On the Restricted and Combined Use of Rüdenberg's Approximations in Crystal Orbital Theories of Hartree-Fock Type

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Dedicated to Prof. Dr. F. F. Seelig on the occasion of his 65 th birthday.

The analysis based on Rüdenberg's well-known letter of 1951 which has been outlined for molecules in the preceding contribution now will be transfered to translational periodic systems in one, two, or three dimensions. Entitled "On the Three- and Four-Center Integrals in Molecular Quantum Mechanics", this letter explicitly presents two approximation formulas for four-center repulsion integrals, only. When applied on some types of three-center repulsion integrals, however, these two recipes still imply considerable oversimplifications. Using both one-electron and two-electron routes of Rüdenberg's expansion, on the other hand, such shortcomings can be avoided strictly. Starting from four simple "Unrestricted and Combined" (U&C) approximation schemes introduced elsewhere, an improved "Restricted and Combined" (R&C) approximation picture for Fock-matrix elements now will be outlined which does not tolerate any unnecessary oversimplifications. Although the simplicity of the U&C scheme is lost in this case, R&C-approximated Fock-matrix elements still can be constructed from one- and two-center integrals alone in an effective way. Moreover, due to their dependence on a single geometric parameter, all types of two-center integrals can be calculated in advance for about one hundred fixed interatomic distances at the desired level of sophistication, and stored once and for all. A cubic spline algorithm may be taken to interpolate the actual integral value from each precomputed list.

1. Introduction

As in the preceding contribution [1], the main topic of this paper is Rüdenberg's letter of 1951 [2] with its two truncated expansions (symbolized by I and II) of diatomic orbital products. In addition to Rüdenberg's proper concepts (R) in the sense commonly used, we distinguish three other kinds of Rüdenberg-type approximations which are closely related to the schemes of Mulliken (M) [3], "Zero Differential Overlap" (ZDO) [4], and "Neglect of Diatomic Differential Overlap" (NDDO) [5]. In particular, we consider their application to the crystal-orbital extension of Roothaan's closed-shell "Restricted Hartree-Fock" theory (RHF) [6] in its generalized "Unrestricted Hartree-Fock" form (UHF) of Pople & Nesbet [7].

In analogy to an equivalent molecular orbital study [8], we have already interpreted the consequences of an "Unrestricted and Combined" use (U&C) of Rüdenberg's approximations in crystal-orbital UHF theory [9], apart from any numerical application. Within this context, the term "Unrestricted" indicated that the considered approximations had been applied irrespectively of the one-, two-, and multi-index or -center quality of the integrals involved. (Note that "Unrestricted" in this sense has nothing to do with the conceptual particularities of the "Unrestricted Hartree-Fock" picture itself).

The analysis of Ref. 9 yielded the following results :

- The U&C use of Rüdenberg's Mulliken-type approximations (M.U&C) led to a completed understanding of the Wolfsberg-Helmholz formula [10] which is a constituent part of the semi-empirical "Extended Hückel Theory" (EHT) [11].
- Furthermore, an improved Rüdenberg-type variant of M.U&C called R.U&C had been proposed which is appropriate for non-empirical computer implementations, since it fulfils the "rotational invariance requirement" [12] of all *ab-initio* quantum chemical concepts.
- Supposing an orthonormal atomic orbital basis set, our M.U&C and R.U&C frameworks immediately converted into two additional "Zero Integral Overlap" (ZIO) and "Neglect of Diatomic Integral Overlap" (NDIO) pictures, which are partially identical with the widely-used ZDO and NDDO approximation schemes, respectively.
- We concluded in pointing out that all these four approximations, which are commonly based on the U&C use of Rüdenberg's ideas, imply considerable oversimplifications.

In order to overcome such shortcomings, another set of four "Restricted and Combined" (R&C) concepts had been sketched. Here, the attribute "Restricted" indicated the avoidance of particular oversimplifications which is consistent with the corresponding level of approximation.

In the present article we now intend to work out this R&C route of Rüdenberg-type approximations for crystal-orbital theories of Hartree-Fock type. For this purpose it is convenient, first of all, to write down the crystal-orbital UHF Fock-matrix representation in a partitive form which separates explicitly the different one-, two-, three-, and four-index or -center interactions from one another in an appropriate way. Each of the four sections which discuss the pictures of Mulliken, ZIO, Rüdenberg, and NDIO type is subdivided into two parts. While the first part intends to explain, how oversimplications generally arise in certain cases of three-index or three-center repulsion integral approximations, the second subsection specifies the "Restricted and Combined" approximation picture for Fock-matrix elements. The equations of these second subsections are constitutive for any forthcoming numerical M.R&C, ZIO.R&C, R.R&C, and NDIO.R&C crystal-orbital investigation.

Finally it should be stressed, that such R&C routes of approximations do not improve the quality of all multi-index or multi-center integrals, in general [13]. Improvements, however, can be expected from the fact that conceptual shortcomings of the standard Mulliken-, ZDO-, Rüdenberg-, and NDDO-pictures are minimized in a way, which is designed to be well-balanced in both attractive and repulsive energy contributions.

2. Basic equations

Introducing periodic boundary conditions according to Born & v. Kármán [14], we consider a three-dimensional crystal ($d = 3$) as being built up of $N_{abc} \equiv N_a N_b N_c$ unit cells, connected by N_a, N_b, and N_c translational symmetry operations along the three crystallographic directions defined through the primitive lattice vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$, respectively. $N_a = N_b = N_c := 1$ corresponds to the zero-dimensional molecular case ($d = 0$). In one-dimensional systems ($d = 1$) only one of the positive integers N_a, N_b, or N_c differs from 1 whereas in two-dimensional lattices ($d = 2$) there are two unit-cell numbers greater than one.

Within the Born-Oppenheimer picture [14] of N_n fixed nuclear positions per unit cell, standard non-empirical quantum chemical methods [14] usually expand the delocalized crystal orbitals of the j-th energy band $\{\Psi_j(\mathbf{k}, \mathbf{r}_i) | j = 1, \ldots, N_o\}$ as linear combinations of N_o symmetry adapted Bloch sums [14] $\{\Phi'_\mu(\mathbf{k}, \mathbf{r}_i) | \mu = 1, \ldots, N_o\}$, constructed from N_o atomic orbitals per unit cell. Each wavevector $\mathbf{k} \equiv \{k^a, k^b, k^c\}$ has components that cover the following ranges defining the first Brillouin zone [14] :

$$-\frac{\pi}{|\mathbf{a}|} < k^a \leq +\frac{\pi}{|\mathbf{a}|} \quad ; \quad -\frac{\pi}{|\mathbf{b}|} < k^b \leq +\frac{\pi}{|\mathbf{b}|} \quad ; \quad -\frac{\pi}{|\mathbf{c}|} < k^c \leq +\frac{\pi}{|\mathbf{c}|} \; . \tag{2.1}$$

In the "Unrestricted Hartree-Fock" theory (UHF) of Pople & Nesbet [7], which is central within the scope of this paper, two different crystal orbital sets have to be determined. The α-spin "Linear Combination of Atomic Orbitals" (LCAO), for instance, reads :

$$\Psi_j^\alpha(\mathbf{k}, \mathbf{r}_i) := \sum_{\mu=1}^{N_o} \Phi'_\mu(\mathbf{k}, \mathbf{r}_i) C'^\alpha_{\mu j}(\mathbf{k}), \qquad j = 1, \ldots, N_o \; , \tag{2.2}$$

with

$$\Phi'_\mu(\mathbf{k}, \mathbf{r}_i) = N_{abc}^{-\frac{1}{2}} \sum_{\mathbf{m}=\mathbf{N}^-}^{\mathbf{N}^+} \exp\left(i[k^a m_a|\mathbf{a}| + k^b m_b|\mathbf{b}| + k^c m_c|\mathbf{c}|]\right) \Phi_\mu(\mathbf{r}_i - \mathbf{R}_\mathbf{m}), \tag{2.3}$$

where we introduced the following abbreviations :

$$\sum_{\mathbf{m}=\mathbf{N}^-}^{\mathbf{N}^+} \equiv \sum_{m_a=N_a^-}^{N_a^+} \sum_{m_b=N_b^-}^{N_b^+} \sum_{m_c=N_c^-}^{N_c^+} \; , \tag{2.4}$$

$$\mathbf{m} \equiv \{m_a, m_b, m_c\} \; , \quad \mathbf{N}^- \equiv \{N_a^-, N_b^-, N_c^-\} \; , \quad \mathbf{N}^+ \equiv \{N_a^+, N_b^+, N_c^+\} \; , \tag{2.5}$$

and

$$\mathbf{R}_\mathbf{m} \equiv m_a\mathbf{a} + m_b\mathbf{b} + m_c\mathbf{c} \; . \tag{2.6}$$

The summation limits are defined as follows :

$$N_a^- := \begin{cases} -(N_a - 2)/2, & \text{if } N_a \text{ even,} \\ -(N_a - 1)/2, & \text{if } N_a \text{ odd,} \end{cases} \quad \text{and} \quad N_a^+ := \begin{cases} +N_a/2, & \text{if } N_a \text{ even,} \\ +(N_a - 1)/2, & \text{if } N_a \text{ odd.} \end{cases} \tag{2.7}$$

Analogous definitions hold for the crystallographic **b** and **c** directions.

An equivalent second ansatz has to be made for spin β. If one should find the unrestricted α- and β-spin orbitals to be identical, they both are of the restricted form according to Roothaan [6]. Hence, Roothaan's "Restricted Hartree-Fock" theory (RHF) is formally included in the more general Pople-Nesbet description. We therefore restrict our discussion to UHF theory. If necessary, all expressions then can be translated easily into the RHF picture.

In order to be more specific, Eqs. (2.2) and (2.3) can be rewritten as follows :

$$\Psi_j^\alpha(\mathbf{k},\mathbf{r}_i) := \sum_{M=1}^{N_n} \sum_{\mu=1}^{n_o(M)} \Phi'_\mu(\mathbf{k},\mathbf{r}_i-\mathbf{R}_M) C'^{\alpha}_{(M,\mu)j}(\mathbf{k}), \qquad j=1,\ldots,N_o \ , \tag{2.8}$$

with

$$\begin{aligned}\Phi'_\mu(\mathbf{k},\mathbf{r}_i-\mathbf{R}_M) = N_{abc}^{-\frac{1}{2}} \sum_{\mathbf{m}=\mathbf{N}^-}^{\mathbf{N}^+} & \exp\left(i[k^a m_a|\mathbf{a}| + k^b m_b|\mathbf{b}| + k^c m_c|\mathbf{c}|]\right) \\ & \times \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M - \mathbf{R}_\mathbf{m}).\end{aligned} \tag{2.9}$$

In contrast to the first notation of Eqs. (2.2) and (2.3), the Eqs. (2.8) and (2.9) explicitly specify the position vector $\mathbf{R}_M \equiv (x_M, y_M, z_M)$ of the M-th atom within each unit cell, to which all $n_o(M)$ basis functions with index μ belong. While the first notation will be chosen in discussing the simple approximation recipe of Mulliken [3] and the "Zero Integral Overlap" scheme (ZIO) [8], the second notation will turn out to be particularly appropriate in the context of Rüdenberg's more elaborate approximation [2] and the "Neglect of Diatomic Integral Overlap" concept (NDIO) [8].

Four types of integrals can be distinguished within both UHF and RHF theories :

- *Overlap integrals*

$$\begin{aligned}&\int \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M)\Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_\mathbf{n}) d\mathbf{r}_i \\ &\equiv \begin{cases} (\mathbf{S_{0n}})_{\mu\nu} & \text{notation 1} \\ \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ \substack{M \\ \mu} & \substack{N \\ \nu} \end{pmatrix} & \text{notation 2 ,} \end{cases}\end{aligned} \tag{2.10}$$

- *kinetic energy integrals*

$$\begin{aligned}&\int \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M)\left[\Delta(\mathbf{r}_i)\Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_\mathbf{n})\right] d\mathbf{r}_i \\ &\equiv \begin{cases} (\mathbf{K_{0n}})_{\mu\nu} & \text{notation 1} \\ (\mathbf{K_{0n}})_{(M,\mu)(N,\nu)} & \text{notation 2 ,} \end{cases}\end{aligned} \tag{2.11}$$

with the Laplacian operator $\Delta(\mathbf{r}_i) = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$, and

- *nuclear attraction integrals*

$$-Z_P \int \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M)|\mathbf{r}_i - \mathbf{R}_P - \mathbf{R_p}|^{-1}\Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R_n})d\mathbf{r}_i$$
$$\equiv \begin{cases} (\mathbf{V_{0n}})_{\mu\nu}[\mathbf{p}P] & \text{notation 1} \\ \begin{pmatrix} \mathbf{0} & \mathbf{p} & \mathbf{n} \\ M & P & N \\ \mu & & \nu \end{pmatrix} & \text{notation 2 ,} \end{cases} \tag{2.12}$$

with the atomic number Z_P of nucleus P, depend on the three Cartesian coordinates $\mathbf{r}_i \equiv (x_i, y_i, z_i)$ of one electron only. Using the chemists' notation, the six-dimensional

- two-electron *repulsion integrals* read as follows :

$$\int\int \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M)\Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R_n})|\mathbf{r}_i - \mathbf{r}_j|^{-1}$$
$$\times\, \Phi_\tau(\mathbf{r}_j - \mathbf{R}_T - \mathbf{R_t})\Phi_\lambda(\mathbf{r}_j - \mathbf{R}_L - \mathbf{R_l})d\mathbf{r}_i d\mathbf{r}_j$$
$$\equiv \begin{cases} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ \mu & \nu & \tau & \lambda \end{array}\right) & \text{notation 1} \\ \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ M & N & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right) & \text{notation 2 .} \end{cases} \tag{2.13}$$

Hence, three-index (notation 1) and three-center (notation 2) integrals can be of attraction and repulsion type, whereas all four-index (notation 1) and four-center (notation 2) integrals are exclusively repulsive.

Atomic units (a.u.) are used throughout this paper. For convenience, all atomic functions are taken to be real, normalized, and locally orthogonal.

2.1. Pople-Nesbet equations of crystal orbital theory

In crystal orbital theory, the coefficient matrices $\mathbf{C}'^\alpha(\mathbf{k})$ of Eq. (2.2) or Eq. (2.8) with the property $\mathbf{C}'^{\alpha\dagger}(\mathbf{k})\mathbf{S}'^\alpha(\mathbf{k})\mathbf{C}'^\alpha(\mathbf{k}) = \mathbf{1}$ are determined by solving the $\mathbf{k}$-dependent Pople-Nesbet equations. Their α-spin part reads as follows :

$$\mathbf{F}'^\alpha(\mathbf{k})\mathbf{C}'^\alpha(\mathbf{k}) = \mathbf{S}'(\mathbf{k})\mathbf{C}'^\alpha(\mathbf{k})\mathbf{E}^\alpha(\mathbf{k}) \ . \tag{2.14}$$

$\mathbf{E}^\alpha(\mathbf{k})$ is the diagonal matrix of crystal-orbital energies :

$$\mathbf{E}^\alpha(\mathbf{k}) = \begin{pmatrix} E_1^\alpha(\mathbf{k}) & 0 & \dots & 0 \\ 0 & E_2^\alpha(\mathbf{k}) & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & E_{N_o}^\alpha(\mathbf{k}) \end{pmatrix} . \tag{2.15}$$

$E_j^\alpha(\mathbf{k})$ belongs to the j-th column of $\mathbf{C}'^\alpha(\mathbf{k})$, where j is the energy-band index. Density matrices of the Bloch basis are defined through :

$$\mathbf{P}'^\alpha(\mathbf{k}) = \mathbf{C}'^\alpha(\mathbf{k})\mathbf{\Omega}^\alpha(\mathbf{k})\mathbf{C}'^{\alpha\dagger}(\mathbf{k}). \tag{2.16}$$

The diagonal matrix $\mathbf{\Omega}^\alpha(\mathbf{k})$ contains the occupation numbers $\Omega_j^\alpha(\mathbf{k})$ of the crystal orbitals $\Psi_j^\alpha(\mathbf{k},\mathbf{r}_i)$:

$$\mathbf{\Omega}^\alpha(\mathbf{k}) = \begin{pmatrix} \Omega_1^\alpha(\mathbf{k}) & 0 & \dots & 0 \\ 0 & \Omega_2^\alpha(\mathbf{k}) & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \Omega_{N_o}^\alpha(\mathbf{k}) \end{pmatrix} , \tag{2.17}$$

with

$$\Omega_j^\alpha(\mathbf{k}) := \begin{cases} 1 & \text{if } \Psi_j^\alpha(\mathbf{k},\mathbf{r}_i) \text{ is occupied ,} \\ 0 & \text{else .} \end{cases} \tag{2.18}$$

The symmetry adapted complex overlap integrals of the Bloch basis are obtained by summing up all real-space overlap integrals according to

$$\mathbf{S}'(\mathbf{k}) = \sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \exp\left(i[k^a n_a|\mathbf{a}| + k^b n_b|\mathbf{b}| + k^c n_c|\mathbf{c}|]\right) \mathbf{S}_{\mathbf{0n}} = \mathbf{S}'^\dagger(\mathbf{k}) \ . \tag{2.19}$$

An equivalent expression holds for the Fock matrix $\mathbf{F}'^\alpha(\mathbf{k})$:

$$\mathbf{F}'^\alpha(\mathbf{k}) = \sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \exp\left(i[k^a n_a|\mathbf{a}| + k^b n_b|\mathbf{b}| + k^c n_c|\mathbf{c}|]\right) \mathbf{F}^\alpha_{\mathbf{0n}} = \mathbf{F}'^{\alpha\dagger}(\mathbf{k}) \ . \tag{2.20}$$

Symmetry properties like $(\mathbf{S}_{\mathbf{0-n}})_{\mu\nu} = (\mathbf{S}_{\mathbf{0n}})_{\nu\mu}$ and $(\mathbf{F}^\alpha_{\mathbf{0-n}})_{\mu\nu} = (\mathbf{F}^\alpha_{\mathbf{0n}})_{\nu\mu}$ can be utilized to accelerate real-space lattice summations from a computational point of view. The summation limits in Eqs. (2.19) and (2.20) have to be chosen in such a way, that the lattice summation includes all non-vanishing contributions. We are going to reconsider this problem below.

2.2. Standard real-space Fock-matrix representations using notation 1

Next, we write down two different, but equivalent formulations of the unrestricted α-spin real-space Fock-matrix representation of Eq. (2.20). Using the first notation we can write :

$$\begin{aligned} (\mathbf{F}^\alpha_{\mathbf{0n}})_{\mu\nu} = (\mathbf{K}_{\mathbf{0n}})_{\mu\nu} &+ \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n} (\mathbf{V}_{\mathbf{0n}})_{\mu\nu}[\mathbf{p}P]}_{\stackrel{\text{def}}{=} (\mathbf{F}^A_{\mathbf{0n}})_{\mu\nu}} \\ &+ \underbrace{\sum_{\mathbf{t},\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau,\lambda=1}^{N_o} (\mathbf{P}^\oplus_{\mathbf{tl}})_{\tau\lambda} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ \mu & \nu \end{pmatrix} \begin{vmatrix} \mathbf{t} & \mathbf{l} \\ \tau & \lambda \end{pmatrix}}_{\stackrel{\text{def}}{=} (\mathbf{F}^C_{\mathbf{0n}})_{\mu\nu}} \\ &- \underbrace{\sum_{\mathbf{t},\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau,\lambda=1}^{N_o} (\mathbf{P}^\alpha_{\mathbf{tl}})_{\tau\lambda} \begin{pmatrix} \mathbf{0} & \mathbf{t} \\ \mu & \tau \end{pmatrix} \begin{vmatrix} \mathbf{n} & \mathbf{l} \\ \nu & \lambda \end{pmatrix}}_{\stackrel{\text{def}}{=} (\mathbf{F}^{\alpha E}_{\mathbf{0n}})_{\mu\nu}} \quad \begin{cases} \mathbf{n} = \mathbf{N}^-, \dots, \mathbf{N}^+ \ , \\ \mu,\nu = 1,\dots,N_o \ . \end{cases} \end{aligned} \tag{2.21}$$

The symbols A, C, and E stand for the Attractive, Coulomb, and Exchange parts of the Fock-representation, respectively.

The real-space density-matrix representation $\mathbf{P}^{\alpha}_{\mathbf{tl}}$ is available from the corresponding complex reciprocal-space $\mathbf{P}'^{\alpha}(\mathbf{k})$ matrices by means of $\mathbf{k}$-space integrations over the Brillouin-zone ranges defined in Eq. (2.1) :

$$(\mathbf{P}^{\alpha}_{\mathbf{tl}})_{\tau\lambda} := \frac{V_d}{(2\pi)^d} \int\int\int \exp\Big\{ i\big[k^a(t_a - l_a)|\mathbf{a}| + k^b(t_b - l_b)|\mathbf{b}| + k^c(t_c - l_c)|\mathbf{c}|\big]\Big\} P'^{\alpha}_{\tau\lambda}(\mathbf{k}) dk^a dk^b dk^c \ . \tag{2.22}$$

V_d denotes the d-dimensional volume of the primitive real-space unit cell ($V_0 := 1$). Again, equivalent expressions for β-spin have to be formulated analogously. The total density matrix is defined through :

$$\mathbf{P}^{\oplus}_{\mathbf{tl}} = \mathbf{P}^{\alpha}_{\mathbf{tl}} + \mathbf{P}^{\beta}_{\mathbf{tl}}, \qquad \mathbf{t},\mathbf{l} = \mathbf{N}^-, \ldots, \mathbf{N}^+. \tag{2.23}$$

In the RHF theory, however, no second equation for β-spin is needed, since in this case the crystal orbitals are restricted to be doubly occupied in general. Consequently one then finds that $\mathbf{P}^{\alpha}_{\mathbf{tl}} = \mathbf{P}^{\beta}_{\mathbf{tl}} = \frac{1}{2}\mathbf{P}^{\oplus}_{\mathbf{tl}}$.

2.3. Partitive real-space Fock-matrix representations mainly using notation 1

With a second formulation of the three definitions in Eq. (2.21) we intend to separate explicitly from one another those terms, which represent four-index and three-index interactions. Furthermore, both groups will be isolated from two- or one-index terms [15].

Since the second notation also specifies the atomic index, it is more appropriate for a partitive formulation of the attractive contributions of the Fock matrix. Exceptionally, notation 2 will be used in this case. Introducing the notations $\mathbf{n}\nu \neq \mathbf{0}\mu \equiv (\mathbf{n} \neq \mathbf{0}) \vee (\nu \neq \mu)$ and $\mathbf{n}N \neq \mathbf{0}M \equiv (\mathbf{n} \neq \mathbf{0}) \vee (N \neq M)$, we therefore write for the off-diagonal attractive part :

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}_{\mathbf{n}N \neq \mathbf{0}M} = \underbrace{\underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n}}_{\mathbf{p}P \neq \mathbf{0}M, \mathbf{n}N} \begin{pmatrix} \mathbf{0} & & \mathbf{n} \\ & \mathbf{p} & \\ M & P & N \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\text{def}}{=} (^{(1)}\mathbf{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}} + \underbrace{\begin{pmatrix} \mathbf{0} & & \mathbf{n} \\ & \mathbf{n} & \\ M & N & N \\ \mu & & \nu \end{pmatrix} + \begin{pmatrix} \mathbf{0} & & \mathbf{n} \\ & \mathbf{0} & \\ M & M & N \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\text{def}}{=} (^{(0)}\mathbf{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}} . \tag{2.24}$$

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{00}})_{(M,\mu)(M,\nu)}}_{\nu \neq \mu} = \underbrace{\underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n}}_{\mathbf{p}P \neq \mathbf{0}M} \begin{pmatrix} \mathbf{0} & & \mathbf{0} \\ & \mathbf{p} & \\ M & P & M \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\text{def}}{=} (^{(1)}\mathbf{A}_{\mathbf{00}})_{(M,\mu)(M,\nu)}} + \underbrace{\begin{pmatrix} \mathbf{0} & & \mathbf{0} \\ & \mathbf{0} & \\ M & M & M \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\text{def}}{=} (^{(0)}\mathbf{A}_{\mathbf{00}})_{(M,\mu)(M,\nu)}} . \tag{2.25}$$

For the diagonal attractive part we write :

$$(\mathbf{F}^A_{\mathbf{00}})_{(M,\mu)(M,\mu)} = \underbrace{\underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{P=1}^{N_n}}_{\mathbf{p}P\neq\mathbf{0}M} \begin{pmatrix} \mathbf{0} & \mathbf{p} & \mathbf{0} \\ M & P & M \\ \mu & & \mu \end{pmatrix}}_{\stackrel{\text{def}}{=}({}^{(1)}\mathbf{A}_{\mathbf{00}})_{(M,\mu)(M,\mu)}} + \underbrace{\begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{0} \\ M & M & M \\ \mu & & \mu \end{pmatrix}}_{\stackrel{\text{def}}{=}({}^{(0)}\mathbf{A}_{\mathbf{00}})_{(M,\mu)(M,\mu)}} . \tag{2.26}$$

For the off-diagonal Coulomb part we write :

$$\begin{aligned}\underbrace{(\mathbf{F}^C_{\mathbf{0n}})_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = & \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu,\mathbf{t}\tau} (\mathbf{P}^{\oplus}_{\mathbf{tl}})_{\tau\lambda} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ \mu & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(1)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu}} + \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}(\mathbf{P}^{\oplus}_{\mathbf{tt}})_{\tau\tau} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{t} \\ \mu & \nu & \tau & \tau \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(2)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu}} \\ & + 2\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}(\mathbf{P}^{\oplus}_{\mathbf{t0}})_{\tau\mu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{0} \\ \mu & \nu & \tau & \mu \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(3)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu}} + 2\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}(\mathbf{P}^{\oplus}_{\mathbf{tn}})_{\tau\nu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{n} \\ \mu & \nu & \tau & \nu \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(4)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu}} + ({}^{(0)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu},\end{aligned} \tag{2.27}$$

with

$$\underbrace{({}^{(0)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} \stackrel{\text{def}}{=} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\mu\mu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{0} & \mathbf{0} \\ \mu & \nu & \mu & \mu \end{array}\right) + (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\nu\nu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{n} \\ \mu & \nu & \nu & \nu \end{array}\right) + 2(\mathbf{P}^{\oplus}_{\mathbf{0n}})_{\mu\nu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{0} & \mathbf{n} \\ \mu & \nu & \mu & \nu \end{array}\right) . \tag{2.28}$$

