Ensemble DFT

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August 7, 2019

(Excited State) Ensemble DFT

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Challenges for TDDFT

Double excitations
- Only singles* from adiabatic approximations

Charge transfer
- Overlap issues

Computational effort
- Lower cost is always better, if accuracy stays comparable

What is Ensemble DFT?

Ensembles built of ground and excited states
- Different kinds, often parameterized weights

Monotonically decreasing weights
- Actually non-increasing, equi-ensembles are okay

Variational method
- Non-perturbative method for excitation energies

Formal structure mirrors a lot of other DFTs
- Difficulties are reminiscent as well…

Variational Principle

$$\sum_{m=0}^{M} \mathrm{w}_m \langle \tilde{\Psi}_m | \hat{H} | \tilde{\Psi}_m \rangle \geq \sum_{m=0}^{M} \mathrm{w}_m E_m$$

Equality holds when trial wavefunctions are lowest M+1 eigenstates of Hamiltonian

Gross, Oliveira, Kohn. PRA (1988). Theophilou (1975).

Energies and Densities

Density matrix:

$$\hat{D}_W = \sum_{m=0}^{M} w_m |\Psi_m\rangle\langle\Psi_m|$$

Ensemble density:

$$n_W(\mathbf{r}) = \text{tr}\{\hat{D}_W \hat{n}(\mathbf{r})\} = \sum_{m=0}^{M} w_m n_m(\mathbf{r})$$

Ensemble energy:

$$E_W = \text{tr}\{\hat{D}_W \hat{H}\} = \sum_{m=0}^{M} w_m E_m$$

Ensemble Kohn-Sham

Ensemble KS Equations:

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\mathrm{s},w}[n_w](\mathbf{r}) \right\} \phi_{j,w}(\mathbf{r}) = \epsilon_{j,w}\phi_{j,w}(\mathbf{r})$$

KS Density matrix:

$$\hat{D}_{\mathrm{s},w} = \sum_{m=0}^{M} w_m |\Phi_m\rangle\langle\Phi_m|$$

Ensemble KS density:

$$n_w(\mathbf{r}) = \sum_{m=0}^{M} w_m n_m(\mathbf{r}) = \sum_{m=0}^{M} w_m n_{\mathrm{s,m}}(\mathbf{r})$$

Ensemble energy via KS:

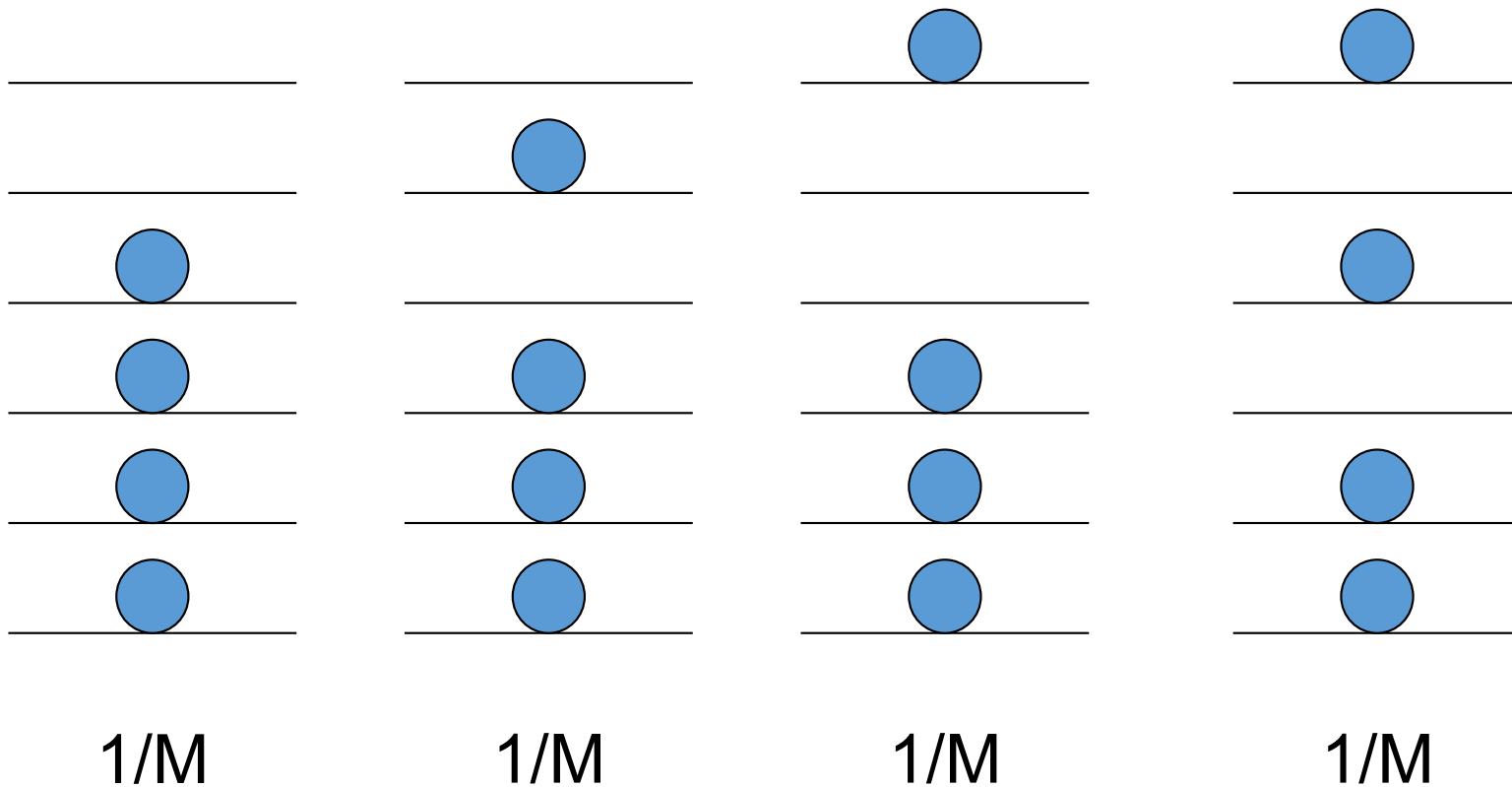$$E_w[n] = T_{\mathrm{s},w}[n] + V[n] + \underline{E_{\mathrm{H}}[n] + E_{\mathrm{XC},w}[n]}$$

Hartree definition
Weight dependence

Ensemble Types

- Finite number of states in an ensemble

- Ensemble structure can vary

- Characterized by weighting scheme
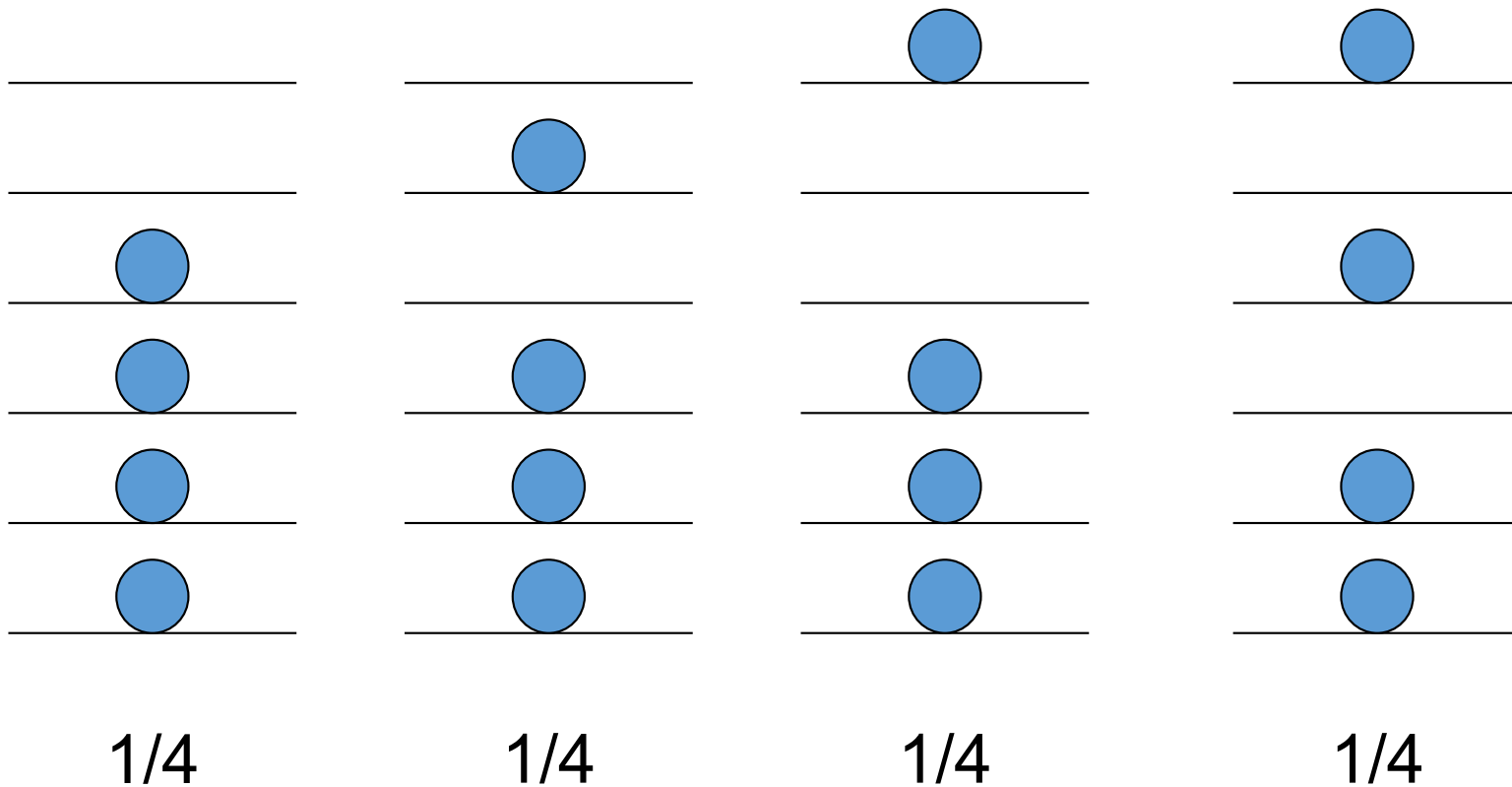
- Most useful ones can be described with parameter

