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Original Investigations

An Examination of UHF Methods for Atoms in the First Three Rows

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The reliability and usefulness of UHF methods of calculating hyperfine parameters has been examined. Comparisons with CI and SEHF methods are made.

A detailed analysis of OPHF calculations for first and second row atoms has shown that various one-electron properties are accurately described by physically reasonable functions of the atomic number Z. In addition there is a strong correlation between these properties. This has led to a method whereby UHF spin densities across a row of atoms can be obtained from UHF calculations of only two atoms in that row.

A strong correlation between experimental and UHF spin densities is shown to exist for atoms of the first three rows. This is used to predict experimental spin densities for atoms in these rows which have not yet been measured experimentally.

Key words: UHF methods, reliability and usefulness of ~

1. Introduction

The problems of finding easy, reliable and accurate methods of calculating hyperfine structure parameters have proved difficult. The hyperfine parameter that has presented the greatest difficulty is the electron spin density at the nucleus, $Q(0)$.

For open shell atoms with no unpaired s electrons non-zero $Q(0)$ values can be interpreted as a spin-dependent distortion of the core s electrons by the unpaired electrons of the open shell [1–3]. This effect is known as "core polarization". Core polarization can be examined theoretically by a variety of methods. In this paper we restrict our attention mainly to $Q(0)$ and to unrestricted Hartree–Fock (UHF) methods [4, 5], which include the spin-polarized Hartree–Fock (SPHF), orbital-polarized Hartree–Fock (OPHF) and self-starting unrestricted Hartree–Fock

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(ssUHF) methods (see [6] for discussion of nomenclature), the spin-extended Hartree–Fock (SEHF) method [7, 8], and the configuration interaction (CI) method [9–12].

In this paper we explicitly define accuracy and reliability in such a way that meaningful comparisons of various theoretical methods can be made. We present a detailed analysis of matrix OPHF calculations for first and second row atoms [12, 16]. Various one electron properties are shown to be described with high accuracy by simple functions of the atomic number, Z. In particular $Q_{ns}(0)/N$, the one-electron contribution per unpaired electron to $Q(0)$, is accurately Z dependent for both first and second row atoms. An extremely good linear correlation between OPHF and experimental $Q(0)/N$ values for first and second row atoms is found to hold. We shall use this correlation to predict the spin densities for carbon, silicon and sulphur which have not as yet been determined experimentally.

Also from the available experimental spin densities of the transition metal atoms we shall obtain a correlation with previous SPHF spin densities [15]. From this correlation we shall predict the experimental $Q(0)$ values of scandium, chromium, iron, nickel and copper.

Using the accurate Z dependence of $\rho_{ns}(0)$, the electron density at the nucleus, and the good linear correlation between $Q_{ns}(0)/N$ and $\rho_{ns}(0)$, we propose a method whereby reliable estimates of UHF spin densities for an entire row of atoms can be obtained from UHF calculations on two atoms within that row. If experimental spin densities for these two atoms can also be obtained, then the experimental spin densities for the remaining atoms can be predicted.

When comparing UHF, SEHF and CI methods for first row atom spin densities we conclude that 1) the difficulty of obtaining accurate results in calculations using analytic basis sets is greater for the CI method than for UHF and SEHF methods, 2) the systematic reliability of UHF methods is slightly better than the CI method and much better than the SEHF method, and 3) the absolute reliability of the CI polarization [10] and first order [11] functions is better than UHF or SEHF methods although it appears likely that the better second order functions [9] would yield $Q(0)$ values which are considerably worse than the polarization and first order functions.

2. Criteria for Reliability and Accuracy

The hyperfine parameter that has presented the greatest difficulty in obtaining reliable theoretical estimates is the electron spin density at the nucleus, $Q(0) = \langle \sum_i \delta(r_i) 2s_{zi} \rangle_{r_i=0}$. There are two main reasons for this. Firstly, the reliability of theoretical $Q(0)$ values depends on the reliability of the wave function at a single point, the nucleus. Thus the best that one could hope for in any theoretical method is results which differ from the true values in some systematic way. Secondly, there are the difficulties associated with the fact that in most methods $Q(0)$ values are obtained as the small difference of large quantities. These are essentially computational difficulties associated with convergence to the true theoretical value. To avoid ambiguities in meaning we shall refer to "accuracy" of a method as the agreement between the calculated theoretical value and the true theoretical value; by the "reliability" of a method we refer to the agreement between the true theoretical value and the true value.

