

Correcting the *GW* self-screening error with a spatially local density functional



MAX-PLANCK-GESELLSCHAFT



**Matt Hodgson
and
Hardy Gross**



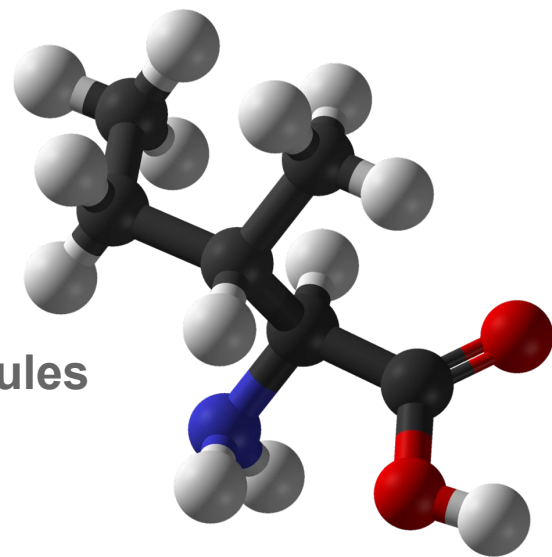
**Jack Wetherell
and
Rex Godby**

What are our aims?

Accurately model the flow of electrons through molecular junctions

Accurately describe the structure of molecules

Accurately predict the excitation properties of molecules



So what's the problem?

The more electrons you have, the more interactions...

...the exact, full-correlated many-body wavefunction quickly becomes impossible to calculate



$$\Psi(x_1)$$

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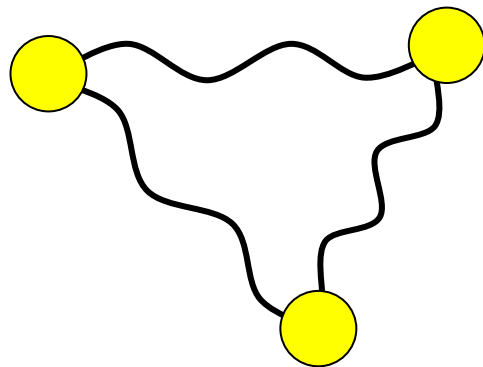
$$\Psi(x_1, x_2)$$

So what's the problem?

The more electrons you have, the more interactions...

...the exact, full-correlated many-body wavefunction quickly becomes impossible to calculate

$$\Psi(x_1, x_2, x_3)$$

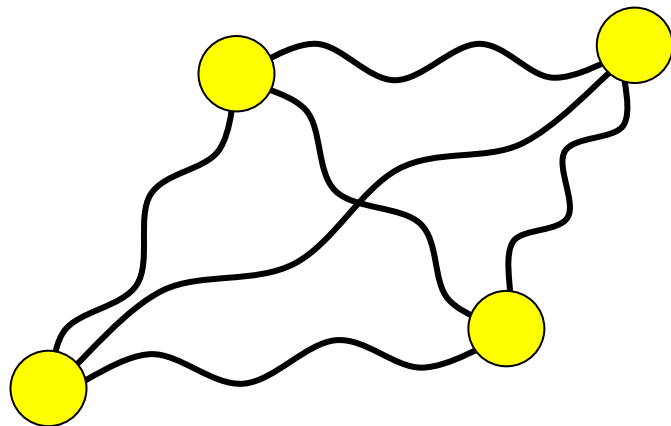


So what's the problem?

The more electrons you have, the more interactions...

