Chapter 7. Calculation of Excited States

The ground state of a system is the lowest energy configuration of the electrons within the various MOs. Excited states are stable, higher energy electronic configurations. Such states are produced when a sample is exposed to UV-visible (UV-vis) radiation. They are relevant to many areas of chemistry, including photochemistry and spectroscopy. Modeling excited states and predicting their properties is a very difficult task.[1]

7.1. Theoretical overview of UV-vis spectroscopy

The UV-vis absorption bands of organic molecules are commonly associated with electronic transitions in the valence shell. These bands are characterized by their position, intensity and shape. These will be discussed in this section.

Electronic absorption frequencies (ν) at which UV-vis absorption bands appear can be obtained from the differences between the energies of the ground (E_i) and excited (E_f) states.

$$\nu = \frac{E_f - E_i}{h} \tag{7.1}$$

Frequency, wavelength (λ), and wavenumber ($\bar{\nu}$) are related by the following expressions:

$$c = \lambda\nu = \frac{\nu}{\bar{\nu}} \tag{7.2}$$

where c is the speed of light. They can be used to describe the position of electronic absorption bands.

Based on the HF approximation, electrons are considered to be in spin-orbitals, but actually due to the electronic correlation and the fact that electrons are fermions, it is better to say that they are in Fermi states that have major contributions of certain spin-orbitals. E_i and E_f would be the initial and final Fermi states.

As a consequence of Brillouin's theorem,[2] singly excited determinants $\left|\Phi_i^a\right\rangle$ (obtained by a single replacement of an occupied spin-orbital χ_i with an unoccupied spin-orbital χ_a) will not interact directly with a reference HF determinant $\left|\Phi_o\right\rangle$. They can mix indirectly with $\left|\Phi_o\right\rangle$ through the doubly excited determinants. Hence, a CIS procedure cannot improve the ground state HF energy ($E_{CIS} = E_{HF}$). However, the CIS treatment is frequently used to calculate excited states from which electronic spectra, are predicted.

The energy required to promote an electron from an occupied orbital "i" to a virtual orbital "a" is given by the expression:[3]

$$\Delta E = \varepsilon_a - \varepsilon_i - J_{ia} + 2K_{ia} \tag{7.3}$$

where ε_a and ε_i are the energies of the initial and final orbitals; J_{ia} is the molecular Coulomb integral:

$$J_{ia} = (ii \mid aa) = \int \phi_i^*(1)\phi_i(1)\frac{1}{r_{12}}\phi_a^*(2)\phi_a(2)d\tau_1 d\tau_2 \tag{7.4}$$

and K_{ia} is the molecular exchange integral:

$$K_{ia} = (ia \mid ai) = \int \phi_i^*(1)\phi_a(1)\frac{1}{r_{12}}\phi_a^*(2)\phi_i(2)d\tau_1 d\tau_2 \tag{7.5}$$

The expression (7.3) refers to the energy associated with singlet-singlet transitions. For singlet-triplet transitions the corresponding expression is: [3]

$$\Delta E = \varepsilon_a - \varepsilon_i - J_{ia} \tag{7.6}$$

These latter transitions will not be treated in this work because usually they do not appear in the electronic spectrum.

Excited states calculated from HF orbitals are in poor agreement with experiment because virtual orbitals are not well optimized, a consequence of the fact that there is no electronic density associated with them. However, they are of great importance in the calculation of spectroscopic data. To improve the calculation of spectra once the ground state has been obtained in a previous geometry optimization (yielding MO coefficients and eigenvalues), a CI calculation must follow.

A single-point calculation (*i.e.*, the calculation of the energy of the system at a specified configuration) on an optimized structure allows us to determined the HF reference electronic configuration associated with the (singlet) ground state of a molecular system. A CIS calculation mixes all single determinant wavefunctions that can be obtained from the ground state by exciting electrons from a subset of the occupied spin-orbitals to a subset of the unoccupied spin-orbitals. These subsets can be specified as a fixed number or by an energy criterion associated with the energy difference between the occupied and unoccupied spin-orbitals. The degree of mixing of states depends primarily upon the energy differences among them. Generally, configurations of high energy do not interact strongly with the reference configuration, and the higher the maximum energy, the greater the number of configurations to be included in the CIS calculation.[4] The Hamiltonian matrix elements between the singly excited determinants are computed, and the matrix is diagonalized to get the spectrum of electronic CIS states, which are expressed (for singlet transitions) as a linear combination of the normalized singly excited Slater determinants:

$$\Psi_{CIS} = 2^{-1/2} \sum_i c_i \left(\left| \Phi_{\bar{i}}^{\bar{a}} \right\rangle - \left| \Phi_i^a \right\rangle \right) \tag{7.7}$$