The criterion previously used to estimate the reliability of methods, although not explicitly stated as such, is to use the ratio between calculated and experimental values (see Ref. [8], pp. 48, 53 and Ref. [15], p. 559; however see also Ref. [17], p. 2031).

We regard a method as being reliable if there is some systematic correlation (over a row of atoms) between the theoretical and true values. We therefore distinguish between absolute reliability and systematic reliability. It is natural to assume that a method whose reliability has been established for certain rows will be reliable for other rows as well.

For the first row, and the second row atoms and the third row transition-metal atoms, where sufficient reliable experimental data is available, there is little practical difference between methods with differing degrees of absolute reliability provided that both are systematically reliable. The established correlation can be used to predict the true $Q(0)$ values for those atoms which have not yet been measured experimentally (or those which have). For rows where no experimental results are available, systematically reliable methods can be used to predict experimental trends with confidence. If two or more experimental results are available then systematically reliable methods can be used to predict experimental values. Here we are assuming that a linear correlation between theoretical and experimental $Q(0)/N$ values holds. This is the case for the first row, and the second row atoms and the third row transition-metal atoms (see Table 4, Eq. (1)).

We now consider the question of accuracy. Various criteria have been used [8, 10, 15]. At this point we would like to stress that, since UHF, SEHF and CI methods have poor absolute reliability (see Tables 1–3) it seems that an undesirable expenditure of effort may be required to attain a high degree of accuracy. Experimental $Q(0)/N$ values across a row of atoms show a good correlation with Z (see Tables 3, 4 and Appendix). We therefore suggest a convenient, practical criterion that guarantees adequate accuracy in methods using analytic basis sets. The size of basis sets should be increased until the theoretical $Q(0)/N$ values for a row of atoms are accurately described by a function of Z of the same form as in the experimental case. This criterion will test if the method is systematically reliable also. If this is so, the theoretical values will then have sufficient internal consistency to make estimates of reliability meaningful. The basis sets used to obtain the OPHF results reported in this paper satisfy this criterion.

3. Results

The OPHF results of this paper were obtained from wave functions with $M_L = L$, $M_S = S$. For boron to fluorine we used the 7/4 s-cusp [18] sets of Goddard [8], while for sodium to chlorine the 8/8 s-cusp sets of Clementi [19] were used. The notation n_1/n_2 indicates a basis set with n_1 different s basis functions and n_2 different p basis functions. For lithium we used the basis set of Clementi [19].

In Table 1 we compare $Q(0)$ values for boron, obtained from a series of CI wave functions.

Table 1. Boron spin densities obtained from various CI wave functions (all quantities in a.u.)

CI function	Ref.	Size of basis set[a]	Number of configurations[b]	E_{corr}[c]	$Q(0)$
Polarization function 1)	[12]		20	$-0.02208 \mp 0.5\%$	0.015
Polarization function 2)	[12]		20	-0.02208	-0.009
Polarization function 3)	[10]	6, 4, 6	53	-0.02223	0.0073
First order function	[11]	6, 6, 6	153	-0.05836	0.0041
Second order function	[9]	4, 3, 4	165	-0.10765	0.0004
187-term function	[9]	4, 3, 4	187	-0.11014	0.0046
Experiment				-0.1289	0.0081

[a] Number of basis functions used in addition to HF basis set; numbers listed in order s, p, d.

[b] Number of L–S configurations; note that the 187-term function contains 1292 unique determinantal functions.

[c] $E_{\mathrm{corr}} = E_{\mathrm{CI}} - E_{\mathrm{HF}}$.

In Table 2 we compare the calculated OPHF values of $Q(0)$ for first and second row atoms against the experimental values (where available). In addition, the one electron contributions to $Q(0)$ are also given.

In Table 3 we compare experimental $Q(0)/N$ values for first row atoms with $Q(0)/N$ values obtained by various UHF, SEHF and CI calculations.

There is a high correlation between experimental and OPHF $Q(0)/N$ values. For first row atoms, boron to fluorine we find

$$[Q(0)/N]_{\mathrm{expt.}} = 0.5754[Q(0)/N]_{\mathrm{OPHF}} - 0.0025 \tag{1a}$$

with a multiple correlation of 0.9950. For second row atoms, aluminium to chlorine, we find

$$[Q(0)/N]_{\mathrm{expt.}} = 0.5447[Q(0)/N]_{\mathrm{OPHF}} + 0.0557 \tag{1b}$$

with a multiple correlation of 0.9998. For the transition-metal atoms scandium to copper, using the SPHF values of Bagus *et al.* [15] we find

$$[Q(0)/N]_{\mathrm{expt.}} = 1.9492[Q(0)/N]_{\mathrm{SPHF}} + 0.0252 \tag{1c}$$

with a multiple correlation of 0.9942.

