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A Study of the Interpretation of Hund's Rule*

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Energy differences between atomic terms belonging to the same configuration are analysed into their components, kinetic energy, nuclear attraction and interelectronic repulsion. The results are discussed from the point of view of the interpretation of Hund's rule. The main conclusion is that the energy differences between terms are essentialy determined by nuclear attraction differences, an obvious contradiction to the traditional interpretation of Hund's rule.

Die Energieunterschiede zwischen Atomtermen mit derselben Konfiguration werden mit Hilfe der Zerlegung in kinetische Energie, Kernanziehung und Elektronenabstoßung untersucht. Die Ergebnisse werden im Hinblick auf die Interpretation der Hundschen Regel diskutiert. Das Hauptergebnis ist, daß die Energiedifferenzen zwischen Termen im wesentlichen durch die Differenzen in der Kernanziehung bestimmt sind; dies stellt einen offensichtlichen Widerspruch zur traditionellen Interpretation der Hundschen Regel dar.

Analyse des différences d'énergie entre termes atomiques appartenant à la même configuration selon leurs composantes: énergie cinétique, attraction nucléaire et répulsion interélectronique. Les résultats sont discutés du point de vue de l'interprétation de la règle de Hund. La conclusion principale est que les différences d'énergie entre les termes sont essentiellement déterminées par les différences d'attraction nucléaire, ce qui est en contradiction évidente avec l'interprétation traditionnelle de la règle de Hund.

1. Introduction

The interpretation of Hund's rule concerning the energetic order of terms belonging to an atomic configuration has recently been reinvestigated [1, 2]. It has been realized that the traditional interpretation according to which the energy differences are due to reduced interelectronic repulsion in the states with high multiplicity is inconsistent with sufficiently accurate computations. The order of levels has been shown to depend on differences in the nuclear attractions rather than the interelectronic repulsions. Actually, in all the cases considered the interelectronic repulsion turned out to be higher in the higher multiplicity states. The origin of the erroneous interpretation of Hund's rule has been shown to be the use of the same atomic orbitals for the different terms, within the one-configuration approximation.

The present contribution extends the above mentioned studies in a number of directions. The minimal improvement over the equal orbitals approximation sufficient to produce the crucial difference from the point of view of the interpretation of Hund's rule is introduced in Sect. 2. In Sects. 3 and 4 the Slater function and SCF results are extended to the positively charged members of the isoelectronic

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series, thereby gaining more precise understanding of the role of interelectronic repulsion, which the consideration of the neutral atom only tends to underestimate too extremely. Inclusion of correlation correction using the Hellmann-Feynman and virial theorems is carried out in Sect. 5 and the treatment of the interpretation of Hund's rule is concluded in Sect. 6 with a suggestive qualitative discussion which seems to justify our confidence in the generality of our conclusions concerning the roles of the various energetic components in establishing the order of terms within atomic configurations.

2. Scaled Atomic Orbitals

The use of the same atomic orbitals for the different terms of a given configuration results in equal one – electron energy values and attributes the whole energetic difference between the terms to the interelectronic repulsion. An obvious drawback of this approach is that the different terms have the same kinetic energy but different values of the total energy, and thus do not satisfy the virial theorem. This can very simply be improved by independently scaling the wavefunction for each one of the terms. The total energy of each term is given, before scaling, by the expression $E=T+L+C$ in which T, L and C are the kinetic energy, nuclear attraction and interelectronic repulsion respectively. The scaling parameter is $\eta=-(L+C)/(2\,T)$ and the scaled expectation values, denoted by primes, are $T'=\eta^2 T$; $L'=\eta L$; $C'=\eta C$. Let A and B be two terms belonging to the same configuration such that $E(A)<E(B)$ in accordance with Hund's rule. Assuming equal atomic orbitals for A and B one obtains the same one – electron expectation values (kinetic energy and nuclear attraction) for the two terms so that $E(A)=T+L+C(A)$ and $E(B)=T+L+C(B)$. Hund's rule being predicted within this simplified scheme $C(A)<C(B)$ so that $\eta(A)>\eta(B)$. Independent scaling of the different wave – functions thus tends to concentrate the electronic charge closer to the nucleus for the lower energy term. This tendency has already been observed for SCF and CI wave-functions [1]. L being negative we further get $L'(A)<L'(B)$, where $L'(A)=L\eta(A)$ and $L'(B)=L\eta(B)$. This already shows that at least part of the energetic difference between the two terms is due to the nuclear attraction contribution. It is encouraging that the nuclear attraction for the lower energy term is greater in magnitude than that for the higher energy term, again in accordance with results of more sophisticated calculations [1, 2]. To evaluate the relative importance of nuclear attraction and interelectronic repulsion in establishing the energy difference between the terms we note that