...the exact, full-correlated many-body wavefunction quickly becomes impossible to calculate

$$\Psi(x_1, x_2, x_3, x_4)$$

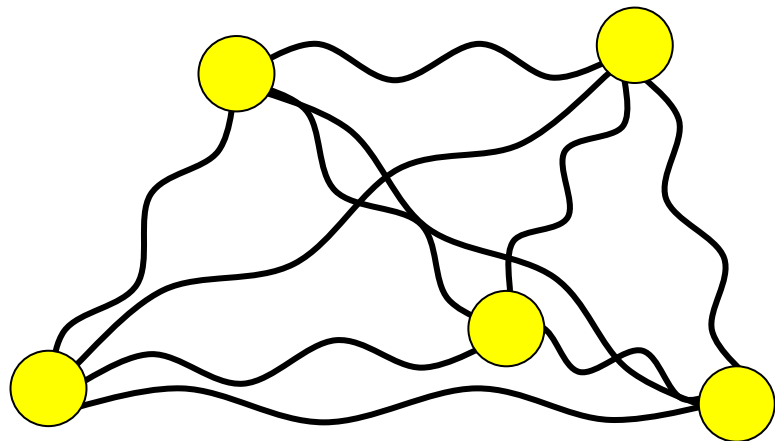


So what's the problem?

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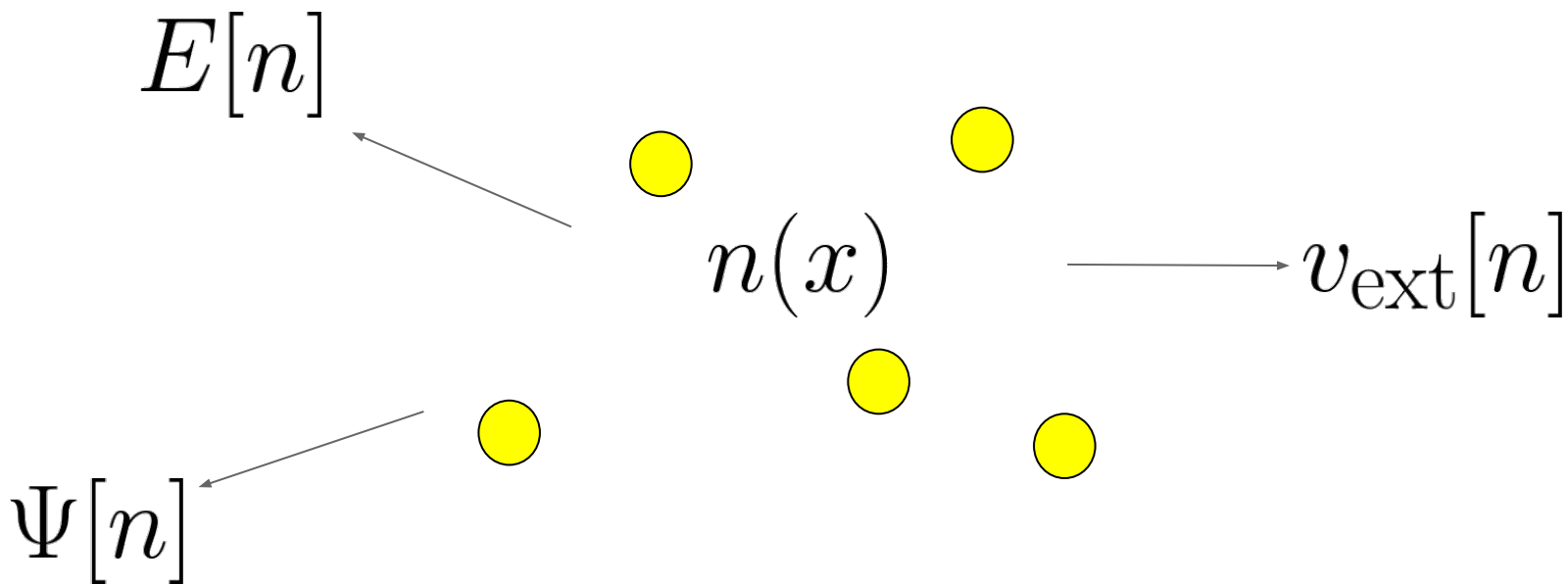
...the exact, full-correlated many-body wavefunction quickly becomes impossible to calculate

