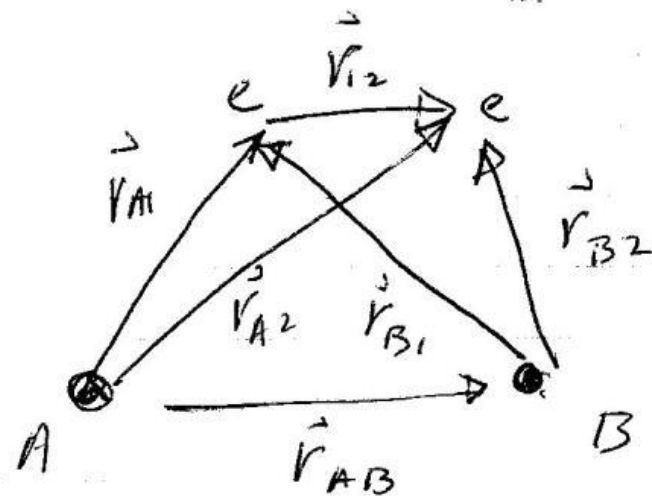
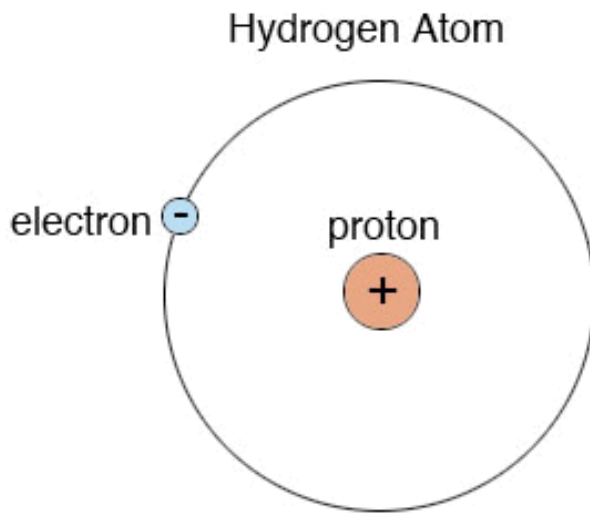


Chapter #2

Hartree-Fock Theory

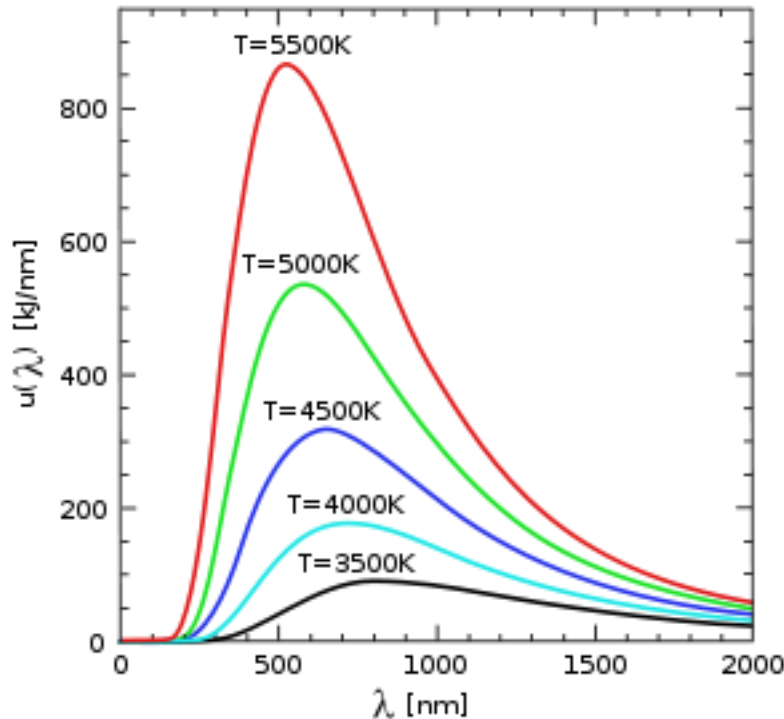
2.1. Need for Probability Distribution Functions

Wouldn't it Be Nice...