For the diagonal Coulomb part we write :

$$\begin{aligned}(\mathbf{F}^C_{\mathbf{00}})_{\mu\mu} = & \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu}\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{t}\tau} (\mathbf{P}^{\oplus}_{\mathbf{tl}})_{\tau\lambda} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{l} \\ \mu & \mu & \tau & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(1)}\mathbf{C}_{\mathbf{00}})_{\mu\mu}} + \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu}(\mathbf{P}^{\oplus}_{\mathbf{00}})_{\tau\tau} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ \mu & \mu & \tau & \tau \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(2)}\mathbf{C}_{\mathbf{00}})_{\mu\mu}} \\ & + 2\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu}(\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\mu\tau} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{0} \\ \mu & \mu & \tau & \mu \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(3)}\mathbf{C}_{\mathbf{00}})_{\mu\mu}} + \underbrace{(\mathbf{P}^{\oplus}_{\mathbf{00}})_{\mu\mu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mu & \mu & \mu & \mu \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(0)}\mathbf{C}_{\mathbf{00}})_{\mu\mu}} .\end{aligned} \tag{2.29}$$

For the off-diagonal exchange part we write :

$$\underbrace{(\mathbf{F}^{\alpha E}_{\mathbf{0n}})_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu,\mathbf{t}\tau} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{\tau\lambda} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{t} & \mathbf{n}\ \mathbf{l} \\ \mu\ \tau & \nu\ \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu}} + \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\alpha}_{\mathbf{tt}})_{\tau\tau} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{t} & \mathbf{n}\ \mathbf{t} \\ \mu\ \tau & \nu\ \tau \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu}}$$

$$+ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\alpha}_{\mathbf{t0}})_{\tau\mu} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{t} & \mathbf{n}\ \mathbf{0} \\ \mu\ \tau & \nu\ \mu \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu}} + \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\alpha}_{\mathbf{tn}})_{\tau\nu} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{t} & \mathbf{n}\ \mathbf{n} \\ \mu\ \tau & \nu\ \nu \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(4)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu}}$$

$$+ \underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\alpha}_{\mathbf{0l}})_{\mu\lambda} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{0} & \mathbf{n}\ \mathbf{l} \\ \mu\ \mu & \nu\ \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu}} + \underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\alpha}_{\mathbf{nl}})_{\nu\lambda} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{n} & \mathbf{n}\ \mathbf{l} \\ \mu\ \nu & \nu\ \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(6)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu}} + ({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu}, \tag{2.30}$$

with

$$\underbrace{({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} \stackrel{\text{def}}{=} (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\mu\mu} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{0} & \mathbf{n}\ \mathbf{0} \\ \mu\ \mu & \nu\ \mu \end{array}\right) + (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\nu\nu} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{n} & \mathbf{n}\ \mathbf{n} \\ \mu\ \nu & \nu\ \nu \end{array}\right)$$
$$+ (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{0} & \mathbf{n}\ \mathbf{n} \\ \mu\ \mu & \nu\ \nu \end{array}\right) + (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{n} & \mathbf{n}\ \mathbf{0} \\ \mu\ \nu & \nu\ \mu \end{array}\right). \tag{2.31}$$

For the diagonal exchange part we write :

$$(\mathbf{F}^{\alpha E}_{\mathbf{00}})_{\mu\mu} = \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{t}\tau} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{\tau\lambda} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{t} & \mathbf{0}\ \mathbf{l} \\ \mu\ \tau & \mu\ \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu}} + \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu} (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\tau\tau} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{t} & \mathbf{0}\ \mathbf{t} \\ \mu\ \tau & \mu\ \tau \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu}}$$

$$2 + \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu} (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\mu\tau} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{t} & \mathbf{0}\ \mathbf{0} \\ \mu\ \tau & \mu\ \mu \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu}} + \underbrace{(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\tau\lambda} \left(\begin{array}{c|c} \mathbf{0}\ \mathbf{0} & \mathbf{0}\ \mathbf{0} \\ \mu\ \mu & \mu\ \mu \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu}}. \tag{2.32}$$

Once again it should be stressed that the ensemble of partitive formulations of Eqs. (2.24) … (2.32) are completely equivalent to the standard formulation of Eq. (2.21).

2.4. Standard real-space Fock-matrix representations using notation 2

Choosing the more specific second notation, the formulas of Eqs. (2.21) and (2.22) then read :

$$(\mathbf{F}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} = (\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n} \begin{pmatrix} \mathbf{0} & \mathbf{p} & \mathbf{n} \\ M & P & N \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\text{def}}{=} (\mathbf{F}^{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}$$

$$+ \underbrace{\sum_{\mathbf{t},\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T,L=1}^{N_n} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\oplus}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ M & N & T & L \\ \mu & \nu & \tau & \lambda \end{array} \right)}_{\stackrel{\text{def}}{=} (\mathbf{F}^{C}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}$$

$$- \underbrace{\sum_{\mathbf{t},\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T,L=1}^{N_n} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{t} & \mathbf{n} & \mathbf{l} \\ M & T & N & L \\ \mu & \tau & \nu & \lambda \end{array} \right)}_{\stackrel{\text{def}}{=} (\mathbf{F}^{\alpha E}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}} \quad \begin{cases} \mathbf{n} = -\mathbf{N}, \ldots, +\mathbf{N} \ , \\ M, N = 1, \ldots, N_n \ , \\ \mu = 1, \ldots, n_o(M) \ , \\ \nu = 1, \ldots, n_o(N) \ , \end{cases} \tag{2.33}$$

and

$$(\mathbf{P}^{\alpha}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)} := \frac{V_d}{(2\pi)^d} \int\int\int \exp\Big\{ i\big[k^a(t_a - l_a)|\mathbf{a}| + k^b(t_b - l_b)|\mathbf{b}| + k^c(t_c - l_c)|\mathbf{c}|\big]\Big\} P'^{\alpha}_{(T,\tau)(L,\lambda)}(\mathbf{k}) dk^a dk^b dk^c \ . \tag{2.34}$$

2.5. Partitive real-space Fock-matrix representations using notation 2

With a second formulation of the three definitions in Eq. (2.40) we intend to separate explicitly from one another those terms, which represent four-center and three-center interactions. Furthermore, both groups will be isolated from two- or one-center terms.

Introducing the notation $\mathbf{n}N \neq \mathbf{0}M \equiv (\mathbf{n} \neq \mathbf{0}) \vee (N \neq M)$, we write for the off-blockdiagonal attractive part :

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}_{\mathbf{n}N \neq \mathbf{0}M} = \underbrace{\underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n}}_{\mathbf{p}P \neq \mathbf{0}M, \mathbf{n}N} \begin{pmatrix} \mathbf{0} & \mathbf{p} & \mathbf{n} \\ M & P & N \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\text{def}}{=} (^{(1)}\mathbf{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}} + \underbrace{\begin{pmatrix} \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & N & N \\ \mu & & \nu \end{pmatrix} + \begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{n} \\ M & M & N \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\text{def}}{=} (^{(0)}\mathbf{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}} . \tag{2.35}$$

For the blockdiagonal attractive part we write :

$$(\mathbf{F}^A_{\mathbf{00}})_{(M,\mu)(M,\nu)} = \underbrace{\underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n}}_{\mathbf{p}P\neq\mathbf{0}M} \begin{pmatrix} \mathbf{0} & \mathbf{p} & \mathbf{0} \\ M & P & M \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\mathrm{def}}{=}({}^{(1)}\mathbf{A_{00}})_{(M,\mu)(M,\nu)}} + \underbrace{\begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{0} \\ M & M & M \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\mathrm{def}}{=}({}^{(0)}\mathbf{A_{00}})_{(M,\mu)(M,\nu)}} \quad . \tag{2.36}$$

For the off-blockdiagonal Coulomb part we write :

$$\begin{aligned}
\underbrace{(\mathbf{F}^C_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = & \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N} \sum_{\tau=1}^{n_o(T)} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N,\mathbf{t}T} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\oplus}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ M & N & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\mathrm{def}}{=}({}^{(1)}\mathbf{C_{0n}})_{(M,\mu)(N,\nu)}} \\
& + \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(T)} (\mathbf{P}^{\oplus}_{\mathbf{tt}})_{(T,\tau)(T,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{t} \\ M & N & T & T \\ \mu & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\mathrm{def}}{=}({}^{(2)}\mathbf{C_{0n}})_{(M,\mu)(N,\nu)}} \\
& + 2 \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{t0}})_{(T,\tau)(M,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{0} \\ M & N & T & M \\ \mu & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\mathrm{def}}{=}({}^{(3)}\mathbf{C_{0n}})_{(M,\mu)(N,\nu)}} \\
& + 2 \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(N)} (\mathbf{P}^{\oplus}_{\mathbf{tn}})_{(T,\tau)(N,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{n} \\ M & N & T & N \\ \mu & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\mathrm{def}}{=}({}^{(4)}\mathbf{C_{0n}})_{(M,\mu)(N,\nu)}} \\
& + ({}^{(0)}\mathbf{C_{0n}})_{(M,\mu)(N,\nu)},
\end{aligned} \tag{2.37}$$

with

$$\underbrace{({}^{(0)}\mathbf{C}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} \stackrel{\text{def}}{=} \sum_{\tau=1}^{n_o(M)} \sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(M,\tau)(M,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{0} & \mathbf{0} \\ M & N & M & M \\ \mu & \nu & \tau & \lambda \end{array}\right)$$
$$+ \sum_{\tau=1}^{n_o(N)} \sum_{\lambda=1}^{n_o(N)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(N,\tau)(N,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{n} \\ M & N & N & N \\ \mu & \nu & \tau & \lambda \end{array}\right) \qquad (2.38)$$
$$+2 \sum_{\tau=1}^{n_o(M)} \sum_{\lambda=1}^{n_o(N)} (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{(M,\tau)(N,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{0} & \mathbf{n} \\ M & N & M & N \\ \mu & \nu & \tau & \lambda \end{array}\right).$$

For the blockdiagonal Coulomb part we write :

$$(\mathbf{F}^{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)} = \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M} \sum_{\tau=1}^{n_o(T)} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{t}T} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\oplus}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=} ({}^{(1)}\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)}}$$
$$+ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(T)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(T,\tau)(T,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=} ({}^{(2)}\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)}}$$
$$+ 2 \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{(M,\lambda)(T,\tau)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{0} \\ M & M & T & M \\ \mu & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=} ({}^{(3)}\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)}}$$
$$+ \underbrace{\sum_{\tau=1}^{n_o(M)} \sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(M,\tau)(M,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ M & M & M & M \\ \mu & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=} ({}^{(0)}\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)}}.$$

(2.39)

For the off-blockdiagonal exchange part we write :

$$
\underbrace{(\mathbf{F}^{\alpha E}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\quad\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N,\mathbf{t}T}\sum_{\lambda=1}^{n_o(L)}(\mathbf{P}^{\alpha}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)}\begin{pmatrix}\mathbf{0} & \mathbf{t} & \mathbf{n} & \mathbf{l}\\ M & T & N & L\\ \mu & \tau & \nu & \lambda\end{pmatrix}}_{\stackrel{\text{def}}{=}({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}
$$

$$
+\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(T)}(\mathbf{P}^{\alpha}_{\mathbf{tt}})_{(T,\tau)(T,\lambda)}\begin{pmatrix}\mathbf{0} & \mathbf{t} & \mathbf{n} & \mathbf{t}\\ M & T & N & T\\ \mu & \tau & \nu & \lambda\end{pmatrix}}_{\stackrel{\text{def}}{=}({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}
$$

$$
+\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(M)}(\mathbf{P}^{\alpha}_{\mathbf{t0}})_{(T,\tau)(M,\lambda)}\begin{pmatrix}\mathbf{0} & \mathbf{t} & \mathbf{n} & \mathbf{0}\\ M & T & N & M\\ \mu & \tau & \nu & \lambda\end{pmatrix}}_{\stackrel{\text{def}}{=}({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}
$$

$$
+\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(N)}(\mathbf{P}^{\alpha}_{\mathbf{tn}})_{(T,\tau)(N,\lambda)}\begin{pmatrix}\mathbf{0} & \mathbf{t} & \mathbf{n} & \mathbf{n}\\ M & T & N & N\\ \mu & \tau & \nu & \lambda\end{pmatrix}}_{\stackrel{\text{def}}{=}({}^{(4)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}
$$

$$
+\underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(L)}(\mathbf{P}^{\alpha}_{\mathbf{0l}})_{(M,\tau)(L,\lambda)}\begin{pmatrix}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{l}\\ M & M & N & L\\ \mu & \tau & \nu & \lambda\end{pmatrix}}_{\stackrel{\text{def}}{=}({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}
$$

$$
+\underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(L)}(\mathbf{P}^{\alpha}_{\mathbf{nl}})_{(N,\tau)(L,\lambda)}\begin{pmatrix}\mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{l}\\ M & N & N & L\\ \mu & \tau & \nu & \lambda\end{pmatrix}}_{\stackrel{\text{def}}{=}({}^{(6)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}
$$

$$
+({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}, \tag{2.40}
$$

with

$$\underbrace{({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} \stackrel{\text{def}}{=} \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{00}})_{(M,\tau)(M,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{0} \\ M & M & N & M \\ \mu & \tau & \nu & \lambda \end{array}\right)$$
$$+ \sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(N)} (\mathbf{P}^{\alpha}_{\mathbf{00}})_{(N,\tau)(N,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{n} \\ M & N & N & N \\ \mu & \tau & \nu & \lambda \end{array}\right)$$
$$+ \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(N)} (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{(M,\tau)(N,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & M & N & N \\ \mu & \tau & \nu & \lambda \end{array}\right)$$
$$+ \sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{(M,\lambda)(N,\tau)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0} \\ M & N & N & M \\ \mu & \tau & \nu & \lambda \end{array}\right). \tag{2.41}$$

For the blockdiagonal exchange part we write :

$$(\mathbf{F}^{\alpha E}_{\mathbf{00}})_{(M,\mu)(M,\nu)} = \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M}\sum_{\tau=1}^{n_o(T)}\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{t}T}\sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{t} & \mathbf{0} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)}}$$
$$+ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(T)} (\mathbf{P}^{\alpha}_{\mathbf{00}})_{(T,\tau)(T,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{t} & \mathbf{0} & \mathbf{t} \\ M & T & M & T \\ \mu & \tau & \nu & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)}}$$
$$+ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{(M,\lambda)(T,\tau)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{t} & \mathbf{0} & \mathbf{0} \\ M & T & M & M \\ \mu & \tau & \nu & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)}}$$
$$+ \underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M}\sum_{\lambda=1}^{n_o(L)}\sum_{\tau=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{0l}})_{(M,\tau)(L,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{l} \\ M & M & M & L \\ \mu & \tau & \nu & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)}}$$
$$+ \underbrace{\sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{00}})_{(M,\tau)(M,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ M & M & M & M \\ \mu & \tau & \nu & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)}}. \tag{2.42}$$

It should be stressed once again that the ensemble of partitive formulations of Eqs. (2.35) ... (2.42) are completely equivalent to the compact formulations of Eq. (2.33).

2.6. Reciprocal-space integrations

Following Ramírez & Böhm [16] we assume that the integrals of Eq. (2.22) (or equivalently those of Eq. (2.34)) can be approximated by discrete summations within the first Brillouin zone :

$$(\mathbf{P}^{\alpha}_{\mathbf{tl}})_{\tau\lambda} := (N^{abc})^{-1} \sum_{u=N^a_-}^{N^a_+} \sum_{v=N^b_-}^{N^b_+} \sum_{w=N^c_-}^{N^c_+} W_{uvw} \times \Re\left\{ \exp\left\{ i\left[k^a_u(t_a - l_a)|\mathbf{a}| + k^b_v(t_b - l_b)|\mathbf{b}| + k^c_w(t_c - l_c)|\mathbf{c}|\right]\right\} P'^{\alpha}_{\tau\lambda}(\mathbf{k}_{uvw})\right\}, \tag{2.43}$$

where

$$W_{uvw} := 1 \quad \text{for all} \quad u = N^a_-, \ldots, N^a_+; v = N^b_-, \ldots, N^b_+; w = N^c_-, \ldots, N^c_+. \tag{2.44}$$

The imaginary part of Eq. (2.43) vanishes so that the $\mathbf{P}^{\alpha}_{\mathbf{tl}}$ matrices are real.

Furthermore, as recommended in Ref. 16, we consider the $N^{abc} \equiv N^a N^b N^c$ discrete wavevectors

$$\{\mathbf{k}_{uvw} \equiv \{k^a_u, k^b_v, k^c_w\} | u = N^a_-, \ldots, N^a_+; v = N^b_-, \ldots, N^b_+; w = N^c_-, \ldots, N^c_+\} \tag{2.45}$$

to form a homogeneously distributed grid. Given the positive integers N^a, N^b, and N^c, we write analogously to Eq. (2.7) :

$$N^a_- := \begin{cases} -(N^a-2)/2, & \text{if } N^a \text{ even,} \\ -(N^a-1)/2, & \text{if } N^a \text{ odd,} \end{cases} \quad \text{and} \quad N^a_+ := \begin{cases} +N^a/2, & \text{if } N^a \text{ even,} \\ +(N^a-1)/2, & \text{if } N^a \text{ odd.} \end{cases} \tag{2.46}$$

The equidistant set of wavenumber components now is selected according to

$$k^a_u := \frac{2\pi}{|\mathbf{a}|} \cdot \frac{u}{N^a}, \quad \text{with} \quad u := N^a_-, \ldots, N^a_+. \tag{2.47}$$

Equivalent definitions hold for the crystallographic **b** and **c** directions. As in the real space, $N^a = N^b = N^c := 1$ also corresponds to the zero-dimensional molecular case, for example.

If the summations of Eq. (2.43) run over the full Brillouin-zone ranges, all reciprocal-space $\mathbf{k}_{uvw}$ points have to be regarded as being equivalent. As indicated above, the weighting factor W_{uvw} is always equal to 1 in this case. Utilizing the symmetry property

$$\mathbf{P}'^{\alpha}(\mathbf{k}) = \mathbf{P}'^{\alpha*}(-\mathbf{k}) \tag{2.48}$$

of the reciprocal-space density matrices, however, we can restrict ourselves to real part summations ranging from $w = 0$ to $w = N^c_+$. All quantities with the exception of those belonging to the two special points $k_0^c = 0$ and $k^c_{+N^c/2} = +\pi/|\mathbf{c}|$ have to be counted twice in this case :

$$(\mathbf{P}^{\alpha}_{\mathbf{tl}})_{\tau\lambda} := (N^{abc})^{-1} \sum_{u=N^a_-}^{N^a_+} \sum_{v=N^b_-}^{N^b_+} \sum_{w=0}^{N^c_+} W_{uvw} \times \Big\{ \cos\big[k^a_u(t_a - l_a)|\mathbf{a}| + k^b_v(t_b - l_b)|\mathbf{b}| + k^c_w(t_c - l_c)|\mathbf{c}|\big] \, \Re\{P'^{\alpha}_{\tau\lambda}(\mathbf{k}_{uvw})\} - \sin\big[k^a_u(t_a - l_a)|\mathbf{a}| + k^b_v(t_b - l_b)|\mathbf{b}| + k^c_w(t_c - l_c)|\mathbf{c}|\big] \, \Im\{P'^{\alpha}_{\tau\lambda}(\mathbf{k}_{uvw})\} \Big\} , \tag{2.49}$$

with

$$W_{uvw} := \begin{cases} 1, & \text{if } w = 0 \text{ or } w = +N^c/2, \\ 2, & \text{otherwise.} \end{cases} \tag{2.50}$$

Moreover, if one uses the symmetry rules developed by Ramírez & Böhm [16], one finally can even restrict $\mathbf{k}$-space summations to the irreducible part of the Brillouin zone. Since the symmetry property of Eq. (2.48) also holds for the matrices

$$\mathbf{F}'^{\alpha}(\mathbf{k}) = \mathbf{F}'^{\alpha *}(-\mathbf{k}), \tag{2.51}$$

$$\mathbf{S}'(\mathbf{k}) = \mathbf{S}'^{*}(-\mathbf{k}), \tag{2.52}$$

$$\mathbf{C}'^{\alpha}(\mathbf{k}) = \mathbf{C}'^{\alpha *}(-\mathbf{k}), \tag{2.53}$$

and

$$\mathbf{E}^{\alpha}(\mathbf{k}) = \mathbf{E}^{\alpha}(-\mathbf{k}), \tag{2.54}$$

such techniques may considerably reduce the preselected number of wavevectors for which the generalized eigenvalue problem of Eq. (2.14) has to be solved.

2.7. Approximations for integrals and Fock-matrix elements

We now turn to the discussion of four approximation methods connected with the names of Mulliken (M) and Rüdenberg (R) and the acronyms ZIO ("Zero Integral Overlap") and NDIO ("Neglect of Diatomic Integral Overlap"). ZIO and NDIO can be regarded as two-electron extensions of the well-known ZDO and NDDO schemes, respectively.

These four approximation methods are commonly based on Rüdenberg's ideas contained in his famous short paper of 1951 [2] entitled "*On the Three- and Four-Center Integrals in Molecular Quantum Mechanics*". Obviously, this title suggests that Rüdenberg does not recommend his approximation for all types of two-center integrals. When applied on certain three-center repulsion integrals, however, his recipe still implies considerable oversimplifications, as we shall see, which have not been discussed explicitly in his contribution. Using both one- and two-electron routes of Rüdenberg's expansion, on the other hand, these shortcomings can be strictly avoided.

The simple recipes of Mulliken type discussed below as well as the even more primitive ZIO scheme will be considered here in the sense of a preliminary study. In general, both simplifications are not invariant with respect to rotations of any local coordinate axes, for instance [12]. Thus, they cannot be applied without imposing additional assumptions. Rüdenberg's integral approximation as well as the NDIO concept, on the other hand, fulfil this rotational invariance requirement automatically. In our view, only these two are of practical interest in connection with a non-empirical LCAO method. Nevertheless, since they are closely related to Mulliken's recipe and the ZIO scheme, an analysis of the two simpler procedures is obligatory, too.

Besides the integral approximations themselves, our interest is focussed on their effect for the evaluation of matrix elements occuring in the UHF representation.

3. Approximations of Mulliken type

3.1. "Unrestricted" and "Restricted" integral approximations

In particular, Mulliken's approximation intends to reduce the four-index repulsion integrals to others with only two indices. According to Rüdenberg, this aim can be reached in two ways. The first (standard) approach consists in reducing a differential two-index one-electron density to the corresponding one-electron overlap integral and the arithmetic mean of the two related differential one-index one-electron densities :

$$\text{(I)}\qquad \{\Phi_\mu(\mathbf{r}_i-\mathbf{R_m})\Phi_\nu(\mathbf{r}_i-\mathbf{R_n})\}^{[\mathrm{M}^{\mathrm{I}}_{\mu\nu}]} := \frac{(\mathbf{S_{0n}})_{\mu\nu}}{2}\Big\{\Phi_\mu(\mathbf{r}_i-\mathbf{R_m})\Phi_\mu(\mathbf{r}_i-\mathbf{R_m}) + \Phi_\nu(\mathbf{r}_i-\mathbf{R_n})\Phi_\nu(\mathbf{r}_i-\mathbf{R_n})\Big\}. \tag{3.1}$$

Alternatively, one can also impose this primitive recipe on six-dimensional two-index two-electron orbital products :

$$\text{(II)}\qquad \{\Phi_\mu(\mathbf{r}_i-\mathbf{R_m})\Phi_\nu(\mathbf{r}_j-\mathbf{R_n})\}^{[\mathrm{M}^{\mathrm{II}}_{\mu\nu}]} := \frac{(\mathbf{S_{0n}})_{\mu\nu}}{2}\Big\{\Phi_\mu(\mathbf{r}_i-\mathbf{R_m})\Phi_\mu(\mathbf{r}_j-\mathbf{R_m}) + \Phi_\nu(\mathbf{r}_i-\mathbf{R_n})\Phi_\nu(\mathbf{r}_j-\mathbf{R_n})\Big\}. \tag{3.2}$$

In a Mulliken-type treatment of four-index repulsion integrals each of both routes have to be passed through twice :

$$\begin{aligned}\text{(I)}\qquad \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{n}&\mathbf{t}&\mathbf{l}\\ \mu&\nu&\tau&\lambda\end{array}\right)^{[\mathrm{M}^{\mathrm{I}}_{\mu\nu}\mathrm{M}^{\mathrm{I}}_{\tau\lambda}]} &:= \frac{(\mathbf{S_{0n}})_{\mu\nu}}{2}\left\{\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{l}\\ \mu&\mu&\tau&\lambda\end{array}\right)^{[\mathrm{M}^{\mathrm{I}}_{\tau\lambda}]} + \left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{n}&\mathbf{t}&\mathbf{l}\\ \nu&\nu&\tau&\lambda\end{array}\right)^{[\mathrm{M}^{\mathrm{I}}_{\tau\lambda}]}\right\}\\ &:= \frac{(\mathbf{S_{0n}})_{\mu\nu}}{2}\frac{(\mathbf{S_{tl}})_{\tau\lambda}}{2}\left\{\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{t}\\ \mu&\mu&\tau&\tau\end{array}\right) + \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{l}&\mathbf{l}\\ \mu&\mu&\lambda&\lambda\end{array}\right) + \left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{n}&\mathbf{t}&\mathbf{t}\\ \nu&\nu&\tau&\tau\end{array}\right) + \left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{n}&\mathbf{l}&\mathbf{l}\\ \nu&\nu&\lambda&\lambda\end{array}\right)\right\},\end{aligned} \tag{3.3}$$

$$\begin{aligned}\text{(II)}\qquad \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{n}&\mathbf{t}&\mathbf{l}\\ \mu&\nu&\tau&\lambda\end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\mu\tau}\mathrm{M}^{\mathrm{II}}_{\nu\lambda}]} &:= \frac{(\mathbf{S_{mt}})_{\mu\tau}}{2}\left\{\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{n}&\mathbf{m}&\mathbf{l}\\ \mu&\nu&\mu&\lambda\end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\nu\lambda}]} + \left(\begin{array}{cc|cc}\mathbf{t}&\mathbf{n}&\mathbf{t}&\mathbf{l}\\ \tau&\nu&\tau&\lambda\end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\nu\lambda}]}\right\}\\ &:= \frac{(\mathbf{S_{mt}})_{\mu\tau}}{2}\frac{(\mathbf{S_{nl}})_{\nu\lambda}}{2}\left\{\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{n}&\mathbf{m}&\mathbf{n}\\ \mu&\nu&\mu&\nu\end{array}\right) + \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{l}&\mathbf{m}&\mathbf{l}\\ \mu&\lambda&\mu&\lambda\end{array}\right) + \left(\begin{array}{cc|cc}\mathbf{t}&\mathbf{n}&\mathbf{t}&\mathbf{n}\\ \tau&\nu&\tau&\nu\end{array}\right) + \left(\begin{array}{cc|cc}\mathbf{t}&\mathbf{l}&\mathbf{t}&\mathbf{l}\\ \tau&\lambda&\tau&\lambda\end{array}\right)\right\}.\end{aligned} \tag{3.4}$$

Having interchanged **n** and ν with **t** and τ, Eq. (3.4) equivalently reads :

$$\begin{aligned}\text{(II)}\qquad \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{t}&\mathbf{n}&\mathbf{l}\\ \mu&\tau&\nu&\lambda\end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\mu\nu}\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]} &:= \frac{(\mathbf{S_{0n}})_{\mu\nu}}{2}\left\{\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{t}&\mathbf{m}&\mathbf{l}\\ \mu&\tau&\mu&\lambda\end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]} + \left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{t}&\mathbf{n}&\mathbf{l}\\ \nu&\tau&\nu&\lambda\end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]}\right\}\\ &:= \frac{(\mathbf{S_{0n}})_{\mu\nu}}{2}\frac{(\mathbf{S_{tl}})_{\tau\lambda}}{2}\left\{\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{t}&\mathbf{m}&\mathbf{t}\\ \mu&\tau&\mu&\tau\end{array}\right) + \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{l}&\mathbf{m}&\mathbf{l}\\ \mu&\lambda&\mu&\lambda\end{array}\right) + \left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{t}&\mathbf{n}&\mathbf{t}\\ \nu&\tau&\nu&\tau\end{array}\right) + \left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{l}&\mathbf{n}&\mathbf{l}\\ \nu&\lambda&\nu&\lambda\end{array}\right)\right\}.\end{aligned} \tag{3.5}$$

In addition to these formulas, which are already contained in Rüdenberg's letter, let us consider the three-index repulsion integrals $\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{l}\\ \mu&\mu&\tau&\lambda\end{array}\right)$ and $\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{t}&\mathbf{m}&\mathbf{l}\\ \mu&\tau&\mu&\lambda\end{array}\right)$.

