Dispersion coefficients based on the local response approximation

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Non empirical determination of the inter-atomic dispersion coefficients are introduced based on the local response approximation due to Dobson and Dinte (DD). [1] In this approximation, the real-space density response function is locally expressed in terms of the total electron density ρ,

$$\chi_{\mathrm{local}}(\mathbf{r},\mathbf{r}',\omega) = \nabla_{\mathbf{r}} \cdot \nabla'_{\mathbf{r}} \left[\frac{\rho(\mathbf{r})\delta^3(\mathbf{r}-\mathbf{r}')}{\omega^2 - \omega_P^2[\rho(\mathbf{r})]} \right], \tag{1}$$

where $\omega_P = \sqrt{4\pi\rho}$ is the local plasma frequency.

Based on the local response and the Zaremba-Kohn expression of the exact second-order dispersion energy, [2] DD derived doubly-local density functional for the dispersion energy between nonoverlapping fragments. [1]

$$E_{\mathrm{disp}} = -\frac{3}{16\pi^{3/2}} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}^6} \frac{\sqrt{\rho(\mathbf{r}_1)}\sqrt{\rho(\mathbf{r}_2)}}{\sqrt{\rho(\mathbf{r}_1)} + \sqrt{\rho(\mathbf{r}_2)}} \tag{2}$$

The same functional was also derived prior to DD by Andersson, Langreth, and Lundqvist (ALL), from the different physical context. [3]

Combining the ALL functional with the long-range corrected (LC) density functional, [4] Kamiya *et al.* [5] and Sato *et al.* [6] have sucessfuly described various inter-molecular interactions. However, the computational cost of the ALL functional is high because of the numerical double integral. The presence of singular $1/r_{12}^6$ term is also problematic.

In the present study, we propose to use the local response (LR) in calculating multipole-expanded dispersion (D) coefficients. The LRD coefficients are then combined with the LC-DFT through the damped atomwise expression.

$$E = E_{\mathrm{LC-DFT}} + \sum_{n\geq 6} \sum_{A>B} C_6^{AB}/R_{AB}^6 \cdot f_{\mathrm{damp}}(R_{AB}) \tag{3}$$

We discuss the new method in terms of its accuracy and efficiency based on several numerical results.

References

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