$$[C'(A)-C'(B)]/[L'(A)-L'(B)]=1-[C(A)+C(B)]/(-L),$$

where $C'(A)=C(A)\,\eta(A)$ and $C'(B)=C(B)\,\eta(B)$. Furthermore, as $E(A)$ and $E(B)$ are negative and T is positive, both $L+C(A)$ and $L+C(B)$ are negative so that $C(A)/(-L)<1$, as well as $C(B)/(-L)$. We therefore obtain $0<[C(A)+C(B)]/(-L)<2$, having also noted that $C(A)$ and $C(B)$ are positive whereas L is negative. Thus $-1<[C'(A)-C'(B)]/[L'(A)-L'(B)]<1$ or $|C'(A)-C'(B)|<|L'(A)-L'(B)|$, showing that the dominant contribution to the energy difference between the terms is that due to nuclear attraction, in obvious contradiction to the situation before scaling, according to which the only contribution is due to interelectronic repulsion. For an isoelectronic series the relative importance of nuclear attraction increases with increased nuclear charge so that $[C(A)+C(B)]/(-L)$ is expected to decrease. This leads immediately to the very interesting observation that $[C'(A)-C'(B)]/[L'(A)-L'(B)]$ increases with the nuclear charge, approaching unity for $Z \rightarrow \infty$. The relative importance of interelectronic repulsion in establishing the difference between the terms is therefore higher for the positive ions, becoming almost equal to that of the nuclear attraction for high enough nuclear charge. This very peculiar high Z behaviour is expected to be confirmed by more accurate calculations.

In order to demonstrate the scaling procedure in connection with the interpretation of Hund's rule let us consider the Slater orbital approximation to the ground configuration of the carbon atom. Optimizing for the ^3P term and using the obtained orbitals for all three terms we obtain the values of the energy components presented in Table 1. Independent scaling of each term gives the values presented in Table 2. It is observed that to the accuracy presented the energy is not changed by scaling, depending on the scaling correction only in second order, but the energy components are changed as expected. The differences between scaled nuclear attraction expectation values are considerably larger than those between corresponding interelectronic repulsions. To check the behaviour along an isoelectronic series we present in the first row of Table 3 the quantity $[C'(^3P)-C'(^1D)]/[L'(^3P)-L'(^1D)]$ for the carbon isoelectronic series, from calculations analogous to the one presented in detail. The results are again in agreement with the general analysis, showing an increase of the relative importance of

Table 1. *Unscaled energy components for carbon in ^3P optimized Slater basis*

	T	L	C	E
^3P	37.622	−88.106	12.861	−37.622
^1D			12.927	−37.556
^1S			13.026	−37.457

Table 2. *Scaled energy components for carbon in ^3P optimized Slater basis*

	η	$T' = -E'$	L'	C'
^3P	1.00000	37.622	−88.106	12.861
^1D	0.99913	37.556	−88.028	12.916
^1S	0.99781	37.457	−87.912	12.998

Table 3. *Relative contribution of interelectronic repulsion and nuclear attraction along the carbon isoelectronic series:* $[C(^3P)-C(^1D)]/[L(^3P)-L(^1D)]$

Z	6	7	8	9	10	20	50	100
Scaled Slater orbitals	0.707	0.737	0.763	0.785	0.804	0.896	0.957	0.978
Optimized Slater orbitals	−0.084	0.120	0.256	0.357	0.426	0.735	0.897	0.950
SCF	−0.216	0.019	0.177	0.289	0.367	0.708		
Exact	−0.37	−0.07	0.06	0.16				

interelectronic repulsion contribution to the energy difference between the two terms, the nuclear attraction difference still remaining dominant. Both contributions have similar effects, lowering the energy of the term predicted to be the lower one by Hund's rule.