(I) Using two one-electron approximations of Mulliken type we get :

$$\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ \mu & \mu & \tau & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{I}}_{\mu\mu}\mathrm{M}^{\mathrm{I}}_{\tau\lambda}]} := \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ \mu & \mu & \tau & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{I}}_{\tau\lambda}]} := \frac{(\mathbf{S_{tl}})_{\tau\lambda}}{2}\left\{\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{t} \\ \mu & \mu & \tau & \tau \end{array}\right) + \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{l} & \mathbf{l} \\ \mu & \mu & \lambda & \lambda \end{array}\right)\right\}, \tag{3.6}$$

$$\begin{aligned} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ \mu & \tau & \mu & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{I}}_{\mu\tau}\mathrm{M}^{\mathrm{I}}_{\mu\lambda}]} &:= \frac{(\mathbf{S_{0t}})_{\mu\tau}}{2}\left\{\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{l} \\ \mu & \mu & \mu & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{I}}_{\mu\lambda}]} + \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ \tau & \tau & \mu & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{I}}_{\mu\lambda}]}\right\} \\ &:= \frac{(\mathbf{S_{0t}})_{\mu\tau}}{2}\frac{(\mathbf{S_{0l}})_{\mu\lambda}}{2}\left\{\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{m} \\ \mu & \mu & \mu & \mu \end{array}\right) + \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{l} & \mathbf{l} \\ \mu & \mu & \lambda & \lambda \end{array}\right) + \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{t} & \mathbf{m} & \mathbf{m} \\ \tau & \tau & \mu & \mu \end{array}\right) + \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{t} & \mathbf{l} & \mathbf{l} \\ \tau & \tau & \lambda & \lambda \end{array}\right)\right\}. \end{aligned} \tag{3.7}$$

(II) Using two two-electron approximations of Mulliken type we get :

$$\begin{aligned} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ \mu & \mu & \tau & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\mu\tau}\mathrm{M}^{\mathrm{II}}_{\mu\lambda}]} &:= \frac{(\mathbf{S_{0t}})_{\mu\tau}}{2}\left\{\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{l} \\ \mu & \mu & \mu & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\mu\lambda}]} + \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ \tau & \mu & \tau & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\mu\lambda}]}\right\} \\ &:= \frac{(\mathbf{S_{0t}})_{\mu\tau}}{2}\frac{(\mathbf{S_{0l}})_{\mu\lambda}}{2}\left\{\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{m} \\ \mu & \mu & \mu & \mu \end{array}\right) + \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{l} & \mathbf{m} & \mathbf{l} \\ \mu & \lambda & \mu & \lambda \end{array}\right) + \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{m} & \mathbf{t} & \mathbf{m} \\ \tau & \mu & \tau & \mu \end{array}\right) + \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{l} & \mathbf{t} & \mathbf{l} \\ \tau & \lambda & \tau & \lambda \end{array}\right)\right\}, \end{aligned} \tag{3.8}$$

$$\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ \mu & \tau & \mu & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\mu\mu}\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]} := \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ \mu & \tau & \mu & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]} := \frac{(\mathbf{S_{tl}})_{\tau\lambda}}{2}\left\{\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{t} \\ \mu & \tau & \mu & \tau \end{array}\right) + \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{l} & \mathbf{m} & \mathbf{l} \\ \mu & \lambda & \mu & \lambda \end{array}\right)\right\}. \tag{3.9}$$

Hence, applying Mulliken's approximation twice implies an oversimplification of the two-index integral $\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{l} \\ \mu & \mu & \mu & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{I}}_{\mu\lambda}]}$ in Eq. (3.7) and of $\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{l} \\ \mu & \mu & \mu & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{II}}_{\mu\lambda}]}$ in Eq. (3.8). Obviously, the formulations of Eqs. (3.6) and (3.9) should be preferred, because Mulliken's simplifying recipe there has been used only once. While the oversimplifying "unrestricted" branch of approximation has been discussed comprehensively elsewhere [9], we now turn to the corresponding "restricted" route which avoids such shortcomings.

3.2. "Restricted and Combined Mulliken" approximations (M.R&C) for Fock-matrix elements

The term ' "Restricted and Combined Mulliken" approximations (M.R&C) ' indicates,

- that both one-electron and two-electron routes of approximation are combined in the sense outlined in Ref. 9, and
- that in this subsection we are going to distinguish four-index and three-index interactions from one another and those of two-index or one-index type. All different types of three-index integrals occuring in Eqs. (2.24) . . . (2.32) will be treated in such a way, that oversimplifications are avoided by applying Mulliken's approximations only once. Furthermore, this time all one- and two-index interactions are considered to be evaluated accurately.

Distinguishing off-diagonal from diagonal matrix elements, we define according to Eq. (2.21) :

$$\underbrace{(\mathbf{F}^{\alpha}_{\mathbf{0n}})^{[\mathrm{M.R\&C}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := (\mathbf{K_{0n}})_{\mu\nu} + (\mathbf{F}^{A}_{\mathbf{0n}})^{[\mathrm{M.R\&C}]}_{\mu\nu} + (\mathbf{F}^{C}_{\mathbf{0n}})^{[\mathrm{M.R\&C}]}_{\mu\nu} - (\mathbf{F}^{\alpha E}_{\mathbf{0n}})^{[\mathrm{M.R\&C}]}_{\mu\nu}, \tag{3.10}$$

$$(\mathbf{F}^{\alpha}_{\mathbf{00}})^{[\mathrm{M.R\&C}]}_{\mu\mu} := (\mathbf{K}_{\mathbf{00}})_{\mu\mu} + (\mathbf{F}^{A}_{\mathbf{00}})_{\mu\mu} + (\mathbf{F}^{C}_{\mathbf{00}})^{[\mathrm{M.R\&C}]}_{\mu\mu} - (\mathbf{F}^{\alpha E}_{\mathbf{00}})^{[\mathrm{M.R\&C}]}_{\mu\mu}. \tag{3.11}$$

For the off-diagonal attractive part we define according to the Eqs. (2.24) and (2.25), respectively :

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{0n}})^{[\mathrm{M.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := ({}^{(0)}\mathbf{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + ({}^{(1)}\mathbf{A}_{\mathbf{0n}})^{[\mathrm{M^I}]}_{(M,\mu)(N,\nu)}. \tag{3.12}$$

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{00}})^{[\mathrm{M.R\&C}]}_{(M,\mu)(M,\nu)}}_{\nu\neq\mu} := ({}^{(0)}\mathbf{A}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + ({}^{(1)}\mathbf{A}_{\mathbf{00}})^{[\mathrm{M^I}]}_{(M,\mu)(M,\nu)}. \tag{3.13}$$

For the off-diagonal Coulomb part we define according to Eq. (2.27) :

$$\begin{aligned}\underbrace{(\mathbf{F}^{C}_{\mathbf{0n}})^{[\mathrm{M.R\&C}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} &:= ({}^{(0)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu} + ({}^{(1)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{M^IM^I}]}_{\mu\nu} + ({}^{(2)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{M^I}]}_{\mu\nu} \\ &+ 2({}^{(3)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{M^{II}}]}_{\mu\nu} + 2({}^{(4)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{M^{II}}]}_{\mu\nu}.\end{aligned} \tag{3.14}$$

For the diagonal Coulomb part we define according to Eq. (2.29) :

$$(\mathbf{F}^{C}_{\mathbf{00}})^{[\mathrm{M.R\&C}]}_{\mu\mu} := ({}^{(0)}\mathbf{C}_{\mathbf{00}})_{\mu\mu} + ({}^{(1)}\mathbf{C}_{\mathbf{00}})^{[\mathrm{M^I}]}_{\mu\mu} + ({}^{(2)}\mathbf{C}_{\mathbf{00}})_{\mu\mu} + 2({}^{(3)}\mathbf{C}_{\mathbf{00}})_{\mu\mu}. \tag{3.15}$$

For the off-diagonal exchange part we define according to Eq. (2.30) :

$$\begin{aligned}\underbrace{(\mathbf{F}^{\alpha E}_{\mathbf{0n}})^{[\mathrm{M.R\&C}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} &:= ({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu} + ({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{M^{II}M^{II}}]}_{\mu\nu} + ({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{M^{II}}]}_{\mu\nu} \\ &+ ({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{M^{II}}]}_{\mu\nu} + ({}^{(4)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{M^{I}}]}_{\mu\nu} + ({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{M^{I}}]}_{\mu\nu} + ({}^{(6)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{M^{II}}]}_{\mu\nu}.\end{aligned} \tag{3.16}$$

For the diagonal exchange part we define according to Eq. (2.32) :

$$(\mathbf{F}^{\alpha E}_{\mathbf{00}})^{[\mathrm{M.R\&C}]}_{\mu\mu} := ({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu} + ({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{00}})^{[\mathrm{M^{II}}]}_{\mu\mu} + ({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu} + 2({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu}. \tag{3.17}$$

Using again the notations
$\mathbf{n}\nu \neq \mathbf{0}\mu \equiv (\mathbf{n} \neq \mathbf{0}) \vee (\nu \neq \mu)$ and $\mathbf{n}N \neq \mathbf{0}M \equiv (\mathbf{n} \neq \mathbf{0}) \vee (N \neq M)$,
the different quantities occuring in Eqs. (3.12) ... (3.17) are defined as follows [15] :

$$\begin{aligned}\underbrace{({}^{(1)}\mathbf{A}_{\mathbf{0n}})^{[\mathrm{M^I}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu \end{pmatrix} \times \frac{1}{2}\Bigg\{ &\underbrace{\underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n}}_{\mathbf{p}P\neq\mathbf{0}M,\mathbf{n}N} \begin{pmatrix} \mathbf{0} & \mathbf{p} & \mathbf{0} \\ M & P & M \\ \mu & & \mu \end{pmatrix}}_{\stackrel{\mathrm{def}}{=}({}^{(1.1)}\mathbf{A}_{\mathbf{0n}})_{(M,\mu,\mu)(N)}} \\ &+ \underbrace{\underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n}}_{\mathbf{p}P\neq\mathbf{0}M,\mathbf{n}N} \begin{pmatrix} \mathbf{n} & \mathbf{p} & \mathbf{n} \\ N & P & N \\ \nu & & \nu \end{pmatrix}}_{\stackrel{\mathrm{def}}{=}({}^{(1.2)}\mathbf{A}_{\mathbf{0n}})_{(M)(N,\nu,\nu)}} \Bigg\},\end{aligned} \tag{3.18}$$

with

$$\underbrace{\left({}^{(1.1)}\mathbf{A}_{\mathbf{0n}}\right)_{(M,\mu,\mu)(N)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{P=1}^{N_n}\begin{pmatrix}\mathbf{0} & & \mathbf{0}\\ & \mathbf{p} & \\ M & & M\\ \mu & P & \mu\end{pmatrix}}_{=(\mathbf{F}^A_{\mathbf{00}})_{(M,\mu)(M,\mu)}} - \begin{pmatrix}\mathbf{0} & & \mathbf{0}\\ & \mathbf{0} & \\ M & & M\\ \mu & M & \mu\end{pmatrix} - \begin{pmatrix}\mathbf{0} & & \mathbf{0}\\ & \mathbf{n} & \\ M & & M\\ \mu & N & \mu\end{pmatrix}, \tag{3.19}$$

and

$$\underbrace{\left({}^{(1.2)}\mathbf{A}_{\mathbf{0n}}\right)_{(M)(N,\nu,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{P=1}^{N_n}\begin{pmatrix}\mathbf{0} & & \mathbf{0}\\ & \mathbf{p} & \\ N & & N\\ \nu & P & \nu\end{pmatrix}}_{=(\mathbf{F}^A_{\mathbf{00}})_{(N,\nu)(N,\nu)}} - \begin{pmatrix}\mathbf{n} & & \mathbf{n}\\ & \mathbf{0} & \\ N & & N\\ \nu & M & \nu\end{pmatrix} - \begin{pmatrix}\mathbf{0} & & \mathbf{0}\\ & \mathbf{0} & \\ N & & N\\ \nu & N & \nu\end{pmatrix}. \tag{3.20}$$

$$\underbrace{\left({}^{(1)}\mathbf{A}_{\mathbf{00}}\right)^{[\mathrm{M}^\mathrm{I}]}_{(M,\mu)(M,\nu)}}_{\nu\neq\mu} := 0. \tag{3.21}$$

$$\begin{aligned}\underbrace{\left({}^{(1)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{M}^\mathrm{I}\mathrm{M}^\mathrm{I}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := (\mathbf{S}_{\mathbf{0n}})_{\mu\nu} \times \frac{1}{2}\Bigg\{ & \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu,\mathbf{t}\tau}(\mathbf{P}^{\oplus}_{\mathbf{tl}})_{\tau\lambda}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{l}\\ \mu & \mu & \tau & \lambda\end{array}\right)^{[\mathrm{M}^\mathrm{I}_{\tau\lambda}]}}_{\stackrel{\mathrm{def}}{=}\left({}^{(1.1)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{M}^\mathrm{I}]}_{\mu\mu}} \\ & + \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu,\mathbf{t}\tau}(\mathbf{P}^{\oplus}_{\mathbf{tl}})_{\tau\lambda}\left(\begin{array}{cc|cc}\mathbf{n} & \mathbf{n} & \mathbf{t} & \mathbf{l}\\ \nu & \nu & \tau & \lambda\end{array}\right)^{[\mathrm{M}^\mathrm{I}_{\tau\lambda}]}}_{\stackrel{\mathrm{def}}{=}\left({}^{(1.2)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{M}^\mathrm{I}]}_{\nu\nu}}\Bigg\},\end{aligned} \tag{3.22}$$

with

$$\begin{aligned}\underbrace{\left({}^{(1.1)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{M}^\mathrm{I}]}_{\mu\mu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} &:= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu,\mathbf{t}\tau}(\mathbf{P}^{\oplus}_{\mathbf{tl}})_{\tau\lambda}(\mathbf{S}_{\mathbf{tl}})_{\tau\lambda} \times \frac{1}{2}\left\{\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t}\\ \mu & \mu & \tau & \tau\end{array}\right) + \left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{l} & \mathbf{l}\\ \mu & \mu & \lambda & \lambda\end{array}\right)\right\} \\ &= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t}\\ \mu & \mu & \tau & \tau\end{array}\right)\left\{((\mathbf{P}^{\oplus}\mathbf{S})_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\nu\tau}(\mathbf{S}_{\mathbf{0t}})_{\nu\tau} - (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau}\right\} \\ &\quad - \left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ \mu & \mu & \nu & \nu\end{array}\right)\left\{((\mathbf{P}^{\oplus}\mathbf{S})_{\mathbf{00}})_{\nu\nu} - 2(\mathbf{P}^{\oplus}_{\mathbf{00}})_{\nu\nu} - (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{\mu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}\right\} \\ &\quad - \left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ \mu & \mu & \mu & \mu\end{array}\right)\left\{(\mathbf{P}^{\oplus}_{\mathbf{00}})_{\mu\nu}(\mathbf{S}_{\mathbf{00}})_{\mu\nu} - (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{\mu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}\right\}.\end{aligned} \tag{3.23}$$

and

$$\underbrace{({}^{(1.2)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{M^I}]}_{\nu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu,\mathbf{t}\tau} (\mathbf{P}^{\oplus}_{\mathbf{tl}})_{\tau\lambda}(\mathbf{S}_{\mathbf{tl}})_{\tau\lambda} \times \frac{1}{2}\left\{\begin{pmatrix}\mathbf{n}\,\mathbf{n} & \mathbf{t}\,\mathbf{t}\\ \nu\,\nu & \tau\,\tau\end{pmatrix} + \begin{pmatrix}\mathbf{n}\,\mathbf{n} & \mathbf{l}\,\mathbf{l}\\ \nu\,\nu & \lambda\,\lambda\end{pmatrix}\right\}$$

$$= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\nu} \begin{pmatrix}\mathbf{0}\,\mathbf{0} & \mathbf{t}\,\mathbf{t}\\ \nu\,\nu & \tau\,\tau\end{pmatrix} \left\{((\mathbf{P}^{\oplus}\mathbf{S})_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\tau\nu}(\mathbf{S}_{\mathbf{0t}})_{\tau\nu} - (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau}\right\}$$
$$- \begin{pmatrix}\mathbf{n}\,\mathbf{n} & \mathbf{0}\,\mathbf{0}\\ \nu\,\nu & \mu\,\mu\end{pmatrix} \left\{((\mathbf{P}^{\oplus}\mathbf{S})_{\mathbf{00}})_{\mu\mu} - 2(\mathbf{P}^{\oplus}_{\mathbf{00}})_{\mu\mu} - (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{\mu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}\right\}$$
$$- \begin{pmatrix}\mathbf{0}\,\mathbf{0} & \mathbf{0}\,\mathbf{0}\\ \nu\,\nu & \mu\,\mu\end{pmatrix} \left\{(\mathbf{P}^{\oplus}_{\mathbf{00}})_{\mu\nu}(\mathbf{S}_{\mathbf{00}})_{\mu\nu} - (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{\mu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}\right\}. \tag{3.24}$$

$$({}^{(1)}\mathbf{C}_{\mathbf{00}})^{[\mathrm{M^I}]}_{\mu\mu} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{t}\tau} (\mathbf{P}^{\oplus}_{\mathbf{tl}})_{\tau\lambda}(\mathbf{S}_{\mathbf{tl}})_{\tau\lambda} \times \frac{1}{2}\left\{\begin{pmatrix}\mathbf{0}\,\mathbf{0} & \mathbf{t}\,\mathbf{t}\\ \mu\,\mu & \tau\,\tau\end{pmatrix} + \begin{pmatrix}\mathbf{0}\,\mathbf{0} & \mathbf{l}\,\mathbf{l}\\ \mu\,\mu & \lambda\,\lambda\end{pmatrix}\right\}$$

$$= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu} \begin{pmatrix}\mathbf{0}\,\mathbf{0} & \mathbf{t}\,\mathbf{t}\\ \mu\,\mu & \tau\,\tau\end{pmatrix} \left\{((\mathbf{P}^{\oplus}\mathbf{S})_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau}\right\}. \tag{3.25}$$

$$\underbrace{({}^{(2)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{M^I}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := (\mathbf{S}_{\mathbf{0n}})_{\mu\nu} \times \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\tau\tau} \begin{pmatrix}\mathbf{0}\,\mathbf{0} & \mathbf{t}\,\mathbf{t}\\ \mu\,\mu & \tau\,\tau\end{pmatrix}}_{\stackrel{\mathrm{def}}{=}({}^{(2.1)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu}}$$
$$+ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\tau\tau} \begin{pmatrix}\mathbf{n}\,\mathbf{n} & \mathbf{t}\,\mathbf{t}\\ \nu\,\nu & \tau\,\tau\end{pmatrix}}_{\stackrel{\mathrm{def}}{=}({}^{(2.2)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu}} \Bigg\}, \tag{3.26}$$

with

$$\underbrace{({}^{(2.1)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\tau\tau} \begin{pmatrix}\mathbf{0}\,\mathbf{0} & \mathbf{t}\,\mathbf{t}\\ \mu\,\mu & \tau\,\tau\end{pmatrix} - (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\nu\nu} \begin{pmatrix}\mathbf{0}\,\mathbf{0} & \mathbf{n}\,\mathbf{n}\\ \mu\,\mu & \nu\,\nu\end{pmatrix}, \tag{3.27}$$

and

$$\underbrace{\left({}^{(2.2)}\mathbf{C}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\nu} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\tau\tau} \begin{pmatrix} \mathbf{0}\ \mathbf{0} & \mathbf{t}\ \mathbf{t} \\ \nu\ \nu & \tau\ \tau \end{pmatrix} - (\mathbf{P}^{\oplus}_{\mathbf{00}})_{\nu\nu} \begin{pmatrix} \mathbf{0}\ \mathbf{0} & \mathbf{0}\ \mathbf{0} \\ \nu\ \nu & \nu\ \nu \end{pmatrix}. \tag{3.28}$$

$$\begin{aligned} \underbrace{\left({}^{(3)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{M^{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := \frac{1}{2}\Bigg\{ & \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{nt}})_{\nu\tau} \begin{pmatrix} \mathbf{0}\ \mathbf{n} & \mathbf{n}\ \mathbf{0} \\ \mu\ \nu & \nu\ \mu \end{pmatrix}}_{\stackrel{\mathrm{def}}{=}\left({}^{(3.1)}\mathbf{C}_{\mathbf{0n}}\right)_{\mu\nu}} \\ & + \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{nt}})_{\nu\tau} \begin{pmatrix} \mathbf{0}\ \mathbf{t} & \mathbf{t}\ \mathbf{0} \\ \mu\ \tau & \tau\ \mu \end{pmatrix}}_{\stackrel{\mathrm{def}}{=}\left({}^{(3.2)}\mathbf{C}_{\mathbf{0n}}\right)_{\mu\nu}} \Bigg\}, \end{aligned} \tag{3.29}$$

with

$$\begin{aligned} \underbrace{\left({}^{(3.1)}\mathbf{C}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o} & (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{0t}})_{\nu\tau} \begin{pmatrix} \mathbf{0}\ \mathbf{n} & \mathbf{n}\ \mathbf{0} \\ \mu\ \nu & \nu\ \mu \end{pmatrix} \\ & -(\mathbf{P}^{\oplus}_{\mathbf{0n}})_{\mu\nu} \begin{pmatrix} \mathbf{0}\ \mathbf{n} & \mathbf{n}\ \mathbf{0} \\ \mu\ \nu & \nu\ \mu \end{pmatrix} \\ & -(\mathbf{P}^{\oplus}_{\mathbf{00}})_{\mu\mu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu} \begin{pmatrix} \mathbf{0}\ \mathbf{n} & \mathbf{n}\ \mathbf{0} \\ \mu\ \nu & \nu\ \mu \end{pmatrix}, \end{aligned} \tag{3.30}$$

and

$$\begin{aligned} \underbrace{\left({}^{(3.2)}\mathbf{C}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu} & (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{0t}})_{\nu\tau} \begin{pmatrix} \mathbf{0}\ \mathbf{t} & \mathbf{t}\ \mathbf{0} \\ \mu\ \tau & \tau\ \mu \end{pmatrix} \\ & -(\mathbf{P}^{\oplus}_{\mathbf{0n}})_{\mu\nu} \begin{pmatrix} \mathbf{0}\ \mathbf{n} & \mathbf{n}\ \mathbf{0} \\ \mu\ \nu & \nu\ \mu \end{pmatrix} \\ -(\mathbf{P}^{\oplus}_{\mathbf{00}})_{\mu\mu}\Big\{(\mathbf{S}_{\mathbf{0n}})_{\mu\nu} - (\mathbf{S}_{\mathbf{00}})_{\mu\nu}\Big\} & \begin{pmatrix} \mathbf{0}\ \mathbf{0} & \mathbf{0}\ \mathbf{0} \\ \mu\ \mu & \mu\ \mu \end{pmatrix}. \end{aligned} \tag{3.31}$$

$$
\underbrace{\left({}^{(4)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{M}^{\mathrm{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\oplus}_{\mathbf{tn}})_{\tau\nu}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau} \left(\begin{matrix}\mathbf{0}\ \mathbf{n}\\ \mu\ \nu\end{matrix}\middle|\begin{matrix}\mathbf{0}\ \mathbf{n}\\ \mu\ \nu\end{matrix}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(4.1)}\mathbf{C}_{\mathbf{0n}}\right)_{\mu\nu}}
$$