"Experimental" $Q(0)/N$ values for the first row, second row atoms and the third row transition-metal atoms that were obtained from Eq. (1) are given in Table 4. The corresponding OPHF or SPHF values and the experimental values (where available) are included for comparison.

Table 2. Comparison of OPHF and experimental values of $Q(0)$ for 1st and 2nd row atoms; contribution of $1s$, $2s$ and $3s$ orbitals to OPHF values of $Q(0)$

Spin density contributions	Li	B	C	N	O	F	Na	Al	Si	P	S	Cl
$1s$	0.0669	−0.0914	−0.3242	−0.7488	−0.7511	−0.5156	0.0468	−0.0543	−0.1701	−0.3617	−0.3301	−0.2134
$2s$	0.1646	0.1106	0.3995	0.9341	0.9476	0.6476	0.0754	0.0367	0.1191	0.2353	0.1967	0.1133
$3s$							0.5254	−0.0912	−0.1048	−0.0161	0.1245	0.1364
Total	0.2315	0.0192	0.0753	0.1853	0.1965	0.1320	0.6476	−0.1088	−0.1558	−0.1425	−0.0089	0.0363
	0.2313	0.00810	—	0.0972	0.1138	0.0717	—	−0.00394	—	0.0972	—	0.0752
	[23]	[24]		[25]	[26]	[26]		[24]		[27]		[28]

Table 3. Comparison of theoretical and experimental $Q(0)/N$ values for first row atoms (all quantities in a.u.)

Function	Ref.	B	C	N	O	F
SPHF	[15]	0.017	0.0385	0.0623	0.0975	0.133
OPHF	[this paper]	0.0192	0.0377	0.0618	0.0983	0.1320
ssUHF	[29]	0.0218	0.0392		0.0970	0.122
SEHF	[8]	0.0362	0.0367	0.0526	0.1069	0.2454
Polarization	[10]	0.0073	0.0139	0.0243	0.0305	0.0470
First order	[11]	0.0041	0.0114	0.0238	0.0314	0.0496
Experiment	[a]	0.0081		0.0324	0.0569	0.0717

[a] See Table 2.

For first row atoms, the correlation between experimental and various theoretical $Q(0)/N$ values is given below.

SPHF a) $y=0.5557x-0.0006$ [0.9955]
b) $y=0.5621x-0.0013$ [0.9930]

Table 4. "Experimental" $Q(0)/N$ values for atoms of first three rows obtained from Eq. (1) (all quantities in a.u.)

		$\frac{Q(0)}{N}$	
Element	Expt. from Eq. (1)	Expt.	OPHF
B	0.0085	0.0081	0.0192
C	0.0192		0.0377
N	0.0331	0.0324	0.0618
O	0.0541	0.0569	0.0983
F	0.0734	0.0717	0.1320
Al	−0.0036	−0.00394	−0.1088
Si	0.0133		−0.0779
P	0.0298	0.0305	−0.0475
S	0.0532		−0.0045
Cl	0.0755	0.0752	0.0363
			SPHF
Sc	−0.0216		−0.0240
Ti	−0.0405	−0.0404	−0.0337
V	−0.0504	−0.0514	−0.0388
Cr	−0.0580		−0.0427
Mn	−0.0676	−0.0657	−0.0476
Fe	−0.0754		−0.0516
Co	−0.0807	−0.0817	−0.0543
Ni	−0.0857		−0.0578
Cu	−0.0980		−0.0632

OPHF	a)	$y=0.5623x-0.0012$	[0.9961]
	b)	$y=0.5754x-0.0025$	[0.9950]
ssUHF	a)	$y=0.6049x-0.0022$	[0.9965]
	b)	$y=0.6380x-0.0056$	[0.9997]
SEHF	a)	$y=0.2922x+0.0080$	[0.8327]
	b)	$y=0.2595x+0.0137$	[0.7776]
Polarization	a)	$y=1.6129x-0.0014$	[0.9665]
	b)	$y=1.6593x-0.0030$	[0.9478]
1st order	a)	$y=1.4867x+0.0014$	[0.9706]
	b)	$y=1.4499x+0.0028$	[0.9543]

where y refers to the experimental $Q(0)/N$ value, while x refers to the appropriate theoretical value; case a) the experimental results for beryllium to fluorine; case b) the experimental results from boron to fluorine. The multiple correlation is given in brackets.

