Hund's Rules, $jj-$coupling and the g^n Electron Configurations

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Abstract

The role of Hund's rules for the determination of the groundstates of superheavy elements is briefly considered.

1. Introduction

More than seventy years ago Felix Hund wrote down his famous rules[1], now known as Hund's rules, for determining the groundstates of electron configurations. His rules have been remarkably successful in the case of equivalent electron configurations $n\ell^N$. Here we restrict our attention to just that type of configuration. In 1966 I published[2] a group classification of the states of the g^n electron configurations. The question "Do Hund's rules apply to g^N configuration?" arises and assumes greater relevance as heavier elements are being created. Maybe in the next century semi-stable elements involving occupation of the $g-$shell will be created and their ground states determined. Will they follow Hund's rules?

Jørgensen[3] has written "Wybourne(1966) has stressed that theoretical calculations for g^2 makes it almost certain that the lowest term is ^3H and not ^3K as expected according to Hund's rules." Kutzelnigg and Morgan[4] have written "That for g^2 configurations Hund's second rule no longer holds strictly appears to have been recognised by Wybourne, who was the first to evaluate the expansion coefficients for g^N configurations". Unfortunately neither statement follows from the quoted article[2] and the observation should be attributed elsewhere[5, 6] and then only tentatively. Our objective here is, in part, to dicuss the relevance, or otherwise, of Hund's rules for superheavy elements.

2. Hund's Rules

Hund's rules, specialised to electron configurations of the type $n\ell^N$, may be formulated as:- The groundstate of the configuration $n\ell^N$ is

1. *the state of maximum spin* S_{max}
2. *with maximal orbital angular momentum* L_{max}
3. *with mminimal total angular momentum* J_{min} *if* $N \leq 2\ell + 1$ or *with maximal total angular momentum* J_{max} *if* $N \geq 2\ell + 2$

Thus for for the electron configuration g^2 the Hund's rule groundstate would be $^3K_6$ rather than $^3H_6$. However, the Hund's rules, given above clearly assume Russell-Saunders $LS-$coupling. Making that assumption and calculating the Coulomb matrix elements one may conclude, with minimal assumptions as to the Coulomb radial integrals[5, 6], that the $LS-$term that is lowest in energy is ^3H rather than ^3K and hence Hund's rules are violated in g^2, the first such case in the periodic table. Such a conclusion is premature.

3. $jj-$coupling

Elements involving $g-$electrons in the ground state configuration could be expected to occur round about atomic number $Z = 122$ and hence to be highly relativistic. The effects of relativity manifest themselves strongly in the actinides where the $5f-$ shell is being occupied. Thus in trivalent Americium Am^{3+} the ground state has less than 50% $|5f^{6\,7}F_0\rangle$ character[7]. Indeed in the actinides many of the states are more realistically described by $jj-$coupling rather than by $LS-$coupling[8].

There are several advantages in calculating in a $jj-$basis as compared to the usual $LS-$basis. Thus in $jj-$coupling spin-orbit interaction in a $nj_1^{N_1}nj_2^{N_2}-$configuration is diagonal in all the quantum numbers with the angular part of the matrix elements for the $N = N_1 + N_2$ configuration with $j_1 = \ell - \frac{1}{2}$ and $j_2 = \ell + \frac{1}{2}$ being just

$$-N_1\frac{\ell+1}{2} + N_2\frac{\ell}{2}$$

The simplicity of the computation of the spin-orbit matrix elements is partially offset by the Coulomb matrix elements being non-diagonal in the j quantum numbers. However, this disadvantage is offset by the fact that whereas in an $LS-$basis the coefficients of fractional parentage for the g^N configuration would fill a very large book those required for the j^N configurations with $j \leq \frac{9}{2}$ are known[9] and occupy just ten pages.

Furthermore, no irreducible representation multiplcities greater than 2 arise compared with a maximum of 26 for g^N configurations[2]. Of course, computing in a $jj-$coupling basis is natural wnere relativistic effects are a major concern.

In the case of $N=2$ the calculations are trivial and the energy matrices for g^2 have been calculated in terms of the Slater Coulomb integrals and the spin-orbit coupling integral$^+$. However, note that a complete relativistic calculation would require use of the small and large components of the Dirac equation. The Coulomb part of the matrices may be checked by diagonalisation and verifying that the eigenvalues accord with those computed in the $LS-$ coupling basis[10].

Inspection of the matrices shows that in the extreme of $jj-$coupling the lowest jj configuration is $(g_{\frac{7}{2}})^2$ with the $J=0,2,4,6$ states being degenerate. This degeneracy is lifted by the Coulomb interaction. Inspection of the diagonal matrix elements indicates that to first order the $J=6$ level should be of lowest energy, as also predicted by Hund's rules. Expansion of the $J=6$ $jj-$coupled state of the $(g_{\frac{7}{2}})^2$ configuration as a linear combination of $LS-$coupled states gives

$$\begin{aligned}|(g_{\frac{7}{2}})^2 J=6\rangle &= -\frac{\sqrt{26}}{39}|^3H_6\rangle + 2\frac{\sqrt{2730}}{117}|^3K_6\rangle + \frac{\sqrt{15}}{9}|^1I_6\rangle \\ &= -0.1307|^3H_6\rangle + 0.8932|^3K_6\rangle + 0.4303|^1I_6\rangle\end{aligned}$$

While the $|^3K_6\rangle$ component is dominant the assertion that Hund's rules are relevant to heavy elements is largely an empty assertion.

4. Back to the Future

A proper understanding of the superheavy elements can be expected to come only from detailed relativistic studies. The simple rules and calculations that were so remarkably successful for light elements must be abandoned as being inappropriate for superheavy elements. The study of superheavy elements will undoubtedly bring many surprises and will require considerable extensions to existing methods.

It is a real pleasure to dedicate this short note to Charlotte Froese Fischer on the occasion of the completion of her seventh decade. There is scarcely an area in atomic physics that her pioneering work has not touched. I look forward to her work during her eighth decade.

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$^+$ The matrices can be found at:- http://www.phys.uni.torun.pl/~bgw/