eQE: The embedded Quantum ESPRESSO software package

Michele Pavanello & friends
@MikPavanello

Department of Chemistry
Rutgers, the State University of New Jersey
Newark, NJ

MolSSI workshop at UB 2018

Pavanello Research Group @ Rutgers

Est. 2012

Embedding is the ~~future~~ present

Embedding is the ~~future~~ present

The playing field as I see it

- Moore's law forces us to go parallel
- (Super)computer architectures typically provide
  - Compute nodes (12-24 procs/node)
  - Infiniband
  - Coprocessors
- The cloud (probably the future)
  - Low on CPU, high on GPU
  - Google colaboratory / Google cloud: python + tensorflow
  - Not aware of any QC/CMT code tailored to AWS

Embedding is the ~~future~~ present

The playing field as I see it

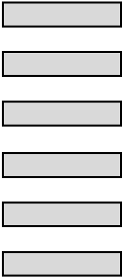
- Moore's law forces us to go parallel
- (Super)computer architectures typically provide
  - Compute nodes (12-24 procs/node)
  - Infiniband
  - Coprocessors
- The cloud (probably the future)
  - Low on CPU, high on GPU
  - Google colaboratory / Google cloud: python + tensorflow
  - Not aware of any QC/CMT code tailored to AWS

The role of Embedding

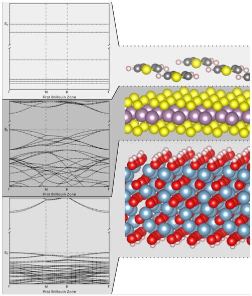
- Naturally work-parallel
- In some formulations also data-parallel
- Embedding is a paradigm:
  - Can embed mathematical quantities (ρ, Ψ, G)
  - Can embed QC/CMT codes

Embedding overlaps with current architectures

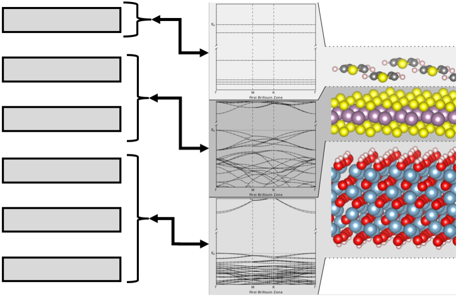
Embedding overlaps with current architectures



Compute nodes

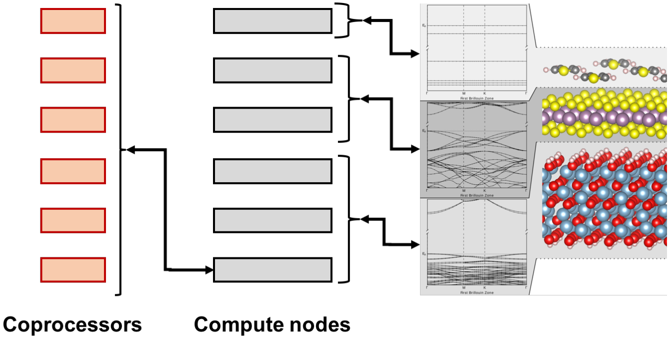


Embedding overlaps with current architectures

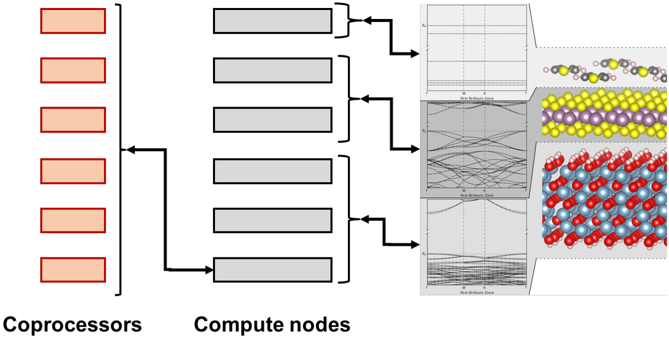


Compute nodes

Embedding overlaps with current architectures



Embedding overlaps with current architectures



The method should:

- Broadcast as little data as possible across compute nodes
- Avoid computing zeros
  - Simple and easy basis set truncation
- Approach excited states and e^{-}–N dynamics

Density Embedding (FDE) / Subsystem DFT

Density Embedding (FDE) / Subsystem DFT

- Split the system into (smaller) interacting subsystems

Density Embedding (FDE) / Subsystem DFT

- Split the system into (smaller) interacting subsystems
- Partition of the total electron density into subsystem contributions

$$\rho(\mathbf{r}) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r}) \qquad \rho_I(\mathbf{r}) = \sum_i^{\infty} n_i^I |\phi_{(i)_I}(\mathbf{r})|^2$$

Density Embedding (FDE) / Subsystem DFT

- Split the system into (smaller) interacting subsystems
- Partition of the total electron density into subsystem contributions

$$\rho(\mathbf{r}) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r}) \qquad \rho_I(\mathbf{r}) = \sum_i^{\infty} n_i^I |\phi_{(i)_I}(\mathbf{r})|^2$$

- The energy functional is almost additive: $E[\rho] \simeq E[\rho_I] + E[\rho_{II}]$

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

Density Embedding (FDE) / Subsystem DFT

- Split the system into (smaller) interacting subsystems
- Partition of the total electron density into subsystem contributions

$$\rho(\mathbf{r}) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r}) \qquad \rho_I(\mathbf{r}) = \sum_i^{\infty} n_i^I |\phi_{(i)_I}(\mathbf{r})|^2$$

- The energy functional is almost additive: $E[\rho] \simeq E[\rho_I] + E[\rho_{II}]$

$$E_{\mathrm{FDE}}[\rho] = E[\rho_I] + E[\rho_{II}] + T_s^{\mathrm{nadd}}[\rho_I, \rho_{II}] + E_{xc}^{\mathrm{nadd}}[\rho_I, \rho_{II}] + V_{\mathrm{Coul}}^{\mathrm{nadd}}[\rho_I, \rho_{II}]$$

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

Density Embedding (FDE) / Subsystem DFT

- Split the system into (smaller) interacting subsystems
- Partition of the total electron density into subsystem contributions

$$\rho(\mathbf{r}) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r}) \qquad \rho_I(\mathbf{r}) = \sum_i^{\infty} n_i^I |\phi_{(i)_I}(\mathbf{r})|^2$$

- The energy functional is almost additive: $E[\rho] \simeq E[\rho_I] + E[\rho_{II}]$

$$E_{\text{FDE}}[\rho] = E[\rho_I] + E[\rho_{II}] + T_s^{\text{nadd}}[\rho_I, \rho_{II}] + E_{xc}^{\text{nadd}}[\rho_I, \rho_{II}] + V_{\text{Coul}}^{\text{nadd}}[\rho_I, \rho_{II}]$$

$$F^{\text{nadd}}[\rho_I, \rho_{II}] = F[\rho] - F[\rho_I] - F[\rho_{II}]$$

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

Density Embedding (FDE) / Subsystem DFT

- Split the system into (smaller) interacting subsystems
- Partition of the total electron density into subsystem contributions

$$\rho(\mathbf{r}) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r}) \qquad \rho_I(\mathbf{r}) = \sum_i^{\infty} n_i^I |\phi_{(i)_I}(\mathbf{r})|^2$$

- The energy functional is almost additive: $E[\rho] \simeq E[\rho_I] + E[\rho_{II}]$

$$E_{\text{FDE}}[\rho] = E[\rho_I] + E[\rho_{II}] + T_s^{\text{nadd}}[\rho_I, \rho_{II}] + E_{xc}^{\text{nadd}}[\rho_I, \rho_{II}] + V_{\text{Coul}}^{\text{nadd}}[\rho_I, \rho_{II}]$$

$$F^{\text{nadd}}[\rho_I, \rho_{II}] = F[\rho] - F[\rho_I] - F[\rho_{II}]$$

- **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

. . . a slide from 2018 QE workshop. . .

