Acta Physica Academiae Scientiarum Hungaricae, 53 (1—2), pp. 247—254 (1982)

COMPARISON OF THE ORBITALS OF NEON, ARGON AND KRYPTON CALCULATED BY THE HARTREE–FOCK AND THE Xα METHODS WITH SEVERAL VALUES OF α *

R. GÁSPÁR and Á. NAGY

INSTITUTE OF THEORETICAL PHYSICS, KOSSUTH LAJOS UNIVERSITY,
4010 DEBRECEN, HUNGARY

The orbitals of Neon, Argon and Krypton were calculated by the Xα method with parameters α theoretically determined by one of the authors [1—3].

It is pointed out by calculating expectation values of some powers of the radius that the orbitals of this method agree well with those of the Hartree–Fock method. For comparison values for the orbitals calculated with $\alpha = 1$ and 2/3 are also presented and some experimental values are included.

Introduction

In 1951 Slater [4] was the first to suggest an approximate exchange potential proportional to the one-third power of the local electronic density. In 1954 Gáspár [5] and later in 1965 Kohn and Sham [6] proposed another exchange potential which was the two-thirds of Slater's. Since that time calculations with several numerical coefficients in the exchange potential have been carried out and this new theory using local exchange potential has been denoted by the term "Xα method".

For the nearly three decades of the Xα method tremendous progress has been made in this theory but the problem of the parameter α still seems to be an unsettled one. In his previous papers [1—3] Gáspár introduced a new, theoretical way of calculation of the exchange parameters α. In this paper a comparison of orbitals of Ne, Ar and Kr calculated with several values of α is presented. It is shown that the orbitals of Gáspár's new method are the nearest in approximating the Hartree–Fock orbitals.

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* Dedicated to Prof. I. Tarján on his 70th birthday.

The theory

The total energy of an electron system is given by

$$\langle EX\alpha\rangle = \sum_i n_i \int u_i^*(1) f_1 u_i(1)\, dv_1 + \frac{1}{2}\int \rho(1)\,\rho(2) g_{12}\, dv_1\, dv_2 + \frac{1}{2}\int [\rho_\uparrow(1)\, U_{X\uparrow}(1) + \rho_\downarrow(1)\, U_{X\downarrow}(1)]\, dv\,, \tag{1}$$

where f_1 is the one-electron operator acting on the first electron, i.e. the sum of the kinetic energy and its potential energy in the field of the nuclei. g_{12} is the two-electron operator, the Coulomb interaction energy of the first and second electrons. The charge densities of the electrons with spin up and down have the form

$$\rho_\uparrow = \sum_{i\uparrow} n_i u_i^* u_i \tag{2}$$

and

$$\rho_\downarrow = \sum_{j\downarrow} n_j u_j^* u_j\,, \tag{3}$$

where u_i are the spin orbitals. The total charge density is

$$\rho = \rho_\uparrow + \rho_\downarrow\,. \tag{4}$$

The last term in the total energy expression provides the exchange energy.

Using the variational principle the Xα one-electron equations are

$$[f_1 + \int \rho(2) g_{12}\, dv_2 + V_{X\alpha\uparrow}(1)]\, u_{i\uparrow}(1) = \varepsilon_{iX\alpha\uparrow} u_{i\uparrow}(1) \tag{5}$$

and similar equations for spin orbitals with spin down. The exchange potential is given by

$$V_{X\alpha\uparrow}(1) = \frac{1}{2}\left[U_{X\uparrow}(1) + \rho_\uparrow(1)\frac{\delta U_{X\uparrow}(1)}{\delta\rho_\uparrow(1)}\right]. \tag{6}$$

In the Xα method the exchange potential in the total energy expression is proportional to the 1/3 power of the charge density

$$U_{X\alpha\uparrow}(1) = -9\alpha\left[\frac{3}{4\pi}\rho_\uparrow(1)\right]^{1/3}. \tag{7}$$

(The energy is in Rydbergs.) The exchange potential in the one-electron equations is

$$V_{X\alpha\uparrow}(1) = -6\alpha\left[\frac{3}{4\pi}\rho_\uparrow(1)\right]^{1/3}. \tag{8}$$

$\alpha=1$ gives the exchange potential proposed by Slater [4] and $\alpha=2/3$ provides the exchange potential suggested by Gáspár [5] and Kohn–Sham [6].

The Xα method of Slater contains a free parameter α. This permits to adjust the Xα method to the Hartree—Fock theory. The parameter α can be chosen so that the total Xα energy should be equal to the Hartree—Fock total energy. These parameters α_{HF} were calculated by Schwarz [9] and a method nearly as good as the Hartree—Fock method itself was obtained. There are, however, some problems with the parameter in the Xα method. Because the value of α is determined by adjusting, the Xα method is often considered as a semiempirical one. The parameter α_{HF} depends on the atomic number Z, it is not quite straightforward how to choose the value of α when the method is used in molecules.

