IJPAC
© Global Research Publications

Vol. 14 • Nos. 1-2 • January-June, 2019
pp. 57-76

Higher excited states of polyatomic molecules by the use of RINDO/S METHOD

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Abstract: In this paper we have studied a brief review of higher excited states of polyatomic molecules by the use of RINDO/S methods.

Key words: polyatomic molecules, RINDO/S methods.

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1. Introduction

The study of any theory of molecular structure gives information about the various physical laws governing the chemical constitutions of molecules in terms of more fundamental universal physical law governing its motions and interactions of the constituents atomic nuclei and electrons. All these things may be understood well by solving appropriate Schrodinger's equations. However, in practice, mathematical and computational complexities make this goal rather difficult and we resort to apaproximate methods.

There are two principles of approximate methods.

(i) Valence Bond Theory (V B Theory)
(ii) Molecular Orbital Theory (MO Theory)

But the difference in the two methods is that in VB method the exchange of two electrons is perfectly correlated. The two electrons are not permitted to enjoy simultaneously the company of a single nucleus. In the MO method no such restriction is placed on the two electrons. Further the VB calculations become more cumbersome as the size of the molecule increases. In this regard the MO method is preferred over the VB method.

Basically an approximate MO method CNDO (complete neglect of differential overlap) was developed by Pople et. Al This method is found capable to interpret valence transitions but the singlet – triplet splittings specially of $n\rightarrow\pi^*$ transitions are not accounted for by the method. The reason lies in the fact that the method ignores one-centre exchange integrals (HvUv). However, these entrails are retained in the INDO (intermediate neglect of differential overlap) method[2] and thus this methods interprets S-T ($n\rightarrow\pi^*$) splits ion a satisfactory manner.

The CNDO and INDO methods are good for interpreting electronic spectra near UV (ultraviolet) region but the higher energy transitions are not well accounted for. Such transitions could, however, be interpreted well by the RCNDO(Rydberg CNDO) method[3]. This method incorporates Rydberg AO's in the valence-basis set as used in the CNDO method. But this method offers intermingling of σ and π configurations because the σ,σ and π,π

interactions are treated on equal footing. To overcome this deficiency Prasad and Singh[4] proposed a method RCNDO/S (Screened RCNDO/S method), which ignore one – center exchange integrals, is in capable to account for the S-T split of n→π* transitions.

Further including Rydberg AO's in the valence basis set as used in INDO and following σ and π separability conditions Singh and Prasad[5] proposed a method RINDO/S (screened RINDO). This method is found capable to interpret the higher energy transitions and the S-T (n→π*) splits are well accounted for. But this method requires calculations of a number of one-center exchange integrals for valence and Rydberg shells. The exchange integrals involving Rydberg shells should, however, contribute insignificantly and hence these can be ignored. Following this idea Prasad and Roy[6] developed a method MRINDO/S (Modified RINDO/S). This method requires less computed time, avoids intermingling of σ and π configurations and yet has the capability to reproduce all the salient features of the RINDO/S method.

It is, therefore, propose in the present work to apply MRINDO/S method on various polyatomic molecules to account for their electronic spectra. In additions, the method provides charge distributions and hence helps us to calculate dipole moments of the molecules. Though the basic set used in the method is limited to pure AO's and there is no provision of polarized or hybrid AO's the calculated depoic moments will lead us to a certain advocacy. It is expected that the calculated results will certainly contribute to the molecular properties and will carry this field forward.

Mayer and Sklar [1-4] used Slater determinants for study the molecular spectrum of benzene. They successfully interpreted the electronic spectra qualitatively agreement with the experimental results but the energy values calculated for all states were too high. Even after several revisions there exists a sufficient gap between the experimental and theoretical results.

By incorporating Parrisar and Parr's[5] assumptions in the Roothan's LCAO-SCF theory Pople [8] extended a semiempirical technique, which is termed as PPP (Pariser, Parr and Pople) method. This method is widely used to solve the π-electron problems. Although the method involves the serious neglect of overlaps and differential overlaps; it accounted for the spectral features of conjugated hydrocarbons quite satisfactorily.

Brown and Hofferman [10,11], for π-electron problem, proposed VESCF (variable electronegative SCF) method which was extended later on by Brown and Harcourt [12] to σ and π-electron systems.

Salahub and Sandorfy [20], with this modified view, proposed a new technique RCNDO (Rydberg Complete Neglect of Differential Overlap) and applied in number of molecules for calculating transition energies. By analysis of the INDO and the RCNDO methods for near and for ultraviolet spectra of molecules it has been concluded that the INDO is quite good for the near ultraviolet spectra but for the higher energy transitions. The RCNDO method is fully capable to describe the higher energy transitions but the method is unable to predict the singlet-triplet (S-T) splittings specially of $n \rightarrow \pi^*$ type transitions. Singh and Haque [25] came forward with new method RINDO scheme which describes S-T splitting in a very satisfactory way.

The new schemes (RCNDO and RINDO) treated this overlap integrals on equal footing, therefore, the two methods cannot account for the effect of σ electrons on the energy level of π electrons. This led Prasad and Singh [27] to introduce a screening parameter for getting distinction in $\sigma -$ and $\pi -$ type interactions. The methods, thus modified with screening parameter, are formed as RCNDO/S and RINDO/S respectively.

Since the RINDO/S method is preferred to RCNDO/S method, so in the present work we employed the RINDO/S method. This method ignores insignificant interactions involving Rydberg atomic orbitals that are required in RINDO method. The method is intermediate in complexity between RCNDO and RINDO/S and termed as MRINDO/S (modified RINDO/S). Here we find that the method interprets electronic spectra of polyatomic molecules in a very satisfactory manner. Prasad and Rai [28] proposed the details of the methodology.

