embedded Quantum ESPRESSO

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#QE2018

A glance at Pavanello Research Group @ Rutgers

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PRG @ Rutgers-Newark since 2012

A glance at Pavanello Research Group @ Rutgers

PRG @ Ru

PRG accepting PhD students!

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- Work alongside
  - 3 postdocs
  - 2 PhD students

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  - New ways to use TDDFT for molecule–surface interactions
  - Nonadiabatic dynamics based on Constrained DFT
  - Orbital-free DFT . . .

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  - Orbital-free DFT . . . that actually works

Some theoretical aspects of embedding

Outline

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- Nature is made of interacting subsystems

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- Nature is made of interacting subsystems
- Multiscale models of ground electronic states
  - Materials modeling: Periodic Subsystem DFT
    - embedded Quantum-ESPRESSO (eQE)
    - Dynamics of liquid, solvated and layered systems
  - Details of the eQE algorithm
  - Details of the eQE parallelization
- One example of excited states calculation

Krishtal, A.; Sinha, D.; Genova, A. & Pavanello, M.

Subsystem Density-Functional Theory as an Effective Tool for Modeling Ground and Excited States, their Dynamics, and Many-Body Interactions

J. Phys.: Condens. Matter, **27**, 183202 (2015)

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- **Frozen Density Embedding** (FDE): Coupled Kohn–Sham equations for each subsystem

$$\frac{\delta E_{\text{FDE}}[\rho_I + \rho_{II}]}{\delta\, \rho_I} = 0 \rightarrow \left[-\frac{1}{2}\nabla^2 + v_{KS}^I(\mathbf{r}) + v_{emb}^I(\mathbf{r}) \right] \phi_{(i)_I}(\mathbf{r}) = \varepsilon_i^I \phi_{(i)_I}(\mathbf{r})$$

Senatore 1986, Cortona 1991, Wesolowski 1993; Jacob, Neugebauer, Carter, ...

Orbital-free DFT interaction between subsystems

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The nonadditive functional for two subsystems

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- Compute $E_x^{nadd}[\rho_I, \rho_{II}]$ in the Dirac approximation, $E_x[\rho] = C_x \int \rho^{4/3}(\mathbf{r})\mathrm{d}\mathbf{r}$
- Compute $E_H^{nadd}[\rho_I, \rho_{II}]$, $E_H[\rho] = \frac{1}{2} \int \int \rho(\mathbf{r}) \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$

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. . . more homework!

- T_s contribution to $v_{emb}(\mathbf{r})$
- E_x contribution to $v_{emb}(\mathbf{r})$
- E_H contribution to $v_{emb}(\mathbf{r})$

Other types of embedding

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Density-based embedding

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Wavefunction, density matrix, and others

- WFT densities in DFT densities [Carter, Wesolowski, Neugebauer]
  $\rho_I(\mathbf{r}) = \langle \Psi_I | \hat{\rho}(\mathbf{r}) | \Psi_I \rangle$

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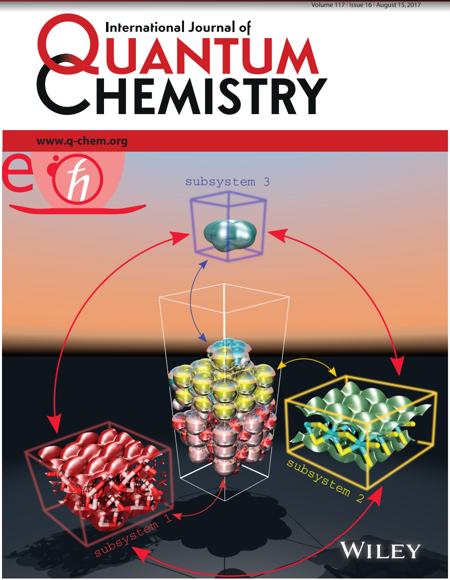
  $\rho_I(\mathbf{r}) = \langle \Psi_I | \hat{\rho}(\mathbf{r}) | \Psi_I \rangle$
- WFT density matrices in DFT density matrices [Manby, Miller, Goodpaster]
  $\gamma_I(\mathbf{r}, \mathbf{r}') = \langle \Psi_I^{HF} | \hat{\gamma}(\mathbf{r}, \mathbf{r}') | \Psi_I^{HF} \rangle$



eQE: An open-source density functional embedding theory code for the condensed phase

