Derivation of Theoretical Formulas for Resonance Integrals from Heisenberg Equation of Motion.
III. Inclusion of Rydberg and/or Inner Atomic Orbitals in the Formalism of NDO-Method Valid for Transition Metal Compounds

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On the basis of the Heisenberg equation of motion and Linderberg-Seamans approximations the analytical formulas for one-electron, two-centre resonance integrals have been derived. The possibility of inclusion of Rydberg and/or inner orbitals to the basis set in the case of d-electron element compounds has been taken into consideration. An application of the derived formulas to the modification of semiempirical, NDO-type methods has been presented. The results of the test INDOL/R version calculations for H_2O molecule and MnO_4^- ion confirm the utility of the method.

1. Introduction

Despite the great progress in computational techniques in the last years, nonempirical calculations for many larger molecular systems including d-electron elements are still time consuming.

For a better understanding and interpretation of the photochemistry and excited states of these systems, the Rydberg orbitals (RO) should be included in the basis set. Of course this extension can increase the basis set twice.

In the case of transition metal complexes the ab initio calculations with such sets are extremenly expensive. For these reasons there is a continued interest in the use of Rydberg orbitals in the simple, semiempirical treatments. Such calculations have been carried out to describe mainly electronic spectra and ground state properties of the s, p-electron element compounds in the CNDO approximation [1, 2, 3], Extended Hückel Theory [4, 5], PPP method [6], and INDO scheme [7, 8, 9] (for a brief review see [9]). As far as we know, these methods have not been extended to the transition metal complexes.

In this paper we consider a new proposal of the INDO-type [14] approach to the d-electron element compounds, which affords possibilities for the inclusion an arbitrary number of the RO or/and inner atomic orbitals to the valence orbital basis set. In our opinion, such a method should enable one to use only one group of parameters for a good reproduction of the ground and excited state properties of the molecules under investigation. On the other hand, the number of nonphysical parameters introduced in this scheme should be reduced and they ought to be substituted by approximate but well founded relations.

Such an approach is possible in the case of the one-electron, two-centre resonance integrals $H_{ij}(\beta_{ij})$. An approximation and parametrisation of the resonance integrals has been a crucial point in every semiempirical method. One of the possible solutions of this problem has been proposed by Linderberg and Seamans [10]. They have derived theoretical

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relations for the resonance integrals between s, p-orbitals using the Heisenberg equation of motion and the second quantization formalism. Recently, we extended Linderberg-Seams method to the derivation of β integrals for the d-electron elements [11], and to the RO inclusion in the case of s, p-electron elements [9].

Application of these formulas to the approximation of the resonance integrals in the INDO-type method gives fairly good results both in the all-valence, as well as the all-valence augmented Rydberg orbitals version [9, 11].

2. Assumptions

We consider resonance integrals between atoms, of which at least one possesses d-type Slater atomic orbitals in the valence or/and in extended basis set. The method of the derivation β integrals has been given by Linderberg and Seamans [10], and we follow their assumptions:

(i) The relation between linear momentum $\boldsymbol{p}$, position $\boldsymbol{r}$ and Hamiltonian $\boldsymbol{H}$ operators is given by the equation of motion

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

(atomic units are used in the paper).

(ii) The Hamiltonian of the electron is the sum of one- ($\boldsymbol{h}$) and two-electron ($\boldsymbol{g}$) parts

$$\boldsymbol{H} = \boldsymbol{h} + \boldsymbol{g}\,. \tag{2}$$

(iii) The position operator commutes with the two-electron part of $\boldsymbol{H}$:

$$[\boldsymbol{r}, \boldsymbol{g}] = 0\,. \tag{3}$$

Under these assumptions, Eq. (1) can be rewritten in matrix form as

$$-i\,\boldsymbol{\nabla} = \boldsymbol{p} = -i\,(\boldsymbol{r}\boldsymbol{h} - \boldsymbol{h}\boldsymbol{r})\,. \tag{4}$$

(iv) The position operator is approximated by the equation

$$\boldsymbol{r}_{\lambda\nu} = (\lambda_{\mathrm{A}}\,|\,\boldsymbol{r}\,|\,\nu_{\mathrm{B}}) = \delta_{\mathrm{AB}}\,[\delta_{\lambda\nu}\,\boldsymbol{R}_{\mathrm{A}} + (\lambda_{\mathrm{A}}\,|\,\boldsymbol{r} - \boldsymbol{R}_{\mathrm{A}}\,|\,\nu_{\mathrm{A}})], \tag{5}$$

where λ, ν are atomic orbitals centered on A and B sites, respectively, and $\boldsymbol{R}_{\mathrm{A}}$ is the position of atom A.

The second term on the right hand side is referred to as the atomic transition moment integral $\mu_{\mathrm{A}}^{\lambda\nu}$ is defined and calculated as previously [11].

Let us now consider a diatomic molecule A–B in which the internuclear distance is equal $\boldsymbol{R}$.

Both the atoms A and B possess an arbitrary number of s, p, and d type atomic orbitals. The use of the assumed approximations and elementary symmetry considerations leads to the following matrix relations between the gradient ($\boldsymbol{\nabla}$) parameters and resonance integrals ($\boldsymbol{\beta}$):

$$\boldsymbol{\nabla}^{\mathrm{ss}} = -R\,\boldsymbol{\beta}^{\mathrm{ss}} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}\,\boldsymbol{\beta}^{\sigma\mathrm{s}} - \boldsymbol{\beta}^{\mathrm{s}\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}, \tag{6}$$

$$\boldsymbol{\nabla}^{\mathrm{s}\pi} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}\,\boldsymbol{\beta}^{\pi\pi} - \boldsymbol{\beta}^{\mathrm{ss}}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}} + \frac{1}{\sqrt{3}}\,\boldsymbol{\beta}^{\mathrm{sd}\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}, \tag{7}$$

$$\boldsymbol{\nabla}^{\mathrm{s}\sigma} = -R\,\boldsymbol{\beta}^{\mathrm{s}\sigma} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}\,\boldsymbol{\beta}^{\sigma\sigma} - \boldsymbol{\beta}^{\mathrm{ss}}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}} - \frac{2}{\sqrt{3}}\,\boldsymbol{\beta}^{\mathrm{sd}\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}, \tag{8}$$

