### Bandgaps and speed

#### Spin-Polarized GLLBSC potential and LCAO-TDDFT for large systems

Possibilities with GPAW code

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### Content

- Potential approximations in general
- How GLLB is related to other approximations?
- Spin polarized extension and results
- Future prospects

- Real time TDDFT, implementation and benchmarks
- Absorption spectrum for Au923

### Idea of model potentials • Usually $v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}$

• Instead of defining complex  $E_{xc}$  and even more complex functional derivative of it just approximate the potential directly  $\delta E_{xc}$ 

$$v_{xc}(r) \approx \frac{\delta E_{xc}}{\delta n(r)}$$

### Model potentials

All xc-potentials can be divided to two parts (details omitted)

$$v_{xc}(r) = v_{scr}(r) + v_{resp}(r)$$

- $v_{scr}(r)$  is the Coulomb potential of exchange correlationhole i.e. Slater potential.
- $v_{resp}(r)$  is the response of the xc-hole potential to density variation. Contains the discontinuity.
- The parts can be approximated separately. There exists several potentials with different approximations to these parts.

### Slater potential

• "Weighted average" exchange potential  $V_s(r) = \sum_{ij}^{occ} \frac{\psi_i(r)\psi_j^*(r)}{n(r)} \int dr' \frac{\psi_i^*(r')\psi_j(r')}{|r-r'|}$ 

- In KLI and LHF approximations used as such.
- In GLLB approximated from GGA-energy density.  $E_x = \frac{1}{2} \int dr V_s(r) n(r) \Rightarrow V_s = 2 \frac{\epsilon^{GGA}(n(r))}{n(r)}$

 In Becke-Roussel approximated using exchange hole of Hydrogen atom (meta-GGA potential).

### **Response potential**

• In OEP: Correct.  

$$V_{resp,\sigma}(\mathbf{r}) = \int d\mathbf{r}' \int d\mathbf{r}'' \sum_{\sigma'\sigma''} \frac{n_{\sigma'}(\mathbf{r}')n_{\sigma''}(\mathbf{r}'')\frac{\delta g_{\sigma\sigma'}(\mathbf{r}',\mathbf{r}'')}{\delta n_{\sigma}(\mathbf{r})}}{|\mathbf{r}'-\mathbf{r}''|}$$

• In GLLB Bapproximated as

$$v_{resp}(\mathbf{r}) = \mathcal{W}_{i} w_{i} \frac{|\psi_{i}(\mathbf{r})|^{2}}{n(\mathbf{r})}, \quad w_{i}^{GLLB} = K_{g} \sqrt{\epsilon_{f} - \epsilon_{i}}$$

In Becke-Johnsson

$$v_{resp}(r) = K_{\sqrt{\frac{\tau}{n(r)}}}, \quad \tau = \sum_{i} |\nabla \psi_i|^2$$

### Common model potentials

- What if one would use  $\epsilon_i, au$  both?
- Is screening potential of GLLB sufficient? What about  $V_s(r) + V_{resp}^{GLLB}(r)$  or  $V_{BR}(r) + V_{resp}^{GLLB}(r)$ .

| Potential     | $v_{scr}(r)$            | $v_{resp}(r)$                                | incgredients                             |
|---------------|-------------------------|--|--|
| OEP-EXX       | $V_s(r)$                | exact  | $\epsilon_i, \epsilon_a, \psi_i, \psi_a$ |
| KLI           | $V_s(r)$                | $\sum_{i} w_{i}^{KLI}  \psi_{i} /n$          | $\psi_{i}$                               |
| LHF           | $V_s(r)$                | $\sum_{ij} w_{ij}^{LHF} \psi_i \psi_j^* / n$ | $\psi_{i}$                               |
| GLLB          | $2\epsilon_{B88}(r)$    | $\sum_{i}^{s} w_{i}^{GLLB}  \psi_{i} /n$     | $\epsilon_i,\psi_i$                      |
| GLLB-SC       | $2\epsilon_{PBEsol}(r)$ | $v_{resp}^{GLLB}$                            |  |
| Becke-Roussel | $v_{BR}(r)$             | -  | $ abla^2,	au$                            |
| Becke-Johnson | $v_{BR}(r)$             | $K\sqrt{	au/n}$                              | $ abla^2,	au$                            |
| Tran-Blaha    | $v_{BR}(r)$             | $(Ka - bC)\sqrt{\tau/n}$                     | $ abla^2,	au$                            |

### **Derivative discontinuity**

- On integer occupation numbers, the xc-potential jumps.
- Local and semilocal xc-functionals do not have this property.
- OEP-EXX, KLI, GLLB and GLLB-SC have this property

$$\Delta_{\mathrm{xc}} = \lim_{\delta \to 0} \left. v_{\mathrm{xc}}(r) \right|_{N+\delta} - \lim_{\delta \to 0} \left. v_{\mathrm{xc}}(r) \right|_{N-\delta},$$

This contributes to quasiparticle band gap

$$E_{\rm QP} = I - A = E_{\rm KS} + \Delta_{\rm xc}$$

### **Results for GLLB-SC**



### Comparison

#### PROS

- Avoid OEP equations, when  $E_{xc}$  is orbital dependent  $\rightarrow$  huge speed up.
- Still good properties of orbital dependent functionals
  - Finite  $\Delta_{xc} \rightarrow$  good band gaps
  - 1/r asymptotic behaviour  $\rightarrow$  good  $\{\epsilon_i\}$
- Almost "Accuracy of GW with speed of GGA"
   → can be used to screen promising materials for further study (see et. al.)