International Journal of Quantum Chemistry, **117**, e25401 (2017)

eQE — embedded Quantum ESPRESSO

eqe.rutgers.edu

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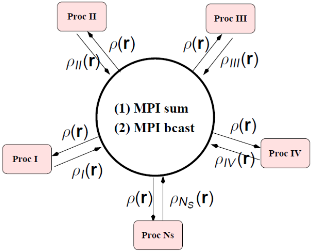
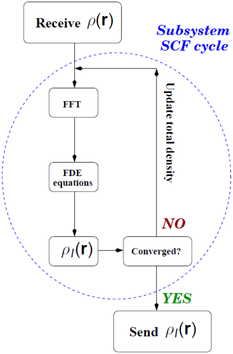
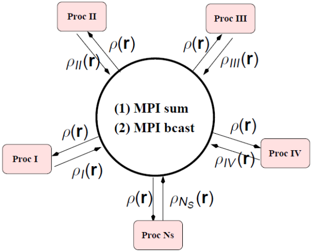
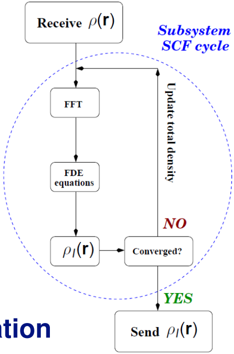




eQE — embedded Quantum ESPRESSO

eqe.rutgers.edu





Massively parallel implementation

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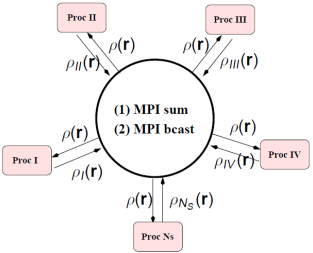
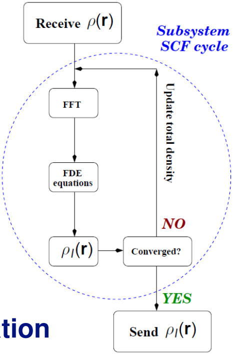
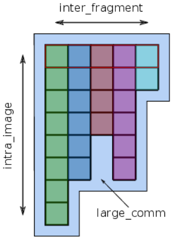


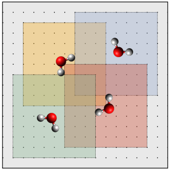


Massively parallel implementation

Rewrite the MPI module of QE

- Subsystem-specific # of CPUs
- Improved latencies (processes wait for others to complete)
- Nested DIIS for $\{\rho_I(\mathbf{r})\}$





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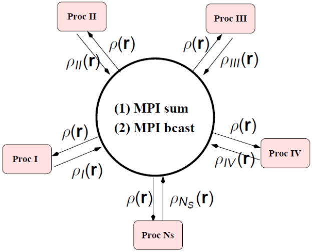

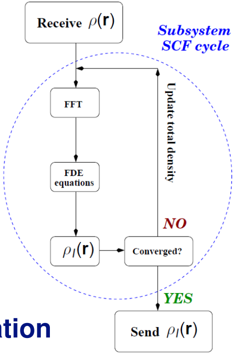

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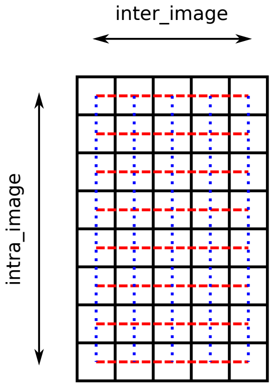
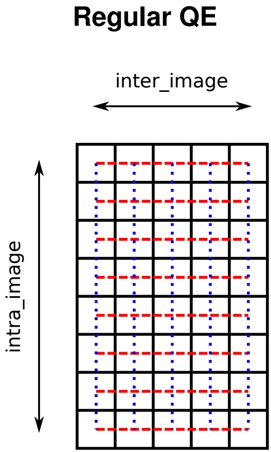
BZ sampling (k-points)

- K-point sampling for (semi)conductors.
- Γ-point for molecules/insulators.