$$\boldsymbol{\nabla}^{\pi\mathrm{s}} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}}\,\boldsymbol{\beta}^{\mathrm{ss}} - \frac{1}{\sqrt{3}}\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{s}} - \boldsymbol{\beta}^{\pi\pi}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}, \tag{9}$$

$$\boldsymbol{\nabla}^{\pi\pi} = -R\,\boldsymbol{\beta}^{\pi\pi} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\pi\pi} - \boldsymbol{\beta}^{\pi\mathrm{d}\pi}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}, \tag{10}$$

$$\boldsymbol{\nabla}^{\pi\sigma} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}}\,\boldsymbol{\beta}^{\mathrm{s}\sigma} - \frac{1}{\sqrt{3}}\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\sigma\sigma} - \boldsymbol{\beta}^{\pi\mathrm{d}\pi}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}, \tag{11}$$

$$\boldsymbol{\nabla}^{\sigma\mathrm{s}} = -R\,\boldsymbol{\beta}^{\sigma\mathrm{s}} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}}\,\boldsymbol{\beta}^{\mathrm{ss}} + \frac{2}{\sqrt{3}}\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{s}} - \boldsymbol{\beta}^{\sigma\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}, \tag{12}$$

$$\boldsymbol{\nabla}^{\sigma\pi} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\pi\pi} - \boldsymbol{\beta}^{\sigma\mathrm{s}}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}} + \frac{1}{\sqrt{3}}\,\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}, \tag{13}$$

$$\begin{aligned}\boldsymbol{\nabla}^{\sigma\sigma} = {} & -R\,\boldsymbol{\beta}^{\sigma\sigma} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}}\,\boldsymbol{\beta}^{\mathrm{s}\sigma} + \frac{2}{\sqrt{3}}\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\sigma\sigma} \\ & - \boldsymbol{\beta}^{\sigma\mathrm{s}}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}} - \frac{2}{\sqrt{3}}\,\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}},\end{aligned} \tag{14}$$

$$\boldsymbol{\nabla}^{\mathrm{sd}\sigma} = -R\,\boldsymbol{\beta}^{\mathrm{sd}\sigma} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}\,\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma} - \frac{2}{\sqrt{3}}\,\boldsymbol{\beta}^{\mathrm{s}\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{15}$$

$$\boldsymbol{\nabla}^{\mathrm{sd}\pi} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}\,\boldsymbol{\beta}^{\pi\mathrm{d}\pi} - \boldsymbol{\beta}^{\mathrm{s}\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{16}$$

$$\boldsymbol{\nabla}^{\pi\mathrm{d}\sigma} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}}\,\boldsymbol{\beta}^{\mathrm{sd}\sigma} - \frac{1}{\sqrt{3}}\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma} + \frac{1}{\sqrt{3}}\,\boldsymbol{\beta}^{\pi\pi}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{17}$$

$$\boldsymbol{\nabla}^{\pi\mathrm{d}\pi} = -R\,\boldsymbol{\beta}^{\pi\mathrm{d}\pi} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi} - \boldsymbol{\beta}^{\pi\pi}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{18}$$

$$\boldsymbol{\nabla}^{\pi\delta} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\delta\delta} - \boldsymbol{\beta}^{\pi\pi}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{19}$$

$$\begin{aligned}\boldsymbol{\nabla}^{\sigma\mathrm{d}\sigma} = {} & -R\,\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}}\,\boldsymbol{\beta}^{\mathrm{sd}\sigma} + \frac{2}{\sqrt{3}}\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma} \\ & - \frac{2}{\sqrt{3}}\,\boldsymbol{\beta}^{\sigma\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}},\end{aligned} \tag{20}$$

$$\boldsymbol{\nabla}^{\sigma\mathrm{d}\pi} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi} - \boldsymbol{\beta}^{\sigma\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{21}$$

$$\boldsymbol{\nabla}^{\mathrm{d}\sigma\mathrm{s}} = -R\,\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{s}} + \frac{2}{\sqrt{3}}\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\,\boldsymbol{\beta}^{\sigma\mathrm{s}} - \boldsymbol{\beta}^{\mathrm{d}\sigma\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}, \tag{22}$$

$$\mathbf{\nabla}^{\mathrm{d}\sigma\pi} = -\frac{1}{\sqrt{3}}\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\pi\pi} - \boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{s}}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}} + \frac{1}{\sqrt{3}}\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}, \tag{23}$$

$$\mathbf{\nabla}^{\mathrm{d}\sigma\sigma} = -R\,\boldsymbol{\beta}^{\mathrm{d}\sigma\sigma} + \frac{2}{\sqrt{3}}\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\sigma\sigma} - \boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{s}}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}} - \frac{2}{\sqrt{3}}\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}, \tag{24}$$

$$\mathbf{\nabla}^{\mathrm{d}\sigma\mathrm{d}\sigma} = -R\,\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma} + \frac{2}{\sqrt{3}}\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma} - \frac{2}{\sqrt{3}}\boldsymbol{\beta}^{\mathrm{d}\sigma\sigma}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{25}$$

$$\mathbf{\nabla}^{\mathrm{d}\sigma\mathrm{d}\pi} = -\frac{1}{\sqrt{3}}\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\pi\mathrm{d}\pi} - \boldsymbol{\beta}^{\mathrm{d}\sigma\sigma}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{26}$$

$$\mathbf{\nabla}^{\mathrm{d}\pi\mathrm{s}} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\sigma\mathrm{s}} - \boldsymbol{\beta}^{\mathrm{d}\pi\pi}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}, \tag{27}$$

$$\mathbf{\nabla}^{\mathrm{d}\pi\pi} = -R\,\boldsymbol{\beta}^{\mathrm{d}\pi\pi} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\pi\pi} - \boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}, \tag{28}$$

$$\mathbf{\nabla}^{\mathrm{d}\pi\sigma} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\sigma\sigma} - \boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}, \tag{29}$$

