jj-Coupling

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The ► vector model provides various ways of calculating the vectorial sum of all the contributing angular momenta l_i (► Spin; Stern–Gerlach experiment; Vector model) and ► spins $s_i = 1/2$ for atoms with more than one ► electron. Either all the l_i are first summed up to one L, and then combined with $S = \sum_i s_i$, or all the l_i and s_i are first summed up separately to j_i with $J = \sum_i j_i$. The noncommutativity of ► operators makes these two procedures in general non-equivalent, yielding different combinatorics, and thus different energy levels and transitions. The first possibility is called ► Russell–Saunders coupling (valid for the lighter, hydrogen-like atoms ► Bohr's atom model). The latter is called jj-coupling, yielding the better approximation for heavier atoms and for the energetically higher terms. jj-coupling assumes a strong interaction between each l_i and the corresponding s_i of each electron. There is thus no definite L and S, but only a well-defined J which also implies that the prohibition of intercombinations with $\Delta S \pm 1$ is no longer in place, and the only ► selection rules applying for jj-coupling are $\Delta J = 0$ or ± 1, and similar for the individual j_i. The ► Landé g-formulae also have to be revised for this case; see [1].

Primary Literature

1. G. Herzberg: *Atomic Spectra and Atomic Structure* (New York: Prentice-Hall 1937, 2nd ed. New York: Dover Publications 1944, 174–5)

Secondary Literature

2. C. Candler: *Atomic Spectra and the Vector Model* (Princeton: Van Nostrand 1937, esp. chaps. 11, 16–18)
3. http://wwwchem.uwimona.edu.jm:1104/courses/RScoupling.html (accessed July 20, 2006)

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