In the Appendix we give the OPHF Z dependence of $\rho_{ns}(0)$, $Q_{ns}(0)/N$, the one electron orbital energies ε_{ns} and the orbital energy splitting per unpaired electron $\Delta\varepsilon_{ns}/N$ for first and second row atoms. The Z dependence of experimental and various theoretical values of $Q(0)/N$ for first row atoms is also given. The Z dependence of experimental and SPHF values of $Q(0)/N$ for transition-metal atoms is included. The correlations between $Q_{ns}(0)/N$ and $\Delta\varepsilon_{ns}/N$, $Q_{ns}(0)/N$ and $\rho_{ns}(0)$, $\Delta\varepsilon_{ns}/N$ and ε_{ns} are also given. For convenience reference the HF and average OPHF values for $\rho_{ns}(0)$ and the OPHF values for $Q_{ns}(0)$ for first and second row atoms are given in Table 5 in the Appendix.

4. Discussion

The matrix OPHF values of $Q_{ns}(0)/N$ for first and second row atoms presented in this paper have, in all cases, a multiple correlation with Z greater than 0.9995 (see Appendix). For first row atoms, the multiple correlation between $Q(0)/N$ and Z for the matrix OPHF values is 0.9984. For the numerical SPHF values [15] it is 0.9994. The multiple correlation for the experimental results is 0.9903 (see Appendix).

Therefore the matrix UHF calculations will have sufficient accuracy and internal consistency so as to enable meaningful conclusions about the reliability of UHF methods to be drawn.

We now compare the convergence behaviour of analytic basis set calculations in the SEHF and CI methods.

The problems of convergence in matrix SEHF calculations are similar to those in UHF calculations [8]. On the other hand the internal consistency of the SEHF method is poor (see Appendix).

In CI calculations the convergence problems are in many ways more serious. If one increases the size of the basis, the number of *L-S* configurations may increase rapidly, depending on the level of the approximation (see Table 1). Each *L-S* configuration (see Ref. [8] for description) will contain many unique determinantal functions. For example, the 187-term function of Schaefer *et al.* [9] contains 1292 unique determinants. Thus the complexity of a calculation will increase significantly as the size of the basis is increased. Yet an examination of $Q(0)$ values for three polarization functions ([10, 12], see Table 1 also) shows how sensitive the calculated values are to variations in the choice or size of the basis set. In the above case the energies agreed to within 0.00015 hartrees. The second order and 187-term functions [9] are very good in the sense that they account for almost 90% of the total correlation error [22]. Yet if one compares the $Q(0)$ values with the $Q(0)$ values obtained from the polarization and first order functions (see Table 1) then it will be noted that the values vary erratically. The accuracy to be expected for the best polarization and first order function $Q(0)$ values is roughly 10% [10].[1]

If the accuracy of $Q(0)$ for the second order and 187-term functions is comparable, then the erratic variation in $Q(0)$ as one proceeds to "better" wave functions is an undesirable feature of the CI method. Certainly there would be little motivation to obtain better wave functions in order to interpret hyperfine effects. On the other hand, if the erratic variation is due to the fact that the accuracy of $Q(0)$ for the second order and 187-term functions is still very inadequate[2] then an excessive expenditure of effort may be necessary to get accurate results.

For first row atoms the internal consistency of the polarization and first order functions is comparable to that of the SPHF, OPHF and ssUHF functions. The multiple correlations between $Q(0)/N$ and Z are 0.9880, 0.9934, 0.9994, 0.9984 and 0.9965 respectively (see Appendix).

We conclude that the accuracy of matrix UHF and SEHF calculations is comparable. The accuracy of analytic basis CI calculations is probably worse, with a major effort required to improve the accuracy. On the other hand the internal consistency of the SEHF method is much worse than that of either UHF methods or CI methods (at the polarization or first order function level). The internal consistency of the latter two methods is comparable. This implies that both UHF and CI methods are systematically reliable while the SEHF method is not.

We now discuss the reliability of UHF methods and compare them to SEHF and CI methods.

It can be seen from Table 2 that the absolute agreement between experimental and OPHF spin densities for atoms of the first two rows is not good. However the OPHF values do reflect the experimental trends for $Q(0)/N$. This is apparent in Table 4, where experimental and SPHF values for the transition-metal atoms are included also. The systematic reliability of the UHF values for atoms of the first three rows is very good. This is shown by the accurate correlation with experimental values given in Eq. (1) (see Results). The "experimental" values obtained using these correlations are given in Table 4. This includes values for C, Si, S, Sc, Cr, Fe,

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[1] Estimated by varying the exponents of the basis functions. On the other hand, the energy is estimated to be accurate to within 0.0001 to 0.00001 hartrees.

