Acta Physica Academiae Scientiarum Hungaricae, Tomus 27, pp. 169—177 (1969)

REMARKS CONCERNING THE THEORETICAL EXPLANATION OF HUND'S RULE* **

By

A. LEMBERGER and R. PAUNCZ

DEPARTMENT OF CHEMISTRY, ISRAEL INSTITUTE OF TECHNOLOGY, HAIFA, ISRAEL

(Received 13. I. 1969)

According to the accepted theoretical explanation of HUND's rule the electronic interaction energy is smallest in the ground state which is of the highest multiplicity. A breakdown of the total energy into one- and two-electron contributions in the case of carbon atom based on self-consistent field calculations and configuration interaction treatment shows that this assumption is not valid. According to our results the main differences in the energies of different terms arising from the same electronic configuration are due to differences in the one-electron energies.

1. Introduction

The simplest treatment of atomic spectra is based on the assumption that a single electronic configuration can be attributed to each atomic energy level. The positions of the different terms arising from a given electronic configuration, are determined theoretically by diagonalizing the matrices of electrostatic and spin-orbit interaction [1, 2, 3]. For light atoms the spin-orbit interaction is weak and can be treated as a perturbation, so that the different terms can still be characterized by their *LS* values and parity.

According to HUND's empirical rule [4], of all terms arising from a certain electronic configuration, the term with highest multiplicity has the lowest energy. This rule predicts correctly the ground state of most atoms, but it usually does not hold for excited states.

The accepted theoretical explanation for this rule is based on the phenomenon of the "Fermi hole". It is well known that antisymmetrization of the wave function introduces strong correlation between electrons with parallel spins. LÖWDIN [5] has shown that the diagonal element of the second order density matrix, $\Gamma(x_1x_2|x_1x_2)$ is zero for $x_1 = x_2$, at least up to the second order; that is, the probability of finding two electrons with parallel spins at the same point in space is zero, whereas the probability of finding two electrons with antiparallel spins at the same point can be different from zero. This can be viewed as if each electron is surrounded by a "hole" — the "Fermi hole" — which cannot be penetrated by electrons with spins parallel to its own. In these

---

* Dedicated to Prof. P. GOMBÁS on his 60th birthday. One of the authors (R. P.) would like to express his gratitude for the stimulus and advice that he received at the beginning of his research work from Professor P. GOMBÁS.

** Part of a thesis (A. L.) submitted to the Senate of the Israel Institute of Technology in partial fulfilment of the requirements for the M. Sc. degree.

circumstances, it may be expected that the electron repulsion energy will be lowest in the term with the highest multiplicity as the latter has the greatest number of electrons with parallel spins.

If we now assume that the one-electron energy is equal, or only slightly different, for the different terms arising from the same electronic configuration, then the energy differences between terms are mainly due to differences in the electron repulsion energy. As the latter is expected to be lowest in the term with highest multiplicity, this term must have the lowest total energy.

When this explanation is examined more carefully, it is worthwhile to pay attention to the following point: The existence of the Fermi hole is a direct result of the antisymmetry of the wave function and does not depend on any approximation method used to calculate the wave function. However the assumption that the one electron energyis equal forthe different terms, arising from the same electronic configuration, is based on the accepted approximation method used in atomic spectroscopy, that is, the attribution of a single configuration to each atomic energy level and the use of the same atomic orbitals for the construction of the wave function of each term. (The way by which the "best" orbitals are found is unimportant to this discussion). This method of approximation has the advantages of being simpler than the usual HF method and it can easily be extended for the perturbation calculation of the magnetic interactions (LS-coupling). SINANOĞLU [6] used this approximation as a convenient starting point for his calculations of the correlation energy.