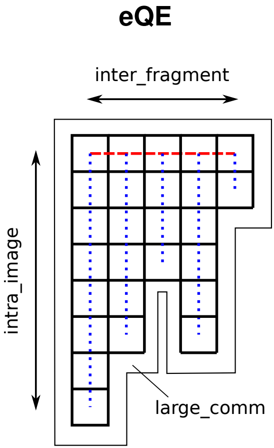
eQE: a note on parallelization

Regular QE





Regular QE
inter_image
intra_image



eQE
inter_fragment
intra_image
large_comm

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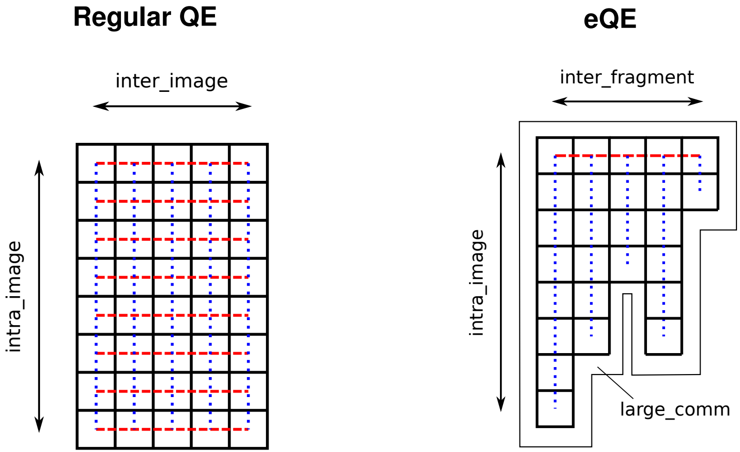

pros & cons

- distributed data communication
- non-polymorphic

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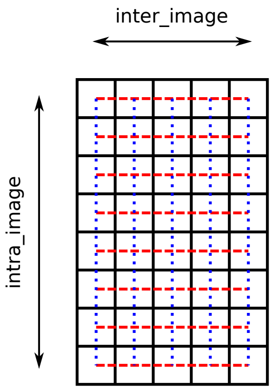

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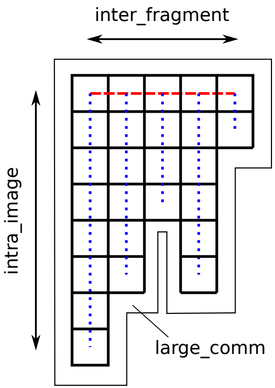

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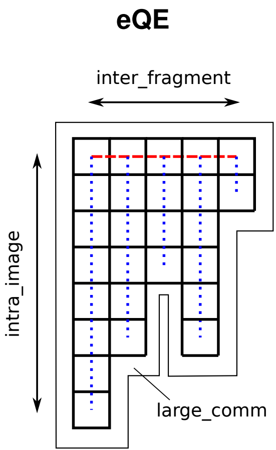
- polymorphic
- gathered data communication

eQE: a note on coding it




```
! dfftp                          :: the fft descriptor of the subsystem electron cell
! dfftl                          :: the fft descriptor of the supersystem simulation cell
! rho%of_r(dfftp%nnr)            :: the subsystem density in the subsystem cell
                                    (grid is distributed over the processes in intra_image_comm)
! rho_fde%of_r(dfftp%nnr)        :: the supersystem density in the subsystem cell
                                    (grid is distributed over the processes in intra_image_comm)
! rho_fde_large%of_r(dfftl%nnr)  :: the supersystem density in the supersystem cell
                                    (grid is distributed over the processes in large_comm)
! %of_g(:)                       :: same quantity in reciprocal space
! aux(dfftp%nnr)                 :: auxiliary vector of the subsystem cell real space
                                    (grid is distributed over the processes in intra_image_comm)
! gaux(ngm)                      :: auxiliary vector of the subsystem cell reciprocal space
! raux(nr1*nr2*nr3)              :: subsystem cell real space auxiliary vector
                                    (whole grid is collected on the ionode proc of intra_image_comm)
! auxl(dfftl%nnr)                :: auxiliary vector of the supersystem cell real space
                                    (grid is distributed over the processes in large_comm)
! gauxl(ngml)                    :: auxiliary vector of the supersystem cell reciprocal space
! rauxl(nr1l*nr2l*nr3l)          :: supersystem (large) cell real space gathered auxiliary vector
                                    (whole grid is collected on the ionode proc of large_comm)
! f2l(nr1*nr2*nr3)               :: subsystem cell to supersystem cell mapping vector.
```