[2] Kaldor *et al.* [12] conclude that configurations of negligible importance for the energy may make decisive contributions to $Q(0)$.

Ni and Cu. Experimental values for these atoms have not yet been published. We expect the values given in Table 4 to be as reliable as those for which a direct experimental comparison is possible.

We conclude that UHF methods have a very high degree of systematic reliability, but the degree of absolute reliability is row dependent. Therefore experimental trends across a row of atoms can be predicted with confidence. On the other hand, if no experimental results are available, then one cannot be certain whether the absolute reliability of UHF spin densities is good or not. If a single experimental result is available then the UHF spin densities can be used to provide better estimates for the remaining atoms of the row. If two or more experimental results within a row are available, then reliable estimates for the remaining atoms can be obtained.

It can be seen from Table 3 that the absolute reliability of the theoretical $Q(0)/N$ values is best for the CI polarization and first order functions and worst for the SEHF method. On the other hand it is possible that the absolute reliability of the "better" second order functions would be very much worse than for the polarization and first order functions (see Table 1).

The systematic reliability of the UHF methods is slightly better than the CI method; again the SEHF method is worst. This is shown by comparing the relevant multiple correlation values (see Results).

For hydrogenic functions, $\rho_{ns}(0)$ has an exact Z^3 dependence (see Appendix). This led to fitting the HF values with a general cubic dependence in Z. It is interesting to note how closely the leading coefficient agrees with the exact hydrogenic value.

One assumes on physical grounds that there is a correlation between $Q_{ns}(0)$ and $\Delta\varepsilon_{ns}$. It is satisfying to note that the OPHF method has sufficient internal consistency to confirm this assumption (see Appendix).

One might expect that, across a row of atoms, the ratio $Q_{ns}(0)/\rho_{ns}(0)$ would vary approximately as the number of unpaired electrons [12]. With the exception of the $3s$ orbitals for second row atoms this is so. For $3s$ orbitals the sign is not even constant. We then noted that the more general relation

$$Q_{ns}(0) = a_1 \rho_{ns}(0) + a_0$$

gave a very accurate correlation (see Appendix).

It is to be expected that ε_{ns} and $\Delta\varepsilon_{ns}$ have a Z dependence across a row of atoms [16]. These are included for convenience in the Appendix. As with $Q_{ns}(0)$ and $\rho_{ns}(0)$, the effect of the number of unpaired electrons on the orbital energy splitting is accurately described by a relationship of the form

$$\Delta\varepsilon_{ns}/N = b_1 \varepsilon_{ns} + b_0 \qquad \text{(see Appendix)}$$

It can be seen that the OPHF method has a very high degree of internal consistency for all the properties examined. It is natural to assume that this will hold in other UHF methods. It should presumably hold for calculations of large atoms, and for molecules as well. This can be of predictive value as we now indicate. If UHF calculations for two atoms in each row of the Periodic Table are obtained then the Z dependence of $\rho_{ns}(0)$ can be extended accurately. Since the correlation between $Q_{ns}(0)$ and $\rho_{ns}(0)$ is linear within rows, the $Q_{ns}(0)$ values for those atoms not calculated can easily be obtained. A cross-check on these values could be obtained from the $Q_{ns}(0)/N$, $\Delta\varepsilon_{ns}/N$ correlation (using the (0, 0) point as well). Thus the systematic trends in $Q(0)/N$ across a row of atoms could be determined. Provided experimental values for the two chosen atoms were also obtained, the linear correlation between theoretical and experimental $Q(0)/N$ values could be used to obtain reliable predictions for the spin densities of the remaining atoms in the row. That is, from observation and calculation of two atoms per row, reliable predictions of the spin densities across a row should be obtainable.

5. Conclusion

In this paper we have explicitly defined accuracy and reliability in such a way so as to enable the value and usefulness of UHF methods to be readily determined.

Accurate spin densities can be obtained from the analytic basis UHF method by using large basis sets. Spin densities of sufficient accuracy to test, and then make use of, the systematic reliability of UHF methods can be obtained from moderately large, optimized s-cusp basis sets.

The systematic reliability of UHF spin densities over the first three rows of the Periodic Table is very good.