$$\mathbf{\nabla}^{\mathrm{d}\pi\mathrm{d}\sigma} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma} + \frac{1}{\sqrt{3}}\boldsymbol{\beta}^{\mathrm{d}\pi\pi}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{30}$$

$$\mathbf{\nabla}^{\mathrm{d}\pi\mathrm{d}\pi} = -R\,\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\pi\mathrm{d}\pi} - \boldsymbol{\beta}^{\mathrm{d}\pi\pi}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{31}$$

$$\mathbf{\nabla}^{\mathrm{d}\pi\delta} = -\boldsymbol{\beta}^{\mathrm{d}\pi\pi}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}, \tag{32}$$

$$\mathbf{\nabla}^{\delta\pi} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\pi\pi} - \boldsymbol{\beta}^{\delta\delta}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}, \tag{33}$$

$$\mathbf{\nabla}^{\delta\mathrm{d}\pi} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\boldsymbol{\beta}^{\pi\mathrm{d}\pi}, \tag{34}$$

$$\mathbf{\nabla}^{\delta\delta} = -R\,\boldsymbol{\beta}^{\delta\delta}. \tag{35}$$

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

$$\mathbf{\nabla}^{ij} = \begin{pmatrix} \mathbf{\nabla}^{i1,j1} & \mathbf{\nabla}^{i1,j2} & \dots & \mathbf{\nabla}^{i1,jm} \\ \mathbf{\nabla}^{i2,j1} & \mathbf{\nabla}^{i2,j2} & \dots & \mathbf{\nabla}^{i2,jm} \\ \vdots & \vdots & & \vdots \\ \mathbf{\nabla}^{in,j1} & \mathbf{\nabla}^{in,j2} & \dots & \mathbf{\nabla}^{in,jm} \end{pmatrix}, \tag{36}$$

where m and n denote the number of "j" and "i" atomic orbitals, respectively.

Due to the properties of $\mathbf{\nabla}$ matrix elements [10] the following relationship between the gradient matrices can be found:

$$\mathbf{\nabla}^{\sigma\pi} = \mathbf{\nabla}^{\pi\sigma} = \mathbf{\nabla}^{\pi\pi'}, \tag{37}$$

$$\mathbf{\nabla}^{\mathrm{s}\sigma} = (R\,\mathbf{\nabla}^{\mathrm{s}\pi})', \tag{38}$$

$$\mathbf{\nabla}^{\sigma\sigma} = R^{-1}(R^2\,\mathbf{\nabla}^{\pi\pi})', \tag{39}$$

$$\mathbf{\nabla}^{\delta\delta} = \mathbf{\nabla}^{\mathrm{d}\pi\delta} = \mathbf{\nabla}^{\delta\mathrm{d}\pi}, \tag{40}$$

$$\mathbf{\nabla}^{\mathrm{d}\pi\mathrm{d}\pi} = R^{-1}(R^2\,\mathbf{\nabla}^{\delta\delta})', \tag{41}$$

$$\sqrt{3}\,\mathbf{\nabla}^{\mathrm{s}\mathrm{d}\sigma} = (R\,\mathbf{\nabla}^{\mathrm{s}\mathrm{d}\pi})', \tag{42}$$

$$\mathbf{\nabla}^{\pi\mathrm{d}\pi} = \mathbf{\nabla}^{\sigma\mathrm{d}\pi}, \tag{43}$$

$$\mathbf{\nabla}^{\mathrm{d}\pi\pi} = \mathbf{\nabla}^{\mathrm{d}\pi\sigma}, \tag{44}$$

$$\mathbf{\nabla}^{\mathrm{d}\sigma\mathrm{d}\pi} = \mathbf{\nabla}^{\mathrm{d}\pi\mathrm{d}\sigma}, \tag{45}$$

$$\mathbf{\nabla}^{\pi\mathrm{d}\pi} = (R\,\mathbf{\nabla}^{\pi\delta})', \tag{46}$$

$$3\,\mathbf{\nabla}^{\sigma\mathrm{d}\sigma} = \sqrt{3}\,R^{-1}(R^2\,\mathbf{\nabla}^{\pi\mathrm{d}\pi})', \tag{47}$$

$$\mathbf{\nabla}^{\mathrm{d}\pi\mathrm{d}\pi} = 2\,\mathbf{\nabla}^{\delta\delta} + \sqrt{3}\,\mathbf{\nabla}^{\mathrm{d}\sigma\mathrm{d}\pi}, \tag{48}$$

$$3\,\mathbf{\nabla}^{\mathrm{d}\sigma\mathrm{d}\sigma} = R^{-1}(R^2\,\mathbf{\nabla}^{\mathrm{d}\pi\mathrm{d}\pi})' + 2\,\mathbf{\nabla}^{\delta\delta}, \tag{49}$$

$$\sqrt{3}\,\mathbf{\nabla}^{\pi\mathrm{d}\sigma} + \mathbf{\nabla}^{\pi\delta} = R(\mathbf{\nabla}^{\pi\delta})', \tag{50}$$

where primes and double primes denote first and second derivatives: $(X)' = \mathrm{d}X/\mathrm{d}R$, $(X)'' = \mathrm{d}^2X/\mathrm{d}R^2$, respectively.

3. Formulas for $\boldsymbol{\beta}$-Resonance Integrals

Here we present explicit formulas for resonance integrals in an A–B molecule, taking into consideration several cases depending on the basis set assumed for atoms A and B.

