Ensemble density-functional theory in real space: 1D models approaching the thermodynamic limit; benchmarks on small molecules; and thermal ensembles

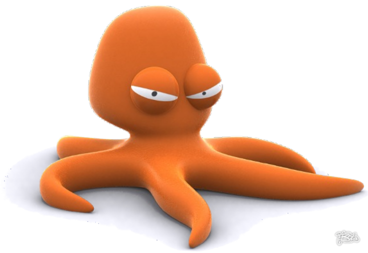
David A. Strubbe,[1] Remi Leano,[2] Uday Panta,[1] Aurora Pribram-Jones[2]
1. Department of Physics, University of California, Merced
2. Department of Chemistry and Biochemistry, University of California, Merced

UNIVERSITY OF CALIFORNIA
MERCED

R. J. Leano, A. Pribram-Jones, and D. A. Strubbe, *Electron. Struct.* 6, 035003 (2024)

U. Panta and D. A. Strubbe, *Electron. Struct.* 6, 045004 (2024)

SAIL
Strubbe
Ab Initio
Laboratory



16 Apr 2025
Benasque TDDFT workshop

Encuentro científico internacional en Benasque

19/09/2016

Duración: 00:04:03 seg

Con: Paco Doblas

El Centro de Ciencias 'Pedro Pascual' del municipio oscense de Benasque acoge entre este 20 y este 23 de septiembre un encuentro de 85 científicos de diversos países que analizarán el comportamiento de los electrones. De esta cita habla en Aragón Radio el profesor de la Universidad de California David Strubbe.

Tags: 2016 Aragón Radio Benasque ciencia científico David Strubbe encuentro septiembre

http://sail.ucmerced.edu/radio.html

Outline

1. Introduction to ensemble DFT
2. Toward the thermodynamic limit
3. Perturbative ensemble DFT (and TDHF) implementation
4. Appearance of thermalization in TDDFT

Ground State Density Functional Theory (GS-DFT)

$$E^{\text{tot}}[\rho]$$

- Excitation energies as a difference of Kohn-Sham eigenvalues.

- GS functional approximations.

$$E_{\text{Hxc}}[\rho]$$

- Band gap with LDA/PBE: Underestimated

Ensemble Density Functional Theory (EDFT)

$$E^{\text{tot}}\left[\sum_{m=1}^{M_I} \mathtt{w}_m \rho_m\right]$$

- Excitation energies extracted from the ensemble energy.

- *Ensemble* functional approximations.

$$E^{w}_{\text{Hxc}}[\rho^{w}]$$

- Calculated band gaps: ***?***

Why bother with EDFT?

Drawbacks of other methods

- GS-DFT underestimates band gaps.

Phys. Rev. A **98**, 022513 (2018)
Phys. Rev. Lett. **51**, 1884 (1983)

- TDDFT inadequately describes double and multiple excitations, and struggles with periodic systems.

Annu. Rev. Phys. Chem. **73**, 117 (2022)

- ΔSCF corrections for standard exchange-correlation approx. go to zero in periodic systems.

Phys. Rev. Lett. **51**, 1888 (1983)
Phys. Rev. Lett. **80**, 3161 (1998)

- Hybrid functionals don’t help with multi-reference excitations.

Prospects of this method

- Based on a variational theorem.
- Can correct GS energies.

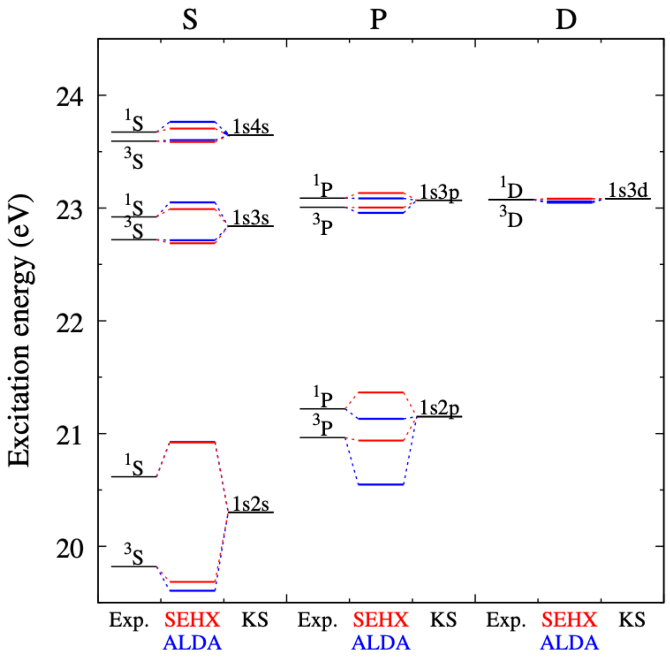
Phys. Rev. A **37**, 2809 (1988)

- Can more easily treat multiple- and charge-transfer excitations.

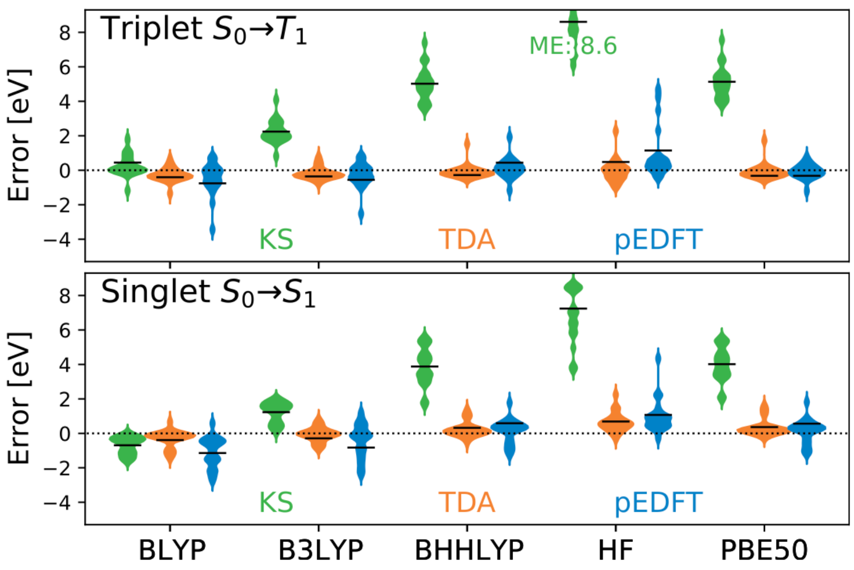
Phys. Rev. B. **95**, 035120 (2017)

Motivation:

- Ensemble DFT has so far been developed and tested for isolated model systems, atoms, and molecules.



Z.-h. Yang, A. Pribram-Jones, K. Burke, and C. A. Ullrich, *Phys. Rev. Lett.* 119, 033003 (2017)



T. Gould, Z. Hashimi, L. Kronik, and S. Dale, *J. Phys. Chem. Lett. 13*, 2452 (2022)

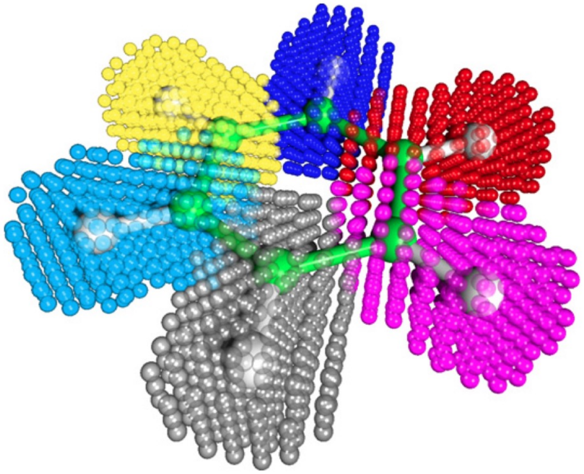
Objectives:

Let’s broaden the scope of applications!

1. Can we use it for periodic systems?
- Does it help with KS-DFT’s band-gap problem for periodic solids?
- Do corrections go to zero?
- What kind of density-functional approximations are needed to obtain non-trivial corrections?

2. Can we use it on larger systems?

Octopus: real-space DFT, TDDFT, etc.



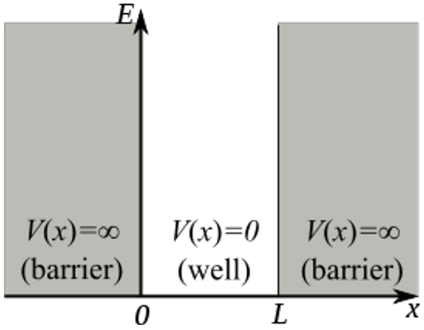
EDFT approaches on real systems have used Gaussian basis sets.
How about real space?

Octopus:

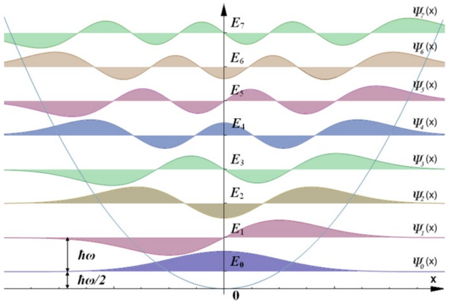
- Derivatives by finite differences with stencils
- Systematically convergeable basis set, like plane waves
- Real-space is most efficient parallelization for very large systems
- Finite or periodic boundary conditions
- Theory levels: all XC functionals of libxc, meta-GGAs, many hybrids, optimized effective potential (e.g. KLI), Hartree, Hartree-Fock
- Model systems (quantum dots, free-electron gas)
- Unusual features: complex scaling for resonances, time-propagation TDDFT, Sternheimer linear response (DFPT), Kohn-Sham inversion, Floquet theory, quantum electrodynamics, ...

