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The Electron Density-Bond Order Matrix and the Spin Density in the Restricted CI Method

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In the frame of the CI method including all singly and doubly excited configurations general expressions for the elements of the electron density-bond order matrix and for the spin density are derived for the ground and excited singlet and triplet molecular states.

Im Rahmen der CI-Methode werden unter Einschluß aller einfach und doppelt angeregten Konfigurationen für den Grundzustand und die angeregten Singulett- und Triplett-Zustände allgemeine Ausdrücke für die Elemente der Elektronendichte- und Bindungsordnungs-Matrix sowie für die Spindichte angegeben.

Dans le cadre de la méthode d'I.C. incluant toutes les configurations mono et diexcitées dans une base d'O.A. orthogonales, on donne les expressions générales pour les éléments de la matrice des densités électroniques et des indices de liaison et pour les densités de spin dans les états fondamentaux et excités singulet ou triplet.

Introduction

The computation of the electronic structure of molecules by the configuration interaction (CI) method is often restricted to singly and doubly excited configurations. The inclusion of more than singly excited configurations leads to a closer description of reactivity, geometry, and other properties of molecules in the ground and excited states. Therefore the knowledge of the distribution of the electron density $P_{\mu\mu}$, the spin density $\varrho_{\mu\mu}$, and the bond orders $P_{\mu\nu}$ computed in this frame will be of value.

An attempt to derive the expression for ${}^1P_{\mu\nu}$ is known [1]. Nevertheless, the formula used in [1] is valid only for the case of mixing of some particular doubly excited configurations, namely those of the types ${}^1\Phi_{\substack{i\to k\\ i\to k}}$ and ${}^1\Phi_{\substack{i\to k\\ j\to l}}$, and of the ground state configuration ${}^1\Phi_0$. An identical formula was erroneously used by the authors of [2–6], who have included singly and/or doubly excited configurations of arbitrary types. The correct formulae for ${}^{1,3}P_{\mu\nu}$ and $\varrho_{\mu\mu}$ with the inclusion of only singly excited configurations are given in [7, 8] where also is indicated that the use of the widely-spread simple formula [1–6] for mixing of configurations of arbitrary types leads sometimes to an even qualitatively incorrect electron density distribution, especially for the states of different multiplicity.

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The present communication is devoted to the derivation of the general expressions for ${}^{1,3}P_{\mu\nu}$ of the ground and excited singlet and triplet molecular states and for $\varrho_{\mu\mu}$ of the triplet states in the frame of the CI method including all singly and doubly excited configurations.

The Wave Functions

The occupied MO's of the ground state of a molecule will be designated by i and j, and the unoccupied MO's by k and l. The single-configurational wave function of the ground state of the system with $2n$ electrons is

$$ {}^1\Phi_0 = (1\bar{1} \ldots i\bar{i}j\bar{j} \ldots n\bar{n}) $$

or for brevity

$$ {}^1\Phi_0 = |i\bar{i}j\bar{j}| \, . $$

The multi-configurational wave functions for the singlet and triplet states, resp., are[1]

$$ \begin{aligned} {}^1\Psi = {} & {}^1X_0\,{}^1\Phi_0 + \sum {}^1X_{i\to k}\,{}^1\Phi_{i\to k} \\ & + \sum {}^1X_{\substack{i\to k\\ i\to k}}\,{}^1\Phi_{\substack{i\to k\\ i\to k}} + \sum {}^1X_{\substack{i\to k\\ j\to k}}\,{}^1\Phi_{\substack{i\to k\\ j\to k}} \\ & + \sum {}^1X_{\substack{i\to k\\ i\to l}}\,{}^1\Phi_{\substack{i\to k\\ i\to l}} + \sum {}^1X'_{\substack{i\to k\\ j\to l}}\,{}^1\Phi'_{\substack{i\to k\\ j\to l}} \\ & + \sum {}^1X''_{\substack{i\to k\\ j\to l}}\,{}^1\Phi''_{\substack{i\to k\\ j\to l}} \, , \end{aligned} $$

$$ \begin{aligned} {}^3\Psi = {} & \sum {}^3X_{i\to k}\,{}^3\Phi_{i\to k} \\ & + \sum {}^3X_{\substack{i\to k\\ j\to k}}\,{}^3\Phi_{\substack{i\to k\\ j\to k}} + \sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3\Phi_{\substack{i\to k\\ i\to l}} \\ & + \sum {}^3X'_{\substack{i\to k\\ j\to l}}\,{}^3\Phi'_{\substack{i\to k\\ j\to l}} + \sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3\Phi''_{\substack{i\to k\\ j\to l}} \\ & + \sum {}^3X'''_{\substack{i\to k\\ j\to l}}\,{}^3\Phi'''_{\substack{i\to k\\ j\to l}} \, , \end{aligned} $$

