Density-driven correlations in many-electron ensembles

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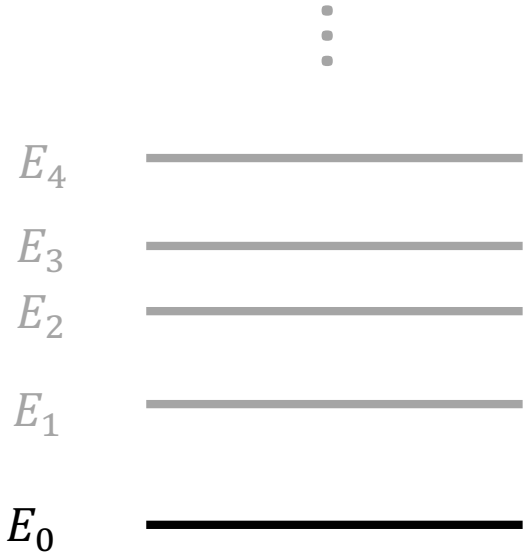
DFT for excited states: From the ground-state to the ensemble picture

$$E_0 = \min_n \left\{ T_s[n] + E_{Hxc}[n] + \int d\mathbf{r}\, v_{ext}(\mathbf{r}) n(\mathbf{r}) \right\}$$



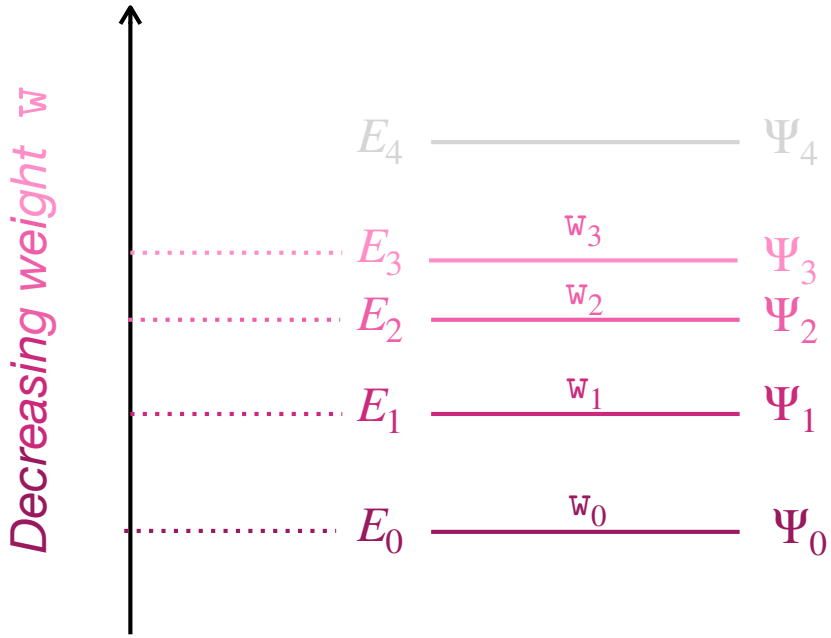
Kohn-Sham equations for a ***pure ground state***:

$$\left[-\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + \left. \frac{\delta E_{Hxc}[n]}{\delta n(\mathbf{r})} \right|_{n=n_0} \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$n_0(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

W. Kohn and L. J. Sham, Phys. Rev. ***140****, A1133 (1965).*

DFT for (canonical) ensembles



Gross-Oliveira-Kohn (GOK) DFT:

The *ensemble energy* $E^{\mathbf{w}} := \sum_{I\geq 0} w_I E_I$ is a functional of the *ensemble density* $n^{\mathbf{w}}(\mathbf{r}) := \sum_{I\geq 0} w_I n_{\Psi_I}(\mathbf{r})$.

A. K. Theophilou, J. Phys. C: Solid State Phys. ***12****, 5419 (1979).*
E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A ***37****, 2805 (1988).*
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L. N. Oliveira, E. K. U. Gross, and W. Kohn, Phys. Rev. A ***37****, 2821 (1988).*

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Ensemble energy

Ensemble Hxc functional

$$\mathbf{w} \equiv (\mathtt{w}_1, \mathtt{w}_2, \ldots)$$

Ensemble weights

$$E_{\rm Hxc}^{\mathbf{w}}[n]$$

A. K. Theophilou, J. Phys. C: Solid State Phys. ***12****, 5419 (1979).*
E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A ***37****, 2805 (1988).*
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K. Deur and E. Fromager, J. Chem. Phys. ***150****, 094106 (2019).*