Orbital-free DFT interaction between subsystems

...a slide from 2018 QE workshop...

The nonadditive functional for two subsystems

$$F^{\text{nadd}}[\rho_I, \rho_{II}] = F[\rho] - F[\rho_I] - F[\rho_{II}]$$

considering that $\rho(r) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r})$.

Orbital-free DFT interaction between subsystems

...a slide from 2018 QE workshop...

The nonadditive functional for two subsystems

$$F^{\text{nadd}}[\rho_I, \rho_{II}] = F[\rho] - F[\rho_I] - F[\rho_{II}]$$

considering that $\rho(r) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r})$.

Homework :)

- Compute $T_s^{nadd}[\rho_I, \rho_{II}]$ in the Thomas-Fermi approximation, $T_s[\rho] = C_{TF} \int \rho^{5/3}(\mathbf{r})\mathrm{d}\mathbf{r}$
- 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 $E_H^{nadd}[\rho_I, \rho_{II}]$, $E_H[\rho] = \frac{1}{2} \int \int \rho(\mathbf{r}) \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$

The nonadditive functional for two subsystems

$$F^{\text{nadd}}[\rho_I, \rho_{II}] = F[\rho] - F[\rho_I] - F[\rho_{II}]$$

considering that $\rho(r) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r})$.

Homework :)

- Compute $T_s^{nadd}[\rho_I, \rho_{II}]$ in the Thomas-Fermi approximation, $T_s[\rho] = C_{TF} \int \rho^{5/3}(\mathbf{r})\mathrm{d}\mathbf{r}$
- 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 $E_H^{nadd}[\rho_I, \rho_{II}]$, $E_H[\rho] = \frac{1}{2} \int \int \rho(\mathbf{r}) \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$

The embedding potential is given by $\frac{\delta E^{\text{nadd}}}{\delta \rho_I(\mathbf{r})}$.

Orbital-free DFT interaction between subsystems

...a slide from 2018 QE workshop...

The nonadditive functional for two subsystems

$$F^{\text{nadd}}[\rho_I, \rho_{II}] = F[\rho] - F[\rho_I] - F[\rho_{II}]$$

considering that $\rho(r) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r})$.

Homework :)

- Compute $T_s^{nadd}[\rho_I, \rho_{II}]$ in the Thomas-Fermi approximation, $T_s[\rho] = C_{TF} \int \rho^{5/3}(\mathbf{r})\mathrm{d}\mathbf{r}$
- 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 $E_H^{nadd}[\rho_I, \rho_{II}]$, $E_H[\rho] = \frac{1}{2} \int \int \rho(\mathbf{r}) \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$

The embedding potential is given by $\frac{\delta E^{\text{nadd}}}{\delta \rho_I(\mathbf{r})}$.

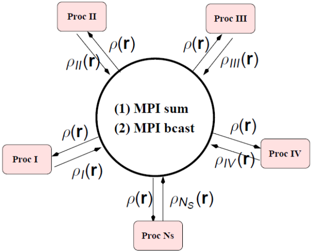
...more homework!

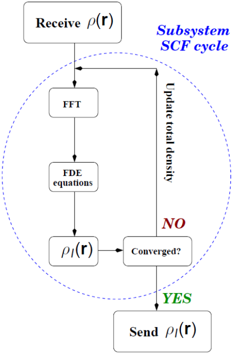
- T_s contribution to $v_{emb}(\mathbf{r})$
- E_x contribution to $v_{emb}(\mathbf{r})$
- E_H contribution to $v_{emb}(\mathbf{r})$

eqe.rutgers.edu

eQE — embedded Quantum Espresso

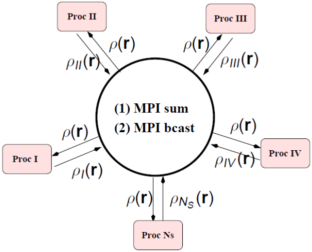
eqe.rutgers.edu

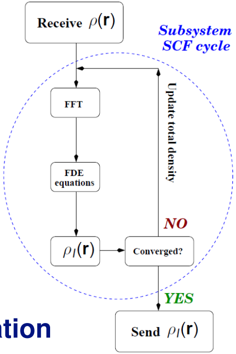




eQE — embedded Quantum Espresso

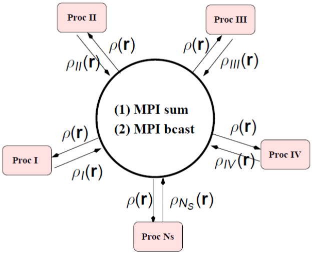
eqe.rutgers.edu

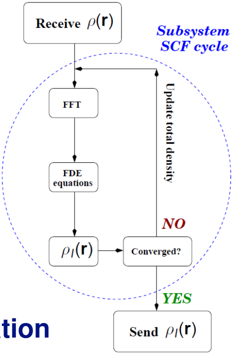




Massively parallel implementation

eqe.rutgers.edu

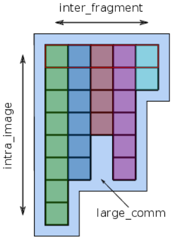


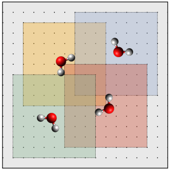


Massively parallel implementation

Rewrite the MPI module of QE

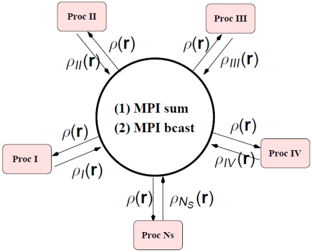
- Subsystem-specific # of CPUs
- Improved latencies (processes wait for others to complete)
- Nested DIIS for $\{\rho_I(\mathbf{r})\}$

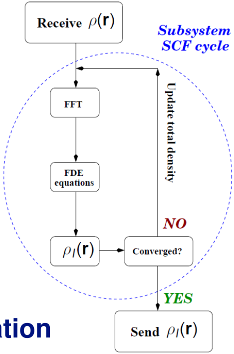




eQE — embedded Quantum Espresso

eqe.rutgers.edu





Massively parallel implementation

Rewrite the MPI module of QE

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

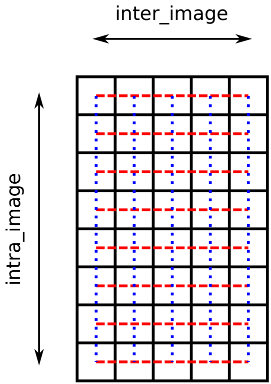
BZ sampling (k-points)

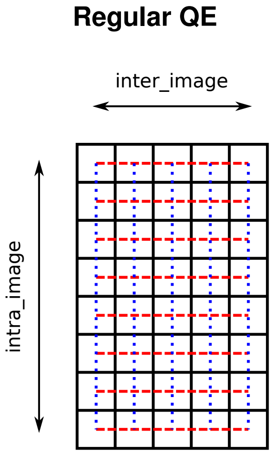
- K-point sampling for (semi)conductors.
- Γ-point for molecules/insulators.