Let us consider now the general case when an atom, say A, possesses n_{A} atomic "s" orbitals, m_{A} "p" type orbitals and l_{A} "d" type ones. When $x_{\mathrm{A}} = y_{\mathrm{A}}$, we denote this case as symmetric (S), $\boldsymbol{\mu}_{\mathrm{A}}^{xy}$ is then a square, otherwise as an unsymmetric case (U). Extending the procedure previously reported [9, 10, 12] and assuming that $n_{\mathrm{A}} = m_{\mathrm{A}}$ and $n_{\mathrm{B}} = m_{\mathrm{B}}$ i.e. $\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}$ and $\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}}$ are square matrices, the following formulas for $\boldsymbol{\beta}$ integrals can be found:

(i) Case I: A(S) – B(S) i.e. $\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}$ and $\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}$ form square matrices:

$$\boldsymbol{\beta}^{\delta\delta} = R^{-1}(\boldsymbol{S}^{\delta\delta})', \tag{51}$$

$$\boldsymbol{\beta}^{\pi\mathrm{d}\pi} = -(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}})^{-1}(\boldsymbol{S}^{\delta\delta})', \tag{52}$$

$$\boldsymbol{\beta}^{\mathrm{d}\pi\pi} = (\boldsymbol{S}^{\delta\delta})'(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1}, \tag{53}$$

$$\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi} = (\boldsymbol{S}^{\delta\delta})'', \tag{54}$$

$$\boldsymbol{\beta}^{\pi\pi} = -(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}})^{-1}\boldsymbol{S}^{\delta\delta}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1}, \tag{55}$$

$$\boldsymbol{\beta}^{\mathrm{d}\sigma\sigma} = \frac{1}{\sqrt{3}}(R\,\boldsymbol{S}^{\delta\delta'})'(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}})^{-1}, \tag{56}$$

$$\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma} = -\frac{1}{\sqrt{3}}(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}})^{-1}(R(\boldsymbol{S}^{\delta\delta})')', \tag{57}$$

$$\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma} = \frac{1}{3R}\left[2(\boldsymbol{S}^{\delta\delta})' + R(\boldsymbol{S}^{\delta\delta})'' + R^2(\boldsymbol{S}^{\delta\delta})'''\right], \tag{58}$$

$$\boldsymbol{\beta}^{\sigma\sigma} = -(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}})^{-1}(R\,\boldsymbol{S}^{\delta\delta})'(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1}, \tag{59}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{s}\sigma} &= \tfrac{1}{3}(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}})^{-1}\{3R(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}})^{-1}\boldsymbol{S}^{\delta\delta}\\ &\quad + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}[4(\boldsymbol{S}^{\delta\delta})' + R(\boldsymbol{S}^{\delta\delta})'']\}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1},\end{aligned} \tag{60}$$

$$\begin{aligned}\boldsymbol{\beta}^{\sigma\mathrm{s}} &= \tfrac{1}{3}(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}})^{-1}\{3R\,\boldsymbol{S}^{\delta\delta}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{2}\\ &\quad + [4(\boldsymbol{S}^{\delta\delta})' + R(\boldsymbol{S}^{\delta\delta})'']\}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}})^{-1},\end{aligned} \tag{61}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{s}\mathrm{d}\sigma} &= \frac{(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}})^{-1}}{3\sqrt{3}\,R}\{[3R^2(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}})^{-1} - 4\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}](\boldsymbol{S}^{\delta\delta})'\\ &\quad - R\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}[4(\boldsymbol{S}^{\delta\delta})'' + R(\boldsymbol{S}^{\delta\delta})''']\},\end{aligned} \tag{62}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{s}} &= \frac{1}{3\sqrt{3}\,R}\{3(\boldsymbol{S}^{\delta\delta})'[3R^2(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1} - 4\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}})]\\ &\quad - R[4(\boldsymbol{S}^{\delta\delta})'' + R(\boldsymbol{S}^{\delta\delta})''']\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}})^{-1},\end{aligned} \tag{63}$$

$$\boldsymbol{\beta}^{\mathrm{ss}} = R^{-1}[(\boldsymbol{S}^{\mathrm{ss}})' + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}\boldsymbol{\beta}^{\sigma\mathrm{s}} - \boldsymbol{\beta}^{\mathrm{s}\sigma}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}]. \tag{64}$$

(ii) Case II: A(U) – B(S) i.e. $\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}$ and $\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}$ are rectangular and square matrices, respectively. Hence, the $\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}$ matrix may not be inverted, and therefore the $\boldsymbol{\beta}^{\delta\delta}$, $\boldsymbol{\beta}^{\mathrm{d}\pi\pi}$ and $\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi}$ integrals can be calculated as in case (i) from (51), (53) and (54), respectively, but the remaining integrals should be calculated from another formula:

$$\boldsymbol{\beta}^{\pi\pi} = \frac{1}{R}[\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}(\boldsymbol{S}^{\delta\delta})' - \boldsymbol{S}^{\pi\mathrm{d}\pi}](\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1}, \tag{65}$$

$$\begin{aligned}\boldsymbol{\beta}^{\pi\mathrm{d}\pi} &= \frac{1}{R}\left\{\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\left[(\boldsymbol{S}^{\delta\delta})'' - \frac{1}{R}(\boldsymbol{S}^{\delta\delta})'\right]\right.\\ &\quad \left. + \frac{1}{R}\boldsymbol{S}^{\pi\mathrm{d}\pi} + (\boldsymbol{S}^{\pi\mathrm{d}\pi})'\right\},\end{aligned} \tag{66}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{d}\sigma\sigma} &= \frac{1}{\sqrt{3}\,R}\left\{[R^2 - (\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}})^2](\boldsymbol{S}^{\delta\delta})'' + \frac{1}{R}(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}})^2(\boldsymbol{S}^{\delta\delta})'\right.\\ &\quad \left. - \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\left[\frac{1}{R}\boldsymbol{S}^{\pi\mathrm{d}\pi} + (\boldsymbol{S}^{\pi\mathrm{d}\pi})'\right]\right\}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1},\end{aligned} \tag{67}$$

$$\boldsymbol{\beta}^{\sigma\sigma} = [\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}(\boldsymbol{S}^{\delta\delta})'' + (\boldsymbol{S}^{\pi\mathrm{d}\pi})'](\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1}, \tag{68}$$