$\left| \Phi_{\bar{i}}^{\bar{a}} \right\rangle$ represents the excitation of an electron between the β spin-orbitals $\chi_{\bar{i}}$ and $\chi_{\bar{a}}$, and $\left| \Phi_i^a \right\rangle$ represents the corresponding excitation between the α spin-orbitals χ_i and χ_a. Triplet CIS states are also obtained but will not be included in this discussion. The coefficients c_i are determined variationally to obtain the lowest CIS energies. The difference in energy between the ground and CIS states determines the energy of the calculated excited electronic states. If N singly excited determinants are considered, N CIS wavefunctions and excited states are obtained.

Detailing the composition of the CIS states, the nature of the calculated electronic transitions (*e.g.* $\sigma\sigma^*$, $\pi\pi^*$, $n\sigma^*$, $n\pi^*$, etc.) can be determined, although there are cases where this assignment is not possible due to a mixture of a great number of states (MOs). The symmetry of the MOs (σ, π, n) implied in the single excitations of the determinants with higher square of the CIS coefficients (c_i^2) will determine the nature of the UV-vis

bands. For a normalized wavefunction, $\sum_i c_i^2 = 1$, that is the reason c_i^2 is the magnitude usually reported, instead of c_i. The symmetry of the MOs can be deduced by considering how they are localized in the molecule, or by analyzing the nature of the AOs that make a major contribution to the MOs.

Various schemes have been proposed to denote the states of a molecule and the absorption bands that correspond to transitions between these states. Some of these schemes are collected in Table 7.1.[5]

Table 7.1. Labeling of electronic transitions.[(a)]

System	State Symbol		Example
Enumerative	S_0	Singlet ground state	$S_0 \rightarrow S_1$
	$S_1, S_2, S_3, \ldots$	Excited singlet states	$S_1 \rightarrow S_2$
	$T_1, T_2, T_3, \ldots$	Triplet states	$T_1 \rightarrow T_2$
Group theory	A, B, E, T (with indices g, u, 1, 2,’,”)	Irreducible representation of the point group of the molecule	$^1A_1 \rightarrow {}^1B_2$ [(b)] $^1A_{1g} \rightarrow {}^3E_{1u}$
Kasha	$\sigma, \pi, n,$	Ground state orbitals	$\pi \rightarrow \pi^*$
	σ^*, π^*	Excited state orbitals	$n \rightarrow \sigma^*$
Platt	A	Ground state	$^1A \rightarrow {}^1B_a$ [(b)]
	B, L (with indices a, b)	Excited states	$^1A \rightarrow {}^1L_b$
Mulliken	N	Ground state	$V \leftarrow N$
	Q, V, R	Excited states	$Q \leftarrow N$
Clar	α, p, β	Intensity and band shape	

[(a)] Reproduced from reference 5; [(b)] The upper left index indicates the multiplicity

In theoretical calculations the intensity of a transition is given by a dimensionless quantity called the oscillator strength (f):

$$f_{i\to f} = \left(\frac{8\pi^2 m_e}{3e^2h^2}\right)(E_f - E_i)|\mu_{fi}|^2 \tag{7.8}$$

where μ_{fi} is the electric dipole transition moment, e and m_e are the charge and rest mass of the electron, respectively, and h is Planck's constant.

The oscillator strength[6] may be interpreted as the ratio of the observed intensity to the intensity of radiation absorbed or emitted by a harmonically bound electron in an atom. For strongly allowed transitions, (*e.g.* $\sigma\sigma^*$, $\pi\pi^*$) f is close to 1; for symmetry forbidden transitions (*e.g.* $n\pi^*$, $n\sigma^*$) f is often close to 0.1, and for spin forbidden transitions (*e.g.* singlet→triplet) f is close to 10^{-5}. The oscillator strength is measured experimentally by determining the integrated absorption intensity, the greater the area under the absorption curve, the greater the intensity of the transition. In practice, the magnitude used to characterize the intensity of an absorption is the molar absorption or extinction coefficient, ε.