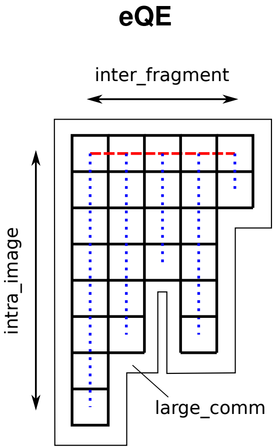
eQE: a note on parallelization

eQE: a note on parallelization

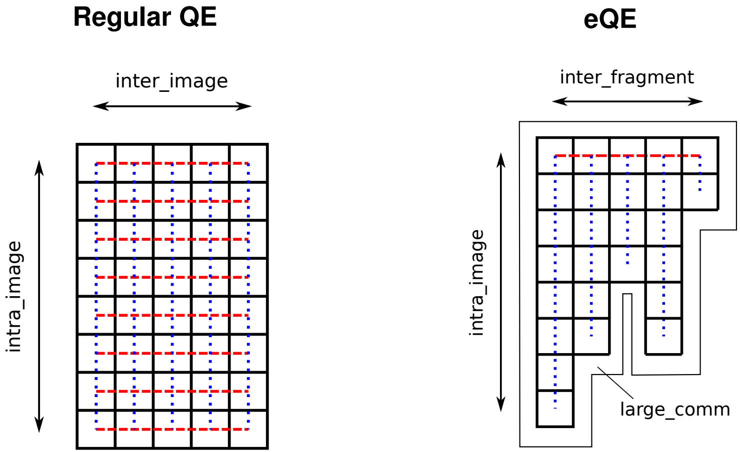
Regular QE




Regular QE
inter_image
intra_image


eQE
inter_fragment
intra_image
large_comm

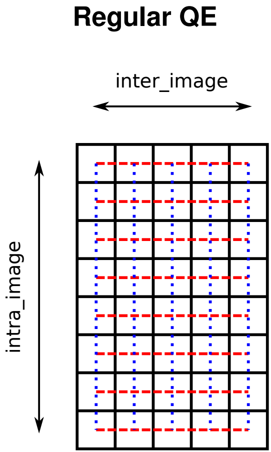
eQE: a note on parallelization

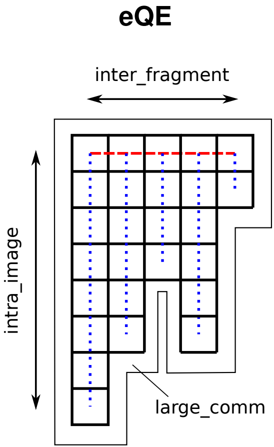


pros & cons

- distributed data communication
- non-polymorphic

eQE: a note on parallelization





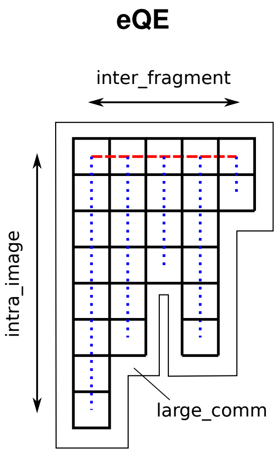
pros & cons

- distributed data communication
- non-polymorphic

pros & cons

- polymorphic
- gathered data communication

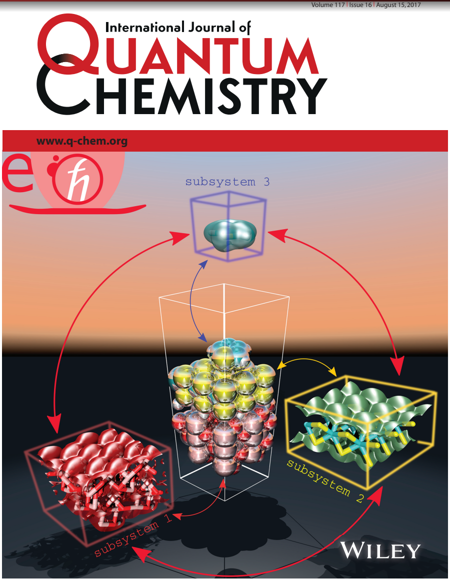
eQE: a note on coding it




```
! 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 — embedded Quantum Espresso



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

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

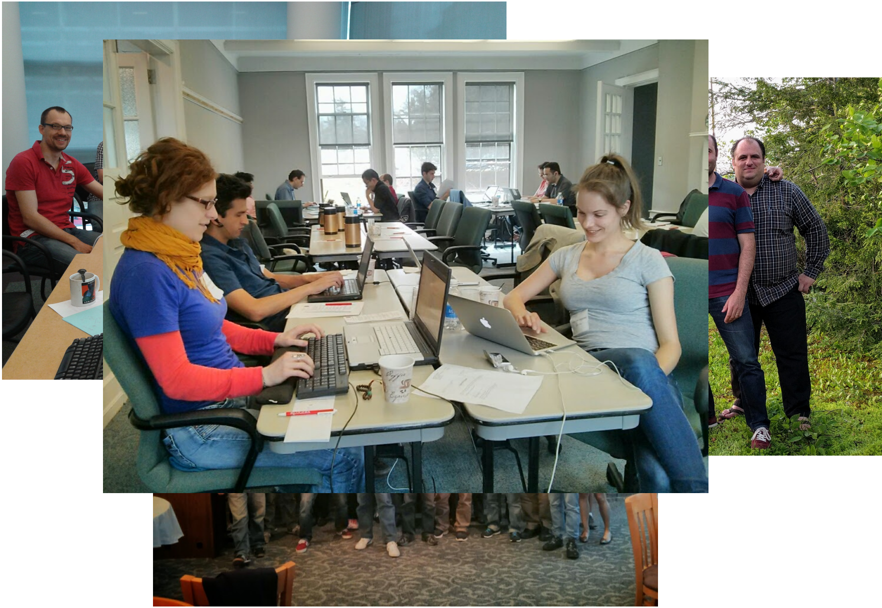
eQE Development: Hackathons are the key

eQE Development: Hackathons are the key

eQE Development: Hackathons are the key

eQE Development: Hackathons are the key

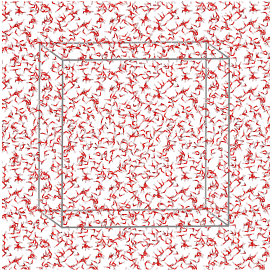
eQE Development: Hackathons are the key



eQE: Performance for molecular periodic systems

eQE: Performance for molecular periodic systems

Water 1024



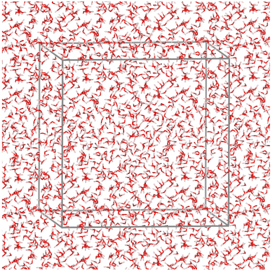
30726 Å^3

Speedup compared to regular QE (all PBE)

24.5 $\times$

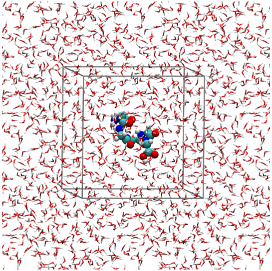
eQE: Performance for molecular periodic systems

Water 1024



$30726\ Å^3$

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

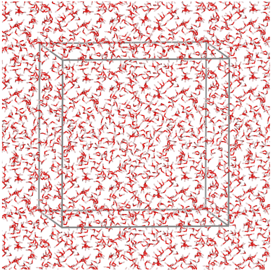
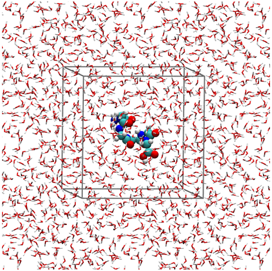
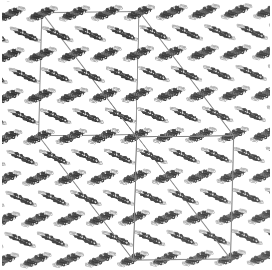


$12656\ Å^3$

Speedup compared to regular QE (all PBE)

24.5 $\times$ **36.5** $\times$

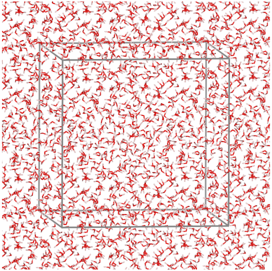
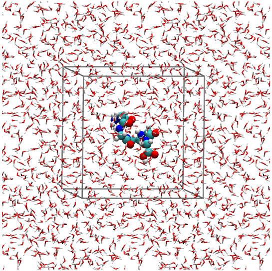
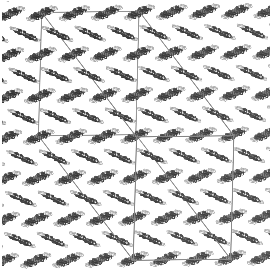
eQE: Performance for molecular periodic systems

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

Speedup compared to regular QE (all PBE)

24.5 $\times$	**36.5** $\times$	**12.5** $\times$

eQE: Performance for molecular periodic systems

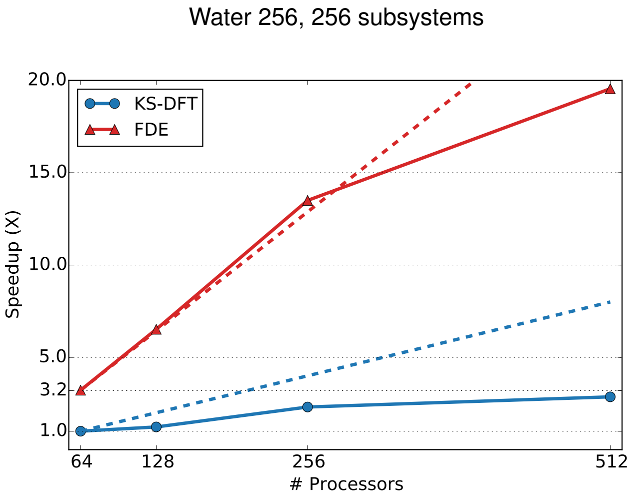
Water 1024	$(GLY)_6$ in $(H_2O)_{395}$	Pentacene $3 \times 3 \times 3$
		
30726 Å^3	12656 Å^3	18243 Å^3

Speedup compared to regular QE (all PBE)

24.5 $\times$	**36.5** $\times$	**12.5** $\times$

Well over one order of magnitude speedup!

eQE vs QE: Parallel scaling for water 256

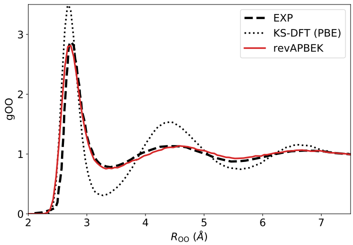


QE–eQE gap widens with increasing # of CPUs

Liquid Water – does eQE get the structure right?

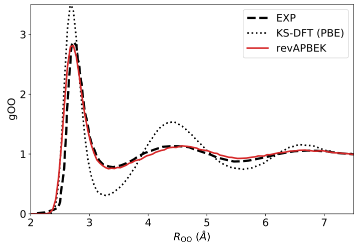
Liquid Water – does eQE get the structure right?

Oxygen–Oxygen RDF

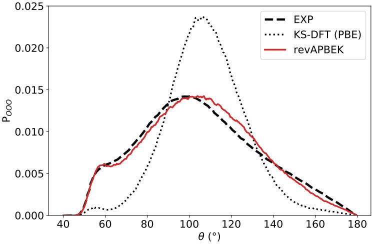


Liquid Water – does eQE get the structure right?

Oxygen–Oxygen RDF

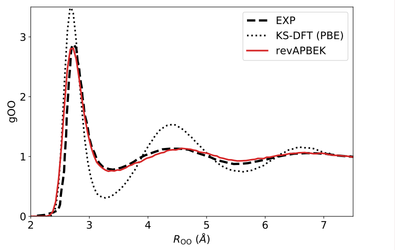


O–O–O ADF

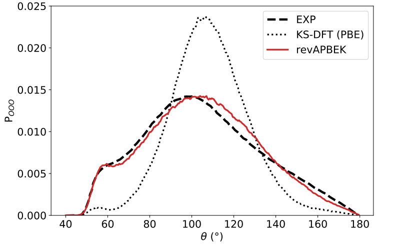


Liquid Water – does eQE get the structure right?

Oxygen–Oxygen RDF



O–O–O ADF