The variation in UHF values for the spin density, χ, across each of the first three rows reflects the actual experimental variations. The widely accepted assumption that χ is constant across a row is, in general, incorrect. Using the correlation between UHF and experimental values we predict that following $Q(0)$ values for the first row, and the second atoms and the third row transition-metal atoms not yet measured; carbon (0.0384 a.u.), silicon (0.0266 a.u.), sulphur (0.1064 a.u.), scandium (−0.0216 a.u.), chromium (−0.2321 a.u.), iron (−0.3015 a.u.), nickel (−0.1750 a.u.), copper (−0.0980 a.u.). The capacity to make reliable predictions satisfactorily answers those doubts raised about UHF methods on the basis of the SPHF spin density for phosphorus.

We expect that the systematic reliability found for the results of the first three rows will apply to other rows of the Periodic Table. We therefore predict that the variation in χ for third row $4p^n$ atoms, shown by SPHF calculations, will reflect the actual experimental variation. Indeed, when another experimental result in this row becomes available, it will be possible to reliably predict the experimental spin densities of the remaining atoms.

The absolute reliability of UHF spin densities is row dependent. It is better for the third row transition-metal atoms than for first and second row atoms. At present there is no way of knowing whether it will be good or bad, although intuitively we exepect it to be better for the various transition series atoms than for other rows.

We have outlined a procedure whereby the variation in experimental spin densities over a row of atoms may be predicted from UHF calculations on two atoms in that row. If experimental results for these atoms are then obtained, the experimental spin densities for the remaining atoms can be predicted. A detailed analysis of OPHF calculations for first and second row atoms has shown that the one electron properties $\rho_{ns}(0)$, $Q_{ns}(0)/N$, ε_{ns} and $\Delta\varepsilon_{ns}/N$ are accurately described by physically plausible functions of the atomic number, Z. In addition these properties are highly correlated. We expect this to apply to other one electron and two electron properties.

The ssUHF version of the UHF method has shown good absolute reliability for the hyperfine parameters $\langle r^{-3}\rangle_l$, $\langle r^{-3}\rangle_d$, $\langle r^{-3}\rangle_q$ [21, 29] for first row atoms. This, coupled with the features mentioned above, and the fact that UHF methods can be applied readily to larger systems, suggests that UHF methods are particularly well suited for use in interpreting hyperfine effects in atoms, molecules and solids. We conclude that UHF methods are more reliable, and have more useful applications, than previously accepted.

For calculations using analytic basis sets, the difficulty in improving accuracy is comparable for the UHF and SEHF methods. For CI methods the difficulties are probably much greater. For first row atoms the systematic reliability of UHF and CI methods is comparable, while the SEHF method much poorer. For first row atoms the absolute reliability of the CI method is better than UHF methods, which are better than the SEHF method.

As one proceeds to higher levels of approximation, the CI method has the undesirable feature that the best wave functions yet obtained for boron provide spin densities which vary erratically. CI methods at these levels cannot be easily applied to large systems.

Appendix

The following Z-dependence for $\rho_{ns}(0)$ and ε_{ns} refer to HF values. Because the OPHF average for $\rho_{ns}(0)$ and ε_{ns} agree very well with the HF values, the corresponding OPHF results are very similar.

For the atoms boron to fluorine and aluminium to chlorine

$$\begin{aligned}
\rho_{1s}(0) &= 0.3208Z^3 - 0.4497Z^2 + 2.5639Z - 7.6796\\
\rho_{2s}(0) &= 0.0432Z^3 - 0.4540Z^2 + 2.3529Z - 4.3393\\
\rho_{3s}(0) &= 0.0065Z^3 - 0.0770Z^2 - 0.0429Z + 1.6103
\end{aligned}$$

all with a multiple correlation of 1.0000.

When the results were extended to include chromium, iron and nickel we obtained,

$$\begin{aligned}
\rho_{1s}(0) &= 0.3178Z^3 - 0.3696Z^2 + 1.8375Z - 5.0984\\
\rho_{2s}(0) &= 0.0381Z^3 - 0.2900Z^2 + 0.7465Z + 0.1313\\
\rho_{3s}(0) &= 0.0038Z^3 + 0.1028Z^2 - 3.4155Z + 10.8378,
\end{aligned}$$

all with a multiple correlation of 1.0000.

Table 5. One-electron contributions to electron densities and spin densities for first and second row atoms (all quantities in a.u.)