Nevertheless, we have no reason to assume a priori that a similar result for the one-electron energy of the terms will be obtained when a more exact calculation of the wave function is made, that is, when the variational calculation is performed separately for each term, within the framework of the single configuration approximation, or when the more exact method of superposition of configurations is used to calculate the wave function. Moreover, it is known that a separate variational calculation for each term may give appreciably different orbitals for different terms [7]. The influence of superposition of configurations can have even more drastic effects on the energy differences between terms [8], especially in the case of Z-degeneracy.

The object of this study was to examine the various contributions to the energy differences between terms, when a variational calculation is carried out separately for each term, and thus to check the validity of the accepted explanation for HUND's rule.

2. Breakdown of the energy for light atoms from SCF calculations

The first step in the investigation consisted in the calculation of the different components of the energy (kinetic energy, nuclear attraction energy and electron interaction energy) for the low lying terms of the atoms from the first

Table I

Energy components for the three lowest terms of the carbon atom as calculated from CLEMENTI's[1] SCF-functions*

Term	Kinetic energy	Nuclear attraction energy	Electronic repulsion energy	Total energy
^3P	37.689	−88.137	12.760	−37.689
^1D	37.632	−87.992	12.728	−37.631
^1S	37.550	−87.769	12.669	−37.550

* Energy values in this and the following tables are given in atomic units.

[1] See [9].

two rows of the periodic table. The calculations were based on self-consistent wave functions obtained by CLEMENTI [9] using the ROOTHAAN — SCF method [10]. These functions were chosen for two reasons: 1. The variational calculation was made separately for each term, thus omitting the usual simplification. 2. The orbitals are of analytic form so they are easy to deal with and still are very close to the Hartree—Fock functions.

The expressions for the energy as a linear combination of radial integrals are tabulated for each term [11]. All the integrals can be calculated exactly by analytic formulas.

Results for the different energy components exhibited the same behaviour in all cases. In the following tables we shall present data for the case of carbon atom as an illustration of the general trend. Table I contains the different components of the energy for the three lowest terms of carbon arising from the electronic configuration $1s^2 2s^2 2p^2$.

The energy sequence of terms is $^3P < {}^1D < {}^1S$ in accordance with experiment and HUND's rule, but the electron repulsion energy is greatest in the ^3P term, in complete contradiction to the accepted explanation for this rule. The factor which determines the energy-sequence of terms turns out to be the different nuclear attraction energy and not the difference in electron repulsion energy.

Closer examination of the results (Tables II, III) shows that the factor responsible for this behaviour is a concentration of the electronic charge of the $2p$ orbital, closer to the nucleus, in the term with highest multiplicity. This causes an appreciable decrease in the nuclear attraction energy, as compared with the other terms, and at the same time, an increase in the repulsion energy of the charge in the $2p$ orbital with the charge in the closed shell, although to a lesser degree. Comparison of the radial charge distribution in the $2p$ orbital for the three terms (Fig. 1) verifies this finding.

The difference in the energies and charge distributions between the closed shell orbitals, $1s$, $2s$, of the three terms are smaller and have smaller influence

Table II

Components of one-electron energy (kinetic energy and nuclear attraction energy) for the three lowest terms of the carbon atom calculated from CLEMENTI'S[1] SCF-functions

Term	Kinetic energy + nuclear attraction energy			
	(1s)	(2s)	(2p)	Total
^3p	−35.869	−7.684	−6.895	−50.448
^1D	−35.870	−7.704	−6.786	−50.360
^1S	−35.871	−7.732	−6.616	−50.219

[1] See [9].

Table III

Components of electronic repulsion energy for the three lowest terms of the carbon atom calculated from CLEMENTI'S[1] SCF-functions

Term	Closed-shell repulsion energy	Inter-shell repulsion energy	Open shell repulsion energy	Total repulsion energy
^3p	7.222	5.048	0.490	12.760
^1D	7.237	4.959	0.532	12.728
^1S	7.260	4.822	0.587	12.669

[1] See [9].