Wouldn't it be nice if we could describe atoms with classical electrodynamics: interaction between moving charged particles.

Planck, 1901: Black Body Radiation

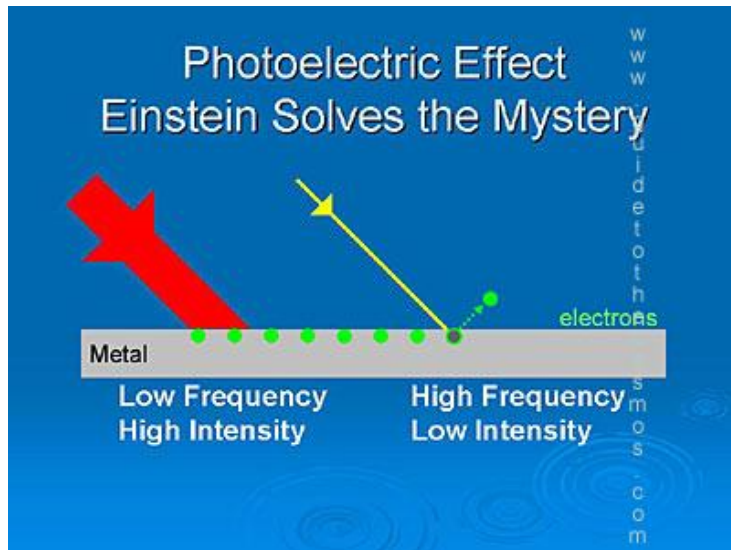


$$I(n, T) = \frac{2h n^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1}$$

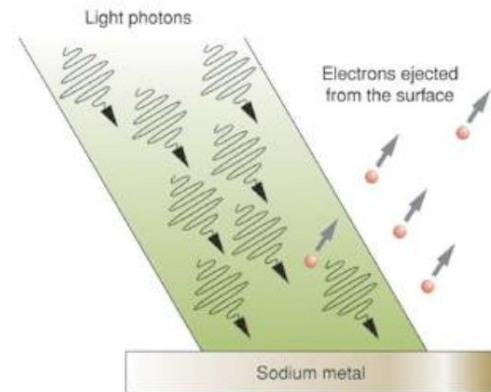
$$E = h\nu$$

The **Planck–Einstein relation** is also referred to as the Einstein relation, Planck's energy–frequency relation, the Planck relation, and the Planck equation.