The energies of the initial and final states of transitions are determined by the CIS eigenvalues, and the transition dipole moments are obtained by using the CIS eigenvectors, that is,

$$\mu_{fi} = \left\langle \Psi_{CIS} \left| \sum_k \hat{m}_k \right| \Phi_o \right\rangle, \qquad \hat{m}_k = -|e|\, r_k \tag{7.9}$$

where k is the sum over electrons. Ψ_{CIS} and Φ_o are the total wavefunctions of the final and initial states. The orientation of μ_{fi} with respect to the molecular axis system is frequently called the absolute polarization direction. It is determined by its highest component.[5]

Absorption occurs only if the light can interact with a transient molecular charge or current distribution characterized by μ_{fi}. The transition dipole moment may be thought of as the dipole moment of the transition density $\left\langle \Psi^*_{CIS}\Phi_o \right\rangle$. The square of the transition

dipole moment is a measure of the change in charge distribution as a result of the electronic transition. The higher $|\mu_{fi}|^2$, the higher the probability of the transition and the greater its intensity.

Selection rules[5] establish the conditions under which the dipole moment of the transition vanishes and allow us to differentiate between formally "allowed" and "forbidden" transitions. A transition with a vanishing transition moment is referred to as forbidden and should have zero intensity. The transition moment of an allowed transition, although non-vanishing, can still be very small, whereas a forbidden transition may be observed in the spectrum with finite intensity if the selection rule is relaxed by an appropriate perturbation.

The shape of a UV-vis absorption band depends on the number and relative intensity of its vibrational components (fine structure). The Franck-Condon principle[7] explains the spectral intensity distribution of the vibrational transitions between two different electronic states of a molecule. This principle states that, because the electron mass is much less than that of the nuclei, the electronic transition in a molecule takes place much more rapidly in comparison to the vibrational motion. As a consequence, the nuclear rearrangement takes place after, not during, the electronic transition. The quantum mechanical basis for the Franck-Condon principle is the extent of overlap between the vibrational wavefunctions of the two electronic states: the more the overlap, the stronger the transition.

Frequently, because of the differences in the bonding characteristics of the upper and the lower states, the potential energy curves are displaced with respect to each other. Consequently, a transition can occur to more than one vibrational level in the excited electronic state (Fig. 7.1). Solvent effects can also alter the shape (besides its position and intensity) of absorption bands, but they will not be discussed in this section.

The accuracy of the computed spectrum depends on the size (*i.e.*, orbital active space) of the CIS calculation (if this is the method employed). In general, the ordering of excited

states is affected only by singly and doubly excited configurations. However, the actual values for the state energies, intensities and polarization directions, are sensitive to higher configurations. Therefore, rational methods for selecting configurations are of great importance. Energy criteria alone are not sufficient for this purpose. Rather, rough estimates of the matrix elements $\langle \Phi_S | \sum_k \hat{m}_k | \Phi_o \rangle$ are needed in order to decide which configurations affect the computed values. Such a scheme was developed, for example, by Downing at *al*.[8]

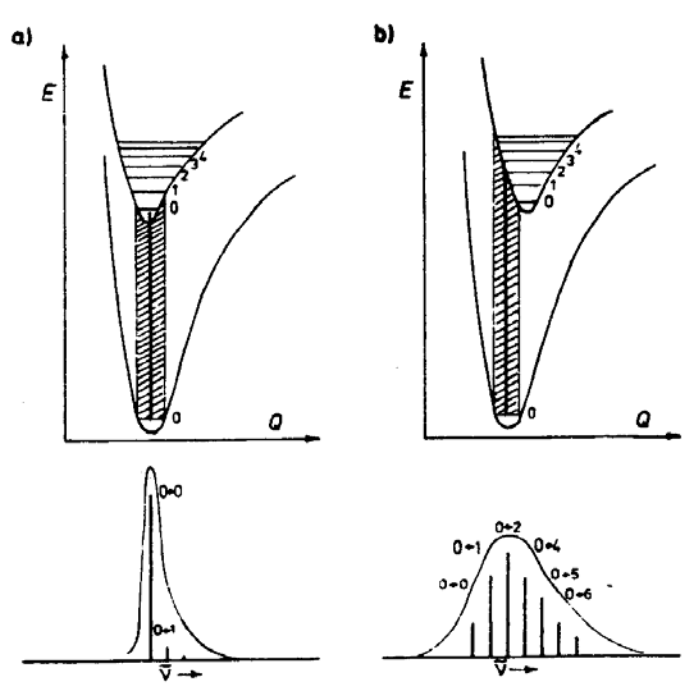

Figure 7.1. Schematic representation of the band shape expected from the Franck-Condon principle: a) approximately equal equilibrium internuclear distances in the ground and excited states; b) internuclear distance in the excited state larger than that of the ground state.
Reproduced from reference 5

