Theoret. Chim. Acta (Berl.) 43, 261-271 (1977)

THEORETICA CHIMICA ACTA

On the Calculation of Multiplet Energies by the Hartree–Fock–Slater Method

Tom Ziegler and Arvi Rauk
Department of Chemistry, University of Calgary, Calgary, Alberta, Canada
T2N 1N4

Evert J. Baerends
Scheikundig Laboratorium Der Vrije Universiteit, De Boelelaan 1083, Amsterdam,
The Netherlands

It is shown that a consistent application of the $\rho^{1/3}$ approximation of the Hartree-Fock-Slater method requires the use of one specific procedure, the sum method, for the calculation of the energy E_S^1 of singlet excited states of closed shell molecules. Further, E_S^1 is found to be in reasonable agreement with experiment for a number of molecules, contrary to the energy E_S^2 obtained according to another method discussed in the literature. The calculation of other multiplet splittings than singlet-triplet in the Hartree-Fock-Slater method is also considered.

Key words: Multiplet energies - Calculation by the Hartree-Fock-Slater method

1. Introduction

The Hartree-Fock-Slater Method [1] has proved itself to be a powerful tool for calculations of excitation energies [2, 3]. Bagus and Bennett [4] have recently shown from numerical results that when singlet-triplet splittings are calculated by the Xα method, using two independent expressions derivable from one-electron theory, the results differ by a large amount. These authors expressed caution at the quantitative value of the splittings and made no mention of the absolute values of the singlet excitation energies.

This communication begins by an analysis of the statistical exchange expression [1] in Sect. 3, where it is shown that the statistical exchange approximation only in general leads to the well-known statistical energy expression [1] for single determinantal wave functions. The results by Bagus and Bennett are discussed in Sect. 4, where it is shown that only one of the two values for the triplet-singlet splitting is consistent with the statistical exchange approximation. Finally, the conditions under which one can calculate multiplet energies by the Hartree-Fock-Slater method are discussed in Sect. 5.

2. Computational Details

The DVXα method by Baerends, Ellis and Ros [5] was used in connection with a double zeta STO basis set [6]. The geometry of all excited states was taken as that of the ground state. The energy of the excited states (relative to ground state) was calculated by the transition state method [1]. A value of 0.7 was used for the exchange parameter, α [5].

3. Statistical Energy Expression

We begin by showing under what conditions the statistical exchange approximation [1] leads to the well-known statistical energy expression [1].

The total energy of a N-electron wave function can be written in a compact form in terms of the one- and two-electron density matrices [1], $\rho_1(x_1, x_1')$ and $\rho_2(x_1, x_2, x_1', x_2')$, as

$$E = \int_{x=x'} f(x_1')\rho_1(x_1, x_1')dx_1 + \tfrac{1}{2}\int \rho_2(x_1, x_2)\frac{1}{r_{12}}dx_1dx_2 \tag{3.1}$$

where the notation $\rho_2(x_1, x_2)$ is used for the diagonal element of the two-electron density matrix (later in the text, $\rho_2(x_1)$ is used for the diagonal element of the corresponding one-electron density matrix). The operator $f(x_1)$ represents the electronic-kinetic energy as well as the attraction between the electrons and the nuclei, and x_i is the general coordinate for an electron with space coordinate, $\mathbf{r}_i$, and spin coordinate, s_i. The function $\rho_2(x_1, x_2)$ can be written in terms of four spin components,

$$\begin{aligned}\rho_2(x_1, x_2) = {} & \rho_2^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)\alpha^2(s_1)\alpha^2(s_2)\\ & + \rho_2^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)\alpha^2(s_1)\beta^2(s_2)\\ & + \rho_2^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2)\beta^2(s_1)\alpha^2(s_2)\\ & + \rho_2^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)\beta^2(s_1)\beta^2(s_2),\end{aligned} \tag{3.2}$$

where $\rho_2^{\alpha\alpha}$ and $\rho_2^{\beta\beta}$ give the probability of finding two electrons of the same spin (α and β, respectively) at $(\mathbf{r}_1, \mathbf{r}_2)$ and $\rho_2^{\alpha\beta}$, $\rho_2^{\beta\alpha}$ the probability of finding two electrons of different spin at $(\mathbf{r}_1, \mathbf{r}_2)$. Substitution of Eq. (3.2) into Eq. (3.1) then yields, after a little manipulation, an energy expression which is suitable for a discussion of the statistical exchange approximation and the corresponding statistical energy expression.