To overcome these shortcomings of the Xα method some refinements have been made. Here the X$\alpha\beta$ method by Herman, Van Dyke and Ortenburger [7, 8] is discussed only. It is argued by these authors that the dependence of the parameter α on the atomic number Z is due to the inhomogeneity in the density distribution and a gradient term is introduced. The main advantage of the X$\alpha\beta$ method is that the parameters α and β are not Z dependent allowing a natural application to molecules and solids. But it has the disadvantage of having two adjustable parameters and a much more difficult way of computation.

One of the authors [1—3] has suggested a new way of theoretical introduction of the parameter in the Xα method. The exchange potential of an electron gas is given by

$$V_{X\uparrow}(1)=-8F(\eta)\left[\frac{3}{4\pi}\rho_{\uparrow}(1)\right], \tag{9}$$

where

$$F(\eta)=\frac{1}{2}+\frac{1-\eta^{2}}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right| \tag{10}$$

and

$$\eta=\frac{k}{k_{\mathrm{F}}} \tag{11}$$

is the reduced momentum of the electron considered and

$$E_{\mathrm{F}\uparrow}=k_{\mathrm{F}\uparrow}^{2}=(6\pi^{2}\rho)^{2/3} \tag{12}$$

is the Fermi energy. By an averaging process in the k space the averaged exchange potential is obtained

$$\bar{V}_{X\uparrow}=-8\left[\frac{3}{4\pi}\rho_{\uparrow}(1)\right]^{1/3}\frac{\int_{\eta_1}^{\eta_2}F(\eta)\eta^{2}\,\mathrm{d}\eta}{\int_{\eta_1}^{\eta_2}\eta^{2}\,\mathrm{d}\eta}. \tag{13}$$

This is an Xα exchange potential with the parameter

$$\alpha = \left\{\frac{1}{2}(\eta^3+\eta) - \frac{1}{4}(\eta^2-1)^2 \ln\left|\frac{1+\eta}{1-\eta}\right|\right\}_{\eta_1}^{\eta_2} [\{\eta^3\}_{\eta_1}^{\eta_2}]^{-1} . \tag{14}$$

If we average over all occupied states, i.e. $\eta_1=0$ and $\eta_2 = \frac{k_F}{k_F} = 1$, the parameter introduced by Slater ($\alpha=1$) is obtained. On averaging over a thin shell near k_F, i.e. $\eta_1 = \frac{k_F-\varepsilon}{k_F}$ and $\eta_2 = \frac{k_F}{k_F} = 1$ with $\varepsilon\to 0$, $\alpha=2/3$ is obtained. Between these two exchange potentials another exchange potential may be constructed by the introduction of an averaging process near the Fermi surface for a layer containing $v_\uparrow$ electrons in the unit volume, i.e. $\eta_1=(1-v_\uparrow/\rho_\uparrow)^{1/3}$ and $\eta_2=1$. $v_\uparrow=u_i^* u_i$ is the density of the reference electron. The exchange potential is given by

$$V_{X\alpha\uparrow} = V_{X\alpha\mathrm{shell}\uparrow} = -6\alpha_{\mathrm{shell}}\left(\frac{3}{4\pi}\rho_\uparrow\right)^{1/3} , \tag{15}$$

where

$$\alpha_{\mathrm{shell}} = \frac{\rho_\uparrow}{v_\uparrow}\left\{1 - \frac{1}{2}\eta^3 - \frac{1}{2}\eta + \frac{1}{4}[\eta^2-1]\ln\left|\frac{1+\eta}{1-\eta}\right|\right\} \tag{16}$$

and

$$\eta = \left(1 - \frac{v_\uparrow}{\rho_\uparrow}\right)^{1/3} . \tag{17}$$

These exchange potentials are different for different shells. It is possible to carry out another averaging process for the electron system with a weight factor n_j

$$\alpha'_\uparrow = \frac{\sum\limits_{j\uparrow} n_j \alpha_{\mathrm{shell}}}{\sum\limits_{j} n_j} , \tag{18}$$

where n_j is the number of electrons in the shell j. Now α'_1 is the same for each electron with the same spin but it depends on the position (1). It is possible to get a constant parameter α_G so that the mean squared deviation of $V_{X\alpha_G\uparrow}$ and $V_{X\alpha'\uparrow}$ be a minimum. The parameter α_G can be determined in a self-consistent way, i.e. starting from a trial atomic (or molecular) potential the spin orbitals u_i are obtained by solving the Xα equations. From the spin orbitals the new exchange parameter α_G is obtained and then the new potential is calculated. This process has to be carried out until self-consistency is achieved.