$$
+ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\oplus}_{\mathbf{tn}})_{\tau\nu}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau} \left(\begin{matrix}\mathbf{t}\ \mathbf{n}\\ \tau\ \nu\end{matrix}\middle|\begin{matrix}\mathbf{t}\ \mathbf{n}\\ \tau\ \nu\end{matrix}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(4.2)}\mathbf{C}_{\mathbf{0n}}\right)_{\mu\nu}} \Bigg\}, \tag{3.32}
$$

with

$$
\underbrace{\left({}^{(4.1)}\mathbf{C}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o} (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\nu\tau}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau} \left(\begin{matrix}\mathbf{0}\ \mathbf{n}\\ \mu\ \nu\end{matrix}\middle|\begin{matrix}\mathbf{0}\ \mathbf{n}\\ \mu\ \nu\end{matrix}\right)
$$

$$
-(\mathbf{P}^{\oplus}_{\mathbf{00}})_{\nu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu} \left(\begin{matrix}\mathbf{0}\ \mathbf{n}\\ \mu\ \nu\end{matrix}\middle|\begin{matrix}\mathbf{0}\ \mathbf{n}\\ \mu\ \nu\end{matrix}\right) \tag{3.33}
$$

$$
-(\mathbf{P}^{\oplus}_{\mathbf{0n}})_{\mu\nu} \left(\begin{matrix}\mathbf{0}\ \mathbf{n}\\ \mu\ \nu\end{matrix}\middle|\begin{matrix}\mathbf{0}\ \mathbf{n}\\ \mu\ \nu\end{matrix}\right),
$$

and

$$
\underbrace{\left({}^{(4.2)}\mathbf{C}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\nu} (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{\nu\tau}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau} \left(\begin{matrix}\mathbf{t}\ \mathbf{0}\\ \tau\ \nu\end{matrix}\middle|\begin{matrix}\mathbf{t}\ \mathbf{0}\\ \tau\ \nu\end{matrix}\right)
$$

$$
-(\mathbf{P}^{\oplus}_{\mathbf{00}})_{\nu\nu}\left\{(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}-1\right\} \left(\begin{matrix}\mathbf{0}\ \mathbf{0}\\ \nu\ \nu\end{matrix}\middle|\begin{matrix}\mathbf{0}\ \mathbf{0}\\ \nu\ \nu\end{matrix}\right) \tag{3.34}
$$

$$
-(\mathbf{P}^{\oplus}_{\mathbf{0n}})_{\mu\nu} \left(\begin{matrix}\mathbf{0}\ \mathbf{n}\\ \mu\ \nu\end{matrix}\middle|\begin{matrix}\mathbf{0}\ \mathbf{n}\\ \mu\ \nu\end{matrix}\right).
$$

$$
\underbrace{\left({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{M}^{\mathrm{II}}\mathrm{M}^{\mathrm{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := (\mathbf{S}_{\mathbf{0n}})_{\mu\nu}\times\frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu,\mathbf{t}\tau} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{\tau\lambda} \left(\begin{matrix}\mathbf{0}\ \mathbf{t}\\ \mu\ \tau\end{matrix}\middle|\begin{matrix}\mathbf{0}\ \mathbf{l}\\ \mu\ \lambda\end{matrix}\right)^{[\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]}}_{\stackrel{\mathrm{def}}{=}\left({}^{(1.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{M}^{\mathrm{II}}]}_{\mu\mu}}
$$

$$
+ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu,\mathbf{t}\tau} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{\tau\lambda} \left(\begin{matrix}\mathbf{n}\ \mathbf{t}\\ \nu\ \tau\end{matrix}\middle|\begin{matrix}\mathbf{n}\ \mathbf{l}\\ \nu\ \lambda\end{matrix}\right)^{[\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]}}_{\stackrel{\mathrm{def}}{=}\left({}^{(1.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{M}^{\mathrm{II}}]}_{\nu\nu}} \Bigg\}, \tag{3.35}
$$

with

$$\underbrace{\left({}^{(1.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{M^{II}}]}_{\mu\mu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu,\mathbf{t}\tau} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{\tau\lambda}(\mathbf{S}_{\mathbf{tl}})_{\tau\lambda} \times \frac{1}{2}\left\{\begin{pmatrix}\mathbf{0}\ \mathbf{t} & \mathbf{0}\ \mathbf{t}\\ \mu\ \tau & \mu\ \tau\end{pmatrix} + \begin{pmatrix}\mathbf{0}\ \mathbf{l} & \mathbf{0}\ \mathbf{l}\\ \mu\ \lambda & \mu\ \lambda\end{pmatrix}\right\}$$

$$= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu} \begin{pmatrix}\mathbf{0}\ \mathbf{t} & \mathbf{0}\ \mathbf{t}\\ \mu\ \tau & \mu\ \tau\end{pmatrix} \left\{((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\nu\tau}(\mathbf{S}_{\mathbf{0t}})_{\nu\tau} - (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau}\right\}$$
$$- \begin{pmatrix}\mathbf{0}\ \mathbf{n} & \mathbf{0}\ \mathbf{n}\\ \mu\ \nu & \mu\ \nu\end{pmatrix} \left\{((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{\nu\nu} - 2(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\nu\nu} - (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}\right\}$$
$$- \begin{pmatrix}\mathbf{0}\ \mathbf{0} & \mathbf{0}\ \mathbf{0}\\ \mu\ \mu & \mu\ \mu\end{pmatrix} \left\{(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\mu\nu}(\mathbf{S}_{\mathbf{00}})_{\mu\nu} - (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}\right\}. \tag{3.36}$$

and

$$\underbrace{\left({}^{(1.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{M^{II}}]}_{\nu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu,\mathbf{t}\tau} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{\tau\lambda}(\mathbf{S}_{\mathbf{tl}})_{\tau\lambda} \times \frac{1}{2}\left\{\begin{pmatrix}\mathbf{n}\ \mathbf{t} & \mathbf{n}\ \mathbf{t}\\ \nu\ \tau & \nu\ \tau\end{pmatrix} + \begin{pmatrix}\mathbf{n}\ \mathbf{l} & \mathbf{n}\ \mathbf{l}\\ \nu\ \lambda & \nu\ \lambda\end{pmatrix}\right\}$$

$$= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\nu} \begin{pmatrix}\mathbf{0}\ \mathbf{t} & \mathbf{0}\ \mathbf{t}\\ \nu\ \tau & \nu\ \tau\end{pmatrix} \left\{((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\tau\nu}(\mathbf{S}_{\mathbf{0t}})_{\tau\nu} - (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau}\right\}$$
$$- \begin{pmatrix}\mathbf{n}\ \mathbf{0} & \mathbf{n}\ \mathbf{0}\\ \nu\ \mu & \nu\ \mu\end{pmatrix} \left\{((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{\mu\mu} - 2(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\mu\mu} - (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}\right\}$$
$$- \begin{pmatrix}\mathbf{0}\ \mathbf{0} & \mathbf{0}\ \mathbf{0}\\ \nu\ \mu & \nu\ \mu\end{pmatrix} \left\{(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\mu\nu}(\mathbf{S}_{\mathbf{00}})_{\mu\nu} - (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}\right\}. \tag{3.37}$$

$$\left({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{00}}\right)^{[\mathrm{M^{II}}]}_{\mu\mu} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{t}\tau} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{\tau\lambda}(\mathbf{S}_{\mathbf{tl}})_{\tau\lambda} \times \frac{1}{2}\left\{\begin{pmatrix}\mathbf{0}\ \mathbf{t} & \mathbf{0}\ \mathbf{t}\\ \mu\ \tau & \mu\ \tau\end{pmatrix} + \begin{pmatrix}\mathbf{0}\ \mathbf{l} & \mathbf{0}\ \mathbf{l}\\ \mu\ \lambda & \mu\ \lambda\end{pmatrix}\right\}$$

$$= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu} \begin{pmatrix}\mathbf{0}\ \mathbf{t} & \mathbf{0}\ \mathbf{t}\\ \mu\ \tau & \mu\ \tau\end{pmatrix} \left\{((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\tau\tau} - (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau}\right\}. \tag{3.38}$$

$$\underbrace{\left({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{M}^{\mathrm{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := (\mathbf{S_{0n}})_{\mu\nu}\times\frac{1}{2}\Bigg\{\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\tau\tau}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{0}&\mathbf{t}\\ \mu&\tau&\mu&\tau\end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(2.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}$$
$$+\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\tau\tau}\left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{t}&\mathbf{n}&\mathbf{t}\\ \nu&\tau&\nu&\tau\end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(2.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}\Bigg\}, \tag{3.39}$$

with

$$\underbrace{\left({}^{(2.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu}(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\tau\tau}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{0}&\mathbf{t}\\ \mu&\tau&\mu&\tau\end{array}\right) - (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\nu\nu}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{0}&\mathbf{n}\\ \mu&\nu&\mu&\nu\end{array}\right), \tag{3.40}$$

and

$$\underbrace{\left({}^{(2.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\nu}(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\tau\tau}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{0}&\mathbf{t}\\ \nu&\tau&\nu&\tau\end{array}\right) - (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\nu\nu}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{0}&\mathbf{0}\\ \nu&\nu&\nu&\nu\end{array}\right). \tag{3.41}$$

$$\underbrace{\left({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{M}^{\mathrm{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := \frac{1}{2}\Bigg\{\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}(\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S_{nt}})_{\nu\tau}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ \mu&\nu&\nu&\mu\end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(3.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}$$
$$+\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}(\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S_{nt}})_{\nu\tau}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{t}&\mathbf{0}\\ \mu&\tau&\tau&\mu\end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(3.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}\Bigg\}, \tag{3.42}$$

with

$$\begin{aligned}\underbrace{\left({}^{(3.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = &\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}(\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S_{0t}})_{\nu\tau}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ \mu&\nu&\nu&\mu\end{array}\right)\\ &-(\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ \mu&\nu&\nu&\mu\end{array}\right)\\ &-(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\mu\mu}(\mathbf{S_{0n}})_{\mu\nu}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ \mu&\nu&\nu&\mu\end{array}\right),\end{aligned} \tag{3.43}$$

and

$$\underbrace{\left({}^{(3.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu}(\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\mu\tau}(\mathbf{S}_{\mathbf{0t}})_{\nu\tau}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{t} & \mathbf{t} & \mathbf{0}\\ \mu & \tau & \tau & \mu\end{array}\right) - (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0}\\ \mu & \nu & \nu & \mu\end{array}\right) - (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\mu\mu}\left\{(\mathbf{S}_{\mathbf{0n}})_{\mu\nu} - (\mathbf{S}_{\mathbf{00}})_{\mu\nu}\right\}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ \mu & \mu & \mu & \mu\end{array}\right). \tag{3.44}$$

$$\underbrace{\left({}^{(4)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{M^I}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}(\mathbf{P}^{\alpha}_{\mathbf{tn}})_{\tau\nu}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ \mu & \mu & \nu & \nu\end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(4.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}} + \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\mu,\mathbf{n}\nu}(\mathbf{P}^{\alpha}_{\mathbf{tn}})_{\tau\nu}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau}\left(\begin{array}{cc|cc}\mathbf{t} & \mathbf{t} & \mathbf{n} & \mathbf{n}\\ \tau & \tau & \nu & \nu\end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(4.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}\Bigg\}, \tag{3.45}$$

with

$$\underbrace{\left({}^{(4.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}(\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\nu\tau}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ \mu & \mu & \nu & \nu\end{array}\right) - (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\nu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ \mu & \mu & \nu & \nu\end{array}\right) - (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ \mu & \mu & \nu & \nu\end{array}\right), \tag{3.46}$$

and

$$\underbrace{\left({}^{(4.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\tau=1}^{N_o}}_{\mathbf{t}\tau\neq\mathbf{0}\nu}(\mathbf{P}^{\alpha}_{\mathbf{0t}})_{\nu\tau}(\mathbf{S}_{\mathbf{0t}})_{\mu\tau}\left(\begin{array}{cc|cc}\mathbf{t} & \mathbf{t} & \mathbf{0} & \mathbf{0}\\ \tau & \tau & \nu & \nu\end{array}\right) - (\mathbf{P}^{\alpha}_{\mathbf{00}})_{\nu\nu}\left\{(\mathbf{S}_{\mathbf{0n}})_{\mu\nu} - 1\right\}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ \nu & \nu & \nu & \nu\end{array}\right) - (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ \mu & \mu & \nu & \nu\end{array}\right). \tag{3.47}$$

$$\underbrace{\left({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{M}^{\mathrm{I}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\alpha}_{\mathbf{0l}})_{\mu\lambda}(\mathbf{S}_{\mathbf{nl}})_{\nu\lambda} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ \mu & \mu & \nu & \nu \end{array}\right)}_{\stackrel{\text{def}}{=}\left({}^{(5.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}$$
$$+ \underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\alpha}_{\mathbf{0l}})_{\mu\lambda}(\mathbf{S}_{\mathbf{nl}})_{\nu\lambda} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{l} & \mathbf{l} \\ \mu & \mu & \lambda & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}\left({}^{(5.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}} \Bigg\}, \tag{3.48}$$

with

$$\underbrace{\left({}^{(5.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o} (\mathbf{P}^{\alpha}_{\mathbf{0l}})_{\mu\lambda}(\mathbf{S}_{\mathbf{0l}})_{\nu\lambda} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ \mu & \mu & \nu & \nu \end{array}\right)$$
$$-(\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ \mu & \mu & \nu & \nu \end{array}\right) \tag{3.49}$$
$$-(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\mu\mu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ \mu & \mu & \nu & \nu \end{array}\right),$$

and

$$\underbrace{\left({}^{(5.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu} (\mathbf{P}^{\alpha}_{\mathbf{0l}})_{\mu\lambda}(\mathbf{S}_{\mathbf{0l}})_{\nu\lambda} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{l} & \mathbf{l} \\ \mu & \mu & \lambda & \lambda \end{array}\right)$$
$$-(\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ \mu & \mu & \nu & \nu \end{array}\right) \tag{3.50}$$
$$-(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\mu\mu}\left\{(\mathbf{S}_{\mathbf{0n}})_{\mu\nu} - (\mathbf{S}_{\mathbf{00}})_{\mu\nu}\right\} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mu & \mu & \mu & \mu \end{array}\right).$$

$$\underbrace{\left({}^{(6)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{M}^{\mathrm{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\alpha}_{\mathbf{nl}})_{\nu\lambda}(\mathbf{S}_{\mathbf{0l}})_{\mu\lambda} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0} \\ \mu & \nu & \nu & \mu \end{array}\right)}_{\stackrel{\text{def}}{=}\left({}^{(6.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}$$
$$+ \underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\mu,\mathbf{n}\nu} (\mathbf{P}^{\alpha}_{\mathbf{nl}})_{\nu\lambda}(\mathbf{S}_{\mathbf{0l}})_{\mu\lambda} \left(\begin{array}{cc|cc} \mathbf{l} & \mathbf{n} & \mathbf{n} & \mathbf{l} \\ \lambda & \nu & \nu & \lambda \end{array}\right)}_{\stackrel{\text{def}}{=}\left({}^{(6.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}} \Bigg\}, \tag{3.51}$$

with

$$\underbrace{\left({}^{(6.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o} (\mathbf{P}^{\alpha}_{\mathbf{0l}})_{\nu\lambda}(\mathbf{S}_{\mathbf{0l}})_{\mu\lambda} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0} \\ \mu & \nu & \nu & \mu \end{array}\right)$$
$$-(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\nu\nu}(\mathbf{S}_{\mathbf{0n}})_{\mu\nu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0} \\ \mu & \nu & \nu & \mu \end{array}\right) \tag{3.52}$$
$$-(\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0} \\ \mu & \nu & \nu & \mu \end{array}\right),$$

and

$$\underbrace{\left({}^{(6.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{\lambda=1}^{N_o}}_{\mathbf{l}\lambda\neq\mathbf{0}\nu} (\mathbf{P}^{\alpha}_{\mathbf{0l}})_{\nu\lambda}(\mathbf{S}_{\mathbf{0l}})_{\mu\lambda} \left(\begin{array}{cc|cc} \mathbf{l} & \mathbf{0} & \mathbf{0} & \mathbf{l} \\ \lambda & \nu & \nu & \lambda \end{array}\right)$$
$$-(\mathbf{P}^{\alpha}_{\mathbf{00}})_{\nu\nu}\left\{(\mathbf{S}_{\mathbf{0n}})_{\mu\nu} - (\mathbf{S}_{\mathbf{00}})_{\mu\nu}\right\} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \nu & \nu & \nu & \nu \end{array}\right) \tag{3.53}$$
$$-(\mathbf{P}^{\alpha}_{\mathbf{0n}})_{\mu\nu} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0} \\ \mu & \nu & \nu & \mu \end{array}\right).$$

4. Approximations of ZIO type

4.1. "Unrestricted" and "Restricted" integral approximations

If one assumes the atomic orbital basis as being not only locally but globally orthonormal, all overlap integrals occuring in the context of Mulliken-type approximations have to be substituted by the corresponding Kronecker symbol ("Zero Integral Overlap", ZIO). What follows is partially identical with the "Zero Differential Overlap" description (ZDO) originally introduced by Parr [3] for an approximate treatment of two-index one-electron densities :

$$\text{(I)} \quad \{\Phi_\mu(\mathbf{r}_i-\mathbf{R_m})\Phi_\nu(\mathbf{r}_i-\mathbf{R_n})\}^{[\mathrm{ZIO}^{\mathrm{I}}_{\mu\nu}]} := \{\Phi_\mu(\mathbf{r}_i-\mathbf{R_m})\Phi_\nu(\mathbf{r}_i-\mathbf{R_n})\}^{[\mathrm{ZDO}_{\mu\nu}]} := \delta_{\mathbf{mn}}\delta_{\mu\nu}\Phi_\mu(\mathbf{r}_i-\mathbf{R_m})\Phi_\mu(\mathbf{r}_i-\mathbf{R_m}). \tag{4.1}$$

This well-known ZDO picture, however, now is supplemented by an analogous two-index two-electron ZIO scheme which also refers to Rüdenberg's fundamental distinction :

$$\text{(II)} \quad \{\Phi_\mu(\mathbf{r}_i-\mathbf{R_m})\Phi_\nu(\mathbf{r}_j-\mathbf{R_n})\}^{[\mathrm{ZIO}^{\mathrm{II}}_{\mu\nu}]} := \delta_{\mathbf{mn}}\delta_{\mu\nu}\Phi_\mu(\mathbf{r}_i-\mathbf{R_m})\Phi_\mu(\mathbf{r}_j-\mathbf{R_m}). \tag{4.2}$$

Again, in a ZIO-type treatment of four-index repulsion integrals each of both routes have to be passed through twice :

$$\text{(I)} \quad \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{n}&\mathbf{t}&\mathbf{l}\\ \mu&\nu&\tau&\lambda\end{array}\right)^{[\mathrm{ZIO}^{\mathrm{I}}_{\mu\nu}\mathrm{ZIO}^{\mathrm{I}}_{\tau\lambda}]} := \delta_{\mathbf{mn}}\delta_{\mu\nu}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{l}\\ \mu&\mu&\tau&\lambda\end{array}\right)^{[\mathrm{ZIO}^{\mathrm{I}}_{\tau\lambda}]} := \delta_{\mathbf{mn}}\delta_{\mu\nu}\delta_{\mathbf{tl}}\delta_{\tau\lambda}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{t}\\ \mu&\mu&\tau&\tau\end{array}\right), \tag{4.3}$$

$$\text{(II)} \quad \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{n}&\mathbf{t}&\mathbf{l}\\ \mu&\nu&\tau&\lambda\end{array}\right)^{[\mathrm{ZIO}^{\mathrm{II}}_{\mu\tau}\mathrm{ZIO}^{\mathrm{II}}_{\nu\lambda}]} := \delta_{\mathbf{mt}}\delta_{\mu\tau}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{n}&\mathbf{m}&\mathbf{l}\\ \mu&\nu&\mu&\lambda\end{array}\right)^{[\mathrm{ZIO}^{\mathrm{II}}_{\nu\lambda}]} := \delta_{\mathbf{mt}}\delta_{\mu\tau}\delta_{\mathbf{nl}}\delta_{\nu\lambda}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{n}&\mathbf{m}&\mathbf{n}\\ \mu&\nu&\mu&\nu\end{array}\right). \tag{4.4}$$

Having interchanged the indices ν and τ, Eq. (4.4) equivalently reads :

$$\text{(II)} \quad \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{t}&\mathbf{n}&\mathbf{l}\\ \mu&\tau&\nu&\lambda\end{array}\right)^{[\mathrm{ZIO}^{\mathrm{II}}_{\mu\nu}\mathrm{ZIO}^{\mathrm{II}}_{\tau\lambda}]} := \delta_{\mathbf{mn}}\delta_{\mu\nu}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{t}&\mathbf{m}&\mathbf{l}\\ \mu&\tau&\mu&\lambda\end{array}\right)^{[\mathrm{ZIO}^{\mathrm{II}}_{\tau\lambda}]} := \delta_{\mathbf{mn}}\delta_{\mu\nu}\delta_{\mathbf{tl}}\delta_{\tau\lambda}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{t}&\mathbf{m}&\mathbf{t}\\ \mu&\tau&\mu&\tau\end{array}\right). \tag{4.5}$$

In addition to these formulas, let us again consider the three-index repulsion integrals $\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{l}\\ \mu&\mu&\tau&\lambda\end{array}\right)$ and $\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{t}&\mathbf{m}&\mathbf{l}\\ \mu&\tau&\mu&\lambda\end{array}\right)$.

(I) Using two one-electron approximations of ZIO type we get :

$$\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{l}\\ \mu&\mu&\tau&\lambda\end{array}\right)^{[\mathrm{ZIO}^{\mathrm{I}}_{\mu\mu}\mathrm{ZIO}^{\mathrm{I}}_{\tau\lambda}]} := \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{l}\\ \mu&\mu&\tau&\lambda\end{array}\right)^{[\mathrm{ZIO}^{\mathrm{I}}_{\tau\lambda}]} := \delta_{\mathbf{tl}}\delta_{\tau\lambda}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{t}\\ \mu&\mu&\tau&\tau\end{array}\right), \tag{4.6}$$

$$\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{t}&\mathbf{m}&\mathbf{l}\\ \mu&\tau&\mu&\lambda\end{array}\right)^{[\mathrm{ZIO}^{\mathrm{I}}_{\mu\tau}\mathrm{ZIO}^{\mathrm{I}}_{\mu\lambda}]} := \delta_{\mathbf{mt}}\delta_{\mu\tau}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{m}&\mathbf{l}\\ \mu&\mu&\mu&\lambda\end{array}\right)^{[\mathrm{ZIO}^{\mathrm{I}}_{\mu\lambda}]} := \delta_{\mathbf{mt}}\delta_{\mu\tau}\delta_{\mathbf{ml}}\delta_{\mu\lambda}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{m}&\mathbf{m}\\ \mu&\mu&\mu&\mu\end{array}\right). \tag{4.7}$$

(II) Using two two-electron approximations of ZIO type we get :

$$\begin{pmatrix} \mathbf{m}\ \mathbf{m} & \mathbf{t}\ \mathbf{l} \\ \mu\ \ \mu & \tau\ \lambda \end{pmatrix}^{[\mathrm{ZIO}^{\mathrm{II}}_{\mu\tau}\mathrm{ZIO}^{\mathrm{II}}_{\mu\lambda}]} := \delta_{\mathbf{mt}}\delta_{\mu\tau}\begin{pmatrix} \mathbf{m}\ \mathbf{m} & \mathbf{m}\ \mathbf{l} \\ \mu\ \ \mu & \mu\ \lambda \end{pmatrix}^{[\mathrm{ZIO}^{\mathrm{II}}_{\mu\lambda}]} := \delta_{\mathbf{mt}}\delta_{\mu\tau}\delta_{\mathbf{ml}}\delta_{\mu\lambda}\begin{pmatrix} \mathbf{m}\ \mathbf{m} & \mathbf{m}\ \mathbf{m} \\ \mu\ \ \mu & \mu\ \ \mu \end{pmatrix}, \tag{4.8}$$

$$\begin{pmatrix} \mathbf{m}\ \mathbf{t} & \mathbf{m}\ \mathbf{l} \\ \mu\ \tau & \mu\ \lambda \end{pmatrix}^{[\mathrm{ZIO}^{\mathrm{II}}_{\mu\mu}\mathrm{ZIO}^{\mathrm{II}}_{\tau\lambda}]} := \begin{pmatrix} \mathbf{m}\ \mathbf{t} & \mathbf{m}\ \mathbf{l} \\ \mu\ \tau & \mu\ \lambda \end{pmatrix}^{[\mathrm{ZIO}^{\mathrm{II}}_{\tau\lambda}]} := \delta_{\mathbf{tl}}\delta_{\tau\lambda}\begin{pmatrix} \mathbf{m}\ \mathbf{t} & \mathbf{m}\ \mathbf{t} \\ \mu\ \tau & \mu\ \tau \end{pmatrix}. \tag{4.9}$$

Hence, like in the discussion above, applying the ZIO scheme twice implies also an oversimplification of the two-index integral $\begin{pmatrix} \mathbf{m}\ \mathbf{m} & \mathbf{m}\ \mathbf{t} \\ \mu\ \ \mu & \mu\ \tau \end{pmatrix}^{[\mathrm{ZIO}^{\mathrm{I}}_{\mu\lambda}]}$ in Eq. (4.7) and of $\begin{pmatrix} \mathbf{m}\ \mathbf{m} & \mathbf{m}\ \mathbf{l} \\ \mu\ \ \mu & \mu\ \lambda \end{pmatrix}^{[\mathrm{ZIO}^{\mathrm{II}}_{\mu\lambda}]}$ in Eq. (4.8). Obviously, the formulations of Eqs. (4.6) and (4.9) should be preferred, since they use the simplifying ZIO recipe only once. While the oversimplifying "unrestricted" branch of approximation has been discussed comprehensively elsewhere [9], we now turn to the corresponding "restricted" route which avoids such shortcomings.

4.2. "Restricted and Combined ZIO" approximations (ZIO.R&C) for Fock-matrix elements

The term ' "Restricted and Combined ZIO" approximations (ZIO.R&C) ' indicates,

- that both one-electron and two-electron routes of approximation are combined in the sense outlined in Ref. 9, and
- that in this subsection we are going to distinguish four-index and three-index interactions from one another and those of two-index or one-index type. All different types of three-index integrals occuring in Eqs. (2.24) ... (2.32) will be treated in such a way that oversimplifications are avoided by applying the ZIO recipe only once. Furthermore, this time all one- and two-index interactions are considered to be evaluated accurately.

