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Optimized Statistical Exchange Parameters α for Atoms with Higher Z*

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The parameter α used in the Xα method for approximating the electron exchange has been optimized for heavier atoms. The variation of the α-values with atomic number Z is analysed in terms of the Xαβ method. Differences between closed shell and open shell system are discussed.

Key words: Statistical exchange – Xα-method – Xαβ-method – Closed shell and open shell systems

1. Introduction

Slater's local statistical (Xα) approximation to the electron exchange [1] is widely used in solid state calculations and more recently also in the SCF-Xα-scattered-wave method [2] for polyatomic molecules and clusters. It has become quite common to optimize the exchange parameter α for free atoms and then to use the same values in molecular and solid state calculations. These optimized α-values are published [3] for the atoms H through Nb.

The purpose of this paper is threefold: (1) to provide optimized α-values for heavier atoms; this is desirable because the SCF-Xα-SW method is particularly useful for clusters with heavy atoms, as was demonstrated e.g. by Boring [4] for the uranyl ion UO_2^{++}; (2) to present an analysis of the Xα method in connection with open shell and closed shell systems; and (3) to investigate the variation of the α-values with atomic number Z in terms of the Xαβ method.

2. Optimized α-Values for Heavier Atoms

The same two criteria for optimization are used in this paper as have been used in Ref. [3] for the lighter atoms: (1) satisfaction of the virial theorem (α_{vt}); and (2) adjustment of the statistical total energy to the configuration averaged Hartree-Fock (HF) total energy (α_{HF}). The method, computation, and nomenclature are the same as in Ref. [3]. From the experience with the lighter atoms we know that α varies linearly with atomic number Z for any particular configurational sequence (i.e. atomic subshell). Therefore only atoms which correspond to the end-points in such a sequence or to special configurations are considered. The results are listed in Table 1; α_{vt} is also displayed in Fig. 1. For the atoms which are not included in Table 1, a linear interpolation between the end-points of the corresponding subshell is sufficiently accurate for most purposes.

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* Dedicated to Professor H. Hartmann on the occasion of his 60th birthday.

Table 1. The optimized exchange parameters α_{vt} and α_{HF} are given for a number of heavier atoms in their ground state

Atom	Configuration	α_{vt}	α_{HF}
Mo 42	[Kr] $+4d^5\ 5s$	0.70311	0.70341
Tc 43	$4d^5\ 5s^2$	0.70269	0.70299
Ru 44	$4d^7\ 5s$	0.70227	0.70253
Rh 45	$4d^8\ 5s$	0.70187	0.70217
Pd 46	$4d^{10}$	0.70128	0.70158
Ag 47	$4d^{10}\ 5s$	0.70114	0.70145
Cd 48	$4d^{10}\ 5s^2$	0.70084	0.70114
In 49	$4d^{10}\ 5s^2\ 5p$	0.70074	0.70102
Xe 54	$4d^{10}\ 5s^2\ 5p^6$	0.69962	0.69984
Cs 55	[Xe] $+\ 6s$	0.69939	0.69961
Ba 56	$6s^2$	0.69906	0.69927
La 57	$5d\ 6s^2$	0.69877	0.69898
Ce 58	$4f\ 5d\ 6s^2$	0.69824	0.69845
Pr 59	$4f^3\ 6s^2$	0.69742	0.69765
Eu 63	$4f^7\ 6s^2$	0.69549	0.69575
Gd 64	$4f^7\ 5d\ 6s^2$	0.69543	0.69566
Tb 65	$4f^8\ 5d\ 6s^2$	0.69501	0.69525
Dy 66	$4f^{10}\ 6s^2$	0.69426	0.69453
Yb 70	$4f^{14}\ 6s^2$	0.69292	0.69317
Lu 71	$4f^{14}5d\ 6s^2$	0.69302	0.69324
Ir 77	$4f^{14}5d^7\ 6s^2$	0.69296	0.69310
Pt 78	$4f^{14}5d^9\ 6s$	0.69292	0.69306
Au 79	$4f^{14}5d^{10}6s$	0.69288	0.69301
Hg 80	$4f^{14}5d^{10}6s^2$	0.69278	0.69290
Tl 81	$4f^{14}5d^{10}6s^2 6p$	0.69280	0.69289
Rn 86	$4f^{14}5d^{10}6s^2 6p^6$	0.69245	0.69248