N. Tancogne-Dejean … D. A. Strubbe ... *et al.*, *J. Chem. Phys.* 152, 124119 (2020)
X. Andrade, D. A. Strubbe, *et al.*, *Phys. Chem. Chem. Phys.* 17, 31371-31396 (2015)

Model Systems in Octopus



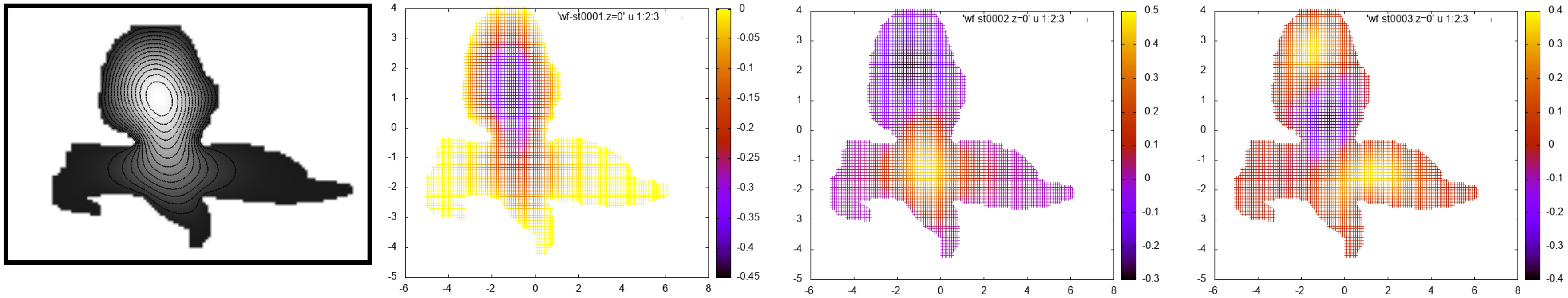
Infinite potential well



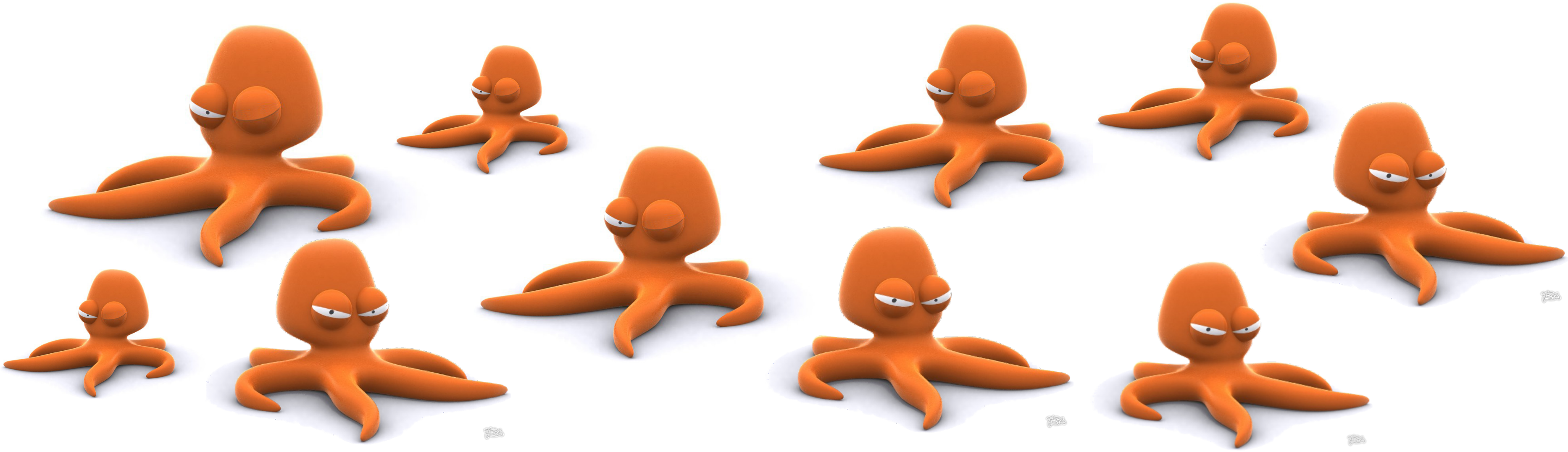
Harmonic Oscillator

Free-electron gas

- Defined naturally in real space, and easily calculated in Octopus.
- May be difficult or impractical to describe potential in plane-waves or wavefunctions in localized orbitals.

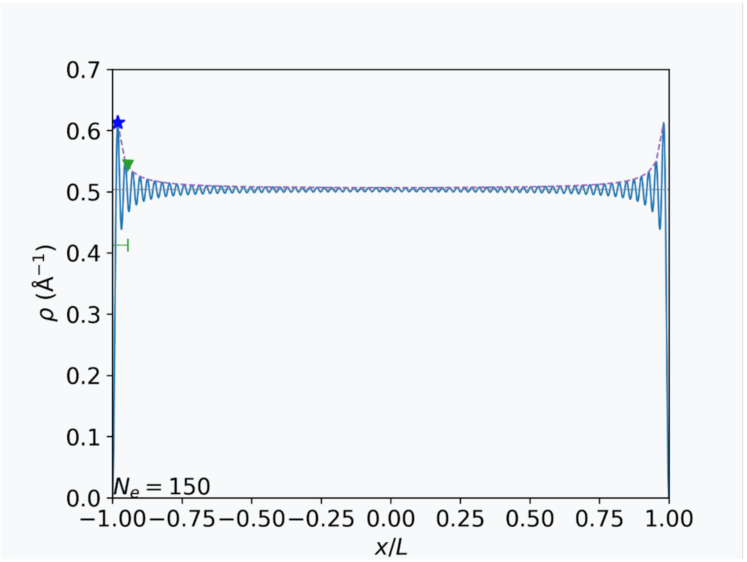


Particle in an Octopus

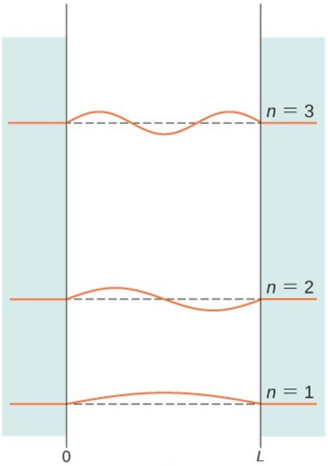


The Thermodynamic Limit: Particle in a Box to Uniform Electron Gas, in 1D

- How can we study periodic systems without a periodic formulation?
- We seek to study DFT in the **thermodynamic limit**, with a 1D particle in a box potential as our *Kohn-Sham potential*. We increase N_e and L while holding the density constant.
- Limit is the uniform electron gas (UEG). Both external and Kohn-Sham potentials are constant in this limit.



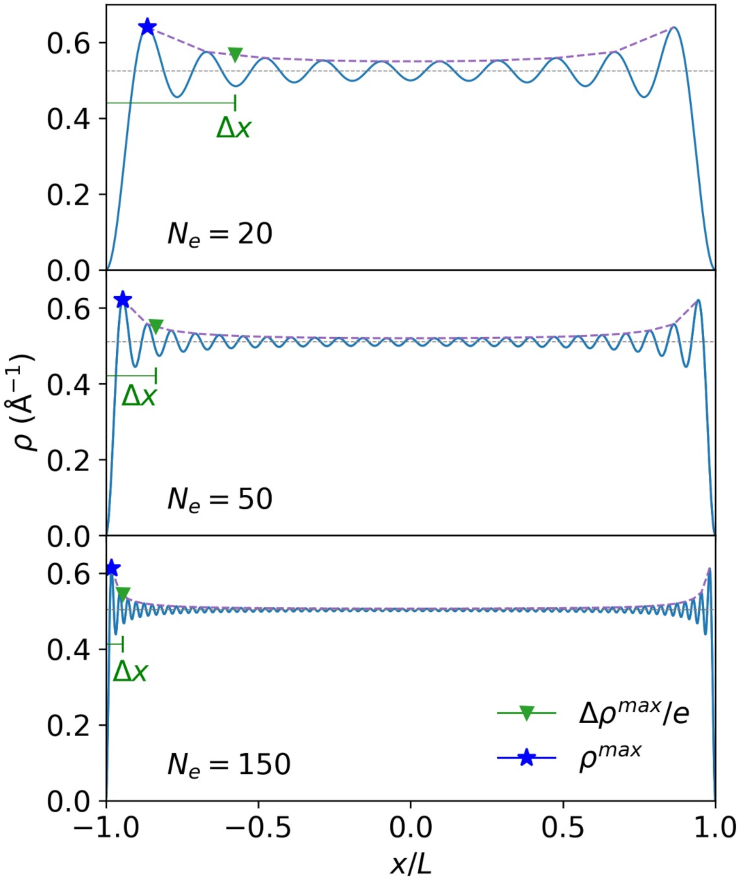
$$\frac{N_e}{2L} = 0.5\ \text{Å}^{-1} \qquad N_e, L \to \infty$$