Distinguishing off-diagonal from diagonal matrix elements, we define according to Eq. (2.21) :

$$\underbrace{(\mathbf{F}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO.R\&C}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := (\mathbf{K}_{\mathbf{0n}})_{\mu\nu} + (\mathbf{F}^{A}_{\mathbf{0n}})^{[\mathrm{ZIO.R\&C}]}_{\mu\nu} + (\mathbf{F}^{C}_{\mathbf{0n}})^{[\mathrm{ZIO.R\&C}]}_{\mu\nu} - (\mathbf{F}^{E}_{\mathbf{0n}})^{[\mathrm{ZIO.R\&C}]}_{\mu\nu}, \tag{4.10}$$

$$(\mathbf{F}^{\alpha}_{\mathbf{00}})^{[\mathrm{ZIO.R\&C}]}_{\mu\mu} := (\mathbf{K}_{\mathbf{00}})_{\mu\mu} + (\mathbf{F}^{A}_{\mathbf{00}})_{\mu\mu} + (\mathbf{F}^{C}_{\mathbf{00}})^{[\mathrm{ZIO.R\&C}]}_{\mu\mu} - (\mathbf{F}^{E}_{\mathbf{00}})^{[\mathrm{ZIO.R\&C}]}_{\mu\mu}. \tag{4.11}$$

For the off-diagonal attractive part we define according to the Eqs. (3.12) and (3.13), respectively :

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{0n}})^{[\mathrm{ZIO.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := ({}^{(0)}\mathbf{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + ({}^{(1)}\mathbf{A}_{\mathbf{0n}})^{[\mathrm{ZIO}^{\mathrm{I}}]}_{(M,\mu)(N,\nu)}. \tag{4.12}$$

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{00}})^{[\mathrm{ZIO.R\&C}]}_{(M,\mu)(M,\nu)}}_{\nu\neq\mu} := ({}^{(0)}\mathbf{A}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + ({}^{(1)}\mathbf{A}_{\mathbf{00}})^{[\mathrm{ZIO}^{\mathrm{I}}]}_{(M,\mu)(M,\nu)}. \tag{4.13}$$

For the off-diagonal Coulomb part we define according to Eq. (3.14) :

$$\underbrace{(\mathbf{F}^{C}_{\mathbf{0n}})^{[\mathrm{ZIO.R\&C}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := ({}^{(0)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu} + ({}^{(1)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{ZIO^{I}ZIO^{I}}]}_{\mu\nu} + ({}^{(2)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{ZIO^{I}}]}_{\mu\nu} + 2({}^{(3)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}}]}_{\mu\nu} + 2({}^{(4)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}}]}_{\mu\nu}. \tag{4.14}$$

For the diagonal Coulomb part we define according to Eq. (3.15) :

$$(\mathbf{F}^{C}_{\mathbf{00}})^{[\mathrm{ZIO.R\&C}]}_{\mu\mu} := ({}^{(0)}\mathbf{C}_{\mathbf{00}})_{\mu\mu} + ({}^{(1)}\mathbf{C}_{\mathbf{00}})^{[\mathrm{ZIO^{I}}]}_{\mu\mu} + ({}^{(2)}\mathbf{C}_{\mathbf{00}})_{\mu\mu} + 2({}^{(3)}\mathbf{C}_{\mathbf{00}})_{\mu\mu}. \tag{4.15}$$

For the off-diagonal exchange part we define according to Eq. (3.16) :

$$\underbrace{(\mathbf{F}^{\alpha E}_{\mathbf{0n}})^{[\mathrm{ZIO.R\&C}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := ({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu} + ({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}ZIO^{II}}]}_{\mu\nu} + ({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}}]}_{\mu\nu} + ({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}}]}_{\mu\nu} + ({}^{(4)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{I}}]}_{\mu\nu} + ({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{I}}]}_{\mu\nu} + ({}^{(6)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}}]}_{\mu\nu}. \tag{4.16}$$

For the diagonal exchange part we define according to Eq. (3.17) :

$$(\mathbf{F}^{\alpha E}_{\mathbf{00}})^{[\mathrm{ZIO.R\&C}]}_{\mu\mu} := ({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu} + ({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{00}})^{[\mathrm{ZIO^{II}}]}_{\mu\mu} + ({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu} + 2({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu}. \tag{4.17}$$

With the additional assumption of a globally orthonormal atomic orbital basis, the different quantities occuring in Eqs. (4.12) ... (4.17) are defined as follows. From the Eqs. (3.18) and (3.21) we get :

$$\underbrace{({}^{(1)}\mathbf{A}_{\mathbf{0n}})^{[\mathrm{ZIO^{I}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := 0. \tag{4.18}$$

From Eqs. (3.22), (3.25), (3.26), (3.29), and (3.32) we get :

$$\underbrace{({}^{(1)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{ZIO^{I}ZIO^{I}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = ({}^{(1)}\mathbf{C}_{\mathbf{00}})^{[\mathrm{ZIO^{I}}]}_{\mu\mu} = \underbrace{({}^{(2)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{ZIO^{I}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{({}^{(3)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{({}^{(4)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := 0. \tag{4.19}$$

From Eqs. (3.35), (3.38), (3.39), (3.42), (3.45), (3.48), and (3.51) we get :

$$\underbrace{({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}ZIO^{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = ({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{00}})^{[\mathrm{ZIO^{II}}]}_{\mu\mu} = \underbrace{({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{({}^{(4)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{I}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{I}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} = \underbrace{({}^{(6)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{ZIO^{II}}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := 0. \tag{4.20}$$

The off-diagonal matrix elements of Eqs. (4.12), (4.14), and (4.16) now can be rewritten :

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{0n}})^{[\mathrm{ZIO.R\&C}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := ({}^{(0)}\mathbf{A}_{\mathbf{0n}})_{\mu\nu}, \tag{4.21}$$

$$\underbrace{(\mathbf{F}^{C}_{\mathbf{0n}})^{[\mathrm{ZIO.R\&C}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := ({}^{(0)}\mathbf{C}_{\mathbf{0n}})_{\mu\nu}, \tag{4.22}$$

$$\underbrace{(\mathbf{F}^{\alpha E}_{\mathbf{0n}})^{[\mathrm{ZIO.R\&C}]}_{\mu\nu}}_{\mathbf{n}\nu\neq\mathbf{0}\mu} := ({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{\mu\nu}. \tag{4.23}$$

And the diagonal matrix elements of Eqs. (2.26), (4.15), and (4.17) finally read :

$$(\mathbf{F}^{A}_{\mathbf{00}})^{[\mathrm{ZIO.R\&C}]}_{\mu\mu} := ({}^{(0)}\mathbf{A}_{\mathbf{00}})_{\mu\mu} + ({}^{(1)}\mathbf{A}_{\mathbf{00}})_{\mu\mu}, \tag{4.24}$$

$$(\mathbf{F}^{C}_{\mathbf{00}})^{[\mathrm{ZIO.R\&C}]}_{\mu\mu} := ({}^{(0)}\mathbf{C}_{\mathbf{00}})_{\mu\mu} + ({}^{(2)}\mathbf{C}_{\mathbf{00}})_{\mu\mu} + 2({}^{(3)}\mathbf{C}_{\mathbf{00}})_{\mu\mu}, \tag{4.25}$$

$$(\mathbf{F}^{\alpha E}_{\mathbf{00}})^{[\mathrm{ZIO.R\&C}]}_{\mu\mu} := ({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu} + ({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu} + 2({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{\mu\mu}. \tag{4.26}$$

5. Approximations of Rüdenberg type

5.1. "Unrestricted" and "Restricted" integral approximations

In particular, Rüdenberg's approximation intends to reduce the four-center repulsion integrals to those of two-center type. According to his letter of 1951, this aim can be reached in two ways. The first (standard) approach consists in expanding a differential two-center one-electron density as follows :

$$
\begin{aligned}
&\text{(I)} \qquad \left\{\Phi_\mu(\mathbf{r}_i - \mathbf{R}_M - \mathbf{R}_\mathbf{m})\Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_\mathbf{n})\right\}^{[\mathrm{R}^{\mathrm{I}}_{MN}]} \\
&:= \frac{1}{2}\Bigg\{\sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M - \mathbf{R}_\mathbf{m})\Phi_{\mu'}(\mathbf{r}_i - \mathbf{R}_M - \mathbf{R}_\mathbf{m}) \\
&\quad + \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_\mathbf{n})\Phi_{\nu'}(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_\mathbf{n})\Bigg\}.
\end{aligned}
\tag{5.1}
$$

Alternatively, one can also impose such an expansion on six-dimensional two-center two-electron orbital products :

$$
\begin{aligned}
&\text{(II)} \qquad \left\{\Phi_\mu(\mathbf{r}_i - \mathbf{R}_M - \mathbf{R}_\mathbf{m})\Phi_\nu(\mathbf{r}_j - \mathbf{R}_N - \mathbf{R}_\mathbf{n})\right\}^{[\mathrm{R}^{\mathrm{II}}_{MN}]} \\
&:= \frac{1}{2}\Bigg\{\sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M - \mathbf{R}_\mathbf{m})\Phi_{\mu'}(\mathbf{r}_j - \mathbf{R}_M - \mathbf{R}_\mathbf{m}) \\
&\quad + \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_\mathbf{n})\Phi_{\nu'}(\mathbf{r}_j - \mathbf{R}_N - \mathbf{R}_\mathbf{n})\Bigg\}.
\end{aligned}
\tag{5.2}
$$

In a Rüdenberg-type treatment of four-center repulsion integrals each of both routes have to be passed through twice :

$$
\begin{aligned}
&\text{(I)} \quad \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ M & N & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{I}}_{MN}\mathrm{R}^{\mathrm{I}}_{TL}]} := \frac{1}{2}\Bigg\{\sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \mu' & \tau & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{I}}_{TL}]} \\
&\qquad + \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{n} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ N & N & T & L \\ \nu' & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{I}}_{TL}]}\Bigg\} \\
&:= \frac{1}{4}\Bigg\{\sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \Bigg[\sum_{\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau' & \lambda \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \mu' & \tau & \tau' \end{array}\right) \\
&\qquad + \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau & \lambda' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{l} & \mathbf{l} \\ M & M & L & L \\ \mu & \mu' & \lambda' & \lambda \end{array}\right)\Bigg] \\
&\quad + \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \Bigg[\sum_{\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau' & \lambda \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{n} & \mathbf{n} & \mathbf{t} & \mathbf{t} \\ N & N & T & T \\ \nu' & \nu & \tau & \tau' \end{array}\right) \\
&\qquad + \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau & \lambda' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{n} & \mathbf{n} & \mathbf{l} & \mathbf{l} \\ N & N & L & L \\ \nu' & \nu & \lambda' & \lambda \end{array}\right)\Bigg]\Bigg\},
\end{aligned}
\tag{5.3}
$$

$$
\begin{aligned}
\text{(II)}\quad \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ M & N & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{MT}\mathrm{R}^{\mathrm{II}}_{NL}]}
&:= \frac{1}{2}\Bigg\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{m} & \mathbf{t} \\ M & T \\ \mu' & \tau \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{n} & \mathbf{m} & \mathbf{l} \\ M & N & M & L \\ \mu & \nu & \mu' & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{NL}]} \\
&\qquad + \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{m} & \mathbf{t} \\ M & T \\ \mu & \tau' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ T & N & T & L \\ \tau' & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{NL}]} \Bigg\} \\
:= \frac{1}{4}\Bigg\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{m} & \mathbf{t} \\ M & T \\ \mu' & \tau \end{pmatrix} &\Bigg[\sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{n} & \mathbf{l} \\ N & L \\ \nu' & \lambda \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{n} & \mathbf{m} & \mathbf{n} \\ M & N & M & N \\ \mu & \nu & \mu' & \nu' \end{array}\right) \\
&\qquad + \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix} \mathbf{n} & \mathbf{l} \\ N & L \\ \nu & \lambda' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{l} & \mathbf{m} & \mathbf{l} \\ M & L & M & L \\ \mu & \lambda' & \mu' & \lambda \end{array}\right) \Bigg] \\
+ \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{m} & \mathbf{t} \\ M & T \\ \mu & \tau' \end{pmatrix} &\Bigg[\sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{n} & \mathbf{l} \\ N & L \\ \nu' & \lambda \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{n} & \mathbf{t} & \mathbf{n} \\ T & N & T & N \\ \tau' & \nu & \tau & \nu' \end{array}\right) \\
&\qquad + \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix} \mathbf{n} & \mathbf{l} \\ N & L \\ \nu & \lambda' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{l} & \mathbf{t} & \mathbf{l} \\ T & L & T & L \\ \tau' & \lambda' & \tau & \lambda \end{array}\right) \Bigg] \Bigg\}.
\end{aligned}
\tag{5.4}
$$

Having interchanged $\mathbf{n}$, N and ν with $\mathbf{t}$, T and τ, respectively, Eq. (5.4) equivalently reads :

$$
\begin{aligned}
\text{(II)}\quad \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{n} & \mathbf{l} \\ M & T & N & L \\ \mu & \tau & \nu & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{MN}\mathrm{R}^{\mathrm{II}}_{TL}]}
&:= \frac{1}{2}\Bigg\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \mu' & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{TL}]} \\
&\qquad + \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{n} & \mathbf{t} & \mathbf{n} & \mathbf{l} \\ N & T & N & L \\ \nu' & \tau & \nu & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{TL}]} \Bigg\} \\
:= \frac{1}{4}\Bigg\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} &\Bigg[\sum_{\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau' & \lambda \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{t} \\ M & T & M & T \\ \mu & \tau & \mu' & \tau' \end{array}\right) \\
&\qquad + \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau & \lambda' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{l} & \mathbf{m} & \mathbf{l} \\ M & L & M & L \\ \mu & \lambda' & \mu' & \lambda \end{array}\right) \Bigg] \\
+ \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{m} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} &\Bigg[\sum_{\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau' & \lambda \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{n} & \mathbf{t} & \mathbf{n} & \mathbf{t} \\ N & T & N & T \\ \nu' & \tau & \nu & \tau' \end{array}\right) \\
&\qquad + \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau & \lambda' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{n} & \mathbf{l} & \mathbf{n} & \mathbf{l} \\ N & L & N & L \\ \nu' & \lambda' & \nu & \lambda \end{array}\right) \Bigg] \Bigg\}.
\end{aligned}
\tag{5.5}
$$

In addition to these formulas, which are already contained in Rüdenberg's letter, let us consider the three-center repulsion integrals $\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)$ and $\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{array}\right)$.

(I) Using two one-electron approximations of Rüdenberg type we get :

$$\begin{aligned}
&\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{l}\\ M&M&T&L\\ \mu&\nu&\tau&\lambda\end{array}\right)^{[\mathrm{R}^{\mathrm{I}}_{MM}\mathrm{R}^{\mathrm{I}}_{TL}]} := \left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{l}\\ M&M&T&L\\ \mu&\nu&\tau&\lambda\end{array}\right)^{[\mathrm{R}^{\mathrm{I}}_{TL}]}\\
&:= \frac{1}{2}\left\{\sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{t}&\mathbf{l}\\ T&L\\ \tau'&\lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{t}\\ M&M&T&T\\ \mu&\nu&\tau&\tau'\end{array}\right) + \sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{t}&\mathbf{l}\\ T&L\\ \tau&\lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{l}&\mathbf{l}\\ M&M&L&L\\ \mu&\nu&\lambda'&\lambda\end{array}\right)\right\},
\end{aligned} \tag{5.6}$$

$$\begin{aligned}
\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{t}&\mathbf{m}&\mathbf{l}\\ M&T&M&L\\ \mu&\tau&\nu&\lambda\end{array}\right)^{[\mathrm{R}^{\mathrm{I}}_{MT}\mathrm{R}^{\mathrm{I}}_{NL}]} &:= \frac{1}{2}\left\{\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{m}&\mathbf{t}\\ M&T\\ \mu'&\tau\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{m}&\mathbf{l}\\ M&M&M&L\\ \mu&\mu'&\nu&\lambda\end{array}\right)^{[\mathrm{R}^{\mathrm{I}}_{ML}]}\right.\\
&\qquad\left. + \sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{m}&\mathbf{t}\\ M&T\\ \mu&\tau'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{t}&\mathbf{t}&\mathbf{m}&\mathbf{l}\\ T&T&M&L\\ \tau'&\tau&\nu&\lambda\end{array}\right)^{[\mathrm{R}^{\mathrm{I}}_{ML}]}\right\}\\
&:= \frac{1}{4}\left\{\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{m}&\mathbf{t}\\ M&T\\ \mu'&\tau\end{pmatrix}\left[\sum_{\nu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{m}&\mathbf{l}\\ M&L\\ \nu'&\lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{m}&\mathbf{m}\\ M&M&M&M\\ \mu&\mu'&\nu&\nu'\end{array}\right)\right.\right.\\
&\qquad\left. + \sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{m}&\mathbf{l}\\ M&L\\ \nu&\lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{l}&\mathbf{l}\\ M&M&L&L\\ \mu&\mu'&\lambda'&\lambda\end{array}\right)\right]\\
&\quad + \sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{m}&\mathbf{t}\\ M&T\\ \mu&\tau'\end{pmatrix}\left[\sum_{\nu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{m}&\mathbf{l}\\ M&L\\ \nu'&\lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{t}&\mathbf{t}&\mathbf{m}&\mathbf{m}\\ T&T&M&M\\ \tau'&\tau&\nu&\nu'\end{array}\right)\right.\\
&\qquad\left.\left. + \sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{m}&\mathbf{l}\\ M&L\\ \nu&\lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{t}&\mathbf{t}&\mathbf{l}&\mathbf{l}\\ T&T&L&L\\ \tau'&\tau&\lambda'&\lambda\end{array}\right)\right]\right\}.
\end{aligned} \tag{5.7}$$

(II) Using two two-electron approximations of Rüdenberg type we get :

$$\begin{aligned}
\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{t}&\mathbf{l}\\ M&M&T&L\\ \mu&\nu&\tau&\lambda\end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{MT}\mathrm{R}^{\mathrm{II}}_{ML}]} &:= \frac{1}{2}\left\{\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{m}&\mathbf{t}\\ M&T\\ \mu'&\tau\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{m}&\mathbf{l}\\ M&M&M&L\\ \mu&\nu&\mu'&\lambda\end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{ML}]}\right.\\
&\qquad\left. + \sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{m}&\mathbf{t}\\ M&T\\ \mu&\tau'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{t}&\mathbf{m}&\mathbf{t}&\mathbf{l}\\ T&M&M&L\\ \tau'&\nu&\tau&\lambda\end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{ML}]}\right\}\\
&:= \frac{1}{4}\left\{\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{m}&\mathbf{t}\\ M&T\\ \mu'&\tau\end{pmatrix}\left[\sum_{\nu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{m}&\mathbf{l}\\ M&L\\ \nu'&\lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{m}&\mathbf{m}&\mathbf{m}\\ M&M&M&M\\ \mu&\nu&\mu'&\nu'\end{array}\right)\right.\right.\\
&\qquad\left. + \sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{m}&\mathbf{l}\\ M&L\\ \nu&\lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{m}&\mathbf{l}&\mathbf{m}&\mathbf{l}\\ M&L&M&L\\ \mu&\lambda'&\mu'&\lambda\end{array}\right)\right]\\
&\quad + \sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{m}&\mathbf{t}\\ M&T\\ \mu&\tau'\end{pmatrix}\left[\sum_{\nu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{m}&\mathbf{l}\\ M&L\\ \nu'&\lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{t}&\mathbf{m}&\mathbf{t}&\mathbf{m}\\ T&M&T&M\\ \tau'&\nu&\tau&\nu'\end{array}\right)\right.\\
&\qquad\left.\left. + \sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{m}&\mathbf{l}\\ M&L\\ \nu&\lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{t}&\mathbf{l}&\mathbf{t}&\mathbf{l}\\ T&L&T&L\\ \tau'&\lambda'&\tau&\lambda\end{array}\right)\right]\right\},
\end{aligned} \tag{5.8}$$

$$\begin{pmatrix} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{pmatrix}^{[\mathrm{R}^{\mathrm{II}}_{MM}\mathrm{R}^{\mathrm{II}}_{TL}]} := \begin{pmatrix} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{pmatrix}^{[\mathrm{R}^{\mathrm{II}}_{TL}]}$$

$$:= \frac{1}{2}\Bigg\{ \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau' & \lambda \end{pmatrix} \begin{pmatrix} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{t} \\ M & T & M & T \\ \mu & \tau & \nu & \tau' \end{pmatrix} + \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau & \lambda' \end{pmatrix} \begin{pmatrix} \mathbf{m} & \mathbf{l} & \mathbf{m} & \mathbf{l} \\ M & L & M & L \\ \mu & \lambda' & \nu & \lambda \end{pmatrix} \Bigg\}. \tag{5.9}$$

Hence, applying Rüdenberg's approximation twice implies an oversimplification of the two-center integral $\begin{pmatrix} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{l} \\ M & M & M & L \\ \mu & \mu' & \nu & \lambda \end{pmatrix}^{[\mathrm{R}^{\mathrm{I}}_{ML}]}$ in Eq. (5.7) and of $\begin{pmatrix} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{l} \\ M & M & M & L \\ \mu & \nu & \mu' & \lambda \end{pmatrix}^{[\mathrm{R}^{\mathrm{II}}_{ML}]}$ in Eq. (5.8). Obviously, the formulations of Eqs. (5.6) and (5.9) should be preferred, since they use Rüdenberg's recipe only once. While the oversimplifying "unrestricted" branch of approximation has been discussed comprehensively elsewhere [9], we now turn to the corresponding "restricted" route which avoids such shortcomings.

5.2. "Restricted and Combined Rüdenberg" approximations (R.R&C) for Fock-matrix elements

The term ' "Restricted and Combined Rüdenberg" approximations (R.R&C) ' indicates,

- that both one-electron and two-electron routes of approximation are combined in the sense outlined in Ref. 9, and
- that in this subsection we are going to distinguish four-center and three-center interactions from one another and those of two-center or one-center type. All different types of three-center integrals occuring in Eqs. (2.35) . . . (2.42) will be treated in such a way that oversimplifications are avoided by applying Rüdenberg's approximations only once. Furthermore, this time all one- and two-center interactions are considered to be evaluated accurately.