2 The SCHRODINGER'S EQUATION

Non realistic time-independent Schrodinger [14] equation basically relates energy of the electronic spectra with its wave function.

$$H\Psi = E\Psi \qquad (1.1)$$

Where H is the total Hamiltonian of the system. In the case of polyatomic molecules with N nuclei and n electrons, the total Hamiltonian is written as,

$$H = -\sum_{A}^{N}\frac{1}{2}\nabla^2 A + \frac{\sum_{A<B} Z_A Z_B}{r_{AB}} - \sum_{i}^{n}\frac{1}{2}\nabla_i^2 - \sum_{A}\sum_{i}\frac{Z_A}{r_i A} + \sum\nolimits_{i<j}\frac{1}{r_{ij}}$$

(1.2)

Here A and i extend overall the N nuclei and n electrons respectively. The first term on R.H.S. represents the nuclear K.E. operator whereas the third term represents the electronic K.E. operator. The second, fourth and fifth terms represents the potential energy operators for the coulomb electrostatic interactions between nuclei A and B, electron i and nuclei A, and electrons i and j respectively.

Considering Born-Openheiner (BO) approximation [30], the first term on RHS of equation (1.2) may be dropped and then we have:

$$[-\sum_{i}^{n}\frac{1}{2}\nabla^2 i - \sum_{A}\sum_{i} Z_A/r_i A + \sum\nolimits_{i<j}\frac{1}{r_{ij}} + \sum_{A<B} Z_A Z_B/r_{AB}]\Psi(r_i, r_A) = E\Psi\,(r_i, r_A)$$

(1.3)

Where E and $\Psi(r_i, r_A)$ represent the total energy and the electronic wave function.

The BO approximation amounts for separating off the nuclear- nuclear kinetic energy from the Hamiltonian. So for convenience the last term is neglected and the remaining Hamiltonian is called electronic Hamiltonian (He) and expressed as

$$H_e = -\sum_{i}^{n} \frac{1}{2} \nabla^2 i \; - \sum_{A} \sum_{i} Z_A / r_i A + \sum_{i<j} \frac{1}{r_{ij}}$$

(1.4)

He is related with H as follows:

$$H = He + \sum_{A<B} Z_A \, Z_B / r_{AB}$$

The total energy of a molecular system is the sum of the total electronic energy and the electrostatic internuclear repulsion energy.

$$E = E_{elect} + \sum_{A<B} Z_A \, Z_B / r_{AB}$$

(1.5)

E_{elect} Stands for the total electronic energy.

3 THE VARIATIONAL PRINCIPLE AND ITS UTILITY:

The perturbation method can only be applied to problems that similar to others exact solutions. For systems which differ substantially from those subject to exact treatment, one may have to write a trial wave function based on an intelligent guess. Then after a strong method, leading to an approximation to the lowest energy eigen value and ground state wave function for the system, can be introduced. The very base of the method is known as variational principle.

A complete solution of Schrodinger equation (1.1) can help to account for the electronic structure of the molecules. But it is not possible to obtain complete solution of Schrodinger equation for many electrons system [16-18]. For many electrons system we apply variational principle to find the approximate solution. The principle states that the energy calculated from all approximate wave functions will always be greater than the lowest eigen value of the Hamiltonian.

The variational principle depends on the concept of complete set of functions which exist in the appropriate space. Supposing an arbitrary wave function Φ in the space spanned by the wave function of the Hamiltonian H, and keeping in view the above principle we may write the expectation value as follows:

$$E = \frac{<\Phi \,|H|\Phi>}{<\Phi|\Phi>} \geq E_0 \qquad (1.6)$$

Where E_0 is the lowest eigen value of H [19].

E approaches E_0 as Φ resembles the exact wave function ψ_0 corresponding to the lowest energy E_0. Conclusively, we say that lower the value E, of the trial function Φ resembles more with the ground state wave function ψ_0. To achieve this, we need to consider a group of trial wave function Φ having a number of parameters $C_1, C_2, C_3 \ldots \ldots etc$. and minimize the expectation value.

$$E\ (C_1, C_2 \ldots\ldots) = \frac{<\Phi\ (r_i, C_1, C_2 \ldots\ldots)\ |H| \Phi\ (r_i, C_1, C_2 \ldots\ldots)>}{<\Phi(r_i, C_1, C_2 \ldots\ldots)|\Phi(r_i, C_1, C_2 \ldots\ldots)>} \qquad (1.7)$$

Where,

$$\frac{\partial E}{\partial C_1} = \frac{\partial E}{\partial C_2} = \ldots\ldots = 0 \qquad (1.8)$$

Eq. No. (1.8) gives the values of $C_1, C_2, \ldots$ etc and the expanded form of the wave function resembling Ψ_0 may be constructed. But due to practical limitations the expansion gets a truncated shape with only a finite number of terms.

4 THE ORBITAL APPROXIMATION

Since each electron is associated with a one electron wave function it is similar to molecular orbital or electron orbit. By the combination of wave functions, Schrodinger equation is an attempt to make a satisfactory approximation for many electrons system. In this orbital approach every function depends upon co-ordinate of one electron only.

Many electron wave function is the product of one electron wave functions, we may write the total wave function as follows:

$$\Phi(1,2,3, \ldots\ldots., n) = \Psi_1(1), \Psi_2(2), \ldots\ldots, \Psi_n(n) \qquad (1.9)$$

One electron functions Ψ_i are termed as orbitals and the product function as a whole is termed as the Hartee product [20]. Further Φ^2 (the probability density function) is the product of one electron probability densities Ψ_i^2. It then vividly implies that the events associated with Ψ_i^2 occur independently of one another. This ensures that the molecular properties can be studied at par with the study of the properties of its electrons.

Due to the presence of the term $1/r_{ij}$ (inter electrons interaction), which is dependent on instantaneous relative coordinates of the two electrons *i* and *j.* The solution of the equation (1.3) is not separable, if the value of $1/r_{ij}$ is equal to zero i.e.

$$\frac{1}{r_{ij}} = 0 \qquad (1.10)$$

Which implies that each electron moves independently in the electrostatic potential field of bare nuclei alone and then the problem becomes easy.

Due to the presence of the term $1/r_{ij}$ the many electron Hamiltonian cannot be expressed simply as the sum of one electron operators. The orbital theories, however, attempt to develop approximate many electron wave function from product function. In fact the concept of the orbital approach to many electrons wave function cannot be lost. Realistic description of the electronic structure is obtained if the inter electronic interaction is incorporated in some average way [21].

