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Relationes

Approximate Radial Functions

I. First-Row Transition-Metal 4s and 3d Atomic Orbitals

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The approximate 4*s* and 3*d* radial wavefunctions of Richardson *et al.* [J. chem. Physics **36**, 1057 (1962)] for first-row transition-metal atoms and ions have been extended to additional electronic configurations. The results suggest several improvements in the 4*s* wavefunction parameters. Formulas are reported for extending the "double-ζ" 3*d* wavefunctions over the range of atomic orbitals d^1 through d^{10}. The results are intended for use in calculations of chemical bonding.

1. Introduction

The extensive use of the approximate Hartree-Fock wavefunctions for first-row transition metals of Richardson *et al.* [1, 2] and a need [3–6] for more consistent wavefunctions of the same type indicate that additional 4*s* and 3*d* wavefunctions are needed for completeness. A common procedure in LCAO-MO calculations is to vary the AO's for the atoms involved in forming the molecule. By using the wavefunctions of the atoms and ions of the species involved some insight is gained about the bonding of the molecule. Although it has been claimed that the one-electron LCAO-MO model is relatively insensitive to the effect of choice of wavefunctions [7], this has not been the case for orbital energies in several MO calculations [5, 6, 8].

The 4*p* wavefunctions of the first-row transition metals are varied extensively in the reports of Richardson and his co-workers [1, 2] as are the 3*d* and 4*s* wavefunctions which are varied over several common oxidation states. Reported in the present article are approximate 4*s* wavefunctions for several additional atomic electronic configuration and formulas for obtaining approximate 3*d* wavefunctions over the entire range of atomic orbitals d^1 through d^{10}.

2. Procedure

By using the procedure similar to that described by Richardson *et al.* [1], we have taken the approximate radial *s* symmetry wavefunctions to have the form

$$R_{ns} = \sum_{k=1}^{n} \chi_{ks} C_{ks,n} \tag{1}$$

where

$$\chi_{kl} = [(2\zeta_{kl})^{2k+1}/(2k)!]^{\frac{1}{2}} r^{k-1} \exp(-\zeta_{kl} r) \tag{2}$$

and

$$\int R_{ns} R_{n's} r^2 \, dr = \delta_{n,n'} \,. \tag{3}$$

Thus we have a linear combination of STO's (Slater type orbitals) which form an orthonormal set over the s symmetry atomic orbitals. We have taken the ground state wavefunction for the $1s$, $2s$, and $3s$ orbitals for each metal to be adequately [9] represented by the Schmidt orthogonal sets given by Richardson *et al.* [1]. The four term $4s$ wavefunctions have been constructed to be Schmidt orthogonal to these orbitals. Consequently the ζ_{4s} parameter is the only variable remaining to be determined. Unlike Richardson *et al.* [1] we have varied the ζ_{4s} extensively until a maximum overlap is obtained between the approximate $4s$ wavefunction and its corresponding Hartree-Fock wavefunction which is taken from Clementi [10] tables.

By utilizing the maximization of overlap as the criterion for the choice of ζ_{4s} for all calculated $4s$ wavefunctions of neutral atoms and ions, the resulting orbitals should be more representative of atomic electronic configuration in MO calculations [11] than those reported by Richardson *et al.* [1,2] who estimated ζ_{4s} values for the ions.

The radial $3d$ wavefunctions obtained by Richardson *et al.* are of the "double-ζ" type with the formula:

$$R_{3d} = C_1 \chi_{3d,1}(\zeta_1) + C_2 \chi_{3d,2}(\zeta_2) \tag{4}$$

with

$$\zeta_1 = 0.20 Z + 0.15\,, \tag{5}$$

$$\zeta_2 = 0.30 Z - 0.20 n - 4.40\,, \tag{6}$$

where Z is the nuclear charge, and n is the number of $3d$ electrons. The values of the coefficients in Eq. (4) were obtained by maximizing the overlap with Hartree-Fock wavefunctions (as were the ζ_1 and ζ_2 initially). Since Eqs. (5) and (6) are compact formulas for obtaining the ζ_1 and ζ_2 values, it would be advantageous to have a compact formula to obtain the coefficients. With this in mind we have in Fig. 1 the C_2 values plotted against their respective ζ_2 values for several of the first-row transition metals. In Fig. 1 we have that C_2 is almost linear with ζ_2. Consequently we have assumed that we can express C_2 for each metal in the following form as a function of ζ_2 for its respective metal:

$$C_2(\mathrm{M}) = \alpha_1 + \alpha_2 \zeta_2 + \alpha_3 \zeta_2^2\,. \tag{7}$$

The values for α_1, α_2 and α_3 for each metal were obtained by a quadratic least square fit of the C_2 and ζ_2 values given by Richardson *et al.* [1]. The remaining C_1 coefficients can be obtained through normalization. With Eqs. (4) thru (7) we now have a systematic procedure for obtaining "double-ζ" $3d$ wavefunctions over the entire range of orbitals from d^1 to d^{10}.