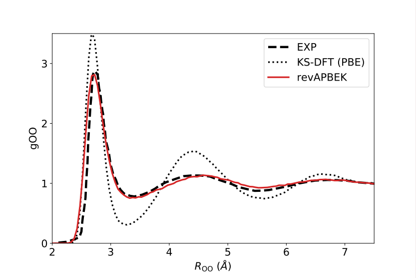


Diffusion coefficient and dipole moment

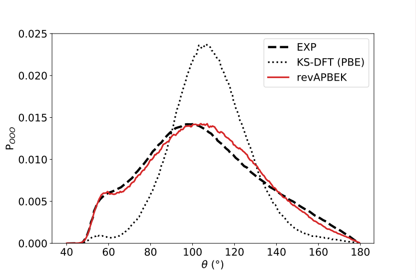
$$\langle D \rangle = 2.97(0.4) \cdot 10^{-5} cm^2 s^{-1}$$
$$\langle \mu \rangle = 2.8(0.2) D$$

Liquid Water – does eQE get the structure right?

Oxygen–Oxygen RDF



O–O–O ADF



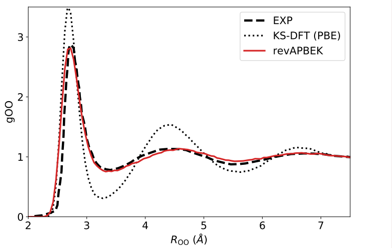
Diffusion coefficient and dipole moment

$$\langle D \rangle = 2.97(0.4) \cdot 10^{-5} cm^2 s^{-1}$$
$$\langle \mu \rangle = 2.8(0.2) D$$

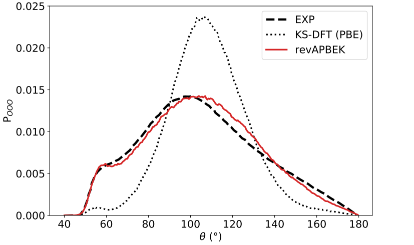
- eQE recovers correct structure
- eQE recovers correct dynamics
- eQE recovers correct e^- structure

Liquid Water – does eQE get the structure right?

Oxygen–Oxygen RDF



O–O–O ADF



Diffusion coefficient and dipole moment

$$\langle D \rangle = 2.97(0.4) \cdot 10^{-5} cm^2 s^{-1}$$
$$\langle \mu \rangle = 2.8(0.2) D$$

- eQE recovers correct structure
- eQE recovers correct dynamics
- eQE recovers correct e^- structure
- **How about e^- excited states?**

Subsystem TDDFT and Related Methods

- effective excitations of active subsystem in environment (leads to "FDEu")
  M.E. Casida, T.A. Wesolowski, *Int. J. Quant. Chem.* **96** (2004), 577; T.A. Wesolowski, *JACS* **126** (2004), 11444.
- general subsystem TDDFT formulation for delocalized excitations ("FDEc")
  J. Neugebauer, *J. Chem. Phys.* **126** (2007), 134116; J. Neugebauer, *J. Chem. Phys.* **131** (2009), 084104
- derivation with focus on subsystem response functions
  M. Pavanello, *J. Chem. Phys.* **138** (2013), 204118.
- fragment-based TDDFT in the context of partition DFT
  M.A. Mosquera, D. Jensen, A. Wasserman, *Phys. Rev. Lett.* **111** (2013), 023001.
- time-dependent potential-functional theory for subsystems
  C. Huang, F. Libisch, Q. Peng, E.A. Carter *J. Chem. Phys.* **140** (2014), 124113.
- real-time subsystem TDDFT
  A. Krishtal, D. Ceresoli, M. Pavanello, *J. Chem. Phys.* **142** (2015), 154116.
- subsystem TDDFT with external orthogonality
  D.V. Chulhai, L. Jensen, *Phys. Chem. Chem. Phys.* **18** (2016), 21032.

Subsytem TDDFT: *Response functions*

$$\delta\rho(\mathbf{r},\omega) = \sum_I \delta\rho_I(\mathbf{r},\omega)$$

Derives directly from $\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$

Subsytem TDDFT: *Response functions*

$$\delta\rho(\mathbf{r},\omega) = \sum_I \delta\rho_I(\mathbf{r},\omega)$$ Derives directly from $\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_I \chi_I(\mathbf{r},\mathbf{r}',\omega)$$ Spectrum is subsystem-additive ?!?

Subsytem TDDFT: *Response functions*

$$\delta\rho(\mathbf{r},\omega) = \sum_I \delta\rho_I(\mathbf{r},\omega)$$

Derives directly from $\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_I \chi_I(\mathbf{r},\mathbf{r}',\omega)$$

Spectrum is subsystem-additive ?!?

$$\chi_I^u = \chi_I^0 + \chi_I^0 K_{II} \chi_I^u$$

Uncoupled/Closed (FDE_u)

Subsytem TDDFT: *Response functions*

$$\delta\rho(\mathbf{r},\omega) = \sum_I \delta\rho_I(\mathbf{r},\omega)$$

Derives directly from $\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_I \chi_I(\mathbf{r},\mathbf{r}',\omega)$$