7.2. The absorption spectra of PAHs

The UV-vis absorption spectra of organic compounds containing π electrons are easy to observe experimentally. The electronic spectra of cyclic conjugated π systems depend

inherently on the number of π electrons. Benzenoid hydrocarbons constitute a class of compounds whose UV-vis spectra have been investigated extensively both experimentally and theoretically.[5,9,10]

Typical UV-vis spectra of aromatic hydrocarbons are shown in Fig. 7.2. For these compounds the notation scheme introduced by Platt[11] is widely used (among others). These spectra contain absorption bands that fall into three categories according to their intensity. Bands of the first type (^1L_b) are of low intensity ($\varepsilon = 10^2$-10^3), may be hidden by the other bands, and often possess a complicated vibrational structure. Bands of the second type (^1L_a or ^1B_a) are moderately intense ($\varepsilon \approx 10^4$); ^1L_a bands usually show a regular vibrational structure. Bands of the third type (^1B_b) are very strong ($\varepsilon > 10^5$) and have little vibrational structure.

As can be seen from Fig. 7.2, the increment in size of the π system from naphthalene to tetracene leads to an extension of the conjugation and consequently, all absorption bands are shifted bathochromically (*i.e.*, to longer wavelengths) and their intensities are also enhanced. Fig. 7.3 shows how the experimentally observed wavelengths for two series of PAHs, the linearly annelated *acenes* and the angularly annelated *phenes*, change with increasing number of benzene rings. The shifts in the ^1L_b and ^1B_b positions are parallel to one another in both series, whereas the bathochromic shift of the ^1L_a band (whose excitation energy is related to the HOMO-LUMO energy difference) of acenes upon annelation is so pronounced that even in anthracene it masks the ^1L_b band.

7.2.1. ***Substituent effects on the spectra of PAHs***

In general, the long-wavelength bands of the spectra of aromatic compounds are most sensitive to substituents. In spite of changes due to substituents, the spectra of substituted derivatives nevertheless possess some resemblance to those of the unsubstituted aromatic hydrocarbon both in the position of bands and in intensity values, although there are exceptions (*e.g.*, quinones, anhydrides, phthalimides, etc.). The spectrum produced by a particular functional group depends to some extent on the position of the substituent. The

substituent position effects are less in molecules of lower symmetry, such as phenanthrene and chrysene, than in molecules of greater symmetry, such as naphthalene, anthracene and pyrene. Moreover, modifications due to position are usually not so great as the difference between the various polynuclear systems.[10]