Einstein, 1905: Photoelectric Effect

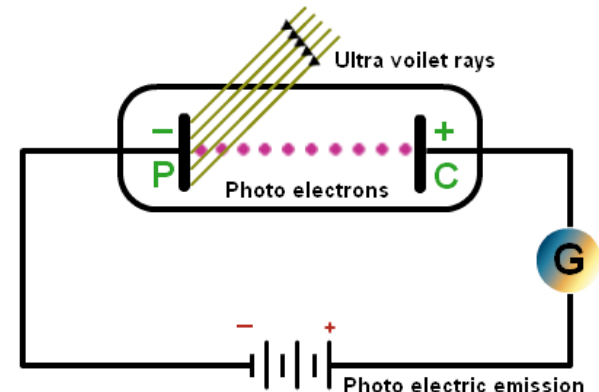


Photoelectric Effect

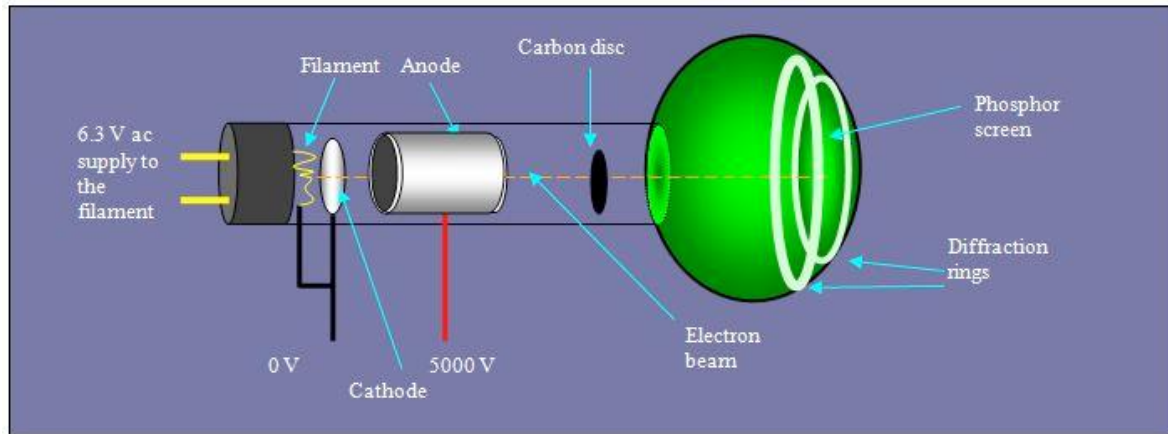


Electrons are only dislodged by the impingement of photons when those photons reach or exceed a threshold frequency (energy). Below that threshold, no electrons are emitted from the metal regardless of the light intensity or the length of time of exposure to the light.

To make sense of the fact that light can eject electrons even if its intensity is low, Einstein proposed that a beam of light is not a wave propagating through space, but rather a collection of discrete wave packets (photons), each with energy $h\nu$.



De Broglie Relation, 1924



To explain diffraction experiments, de Broglie suggested that particles can exhibit properties of waves. Equation used to describe the wave properties of matter, specifically, the wave nature of the electron: $\lambda = h/mv$ where λ is wavelength, h is Planck's constant, m is the mass of a particle, moving at a velocity v .

Heisenberg Uncertainty

1927



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Heisenberg Uncertainty Principle

The operators for momentum and position do not commute. In 1-D:

$$[\hat{x}, \hat{p}_x] = i\hbar \quad (1)$$

As a consequence, \hat{x} and \hat{p}_x cannot share the same set of eigenfunctions, and *it is impossible to specify simultaneously and precisely the momentum and position of the particle*. In fact, it can be shown that there is a fundamental limit to the precision with which both can be known:

$$\boxed{\Delta x \Delta p_x \geq \frac{\hbar}{2}} \quad (2)$$

Δx and Δp_x are the standard deviations in the distribution of position and momentum respectively, defined (as in statistics) to be:

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \quad \text{and} \quad \Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} \quad (3)$$

We need a "Wave Function"

We need a Probability Distribution

For example, the particle-in-a-box stationary states are not eigenfunctions of either \hat{x} or \hat{p}_x , so there is some uncertainty about what the values of the particle's position and momentum will be before a measurement is performed. The particle's position is given by the probability distribution $\psi^*\psi$ (the Born interpretation) and so clearly has an uncertainty about it. The *magnitude* of the particle's momentum is known, because it is in a state of definite kinetic energy (ψ is an eigenfunction of the Hamiltonian, \hat{H} , which gives the *total* energy and inside the box it has no potential energy):

$$T_n = E_n = \frac{h^2 n^2}{8mL^2} = \frac{p^2}{2m} \Rightarrow p = \pm \frac{hn}{2L} = \pm \frac{\hbar n \pi}{L} \quad (4)$$

However, the sign of the particle's momentum is not determined - the particle could be found to be moving to the right or to the left in the box. The above is consistent with the De Broglie relationship between wavelength and momentum, $|p| = h/\lambda$, because the wavelength of the wavefunction is

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \Rightarrow \frac{n\pi x}{L} = \frac{2\pi x}{\lambda} \Rightarrow \lambda = \frac{2L}{n} \Rightarrow |p| = \frac{h}{\lambda} = \frac{\hbar n}{2L} \quad (5)$$

Chapter #2

Hartree-Fock Theory

2.2. Schroedinger Equation and Variational Theorem

Schrodinger Equation

$$Hy = Ey$$

H = Hamiltonian Operator

Once we have the “Wave Function”, then the application of the “Hamiltonian Operator” on the “Wave Function” produces the Energy Eigenvalues.

