Orbital-Dependent Energy Expressions for Kohn–Sham Potentials

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Suppose we are given an exchange-correlation Kohn–Sham potential $v_{\rm xc}([\rho];\mathbf{r})$ whose parent functional is unknown. One can obtain the energy corresponding to this potential by integrating $v_{\rm xc}([\rho_t];\mathbf{r})$ along a path of suitably parametrized densities $\rho_t(\mathbf{r})$. If the parent functional exists, then every path yields the same result; otherwise, the energy is path-dependent. For potentials that are not functional derivatives (i.e., for most *model* Kohn–Sham potentials), the path of uniformly scaled densities, $\rho_t(\mathbf{r}) = t^3\rho(t\mathbf{r})$, usually gives the most sensible results. We explore a distinctly different path in which intermediate densities are constructed by filling Kohn–Sham orbitals with fractions of an electron in accordance with the *Aufbau* principle,

$$\rho_t^J(\mathbf{r}) = \sum_{i=1}^{J-1} |\phi_i(\mathbf{r})|^2 + t|\phi_J(\mathbf{r})|^2, \qquad \begin{array}{l} J = 1, 2, \ldots, N \\ 0 \leqslant t \leqslant 1 \end{array}$$

Here N is the total number of electrons in the system and $\phi_i(\mathbf{r})$ is the spatial part of the ith spin-orbital. Two versions of this method are examined: (i) one in which the orbitals are found once by solving the N-electron Kohn–Sham equations with $v_{\rm xc}([\rho];\mathbf{r})$ and then kept frozen along the entire path; (ii) using relaxed and fully self-consistent Kohn–Sham orbitals at each point of the path. The frozen-orbital *Aufbau* path leads to the following orbital-dependent energy expression

$$E_{\rm xc}[\rho] = \int d\mathbf{r} \sum_{J=1}^{N} \int_0^1 v_{\rm xc}([\rho_t^J];\mathbf{r})\, |\phi_J(\mathbf{r})|^2\, dt.$$

The relaxed-orbital path is shown to give the same result as the Janak theorem,

$$E[\rho] = \sum_{J=1}^{N} \int_0^1 \epsilon_{\rm HOMO}(J-t)\, dt,$$

where E is the total energy and $\epsilon_{\rm HOMO}(J-t)$ is the highest occupied Kohn–Sham orbital of the $(J-t)$-electron system. Possible applications of *Aufbau* paths are discussed and numerical results for several model potentials are presented.