Ground-State Energy as a Simple Sum of Orbital Energies in Kohn-Sham Theory: A Shift in Perspective through a Shift in Potential.

M. Levy and F. Zahariev, Phys. Rev. Lett. 113, 113002 (2014).

$$E_{gs} = \min_{\rho} \left\{ \int v(\boldsymbol{r}) \rho(\boldsymbol{r}) \, d\boldsymbol{r} + T_s[\rho] + E_{Hxc}[\rho] \right\}$$

$$E_{gs} = \int v(\boldsymbol{r}) \rho_{gs}(\boldsymbol{r}) \, d\boldsymbol{r} + T_s\left[\rho_{gs}\right] + E_{Hxc}\left[\rho_{gs}\right]$$

$E_{Hxc}[\rho]$ is a sum of Hartree energy and exchange-correlation energy

Kohn-Sham Theory

where $\rho_{gs}(\mathbf{r})$ and $T_s[\rho_{gs}]$ are obtained from the KS Equations,

$$\left[-\frac{1}{2}\nabla^2 + v(\boldsymbol{r}) + v_{Hxc}\left([\rho_{GS}];\boldsymbol{r}\right)\right]\varphi_i(\boldsymbol{r}) = \varepsilon_i\varphi_i(\boldsymbol{r})$$

$$\left(i = 1,2,\ldots,N\right)$$

where $$v_{Hxc}\left([\rho_{GS}];\boldsymbol{r}\right) = \left(\frac{\delta E_{Hxc}[\rho]}{\delta\rho(\boldsymbol{r})}\right)\Big|_{\rho=\rho_{GS}}$$

Direct Energy KS Theory

To obtain the alternative "Direct Energy KS Equations", form

$$\bar{v}_{Hxc}\left([\rho];\mathbf{r}\right)=v_{Hxc}\left([\rho];\mathbf{r}\right)+c\left([\rho]\right)$$

so that

$$E_{Hxc}[\rho]=\int\bar{v}_{Hxc}\left([\rho];\mathbf{r}\right)\rho(\mathbf{r})\,d\mathbf{r}$$

$$E_{Hxc}\left[\rho\right]=\int\bar{v}_{Hxc}\left(\left[\rho\right];\mathbf{r}\right)\rho\left(\mathbf{r}\right)d\mathbf{r}$$

which means

$$E_{Hxc}\left[\rho_{gs}\right]=\sum_{i=1}^{N}\left\langle\varphi_i\middle|\bar{v}_{Hxc}\left(\left[\rho\right]\right)\middle|\varphi_i\right\rangle$$

Direct Energy Kohn-Sham Equations

Now ρ_{gs} and E_{gs} are obtained directly from the following "Direct Energy KS Equations",

$$\left[-\frac{1}{2}\nabla^2 + v(\boldsymbol{r}) + \bar{v}_{Hxc}\left(\left[\rho_{GS}\right];\boldsymbol{r}\right)\right]\varphi_i(\boldsymbol{r}) = \bar{\varepsilon}_i\varphi_i(\boldsymbol{r})$$

$$\left(\boldsymbol{i} = 1,2,\ldots,N\right)$$

where <u>now</u>

$$E_{GS} = \sum_{i=1}^{N}\bar{\varepsilon}_i$$

Key Properties of $\bar{v}_{Hxc}([\rho];\boldsymbol{r})$ in "Direct Energy KS Theory"

$$\int \left(\frac{\partial \bar{v}_{Hxc}\left(\left[\rho(\boldsymbol{r}) + \varepsilon \Delta\rho(\boldsymbol{r})\right];\boldsymbol{r}\right)}{\partial \varepsilon} \right)_{\varepsilon=1} \rho(\boldsymbol{r})\, d\boldsymbol{r} = 0$$

for an *arbitrary isoelectronic* $\Delta\rho(\boldsymbol{r})$

As a result, it can be shown that it follows that

$$\int \left(\frac{\partial \overline{v}_{Hxc}\left(\left[\rho + \varepsilon \Delta\rho\right]; \boldsymbol{r}\right)}{\partial \varepsilon} \right)^2_{\varepsilon=0} \rho\left(\boldsymbol{r}\right) d\boldsymbol{r}$$

$$\leq \int \left(\frac{\partial v_{Hxc}\left(\left[\rho + \varepsilon \Delta\rho\right]; \boldsymbol{r}\right)}{\partial \varepsilon} \right)^2_{\varepsilon=0} \rho\left(\boldsymbol{r}\right) d\boldsymbol{r}$$

In other words, as ρ changes, the Direct Energy KS Potential $\overline{v}_{Hxc}$ changes less than the original KS Potential v_{Hxc} changes.

$v_{Hxc}\left([\rho];\boldsymbol{r}\right)$ has a Discontinuity with the onset of Fractional Particle Number

$$\lim_{\varepsilon \to +0} v_{Hxc}\left(\left[\rho_{N+\varepsilon}\right];\boldsymbol{r}\right) = v_{Hxc}\left(\left[\rho_{N}\right];\boldsymbol{r}\right) + b$$

(for all finite $\boldsymbol{r}$)

$\overline{v}_{Hxc}([\rho];\boldsymbol{r})$ has No Discontinuity with the onset of Fractional Particle Number

$$\overline{v}_{Hxc}([\rho];\boldsymbol{r}) = v_{Hxc}([\rho];\boldsymbol{r}) + \frac{E_{Hxc}[\rho] - \int v_{Hxc}([\rho];\boldsymbol{r})\rho(\boldsymbol{r})\,d\boldsymbol{r}}{\int \rho(\boldsymbol{r})\,d\boldsymbol{r}}$$

$$\lim_{\varepsilon\to+0} \overline{v}_{Hxc}([\rho_{N+\varepsilon}];\boldsymbol{r}) = \overline{v}_{Hxc}([\rho_N];\boldsymbol{r})$$