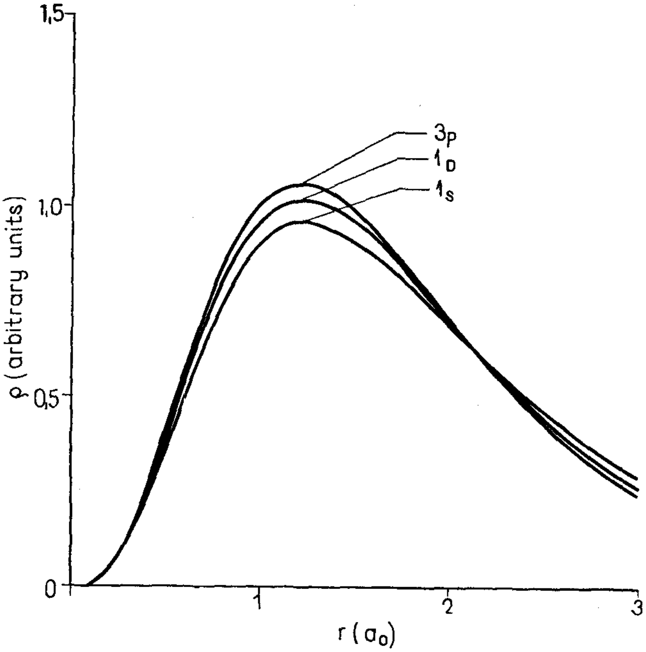

Fig. 1. Mean charge distribution in the $2p$-orbital for the three lowest terms of carbon atom calculated from CLEMENTI'S SCF functions

on the energy differences between the terms. This result could be expected since the inner shell of the atom is known to be influenced only slightly by changes in the outer shell.

Another interesting point which is observed in Table III is that the repulsion energy in the open shell only is in the order $^3P < {}^1D < {}^1S$. That is although there are differences in the $2p$ orbitals of the three terms, it can still be observed that antisymmetrization of the wave function introduces a measure of correlation between electrons with parallel spins. However, this correlation has a slight influence on the energy differences between terms and the main factor is, as was mentioned above, the difference in nuclear attraction energy of the $2p$ orbital.

Exactly analogous results were obtained for the other atoms examined — N($^4S^0$, $^2D^0$, $^2P^0$), O(^3P, ^1D, ^1S) and their counterparts in the second row of the periodic table — Si, P, S.

3. Configuration interaction calculations

In order to ascertain whether the above results are not limited to the single configuration approximation (it is well known that SCF-functions do not yield a good description of two electron observables) the different components of the total energy were calculated for the three lowest terms of carbon, using CI functions.

These functions were calculated by us following a previous calculation made by Boys [12]. The first step consisted in recalculating Boys' results and in the second — other configurations were added to the function in view of improving the energy. Computer programs have been written for the calculation of matrix elements between the atomic configurations involved and for the solution of the secular equation. For the latter we used the partitioning technique of Löwdin [13], which was found to be very convenient for such calculations.

Results for the wave functions and energies are listed in Table IV. Comparison of the energy values obtained in the different approximations is given in Table V. The fourth column presents the best values known in literature for the carbon atom, published recently by Weiss [14]. Another comparison to experiment is obtained by the interval-ratio ^1S—^1D/^1D—^3P for carbon (Table VI).

Superposition of configurations appreciably improves the quantitative agreement of the interval-ratio with experiment, so that it can be expected that these functions will give a better description of the energy-differences between the various terms of the carbon atom. Results for the different components of the energy as calculated from these functions are given in Table VII

Table IV

CI functions and energies for the three lowest terms of the carbon atom (present work)

