# Lecture 9

# Hartree – Fock Method and Koopman's Theorem

$\Psi(N)$ is approximated as a single slater determinant $\Phi$ of N orthogonal
One electron spin-orbitals.
One electron orbital $\phi_i = \phi_i(r)\ \chi_i(\sigma)$
$\chi_i(\sigma) = \alpha(m_s = +1/2)$ or $\beta\ (m_s = -1/2)$
The orthogonality relations are,
$\int \phi^*_i(r)\ \phi_j(r)\ dt \equiv <\phi_i|\phi_j> = S_{ij}$
$\int \chi_i^*(\sigma)\ \chi_j(\sigma)\ dt \equiv <\chi_i\ |\ \chi_j> = S_{msi,msj} = \{1$ for $\alpha\ \alpha$ or $\beta\ \beta$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad 0$ for $\alpha\ \beta$ or $\beta\ \alpha$

$\Psi \approx \Phi = 1/\sqrt{N!} \begin{vmatrix} \phi_1(1)\chi_1(1)\ \phi_2(1)\ \chi_2(1)\ \dots\ \phi_{N-1}(1)\ \chi_{N-1}(1)\ \phi_N(1)\chi_N(1) \\ \phi_1(2)\chi_1(2)\ \phi_2(2)\ \chi_2(2)\ \dots\ \phi_{N-1}(2)\ \chi_{N-1}(2)\ \phi_N(2)\chi_N(2) \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \end{vmatrix}$

1 …. N label the space and spin co-ordinates of each orbital

The orbitals are assumed to have the symmetry of the molecule

In atoms the orbitals are of the form,

$[-1/2 \quad - \quad \Sigma_{l=1}^{p} Z_l/r_{1l}] \phi_i(1) + [\Sigma_{j=1}^{N} \int \phi_j^*(2) \, 1/r_{12} \, \phi_j(2) \, d\tau_2] \phi_i(1)$
Kinetic  e-n attraction          e-e coulombic repulsion

$-\delta_{msi,msj} \Sigma_{j=1}^{N} [\int \phi_j^*(2) \, 1/r_{12} \, \phi_j(2) \, dt_2] \phi_j(w) = \Sigma_i \phi_i(1)$ I = 1, 2, ...N
                    e-e exchange

$\Sigma_l$'s are the one electron orbital energies. Exchange is possible only for
Electron with parallel spins. ($\alpha\alpha$ or $\beta\beta$)

Kronecker delta allows this.

This equation expressed in terms of Fock operators,

$$F(l)\phi_i(1) = [-1/2 \ -\Sigma_{l=1}^{P} Z_l/r_{l1} + \Sigma_{j=1}^{N} [\hat{J}_j - \delta_{msi, \ msj} K_j] \ \phi_i(1) = \in_i \phi_i(1)$$

The Coulomb and exchange operators $\hat{J}_j$ and $K_j$ are

$$\hat{J}_j\phi_i(1) = \int\phi_j^*(2) \ 1/r_{12} \ \phi_i(2) \ \phi_i(1) \ dt_2$$

$$K_j \ \phi_l(1) = \int \phi_j^*(2) \ 1/r_{12} \ \phi_i(2) \ \phi_j(2) \ dt_2$$

The coulomb and exchange integrals are,

$$J_{ij} = < \phi_i(1)| \ \hat{J}_j \ | \ \phi_j(1)> = \int\int \phi_i^*(1) \ \phi_j^*(2) \ 1/r_{12} \ \phi_i(1) \ \phi_j(2) \ dt_1 \ dt_2$$

$$K_{ij} = < \phi_i(1)| \ \hat{J}_j| \ \phi_i(1)> = \int\int \phi_i^*(1) \ \phi_j^*(2) \ 1/r_{12} \ \phi_i(2) \ \phi_j(1) \ dt_1 \ dt_2$$

Thus $J_{ij} = J_{ji}$, $K_{ij} = K_{ji}$  $J_{ii} = K_{ii}$

Once the SCF is performed, the orbital  energies can be obtained from

$$\phi_{nlml}(r, \theta, \phi) = R_{nl}(r) \qquad Y_{lmi}(\theta, \phi)$$

radial part     Angular parat
Spherical harmonics

In molecules the symmetry types such as $1\sigma$, $3\pi g$ arise.

Orbitals are approximated as linear combinations of atomic orbitals.

In solids, translational periodicity requires that delocalised orbitals
are of Bloch-type

$$\phi_k(r) = u_k(r) \exp(i\,k - r)$$

K is the wave vector of the lattice and $n_k(r)$ is a function characteristic
Of $\phi_k$ which has the same translational periodicity as the lattice.

A free electron will have a constant $u_k(r)$ and will yield,

$\phi_k(r) = C \exp(i\ k.r)$
C is a normalisation constant.

