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Derivation of Theoretical Formulas for Resonance Integrals from Heisenberg Equation of Motion

II. Inclusion of Rydberg and/or Inner Atomic Orbitals in the Formalism of NDO-Methods

Józef Lipiński

Institute of Organic and Physical Chemistry, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, PL-50-370 Wrocław, Poland

Jerzy Leszczyński

Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, PL-50-370 Wrocław, Poland

On the basis of the Heisenberg equation of motion and Linderberg–Seamans approximations useful formulas for β-resonance integrals in the NDO-like semiempirical methods have been derived. The case of *s*, *p*-electron elements has been investigated. The possibility of inclusion of Rydberg and/or inner orbitals in the basis set of the valence orbitals has been taken into consideration. The results of the test INDOL/R method calculations of vertical transition energies for H_2 and H_2O molecules has been presented.

Key words: Resonance integrals – Heisenberg equation of motion – Rydberg orbitals – NDO methods.

1. Introduction

Investigation of the Rydberg states in molecules is an important step to better understanding and interpretation of the electronic spectra [1–3], as well as photochemistry [2, 4] of various molecules. At present, calculations of the electronic spectra (taking into consideration the Rydberg states) have been performed in an *ab initio* SCF CI scheme by adding appropriate diffuse atomic orbitals

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Offprint requests to J. Lipiński

(Rydberg orbitals) to the usual basis set. These calculations are very time-consuming, and therefore they are restricted to rather small molecules. The various aspects of these calculations have been recently described by a few workers [4–8].

Usually, in the approximate NDO-type methods a minimum basis set of valence shell atomic orbitals (AO) has been used, which could not account for electronic transition involving a change in principal quantum number (Rydberg transition). The use of extended basis set in semiempirical methods has received little attention.

Kato et al. [9] and Watson et al. [10] included Rydberg orbitals (RO) in Extended Hückel method in a study of molecular properties of some molecules in the ground state [9], as well as in the calculations of valence and Rydberg transitions in mono-olefinic hydrocarbons [10]. In a few papers Rydberg orbitals have been included in the studies of the electronic spectra of indole (PPP approximations) [11] and in the CNDO calculations of the ground state properties of tiophene [12].

In 1971, Salahub and Sandorfy [13, 14], in a systematic study, have extended the CNDO method by including Rydberg orbitals in the basis set and performed calculations (mainly electronic spectra) on the first row atom molecules in which the heavy atom and hydrogen atom basis sets were augmented by $3s$, $3p$, and $2s$, $2p$ Slater type atomic orbitals, respectively.

Recently, Hague [15] and Singh and Prasad [16] also have used a similar approach (and have extended it to INDO scheme) in the studies of Rydberg electronic transitions in various simple molecular systems.

It seems, however, that Robin's comment: "... there seems outwardly to be good agreement with experiment, but closer inspection shows that in many cases, the theoretical valence shell excitations have been assigned to experimental Rydberg states ..." [1, I p. 49] can be applied to all above mentioned semiempirical calculations [10, 13–16] of Rydberg electronic transitions. Nevertheless, it appears, that semiempirical methods (with basis set including RO) can be useful technique for studying Rydberg states, when appropriate parametrization will be adopted. These methods may be fruitful, especially for larger molecules.

The most important point in every semiempirical scheme is the approximation of the $H_{ij}(\beta_{ij})$ one-electron, two-centre resonance integrals. Theoretical relations for the resonance integrals between s, p-electron elements have been derived by Linderberg and Seamans [17] using the Heisenberg equation of motion and the second quantization formalism. Application of their formulas to the calculations of the resonance integrals in the all-valence INDO-type method reproduces fairly well both ground and excited state properties of a wide range of the tested molecules and molecular complexes (see references cited in [18]). Recently, we extended Linderberg-Seamans formalism to d-orbitals [18].

The original Linderberg-Seamans formulas apply to the case when an atom possesses only one s type and one p type orbital. Therefore, in the present paper we derived theoretical relations for resonance integrals for the case of the atom (s) which possess an arbitrary number of both s and p type Slater atomic orbitals.