Results and discussion

The expectation values of powers of the radius $\langle \frac{1}{r} \rangle$, $\langle r \rangle$ and $\langle r^2 \rangle$, in atomic units, are calculated by the Hartree—Fock and the Xα method with parameters $\alpha=1$, $\alpha=2/3$, α_{HF} and α_G and they are presented in Tables I—III, which show that there is a good agreement between these orbitals. It is the results gained with the parameter α_G that are closest to the Hartree—Fock values [10]. The expectation values with α_{HF} are nearly as close to the Hartree—Fock values as those calculated with α_G. Results with $\alpha_S = 1$ and $\alpha_{GKS}=2/3$ are farther from the Hartree—Fock ones, though the expectation value obtained with α_{GKS} are sometimes rather close to the Hartree—Fock ones.

These expectation values show the behaviour of the orbitals at different values of the radius. The values $\langle \frac{1}{r} \rangle$ are sensitive to the behaviour of the orbitals near the nucleus. The expectation values $\langle r \rangle$ and $\langle r^2 \rangle$ show how good the orbitals are in the middle and outer regions of the atom.

The expectation value $\langle r^2 \rangle$ of the atom is proportional to the experimentally measurable diamagnetic susceptibility. These values calculated by different methods and gained from experiment can be found in Table IV. A comparison shows a good agreement between the results obtained by Hartree—Fock and Xα calculations with α_G and α_{HF} and the experiment. Unfortunately, the uncertainties in experimental values do not make it possible to decide which orbitals are the best.

Table I

Expectation values of powers of the radius for some orbitals in Ne (in atomic units)

		$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
1*s*				
HF		9.618 09	0.157 63	0.033 47
Xα	$\alpha=1$	9.674 32	0.156 84	0.033 15
	$\alpha=2/3$	9.558 68	0.158 98	0.034 09
	α_{HF}	9.581 28	0.158 65	0.033 90
	α_G	9.588 70	0.158 42	0.033 84
2*s*				
HF		1.632 56	0.892 11	0.967 08
Xα	$\alpha=1$	1.674 14	0.874 38	0.928 68
	$\alpha=2/3$	1.624 51	0.906 00	1.004 67
	α_{HF}	1.633 58	0.899 97	0.989 88
	α_G	1.636 77	0.897 91	0.984 86
2*p*				
HF		1.435 35	0.965 27	1.228 46
Xα	$\alpha=1$	1.514 19	0.912 78	1.097 49
	$\alpha=2/3$	1.431 03	0.989 98	1.326 81
	α_{HF}	1.447 22	0.973 66	1.275 64
	α_G	1.452 79	0.968 24	1.259 00

Table II

Expectation values of powers of radius for some orbitals in Ar (in atomic units)

		$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
1*s*				
HF		17.553 31	0.086 10	0.009 96
Xα	$\alpha=1$	17.611 85	0.085 82	0.009 89
	$\alpha=2/3$	17.500 58	0.086 43	0.010 03
	α_{HF}	17.519 25	0.086 33	0.010 01
	α_G	17.517 09	0.086 34	0.010 01
2*s*				
HF		3.555 33	0.412 28	0.201 22
Xα	$\alpha=1$	3.574 70	0.410 78	0.200 01
	$\alpha=2/3$	3.511 07	0.418 14	0.207 47
	α_{HF}	3.521 58	0.416 90	0.206 20
	α_G	3.520 38	0.417 04	0.206 34
2*p*				
HF		3.449 99	0.375 33	0.174 34
Xα	$\alpha=1$	3.507 87	0.369 77	0.169 57
	$\alpha=2/3$	3.437 86	0.378 41	0.178 02
	α_{HF}	3.449 44	0.376 95	0.176 57
	α_G	3.448 15	0.377 12	0.176 74
3*s*				
HF		0.961 98	1.422 17	2.350 41
Xα	$\alpha=1$	1.013 57	1.370 21	2.179 14
	$\alpha=2/3$	0.984 33	1.417 94	2.347 82
	α_{HF}	0.988 95	1.410 09	2.319 55
	α_G	0.988 45	1.410 96	2.322 68
3*p*				
HF		0.814 07	1.662 96	3.310 85
Xα	$\alpha=1$	0.875 21	1.563 80	2.918 47
	$\alpha=2/3$	0.824 67	1.682 10	3.435 21
	α_{HF}	0.833 15	1.660 68	3.337 15
	α_G	0.832 22	1.663 04	3.347 93

In conclusion, we can state that the new way in the calculation of the exchange parameter α in the Xα method provides good orbitals. Although the orbitals obtained with the parameter α_{HF} are nearly as good as those calculated with α_G, this new method has two very important advantages. First, this method contains no adjustable parameters and so it can be regarded as an ab initio method. Second, this method can be applied to any system of molecules or solids without further theoretical difficulties.