Collect the subsystem density from all the `intra_image` processes into a single array (`raux`).

```
call grid_gather(rho_fde%of_r(:,is), raux)

if (ionode) then
```

Copy each subsystem density into an array of the supersystem cell (`rauxl`), using mapping (`f2l`).

```
    rauxl = 0.d0
    rauxl(f2l(:)) = raux(:)
```

Allreduce `rauxl` across the processes in `inter_fragment` to build the supersystem density in the supersystem cell.

```
    call mp_sum(rauxl, inter_fragment_comm)
```

Using the `f2l` mapping, copy the supersystem density into each subsystem cell.

```
    raux = 0.d0
    raux(:) = rauxl(f2l(:))

endif
```

Distribute the supersystem density over all processes in the communicators spanning the supersystem and subsystem cells.

```
call grid_scatter_large(rauxl, rho_fde_large%of_r(:,is))
call grid_scatter(raux, rho_fde%of_r(:,is))
```

FFT to obtain the reciprocal space representation of the supersystem density in both the subsystem and the supersystem cells.

```
gauxl(:) = cmplx(rho_fde_large%of_r(:,is), 0.d0, kind=dp)
call fwfft ('Custom', gauxl, dfftl)
rho_fde_large%of_g(1:ngml,is) = gauxl(nll(1:ngml))

gaux(:) = cmplx(rho_fde%of_r(:,is), 0.d0, kind=dp)
call fwfft ('Dense', gaux, dfftp)
```

eQE: Performance for molecular periodic systems

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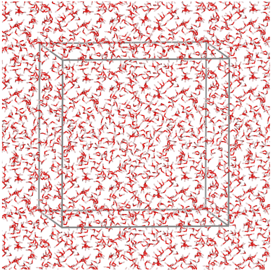
Water 1024



30726 Å^3

Speedup compared to regular QE (all PBE)

24.5 $\times$

eQE: Performance for molecular periodic systems

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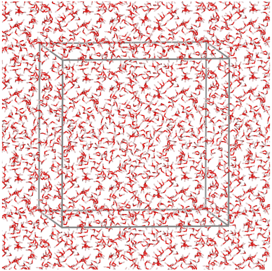
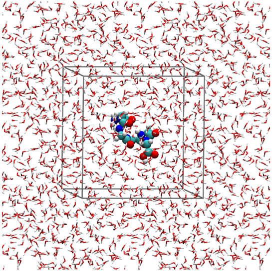


30726 Å^3

$(\mathrm{GLY})_6$ in $(H_2O)_{395}$



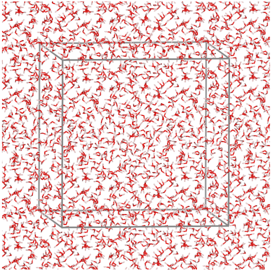
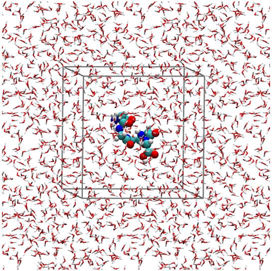
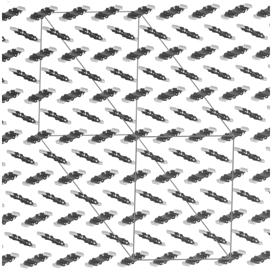
12656 Å^3

Speedup compared to regular QE (all PBE)

24.5 $\times$

36.5 $\times$

eQE: Performance for molecular periodic systems

Water 1024	$(\mathrm{GLY})_6$ in $(H_2O)_{395}$	Pentacene $3 \times 3 \times 3$
		
30726 Å^3	12656 Å^3	18243 Å^3

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eQE: Performance for molecular periodic systems