#### CONS

- Lose total energy
   → No geometry or energetics
- Depending on  $v_{xc}$  may lose size consistency.
- Relatively rare (at the moment) → PBE is well studied in 10000s of publications, less in known about model potential

# Spin polarized GLLB-SC with Transition Metal Oxides

- LDA/GGA are known to fail with stronly correlated transition metal oxides
- More accurate treatment of exchange (e.g. EXX) seem to improve description
- We use spin-polarized extension to GLLB-SC potential for study.
- Also some ferromagnetics and single half-metal

## Spin Polarized band gaps for transition metal oxides

- In predicting the semiconducting state GLLB-SC performs as badly as LDA: CoO and FeO metallic.
- MnO and NiO improved.
- Self-interaction error? Could improving the screening part of GLLB help.

|     | PBEsol | GLLB | GLLBSC | exp. |
|-----|--------|------|--------|------|
| MnO | 0.65   | 4.02 | 3.52   | 3.9  |
| NiO | 0.66   | 2.95 | 2.89   | 4.0  |
| CoO | 0.00   | 0.00 | 0.00   | 2.5  |
| FeO | 0.10   | 0.09 | 0.00   | 2.4  |

### Magnetic moments

- Improves local magnetic moments for antiferromagnetic metal oxides
- Co2FeSi also is improved. DOS of minority spin is split to two parts as with LDA+U. (however, still metallic, not semi-metallic).
- Overestimates the magnetic moment of ferromagnetic metals

|        | Co2FeSi | Fe   | $\operatorname{Co}$ | Ni   | MnO     | FeO  | CoO     | NiO       |
|--------|---------|------|---------------------|------|---------|------|---------|-----------|
| LDA    | 5.02    | 2.17 | 1.59                | 0.61 |         |      |         |           |
| PBEsol | 5.29    | 2.02 | 1.62                | 0.65 | 4.29    | 3.43 | 2.41    | 1.33      |
| GLLB   | 6.06    | N/A  | N/A                 | 0.78 | 4.71    | 3.81 | 2.76    | 1.65      |
| GLLBSC | 6.17    | 3.08 | 2.01                | 0.83 | 4.61    | 3.82 | 2.77    | 1.67      |
| $\exp$ | 6       | 2.22 | 1.7                 | 0.7  | 4.6-4.8 | 4.2  | 3.4-4.0 | 1.6 - 1.9 |

## Conclusions for spin polarized GLLB-SC

- Doesn't work as well as with spin-paired semiconductors.
- The role of self interaction error should be checked (and more knowledge of connections between Becke-Johnsson and GLLB is required also)
  - Code Slater potential to GPAW/Code GLLB to Octopus/Code Becke-Roussel/Use with SIC etc.
- Nevertheless, band gaps are improved on some systems with still only the effort of GGA.

### Optical Properties of Metal Clusters

- Optical properties important (used as markers)
- Have strong absorption due to plasmon resonance
- Problems: Large number of valence electrons (~10000), ab initio programs are at their limits.
  - → Must use real time propagation.
    → Must use small basis sets.
- This is implemented to gpaw branch Icaotddft. Results are promising, Au931 with 20000 orbitals was easy.

### Time propagation

- Propagation is done with a basis set, hamiltonian and overlap are "small" matrices.
- Stable! Timesteps can be larger than with grid.
- Uses full matrix algebra parallerized with scaLAPACK.
- Crank-Nicholson:  $U(dt) = \frac{O \frac{1}{2}iHdt}{O + \frac{1}{2}iHdt}$

$$\begin{split} \psi(t+dt) &= U(dt,H(t))\psi(t) \twoheadrightarrow H(t+dt) \\ H(t+dt/2) \approx \frac{1}{2}H(t) + \frac{1}{2}H(t+dt) \\ \psi(t+dt) &= U(dt,H(t+dt/2))\psi(t) \end{split}$$

#### Basis set issues

- Good TD-DFT response requires good dynamic polarizability from basis sets.
  - Basis sets are optimized for good static polarizability → partially optimizes dynamic polarizability also.
- Thus, organic molecule excitations are in general between delocalized orbitals of partially occupied s and p-states ("intraband"). Represented well with valence lcao (say dzp).
- Noble atoms have a low lying atomic ("interband") excitations.
   le. Au: 6s → 6p, Ag: 5s → 5p. → Adding atomic excited states to basis set is easy and improves spectrum a lot (more than dzp → tzdp).

### Organic molecule

- 250 atom graphene nano flake, LCAO-RT-TDDFT (dzp) vs. GRID-RT-TDDFT
- 50x speed up, essential properties identical, quantitative differences.
- 250 atoms with dzp is plausible with just single processor!
- In Au55 cluster, the speedup even larger



### Metallic excitations: Need for excited state basis

Photoabsorption spectrum of Au55 cluster



### References

- PBE relaxed 55atom AuAg clusters with PBE TDDFT absorption spectrum.
- Comparison with octopus grid code.
- Fast! One day with a single core.



2

2.5

3

3.5

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4.5

5

### Icosahedral Au92

- dzp-basis + 6p atomic state
- 10152 valence electrons, 19383 basis function
- GRID-RT-TDDFT practically impossible(?)
- 512 cores (32x16, 128 BLACS grid) Scaling not tested, might be inefficient configuration.
- 20fs in 36 wall-hours. Only 18000 cpu-hours.
- O(N^3) scaling from full matrix linear solver dominates.



### Conclusions

- Spin Polarized GLLB-SC needs more investigation. Different approaches should be analyzed properly.
- LCAO-TDDFT enables optical calculations which were not previously available with GPAW. Upper limit is still unknown. Basis set benchmarking important.
- Furthermore: GLLB-SC TDDFT could be interesting. Derivative discontinuity appears as counteracting xc-field, which in is provided by the GLLB response potential.

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### Thanks!