Spectrum is subsystem-additive ?!?

$$\chi_I^u = \chi_I^0 + \chi_I^0 K_{II} \chi_I^u$$

Uncoupled/Closed (FDE_u)

$$\chi_I = \chi_I^u$$

Subsytem TDDFT: *Response functions*

$$\delta\rho(\mathbf{r},\omega) = \sum_I \delta\rho_I(\mathbf{r},\omega)$$ Derives directly from $\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_I \chi_I(\mathbf{r},\mathbf{r}',\omega)$$ Spectrum is subsystem-additive ?!?

$$\chi_I^u = \chi_I^0 + \chi_I^0 K_{II} \chi_I^u$$ Uncoupled/Closed ($\mathrm{FDE_u}$)

$$\chi_I = \chi_I^u + \sum_{J\neq I} \chi_I^u K_{IJ} \chi_J$$ Coupled/Open ($\mathrm{FDE_c}$) – Holographic theory

The K_{IJ} coupling

$$K_{IJ}(\mathbf{r}_1,\mathbf{r}_2,t-t') = \frac{\delta(t-t')}{|\mathbf{r}_1-\mathbf{r}_2|} + \frac{\delta^2 E_{\mathrm{xc}}}{\delta\rho(\mathbf{r}_1,t)\delta\rho(\mathbf{r}_2,t')} + \frac{\delta^2 T_{\mathrm{s}}}{\delta\rho(\mathbf{r}_1,t)\delta\rho(\mathbf{r}_2,t')}$$

Subsytem TDDFT: *Response functions*

$$\delta\rho(\mathbf{r},\omega) = \sum_I \delta\rho_I(\mathbf{r},\omega)$$

Derives directly from $\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_I \chi_I(\mathbf{r},\mathbf{r}',\omega)$$

Spectrum is subsystem-additive ?!?

$$\chi_I^u = \chi_I^0 + \chi_I^0 K_{II} \chi_I^u$$

Uncoupled/Closed (FDE$_u$)

$$\chi_I = \chi_I^u + \sum_{J \neq I} \chi_I^u K_{IJ} \chi_J$$

Coupled/Open (FDE$_c$) – Holographic theory

The K_{IJ} coupling

$$K_{IJ}(\mathbf{r}_1,\mathbf{r}_2,t-t') = \frac{\delta(t-t')}{|\mathbf{r}_1-\mathbf{r}_2|} + \frac{\delta^2 E_{\mathrm{xc}}}{\delta\rho(\mathbf{r}_1,t)\delta\rho(\mathbf{r}_2,t')} + \frac{\delta^2 T_{\mathrm{s}}}{\delta\rho(\mathbf{r}_1,t)\delta\rho(\mathbf{r}_2,t')}$$

Subsystem TDDFT is a general theory for open systems
Let's apply it to liquid water!

The Optical Spectrum of Liquid Water

The Optical Spectrum of Liquid Water

Cooperation and Environment Characterize the Low-Lying Optical Spectrum of Liquid Water

J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

The Optical Spectrum of Liquid Water

Cooperation and Environment Characterize the Low-Lying Optical Spectrum of Liquid Water

J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

Details of the calculation

- Real-time subsystem TD-DFT, coded in eQE
  A. Krishtal, D. Ceresoli, M. Pavanello JCP **142**, *154116 (2015)*

The Optical Spectrum of Liquid Water

Cooperation and Environment Characterize the Low-Lying Optical Spectrum of Liquid Water

J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

Details of the calculation

- Real-time subsystem TD-DFT, coded in eQE
  A. Krishtal, D. Ceresoli, M. Pavanello JCP **142**, *154116 (2015)*
- Ultrasoft pseudopotentials
  X. Qian, J. Li, X. Lin, S. Yip PRB **73**, *035408 (2006)*

The Optical Spectrum of Liquid Water

Cooperation and Environment Characterize the Low-Lying Optical Spectrum of Liquid Water

J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

Details of the calculation

- Real-time subsystem TD-DFT, coded in eQE
  A. Krishtal, D. Ceresoli, M. Pavanello JCP **142**, *154116 (2015)*