The momentum P and energy E are,
$P = \hbar k$
$E = E_{kin=} P^2/2m = \hbar k^2/2m$

The Hamiltonian can be used with variational principle to find optimum $\phi$, So that the total energy $E = <\phi|\hat{H}|\phi>$ is minimum. The Hartree – Fock equations are obtained this way.

These equations in the diagonal form are,
$\in_i = \in_i^0 + \Sigma_{j=1}^N (J_{ij} - \delta_{msi,msj}\ k_{ij})$

$\in_i^0$ is the expectation value of the one-electron operator for kinetic Energy and electron – nuclear attraction.

$$\in_i^0 = <\phi_i(1) | -1/2 \quad - \Sigma_{l=1}^p Z_l/r_{1l} \, \phi_i(1)>$$

The total energy is given by,

$$E = < \phi|\hat{H}|\phi> = \Sigma_{i=1}^N \in_i^0 + \Sigma_{i=1}^N \Sigma_{j>i}^N (J_{ij} - \delta_{msi,msj} k_{ij}) + \Sigma_{l=1}^p \Sigma_{m>l} Z_l 2m/r_{lm}$$

Measured total energy is not the sum of orbital energies.

The best H-F method of determining the binding energy is to compute The energy difference between $E^f(N-1,k)$ and $E^i(N)$ corresponding to $\Psi^f_{(N-1, k)}$ and $\Psi^i(N)$. Since electron emission is faster ($10^{-16}$ sec) than nuclear coordinates can be identical in both the states, therefore nuclear-nuclear repulsion cancell each other. The ionic state potential minimum, however, may have different nuclear coordinates and Therefore, vibrational excitations are possible.

If these excitations are fast compared to the motions of remaining N-1 electrons (called sudden approximation) different excited states can be reached. Due to excitation, The remaining N-1 electrons will not have the same spatial distribution.

The spatial form may not change much but the calculated Bes can change greatly. The relaxation effects can be important. Relativistic Correction - orbital velocity/c

Correlation correction is taken in the form of pair correlation energies. For a Ne 1s hole correlation correction can be written,

$$\delta E_{corr} = \in(1s\alpha, 1s\beta) + \in(1s\alpha, 2s\alpha) + \in(1s\alpha, 2s\alpha) + 3\in(1s\alpha, 2p\beta) + 3\in(1s\alpha, 2p\alpha) + 3\in(1s\alpha, 2p\beta)$$

This is only a first approximation. All types of correlation in Both Ne and Ne+ with a 1s hole will be a better estimate.

Studies show that core hole is not delocalised.
An LCAO HF calculation gives +1/2e charge on each $\sigma_g 1s$ and $\sigma_g 1s$
for a 1s hole.
But the energy state is not the minimum.  That corresponds to the state
for which 1s hole is localised on 1 atom.

For valence states delocalisation may be involved.  Some orbitals
such as non-bonding orbitals are essentially atomic and
electron emission can be assumed to lead to localised hole states.

To avoid difficulties associated with hole state calculation,
Koopmans' approximation is used. The assumption is that the initial
one electron orbitals $\phi_i^s$ making up the, $\Phi^I(N)$ state is the same
as the final orbitals $\phi_i'^s$ making up the $\Phi^f(N-1, k)$. state.
The energy for $E^f(N-1, K)$ can be calculated from $E^i(N)$ by eleminting
K state occupancy

$$E^f_{(N-1,\,k)}{}^{kT} = \Sigma_{i \neq k}{}^N \in_i^0 + \Sigma_{i \neq k}{}^N \Sigma_{j>I,\ j \neq k} (J_{ij} - \delta_{msi,msj}\, k_{ij})$$

This neglects nuclear repulsion.

$$= \Sigma_{i \neq k}{}^N \in_i^0 + \Sigma_{i=1}{}^N \Sigma_{j>i}{}^N (J_{ij} - \delta_{msi,msj}\, k_{ij}) - \Sigma_{i=1}{}^N (J_{ik} - \delta_{msi,}m_{sk}\, k_{ik})$$

Binding energy of the $K^{th}$ electron can be given by the difference method,

$$E_b{}^v(k)^{KT} = E^f_{(N-1,\,k)}{}^{KT} - E^i(N)$$

$$= -\in_k^0 - \Sigma_{i=1}{}^N (J_{ik} - \delta_{msi,msk}\, k_{in})$$

Making use of the expression for $\in_k$

$$E_b{}^v(k)^{KT} = -\in_k$$

For occupied orbitals $\in_k$ is –ve and $E_b^\nu(k)$ is +ve. Since relaxation and other effects are neglected, KT binding energies are lower than theoretical estimates. The error due to relaxation $\delta E_{relax} > 0$,

$$E_b^\nu(k) = E_b^\nu(k)^{KT} - \delta E_{relax}$$
$$= -e_k - \delta E_{relax}$$

This derivation of KT is valid only for closed shell systems represented say single Slater determinant with doubly occupied one-electron orbitals or solids highly delocalised orbitals with quasi – continuous energy eigen values.

