Plasmon, exciton and RPA correlation energy : implementations and applications based on the linear density response function

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Linear response TDDFT

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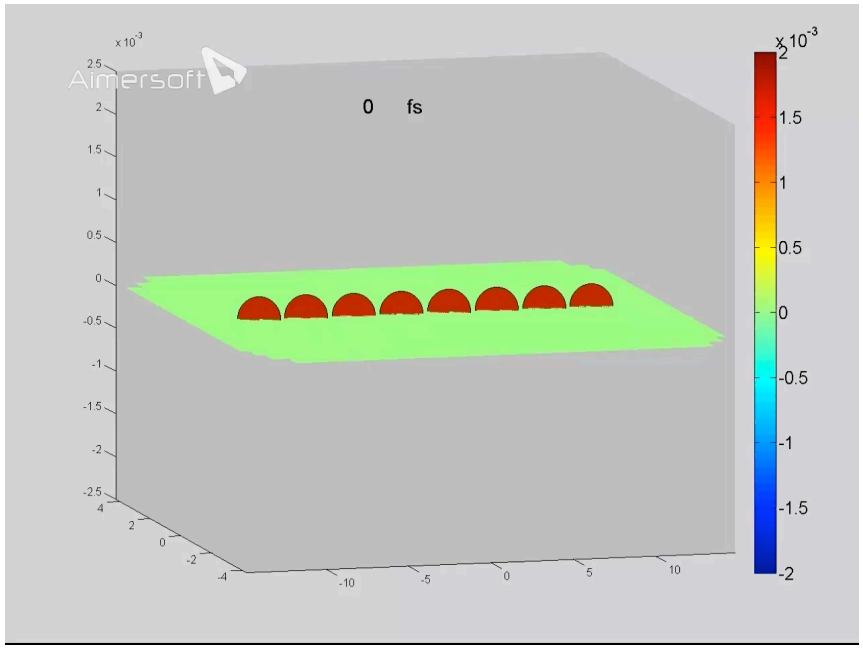

$$\delta n(\mathbf{r},t) = \int d\mathbf{r}'\chi(\mathbf{r},\mathbf{r}',t)V_{ext}(\mathbf{r}',t)$$

V_{ext} : external field

δn : induced density

$$\chi = \chi^0 + \chi^0 K \chi$$

K : Coulomb (+xc) kernel

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \frac{2}{V_{\mathrm{BZ}}}\sum_{k,nm}(f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}})\frac{\langle\psi_{n\mathbf{k}}|\, e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\,|\psi_{m\mathbf{k}+\mathbf{q}}\rangle\,\langle\psi_{m\mathbf{k}+\mathbf{q}}|\, e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}\,|\psi_{n\mathbf{k}}\rangle}{\omega + \epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}} + i\eta}$$

Jun Yan, Jens. J. Mortensen, Karsten W. Jacobsen and Kristian S. Thygesen, Phys. Rev. B 83, 245122 (2011).

Overview

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Implementations	Applications
Density Response Function	**Plasmons** (robust, well documentation and tutorial) • Substrate effect on the plasmon excitations in graphene • Adsorbate effect : H monolayer on Ag(111) surface • Acoustic surface plasmons
Bethe-Salpeter Equation Bootstrap kernel with TDDFT	**Excitons** (documented, no tutorial, slow, problem with W) • Boron nitride sheet on graphene
RPA on GPUs	**EXX+RPA total energy** (robust, doc/tutorial only for CPU version) • Formation energy of metal oxides

Others :

GW (Falco)	Plasmons (Kirstan)
RPA, rALDA (Thomas)	Solar cell (Ivano)
	...

Plasmon : nanoplasmonic applications

Plasmon : quanta of collective electronic excitations

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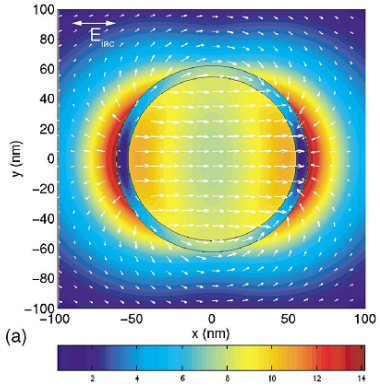
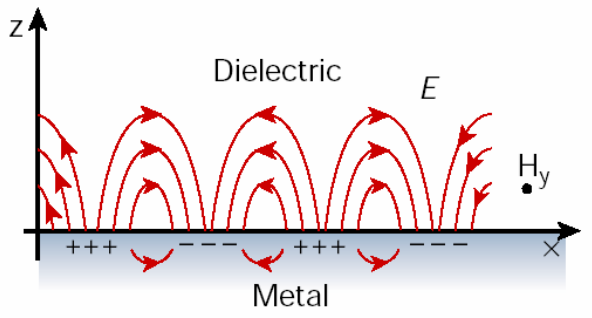
localized plasmon



Propagating plasmon



Localized plasmons depend sensitively on the size, shape and dielectric environment of the nanoparticles, they can localize and enhance electromagnetic wave.

Applications :
- Surface enhanced Raman spectroscopy,
- Chemical and biological sensing,
- Plasmon enhanced photocatalyst

Propagating plasmons can recover evanescent wave at interface, have negative refractive index

Applications:
- Photonic circuit
- Optical imaging

Plasmonic Field : Classical -> Quantum

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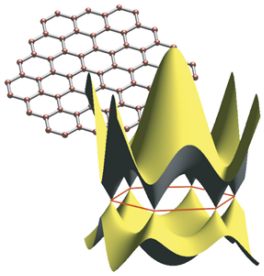
The effect of substrate at the weak interaction limit

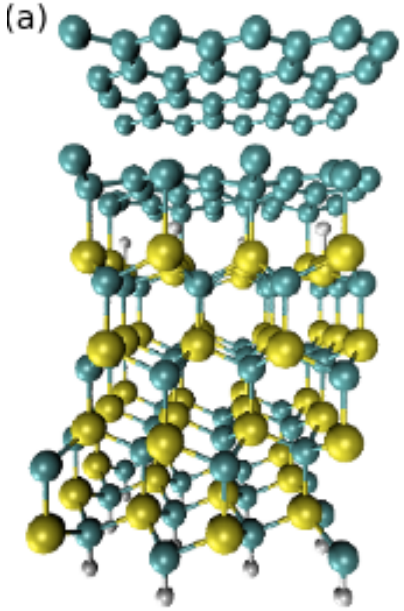


Substrate:

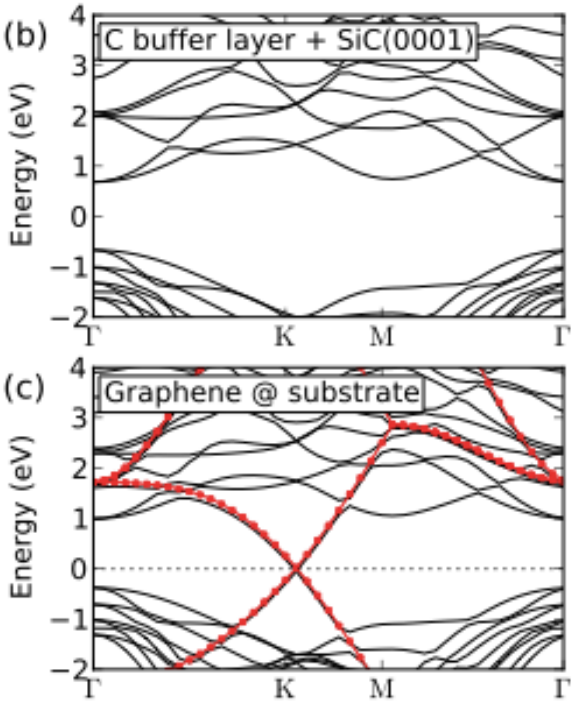
- Change the interface structure / electronic structure
- Introduce doping
- Dielectric screening

Static Vs Dynamical effects

Graphene / SiC(0001)



Bandstructure



Graphene is weakly bounded to the SiC substrate.
Fermi level is shifted upward by 0.05 eV.