Distinguishing off-blockdiagonal from blockdiagonal matrix elements we define according to Eq. (2.33) :

$$\underbrace{(\mathbf{F}^{\alpha}_{\mathbf{0n}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := (\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + (\mathbf{F}^{A}_{\mathbf{0n}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(N,\nu)} + (\mathbf{F}^{C}_{\mathbf{0n}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(N,\nu)} - (\mathbf{F}^{\alpha E}_{\mathbf{0n}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(N,\nu)}, \tag{5.10}$$

$$(\mathbf{F}^{\alpha}_{\mathbf{00}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(M,\nu)} := (\mathbf{K}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + (\mathbf{F}^{A}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + (\mathbf{F}^{C}_{\mathbf{00}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(M,\nu)} - (\mathbf{F}^{\alpha E}_{\mathbf{00}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(M,\nu)}. \tag{5.11}$$

For the off-blockdiagonal attractive part we define according to Eq. (2.35) :

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{0n}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := ({}^{(0)}\mathbf{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + ({}^{(1)}\mathbf{A}_{\mathbf{0n}})^{[\mathrm{R}^{\mathrm{I}}]}_{(M,\mu)(N,\nu)}. \tag{5.12}$$

For the off-blockdiagonal Coulomb part we define according to Eq. (2.37) :

$$\underbrace{(\mathbf{F}^{C}_{\mathbf{0n}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := ({}^{(0)}\mathbf{C}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + ({}^{(1)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{R^I R^I}]}_{(M,\mu)(N,\nu)} + ({}^{(2)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{R^I}]}_{(M,\mu)(N,\nu)} + 2({}^{(3)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{R^{II}}]}_{(M,\mu)(N,\nu)} + 2({}^{(4)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{R^{II}}]}_{(M,\mu)(N,\nu)}. \tag{5.13}$$

For the blockdiagonal Coulomb part we define according to Eq. (2.39) :

$$\begin{aligned}(\mathbf{F}^{C}_{\mathbf{00}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(M,\nu)} :=& ({}^{(0)}\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + ({}^{(1)}\mathbf{C}_{\mathbf{00}})^{[\mathrm{R^I}]}_{(M,\mu)(M,\nu)} \\ &+ ({}^{(2)}\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + 2({}^{(3)}\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)}.\end{aligned} \tag{5.14}$$

For the off-blockdiagonal exchange part we define according to Eq. (2.40) :

$$\begin{aligned}\underbrace{(\mathbf{F}^{\alpha E}_{\mathbf{0n}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} :=& ({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + ({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{R^{II}R^{II}}]}_{(M,\mu)(N,\nu)} + ({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{R^{II}}]}_{(M,\mu)(N,\nu)} \\ &+ ({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{R^{II}}]}_{(M,\mu)(N,\nu)} + ({}^{(4)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{R^{I}}]}_{(M,\mu)(N,\nu)} \\ &+ ({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{R^{I}}]}_{(M,\mu)(N,\nu)} + ({}^{(6)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{R^{II}}]}_{(M,\mu)(N,\nu)}.\end{aligned} \tag{5.15}$$

For the blockdiagonal exchange part we define according to Eq. (2.57) :

$$\begin{aligned}(\mathbf{F}^{\alpha E}_{\mathbf{00}})^{[\mathrm{R.R\&C}]}_{(M,\mu)(M,\nu)} :=& ({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + ({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{00}})^{[\mathrm{R^{II}}]}_{(M,\mu)(M,\nu)} + ({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)} \\ &+ ({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + ({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)}.\end{aligned} \tag{5.16}$$

Using again the notation $\mathbf{n}N \neq \mathbf{0}M \equiv (\mathbf{n} \neq \mathbf{0}) \vee (N \neq M)$, the different quantities occuring in Eqs. (5.12) ... (5.16) are defined as follows [15] :

$$\begin{aligned}\underbrace{({}^{(1)}\mathbf{A}_{\mathbf{0n}})^{[\mathrm{R^I}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \frac{1}{2}\Bigg\{ & \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \underbrace{\underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n}}_{\mathbf{p}P\neq\mathbf{0}M,\mathbf{n}N} \begin{pmatrix} \mathbf{0} & \mathbf{p} & \mathbf{0} \\ M & P & M \\ \mu & & \mu' \end{pmatrix}}_{\stackrel{\mathrm{def}}{=}({}^{(1.1)}\mathbf{A}_{\mathbf{0n}})_{(M,\mu,\mu')(N)}} \\ &+ \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \underbrace{\underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n}}_{\mathbf{p}P\neq\mathbf{0}M,\mathbf{n}N} \begin{pmatrix} \mathbf{n} & \mathbf{p} & \mathbf{n} \\ N & P & N \\ \nu' & & \nu \end{pmatrix}}_{\stackrel{\mathrm{def}}{=}({}^{(1.2)}\mathbf{A}_{\mathbf{0n}})_{(M)(N,\nu',\nu)}} \Bigg\},\end{aligned} \tag{5.17}$$

with

$$\underbrace{\left({}^{(1.1)}\mathbf{A}_{\mathbf{0n}}\right)_{(M,\mu,\mu')(N)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{P=1}^{N_n}\begin{pmatrix} \mathbf{0} & \mathbf{p} & \mathbf{0} \\ M & P & M \\ \mu & & \mu' \end{pmatrix}}_{=(\mathbf{F}^A_{\mathbf{00}})_{(M,\mu)(M,\mu')}} - \begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{0} \\ M & M & M \\ \mu & & \mu' \end{pmatrix} - \begin{pmatrix} \mathbf{0} & \mathbf{n} & \mathbf{0} \\ M & N & M \\ \mu & & \mu' \end{pmatrix}, \tag{5.18}$$

and

$$\underbrace{\left({}^{(1.2)}\mathbf{A}_{\mathbf{0n}}\right)_{(M)(N,\nu',\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{P=1}^{N_n}\begin{pmatrix} \mathbf{n} & \mathbf{p} & \mathbf{n} \\ N & P & N \\ \nu' & & \nu \end{pmatrix}}_{=(\mathbf{F}^A_{\mathbf{00}})_{(N,\nu')(N,\nu)}} - \begin{pmatrix} \mathbf{n} & \mathbf{0} & \mathbf{n} \\ N & M & N \\ \nu' & & \nu \end{pmatrix} - \begin{pmatrix} \mathbf{n} & \mathbf{n} & \mathbf{n} \\ N & N & N \\ \nu' & & \nu \end{pmatrix}. \tag{5.19}$$

Introducing the abbreviations

$$(\mathbf{Q}^{\oplus}_{\mathbf{0n}})_{(M)(N,\nu,\nu')} \stackrel{\text{def}}{=} \sum_{\mu=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \tag{5.20}$$

and

$$(\mathbf{Q}^{\oplus}_{\mathbf{0n}})_{(M,\mu,\mu')(N)} \stackrel{\text{def}}{=} \sum_{\nu=1}^{n_o(N)} (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \tag{5.21}$$

we define :

$$\underbrace{\left({}^{(1)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{R^I R^I}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} :=$$

$$\frac{1}{2}\Bigg\{\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N,\mathbf{t}T}\sum_{\lambda=1}^{n_o(L)}(\mathbf{P}^{\oplus}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)}\left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \mu' & \tau & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{I}}_{TL}]}}_{\stackrel{\text{def}}{=}\left({}^{(1.1)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{R^I}]}_{(M,\mu,\mu')(N)}}$$

$$+\sum_{\nu'=1}^{n_o(N)}\begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N,\mathbf{t}T}\sum_{\lambda=1}^{n_o(L)}(\mathbf{P}^{\oplus}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)}\left(\begin{array}{cc|cc} \mathbf{n} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ N & N & T & L \\ \nu' & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{R}^{\mathrm{I}}_{TL}]}}_{\stackrel{\text{def}}{=}\left({}^{(1.2)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{R^I}]}_{(M)(N,\nu',\nu)}}\Bigg\}, \tag{5.22}$$

with

$$\begin{aligned}
&\underbrace{\left({}^{(1.1)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{R}^{\mathrm{I}}]}_{(M,\mu,\mu')(N)}}_{\mathbf{n}N\neq\mathbf{0}M} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\ \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N,\mathbf{t}T}\ \sum_{\lambda=1}^{n_o(L)}(\mathbf{P}^{\oplus}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)}\\
&\qquad\times\frac{1}{2}\left\{\sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{t}&\mathbf{l}\\ \\ T&L\\ \tau'&\lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{t}&\mathbf{t}\\ \\ M&M&T&T\\ \mu&\mu'&\tau&\tau'\end{array}\right)+\sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{t}&\mathbf{l}\\ \\ T&L\\ \tau&\lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{l}&\mathbf{l}\\ \\ M&M&L&L\\ \mu&\mu'&\lambda'&\lambda\end{array}\right)\right\}\\
&=\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M}\sum_{\tau,\tau'=1}^{n_o(T)}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{t}&\mathbf{t}\\ \\ M&M&T&T\\ \mu&\mu'&\tau&\tau'\end{array}\right)\Big\{((\mathbf{P}^{\oplus}\mathbf{S})_{\mathbf{00}})_{(T,\tau)(T,\tau')}\\
&\qquad\qquad -(\mathbf{P}^{\oplus}_{\mathbf{00}})_{(T,\tau)(T,\tau')}-(\mathbf{Q}^{\oplus}_{\mathbf{0t}})_{(N)(T,\tau,\tau')}-(\mathbf{Q}^{\oplus}_{\mathbf{0t}})_{(M)(T,\tau,\tau')}\Big\}\\
&\quad-\sum_{\tau,\tau'=1}^{n_o(N)}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{n}&\mathbf{n}\\ \\ M&M&N&N\\ \mu&\mu'&\tau&\tau'\end{array}\right)\Big\{((\mathbf{P}^{\oplus}\mathbf{S})_{\mathbf{00}})_{(N,\tau)(N,\tau')}\\
&\qquad\qquad -2(\mathbf{P}^{\oplus}_{\mathbf{00}})_{(N,\tau)(N,\tau')}-(\mathbf{Q}^{\oplus}_{\mathbf{0n}})_{(M)(N,\tau,\tau')}\Big\}\\
&\quad-\sum_{\tau,\tau'=1}^{n_o(M)}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{0}&\mathbf{0}\\ \\ M&M&M&M\\ \mu&\mu'&\tau&\tau'\end{array}\right)\Big\{(\mathbf{Q}^{\oplus}_{\mathbf{00}})_{(N)(M,\tau,\tau')}-(\mathbf{Q}^{\oplus}_{\mathbf{0n}})_{(M,\tau,\tau')(N)}\Big\}.
\end{aligned}\tag{5.23}$$

and

$$\begin{aligned}
&\underbrace{\left({}^{(1.2)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{R}^{\mathrm{I}}]}_{(M)(N,\nu',\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\ \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N,\mathbf{t}T}\ \sum_{\lambda=1}^{n_o(L)}(\mathbf{P}^{\oplus}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)}\\
&\qquad\times\frac{1}{2}\left\{\sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{t}&\mathbf{l}\\ \\ T&L\\ \tau'&\lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{n}&\mathbf{t}&\mathbf{t}\\ \\ N&N&T&T\\ \nu'&\nu&\tau&\tau'\end{array}\right)+\sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{t}&\mathbf{l}\\ \\ T&L\\ \tau&\lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{n}&\mathbf{l}&\mathbf{l}\\ \\ N&N&L&L\\ \nu'&\nu&\lambda'&\lambda\end{array}\right)\right\}\\
&=\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}N}\sum_{\tau,\tau'=1}^{n_o(T)}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{t}&\mathbf{t}\\ \\ N&N&T&T\\ \nu'&\nu&\tau&\tau'\end{array}\right)\Big\{((\mathbf{P}^{\oplus}\mathbf{S})_{\mathbf{00}})_{(T,\tau)(T,\tau')}\\
&\qquad\qquad -(\mathbf{P}^{\oplus}_{\mathbf{00}})_{(T,\tau)(T,\tau')}-(\mathbf{Q}^{\oplus}_{\mathbf{0t}})_{(N)(T,\tau,\tau')}-(\mathbf{Q}^{\oplus}_{\mathbf{0t}})_{(M)(T,\tau,\tau')}\Big\}\\
&\quad-\sum_{\tau,\tau'=1}^{n_o(M)}\left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{n}&\mathbf{0}&\mathbf{0}\\ \\ N&N&M&M\\ \nu'&\nu&\tau&\tau'\end{array}\right)\Big\{((\mathbf{P}^{\oplus}\mathbf{S})_{\mathbf{00}})_{(M,\tau)(M,\tau')}\\
&\qquad\qquad -2(\mathbf{P}^{\oplus}_{\mathbf{00}})_{(M,\tau)(M,\tau')}-(\mathbf{Q}^{\oplus}_{\mathbf{0n}})_{(M,\tau,\tau')(N)}\Big\}\\
&\quad-\sum_{\tau,\tau'=1}^{n_o(N)}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{0}&\mathbf{0}\\ \\ N&N&N&N\\ \nu'&\nu&\tau&\tau'\end{array}\right)\Big\{(\mathbf{Q}^{\oplus}_{\mathbf{00}})_{(M)(N,\tau,\tau')}-(\mathbf{Q}^{\oplus}_{\mathbf{0n}})_{(M)(N,\tau,\tau')}\Big\}.
\end{aligned}\tag{5.24}$$

$$
\left({}^{(1)}\mathbf{C}_{\mathbf{00}}\right)^{[\mathrm{R}^{\mathrm{I}}]}_{(M,\mu)(M,\nu)} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M} \sum_{\tau=1}^{n_o(T)} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{t}T} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\oplus}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)}
$$

$$
\times\frac{1}{2}\left\{ \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau' & \lambda \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \nu & \tau & \tau' \end{array}\right) + \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix} \mathbf{t} & \mathbf{l} \\ T & L \\ \tau & \lambda' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{l} & \mathbf{l} \\ M & M & L & L \\ \mu & \nu & \lambda' & \lambda \end{array}\right) \right\}
$$

$$
= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M} \sum_{\tau=1}^{n_o(T)} \sum_{\tau'=1}^{n_o(T)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \nu & \tau & \tau' \end{array}\right) \Big\{ ((\mathbf{P}^{\oplus}\mathbf{S})_{\mathbf{00}})_{(T,\tau)(T,\tau')}
$$

$$
- (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(T,\tau)(T,\tau')} - (\mathbf{Q}^{\oplus}_{\mathbf{0t}})_{(M)(T,\tau,\tau')} \Big\}. \tag{5.25}
$$

$$
\underbrace{\left({}^{(2)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{R}^{\mathrm{I}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \frac{1}{2}\Bigg\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N} \sum_{\tau,\lambda=1}^{n_o(T)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(T,\tau)(T,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \mu' & \tau & \lambda \end{array}\right)}_{\stackrel{\mathrm{def}}{=}({}^{(2.1)}\mathbf{C}_{\mathbf{0n}})_{(M,\mu,\mu')(N)}}
$$

$$
+ \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N} \sum_{\tau,\lambda=1}^{n_o(T)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(T,\tau)(T,\lambda)} \left(\begin{array}{cc|cc} \mathbf{n} & \mathbf{n} & \mathbf{t} & \mathbf{t} \\ N & N & T & T \\ \nu' & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\mathrm{def}}{=}({}^{(2.2)}\mathbf{C}_{\mathbf{0n}})_{(M)(N,\nu',\nu)}} \Bigg\}, \tag{5.26}
$$

with

$$
\underbrace{\left({}^{(2.1)}\mathbf{C}_{\mathbf{0n}}\right)_{(M,\mu,\mu')(N)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M} \sum_{\tau,\lambda=1}^{n_o(T)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(T,\tau)(T,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \mu' & \tau & \lambda \end{array}\right)
$$

$$
- \sum_{\tau,\lambda=1}^{n_o(N)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(N,\tau)(N,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & M & N & N \\ \mu & \mu' & \tau & \lambda \end{array}\right), \tag{5.27}
$$

and

$$
\underbrace{\left({}^{(2.2)}\mathbf{C}_{\mathbf{0n}}\right)_{(M)(N,\nu',\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}N} \sum_{\tau,\lambda=1}^{n_o(T)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(T,\tau)(T,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ N & N & T & T \\ \nu' & \nu & \tau & \lambda \end{array}\right)
$$

$$
- \sum_{\tau,\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(M,\tau)(M,\lambda)} \left(\begin{array}{cc|cc} \mathbf{n} & \mathbf{n} & \mathbf{0} & \mathbf{0} \\ N & N & M & M \\ \nu' & \nu & \tau & \lambda \end{array}\right). \tag{5.28}
$$

$$
\underbrace{\left({}^{(3)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{R}^{\mathrm{II}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{(M,\lambda)(T,\tau)} \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix}\mathbf{n} & \mathbf{t}\\ N & T\\ \nu' & \tau\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ M&N&N&M\\ \mu&\nu&\nu'&\lambda\end{array}\right)}_{\stackrel{\mathrm{def}}{=}({}^{(3.1)}\mathbf{C}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}
$$

$$
+ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{(M,\lambda)(T,\tau)} \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix}\mathbf{n} & \mathbf{t}\\ N & T\\ \nu & \tau'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{t}&\mathbf{0}\\ M&T&T&M\\ \mu&\tau'&\tau&\lambda\end{array}\right)}_{\stackrel{\mathrm{def}}{=}({}^{(3.2)}\mathbf{C}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}}\Bigg\}, \tag{5.29}
$$

with

$$
\underbrace{\left({}^{(3.1)}\mathbf{C}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{(M,\lambda)(T,\tau)} \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix}\mathbf{0} & \mathbf{t}\\ N & T\\ \nu' & \tau\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ M&N&N&M\\ \mu&\nu&\nu'&\lambda\end{array}\right)
$$

$$
- \sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{(M,\lambda)(N,\tau)} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ M&N&N&M\\ \mu&\nu&\tau&\lambda\end{array}\right)
$$

$$
- \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(M,\lambda)(M,\tau)} \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \tau & \nu'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ M&N&N&M\\ \mu&\nu&\nu'&\lambda\end{array}\right), \tag{5.30}
$$

and

$$
\underbrace{\left({}^{(3.2)}\mathbf{C}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{0t}})_{(M,\lambda)(T,\tau)} \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix}\mathbf{0} & \mathbf{t}\\ N & T\\ \nu & \tau'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{t}&\mathbf{0}\\ M&T&T&M\\ \mu&\tau'&\tau&\lambda\end{array}\right)
$$

$$
- \sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{(M,\lambda)(N,\tau)} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ M&N&N&M\\ \mu&\nu&\tau&\lambda\end{array}\right)
$$

$$
- \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(M,\lambda)(M,\tau)} \sum_{\tau'=1}^{n_o(M)} \left\{ \begin{pmatrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \tau' & \nu\end{pmatrix} - \begin{pmatrix}\mathbf{0} & \mathbf{0}\\ M & N\\ \tau' & \nu\end{pmatrix}\right\}\left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{0}&\mathbf{0}\\ M&M&M&M\\ \mu&\tau'&\tau&\lambda\end{array}\right). \tag{5.31}
$$

$$\underbrace{\left({}^{(4)}\mathbf{C}_{\mathbf{0n}}\right)^{[\mathrm{R^{II}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(N)} \left(\mathbf{P}^{\oplus}_{\mathbf{tn}}\right)_{(T,\tau)(N,\lambda)} \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{t} \\ M & T \\ \mu' & \tau \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{0} & \mathbf{n} \\ M & N & M & N \\ \mu & \nu & \mu' & \lambda \end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(4.1)}\mathbf{C}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}$$

$$+ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(N)} \left(\mathbf{P}^{\oplus}_{\mathbf{tn}}\right)_{(T,\tau)(N,\lambda)} \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{0} & \mathbf{t} \\ M & T \\ \mu & \tau' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{n} & \mathbf{t} & \mathbf{n} \\ T & N & T & N \\ \tau' & \nu & \tau & \lambda \end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(4.2)}\mathbf{C}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}} \Bigg\}, \tag{5.32}$$

with

$$\underbrace{\left({}^{(4.1)}\mathbf{C}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(N)} \left(\mathbf{P}^{\oplus}_{\mathbf{0t}}\right)_{(N,\lambda)(T,\tau)} \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{t} \\ M & T \\ \mu' & \tau \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{0} & \mathbf{n} \\ M & N & M & N \\ \mu & \nu & \mu' & \lambda \end{array}\right)$$
$$- \sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(N)} \left(\mathbf{P}^{\oplus}_{\mathbf{00}}\right)_{(N,\tau)(N,\lambda)} \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \tau \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{0} & \mathbf{n} \\ M & N & M & N \\ \mu & \nu & \mu' & \lambda \end{array}\right)$$
$$- \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(N)} \left(\mathbf{P}^{\oplus}_{\mathbf{0n}}\right)_{(M,\tau)(N,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{0} & \mathbf{n} \\ M & N & M & N \\ \mu & \nu & \tau & \lambda \end{array}\right), \tag{5.33}$$

and

$$\underbrace{\left({}^{(4.2)}\mathbf{C}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(N)} \left(\mathbf{P}^{\oplus}_{\mathbf{0t}}\right)_{(N,\lambda)(T,\tau)} \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{0} & \mathbf{t} \\ M & T \\ \mu & \tau' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{t} & \mathbf{0} & \mathbf{t} & \mathbf{0} \\ T & N & T & N \\ \tau' & \nu & \tau & \lambda \end{array}\right)$$
$$- \sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(N)} \left(\mathbf{P}^{\oplus}_{\mathbf{00}}\right)_{(N,\tau)(N,\lambda)} \sum_{\tau'=1}^{n_o(N)} \left\{ \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \tau' \end{pmatrix} - \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ M & N \\ \mu & \tau' \end{pmatrix} \right\} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ N & N & N & N \\ \tau' & \nu & \tau & \lambda \end{array}\right)$$
$$- \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(N)} \left(\mathbf{P}^{\oplus}_{\mathbf{0n}}\right)_{(M,\tau)(N,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{n} & \mathbf{0} & \mathbf{n} \\ M & N & M & N \\ \mu & \nu & \tau & \lambda \end{array}\right). \tag{5.34}$$

Introducing the abbreviations

$$\left(\mathbf{Q}^{\alpha}_{\mathbf{0n}}\right)_{(M)(N,\nu,\nu')} \stackrel{\mathrm{def}}{=} \sum_{\mu=1}^{n_o(M)} \left(\mathbf{P}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \tag{5.35}$$

and

$$\left(\mathbf{Q}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu,\mu')(N)} \stackrel{\mathrm{def}}{=} \sum_{\nu=1}^{n_o(N)} \left(\mathbf{P}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \tag{5.36}$$

we define :

$$
\begin{aligned}
&\underbrace{\left({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{R^{II}R^{II}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \\
&\quad \frac{1}{2}\Bigg\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \mu' & \nu\end{pmatrix} \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N,\mathbf{t}T}\sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{0}&\mathbf{l}\\ M&T&M&L\\ \mu&\tau&\mu'&\lambda\end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{TL}]}}_{\stackrel{\mathrm{def}}{=}\left({}^{(1.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{R^{II}}]}_{(M,\mu,\mu')(N)}} \\
&\quad + \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \mu & \nu'\end{pmatrix} \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N,\mathbf{t}T}\sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc}\mathbf{n}&\mathbf{t}&\mathbf{n}&\mathbf{l}\\ N&T&N&L\\ \nu'&\tau&\nu&\lambda\end{array}\right)^{[\mathrm{R}^{\mathrm{II}}_{TL}]}}_{\stackrel{\mathrm{def}}{=}\left({}^{(1.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{R^{II}}]}_{(M)(N,\nu',\nu)}} \Bigg\},
\end{aligned}
\tag{5.37}
$$

with

$$
\begin{aligned}
&\underbrace{\left({}^{(1.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{R^{II}}]}_{(M,\mu,\mu')(N)}}_{\mathbf{n}N\neq\mathbf{0}M} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N,\mathbf{t}T}\sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)} \\
&\qquad \times\frac{1}{2}\Bigg\{ \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix}\mathbf{t} & \mathbf{l}\\ T & L\\ \tau' & \lambda\end{pmatrix} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{0}&\mathbf{t}\\ M&T&M&T\\ \mu&\tau&\mu'&\tau'\end{array}\right) + \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix}\mathbf{t} & \mathbf{l}\\ T & L\\ \tau & \lambda'\end{pmatrix} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{l}&\mathbf{0}&\mathbf{l}\\ M&L&M&L\\ \mu&\lambda'&\mu'&\lambda\end{array}\right)\Bigg\} \\
&= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M}\sum_{\tau,\tau'=1}^{n_o(T)} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{0}&\mathbf{t}\\ M&T&M&T\\ \mu&\tau&\mu'&\tau'\end{array}\right) \Bigg\{ \frac{1}{2}\Big[((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{(T,\tau)(T,\tau')} + ((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{(T,\tau')(T,\tau)}\Big] \\
&\qquad -(\mathbf{P}^{\alpha}_{\mathbf{00}})_{(T,\tau)(T,\tau')} - \frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{0t}})_{(N)(T,\tau,\tau')} + (\mathbf{Q}^{\alpha}_{\mathbf{0t}})_{(N)(T,\tau',\tau)}\Big] \\
&\qquad - \frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{0t}})_{(M)(T,\tau,\tau')} + (\mathbf{Q}^{\alpha}_{\mathbf{0t}})_{(M)(T,\tau',\tau)}\Big]\Bigg\} \\
&\quad - \sum_{\tau,\tau'=1}^{n_o(N)} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{0}&\mathbf{n}\\ M&N&M&N\\ \mu&\tau&\mu'&\tau'\end{array}\right) \Bigg\{ \frac{1}{2}\Big[((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{(N,\tau)(N,\tau')} + ((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{(N,\tau')(N,\tau)}\Big] \\
&\qquad -2(\mathbf{P}^{\alpha}_{\mathbf{00}})_{(N,\tau)(N,\tau')} - \frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{0n}})_{(M)(N,\tau,\tau')} + (\mathbf{Q}^{\alpha}_{\mathbf{0n}})_{(M)(N,\tau',\tau)}\Big]\Bigg\} \\
&\quad - \sum_{\tau,\tau'=1}^{n_o(M)} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{0}&\mathbf{0}\\ M&M&M&M\\ \mu&\tau&\mu'&\tau'\end{array}\right) \Bigg\{ \frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{00}})_{(N)(M,\tau,\tau')} + (\mathbf{Q}^{\alpha}_{\mathbf{00}})_{(N)(M,\tau',\tau)}\Big] \\
&\qquad - \frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{0n}})_{(M,\tau,\tau')(N)} + (\mathbf{Q}^{\alpha}_{\mathbf{0n}})_{(M,\tau',\tau)(N)}\Big]\Bigg\}.
\end{aligned}
\tag{5.38}
$$

and

$$\underbrace{\left({}^{(1.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{R^{II}}]}_{(M)(N,\nu',\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N,\mathbf{t}T}\sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)}$$

$$\times\frac{1}{2}\left\{\sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{t} & \mathbf{l}\\ T & L\\ \tau' & \lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{n} & \mathbf{t} & \mathbf{n} & \mathbf{t}\\ N & T & N & T\\ \nu' & \tau & \nu & \tau'\end{array}\right)+\sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{t} & \mathbf{l}\\ T & L\\ \tau & \lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{n} & \mathbf{l} & \mathbf{n} & \mathbf{l}\\ N & L & N & L\\ \nu' & \lambda' & \nu & \lambda\end{array}\right)\right\}$$

$$= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}N}\sum_{\tau,\tau'=1}^{n_o(T)}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{t} & \mathbf{0} & \mathbf{t}\\ N & T & N & T\\ \nu' & \tau & \nu & \tau'\end{array}\right)\left\{\frac{1}{2}\Big[((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{(T,\tau)(T,\tau')}+((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{(T,\tau')(T,\tau)}\Big]\right.$$

$$-(\mathbf{P}^{\alpha}_{\mathbf{00}})_{(T,\tau)(T,\tau')}-\frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{0t}})_{(N)(T,\tau,\tau')}+(\mathbf{Q}^{\alpha}_{\mathbf{0t}})_{(N)(T,\tau',\tau)}\Big]$$

$$\left.-\frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{0t}})_{(M)(T,\tau,\tau')}+(\mathbf{Q}^{\alpha}_{\mathbf{0t}})_{(M)(T,\tau',\tau)}\Big]\right\}$$

$$-\sum_{\tau,\tau'=1}^{n_o(M)}\left(\begin{array}{cc|cc}\mathbf{n} & \mathbf{0} & \mathbf{n} & \mathbf{0}\\ N & M & N & M\\ \nu' & \tau & \nu & \tau'\end{array}\right)\left\{\frac{1}{2}\Big[((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{(M,\tau)(M,\tau')}+((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{(M,\tau')(M,\tau)}\Big]\right.$$

$$\left.-2(\mathbf{P}^{\alpha}_{\mathbf{00}})_{(M,\tau)(M,\tau')}-\frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{0n}})_{(M,\tau,\tau')(N)}+(\mathbf{Q}^{\alpha}_{\mathbf{0n}})_{(M,\tau',\tau)(N)}\Big]\right\}$$

$$-\sum_{\tau,\tau'=1}^{n_o(N)}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ N & N & N & N\\ \nu' & \tau & \nu & \tau'\end{array}\right)\left\{\frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{00}})_{(M)(N,\tau,\tau')}+(\mathbf{Q}^{\alpha}_{\mathbf{00}})_{(M)(N,\tau',\tau)}\Big]\right.$$

$$\left.-\frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{0n}})_{(M)(N,\tau,\tau')}+(\mathbf{Q}^{\alpha}_{\mathbf{0n}})_{(M)(N,\tau',\tau)}\Big]\right\}. \tag{5.39}$$

$$\left({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{00}}\right)^{[\mathrm{R^{II}}]}_{(M,\mu)(M,\nu)} := \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M}\sum_{\tau=1}^{n_o(T)} \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{t}T}\sum_{\lambda=1}^{n_o(L)} (\mathbf{P}^{\alpha}_{\mathbf{tl}})_{(T,\tau)(L,\lambda)}$$