DFT for excited states: From the ground-state to the ensemble picture

$$E^{\mathbf{w}} := \sum_{I\geq 0} \mathtt{w}_I E_I = \min_n \left\{ T_{\mathrm{s}}^{\mathbf{w}}[n] + E_{\mathrm{Hxc}}^{\mathbf{w}}[n] + \int d\mathbf{r}\, v_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

Ensemble energy

Kohn-Sham equations for ***an ensemble***:

$$\left[-\frac{\nabla^2}{2} + v_{\mathrm{ext}}(\mathbf{r}) + \frac{\delta E_{\mathrm{Hxc}}^{\mathbf{w}}[n]}{\delta n(\mathbf{r})}\bigg|_{n=n^{\mathbf{w}}} \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$n^{\mathbf{w}}(\mathbf{r}) = \sum_{I\geq 0} \mathtt{w}_I \sum_{i\in\Phi_I^{\mathbf{w}}} |\varphi_i(\mathbf{r})|^2$$

Ensemble density

A. K. Theophilou, J. Phys. C: Solid State Phys. ***12****, 5419 (1979).*
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$$E_J - E_0 = \frac{\partial E^{\mathbf{w}}}{\partial \mathtt{w}_J}$$

Excitation energy

A. K. Theophilou, J. Phys. C: Solid State Phys. ***12****, 5419 (1979).*
E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A ***37****, 2805 (1988).*
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K. Deur and E. Fromager, J. Chem. Phys. ***150****, 094106 (2019).*

Approximations to the ensemble correlation energy

*Recycling **standard** density-functional **approximations** …*

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] \approx \sum_{I\geq 0} \mathtt{w}_I \, E_{\mathrm{c}}[n_{\Phi_I^{\mathbf{w}}}]$$

***Ground-state** correlation functional*

Approximations to the ensemble correlation energy

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***Ground-state** correlation functional*

$$E_{\mathrm{c}}[n] = \langle \Psi[n] \,|\, \hat{T} + \hat{W}_{\mathrm{ee}} \,|\, \Psi[n] \rangle - \langle \Phi^{\mathrm{KS}}[n] \,|\, \hat{T} + \hat{W}_{\mathrm{ee}} \,|\, \Phi^{\mathrm{KS}}[n] \rangle$$

Approximations to the ensemble correlation energy

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Same density!

Approximations to the ensemble correlation energy

✓ *Recycling **standard** density-functional **approximations** …*

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] \approx \sum_{I\geq 0} \mathtt{w}_I \, E_{\mathrm{c}}[n_{\Phi_I^{\mathbf{w}}}]$$

✓ *Designing density-functional **approximations for ensembles** …*

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] \approx \sum_{I\geq 0} \mathtt{w}_I \, E_{\mathrm{c},I}^{\mathrm{LDA}}\left[n^{\mathbf{w}}\right]$$

More recent strategy[1,2]

[1] *P.-F. Loos and E. Fromager, J. Chem. Phys. **152**, 214101 (2020).*

[2] *C. Marut, B. Senjean, E. Fromager, and P.-F. Loos, Faraday Discussions, 2020, DOI: 10.1039/D0FD00059K.*

Approximations to the ensemble correlation energy

✓ *Recycling **standard** density-functional **approximations** …*

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] \approx \sum_{I\geq 0} \mathtt{w}_I \, E_{\mathrm{c}}[n_{\Phi_I^{\mathbf{w}}}]$$

✓ *Designing density-functional **approximations for ensembles** …*

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] \approx \sum_{I\geq 0} \mathtt{w}_I \, E_{\mathrm{c},I}^{\mathrm{LDA}}\left[n^{\mathbf{w}}\right]$$

*Extracted from **uniform** electron gas models*

$$E_{\mathrm{c},I}^{\mathrm{LDA}}[n] \equiv \langle \Psi_I(n) \,|\, \hat{T} + \hat{W}_{\mathrm{ee}} \,|\, \Psi_I(n) \rangle - \langle \Phi_I(n) \,|\, \hat{T} + \hat{W}_{\mathrm{ee}} \,|\, \Phi_I(n) \rangle$$

Same density!