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Jun Yan, Kristian S. Thygesen and Karsten W. Jacobsen, Phys. Rev. Lett. 106, 146803 (2011).

Graphene @ semiconducting SiC(0001) substrate

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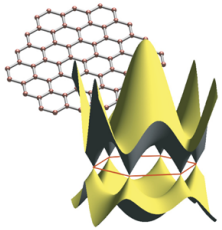
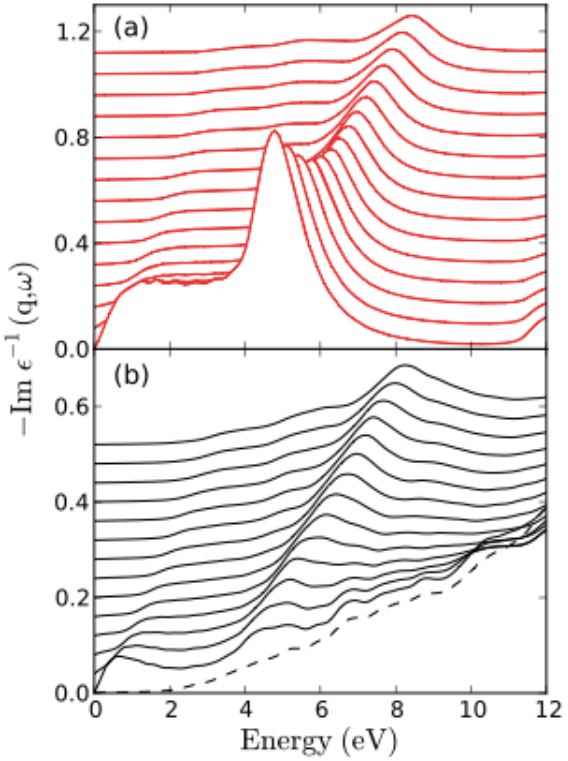


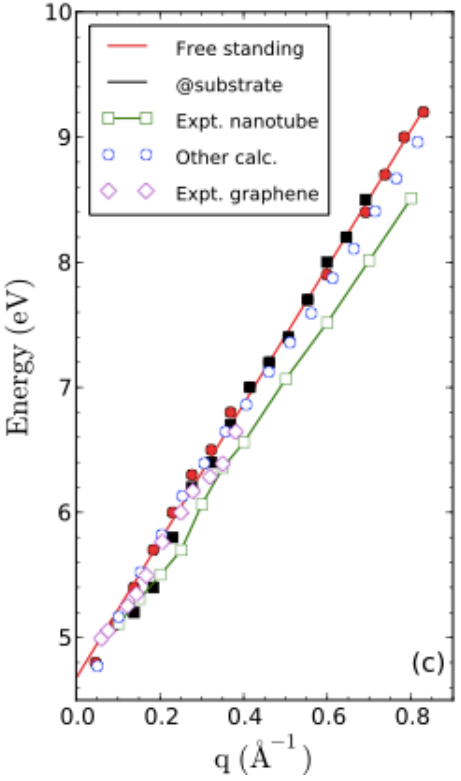
Free standing graphene →

Graphene / SiC →

Loss spectra



Plasmon dispersion



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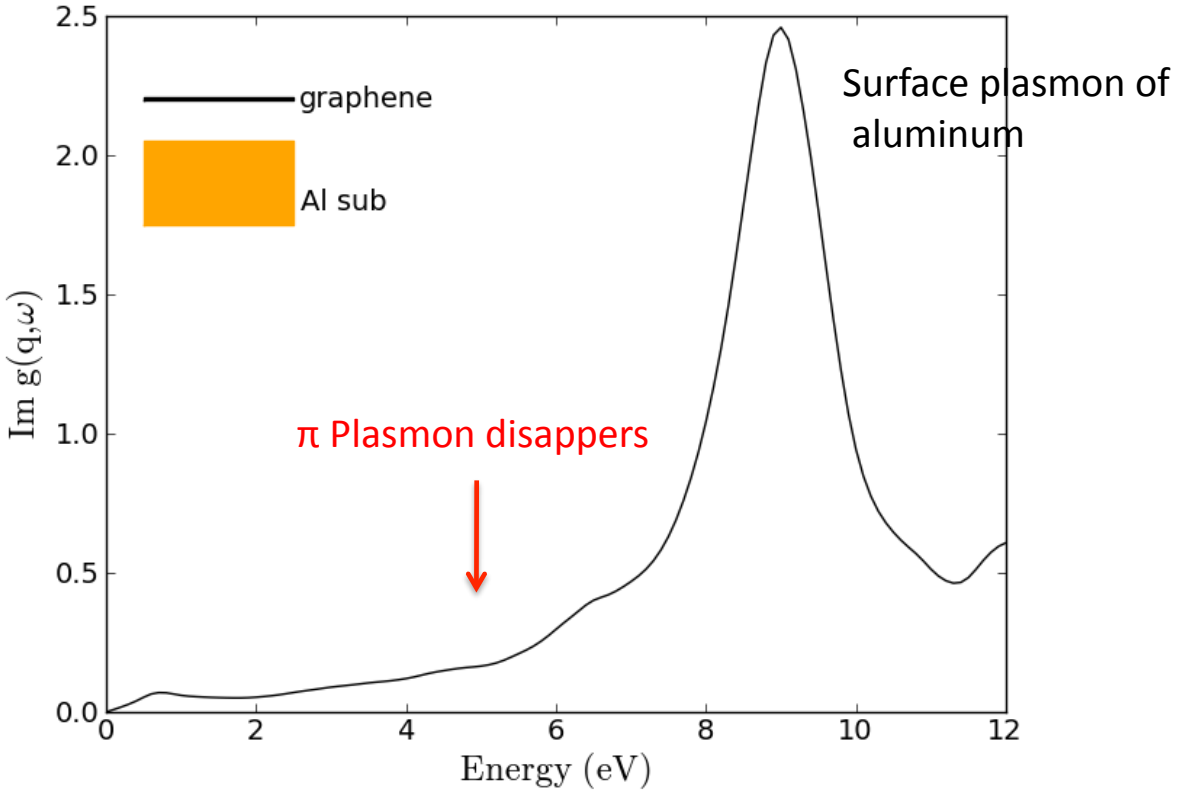
Graphene @ metallic Al(111) substrate



- Plasmon is completely quenched by a metallic aluminum substrate.