$$\Psi(x_1, x_2, x_3, x_4, \dots)$$



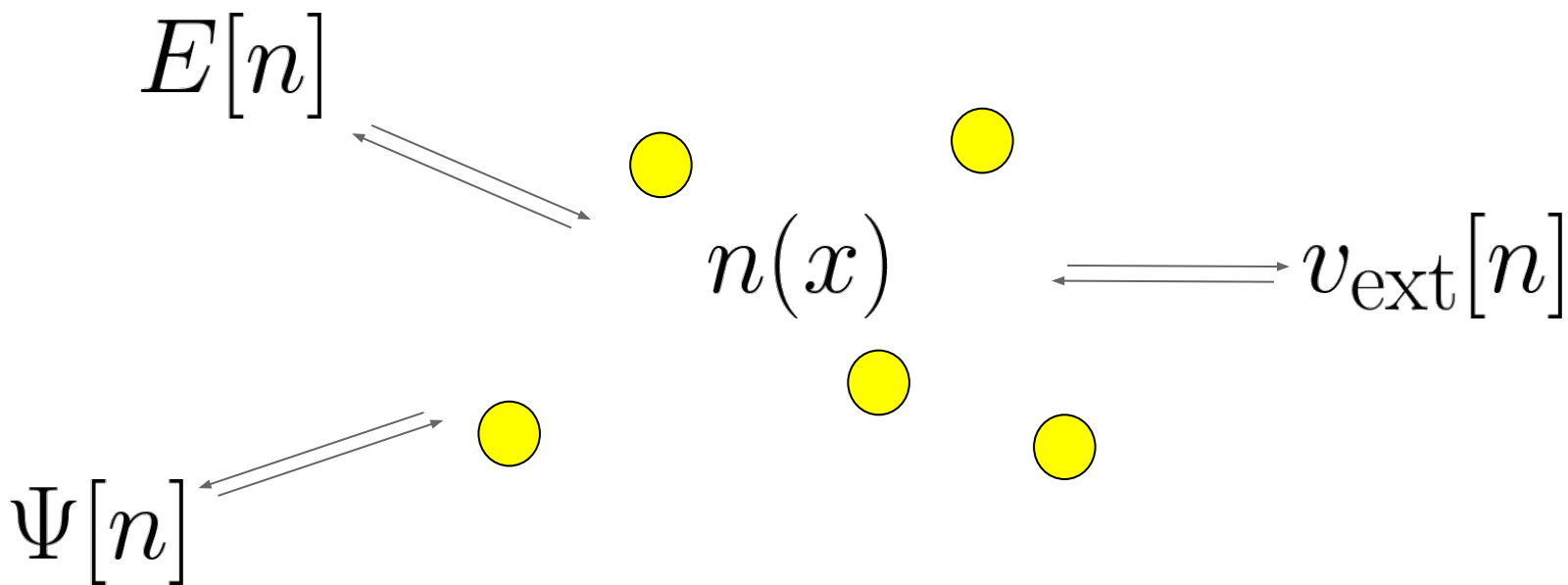
Density functional theory

Replace the wavefunction with the *density* – P. Hohenberg and W. Kohn Phys. Rev. **136**, B864