Exact correlation energy of an ensemble

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{I\geq 0} \mathtt{w}_I \, \mathscr{E}_{\mathrm{c},I}^{\mathbf{w}}\left[n^{\mathbf{w}}\right]$$

Individual ***components***

$$\mathscr{E}_{\mathrm{c},I}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] := \langle \Psi_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi_I \rangle - \langle \Phi_I^{\mathbf{w}} | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi_I^{\mathbf{w}} \rangle$$

KS determinant (within the ensemble)

T. Gould and S. Pittalis, Phys. Rev. Lett. ***123****, 016401 (2019).*

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$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{I\geq 0} \mathtt{w}_I \, \mathscr{E}_{\mathrm{c},I}^{\mathbf{w}}\left[n^{\mathbf{w}}\right]$$

Individual ***components***

$$\mathscr{E}_{\mathrm{c},I}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] := \langle \Psi_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi_I \rangle - \langle \Phi_I^{\mathbf{w}} | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi_I^{\mathbf{w}} \rangle$$

KS determinant (within the ensemble)

Ensemble density constraint

$$\sum_{I\geq 0} \mathtt{w}_I \, n_{\Psi_I}(\mathbf{r}) = \sum_{I\geq 0} \mathtt{w}_I \, n_{\Phi_I^{\mathbf{w}}}(\mathbf{r}) \quad \not\Longrightarrow \quad n_{\Psi_I}(\mathbf{r}) = n_{\Phi_I^{\mathbf{w}}}(\mathbf{r})$$

WRONG!

T. Gould and S. Pittalis, Phys. Rev. Lett. ***123****, 016401 (2019).*

Exact correlation energy of an ensemble

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{I\geq 0} \mathtt{w}_I \, \mathscr{E}_{\mathrm{c},I}^{\mathbf{w}}\left[n^{\mathbf{w}}\right]$$

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$$\mathscr{E}_{\mathrm{c},I}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] := \langle \Psi_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi_I \rangle - \langle \Phi_I^{\mathbf{w}} | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi_I^{\mathbf{w}} \rangle$$

Different densities!

T. Gould and S. Pittalis, Phys. Rev. Lett. ***123****, 016401 (2019).*

Exact correlation energy of an ensemble

$$\sum_{I \geq 0} \mathtt{w}_I \, \mathscr{E}^{\mathbf{w}}_{\mathrm{c},I}\left[n^{\mathbf{w}}\right] = E^{\mathbf{w}}_{\mathrm{c}}\left[n^{\mathbf{w}}\right]$$

Gould-Pittalis ***decomposition***

Same density!

state-driven (SD) correlation

$$\mathscr{E}^{\mathbf{w}}_{\mathrm{c},I}\left[n^{\mathbf{w}}\right] := \langle \Psi_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi_I \rangle - \langle \overline{\Phi}^{\mathbf{w}}_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \overline{\Phi}^{\mathbf{w}}_I \rangle$$

$$- \left[\langle \Phi^{\mathbf{w}}_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi^{\mathbf{w}}_I \rangle - \langle \overline{\Phi}^{\mathbf{w}}_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \overline{\Phi}^{\mathbf{w}}_I \rangle \right]$$

Different densities!

density-driven (DD) correlation

T. Gould and S. Pittalis, Phys. Rev. Lett. ***123****, 016401 (2019).*

Exact correlation energy of an ensemble

$$\sum_{I\geq 0} \mathtt{w}_I \, \mathscr{E}^{\mathbf{w}}_{\mathrm{c},I}\left[n^{\mathbf{w}}\right] = E^{\mathbf{w}}_{\mathrm{c}}\left[n^{\mathbf{w}}\right]$$

non-uniqueness,
v-representability issues

$$\mathscr{E}^{\mathbf{w}}_{\mathrm{c},I}\left[n^{\mathbf{w}}\right] := \langle \Psi_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi_I \rangle - \langle \overline{\Phi}^{\mathbf{w}}_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \overline{\Phi}^{\mathbf{w}}_I \rangle$$

$$- \left[\langle \Phi^{\mathbf{w}}_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi^{\mathbf{w}}_I \rangle - \langle \overline{\Phi}^{\mathbf{w}}_I | \hat{T} + \hat{W}_{\mathrm{ee}} | \overline{\Phi}^{\mathbf{w}}_I \rangle \right]$$

T. Gould and S. Pittalis, Phys. Rev. Lett. ***123****, 016401 (2019).*
E. Fromager, Phys. Rev. Lett. ***124****, 243001 (2020).*

Density-driven correlation without additional KS systems

Alternative evaluation of the ***exact*** ensemble correlation energy:

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{J\geq 0} \mathtt{w}_J \, E_{\mathrm{c},J}^{\mathbf{w}}\left[n^{\mathbf{w}}\right]$$

True individual correlation energy

Density-driven correlation without additional KS systems

Alternative evaluation of the ***exact*** ensemble correlation energy:

*Individual **component***

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{J\geq 0} \mathtt{w}_J \, E_{\mathrm{c},J}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{J\geq 0} \mathtt{w}_J \, \mathscr{E}_{\mathrm{c},J}^{\mathbf{w}}\left[n^{\mathbf{w}}\right]$$

True individual correlation energy

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Alternative evaluation of the ***exact*** ensemble correlation energy:

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True individual correlation energy

WRONG!

because $n_{\Psi_J}(\mathbf{r}) \neq n_{\Phi_J^{\mathbf{w}}}(\mathbf{r})$ …

Density-driven correlation without additional KS systems

Alternative evaluation of the ***exact*** ensemble correlation energy:

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{J\geq 0} \mathtt{w}_J \, E_{\mathrm{c},J}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{J\geq 0} \mathtt{w}_J \, \mathscr{E}_{\mathrm{c},J}^{\mathbf{w}}\left[n^{\mathbf{w}}\right]$$

Linearity *of the ensemble energy*

$$E_J = E_0 + \left(E_J - E_0\right) = E^{\mathbf{w}} - \sum_{I>0} \mathtt{w}_I \frac{\partial E^{\mathbf{w}}}{\partial \mathtt{w}_I} + \left(\frac{\partial E^{\mathbf{w}}}{\partial \mathtt{w}_J}\right)$$

$$E_{\mathrm{c},J}^{\mathbf{w}}[n^{\mathbf{w}}] = \mathscr{E}_{\mathrm{c},J}^{\mathbf{w}}[n^{\mathbf{w}}] + \sum_{K\geq 0} \mathtt{w}_K \sum_{I>0} (\delta_{IJ} - \mathtt{w}_I) \frac{\partial \left(\mathscr{E}_{\mathrm{c},K}^{\mathbf{w}}[n^{\mathbf{w}}]\right)}{\partial \mathtt{w}_I} + \ldots$$

Summation over ***all*** *the states*

Density-driven correlation without additional KS systems

Alternative evaluation of the ***exact*** ensemble correlation energy:

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{J\geq 0} \mathtt{w}_J \, E_{\mathrm{c},J}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{J\geq 0} \mathtt{w}_J \, \mathscr{E}_{\mathrm{c},J}^{\mathbf{w}}\left[n^{\mathbf{w}}\right]$$

State-driven correlation!

State J:

$$E_{\mathrm{c},J}^{\mathbf{w}}[n^{\mathbf{w}}] = \mathscr{E}_{\mathrm{c},J}^{\mathbf{w}}[n^{\mathbf{w}}] + \sum_{K\geq 0} \mathtt{w}_K \sum_{I>0} (\delta_{IJ} - \mathtt{w}_I) \frac{\partial \left(\mathscr{E}_{\mathrm{c},K}^{\mathbf{w}}[n^{\mathbf{w}}]\right)}{\partial \mathtt{w}_I} + \ldots$$

$K = J$

Density-driven correlation without additional KS systems

Alternative evaluation of the ***exact*** ensemble correlation energy:

$$E_{\mathrm{c}}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{J\geq 0} \mathtt{w}_J \, E_{\mathrm{c},J}^{\mathbf{w}}\left[n^{\mathbf{w}}\right] = \sum_{J\geq 0} \mathtt{w}_J \, \mathscr{E}_{\mathrm{c},J}^{\mathbf{w}}\left[n^{\mathbf{w}}\right]$$

Density-driven correlation!

State J:

$$E_{\mathrm{c},J}^{\mathbf{w}}[n^{\mathbf{w}}] = \mathscr{E}_{\mathrm{c},J}^{\mathbf{w}}[n^{\mathbf{w}}] + \sum_{K\geq 0} \mathtt{w}_K \sum_{I>0} (\delta_{IJ} - \mathtt{w}_I) \frac{\partial\left(\mathscr{E}_{\mathrm{c},K}^{\mathbf{w}}[n^{\mathbf{w}}]\right)}{\partial \mathtt{w}_I} + \ldots \qquad K \neq J$$