- Ultrasoft pseudopotentials
  X. Qian, J. Li, X. Lin, S. Yip PRB **73**, *035408 (2006)*
- Reduce the # of Plane Waves by 80%
  A. Genova, D. Ceresoli, M. Pavanello JCP **144**, *234105 (2016)*

The Optical Spectrum of Liquid Water

Cooperation and Environment Characterize the Low-Lying Optical Spectrum of Liquid Water

J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

Details of the calculation

- Real-time subsystem TD-DFT, coded in eQE
  A. Krishtal, D. Ceresoli, M. Pavanello JCP **142**, *154116 (2015)*
- Ultrasoft pseudopotentials
  X. Qian, J. Li, X. Lin, S. Yip PRB **73**, *035408 (2006)*
- Reduce the # of Plane Waves by 80%
  A. Genova, D. Ceresoli, M. Pavanello JCP **144**, *234105 (2016)*
- Γ point for each water molecule

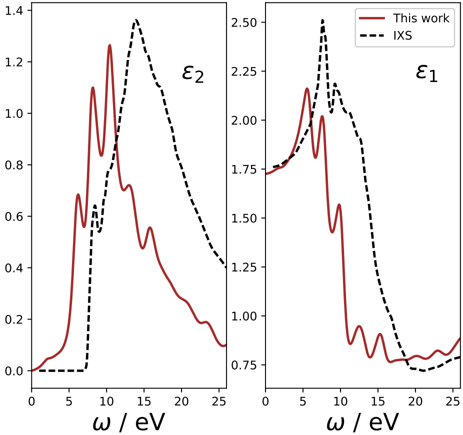
Optical Properties of Liquid Water: ϵ_1 & ϵ_2

Computation of ϵ

Optical Properties of Liquid Water: ϵ_1 & ϵ_2

Computation of ϵ

- 10 snapshots of water 64
- Average of 640 spectra

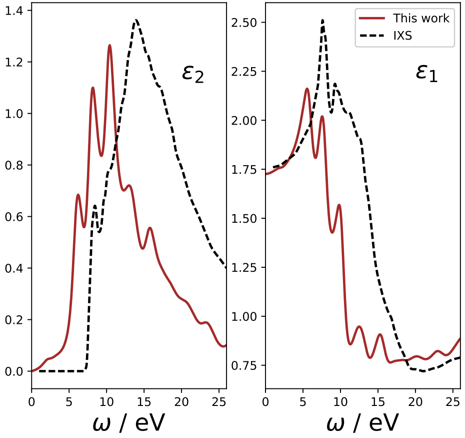


Kumar P., S. & Genova, A. & MP, J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

Optical Properties of Liquid Water: ϵ_1 & ϵ_2

Computation of ϵ

- 10 snapshots of water 64
- Average of 640 spectra
- Match experimental sum-rule in 0-25 eV window



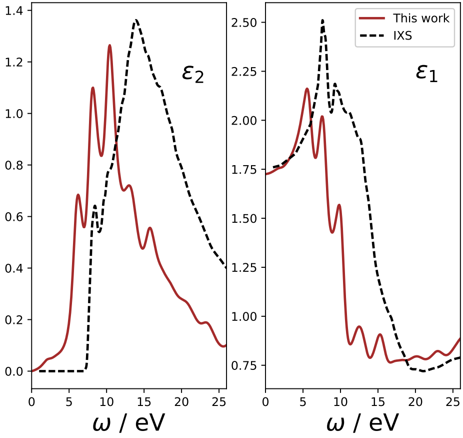
Kumar P., S. & Genova, A. & MP, J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

Optical Properties of Liquid Water: ϵ_1 & ϵ_2

Computation of ϵ

- 10 snapshots of water 64
- Average of 640 spectra
- Match experimental sum-rule in 0-25 eV window

We find. . .



Kumar P., S. & Genova, A. & MP, J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

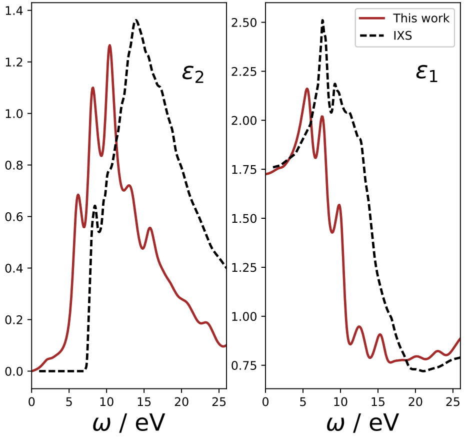
Optical Properties of Liquid Water: ϵ_1 & ϵ_2

Computation of ϵ

- 10 snapshots of water 64
- Average of 640 spectra
- Match experimental sum-rule in 0-25 eV window

We find...

- Overall good agreement across wide window of ω



Kumar P., S. & Genova, A. & MP, J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

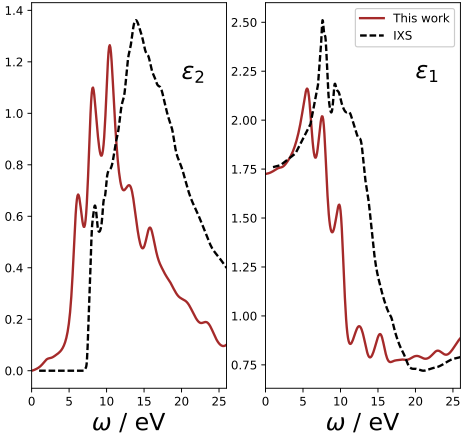
Optical Properties of Liquid Water: ϵ_1 & ϵ_2

Computation of ϵ

- 10 snapshots of water 64
- Average of 640 spectra
- Match experimental sum-rule in 0-25 eV window

We find. . .

- Overall good agreement across wide window of ω
- KS Exciton binding energy
  - $\rightarrow$ *KS gap* ~ 7.0 *eV*
  - $\rightarrow$ *Optical gap* ~ 6.4 *eV*



Kumar P., S. & Genova, A. & MP, J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

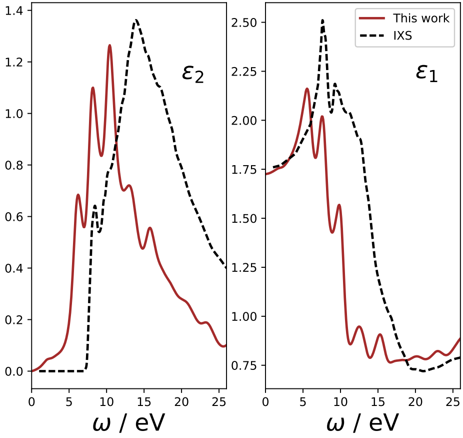
Optical Properties of Liquid Water: ϵ_1 & ϵ_2

Computation of ϵ

- 10 snapshots of water 64
- Average of 640 spectra
- Match experimental sum-rule in 0-25 eV window

We find…

- Overall good agreement across wide window of ω
- KS Exciton binding energy
  - $\rightarrow$ *KS gap* ~ 7.0 *eV*
  - $\rightarrow$ *Optical gap* ~ 6.4 *eV*
- Index of refraction $n = 1.68$



Kumar P., S. & Genova, A. & MP, J. Phys. Chem. Lett., 8 (20), pp 5077-5083 (2017)

Optical Properties of Liquid Water: ϵ_1 & ϵ_2