where

$$ {}^1\Phi_{i\to k} = \frac{1}{\sqrt{2}} (|i\bar{k}j\bar{j}| - |\bar{i}kj\bar{j}|) \, , $$

$$ {}^1\Phi_{\substack{i\to k\\ i\to k}} = |k\bar{k}j\bar{j}| \, , $$

$$ {}^1\Phi_{\substack{i\to k\\ j\to k}} = \frac{1}{\sqrt{2}} (|i\bar{k}\bar{j}k| + |\bar{i}kj\bar{k}|) \, , $$

$$ {}^1\Phi_{\substack{i\to k\\ i\to l}} = \frac{1}{\sqrt{2}} (|k\bar{l}j\bar{j}| + |l\bar{k}j\bar{j}|) \, , $$

$$ {}^1\Phi'_{\substack{i\to k\\ j\to l}} = \frac{1}{2} (|i\bar{k}\bar{j}l| + |\bar{i}kj\bar{l}| - |ikj\bar{l}| - |\bar{i}\bar{k}jl|) \, , $$

[1] Here and in the following equations the summation indexes over MO's are omitted supposing that they run independently over all possible values.

$$
\begin{aligned}
{}^1\Phi''_{\substack{i\to k\\ j\to l}} &= \frac{1}{\sqrt{12}}\left(|i\bar{k}\bar{j}l| + |\bar{i}kj\bar{l}| + |ikj\bar{j}\bar{l}|' + |\bar{i}\bar{k}jl|\right.\\
&\quad \left. - 2|i\bar{k}j\bar{l}| - 2|\bar{i}k\bar{j}l|\right),
\end{aligned}
$$

$$ {}^3\Phi_{i\to k} = |ikj\bar{j}|, $$

$$ {}^3\Phi_{\substack{i\to k\\ j\to k}} = |i\bar{k}jk|, $$

$$ {}^3\Phi_{\substack{i\to k\\ i\to l}} = |klj\bar{j}|, $$

$$ {}^3\Phi'_{\substack{i\to k\\ j\to l}} = \frac{1}{\sqrt{2}}\left(|\bar{i}kjl| - |ikj\bar{l}|\right), $$

$$ {}^3\Phi''_{\substack{i\to k\\ j\to l}} = \frac{1}{\sqrt{6}}\left(|\bar{i}kjl| + |ikj\bar{l}| - 2|ik\bar{j}l|\right), $$

$$ {}^3\Phi'''_{\substack{i\to k\\ j\to l}} = \frac{1}{\sqrt{12}}\left(|\bar{i}kjl| + |ikj\bar{l}| + |ik\bar{j}l| - 3|i\bar{k}jl|\right). $$

The Expectation Value of a One-Electron Operator

Let the one-electron operator be given

$$ \hat{q} = \sum_t \hat{Q}(t). $$

There should be found its average values

$$ {}^1\langle\hat{q}\rangle = \langle {}^1\Psi|\hat{q}|{}^1\Psi\rangle $$

and

$$ {}^3\langle\hat{q}\rangle = \langle {}^3\Psi|\hat{q}|{}^3\Psi\rangle. $$

In order to calculate the matrix elements of $\hat{q}$ on the determinantal functions contained in ${}^1\Psi$ and ${}^3\Psi$ one may use the known expansion [9]

$$ \langle U|\hat{q}|V\rangle = \sum_{rs} \langle u_r|\hat{Q}|v_s\rangle D(r|s), $$

where

$$ U = (u_1 u_2 \ldots u_N), $$
$$ V = (v_1 v_2 \ldots v_N), $$

and $D(r|s)$ is a minor of the determinant

$$ D = \langle U|V\rangle, $$

received by crossing in D the column r and the row s.

Tedious calculations lead to the following expressions for ${}^1\langle\hat{q}\rangle$ through the matrix elements of $\hat{Q}$ in the MO representation and for ${}^3\langle\hat{q}\rangle$ in the spin-MO representation[2]:

$$\begin{aligned}
{}^1\langle\hat q\rangle = {} & 2\sum_{i=1}^{n} Q_{ii} + \sum {}^1X_{i\to k}\,{}^1X_{i'\to k'}(Q_{kk'}\delta_{ii'} - Q_{ii'}\delta_{kk'}) \\
& + 2\sum {}^1X^2_{\substack{i\to k\\ i\to k}}(Q_{kk} - Q_{ii}) + \sum {}^1X_{\substack{i\to k\\ j\to k}}\,{}^1X_{\substack{i'\to k\\ j'\to k}}(2Q_{kk}\delta_{ii'}\delta_{jj'} - Q_{ii'}\delta_{jj'} - Q_{jj'}\delta_{ii'}) \\
& + \sum {}^1X_{\substack{i\to k\\ i\to l}}\,{}^1X_{\substack{i\to k'\\ i\to l'}}(-2Q_{ii}\delta_{kk'}\delta_{ll'} + Q_{ll'}\delta_{kk'} + Q_{kk'}\delta_{ll'}) \\
& + \sum \left({}^1X'_{\substack{i\to k\\ j\to l}}\,{}^1X'_{\substack{i'\to k'\\ j'\to l'}} + {}^1X''_{\substack{i\to k\\ j\to l}}\,{}^1X''_{\substack{i'\to k'\\ j'\to l'}}\right)(Q_{kk'}\delta_{ii'}\delta_{jj'}\delta_{ll'} + Q_{ll'}\delta_{ii'}\delta_{jj'}\delta_{kk'} \\
& - Q_{ii'}\delta_{jj'}\delta_{kk'}\delta_{ll'} - Q_{jj'}\delta_{ii'}\delta_{kk'}\delta_{ll'}) + 2\sqrt{2}\sum {}^1X_{i\to k}\left({}^1X_0 + {}^1X_{\substack{i\to k\\ i\to k}}\right)Q_{ik} \\
& - 2\sum {}^1X_{i\to k}\,{}^1X_{\substack{i\to k\\ j\to k}}Q_{jk} + 2\sum {}^1X_{i\to k}\,{}^1X_{\substack{i\to k\\ i\to l}}Q_{il} \\
& - \sqrt{2}\sum {}^1X_{i\to k}\left({}^1X'_{\substack{i\to k\\ j\to l}} + \sqrt{3}\,{}^1X''_{\substack{i\to k\\ j\to l}}\right)Q_{jl} \\
& + 2\sqrt{2}\sum \left({}^1X_{\substack{i\to k\\ i\to k}}\,{}^1X_{\substack{i\to k\\ j\to k}} + {}^1X_{\substack{i\to k\\ i\to l}}\,{}^1X'_{\substack{i\to k\\ j\to l}}\right)Q_{ij} \\
& + 2\sqrt{2}\sum \left({}^1X_{\substack{i\to k\\ i\to k}}\,{}^1X_{\substack{i\to k\\ i\to l}} + {}^1X_{\substack{i\to k\\ j\to k}}\,{}^1X'_{\substack{i\to k\\ j\to l}}\right)Q_{kl},
\end{aligned}$$

$$\begin{aligned}
{}^3\langle\hat q\rangle = {} & \sum_{i=1}^{n}(Q_{ii} + Q_{\bar i\bar i}) + \sum {}^3X_{i\to k}\,{}^3X_{i'\to k'}(Q_{kk'}\delta_{ii'} - Q_{\bar i\bar i'}\delta_{kk'}) \\
& + \sum {}^3X_{\substack{i\to k\\ j\to k}}\,{}^3X_{\substack{i'\to k\\ j'\to k}}[(Q_{kk} + Q_{\bar k\bar k})\delta_{ii'}\delta_{jj'} - Q_{\bar i\bar i'}\delta_{jj'} - Q_{\bar j\bar j'}\delta_{ii'}] \\
& + \sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X_{\substack{i\to k'\\ i\to l'}}[-(Q_{ii} + Q_{\bar i\bar i})\delta_{kk'}\delta_{ll'} + Q_{kk'}\delta_{ll'} + Q_{ll'}\delta_{kk'}] \\
& + \sum {}^3X'_{\substack{i\to k\\ j\to l}}\,{}^3X'_{\substack{i'\to k'\\ j'\to l'}}\Big[Q_{kk'}\delta_{ii'}\delta_{jj'}\delta_{ll'} - Q_{\bar j\bar j'}\delta_{ii'}\delta_{kk'}\delta_{ll'} \\
& + \frac{1}{2}(Q_{ll'} + Q_{\bar l\bar l'})\delta_{ii'}\delta_{jj'}\delta_{kk'} - \frac{1}{2}(Q_{ii'} + Q_{\bar i\bar i'})\delta_{jj'}\delta_{kk'}\delta_{ll'}\Big] \\
& + \frac{1}{6}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3X''_{\substack{i'\to k'\\ j'\to l'}}[6Q_{kk'}\delta_{ii'}\delta_{jj'}\delta_{ll'} + (5Q_{ll'} + Q_{\bar l\bar l'})\delta_{ii'}\delta_{jj'}\delta_{kk'} \\
& - (4Q_{jj'} + 2Q_{\bar j\bar j'})\delta_{ii'}\delta_{kk'}\delta_{ll'} - (Q_{ii'} + 5Q_{\bar i\bar i'})\delta_{jj'}\delta_{kk'}\delta_{ll'}] \\
& + \frac{1}{12}\sum {}^3X'''_{\substack{i\to k\\ j\to l}}\,{}^3X'''_{\substack{i'\to k'\\ j'\to l'}}[(3Q_{kk'} + 9Q_{\bar k\bar k'})\delta_{ii'}\delta_{jj'}\delta_{ll'} \\
& + (11Q_{ll'} + Q_{\bar l\bar l'})\delta_{ii'}\delta_{jj'}\delta_{kk'} - (Q_{ii'} + 11Q_{\bar i\bar i'})\delta_{jj'}\delta_{kk'}\delta_{ll'} \\
& - (11Q_{\bar j\bar j'} + Q_{jj'})\delta_{ii'}\delta_{kk'}\delta_{ll'}] - 2\sum {}^3X_{i\to k}\,{}^3X_{\substack{i\to k\\ j\to k}}Q_{\bar j\bar k} \\
& - 2\sum {}^3X_{i\to k}\,{}^3X_{\substack{i\to k\\ i\to l}}Q_{il} - \sqrt{2}\sum {}^3X_{i\to k}\,{}^3X'_{\substack{i\to k\\ j\to l}}Q_{\bar j\bar l} \\
& + \sqrt{\frac{2}{3}}\sum {}^3X_{i\to k}\,{}^3X''_{\substack{i\to k\\ j\to l}}(2Q_{jl} + Q_{\bar j\bar l})
\end{aligned}$$