$$\begin{aligned}E = {} & \int_{x=x'} \rho_1(x_1, x_1')f(x_1')dx_1 + \tfrac{1}{2}\int \rho_1(x_1)\rho_1(x_2)\frac{1}{r_{12}}dx_1dx_2\\ & + \tfrac{1}{2}\int \rho_1^{\alpha}(\mathbf{r}_1)\rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)\alpha^2(s_1)\alpha^2(s_2)\frac{1}{r_{12}}dx_1dx_2\\ & + \tfrac{1}{2}\int \rho_1^{\beta}(\mathbf{r}_1)\rho_x^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)\beta^2(s_1)\beta^2(s_2)\frac{1}{r_{12}}dx_1dx_2\end{aligned}$$

$$+\tfrac{1}{2}\int \rho_1^{\alpha}(\mathbf{r}_1)\rho_x^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)\alpha^2(s_1)\beta^2(s_2)\,\frac{1}{r_{12}}\,dx_1dx_2$$

$$+\tfrac{1}{2}\int \rho_1^{\beta}(\mathbf{r}_1)\rho_x^{\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2)\beta^2(s_1)\alpha^2(s_2)\,\frac{1}{r_{12}}\,dx_1dx_2 \tag{3.3}$$

where

$$\rho_x^{\alpha\alpha}(r_1,r_2)=\left[\frac{\rho_2^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)}{\rho_1^{\alpha}(\mathbf{r}_1)}-\rho_1^{\alpha}(\mathbf{r}_2)\right]. \tag{3.4}$$

and

$$\rho_x^{\alpha\beta}(r_1,r_2)=\left[\frac{\rho_2^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)}{\rho_1^{\alpha}(\mathbf{r}_1)}-\rho_1^{\beta}(\mathbf{r}_2)\right]. \tag{3.5}$$

Analogous expressions are obtained for the function $\rho_x^{\beta\beta}$ by replacing α for β in Eq. (3.4), and for the function $\rho_x^{\beta\alpha}$ by permuting α and β in Eq. (3.5). ρ_1^{α} and ρ_1^{β} are the spin densities corresponding to ρ_1.

The application of the statistical exchange approximation [7],

$$\int \rho_1^{\alpha}(\mathbf{r}_1)\rho_x^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)\,\frac{1}{r_{12}}\,d\mathbf{r}_1d\mathbf{r}_2 \simeq -K\int \rho_1^{\alpha}(\mathbf{r}_1)\,[\rho_1^{\alpha}(\mathbf{r}_1)]^{1/3} \tag{3.6}$$

with a similar expression involving $\rho_x^{\beta\beta}$ now gives

$$E \simeq E(\rho_1)+E^{\alpha\beta} \tag{3.7}$$

where

$$E(\rho_1)=\int_{x=x'} \rho_1(x_1,x_1')f(x_1')dx_1+\tfrac{1}{2}\int \rho_1(x_1)\rho_1(x_2)\,\frac{1}{r_{12}}\,dx_1dx_2$$

$$-K\int \rho_1^{\alpha}(\mathbf{r}_1)\,[\rho_1^{\alpha}(\mathbf{r}_1)]^{1/3}\,d\mathbf{r}_1-K\int \rho_1^{\beta}(\mathbf{r}_1)\,[\rho_1^{\beta}(\mathbf{r}_1)]^{1/3}\,d\mathbf{r}_1 \tag{3.8}$$

is the well-known expression for the statistical energy [1], and

$$E^{\alpha\beta}=\tfrac{1}{2}\int \rho^{\alpha}(\mathbf{r}_1)\rho_x^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)\alpha^2(\mathbf{r}_1)\beta^2(\mathbf{r}_2)\,\frac{1}{r_{12}}\,dx_1dx_2$$

$$+\tfrac{1}{2}\int \rho^{\beta}(\mathbf{r}_1)\rho_x^{\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2)\beta^2(\mathbf{r}_1)\alpha^2(\mathbf{r}_2)\,\frac{1}{r_{12}}\,dx_1dx_2. \tag{3.9}$$

