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THE HYPERFINE INTERACTION PARAMETER $\rho(0)$ CALCULATED BY THE $X\alpha$ METHOD WITH AB INITIO SELF-CONSISTENT EXCHANGE PARAMETER

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The total electronic density at the nucleus for atoms has been calculated by the $X\alpha$ method with ab initio exchange parameter α_{SCF}. Calculations have been done for a few atoms with the exchange parameter 2/3, 1 and α_{HF}, too. It has been found that the values obtained with α_{HF} and α_{SCF} show the best agreement with the Hartree–Fock data.

Introduction

Since the $X\alpha$ method was proposed by Slater [1], it has been a fascinating question how to select the value of α. In 1974 Gáspár [2] suggested a method of calculating an ab initio exchange parameter α. In a recent article [3] a comparison has been made between the Hartree–Fock and $X\alpha$ orbitals studying the expectation values of some powers of the radius. It has been found that the $X\alpha$ orbitals calculated with the SCF exchange parameters well approximate the HF ones.

There is another parameter which is very sensitive to the accuracy of the wave function. The Mössbauer isomer shift is proportional to the total electronic density at the nucleus

$$\rho(0) = \sum_i n_i |u_i(0)|^2, \tag{1}$$

where n_i is the occupation number of the orbital u_i. The sum includes only the s orbitals. There are a few $X\alpha$ studies on the hyperfine interactions [4], however systematic investigation is still lacking. Here, only the parameter $\rho(0)$ for light atoms has been determined by the $X\alpha$ method having SCF exchange parameter α. For a few cases, calculations have been done using several values of α, including 1, 2/3, α_{HF} and α_{SCF}. It has been found that the results obtained with α_{HF} and α_{SCF} are the best ones in approximating the HF values.

The method

Here the method is briefly reviewed. For details we refer to [2]. The derivation of the theory is based on the free-electron gas model. The exchange parameter suggested by Slater [1]($\alpha = 1$) can be obtained averaging the exchange potential

over the whole Fermi sphere. An average over a layer with a thickness of ϵ near the Fermi surface and $\epsilon \to 0$, gives the value of 2/3 for the exchange parameter. This is the Gáspár, Kohn–Sham [5] case. The average suggested by Gáspár [2] is between these extreme ones: it is over a layer containing $\nu_\uparrow$ electrons in the unit volume near the Fermi surface. The exchange parameter for the orbital j is given by

$$\alpha_j = \frac{1}{1-\eta_j^3}\left\{1 - \frac{1}{2}\eta_j - \frac{1}{2}\eta_j^3 + \frac{1}{4}(\eta_j^2 - 1)^2 \ln\left|\frac{1+\eta_j}{1-\eta_j}\right|\right\}, \tag{2}$$

where

$$\eta_j = (1 - \frac{\nu_\uparrow^j}{\rho_\uparrow}). \tag{3}$$

$\nu_\uparrow^j$ is the charge density of the orbital j and $\rho_\uparrow$ is the total electron density of electrons with spin up. An average over the shells leads to the exchange parameter

$$\alpha = \frac{\sum_j n_j \alpha_j}{\sum_j n_j}, \tag{4}$$

where n_j is the occupation number of the shell j. Solving the one-electron $X\alpha$ equations, this exchange parameter can be calculated self-consistently. That is why the term of self-consistent exchange parameter α_{SCF} is used.

Results and discussion

The value of $\rho(0)$ has been calculated by the $X\alpha$ method for several atoms. In Tables I–III the electronic density of orbitals at the nucleus $n_i|u_i(0)|^2$ are also presented. Hartree–Fock data [6] are also shown for comparison. The $X\alpha$ calculations have been carried out using several values of α. Tables I–III include the results obtained with the exchange parameter 2/3, 1 α_{HF} and α_{SCF}. While there is considerable difference between the HF and $X\alpha$ values for the orbitals — $n_i|u_i(0)|^2$ — there is agreement between the values of $\rho(0)$ obtained by the $X\alpha$ and HF methods. It suggests that the $X\alpha$ method — as it is expected — should be a better approximation for the atom as a whole than for the individual orbitals. The best agreement between the $X\alpha$ and HF results has been found for the exchange parameters α_{SCF} and α_{HF}. As it is well known α_{HF} is the value of α for which the total $X\alpha$ energy is equal to the HF one [6]. Table IV includes the values $\rho(0)$ of several atoms calculated by the HF and $X\alpha$ methods with self-consistent exchange parameters. The difference between them is about 0.2–0.3 per cent except for very small atomic numbers ($Z = 3 - -5$).