Dielectric Constant – Many Body Effects

Dielectric Constant – Many Body Effects

- One Body (closed):

$$\chi = \sum_I \chi_I^u$$

Dielectric Constant – Many Body Effects

- One Body (closed):

$$\chi = \sum_I \chi_I^u$$

- Many Body (open):

$$\chi = \sum_I \chi_I^u + \\ + \sum_{I \neq J} \chi_I^u K_{IJ} \chi_J$$

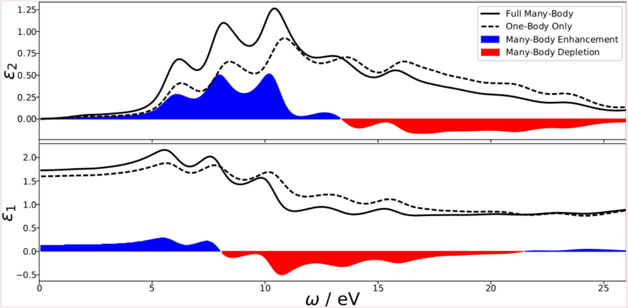
Dielectric Constant – Many Body Effects

- One Body (closed):

$$\chi = \sum_I \chi_I^u$$

- Many Body (open):

$$\chi = \sum_I \chi_I^u + \sum_{I \neq J} \chi_I^u K_{IJ} \chi_J$$



[a] D. Pan, Q. Wan, and G. Galli, Nat. Commun., 5, 3919 (2014)

Optical Properties of Liquid Water: ϵ_1 & ϵ_2

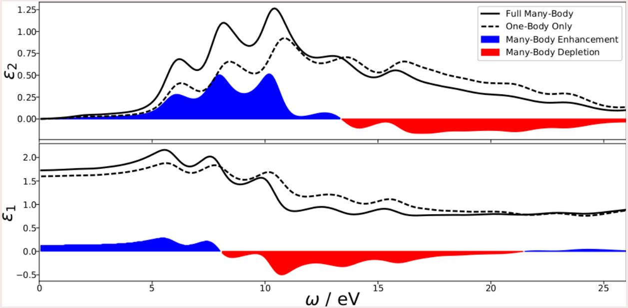
Dielectric Constant – Many Body Effects

- One Body (closed):

$$\chi = \sum_I \chi_I^u$$

- Many Body (open):

$$\chi = \sum_I \chi_I^u + \sum_{I \neq J} \chi_I^u K_{IJ} \chi_J$$



1. Oscillator strength enhanced in low-lying excitations

[a] D. Pan, Q. Wan, and G. Galli, Nat. Commun., 5, 3919 (2014)

Optical Properties of Liquid Water: ϵ_1 & ϵ_2

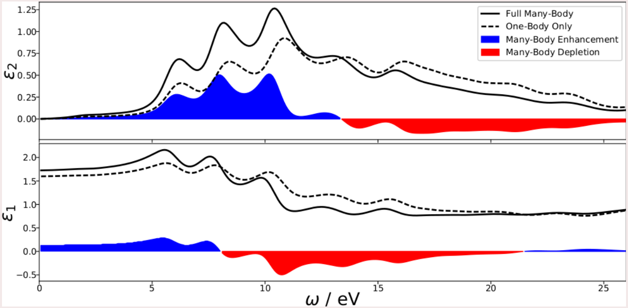
Dielectric Constant – Many Body Effects

- One Body (closed):

$$\chi = \sum_I \chi_I^u$$

- Many Body (open):

$$\chi = \sum_I \chi_I^u + \sum_{I \neq J} \chi_I^u K_{IJ} \chi_J$$



1. Oscillator strength enhanced in low-lying excitations
2. Oscillator strength depleted in high-lying excitations

[a] D. Pan, Q. Wan, and G. Galli, Nat. Commun., 5, 3919 (2014)

Optical Properties of Liquid Water: ϵ_1 & ϵ_2

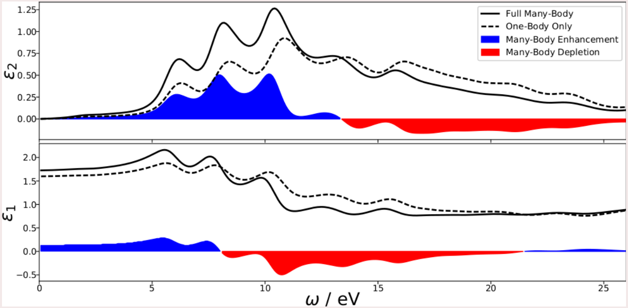
Dielectric Constant – Many Body Effects

- One Body (closed):

$$\chi = \sum_I \chi_I^u$$

- Many Body (open):

$$\chi = \sum_I \chi_I^u + \sum_{I \neq J} \chi_I^u K_{IJ} \chi_J$$



1. Oscillator strength enhanced in low-lying excitations
2. Oscillator strength depleted in high-lying excitations
3. Many-body effects do not change first peak position

[a] D. Pan, Q. Wan, and G. Galli, Nat. Commun., 5, 3919 (2014)

Optical Properties of Liquid Water: ϵ_1 & ϵ_2

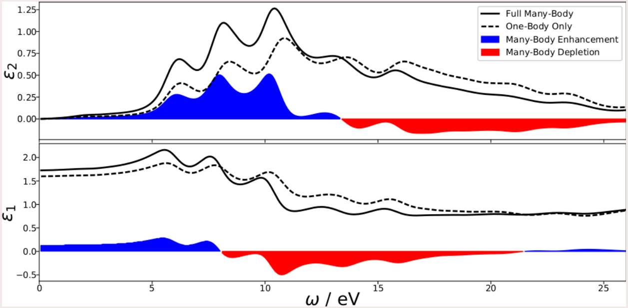
Dielectric Constant – Many Body Effects

- One Body (closed):

$$\chi = \sum_I \chi_I^u$$

- Many Body (open):

$$\chi = \sum_I \chi_I^u + \sum_{I \neq J} \chi_I^u K_{IJ} \chi_J$$



1. Oscillator strength enhanced in low-lying excitations
2. Oscillator strength depleted in high-lying excitations
3. Many-body effects do not change first peak position
4. Consistent with Galli's explanation for increased index of refraction with pressure[a]

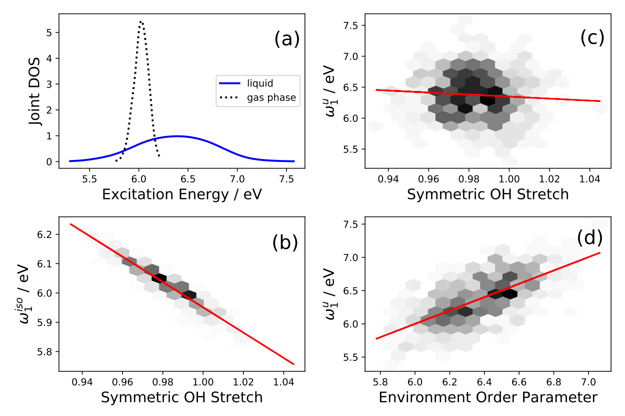
[a] D. Pan, Q. Wan, and G. Galli, Nat. Commun., 5, 3919 (2014)

First Absorption Band of Liquid Water: ω_1

Role of the Environment: Urbach tail and ω_1 peak position

First Absorption Band of Liquid Water: ω_1

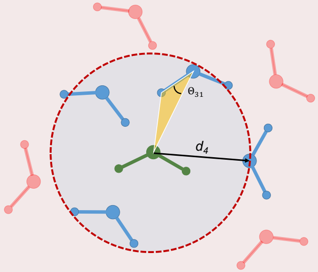
Role of the Environment: Urbach tail and ω_1 peak position

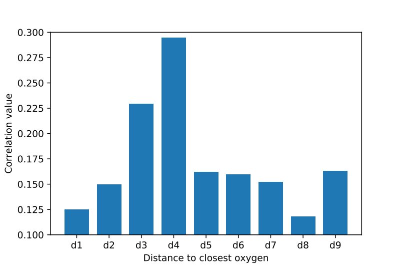


- Urbach tail entirely due to environment
- ω_1 and OH stretching do not correlate in the liquid
- Environment Order Parameter (**EOP**): Regression of 300+ descriptors