[2] Since we are going to derive ${}^3P_{\mu\nu}$ and $\varrho_{\mu\mu}$ the expression for ${}^3\langle\hat q\rangle$ is written without summation over the spin variables.

$$
\begin{aligned}
&+\frac{1}{\sqrt{3}}\sum_{j\to l} {}^3X_{i\to k}\,{}^3X'''_{i\to k}(Q_{\bar{j}\bar{l}}-Q_{jl})\\
&+\sqrt{2}\sum {}^3X'_{\substack{i\to k\\ j\to k}}\left({}^3X'_{\substack{i\to k\\ j\to l}}-\frac{1}{\sqrt{3}}\,{}^3X''_{\substack{i\to k\\ j\to l}}\right)Q_{\bar{k}\bar{l}}\\
&-\frac{1}{\sqrt{3}}\sum {}^3X_{\substack{i\to k\\ j\to k}}\,{}^3X'''_{\substack{i\to k\\ j\to l}}(3Q_{kl}+Q_{\bar{k}\bar{l}})\\
&+\sqrt{2}\sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X'_{\substack{i\to k\\ j\to l}}Q_{\bar{i}\bar{j}}+\sqrt{\frac{2}{3}}\sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X''_{\substack{i\to k\\ j\to l}}(Q_{\bar{i}\bar{j}}+2Q_{ij})\\
&+\frac{1}{\sqrt{3}}\sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X'''_{\substack{i\to k\\ j\to l}}(Q_{\bar{i}\bar{j}}-Q_{ij})\\
&+\frac{1}{\sqrt{3}}\sum\left[{}^3X'_{\substack{i\to k\\ j\to l}}\left({}^3X''_{\substack{i'\to k\\ j\to l'}}+\frac{1}{\sqrt{2}}\,{}^3X'''_{\substack{i'\to k\\ j\to l'}}\right)\right][(Q_{ll'}-Q_{\bar{l}\bar{l}'})\delta_{ii'}\\
&+(Q_{\bar{i}\bar{i}'}-Q_{ii'})\delta_{ll'}]\\
&+\frac{\sqrt{2}}{6}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3X'''_{\substack{i'\to k\\ j'\to l'}}[(Q_{\bar{l}\bar{l}'}-Q_{ll'})\delta_{ii'}\delta_{jj'}\\
&+(Q_{\bar{i}\bar{i}'}-Q_{ii'})\delta_{jj'}\delta_{ll'}+2(Q_{jj'}-Q_{\bar{j}\bar{j}'})\delta_{ii'}\delta_{ll'}]\,. \qquad (1)
\end{aligned}
$$

The Electron Density-Bond Order Matrix and the Spin Density

Expanding the MO's in linear combination of AO's

$$\varphi_r=\sum_\mu C_{\mu r}\chi_\mu \qquad (2)$$

one can introduce the matrix elements

$$Q_{\mu\nu}=\langle\chi_\mu|\hat{Q}|\chi_\nu\rangle$$

and obtains an expression for ${}^1\langle\hat{q}\rangle$ in terms of the expansion coefficients $C_{\mu r}$. Comparing it with the known expression

$${}^{1,3}\langle\hat{q}\rangle=\sum_{\mu\nu}{}^{1,3}P_{\mu\nu}Q_{\mu\nu} \qquad (3)$$