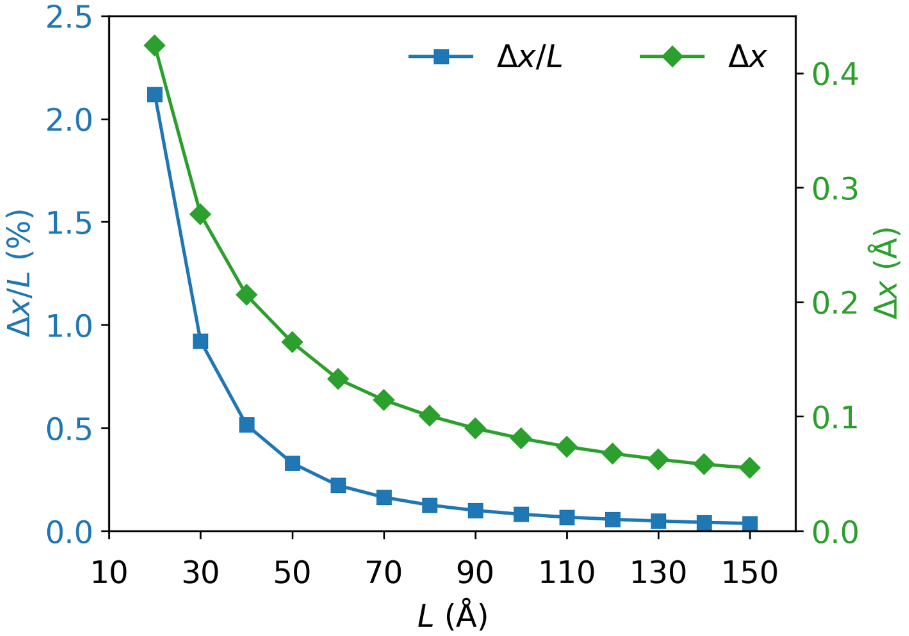


$$\hat{\mathcal{H}}^{\text{1D-PIB}}_{\text{non-int}} = -\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2} + V(x)$$

$$V(x) = \begin{cases} 0, & -L < x < L \\ \infty, & x \le -L \text{ or } x \ge L \end{cases}$$

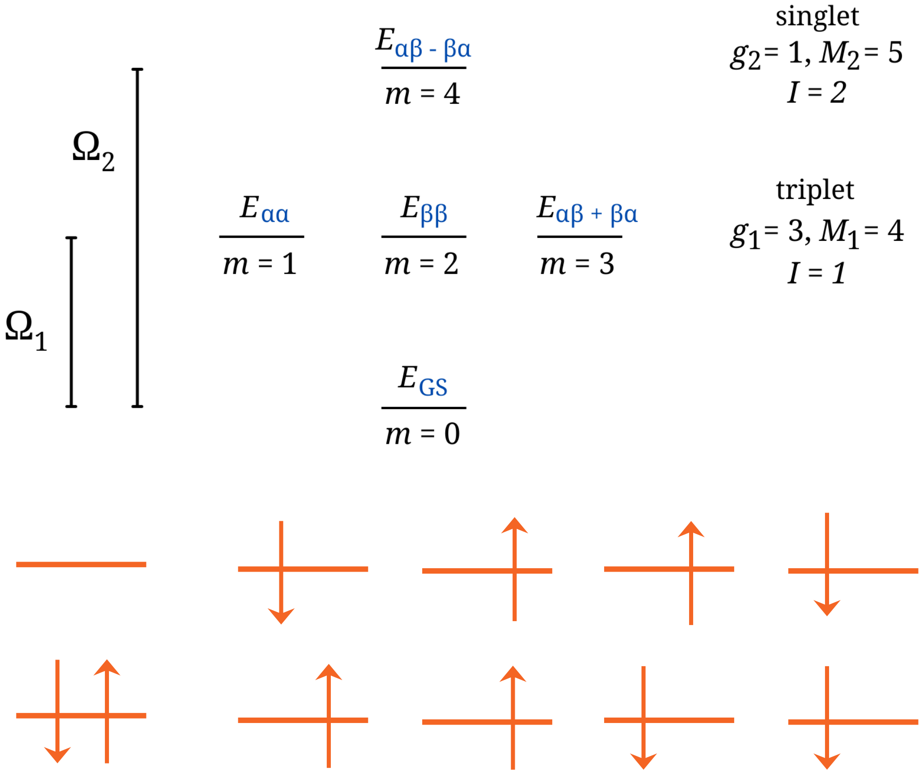
Density Approaches the Uniform Electron Gas





As the number of particles considered increases, the density becomes more uniform, and the edges become smaller. With increasing N_e, the edge region shrinks relatively **and in absolute size.**

Constructing Ensembles and Corrections



Ω_2

Ω_1

$E_{\alpha\beta\,-\,\beta\alpha}$
$m = 4$

$E_{\alpha\alpha}$
$m = 1$

$E_{\beta\beta}$
$m = 2$

$E_{\alpha\beta\,+\,\beta\alpha}$
$m = 3$

E_{GS}
$m = 0$

singlet
$g_2 = 1, M_2 = 5$
$I = 2$

triplet
$g_1 = 3, M_1 = 4$
$I = 1$

GOK-I ensemble

$$\mathtt{w}_m = \begin{cases} \frac{1-\mathtt{w}g_I}{M_I-g_I} & m < M_I - g_I, \\ \mathtt{w} & m \geq M_I - g_I, \end{cases}$$

E. K. U. Gross *et al.*, *Phys. Rev. A* 37, 2809 (1988)

Density-Functional Approximations (DFAs) for EDFT

Many DFAs have been developed; an ongoing challenge. Let’s see what happens with a very simple one.

Consider two options for Hartree term:

“traditional” (weight-independent)

$$E_{\mathrm{H}}^{\mathrm{trad}}[\rho] = E_{\mathrm{H}}\left[\sum_{m=0}^{M_I-1} \mathtt{w}_m \rho_m(r)\right]$$

ensemble-generalized Hartree

$$E_{\mathrm{H},w}[\rho] = \sum_{m=0}^{M_I-1} \mathtt{w}_m E_{\mathrm{H}}[\rho_m(r)]$$

ensemble-generalized Local Spin Density Approximation (LSDA)

$$E_{\mathrm{xc},w}^{\mathrm{LSDA}}[\rho] = \sum_{m=0}^{M_I-1} \mathtt{w}_m E_{\mathrm{xc}}^{\mathrm{LSDA}}[\rho_m(r)]$$

soft Coulomb potential with *a* = 1 Bohr

$$v_{\mathrm{sc}}(x) = \frac{1}{\sqrt{x^2+a^2}}$$

1D LSDA for this interaction from Quantum Monte Carlo:

N. Helbig, J. I. Fuks, M. Casula, M. J. Verstraete, M. A. L. Marques, I. V. Tokatly, and A. Rubio, *Phys. Rev. A* 83, 032503 (2011).
M. Casula, S. Sorella, and G. Senatore, *Phys. Rev. B* 74, 245427 (2006).

Traditional Hartree -> no contribution, “XC.” Ensemble-generalized -> contributes, “HXC.”

Can we just apply EDFT to a periodic system?

$$\mathtt{w}_m = \begin{cases} \frac{1-\mathtt{w}g_I}{M_I-g_I} & m < M_I - g_I, \\ \mathtt{w} & m \geq M_I - g_I, \end{cases}$$

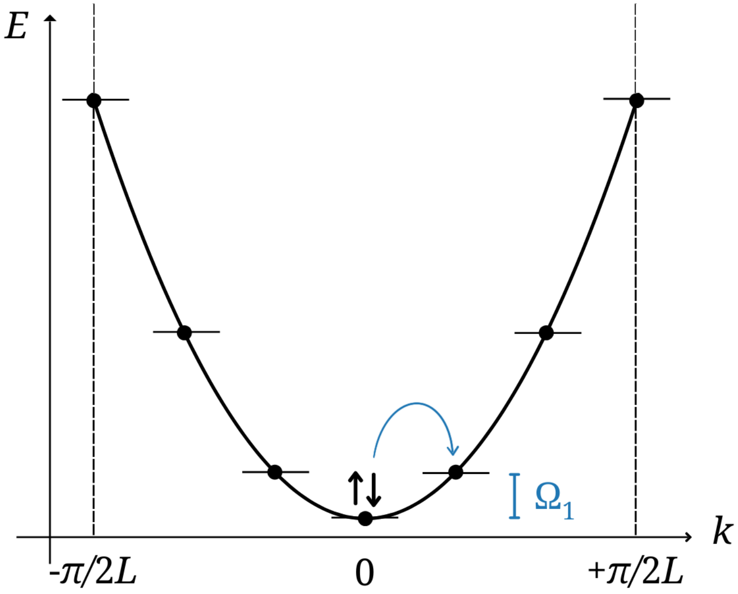
E. K. U. Gross *et al.*, *Phys. Rev. A* 37, 2809 (1988)

GOK-I ensemble is based on a discrete set of states.
But solids have a continuous spectrum.

What if we just artificially discretize the *k*-points?
In a UEG, all densities are constant and equal.

