

Hund's rule

BOYD¹ recently suggested an explanation of Hund's rule in terms of electron correlation. A previous investigation of this approach² gave rise to a richer interpretation of two-electron spectra in terms of an alternating rule, in place of the usual Hund rule first noted by Russell and Meggers³ for the spectrum of scandium. The alternating rule states that, within a given configuration, the energy ordering of singlet and triplet states reverses each time the angular momentum changes by one unit. For the term of greatest angular momentum, the triplet lies lowest. The rule reliably orders singlet-triplet energy levels in ~90% of known cases.

The alternating rule follows from the assumption that the state with the larger average value of the inter-electronic angle, θ_{12} , has less shielding and therefore a lower energy. This is not far from Boyd's approach. One might expect a triplet always to have less shielding, owing to the Fermi hole, but wavefunction antisymmetry can give rise to features in the singlet which resemble the triplet hole². As the charge density $\rho(\theta_{12})$ has been found to obey the alternating rule², the Fermi hole argument is too simplistic.

The alternating rule helps in explaining cases deviating from Hund's first rule, but many exceptions are known. When the second rule fails, a singlet can be the lowest term in a configuration. An example is the 2p3d configuration of carbon, where the ¹D lies below the ³F, contrary to Hund's first rule. The alternating rule, however, is obeyed: the ¹D lies

below the ³D, and the ³F is below the ¹F. For the $npn'd$ configuration, Hund's rules work only in ~50% of the cases² and many of the exceptions may be caused by a failure of Hund's second rule.

Recent studies of electron distributions in two-electron atoms^{4,5} are beginning to yield a new and more comprehensive picture. Some states, for example, the doubly-excited states of helium-like atoms, exhibit very strong angular correlations, much greater than in singly-excited states, to the extent that collective, quasi-molecular quantization, with near-rigid rotations and bending and stretching vibrations, describes the electron distribution. Even the alkaline-earth atoms and alkali negative ions show considerable A—B—A molecular behaviour, although these systems have less rigid structures than He^{**}.

That radial correlation sometimes dominates the energy orderings is difficult to reconcile with shielding concepts². The 2s3s states of helium have similar angular electron distributions, much like that of the 2s², ¹S state, but the radial distributions are all quite different. Both the 2s3s states have strong angular correlation expected for a linear quasi-molecular system, with $\rho(\theta_{12})$ centred around π . The triplet corresponds to one quantum of excitation in the antisymmetric stretching mode for the A—B—A molecule; it has a lower energy than the singlet because the antisymmetric stretching has a lower frequency when A is lighter than B. The 2s2p, ³P helium state, with a strong maximum in $\rho(\theta_{12})$ near π , corresponds to the first-excited rotor state, with no bending excitation. The angular distribution in the 2s2p, ¹P state is very

different, with the maximum at slightly more than $\pi/2$, and with finite probability density at $\theta_{12}=0$. This singlet is one of two partners in a nearly degenerate pair with one quantum in the bending vibration; the other is the lower energy 2p², ³P, having almost the same angular distribution, but no electron density at $\theta_{12}=0$.

In the quasi-molecular picture, the appropriate comparisons, as exemplified above, may be between states of different configurations. When electron correlation and configuration interaction are large, it is inappropriate to classify states in terms of a one-electron configuration, and Hund's rule loses its meaning. Nevertheless, it is interesting to ask under what circumstances a shielding argument can predict the energy orderings. The alternating rule has many exceptions for the $npn'd$, P and D terms, and future considerations of this problem should perhaps focus on physical interactions, such as collective motion kinematics and shielding, rather than on quantum numbers associated with a specific model and representation.

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1. Boyd, R. J. *Nature* **310**, 480-481 (1984).
2. Warner, J. W., Bartell, L. S. & Blinder, S. M. *Int. J. Quantum Chem.* **18**, 921-932 (1980).
3. Russell, N. H. & Meggers, W. F. *Sci. Pap. natn Bur. Stand.* **22**, 364-371 (1927).
4. Rehmus, P. D. & Berry, R. S. *Chem. Phys.* **38**, 247-275 (1979).
5. Ezra, G. & Berry, R. S. *Phys. Rev. A* **28**, 1974-1988 (1983).