5 ANTISYMMETRY PRINCIPLE AND DETERMINANTAL WAVE FUNCTION:

For MO calculations the antisymmetry behaviour of many electrons wave function in essential required. The product wave function must be antisymmetry under interchange of coordinates of electrons. The antisymmetry principle states that the wave function Φ describing any state of n-electron system is antisymmetrie under any permutation of the electrons. Mathematically, it is expressed as:

$$P_{ij}\Phi = E\rho\Phi \qquad (1.11)$$

Where P_{ij} is permutation operator that interchanges all the coordinates of electron *i* and *j* and $E_\rho = \pm 1$ for permutation of even and odd parity respectively. This is quantum mechanical generalisation of Pauli's principle [22] which states that no two electrons may be assigned to the same orbital.

Keeping in view the antisymmetry principle and the Hartee-Fock criterion of self-consistency [23], the many electron wave function for 2n electron system consisting to electrons per spatial orbital as a determinant of the 2n spin orbitals involved can be written as,

$$\Phi = \frac{1}{\sqrt{(2n)!}} - \begin{vmatrix} \Psi_1(1)\overline{\Psi_1}(1)\overline{\Psi_2}(1) \ldots\ldots\ldots\ldots\ldots\ldots\ldots . \overline{\Psi_n}(1) \\ \Psi_1(2)\overline{\Psi_1}(2)\overline{\Psi_2}(2) \ldots\ldots\ldots\ldots\ldots\ldots\ldots . \overline{\Psi_n}(2) \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots\;\vdots \\ \Psi_1(2n)\overline{\Psi_1}(2n)\overline{\Psi_2}(2n) \ldots\ldots\ldots\ldots\ldots\ldots\ldots . \overline{\Psi_n}(2n) \end{vmatrix} \qquad (1.12)$$

Equation (1.12) conclusively may be written as -

$$\Phi = \frac{1}{\sqrt{(2n)!}} = |\Psi_1(1)\overline{\Psi_1}(1) \ldots\ldots\ldots\ldots\ldots\ldots\ldots . \overline{\Psi_n}(2n)| \qquad (1.13)$$

Where the unbared orbitals represent α and β spins otherwise. Such spin orbital determinants are Slater determinants [24]. If the two electrons have the same spin orbital two columns of the Slater determinants are identical and the determinant vanishes. This is nothing but Pauli Exclusion Principle, which assures that non zero function cannot be saved if the two electrons are assigned to the same spin orbital. The factor $\frac{1}{\sqrt{(2n)!}}$ in the equation (1.12) is the normalization factor insuring that,

$\int \Phi^*\Phi \; d\tau = 1$ of the ground state determinant Φ is written as [25].

6 IONIZATION POTENTIAL AND EXCITATION ENERGY:

The ionized and excited states have been treated using approximate wave functions constructed from SCF ground state configuration itself.

The approximate wave function for singly ionized state corresponding to the removal of one electron from one of the MO's, Ψ_1 of the ground state determinant Φ is written as [25]

$$2\Phi_{\mathrm{i}} = \frac{1}{\sqrt{(2n)!}} \times det \left| \Psi_1(1)\overline{\Psi_1}(2) \ldots \Psi_{i-1}(2i-3)\, \overline{\Psi_{\iota-1}}(2i-2) \times \begin{Bmatrix} \Psi_{\mathrm{i}}(2\mathrm{i}-1) \\ \Psi_{\mathrm{i}}(2\mathrm{i}) \end{Bmatrix} \Psi_{\mathrm{i}+1}(2\mathrm{i}+1)\, \overline{\Psi}_{\mathrm{i}+1}(2\mathrm{i}+2) \ldots \ldots\ \Psi_{\mathrm{n}}(2\mathrm{n}) \right| \qquad (1.15)$$

The wave function describes a doublet state of the molecular ion of an electron in Ψ_{i} MO. The difference of energy for the states described by equations (1.15) and (1.13) is [24].

$$E^2(\Phi_i) - E(\Phi) = -H_i - \sum_j^2 \left(J_{ij} - K_{ij}\right) = -\varepsilon_i \qquad (1.16)$$

This is the ionization energy (potential) or molecular ionization potential equal to the negative of the orbital energy for the orbital occupied by the removed electron this important theorem is known as Koopmans theorem [25].

For describing low-lying excited States we replace a MO's, Ψ_{i}, in the Slater determinant of the ground state is replaced by an excited orbital $\Psi_{\dot{\mathrm{a}}}$. This is the virtual orbital (VO) approximation for the excited state. This low-lying excited states are formed by exciting an electron from Ψ_{i} to Ψ_{a}. They involve oxidation of one electron at a time [26].

if you consider the relative spins of electron in Ψ_{i} and Ψ_{a} the excited state wave functions are given as follows:

$$\Phi_i^a = \det \left| \Psi_1(1)\overline{\Psi}_1(2) \ldots \ldots \ldots\ \Psi_{\mathrm{i}-1}(2\mathrm{i}-3)\, \overline{\Psi}_{\mathrm{i}-1}(2\mathrm{i}-2) \times \begin{vmatrix} \Psi_{\mathrm{i}}(2\mathrm{i}-1)\overline{\Psi}_{\mathrm{a}}(2\mathrm{i}) \\ \Psi_{\mathrm{i}}(2\mathrm{i}-1)\overline{\Psi}_{\mathrm{a}}(2\mathrm{i}) \\ \Psi_{\mathrm{i}}(2\mathrm{i}-1)\overline{\Psi}_{\mathrm{a}}(2\mathrm{i}) \\ \Psi_{\mathrm{i}}(2\mathrm{i}-1)\overline{\Psi}_{\mathrm{a}}(2\mathrm{i}) \end{vmatrix} \Psi_{\mathrm{i}+1}(2\mathrm{i}+1)\overline{\Psi}_{\mathrm{i}+1}(2\mathrm{i}+2) \ldots \ldots \ldots \ldots\ \overline{\Psi}_{\mathrm{n}}(2\mathrm{n}) \right| \qquad (1.17)$$

