45 Structure and Bonding

Göran Wendin

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Göran Wendin

Institute of Theoretical Physics, Chalmers University of Technology, S-41296 Göteborg, Sweden
and Department of Physics, Brookhaven National Laboratory, Upton, L.I., NY 11973, USA

The purpose of this review is to describe some spectacular effects of many-electron interactions in certain core levels in heavy atoms, as well as to give an overview of closely related phenomena in molecules, solids and adsorbates. The central concept will be what we shall call *giant Coster-Kronig (gCK) fluctuation and decay* of a hole level, involving ineraction of a single hole with configurations with primarily two holes and one excited electron. In systems with an open "valence shell" structure, i.e. with empty levels spacially as compact as the occupied ones, the interaction process can become extremely strong and lead to a breakdown of the one-electron picture. In some cases, there is even a complete breakdown of the quasi-particle picture, in which case the spectral strength has no prominent discret features and rather shows a continuum-like distribution.

The breakdown of the one-electron picture can be associated with symmetry breaking and localization, in a wide sense, of the hole. Due to the gCK fluctuation process (configuration interaction), a hole has to be described in terms of a wave-packet of one-electron symmetry states. As a consequence, in a number of cases, an atomic hole cannot be confined to a proper subshell but will move in a polarized subshell. In molecules, a hole will often not be confined to a molecular symmetry orbital but will be localized to varying degrees. Finally, in a metal, a hole in a narrow band often cannot be described in terms of extended states, in which case the non-validity of a ground state band picture may show up as band narrowing or shifted band structure. Particularly spectacular effects of localization occur in the case of two holes in a narrow band.

Examples of atomic levels showing very strong many-electron effects are $4\underline{s}$, 4 p-like holes in Cd to Gd and $5\underline{s}$, 5 p-like holes in Bi to Pu, where the gCK process takes the form $ns \leftrightarrows np^5nd^9nf,\varepsilon f$ and $np^5 \leftrightarrows nd^8nf,cf,\bar{w}$ith n=4 and 5, resp. These spectra represent a partial or complete breakdown of the quasi-particle picture. In molecules one has found a large number of cases of partial or complete breakdown of the quasi-particle picture in the inner valence region of e.g. N_2, N_2O_4, C_2H_2, CS_2, to mention only a few examples. This type of behaviour seems to be the rule rather than the exception due to the high density of two-hole-one-electron levels in the inner valence region. Finally, in metallic Ni a hole in the 3 d-valence band has been found to show pronounced effects of localization, giving rise to a narrowing of the 3 d-band in comparison with the calculated ground-state band structure.

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