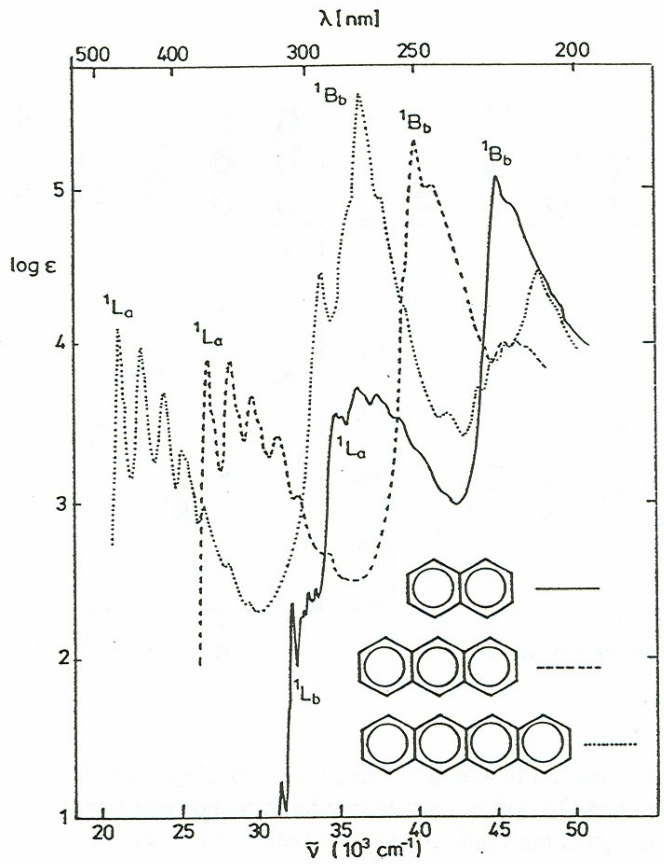

Figure 7.2. Examples of typical absorption spectra of PAHs.
Reproduced from reference 5

Alkyl substituents shift bathochromically all the transitions, and sometimes alter the total number of spectral bands but these changes usually occur in the very weak bands at long wavelengths. The presence of more than one alkyl group increases the bathochromic shift, but usually not as much as a single alkyl group does. Friedel and Orchin, after

examining the spectra of various alkyl-substituted naphthalenes and 1,2-benzanthracenes, have also stated the non-existence of a correlation between the size of the shift and the number of substituents, or their position on the ring. Askew[12] has indicated that alkylphenanthrenes substituted in the 1-position generally give the greatest bathochromic shift.

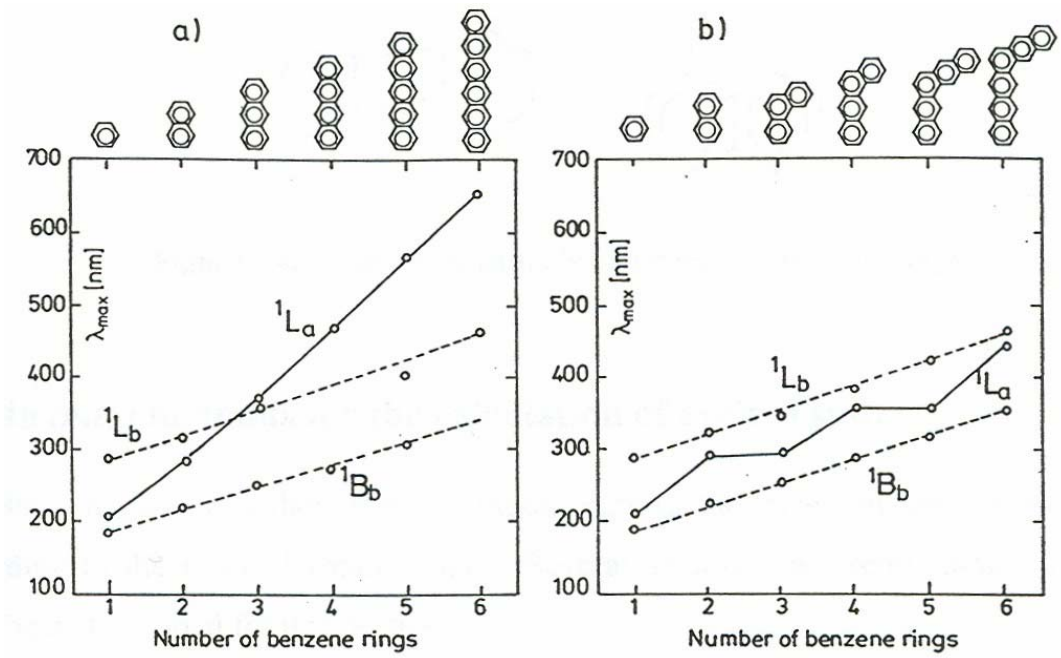

Figure 7.3. Wavelengths of ^1L_b, ^1L_a or ^1B_b bands of condensed aromatic hydrocarbons plotted versus the number of benzene rings a) linearly annelated and, b) angularly annelated aromatics. Reproduced from reference 5

The difference in chain length of the alkyl substituent on PAHs has little effect. In the series methylbenzene to *n*-hexylbenzene, there is a slight shift and decrease of fine structure with increasing size of alkyl group, and this effect becomes progressively less as one approaches *n*-hexylbenzene.[13] In more highly condensed aromatic systems, alkyl groups of various sizes have little or no effect because of the relatively large size of the aromatic nucleus.