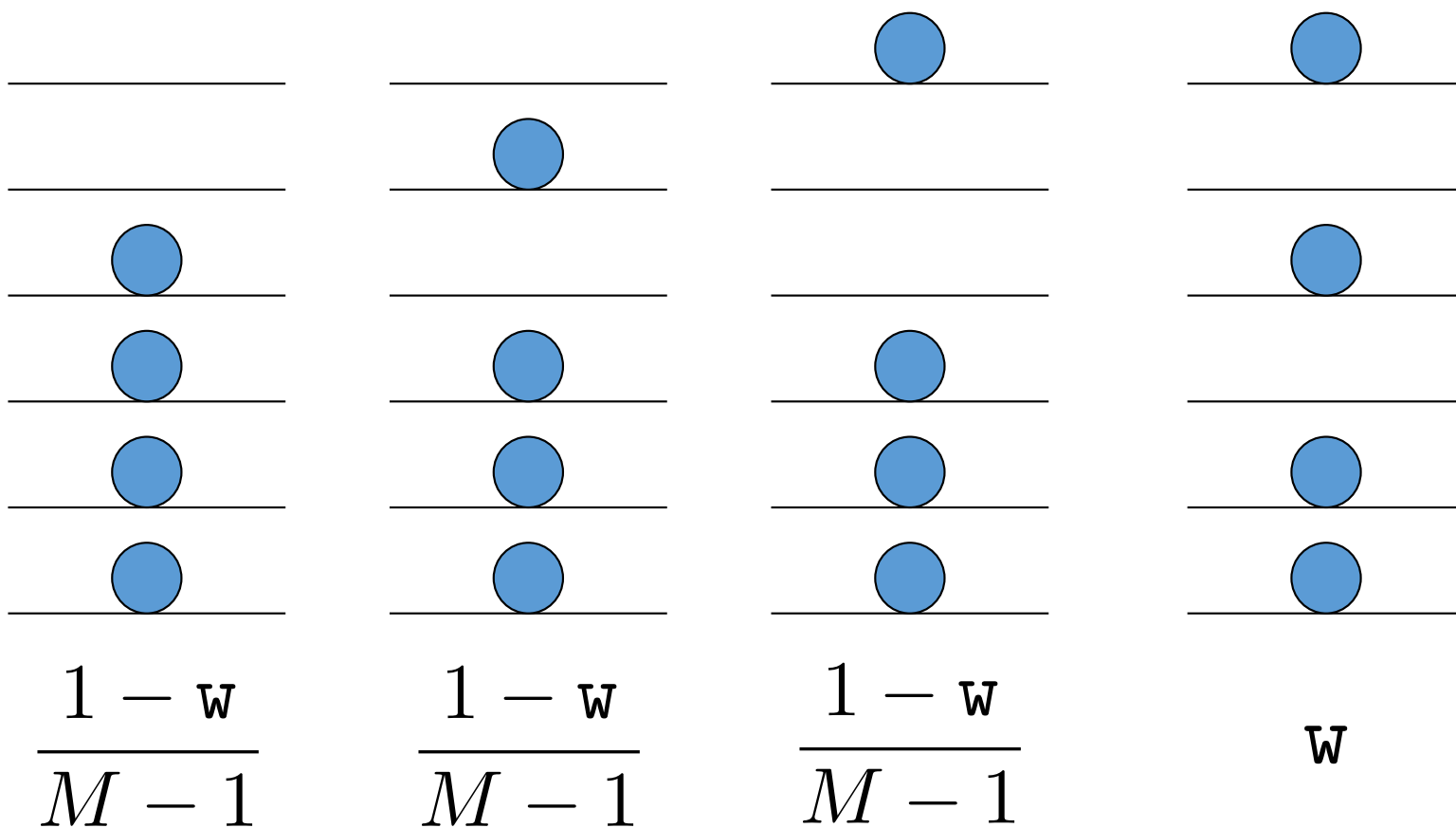# Equi-Ensemble

Number of states = M = 4

| 1/M | 1/M | 1/M | 1/M |

Equi-Ensemble

Number of states = M = 4

| 1/4 | 1/4 | 1/4 | 1/4 |

Not-Quite-Equi-Ensemble
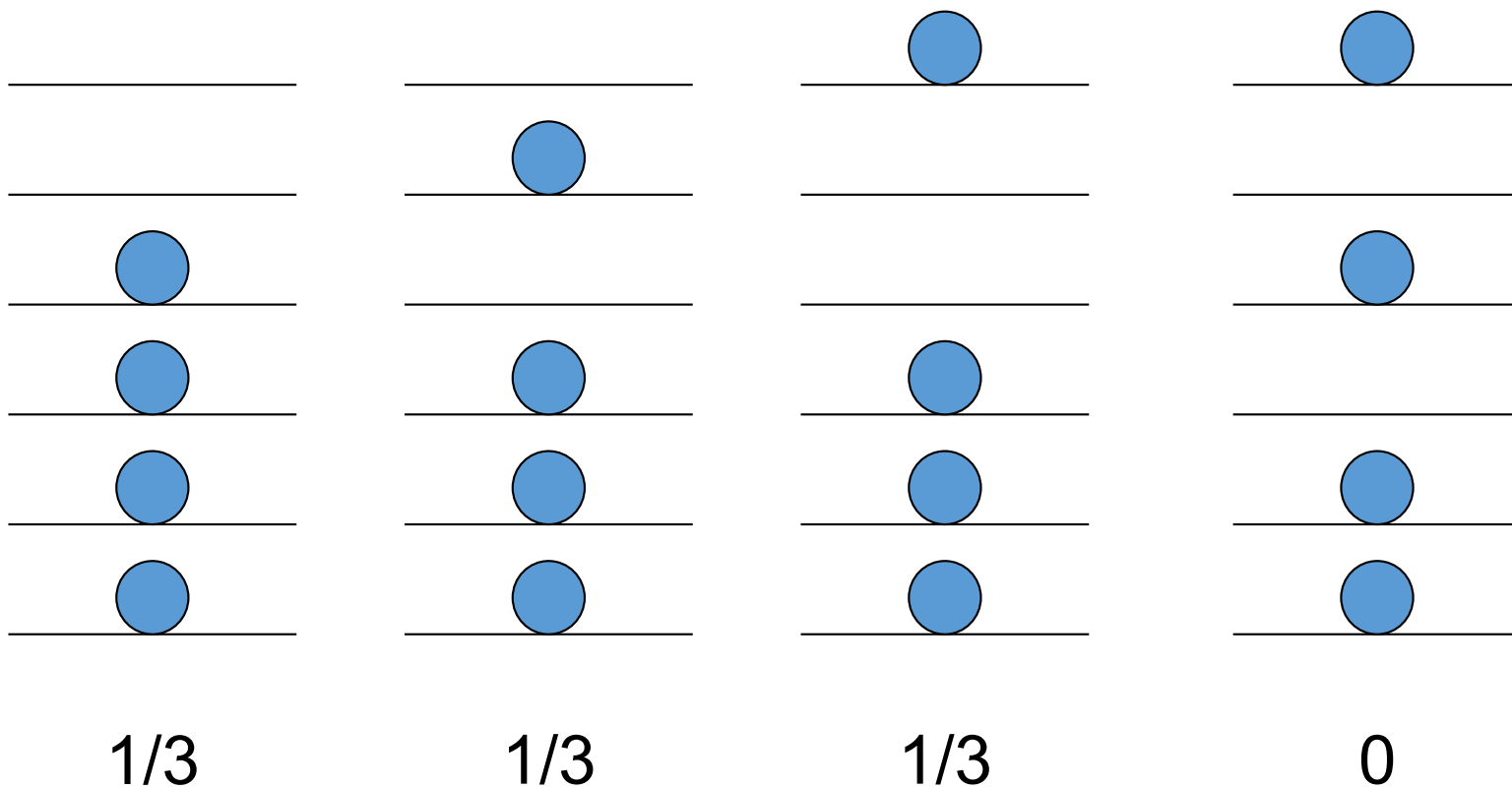
Number of states = M = 4

$$\frac{1-\mathrm{w}}{M-1} \qquad \frac{1-\mathrm{w}}{M-1} \qquad \frac{1-\mathrm{w}}{M-1} \qquad \mathrm{w}$$

