Higher-order derivatives in density-functional theory, especially the hardness derivative ??/?N

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Several third derivatives of the ground-state electronic energy E with respect to the electron number N and/or the external potential ?, as defined in density-functional theory, are studied. These include the first derivatives of the hardness ?. Legendre transforms of ?[N,?] are constructed and corresponding Maxwell relations derived. Various new functions and relations are found. The derivative of the hardness with respect to the electron number at constant potential ? is studied numerically for atoms and positive ions, and suggested values are displayed and discussed. Recommended values of ? are positive for most spherical atoms, negative otherwise. Power series expansions of E(N) are not recommended for reasons given. Simple analytical representations are recommended instead.