Application II : H monolayer @ Ag(111) surface

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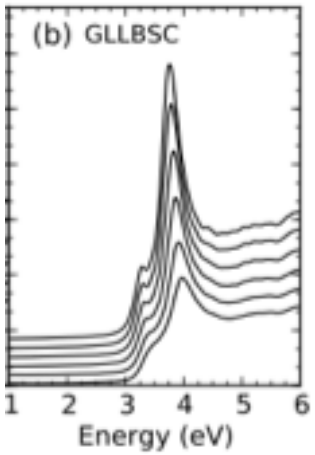
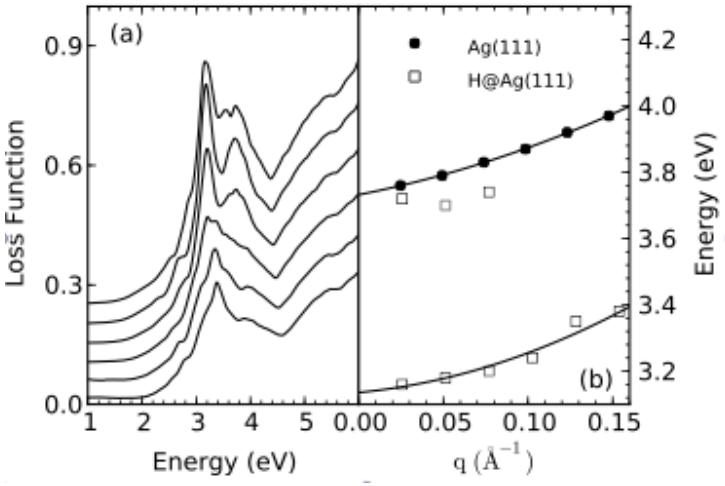
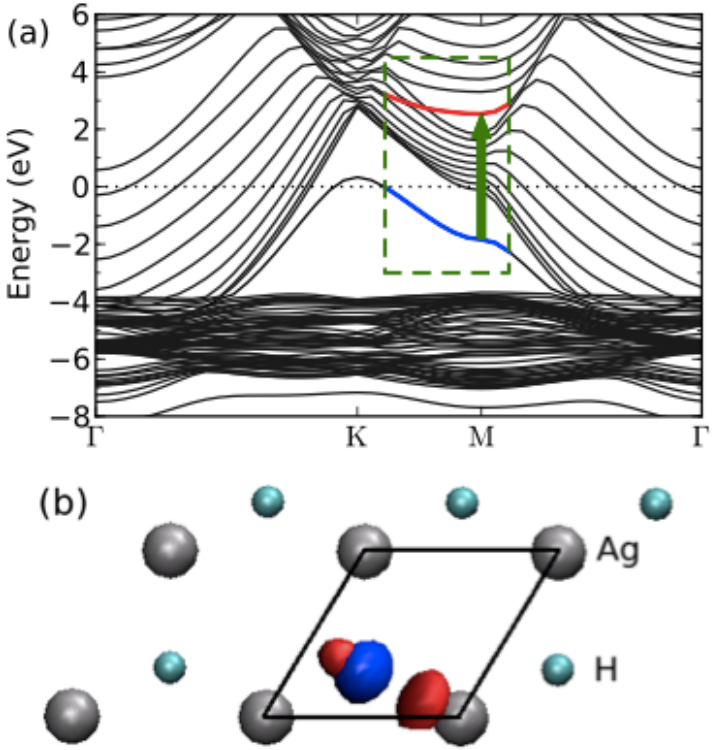
The effect of adsorbate with strong interaction :
a charge-transfer like excitation

clean surface



H/Ag(111)





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Jun Yan, Karsten W. Jacobsen and Kristian S. Thygesen, Phys. Rev. B 84, 235430 (2011).

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Application III: acoustic plasmons at noble metal surfaces

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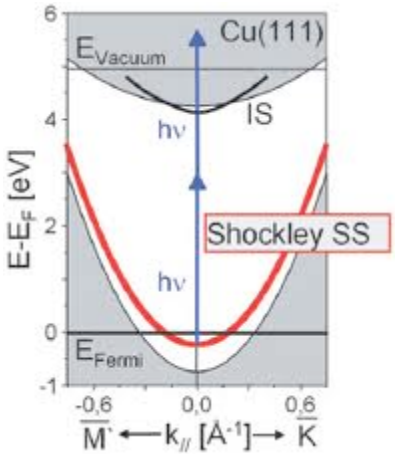
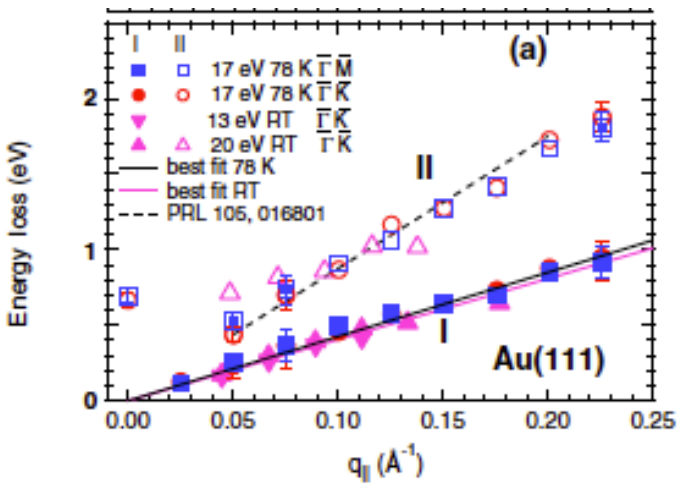
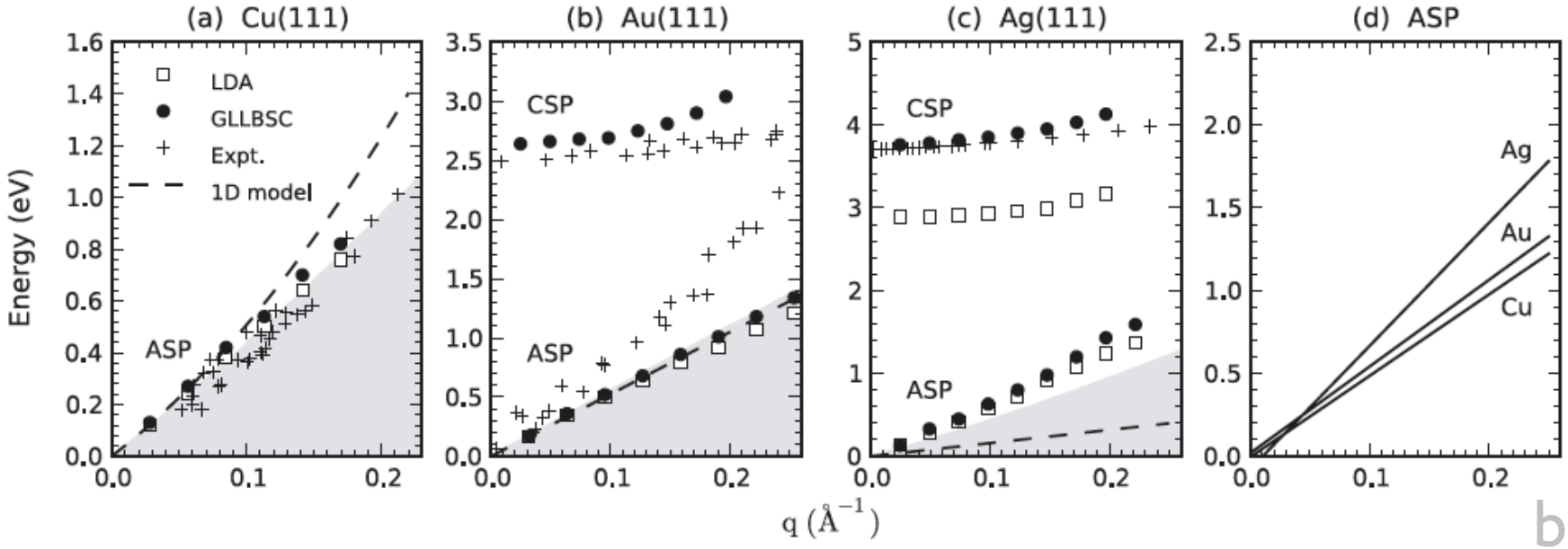


Expt : M. Rocca, Phys. Rev. Lett. 110, 127405 (2013)





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Jun Yan, Karsten W. Jacobsen and Kristian S. Thygesen, Phys. Rev. B 86, 241402(R) (2012).