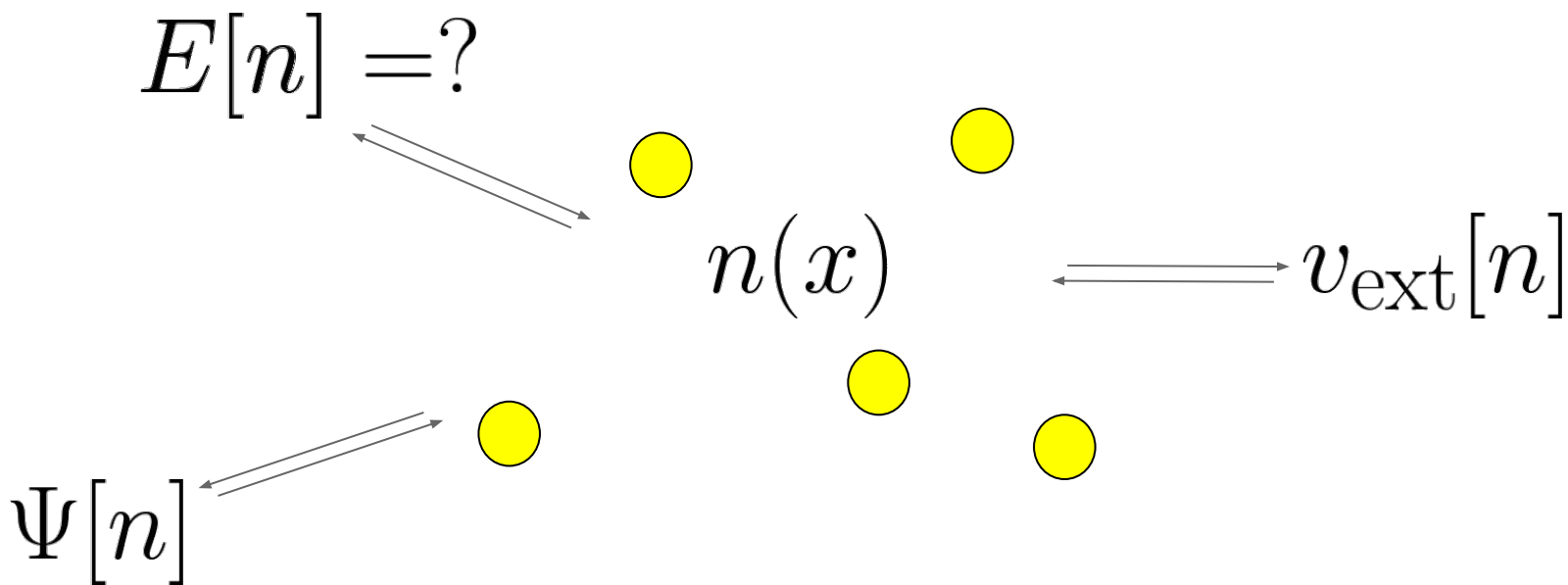
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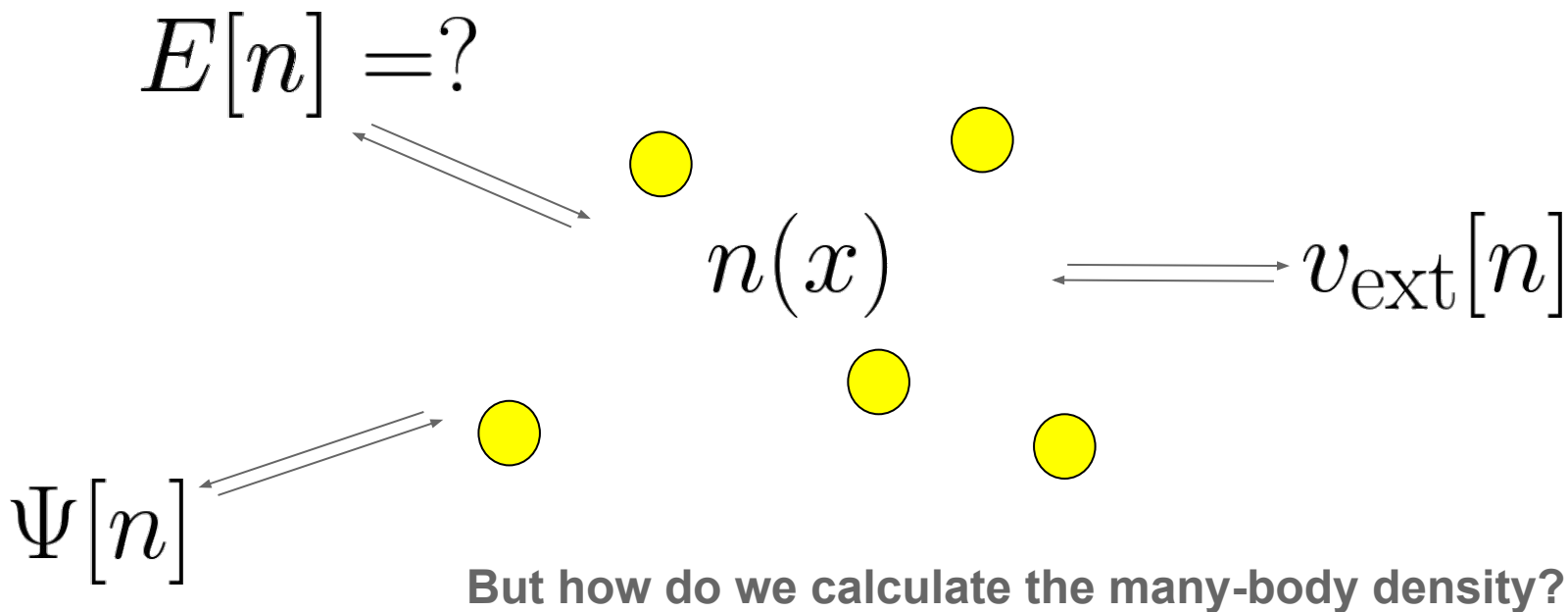
Density functional theory