What is H? What is ψ ?

Hamiltonian

$$T + V = E$$

The kinetic energy can be rewritten

$$\frac{p^2}{2m} + V = E$$

We can multiply this equation by Ψ

$$\frac{p^2}{2m} \Psi + V \Psi = E \Psi$$

What the heck?

$$p := \frac{\hbar}{i} \frac{\partial}{\partial x}$$

$$p^2 = -\hbar^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\hbar^2 \nabla^2$$

Laplacian

Hamiltonian for Atoms and Molecules

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i < j} \frac{e^2}{r_{ij}} + \sum_{k < l} \frac{e^2 Z_k Z_l}{r_{kl}}$$

Kinetic
Energy
Electrons

Kinetic
Energy
Nuclei

Electron
Nuclear

EE

NN

BORN-
OPPENHEIMER
APPROXIMATION

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i < j} \frac{e^2}{r_{ij}} + \sum_{k < l} \frac{e^2 Z_k Z_l}{r_{kl}}$$

BO Approximation assumes that the electrons can follow nuclear motions without any delay. BOA becomes weak if the electrons become very heavy because of very high kinetic energy.

Integrate SE from Left

$$H\psi = E\psi$$

Many eigenfunctions

$$H\psi_i = E_i\psi_i$$

We want orthogonal
eigenfunctions

$$\int \psi_j \psi_i dr = \delta_{ij}$$

Kronecker
Delta

$$\int \psi_j H\psi_i dr = \int \psi_j E_i\psi_i dr = E_i\delta_{ij}$$

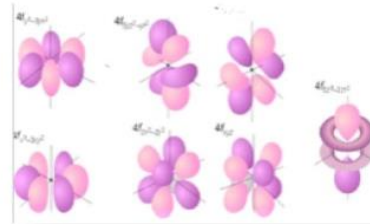
Once we have the eigenfunction,
we can compute its energy

Orthogonal Eigenfunctions, Atoms

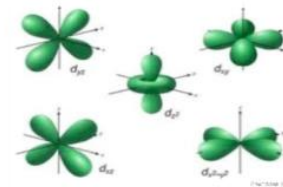
$$\delta_{ij} = \iiint \psi_i \psi_j dx dy dz$$

$$\delta_{ij} = \int \psi_i \psi_j dr$$

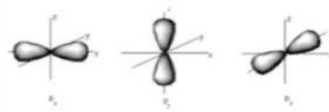
f orbitals



d orbitals



p orbitals



s orbital



ENERGY

Trial Function

Upper
case
PHI

$$\Phi = \sum_i c_i \psi_i$$

Lower
case
PSI

$$1 = \sum_i c_i^2$$

Coefficients
are constrained
by normalization

The trial function Φ is a linear combination of orthogonal **molecular wave functions ψ_i** (which we do not know yet).
The molecular wave function is normalized.

Normality of the Trial Function

$$\begin{aligned}\int \Phi^2 dr &= 1 = \int \left(\sum_i c_i \psi_i \right) \left(\sum_j c_j \psi_j \right) dr \\ &= \sum_{ij} c_i c_j \int \psi_i \psi_j dr \\ &= \sum_{ij} c_i c_j \delta_{ij} \\ &= \sum_i c_i^2\end{aligned}$$

The normality of the trial function imposes a constraint on the coefficients.