$$\times\frac{1}{2}\left\{\sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{t} & \mathbf{l}\\ T & L\\ \tau' & \lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{t} & \mathbf{0} & \mathbf{t}\\ M & T & M & T\\ \mu & \tau & \nu & \tau'\end{array}\right)+\sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{t} & \mathbf{l}\\ T & L\\ \tau & \lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{l} & \mathbf{0} & \mathbf{l}\\ M & L & M & L\\ \mu & \lambda' & \nu & \lambda\end{array}\right)\right\}$$

$$= \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M}\sum_{\tau=1}^{n_o(T)}\sum_{\tau'=1}^{n_o(T)}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{t} & \mathbf{0} & \mathbf{t}\\ M & T & M & T\\ \mu & \tau & \nu & \tau'\end{array}\right)\left\{\frac{1}{2}\Big[((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{(T,\tau)(T,\tau')}+((\mathbf{P}^{\alpha}\mathbf{S})_{\mathbf{00}})_{(T,\tau')(T,\tau)}\Big]\right.$$

$$\left.-(\mathbf{P}^{\alpha}_{\mathbf{00}})_{(T,\tau)(T,\tau')}-\frac{1}{2}\Big[(\mathbf{Q}^{\alpha}_{\mathbf{0t}})_{(M)(T,\tau,\tau')}+(\mathbf{Q}^{\alpha}_{\mathbf{0t}})_{(M)(T,\tau',\tau)}\Big]\right\}. \tag{5.40}$$

$$\underbrace{\left({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{R}^{\mathrm{II}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \frac{1}{2}\Bigg\{\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \mu' & \nu\end{pmatrix}\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau,\lambda=1}^{n_o(T)}\left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(T,\tau)(T,\lambda)}\left(\begin{matrix}\mathbf{0} & \mathbf{t}\\ M & T\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\mathbf{0} & \mathbf{t}\\ M & T\\ \mu' & \lambda\end{matrix}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(2.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu,\mu')(N)}}$$

$$+\sum_{\nu'=1}^{n_o(N)}\begin{pmatrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \mu & \nu'\end{pmatrix}\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau,\lambda=1}^{n_o(T)}\left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(T,\tau)(T,\lambda)}\left(\begin{matrix}\mathbf{n} & \mathbf{t}\\ N & T\\ \nu' & \tau\end{matrix}\middle|\begin{matrix}\mathbf{n} & \mathbf{t}\\ N & T\\ \nu & \lambda\end{matrix}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(2.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M)(N,\nu',\nu)}}\Bigg\}, \tag{5.41}$$

with

$$\underbrace{\left({}^{(2.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu,\mu')(N)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M}\sum_{\tau,\lambda=1}^{n_o(T)}\left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(T,\tau)(T,\lambda)}\left(\begin{matrix}\mathbf{0} & \mathbf{t}\\ M & T\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\mathbf{0} & \mathbf{t}\\ M & T\\ \mu' & \lambda\end{matrix}\right) - \sum_{\tau,\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(N,\tau)(N,\lambda)}\left(\begin{matrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \mu' & \lambda\end{matrix}\right), \tag{5.42}$$

and

$$\underbrace{\left({}^{(2.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M)(N,\nu',\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}N}\sum_{\tau,\lambda=1}^{n_o(T)}\left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(T,\tau)(T,\lambda)}\left(\begin{matrix}\mathbf{0} & \mathbf{t}\\ N & T\\ \nu' & \tau\end{matrix}\middle|\begin{matrix}\mathbf{0} & \mathbf{t}\\ N & T\\ \nu & \lambda\end{matrix}\right) - \sum_{\tau,\lambda=1}^{n_o(M)}\left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(M,\tau)(M,\lambda)}\left(\begin{matrix}\mathbf{n} & \mathbf{0}\\ N & M\\ \nu' & \tau\end{matrix}\middle|\begin{matrix}\mathbf{n} & \mathbf{0}\\ N & M\\ \nu & \lambda\end{matrix}\right). \tag{5.43}$$

$$
\underbrace{\left({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{R}^{\mathrm{II}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N} \sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{(M,\lambda)(T,\tau)} \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix}\mathbf{n}&\mathbf{t}\\ N&T\\ \nu'&\tau\end{pmatrix} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ M&N&N&M\\ \mu&\nu'&\nu&\lambda\end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(3.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}
$$

$$
+ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N} \sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{(M,\lambda)(T,\tau)} \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix}\mathbf{n}&\mathbf{t}\\ N&T\\ \nu&\tau'\end{pmatrix} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{t}&\mathbf{0}\\ M&T&T&M\\ \mu&\tau&\tau'&\lambda\end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(3.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}} \Bigg\}, \tag{5.44}
$$

with

$$
\underbrace{\left({}^{(3.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{(M,\lambda)(T,\tau)} \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix}\mathbf{0}&\mathbf{t}\\ N&T\\ \nu'&\tau\end{pmatrix} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ M&N&N&M\\ \mu&\nu'&\nu&\lambda\end{array}\right)
$$

$$
- \sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{(M,\lambda)(N,\tau)} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ M&N&N&M\\ \mu&\tau&\nu&\lambda\end{array}\right)
$$

$$
- \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{00}})_{(M,\lambda)(M,\tau)} \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix}\mathbf{0}&\mathbf{n}\\ M&N\\ \tau&\nu'\end{pmatrix} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ M&N&N&M\\ \mu&\nu'&\nu&\lambda\end{array}\right), \tag{5.45}
$$

and

$$
\underbrace{\left({}^{(3.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{0t}})_{(M,\lambda)(T,\tau)} \sum_{\tau'=1}^{n_o(T)} \begin{pmatrix}\mathbf{0}&\mathbf{t}\\ N&T\\ \nu&\tau'\end{pmatrix} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{t}&\mathbf{t}&\mathbf{0}\\ M&T&T&M\\ \mu&\tau&\tau'&\lambda\end{array}\right)
$$

$$
- \sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{(M,\lambda)(N,\tau)} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{n}&\mathbf{n}&\mathbf{0}\\ M&N&N&M\\ \mu&\tau&\nu&\lambda\end{array}\right)
$$

$$
- \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(M)} (\mathbf{P}^{\alpha}_{\mathbf{00}})_{(M,\lambda)(M,\tau)} \sum_{\tau'=1}^{n_o(M)} \left\{ \begin{pmatrix}\mathbf{0}&\mathbf{n}\\ M&N\\ \tau'&\nu\end{pmatrix} - \begin{pmatrix}\mathbf{0}&\mathbf{0}\\ M&N\\ \tau'&\nu\end{pmatrix} \right\} \left(\begin{array}{cc|cc}\mathbf{0}&\mathbf{0}&\mathbf{0}&\mathbf{0}\\ M&M&M&M\\ \mu&\tau&\tau'&\lambda\end{array}\right). \tag{5.46}
$$

$$\underbrace{\left({}^{(4)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{R}^{\mathrm{I}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{tn}}\right)_{(T,\tau)(N,\lambda)}\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{0} & \mathbf{t}\\ M & T\\ \mu' & \tau\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ M & M & N & N\\ \mu & \mu' & \nu & \lambda\end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(4.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}$$

$$+\underbrace{\underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{tn}}\right)_{(T,\tau)(N,\lambda)}\sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{0} & \mathbf{t}\\ M & T\\ \mu & \tau'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{t} & \mathbf{t} & \mathbf{n} & \mathbf{n}\\ T & T & N & N\\ \tau' & \tau & \nu & \lambda\end{array}\right)}_{\stackrel{\mathrm{def}}{=}\left({}^{(4.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}\Bigg\}, \tag{5.47}$$

with

$$\underbrace{\left({}^{(4.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{0t}}\right)_{(N,\lambda)(T,\tau)}\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{0} & \mathbf{t}\\ M & T\\ \mu' & \tau\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ M & M & N & N\\ \mu & \mu' & \nu & \lambda\end{array}\right)$$
$$-\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(N,\tau)(N,\lambda)}\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \mu' & \tau\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ M & M & N & N\\ \mu & \mu' & \nu & \lambda\end{array}\right)$$
$$-\sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{0n}}\right)_{(M,\tau)(N,\lambda)}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ M & M & N & N\\ \mu & \tau & \nu & \lambda\end{array}\right), \tag{5.48}$$

and

$$\underbrace{\left({}^{(4.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}N}\sum_{\tau=1}^{n_o(T)}\sum_{\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{0t}}\right)_{(N,\lambda)(T,\tau)}\sum_{\tau'=1}^{n_o(T)}\begin{pmatrix}\mathbf{0} & \mathbf{t}\\ M & T\\ \mu & \tau'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{t} & \mathbf{t} & \mathbf{0} & \mathbf{0}\\ T & T & N & N\\ \tau' & \tau & \nu & \lambda\end{array}\right)$$
$$-\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(N,\tau)(N,\lambda)}\sum_{\tau'=1}^{n_o(N)}\left\{\begin{pmatrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \mu & \tau'\end{pmatrix}-\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ M & N\\ \mu & \tau'\end{pmatrix}\right\}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ N & N & N & N\\ \tau' & \tau & \nu & \lambda\end{array}\right)$$
$$-\sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{0n}}\right)_{(M,\tau)(N,\lambda)}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n}\\ M & M & N & N\\ \mu & \tau & \nu & \lambda\end{array}\right). \tag{5.49}$$

$$\underbrace{\left({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{R}^{\mathrm{I}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N} \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(L)} \left(\mathbf{P}^{\alpha}_{\mathbf{0l}}\right)_{(M,\tau)(L,\lambda)} \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{n} & \mathbf{l} \\ N & L \\ \nu' & \lambda \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & M & N & N \\ \mu & \tau & \nu & \nu' \end{array}\right)}_{\overset{\mathrm{def}}{=}\left({}^{(5.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}$$

$$+ \underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N} \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(L)} \left(\mathbf{P}^{\alpha}_{\mathbf{0l}}\right)_{(M,\tau)(L,\lambda)} \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix} \mathbf{n} & \mathbf{l} \\ N & L \\ \nu & \lambda' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{l} & \mathbf{l} \\ M & M & L & L \\ \mu & \tau & \lambda' & \lambda \end{array}\right)}_{\overset{\mathrm{def}}{=}\left({}^{(5.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}} \Bigg\}, \tag{5.50}$$

with

$$\underbrace{\left({}^{(5.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}\sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(L)} \left(\mathbf{P}^{\alpha}_{\mathbf{0l}}\right)_{(M,\tau)(L,\lambda)} \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{0} & \mathbf{l} \\ N & L \\ \nu' & \lambda \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & M & N & N \\ \mu & \tau & \nu & \nu' \end{array}\right)$$
$$- \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(N)} \left(\mathbf{P}^{\alpha}_{\mathbf{0n}}\right)_{(M,\tau)(N,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & M & N & N \\ \mu & \tau & \nu & \lambda \end{array}\right)$$
$$- \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(M)} \left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(M,\tau)(M,\lambda)} \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \lambda & \nu' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & M & N & N \\ \mu & \tau & \nu & \nu' \end{array}\right), \tag{5.51}$$

and

$$\underbrace{\left({}^{(5.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M}\sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(L)} \left(\mathbf{P}^{\alpha}_{\mathbf{0l}}\right)_{(M,\tau)(L,\lambda)} \sum_{\lambda'=1}^{n_o(L)} \begin{pmatrix} \mathbf{0} & \mathbf{l} \\ N & L \\ \nu & \lambda' \end{pmatrix} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{l} & \mathbf{l} \\ M & M & L & L \\ \mu & \tau & \lambda' & \lambda \end{array}\right)$$
$$- \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(N)} \left(\mathbf{P}^{\alpha}_{\mathbf{0n}}\right)_{(M,\tau)(N,\lambda)} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & M & N & N \\ \mu & \tau & \nu & \lambda \end{array}\right)$$
$$- \sum_{\tau=1}^{n_o(M)}\sum_{\lambda=1}^{n_o(M)} \left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(M,\tau)(M,\lambda)} \sum_{\lambda'=1}^{n_o(M)} \left\{ \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \lambda' & \nu \end{pmatrix} - \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ M & N \\ \lambda' & \nu \end{pmatrix} \right\} \left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ M & M & M & M \\ \mu & \tau & \lambda' & \lambda \end{array}\right). \tag{5.52}$$

$$\underbrace{\left({}^{(6)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)^{[\mathrm{R}^{\mathrm{II}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := \frac{1}{2}\Bigg\{ \underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(L)}\left(\mathbf{P}^{\alpha}_{\mathbf{nl}}\right)_{(N,\tau)(L,\lambda)}\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{0} & \mathbf{l}\\ M & L\\ \mu' & \lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0}\\ M & N & N & M\\ \mu & \tau & \nu & \mu'\end{array}\right)}_{\overset{\mathrm{def}}{=}\left({}^{(6.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}$$

$$+\underbrace{\underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}M,\mathbf{n}N}\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(L)}\left(\mathbf{P}^{\alpha}_{\mathbf{nl}}\right)_{(N,\tau)(L,\lambda)}\sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{0} & \mathbf{l}\\ M & L\\ \mu & \lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{l} & \mathbf{n} & \mathbf{n} & \mathbf{l}\\ L & N & N & L\\ \lambda' & \tau & \nu & \lambda\end{array}\right)}_{\overset{\mathrm{def}}{=}\left({}^{(6.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}\Bigg\}, \tag{5.53}$$

with

$$\underbrace{\left({}^{(6.1)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(L)}\left(\mathbf{P}^{\alpha}_{\mathbf{0l}}\right)_{(N,\tau)(L,\lambda)}\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{0} & \mathbf{l}\\ M & L\\ \mu' & \lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0}\\ M & N & N & M\\ \mu & \tau & \nu & \mu'\end{array}\right)$$

$$-\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(N,\tau)(N,\lambda)}\sum_{\mu'=1}^{n_o(M)}\begin{pmatrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \mu' & \lambda\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0}\\ M & N & N & M\\ \mu & \tau & \nu & \mu'\end{array}\right)$$

$$-\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(M)}\left(\mathbf{P}^{\alpha}_{\mathbf{0n}}\right)_{(M,\lambda)(N,\tau)}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0}\\ M & N & N & M\\ \mu & \tau & \nu & \lambda\end{array}\right), \tag{5.54}$$

and

$$\underbrace{\left({}^{(6.2)}\mathbf{E}^{\alpha}_{\mathbf{0n}}\right)_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{L=1}^{N_n}}_{\mathbf{l}L\neq\mathbf{0}N}\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(L)}\left(\mathbf{P}^{\alpha}_{\mathbf{0l}}\right)_{(N,\tau)(L,\lambda)}\sum_{\lambda'=1}^{n_o(L)}\begin{pmatrix}\mathbf{0} & \mathbf{l}\\ M & L\\ \mu & \lambda'\end{pmatrix}\left(\begin{array}{cc|cc}\mathbf{l} & \mathbf{0} & \mathbf{0} & \mathbf{l}\\ L & N & N & L\\ \lambda' & \tau & \nu & \lambda\end{array}\right)$$

$$-\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(N)}\left(\mathbf{P}^{\alpha}_{\mathbf{00}}\right)_{(N,\tau)(N,\lambda)}\sum_{\lambda'=1}^{n_o(N)}\left\{\begin{pmatrix}\mathbf{0} & \mathbf{n}\\ M & N\\ \mu & \lambda'\end{pmatrix}-\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ M & N\\ \mu & \lambda'\end{pmatrix}\right\}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ N & N & N & N\\ \lambda' & \tau & \nu & \lambda\end{array}\right)$$

$$-\sum_{\tau=1}^{n_o(N)}\sum_{\lambda=1}^{n_o(M)}\left(\mathbf{P}^{\alpha}_{\mathbf{0n}}\right)_{(M,\lambda)(N,\tau)}\left(\begin{array}{cc|cc}\mathbf{0} & \mathbf{n} & \mathbf{n} & \mathbf{0}\\ M & N & N & M\\ \mu & \tau & \nu & \lambda\end{array}\right). \tag{5.55}$$

6. Approximations of NDIO type

6.1. “Unrestricted” and “Restricted” integral approximations

If one assumes the atomic orbital basis as being not only locally but globally orthonormal, all diatomic overlap integrals occuring in the context of Rüdenberg-type approximations have to be supplemented by the corresponding diatomic Kronecker symbol (“Neglect of Diatomic Integral Overlap”, NDIO). What follows is partially identical with the “Neglect of Diatomic Differential Overlap” description (NDDO) originally introduced by Pople, Santry, & Segal [5] for an approximate treatment of two-center one-electron densities :

$$
\begin{aligned}
\text{(I)}\qquad & \left\{\Phi_\mu(\mathbf{r}_i-\mathbf{R}_M-\mathbf{R}_\mathbf{m})\Phi_\nu(\mathbf{r}_i-\mathbf{R}_N-\mathbf{R}_\mathbf{n})\right\}^{[\mathrm{NDIO}^{\mathrm{I}}_{MN}]}\\
&:= \left\{\Phi_\mu(\mathbf{r}_i-\mathbf{R}_M-\mathbf{R}_\mathbf{m})\Phi_\nu(\mathbf{r}_i-\mathbf{R}_N-\mathbf{R}_\mathbf{n})\right\}^{[\mathrm{NDDO}_{MN}]}\\
&:= \delta_{\mathbf{mn}}\delta_{MN}\Phi_\mu(\mathbf{r}_i-\mathbf{R}_M-\mathbf{R}_\mathbf{m})\Phi_\nu(\mathbf{r}_i-\mathbf{R}_M-\mathbf{R}_\mathbf{m}).
\end{aligned}
\tag{6.1}
$$

This well-known NDDO picture, however, now is extended by an analogous two-center two-electron NDIO scheme which also refers to Rüdenberg’s fundamental distinction :

$$
\begin{aligned}
\text{(II)}\qquad & \left\{\Phi_\mu(\mathbf{r}_i-\mathbf{R}_M-\mathbf{R}_\mathbf{m})\Phi_\nu(\mathbf{r}_j-\mathbf{R}_N-\mathbf{R}_\mathbf{n})\right\}^{[\mathrm{NDIO}^{\mathrm{II}}_{MN}]}\\
&:= \delta_{\mathbf{mn}}\delta_{MN}\Phi_\mu(\mathbf{r}_i-\mathbf{R}_M-\mathbf{R}_\mathbf{m})\Phi_\nu(\mathbf{r}_j-\mathbf{R}_M-\mathbf{R}_\mathbf{m}).
\end{aligned}
\tag{6.2}
$$

Again, in a NDIO-type treatment of four-center repulsion integrals each of both routes have to be passed through twice :

$$
\begin{aligned}
\text{(I)}\quad \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ M & N & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{I}}_{MN}\mathrm{NDIO}^{\mathrm{I}}_{TL}]}
&:=\delta_{\mathbf{mn}}\delta_{MN}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{I}}_{TL}]}\\
&:=\delta_{\mathbf{mn}}\delta_{MN}\delta_{\mathbf{tl}}\delta_{TL}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \nu & \tau & \lambda \end{array}\right),
\end{aligned}
\tag{6.3}
$$

$$
\begin{aligned}
\text{(II)}\quad \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ M & N & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{II}}_{MT}\mathrm{NDIO}^{\mathrm{II}}_{NL}]}
&:=\delta_{\mathbf{mt}}\delta_{MT}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{n} & \mathbf{m} & \mathbf{l} \\ M & N & M & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{II}}_{NL}]}\\
&:=\delta_{\mathbf{mt}}\delta_{MT}\delta_{\mathbf{nl}}\delta_{NL}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{n} & \mathbf{m} & \mathbf{n} \\ M & N & M & N \\ \mu & \nu & \tau & \lambda \end{array}\right).
\end{aligned}
\tag{6.4}
$$

Having interchanged the indices N and ν with T and τ, respectively, Eq. (6.4) equivalently reads :

$$
\begin{aligned}
\text{(II)}\quad \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{n} & \mathbf{l} \\ M & T & N & L \\ \mu & \tau & \nu & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{II}}_{MN}\mathrm{NDIO}^{\mathrm{II}}_{TL}]}
&:=\delta_{\mathbf{mn}}\delta_{MN}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{II}}_{TL}]}\\
&:=\delta_{\mathbf{mn}}\delta_{MN}\delta_{\mathbf{tl}}\delta_{TL}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{t} \\ M & T & M & T \\ \mu & \tau & \nu & \lambda \end{array}\right).
\end{aligned}
\tag{6.5}
$$

In addition to these formulas let us again consider the three-center repulsion integrals $\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)$ and $\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{array}\right)$.

(I) Using two one-electron approximations of NDIO type we get :

$$\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{I}}_{MM}\mathrm{NDIO}^{\mathrm{I}}_{TL}]} := \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{I}}_{TL}]} := \delta_{\mathbf{tl}}\delta_{TL}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \nu & \tau & \lambda \end{array}\right), \tag{6.6}$$

$$\begin{aligned} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{I}}_{MT}\mathrm{NDIO}^{\mathrm{I}}_{NL}]} &:= \delta_{\mathbf{mt}}\delta_{MT}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{l} \\ M & M & M & L \\ \mu & \tau & \nu & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{I}}_{ML}]} \\ &:= \delta_{\mathbf{mt}}\delta_{MT}\delta_{\mathbf{ml}}\delta_{ML}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{m} \\ M & M & M & M \\ \mu & \tau & \nu & \lambda \end{array}\right). \end{aligned} \tag{6.7}$$

(II) Using two two-electron approximations of NDIO type we get :

$$\begin{aligned} \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{II}}_{MT}\mathrm{NDIO}^{\mathrm{II}}_{ML}]} &:= \delta_{\mathbf{mt}}\delta_{MT}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{l} \\ M & M & M & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{II}}_{ML}]} \\ &:= \delta_{\mathbf{mt}}\delta_{MT}\delta_{\mathbf{ml}}\delta_{ML}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{m} \\ M & M & M & M \\ \mu & \nu & \tau & \lambda \end{array}\right), \end{aligned} \tag{6.8}$$

$$\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{II}}_{MM}\mathrm{NDIO}^{\mathrm{II}}_{TL}]} := \left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{II}}_{TL}]} := \delta_{\mathbf{tl}}\delta_{TL}\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{t} \\ M & T & M & T \\ \mu & \tau & \nu & \lambda \end{array}\right). \tag{6.9}$$

Hence, like in the discussion above, applying the NDIO scheme twice implies also an oversimplification of the two-center integral $\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{l} \\ M & M & M & L \\ \mu & \tau & \nu & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{I}}_{ML}]}$ in Eq. (6.7) and of $\left(\begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{l} \\ M & M & M & L \\ \mu & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{NDIO}^{\mathrm{II}}_{ML}]}$ in Eq. (6.8). Obviously, the formulations (6.6) and (6.9) should be preferred, since they use the simplifying NDIO recipe only once. While the oversimplifying "unrestricted" branch of approximation has been discussed comprehensively elsewhere [9], we now turn to the corresponding "restricted" route which avoids such shortcomings.

6.2. "Restricted and Combined NDIO" approximations (NDIO.R&C) for Fock-matrix elements

The term ' "Restricted and Combined NDIO" approximations (NDIO.R&C) ' indicates,

- that both one-electron and two-electron routes of approximation are combined in the sense outlined in Ref. 9, and
- that in this subsection we are going to distinguish four-center and three-center interactions from one another and those of two-center or one-center type. All different types of three-center integrals occuring in Eqs. (2.35) . . . (2.42) will be treated in such a way that oversimplifications are avoided by applying the NDIO

recipe only once. Furthermore, this time all one- and two-center interactions are considered to be evaluated accurately.

