Hartree – Fock Method and Koopman’s Theorem

$\Psi_{tot}(N) = \Psi_{tot}(r_1, \sigma_1, r_2, \sigma_2 \ldots. r_N \sigma_N;\ \ R_1, R_2 \ldots R_P)$

Nuclear coordinates can be neglected in the resolution scale of electron spectroscopy. In the non-relativistic limit, the Hamiltonian in electrostatic units,

$$\hat{H}_{tot} = \hbar^2/2m\, \Sigma_{i=1}^{N}\, \nabla_i^2 - \Sigma_{i=1}^{N} \Sigma_{l=1}^{P} Z_l e^2/r_{il} + \Sigma_{i=1}^{N} \Sigma_{j>i}^{N} e^2/r_{ij}$$

e-kinetic e-n attraction e-e repulsion

$$+ \Sigma_{l=1}^{P} \Sigma_{m>l}^{P} Z_l Z_m e^2/r_{lm} - \hbar^2/2\, \Sigma_{l\,=\,1}^{P}\ {}_{l}\nabla_l^2/ M_l$$

n-n repulsion Nuclear kinetic

M – electron mass, Z_l charge of l^{th} nucleus $r_{il} = |r_i - R_l|$, $r_{ij} = |r_j - r_j|$,
$R_{lm} = |R_l - R_m|$, M_l – mass of l^{th} nucleus.

To this relativistic effects may be added by perturbation. Hamiltonian most often added is due to spin-orbit splitting.

The total wave function must satisfy the time independent Schroedinger equation,

$$\hat{H}_{tot}\Psi_{tot}(N) = E_{tot}(N)\,\Psi_{tot}(N)$$

Bohn-oppenheimer approximation permits separation of the total wave function into a product of electronic and nuclear parts.

$$\Psi_{tot}(r_1 \;....\; r_N;\, R_1 \;....\; R_p) = \Psi(r_1, \sigma_1 \;...\; r_N\, \sigma_N)\, \Psi_{nuc}(R_1 ... R_p)$$

$\Psi(N)$, the electronic wave function depends on $R_1 \;...\; R_P$ only parametrically through nuclear-nuclear coulombic repulsion.

The electronic Hamiltonian will be $\hat{H}_{tot}$ minus the nuclear kinetic term.

$$(\hat{H}_{tot} + \hbar^2/2\,\Sigma_{I=1}{}^{P}\,\nabla_I{}^2/M_I)\ \Psi(N) \equiv \hat{H}(N)\ \Psi(N) = E(N)\ \Psi(N)$$

$\hat{H}_{tot}$ can be include S-O effects. The total energy

$$E_{tot} = E + E_{nuc}$$

$$= E + E_{vib} + E_{tot} + E_{trans} + \ldots.$$

The quantum number K (representing nuclear motion) should represent all forms of motion, vibrational, rotational,.

For diatomic harmonic oscillator,
$E_{vib} = \hbar\nu_{vib}(v + ½)$
$v = 0, 1, 2, \ldots.$

Translational motions of the atom or molecule can influence the energies in two ways.

1. Conservation of linear momentum requires

$P_{h\nu}$ + 0 = $P^f + P_r$
$P_{h\nu} \rightarrow$ Photon momentum $h\nu/c$, momentum of E^i taken to be zero.
$P^f \rightarrow$ photoelectron momentum, P_r recoil momentum of the atom.

Recoil energy of two atom vary as $E_r = P^2/2m$ and increases with decreasing at. no. For Al K_α, the E_r value for various elements are, H – 0.9 eV, Li – 0.1 eV, Na –0.04 eV, K – 0.02 eV Rb – 0.01 eV.

Therefore, this is important only in H, as far as XPS in concerned XPS instrumental line widths are 0.4 – 0.9 eV. Thus E_r can be neglected.

2. Doppler broadening can be significant.

Thermal motion of emitters.
If the atom of mass M moves with a centre of mass velocity V, the electron kinetic energy
$E_{kin}'' = (\frac{1}{2})\, m\, |\nu - V|^2$

The measured $E_{kin} = (\frac{1}{2}) m \nu^2$ will be different from this. The difference depends on thermal velocities. If the mean kinetic energy measured is E_{kin}, the Doppler width, ΔE_d

$$= 0.723 \times 10^{-3} \, (T.\, E_{kin}/M)^{1/2} \text{ (in eV)}$$

E_{kin} refers to the average kinetic energy of the ion.