Partially hydrogenated aromatic rings are compounds in which at least one non-aromatic ring (with or without olefin bond) is attached to an aromatic skeleton (Fig. 7.4). Steric hindrance cannot appreciably affect the resonance in this class of olefins because the ring structure compels the olefin bond to remain approximately in the same plane as the aromatic system.[5]

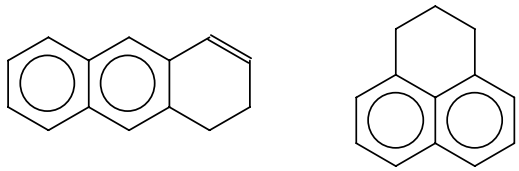

Figure 7.4. Examples of partially hydrogenated aromatic rings.

7.3. *Ab initio* methods for the calculation of excited states

Quantum chemical calculations of excitation energies and transition dipole moments vary according to the level of sophistication. Several *ab initio* and semi-empirical methods have been developed for this purpose.

For a detailed *ab initio* description of excited states[5] it is necessary to use diffuse basis functions. In addition, electron correlation effects for the ground state and the open-shell excited state must be considered. A widely used scheme for such calculations is the MRD-CI (multi-reference double excitation CI), which considers all doubly excited configurations with respect to a number of reference configurations. The number of elements in the CI matrix may easily exceed $5 \cdot 10^5$. The CI expansion is therefore truncated by appropriate selection criteria and energy extrapolations are used to approximate the contributions from omitted configurations.[14]

The most accurate data for excited states are obtained from CASSCF calculations[1,15] and a subsequent step is the use of the second-order perturbation theory with the CASSCF wavefunction as a reference state.[16]

In general, these methods lead to very good agreement between calculated and observed values. Rydberg states (unoccupied orbitals outside of the valence shell, characterized by high quantum number orbitals, which are much more extended than valence orbitals) are also described well. For $\pi\pi^*$ transitions, agreement with experiment is more difficult to achieve.

Modeling excited states as combinations of single substitutions from the HF ground state at the *ab initio* level, that is, without parameterizations and solving explicitly all the integrals and matrix elements, give rise to a method to which reference has been made in previous sections, CIS. This method is comparable to HF theory for ground state systems in that it is qualitatively accurate if not always highly quantitatively predictive. Like HF theory, CIS is an inexpensive method that can be applied to large systems.[1,17]

Time-dependent calculations often result in obtaining a wavefunction that oscillates between the ground and first excited states. From this solution, it is possible to extract both these states.[18] Time-dependent HF (TD-HF) is the HF approximation for the time-dependent Schrödinger equation:

$$\hat{H}\Psi = i\frac{h}{2\pi}\left(\frac{\partial\Psi}{\partial t}\right) \tag{7.10}$$

TD-HF, together with other time-dependent methods, is also used in computing non-linear optical properties.[19]

In the last several years, time-dependent DFT has emerged as an attractive method for the calculation of excited states.[20] Its success in predicting excited states for PAHs has also been demonstrated.[21] At its simplest, TD-DFT is the translation of the random phase approximation (RPA, a time-dependent *ab initio* method with a formulation and results equivalent to TD-HF) into DFT.[22]

7.4. Semi-empirical methods for the calculation of excited states

Over the past decades the semi-empirical MO methods of quantum chemistry have been widely used in computational studies. SCF π-electron calculations have been carried out since the 1950s and valence-electron calculations since the 1960s. Several books[23] and reviews[24,25] describe the underlying theory, the variants of semi-empirical methods, and the numerical results in much detail. Section 2.7 covers this topic in a general way.

The HMO[26] model is the easiest way of calculating excited states, but the spectra of PAHs cannot be well reproduced. Excited states are described by just one singly excited configuration (this is frequently possible to a good approximation for transitions from the highest occupied MO (HOMO) into the lowest unoccupied MO (LUMO)), and because electronic repulsions are not explicitly considered, the formulae for the excitation energies (linearly related to orbital energy differences) and the transition moments are considerably simplified.

The PPP method[27,23a] was an important stage in the calculation of electronic excitation properties of organic molecules. This theory was designed for the correlation and prediction of the wavelengths and intensities of the first main UV-vis absorption bands and other properties of complex unsaturated molecules. CI and SCF procedures are combined in a simple and economical way, and although it is limited to π electrons, it has been used extensively and with great success.