Distinguishing atomic off-blockdiagonal from blockdiagonal matrix elements, we define according to Eq. (2.33) :

$$\underbrace{(\mathbf{F}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := (\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + (\mathbf{F}^{A}_{\mathbf{0n}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(N,\nu)} + (\mathbf{F}^{C}_{\mathbf{0n}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(N,\nu)} - (\mathbf{F}^{\alpha E}_{\mathbf{0n}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(N,\nu)}, \tag{6.10}$$

$$(\mathbf{F}^{\alpha}_{\mathbf{00}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(M,\nu)} := (\mathbf{K}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + (\mathbf{F}^{A}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + (\mathbf{F}^{C}_{\mathbf{00}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(M,\nu)} - (\mathbf{F}^{\alpha E}_{\mathbf{00}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(M,\nu)}. \tag{6.11}$$

For the off-blockdiagonal attractive part we define according to Eq. (5.12) :

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{0n}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := {}^{(0)}(\mathbf{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + {}^{(1)}(\mathbf{A}_{\mathbf{0n}})^{[\mathrm{R^I}]}_{(M,\mu)(N,\nu)}. \tag{6.12}$$

For the off-blockdiagonal Coulomb part we define according to Eq. (5.13) :

$$\underbrace{(\mathbf{F}^{C}_{\mathbf{0n}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := {}^{(0)}(\mathbf{C}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + {}^{(1)}(\mathbf{C}_{\mathbf{0n}})^{[\mathrm{NDIO^I NDIO^I}]}_{(M,\mu)(N,\nu)} + {}^{(2)}(\mathbf{C}_{\mathbf{0n}})^{[\mathrm{NDIO^I}]}_{(M,\mu)(N,\nu)} + 2^{(3)}(\mathbf{C}_{\mathbf{0n}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(N,\nu)} + 2^{(4)}(\mathbf{C}_{\mathbf{0n}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(N,\nu)}. \tag{6.13}$$

For the blockdiagonal Coulomb part we define according to Eq. (5.14) :

$$(\mathbf{F}^{C}_{\mathbf{00}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(M,\nu)} := {}^{(0)}(\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + {}^{(1)}(\mathbf{C}_{\mathbf{00}})^{[\mathrm{NDIO^I}]}_{(M,\mu)(M,\nu)} + {}^{(2)}(\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + 2^{(3)}(\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)}. \tag{6.14}$$

For the off-blockdiagonal exchange part we define according to Eq. (5.15) :

$$\underbrace{(\mathbf{F}^{\alpha E}_{\mathbf{0n}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(N,\nu)}}_{N\neq M} := {}^{(0)}(\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + {}^{(1)}(\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{II} NDIO^{II}}]}_{(M,\mu)(N,\nu)} + {}^{(2)}(\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(N,\nu)} + {}^{(3)}(\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(N,\nu)} + {}^{(4)}(\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{I}}]}_{(M,\mu)(N,\nu)} + {}^{(5)}(\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{I}}]}_{(M,\mu)(N,\nu)} + {}^{(6)}(\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(N,\nu)}. \tag{6.15}$$

For the blockdiagonal exchange part we define according to Eq. (5.16) :

$$(\mathbf{F}^{\alpha E}_{\mathbf{00}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(M,\nu)} := {}^{(0)}(\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + {}^{(1)}(\mathbf{E}^{\alpha}_{\mathbf{00}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(M,\nu)} + {}^{(2)}(\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + {}^{(3)}(\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + {}^{(5)}(\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)}. \tag{6.16}$$

With the additional assumption of a globally orthonormal atomic orbital basis the different quantities occuring in Eqs. (6.12) ... (6.16) are defined as follows. From Eq. (5.17) we get :

$$\underbrace{({}^{(1)}\mathbf{A}_{\mathbf{0n}})^{[\mathrm{NDIO^I}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := 0. \tag{6.17}$$

From Eqs. (5.21), (5.24), (5.25), (5.28), and (5.31) we get :

$$\begin{aligned}\underbrace{({}^{(1)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{NDIO^I NDIO^I}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} &= ({}^{(1)}\mathbf{C}_{\mathbf{00}})^{[\mathrm{NDIO^I}]}_{(M,\mu)(M,\nu)} = \underbrace{({}^{(2)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{NDIO^I}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} \\ &= \underbrace{({}^{(3)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{NDIO^{II}}]}_{\mu\nu}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{({}^{(4)}\mathbf{C}_{\mathbf{0n}})^{[\mathrm{NDIO^{II}}]}_{\mu\nu}}_{\mathbf{n}N\neq\mathbf{0}M} := 0.\end{aligned} \tag{6.18}$$

From Eqs. (5.35), (5.38), (5.39), (5.42), (5.45), (5.48), and (5.51) we get :

$$\begin{aligned}\underbrace{({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{II} NDIO^{II}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} &= ({}^{(1)}\mathbf{E}^{\alpha}_{\mathbf{00}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(N,\nu)} = \underbrace{({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} \\ &= \underbrace{({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{({}^{(4)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{I}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} \\ &= \underbrace{({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{I}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} = \underbrace{({}^{(6)}\mathbf{E}^{\alpha}_{\mathbf{0n}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := 0.\end{aligned} \tag{6.19}$$

The off-blockdiagonal matrix elements of Eqs. (6.12), (6.13), and (6.15) now can be rewritten :

$$\underbrace{(\mathbf{F}^{A}_{\mathbf{0n}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := ({}^{(0)}\mathbf{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}, \tag{6.20}$$

$$\underbrace{(\mathbf{F}^{C}_{\mathbf{0n}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := ({}^{(0)}\mathbf{C}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}, \tag{6.21}$$

$$\underbrace{(\mathbf{F}^{\alpha E}_{\mathbf{0n}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(N,\nu)}}_{\mathbf{n}N\neq\mathbf{0}M} := ({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}. \tag{6.22}$$

And the blockdiagonal matrix elements of Eqs. (2.36), (6.14), and (6.16) finally read :

$$(\mathbf{F}^{A}_{\mathbf{00}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(M,\nu)} := ({}^{(0)}\mathbf{A}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + ({}^{(1)}\mathbf{A}_{\mathbf{00}})_{(M,\mu)(M,\nu)}, \tag{6.23}$$

$$(\mathbf{F}^{C}_{\mathbf{00}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(M,\nu)} := ({}^{(0)}\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + ({}^{(2)}\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + 2({}^{(3)}\mathbf{C}_{\mathbf{00}})_{(M,\mu)(M,\nu)}, \tag{6.24}$$

$$\begin{aligned}(\mathbf{F}^{\alpha E}_{\mathbf{00}})^{[\mathrm{NDIO.R\&C}]}_{(M,\mu)(M,\nu)} := {}&({}^{(0)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + ({}^{(2)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)} \\ &+ ({}^{(3)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)} + ({}^{(5)}\mathbf{E}^{\alpha}_{\mathbf{00}})_{(M,\mu)(M,\nu)}.\end{aligned} \tag{6.25}$$

7. Real-space lattice summations including long-range interactions

7.1. Long-range correction of the Fock matrix

We now return to the problem mentioned above in connection with the Eqs. (2.19) and (2.20) concerning real-space lattice sums. With respect to Eq. (2.19), the choice of unit-cell numbers N_a, N_b, and N_c, which governs the expense of real-space lattice summations in general, can be kept small, since the matrices $(\mathbf{S_{0n}})$ decay rather quickly with increasing intercellular distances $|\mathbf{R_0} - \mathbf{R_n}|$. The Fock-matrix representation of Eq. (2.20), on the other hand, contains long-ranging two-center integrals of Coulomb type. For large internuclear distances, these Coulomb-type attraction and repulsion integrals can be identified approximately with classical Coulomb interaction energies :

$$\begin{pmatrix} \mathbf{0} & \mathbf{t} & \mathbf{0} \\ \begin{smallmatrix} M \\ \mu \end{smallmatrix} & T & \begin{smallmatrix} M \\ \mu \end{smallmatrix} \end{pmatrix}_{\infty} := -Z_T |\mathbf{R}_M - [\mathbf{R}_T - \mathbf{R_t}]|^{-1} \quad \text{for all} \quad \mu \; , \tag{7.1}$$

$$\left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ \begin{smallmatrix} M \\ \mu \end{smallmatrix} & \begin{smallmatrix} M \\ \mu \end{smallmatrix} & \begin{smallmatrix} T \\ \tau \end{smallmatrix} & \begin{smallmatrix} T \\ \tau \end{smallmatrix} \end{array}\right)_{\infty} := |\mathbf{R}_M - [\mathbf{R}_T - \mathbf{R_t}]|^{-1} \quad \text{for all} \quad \mu, \tau \; . \tag{7.2}$$

Assuming that all integrals except those of Eqs. (7.1) and (7.2) have decayed sufficiently, if

$$(\mathbf{S}_{\mathbf{0}\{N_a^+,0,0\}}) \approx (\mathbf{S}_{\mathbf{0}\{0,N_b^+,0\}}) \approx (\mathbf{S}_{\mathbf{0}\{0,0,N_c^+\}}) \approx \mathbf{0} \; , \tag{7.3}$$

we additionally have to specify the following long-range corrections. Using the atomic charge definition for a locally orthonormalized basis set

$$q_M^{\infty} \stackrel{\text{def}}{=} Z_M - \sum_{\mu=1}^{n_o(M)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(M,\mu)(M,\mu)} \; , \tag{7.4}$$

we distinguish two off-diagonal cases and the diagonal one. For the diatomic off-diagonal case we write :

$$\begin{aligned} \underbrace{F'^{\alpha}_{(M,\mu)(N,\nu)}(\mathbf{k})}_{N\neq M} := & \sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \exp\left(i[k^a n_a|\mathbf{a}| + k^b n_b|\mathbf{b}| + k^c n_c|\mathbf{c}|]\right) (\mathbf{F}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \\ & + F'^{\alpha\infty}_{(M,\mu)(N,\nu)}(\mathbf{k}) - F'^{\alpha\circ}_{(M,\mu)(N,\nu)}(\mathbf{k}) \; . \end{aligned} \tag{7.5}$$

From the Eqs. (2.35) ... (2.42) we pick out all long-range terms and collect them in $F'^{\alpha\infty}_{(M,\mu)(N,\nu)}(\mathbf{k})$:

$$\begin{aligned} \underbrace{F'^{\alpha\infty}_{(M,\mu)(N,\nu)}(\mathbf{k})}_{N\neq M} \stackrel{\text{def}}{=} & -\sum_{\mathbf{n}=-\infty}^{+\infty} \exp\left(i[k^a n_a|\mathbf{a}| + k^b n_b|\mathbf{b}| + k^c n_c|\mathbf{c}|]\right) \\ & \times (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \underbrace{\left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ \begin{smallmatrix} M \\ \mu \end{smallmatrix} & \begin{smallmatrix} M \\ \mu \end{smallmatrix} & \begin{smallmatrix} N \\ \nu \end{smallmatrix} & \begin{smallmatrix} N \\ \nu \end{smallmatrix} \end{array}\right)_{\infty}}_{:=|\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R_n}]|^{-1}} \; . \end{aligned} \tag{7.6}$$

Using Eq. (2.34), we rewrite

$$(\mathbf{P}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} := \frac{V_d}{(2\pi)^d}\int\int\int \exp\Big\{-i\big[k'^a n_a|\mathbf{a}| + k'^b n_b|\mathbf{b}| + k'^c n_c|\mathbf{c}|\big]\Big\} P'^{\alpha}_{(M,\mu)(N,\nu)}(\mathbf{k}')dk'^a dk'^b dk'^c \ . \qquad ()$$

Inserting Eq. () into Eq. (7.6) we get :

$$\underbrace{F'^{\alpha\infty}_{(M,\mu)(N,\nu)}(\mathbf{k})}_{N\neq M} := -\frac{V_d}{(2\pi)^d}\int\int\int \sum_{\mathbf{n}=-\infty}^{+\infty} \exp\Big\{i[(k^a-k'^a)n_a|\mathbf{a}| + (k^b-k'^b)n_b|\mathbf{b}| + (k^c-k'^c)n_c|\mathbf{c}|]\Big\} \times P'^{\alpha}_{(M,\mu)(N,\nu)}(\mathbf{k}')dk'^a dk'^b dk'^c |\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_{\mathbf{n}}]|^{-1} \qquad ()$$

$$= -P'^{\alpha}_{(M,\mu)(N,\nu)}(\mathbf{0}) \sum_{\mathbf{n}=-\infty}^{+\infty} \exp\big(i[k^a n_a|\mathbf{a}| + k^b n_b|\mathbf{b}| + k^c n_c|\mathbf{c}|]\big)\, |\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_{\mathbf{n}}]|^{-1} \ . \qquad ()$$

$F'^{\alpha\circ}_{(M,\mu)(N,\nu)}(\mathbf{k})$ represents the sum of those classical contributions which had already been included non-classically :

$$\underbrace{F'^{\alpha\circ}_{(M,\mu)(N,\nu)}(\mathbf{k})}_{N\neq M} \stackrel{\text{def}}{=} -\sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \exp\big(i[k^a n_a|\mathbf{a}| + k^b n_b|\mathbf{b}| + k^c n_c|\mathbf{c}|]\big) \times (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} |\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_{\mathbf{n}}]|^{-1} \ . \qquad (7.7)$$

$$= -P'^{\alpha}_{(M,\mu)(N,\nu)}(\mathbf{0}) \sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \exp\big(i[k^a n_a|\mathbf{a}| + k^b n_b|\mathbf{b}| + k^c n_c|\mathbf{c}|]\big)\, |\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_{\mathbf{n}}]|^{-1} \ . \qquad ()$$

For the one-center off-diagonal case we simply get :

$$\underbrace{F'^{\alpha}_{(M,\mu)(M,\nu)}(\mathbf{k})}_{\nu\neq\mu} := \sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \exp\big(i[k^a n_a|\mathbf{a}| + k^b n_b|\mathbf{b}| + k^c n_c|\mathbf{c}|]\big)\, (\mathbf{F}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(M,\nu)} \ . \qquad (7.8)$$

For the diagonal elements we define :

$$F'^{\alpha}_{(M,\mu)(M,\mu)}(\mathbf{k}) := \sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \exp\big(i[k^a n_a|\mathbf{a}| + k^b n_b|\mathbf{b}| + k^c n_c|\mathbf{c}|]\big)\, (\mathbf{F}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(M,\mu)} + F^{\infty}_{(M,\mu)(M,\mu)} - F^{\circ}_{(M,\mu)(M,\mu)} \ . \qquad (7.9)$$

Again, from the Eqs. (2.35) ... (2.42) we pick out all long-range terms and collect them in $F^{\infty}_{(M,\mu)(M,\mu)}$:

$$F^{\infty}_{(M,\mu)(M,\mu)} \stackrel{\text{def}}{=} \underbrace{\sum_{\mathbf{t}=-\boldsymbol{\infty}}^{+\boldsymbol{\infty}} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M} \Bigg\{ \underbrace{\begin{pmatrix} \mathbf{0} & \mathbf{t} & \mathbf{0} \\ M & T & M \\ \mu & & \mu \end{pmatrix}_{\infty}}_{:=-Z_T|\mathbf{R}_M-[\mathbf{R}_T-\mathbf{R}_\mathbf{t}]|^{-1}} + \underbrace{\sum_{\tau=1}^{n_o(T)} (\mathbf{P}^{\oplus}_{\mathbf{00}})_{(T,\tau)(T,\tau)}}_{:=Z_T-q^{\infty}_T} \underbrace{\left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \mu & \tau & \tau \end{array}\right)_{\infty}}_{:=|\mathbf{R}_M-[\mathbf{R}_T-\mathbf{R}_\mathbf{t}]|^{-1}} \Bigg\}$$
$$= \underbrace{\sum_{\mathbf{t}=-\boldsymbol{\infty}}^{+\boldsymbol{\infty}} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M} (-q^{\infty}_T)|\mathbf{R}_M - [\mathbf{R}_T - \mathbf{R}_\mathbf{t}]|^{-1} \quad \text{for all } \mu \ . \tag{7.10}$$

Correspondingly, we write :

$$F^{\circ}_{(M,\mu)(M,\mu)} \stackrel{\text{def}}{=} \underbrace{\sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n}}_{\mathbf{t}T\neq\mathbf{0}M} (-q_T)|\mathbf{R}_M - [\mathbf{R}_T - \mathbf{R}_\mathbf{t}]|^{-1} \quad \text{for all } \mu \ . \tag{7.11}$$

Following Ramírez & Böhm [16], Eq. (7.10) can be interpreted as follows : For large internuclear distances each non-zero Fock-matrix element $F^{\infty}_{(M,\mu)(M,\mu)}$ belonging to an atom M represents the Madelung potential of an electronic point charge at center M of the reference cell. Such Madelung potentials can be evaluated using Ewald-summation techniques [17].

Off-diagonal contributions, however, which stem from long-range exchange interactions, have no classical counterpart in our description. Since the infinite sums of Eq. (7.6) are only conditionally convergent, their evaluation causes severe problems in solid-state Hartree-Fock theories [18]. Numerous techniques and recipes have been proposed to overcome such difficulties (cf. [14] and references therein).

7.2. Long-range correction of the total energy per unit cell

Finally, we discuss real-space lattice summations in the computation of the total energy per unit cell :

$$\mathcal{E}_t = \frac{1}{2} \sum_{M=1}^{N_n} \sum_{\mu=1}^{n_o(M)} \sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{N=1}^{N_n} \sum_{\nu=1}^{n_o(N)} \Big\{ (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \Big[(\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + (\mathbf{F}^{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \Big] + (\mathbf{P}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} (\mathbf{F}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + (\mathbf{P}^{\beta}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} (\mathbf{F}^{\beta}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \Big\}$$

$$+\underbrace{\frac{1}{2}\sum_{M=1}^{N_n} Z_M \underbrace{\sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{N=1}^{N_n}}_{\mathbf{n}N\neq\mathbf{0}M} Z_N|\mathbf{R}_M-[\mathbf{R}_N-\mathbf{R}_\mathbf{n}]|^{-1}}_{\stackrel{\text{def}}{=}\mathcal{E}_n} +\mathcal{E}_{t\infty}-\mathcal{E}_{t\circ}\ . \tag{7.13}$$

According to Eq. (2.33) we can also write :

$$\begin{aligned}\mathcal{E}_t = \frac{1}{2}\sum_{M=1}^{N_n}\sum_{\mu=1}^{n_o(M)}\sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{N=1}^{N_n}\sum_{\nu=1}^{n_o(N)} \Big\{ (\mathbf{P}^{\oplus}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \Big[& 2(\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \\ & +2(\mathbf{F}^{A}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \\ & +(\mathbf{F}^{C}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}\Big] \\ -(\mathbf{P}^{\alpha}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} & (\mathbf{F}^{\alpha E}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \\ -(\mathbf{P}^{\beta}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} & (\mathbf{F}^{\beta E}_{\mathbf{0n}})_{(M,\mu)(N,\nu)}\Big\} \\ & +\mathcal{E}_n+\mathcal{E}_{t\infty}-\mathcal{E}_{t\circ}\ .\end{aligned} \tag{7.14}$$

As before, we pick out all long-range terms from $\mathcal{E}_n$ and the Eqs. (2.35) ... (2.42) and collect them in $\mathcal{E}_{t\infty}$:

$$\begin{aligned}\mathcal{E}_{t\infty} \stackrel{\text{def}}{=} & \frac{1}{2}\sum_{M=1}^{N_n} Z_M \underbrace{\sum_{\mathbf{n}=-\infty}^{+\infty}\sum_{N=1}^{N_n}}_{\mathbf{n}N\neq\mathbf{0}M} Z_N|\mathbf{R}_M-[\mathbf{R}_N-\mathbf{R}_\mathbf{n}]|^{-1} \\ & +\sum_{M=1}^{N_n}\underbrace{\sum_{\mu=1}^{n_o(M)}(\mathbf{P}^{\oplus}_{\mathbf{00}})_{(M,\mu)(M,\mu)}}_{:=(Z_M-q_M)} \underbrace{\sum_{\mathbf{n}=-\infty}^{+\infty}\sum_{N=1}^{N_n}}_{\mathbf{n}N\neq\mathbf{0}M} \underbrace{\begin{pmatrix} \mathbf{0} & & \mathbf{0} \\ & \mathbf{n} & \\ M & N & M \\ \mu & & \mu \end{pmatrix}_\infty}_{:=-Z_N|\mathbf{R}_M-[\mathbf{R}_N-\mathbf{R}_\mathbf{n}]|^{-1}} \\ & +\frac{1}{2}\sum_{M=1}^{N_n}\underbrace{\sum_{\mu=1}^{n_o(M)}(\mathbf{P}^{\oplus}_{\mathbf{00}})_{(M,\mu)(M,\mu)}}_{:=(Z_M-q_M)} \underbrace{\sum_{\mathbf{n}=-\infty}^{+\infty}\sum_{N=1}^{N_n}}_{\mathbf{n}N\neq\mathbf{0}M} \underbrace{\sum_{\nu=1}^{n_o(N)}(\mathbf{P}^{\oplus}_{\mathbf{00}})_{(N,\nu)(N,\nu)}}_{:=(Z_N-q_N)} \underbrace{\left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & M & N & N \\ \mu & \mu & \nu & \nu \end{array}\right)_\infty}_{:=|\mathbf{R}_M-[\mathbf{R}_N-\mathbf{R}_\mathbf{n}]|^{-1}} \\ & -\frac{1}{2}\sum_{M=1}^{N_n}\sum_{\mu=1}^{n_o(M)}\underbrace{\sum_{\mathbf{n}=-\infty}^{+\infty}\sum_{N=1}^{N_n}}_{\mathbf{n}N\neq\mathbf{0}M}\sum_{\nu=1}^{n_o(N)}(\mathbf{P}^{\alpha}_{\mathbf{0n}})^2_{(M,\mu)(N,\nu)} \underbrace{\left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & M & N & N \\ \mu & \mu & \nu & \nu \end{array}\right)_\infty}_{:=|\mathbf{R}_M-[\mathbf{R}_N-\mathbf{R}_\mathbf{n}]|^{-1}} \\ & -\frac{1}{2}\sum_{M=1}^{N_n}\sum_{\mu=1}^{n_o(M)}\underbrace{\sum_{\mathbf{n}=-\infty}^{+\infty}\sum_{N=1}^{N_n}}_{\mathbf{n}N\neq\mathbf{0}M}\sum_{\nu=1}^{n_o(N)}(\mathbf{P}^{\beta}_{\mathbf{0n}})^2_{(M,\mu)(N,\nu)} \underbrace{\left(\begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{n} & \mathbf{n} \\ M & M & N & N \\ \mu & \mu & \nu & \nu \end{array}\right)_\infty}_{:=|\mathbf{R}_M-[\mathbf{R}_N-\mathbf{R}_\mathbf{n}]|^{-1}}\end{aligned}$$

$$= \underbrace{\frac{1}{2}\sum_{M=1}^{N_n} q_M^{\infty} \underbrace{\sum_{\mathbf{n}=-\infty}^{+\infty}\sum_{N=1}^{N_n}}_{\mathbf{n}N\neq\mathbf{0}M} q_N^{\infty}|\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_{\mathbf{n}}]|^{-1}}_{\stackrel{\text{def}}{=}\ \mathcal{E}_{t\infty}^{\mathcal{M}}} + \mathcal{E}_{t\infty}^{E} \ , \tag{7.15}$$

where

$$\mathcal{E}_{t\infty}^{E} \stackrel{\text{def}}{=} -\frac{1}{2}\sum_{M=1}^{N_n} \underbrace{\sum_{\mathbf{n}=-\infty}^{+\infty}\sum_{N=1}^{N_n}}_{\mathbf{n}N\neq\mathbf{0}M} |\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_{\mathbf{n}}]|^{-1} \times \sum_{\mu=1}^{n_o(M)}\sum_{\nu=1}^{n_o(N)} \left[(\mathbf{P}_{\mathbf{0n}}^{\alpha})^2_{(M,\mu)(N,\nu)} + (\mathbf{P}_{\mathbf{0n}}^{\beta})^2_{(M,\mu)(N,\nu)}\right] , \tag{7.16}$$

and

$$\mathcal{E}_{t\circ} \stackrel{\text{def}}{=} \underbrace{\frac{1}{2}\sum_{M=1}^{N_n} q_M \underbrace{\sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{N=1}^{N_n}}_{\mathbf{n}N\neq\mathbf{0}M} q_N|\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_{\mathbf{n}}]|^{-1}}_{\stackrel{\text{def}}{=}\ \mathcal{E}_{t\circ}^{\mathcal{M}}} + \mathcal{E}_{t\circ}^{E} \ , \tag{7.17}$$

with

$$\mathcal{E}_{t\circ}^{E} \stackrel{\text{def}}{=} -\frac{1}{2}\sum_{M=1}^{N_n} \underbrace{\sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+}\sum_{N=1}^{N_n}}_{\mathbf{n}N\neq\mathbf{0}M} |\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_{\mathbf{n}}]|^{-1} \times \sum_{\mu=1}^{n_o(M)}\sum_{\nu=1}^{n_o(N)} \left[(\mathbf{P}_{\mathbf{0n}}^{\alpha})^2_{(M,\mu)(N,\nu)} + (\mathbf{P}_{\mathbf{0n}}^{\beta})^2_{(M,\mu)(N,\nu)}\right] . \tag{7.18}$$

Again, $\mathcal{E}_{t\infty}^{\mathcal{M}}$ is the Madelung energy of a crystalline system with point charges q_M at $\mathbf{R}_M$ and q_N at $(\mathbf{R}_N - \mathbf{R}_n)$. It can also be evaluated by means of Ewald-summation techniques [17]. How the infinite sum of Eq. (7.16) can be treated, which arises from long-range off-diagonal exchange contributions, is again a hard problem of any *ab-initio* solid-state theory of Hartree-Fock type (cf. [14] and references therein) [19].

8. Concluding remarks

The present contribution shows that the insights of the preceding paper obtained for the molecular case [1] can be extended to a related quantum chemical solid-state formalism.

Within a picture gained by an "Restricted and Combined" application (R&C), the four approximations

- of Mulliken type (M),
- of "Zero Integral Overlap" type (ZIO),
- of Rüdenberg type (R), and
- of "Neglect of Diatomic Integral Overlap" type (NDIO)

considered here are interconnected in the following way :

Rotational invariance	Globally orthogonal atomic orbital basis	Locally orthogonal atomic orbital basis
violated	ZIO.R&C	M.R&C
fulfilled	NDIO.R&C	R.R&C

ZIO.R&C, NDIO.R&C or M.R&C might prove to be useful as modifications of numerous computational concepts in semi-empirical quantum chemistry [20]. For a non-empirical orbital theory, however, only those concepts can be important, which neither assume a globally orthogonal basis set, nor violate the rotational invariance condition. Hence, for practical purposes, we are particularly interested in the R.R&C branch which requires a computational procedure for the accurate evaluation of all two-center integrals.

Due to their dependence on a single geometric parameter, all types of two-center integrals can be calculated in advance for about one hundred fixed interatomic distances at the desired level of sophistication [21] and stored once and for all. A cubic spline algorithm [22] may be taken to interpolate the actual integral value from each precomputed list. Such techniques, particularly appropriate for minimal basis sets, have been incorporated in a non-empirical crystal orbital procedure based on Rüdenberg's ideas.

Acknowledgement

About twenty years ago, I first became acquainted with the theory of (one-dimensional) crystals through Professor Seelig's quantum chemical lectures. Later on, he invited me to join his working group to perform band-structure calculations at the "Extended-Hückel" level which seemed to be appropriate for our purposes and computer facilities at that time. While conserving its conceptual simplicity, my scientific efforts of the following years intended to improve this simple semi-empirical picture. The distilled result, which is outlined in the present contribution, appears as a non-empirical variant of Professor Seelig's early concept [23].
I would like to express my gratitude for the many years of cooperation in our small department for Theoretische Chemie, together with sincere congratulations that include best wishes for our Professor's and his family's future.

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$$\underbrace{F'^{\alpha\infty[\mathrm{X.U\&C}]}_{(M,\mu)(N,\nu)}(\mathbf{k})}_{N\neq M} - \underbrace{F'^{\alpha\circ[\mathrm{X.U\&C}]}_{(M,\mu)(N,\nu)}(\mathbf{k})}_{N\neq M} := 0 \ , \quad \mathrm{X} = \mathrm{M}, \mathrm{ZIO}, \mathrm{R}, \mathrm{NDIO} \ .$$

[19] In the already mentioned U&C variant [9], however, the long-range contribution of Eqs. (7.16) again disappears :

$$\mathcal{E}^{E[\mathrm{X.U\&C}]}_{t\infty} - \mathcal{E}^{E[\mathrm{X.U\&C}]}_{t\circ} := 0 \ , \quad \mathrm{X} = \mathrm{M}, \mathrm{ZIO}, \mathrm{R}, \mathrm{NDIO} \ .$$

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