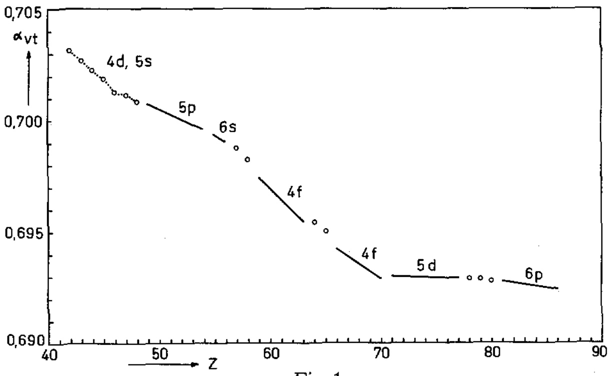

Fig.1

3. Quantitative Explanation of the Variation of α_{vt} with Z

The Z-dependence of α_{vt} is greatly reduced for atoms with Z larger than thirty compared with that for lighter atoms. It is interesting to note that the α_{vt}-values even for atoms with Z around 80 are significantly above two-thirds. These results can be understood in terms of the X$\alpha\beta$ method [5, 6], in which the exchange potential in the one-electron Schrödinger equation is given by

$$V_{X\alpha\beta} = V_{X\alpha}\left[1+\frac{\beta}{\alpha}G(\varrho)\right] = V_{XS}[\alpha+\beta\, G(\varrho)] \tag{1}$$

where V_{XS} is Slater's original exchange potential [7] and $G(\varrho)$ is the inhomogeneity correction as a function of the electron charge density ϱ [5, 6] (the "converence factors" [6, 8, 9, 11] for $G(\varrho)$ have been omitted in the above equation, because they are irrelevant for the following arguments).

It has been pointed out that in the X$\alpha\beta$ method α can be fixed to two thirds and β to 0.003 for all atoms in the periodic table [8–10]. This universal, Z-independent exchange approximation with α and β fixed (indicated by F) will be denoted by XF$\alpha\beta$-method [8].

In a qualitative way the variation of α_{vt} with Z can be understood by recalling from the XF$\alpha\beta$-method [6, 8] that close to the main peak of each individual orbital the inhomogeneity term $\frac{\beta}{\alpha}G(\varrho)$ exhibits a maximum. Thus, in the radial range where the probability of finding a particular electron is large, the factor multiplying V_{XS} can be considered as an effective exchange parameter for that orbital. This factor is always larger than two-thirds.

Using this picture the deviation from two-thirds of the α-values in the Xα-method can be interpreted to be an average over the inhomogeneity contributions of all orbitals. The variation of α with Z can then be explained in the following way: For the lighter atoms $G(\varrho)$ has only a few large peaks (one for every main shell, cf. Fig. 2 of Ref. [6]), but for heavier atoms the inhomogeneity becomes less pronounced, in the sense that $G(\varrho)$ has more peaks which are smaller in magnitude. Therefore α decreases with increasing Z. The fact that α remains above two-thirds indicates that even for the heavy atoms the inhomogeneity corrections are not negligible. A more quantitative explanation will be given in Section 5.

4. Closed Shell and Open Shell Atoms

Closed shell and open shell systems will be analyzed in this section by comparing total energy terms of the HF-method and the statistical approximation (Xα and X$\alpha\beta$). This analysis should lead to a better understanding of the approximations made in the Xα-method [12]. At the same time it can be found which terms have approximately the same value in the Xα or X$\alpha\beta$-method. Utilizing these results the variation of α_{vt} with atomic number can be explained quantitatively by the XF$\alpha\beta$-method (Section 5).

