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Variational Calculation of the Multiplet Spacings in the $(3d)^2$ Electron Configurations

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The effect of spatial correlation of the two valence electrons on the multiplet spacings has been investigated for atoms with the $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2$ ground configuration. The atom is taken as a two-electron system with each electron moving in a Hartree-Fock effective potential. The zeroth-order wave function is taken to be a Clebsch-Gordan combination of products of one-electron Hartree-Fock orbitals. A variational function of the form $1+cr_{12}+c'(r_1-r_2)^2$ is inserted into this wave function for each of the multiplet members, and c and c' are determined by the variational method. When unrestricted Hartree-Fock functions are used as the zeroth-order basis set, good results which are insensitive to c' are obtained for the multiplet spacings. The ${}^1G$-${}^3F$ spacing is overcorrected by about -12% compared to $+23\%$ without correlation, while the ${}^1D$-${}^3F$ spacing is overcorrected by -3% compared to $+34\%$ without correlation.

I. INTRODUCTION

It is well known that the Hartree-Fock theory gives good average energies and ionization energies for many-electron atoms but gives poor results for the multiplet spacings for open-shell atoms. This is because the multiplet spacings, in the case of $(3d)^2$, depend on two Slater-Condon integrals and the Hartree-Fock theory overestimates these integrals by 20–30%. Apparently these poor results are due to the inadequate inclusion of the electron correlations. In an early paper[1] on the subject, an old technique due to Hylleraas[2] was applied to the separate multiplet levels of the $(3d)^2$ electron configuration in an effort to correct the multiplet spacings without disturbing the Hartree-Fock (HF) average energies. In this case, a variational function of the form $1+cr_{12}$ was inserted into the wave function for each multiplet level, and the value of c was determined by the variation method. The zeroth-order wave function for this two-electron system was taken as a Clebsch-Gordan combination of products of one-electron orbitals. These orbitals were chosen as analytic HF average-of-configuration (HFAC) functions. The multiplet spacings were found to be overcorrected by 13–25% in the case of Ti III. It was conjectured that the simple one-parameter variation function and the way in which the core model was employed were responsible for the major part of the discrepancy from the experimental-term values.

This conjecture was investigated further[3] in a study of the multiplet structure of the $(2p)^2$ configuration. This carbonlike configuration was chosen as a test of the core model because of the penetrating nature of the $2p$ orbital. It was thought that the inadequacy of the core model would manifest itself in poor results for the multiplet spacings. However, it was found that the use of a one-parameter variation function and unrestricted Hartree-Fock (UHF) orbitals gave results in satisfactory agreement with experiment. Thus, the core model using UHF functions seemed to be a reasonable approach, and it remained only to study the variational function. This was done by inserting a two-parameter function of the form $1+cr_{12}+c'(r_1-r_2)^2$ into the UHF function for each multiplet level and again using the variation method to determine c and c'. Again, good agreement with experiment was obtained for the carbon isoelectronic sequence.[4] The conclusion from these studies was that, in spite of the expected large $2s$-$2p$ correlations,[5] the core model as represented by the UHF functions was adequate and that a two-parameter variation function could slightly improve the results.

In this paper, the results of a similar calculation on the $(3d)^2$ configuration are reported. A two-parameter variation function of the above type is used in conjunction with UHF zeroth-order functions. It will be seen that the multiplet separations are in good agreement with experimental-term values and are much improved over those of Ref. 1 where HFAC functions were used. Furthermore, results are presented for all the transition metal ions through Ni IX. Section II contains a brief discussion of the theory and UHF wave functions, and the results are discussed in Sec. III. Section IV contains some concluding remarks.

II. THEORY

The formulation of this semiempirical method is identical to that presented in Ref. 4 and need not be repeated here. However, some comment regarding the UHF functions is necessary. Clementi[6] has derived these functions for only the ^3F multiplet for these ions, and it was necessary to generate them for the other multiplet levels as well. The Roothaan method[7] was used for this purpose. For the core electrons, the same size basis set as Clementi's was used, but for the two open-shell electrons, a three-term basis set was used. Since the open-shell basis set was two terms shorter than Clementi's, this made it necessary to reoptimize the orbital exponents and expansion coefficients for the core electrons. The virial theorem was always satisfied to 6 or 7 significant figures, and where it was possible, comparison with Clementi's results[6] showed that the total energies and orbital energies always agreed out to 3 or 4 decimal places.[8] The reduced size of the d-orbital basis set resulted in a twofold saving of much computer time, first in generating the UHF functions for the higher multiplet levels which are already slowly convergent and, second, in using these functions in the subsequent variational calculation. The slight loss in accuracy, which is insignificant for the purposes of this paper, seemed justified by this saving of computer time. Since there are undoubtedly other applications in which only the d orbitals are needed, these shorter functions could be very useful and will be reported in another paper.