Not-Quite-Equi-Ensemble

Number of states = M = 4

1/3   1/3   1/3   0

Not-Quite-Equi-Ensemble

Number of states = M = 4

$$\frac{1-\text{w}}{M-1} \qquad \frac{1-\text{w}}{M-1} \qquad \frac{1-\text{w}}{M-1} \qquad \text{w}$$
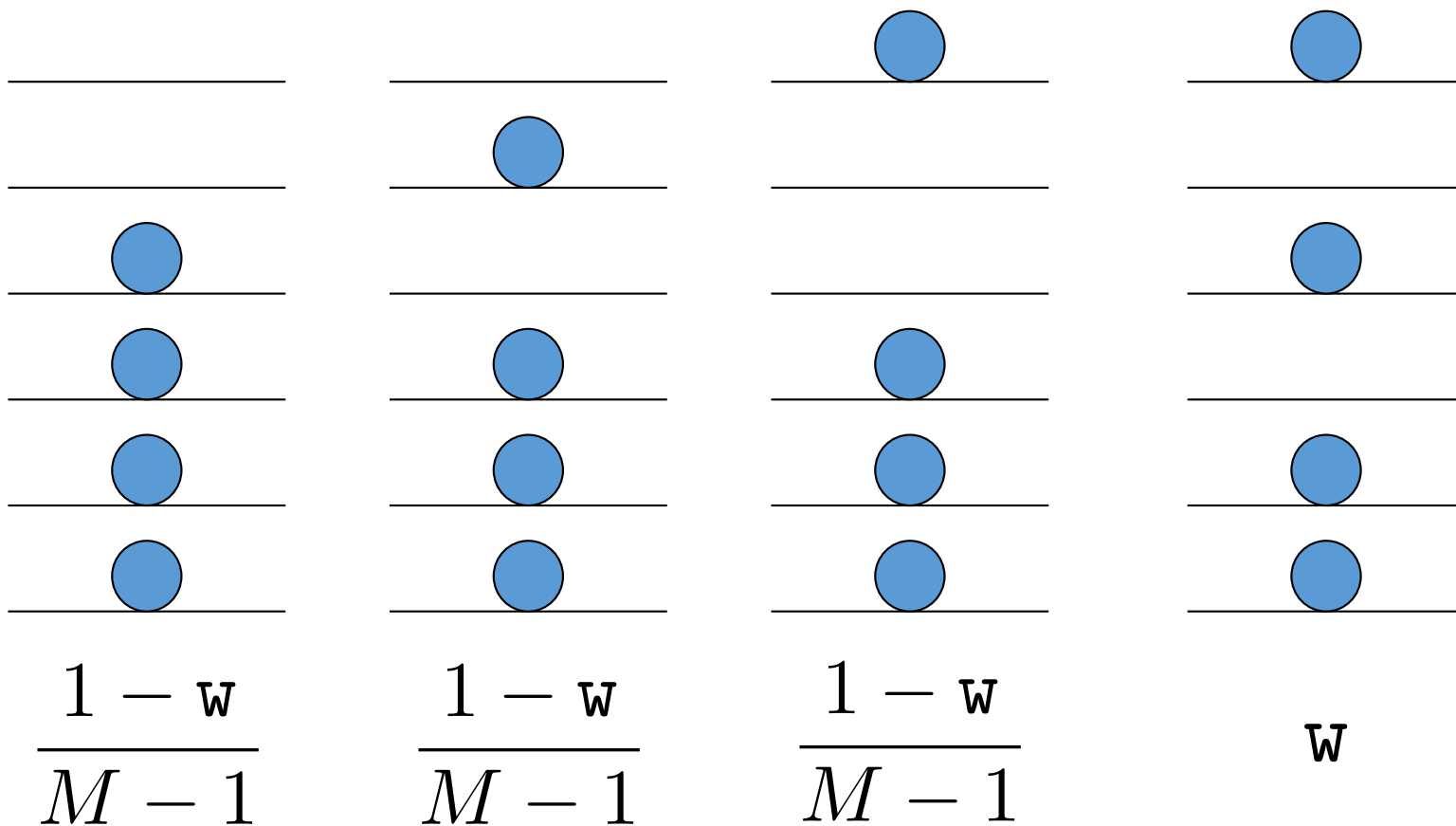
Not-Quite-Equi-Ensemble

Number of states = M = 4

| 1/4 | 1/4 | 1/4 | 1/4 |
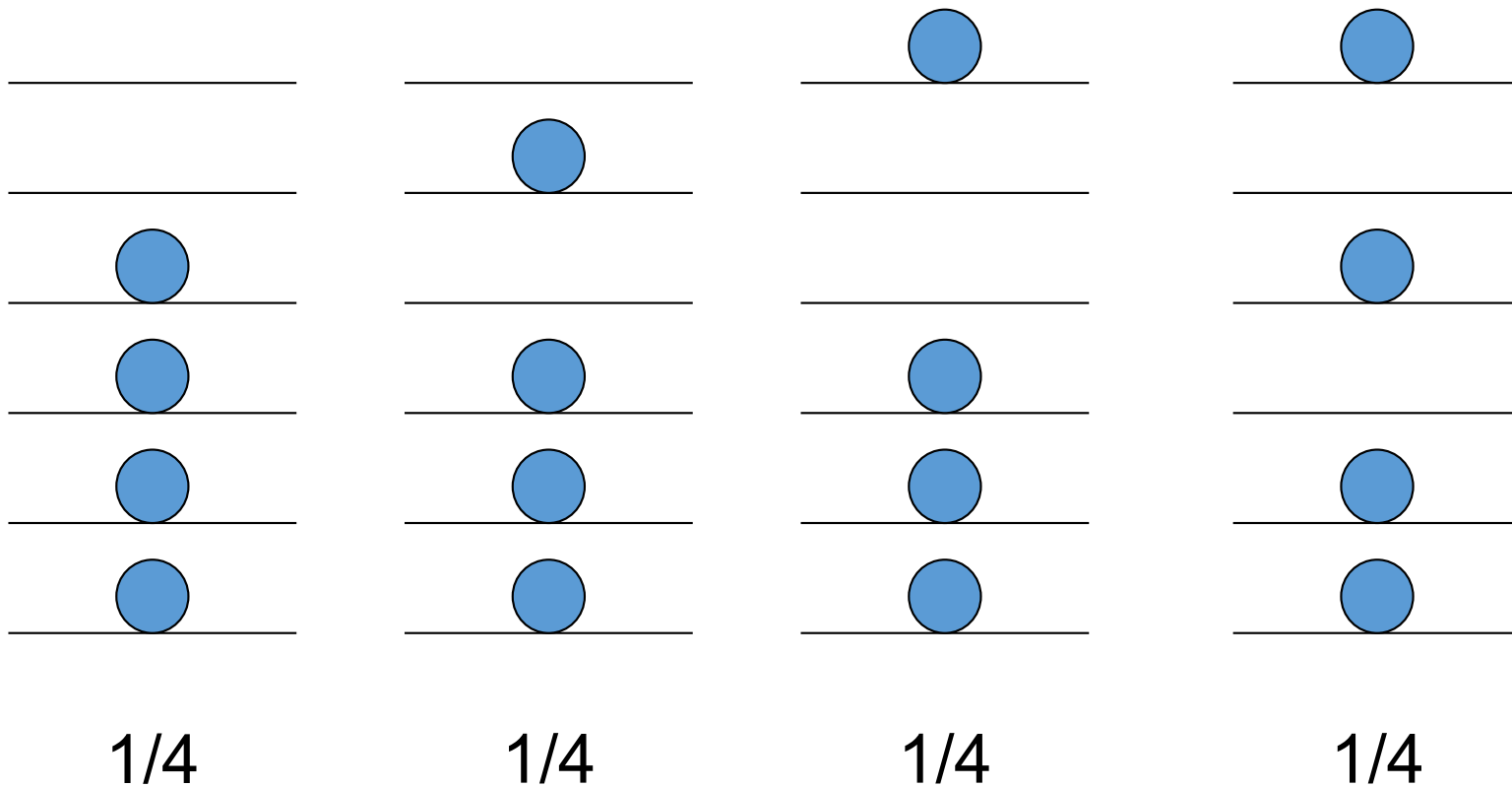
GOK Ensemble

"Interpolates between equi-ensembles"

$$\frac{1-\mathrm{w}}{M-1} \qquad \frac{1-\mathrm{w}}{M-1} \qquad \frac{1-\mathrm{w}}{M-1} \qquad \mathrm{w}$$
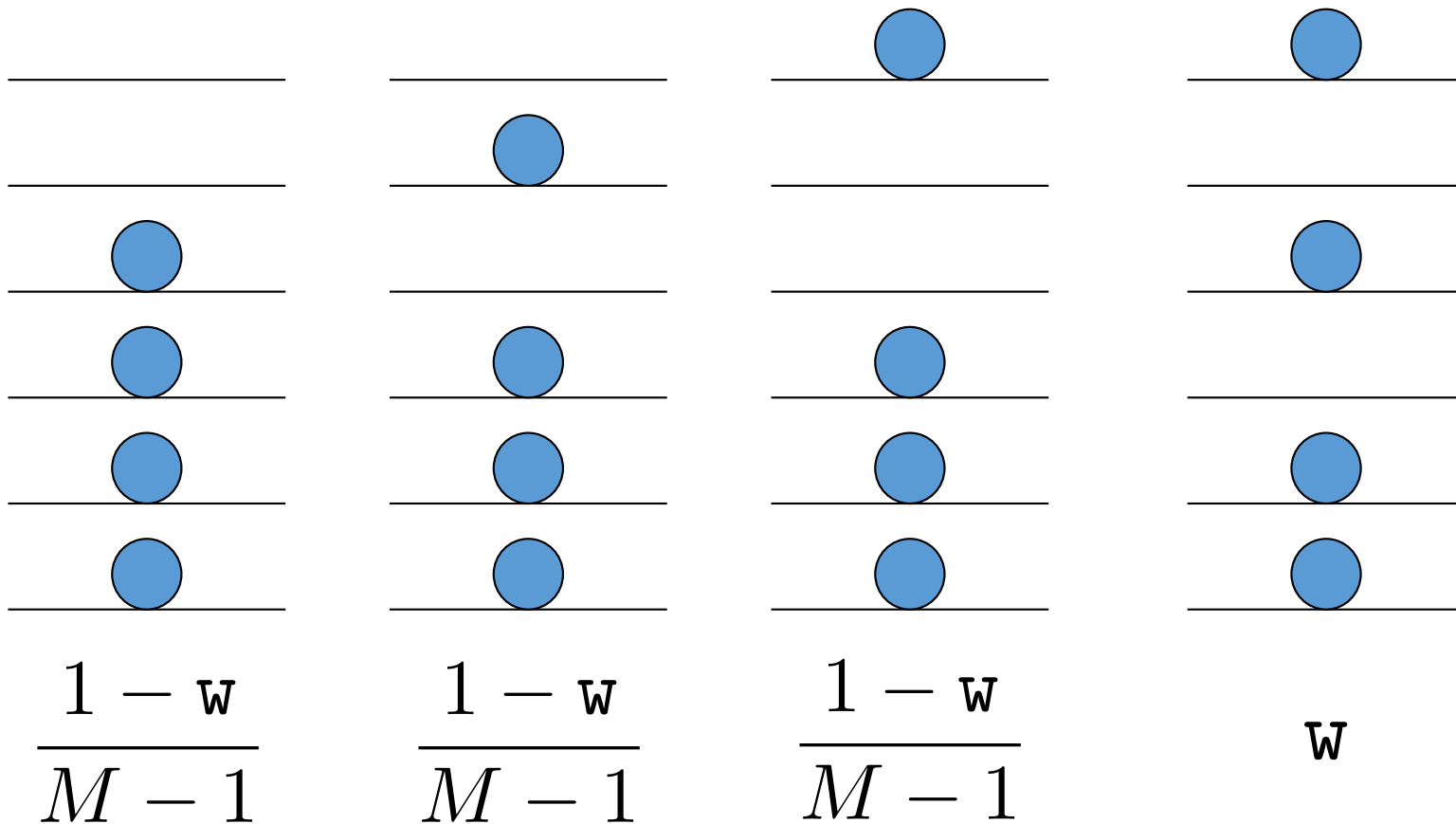
GOK II Ensemble