(for all finite $\boldsymbol{r}$)

Approximating $\bar{v}_{Hxc}([\rho];\boldsymbol{r})$

$$\bar{v}_{Hxc}([\rho];\boldsymbol{r}) \approx c_1 \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' + c_2 \rho^{\frac{1}{3}}(\boldsymbol{r}) + c_3 f\left(\frac{|\nabla \rho(\boldsymbol{r})|^m}{\rho(\boldsymbol{r})^n} \right)$$

Approximating $\bar{v}_{Hxc}\left(\left[\rho\right];\mathbf{r}\right)$

S. Vuckovic, L. O. Wagner, A. Mirtschink, and P. Gori-Giorgi, J. Chem. Theory Comput. 11, 3153 (2015) have determined the exact $C\left[\rho\right]$ for H_2, in the strictly correlated regime, by the dual Kantorovich formulation

V. U. Nazarov and G. Vignale, J. Phys. Chem. **143**, 064111 (2015) have put forth an exchange potential that naturally incorporates an approximation for $C\left[\rho\right]$

Approximating $\bar{v}_{Hxc}([\rho];\boldsymbol{r})$

An important practical test for the approximation of $\bar{v}_{Hxc}([\rho];\boldsymbol{r})$ is the requirement that the value of $\sum_{i=1}^{N}\bar{\varepsilon}_i$ from an output density must not be higher than the value from the corresponding input density at each direct-energy KS iteration towards self-consistency. This constraint, which embodies several exact properties of $\bar{v}_{Hxc}([\rho];\boldsymbol{r})$, is dictated by the recent result in

L. O. Wagner, E. M. Stoudenmire, K. Burke, and S. R. White, Phys. Rev. Lett. 111, 093003 (2013); 112, 019901(E) (2014).

Ne	ε_{1s}	ε_{2s}	ε_{2p_m} $(m = x, y, z)$
Exact	-30.82	-1.654	-0.797
SVWN	-30.30 (+0.52/1.69)	-1.323 (+0.331/20.01)	-0.498 (+0.299/37.52)
BLYP	-30.52 (+0.30/0.97)	-1.329 (+0.325/19.65)	-0.491 (+0.306/38.39)
PBE	-30.49 (+0.33/1.07)	-1.333 (+0.321/19.41)	-0.490 (+0.307/38.52)
M11-L	-31.26 (-0.44/1.43)	-1.555 (+0.099/5.99)	-0.533 (+0.264/33.12)
revTPSS	-30.69 (+0.13/0.42)	-1.368 (+0.286/17.29)	-0.504 (+0.293/36.76)

Ne	$\overline{\varepsilon}_{1s}$	$\overline{\varepsilon}_{2s}$	$\overline{\varepsilon}_{2p_m}$ $(m = x, y, z)$	$E_{GS} = \sum_{i=1s,2s,2p_x,2p_y,2p_z} \overline{\varepsilon}_i$
Exact	-36.74	-7.573	-6.716	-128.93
SVWN	-36.50 (+0.24/0.65)	-7.522 (+0.051/0.67)	-6.697 (+0.019/0.28)	-128.23 (+0.70/0.54)
BLYP	-36.76 (-0.02/0.05)	-7.561 (+0.012/0.16)	-6.723 (-0.007/0.10)	-128.97 (-0.04/0.03)
PBE	-36.72 (+0.02/0.05)	-7.561 (+0.012/0.16)	-6.718 (-0.002/0.03)	-128.87 (+0.06/0.05)
M11-L	-37.27 (-0.53/1.44)	-7.568 (+0.005/0.07)	-6.546 (+0.170/2.53)	-128.95 (-0.02/0.02)
revTPSS	-36.88 (-0.14/0.38)	-7.558 (+0.015/0.20)	-6.694 (+0.022/0.33)	-129.04 (-0.11/0.08)

Orbital energies

$$\bar{\varepsilon}_{N+j} - \bar{\varepsilon}_i = \varepsilon_{N+j} - \varepsilon_i$$

$$I_N = -\bar{\varepsilon}_N + \bar{v}_{Hxc}\left(\left[\rho_N\right]; \boldsymbol{r} \to \infty\right)$$

$$\bar{v}_{Hxc}\left(\left[\rho_N\right]; \boldsymbol{r} \to \infty\right) = \sum_{i=1}^{N-1}\left[\bar{\varepsilon}_i\left(N-1\right) - \bar{\varepsilon}_i\left(N\right)\right]$$

Spin-dependence

$$\bar{v}_{Hxc,\uparrow}\left(\left[\rho_\uparrow,\rho_\downarrow\right];\boldsymbol{r}\right)=v_{Hxc,\uparrow}\left(\left[\rho_\uparrow,\rho_\downarrow\right];\boldsymbol{r}\right)+\frac{E_{Hxc}\left[\rho_\uparrow,\rho_\downarrow\right]}{\int\left(\rho_\uparrow\left(\boldsymbol{r}\right)+\rho_\downarrow\left(\boldsymbol{r}\right)\right)d\boldsymbol{r}}-\frac{\int v_{Hxc,\uparrow}\left(\left[\rho_\uparrow,\rho_\downarrow\right];\boldsymbol{r}\right)\rho_\uparrow\left(\boldsymbol{r}\right)d\boldsymbol{r}}{\int\rho_\uparrow\left(\boldsymbol{r}\right)d\boldsymbol{r}}$$