The energy E in Eq. (3.7) is not identical to the statistical energy $E(\rho_1)$ unless $E^{\alpha\beta}$ is zero. This is the case for a single determinantal wave function where one has,

$$\rho_2^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)=\rho_1^{\alpha}(\mathbf{r}_1)\rho_1^{\beta}(\mathbf{r}_2),\qquad \rho_2^{\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2)=\rho_1^{\beta}(\mathbf{r}_1)\rho_1^{\alpha}(\mathbf{r}_2), \tag{3.10}$$

and correspondingly $\rho_x^{\alpha\beta}=\rho_x^{\beta\alpha}=0$. The term $E^{\alpha\beta}$ is in general not zero for multiplets with a multideterminantal wave function. In those cases, it is not consistent with the statistical exchange approximation to calculate the energy E of Eq. (3.7) from the statistical energy expression, $E(\rho_1)$.

It is, however, possible in a number of cases to express a multiplet energy, H, as a weighted sum of one-determinantal energies $E(D_i)$,

$$H = \sum_i C_i E(D_i) \tag{3.11}$$

and one might in those cases try to calculate H approximately by replacing $E(D_i)$ with the statistical energy $E(\rho_1^i)$. We get

$$H \simeq \sum_i C_i E(\rho_1^i) \tag{3.12}$$

where ρ_1^i is the density corresponding to the one-determinantal wave function D_i. This procedure, which we call the *sum method* and discuss in the next section, allows us to approximate the averaged configuration energy (the average energy of all possible determinants in a given configuration) in the following way,

$$E_{\mathrm{av}} \simeq \frac{1}{N}\sum_{i=1} E(\rho_1^i), \tag{3.13}$$

where N is the total number of different one-determinantal wave functions (with densities, ρ_1^i) due to a given electronic configuration.

It might appear that one could avoid the troublesome term $E^{\alpha\beta}$ by applying the statistical exchange approximation to the last two terms of the following expression for the total energy:

$$\begin{aligned} E = {} & \int_{x=x'} \rho_1(x_1, x_1')f(x_1')dx_1 + \tfrac{1}{2}\int \rho_1(x_1)\rho_1(x_2)\frac{1}{r_{12}}\,dx_1dx_2 \\ & + \tfrac{1}{2}\int \rho_1^{\alpha}(\mathbf{r}_1)\left\{\rho_x^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) + \rho_x^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)\right\}\,\alpha^2(s_1)\alpha^2(s_2)\frac{1}{r_{12}}\,dx_1dx_2 \\ & + \tfrac{1}{2}\int \rho_1^{\beta}(\mathbf{r}_1)\left\{\rho_x^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2) + \rho_x^{\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2)\right\}\,\beta^2(s_1)\beta^2(s_2)\frac{1}{r_{12}}\,dx_1dx_2. \end{aligned} \tag{3.15}$$

This proposal has some merit since the energy of Eq. (3.15) has the same value numerically as the energy of Eq. (3.3). It is shown in the Appendix 1, that this would require

$$\rho_x^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) + \rho_x^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2) \xrightarrow[\mathbf{r}_1\to\mathbf{r}_2]{} -\rho_1^{\alpha}(\mathbf{r}_2) \tag{3.16}$$

with a similar condition for $\rho_x^{\beta\beta} + \rho_x^{\beta\alpha}$. Since $\rho_x^{\alpha\alpha}$ goes to $-\rho_1^{\alpha}(r_2)$ as $\mathbf{r}_1$ goes to $\mathbf{r}_2$ we are left with a condition that is generally true only for single determinantal wave functions, namely that $\rho_x^{\alpha\beta}(\mathbf{r}_2,\mathbf{r}_2)$ is zero.

Slater has on several occasions [1, 7] given an expression for the statistical energy of an averaged configuration which has the form, $E(\rho_1^{\mathrm{av}})$. The function $E(\rho_1)$ is defined in Eq. (3.8), and ρ_1^{av} is the averaged density of all single determinantal wave functions due to a given configuration. The expression $E(\rho_1^{\mathrm{av}})$, which in general differs from that proposed in Eq. (3.13), is obtained by writing the averaged configuration energy, E_{av}, in the form given in Eq. (3.15) and then applying the statistical exchange approximation to the last two terms. It is shown in Appendix 2 that such a procedure is inconsistent with the statistical exchange approximation in the sense that $\rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_1) + \rho_x^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_1) \neq -\rho^{\alpha}(r_1)$. We will return to Slater's expression in the next section.