Equation (1.17) represents equivalent configuration and hence we can obtain singlet, ${}^1\Phi_{\mathrm{i}}^{\mathrm{a}}$, and the three components of the triplet, ${}^3\Phi_{\mathrm{i}}^{\mathrm{a}}$, states by taking their suitable linear combinations. Thus,

$$1\Phi_{\mathrm{i}}^{\mathrm{a}} = \det \left| \Psi_1(1)\overline{\Psi}_1(2) \ldots \ldots \ldots\ \Psi_{\mathrm{i}-1}(2\mathrm{i}-3)\, \overline{\Psi}_{\mathrm{i}-1}(2\mathrm{i}-2) \times \frac{1}{\sqrt{2}}\{\Psi_{\mathrm{i}}(2\mathrm{i}-1)\overline{\Psi}_{\mathrm{a}}(2\mathrm{i}) - \Psi_{\mathrm{i}}(2\mathrm{i}-1)\, \overline{\Psi}_{\mathrm{a}}(2\mathrm{i})\} \times \Psi_{\mathrm{i}+1}(2\mathrm{i}+1)\overline{\Psi}_{\mathrm{i}+1}(2\mathrm{i}+2) \ldots \ldots \ldots\ \overline{\Psi}_{\mathrm{n}}(2\mathrm{n}) \right| \qquad (1.18)$$

and

$$3\Phi_{\mathrm{i}}^{\mathrm{a}} = \det[\Psi_1(1)\overline{\Psi}_1(2) \ldots \ldots \ldots\ \Psi_{\mathrm{i}-1}(2\mathrm{i}-3)\, \overline{\Psi}_{\mathrm{i}-1}(2\mathrm{i}-2) \times \begin{bmatrix} \Psi_{\mathrm{i}}(2\mathrm{i}-1)\overline{\Psi}_{\mathrm{a}}(2\mathrm{i}) \\ \frac{1}{\sqrt{2}}\, \Psi_{\mathrm{i}}(2\mathrm{i}-1)\overline{\Psi}_{\mathrm{a}}(2\mathrm{i}) - \Psi_{\mathrm{i}}(2\mathrm{i}-1)\, \overline{\Psi}_{\mathrm{a}}(2\mathrm{i}) \\ \Psi_{\mathrm{i}}(2\mathrm{i}-1)\overline{\Psi}_{\mathrm{a}}(2\mathrm{i}) \end{bmatrix}$$

$$\times \Psi_{\mathrm{i}+1}(2\mathrm{i}+1)\overline{\Psi}_{\mathrm{i}+1}(2\mathrm{i}+2) \ldots \ldots \ldots\ \overline{\Psi}_{\mathrm{n}}(2\mathrm{n}) \qquad (1.19)$$

The expectation value of the electronic Hamiltonian in the excited states are given as [27].

$$E(\ {}^{1,3}\Phi_i^a) = <^{1,3}\ \Phi_1^a\ |He|^{1,3}\ \Phi_1^a >$$

$$= \left\{2\sum \mathrm{H_j} + \sum_{\mathrm{j,k}} (2\mathrm{J_{jk}} - \mathrm{K_{jk}})\right\} + \left\{\mathrm{H_a} + \sum_{\mathrm{j}} (2\mathrm{J_{ia}} - \mathrm{K_{ja}})\right\} - \left\{\mathrm{H_i} + \sum_{\mathrm{j}} (2\mathrm{J_{ij}} - \mathrm{K_{ij}})\right\} - (\mathrm{J_{ia}} - \mathrm{K_{ja}}) \pm \mathrm{K_{ia}}$$

$$= \mathrm{E}(\Phi) - \varepsilon_a - \varepsilon_i - (\mathrm{J_{ai}} \pm \mathrm{K_{ia}}) \tag{1.20}$$

the plus sign of the last term represents the singlet-state while minus sign holds for the triplet-state .

If Ψ_i and Ψ_a belong to degenerate sets of MO's then the wave function represented by the equations (1.18) and (1.19) may not be a good approximations to the exact wave function. The reason is obvious that $^{1,3}\Phi_i^a$ are not good symmetry functions. However, suitable linear combination of configuration to from the functions of the correct symmetry are obtained by incorporating a CI procedure in the calculations [28].

1.7 ELECTRONIC TRANSITION

A) Rydberg character

Rydberg character characterizes the nature of transition to be Rydberg, valence or valance - Rydberg type. The Rydberg levels, in the LCAO approximation, can be discussed in the terms of Rydberg character obtained from the population analysis for the upper state of an electronic transition [29]. Generally the spectral bands due to the Rydberg transitions fall in the far ultra-violet region.

The Rydberg bands are the consequences of the excitation of an electron from one of the occupied ground state orbitals to a MO in which the AO's of higher principal quantum numbers have the largest AO coefficients. This gives rise to Rydberg series of electronic states, which can be expressed by the formula,

$$\nu = I - \frac{R}{(n-\delta)^2} \tag{1.21}$$

Where ν is the frequency of the transition, I the ionization potential, R the Rydberg constant, δ the quantum defect and n is the principal quantum number on which the Rydberg electron is mainly populated.

The Rydberg character (C_R) for state 'i' is defined as

$$C_R = \sum_P C_{ip}^2 \sum_r C_{ra}^2 \tag{1.22}$$

The Rydberg character (C_R) obtained from the population analysis for upper state of an electronic transition, describes the Rydberg state in LCAO approximation. Where the first summation is overall configurations considered in the CI procedure C_{ip} is the contribution of the p^{th}configuration to the i$^{\mathrm{th}}$ state. The second summation is overall the Rydberg AO's and $C_{ra}$is the LACO coefficient for the upper MO in the p$^{\mathrm{th}}$ configuration.

The equation (1.22) describes Rydberg character in percent. If CR = 1, the contribution due to the Rydberg transition is considered to be sent percent. The small value of CR is indicative of valence transition while a moderate value of it indicates the mixture of valence and Rydberg transitions.