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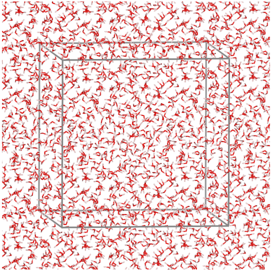	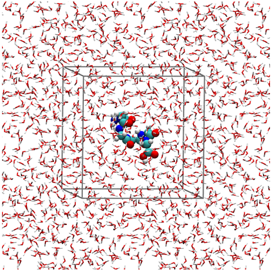	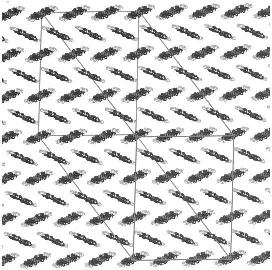
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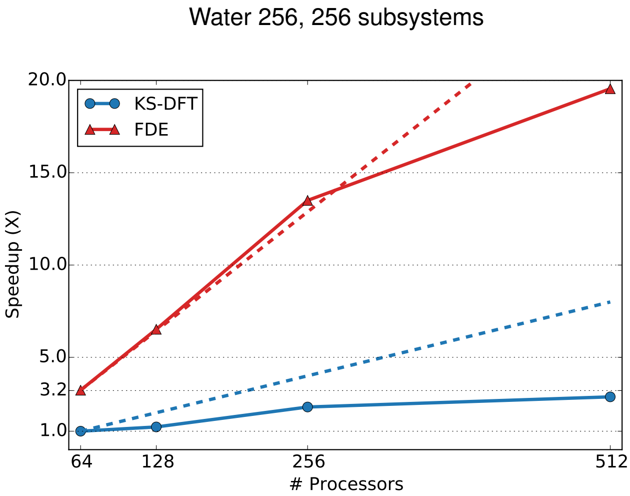
Well over one order of magnitude speedup!

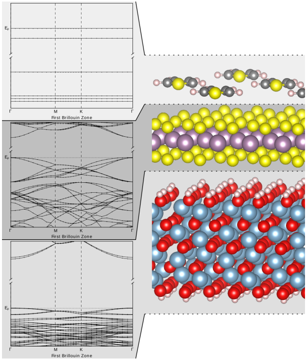
eQE vs QE: Parallel scaling for water 256



QE–eQE gap widens with increasing # of CPUs

eQE: Computational savings for truly periodic systems

System relevant for catalysis:



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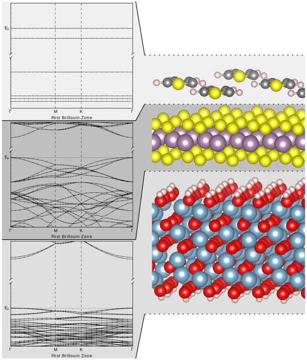

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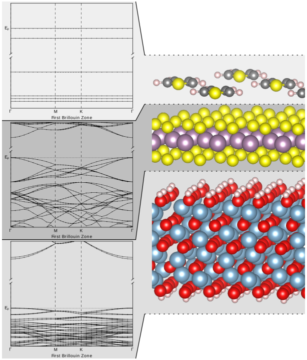

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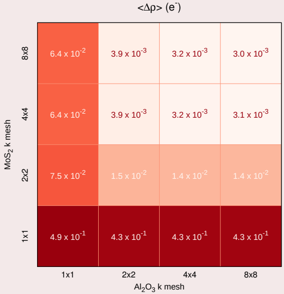

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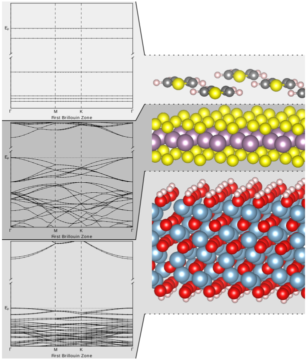

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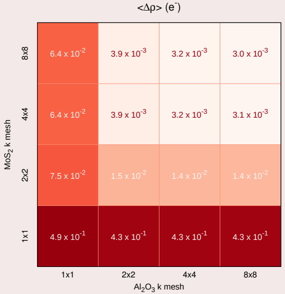

The MoS_2 layer must be well sampled!