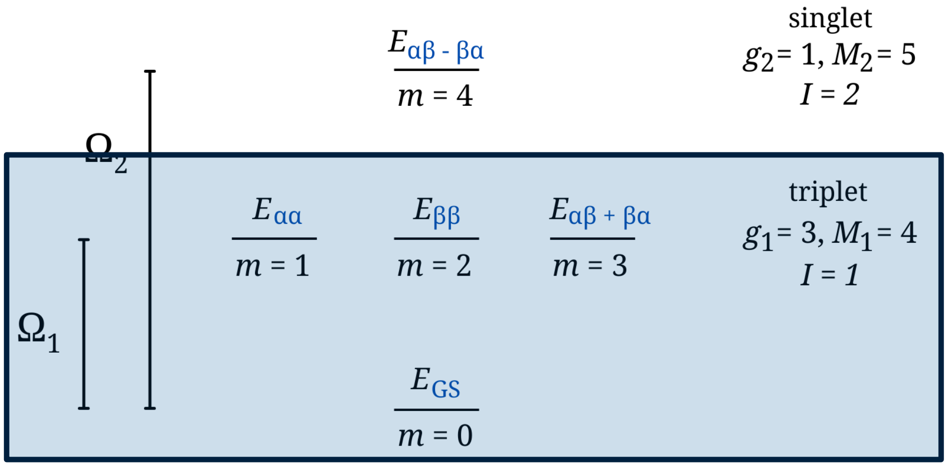
$$\rho_{\alpha\alpha}(r) = \left|\sqrt{\frac{1}{2L}}e^{ik_1x}\alpha(\omega)\right|^2 + \left|\sqrt{\frac{1}{2L}}e^{ik_2x}\alpha(\omega)\right|^2 = \frac{1}{L}$$

$$\left.\frac{\partial E^w_{\mathrm{Hxc}}[\rho]}{\partial \mathtt{w}}\right|_{\rho=\rho^w} = -3E_{\mathrm{Hxc}}[\rho_{\mathrm{GS}}] + E_{\mathrm{Hxc}}[\rho_{\alpha\alpha}] + E_{\mathrm{Hxc}}[\rho_{\beta\beta}] + E_{\mathrm{Hxc}}[\rho_{\alpha\beta\pm\beta\alpha}] = 0$$



Corrections always vanish.
Not a useful approach.
(Theoretical justification unclear anyway.)

Bi-ensemble



$E_{\alpha\beta\text{ - }\beta\alpha}$

$m = 4$

singlet

$g_2 = 1$, $M_2 = 5$

$I = 2$

Ω_2

$E_{\alpha\alpha}$

$m = 1$

$E_{\beta\beta}$

$m = 2$

$E_{\alpha\beta\text{ + }\beta\alpha}$

$m = 3$

triplet

$g_1 = 3$, $M_1 = 4$

$I = 1$

Ω_1

E_{GS}

$m = 0$

$$\mathtt{w}_m = \begin{cases} 1 - 3\mathtt{w} & m < 1, \\ \mathtt{w} & m \geq 1. \end{cases}$$

$$\Omega_1 = \epsilon_{n=N_e/2+1} - \epsilon_{n=N_e/2} + \frac{1}{3}\left.\frac{\partial E^{w,I=2}_{\text{Hxc}}[\rho]}{\partial \mathtt{w}}\right|_{\rho=\rho^w_{I=2}}$$

$$\left.\frac{\partial E^{w,I=2}_{\text{Hxc}}[\rho]}{\partial \mathtt{w}}\right|_{\rho=\rho^w_{I=2}} = -3E_{\text{Hxc}}[\rho_{\text{GS}}] + 2E_{\text{Hxc}}[\rho_{\alpha\alpha}] + E_{\text{Hxc}}[\rho_{\alpha\beta\pm\beta\alpha}] \, .$$

Same density as singlet;
LSDA can’t distinguish.

$$\left.\frac{\partial E^{w,I=2}_{\text{Hxc}}[\rho]}{\partial \mathtt{w}}\right|_{\rho=\rho^w_{I=2}} = -3E_{\text{Hxc}}[\rho_{\text{GS}}] + 3E_{\text{Hxc}}[\rho_{\alpha\alpha}] \, ,$$

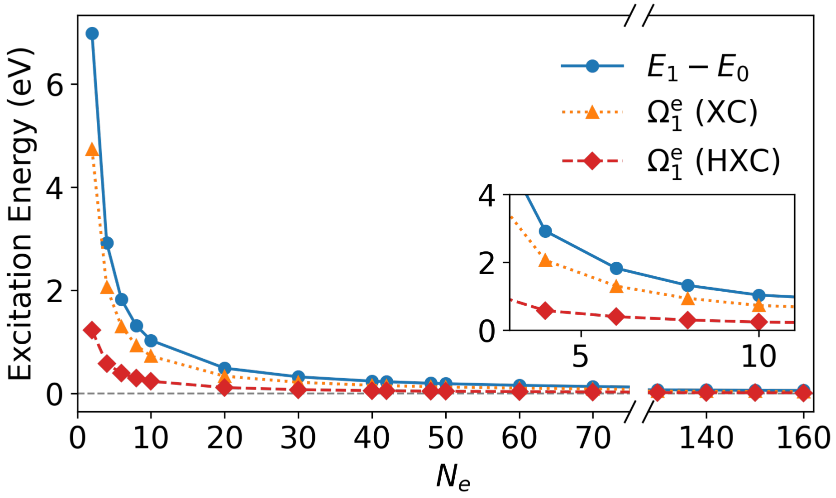
A) Symmetry-enforced

$$\left.\frac{\partial E^{w,I=2}_{\text{Hxc}}[\rho]}{\partial \mathtt{w}}\right|_{\rho=\rho^w_{I=2}} = -3E_{\text{Hxc}}[\rho_{\text{GS}}] + 2E_{\text{Hxc}}[\rho_{\alpha\alpha}] + E_{\text{Hxc}}[\rho_{\alpha\beta\pm\beta\alpha}] \, .$$

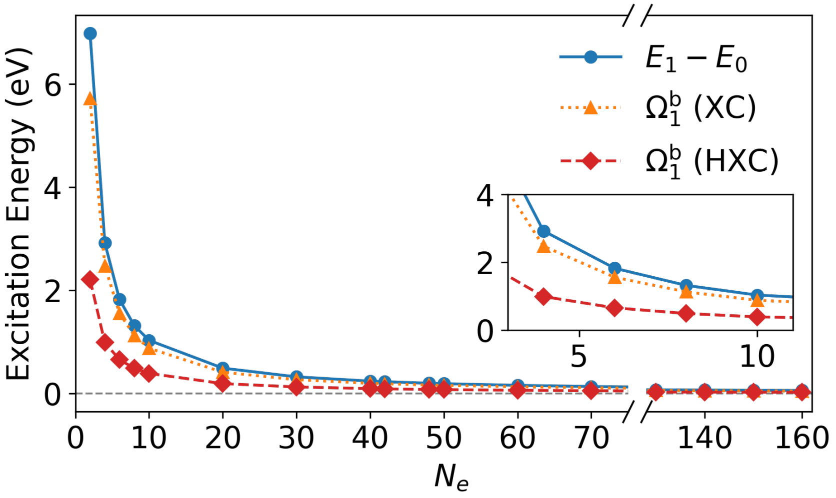
B) Symmetry-broken

Bi-ensemble: triplet excitation energies

Symmetry-enforced



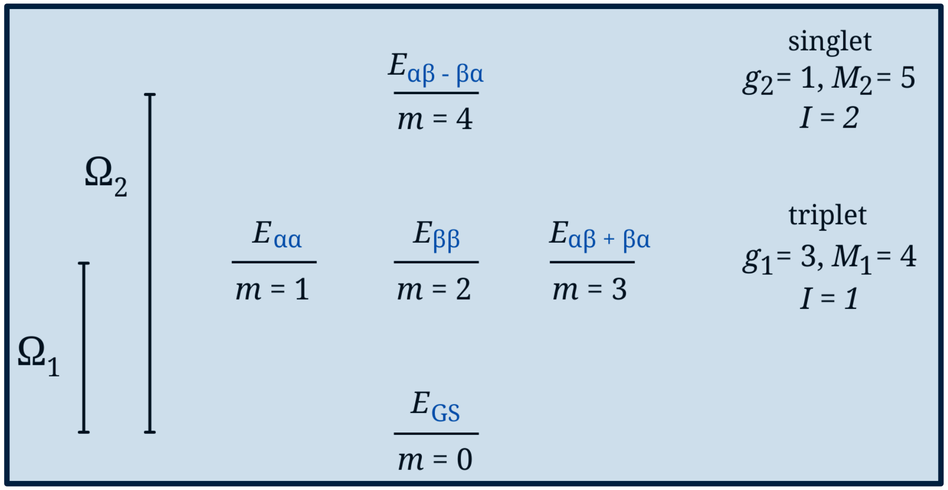
Symmetry-broken



All corrections positive (no triplet instability) and tend to zero (it’s a metal).

Reduced excitation energy vs KS.
HXC is much less than XC.