4. Calculation of the Singlet-Triplet Splitting

Bagus and Bennett [4] discussed an electronic configuration consisting of closed shells plus two singly occupied molecular orbitals. Since, for the following discussion, the closed shells are irrelevant, the configuration can be represented simply as $(a)^1(b)^1$, from which one can write the usual four state functions,

$$^3_1\Psi = |\overset{+}{a}\overset{+}{b}|, \qquad ^3_0\Psi = \frac{1}{\sqrt{2}}(|\overset{+}{a}\overset{-}{b}| + |\overset{-}{a}\overset{+}{b}|), \qquad ^3_{-1}\Psi = |\overset{-}{a}\overset{-}{b}|, \qquad \text{and}$$

$$^1_0\Psi = \frac{1}{\sqrt{2}}(|\overset{+}{a}\overset{-}{b}| - |\overset{-}{a}\overset{+}{b}|).$$

The sum method described in Sect. 3 affords a triplet energy E_T and a singlet energy, E_s^1, in the following way[1].

The statistical energy of D_1, which we will call $E_T(D_1)$ since it is a triplet energy calculated from the density of $D_1 = |\overset{+}{a}\overset{+}{b}|$, is given by

$$E_T(D_1) = E^0 - K \int \{a(1)a(1) + b(1)b(1)\} \; [a(1)a(1) + b(1)b(1)]^{1/3} \cdot d\tau_1 \tag{4.1}$$

where K is a positive constant, and E^0 is the part of the energy common for the three expressions in Eq. (4.1), Eq. (4.2) and Eq. (4.3). The statistical energy of $D_2 = |\overset{+}{a}\overset{-}{b}|$, half triplet and half singlet, is given by

$$\tfrac{1}{2}(E_T(D_2) + E_S(D_2)) = E^0 - K \int a(1)a(1) \; [a(1)a(1)]^{1/3} \cdot d\tau_1$$
$$-K \int b(1)b(1) \; [b(1)b(1)]^{1/3} \cdot d\tau_1. \tag{4.2}$$

Eq. (4.1) directly gives a triplet energy which, when substituted into Eq. (4.2) in turn gives the singlet energy, E_S^1. Calculated values of E_T and E_S^1 are shown in Table 1 for a number of molecules. They compare well with experiment. The averaged configuration energy consistent with the sum method (Eq. (3.13)) is $\frac{1}{4}\{2E_T(D_1) + E_T(D_2) + E_S(D_2)\}$. We will now make a comparison with Slater's expression given by

$$\tfrac{3}{4}E_T(D_3) + \tfrac{1}{4}E_S(D_3) = E^0 - K \int \{a(1)a(1) + b(1)b(1)\}$$
$$\times \tfrac{1}{2}(a(1)a(1) + b(1)b(1))]^{1/3}\} d\tau_1 \tag{4.3}$$

---

[1] Strictly speaking, the subscripted E's E_S and E_T, of this section should be replaced by H's to conform with our general notation for a multiplet energy. However, we feel that in the discussion of the particular case of singlet and triplet energies, the notation adopted is less awkward.

Table 1. Calculation of triplet and singlet transition energies (eV)[a, b]