one finally obtains

$$
\begin{aligned}
{}^1P_{\mu\nu}&=2\sum_{i=1}^{n}C_{\mu i}C_{\nu i}+\sum {}^1X_{i\to k}\,{}^1X_{i'\to k'}(C_{\mu k}C_{\nu k'}\delta_{ii'}-C_{\mu i}C_{\nu i'}\delta_{kk'})\\
&+2\sum_{i\to k}{}^1X^2_{i\to k}(C_{\mu k}C_{\nu k}-C_{\mu i}C_{\nu i})\\
&+\sum {}^1X_{\substack{i\to k\\ j\to k}}\,{}^1X_{\substack{i'\to k\\ j'\to k}}(2C_{\mu k}C_{\nu k}\delta_{ii'}\delta_{jj'}-C_{\mu i}C_{\nu i'}\delta_{jj'}-C_{\mu j}C_{\nu j'}\delta_{ii'})\\
&+\sum {}^1X_{\substack{i\to k\\ i\to l}}\,{}^1X_{\substack{i\to k'\\ i\to l'}}(-2C_{\mu i}C_{\nu i}\delta_{kk'}\delta_{ll'}+C_{\mu k}C_{\nu k'}\delta_{ll'}+C_{\mu l}C_{\nu l'}\delta_{kk'})\\
&+\sum\left({}^1X'_{\substack{i\to k\\ j\to l}}\,{}^1X'_{\substack{i'\to k'\\ j'\to l'}}+{}^1X''_{\substack{i\to k\\ j\to l}}\,{}^1X''_{\substack{i'\to k'\\ j'\to l'}}\right)(C_{\mu k}C_{\nu k'}\delta_{ii'}\delta_{jj'}\delta_{ll'}\\
&+C_{\mu l}C_{\nu l'}\delta_{ii'}\delta_{jj'}\delta_{kk'}-C_{\mu i}C_{\nu i'}\delta_{jj'}\delta_{kk'}\delta_{ll'}-C_{\mu j}C_{\nu j'}\delta_{ii'}\delta_{kk'}\delta_{ll'})
\end{aligned}
$$

$$+2\sqrt{2}\sum {}^1X_{i\to k}\Big({}^1X_0 + {}^1X_{\substack{i\to k\\ i\to k}}\Big)C_{\mu i}C_{\nu k}$$
$$-2\sum {}^1X_{i\to k}{}^1X_{\substack{i\to k\\ j\to k}}C_{\mu j}C_{\nu k} + 2\sum {}^1X_{i\to k}{}^1X_{\substack{i\to k\\ i\to l}}C_{\mu i}C_{\nu l}$$
$$-\sqrt{2}\sum {}^1X_{i\to k}\Big({}^1X'_{\substack{i\to k\\ j\to l}} + \sqrt{3}\,{}^1X''_{\substack{i\to k\\ j\to l}}\Big)C_{\mu j}C_{\nu l}$$
$$+2\sqrt{2}\sum\Big({}^1X_{\substack{i\to k\\ i\to k}}{}^1X_{\substack{i\to k\\ j\to k}} + {}^1X_{\substack{i\to k\\ i\to l}}{}^1X'_{\substack{i\to k\\ j\to l}}\Big)C_{\mu i}C_{\nu j}$$
$$+2\sqrt{2}\sum\Big({}^1X_{\substack{i\to k\\ i\to k}}{}^1X_{\substack{i\to k\\ i\to l}} + {}^1X_{\substack{i\to k\\ j\to k}}{}^1X'_{\substack{i\to k\\ j\to l}}\Big)C_{\mu k}C_{\nu l}\,. \tag{4}$$

In order to calculate $\varrho_{\mu\mu}$ let put in (1)

