \quad c_i \in \mathbb{C}, \text{ for a discrete case}$$

$$|\phi\rangle = \int c(r) |r\rangle dr \quad \text{with} \quad c(r) \in \mathbb{C}, \text{ for a continuous case}$$

- **Hermiticity of quantum-mechanical operators $\hat{\Omega}$ corresponding to a physical observables Ω are the basis for concepts such as hybridization and linear combination of atomic orbitals**

Born Interpretation of the Wavefunction

- probability density $\rho(r,t)$ to find a particle at the location r at time t is given by the square modulus of the complex wave function (which implies the density is always a real number)

$$\rho(r,t) = |\psi(r,t)|^2 = \psi^*(r,t)\psi(r,t)$$

- probability $P(t)$ to find a particle in an infinitesimal volume $d\tau$ around a location r at time t is

$$P(t) = \int |\psi|^2 d\tau$$

- normalization: the probability integrated over the entire space equals to 1

$$\int |N\psi|^2 d\tau = 1 \quad \Leftrightarrow \quad N = \left\{ \int |N\psi|^2 d\tau \right\}^{-1/2}$$

- **due to Hermiticity, Eigenfunctions resulting from Eigenequations with quantum-mechanical operators $\hat{\Omega}$ corresponding to a physical observables Ω are normalized**

Quantization Resulting from the Constraints of the Born Interpretation

- an acceptable wavefunction must hence be square-integrable and normalizable function mapping each point of 3D space to a complex number
- Born interpretation further implies that the wavefunction is
  - single-valued at every location r
  - not infinite over a non-infinitesimal region
  - continuous in slope and curvature
- **these conditions limits the choice of acceptable mathematical functions**
- **quantization of the allowed energies of a particle is the result of the finite probability density and the resulting constraints for the selection of acceptable wavefunctions**