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Exciton : solar cell applications

Implementing the Bethe-Salpeter Equation

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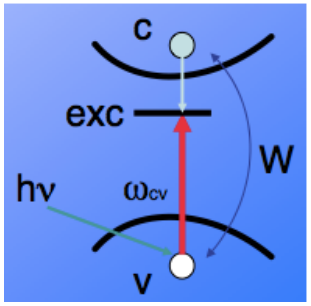
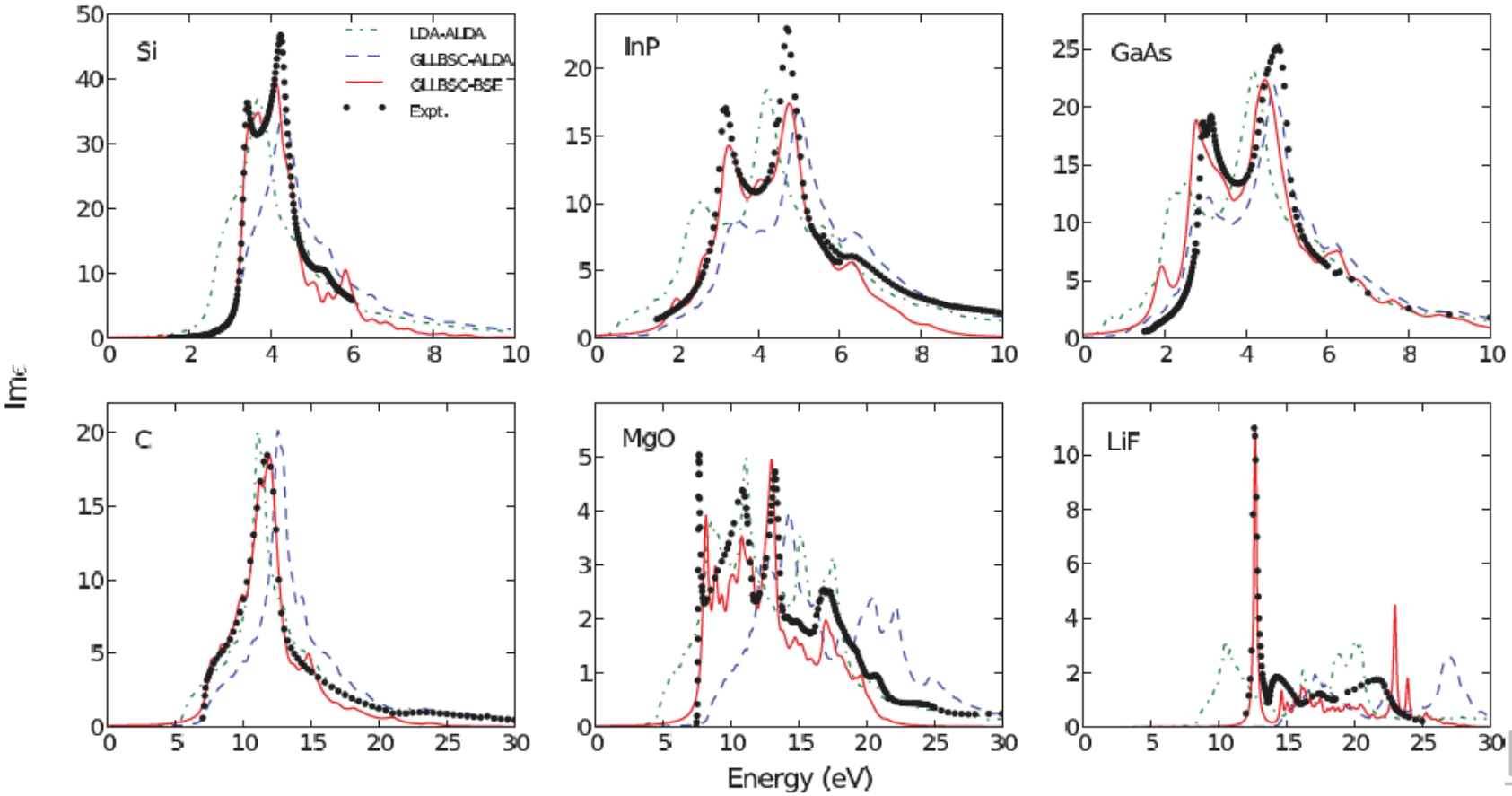
- TDDFT with adiabatic kernel fails to reproduce the excitonic effect



$$(E_{c\vec{k}} - E_{v\vec{k}})A^S_{cv\vec{k}} + \sum_{c'v'\vec{k}'} \left\langle cv\vec{k} \left| K^{eh} \right| c'v'\vec{k}' \right\rangle A^S_{c'v'\vec{k}'} = \Omega^S A^S_{cv\vec{k}}$$



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Jun Yan, Karsten W. Jacobsen and Kristian S. Thygesen, Phys. Rev. B 86, 045208 (2012).

TDDFT with non-adiabatic kernel : bootstrap kernel

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- BSE calculation is too expensive

  The kernel is supposed to have a form of $\frac{\alpha}{q^2}$ where q is a wave vector and alpha is constant. The adiabatic kernel is independent of q.

- An approximate bootstrap kernel with TDDFT

Bootstrap kernel

$$f_{\mathrm{xc}}^{\mathrm{BS}}(\mathbf{q},\omega) = -\frac{\varepsilon^{-1}(\mathbf{q},\omega=0)v(\mathbf{q})}{\varepsilon_0(\mathbf{q},\omega=0)-1}$$

fxc updated self-consistently
It can reproduce bulk tests very well.
The performance for surfaces or 2D systems is unclear.

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S. Sharma, J.K. Dewhurst, A. Sanna, and E.K.U.Gross, Phys. Rev. Lett. 107, 186401 (2011)

RPA correlation energy

EXX + RPA total energy

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RPA correlation energy :

$$E_c^{\mathrm{RPA}} = \int_0^\infty \frac{d\omega}{2\pi} \sum_{\mathbf{q}}^{\mathrm{BZ}} \mathrm{Tr}\left\{\ln[1 - \chi^0_{\mathbf{GG'}}(\mathbf{q}, i\omega)V_{\mathbf{G'}}(\mathbf{q})] + \chi^0_{\mathbf{GG'}}(\mathbf{q}, i\omega)V_{\mathbf{G'}}(\mathbf{q})\right\}$$

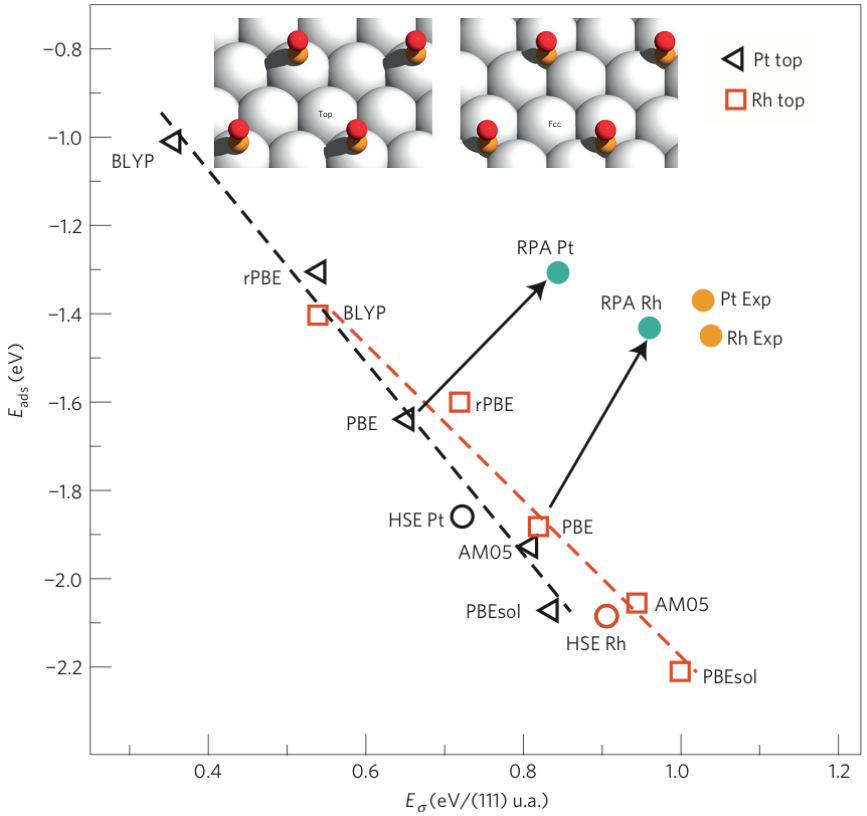
EXX + RPA total energy :

$$E = E^{\mathrm{DFT}} - E_{xc}^{\mathrm{DFT}} + E_x^{\mathrm{EXX}} + E_c^{\mathrm{RPA}}$$