III. RESULTS

The variational calculation was made using both UHF and HFAC zeroth-order functions, but as found in the $(2p)^2$ case, the HFAC results were never as good as the UHF results. Therefore, only the latter are presented here. Also, the same calculation was made with and without c' in the variational function. These results always showed, as expected, that the separate multiplet energies were lower when the c' term was included, but the differ-

TABLE I. UHF results for $(3d)^2$ with c' zero in the variational function. All energies in uncorrected a.u.

Atom	^1S	^1G	^3P	^1D	^3F
			Total energy with correlation		
Ti	−847.62078	−847.68041	−847.69069	−847.69914	−847.73592
V	−940.99334	−941.07122	−941.08477	−941.09535	−941.14242
Cr	−1039.52611	−1039.62151	−1039.63821	−1039.65067	−1039.70699
Mn	−1143.20551	−1143.31833	−1143.33804	−1143.35214	−1143.41729
Fe	−1252.02311	−1252.15330	−1252.17602	−1252.19168	−1252.26552
Co	−1365.97354	−1366.12091	−1366.14660	−1366.16381	−1366.24617
Ni	−1485.05261	−1485.21724	−1485.24588	−1485.26456	−1485.35519
			Effect on HF energy		
Atom	^1S	^1G	^3P	^1D	^3F
Ti	−0.080	−0.029	−0.022	−0.020	−0.006
V	−0.092	−0.032	−0.023	−0.021	−0.006
Cr	−0.100	−0.033	−0.024	−0.022	−0.006
Mn	−0.107	−0.034	−0.024	−0.023	−0.006
Fe	−0.111	−0.035	−0.025	−0.023	−0.006
Co	−0.116	−0.036	−0.025	−0.024	−0.006
Ni	−0.119	−0.037	−0.026	−0.024	−0.006

TABLE II. UHF variational parameter c in reciprocal a.u. for c' zero in the correlation correction for $(3d)^2$.

Atom	$c(^1S)$	$c(^1G)$	$c(^3P)$	$c(^1D)$	$c(^3F)$
Ti	0.434	0.222	0.189	0.172	0.084
V	0.446	0.224	0.188	0.174	0.084
Cr	0.450	0.224	0.187	0.174	0.084
Mn	0.450	0.224	0.186	0.175	0.084
Fe	0.449	0.223	0.185	0.175	0.084
Co	0.449	0.223	0.184	0.175	0.084
Ni	0.448	0.223	0.183	0.175	0.084

ences in the multiplet energies, to the accuracy of the calculation, were completely insensitive to this term. In fact, the improvement in total energies resulting from the c' term borders on the limit of accuracy of the calculation. This has led to the conclusion that including the c' term in the variational function is not practical since it increases the computer time many-fold and the results do not justify this. Therefore, all results presented here are obtained with c' set to zero.

Table I gives the total energies, in hartree units, for each multiplet level and the effect of the spatial correlation on these energies. This information also allows one to calculate the total energies with-

TABLE III. Multiplet spacings in a.u. for $(3d)^2$ configuration.