2. Assumptions

The detailed assumptions made in the derivation of theoretical formulas for resonance integrals are presented in the Linderberg-Seamans paper [17] and only the most important ones will be briefly given here.

We started from the equation of motion

$$\boldsymbol{p} = -i[\boldsymbol{r}, H] \tag{1}$$

(in atomic units, which will be used throughout the paper), where $\boldsymbol{p}$, $\boldsymbol{r}$ and H denote linear momentum, position and Hamiltonian operators, respectively. Assuming that

(i) Hamiltonian of electrons is the sum of one- and two-electron parts $H = h + g$, and

(ii) the position operator $\boldsymbol{r}$ commutes with the two-electron part (g) of H, Eq. (1) can be rewritten in matrix form as

$$-i\boldsymbol{\nabla} = \boldsymbol{p} = -i(\boldsymbol{rh} - \boldsymbol{hr}). \tag{2}$$

Another important assumption concerns position operator approximated by the equation

$$\boldsymbol{r}_{\mu\nu} = (\mu_A|\boldsymbol{r}|\nu_B) = \delta_{AB}[\delta_{\mu\nu}\boldsymbol{R}_A + (\mu_A|\boldsymbol{r} - \boldsymbol{R}_A|\nu_A)] \tag{3}$$

where μ, ν are atomic orbitals centered on A and B sites, respectively, and $\boldsymbol{R}_A$ is the position of atom A. The second term on right hand side is referred to as the atomic transition moment integral.

Let us now consider a diatomic molecule A–$B(R_{AB} = R)$, in which both the atoms possess an arbitrary number of s and p type orbitals. The use of elementary symmetry considerations and introduced approximations enabled us to derive from Eq. (2) the following matrix relations between the gradient ($\boldsymbol{\nabla}$) parameters and two center $\boldsymbol{\beta}$ integrals

$$\boldsymbol{\nabla}^{ss} = -R\boldsymbol{\beta}^{ss} + \boldsymbol{\mu}_A^{sp}\boldsymbol{\beta}^{\sigma s} - \boldsymbol{\beta}^{s\sigma}\boldsymbol{\mu}_B^{ps} \tag{4}$$

$$\boldsymbol{\nabla}^{\sigma\sigma} = -R\boldsymbol{\beta}^{\sigma\sigma} + \boldsymbol{\mu}_A^{ps}\boldsymbol{\beta}^{s\sigma} - \boldsymbol{\beta}^{\sigma s}\boldsymbol{\mu}_B^{sp} \tag{5}$$

$$\boldsymbol{\nabla}^{\pi\pi} = -R\boldsymbol{\beta}^{\pi\pi} \tag{6}$$

$$\boldsymbol{\nabla}^{s\sigma} = -R\boldsymbol{\beta}^{s\sigma} + \boldsymbol{\mu}_A^{sp}\boldsymbol{\beta}^{\sigma\sigma} - \boldsymbol{\beta}^{ss}\boldsymbol{\mu}_B^{sp} \tag{7}$$

$$\boldsymbol{\nabla}^{s\pi} = \boldsymbol{\mu}_A^{sp}\boldsymbol{\beta}^{\pi\pi} - \boldsymbol{\beta}^{ss}\boldsymbol{\mu}_B^{sp} \tag{8}$$

$$\boldsymbol{\nabla}^{\sigma s} = -R\boldsymbol{\beta}^{\sigma s} + \boldsymbol{\mu}_A^{ps}\boldsymbol{\beta}^{ss} - \boldsymbol{\beta}^{\sigma\sigma}\boldsymbol{\mu}_B^{ps} \tag{9}$$

$$\boldsymbol{\nabla}^{\pi s} = \boldsymbol{\mu}_A^{ps}\boldsymbol{\beta}^{ss} - \boldsymbol{\beta}^{\pi\pi}\boldsymbol{\mu}_B^{ps} \tag{10}$$

$$\mathbf{\nabla}^{\pi\sigma} = \boldsymbol{\mu}_A^{ps}\boldsymbol{\beta}^{s\sigma} \tag{11}$$

$$\mathbf{\nabla}^{\sigma\pi} = -\boldsymbol{\beta}^{\sigma s}\boldsymbol{\mu}_B^{sp}. \tag{12}$$

When both the atoms have only one s and one p orbital the matrix equations reduce to Linderberg-Seamans ones [17].