$$\begin{aligned}\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma} &= -\frac{1}{\sqrt{3}\,R}\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\{[(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}})^2 + R^2](\boldsymbol{S}^{\delta\delta})''\\ &\quad \left. - \frac{1}{R}(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}})^2(\boldsymbol{S}^{\delta\delta})' + R(\boldsymbol{S}^{\pi\mathrm{d}\pi})' + \boldsymbol{S}^{\pi\mathrm{d}\pi}\right\}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-2}\\ &\quad - \frac{2}{\sqrt{3}}[R(\boldsymbol{S}^{\delta\delta})']'(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1},\end{aligned} \tag{69}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma} &= \frac{1}{3R}\left\{\frac{6}{\sqrt{3}}[\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma} - \boldsymbol{\beta}^{\mathrm{d}\sigma\sigma}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}]\right.\\ &\quad \left. + R^2(\boldsymbol{S}^{\delta\delta})''' + 5R(\boldsymbol{S}^{\delta\delta})'' + 6(\boldsymbol{S}^{\delta\delta})'\right\},\end{aligned} \tag{70}$$

$$\boldsymbol{\beta}^{\mathrm{s}\sigma} = (\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}})^{-1}\left(R\,\boldsymbol{\beta}^{\pi\pi} + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\boldsymbol{\beta}^{\mathrm{d}\pi\pi} + \frac{1}{\sqrt{3}}\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\boldsymbol{\beta}^{\mathrm{d}\sigma\sigma}\right), \tag{71}$$

$$\boldsymbol{\beta}^{\sigma\mathrm{s}} = -\left(R\,\boldsymbol{\beta}^{\pi\pi} - \boldsymbol{\beta}^{\pi\mathrm{d}\pi}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}} - \frac{1}{\sqrt{3}}\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\right)(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}})^{-1} \tag{72}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{s}\mathrm{d}\sigma} &= \frac{1}{\sqrt{3}}(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}})^{-1}\{-R\,\boldsymbol{\beta}^{\pi\mathrm{d}\pi}\\ &\quad + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}(\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi} + \boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma} - 2\boldsymbol{\beta}^{\delta\delta})\},\end{aligned} \tag{73}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{s}} &= -\frac{1}{\sqrt{3}}\{R\,\boldsymbol{\beta}^{\mathrm{d}\pi\pi}\\ &\quad + (\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi} + \boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma} - 2\boldsymbol{\beta}^{\delta\delta})\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}})^{-1},\end{aligned} \tag{74}$$

$$\boldsymbol{\beta}^{\mathrm{ss}} = \frac{1}{R}[(\boldsymbol{S}^{\mathrm{ss}})' + \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}\boldsymbol{\beta}^{\sigma\mathrm{s}} - \boldsymbol{\beta}^{\mathrm{s}\sigma}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}]. \tag{75}$$

(iii) Case III: A(U) – B(U) i.e. both $\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}$ and $\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}$ are rectangular matrices, and the inverted matrices $(\boldsymbol{\mu}_{\mathrm{K}}^{\mathrm{dp}})^{-1}$ may not exist. Thus the $\boldsymbol{\beta}^{\delta\delta}$ and $\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi}$ integrals can be calculated as in the cases (i) and (ii).

For the remaining integrals the following formulas can be derived:

$$\boldsymbol{\beta}^{\pi\mathrm{d}\pi} = \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\left[\frac{1}{R}(\boldsymbol{S}^{\delta\delta})'\right]' + \left[\frac{1}{R}(\boldsymbol{S}^{\pi\mathrm{d}\pi})\right]', \tag{76}$$

$$\boldsymbol{\beta}^{\mathrm{d}\pi\pi} = -\left[\frac{1}{R}(\boldsymbol{S}^{\delta\delta})'\right]'\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}} + \left[\frac{1}{R}(\boldsymbol{S}^{\mathrm{d}\pi\pi})\right]', \tag{77}$$

$$\begin{aligned}\boldsymbol{\beta}^{\pi\pi} &= -\frac{1}{R}\left\{2\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}R\left[\frac{1}{R}(\boldsymbol{S}^{\delta\delta})'\right]'\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\right.\\ &\quad + \left[\frac{1}{R}(\boldsymbol{S}^{\pi\mathrm{d}\pi})\right]'\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\\ &\quad \left. - \boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\left[\frac{1}{R}(\boldsymbol{S}^{\mathrm{d}\pi\pi})\right]' + (\boldsymbol{S}^{\pi\pi})'\right\},\end{aligned} \tag{78}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma} &= \frac{1}{3R}\left\{R^2(\boldsymbol{S}^{\delta\delta})''' + R(\boldsymbol{S}^{\delta\delta})'' + 6(\boldsymbol{S}^{\delta\delta})'\right.\\ &\quad + 2\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\left[\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\left(\frac{1}{R}(\boldsymbol{S}^{\delta\delta})'\right)' + \left(\frac{1}{R}\boldsymbol{S}^{\pi\mathrm{d}\pi}\right)'\right]\\ &\quad \left. + 2\left[\left(\frac{1}{R}(\boldsymbol{S}^{\delta\delta})'\right)'\right]\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}} - \left(\frac{1}{R}\boldsymbol{S}^{\mathrm{d}\pi\pi}\right)'\right\}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}},\end{aligned} \tag{79}$$

$$\begin{aligned}\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma} &= -\frac{1}{\sqrt{3}}\Big\{3\,\boldsymbol{\beta}^{\pi\mathrm{d}\pi}+\frac{1}{R}\,[\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}(2\,\boldsymbol{\beta}^{\delta\delta}-\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi}\\ &\quad -3\,\boldsymbol{\beta}^{\mathrm{d}\delta\mathrm{d}\sigma})+2\,\boldsymbol{\beta}^{\pi\pi}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}}]\Big\}+\frac{1}{R}\,(\boldsymbol{S}^{\sigma\mathrm{d}\sigma})',\end{aligned}\tag{80}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{d}\sigma\sigma} &= -\frac{1}{\sqrt{3}}\Big\{3\,\boldsymbol{\beta}^{\mathrm{d}\pi\pi}+\frac{1}{R}\,[(-2\,\boldsymbol{\beta}^{\delta\delta}+\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi}\\ &\quad +3\,\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma})\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}-2\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{dp}}\,\boldsymbol{\beta}^{\pi\pi}]\Big\}+\frac{1}{R}\,(\boldsymbol{S}^{\mathrm{d}\sigma\sigma})',\end{aligned}\tag{81}$$