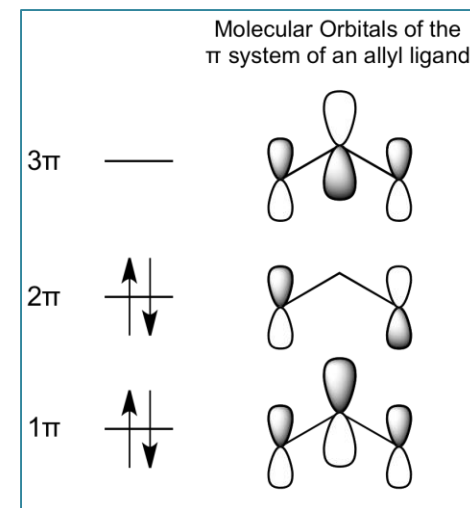
Energy of the Trial Function

$$\int \Phi H \Phi dr = \int \left(\sum_i c_i \psi_i \right) H \left(\sum_j c_j \psi_j \right) dr$$

$$\int \Phi H \Phi dr = \sum_{ij} c_i c_j \int \psi_i H \psi_j dr$$

$$\int \Phi H \Phi dr = \sum_{ij} c_i c_j E_i \delta_{ij}$$

$$\int \Phi H \Phi dr = \sum_i c_i^2 E_i$$



Variational Theorem

Normalization
Always applies

$$\int \Phi H \Phi dr = \sum_i c_i^2 E_i$$

$$\int \Phi^2 dr = \sum_i c_i^2 \text{ or } E_0 \int \Phi^2 dr = \sum_i c_i^2 E_0$$

Row 1 – Row 2

$$\int \Phi H \Phi dr - E_0 \int \Phi^2 dr = \sum_i c_i^2 E_i - \sum_i c_i^2 E_0$$

$$E_i > E_0$$

$$\int \Phi H \Phi dr - E_0 \int \Phi^2 dr \geq 0$$

$$\frac{\int \Phi H \Phi dr}{\int \Phi^2 dr} \geq E_0$$

The lower,
the better.

Chapter #2

Hartree-Fock Theory

2.3. LCAO Basis Set Approach and Secular Determinant

LCAO Basis Set Approach

Upper
case
PHI

$$\Psi = \sum_i c_i \phi_i$$

Lower
case
PSI

$$1 = \sum_i c_i^2$$

Coefficients
are constrained by normalization

Lower
case
PHI

$$\Psi = \sum_i a_i \phi_i$$

Alternate
Lower case
PHI

The molecular wave function is a linear combination of atomic orbitals, LCAO.
The AOs located at different atoms are not orthogonal.
Much more on basis sets, see Chapter 6.

Variational Theorem meets LCAO

$$\frac{\int \left(\sum_i a_i \varphi_i \right) H \left(\sum_j a_j \varphi_j \right) dr}{\int \left(\sum_i a_i \varphi_i \right) \left(\sum_j a_j \varphi_j \right) dr} = E$$

$$\frac{\sum_{ij} a_i a_j \int \varphi_i H \varphi_j dr}{\sum_{ij} a_i a_j \int \varphi_i \varphi_j dr} = E$$

Find a values that give the
lowest E !

$$H_{ij} = \int \varphi_i H \varphi_j dr$$

$$S_{ij} = \int \varphi_i \varphi_j dr$$

Overlap
Integral

Set of N Equations

Differentiate E with regard to every coefficient

$$\frac{\sum_{ij} a_i a_j H_{ij} dr}{\sum_{ij} a_i a_j S_{ij} dr} = E$$

$$\sum_{i=1}^N a_i (H_{ik} - ES_{ik}) = 0$$

Secular Determinant

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

- (1) Select Basis Functions
- (2) Determine all S_{ij} (relatively easy)
- (3) Determine all H_{ij} (not so easy)
- (4) Determine the E_j values from the secular equation
- (5) Determine the MO coefficients for each E_j

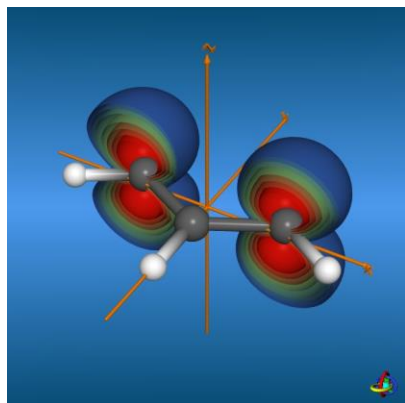


Hückel Theory

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

- (1) Only one p-AO per atom.
- (2) Only self-overlap $S_{ij} = \delta_{ij}$.
- (3) Ionization energy of p-AO: $H_{ii} = \alpha$.
- (4) Resonance energy with neighbor: $H_{ij} = \beta$.