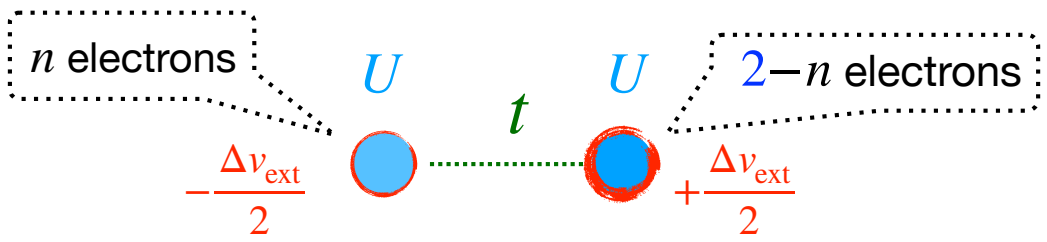
Density-driven correlation without additional KS systems

Ensemble density-driven (DD) correlation energy expression:

$$E_{\mathrm{c}}^{\mathbf{w},\mathrm{DD}}\left[n^{\mathbf{w}}\right] = 2\sum_{J\geq 0} \mathtt{w}_J^2 \sum_{I>0} (\delta_{IJ} - \mathtt{w}_I) \left\langle \Phi_J^{\mathrm{KS},\mathbf{w}} \middle| \hat{T} + \hat{W}_{\mathrm{ee}} \middle| \frac{\partial \Phi_J^{\mathrm{KS},\mathbf{w}}}{\partial \mathtt{w}_I} \right\rangle$$

