Why the traditional concept of local hardness does not work

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Finding a proper local measure of chemical hardness has been a long-standing aim of density functional theory. The traditional approach to defining a local hardness index, by the derivative of the chemical potential with respect to the electron density subject to the constraint of a fixed external potential, has raised several questions, and its chemical applicability has proved to be limited. Here, we point out that the only actual possibility to obtain a local hardness measure in the traditional approach emerges if the external potential constraint is dropped; consequently, utilizing the ambiguity of a restricted chemical potential derivative is not an option to gain alternative definitions of local hardness. At the same time, however, the arising local hardness concept turns out to be fatally undermined by its inherent connection with the asymptotic value of the second derivative of the universal density functional. The only other local hardness concept one may deduce from the traditional definition is the one that gives a constant value, the global hardness itself, throughout an electron system in its ground state. Consequently, the traditional approach is in principle incapable of delivering a local hardness indicator. The parallel case of defining a local version of the chemical potential itself is also outlined, arriving at a similar conclusion. Namely, the only local chemical potential concept that can be gained from a definition dE[n]/dn(r)|v is the one that gives a constant, mu itself, for electron systems in their ground state.

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