Atom	Multiplet spacing	Expt[a]	UHF No corr.	Deviation from expt	UHF with c	Deviation from expt
Ti III	^1S-^3F	0.063	0.190	...	0.115	...
	^1G-^3F	0.064	0.079	23%	0.056	−13%
	^3P-^3F	0.047	0.061	30%	0.045	−4%
	^1D-^3F	0.038	0.051	34%	0.037	−3%
V IV	^1S-^3F	...	0.235	...	0.149	...
	^1G-^3F	0.082	0.097	18%	0.071	−13%
	^3P-^3F	0.059	0.075	27%	0.058	−2%
	^1D-^3F	0.048	0.062	29%	0.047	−2%
Cr V	^1S-^3F	...	0.275	...	0.181	...
	^1G-^3F	0.098	0.113	15%	0.085	−14%
	^3P-^3F	0.069	0.087	26%	0.069	0
	^1D-^3F	0.057	0.073	28%	0.056	−2%
Mn VI	^1S-^3F	...	0.312	...	0.212	...
	^1G-^3F	0.112	0.127	13%	0.099	−12%
	^3P-^3F	0.079	0.098	24%	0.079	0
	^1D-^3F	0.065	0.082	26%	0.065	0
Fe VII	^1S-^3F	...	0.348	...	0.242	...
	^1G-^3F	0.126	0.142	13%	0.112	−11%
	^3P-^3F	0.089	0.108	21%	0.090	+1%
	^1D-^3F	0.073	0.091	25%	0.074	+1%
Co VIII	^1S-^3F	...	0.382	...	0.273	...
	^1G-^3F	...	0.155	...	0.125	...
	^3P-^3F	...	0.119	...	0.100	...
	^1D-^3F	...	0.100	...	0.082	...
Ni IX	^1S-^3F	...	0.416	...	0.303	...
	^1G-^3F	...	0.169	...	0.138	...
	^3P-^3F	...	0.129	...	0.109	...
	^1D-^3F	...	0.109	...	0.091	...

[a] Experimental energies averaged over the J values were taken from C. E. Moore, Atomic Energy Levels, Natl. Bur. Std. (U.S.), Circ. No. 467 (Government Printing Office, Washington, D.C., 1949).

out correlation and thus obtain a result due only from the shorter UHF functions, i.e., the zeroth-order energies. Table II gives the corresponding values of c for each level in reciprocal atomic length units. None of the results have been corrected for the finite nuclear mass since such a correction lies within the round-off error of the IBM 360/50 computer which was used. The multiplet separations, which are the prime concern of this paper, are given in Table III and are accurate to the number of significant figures shown.

It is interesting to observe from Tables I and II the constancy of the correlation effect as a function of the atomic number Z. From Table I, the effect of the correlation on the HF energy for each multiplet level is practically constant in Z. This is particularly true for the value of c from Table II. This means that the correlation of the two open-shell electrons can be transferred from one ion to another for a given level. This was also approximately true in the $(2p)^2$ case.[4] Öksüz and Sinanoğlu[9] have recently studied three types of correlations in nonclosed shell atoms; namely, (1) the "internal," (2) "polarization and semiinternal," and (3) the "all-external" correlations. The first two of these were found to be strongly dependent on the number of electrons, symmetry, and Z, while the all-external correlations were Z transferable in 113 species arising from the $(1s)^2(2s)^n(2p)^m$ configurations. Therefore, it appears that the semiempirical method outlined in this paper and in Ref. 4 is a rather simple way to account for some of the all-external correlations. This is not unexpected since, by definition, these correlations arise from the excitation of two electrons from the HF sea into a pair correlation function of the type used here. Also, from Table III the percentage deviation of the "UHF with c" spacing from the observed spacing is practically independent of Z, which again reflects the importance of the all-external correlation in the multiplet structure.

The correlation or variational function used here is multiplicative, whereas it is additive in Sinagoğlu's theory. However, it is easy to show[8] that orthogonalization of the zeroth-order function with each part of the variational function produces an additive correlation correction but does not change the total energies or the effect on the HF energies, although the value of c does change slightly.

IV. CONCLUSION

Only now is it possible to make some general remarks about the semiempirical method used in these studies. (1) For the multiplet structure arising from the open-shell electrons, the UHF potential is an adequate representation of the atomic core. (2) Inclusion of the pure radial correlation term in the variational function is not practical since the improvement of the results due to c' is insignificant. These two conclusions also hold for the $(2p)^2$ configuration. (3) The results of a similar calculation on the $(3p)^2$ configuration were not good. This apparently was due to the node in the $3p$ function which causes correlations between open-shell electrons and core electrons to be more important. (4) The semiempirical method used in these studies is not intended to supplant the more rigorous "Many Electron Theory" of Sinanoğlu, but it can be formulated in a rather simple manner, and the results agree quite well with experiment for the case of two equivalent electrons outside a closed shell, each with $l = n - 1$. (5) The all-external correlations between the two open-shell electrons seem to be accounted for by this method, and the results are transferable from one ion to another for a given multiplet level. (6) The remaining discrepancy between theory and experiment could probably be removed by including the internal and the polarization plus semiinternal correlations.

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