Matrices $\mathbf{\nabla}$, $\boldsymbol{\mu}_K$ and $\boldsymbol{\beta}$ are defined in the same way and, for example

$$\mathbf{\nabla}^{ij} = \begin{pmatrix} \nabla^{i1,j1} & \nabla^{i1,j2} & \dots & \nabla^{i1,jm} \\ \nabla^{i2,j1} & \nabla^{i2,j2} & \dots & \nabla^{i2,jm} \\ \vdots & \vdots & & \vdots \\ \nabla^{in,j1} & \nabla^{in,j2} & \dots & \nabla^{in,jm} \end{pmatrix}$$

where m and n denotes number of "j" and "i" type atomic orbitals, respectively.

Generally, the matrices $\mathbf{\nabla}$, $\boldsymbol{\mu}_K$ and β are rectangular. The μ_K symbol denotes the atomic transition moment integral defined and calculated as previously [18].

Due to the properties of $\mathbf{\nabla}$ matrix elements [17–19] the following relationships between the gradient matrices can be found

$$\mathbf{\nabla}^{\pi\pi} = \mathbf{\nabla}^{\pi\sigma} = \mathbf{\nabla}^{\sigma\pi} \tag{13}$$

$$\mathbf{\nabla}^{s\sigma} = (R\mathbf{\nabla}^{s\pi})' \tag{14a}$$

$$\mathbf{\nabla}^{\sigma s} = (R\mathbf{\nabla}^{\pi s})' \tag{14b}$$

$$\mathbf{\nabla}^{\sigma\sigma} = R^{-1}(R^2\mathbf{\nabla}^{\pi\pi})' \tag{15}$$

where prime denotes a first derivative, $(X)' = dX/dR$, and R is the internuclear distance.

3. Formulas for β-integrals

In this section we present general formulas for β integrals in A–B molecule, taking into consideration several cases depending on basis set assumed on atoms A and B.

Let us consider now a general case when an atom, say A possesses n_A atomic "s" orbitals and m_A "p" type ones. For example, in the case of a heavy atom (say carbon) with valence and Rydberg orbitals, the basis set contains $2s$, $3s$ and $2p$, $3p$ orbitals, so that $n_A = 2$ and $m_A = 2$. In the case of hydrogen atom the basis set can be $1s$, $2s$ and $2p$ orbitals and thus $n_A = 2$, $m_A = 1$, etc. The Linderberg-Seamans formulas were restricted to $n_A = m_A = 1$ for heavy atoms and to $n_A = 1$, $m_A = 0$ for hydrogen atom.

When $n_A = m_A$, we denote this case as symmetric $(S)\boldsymbol{\mu}_A$ is then square, otherwise as unsymmetric (U). Thus, depending on the basis set used on atoms A and B, three cases will be considered.

(i) Case I: $A(S) - B(S)$ i.e. both atoms form square matrices $\boldsymbol{\mu}$, $n_A = m_A$, $n_B = m_B$. This case includes also subcases when $n_A = n_B$ and when $n_A \neq n_B$.