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Density functional theory

Replace the wavefunction with the *density* – P. Hohenberg and W. Kohn Phys. Rev. **136**, B864



Kohn-Sham theory

Define an auxiliary system of fully non-interacting electrons:

$$E = \min_{n \rightarrow N} \left(T_s[n] + U[n] + E_{\text{xc}}[n] + \int n(x)v_{\text{ext}}(x)dx \right)$$

which yields the exact many-body density!

Kohn-Sham theory

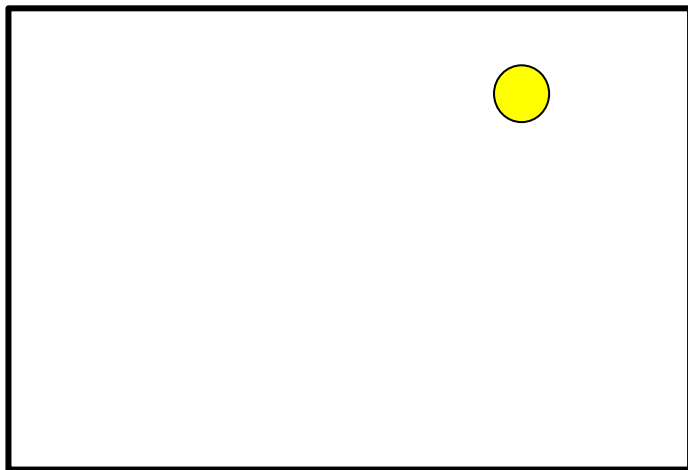
Auxiliary system of fully non-interacting electrons which experience a local effective potential – the Kohn-Sham potential

$$\left(-\frac{1}{2} \frac{d^2}{dx^2} + v_s(x) \right) \phi_i(x) = \varepsilon_i \phi_i(x) \quad n(x) = \sum_i |\phi_i(x)|^2$$

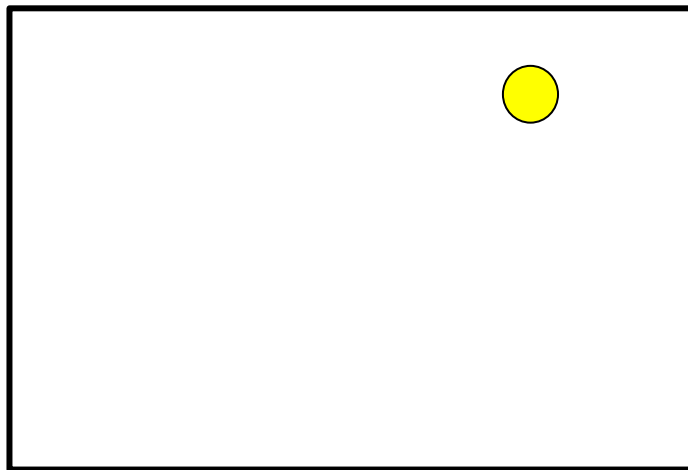
$$v_s(x) = v_{\text{ext}}(x) + v_{\text{H}}(x) + v_{\text{xc}}(x)$$