$$\begin{aligned}\boldsymbol{\beta}^{\sigma\sigma} &= \frac{1}{R}\Big\{\frac{1}{R}\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,[4\,\boldsymbol{\beta}^{\delta\delta}-2\,\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi}-6\,\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma}]\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\\ &\quad -4\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\pi\pi}+4\,\boldsymbol{\beta}^{\pi\mathrm{d}\pi}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\\ &\quad +\frac{2}{R}\,(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}})^2\,\boldsymbol{\beta}^{\pi\pi}+\boldsymbol{\beta}^{\pi\pi}\,(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^2\\ &\quad +\frac{\sqrt{3}}{R}\,[\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,(\boldsymbol{S}^{\mathrm{d}\sigma\sigma})'+(\boldsymbol{S}^{\sigma\mathrm{d}\sigma})'\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}]+(\boldsymbol{S}^{\pi\pi})'\Big\},\end{aligned}\tag{82}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{sd}\sigma} &= \frac{1}{\sqrt{3}}\,(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}})^{-1}\,\{-R\,\boldsymbol{\beta}^{\pi\mathrm{d}\pi}\\ &\quad +\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,(\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi}+\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma}-2\,\boldsymbol{\beta}^{\delta\delta})\},\end{aligned}\tag{83}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{s}} &= -\frac{1}{\sqrt{3}}\,\{-R\,\boldsymbol{\beta}^{\mathrm{d}\pi\pi}\\ &\quad -(\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi}+\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma}-2\,\boldsymbol{\beta}^{\delta\delta})\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\}\,(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}})^{-1},\end{aligned}\tag{84}$$

$$\begin{aligned}\boldsymbol{\beta}^{\sigma\mathrm{s}} &= -\frac{1}{3R}\,\{\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,(2\,\boldsymbol{\beta}^{\delta\delta}-\boldsymbol{\beta}^{\mathrm{d}\pi\mathrm{d}\pi}-3\,\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma})\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\\ &\quad -3R\,(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\pi\pi}-\boldsymbol{\beta}^{\pi\mathrm{d}\pi}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}})+2\,\boldsymbol{\beta}^{\pi\pi}\,(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^2\\ &\quad -\sqrt{3}\,(\boldsymbol{S}^{\sigma\mathrm{d}\sigma})'\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}-(\boldsymbol{S}^{\pi\pi})'\}\,(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}})^{-1},\end{aligned}\tag{85}$$

$$\begin{aligned}\boldsymbol{\beta}^{\mathrm{s}\sigma} &= \frac{1}{3R}\,(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}})^{-1}\{\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,(2\,\boldsymbol{\beta}^{\delta\delta}-\boldsymbol{\beta}^{\pi\mathrm{d}\pi}+3\,\boldsymbol{\beta}^{\mathrm{d}\sigma\mathrm{d}\sigma})\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\\ &\quad -3R\,(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,\boldsymbol{\beta}^{\mathrm{d}\pi\pi}-\boldsymbol{\beta}^{\pi\mathrm{d}\pi}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}})-2\,(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}})^2\,\boldsymbol{\beta}^{\pi\pi}\\ &\quad +\sqrt{3}\,\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}\,(\boldsymbol{S}^{\mathrm{d}\sigma\sigma})'-(\boldsymbol{S}^{\pi\pi})'\},\end{aligned}\tag{86}$$

$$\boldsymbol{\beta}^{\mathrm{ss}} = \frac{1}{R}\,\{(\boldsymbol{S}^{\mathrm{ss}})'+\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}\,\boldsymbol{\beta}^{\sigma\mathrm{s}}-\boldsymbol{\beta}^{\mathrm{s}\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}\}.\tag{87}$$

(iv) Case IV: $\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}=0$, B(S) i.e. atom A possesses only an s, p orbital basis set and $\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}$ is a square matrix.

In this case, expressions for gradient elements reduce considerably due to the relation $\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}=0$. The β integrals can be found from the relations

$$\boldsymbol{\beta}^{\pi\pi} = \frac{1}{R}\,\boldsymbol{S}^{\pi\mathrm{d}\pi}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1},\tag{88}$$

$$\boldsymbol{\beta}^{\pi\mathrm{d}\pi} = \left(\frac{1}{R}\,\boldsymbol{S}^{\pi\mathrm{d}\pi}\right)',\tag{89}$$

$$\boldsymbol{\beta}^{\mathrm{s}\sigma} = (\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}})^{-1}\,\boldsymbol{S}^{\pi\mathrm{d}\pi}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1},\tag{90}$$

$$\boldsymbol{\beta}^{\sigma\sigma} = (\boldsymbol{S}^{\pi\mathrm{d}\pi})'\,(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}})^{-1},\tag{91}$$

$$\boldsymbol{\beta}^{\mathrm{sd}\sigma} = -\frac{R}{\sqrt{3}}\,(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}})^{-1}\left(\frac{1}{R}\,\boldsymbol{S}^{\pi\mathrm{d}\pi}\right)',\tag{92}$$

$$\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma} = \frac{1}{\sqrt{3}\,R^2}\,[R^2\,(\boldsymbol{S}^{\pi\mathrm{d}\pi})''-R\,(\boldsymbol{S}^{\pi\mathrm{d}\pi})'+\boldsymbol{S}^{\pi\mathrm{d}\pi}],\tag{93}$$

$$\begin{aligned}\boldsymbol{\beta}^{\sigma\mathrm{s}} &= \boldsymbol{S}^{\pi\mathrm{d}\pi}(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{pd}})^{-1}\,(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}})^{-1}\\ &\quad +\frac{1}{3}\left[\left(\boldsymbol{S}^{\pi\mathrm{d}\pi}\right)''+2\left(\frac{1}{R}\,\boldsymbol{S}^{\pi\mathrm{d}\pi}\right)'\right]\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\,(\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}})^{-1},\end{aligned}\tag{94}$$

$$\boldsymbol{\beta}^{\mathrm{ss}} = \frac{1}{R}\,[(\boldsymbol{S}^{\mathrm{ss}})'+\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}\,\boldsymbol{\beta}^{\sigma\mathrm{s}}-\boldsymbol{\beta}^{\mathrm{s}\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}].\tag{95}$$