Tri-ensemble



$$\mathtt{w}_m = \begin{cases} \frac{1-\mathtt{w}}{4} & m < 4, \\ \mathtt{w} & m \geq 4. \end{cases}$$

$$\Omega_2 \approx \epsilon^{w_2}_{n=N_e/2+1} - \epsilon^{w_2}_{n=N_e/2} + \left.\frac{\partial E^{w,I=3}_{\rm Hxc}[\rho]}{\partial \mathtt{w}}\right|_{\rho=\rho^w_{I=3}} + \frac{1}{4}\left.\frac{\partial E^{w,I=2}_{\rm Hxc}[\rho]}{\partial \mathtt{w}}\right|_{\rho=\rho^w_{I=2}}$$

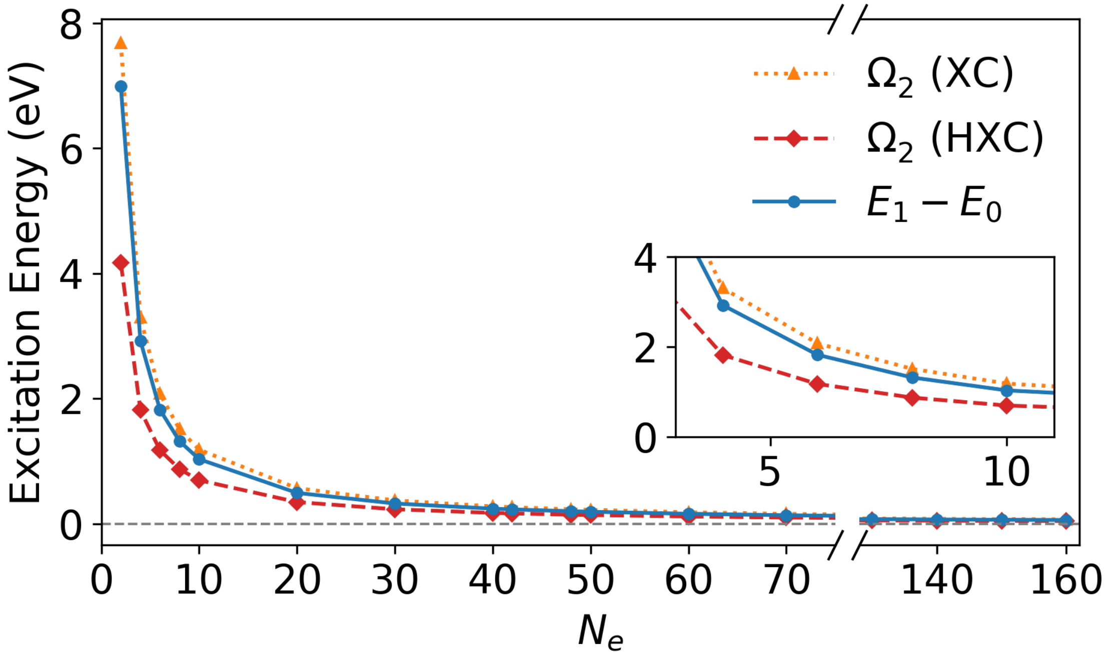
after a lot of algebraic derivation.

$$\left.\frac{\partial E^{w,I=3}_{\rm Hxc}[\rho]}{\partial \mathtt{w}}\right|_{\rho=\rho^w_{I=3}} = -\frac{1}{4}\left(E_{\rm Hxc}[\rho_{\rm GS}] + E_{\rm Hxc}[\rho_{\alpha\alpha}] + E_{\rm Hxc}[\rho_{\beta\beta}] + E_{\rm Hxc}[\rho_{\alpha\beta+\beta\alpha}]\right) + E_{\rm Hxc}[\rho_{\alpha\beta-\beta\alpha}]\,.$$

$$\Omega_2 \approx \epsilon_{n=N_e/2+1} - \epsilon_{n=N_e/2} - E_{\rm Hxc}[\rho_{\rm GS}] + E_{\rm Hxc}[\rho_{\alpha\beta\pm\beta\alpha}]\,.$$

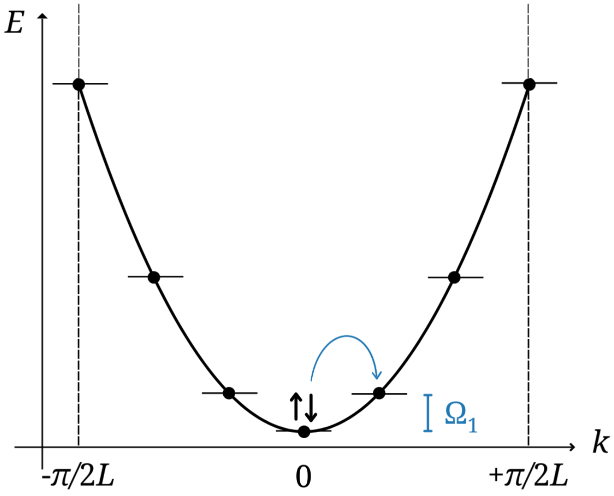
Ends up the same whether symmetry-enforced or symmetry-broken.

Tri-ensemble: singlet excitation energies



Excitation energies are positive but tend to zero (again, metal).
XC contribution is positive.
H contribution is negative.

Effective Masses: does everything just vanish?



$$E = \frac{\hbar^2 k^2}{2m^*}$$

Classic approach for metals and semiconductors: fit curvature of parabolic band, or parametrize from experiments like Hall effect

Due to interactions in general: in lattice in real systems, but also electron-electron interactions, like here.

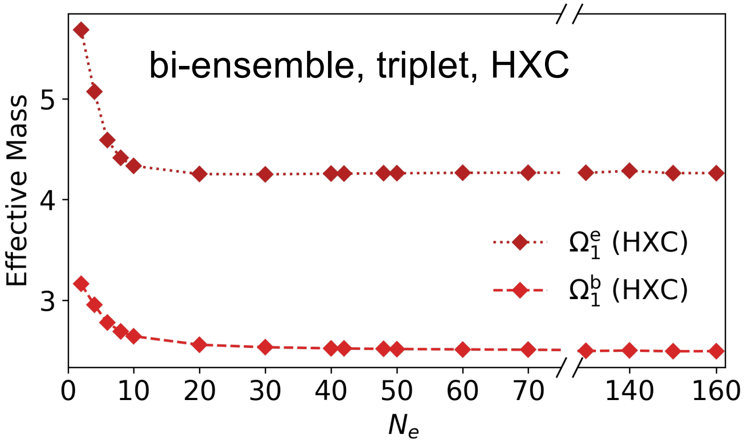
Description of effective masses is classic test of interactions in many-body methods, e.g. quantum Monte Carlo.

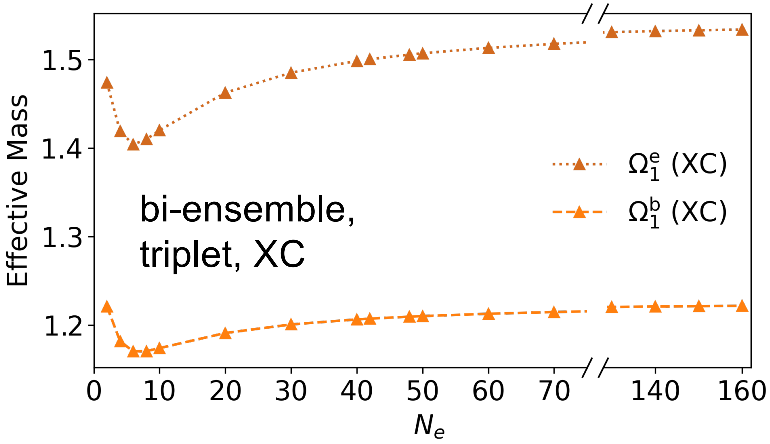
Can show analytically: LDA in UEG gives bare mass, no renormalization.

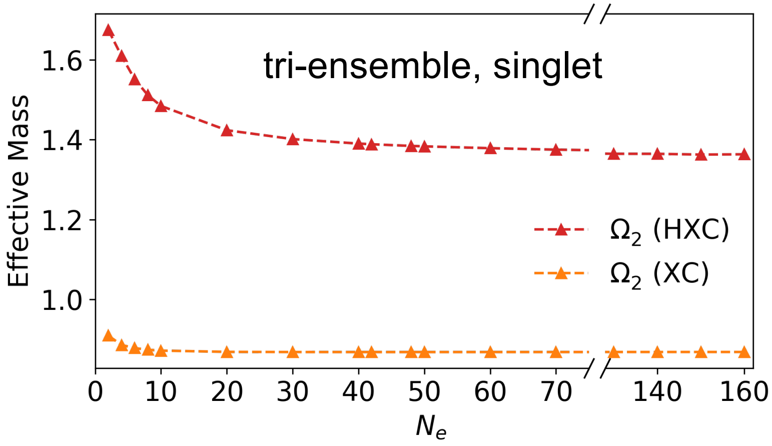
We can estimate an effective mass from our results assuming this picture:

$$\frac{\Delta E^{\text{ip}}}{\Delta E^{\text{int}}} = \frac{E_I - E_0}{\Omega_I} = \frac{\frac{\hbar^2 k_2{}^2}{2m_e} - \frac{\hbar^2 k_1{}^2}{2m_e}}{\frac{\hbar^2 k_2{}^2}{2m^*} - \frac{\hbar^2 k_1{}^2}{2m^*}} = \frac{m^*}{m_e}$$

Effective Masses, toward the thermodynamic limit







Effective masses in comparison to 2D and 3D uniform electron gas

	Excitation	HXC	XC
triplet	Ω_1^{e}	4.263	1.534
triplet	Ω_1^{b}	2.495	1.222
singlet	Ω_2	1.363	0.8684

density parameter
(Wigner-Seitz radius)

$$r_s^{3\mathrm{D}} = \frac{3}{4\pi}\frac{a_0}{\rho^{1/3}}$$

$$r_s^{1\mathrm{D}} = \frac{a_0}{2\rho} = 1.89$$

in our case

1D, GW, contact interaction not soft Coulomb): **1** to **2.5**.
B. Tanatar and E. Demirel, *phys. status solidi b* 220, 909–22 (2000)

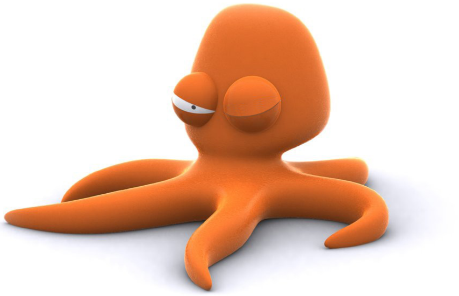
2D: **0.955(2)** for $r_s = 1$; **1.04(2)** for $r_s = 4$. (paramagnetic)
N. D. Drummond and R. J. Needs, *Phys. Rev. B* 87, 045131 (2013).