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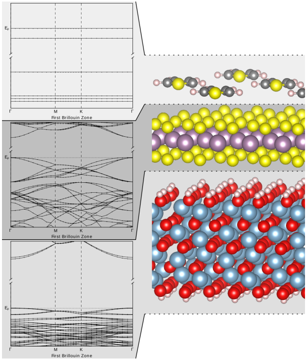

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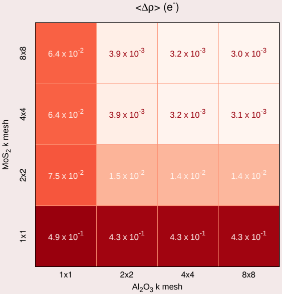

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Computational complexity [Genova & Pavanello JPCM (2015)]

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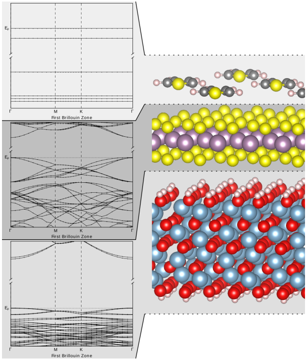

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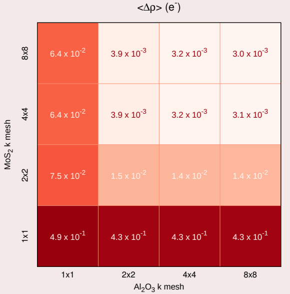

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Computational complexity [Genova & Pavanello JPCM (2015)]

	KS	FDE (bare)	FDE (optimized)
Speedup	$1.0\times$	$0.9\times$	$6.2\times$
Time / Cycle (s)	195	220	31
# of Cycles	17	88	24

eQE for periodic systems: does it work?

Water on Pt(100)

[a]Genova, Ceresoli, & MP, J. Chem. Phys., **141**, 174101 (2014)

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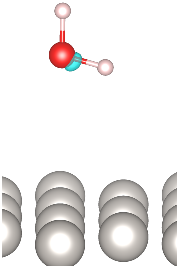

$\langle \Delta\rho \rangle = 0.02$
$\Delta E_{\text{int}} = -0.2$ kcal/mol
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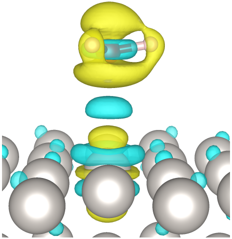

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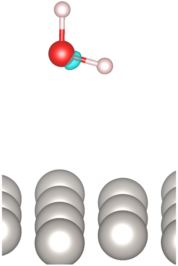

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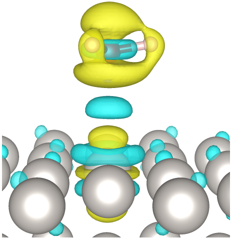

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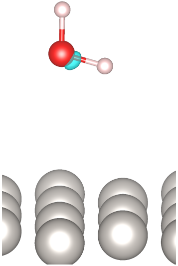

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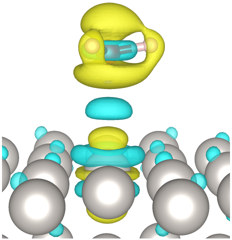

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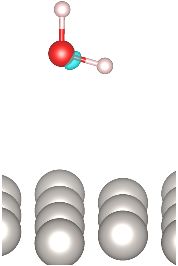

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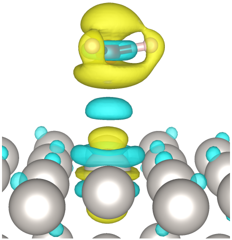

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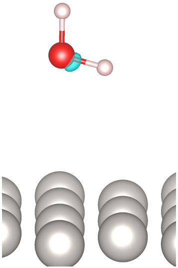

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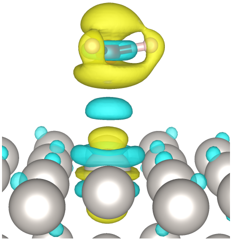

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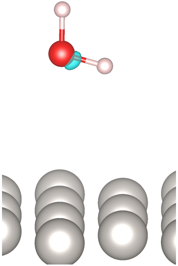

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Liquid Water – does eQE get the structure right?