	$\rho_{1s}(0)$			$\rho_{2s}(0)$			$\rho_{3s}(0)$		
Element	HF	OPHF average	$Q_{1s}(0)$	HF	OPHF average	$Q_{2s}(0)$	HF	OPHF average	$Q_{3s}(0)$
Li	6.8338	6.8447	0.0669	0.1674	0.1646				
B	33.9195	34.5799	−0.0914	1.4099	1.4022	0.1106			
C	60.9823	61.0094	−0.3242	2.7698	2.7483	0.3995			
N	98.2078	98.2940	−0.7488	4.7687	4.7191	0.9341			
O	148.2711	148.2566	−0.7511	7.6371	7.5941	0.9476			
F	212.8527	212.8561	−0.5156	11.4048	11.3751	0.6476			
Na	392.9400	392.9431	0.0468	23.4132	23.4163	0.0754	0.5285	0.5254	
Al	654.4880	654.4865	−0.0543	44.1778	44.1782	0.0367	2.3558	2.3579	−0.0912
Si	820.3829	820.3891	−0.1701	58.0813	58.0791	0.1191	3.8070	3.8098	−0.1048
P	1012.4321	1012.4330	−0.3616	74.6022	74.6024	0.2353	5.6265	5.6225	−0.0160
S	1232.2641	1232.2652	−0.3301	93.9798	93.9801	0.1967	7.9120	7.9087	0.1245
Cl	1482.1324	1482.1428	−0.2134	116.3820	116.3797	0.1133	10.6440	10.6411	0.1364

For hydrogenic atoms,

$$\rho_{1s}(0)=0.3183Z^3$$
$$\rho_{2s}(0)=0.0398Z^3$$
$$\rho_{3s}(0)=0.0118Z^3$$

For the atoms boron to fluorine

$$\varepsilon_{1s}=0.3503Z^2+0.2326Z-0.1023$$

and

$$\varepsilon_{2s}=0.0210Z^2+0.0247Z-0.0937$$

with multiple correlations of 1.0000 and 0.9999 respectively, whereas for the atoms aluminium to chlorine

$$\varepsilon_{1s}=0.4297Z^2+1.2938Z-2.7093$$
$$\varepsilon_{2s}=0.0603Z^2+0.3872Z+0.2513$$
$$\varepsilon_{3s}=-0.0086Z^2+0.0888Z-0.0910$$

with multiple correlations of 1.0000, 1.0000 and 0.9999 respectively

Given the Z-dependence of $\rho_{ns}(0)$ it is reasonable to expect that $Q_{ns}(0)$ could be accurately described by a quadratic Z-dependence. The following results refer to the OPHF values of this paper.

For the atoms boron to fluorine

$$Q_{1s}(0)/N=-0.0127Z^2+0.0709Z-0.1301$$
$$Q_{2s}(0)/N=0.0157Z^2-0.0852Z+0.1436$$

with multiple correlations of 0.9997 and 0.9996 respectively whereas for the atoms aluminium to chlorine

$$Q_{1s}(0)/N=-0.0032Z^2+0.0549Z-0.2344$$
$$Q_{2s}(0)/N=-0.0011Z^2+0.0509Z-0.4465$$
$$Q_{3s}(0)/N=0.0065Z^2-0.1382Z+0.6062$$

with multiple correlations of 0.9999, 0.9995 and 0.9997 respectively.

The Z-dependence of $Q(0)/N$ for first row atoms is given below

SPHF

a) $2.630\times10^{-3}Z^2-7.615\times10^{-3}Z-0.0113$ [0.9994]
b) $2.814\times10^{-3}Z^2-1.030\times10^{-3}Z-0.0018$ [0.9993]

OPHF

a) $2.580\times10^{-3}Z^2-7.219\times10^{-3}Z-0.0115$ [0.9985]
b) $3.057\times10^{-3}Z^2-14.180\times10^{-3}Z+0.0131$ [0.9983]

SEHF

a) $12.977\times10^{-3}Z^2-127.127\times10^{-3}Z+0.3198$ [0.9361]
b) $22.457\times10^{-3}Z^2-265.540\times10^{-3}Z+0.8090$ [0.9847]

Polarization

a) $0.793\times 10^{-3}Z^2-1.307\times 10^{-3}Z-0.0068$ [0.9905]
b) $1.114\times 10^{-3}Z^2-6.000\times 10^{-3}Z+0.0098$ [0.9879]

1st Order

a) $1.280\times 10^{-3}Z^2-6.865\times 10^{-3}Z+0.0068$ [0.9930]
b) $1.214\times 10^{-3}Z^2-5.900\times 10^{-3}Z+0.0034$ [0.9904]

Experimental

a) $1.483\times 10^{-3}Z^2-4.509\times 10^{-3}Z-0.0061$ [0.9927]
b) $1.264\times 10^{-3}Z^2-1.302\times 10^{-3}Z-0.0175$ [0.9888]

a) Be to F; b) B to F.