Hückel Theory: Allyl



C1 connected to C2
C2 connected to C3

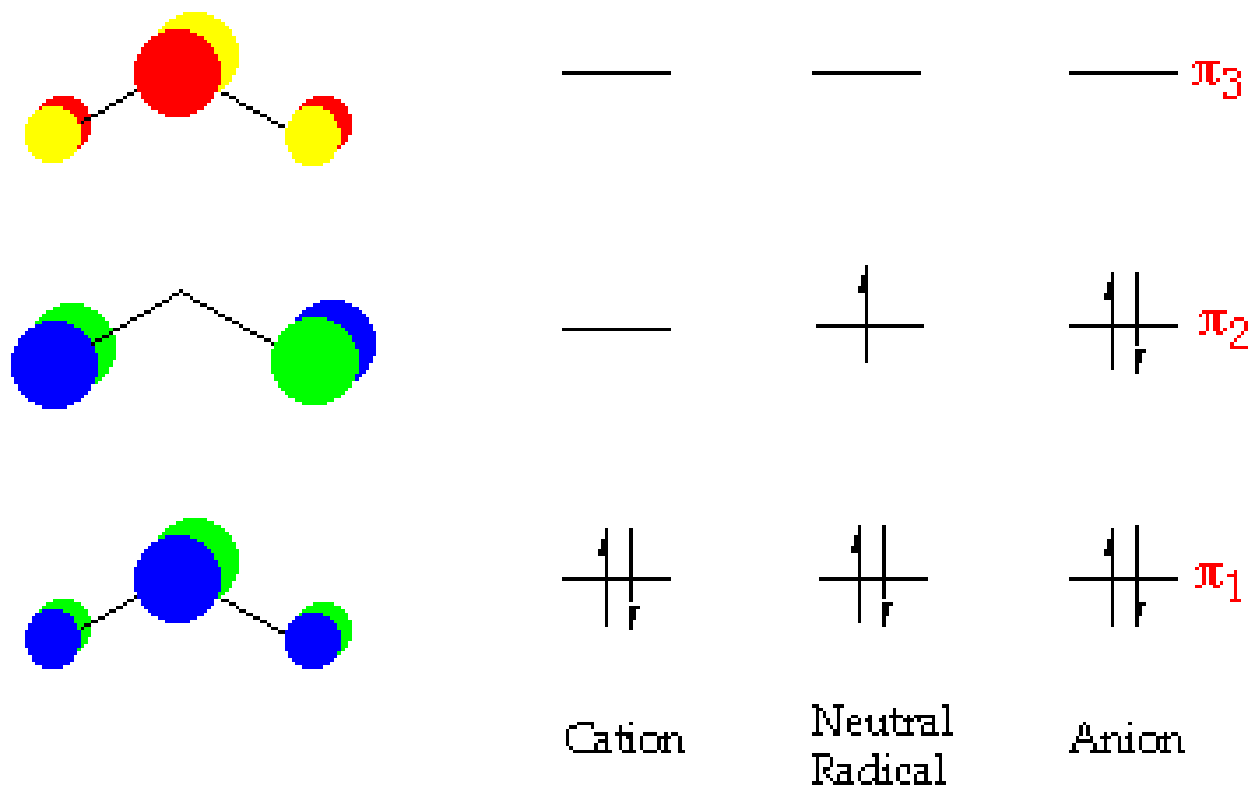
$$\begin{vmatrix} a - E & b & 0 \\ b & a - E & b \\ 0 & b & a - E \end{vmatrix} = 0$$