3D: **0.955(1)** for $r_s = 1$ and **0.996(3)** at $r_s = 4$. K. Haule and K. Chen, *Sci. Rep.* 12, 2294 (2022).
0.85 at $r_s \approx 4$. S. Azadi, N. D. Drummond, and W. M. C. Foulkes, *Phys. Rev. Lett.* 127, 086401 (2021).
< 1 at $r_s \leq 1$ (high-density regime). A. Krakovsky and J. K. Percus, *Phys. Rev. B* 53, 7352–7356 (1996).

Conclusions

- Approach to the thermodynamic limit with ensemble-generalized LSDA gives zero gap corrections, as expected.
- Non-trivial effective mass renormalization, similar to 2D and 3D electron gas results.
- Spin-symmetry-breaking effects of LSDA have only a moderate effect.
- Ensemble-generalized Hartree reduces excitation energies, may be less physical.
- Promising indications for development of a periodic EDFT: could give useful results even from simple approximations.
- Next: semiconducting Kronig-Penney model.

R. J. Leano, A. Pribram-Jones, and D. A. Strubbe, *Electron. Struct.* 6, 035003 (2024)



Excitation Energies

- Traditional Time-dependent Density Functional Theory (TDDFT) approach is computationally expensive and cannot handle multiple naturally.

TDDFT:

Tamm-Dancoff Approximation:

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|r_{12}^{-1} + f_{xc}|jb)$$ Unocc-occ basis

Hirata, S. *et al.*, *Chem. Phys. Lett.* 314, 291-299 (1999)

- Ensemble DFT (EDFT) can inherently handle multiple excitations while being less expensive. However, EDFT approaches have not been tested on variety of systems.

Perturbative EDFT (pEDFT): (start with Kohn-Sham reference)

HOMO-LUMO approach: correction to unoccupied level energy

$$A_{a,b} = \left\langle a|\hat{H}_{KS}|b\right\rangle + \left\langle a|v_{xc}^{eff}|b\right\rangle$$ Smaller space (unocc basis)

Gould, T. *et al., J Phys Chem Lett*, *13*, 2452 (2022)

DEC approach: correction to KS eigenvalue difference

$$\Delta\omega_I^{\mathrm{SEHX}} = H_I/g_I - H_0/g_0.$$ No diagonalization

Yang, Zeng-hui et al., *Phys Rev Lett* 119, 033003 (2017)

- However, oscillator strength for EDFT approaches is unknown.

Comparisons of real space and Gaussian-type orbitals

- Real-space codes cannot practically do all-electron full-potential calculations, due to divergence of 1/*r*. Instead pseudopotentials are used (LDA or PBE).

- Basis set is far larger. e.g. acetaldehyde aug-cc-pvtz has 496 orbitals, but sphere of radius 10 Å and spacing 0.1 Å has 4 million grid points.

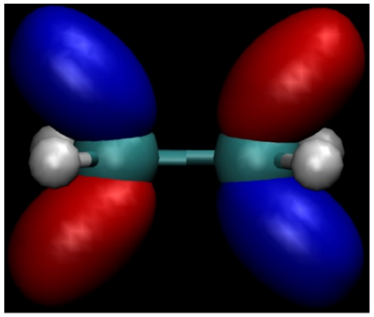
- Real space easily describes states extending far from atoms, but GTOs can need very diffuse orbitals.

e.g. for nonlinear response properties of $CHCl_3$ molecule
F. Vila, D. A. Strubbe *et al.*, *J. Chem. Phys.* 133, 034111 (2010)

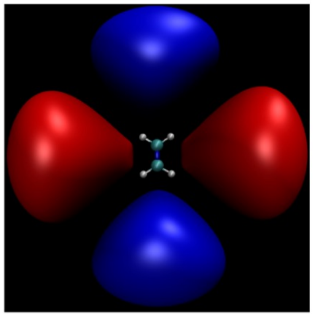
Comparisons of real space and Gaussian-type orbitals

- Real space has many vacuum and Rydberg excited states
- Must search for orbitals corresponding to GTO to compare excitations, by symmetry and localization

a) GTO Valence LUMO+4 at 2.50 eV

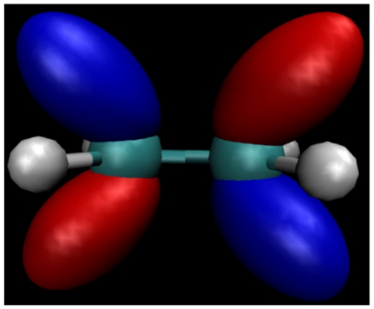


b) Real-space Rydberg LUMO+4 at 1.25 eV



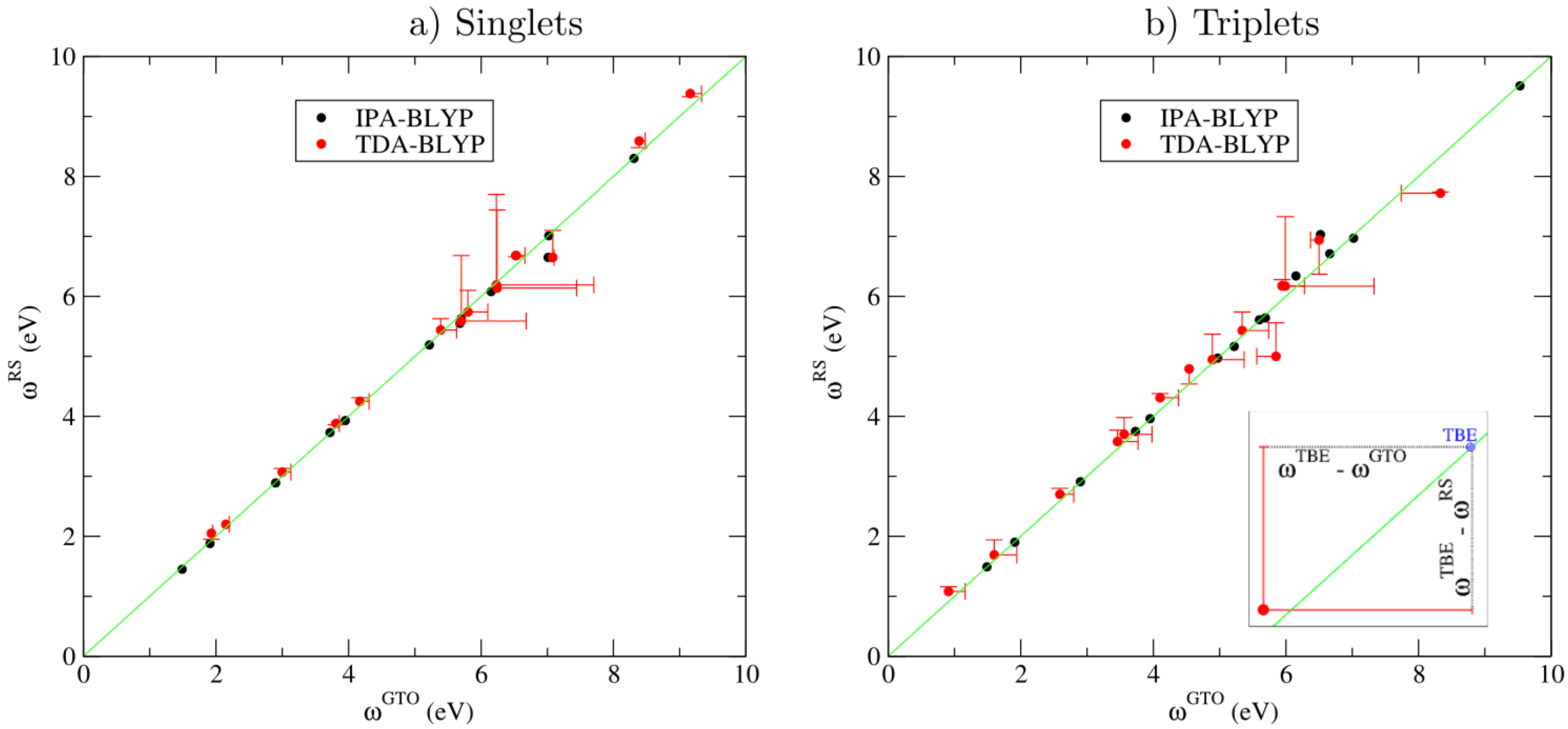
c) Real-space Valence LUMO+29 at 2.82 eV

ethylene



GTO: Psi4, aug-cc-pvtz. Octopus: sphere of radius 10 Å and spacing 0.1 Å.