Starting from Eqs. (6), (11), (12) and relation (13) we get

$$\boldsymbol{\beta}^{\pi\pi} = R^{-1}(\boldsymbol{s}^{\pi\pi})' \tag{16}$$

$$\boldsymbol{\beta}^{s\sigma} = -(\boldsymbol{\mu}_A^{ps})^{-1}(\boldsymbol{s}^{\pi\pi})' \tag{17}$$

$$\boldsymbol{\beta}^{\sigma s} = (\boldsymbol{s}^{\pi\pi})'(\boldsymbol{\mu}_B^{sp})^{-1}. \tag{18}$$

Substituting Eq. (15) by (5) and employing relation (13) we see that

$$\boldsymbol{\beta}^{\sigma\sigma} = (\boldsymbol{s}^{\pi\pi})''. \tag{19}$$

Finally, $\boldsymbol{\beta}^{ss}$ matrix can be obtained from Eq. (14)

$$\boldsymbol{\beta}^{ss} = -(\boldsymbol{\mu}_A^{ps})^{-1}\boldsymbol{s}^{\pi\pi}(\boldsymbol{\mu}_B^{sp})^{-1}. \tag{20}$$

In these equations $\boldsymbol{S}^{\pi\pi}$ denotes $\pi-\pi$ overlap integrals matrix whereas prime and double prime denote first and second derivative $(S^{\pi\pi})' = dS/dR$, $(S^{\pi\pi})'' = d^2S/dR^2$, respectively. The general expression for the overlap integral derivative is given in [18].

Practically, the matrices $\boldsymbol{\mu}_K$ can be always inverted except the cases when

(a) basis set is linearly dependent, and

(b) accidentally when the Slater orbital exponent ξ for the orbital with a higher principal quantum number is greater than that for the orbital with a smaller quantum number, i.e. when, for example $\xi_{3s} > \xi_{2s}$ etc. Actually, the latter case is never fulfilled.

(ii) Case II: $A(U)-B(S)$ i.e. $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$ are rectangular and square matrices, respectively. Hence, $\boldsymbol{\mu}_A$ matrix may not be inverted and therefore $\beta^{\pi\pi}$, $\beta^{\sigma\sigma}$ and $\beta^{\sigma s}$ integrals can be calculated as in the case (i) i.e. from Eqs. (16), (19) and (18), respectively, but remaining integrals should be calculated from another formula. Namely, from Eq. (14) we have

$$\boldsymbol{\beta}^{s\sigma} = (\boldsymbol{\beta}^{ss})'\boldsymbol{\mu}_B^{sp}. \tag{21}$$

Substituting the result to Eq. (7) and integrating over R we obtain

$$\boldsymbol{\beta}^{ss} = R^{-1}[\boldsymbol{S}^{s\sigma} + \boldsymbol{\mu}_A^{sp}(\boldsymbol{S}^{\pi\pi})'](\boldsymbol{\mu}_B^{sp})^{-1} \tag{22}$$

and utilizing Eq. (21) we have

$$\boldsymbol{\beta}^{s\sigma} = \left(\frac{\boldsymbol{S}^{s\sigma} + \boldsymbol{\mu}_A^{sp}(\boldsymbol{S}^{\pi\pi})'}{R}\right)'. \tag{23}$$

(iii) Case III: $A(U)-B(U)$ i.e. both $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$ are rectangular matrices, and the inverted matrices $(\boldsymbol{\mu}_K)^{-1}$ may not exist. Thus $\boldsymbol{\beta}^{\pi\pi}$, $\boldsymbol{\beta}^{\sigma\sigma}$ can be calculated as in the cases (i) and (ii), $\boldsymbol{\beta}^{s\sigma}$ as in the case (ii) (see Eq. 23). The expression for $\boldsymbol{\beta}^{\sigma s}$ may be derived in the way similar to that employed in the derivation of $\boldsymbol{\beta}^{s\sigma}$ in the case (ii). It reads

$$\boldsymbol{\beta}^{\sigma s} = \left(\frac{\boldsymbol{S}^{\sigma s} - (\boldsymbol{S}^{\pi\pi})'\boldsymbol{\mu}_B^{ps}}{R}\right)'. \tag{24}$$