$$(a - E) \begin{vmatrix} a - E & b \\ b & a - E \end{vmatrix} - b \begin{vmatrix} b & 0 \\ 0 & b \end{vmatrix} + 0 = 0$$

$$(a - E)^3 - (a - E)b^2 - b^3 = 0$$

$$(a + \sqrt{2b}), \quad a, \quad (a - \sqrt{2b})$$

Hückel Theory: Allyl MOs



Chapter #2

Hartree-Fock Theory

2.4. One-Electron Hamiltonian, Hartree Product, and Hartree Hamiltonian

One-Electron Hamiltonian for Molecule

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i < j} \frac{e^2}{r_{ij}} + \sum_{k < l} \frac{e^2 Z_k Z_l}{r_{kl}}$$

Kinetic
Energy
Electrons

Kinetic
Energy
Nuclei

Electron
Nuclear

EE

NN

BO-Approximation
One-Electron Hamiltonian
No Electron-Electron Repulsion

$$H = \sum_i h_i$$

$$h_i = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k^M \frac{e^2 Z_k}{r_{ik}}$$

Hartree Product

Pretending that a many-electron problem really is just a one-electron problem.

Hartree Product

$$\Psi_{HP} = \psi_1 \psi_2 \cdots \psi_N$$

Energy of the Hartree
Product

$$E_{HP} = \sum_i \epsilon_i$$

Allyl Radical - Hückel

There are no electron-electron repulsion terms in HMO theory

Hartree Product

$$Y_{Allyl} = y_{MO1} y_{MO1} y_{MO2}$$

Energy of the Hartree
Product

$$E_{Allyl} = e_{MO1} + e_{MO1} + e_{MO2}$$

Hartree Hamiltonian

BO

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i < j} \frac{e^2}{r_{ij}}$$

Kinetic
Energy
Electrons

Electron
Nuclear

EE

One-Electron Hamiltonian
Average EE-Repulsion

$$H = \sum_i h_i$$

$$h_i = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{j \neq i} \int \frac{\rho_j}{r_{ij}}$$

Pretending that a many-electron problem really is just a one-electron problem and then trying to make up for it.

Self-Consistent Field, SCF

$$H = \sum_i h_i$$
$$h_i = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k^M \frac{e^2 Z_k}{r_{ik}} + \sum_{j \neq i} \int \frac{\rho_j}{r_{ij}}$$

The wavefunction is needed
To find the wavefunction

Requires Iterative Methods



Hartree Product & Hartree Energy

Eigenfunctions of the
Hartree Hamiltonian

Hartree Product

$$\Psi_{HP} = \psi_1 \psi_2 \cdots \psi_N$$

Energy of Hartree Product

No longer
just the sum of
MO eigenvalues

$$E_{HP} \neq \sum_i \varepsilon_i$$

$$E_{HP} = \sum_i \varepsilon_i - \frac{1}{2} \sum_{i \neq j} \iint \frac{|\psi_i|^2 |\psi_j|^2}{r_{ij}} dr^2$$

Chapter #2

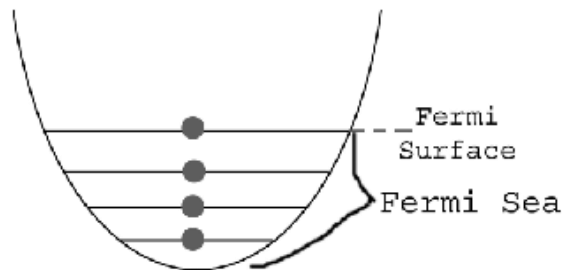
Hartree-Fock Theory

2.5. Electron Spin, Antisymmetry, and Slater Determinants

Fermion vs. Bosons

Fermions:

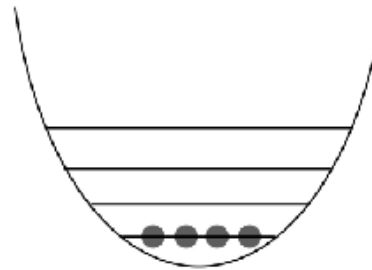
No two fermions can occupy the same state, so in the ground state ($T=0$), fermions stack from the lowest energy level to higher energy levels, leaving no holes.



