Weight dependence of local exchange–correlation functionals in ensemble density-functional theory: double excitations in two-electron systems

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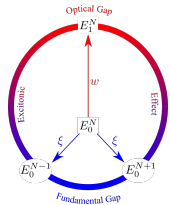
New horizons in density-functional theory — Faraday Discussion



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Ensemble density:

$$n^{\mathbf{w}} = (1 - w_1 - w_2)n^{(0)} + w_1 n^{(1)} + w_2 n^{(2)}$$

Ensemble energy:

$$\boxed{E^{\mathbf{w}} = (1 - w_1 - w_2)E^{(0)} + w_1 E^{(1)} + w_2 E^{(2)}}$$

Excitation energies:

$$\frac{\partial E^{\mathbf{w}}}{\partial w_1} = E^{(1)} - E^{(0)} = \Omega^{(1)} \qquad \frac{\partial E^{\mathbf{w}}}{\partial w_2} = E^{(2)} - E^{(0)} = \Omega^{(2)}$$

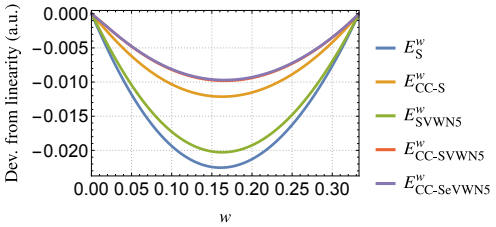
Ensemble energy in practice:

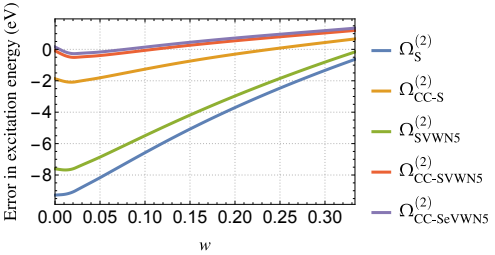
$$E^{\mathbf{w}} = \min_n \left\{ F^{\mathbf{w}}[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\} \qquad F^{\mathbf{w}}[n] = T_{\text{s}}^{\mathbf{w}}[n] + E_{\text{H}}[n] + E_{\text{xc}}^{\mathbf{w}}[n]$$

$$\left\{ -\frac{\nabla^2}{2} + v_{\text{ne}}(\mathbf{r}) + \int \frac{n^{\mathbf{w}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}^{\mathbf{w}}[n^{\mathbf{w}}]}{\delta n(\mathbf{r})} \right\} \phi_p^{\mathbf{w}}(\mathbf{r}) = \varepsilon_p^{\mathbf{w}} \phi_p^{\mathbf{w}}(\mathbf{r}),$$

Ensemble derivative:

$$\boxed{\frac{\partial E^{\mathbf{w}}}{\partial w_I} = \mathcal{E}_I^{\mathbf{w}} - \mathcal{E}_0^{\mathbf{w}} + \left. \frac{\partial E_{\text{xc}}^{\mathbf{w}}[n]}{\partial w_I} \right|_{n = n^{\mathbf{w}}(\mathbf{r})} \qquad E_{\text{xc}}^{\mathbf{w}}[n] = \int \epsilon_{\text{xc}}^{\mathbf{w}}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}}$$





Slater-Dirac LDA exchange functional:

$$\epsilon_x^S(n) = C_x n^{1/3} \qquad C_x = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

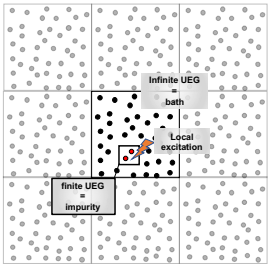
Curvature-corrected (CC) LDA exchange functional:

$$\epsilon_x^{w_2,\text{CC-S}}(n) = C_x^{w_2} n^{1/3} \qquad \frac{C_x^{w_2}}{C_x} = 1 - w_2(1-w_2)\left[\alpha + \beta(w_2 - 1/2) + \gamma(w_2 - 1/2)^2\right]$$

Stein, Kronik & Baer JACS 131 (2009) 2818

Three-state ensemble correlation functional:

$$\tilde{\epsilon}_c^{w_1,w_2}(n) = (1 - w_1 - w_2)\epsilon_c^{(0)}(n) + w_1\epsilon_c^{(1)}(n) + w_2\epsilon_c^{(2)}(n)$$



LDA-centered functionals:

$$\bar{\epsilon}_c^{(I)}(n) = \epsilon_c^{(I)}(n) + \epsilon_c^{\mathrm{LDA}}(n) - \epsilon_c^{(0)}(n)$$

$$\tilde{\epsilon}_c^{w_1,w_2}(n) \to \epsilon_c^{w_1,w_2}(n) = (1 - w_1 - w_2)\bar{\epsilon}_c^{(0)}(n) + w_1\bar{\epsilon}_c^{(1)}(n) + w_2\bar{\epsilon}_c^{(2)}(n)$$

Weight-dependent LDA functional for ensembles "eLDA":

$$\boxed{\epsilon_c^{w_1,w_2}(n) = \epsilon_c^{\mathrm{LDA}}(n) + w_1\left[\epsilon_c^{(1)}(n) - \epsilon_c^{(0)}(n)\right] + w_2\left[\epsilon_c^{(2)}(n) - \epsilon_c^{(0)}(n)\right]}$$

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