"Footnote Ensemble"
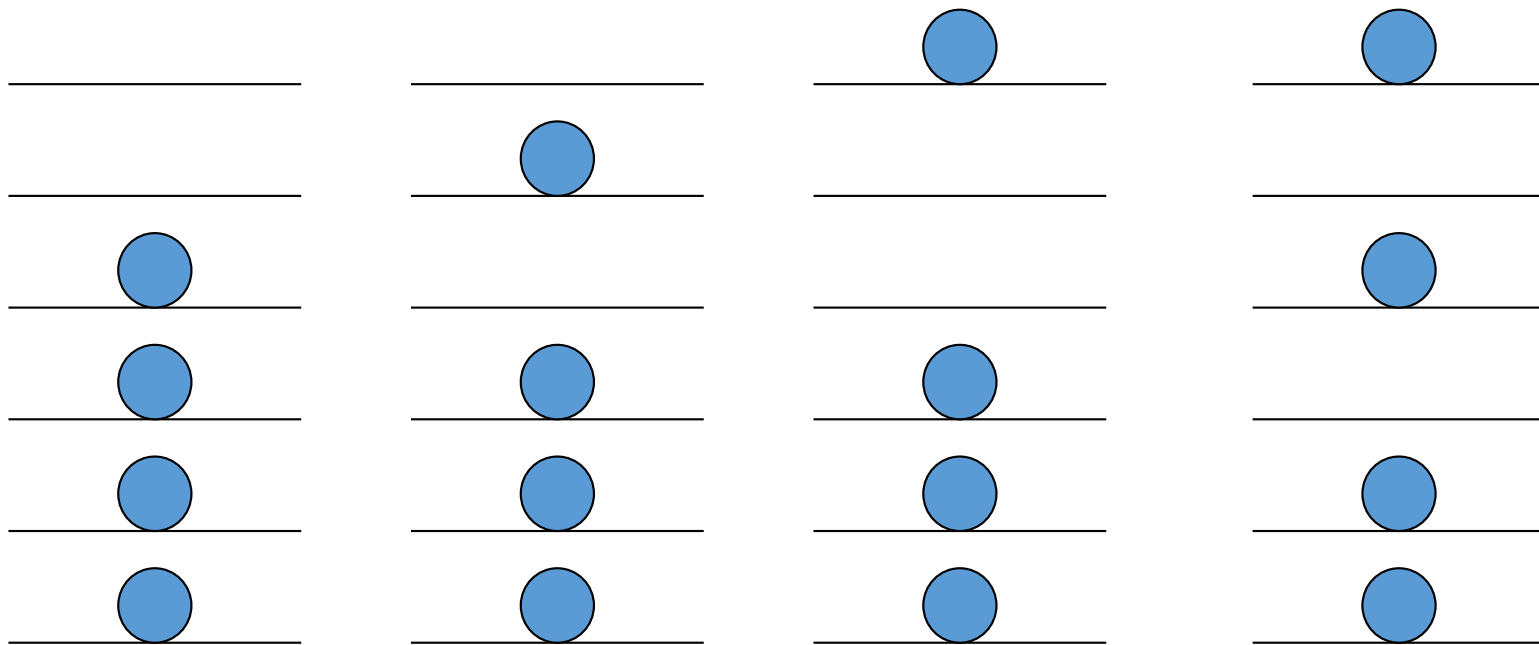
$$1 - (M-1)\mathtt{w} \qquad \mathtt{w} \qquad \mathtt{w} \qquad \mathtt{w}$$
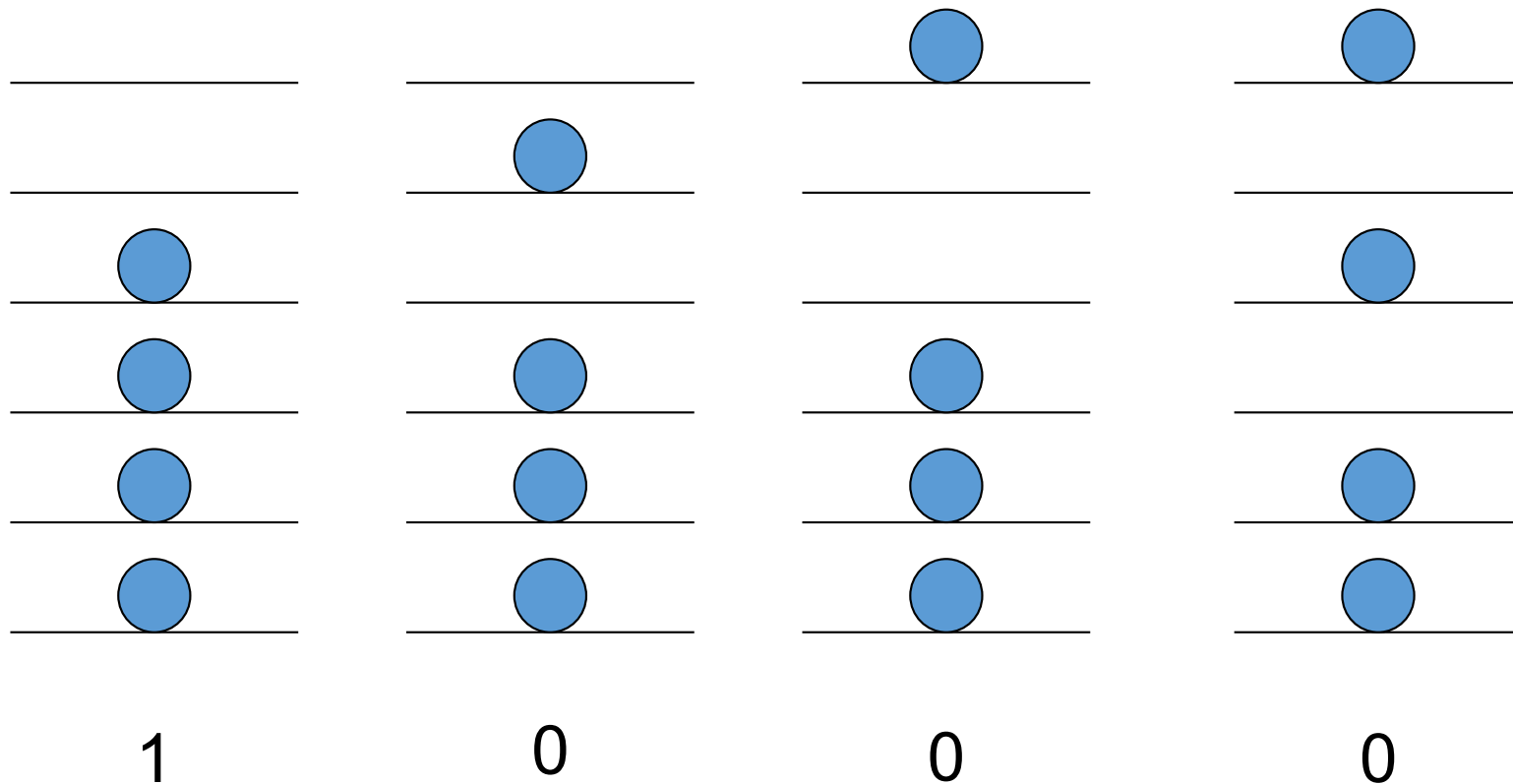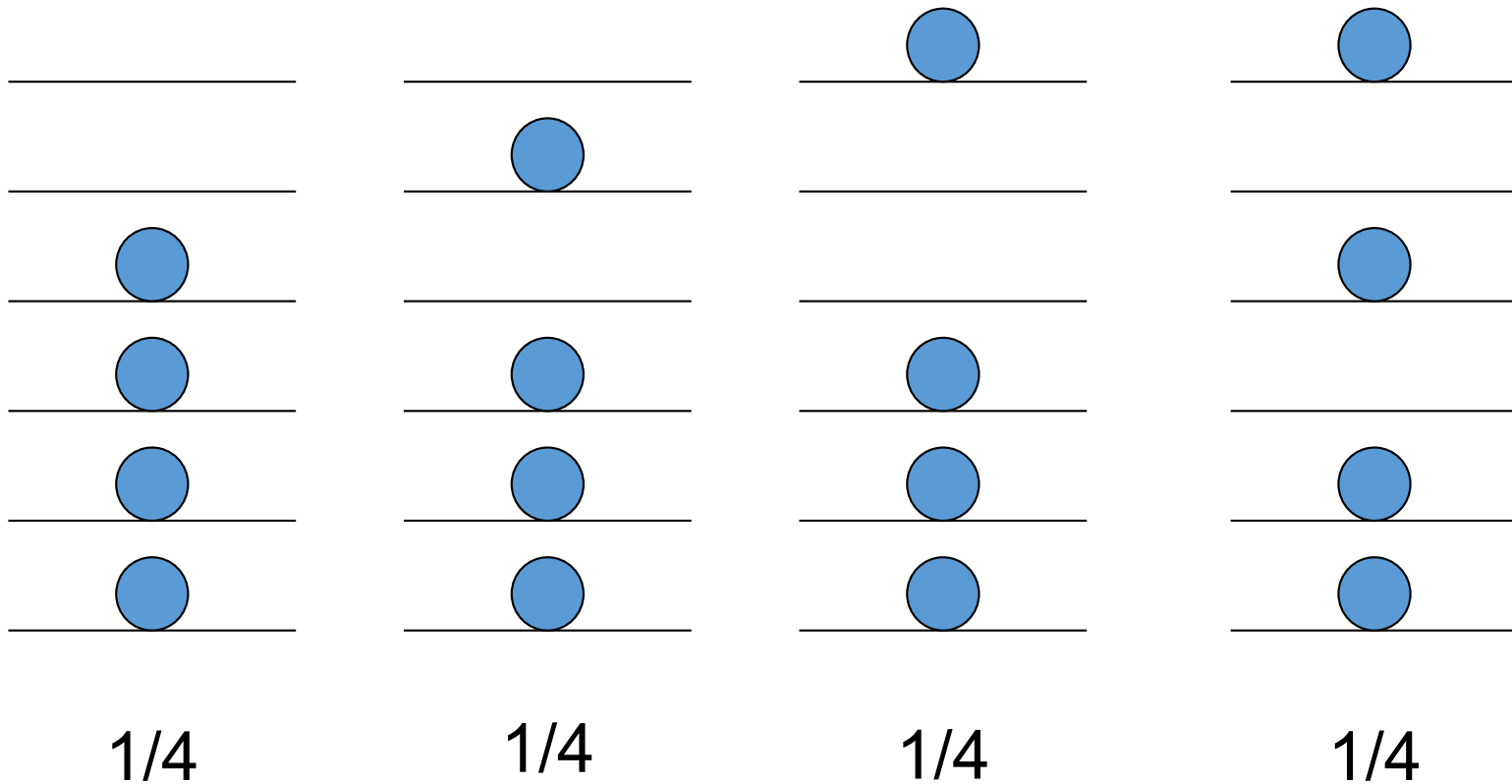
GOK II Ensemble