$$\hat{q} = \sum_t \hat{s}_z(t)\,.$$

Taking into account that

$$(\hat{s}_z)_{ij} = -(\hat{s}_z)_{\bar{i}\bar{j}}$$

and using the AO basis one obtains after some manipulations

$$\Big\langle\sum_t \hat{s}_z(t)\Big\rangle = \frac{1}{2}\sum {}^3X_{i\to k}{}^3X_{i'\to k'}\sum_\mu (C_{\mu k}C_{\mu k'}\delta_{ii'} + C_{\mu i}C_{\mu i'}\delta_{kk'})$$
$$+\frac{1}{2}\sum {}^3X_{\substack{i\to k\\ j\to k}}{}^3X_{\substack{i'\to k\\ j'\to k}}\sum_\mu (C_{\mu j}C_{\mu j'}\delta_{ii'} + C_{\mu i}C_{\mu i'}\delta_{jj'})$$
$$+\frac{1}{2}\sum {}^3X_{\substack{i\to k\\ i\to l}}{}^3X_{\substack{i\to k'\\ i\to l'}}\sum_\mu (C_{\mu k}C_{\mu k'}\delta_{ll'} + C_{\mu l}C_{\mu l'}\delta_{kk'})$$
$$+\frac{1}{2}\sum {}^3X'_{\substack{i\to k\\ j\to l}}{}^3X'_{\substack{i\to k'\\ j'\to l}}\sum_\mu (C_{\mu k}C_{\mu k'}\delta_{jj'} + C_{\mu j}C_{\mu j'}\delta_{kk'})$$
$$+\frac{1}{6}\sum {}^3X''_{\substack{i\to k\\ j\to l}}{}^3X''_{\substack{i'\to k'\\ j'\to l'}}\sum_\mu (3C_{\mu k}C_{\mu k'}\delta_{ii'}\delta_{jj'}\delta_{ll'}$$
$$+2C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}\delta_{kk'} + 2C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{kk'}\delta_{ll'} - C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{kk'}\delta_{ll'})$$
$$+\frac{1}{12}\sum {}^3X'''_{\substack{i\to k\\ j\to l}}{}^3X'''_{\substack{i'\to k'\\ j'\to l'}}\sum_\mu (5C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{kk'}\delta_{ll'}$$
$$+5C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{kk'}\delta_{ll'} + 5C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}\delta_{kk'}$$
$$-3C_{\mu k}C_{\mu k'}\delta_{ii'}\delta_{jj'}\delta_{ll'})$$
$$+\sum {}^3X_{i\to k}{}^3X_{\substack{i\to k\\ j\to k}}\sum_\mu C_{\mu j}C_{\mu k} - \sum {}^3X_{i\to k}{}^3X_{\substack{i\to k\\ i\to l}}\sum_\mu C_{\mu i}C_{\mu l}$$
$$+\frac{1}{2}\sum {}^3X_{i\to k}\Bigg(\sqrt{2}\,{}^3X'_{\substack{i\to k\\ j\to l}} + \sqrt{\frac{2}{3}}\,{}^3X''_{\substack{i\to k\\ j\to l}}$$
$$-\frac{2}{\sqrt{3}}\,{}^3X'''_{\substack{i\to k\\ j\to l}}\Bigg)\sum_\mu C_{\mu j}C_{\mu l} + \frac{1}{2}\sum {}^3X_{\substack{i\to k\\ j\to k}}\Bigg(-\sqrt{2}\,{}^3X'_{\substack{i\to k\\ j\to l}}$$
$$+\sqrt{\frac{2}{3}}\,{}^3X''_{\substack{i\to k\\ j\to l}} - \frac{2}{\sqrt{3}}\,{}^3X'''_{\substack{i\to k\\ j\to l}}\Bigg)\sum_\mu C_{\mu k}C_{\mu l}$$

$$+\frac{1}{2}\sum {}^3X_{\substack{i\to k\\ i\to l}}\Big(-\sqrt{2}\,{}^3X'_{\substack{i\to k\\ j\to l}}+\sqrt{\frac{2}{3}}\,{}^3X''_{\substack{i\to k\\ j\to l}}$$
$$-\frac{2}{\sqrt{3}}\,{}^3X'''_{\substack{i\to k\\ j\to l}}\Big)\sum_\mu C_{\mu i}C_{\mu j}+\frac{1}{\sqrt{3}}\sum {}^3X'_{\substack{i\to k\\ j\to l}}\Big({}^3X''_{\substack{i'\to k\\ j\to l'}}$$
$$+\frac{1}{\sqrt{2}}\,{}^3X'''_{\substack{i\to k\\ j\to l'}}\Big)\sum_\mu (C_{\mu l}C_{\mu l'}\delta_{ii'}-C_{\mu i}C_{\mu i'}\delta_{ll'})$$
$$+\frac{\sqrt{2}}{6}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3X'''_{\substack{i'\to k\\ j'\to l'}}\sum_\mu (2C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{ll'}$$
$$-C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{ll'}-C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}).$$

On the other hand

$$\Big\langle\sum_t \hat{s}_z(t)\Big\rangle=\frac{1}{2}\sum_\mu \varrho_{\mu\mu},$$