Compound	Transition	$\frac{3}{4}E_T(D_3) + \frac{1}{4}E_S(D_3)$	$\frac{1}{2}E_T(D_2) + \frac{1}{2}E_S(D_2)$	$E_T(D_1)$	${}^{c}E_S^1$	${}^{d}E_S^2$	E_S^{exp}	E_T^{exp}
H_2CO	$2b_2 \rightarrow 2b_1$	(4.22)	3.48 (4.32)	3.18 (3.14)	3.70 (3.70)	7.34 (7.46)	3.50^{e}	3.21^{e}
C_2H_2	$\pi \rightarrow \pi^*$	(6.08)	6.01 (6.01)	4.57 (4.63)	7.45 (7.39)	10.61 (10.43)	7.6^{f}	4.6^{f}
C_4H_6	$1b_g \rightarrow 2a_u$	(4.22)	4.18 (4.19)	3.31 (3.36)	5.05 (5.02)	6.95 (6.80)	5.9^{g}	3.22^{g}
CO	$5\sigma \rightarrow 2\pi$	(7.35)	6.90 (6.81)	5.81 (5.80)	7.99 (7.81)	11.97 (12.00)	8.4^{h}	6.3^{h}
N_2	$3\sigma_g \rightarrow 1\pi_g$	(8.86)	8.48 (8.48)	7.83 (7.83)	9.13 (9.13)	11.95 (11.95)	9.3^{i}	8.1^{i}
	$2\sigma_u \rightarrow 1\pi_g$	(11.70)	11.51 (11.47)	10.68 (10.73)	12.34 (12.21)	14.76 (14.61)	12.8^{i}	11.1^{i}

[a] The numbers in parentheses correspond to calculations based on orbitals optimized with respect to D_3, see text.

[b] The numbers not in parentheses correspond to calculations where the orbitals have been optimized separately for D_1, D_2 and D_3, see text.

[c] Singlet energy calculated from $E_T(D_1)$ and $\frac{1}{2}E_T(D_2) + \frac{1}{2}E_S(D_2)$.

[d] Singlet energy calculated from $E_T(D_1)$ and $\frac{3}{4}E_T(D_3) + \frac{1}{4}E_S(D_3)$.

[e] Ref. [8]. [f] Ref. [9]. [g] Ref. [10]. [h] Ref. [11]. [i] Ref. [12].

where the index D_3 indicates that the density used in Eq. (4.3) is the average of the densities of the singlet state and the three components of the triplet state. The identification is made implicit in the left-hand side of Eq. (4.3). The energy in Eq. (4.3) is clearly higher than $E_T(D_1)$ of Eq. (4.1) but, what is more important, is also higher than $\frac{1}{2}\{E_T(D_2) + E_S(D_2)\}$ of Eq. (4.2). The latter point is shown numerically in Table 1 and follows from the reasonable assumption that the exchange integral

$$\int u_i(1)u_i(1) \cdot [\, \lambda \cdot u_i(1)u_i(1) + (\sqrt{1-\lambda^2})\, u_j(1)u_j(1)]^{1/3} \cdot d\tau_1$$

has its maximum for $\lambda = 1$. The singlet energy, E_S^2, which one can calculate by substituting $E_T(D_1)$ for $E_T(D_3)$ in Eq. (4.3) is consequently higher than E_S^1, and this is still the case if one calculates, E_S^1, E_S^2, from a set of orbitals (a, b) optimized with respect to Eq. (4.3) as shown in Table 1 (by the numbers in parentheses). It is therefore clear that the discrepancies noted by Bagus and Bennett (4) between $(E_S^1 - E_T)$ and $(E_S^2 - E_T)$ are not primarily due to the use of not properly optimized orbitals in the different energy expressions, but come from the inconsistent use of Eq. (4.3) in connection with the sum method.

We now return to the sum method and discuss its application to a general electronic configuration. The energy $E(D_i)$ of each possible single determinant D_i in a given configuration is, in general, a weighted sum of multiplet energies H_j,

$$E(D_i) = \sum_j C_{ij}H_j. \tag{4.4}$$

The idea of the sum method is to replace $E(D_i)$ in Eq. (4.4) by the corresponding statistical energy $E(\rho_i)$ and in this way obtain a set of equations

$$E(\rho_i) = \sum_j C_{ij}H_j \tag{4.5}$$

from which one can find the multiplet energies H_j, provided that the number of determinants of different energy, $E(\rho_i)$, is the same as the number of multiplets with different energy.

We amplify these remarks in the next section.

5. Spatial Multiplets

If an excited configuration gives rise to two or more state functions with the same symmetry and the same spin, calculation of the individual energies of these state functions goes beyond any one electron model. For example, in the case of CrO_4^{3-}, it is not possible to derive the energies of the two singlet states of A_1 symmetry which arise from the configuration $(t_1)^5(2e)^1(5t_2)^1$ [16] either by the Hartree-Fock or by the Hartree-Fock-Slater method without configuration interaction.