"Interpolates between ground state and equi-ensemble"

1   0   0   0

GOK II Ensemble

"Interpolates between ground state and equi-ensemble"

| 1/4 | 1/4 | 1/4 | 1/4 |

Your Turn

Using the definitions, write down the expression for a bi-ensemble's density and energy in terms of n_0, n_1, E_0, E_1, and w. Next, rearrange the energy terms to yield a method for getting the 1st excitation energy.

Ensemble energy:

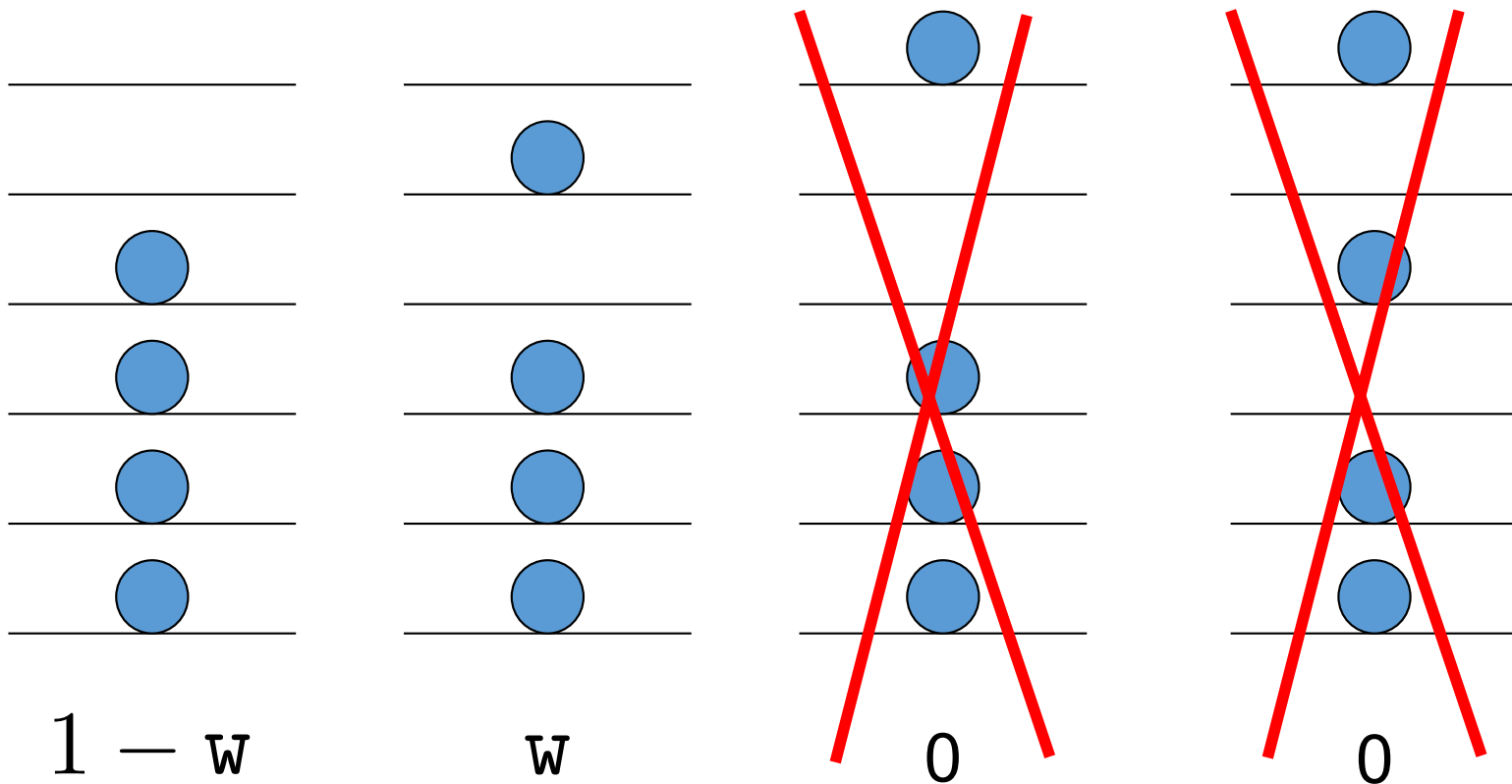$$E_w = \sum_{m=0}^{M} w_m E_m$$

Ensemble density:

$$n_w(\mathbf{r}) = \sum_{m=0}^{M} w_m n_m(\mathbf{r})$$

Check Yourself: A Bi-Ensemble

w "switches on" the ensemble behavior

$1 - \mathtt{w}$ $\mathtt{w}$ 0 0

Check Yourself: Excitation Energy

Ensemble density and energy:

$$n_{\mathtt{w}}(\mathbf{r}) = (1 - \mathtt{w})n_0(\mathbf{r}) + \mathtt{w}\, n_1(\mathbf{r})$$

$$E_{\mathtt{w}} = (1 - \mathtt{w})E_0 + \mathtt{w}\, E_1$$

Rearrange energy terms for excitation energy:

$$E_{\mathtt{w}} = E_0 + \mathtt{w}(E_1 - E_0)$$

$$\omega_1 = \frac{dE_{\mathtt{w}}}{d\mathtt{w}}$$

GOK Excitation Energies

In general:

$$\omega_I = \frac{1}{g_I} \left.\frac{\partial E_{I,\mathrm{w}}}{\partial \mathrm{w}}\right|_{\mathrm{w}=\mathrm{w}_I} + \sum_{i=0}^{I-1} \frac{1}{M_i} \left.\frac{\partial E_{i,\mathrm{w}}}{\partial \mathrm{w}}\right|_{\mathrm{w}=\mathrm{w}_i}$$

For the first excitation energy:

$$\omega_1 = \omega_{\mathrm{s},1,\mathrm{w}} + \left.\frac{\partial E_{\mathrm{XC,w}}[n]}{\partial \mathrm{w}}\right|_{n=n_{\mathrm{w}}}$$