B) OSCILLATOR STRENGTH

The allowedness of an electronic transition is governed by the selection rules. The allowedness of a given electronic transition $m - \sim\sim\sim p$ is accounted for by the matrix elements of the transition moment,

$$\underline{M}_{mp} = \int \Phi_{\mathrm{m}} \mathrm{M} \Phi_{\mathrm{p}} \mathrm{d}\tau \qquad (1.23)$$

Here Φ_{m} and Φ_{p} the state functions for the electronic energy levels m and p respectively. The symbol $\underline{M}$ is a transition moment operator of various kinds. The most commonest type of transition is the electronic dipole allowed transition with the components –

$$\sum_i e_i x\,, \sum_i e_i\, y_i, \text{and } \sum_i e z_i,$$

The transition is allowed if the matrix element $\underline{M}_{mp}$ of equation (1.23) is non zero. This is possible only when the state functions Φ_{m} and Φ_{p} belong to the same irreducible representation of the molecular point group and the direct product of symmetry species is non-zero.

$$\Gamma_m \Gamma_p = \Gamma_T \qquad (1.24)$$

Where Γ represents a symmetry species and T refers to a transition [30]. In the case when $\underline{M}_{mp}$ is zero, the transition is said to be symmetry forbidden. However, such forbidden transitions are sometimes observed as weak bands which are attributed to the vibronic interaction. The transition may be weakly allowed as a magnetic dipole or electric quadrupole-transition. Thus, in such cases, we have

$$\Gamma_m \Gamma_p = \Gamma_R$$

Where Γ_R is the symmetry species of a rotation.

The oscillator strength, f, is one of the measures of the intensity of a transition. It is defined as the ratio of the square of the observed transition moment to the square of the transition moment of the electron as an harmonic oscillator [31].

Mathematically, it is expressed as –

$$f = \frac{8\pi^2 m_c C}{3h^2 e^2} \left(E_m - E_p\right) \left[\underline{M}_{mp}\right]^2 \qquad (1.25)$$

Here $\left(E_m = E_p\right)$ in the transition energy, m_e, e, h and c are mass of electron, charge of electron, Planck's constant and velocity of light respectively. The X-component of the transition moment for transitions from the ground to the excited States described by Φ and $\Phi_{\mathrm{i}}^{\mathrm{a}}$ [equations (1.12) and (1.18)] is given as

$$(M_x)_{mp} = e\sqrt{2} \int \psi_i \times \psi_a \, \mathrm{dv}$$

Here dv is an element of the configuration space.

In LCAO approximation, where $\psi_i = \sum C_{i\mu} \Phi_\mu$ the above equation may be written as –

$$(M_x)_{mp} = e\sqrt{2} \sum_{\mu,v} C_{i\mu} C_{av} \int \Phi_\mu \times \Phi_v \, \mathrm{dv} \tag{1.26}$$

$$= e\sqrt{2} \sum_{\mu} [C_{i\mu} C_{av} \int \Phi_\mu \times \Phi_\mu \, dv + \sum_{v \neq \mu} C_{i\mu} C_{av} \int \Phi_\mu \times \Phi_\mu \, \mathrm{dv}]$$

$$= e\sqrt{2} \sum_{\mu} [C_{i\mu} C_{av} X_A + \sum_{v \neq \mu} C_{i\mu} C_{av} \left(\frac{1}{2}\right) (X_A + X_B) S\mu v \, \mathrm{dv}]$$

Where X_A and X_B are the coordinates of the nuclei A and B on which Φ_μ and Φ_v are centered respectively. The second summation in the above equation contributes little to the transition moment and hence it is neglected. Thus, we have

$$(M_x)_{mp} = e\sqrt{2} \sum C_{i\mu} C_{a\mu} X_A \tag{1.27}$$

Similarly expressions for Y and Z - components may be derived. Finally, the simplified expression for oscillator strength (1.25) becomes as following.

$$f = 1.085 \times 10^{-5} \omega_{mp} \times 2 \left\{ \left(\sum_{\mu} C_{i\mu} C_{a\mu} X_A \right)^2 + \left(\sum_{\mu} C_{i\mu} C_{a\mu} Y_A \right)^2 + \left(\sum_{\mu} C_{i\mu} C_{a\mu} Z_A \right)^2 \right\} \tag{1.28}$$

Where ω_{mp} is the wave number expressed in cm^{-1} and the atomic coordinates are in Angstroms.

8 Configuration interaction:

The molecular orbital functions become in capable to give correct description of electronic transitions, molecular dissociation etc because these neglect electron correlation. This can however, be taken care of by introducing configuration interaction technique in the MO calculations. The correlation energy is defined as [32].

$$E_{corr} = E_{HF} - E_{EXPT} \tag{1.29}$$

Where E_{HF} and E_{EXPT} are the Hartee Fock energy and the experimental energy respectively.

However, the HF procedure keeps the electron with parallel is spins apart due to Pauli's Exclusion Principle. Thus the electron correlation arises due to the mutual interaction between the electrons with opposite spins.

But in the molecular orbital calculation for closed shell configuration two electrons with opposite signs are associated with the same MO and show the possibility for one electron to come closer to the other is quite natural which constitute correlation. Actually, for an electronic transition it is the relative correlation of the excited state.

In a CI procedure the Slater determinants are taken as basis functions and by mixing them to have a linear combination of Slater determinants. Since each Slater determinant represents an electronic configuration, we really mix configuration for closed shell systems, the wave function is expanded in terms of Slater determinants formed by selecting 2n orbitals at a time from a complete set of orthonormal MSO's. This assures us to have a complete orthonormal set $\{\Phi_j\}$ of Slater determinants, the procedure itself being called a complete CI procedure [33]. Thus, the exact solution for the wave function would be of the form –

$$\Psi_i = \sum_j^{\infty} C_{ij}\Phi_j \tag{1.30}$$

Where C_{ij}'s are the expansion coefficients. This may be obtained from the secular equation

$$\sum_j^{\infty} C_{ij}\left(H_{ij} - E\partial_{ij}\right) = 0 \tag{1.31}$$

Where, $H_{ij} = \bar{H}_{ij} = \int \Phi_i H_e \Phi_j d\tau$ (1.32)

$\partial_{ij} = \int \Phi_i \Phi_j d\tau$ (1.33)

The summation in Eq. (1.30) extends over infinity. But due to practical limitations we restrict our idea for considering only a finite set of orbitals. The finite set {Φ} thus formed from them would comprise of the HF function and M-1 determinants obtained from it by replacing one or more ground state orbitals by the excited orbitals. The single replacement referred to the singly excited configuration, Δ the double replacements to the doubly excited configuration and so on in this way we have M determinants in all, and consequently equations (1.30) and (1.31) would reduced to –

$$\Psi_i = \sum_j^{M} C_{ij}\,\Phi \tag{1.34}$$

and

$$\sum_j^{M} C_{ij}\left(H_{ij} - E\partial_{ij}\right) = 0 \tag{1.35}$$

Which would have non trivial solution if,

$$\det\left|H_{ij} - E\partial_{ij}\right| = 0$$

here a full CI treatment is adopted in which only those determinants are utilized in eqn. (1.34) belonging to a given irreducible representation of symmetry group. This treatment still seems to be rather cumbersome and impracticable for larger molecules having larger set of MO's. Thus to make this work easy we truncate the expansion,

$$K_{ij} = \int\int \Psi_i^*(1)\,\Psi_j^*(2)(1/r_{12})\Psi_j(1)\Psi_i(2)d\tau_1 d\tau_2 \qquad (1.36)$$

and

$$H(1) = \left(-\frac{1}{2}\right)\nabla_1 - \sum_A Z_A/r_iA$$

Here H_{ij} indicates the energy of an electron in a molecular orbital Ψ_i in the field of nuclei alone. J_{ij} and K_{ij} are the coulomb integrals and exchange integrals respectively.