On the basis of these results it can be concluded that the $X\alpha$ method with self-consistent exchange parameter α_{SCF} provides sufficiently good electronic density.

Table I
Values of $\rho(0)$ of Ne calculated by the HF [6] and $X\alpha$ methods with exchange parameters 2/3, 1, α_{HF} and α_{SCF}

Orbital	HF	$X\alpha$			
		$\alpha = \frac{2}{3}$	$\alpha = 1$	α_{HF}	α_{SCF}
1*s*	587.535	581.319	597.203	597.194	585.403
2*s*	32.400	32.910	34.815	34.815	33.372
total	619.935	614.229	632.018	632.009	618.775

Table II
Values of $\rho(0)$ of Ar calculated by the HF [6] and $X\alpha$ methods with exchange parameters 2/3, 1, α_{HF} and α_{SCF}

Orbital	HF	$X\alpha$			
		$\alpha = \frac{2}{3}$	$\alpha = 1$	α_{HF}	α_{SCF}
1*s*	3527.724	3508.710	3559.603	3517.202	3516.218
2*s*	284.369	278.766	289.248	280.476	280.283
3*s*	27.772	31.101	32.743	31.353	31.327
total	3839.865	3818.577	3881.594	3829.031	3827.828

Table III
Values of $\rho(0)$ of Kr determined by the HF [6] and $X\alpha$ methods with exchange parameters 2/3, 1, α_{HF} and α_{SCF}

Orbital	HF	$X\alpha$			
		$\alpha = \frac{2}{3}$	$\alpha = 1$	α_{HF}	α_{SCF}
1*s*	28871.115	28800.648	29005.201	28824.191	28816.290
2*s*	2858.533	2830.345	2873.074	2835.335	2833.611
3*s*	460.166	458.334	470.859	459.757	459.295
4*s*	46.688	54.591	57.944	54.968	54.846
total	32236.502	32143.918	32407.078	32174.251	32164.042

Table IV
The total electron density at the atomic nucleus of atoms determined by the HF and the $X\alpha$ methods applying the self-consistent exchange parameter α_{SCF}

Z	HF	$X\alpha$
3	13.815	13.570
4	35.388	34.993
5	71.923	72.459
6	127.461	128.183
7	205.973	206.576
8	311.668	311.819
9	448.331	447.911
10	619.935	618.775
11	833.776	829.071
12	1093.744	1090.142
13	1402.875	1397.100
14	1765.646	1759.724
15	2186.363	2179.276
16	2669.519	2660.927
17	3219.247	3208.992
18	3839.865	3827.828
19	4538.725	4520.746
20	5319.719	5299.928
21	6182.441	6163.075
22	7133.395	7112.034
23	8177.116	8153.576
24	9318.062	9291.944
25	10560.309	10531.749
26	11908.955	11877.441
27	13367.667	13332.907
28	14940.899	14902.792
29	16632.956	16591.480
30	18448.022	18403.162
31	20397.625	20546.315
32	22480.511	22426.314
33	24701.383	24643.206
34	27064.951	27001.915
35	29575.097	29507.450
36	32236.502	32164.042

References

1. J.C. Slater, Phys. Rev., *81*, 385, 1951.
2. R. Gáspár, Acta Phys. Hung., *35*, 213, 1974.
3. R. Gáspár and Á.Nagy, Acta Phys. Hung., *53*, 247, 1982.
4. S.K. Lie, D.M.S. Esquivel and D. Guenzburger, Chem. Phys. Lett., *57*, 458, 1978.
5. R. Gáspár, Acta Phys. Hung., *3*, 263, 1954; W. Kohn and L.I. Sham, Phys Rev., *140A*, 1133, 1965.
6. C. Froese- Fischer, Atomic Data, *4*, 301, 1972.