(v) Case V: $\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{pd}}=0$, B(U). Hence the $\boldsymbol{\beta}^{\pi\mathrm{d}\pi}$ and $\boldsymbol{\beta}^{\mathrm{sd}\sigma}$ integrals can be calculated as in case IV, i.e. from (89) and (92), respectively, but the remaining resonance integrals should be expressed by the following formulas:

$$\boldsymbol{\beta}^{\pi\pi} = \frac{1}{R}\left[(\boldsymbol{S}^{\pi\pi})'-\left(\frac{1}{R}\,\boldsymbol{S}^{\pi\mathrm{d}\pi}\right)'\right],\tag{96}$$

$$\boldsymbol{\beta}^{\sigma\mathrm{d}\sigma} = \frac{1}{\sqrt{3}\,R}\left[2\,(\boldsymbol{S}^{\pi\mathrm{d}\pi})'+R\left(\frac{1}{R}\,\boldsymbol{S}^{\pi\mathrm{d}\pi}\right)'-\sqrt{3}\,(\boldsymbol{S}^{\sigma\mathrm{d}\sigma})'\right],\tag{97}$$

$$\begin{aligned}\boldsymbol{\beta}^{\sigma\sigma} &= \frac{1}{R^2}\left\{4\,(\boldsymbol{S}^{\pi\mathrm{d}\pi})'-\frac{2}{R}\,(\boldsymbol{S}^{\pi\mathrm{d}\pi})'-\sqrt{3}\,(\boldsymbol{S}^{\sigma\mathrm{d}\sigma})'\right\}\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}\\ &\quad -\frac{1}{R}\,(\boldsymbol{S}^{\pi\pi})',\end{aligned}\tag{98}$$

$$\boldsymbol{\beta}^{\mathrm{s}\sigma} = (\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}})^{-1}\left[\left(\frac{1}{R}\,\boldsymbol{S}^{\pi\mathrm{d}\pi}\right)'\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{dp}}-(\boldsymbol{S}^{\pi\pi})'\right],\tag{99}$$

$$\begin{aligned}\boldsymbol{\beta}^{\sigma\mathrm{s}} &= -\frac{1}{3R}\left[2\,(\boldsymbol{S}^{\pi\mathrm{d}\pi})'+R\left(\frac{1}{R}\,\boldsymbol{S}^{\pi\mathrm{d}\pi}\right)'\right.\\ &\quad \left.-\sqrt{3}\,(\boldsymbol{S}^{\sigma\mathrm{d}\sigma})'-3R\,(\boldsymbol{S}^{\pi\pi})'\right](\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{sp}})^{-1},\end{aligned}\tag{100}$$

$$\boldsymbol{\beta}^{\mathrm{ss}} = \frac{1}{R}\,[(\boldsymbol{S}^{\mathrm{ss}})'+\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}\,\boldsymbol{\beta}^{\sigma\mathrm{s}}-\boldsymbol{\beta}^{\mathrm{s}\sigma}\,\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}],\tag{101}$$

$$\boldsymbol{\beta}^{\mathrm{sd}\sigma} = -\frac{R}{\sqrt{3}}\,(\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{ps}})^{-1}\left(\frac{1}{R}\,\boldsymbol{S}^{\pi\mathrm{d}\pi}\right)'.\tag{102}$$

In all the considered cases we ought to include also subcases when the assumption that the $\boldsymbol{\mu}_{\mathrm{A}}^{\mathrm{sp}}$ and $\boldsymbol{\mu}_{\mathrm{B}}^{\mathrm{ps}}$

matrices are square is not fulfilled, and the inverted matrices $(\boldsymbol{\mu}_K)^{-1}$ may not exist. When the $\boldsymbol{\mu}_A^{sp}$ matrix is rectangular we have to replace (60), (71), (86), (90) and (99) by the relation

$$\begin{aligned}\boldsymbol{\beta}^{s\sigma} = \frac{3}{\sqrt{3}\,R^2}\Big[\boldsymbol{\mu}_A^{sp}\Big(\boldsymbol{\beta}^{\sigma d\sigma} - \frac{2}{\sqrt{3}}\boldsymbol{\beta}^{\pi d\pi}\Big) & \\ + (\boldsymbol{S}^{sd\sigma})' - \frac{2}{R}\boldsymbol{S}^{sd\sigma}\Big]\boldsymbol{\mu}_B^{dp} + \frac{1}{R}\boldsymbol{\mu}_A^{sp}(\boldsymbol{\beta}^{\sigma\sigma} - \boldsymbol{\beta}^{\pi\pi}) & \\ + \frac{1}{R}(\boldsymbol{S}^{s\sigma})' - \frac{1}{R^2}\boldsymbol{S}^{s\sigma} & \end{aligned} \tag{103}$$

and (62), (73), (83) and (92) by

$$\boldsymbol{\beta}^{sd\sigma} = \frac{1}{R}\Big[\boldsymbol{\mu}_A^{sp}\Big(\boldsymbol{\beta}^{\sigma d\sigma} - \frac{2}{\sqrt{3}}\boldsymbol{\beta}^{\pi d\pi}\Big) + (\boldsymbol{S}^{sd\sigma})' - \frac{2}{R}\boldsymbol{S}^{sd\sigma}\Big]. \tag{104}$$