The orbital Ψ_i's are those which make the energy minimum. This implies that the energy given by eqn. (1.37) should be minimized. This orbital also satisfies the condition of orthonormality. This leads to the Hartee-Fock equation [34].

$$\left[H(1) + \sum_j^n (2J_i)(1) - K_j(1)\right]\Psi_i = \varepsilon_i\Psi_i(1) \qquad (1.37)$$

Where J_i and K_j represent coulomb and exchange operations respectively and given by,

$$J_i(1)\Psi_i(1) = \left[\int \Psi_i^*(2)(1/_{n2})\Psi_j(2)\, d\tau_2\right]\Psi_i(1)$$

$$K_j(1)\Psi_i(1) = \left[\int \Psi_j^*(2)(1/_{n2})\Psi_i(2)\, d\tau_2\right]\Psi_j(1) \qquad (1.38)$$

The equation (1.37) represents n one electron wave equations for orbitals $\Psi_1, \Psi_2, \ldots\ldots\ldots, \Psi_n$. The quantity within the square bracket is known as Fock Hamiltonian F.

$$F(1) = H(1) + \sum_j^n \left(2J_j(1) - k_j(1)\right) \qquad (1.39)$$

and the wave equation is expressed as,

$$F(1)\Psi_i(1) = \varepsilon_i\Psi_i(1) \qquad (1.40)$$

Where ε_i is the orbital energy and $i = 1,2, \ldots\ldots, n$. The solved equations are

$$F\Psi = \varepsilon\Psi \qquad (1.41)$$

The solutions of the equation (1.45) comprise not only the n solutions Ψ_i; $i = 1,2, \ldots\ldots, n$ of equation (1.40) but also those that corresponding to electrons which move in the field of 2n - electrons these remaining Eigen functions of F are called excited orbitals in contrast to the n – functions Ψ_i which are called ground state orbitals.

We make an initial guess at the n-solutions Ψ_i, complete the average potential$\sum_j(2J_j - k_j)$ and solve equation (1.40). Obtained Ψ_i's are generally improved over the initially assumed one. On the basis of these first improved solutions, in the second cycle, the above procedure is repeated. Now we have second improved solution. This process is continued till the new improved solutions become identical with previous cycle, i.e., the potential field obtained from a set of solutions generate almost the same solution. The field becomes consistent with itself. This is called SCF approach (Method). The total electronic energy can be written as –

$$E_{clcc}. = \sum_i^n H_i + \left[H_i + \sum_j (2J_{ij} - K_{ij}) \right] = \sum_j^n (H_i + \varepsilon_i) \tag{1.42}$$

9 APPROXIMATE MO METHOD:

Now we discuss some important approximate methods in briefs. Methods are semi empirical.

[A] THE CNDO METHOD:

The Complete Neglect of Differential Overlap {CNDO} method is the most basic theory relating the main features of electron repulsion introduced by People, Sentry and Segal [34, 35]. In this method only the valence electrons are considered explicitly and the inner shells are supposed to be the rigid core.

Following are some basic characteristics of the approximations made under this approach [36]. They are:

A_1> The overlap integrals are orthogonal

$$S_{\mu v} = \delta_{\mu v} \tag{1.43}$$

A_2> The differential overlaps in all two electron integrals are neglected so that

$$\mu v / \lambda \sigma = \delta_{\mu v} \delta_{\lambda \sigma} (\mu\mu / \lambda\lambda) \tag{1.44}$$

A_3> The coulomb integrals are supposed to depend only on the nature of the atoms A and B to which the AO's $\Phi_\mu$and Φ_v belong but not on the nature of orbitals, for example -

$$\mu\mu / \lambda\lambda = \gamma AB \ \Phi_\mu \rightarrow \ \mathrm{A}; \ \Phi_\varepsilon \rightarrow \mathrm{B} \tag{1.45}$$

A_4> The monatomic differential overlap is neglected in the interaction integrals implicating in the case of atoms.

$$\mu / \nu B / \upsilon = \delta_{\mu v} \nu_{AB} \tag{1.46}$$

A_5> The diatomic off diagonal core-matrix elements are supposed to be proportional to the corresponding overlap integrals,

$$H_{\mu v} = \beta_{AB}^0 S_{\mu v} \Phi_\mu \rightarrow A : \Phi_\varepsilon \rightarrow B \tag{1.47}$$

Considering all the above approximations($A_1, A_2, A_3, A_4$and A_5), the matrix elements of the Fock-Hamiltonian are.

$$F_{\mu\mu} = U\mu\mu + \left(P_{AA} - \frac{1}{2}P_{\mu\mu}\right)\gamma_{AA} + \sum_{B(\neq A)} \left(P_{BB\gamma AB} - V_{AB}\right) \tag{1.48}$$

$$F_{\mu\upsilon} = \beta_{AB}^{0} S_{\mu\upsilon} - \tfrac{1}{2} P_{\mu\upsilon}\gamma_{AB}, \mu \neq \upsilon; \tag{1.49}$$

Here γ_{AB} is the average electronic repulsion between electrons on the atoms A and B, $U_{\mu\mu}$ is stands for one centre term, P_{BB} represents the total electron density associated with atom B and the constant β_{AB}^{0} is selected to depend only on the nature of atoms A and B. The eqn. (1.64) can be rearranged as follows -

$$F_{\mu\mu} = U_{\mu\mu} + \left(P_{AA} - \frac{1}{2}P\mu\upsilon\right)\gamma_{AB} + \sum_{B(\neq A)} [-\Theta_b\gamma_{AB} + (Z_B\gamma_{AB} - \nu_{AB})] \tag{1.50}$$