At room temperature, for XPS energy of 1000 eV, the value of $\Delta E_d \leq 0.1$ eV for $M \geq 10$. Thus it is not significant in comparison with FWHM. But important in gas phase.

Normally it is a practice to neglect nuclear motion.

The N and N – 1 electron states represent the various irreducible representations of the point group.

In atoms where spin-orbit splitting is small, the states are specified by L, S and perhaps also M_L and M_S. M_L and M_s are z components of L and S. For zero spin orbit splitting, energies depend only on L and S. and the degeneracies would be (2L + 1) (2S + 1). Such states also occur in molecules, but they are seldom used.

$\Psi(N)$ is approximated as a single Slater determinant Φ 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,

$\int \phi^*_i(r)\ \phi_j(r)\ dt \equiv <\phi_i|\phi_j> = \delta_{ij}$

$\int \chi_i^*(\sigma)\ \chi_j(\sigma)\ dt \equiv <\chi_i \mid \chi_j> = \delta_{msi,msj} = \begin{cases} 1 \text{ for } \alpha\ \alpha \text{ or } \beta\ \beta \\ 0 \text{ for } \alpha\ \beta \text{ or } \beta\ \alpha \end{cases}$

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

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

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

radial part   Angular parat
Spherical harmonics

In molecules the symmetry types such as 1σ, $3\pi g$ 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 ϕ_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 ϕ, So that the total energy $E = < \phi|\hat{H}|\phi>$ is minimum.

The Hartree – Fock equations are obtained this way.

We get Hartree-Fock equations.

The orbitals are assumed to have the symmetry of the molecule

HF equations are,

$[-1/2\ \nabla_1^{2}\ -\ \Sigma_{l=1}^{p} Z_l/r_{1l}]\ \phi_i(1) + [\Sigma_{j=1}^{N} \int \phi_j^{*}(2)\ 1/r_{12}\ \phi_j(2)\ d\tau_2]\ \phi_i(1)$
Kinetic e-n attraction e-e coulombic repulsion

$-\delta_{msi,msj}\ \Sigma_{j=1}^{N} [\int \phi_j^{*}(2)\ 1/r_{12}\ \phi_i(2)\ d\tau_{2}]\ \phi_j(1) = \varepsilon_i\ \phi_i(1)$ i = 1, 2, …N
e-e exchange

ε_i's are the one electron orbital energies.

Exchange interaction 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,

$F(1)\phi_i(1) = [-1/2\ \nabla_1^2 - \Sigma_{l=1}^{P} Z_l/r_{1l} + \Sigma_{j=1}^{N} [\hat{J}_j - \delta_{msi,\ msj} K_j]\ \phi_i(1) = \in_i \phi_i(1)$

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

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.

$$\in_i^0 = <\phi_i(1) \mid [-1/2 \blacktriangledown_1^2 - \Sigma_{l=1}^p Z_l/r_{1l}] \phi_i(1)>$$

The total energy is given by,

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

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.

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 ϕ_i^s making up the, $\Phi^I(N)$ state is the same as the final orbitals $\phi_i^{\prime s}$ 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 eliminating k state occupancy

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,

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

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

$$E^{f}{}_{(N-1,\, k)}{}^{kT} = \Sigma_{i\neq k}{}^{N} \in_{i}{}^{0} + \Sigma_{i\, \neq k}{}^{N}\, \Sigma_{j>I,\; j\neq k} (J_{ij} - \delta_{msi,msj} K_{ij})$$

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 kth electron can be given by the difference method,

$$E_{b}{}^{v}(k)^{KT} = E^{f}{}_{(N-1,\, k)}{}^{KT} - E^{i}(N)$$

$$= -\ \in_{k}{}^{0} - \Sigma_{i=1}{}^{N} (J_{ik} - \delta_{msi,msk} K_{ik})$$

Making use of the expression for $\in_k$

$$E_{b}{}^{v}(k)^{KT} = -\in_{k}$$

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

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

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 δE_{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 → calculation with 1071 configuration.

The coefficients are the following:

Φ_1 -$1s^2 2s^2 2p^6$ - 0.984

Φ_2 - $1s^2 2s^1 2p^6 3s^1$ - 0.005

Φ_3 -$1s^2 2s^2 2p^5 3p$ - 0.009

Φ_4 - $1s^2 2s^2 2p^4 4p^2$ - 0.007 - 0.030

Φ_5 -$1s^2 2s^2 2p^4 3p4p$ - 0.007 - 0.002