If all state functions of the same spin have different space symmetries, it is possible to derive their energies by the Hartree-Fock method but not necessarily by the Hartree-Fock-Slater method. As stated in the previous section, the general condition for

Table 2. Some triplet and singlet energies for CO, N_2, C_6H_6 and CrO_4^{2-} in eV

Compound	Excited Configuration	State Symmetry	E_T^{cal}	E_S^{cal}	E_T^{exp}	E_S^{exp}
CO^a	$(1\pi)^3(2\pi)^1$	Δ	9.65	10.20	9.2^b	10.5^b
$N_2{}^a$	$(1\pi_u)^3(2\pi_g)^1$	Δ	8.70	10.58	8.9^c	10.3^c
C_6H_6	$(1e_g)^3(2e_u)^1$	E_{2u}	4.65	6.18	4.6^d	6.9^d
CrO_4^{2-}	$(t_1)^5(2e)^1$	T_1	2.71	2.83	-	2.8^e
		T_2	2.79	3.28	-	3.32^e

[a] The configuration $(1\pi)^3(2\pi)^1$ in CO and N_2 has the states $^{(1,3)}\Sigma^{(-)}$, $^{(1,3)}\Sigma^{(+)}$ and $^{(1,3)}\Delta$. Only the $^{(1,3)}\Delta$ states can be resolved by the HFS method.

[b] Ref. [11]. [c] Ref. [13]. [d] Ref. [14]. [e] Ref. [15].

calculating the energy of all multiplets in a given configuration is that the number of determinants with different energy is the same as the number of multiplets with different energy. The excited configuration $(t_1)^5(2e)^1$ in CrO_4^{2-} generates the four states [16] $^{3,1}T_1$, $^{3,1}T_2$, and the determinants, $D_1 = |t_{1z}^{+}2\bar{e}_a|$, $D_2 = |t_{1z}^{+}2\overset{+}{e}_a|$, $D_3 = |t_{1z}^{+}2\bar{e}_b|$ and $D_4 = |t_{1z}^{+}2\overset{+}{e}_b|$, all of different energy. From D_1 and D_2 one can obtain the energy of $^{3,1}T_1$ and from D_3 and D_4, the energy of $^{3,1}T_2$. An example in which not all multiplets can be calculated is the first excited configuration of benzene, $(e_{1g})^3(e_{2u})^1$, which gives rise to six states $^{3,1}E_{1u}$, $^{3,1}B_{1u}$ and $^{3,1}B_{2u}$ [16], but for which one has only four determinants of different energy, $D_1 = |e_{1ga}^{+}e_{2ua}^{-}|$, $D_2 = |e_{1ga}^{+}e_{2ua}^{+}|$, $D_3 = |e_{1ga}^{+}e_{2ub}^{+}|$ and $D_4 = |e_{1ga}^{+}e_{2ub}^{-}|$. One can derive from D_1 and D_2 the energy of $^{3,1}E_{1u}$, whereas D_3 and D_4 can only give the average triplet and average singlet energy of B_{1u} and B_{2u}. In Table 2 we give some calculated results for CrO_4^{2-}, C_6H_6, N_2 and CO. As was seen in Table 1, quite satisfactory agreement is obtained between calculated and experimental multiplet energies where these can be compared.

Acknowledgement. We thank the National Research Council of Canada for financial support of this work. We would also like to thank Dr. W. Heijser for the use of his unrestricted-HFS version of the DVM-HFS program system.

Appendix 1

The Statistical Exchange Approximation

In this appendix, we provide an analysis of the assumptions which leads to the statistical exchange approximation [1] given by

$$\int \rho_1^{\alpha}(\mathbf{r}_1)\rho_x^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)\frac{1}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2 \simeq -K\int \rho_1^{\alpha}(\mathbf{r}_1)\,[\rho_1^{\alpha}(\mathbf{r}_1)]^{1/3}d\mathbf{r}_1. \tag{A.1}$$