3. Results

Overlaps, S, with Hartree-Fock wave functions and parameters for $4s$ radial functions are presented in Table 1. From the values of S in this table we see that the best approximate wavefunctions are obtained for the $+1$ metal ions for each of the metals with a decrease in accuracy with increasing atomic number. The least accurate representations are obtained with the -1 metal ions, although these are

Table 1. Parameters and overlaps with Hartree-Fock wavefunctions for 4s radial functions

Metal	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
[a] ζ_{1s}	21.40	22.395	23.39	24.385	25.38	26.375	27.37	28.365
ζ_{2s}	8.05	8.475	8.90	9.325	9.75	10.175	10.60	11.025
ζ_{3s}	3.64	3.85	4.06	4.27	4.48	4.69	4.90	5.11

System	ζ_{4s}	C_1	C_2	C_3	C_4	S[b]
Ti s^2d^1	1.4779	−0.03614	0.12603	−0.33192	1.04515	0.998
s^2d^2	1.2077	−0.02266	0.07875	−0.20184	1.01691	0.993
s^2d^3	0.8133	−0.00774	0.02679	−0.06655	1.00185	0.96
V s^2d^2	1.5364	−0.03541	0.12267	−0.31947	1.04177	0.998
s^2d^3	1.2582	−0.02222	0.07671	−0.19462	1.01569	0.993
s^2d^4	0.8390	−0.00731	0.02514	−0.06183	1.00159	0.96
Cr s^2d^3	1.5918	−0.03459	0.11910	−0.30702	1.03852	0.997
s^2d^4	1.3061	−0.02172	0.07451	−0.18731	1.01450	0.992
s^2d^5	0.8608	−0.00684	0.02337	−0.05695	1.00135	0.96
Mn s^2d^4	1.6456	−0.03379	0.11564	−0.29526	1.03558	0.997
s^2d^6	1.3486	−0.02105	0.07182	−0.17894	1.01320	0.991
s^2d^7	0.8998	−0.00682	0.02316	−0.05602	1.00130	0.95
Fe s^2d^5	1.6954	−0.03286	0.11191	−0.28317	1.03269	0.996
s^2d^6	1.3997	−0.02076	0.07049	−0.17429	1.01250	0.990
s^2d^7	0.9290	−0.00658	0.02224	−0.05340	1.00118	0.95
Co s^2d^6	1.7504	−0.03224	0.10927	−0.27432	1.03063	0.996
s^2d^7	1.4466	−0.02035	0.06877	−0.16881	1.01170	0.99
s^2d^8	0.9605	−0.00641	0.02158	−0.05147	1.00109	0.95
Ni s^2d^7	1.8013	−0.03148	0.10625	−0.26483	1.02852	0.996
s^2d^8	1.4913	−0.01989	0.06691	−0.16320	1.01092	0.99
s^2d^{10}	0.9881	−0.00618	0.02072	−0.04912	1.00099	0.96
Cu s^2d^9	1.5343	−0.01940	0.06504	−0.15766	1.01017	0.99
s^2d^{10}	1.3505	−0.01380	0.04620	−0.11079	1.00503	0.98
s^2d^{10}	1.0085	−0.00584	0.01951	−0.04597	1.00087	0.95

[a] ζ_{1s}, ζ_{2s} and ζ_{3s} values were taken from Richardson *et al.* J. chem. Physics **36**, 1057 (1962).

[b] .S is the overlap between the approximate and the Hartree-Fock wavefunctions.

probably adequate for most purposes. The accuracy obtained for the neutral ground state wavefunctions is intermediate to that of the +1 and −1 ions. A close look at the Hartree-Fock wavefunctions [10] gives some indication as to the inaccuracy of the −1 ion wavefunctions. Since the +1 ion and neutral atom wavefunctions have only one or two dominant terms to be represented by the approximate wavefunction, they can be represented fairly accurately. The −1 ion Hartree-Fock wavefunctions have three dominant terms which contain a greater range of zeta values and thus can only be poorly represented by one dominant term containing ζ_{4s}.