Using a short-hand notation the HF total energy can be written

$$\langle \mathrm{HF}\rangle = I + \frac{1}{2}\left(F - \frac{G}{2}\right). \tag{2}$$

For our purpose all terms will be evaluated using the HF expressions but with Xα (resp. X$\alpha\beta$) orbitals, which agree closely with HF orbitals. This scheme will be denoted by HF (Xα). The statistical total energy is given by

$$E_{st} = \sum I_{nl} + \frac{1}{2}\int \frac{2\varrho(1)\,\varrho(2)}{r_{12}}\,d\tau_1\,d\tau_2 + \frac{1}{2}\int \varrho(1)\,U_X\,d\tau_1 \tag{3}$$

or again in short hand notation:

$$E_{st} = I + \tfrac{1}{2} E_C^{\text{el}} + \tfrac{1}{2} E_{\text{X}} \tag{4}$$

(Rydberg atomic units are used throughout this paper). The three terms in Eqs. (2)–(4) denote in turn the one-electron-integral-, the electronic-Coulomb-, and the exchange-term.

In the X$\alpha\beta$-method the exchange potential for the total energy U_{X} (to be distinguished from $V_{\text{X}\alpha\beta}$ of Eq. (1)) is given by

$$U_{\text{X}\alpha\beta} = [\tfrac{3}{2}\alpha + 3\beta G(\varrho)]\, V_{\text{XS}}\,. \tag{5}$$

The results are summarized for a closed shell system (neon, cf. Table 2) and an open shell system (fluorine, cf. Table 3). The one-electron-integral terms (I) are the same for HF(Xα) and Xα. A comparison of these two schemes is made for (a) the Coulomb-, (b) the exchange-, (c) the Coulomb plus exchange-term, and (d) the total energy.

In the Xα-method α_{vt} is the α-value for which the HF(Xα) virial theorem is satisfied by construction [3]. Within the Xα-method itself it is always valid because of the variational principle. Since the kinetic energy is the same for HF(Xα) and Xα, the corresponding total energies must be equal:

$$\langle \text{HF}(\text{X}\alpha_{vt}) \rangle = E_{st}(\text{X}\alpha_{vt}). \tag{6}$$

It also follows that for the two methods the Coulomb plus exchange energy must be equal for α_{vt}, i.e.

$$F - \frac{G}{2} = E_C^{\text{el}} + E_{\text{X}\alpha}\,. \tag{7}$$

All the equalities just mentioned can be seen in Tables 2 and 3 to be satisfied with reasonable accuracy. (It should be noted, however, that α_{vt} taken from

Table 2. Comparison of total-energy-terms between HF(Xα) resp. HF(XF$\alpha\beta$) and the statistical approximations Xα (with $\alpha_{vt} = 0.72997$) and XF$\alpha\beta$ is tabulated for neon. The entries are: (1) the one-electron-integral term, (2) the electronic-Coulomb term, (3) the exchange-energy term, (4) the Coulomb plus exchange energy, and (5) the total energy. In the case of the Xα-method a further breakup of the terms into contributions from each orbital is listed. For the XF$\alpha\beta$-method only the weighted sum is given

HF	Stat.	1s	2s	2p	Weighted sum	
					Xα_{vt}	$\text{X}_{\text{F}\alpha\beta}$
I		-99.78108	-22.16100	-20.20917	-365.13918	-364.63200
F		46.70223	21.71090	21.26348	264.40714	263.32758
	E_C^{el}	46.70223	21.71090	21.26348	264.40713	263.32758
$-G/2$		-12.40216	-3.41897	-2.76987	-48.26146	-48.22270
	$E_{\text{X}\alpha\beta}$	-11.75047	-3.26804	-3.03738	-48.26128	-49.49644
$F-G/2$		34.30007	18.29193	18.49361	216.14567	215.10488
	$E_C^{\text{el}} + E_{\text{X}\alpha\beta}$	34.95176	18.44286	18.22610	216.14585	213.83114
$\langle$HF$\rangle$		-82.63104	-13.01503	-10.96237	-257.06634	-257.07956
	E_{st}	-82.30520	-12.93957	-11.09612	-257.06626	-257.71643

Table 3. Comparison of total-energy terms for fluorine similar to Table 2. In the Xα-method $\alpha_{vt} = 0.73651$. For the XF$\alpha\beta$-method the α and β term of the exchange energy are listed separately. In addition to the entries of Table 2 the virial coefficient (ratio of potential to kinetic energy) is given