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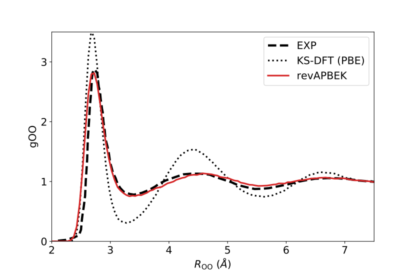
Oxygen–Oxygen RDF



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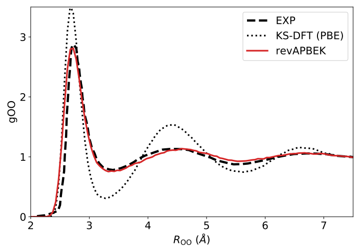

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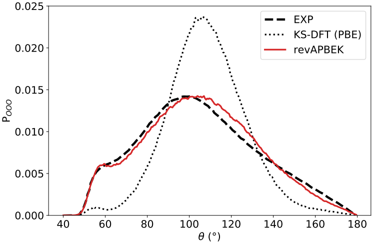

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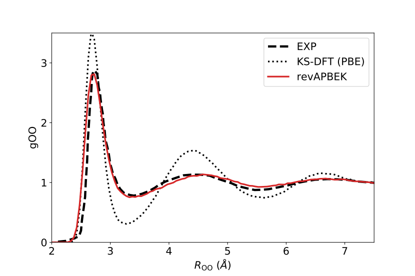

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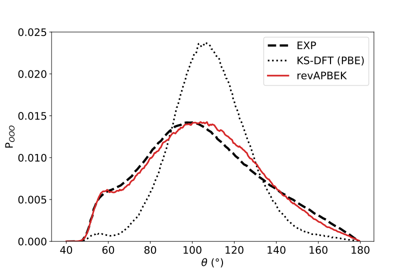

Diffusion coefficient and dipole moment

$$\langle D \rangle = 2.97(0.4) \cdot 10^{-5} cm^2 s^{-1}$$

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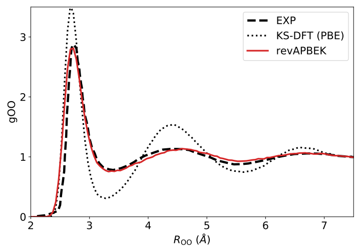

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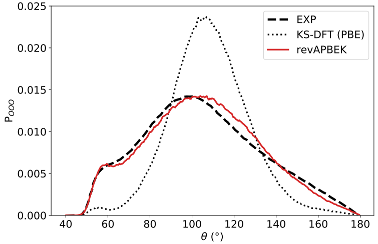

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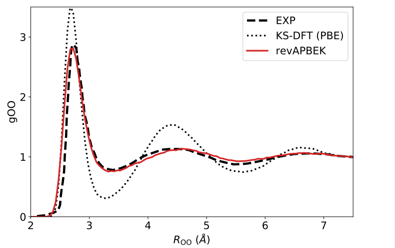

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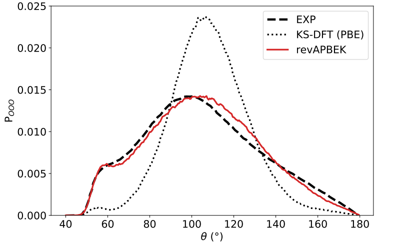

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- **How about e^- excited states?**

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Computation of ϵ

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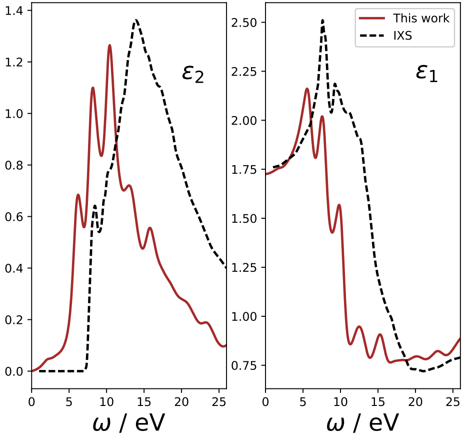