In general for open shell systems there can be more than one way of compiling the angular moments and different final states result. For atoms there states can be described in terms of L and S. A linear combination of Slater determinants are needed. But slater has shown that if average total energies of initial and final state are taken,

$$E_b^v(k)^{KT} = E^f(k)^{KT} - E^i(k) = -\in_k$$

The best way to calculate $\delta E_{relax}$ is to carry out SCF calculations on initial and final states and compare the energy difference with $\in_i$.

The binding energy can be approximated by,

$$E_b^v(k) = -\in_k - \delta E_{relax} + \delta E_{relax} + \delta E_{corr}$$

More accurate wave function and CI
N electron wave function is written in terms of linear combination of states determinates $\phi_j(N)$

$\Psi(N) = \Sigma_j \, c_j \Phi_j \, (N)$

For Ne $\rightarrow$ calculation with 1071 configuration.
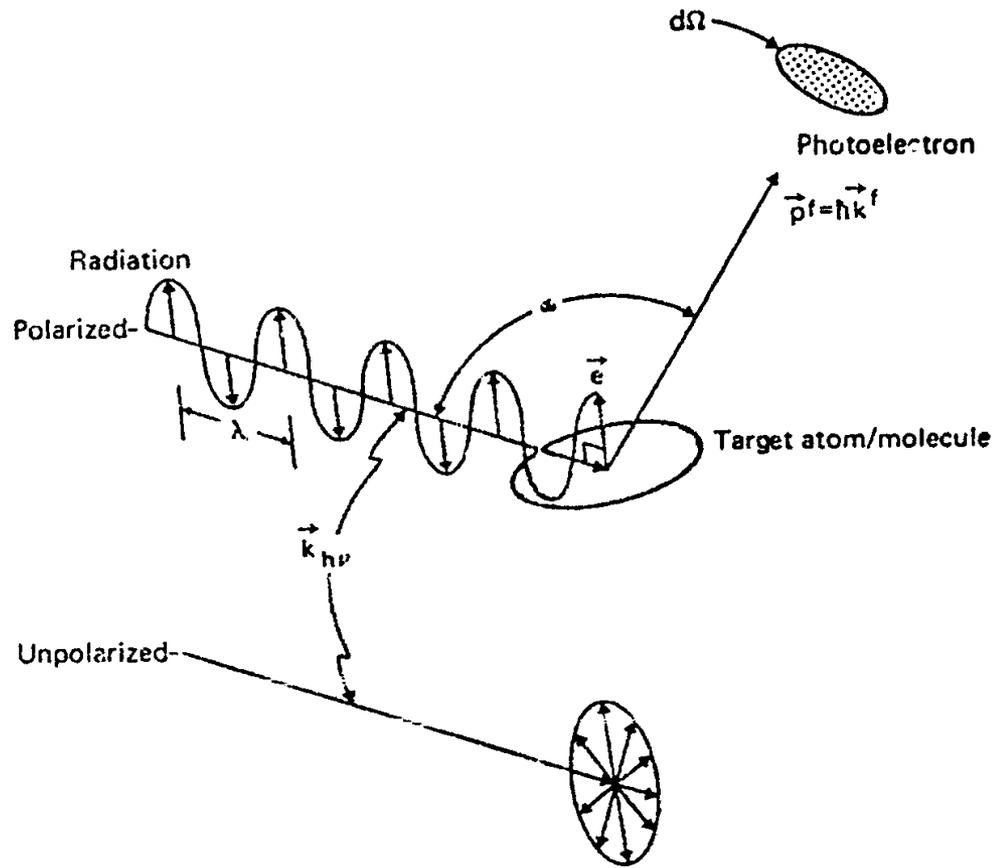The coefficients are the following:
$\Phi_1$ -$1s^2$ $2s^2$ $2p^6$ - 0.984
$\Phi_2$ - $1s^2$ $2s^1$ $2p^6$ $3s^1$ - 0.005
$\Phi_3$ -$1s^2$ $2s^2$ $2p^5$ $3p$ - 0.009
$\Phi_4$ - $1s^2$ $2s^2$ $2p^4$ $4p^2$ - 0.007 - 0.030
$\Phi_5$ -$1s^2$ $2s^2$ $2p^4$ $3p4p$ - 0.007 - 0.002

General geometry for defining the differential cross-section $d\sigma/d\Omega$, Showing both polarized and unpolarized incident radiation. The Polarization vector e is parallel to the electric field E of the radiation. In order for the dipole approximation to be valid, the radiation wave length $\lambda$ should be much larger than typical target dimensions