so that finally

$$\varrho_{\mu\mu}=\sum {}^3X_{i\to k}\,{}^3X_{i'\to k'}(C_{\mu k}C_{\mu k'}\delta_{ii'}+C_{\mu i}C_{\mu i'}\delta_{kk'})$$
$$+\sum {}^3X_{\substack{i\to k\\ j\to k}}\,{}^3X_{\substack{i'\to k\\ j'\to k}}(C_{\mu i}C_{\mu i'}\delta_{jj'}+C_{\mu j}C_{\mu j'}\delta_{ii'})$$
$$+\sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X_{\substack{i\to k'\\ i\to l'}}(C_{\mu k}C_{\mu k'}\delta_{ll'}+C_{\mu l}C_{\mu l'}\delta_{kk'})$$
$$+\sum {}^3X'_{\substack{i\to k\\ j\to l}}\,{}^3X'_{\substack{i\to k'\\ j'\to l}}(C_{\mu k}C_{\mu k'}\delta_{jj'}+C_{\mu j}C_{\mu j'}\delta_{kk'})$$
$$+\frac{1}{3}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3X''_{\substack{i'\to k'\\ j'\to l'}}(3C_{\mu k}C_{\mu k'}\delta_{ii'}\delta_{jj'}\delta_{ll'}$$
$$+2C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}\delta_{kk'}+2C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{kk'}\delta_{ll'}-C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{kk'}\delta_{ll'})$$
$$+\frac{1}{6}\sum {}^3X'''_{\substack{i\to k\\ j\to l}}\,{}^3X'''_{\substack{i'\to k'\\ j'\to l'}}(5C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{kk'}\delta_{ll'}$$
$$+5C_{\mu j}C_{\mu j'}\delta_{kk'}\delta_{ll'}\delta_{ii'}-3C_{\mu k}C_{\mu k'}\delta_{ii'}\delta_{jj'}\delta_{ll'}$$
$$+5C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}\delta_{kk'})+2\sum {}^3X_{i\to k}\,{}^3X_{\substack{i\to k\\ j\to k}}C_{\mu j}C_{\mu k}$$
$$-2\sum {}^3X_{i\to k}\,{}^3X_{\substack{i\to k\\ i\to l}}C_{\mu i}C_{\mu l}+\sqrt{\frac{2}{3}}\sum {}^3X_{i\to k}\Big(\sqrt{3}\,{}^3X'_{\substack{i\to k\\ j\to l}}$$
$$+{}^3X''_{\substack{i\to k\\ j\to l}}-\sqrt{2}\,{}^3X'''_{\substack{i\to k\\ j\to l}}\Big)C_{\mu j}C_{\mu l}+\sqrt{\frac{2}{3}}\sum\Big(-\sqrt{3}\,{}^3X'_{\substack{i\to k\\ j\to l}}$$
$$+{}^3X''_{\substack{i\to k\\ j\to l}}-\sqrt{2}\,{}^3X'''_{\substack{i\to k\\ j\to l}}\Big)\Big({}^3X_{\substack{i\to k\\ j\to k}}C_{\mu k}C_{\mu l}$$
$$+{}^3X_{\substack{i\to k\\ i\to l}}C_{\mu i}C_{\mu j}\Big)+\sqrt{\frac{2}{3}}\sum {}^3X'_{\substack{i\to k\\ j\to l}}\Big(\sqrt{2}\,{}^3X''_{\substack{i'\to k\\ j\to l'}}$$
$$+{}^3X'''_{\substack{i'\to k\\ j\to l'}}\Big)(C_{\mu l}C_{\mu l'}\delta_{ii'}-C_{\mu i}C_{\mu i'}\delta_{ll'})$$
$$+\frac{\sqrt{2}}{3}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3X'''_{\substack{i'\to k\\ j'\to l'}}(2C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{ll'}$$
$$-C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{ll'}-C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}).\tag{5}$$

The expression (1) also permits to obtain the formula for ${}^3P_{\mu\nu}$. Let us carry out the summation in (1) over the spin variables taking the normalization condition of ${}^3\Psi$ into account. Using the AO representation and comparing the expression derived so far with (3) one finally obtains