The inclusion of all valence electrons in the framework of semi-empirical procedures to calculate excited states of organic molecules occurred 15 years later, when del Bene and Jaffé published the papers related to their CNDO/S method[28] (spectroscopic CNDO) after the development of CNDO-INDO routines by Pople et *al.* in 1965.[23c] It is a modified CNDO/2 method extended to spectroscopic calculations. A new empirical parameter is introduced to differentiate resonance integrals between σ orbitals from those between π orbitals, and the semi-empirical Coulomb integrals are substituted with similar integrals to those used in the PPP method. The changes introduced in this method made possible

the study of $n\pi^*$ transitions and calculations for non-planar π systems, for which the PPP method was not applicable. When limited CI including singly and doubly excited configurations is considered,[29] fairly good agreement between computed and experimental results is obtained for singlet as well as triplet excitation energies. Some applications to excited state calculations of aromatic hydrocarbons are cited in reference 30.

CNDOL[31] is another approach, based on the CNDO approximation, which has been used to calculate excited states.[32] This method only uses parameters that are chosen *a priori*: STO exponents, valence state ionization potentials and electron affinities of each *l* azimuthal quantum number type of valence atomic orbital. That is, no parameters are empirically adjusted to fit results to experimental or previous accurate theoretical data. This method is combined with a single CI variational procedure.

The PCILO (perturbative CI using totally localized orbitals) method[33] is one of the methods which bypass the SCF stage by using a perturbational CI scheme in its place. This non-iterative method is based on the idea of treating a molecule as a system of localized bonds. First, the bond orbitals are obtained from a standard STO basis by minimizing the bond-bond overlap through construction of hybrid orbitals. Next, the various integrals over the resulting hybrid AOs are determined either by approximation formulae (semi-empirical method) or *ab initio*.[34] In particular, it is possible to adopt the ZDO approximation at the CNDO or INDO[35] levels. The PCILO method is especially interesting in the case of highly localized systems, where the bond-orbital description is quite satisfactory.

Another semi-empirical alternative for the calculation of ionization potentials and electronic transition energies of valence electrons is called LNDO/S (LNDO for spectroscopy).[36] This method is distinguished by explicit inclusion of electron correlation in a semi-empirical frame on the basis of large CI calculations. Simplifications in the SCF part of the method are achieved by use of the LNDO (local neglect of differential overlap) approximation. It is an approximation intermediate between CNDO and INDO

on the one hand and NDDO on the other. The basic idea is contained in the application of the ZDO approximation in the local instead of the molecular coordinate system. In this approximation all integrals except the Coulomb integrals are set equal to zero. Moreover, different types of Coulomb integrals may be used. This method has shown promising results.[36,37]

A frequent problem in excited-state applications of semi-empirical valence-electron methods including CI with multiply excited configurations is that the parameterization already may have been determined so as to include correlation effects for the ground-state results, and these are thus counted twice. Thiel in 1981 proposed the semi-empirical MNDOC method,[38] a reparameterization of the MNDO model[39] with explicit inclusion of electron correlation (C for correlation) by CI. Together with appropriate selection criteria for truncating the CI and with the possibility of using different reference configurations for different states, this method is well suited for calculating excitation energies, potential energy surfaces, and hence geometries of excited states,[40] but the basic shortcomings of the ZDO approximation remain in effect and again lead to excitation energies that are usually too small.[5,24]

7.4.1. ***The INDO/S method***

INDO/S[41] (spectroscopic INDO, also called ZINDO/S or ZINDO) has been designed for calculating electronic spectra, particularly vertical excitation energies at given ground-state geometries. It is a semi-empirical CI method parameterized at the CIS level, like the CNDO methods previously mentioned, that employs the INDO approximation.[42] Without using an extensive parameterization, it has been quite successful in calculating electronic spectra of large molecules.[41,43] ZINDO often gives poor results when used for geometry optimizations.

The INDO approximation includes the one-centre exchange integrals (neglected in the CNDO approximation) necessary in accurately separating different terms from within a configuration (e.g., the singlet and triplet states arising from $n\pi^*$ transitions are degenerate within the CNDO approximation). In addition, it has been found [41a] that these

integrals increase the interaction between states arising from $\pi\pi^*$ and $\sigma\sigma^*$ transitions, in many cases reducing the calculated transition energies and oscillator strengths.