3. Optimized Atomic Orbitals

A somewhat better approximation than the described scaling procedure is the independent optimization of the orbitals for each term, still within the Slater orbital approximation. Representative results for carbon are given in Table 4. It is noted that $C(^3P) > C(^1D) > C(^1S)$, in contradiction with the traditional interpretation of Hund's rule but in agreement with the SCF and CI calculations of Lemberger and Pauncz [1]. The contribution responsible for the order of levels is the nuclear attraction. A further comparison is furnished by the exponential parameters of the Slater functions, presented in Table 5. The values show a slight expansion of the 1*s* and 2*s* orbitals in the lower energy terms with respect to the higher, whereas the 2*p* orbital is most contracted in the lowest energy term. These finer details which cannot be obtained by simple scaling are in agreement with the analysis of the carbon SCF wave-function given in Ref. [1].

Table 4. *Energy components for an optimized Slater basis approximation of carbon*

	L	C	$E = -T$
^3P	−88.106	12.861	−37.622
^1D	−87.963	12.849	−37.557
^1S	−87.746	12.824	−37.461

Table 5. *Slater function optimized exponential parameters for carbon*

	1*s*	2*s*	2*p*
^3P	5.6726	1.608	1.568
^1D	5.6730	1.614	1.536
^1S	5.6735	1.623	1.487

The reversed order of interelectronic repulsions disappears in the positive isoelectronic ions. Hund's rule is obeyed all over the series and nuclear attraction is the dominant contribution to the energy difference between the terms. This is manifested in the appropriate row of Table 3.

4. Analysis of SCF Results

The analysis of SCF results for light neutral atoms, presented in Refs. [1], and [2], has been the first indication of the inadequacy of the traditional interpretation of Hund's rule. In the present section we report the extension of this analysis to an isoelectronic series including a number of positive ions. The isoelectronic series considered is that of carbon, the analysis of SCF [3] results for which is presented in Table 6, as well as in the appropriate row of Table 3. It is noted that the dominance of the nuclear attraction contribution in determining the energy difference between terms is preserved along the series. However, the order of interelectronic repulsions changes from the reversed one for the neutral atom, observed in Ref. [1], to the normal one, namely $C(^3P) < C(^1D) < C(^1S)$ for the positive ions. This behaviour is closely similar to that observed for the same isoelectronic series with the cruder Slater function approximation.

Table 6. SCF *energy components for the carbon isoelectronic series*

Z	$C(^3P)$	$C(^1D)$	$C(^1S)$	$L(^3P)$	$L(^1D)$	$L(^1S)$
6	12.760	12.728	12.667	−88.138	−87.990	−87.765
7	16.175	16.178	16.170	−123.951	−123.792	−123.550
8	19.531	19.562	19.594	−165.731	−165.556	−165.286

Table 7. *Exact energy components for the carbon isoelectronic series*

Z	$C(^3P)$	$C(^1D)$	$C(^1S)$	$L(^3P)$	$L(^1D)$	$L(^1S)$
6	12.50	12.44	12.41	−88.20	−88.04	−87.91
7	15.91	15.90	15.85	−124.02	−123.88	−123.67
8	19.24	19.25	19.26	−165.79	−165.62	−165.42
9	22.55	22.58	22.63	−213.55	−213.36	−213.16