Configuration	coefficient		
	^3P	^1D	^1S
$(sA^2)(sB^2)pA^2$	1.0	1.0	1.0
$(sAsC)(sB^2)pA^2$	0.00931	0.00925	0.00907
$(sC^2)(sB^2)pA^2$	−0.01511	−0.01510	−0.01505
$(pC^2)(sB^2)pA^2$	0.01604	0.01604	0.01602
$(sA^2)pA^4$	0.12462	−0.12361	−0.24778
$(sA^2)(sBsC)pA^2$	0.00797	0.00905	0.01469
$(sA^2)(sBsD)pA^2$	−0.07872	−0.08039	−0.09033
$(sA^2)(sB^2)pApB$	0.04275	0.07925	0.13294
$(sA^2)(sBdA)^3\,D(pA^2)^3p$	0.09996	0.14982	—
$(sA^2)(sBdA)^3\,D(pA^2)^1D$	0.12085	—	—
$(sA^2)(sBsC)pApB$	0.03357	0.03387	0.03473
$(sA^2)(sBsD)pApB$	−0.05449	−0.05736	−0.06209
$(sA^2)(sB^2)pB^2$	−0.04089	−0.05698	−0.07736
$(sA^2)(sB^2)dA^2$	0.03614	0.04780	0.09714
$(sA^2)(sB^2)pApD'$*	0.13952	0.17279	0.22358
$(sA^2)(sB^2)pApC$	0.03912	0.04454	0.05233
$(sA^2)(dA^2)pA^2$	−0.03496	−0.03482	−0.00544
$(sA^2)(pB^2)pA^2$	0.01861	0.01893	0.00278
$(sAsB)(sC^2)pA^2$	−0.00542	−0.00543	−0.00549
$(sB^2)(sCsD)pA^2$	−0.00375	−0.00376	−0.00380
E(a.u.)	−37.7600	−37.7030	−37.6416

* The orbital pD' is not the one used by BOYS — it is rather a linear combination of BOYS' pD and pC, which is orthogonal to pC.

Table V

Comparison of energies for different calculations for the carbon atom

Term	SCF (CLEMENTI¹)	CI (BOYS²)	CI (present work)	CI (WEISS³)	Exp.²
^3P	−37.689	−37.747	−37.760	−37.779	−37.841
^1D	−37.631	−37.689	−37.703	−37.731	−37.795
^1S	−37.550	−37.633	−37.642	−37.679	−37.742

[1] See [9].
[2] See [12].
[3] See [14].

Table VI

Comparison of the interval ratio $(^1S-^1D)/(^1D-^3P)$ for the different calculations

SLATER[1]	SCF (CLEMENTI[2])	CI (present work)	CI (WEISS[3])	Exp.[4]
1.50	1.43	1.08	1.09	1.13

[1] See [2]
[2] See [9]
[3] See [14]
[4] See [2]

Table VII

Energy components for the three lowest terms of the carbon atom, calculated from the CI functions of Table IV

Term	Kinetic energy	Nuclear attraction energy	Electronic repulsion energy	Total energy
^3P	37.635	—87.958	12.563	—37.760
^1D	37.583	—87.821	12.535	—37.703
^1S	37.553	—87.677	12.483	—37.642

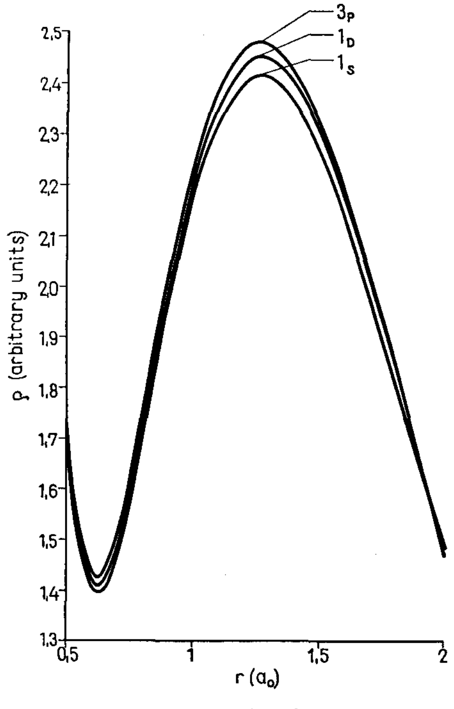

Fig. 2. Mean charge distribution in the L-shell for the three lowest terms of carbon atom as calculated from the CI functions given in Table IV

These results indicate exactly the same behaviour as the one observed using SCF functions: The electron repulsion energy is highest in the term with highest multiplicity and the factor responsible for the order $^3P < ^1D < ^1S$ is the difference in nuclear attraction energy.