RPA improves:

- Lattice constants
- Surface energies
- Adsorption sites
- Adsorption energies

Despite : PBE structure, none-self-consistency, underbinds for atomization/cohesive/ adsorption energies



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L. Schimka, J. Harl, A. Stroppa, A. Gruneis, M. Marsman, F. Mittendorfer, and G. Kresse, Nature Materials 9, 741 (2010)
X. Ren, P. Rinke and M. Scheffler, Phys. Rev. B 80, 045402 (2009)

Response function - convergence parameters

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$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \frac{2}{V_{\mathrm{BZ}}} \sum_{k,nm} (f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}) \frac{\langle \psi_{n\mathbf{k}} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{m\mathbf{k}+\mathbf{q}} \rangle \langle \psi_{m\mathbf{k}+\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | \psi_{n\mathbf{k}} \rangle}{\omega + \epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}} + i\eta}$$

Number of frequency points

Number of (empty) bands

Number of k-points

Number of (irreducible) q-points, q = k - k'

Number of plane waves (reciprocal lattice vectors)

Convergence parameters

Parallelized over q, k (or bands), w and G.
The parallelization over q and k (or bands) has almost 100% efficiency.

Frequency integration

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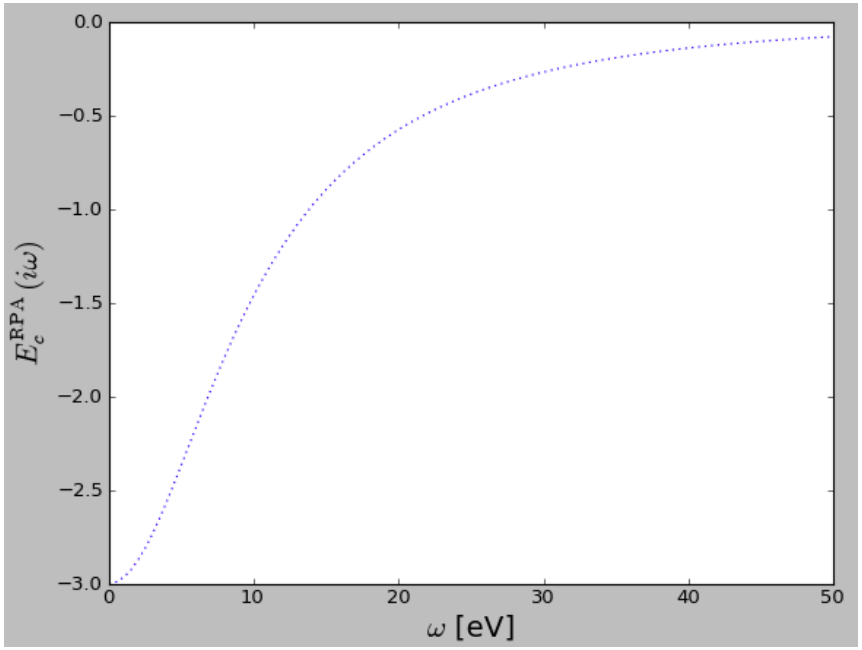
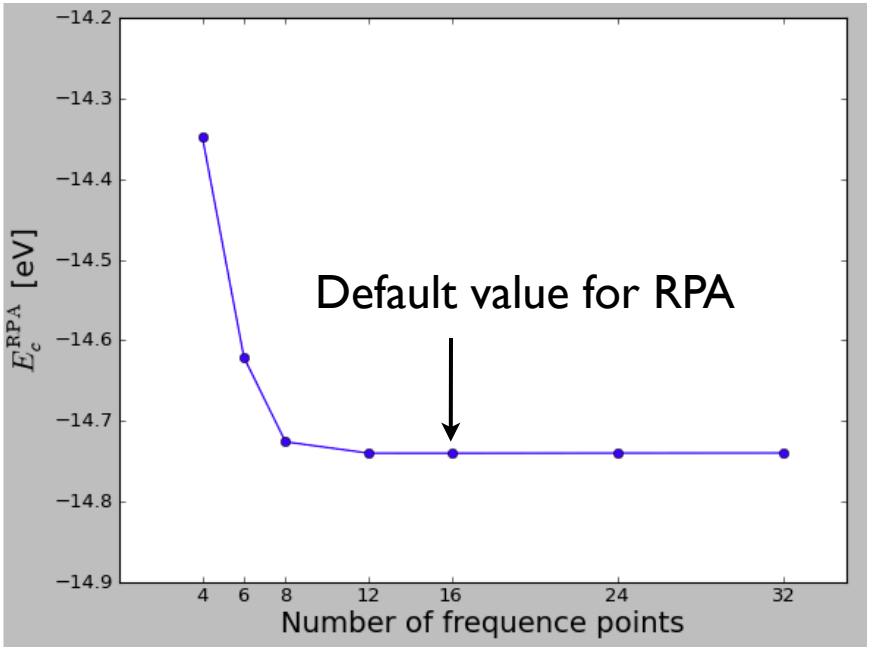
- Use imaginary frequencies



- Use Gauss-Legendre integration method



Free electron gas limit at high energy cutoff

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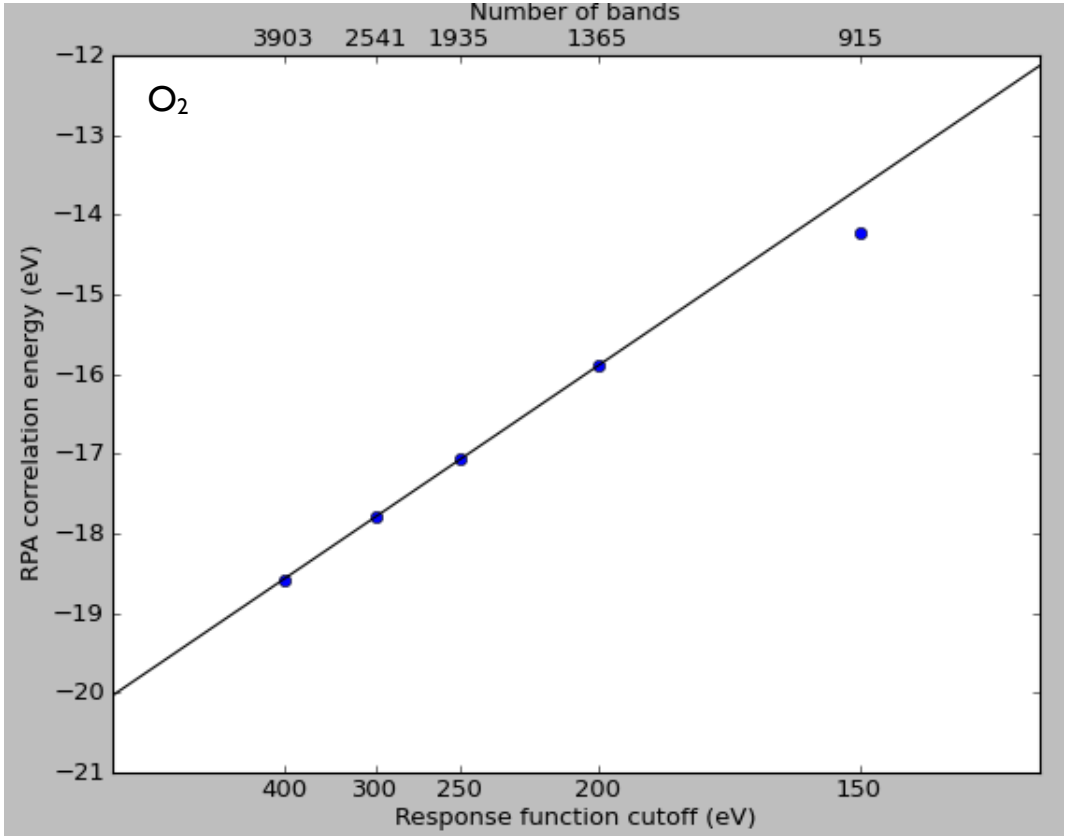
For free electrons the non-interacting response function is known as the Lindhard function and for high energies its RPA correlation energy scales as:

$$E_c = E_c^{\infty} + \frac{A}{(E_{\mathrm{cut}})^{3/2}}$$



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Speed up ground state calculation

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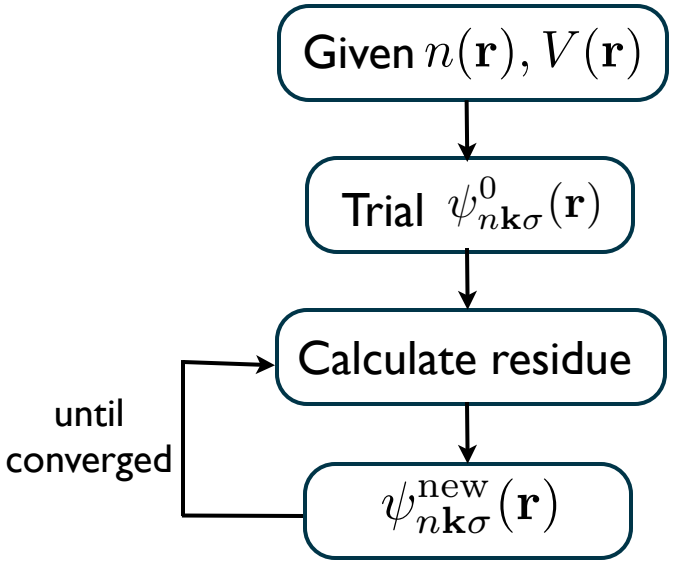
100-400 times speed up

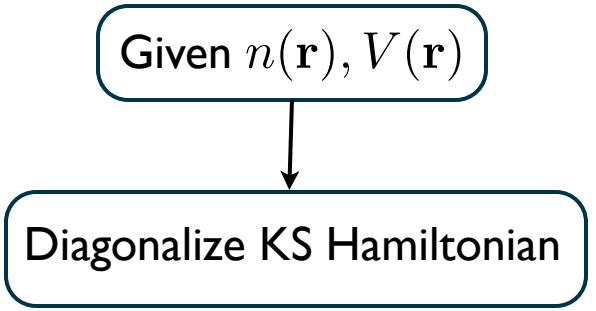
Grid basis ⟶ **Plane wave basis**

N_2/Ru(001): 40 hours on 40 cores 2 hours 13 mins on 8 cores

The key reason for such speed up is that using plane wave basis, the KS equation is diagonalized directly instead of solving iteratively.

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right]\psi_{n\mathbf{k}\sigma}(\mathbf{r}) = E_{n\mathbf{k}\sigma}\psi_{n\mathbf{k}\sigma}(\mathbf{r})$$





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RPA bottlenecks

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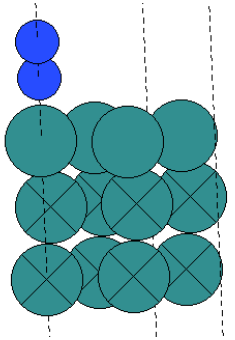
Response function takes most of the time (>99.5%)

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, i\omega) = \frac{2}{V_{\mathrm{BZ}}} \sum_{k,nm} (f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}) \frac{\langle \psi_{n\mathbf{k}} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{m\mathbf{k}+\mathbf{q}} \rangle \langle \psi_{m\mathbf{k}+\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{n\mathbf{k}} \rangle}{i\omega + \epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}} + i\eta}$$

Example : N_2/Ru(001) 2*2*3 slab

16 (k-point) * 60 (occ bands) * 3000 (unocc bands) * 16 (w points) * 5 (q-points) = 230,400,000 loops, which takes 80 cores for 50 hours.



For a given n, m, k, q, define density matrix :

$$n(\mathbf{G}) \equiv \langle \psi_{n\mathbf{k}} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{m\mathbf{k}+\mathbf{q}} \rangle$$

The computing of the response functions consists of :

1. Calculate $n(\mathbf{G})$

   A few hundred lines of code, takes 10% of total computing time for the response function.

2. Perform $C(i\omega) n(\mathbf{G}) n^*(\mathbf{G}')$ and add to $\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, i\omega)$

   A few lines code, takes 90% of total computing time.

16 complex matrices of size 4000×4000 : 4G memory

Speed up RPA using Graphic Processing Units (GPUs)

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Bottleneck :

$$\chi^0_{\mathbf{GG'}}(i\omega) = \sum_{\mathbf{k},nn'} A(i\omega) n(\mathbf{G}) n^*(\mathbf{G'}),$$

It is calculated using zher routine in blas. Move this function to cuda using cublas gains 13x speed up.

Group multiple charge density matrices together and use zherk instead of zher routine.

$$\chi^0_{\mathbf{GG'}}(i\omega) = \sum_{\mathbf{k},n,u\subset n'} A(u, i\omega) n(u, \mathbf{G}) n^*(u, \mathbf{G'}),$$

No.	Function	250
3)	get_wfs	16.0×
4)	transform_wfs	15.4×
5)	fft	12.3×
6)	mapG	53.4×
7)	paw_P_ai	242.2×
8)	paw_P_ap	56.7×
9)	paw_add	136.2×
10)	optical_limit	19.2×
11)	zherk	26.9×
	Total, $\mathbf{q} \to 0$	30.6×
	Total, $\mathbf{q} \neq 0$	39.6×

Final speed up

Special kernel for PAW terms

$$n_{n\mathbf{k},n'\mathbf{k}+\mathbf{q}}(\mathbf{G}) = \tilde{n}_{n\mathbf{k},n'\mathbf{k}+\mathbf{q}}(\mathbf{G}) + \sum_{a,ij} \langle \tilde{\psi}_{n\mathbf{k}} | \tilde{p}^a_i \rangle \langle \tilde{p}^a_j | \tilde{\psi}_{n'\mathbf{k}+\mathbf{q}} \rangle Q^a_{ij}(\mathbf{q}+\mathbf{G})$$

6000 lines of python, 1000 lines of C/CUDA (and re-uses many GPAW functions)

Techniques:
Use BLAS3 “zherk” instead of BLAS2 “zher”
Batch FFTs
GPU kernels parallelized over atoms/bands/projector-functions
No thunking: all calculations on GPU

Performance over different systems

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System	Phase	N_a	N_e	Spin	k-points	Improvement	t_{gpu}
O_2	gas	2	12	True	1	11.3x	41 sec
Li_2O	bulk	3	8	False	$4 \times 4 \times 4$	10.5x	63 sec
MoO_3	bulk	16	96	False	$4 \times 2 \times 4$	35.3x	1.0 h
N_2/Ru(0001)	surface	14	202	False	$4 \times 4 \times 1$	36.1x	1.4 h
CO/Ni(111)	surface	22	210	True	$4 \times 4 \times 1$	37.0x	5.5 h

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Jun Yan, Lin Li and Christopher O'Grady, submitted, 2013.