HF	Xα_{vt}	X$_{F\alpha\beta}$	Stat.	Xα_{vt}	X$_{F\alpha\beta}$
I	−278.56858	−278.09937	I	−278.56858	−278.09937
F	197.71684	196.73422	E_C^{el}	199.43519	198.43405
			$E_{X\alpha}$	− 39.89128	− 36.03453
			$E_{X\beta}$		− 4.87184
$-G/2$	− 38.17273	− 38.15074	$E_{X\alpha\beta}$	− 39.89128	− 40.90637
$F-G/2$	159.54410	158.58348	$E_C^{el} + E_{X\alpha\beta}$	159.54391	157.52768
$I+\frac{1}{2}F$	−179.71016	−179.73226	$I+\frac{1}{2}E_C^{el}$	−178.85098	−178.88234
⟨HF⟩	−198.79652	−198.80763	E_{st}	−198.79662	−199.33553
virial	− 2.00000	− 1.99798	virial	− 2.00000	− 2.00063

Ref. [3] has been determined by the virial coefficient and not by the equalities given here.)

It is found from Table 2 that for a closed shell system (Ne) the Coulomb energies agree term-wise for every orbital between HF(Xα) and Xα. The exchange energies do not agree for every orbital, as one would expect from a statistical method, but only in their sum. The same type of agreement is found for the total energy.

We would come to almost the same general conclusions for the X$\alpha\beta$-method if we would use two-thirds for α and β_{vt}, the varial theorem value [8] for β. However, if we employ the universal, Z-independent exchange potential in form of the XF$\alpha\beta$-method with its obvious advantages, then the HF(XF$\alpha\beta$) virial theorem is not satisfied (Table 3). The reason that the virial theorem is not even valid within the X$\alpha\beta$-scheme is due to the use of the "convergence factor" for $G(\varrho)$ [11].

In Table 3 the weighted sums of the particular terms to the total energies are listed for an open shell system (fluorine). If we first concentrate on the Xα_{vt} results, it can be seen that, in contrast to a closed shell system, the Coulomb and exchange terms do not agree seperately between HF(Xα) and Xα, but only in their sum.

Summarizing, we find that for a closed shell atom the Xα-method differs only in the exchange term from HF. This term is replaced by a statistical approximation which leads to the same total exchange energy. For an open shell system only the sum of the total exchange energy plus the Coulomb energy remain the same for HF and Xα with α_{vt}, as mentioned in Ref. [12].

5. Z-Dependence of α_{vt} Analyzed in Terms of the XF$\alpha\beta$-Method

For a number of atoms XF$\alpha\beta$ calculations have been performed as described in Ref. [8]. From these results the Z-dependence of α_{vt} in the Xα-method can be explained quantitatively. A qualitative understanding has already been given in Section 3.

The general idea is to find an $\tilde{\alpha}$ which would lead to the same exchange energy in a hypothetical Xα-calculation (using X$\alpha\beta$ orbitals) than the current X$\alpha\beta$ calculation has given. If we would use β_{vt} instead of the fixed β-value of 0.003, it would be sufficient to look at the exchange energy. But in the XF$\alpha\beta$-method we have to correct for this fixed β, because the exchange energy and therefore also the statistical total energy are different for $X\alpha_{vt}$ and $XF\alpha\beta$. This result can be checked in Tables 2 and 3. It can also be seen that the HF total energy computed with $XF\alpha\beta$ orbitals is very nearly the same as that computed with $X\alpha_{vt}$ orbitals, i.e.

$$\langle \mathrm{HF}(\mathrm{XF}\alpha\beta)\rangle \simeq \langle \mathrm{HF}(\mathrm{X}\alpha_{vt})\rangle = E_{st}(\mathrm{X}\alpha_{vt}) \tag{8}$$

where the last equality follows from (6). Using (4) the statistical total energy for α_{vt} is given by the formula

$$E_{st}(\mathrm{X}\alpha_{vt}) = (I + \tfrac{1}{2}E_C^{\mathrm{el}})_{\mathrm{X}\alpha_{vt}} + \tfrac{1}{2}E_{\mathrm{X}\alpha_{vt}} \tag{9}$$

