

Orbital dependent functionals and OEP

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Introduction to KS-DFT

Summary

- **1. HK:** There is an energy functional of the density
- **2. HK:** There is a variational principle
- **1. KS:** V-representability of $\rho(\mathbf{r})$
- **2. KS:** Decompose energy and approximate unknown
- **Optimize:** Find $v_{S,0}(\mathbf{r}) = \left. \frac{\delta[W_{\text{ext}} + W_{\text{Coul}} + E_{\text{xc}}]}{\delta\rho(\mathbf{r})} \right|_{\rho_0(\mathbf{r})}$

Introduction to OEP

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}$$

LDA

ODF

- $E_x^{\text{LDA}} = C \int \rho(\mathbf{r})^{\frac{4}{3}} d\mathbf{r}$

- $E^{\text{EXX}} = -\frac{1}{2} \sum_{ij} [ij|ji]$

- $\frac{\delta E_x^{\text{LDA}}}{\delta \rho(\mathbf{r})} = V_x^{\text{LDA}} = D\rho(\mathbf{r})^{\frac{1}{3}}$

- $\frac{\delta E^{\text{EXX}}}{\delta \rho(\mathbf{r})} = V^{\text{EXX}}(\mathbf{r}) = ?$

$$[ij|ji] = \int \int \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Introduction to OEP

Chain rule for differentiation

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})} = \sum_i \int \frac{\delta E_{\text{xc}}}{\delta \phi_i(\mathbf{r}_1)} \frac{\delta \phi_i(\mathbf{r}_1)}{\delta \rho(\mathbf{r})} d\mathbf{r}_1 =$$
$$\sum_i \int \frac{\delta E_{\text{xc}}}{\delta \phi_i(\mathbf{r}_1)} \frac{\delta \phi_i(\mathbf{r}_1)}{\delta V_S(\mathbf{r}_2)} \frac{\delta V_S(\mathbf{r}_2)}{\delta \rho(\mathbf{r})} d\mathbf{r}_1 d\mathbf{r}_2$$

The inverse of the response function, $\frac{\delta V_S(\mathbf{r}_2)}{\delta \rho(\mathbf{r})}$, is difficult to calculate

Introduction to OEP

Search all allowed $V_S(\mathbf{r})$

Allowed are local, i.e. multiplicative Potentials

$$V_S(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_0(\mathbf{r}) + \sum_t b_t g_t(\mathbf{r})$$

The potential is divided into

- the external potential
- an arbitrary guess potential
- rest term

The rest term is expanded in a set of functions

How to find the minimum

Chain rule for differentiation

$$0 = \frac{\delta E}{\delta V_S(\mathbf{r})} = \sum_i \int \frac{\delta E}{\delta \phi_i(\mathbf{r}_1)} \frac{\delta \phi_i(\mathbf{r}_1)}{\delta V_S(\mathbf{r})} d\mathbf{r}_1 =$$
$$\sum_i \int \frac{\delta E}{\delta \phi_i(\mathbf{r}_1)} \frac{\delta \phi_i(\mathbf{r}_1)}{\delta V_S(\mathbf{r})} \frac{\partial V_S(\mathbf{r}_2)}{\partial b_t} d\mathbf{r}_1 d\mathbf{r}_2$$

The parameters can be optimized directly

Introduction to OEP

Summary

- Self-consistent calculations for $\frac{\delta E}{\delta \rho(\mathbf{r})} = 0, \{v_S(\mathbf{r}), \rho(\mathbf{r})\}$
- Problem to calculate $\frac{\delta v_S(\mathbf{r}_2)}{\delta \rho(\mathbf{r})}$
- Direct optimization $\frac{\delta E}{\delta v_S(\mathbf{r})} = 0$

Objectives

- Find minimum energy for ODF
- Find $v_S(\mathbf{r})$ for
 - use in TDDFT
 - studying the xc-potential

Results for ODFs

Proposed functionals

- Perturbation theory based functionals

- $E_{xc} = \sum_{ia} \frac{f(i,a)}{\varepsilon_i - \varepsilon_a}$

- Corrected Hartree functional

- $E_{xc} = \sum_{pr} f(p,r)[pr|rp]$

Direct minimization for He

- Obtain (near-)degeneracy for HOMO and LUMO
- Variational collapse of the perturbation theory based functional
- Variational "collapse" of the Corrected Hartree functional

Benchmarking

EXX for two-electron systems

- It is really a density functional

- $T_S = \langle \sqrt{\rho(\mathbf{r})} | -1/2\nabla^2 | \sqrt{\rho(\mathbf{r})} \rangle$

- $W_{\text{ext}} = \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r}$

- $W_{\text{coul}} = \int \rho(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}_1|} \rho(\mathbf{r}_1) d\mathbf{r} d\mathbf{r}_1$

- $E_{\text{xc}} = -\frac{1}{2} \int \rho(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}_1|} \rho(\mathbf{r}_1) d\mathbf{r} d\mathbf{r}_1$

- The potential is exactly known

- $\frac{\delta W_{\text{ext}}}{\delta \rho(\mathbf{r})} = V_{\text{ext}}(\mathbf{r})$

- $\frac{\delta W_{\text{coul}}}{\delta \rho(\mathbf{r})} = \int \frac{1}{|\mathbf{r}-\mathbf{r}_1|} \rho(\mathbf{r}_1) d\mathbf{r}_1$

- $\frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})} = -\frac{1}{2} \int \frac{1}{|\mathbf{r}-\mathbf{r}_1|} \rho(\mathbf{r}_1) d\mathbf{r}_1$

- The correct total energy coincides with HF

Benchmark calculations

$$V_S(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_0(\mathbf{r}) + \sum_t b_t g_t(\mathbf{r})$$

H₂ in uncontracted cc-pv5z (orbitals + potential)

Energies in Hartree for EXX functional

$V_0(\mathbf{r})$	difference in total energy	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$
Zero	10^{-12}	-0.594653	-0.161900	-0.102045
LDA	10^{-12}	-0.594653	-0.153790	-0.090312
Amaldi	10^{-12}	-0.594653	-0.157222	-0.095787
EXX	-	-0.594653	-0.157193	-0.095791

Benchmark calculations

$$V_S(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_0(\mathbf{r}) + \sum_t b_t g_t(\mathbf{r})$$

H₂ in uncontracted cc-pv5z (orbitals + potential)

Energies in Hartree for LDA functional

$V_0(\mathbf{r})$	difference in total energy	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$
Zero	10^{-11}	-0.377341	0.026300	0.076294
Amaldi	10^{-11}	-0.377341	0.031188	0.081848
LDA	-	-0.377341	0.026800	0.076294

Summary

Summary

- Proposed ODFs are bad approximations
- Benchmark calculations obtain correct total energy
- Orbital energy differences between 10^{-3} and 10^{-6} Hartree

Conclusion

- Correct potential couldn't be found
- Different potentials yield same density
- This is true for any density not only HF density
- **REASON:** finite orbital basis