In Table 2 we have tabulated the calculated ζ_{4s} values and several estimated values. The many trends within the calculated values lend considerable confidence to the estimated values. An average value for the differences between successive calculated ζ_{4s} values, $\Delta\zeta_{4s}$, for each horizontal series reveals that each sequence is uniform and has an almost linear increase. This trend is found in the ground state $\zeta_{4s}(3d^n4s^2)$ values reported by Richardson *et al.* [1], but is not found in their

Table 2. Calculated and estimated ζ_{4s} values[a]

Metal System	Ti $n=2$	V 3	Cr 4	Mn 5	Fe 6	Co 7	Ni 8	Cu 9	$\Delta\zeta_{4s}$
$3d^{n+1}4s^2$	0.8133	0.8390	0.8608	0.8998	0.9290	0.9605	(0.986)	1.0085	0.029
$4s^1$	(1.08)	(1.12)	(1.16)	(1.20)	(1.24)	(1.28)	(1.32)	1.3505	(0.04)
$3d^n\ 4s^2$	1.2077	1.2582	1.3061	1.3486	1.3997	1.4466	1.4913	1.5343	0.046
$4s^1$	(1.39)	(1.44)	(1.49)	(1.55)	(1.59)	(1.65)	(1.70)	(1.75)	(0.05)
$3d^{n-1}4s^2$	1.4779	1.5364	1.5918	1.6456	1.6954	1.7504	1.8013	(1.85)	0.054
$4s^1$	(1.60)	(1.66)	(1.72)	(1.78)	(1.83)	(1.94)	(1.94)	(1.99)	(0.06)
$3d^{n-2}4s^2$	(1.66)	(1.72)	(1.78)	(1.85)	(1.90)	(1.95)	(2.01)	(2.06)	(0.06)

[a] Values in parentheses are estimated values.

estimated values of ζ_{4s} for ions. On comparison, the values reported in Table 4 of Ref. [1] are consistently lower on the Ti end of a horizontal sequence and high on the Ni end of the sequence (*e.g.*, $3d^{n-1}4s^2$, Ti $\zeta_{4s} = 1.45$ as compared with 1.48 reported here; and Ni $\zeta_{4s} = 1.90$ as compared with 1.80). By combining the above mentioned trends with changes in vertical sequences we have made several estimates for additional ζ_{4s} values. Some of the values estimated (and also calculated) are similar to those reported by Richardson *et al.*, but several are markedly different.

The coefficients obtained for Eq. (7) for each of the metals considered are given in Table 3. A standard estimate of error, σ, is also given for each curve and indicates an accuracy of about three significant figures. By comparing graphically the values reported by Richardson *et al.* in Fig. 1 with those obtained by extrapolating with Eq. (7), there seems to be reasonable accuracy except for the case of Ti. Since there are only four reported [1] values for the C_2 coefficients for Ti, it should be expected that a fairly good quadratic least square fit would be obtained. But we should not place much confidence in the result as shown by curve 1 in

Table 3. Coefficients obtained from quadratic least square fits of $3d$ wavefunction C_2 coefficients as a function of ζ_2 for the first-row transition metals. Coefficients obtained from a linear least square fit for Ti are also given[a]

Metal	α_1	α_2	α_3	$\sigma \times 10^4$	N
Ti	0.90085	0.03268	−0.08312	9.6	4
	1.13693	−0.24994		47.5	6
V	1.09163	−0.21257	−0.00892	14.3	5
Cr	1.14006	−0.28382	0.01383	17.0	6
Mn	1.10747	−0.26185	0.01071	6.0	6
Fe	1.04582	−0.21241	0.00133	8.3	6
Co	1.03985	−0.21358	0.00312	9.5	6
Ni	1.03482	−0.21017	0.00352	17.0	6
Cu	1.13194	−0.28572	0.01895	10.7	5
Average[b]	1.0845	−0.2400	0.0075		

[a] σ is the standard estimate of error (standard deviation) and N is the number of data points used for the least square fit.

[b] The average α_i coefficients do not include Ti results.