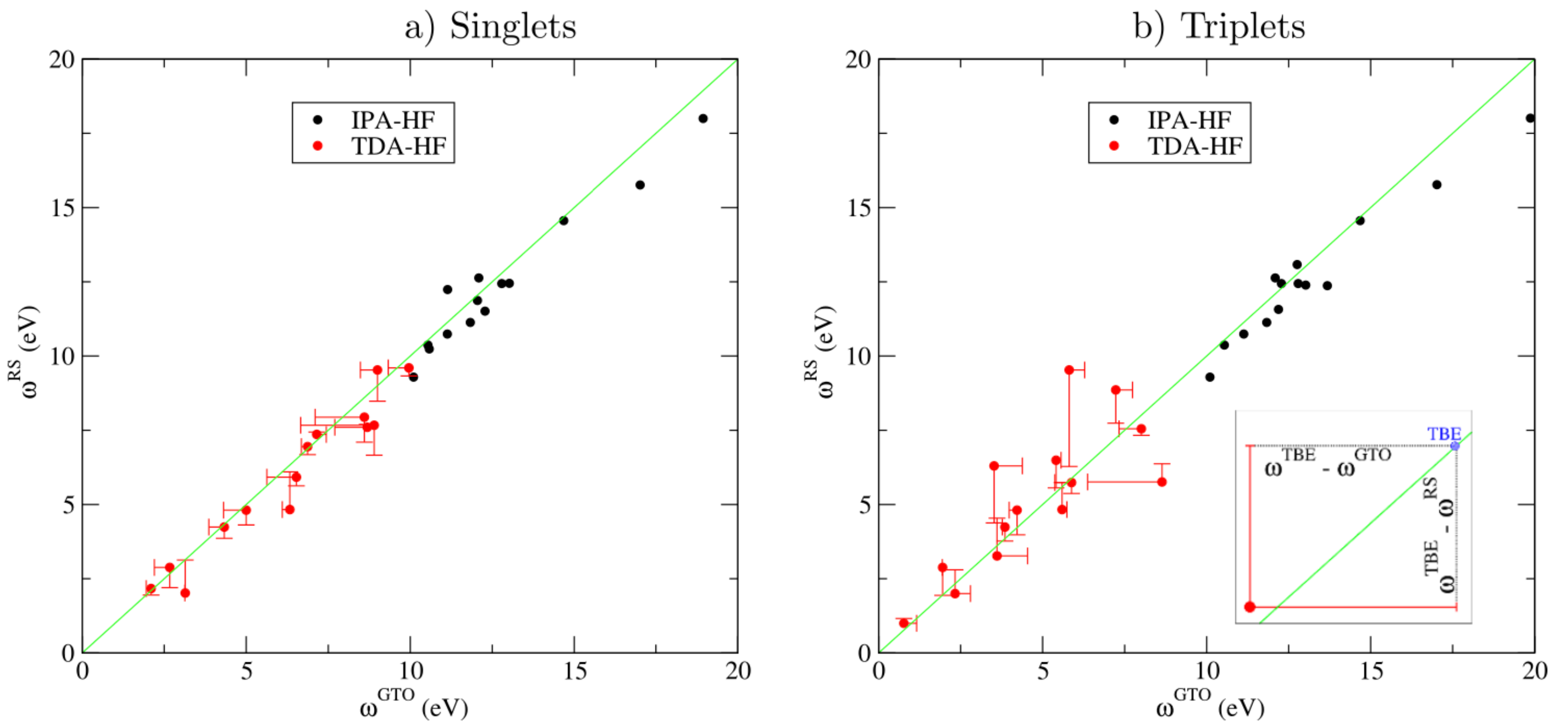
Benchmarking TDDFT (TDA, BLYP) for 14 small molecules



Error bars show deviation vs. Theoretical best estimate (TBE)
P. F. Loos *et al.*, *J. Chem. Theory Comput.* 14, 4360 (2018)

GTOs in Psi4, T. Gould *et al., J. Phys. Chem. Lett. 13*, 2452 (2022)

Benchmarking TDHF (TDA) for 14 small molecules



Error bars show deviation vs. Theoretical best estimate (TBE)
P. F. Loos *et al.*, *J. Chem. Theory Comput.* 14, 4360 (2018)

GTOs in Psi4, T. Gould *et al., J. Phys. Chem. Lett. 13*, 2452 (2022)

Benchmarking TDHF (TDA) for 14 small molecules

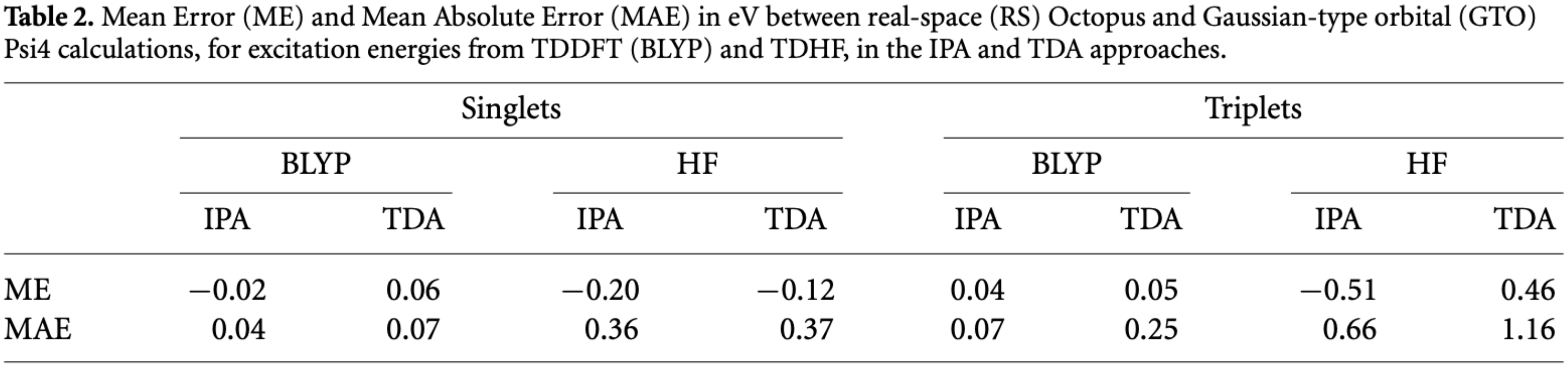


Table 2. Mean Error (ME) and Mean Absolute Error (MAE) in eV between real-space (RS) Octopus and Gaussian-type orbital (GTO) Psi4 calculations, for excitation energies from TDDFT (BLYP) and TDHF, in the IPA and TDA approaches.

	Singlets				Triplets			
	BLYP		HF		BLYP		HF	
	IPA	TDA	IPA	TDA	IPA	TDA	IPA	TDA
ME	−0.02	0.06	−0.20	−0.12	0.04	0.05	−0.51	0.46
MAE	0.04	0.07	0.36	0.37	0.07	0.25	0.66	1.16

Most of TDHF discrepancies are due to HF eigenvalues, i.e. inherent differences between real space and GTOs.

Discrepancies are larger than for BLYP:

Note: adaptive compressed exchange (ACE) used for HF, implementation by Nicolas Tancogne-Dejean.

Lin Lin, *J. Chem. Theory Comput. 12,* 2242 (2016)

Direct Ensemble Correction (DEC)

$$\Delta\omega_I^{SEHX} = \frac{1}{2} tr\left\{V(r,r').\left(\frac{Q_I}{g_I} - \frac{Q_{GS}}{g_{GS}}\right)\right\} - \int d^3r v_{HX}(\vec{r})\left[\frac{\tilde{n}_I(\vec{r})}{g_I} - \frac{\tilde{n}_{GS}(\vec{r})}{g_{GS}}\right]$$

$$V_{\mu\nu\kappa\lambda} = \frac{1}{2}\left[(\mu\kappa|\nu\lambda)\,\delta_{\sigma_\mu,\sigma_\kappa}\delta_{\sigma_\nu,\sigma_\lambda} - (\mu\lambda|\nu\kappa)\,\delta_{\sigma_\mu,\sigma_\lambda}\delta_{\sigma_\nu,\sigma_\kappa}\right]$$

μ,ν,κ,λ can be any orbital.

DEC is heavily dependent on the exchange integrals.

$v_{\mathrm{HX}}(\mathbf{r})$ is the ground-state Hartree-exchange potential.

symmetry-eigenstate
Hartree-exchange (SEHX)
(no correlation)

Singlet (S) and triplet (T)
excitation energies

Similar results for KLI
and HF ground state

Literature: Z.-h. Yang *et al., Phys. Rev. Lett.* 119, 033003 (2017)

pEDFT

HOMO-LUMO Gap

$$A_{a,b} = \left\langle a|\hat{H}_{KS}|b\right\rangle + \left\langle a|v_{xc}^{eff}|b\right\rangle$$

a and *b* are unoccupied orbitals.

To calculate the excitation energy for transition *i* → *p*, solve for v_{eff}, *a* and *b* **self-consistently** until p^{th} unoccupied state converges

$$v_{xc}^{eff,T} = v_{xc}^{\uparrow}\left[\rho_{GS}^{\uparrow} + \rho_p, \rho_{GS}^{\downarrow} - \rho_i\right] - v_{xc}^{\uparrow}\left[\rho_{GS}^{\uparrow}, \rho_{GS}^{\downarrow}\right]$$ for Triplet excitations.

For Singlet excitations.

$$A_{a,b} = A_{a,b}^{T} + 2\left\langle ai|ib\right\rangle$$

T. Gould *et al., J. Phys. Chem. Lett.* 13, 2452 (2022)

So far, our implementation expands in unoccupied orbitals like for GTOs.
Under development: work directly in real space, projecting out occupied orbitals.