“An ‘exactification’ of the Hartree equations”

Many-body system



Kohn-Sham system

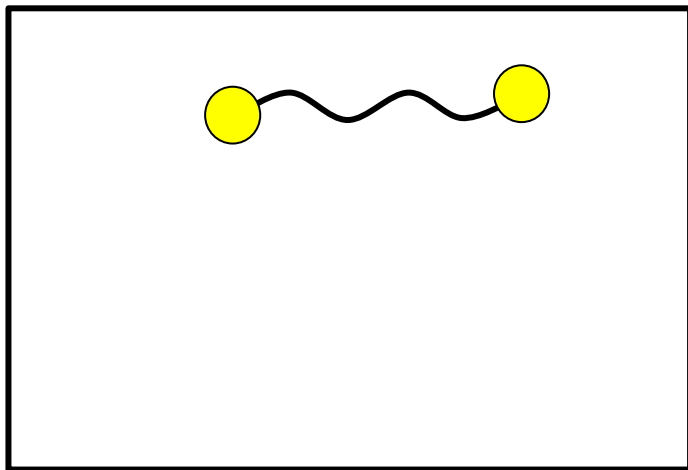


The electron densities are the same

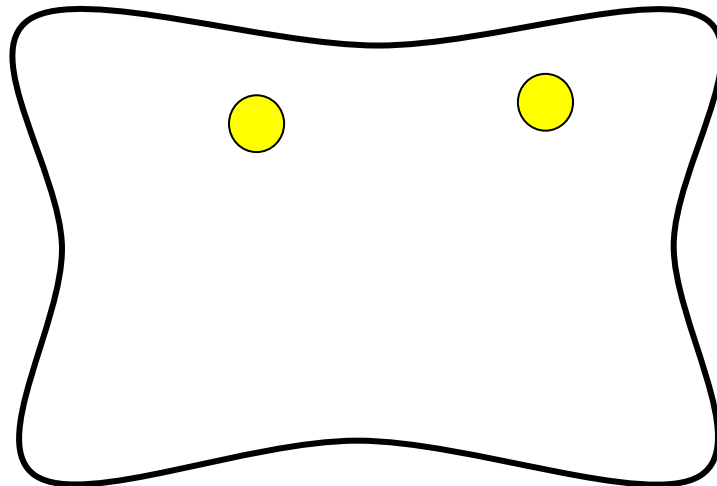
Computational scaling: k^1

Computational scaling: $1 \cdot k$

Many-body system



Kohn-Sham system

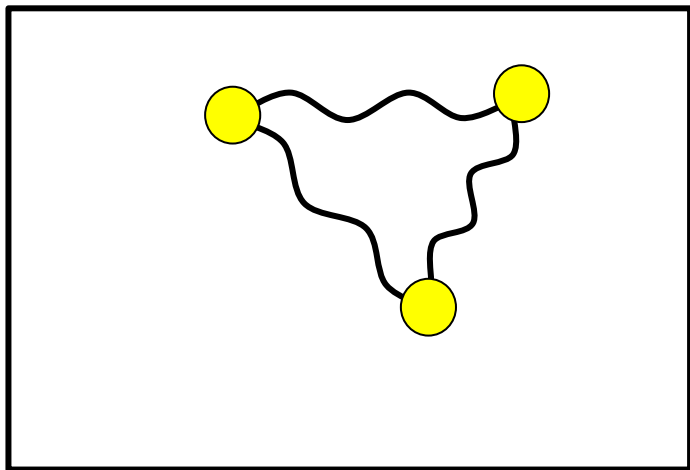


The electron densities are the same

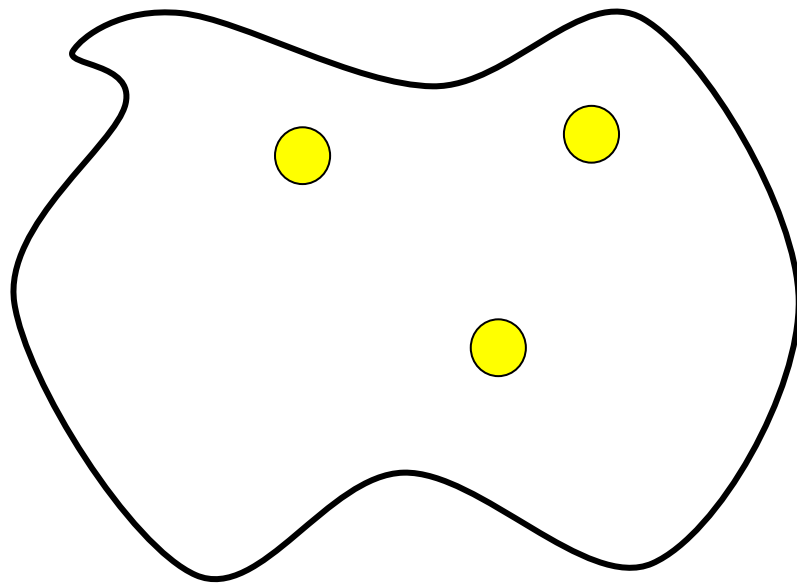
Computational scaling: k^2

Computational scaling: $2 \cdot k$

Many-body system



Kohn-Sham system

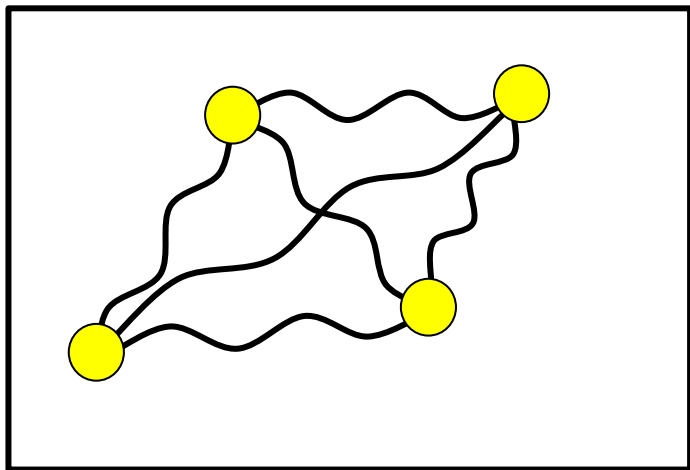


The electron densities are the same