Non-Integer Spin

Bosons:

In the ground state ($T=0$), all bosons occupy lowest energy state.



Integer Spin

Pauli Principle: MO can be occupied by 2 electrons with opposite spin.

Dirac Theory: For fermions, the exchange of two electrons should change the sign of the wave function.

Antisymmetry of Diradical Triplet

No
Sign
Change

$${}^3Y_{SD} = y_1(1)a(1)y_2(2)a(2)$$

$${}^3Y_{SD} = y_1(2)a(2)y_2(1)a(1)$$

Exchange of electrons should change the sign of the
wave function

Sign
Change

$${}^3Y_{SD} = \frac{1}{\sqrt{2}} [y_1(1)a(1)y_2(2)a(2) - y_1(2)a(2)y_2(1)a(1)]$$

$${}^3Y_{SD} = -\frac{1}{\sqrt{2}} [y_1(2)a(2)y_2(1)a(1) - y_1(1)a(1)y_2(2)a(2)]$$

Slater Determinants

$${}^3Y_{SD} = \frac{1}{\sqrt{2}} [y_1(1)a(1)y_2(2)a(2) - y_1(2)a(2)y_2(1)a(1)]$$

$${}^3\Psi_{SD} = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_2(1)\alpha(1) \\ \psi_1(2)\alpha(2) & \psi_2(2)\alpha(2) \end{vmatrix}$$

Spin Orbital
Lower case Chi
MO x Spin Function

$$\Psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_1(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_2(2) \\ \vdots & \vdots & & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix}$$

Hartree-Fock Theory: Hartree's SCF procedure with Slater Determinants

SD and Exchange Correlation

$${}^3Y_{SD} = \frac{1}{\sqrt{2}} [y_1(1)a(1)y_2(2)a(2) - y_1(2)a(2)y_2(1)a(1)]$$

$$\int {}^3\Psi_{SD} \frac{1}{r_{12}} {}^3\Psi_{SD} =$$

$$\frac{1}{2} \left[\int |\psi_1(1)|^2 |\alpha(1)|^2 \frac{1}{r_{12}} |\psi_2(2)|^2 |\alpha(2)|^2 \right]$$

$$-2 \int \psi_1(1)\psi_2(1) |\alpha(1)|^2 \frac{1}{r_{12}} \psi_2(2)\psi_1(2) |\alpha(2)|^2$$

$$+ \left[\int |\psi_1(2)|^2 |\alpha(2)|^2 \frac{1}{r_{12}} |\psi_2(1)|^2 |\alpha(1)|^2 \right]$$

$$= J_{12} - K_{12}$$

Exchange
Reduces
EE-Repulsion
Between
same-spin
Electrons

SD and Repulsion in Singlet

$$^3\Psi_{SD} = \frac{1}{\sqrt{2}} [\psi_1(1)\alpha(1)\psi_2(2)\beta(2) - \psi_1(2)\alpha(2)\psi_2(1)\beta(1)]$$

$$\int \Psi_{SD} \frac{1}{r_{12}} \Psi_{SD} =$$

$$\frac{1}{2} \left[\int |\psi_1(1)|^2 |\alpha(1)|^2 \frac{1}{r_{12}} |\psi_2(2)|^2 |\beta(2)|^2 \right]$$

$$- 2 \int \psi_1(1)\psi_2(1) |\alpha(1)| |\beta(1)| \frac{1}{r_{12}} \psi_2(2)\psi_1(2) |\alpha(2)| |\beta(2)|$$

$$+ \left[\int |\psi_1(2)|^2 |\alpha(2)|^2 \frac{1}{r_{12}} |\psi_2(1)|^2 |\beta(1)|^2 \right]$$

$$= J_{12}$$

Alpha and beta
spin orbitals are
orthogonal and K
disappears.