In the subcase when the $\boldsymbol{\mu}_B^{ps}$ matrix is rectangular, (61), (72), (85), (94) and (100) should be replaced by

$$\begin{aligned}\boldsymbol{\beta}^{\sigma s} = \frac{3}{\sqrt{3}\,R^2}\Big[\Big(\boldsymbol{\beta}^{d\sigma\sigma} - \frac{2}{\sqrt{3}}\boldsymbol{\beta}^{d\pi\pi}\Big)\boldsymbol{\mu}_B^{ps} & \\ - (\boldsymbol{S}^{d\sigma s})' + \frac{2}{R}\boldsymbol{S}^{d\sigma s}\Big] & \\ - \frac{1}{R}(\boldsymbol{\beta}^{\sigma\sigma} - \boldsymbol{\beta}^{\pi\pi})\boldsymbol{\mu}_B^{ps} + \frac{1}{R}(\boldsymbol{S}^{\sigma s})' - \frac{1}{R^2}\boldsymbol{S}^{\sigma s} & \end{aligned} \tag{105}$$

and (63), (74) and (84) by

$$\begin{aligned}\boldsymbol{\beta}^{d\sigma s} = -\frac{1}{R}\Big[\Big(\boldsymbol{\beta}^{d\sigma\sigma} - \frac{2}{\sqrt{3}}\boldsymbol{\beta}^{d\pi\pi}\Big)\boldsymbol{\mu}_B^{ps} & \\ - (\boldsymbol{S}^{d\sigma s})' + \frac{2}{R}\boldsymbol{S}^{d\sigma s}\Big], & \end{aligned} \tag{106}$$

respectively.

4. Discussion and Test Calculations

The usefulness of the Linderberg-Seamans' type formulas to semiempirical calculations has been proved in our previous papers [9, 12, 13].

Zerner and Parr have used successfully the molecular orbital theory, the Heisenberg equation of motion and the virial theorem to derive their expressions for force constants [15].

The formulas derived here can be considered as a generalization of those derived previously, for the case when $m_A = n_A = l_A = 1$ [11] or $l_A = 0$ [9]. To avoid the troublesome calculations of second and third derivatives of overlap integrals one can use relations for reducing them to the first one [11].

The formulas for resonance integrals presented here can be used as a basis for the elaboration of the NDO-like method which takes into account not only the valence shell, but also Rydberg and/or inner ones. As an illustration we carried out initial calculations of the INDO type, even though the theory is more general, including even the NDDO scheme. The modified INDO CI method [13] was used in the valence electron approximation (INDOL/V) as well as with basis set orbitals augmented by the RO (INDOL/R) version.

To study the influence of higher Rydberg orbitals on the vertical transition energies we chose the water molecule, very well known theoretically as well as experimentally. Singly excited configurations (in all considered cases 60 lowest excitations) were taken into account. In our previous paper [9] we used a 1s, 2s, 2p basis set for the hydrogen and a 2s, 2p, 3s, 3p one for the oxygen atom. In the present study this oxygen basis set was augmented by 3d, 4s, 4p and 4d orbitals. The Slater orbital exponents were used for oxygen orbitals, and $\xi_{1s} = 1.2$, $\xi_{2s} = \xi_{2p} = 0.6$ for hydrogen ones. The all one-centre integrals involving RO were calculated analytically using the above exponents.

The vertical transition energies do not change by more than 0.1 eV in relation to those reported in the previous article [9]. However, there appear the new transitions to the 3d and 4s Rydberg oxygen orbitals (Table 1).

It should be noted that there exists quite good agreement between our calculations and ab initio results [16].

Table 1. The calculated vertical transition energies (in eV) connected with excitations on higher RO for water molecule.

State	Main configuration	INDOL/R	Ab initio [16]
$^1A_2$	1 b_1 → 3d b_2	10.37	10.87
$^1B_1$	1 b_1 → 4s a_1	10.30	10.64
$^1B_1$	1 b_1 → 3d a_1	10.52	11.07
$^1A_1$	1 b_1 → 3d b_1	10.59	11.17

Table 2. The calculated occupied orbital energies (in a.u.) for MnO_4^- ion.

Orbital	INDOL/V	INDOL/R
$1a$	-1.306	-1.342
$1t_2$	-1.152	-1.168
$2t_2$	-0.410	-0.434
$1e$	-0.354	-0.364
$3t_2$	-0.328	-0.344
$2a$	-0.323	-0.341
$1t_1$	-0.224	-0.240

Table 3. The calculated valence and Rydberg orbital populations P_i (in e) and the metal charge Q for the permanganate ion.

Populations	INDOL/V	INDOL/R	
		Valence	Rydberg
P_s	0.474	0.469	0.055
P_p	1.375	1.390	0.033
P_d	4.640	4.610	0.024
Q_{Mn}	0.511	0.530	-0.112

Table 4. Experimental and calculated vertical transition enegies (in eV) for MnO_4^- ion.

State	INDOL/V	INDOL/R	Exp. [19, 20]
T_1	1.75	1.64	1.80
T_2	2.47	2.39	2.30
T_2	3.65	3.70 $(t_1 \rightarrow s_R)$	3.50
T_2	4.73	4.81 $(t_1 \rightarrow p_R)$	4.10

As a second example, the permanganate ion – a "guinea pig" for quantum chemical calculations on d-electron element compounds – was choosen. The Slater orbital exponents for oxygen 2s, 2p, 3s, 3p orbitals and the Gouterman-Zerner basis set [17] for 3d, 4s and 4p manganese valence orbitals were used with $\xi_{4d} = \xi_{5s} = \xi_{5p} = 0.3$ for RO. The experimental geometry ($R_{Mn-O} = 1.63$ Å) was assumed [18] for the tetrahedral ion in T_d symmetry group. We compare our valence electron approximation (INDOL/V with INDOL/R) results. The same set of parameters for the valence matrix elements was used in both methods.

Tables 2 and 3 show the calculated energy of the occupied molecular orbitals and populations of manganese valence and Rydberg orbitals. It is evident that no essential differences in the calculated ground state properties have been found for the INDOL/V and INDOL/R results. The main difference between these two versions of modified INDO methods lays in the interpretation of the electronic spectrum. However, the energy values of the calculated excitations for both versions are in very good agreement with the experimental results, but a closer inspection of the INDOL/R values shows that begining from the second T_2 symmetry excitation the final states in these transitions have at least 90 percent of Rydberg character. The results of our calculations show that inclusion of RO should distinctly change the interpretation of higher-energy electronic spectra, especially for transition element compounds.

The only disadvantage of the proposed method is a 4 to 6 times longer calculation time if compared to the INDOL/V version. However, the calculation time is still relatively short.

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