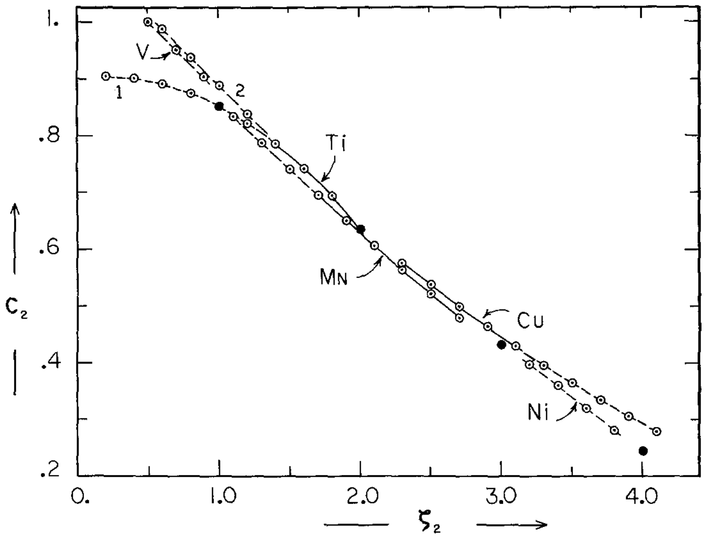

Fig. 1. Typical C_2 versus ζ_2 relations for "double-ζ" $3d$ wavefunctions. Solid curves for the metals shown are from those reported by Richardson *et al.* [J. chem. Physics **36**, 1057 (1962)]. Dashed curves are obtained by using Eq. (7) with the α_i coefficients given in Table 3. Curve 1 is the quadratic extension of C_2 (Ti) and curve 2 is the linear extension of C_2 (Ti). The solid black points, ●, are obtained by using the general relation given in Eq. (8)

Fig. 1. A more acceptable curve is obtained with a linear least square fit for C_2 (Ti) as illustrated by curve 2 in Fig. 1. This is borne out by considering the trends of the other metals. Although the C_2 (Ti) results are probably the poorest, the remaining curves indicate at least an internal consistency.

By taking an average value for each α_i (excluding Ti), we have obtained an equation that has general validity over the entire range of metals except for Ti and Cu which are at the ends of the series. The equation is as follows:

$$C_2 = 1.0845 - 0.2400\zeta_2 + 0.0075\zeta_2^2 . \tag{8}$$

On combining Eq. (8) with Eqs. (4), (5), and (6) we complete the set of equations for obtaining "double-ζ" $3d$ wavefunctions that are fairly accurate from vanadium through nickel. The solid black points, ●, in Fig. 1 are obtained from Eq. (8) and illustrate the validity of this equation.

4. Conclusions

Although many of the results obtained by this study are similar to those of Richardson *et al.* [1, 2] a more reasonable set of ζ_{4s} values is reported for a larger range of electronic configurations. By reasonable we mean that the wavefunctions give a fairly good representation of atomic electronic configurations in MO calculations for approximate $4s$ wavefunctions. The internal consistency of estimated ζ_{4s} values indicate several improvements over previously reported values.

With Eqs. (4), (5), (6), and (8) we are now able to obtain "double-ζ" $3d$ wavefunctions for the sequence of metals from vanadium through nickel with reasonable accuracy for the entire range of electronic configurations from d^1 through d^{10}. A more accurate representation of the wavefunction can be obtained for each metal in the sequence from Ti through Cu by using Eq. (7) instead of Eq. (8). Only the $3d$ wavefunctions of Ti seem to be questionable on being extended to additional oxidation states.

References

1. Richardson, J. W., Nieuwpoort, W. C., Powell, R. R., Edgell, W. F.: J. chem. Physics **36**, 1057 (1962).
2. — Powell, R. R., Nieuwpoort, W. C.: J. chem. Physics **38**, 796 (1963).
3. Brown, R. D., James, B. H., O'Dwyer, M. F.: Theoret. chim. Acta (Berl.) **17**, 264 (1970).
4. Fenske, R. F., Caulton, K. G., Radtke, D. D., Sweeney, C. C.: Inorg. Chemistry **5**, 951 (1966).
5. Dahl, J. P., Johansen, H.: Theoret. chim. Acta (Berl.) **11**, 8 (1968).
6. Becker, C. A. L., Dahl, J. P.: Theoret. chim. Acta (Berl.) **14**, 26 (1969).
7. Shulman, R. G.: Bell Telephone Laboratories, Memorandum for File, Case 38140-13.
8. Copeland, D. A., Ballhausen, C. J.: Theoret. chim. Acta (Berl.) **20**, 317 (1971).
9. Watson, R. E.: Physic. Rev. **118**, 1036 (1960); **119**, 1934 (1960).
10. Clementi, E.: IBM J. Res. Devel. **9**, 2 (1965) and the supplement to this paper.
11. Burns, G.: J. chem. Physics **41**, 1521 (1964).

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