where the subscript on the RHS indicates that these integrals have been evaluated using $X\alpha_{vt}$-orbitals. The LHS can be approximated by $\langle \mathrm{HF}(\mathrm{XF}\alpha\beta)\rangle$. From Tables 2 or 3 we see that the first two terms in the statistical total energy agree fairly well between $X\alpha_{vt}$ and $XF\alpha\beta$. Thus we can use the value obtained from the $XF\alpha\beta$-calculation. The remaining term in (9) is the exchange energy. The α-term (from the first term in Eq. (5) of the $X\alpha\beta$ exchange $(E_{\mathrm{X}\alpha\beta})$ can be scaled by a new exchange parameter $\tilde{\alpha}$ in order to approximate $E_{\mathrm{X}\alpha_{vt}}$. Using these approximations (9) can be rewritten

$$\langle \mathrm{HF}(\mathrm{XF}\alpha\beta)\rangle = \left(I + \frac{1}{2}E_C^{\mathrm{el}}\right)_{\mathrm{XF}\alpha\beta} + \frac{1}{2}\tilde{\alpha}\left(\frac{E_{\mathrm{X}\alpha}}{\alpha}\right)_{\mathrm{XF}\alpha\beta}. \tag{10}$$

Adding and subtracting to the RHS $\tfrac{1}{2}E_{\mathrm{X}\alpha\beta}$ we obtain $E_{st}(\mathrm{XF}\alpha\beta)$. From this equation a formula for $\tilde{\alpha}$ can be derived which contains only results from an $XF\alpha\beta$-calculation. Using the fact that α is chosen to be two-thirds in $XF\alpha\beta$, we get

$$\tilde{\alpha} = \frac{2}{3}\,\frac{E_{\mathrm{X}\alpha\beta} + 2[\langle \mathrm{HF}(\mathrm{XF}\alpha\beta)\rangle - E_{st}(\mathrm{XF}\alpha\beta)]}{E_{\mathrm{X}\alpha}}. \tag{11}$$

If we would have used β_{vt} instead of the fixed β-value, the term in the square bracket vanishes and the formula for $\tilde{\alpha}$ simplifies to

$$\tilde{\alpha} = \frac{2}{3}\left(\frac{E_{\mathrm{X}\alpha\beta}}{E_{\mathrm{X}\alpha}}\right)_{\mathrm{X}\alpha\beta}. \tag{12}$$

The additional term in (11) is just for the correction for not having used β_{vt} in the $XF\alpha\beta$-method.

Equation (12) can be interpreted in the following way: Instead of adding the inhomogeneity correction [β-term in Eq. (5)] to the $X\alpha$-exchange with α equal to two-thirds, the same exchange energy can be obtained purely within the $X\alpha$-exchange framework by increasing α from two-thirds to $\tilde{\alpha}$.

Table 4 lists $\tilde{\alpha}$-values computed within $XF\alpha\beta$ calculations as described in Ref. [8] using Eq. (11). A comparison with the corresponding α_{vt}-values shows a remarkable good agreement. This demonstrates that the Z-dependence of α_{vt} can be explained in a quantitative way by means of the $X\alpha\beta$-method. The qualitative picture given in Section 3 is also correct.

Table 4. Comparison of α_{vt} with $\tilde{\alpha}$, an α-average obtained within an XFαβ calculation using Eq. (11)

Atom	$\tilde{\alpha}$	α_{vt}
He 2	0.77243	0.77236
F 9	0.73727	0.73651
Si 14	0.72758	0.72696
Fe 26	0.71119	0.71094
Rh 45	0.70204	0.70187
Tb 65	0.69511	0.69501
Rn 86	0.69244	0.69245

6. Conclusion

The exchange parameter α in the Xα-method has been optimized for heavier atoms (up to Rn). The variation of α with atomic number Z can be explained in terms of the Xαβ-method: (a) qualitatively, by calling attention to the fact that the inhomogeneity correction (β-term) becomes less pronounced for heavier atoms, (b) quantitatively, by scaling the Xα-exchange in order to match between Xα and Xαβ.

From a comparison between HF and Xα it has been found that for closed shell systems it is just the exchange which is approximated in the Xα-method. In open shell systems, however, only the sum of the Coulomb plus exchange energy remains the same for HF and Xα.

Both, the interpretation of the Z-dependence of α in terms of the Xαβ-method and also the differences, which occur for closed shell and open shell systems, should provide additional insight in the statistical approximations in form of the Xα or Xαβ-method.

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