Exact vs. KS Excitation Energies
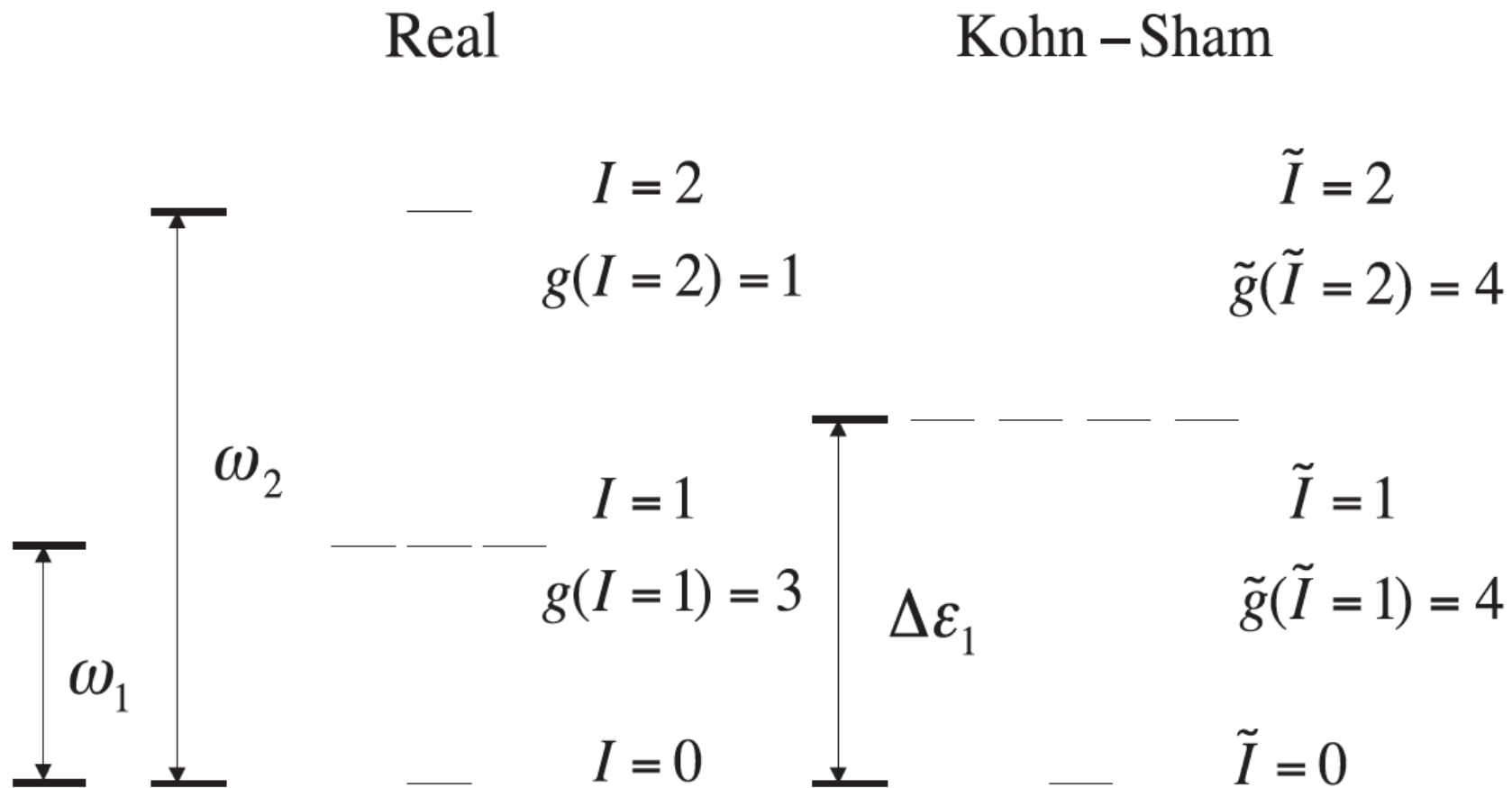
APJ, Yang, Trail, Needs, Burke, Ullrich. JCP (2014).

Your Turn Again

Think for a minute, then discuss with your neighbors…

We talked about how w "turns on" the ensemble as it goes from 0 to a very small positive number. What do you think happens to the XC potential when that "switch on" happens? Is it a smooth transition?

In other words, what does the KS or XC potential do when you first begin to occupy the excited state in a bi-ensemble?
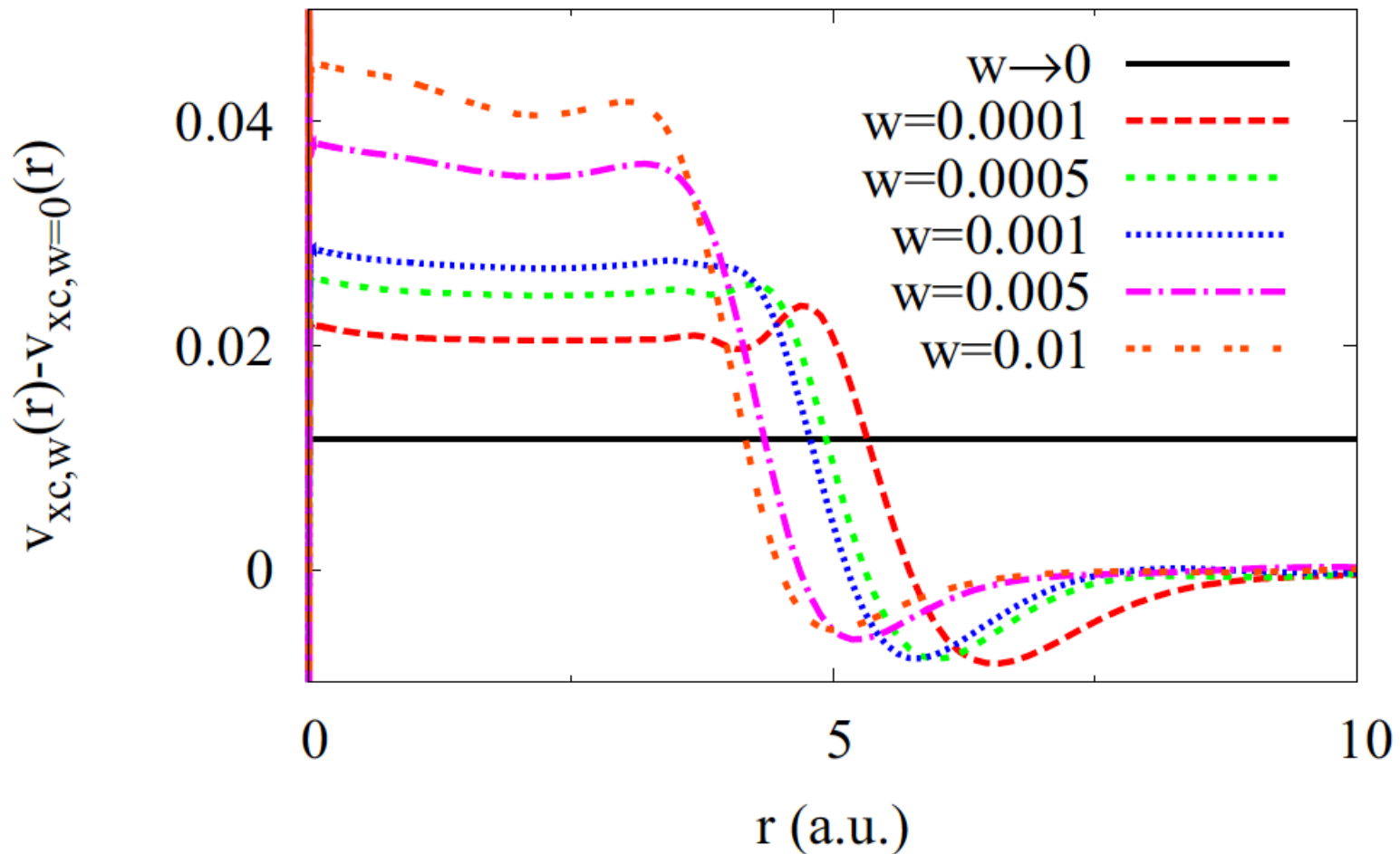
Your Turn Again

We talked about how w "turns on" the ensemble as it goes from 0 to a very small positive number. What do you think happens to the XC potential when that "switch on" happens? Is it a smooth transition? NOPE!

Levy's ensemble derivative discontinuity:

$$\Delta v_{XC} = \lim_{w \to 0} \left. \frac{\partial E_{XC,w}[n]}{\partial w} \right|_{n=n_w}$$

$$= \left[\lim_{w \to 0} v_{XC,w}[n_w](\mathbf{r}) \right] - v_{xc,w=0}[n_{w=0}](\mathbf{r})$$

Levy. Phys. Rev. A 52, R4313 (1995).

Derivative Discontinuity

Δv_{XC} for helium:

Yang, Trail, APJ, Needs, Burke, Ullrich. PRA (2014).

Fundamental and Optical Gaps

Senjean and Fromager: tie ensemble optical gap to fundamental gap
- Traditional DFT derivative discontinuity/gap problem related to the ensemble derivative discontinuity!

$$E_g^N = \varepsilon_L^{\{N,\xi\}} - \varepsilon_H^{\{N,\xi\}} + \left.\frac{\partial E_{xc}^{\{N,\xi\}}[n]}{\partial \xi}\right|_{n=n_{\hat{\Gamma}_0^{\{N,\xi\}}}}$$

Senjean and Fromager, *PRA 98, 022513 (2018)*

Challenges for Ensemble DFT

Hartree Definition

- Pick: nice potentials with ghosts or OEP without

Need new XC functional approximations

- Using g.s. functional approximations ineffective

Computational effort

- Need a lot of ensemble DFT calculations, so not as low-cost as gs DFT

Traditional Hartree Definition

Familiar, ground-state Hartree:

$$U[n] = \frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \frac{n(\mathbf{r})n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$

If we "plug in" ensemble densities:

$$E_{\mathrm{H,W}}^{\mathrm{trad}} = U[n_{\mathrm{W}}]$$

get some troubling results…

Another Question

If you use your definitions of a bi-ensemble density and the traditional Hartree definition, what troubles do you see with the result?

$$n_{\mathtt{w}}(\mathbf{r}) = (1 - \mathtt{w})n_0(\mathbf{r}) + \mathtt{w}\, n_1(\mathbf{r})$$

$$U[n] = \frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, \frac{n(\mathbf{r})n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$

$$E_{\mathrm{H},\mathtt{w}}^{\mathrm{trad}} = U[n_{\mathtt{w}}]$$

Another Response: Ghosts

Traditional Hartree with an ensemble density leads to interactions between the ground and excited state.