Comparison of the mean radial charge distribution of the three terms indicates that the differences in the inner shell (K shell) are very small but there are differences in the outer shell (L shell). The radial charge distribution in the L shell of carbon for the three lowest terms is given in Fig. 2.

The charge in the ^3P-term is concentrated closer to the nucleus than in the other terms, and this seems to be the reason for the decrease in nuclear attraction energy and for the increase in the electron repulsion energy.

4. Summary

Results of the calculations indicate that the accepted explanation for Hund's rule is based on an approximation and it does not remain valid if more elaborate methods are used for the determination of the atomic wave function. It seems that at least for the three lowest terms of the carbon atom the differences in term energies are due to changes in spatial charge distribution, so that the main factor responsible for the order of energies is the difference in nuclear attraction energy, not in the electron repulsion energy.

Although we cannot conclude that this result is characteristic of all atoms (it is probably not the case with positive ions), the above results still emphasize the fact that the differences in one-electron energy between various terms are of the same order of magnitude as the differences in electron repulsion energy and their neglection is, therefore, unjustified.

REFERENCES

1. E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, Cambridge University Press, New York, 1959.
2. J. C. Slater, Quantum Theory of Atomic Structure, Vol. I., McGraw Hill Book Co. Inc., New York, 1960.
3. P. Gombás, Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellenmechanik, Birkhäuser, Basel, 1950.
4. F. Hund, Linienspektren und periodisches System der Elemente, Springer, Berlin, 1927.
5. P.-O. Löwdin, Advances in Chemical Physics, ed. I. Prigogine, Vol. II, Interscience Publishers, New York, 1959.
6. O. Sinanoğlu, Advances in Chemical Physics, ed. I. Prigogine, Vol. VI, Interscience Publishers, New York, 1964.
7. D. R. Hartree and W. Hartree, Proc. Roy. Soc. London, **A 154**, 588, 1936.
8. R. N. Zare, J. Chem. Phys., **45**, 1966, 1966.
9. a. E. Clementi, IBM Journal of Research and Development, **9**, 2, 1965.
   b. E. Clementi, Tables of Atomic Functions, a supplement to (a), table 01.
10. C. C. J. Roothaan and P. Bagus, Methods of Computational Physics, ed. B. Alder, Vol. 2, Academic Press Inc., New York, 1963.

11. J. C. SLATER, Quantum Theory of Atomic Structure, Vol. II, McGraw Hill Book Co. Inc., New York, 1960, appendix 21.
12. S. F. BOYS, Proc. Roy. Soc. London, A **217**, 235, 1953.
13. P.-O. LÖWDIN, Technical note from the Uppsala Quantum Chemistry Group, April 23, 1958.
14. A. W. WEISS, Phys. Rev., **162**, 71, 1967.

ПРИМЕЧАНИЯ ОТНОСИТЕЛЬНО ТЕОРЕТИЧЕСКОГО ТОЛКОВАНИЯ ПРАВИЛА ГУНДА

А. ЛЕМБЕРГЕР и Р. ПАУНЦ

Резюме

Согласно принятому теоретическому толкованию правила Гунда энергия электронного взаимодействия наиболее низка в основном состоянии, что обусловливается высокой мультиплетностью. Распад полной энергии в одно- и двухэлектронный вклады в случае атома углерода, определенный на базе метода самосогласованного поля и конфигурационного взаимодействия, говорит о недействительности данного предположения. Наши результаты показывают, что главное различие в энергиях различных термов, происходящих от одной и той же электронной конфигурации, обусловливается различием в одноэлектронных энергиях.