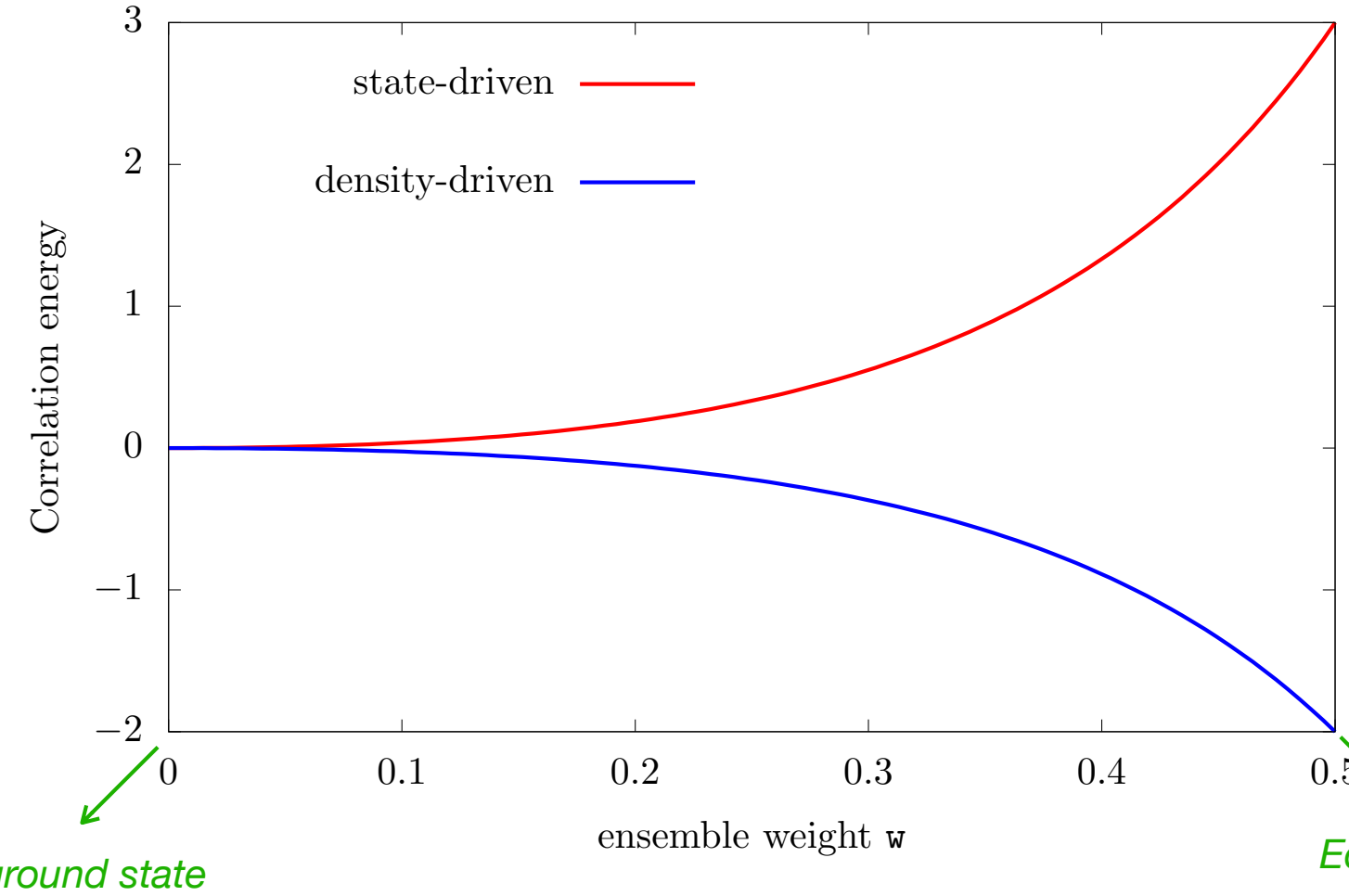
Static linear response

Application to the Hubbard dimer: the bi-ensemble case



$$\frac{\Delta v_{\text{ext}}}{t} << \frac{t}{U} << 1$$

First (singlet) **excited-state** correlation energy per unit of $U(U\Delta v_{\text{ext}})^2/(4t^4)$



E. Fromager, Phys. Rev. Lett. ***124****, 243001 (2020).*

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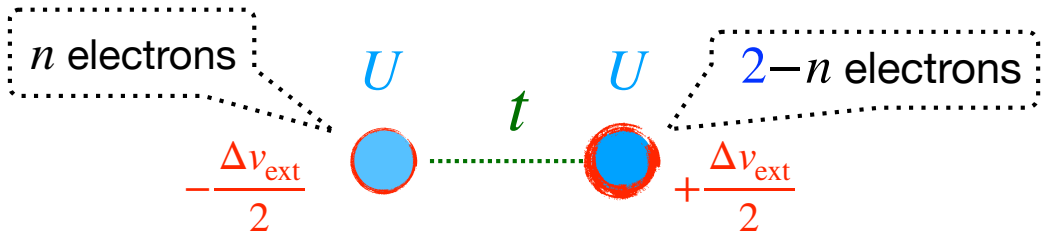
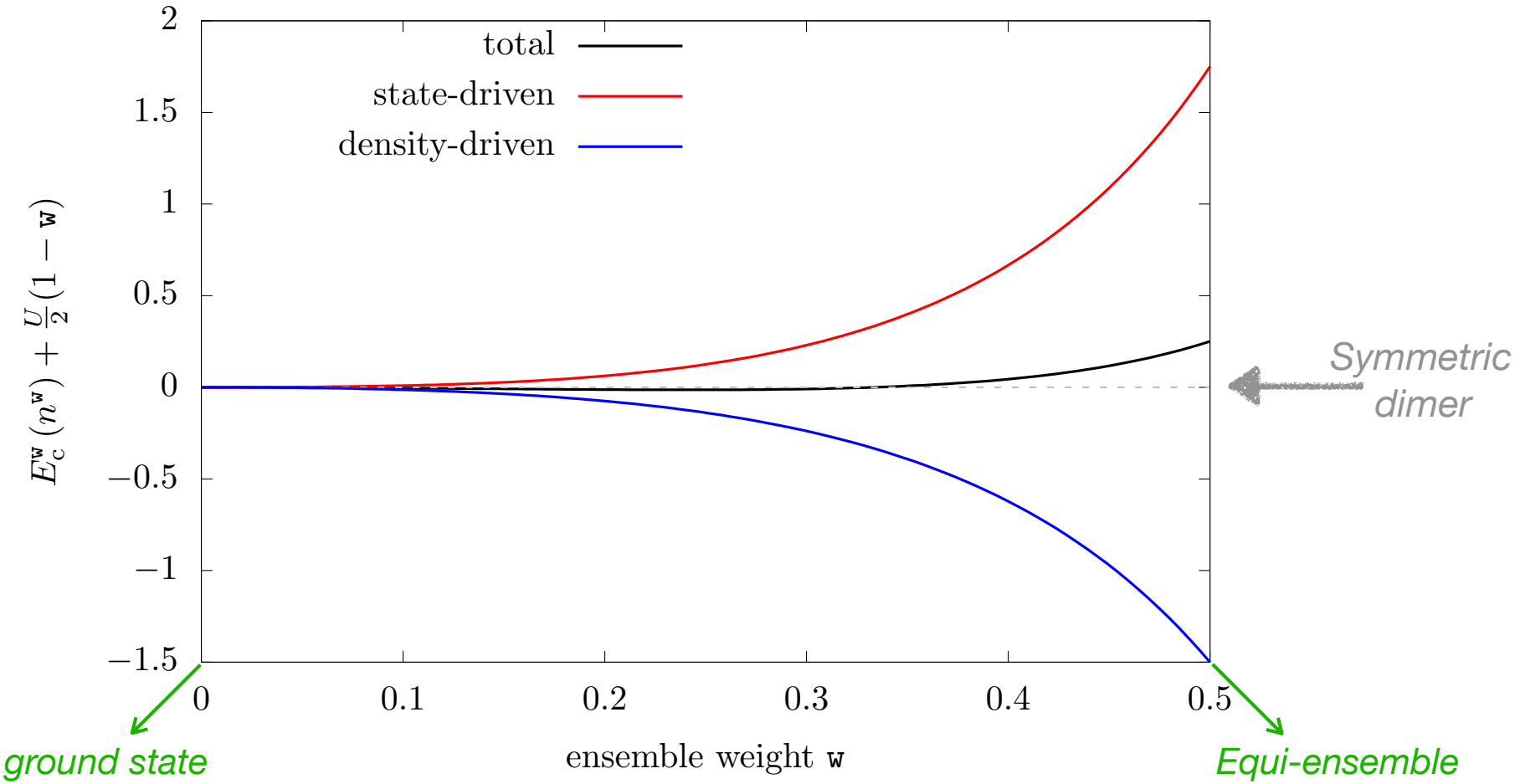


