NON-LOCAL POLARIZABILITY DENSITY AND DFT

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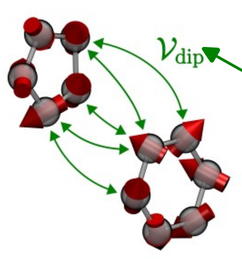
Motivation

Different ideas for handling dispersion in density functionals:

- Expanded methods



Approximate interaction

$$V = V_{\text{mon.}} + V_{\text{dip.}} + V_{\text{quad.}} + \dots$$

Infinite order

Coarse-graining possible

- Non-expanded methods

Exact interaction via non-local response

$$E_{corr} = -\frac{1}{2\pi}\int_0^\infty d\omega \int_0^1 d\lambda \,\mathrm{Tr}[(\chi_\lambda - \chi_0)v]$$

Only pair-wise

Objective: build a non-local many body model that can be coarse-grained

Main transformation

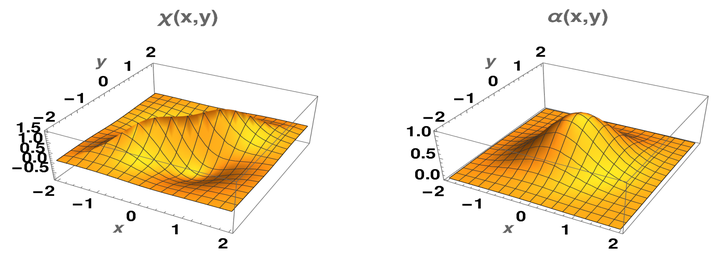
Rewrite the ACFDT formula with polarizability [1]

$$E_c = -\int_0^\infty \frac{du}{2\pi}\int_0^1 d\lambda \iint d\boldsymbol{r}d\boldsymbol{r'}\,[\chi_\lambda(\boldsymbol{r},\boldsymbol{r'},u) - \chi_0(\boldsymbol{r},\boldsymbol{r'},u)]\,v(\boldsymbol{r},\boldsymbol{r'})$$

$$\chi(\boldsymbol{r},\boldsymbol{r'}) = -\nabla_{\boldsymbol{r}}\cdot\nabla_{\boldsymbol{r'}}\cdot\boldsymbol{\alpha}(\boldsymbol{r},\boldsymbol{r'})$$

$$E_c = -\int_0^\infty \frac{du}{2\pi}\int_0^1 d\lambda \int\int d\boldsymbol{r}d\boldsymbol{r'}\,[\boldsymbol{\alpha}_\lambda(\boldsymbol{r},\boldsymbol{r'},u) - \boldsymbol{\alpha_0}(\boldsymbol{r},\boldsymbol{r'},u)]\,\mathbf{T}(\boldsymbol{r},\boldsymbol{r'})$$

Polarizability is localizable [2] $\iint \boldsymbol{\alpha}(\boldsymbol{r},\boldsymbol{r'})d\boldsymbol{r}d\boldsymbol{r'} = \alpha_1 \neq 0$



Conclusions

- Correlation energy can be reformulated in terms of non-local polarizability

$$E_c = -\int_0^\infty \frac{du}{2\pi}\int_0^1 d\lambda \int\int d\boldsymbol{r}d\boldsymbol{r'}\,[\boldsymbol{\alpha}_\lambda(\boldsymbol{r},\boldsymbol{r'},u) - \boldsymbol{\alpha_0}(\boldsymbol{r},\boldsymbol{r'},u)]\,\mathbf{T}(\boldsymbol{r},\boldsymbol{r'})$$

- The theory of non-local polarizability is written using spatial correlation functions

- Polarizability is more prone to localization than susceptibility

Non-local polarizability framework

In the linear response regime, second order perturbation theory is used

$$\chi(\boldsymbol{r},\boldsymbol{r'}) = \sum_{n\neq 0}\frac{\langle 0|\hat{\rho}(\boldsymbol{r})|n\rangle\langle n|\hat{\rho}(\boldsymbol{r'})|0\rangle}{E_n - E_0} \qquad \boldsymbol{\alpha}(\boldsymbol{r},\boldsymbol{r'}) = \sum_{n\neq 0}\frac{\langle 0|\hat{\boldsymbol{P}}(\boldsymbol{r})|n\rangle\langle n|\hat{\boldsymbol{P}}(\boldsymbol{r'})|0\rangle}{E_n - E_0}$$