The $\boldsymbol{\beta}^{ss}$ integral matrix cannot be expressed solely in terms of $S^{\pi\pi}$, $S^{s\sigma}$ and $S^{\sigma s}$ and therefore Eq. (4) must be used

$$\boldsymbol{\beta}^{ss} = R^{-1}(\boldsymbol{S}^{ss})' + \frac{1}{R}\left(\frac{\boldsymbol{\mu}_A^{sp}\boldsymbol{S}^{\sigma s} - \boldsymbol{S}^{s\sigma}\boldsymbol{\mu}_B^{sp}}{R}\right)' - \frac{2}{R}\left(\frac{\boldsymbol{\mu}_A^{sp}(\boldsymbol{S}^{\pi\pi})'\boldsymbol{\mu}_B^{ps}}{R}\right)'. \tag{25}$$

In the derivation of this formula, Eq. (23) and (24) have been used.

When both the atoms possess either only s or $p(\pi)$ type orbitals, then

$$\boldsymbol{\beta}^{ss} = R^{-1}(\boldsymbol{S}^{ss})' \tag{26}$$

and

$$\boldsymbol{\beta}^{\pi\pi} = R^{-1}(\boldsymbol{S}^{\pi\pi})', \qquad (26)$$

respectively.

The calculation of the second derivative of overlap intergrals is troublesome for orbitals with higher principal quantum number. Therefore in [18] we give useful relation for reducing the second derivative of $S^{\pi\pi}$ to the first one.

The Rydberg orbitals can be placed at the nuclear centres or in the "midpoint" of the molecule [7,8]. The latter location has computational advantages even in semiempirical methods. Thus, Rydberg orbitals are ghost orbitals (GO) centred on "atom" with nuclear charge equal to zero and atoms have a "normal" basis set. Inclusion of these GO's in NDO scheme has been proposed in our earlier papers [20–22]. In this case resonance integrals can be also calculated from the respective equations of the present paper and, for example $\boldsymbol{\beta}^{s\sigma}$ integrals between hydrogen atom (one s orbital) and Rydberg ghost orbitals can be calculated from Eq. (23). $\boldsymbol{\beta}^{ss}$ integrals can be obtained from Eq. (22) when $\boldsymbol{\mu}$ for RO forms a square matrix, otherwise from Eq. (25), putting in all these formulas $\boldsymbol{\mu}_H = 0$.

4. Discussion and Test Calculations

Theoretical formulas for resonance integrals in NDO-like methods presented here can be used as a basis for the elaboration of an approximate method which takes into consideration not only valence shell orbitals, but also Rydberg and/or inner ones. Such work has been finished and the results will be published elsewhere. Inclusion of inner and/or Rydberg orbitals is relatively simple, but requires modification of approximation in two electron parts of the Hamiltonian [23].

In the previous CNDO/INDO calculations [13–16] the resonance integrals were approximated by formula $\beta_{ij} = k_1 k_2 (I_i + I_j) S_{ij}$ where I_x and k_y are ionization energies and constant parameters, respectively. The k_1 parameter was put equal to about 0.4 for valence-valence interaction and about 0.04 otherwise (i.e. for valence–Rydberg and Rydberg–Rydberg overlap). Additionally, k_2 was set equal to 1.0 except π–π interaction where the value of ~0.6 was adopted. Numerical comparison of these results with our formulas (which do not contain any adjustable parameters) shows qualitative agreement only. The closer analysis indicates that our β values between valence–Rydberg (Rydberg–Rydberg) and valence-valence orbitals are smaller (20–80%) and greater (about 30%) than those of CNDO/INDO, respectively, in the tested C–C and H–H bond cases.

We also noted another difference. Namely k_2 and especially k_1 are strongly ξ and R dependent. On the other hand, it is known, that the energy of the Rydberg states are rather strongly dependent on the choice of Rydberg orbital exponent [24], thus optimization on ξ via CNDO/INDO type relation for β integrals may be equivocal, because both the k parameter and overlap integral are ξ dependent. In this context presented formulas should be more useful.