$$\frac{\Delta v_{\text{ext}}}{t} << \frac{t}{U} << 1$$

Exact **ensemble correlation** energy per unit of $U(U\Delta v_{\text{ext}})^2/(4t^4)$



E. Fromager, Phys. Rev. Lett. ***124****, 243001 (2020).*

Conclusions and perspectives

- Many-electron ensembles exhibit *density-driven (DD) correlations*.
- DD correlations do *not* exist in *standard* ground-state *DFT*.
- A *general* DD correlation energy *expression* has been derived[1]:

$$E_{\mathrm{c}}^{\mathbf{w},\mathrm{DD}}\left[n^{\mathbf{w}}\right] = 2\sum_{J\geq 0} \mathtt{w}_J^2 \sum_{I>0} (\delta_{IJ} - \mathtt{w}_I) \left\langle \Phi_J^{\mathrm{KS},\mathbf{w}} \middle| \hat{T} + \hat{W}_{\mathrm{ee}} \middle| \frac{\partial \Phi_J^{\mathrm{KS},\mathbf{w}}}{\partial \mathtt{w}_I} \right\rangle$$

- DD correlations were shown to be *significant* (in model systems).
- Our formalism applies also to ensembles with *charged excitations*[2,3,4] (work in progress).

[1] *E. Fromager, Phys. Rev. Lett.* ***124****, 243001 (2020).*
[2] *B. Senjean and E. Fromager, Phys. Rev. A* ***98****, 022513 (2018).*
[3] *B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190.*
[4] *M. J. P. Hodgson, J. Wetherell, and E. Fromager,* ***arXiv:2010.05642*** *(2020).*

N-centered grand canonical ensembles

density:

$$n^{\mathcal{N}}(\mathbf{r}) = (1-\alpha)n^{N}(\mathbf{r}) + \alpha\, n^{N-1}(\mathbf{r})$$