Enthalpy of Formation per Oxygen

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$$\Delta E_{\mathrm{O}} = \frac{1}{y}E(\mathrm{A}_x\mathrm{O}_y) - \frac{x}{y}E(\mathrm{A}) - \frac{1}{2}E(\mathrm{O}_2),$$

- Selection of oxides

Alkali and Alkali Earth Metal Oxides
with oxidization states
O^{2-} (oxide),
O_2^{2-}(peroxide) ,
O_2^{-}(superoxide).

Transition Metal Oxides
with simple structures
and spin configurations

PBE values < 0.1 eV difference compared with Materials project database

	PBE	EXX	EXX+RPA @ PBE	Expt T=0	Expt RT
Li_2O	-5.35	-5.72	-5.69	-6.14	-6.21[a]
Li_2O_2	-2.80	-2.61	-3.05	-	-3.28[a]
LiO_2	-1.42	-0.24	-1.38	-	-1.37 to -1.50[b]
Na_2O	-3.62	-3.38	-3.93	-4.28	-4.33[a]
Na_2O_2	-2.14	-1.88	-2.41	-2.63	-2.66[a]
NaO_2	-1.22	-0.22	-1.26	-1.37	-1.35[a]
K_2O	-3.07	-2.14	-3.54	-	-3.76[a]
K_2O_2	-2.11	-1.55	-2.42	-	-2.57[a]
KO_2	-1.34	-0.21	-1.45	-1.48	-1.47[a]
Rb_2O	-2.70	-1.59	-3.30	-	-3.51[c]
Rb_2O_2	-2.02	-1.43	-2.42	-	-2.48[c]
RbO_2	-1.31	0.12	-1.43	-	-1.45[c]
Cs_2O	-3.02	-1.42	-3.50	-	-3.58[c]
Cs_2O_2	-2.08	-1.30	-2.47	-	-2.58[c]
CsO_2	-1.36	0.15	-1.43	-	-1.48[c]
BeO	-5.45	-6.31	-5.89	-6.27	-6.31[a]
MgO	-5.57	-6.04	-5.94	-6.19	-6.23[a]
CaO	-6.05	-6.10	-6.48	-6.55	-6.58[a]
CaO_2	-2.86	-2.71	-3.12	-	-3.17[e]
SrO	-5.49	-5.51	-5.90	-6.11	-6.14[a]
BaO	-5.08	-5.14	-5.62	-5.67	-5.68[a]
TiO_2	-4.59	-5.35	-4.79	-4.87	-4.90[a]
RuO_2	-1.56	-0.75	-1.59	-	-1.58[d]
MAE	0.44	0.96	0.15		
MAE-s	0.21		0.10		

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Enthalpy of Formation per Oxygen

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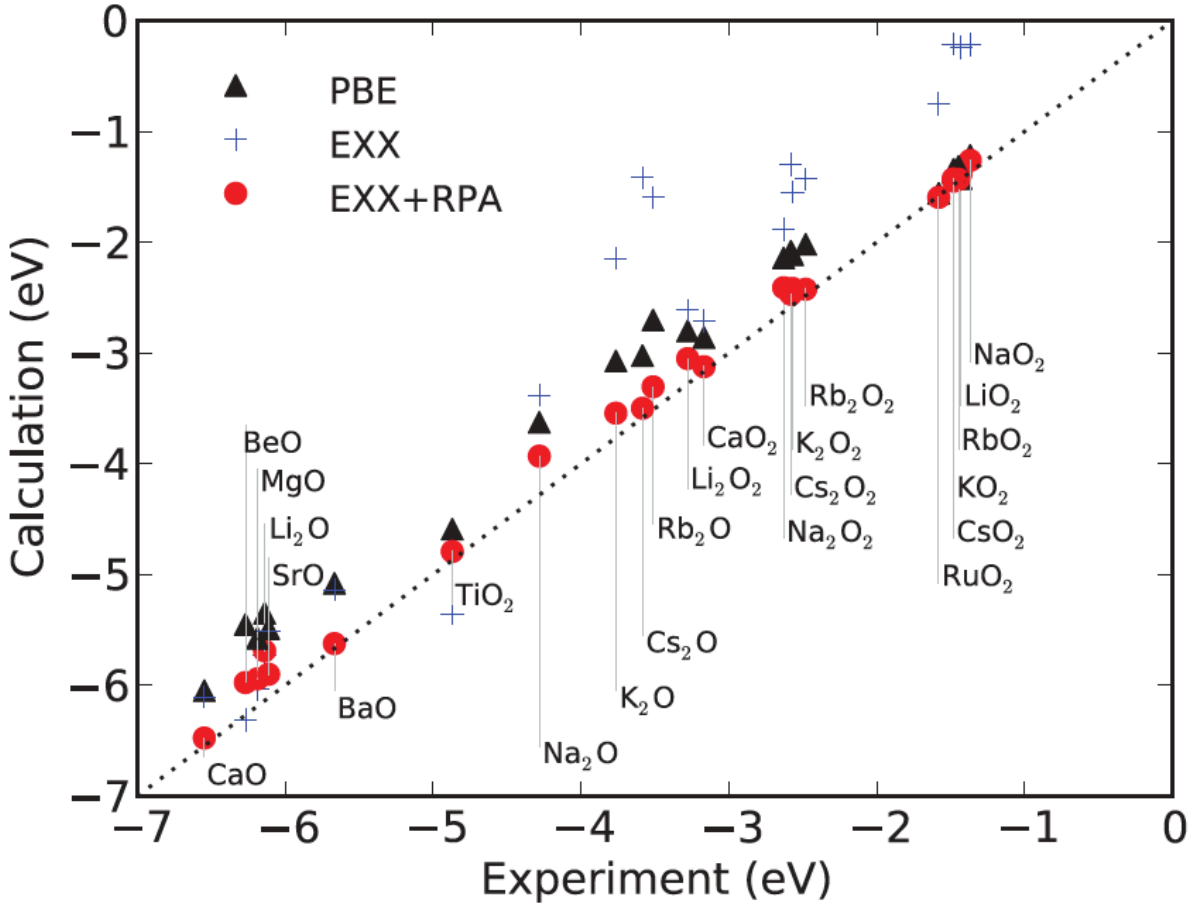

Mean absolute error:
PBE : 0.44 eV
RPA : 0.15 eV

Jun Yan, Jens S. Hummelshøj, and Jens K. Nørskov, Phys. Rev. B 87, 075207 (2013)