Table 1. Calculated vertical transition energies (in eV) for hydrogen molecule

State	Main configuration	% Rydberg character	INDOL/R	*Ab initio* CI [8]	Accurate [26]	INDOL/V
${}^1\Sigma_u^+$	$1s \to 2p\sigma$	95	13.23	12.73	12.81	15.70
${}^1\Sigma_g^+$	$1s \to 2s$	100	13.62	13.08	13.42	—
${}^3\Sigma_u^+$	$1s \to 2p\sigma$	94	10.90	9.97	10.65	12.99
${}^3\Sigma_g^+$	$1s \to 2s$	99	13.02	12.03	12.56	—

Table 2. Experimental (Exp.) and calculated vertical transition energies (in eV) for water molecule

State	Main configuration	% Rydberg character	INDOL/R	*Ab initio* [7]	*Ab initio* CI[27]	Exp.[a]	INDOL/V
${}^1A_1$	$\sigma \to 3s\,a_1$	93	9.44	9.80	9.82	9.73	11.24
${}^1A_1$	$n \to 3p\,b_1$	88	10.22	10.32	10.16	10.17	17.49
${}^1A_1$	$\sigma \to 3p\,a_1$	94	12.69	11.53	12.08	12.10	30.31
${}^3A_1$	$\sigma \to 3s\,a_1$	80	8.20	9.01	9.44	9.35	9.44
${}^3A_1$	$n \to 3p\,b_1$	77	9.73	9.65	9.74	9.81	14.84
${}^3A_1$	$\sigma \to 3p\,a_1$	95	11.89	—	11.77	11.80	26.59
${}^1A_2$	$n \to 3p\,b_2$	77	8.96	9.20	9.46	9.20	9.73
${}^1A_2$	mixed V/R	38	10.25	—	—	—	—
${}^3A_2$	$n \to 3p\,b_2$	62	8.90	9.04	9.34	9.10	8.93
${}^3A_2$	mixed V/R	37	9.60	—	—	—	—
${}^1B_2$	$\sigma \to 3p\,b_2$	99	11.58	11.21	11.47	11.40	13.64
${}^1B_2$	$\sigma \to 3p\,b_2$	74	12.19	—	—	—	14.78
${}^3B_2$	$\sigma \to 3p\,b_2$	74	10.45	10.99	11.11	11.10	11.49
${}^3B_2$	$\sigma \to 3p\,b_2$	64	12.14	—	—	—	13.23
${}^1B_1$	$n \to 3s\,a_1$	80	6.65	7.30	7.61	7.49	7.11
${}^1B_1$	mixed V/R	56	8.77	—	—	—	—
${}^1B_1$	$n \to 3p\,a_1$	59	9.97	9.90	10.06	10.00	—
${}^1B_1$	$\sigma \to 3p\,b_1$	95	12.75	11.72	11.92	11.90	—
${}^3B_1$	$n \to 3s\,a_1$	82	6.23	6.90	7.26	7.14	5.87
${}^3B_1$	mixed V/R	40	7.63	—	—	—	—
${}^3B_1$	$n \to 3p\,a_1$	85	9.51	9.84	9.99	9.93	—
${}^3B_1$	$\sigma \to 3p\,b_1$	95	12.67	11.68	11.87	11.90	—

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[a] Cited according to ref. [27].

As an illustration of the application of the relations derived here, we calculated vertical transition energies of hydrogen (Table 1) and water (Table 2) molecules, using modified INDO CI method [25] in the valence electron approximation (INDOL/V), as well as including Rydberg orbitals (INDOL/R). The all one-centre integrals involving Rydberg orbitals were calculated analytically, using Slater exponents for oxygen $2s, 2p, 3s$ and $3p$ orbitals, and $\xi_{1s} = 1.2, \xi_{2s} = \xi_{2p} = 0.6$ values for hydrogen $1s$, $2s$ and $2p$ orbitals.

It should be noted that quite good agreement with *ab initio* calculations as well as with the experimental results exists. The results of our calculations show that inclusion of Rydberg orbitals distinctly improve interpretation of electronic spectra, especially in the high-energy region.

The subsequent examples of the electronic spectra calculations involving Rydberg states of varous molecules using INDOL/R method will be published [28].

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