5. Inclusion of Correlation Correction

Partial inclusion of correlation correction is possible by performance of a (necessarily restricted) CI calculation. It is, however, possible to obtain reasonably accurate estimates of the exact correlation corrections of the nuclear attraction and interelectronic repulsion by the analysis of the available "experimental" correlation energies for atomic isoelectronic series [4] with the aid of the Hellmann-Feynman and virial theorems. The Hellmann-Feynman theorem with respect to the nuclear charge is obeyed by both the exact and SCF energies, and therefore by their difference, the correlation energy. The same is true of the virial theorem. From the Hellmann-Feynman theorem one obtains for the correlation correction to the nuclear attraction the following expression

$$Lc = Z\partial Ec/\partial Z.$$

Using the virial theorem, the correlation correction of the interelectronic repulsion is given by $Cc = 2Ec - Lc$. A polynomial best fit of the experimental correlation energies for the various relevant isoelectronic series has been differentiated to obtain Lc from which Cc was also computed. Together with the SCF results obtained in the previous section they provide the exact values of the energy components, presented in Table 7 and used for the computation of the last row of Table 3. It is observed that correlation decreases the interelectronic repulsion, as one would expect. Its effect is highest on the ^1S interelectronic repulsion, thus tending to increase the role of nuclear attraction versus interelectronic repulsion with respect to term energy differences.

6. Discussion

The various stages of approximation discussed have in common some essential features, the central being the obvious role of nuclear attraction differences between terms in determining the energy difference between them. It is intuitively suggestive, and verified by a large amount of available data, that the energy difference between terms of any atomic configuration, $\Delta E = E(A) - E(B)$ such that $E(A)$ is the lower energy term, is a decreasing function of the nuclear charge within the appropriate isoelectronic series, i.e., increasing in absolute value. Application of the Hellmann-Feynman theorem therefore suggests that the corresponding difference between nuclear attractions, $\Delta L = Z\partial\Delta E/\partial Z$, is negative, namely operates in the right direction. The interelectronic repulsion difference, given by the virial theorem as $\Delta C = 2\Delta E - \Delta L$, is not necessarily either positive or negative. Consideration based on a perturbative expansion of the energy in terms of $1/Z$ suggests a qualitatively reasonable form of the term energy difference, namely $\Delta E = \alpha(Z - Z_0)$. α is expected to be negative for ΔE to decrease with Z, and $Z_0 > 0$ is probably reasonably close to the minimal charge below which the outer electrons become unbound. Then $\Delta L = \alpha Z$ and $\Delta C = \alpha(Z - 2Z_0)$. ΔL is therefore always negative whereas ΔC is positive for $Z < 2Z_0$ and negative for $Z > 2Z_0$. This qualitative argument agrees with the previously presented results and emphasizes in a very transparent and appealing way the conclusion already reached before concerning the interpretation of Hund's rule. It is further noted that $\Delta C/\Delta L = 1 - 2Z_0/Z$ so that $\Delta C/\Delta L < 1$, approaching unity for $Z \to \infty$, again in excellent qualitative agreement with the results presented.

As a final demonstration of the main points of our discussion we present in Table 8 a Hellmann-Feynman type analysis of the energy difference between extensive CI calculated energies of the ^3D and ^1D isoelectronic series of helium [5]. The essential features revealed leave little to be desired.

Table 8. *Energy component differences for the $^3D - {}^1D$ states of the helium isoelectronic series*

Z	ΔL	ΔC
2	$-1.2 \cdot 10^{-4}$	$0.8 \cdot 10^{-4}$
3	$-5.5 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$
4	$-1.1 \cdot 10^{-3}$	$3.5 \cdot 10^{-4}$
5	$-1.7 \cdot 10^{-3}$	$3.2 \cdot 10^{-4}$
6	$-2.3 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$
7	$-2.8 \cdot 10^{-3}$	$-0.5 \cdot 10^{-4}$
8	$-3.4 \cdot 10^{-3}$	$-3.3 \cdot 10^{-4}$
9	$-3.9 \cdot 10^{-3}$	$-6.2 \cdot 10^{-4}$

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