→ Spurious or ghost interactions first corrected by Gidopoulos, Papaconstantinou, and Gross in 2002, used to correct atomic excitation energies.

→ Ghost interaction correction (GIC) in 2016 for range-separated ensemble DFT.

Gidopoulos, Papaconstantinou, Gross. PRL, 88 (3). (2002); Alam, Knecht, Fromager. PRA 94, 012511 (2016).

Ensemble Hartree Definition

Based on ensemble-weighted HX:

$$E_{\mathrm{HX},w} = \mathrm{tr}\{\hat{D}_{\mathrm{s},w}\hat{V}_{\mathrm{ee}}\} = \sum_{m=0}^{M} \mathrm{w}_m \langle \Phi_m | \hat{V}_{\mathrm{ee}} | \Phi_m \rangle.$$

Ensemble Hartree definition (Nagy, 2001):

$$E_{\mathrm{H,w}}^{\mathrm{ens}} = \sum_{m=0}^{M} \mathrm{w}_m U[n_m]$$

- Nagy ('94 through '02) used to derive exact conditions, OEP for ensembles, etc.

X Only: EEXX Approximation

Defines Hartree-exchange energy as

$$\mathcal{E}_{Hx}[n] := \lim_{\lambda \to 0^+} \frac{\mathcal{F}^\lambda[n] - \mathcal{T}_s[n]}{\lambda}$$

which can also be written as a minimization (over set of non-int ensembles that yield n and exact non-int KE):

$$\mathcal{E}_{Hx}[n] \equiv \min_{\hat{\Gamma} \in \mathcal{G}^{n,\lambda=0}} \mathrm{Tr}[\hat{\Gamma}\hat{W}]$$

- Avoids non-uniqueness issues from direct trace
- No ghosts (GPG02 and SEHX are special cases)
- Admits multireference states
- New insights into correlation for ensembles

Gould and Pittalis. PRL 119, 243001 (2017).

X Only: Charge Transfer from EEXX
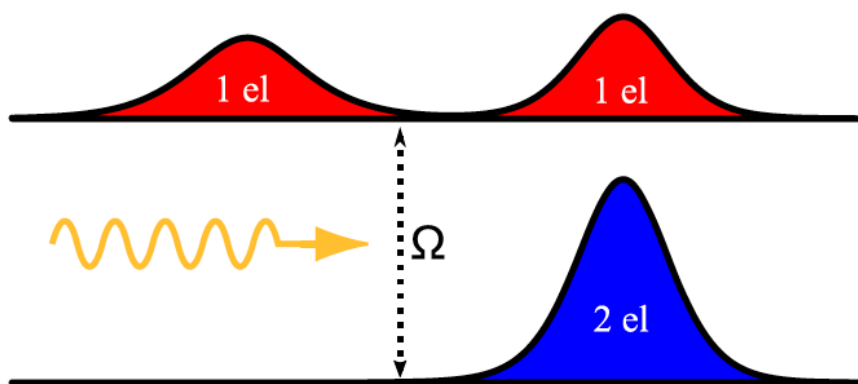
- Charge transfer excitation energies within few tenths of eV, (exchange-only, weight-dependent approximation to XC)

Gould, Kronik, Pittalis. J. Chem. Phys. 148, 174101 (2018)
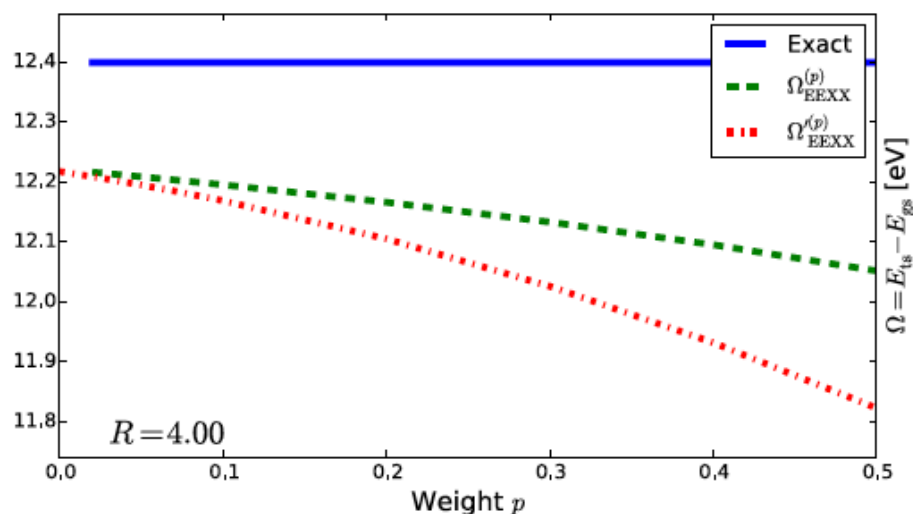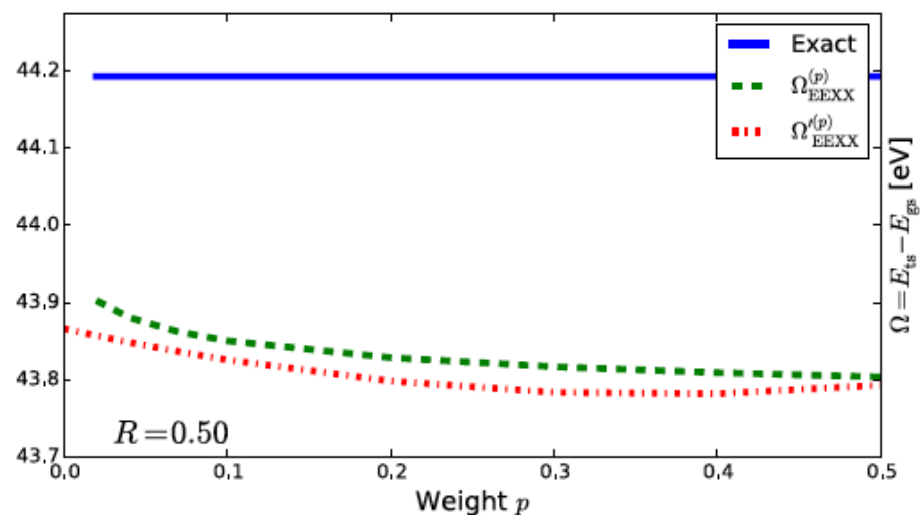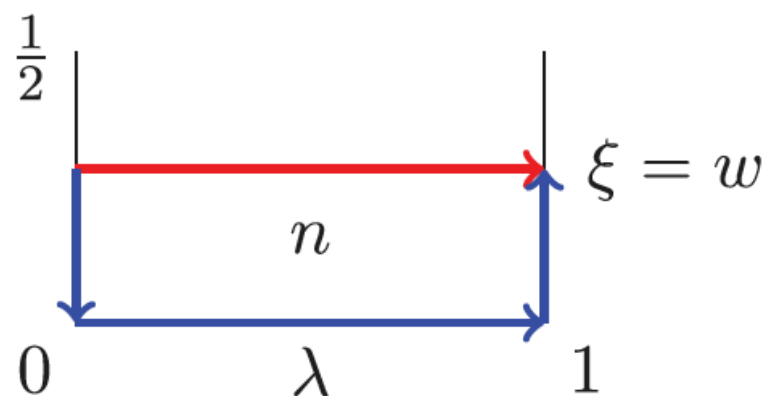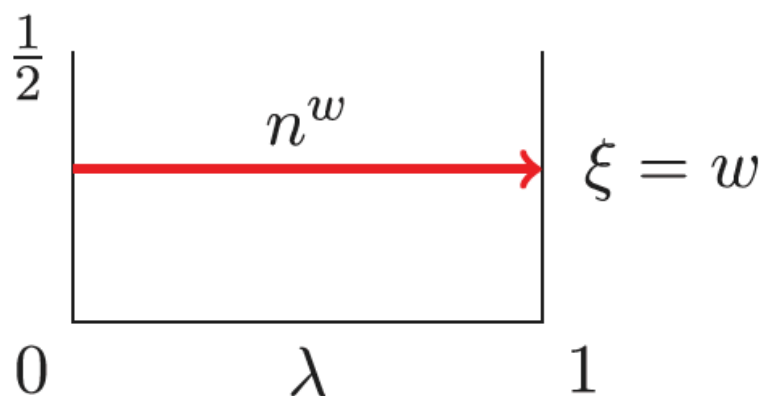
XC approximations: GACE and GIC

RESEARCH ARTICLE

Generalised adiabatic connection in ensemble density-functional theory for excited states: example of the H_2 molecule

Odile Franck and Emmanuel Fromager*

Laboratoire de Chimie Quantique, Institut de Chimie, CNRS/Université de Strasbourg, Strasbourg, France