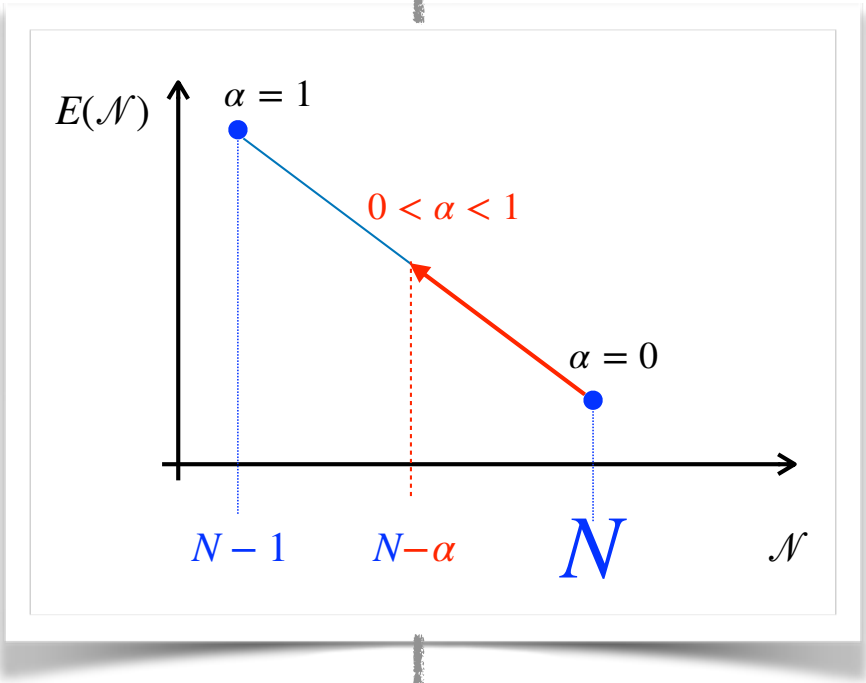
Look at me!

electron **number**:

$$\mathcal{N} = N-\alpha$$

energy:

$$E\left(\mathcal{N}\right) = (1-\alpha)E^{N} + \alpha E^{N-1}$$



density:

$$n^{\{N,\alpha\}}(\mathbf{r}) = (1-\alpha)n^{N}(\mathbf{r}) + \frac{N\alpha}{N-1}\, n^{N-1}(\mathbf{r})$$

Look at me!

electron **number**:

$$N$$

energy:

$$\mathscr{E}^{\{N,\alpha\}} = (1-\alpha)E^{N} + \frac{N\alpha}{N-1}E^{N-1}$$

$$\left[\left(1-\frac{\alpha}{N}\right) - \frac{\alpha(1-\alpha)}{N}\frac{\partial}{\partial\alpha}\right]$$

Conventional *picture*

N-centered picture

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. (2020), ***DOI: 10.1002/qua.26190***

$$E_J = \langle \Phi_J^{\mathrm{KS,w}} | \hat{H} | \Phi_J^{\mathrm{KS,w}} \rangle + E_{\mathrm{c},J}^{\mathrm{w}}[n^{\mathrm{w}}]$$

$$E_{\mathrm{c},J}^{\mathrm{w}}[n^{\mathrm{w}}] = \mathscr{E}_{\mathrm{c},J}^{\mathrm{w}}[n^{\mathrm{w}}] + \sum_{K\geq 0} \mathtt{w}_K \sum_{I>0} (\delta_{IJ} - \mathtt{w}_I) \frac{\partial \left(\mathscr{E}_{\mathrm{c},K}^{\mathrm{w}}[n^{\mathrm{w}}] \right)}{\partial \mathtt{w}_I} + \sum_{K\geq 0} \mathtt{w}_K \int d\mathbf{r} \frac{\delta \mathscr{E}_{\mathrm{c},K}^{\mathrm{w}}[n^{\mathrm{w}}]}{\delta n(\mathbf{r})} \left(n_{\Phi_J^{\mathrm{KS,w}}}(\mathbf{r}) - n_{\Psi_J}(\mathbf{r}) \right)$$

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$$E^{\mathbf{w}} := \sum_{I\geq 0} \mathtt{w}_I E_I = \min_n \left\{ T_{\mathrm{s}}^{\mathbf{w}}[n] + E_{\mathrm{Hxc}}^{\mathbf{w}}[n] + \int d\mathbf{r}\, v_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

Ensemble energy

Kohn-Sham equations for ***an ensemble***

$$n^{\mathbf{w}}(\mathbf{r}) = \sum_{I\geq 0} \mathtt{w}_I \sum_{i\in\Phi_I^{\mathbf{w}}} |\varphi_i(\mathbf{r})|^2$$

Ensemble density

$$\left[-\frac{\nabla^2}{2} + v_{\mathrm{ext}}(\mathbf{r}) + \left. \frac{\delta E_{\mathrm{Hxc}}^{\mathbf{w}}[n]}{\delta n(\mathbf{r})} \right|_{n=n^{\mathbf{w}}} \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$E_J - E_0 = \frac{\partial E^{\mathbf{w}}}{\partial \mathtt{w}_J}$$

Excitation energy

A. K. Theophilou, J. Phys. C: Solid State Phys. ***12****, 5419 (1979).*
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