- Correlation of EOP to ω_1 is 0.65

Optical Properties of Liquid Water

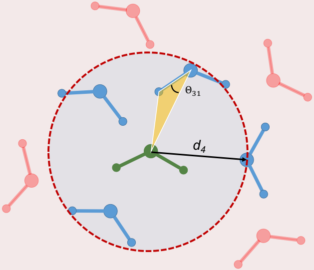
Environment Order Parameter: Simplified depiction

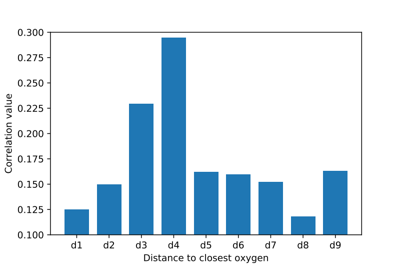




Optical Properties of Liquid Water

Environment Order Parameter: Simplified depiction

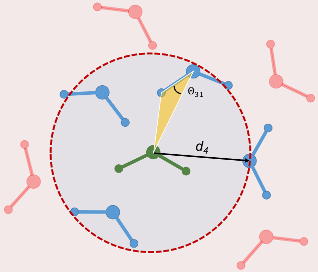


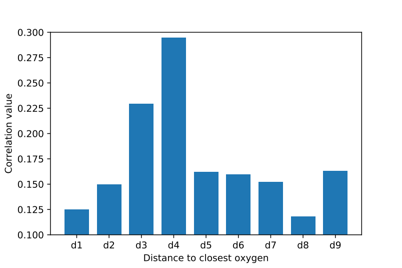


What is “Environment Order Parameter” made of?

Optical Properties of Liquid Water

Environment Order Parameter: Simplified depiction



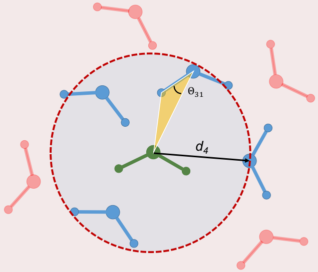


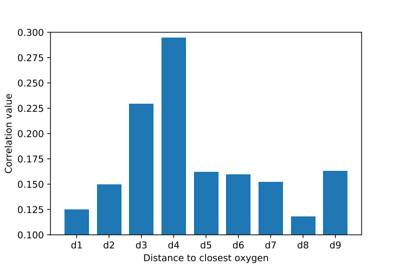
What is “Environment Order Parameter” made of?

- Accepted Hydrogen Bonds is the highest contribution to EOP

Optical Properties of Liquid Water

Environment Order Parameter: Simplified depiction



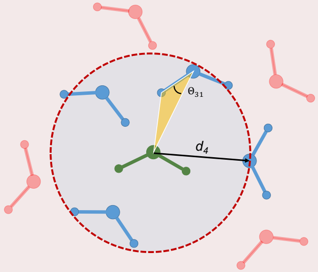


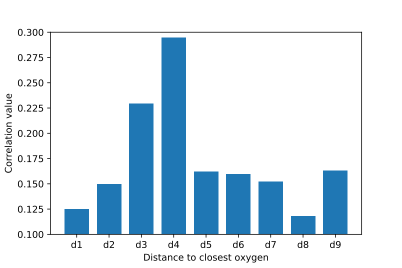
What is "Environment Order Parameter" made of?

- Accepted Hydrogen Bonds is the highest contribution to EOP
- Distances and angles within the 1st solvation shell

Optical Properties of Liquid Water

Environment Order Parameter: Simplified depiction



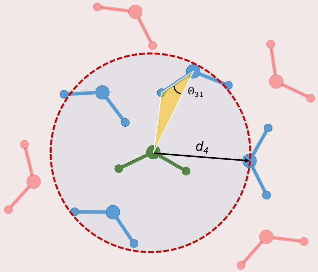


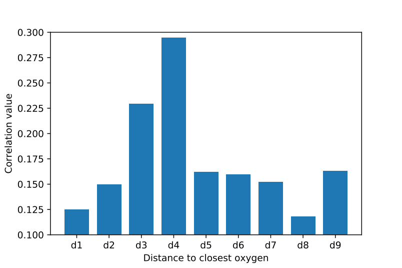
What is "Environment Order Parameter" made of?

- Accepted Hydrogen Bonds is the highest contribution to EOP
- Distances and angles within the 1^{st} solvation shell
- Linear and Neural Network regressions lead to the same result

Optical Properties of Liquid Water

Environment Order Parameter: Simplified depiction



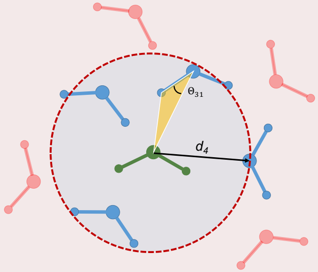


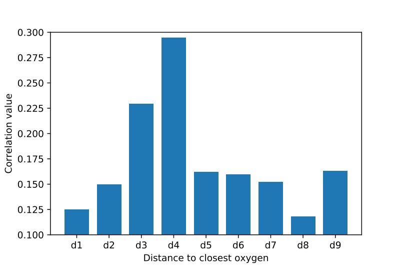
What is "Environment Order Parameter" made of?

- Accepted Hydrogen Bonds is the highest contribution to EOP
- Distances and angles within the 1^{st} solvation shell
- Linear and Neural Network regressions lead to the same result
- Same correlations between EOP and KS eigenvalue difference

Optical Properties of Liquid Water

Environment Order Parameter: Simplified depiction





What is "Environment Order Parameter" made of?

- Accepted Hydrogen Bonds is the highest contribution to EOP
- Distances and angles within the 1st solvation shell
- Linear and Neural Network regressions lead to the same result
- Same correlations between EOP and KS eigenvalue difference

. . . we have dissected liquid water. . .

Acknowledgments

Postdocs, Students & Collaborators

Current PRG members

Postdocs:

- Dr. Wenhui Mi
- Dr. Muhammed Acikgoz
- Dr. Pablo Ramos

Graduate Students:

- Rupali Chawla
- Alina Umerbekova
- Jack Maranhao

Funding:

- NSF CAREER
- DOE CTC

Alumni & Collaborators

Alumni:

- **Johannes Tölle (Münster University)**
- **Dr. Alessandro Genova (@ Kitware)**
- **Prof. Alisa Krishtal (@ NJIT)**
- **Dr. Debalina Sinha (@ L'Oreal)**

Collaborators:

- **Dr. Davide Ceresoli (CNR)**
- **Prof. Rob DiStasio (Cornell)**
- **Dr. Andre Gomes (CNRS)**
- **Prof. Oliviero Andreussi (North Texas)**
- **Prof. Henk Eshuis (Montclair State)**
- **Dr. Damien Riedel (Paris Sud)**