Here $\rho_1^\alpha(\mathbf{r}_1)$ is the one-electron density matrix for electrons with α spin, and $\rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)$ is a function defined in Eq. (3.4). $\rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)$ depends on the two-electron density $\rho_2^{\alpha\alpha}$. The function $\rho_2^{\alpha\alpha}$ has the following properties, provided it is constructed from an antisymmetric wave function: 1) it goes to zero when $\mathbf{r}_1$ goes to $\mathbf{r}_2$; 2) it converges to the uncorrelated two-electron density $\rho_1^\alpha(\mathbf{r}_1)\rho_1^\alpha(\mathbf{r}_2)$ on infinite separation of the two electrons; and 3) it equals $(n-1)\rho_1^\alpha(\mathbf{r}_1)$ after integration over $\mathbf{r}_2$, where n is the number of electrons with α-spin. This gives the following properties for $\rho_x^{\alpha\alpha}$:

(1) $\rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) \xrightarrow[|\mathbf{r}_1 - \mathbf{r}_2| \to 0]{} -\rho_1^\alpha(\mathbf{r}_1)$

(2) $\rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) \xrightarrow[|\mathbf{r}_1 - \mathbf{r}_2| \to \infty]{} 0$

(3) $\int \rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_2 = -1.$

In the statistical exchange approximation, $\rho_x^{\alpha\alpha}$ is replaced by the function $g^\alpha(r_{12})$ defined as

$$g^\alpha(r_{12}) = \begin{cases} \rho_1^\alpha(\mathbf{r}_1) & r_{12} \leq R \\ 0 & r_{12} > R. \end{cases} \tag{A.2}$$

The new function $g^\alpha(r_{12})$ is clearly constructed in such a way that it satisfies (1) and (2), and by requiring that it also satisfies (3) we get an expression for the parameter R in terms of $\rho_1^\alpha(\mathbf{r}_1)$. Thus,

$$\int g^\alpha(r_{12})d\mathbf{r}_2 = -\int_0^R \rho_1^\alpha(\mathbf{r}_1)dr_{12} = -1 \tag{A.3}$$

or

$$R = \left(\frac{3\pi}{4}\rho_1^\alpha(\mathbf{r}_1)\right)^{1/3}. \tag{A.4}$$

Substituting $g^\alpha(r_{12})$ for $\rho_x^{\alpha\alpha}$ then gives us

$$\iint \rho_1^\alpha(\mathbf{r}_1)\rho_x^{\alpha\alpha}(r_1, r_2)\frac{1}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2 \simeq -\int d\mathbf{r}_1 \int_0^R \rho_1^\alpha(\mathbf{r}_1)\rho_1^\alpha(\mathbf{r}_1)\frac{1}{r_{12}}dr_{12} \tag{A.5}$$

or

$$\iint \rho_1^\alpha(\mathbf{r}_1)\rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)\frac{1}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2 \simeq -\left[\frac{9\pi}{2}\right]^{1/3}\int \rho_1^\alpha(\mathbf{r}_1)\;[\rho_1^\alpha(\mathbf{r}_1)]^{1/3}d\mathbf{r}_1. \tag{A.6}$$

The scale factor K of Sect. 4 has in our derivation the value $[9\pi/2]^{1/3}$. It has become common practice to use a scale factor of the form $\frac{9}{2}\alpha[3/4\pi]^{1/3}$ where α is an adjustable parameter.

Appendix 2

Slater writes the averaged configuration energy, E_{av}, in the form of Eq. (3.15), see i.e. Eq. (A.13) and the left side of Eq. (A.14) in Ref. [7]. The statistical energy expression $E(\rho)$, is then arrived at by applying the statistical exchange approximation to the last two terms of Eq. (3.15). Such a procedure is only justified provided that $p_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_1) + \rho_x^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_1) = -\rho_x^{\alpha}(\mathbf{r}_1)$ for all values of $\mathbf{r}_1$. We will now demonstrate that this is not true for an averaged configuration by showing that in this case $\rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_1) = -\rho_x^{\alpha}(\mathbf{r}_1)$ for all $\mathbf{r}_1$ and that $\rho_x^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_1)$ is different from zero (negative) at least for some values of $\mathbf{r}_1$. We have according to Ref. [7] for the appropriate terms