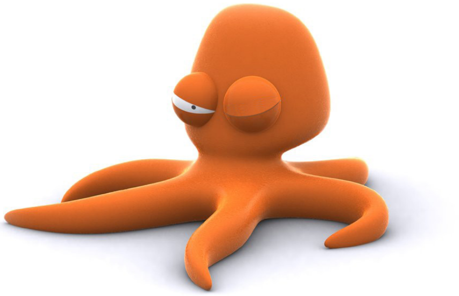
Conclusions

- Approach to the thermodynamic limit with ensemble-generalized LSDA gives zero gap corrections, as expected.
- Non-trivial effective mass renormalization, similar to 2D and 3D electron gas results.
- Spin-symmetry-breaking effects of LSDA have only a moderate effect.
- Ensemble-generalized Hartree reduces excitation energies, may be less physical.
- Promising indications for development of a periodic EDFT: could give useful results even from simple approximations.
- Next: semiconducting Kronig-Penney model.

R. J. Leano, A. Pribram-Jones, and D. A. Strubbe, *Electron. Struct.* 6, 035003 (2024)

- Working implementation of TDHF and two EDFT approaches, DEC and HOMO-LUMO pEDFT, in the real-space Octopus code.
- Opens the way to new kinds of applications and new kinds of comparisons.

U. Panta and D. A. Strubbe, *Electron. Struct.* 6, 045004 (2024).
U. Panta and D. A. Strubbe, *in preparation.*



Thermalization in TDDFT

TDDFT propagated orbitals – *which preserve original pure-state occupations*

$$H_{\mathrm{KS}}(t)\psi_i(t) = \epsilon_i(t)\psi_i(t)$$

ground-state Kohn-Sham orbitals

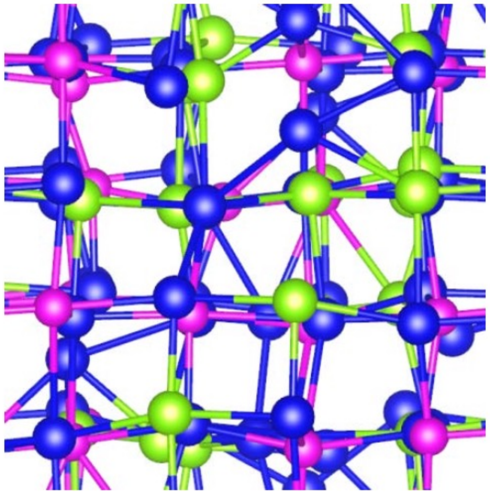
$$H_{\mathrm{KS}}^{t=0}\phi_i = \epsilon_i^{t=0}\phi_i$$

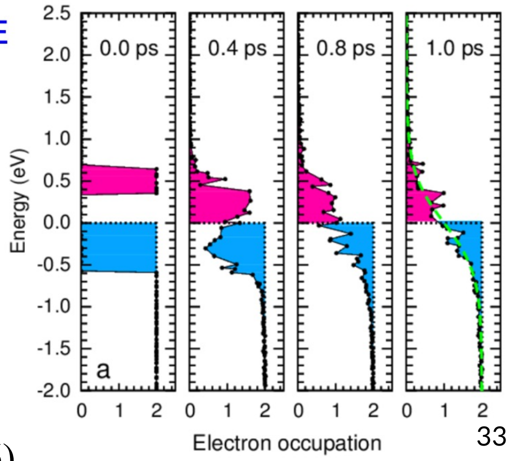
effective occupations by projection on ground state

$$f_i(t) = \sum_j f_j^0 |\langle\phi_i|\psi_j(t)\rangle|^2$$

Semiconductor + Ehrenfest dynamics → Fermi-Dirac for projected occupations
(presented by Junhyeok Bang at Benasque 2016)

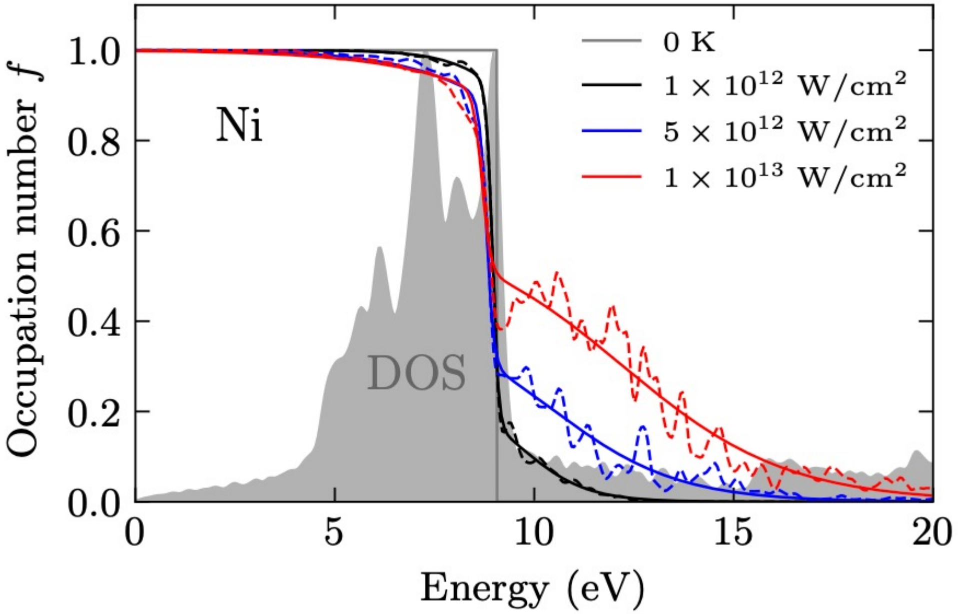
J. Bang, Y. Y. Sun, X.-Q. Liu, F. Gao, and S. B. Zhang, *Phys. Rev. Lett.* 117, 126402 (2016)





LEE

Thermalization in TDDFT



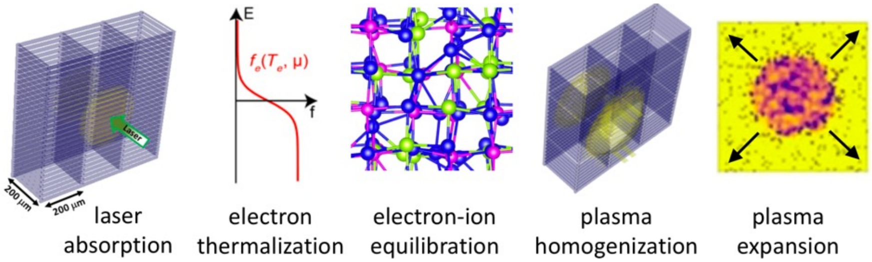
$$f = \frac{\beta}{1 + \exp\left(\frac{\epsilon - \mu_{sp}}{k_b T_{sp}}\right)} + \frac{1-\beta}{1 + \exp\left(\frac{\epsilon - \mu_d}{k_b T_d}\right)}$$

transition metals + TDDFT (no Ehrenfest) → Fermi-Dirac separately for *sp* and *d* bands
thermalization only occurs during pulse, 7 fs long.

E. P. Silaeva, E. Bevillon, R. Stoian, and J. P. Colombier, *Phys. Rev. B* 98, 094306 (2018).

Thermalization in TDDFT

How does a solid irradiated by intense laser pulses become a plasma? For inertial confinement fusion.



Our work: graphene (semimetal) + TDDFT (no Ehrenfest) → single effective Fermi-Dirac distribution

Mysteries: Is this physical? How does it depend on functional?
What is role of electronic structure, dimensionality, external field, and ionic motion?

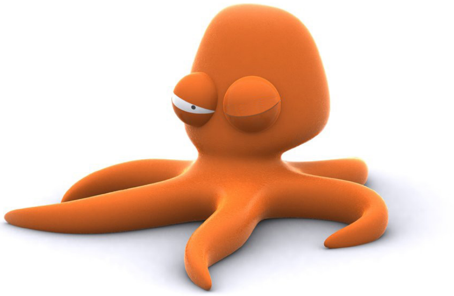
Conclusions

- Approach to the thermodynamic limit with ensemble-generalized LSDA gives zero gap corrections, as expected.
- Non-trivial effective mass renormalization, similar to 2D and 3D electron gas results.
- Promising indications for development of a periodic EDFT: could give useful results even from simple approximations.
- Next: semiconducting Kronig-Penney model.

R. J. Leano, A. Pribram-Jones, and D. A. Strubbe, *Electron. Struct.* 6, 035003 (2024)

- Working implementation of TDHF and two EDFT approaches, DEC and HOMO-LUMO pEDFT, in the real-space Octopus code.
- Opens the way to new kinds of applications and new kinds of comparisons.

U. Panta and D. A. Strubbe, *Electron. Struct.* 6, 045004 (2024).
U. Panta and D. A. Strubbe, *in preparation.*



- Graphene without ionic motion can thermalize in TDDFT.
- Mysteries remain about these thermalization processes.

Acknowledgments

SAIL
Strubbe
Ab Initio
Laboratory

Grad students: Remi Leano, Uday Panta
Postdoc: Tobias Zier
Collaborator: Prof. Aurora Pribram-Jones

UNIVERSITY
OF
CALIFORNIA

CfHEDS
Consortium for High Energy Density Science
Fostering Growth and Opportunities
for Minorities in High Energy Density Science

NNSA
National Nuclear Security Administration

NSF

ONDESA
CONVERGENCE OF NANO-ENGINEERED DEVICES FOR
ENVIRONMENTAL AND SUSTAINABLE APPLICATIONS

UNIVERSITY OF CALIFORNIA
MERCED

U.S. DEPARTMENT OF
ENERGY
Office of
Science

RESEARCH CORPORATION
for SCIENCE ADVANCEMENT

**MERCED and
Pinnacles
clusters**

NERSC
supercomputer time

**ccCAT (Center for
Chemical Computation
and Theory)**