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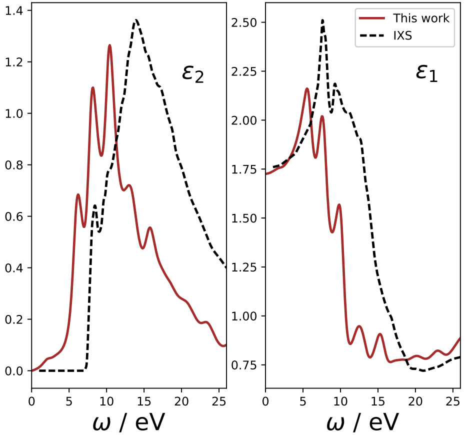

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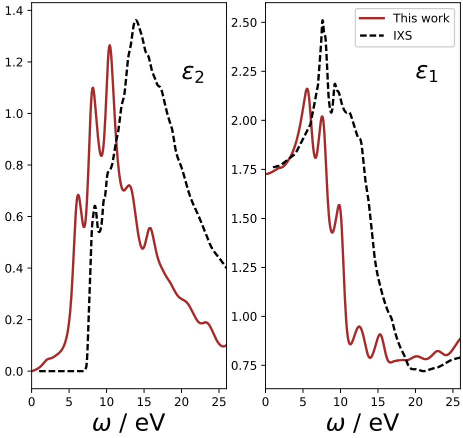

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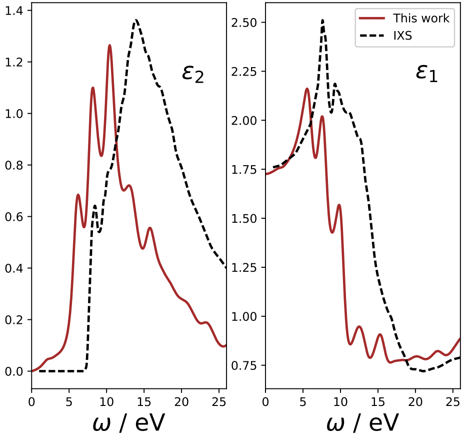

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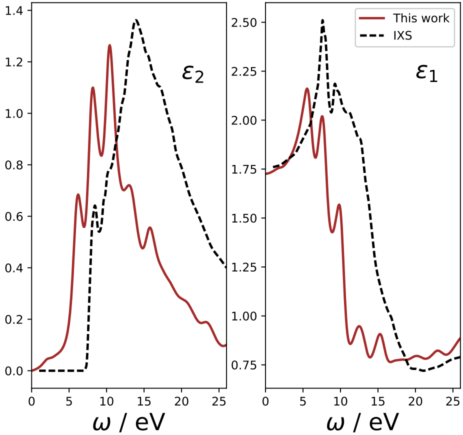

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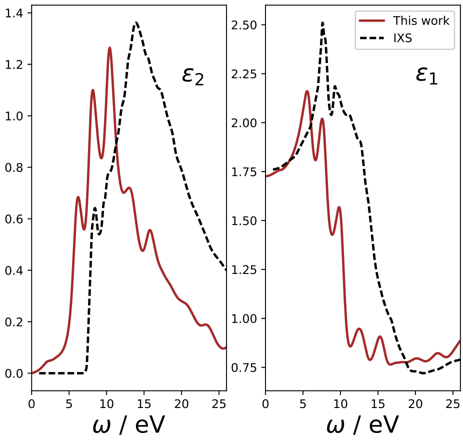

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- Dr. Wenhui Mi
- Dr. Muhammed Acikgoz
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- Johannes Tölle (visitor)
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- **Dr. Debalina Sinha (@ L'Oreal)**
- **Dr. Davide Ceresoli (CNR)**
- **Prof. Oliviero Andreussi (North Texas)**
- **Dr. Andre Gomes (CNRS)**
- **Prof. Rob DiStasio (Cornell)**
- **Prof. Henk Eshuis (Montclair State)**
- **Dr. Damien Riedel (CNRS)**

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