Bulk Volumes with RPA

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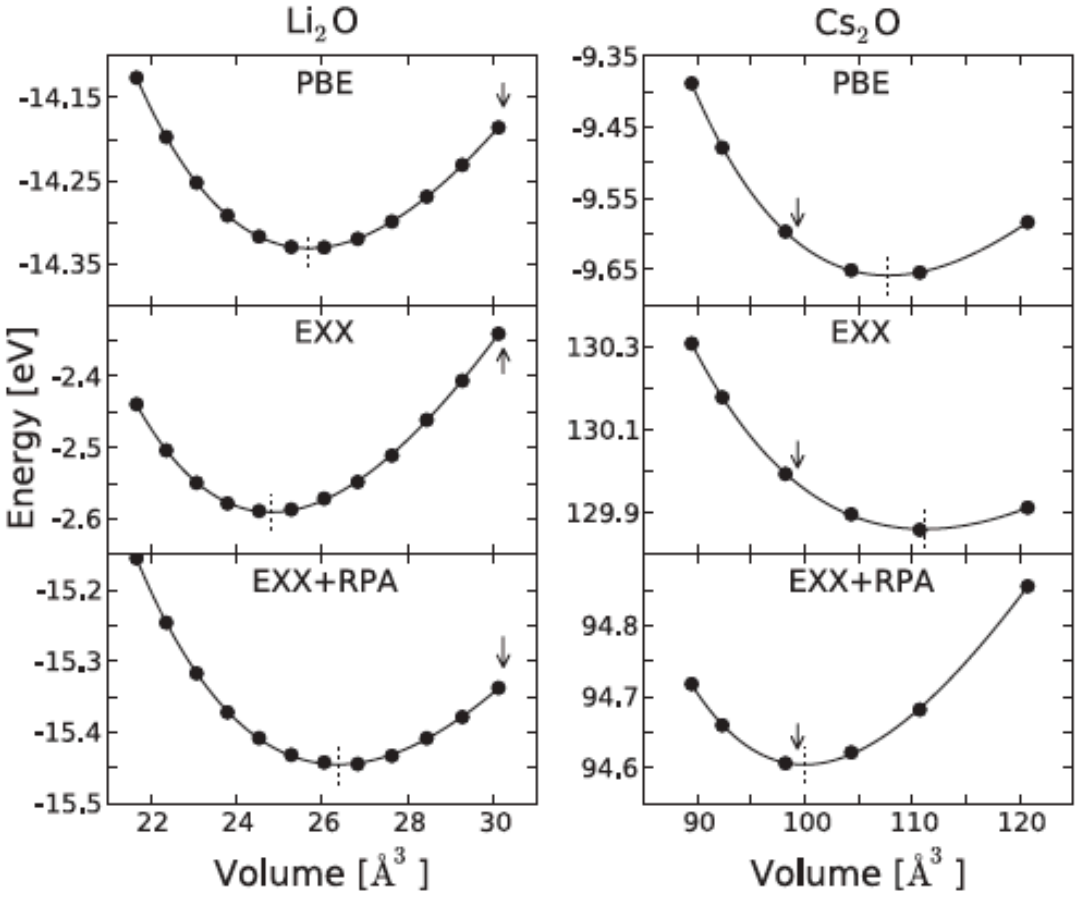
Two representative oxides:

- Li_2O : PBE volume 16.3% smaller than Expt. one
- Cs_2O : PBE volume 16.4% larger than Expt. one

Other oxides : volume error -3% to 6%



RPA volume is 5 and 44 meV lower in total energy for Li_2O and Cs_2O, respectively

Jun Yan, Jens S. Hummelshøj, and Jens K. Nørskov, Phys. Rev. B 87, 075207 (2013)

Different Oxidation States

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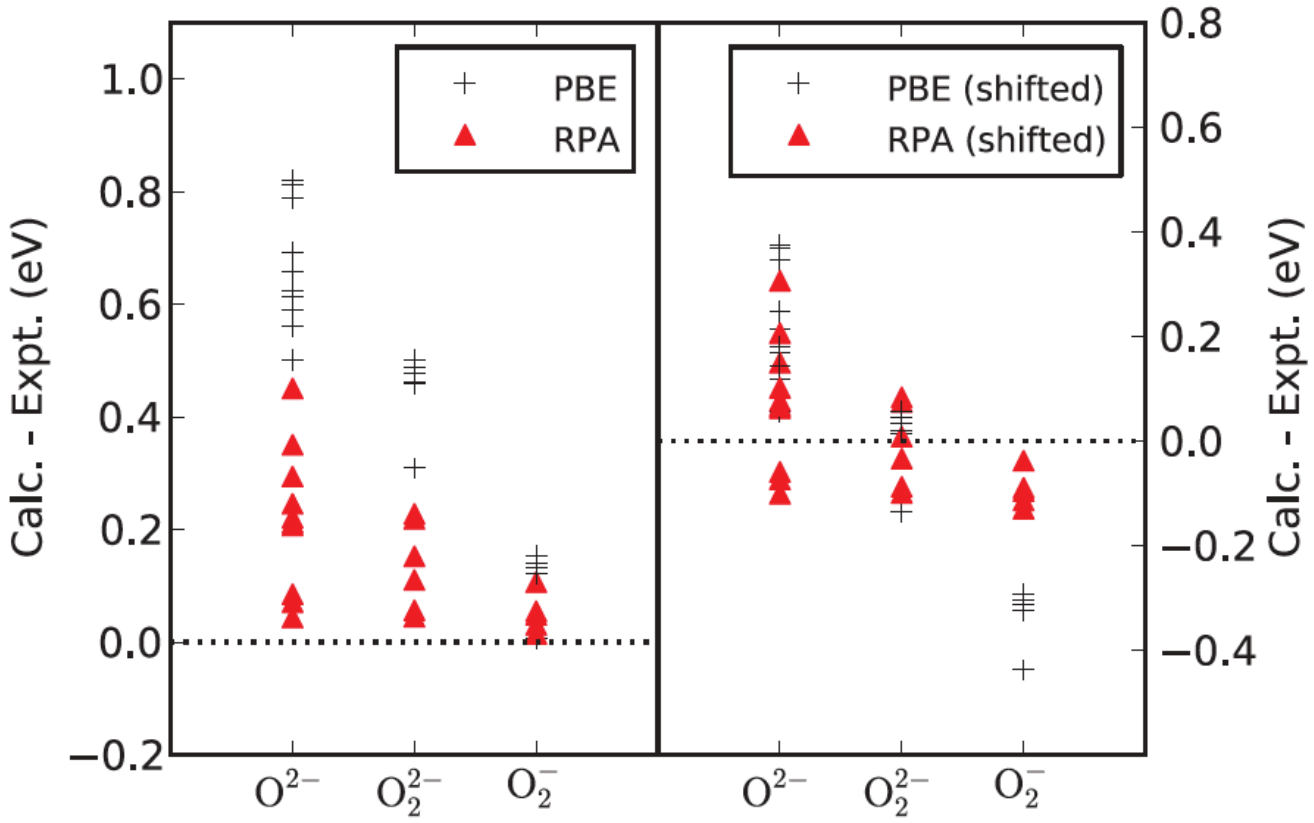
		PBE	EXX	RPA	EXX+RPA	Expt.
O_2	Ours	6.25	1.10	3.82	4.92	5.25
	Ref.	6.24	1.08	3.82	4.90	



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Summary

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- **Plasmons** (easy to calculate and measure in Expt, meaningful results even when not converged)
  - Substrate effect : dynamical screening at weak interacting limit
  - Adsorbate effect : charge transfer like excitation at strong interacting limit
  - Low energy acoustic mode : predicted plasmon energies at Au and Ag surface
- **Excitons** (easy to measure, difficult to calculate and achieve k-point convergence)
  - Single layer boron nitride on graphene
- **RPA correlation energy** (not directly measured, robust on GPU, hard to converge for metals)
  - Benchmark formation energy of 23 metal oxides :
    Mean absolute error 0.44 eV (PBE) -> 0.15 eV (RPA)
- **Implementations**
  - TDDFT with ALDA and bootstrap fxc kernel : well documented and detail tutorials, robust code
  - BSE : documented, no tutorial, hard to converge with k-points
  - RPA (on GPUs) : robust, difficult to converge with k-points for metals
- **Other talks**
  - Plasmonics with GPAW (Kristian), GW (Falco),
  - Extending RPA with renormalized kernel (Thomas), Thin film solar cells (Ivano)

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CASE
Catalysis for Sustainable Energy

neec
Center on Nanostructuring for Efficient Energy Conversion

DTU

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Thank you for your attention !

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