$$\begin{aligned}
{}^3P_{\mu\nu} = 2 \sum_{i=1}^{n} C_{\mu i} C_{\nu i} &+ \sum {}^3X_{i\to k}\, {}^3X_{i'\to k'} (C_{\mu k} C_{\nu k'} \delta_{ii'} - C_{\mu i} C_{\nu i'} \delta_{kk'}) \\
&+ \sum {}^3X_{\substack{i\to k\\ j\to k}}\, {}^3X_{\substack{i'\to k\\ j'\to k}} (2C_{\mu k} C_{\nu k} \delta_{ii'} \delta_{jj'} - C_{\mu i} C_{\nu i'} \delta_{jj'} - C_{\mu j} C_{\nu j'} \delta_{ii'}) \\
&+ \sum {}^3X_{\substack{i\to k\\ i\to l}}\, {}^3X_{\substack{i\to k'\\ i\to l'}} (-2C_{\mu i} C_{\nu i} \delta_{kk'} \delta_{ll'} + C_{\mu k} C_{\nu k'} \delta_{ll'} + C_{\mu l} C_{\nu l'} \delta_{kk'}) \\
&+ \sum \Big({}^3X'_{\substack{i\to k\\ j\to l}}\, {}^3X'_{\substack{i'\to k'\\ j'\to l'}} + {}^3X''_{\substack{i\to k\\ j\to l}}\, {}^3X''_{\substack{i'\to k'\\ j'\to l'}} \\
&+ {}^3X'''_{\substack{i\to k\\ j\to l}}\, {}^3X'''_{\substack{i'\to k'\\ j'\to l'}} \Big) (C_{\mu k} C_{\nu k'} \delta_{ii'} \delta_{jj'} \delta_{ll'} \\
&+ C_{\mu l} C_{\nu l'} \delta_{ii'} \delta_{jj'} \delta_{kk'} - C_{\mu i} C_{\nu i'} \delta_{jj'} \delta_{kk'} \delta_{ll'} \\
&- C_{\mu j} C_{\nu j'} \delta_{ii'} \delta_{kk'} \delta_{ll'}) - 2 \sum {}^3X_{i\to k}\, {}^3X_{\substack{i\to k\\ j\to k}} C_{\mu j} C_{\nu k} \\
&- 2 \sum {}^3X_{i\to k}\, {}^3X_{\substack{i\to k\\ i\to l}} C_{\mu i} C_{\nu l} \\
&- \sqrt{2} \sum {}^3X_{i\to k} \Big({}^3X'_{\substack{i\to k\\ j\to l}} - \sqrt{3}\, {}^3X''_{\substack{i\to k\\ j\to l}} \Big) C_{\mu j} C_{\nu l} \\
&+ \sqrt{\frac{2}{3}} \sum {}^3X_{\substack{i\to k\\ j\to k}} \Big(\sqrt{3}\, {}^3X'_{\substack{i\to k\\ j\to l}} - {}^3X''_{\substack{i\to k\\ j\to l}} - 2\sqrt{2}\, {}^3X'''_{\substack{i\to k\\ j\to l}} \Big) C_{\mu k} C_{\nu l} \\
&+ \sqrt{2} \sum {}^3X'_{\substack{i\to k\\ i\to l}} \Big({}^3X'_{\substack{i\to k\\ j\to l}} + \sqrt{3}\, {}^3X''_{\substack{i\to k\\ j\to l}} \Big) C_{\mu i} C_{\nu j} \,. \qquad (6)
\end{aligned}$$

The expressions (4)–(6) immediately lead to the formulae [7, 8]

$${}^{1,3}P_{\mu\nu} = 2 \sum_{i=1}^{n} C_{\mu i} C_{\nu i} + \sum {}^{1,3}X_{i\to k}\, {}^{1,3}X_{i'\to k'} (C_{\mu k} C_{\nu k'} \delta_{ii'} - C_{\mu i} C_{\nu i'} \delta_{kk'}) \,, \qquad (7)$$

and

$$\varrho_{\mu\mu} = \sum {}^3X_{i\to k}\, {}^3X_{i'\to k'} (C_{\mu k} C_{\mu k'} \delta_{ii'} + C_{\mu i} C_{\mu i'} \delta_{kk'}) \,, \qquad (8)$$

which are valid for the case of including *only singly* excited configurations.

The formula for ${}^1P_{\mu\nu}$ erroneously used in [2–6] may be obtained from (7) if the summation in the latter is restricted by the condition $i = i'$ and $k = k'$. The validity of the expression for ${}^1P_{\mu\nu}$ used in [1] follows from (4) when accounting only for some particular configurations, namely those of type ${}^1\Phi_0$, ${}^1\Phi_{\substack{i\to k\\ i\to k}}$, and ${}^1\Phi_{\substack{i\to k\\ j\to l}}$ which have been included by these authors.

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References

1. Egorova, L. I., V. N. Mochalkin, R. I. Rakauskas, L. A. Borovinsky, and A. B. Bolotin: Theoret. i Eksperim. Khimiya (U.S.S.R.) **2**, 291 (1966).
2. Kagan, G. I., I. N. Fundiler, and G. M. Kagan: Theoret. i Eksperim. Khimiya (U.S.S.R.) **2**, 589 (1966).
3. Mochalkin, V. N.: Theoret. i Eksperim. Khimiya (U.S.S.R.) **2**, 729 (1966).

4. — L. I. Egorova, and L. A. Borovinsky: Theoret. i Eksperim. Khimiya (U.S.S.R.) **3**, 398 (1967).
5. Imamura, A., H. Fujita, and C. Nagata: Bull. chem. Soc. Japan **40**, 21 (1967).
6. Pukanic, G. W., D. R. Forshey, B. J. D. Wegener, and J. B. Greensfields: Theoret. chim. Acta (Berl.) **9**, 38 (1967).
7. Danilov, V. I.: Quantum-mechanical study of the nucleic acids components in connection with the molecular mechanisms of mutagenesis, Ph. D. Thesis, Institute of Physical Chemistry, Academy of Sciences of the Ukrainian S.S.R., Kiev, 1968.
8. Kruglyak, Yu. A.: On calculation of electronic structure of conjugated molecules and radicals by self-consistent and configuration interaction methods. In: L. P. Kayushin, M. K. Pulatova, and K. M. Lvov: Investigation of paramagnetic centers in γ-irradiated proteins. Moscow: Publishing House "Nauka" (in press).
9. Löwdin, P.-O.: Physic. Rev. **97**, 1474 (1955).

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