$$\begin{aligned}\rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_1) = -[\rho^{\alpha}(\mathbf{r}_1)]^{-1} \cdot \sum_i q_i \Bigg[& \frac{(q_{i0} - q_i)\sum_{kl} u_{ik}(\mathbf{r}_1)u_{ik}(\mathbf{r}_1)u_{il}(\mathbf{r}_1)u_{il}(\mathbf{r}_1)}{q_{i0} \cdot q_{i0}(q_{i0} - 1)} \\ & + (q_i - 1)\sum_{kl} \frac{u_{ik}(\mathbf{r}_1)u_{ik}(\mathbf{r}_1)u_{il}(\mathbf{r}_1)u_{il}(\mathbf{r}_1)}{q_{i0} \cdot (q_{i0} - 1)} \\ & + \sum_{j \neq i} q_j \sum_{kl} \frac{u_{ik}(\mathbf{r}_1)u_{ik}(\mathbf{r}_1)u_{jl}(\mathbf{r}_1)u_{jl}(\mathbf{r}_1)}{q_{i0} \cdot q_{j0}} \Bigg] \end{aligned} \tag{A.7}$$

$$\rho_x^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_1) = -[\rho^{\alpha}(\mathbf{r}_1)]^{-1} \cdot \sum_i q_i \left[\frac{(q_{i0} - q_i)}{q_{i0}} \sum_{kl} \frac{u_{ik}(\mathbf{r}_1)u_{ik}(\mathbf{r}_1)u_{il}(\mathbf{r}_1)u_{il}(\mathbf{r}_1)}{q_{i0} \cdot (q_{i0} - 1)} \right] \tag{A.8}$$

and

$$p^{\alpha}(\mathbf{r}_1) = \sum_i \frac{q_i}{q_{i0}} u_i(\mathbf{r}_1)u_i(\mathbf{r}_1). \tag{A.9}$$

Here i and j count the number of shells for which the actual and maximal occupation numbers are q_i and q_{i0}, and k, l run over spatial orbitals. It follows immediately from Eq. (A.8) that $\rho_x^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_1)$ will be negative for some values of $\mathbf{r}_1$, and a straightforward collection of the three terms in Eq. (A.7) will give us $\rho_x^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_1) = -\rho^{\alpha}(\mathbf{r}_1)$.

References

1. Slater, J. C.: Advan. Quantum Chem. **6**, 1 (1972)
2. Johnson, K. H., Norman, J. G., Jr., Connolly, J. W. D.: In: Computational methods for large molecules and localised states in solids, F. Herman, A. D. McLean, and R. K. Nesbet, Eds., p. 161. New York: Plenum Press 1973
3. Parameswaren, T., Ellis, D. E.: J. Chem. Phys. **58**, 2088 (1973)
4. Bagus, P. S., Bennett, B. I.: Intern. J. Quantum Chem. **9**, 143 (1975)
5. Baerends, E. J., Ellis, D. E., Ros, P.: Chem. Phys. **2**, 52 (1973)
6. Roetti, C., Clementi, E.: J. Chem. Phys. **60**, 4725 (1974)
7. Slater, J. C.: Quantum theory of molecules and solids, Vol. 4. New York: McGraw-Hill 1974
8. Herzberg, G.: Electronic spectra and electronic structure of polyatomic molecules. New York: Van Nostrand 1966
9. Merer, A. J., Mulliken, R. S.: Chem. Rev. **69**, 639 (1969)
10. Shih, S., Buenker, R. J., Peyerimhoff, S. D.: Chem. Phys. Letters **16**, 6042 (1969)
11. Meyer, V., Skerbele, A., Lassettre, E.: J. Chem. Phys. **43**, 805 (1965)
12. Vanderslice, J. T., Tilford, S. G., Wilkinson, P. G.: Astrophys. J. **142**, 1227 (1965)
13. Benesch, W., Saum, K. A.: J. Phys. **B4**, 732 (1971)

14. Katz, B., Brith, M., Ron, A., Sharf, A., Jortner, J.: Phys. Letters **2**, 189 (1968)
15. Ballhausen, C. J., Dahl, J. P., Trabjerg, I.: National Na 191 Paris, 69 (1969)
16. For construction of the different multiplet wavefunctions due to a given configuration see: Koster, G. F., Dimmock, J., Wheeler, R. G., Statz, H.: Properties of the thirty-two point groups. Cambridge, Massachusetts: M.I.T. Press 1963

Received August 6, 1976