Under the CNDO approximation the two electron integrals:

$$(ij \mid kl) = \int \phi_i^*(1)\phi_j(1)\frac{1}{r_{12}}\phi_k^*(2)\phi_l(2)d\tau_1 d\tau_2 = \sum_{\alpha\beta\gamma\delta} C_{i\alpha}C_{j\beta}C_{k\gamma}C_{l\delta}(\alpha\beta \mid \gamma\delta) \tag{7.11}$$

(where the indices i, j, k, l refer to MOs; the α, β, γ, δ, refer to AOs) reduce to:

$$(ij \mid kl)_{CNDO} = \sum_{\alpha\gamma} C_{i\alpha}C_{j\alpha}C_{k\gamma}C_{l\gamma}\gamma_{\alpha\gamma} \tag{7.12}$$

This term is equal to zero when α and γ are σ and π orbitals, respectively.

Under the INDO approximation many terms of equation (3.10) do not reduce to zero, as indeed they should not:

$$(ij \mid kl) = \sum_{\alpha\neq\beta,\gamma\neq\delta} C_{i\alpha}C_{j\beta}C_{k\gamma}C_{l\delta}(\alpha\beta \mid \gamma\delta)\delta^{AB}\delta^{CD}\delta^{AC} + \sum_{\alpha\gamma} C_{i\alpha}C_{j\alpha}C_{k\gamma}C_{l\gamma}\delta^{AC}\Delta_{\alpha\gamma} + (ij \mid kl)_{CNDO} \tag{7.13}$$

$$\alpha\in A,\ \beta\in B,\ \gamma\in C,\ \delta\in D$$

$$\Delta_{\alpha\gamma} \equiv (\alpha\alpha \mid \gamma\gamma) - F^{\circ}(\alpha\gamma)$$

The first term refers to the situation when α, β, γ and δ are all on one centre; the second term refers to the situation when α and γ are on the same centre. $F^{\circ}(\alpha\gamma)$ represents the one-centre two-electron integrals.

The transition energies calculated with equation (7.3) are the diagonal elements of the CI Hamiltonian matrix, $\left\langle {}^1\Phi_{i\to a} \middle| \hat{H} \middle| {}^1\Phi_{i\to a} \right\rangle$. The off-diagonal elements are:

$$\left\langle {}^1\Phi_{o} \middle| \hat{H} \middle| {}^1\Phi_{i\to a} \right\rangle = 0 \quad \text{(Brillouin's theorem)}$$

$$\left\langle {}^1\Phi_{i\to a} \middle| \hat{H} \middle| {}^1\Phi_{j\to b} \right\rangle = 2(ai \mid jb) - (ab \mid ij) \tag{7.14}$$

During the parameterization of the method several factors appear. The developers of ZINDO found that the parameters required to reproduce orbital energy orderings and UV-vis spectra are different from those required to reproduce accurate structures by geometry

optimizations. Empirical overlap weighting factors (f_π and f_σ) are introduced to account for this. They are used to scale down the π-π two-centre interactions, and scale up the σ-σ interactions. Their effect is to modify the resonance integrals for the off-diagonal elements of the Hamiltonian matrix.[41a]

In semi-empirical formulations, resonance integrals account for σ and π bonding patterns in molecules. These one-electron two-centre integrals represent the kinetic and electron-nuclear attraction energies associated with a charge distribution that lies between two atoms (overlap distribution). The actual magnitude of the resonance integral is proportional to the overlap integral $S_{\mu\nu}$. There are two types of atomic orbital overlap: σ-σ and π-π. The σ-π overlap is generally absent due to orthogonality conditions. Adjusting the weights provides a mechanism to account for the relative contributions of σ versus π bonding.

Usually a value of 1.267 is given to $f_{\sigma.}$[41b] Several different values have been used in the literature for f_π, for UV-vis spectra and orbital eigenvalues of organic molecules, 0.585 is commonly used,[26c] and for transition metal complexes,[41c] 0.640 has been recommended.
As in many computational methods trends and differences are determined more accurately than absolute values. ZINDO calculations on several substituted benzenes underestimate the wavelengths of the major UV absorption by about 20 nm, but the relative values are very well reproduced.

Sophisticated *ab initio*-CI methods for excited states calculations are available, but their computational cost is too high. Such calculations are not expected to become routine for large molecules in the near future. Therefore the semi-empirical valence-electron procedures continue to present an important way out of this dilemma.

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