Convexity in Density Functional Theory

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One of the most fundamental questions in molecular quantum chemistry is whether the vertical ionization potential of a molecule is always greater than its vertical electron affinity, that is, whether the energy is a convex function of the number of electrons. If so, the fundamental gap and chemical hardness of molecules is always positive, the Pariser-Parr estimate for the electron- electron repulsion integral is positive (ergo reasonable), and all *N*-electron ground states are accessible in density functional theory. If there are systems where $I - A < 0$, however, these statements are no longer true. We explore this issue, which was one of the abiding concerns of the later Robert Parr, as well as its extension to spin-polarized systems, concluding that convexity of the energy is a much more subtle issue than has been heretofore appreciated.