Table III

Expectation values of powers of radius for some orbitals in Kr (in atomic units)

		$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
1*s*				
HF		35.498 28	0.042 44	0.002 41
Xα	$\alpha=1$	35.558 67	0.042 36	0.002 40
	$\alpha=2/3$	35.448 83	0.042 51	0.002 42
	α_{HF}	35.461 54	0.042 49	0.002 42
	α_G	35.457 28	0.042 50	0.002 42
2*s*				
HF		7.918 84	0.187 26	0.041 28
Xα	$\alpha=1$	7.933 53	0.186 83	0.041 07
	$\alpha=2/3$	7.877 25	0.188 10	0.041 63
	α_{HF}	7.883 86	0.187 95	0.041 56
	α_G	7.881 58	0.187 99	0.041 59
2*p*				
HF		7.868 44	0.161 88	0.032 00
Xα	$\alpha=1$	7.927 18	0.160 68	0.031 51
	$\alpha=2/3$	7.866 26	0.162 02	0.032 06
	α_{HF}	7.873 44	0.161 86	0.031 99
	α_G	7.870 93	0.161 91	0.032 01
3*s*				
HF		2.637 56	0.537 80	0.331 73
Xα	$\alpha=1$	2.655 90	0.535 56	0.329 27
	$\alpha=2/3$	2.620 19	0.542 90	0.338 73
	α_{HF}	2.624 30	0.542 04	0.337 61
	α_G	2.622 95	0.542 33	0.337 98
3*p*				
HF		2.522 78	0.542 63	0.343 54
Xα	$\alpha=1$	2.555 17	0.537 01	0.336 86
	$\alpha=2/3$	2.514 25	0.546 44	0.349 36
	α_{HF}	2.518 99	0.545 32	0.347 87
	α_G	2.517 44	0.545 69	0.348 36
3*d*				
HF		2.276 94	0.550 88	0.317 48
Xα	$\alpha=1$	2.331 40	0.538 32	0.355 08
	$\alpha=2/3$	2.274 53	0.554 86	0.379 33
	α_{HF}	2.281 22	0.552 86	0.376 34
	α_G	2.279 05	0.553 51	0.377 31
4*s*				
HF		0.804 19	1.629 38	3.040 32
Xα	$\alpha=1$	0.858 89	1.551 35	2.751 59
	$\alpha=2/3$	0.833 03	1.603 68	2.955 21
	α_{HF}	0.835 98	1.597 51	2.930 78
	α_G	0.835 02	1.599 54	2.938 83
4*p*				
HF		0.669 22	1.951 61	4.455 08
Xα	$\alpha=1$	0.720 58	1.835 61	3.926 51
	$\alpha=2/3$	0.677 37	1.970 73	4.595 63
	α_{HF}	0.682 56	1.953 17	4.504 42
	α_G	0.680 84	1.958 98	4.534 54

Table IV

Expectation values $\langle r^2 \rangle$ calculated with the total radial density of the atom for Ne, Ar and Kr. (Expectation values are in atomic units.) The experimental results are obtained from diamagnetic susceptibility [11]

		Ne	Ar	Kr
HF		9.372	26.034	39.530
$X\alpha$	$\alpha=1$	8.509	23.306	35.569
	$\alpha=2/3$	10.038	26.810	40.331
	α_{HF}	9.701	26.154	39.694
	α_G	9.591	26.226	39.904
Exp [11]		8.4—9.8	14.2—24.9	34.8—36.9

References

1. R. Gáspár, Acta Phys. Hung., **35**, 213, 1974.
2. R. Gáspár, Acta Phys. et Chim. Debr., XIX, 7, 1974.
3. R. Gáspár, Acta Phys. et Chim. Szeged., XX, 321, 1974.
4. J. C. Slater, Phys. Rev., **81**, 385, 1951.
5. R. Gáspár, Acta Phys. Hung., **3**, 263, 1954.
6. W. Kohn and L. J. Sham, Phys. Rev., **140A**, 1133, 1965.
7. F. Herman, J. P. Van Dyke and I. B. Ortenburger, Phys. Rev. Lett., **22**, 807, 1969.
8. F. Herman, J. P. Van Dyke and I. B. Ortenburger, Int. J. Quant. Chem., **S3**, 827, 1970.
9. K. Schwarz, Phys. Rev., **B5**, 2466, 1972.
10. C. Froese-Fischer, Atomic Data, **4**, 301, 1972.
11. Landolt-Börnstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik (Springer-Verlag, Berlin, 1950), 6 Auflage, Band I.