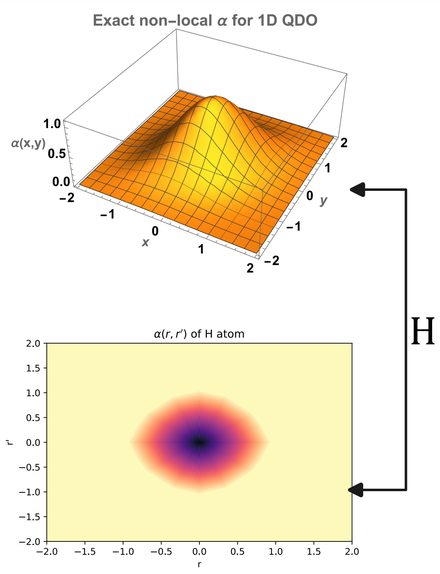
Charge density operator is known, polarization density operator is found [3]

$$\nabla\cdot\boldsymbol{P}(\boldsymbol{r}) = -\rho(\boldsymbol{r}) \qquad \boldsymbol{P}(\boldsymbol{r}) = \sum_{n=1}^{N} q_n \int_0^1 d\lambda(\boldsymbol{q_n} - \boldsymbol{R})\delta^3(\boldsymbol{r} - \boldsymbol{R} - \lambda(\boldsymbol{q_n} - \boldsymbol{R}))$$

Infinite sum could be evaluated for model systems

Contains exact contribution from all multipoles

Response functions for real systems



H atom

Independent particle approximation

$$\chi_0(r,r') = \sum_{i\in occ.,j\in virt.}\frac{\phi_i(r)\phi_j(r')\phi_j(r)\phi_i(r')}{\varepsilon_j - \varepsilon_i}$$

Correlation via Dyson eq. (eg. MBD [4])

$$\chi(r,r') = \chi_0(r,r') + \chi_0(r,r')v(r',r'')\chi(r'',r')$$

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Four-Dimensional Scaling of Dipole Polarizability in Quantum Systems

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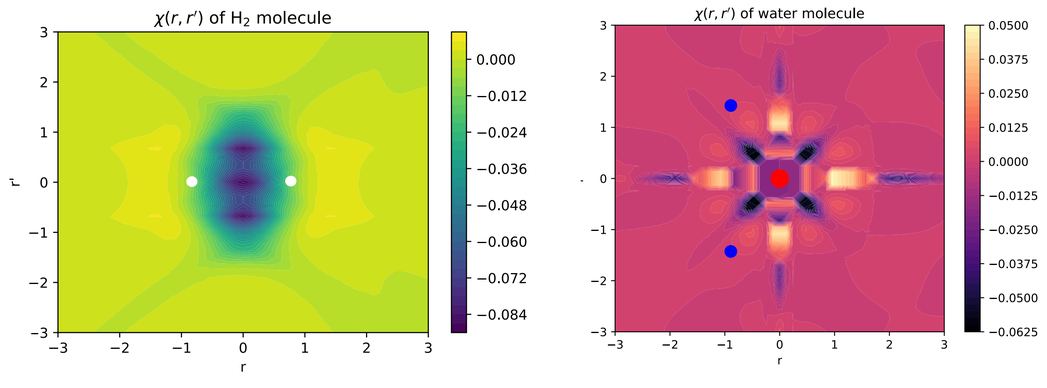
Direct differentiation of electron density $\chi(r,r') = \dfrac{\partial\rho(r)}{\partial v(r')}$



Plots made using an in-house implementation based on PySCF with the help of GF von Rudorff

[1] J. F. Dobson, B. P. Dinte: Constraint Satisfaction in Local and Gradient Susceptibility Approximations: Application to a van der Waals Density Functional, PRL 76, 1780
[2] J. Hermann, R. A. DiStasio Jr., A. Tkatchenko: First-Principles Models for van der Waals Interactions in Molecules and Materials: Concepts, Theory, and Applications, Chem. Rev. 2017, 117, 6, 4714–4758
[3] M. Babiker, R. Loudon: Derivation of the Power-Zienau-Woolley Hamiltonian in Quantum Electrodynamics by Gauge Transformation
[4] A. Ambrosetti, A. M. Reilly, R. A. DiStasio Jr., A. Tkatchenko: Long-range correlation energy calculated from coupled atomic response functions, JCP 140, 18A508 (2014)

Outlook

- ACFDT-based correlation energy expression
- Polarizability models can be built on fragments
- QDO model lends to explicit many-body dispersion

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