XC approximations: Hubbard

Sagredo and Burke: errors of doubles with X only
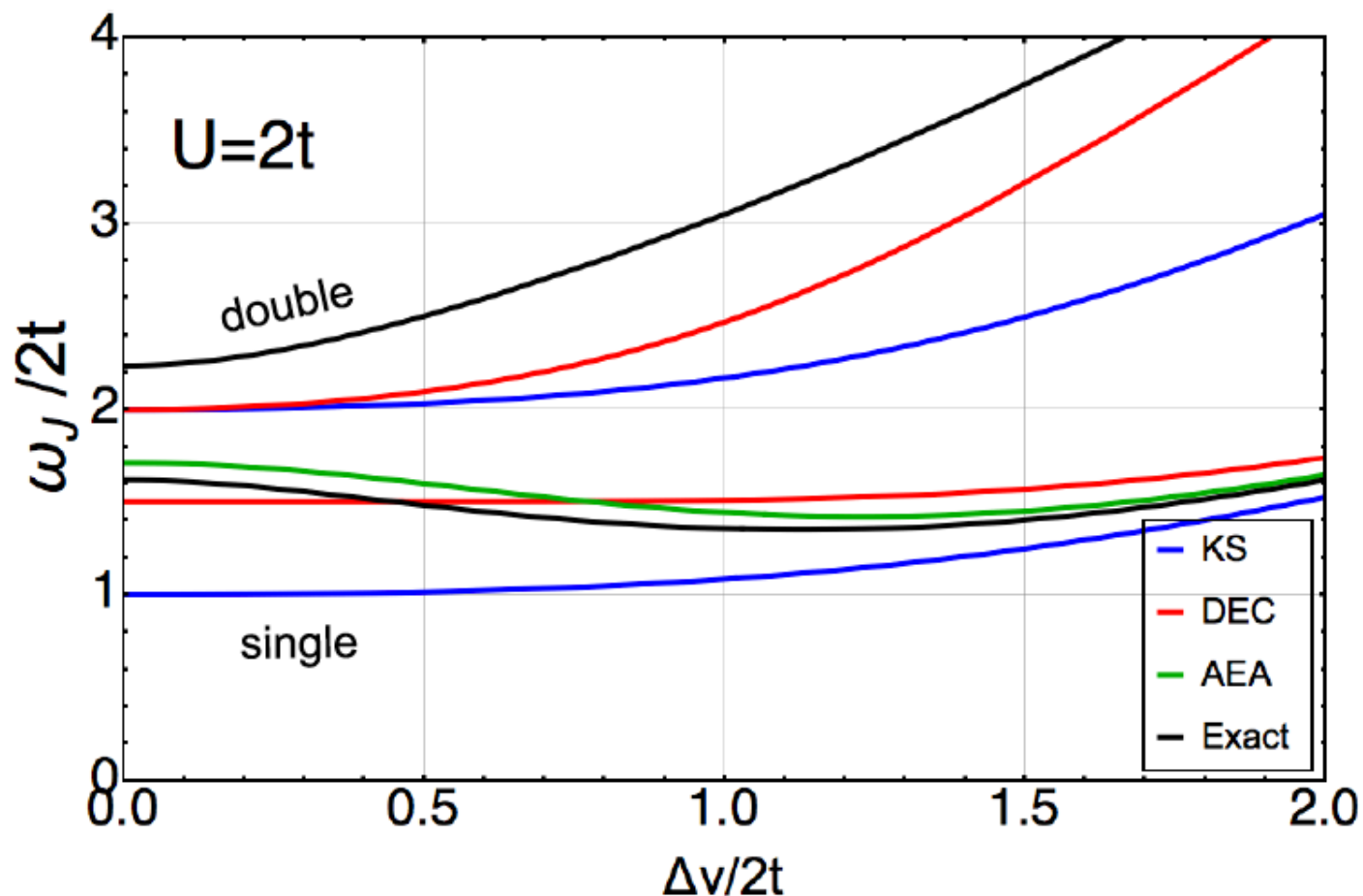
Francisca Sagredo and Kieron Burke, *Journal of Chemical Physics* **149**, 134103 (2018)

Correcting KS Excitations

Direct Ensemble Correction (DEC)

- Essentially same cost as expensive g.s. KS
- Captures double excitations
- Fixes mis-ordering
- Only has exchange so far (implementation is with SEHX based on handy cancellation of terms)

Yang, APJ, Burke, Ullrich. PRL (2017).

Correcting KS Excitations: DEC

- GOKII excitation energies: take weight to 0
- KS eigenvalues and densities: same for I and $I-1$

- _Direct ensemble correction to KS excitations_

$$\Delta\omega_I = \frac{1}{g_I} \frac{d}{d\mathbf{w}}\bigg|_{\mathbf{w}=0} \left(E_{\mathrm{XC,I}}^{\mathrm{GOKII}} - E_{\mathrm{XC,I-1}}^{\mathrm{GOKII}}\right)$$

- Cost of single ground-state calculation if we know ensemble XC as density functional

Yang, APJ, Burke, Ullrich. PRL (2017).

DEC/SEHX

Using SEHX approximation, all intermediate levels cancel
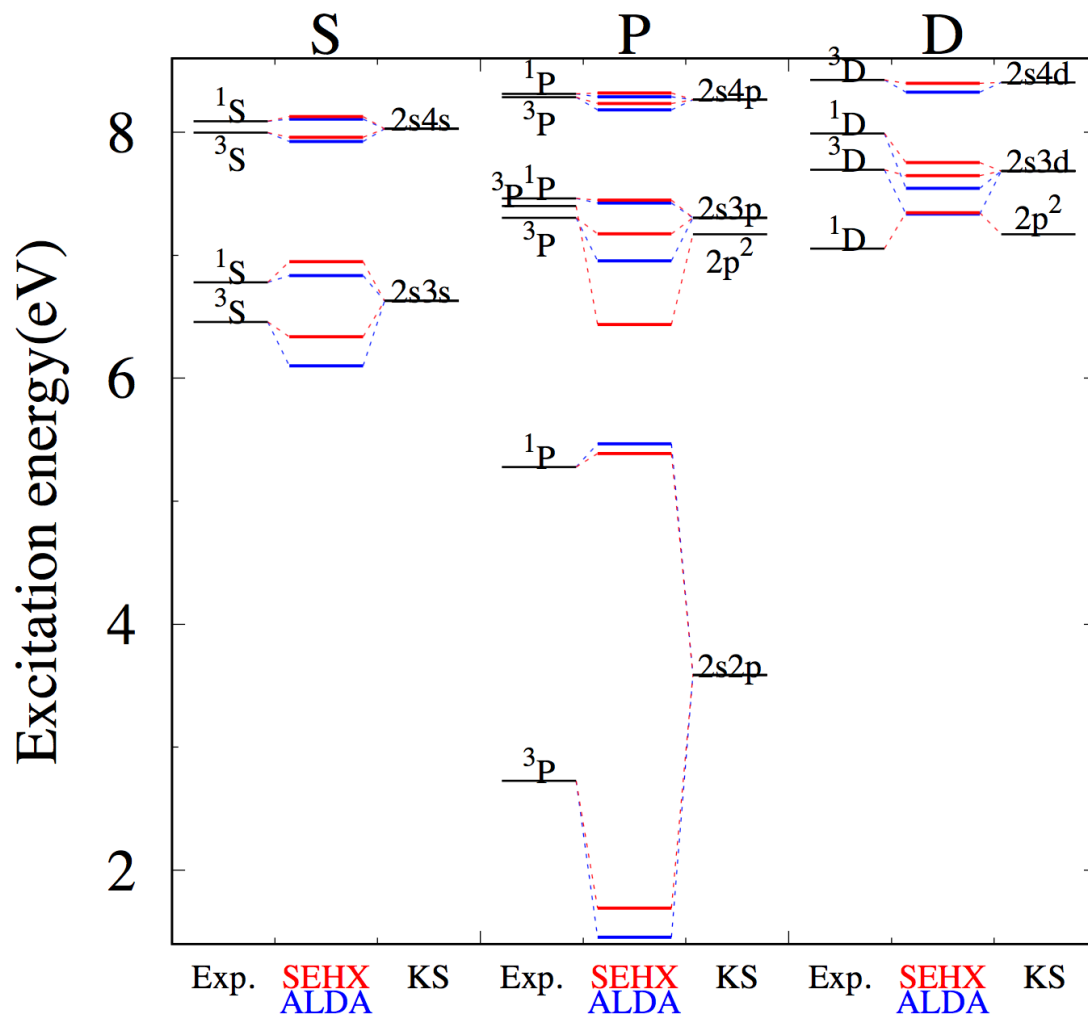
$$\omega_I[n_0] = \omega_I^{KS}[n_0] + H_I/g_I - H_0/g_0$$

where

$$H_i = \frac{1}{2}\int\int \frac{drdr'}{|r-r'|} \text{tr}\{\mathbf{P}(r,r')\cdot\mathbf{Q}_i\} - \int dr V_{\text{HX}}(r) n_i(r)$$

products of KS orbitals

orbital occupation factors & symmetrization coefficients of KS determinants

Yang, APJ, Burke, Ullrich. PRL (2017).

DEC Results: Doubles in Be atom

Yang, APJ, Burke, Ullrich. PRL (2017).

DEC Results: Hooke's Atom

I	ω_{KS}	exact	TDDFT AEXX	DEC SEHX	exact	TDDFT dressed
					$\Delta\omega_I$	
Singles						
1	962	38	39	39	38	39
3	1953	47	30	30	48	49
5	2948	52	25	27	51	54
Doubles						
2	1923	41	—	58	41	39
4	2915	49	—	77	49	47

Yang, APJ, Burke, Ullrich. PRL (2017).

Summary

Ensemble DFT is alternative way of calculating excitation energies.

Things to consider:
- **Definition of Hartree energy**
- **Ensemble weight-dependent XC approximation**
- **Which ensemble will you use?**
- **Do you need more than just energy differences?**

Things to watch:
- **New XC approximations**
- **Newly accessible properties**
- **Periodic systems, gaps, model systems, and exact conditions**

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