Here Θ_b is the net charge on atom B and in equal to,

$$\Theta_b = Z_B - P_{BB} \tag{1.51}$$

The difference between the potential due to valence electrons and the core of the natural atom B is represented by the quantity($Z_B\gamma_{AB} - \nu_{AB}$). the total energy is calculated by –

$$E_{total} = \frac{1}{2}\sum_{\mu\upsilon} P_{\mu\upsilon}\left(H_{\mu\upsilon} + F_{\mu\upsilon}\right) + \sum_{A<B} Z_A Z_B \gamma^{-1} AB \tag{1.52}$$

[B] THE INDO METHOD:

The Intermediate Neglect of Differential Overlap (INDO) method is an improvement of the CNDO method which neglects the monoatomic exchange integrals ($\mu\upsilon/\mu\upsilon$), due to this it cannot explain the separation of states related to the same configuration.

Pople, Beveridge and Dobash [48] introduced the INDO method. In this the differential overlap is neglected in all electron interaction integrals in excluding those which involves one centre only. The HF matrices are given as –

$$F_{\mu\mu} = U_{\mu\mu} + \sum_{\lambda}^{A} P_{\lambda\lambda}\left[(\mu\mu/\lambda\lambda) - \frac{1}{2}(\mu\lambda/\mu\lambda)\right] + \sum_{B\neq A} (P_{BB} - Z_B)\gamma_{AB'}; \mu \rightarrow A \tag{1.53}$$

$$F_{\mu\upsilon} = P_{\mu\upsilon}\left[\tfrac{3}{2}(\mu\upsilon/\mu\upsilon) - \tfrac{1}{2}(\mu\mu/\upsilon\upsilon),\right]\mu \neq \upsilon \rightarrow A \tag{1.54}$$

$$F_{\mu\upsilon} = \beta_{AB}^{0} S_{\mu\upsilon} - \tfrac{1}{2} P_{\mu\upsilon} V_{AB'};\ \mu \rightarrow A, \upsilon \rightarrow B \tag{1.55}$$

and

$$U_{\mu\mu} = -\tfrac{1}{2}\left(I_\mu + A_\mu\right) - \left(Z_A - \tfrac{1}{2}V_{AB}\right) \qquad (1.56)$$

$$(\mu\upsilon/\lambda\sigma) = \int\int \Phi_\mu^*\,(1)\,\Phi_\lambda^*(2)(1/r_{12})\,\Phi_\sigma(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \qquad (1.57)$$

[C] The RCNDO method:

This method, well known as the Rydberg Complete Neglect of Differential Overlap (RCNDO) method, includes Rydberg AO's in the extended basis set. Following assumptions are made under this scheme [36].

C_1) The electron repulsion integrals $\gamma_{\mu\upsilon}$ depend only on the atoms (to which AO/s μ and υ belong) and on their principal quantum number,

$$V_{\mu\upsilon} = \underset{A\,B}{V_{n1n2}}, \mu \to \underset{A}{n1}, \upsilon \to \underset{B}{n2} \qquad (1.58)$$

C_2) The core integrals are given by –

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B\neq A}(\mu|V_B|\upsilon)\;\; \mu,\upsilon \to A \qquad (1.59)$$

$$H_{\mu\upsilon} = U_{\mu\upsilon} - \sum_{B\neq A}(\mu|V_B|\upsilon)\;\; \mu,\upsilon \to A \qquad (1.60)$$

$$= B\mu\varepsilon, \mu \to A, \upsilon \to B \qquad (1.61)$$

C_3> The resonance integrals $\beta_{\mu\upsilon}$ were supposed to be proportional to the corresponding overlap integral and are given as –

$$\beta_{\mu\upsilon} = \beta_A^{n1}{}_B^{n2}S_{\mu\upsilon} \qquad (1.62)$$

C_4> The coulomb type integrals were taken equal for all orbitals, i.e.,

$$(\mu|V_B|\mu) = \underset{A\,B}{V_{n1}} \qquad (1.63)$$

Which was further estimated as,

$$\underset{A\;\;B}{V_{n1}} = Z_B\gamma_A^{n1}{}_B^{n2} \qquad (1.64)$$

C_5> The term $U_{\mu\upsilon}$ is treated in the semi- empirical manner –

$$U_{\mu\upsilon} = -\tfrac{1}{2}\left(I_\mu + A_\mu\right) - (Z_A - 1).V_{\underset{A}{n1}\;\underset{A}{n1}} - \tfrac{1}{2}V_{\underset{A}{n1}\;\underset{A}{n1}} \qquad (1.65)$$

Thus the HF matrix elements assume the form,

$$F_{\mu\mu} = -\frac{1}{2}\left(i_\mu = A_\mu\right) + \sum_{n2}^{A} P_{\underset{B}{n2}\;\underset{B}{n2}}\gamma_{\underset{A}{n1}\;\underset{A}{n2}} - \frac{1}{2}\left(P_{\mu\mu} + 1\right)\left(V_{\underset{A}{n1}\;\underset{A}{n1}} + V_{\underset{A}{n1}\;\underset{A}{n1}}\right) + \sum_{B\neq A}\sum_{n2}^{B} P_{\underset{B}{n2}\;\underset{B}{n2}}V_{\underset{A}{n1}\;\underset{B}{n1}} - \sum_{B} Z_B\,V_{\underset{A}{n1}\;\underset{B}{n2}}$$

(1.66)

$$F_{\mu\upsilon} = \beta^{0}\underset{A}{n1}\,\underset{B}{n2}S_{\mu\upsilon} - \left(\tfrac{1}{2}\right)P_{\mu\upsilon}V_{\underset{A}{n1}\ \underset{B}{n2}} \tag{1.67}$$

[D] THE RINDO/S METHOD:

Singh and Haque [22] introduced Rydberg Intermediate Neglect of Differential Overlap (RINDO) method which describes the S-T splitting in a rather satisfactory way. The method incorporates the monoatomic exchange integrals (which were ignored by RCNDO method) and to Rydberg AO's also. The matrix elements under this scheme are

$$F_{\mu\mu} = U_{\mu\upsilon} + \sum_{\lambda}^{A,n1} P_{\lambda\lambda}\left[(\mu\mu/\lambda\lambda) - \left(\frac{1}{2}\right)(\mu\lambda/\mu\lambda)\right] + \sum_{n2\neq n1} P_{\underset{A}{n2}\ \underset{A}{n2}}V_{\underset{A}{n1}\ \underset{A}{n1}}$$
$$+ \sum_{B\neq A}\left[\sum_{n2}^{B} P_{\underset{B}{n2}\ \underset{B}{n2}}V_{\underset{A}{n1}\ \underset{A}{n1}} - Z_B V_{\underset{B}{n1}\ \underset{B}{n2}}\right], \mu \rightarrow n16; \tag{1.68}$$

$$F_{\mu\upsilon} = P_{\mu\upsilon}\left[\tfrac{3}{2}(\mu\upsilon/\mu\upsilon) - \left(\tfrac{1}{2}\right)\mu\mu/\upsilon\upsilon\right], \mu\neq\upsilon \rightarrow \underset{A}{n1} \tag{1.69}$$

and also,

$$F_{\mu\upsilon} = \beta^{0}{}_{\underset{A}{n1}\ \underset{B}{n2}}S_{\mu\upsilon} - \left(\tfrac{1}{2}\right)P_{\mu\upsilon}V_{\underset{A}{n1}\ \underset{B}{n2}},\ \mu \rightarrow_{\underset{A}{n1}},\ \upsilon \rightarrow_{\underset{B}{n2}} \tag{1.70}$$

The term $U_{\mu\mu}$ is defined as in equn. (1.65).

[E] THE RINDO/S METHOD:

Though the assumptions made in both the methods (RINDO and RINDO/s) are the same, the screened RINDO/s method is more convenient than RINDO method, due to the difference in the treatment of overlap terms $S_{\mu\upsilon}$ of equation (1.70). The term is replaced by –

$S_{\mu\upsilon} = S\_\mu\upsilon$ for σ symmetry

$= \kappa S_{\mu\upsilon}$ for π symmetry (1.71)

Where κ is a screening parameter and its value is equal to 0.585 as proposed by Del Bene and Jaffe [12]. In this present work, the values of κ are chosen as –

$\kappa = 0.585$ for valence interactions.

and $\kappa' = 0.595$ for all others.

When $\kappa = \kappa' = 1$, RINDO/s reduces to RINDO.

[F] THE RCNDO/S METHOD:

The Rydberg Complete Neglect of Differential Overlap by screening method (RCNDO/S) provides the same at Hartee-Fock matrix elements. For distinguishing σ and $\pi -$ type interactions are same as used in the RINDO/S method

1.10 PARAMETERS AND INTEGRAL EVALUATIONS:

We can calculate molecular energies of right order of magnitude only if the parameters like $U_{\mu\mu}$ and $V_{\underset{A}{n1}\ \underset{A}{n2}}$ are approximately correct. $U_{\mu\mu}$ and $V_{\underset{A}{n1}\ \underset{A}{n2}}$ determine the energy levels of separate atoms. The excited states are satisfactorily described if $U_{\mu\mu}$ be computed in the manner of Pople and Segal from ionization potentials (IP) and electron affinities (EA) associated with the average states of atoms [34] and $V_{\underset{A}{n1}\ \underset{B}{n2}}$ be replaced by the difference between these IP and EA [5,14]. The values of IP and EA of H, C, N, O and F are given in table C – I (Appendix C). They are from Salahub [11]. Ionization potential and electron affinities for valence orbital's have been taken from Pople and Segal [40] for computing core integrals.

Two electron integrals were calculated in the following way.

i) One orbital integrals

$$(\mu\mu/\mu\mu) = V_{\underset{A}{n1}\ \underset{A}{n2}} = I_{\underset{A}{n1}} - I_{\underset{A}{n1}} \tag{1.72}$$

The values for p electron where taken from Del Bene and Jaffe work [12,15].

ii) Two centre integrals $V_{\underset{A}{n1}\ \underset{B}{n2}}$ where are obtained by using Parriser and Parr's uniformly extrapolation technique [6].

iii) One centre to orbital integrals where mentioned as [17].

$$V_{\underset{A}{n1}\ \underset{A}{n2}} = \left(\frac{1}{2}\right)\left(V_{\underset{A}{n1}\ \underset{A}{n2}} + V_{\underset{A}{n1}\ \underset{A}{n2}}\right) \tag{1.73}$$

The values of integrals within brackets along with $U_{\mu\mu}$ are listed in table C – 3 (See Appendix C).

iv) The MRINDO/S method requires evaluation of one-centre exchange integrals $(\mu\, \upsilon/\mu\, \upsilon)$ also. These were computed from Slater-Condon (S-C) factors as Pople and his coworkers did [35]. Such (S-C) factors for excited AO's were determined by Fischer [48] using multi-configuration Hatree-Fock Program [49]; except in the case of hydrogen where we have used in the values obtained by Lewis [50]. The F-C factors are collected in Table C-2 (See Appendix C).

v) In the present calculation we require larger number of bonding parameters -12 as against 3 needed in the INDO method for a given pair of atoms. We have, therefore, use a semi empirical relation [46].

$$\beta^0{}_{\underset{A}{n1}\ \underset{B}{n2}} = n\left(I_{\underset{A}{n1}} + I_{\underset{A}{n1}}\right) \tag{1.74}$$

Where I_n is the average ionization potential for S and P electrons of principal quantum number n_1 on atom A and n is an adjustable parameter having value 0.42 for valence-valance interactions and 0.045 for all other interactions.

vi) The overlap integrals $S_{\mu v}$ are obtained by using formula of Mulliken, Ricka and Orloff [51], considering Slater exponents, except for H, where

$\varepsilon 1S = 1.2$ and $\varepsilon 2S = \varepsilon 2P = 0.6$

The present calculations are followed by configuration interaction technique in which the lowest thirty singly excited configuration have been considered for both singlets and triplets. The CI matrix elements and molecules integrals required in the present calculations are given in Appendix A and B.

In Appendix D, the computer program for present work has been briefly discussed.

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