The multiple correlation for the Z-dependence is given in brackets. For the SEHF results, the multiple correlation is artificially high. The best fit quadratic for $Z=5$ to 9 has a minimum at $Z\sim 6$. The best fit quadratic for $Z=4$ to 9 has a minimum at $Z\sim 5$. The experimental results increase from $Z=4$ to $Z=9$.

The Z-dependence of the third row transition-metal atoms is given below.

Experimental

$Q(0)/N=2.160\times 10^{-4}Z^2-18.643\times 10^{-3}Z+0.2645$ [0.9966]

SPHF

$Q(0)/N=2.357\times 10^{-4}Z^2-16.269\times 10^{-3}Z+0.2119$ [0.9897]

The Z-dependence of the OPHF values for $\Delta\varepsilon_{ns}/N$ and the correlation between OPHF values for $Q_{ns}(0)/N$ and $\Delta\varepsilon_{ns}/N$ follow.

For the atoms boron to fluorine

$$\Delta\varepsilon_{1s}/N=-0.0084Z+0.0276$$
$$\Delta\varepsilon_{2s}/N=-0.0249Z+0.0270$$

with multiple correlations of 0.9996 and 0.9973 respectively whereas for the atoms aluminium to chlorine

$$\Delta\varepsilon_{1s}/N=-0.0023Z+0.0268$$
$$\Delta\varepsilon_{2s}/N=-0.0020Z+0.0227$$
$$\Delta\varepsilon_{3s}/N=-0.0157Z+0.1430$$

with multiple correlations of 0.9982, 0.9997 and 0.9991 respectively.

For the atoms boron to fluorine

$$Q_{1s}(0)/N=-131.8093(\Delta\varepsilon_{1s}/N)^2+4.3572(\Delta\varepsilon_{1s}/N)+0.0008$$
$$Q_{2s}(0)/N=21.9417(\Delta\varepsilon_{2s}/N)^2+1.0437(\Delta\varepsilon_{2s}/N)+0.0030$$

both with multiple correlations of 0.9999.

For the atoms aluminium to chlorine

$$Q_{1s}(0)/N = -114.0846(\Delta\varepsilon_{1s}/N)^2 + 16.0968(\Delta\varepsilon_{1s}/N) - 0.0019$$
$$Q_{2s}(0)/N = -169.5805(\Delta\varepsilon_{2s}/N)^2 - 11.9955(\Delta\varepsilon_{2s}/N) + 0.0003$$
$$Q_{3s}(0)/N = 40.1835(\Delta\varepsilon_{3s}/N)^2 + 3.8236(\Delta\varepsilon_{3s}/N) - 0.0010$$

where the multiple correlations are 0.9990, 0.9998 and 0.9978 respectively.

In all cases the point (0, 0) was assumed to be a physically reasonable data point. The small value of the constant that is obtained in all cases is consistent with this assumption.

The correlation between the OPHF values for $Q_{ns}/(0)/N$ and $\rho_{ns}(0)$ and for $\Delta\varepsilon_{ns}/N$ and ε_{ns} follows.

For the atoms boron to fluorine,

$$Q_{1s}(0)/N = -0.002375\rho_{1s}(0) - 0.01558$$
$$Q_{2s}(0)/N = 0.05366\rho_{2s}(0) + 0.4823$$

with a multiple correlation of 0.9990 and 0.9965 respectively whereas for the atoms aluminium to chlorine

$$Q_{1s}(0)/N = -0.0001928\rho_{1s}(0) + 0.07294$$
$$Q_{2s}(0)/N = 0.001409\rho_{2s}(0) - 0.00398$$
$$Q_{3s}(0)/N = 0.02760\rho_{3s}(0) - 0.15751$$

with a multiple correlation of 0.9997, 0.9747 and 0.9996 respectively.

For the atoms boron to fluorine,

$$\Delta\varepsilon_{1s}/N = 0.001786\varepsilon_{1s} - 0.00178$$
$$\Delta\varepsilon_{2s}/N = 0.09164\varepsilon_{2s} - 0.05610$$

with a multiple correlation of 0.9978 and 0.9938 respectively whereas for the atoms aluminium to chlorine

$$\Delta\varepsilon_{1s}/N = 0.0001962\varepsilon_{1s} + 0.00852$$
$$\Delta\varepsilon_{2s}/N = 0.001406\varepsilon_{2s} + 0.00339$$
$$\Delta\varepsilon_{3s}/N = 0.09207\varepsilon_{3s} - 0.02683$$

with a multiple correlation of 0.9998, 0.9967 and 0.9924 respectively.

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