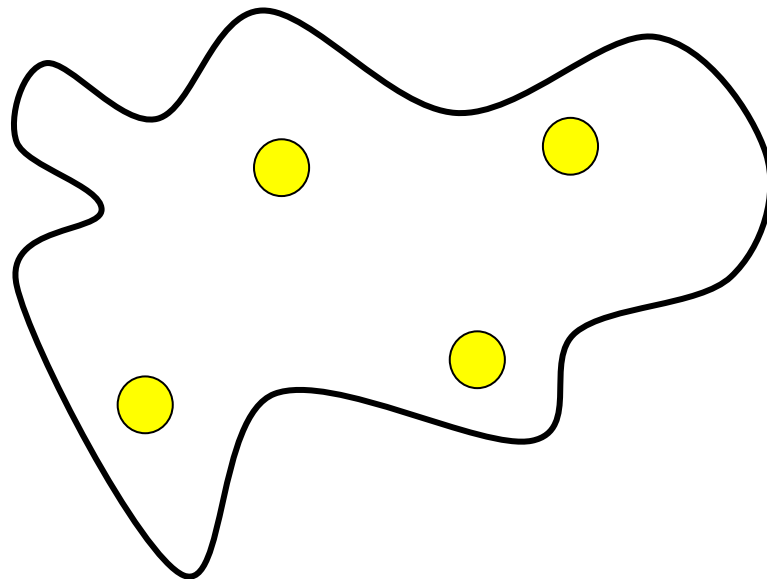
Computational scaling: k^3

Computational scaling: $3 \cdot k$

Many-body system



Kohn-Sham system

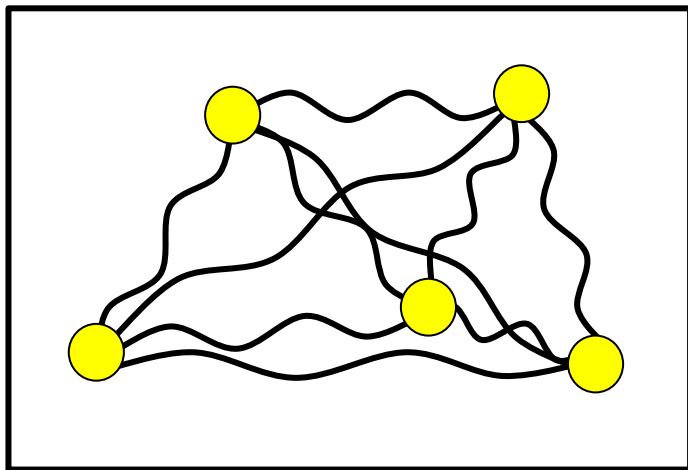


The electron densities are the same

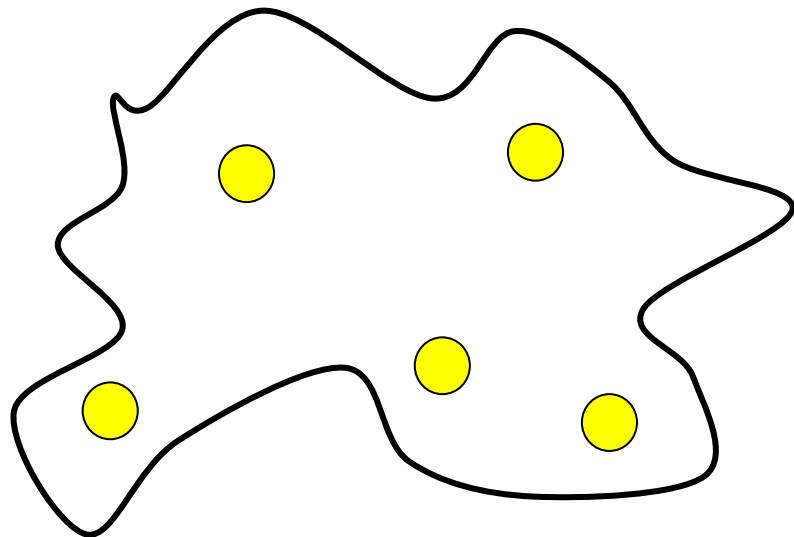
Computational scaling: k^4

Computational scaling: $4 \cdot k$

Many-body system



Kohn-Sham system



The electron densities are the same

Computational scaling: k^5

Computational scaling: $5 \cdot k$

Density functional theory: successes and limitations

- Very computationally efficient
- Very successful in solid state physics
- Less successful for molecules – advanced approximations to the (time-dependent) Kohn-Sham exchange-correlation potential required
- Auxiliary Kohn-Sham system not designed to yield quasiparticle energies

Many-body perturbation theory

Hartree-Fock approximation:

Assume the many-body wavefunction is a single Slater Determinant: $\Psi \approx \Phi$

$$E_{\text{HF}} = \min \langle \Phi | \hat{H} | \Phi \rangle$$

Quasiparticle energies

$$\left(-\frac{1}{2} \frac{d^2}{dx^2} + v_{\text{ext}}(x) + v_{\text{H}}(x) \right) \phi_i(x) + \int dx' \Sigma_{\text{x}}(x, x') \phi_i(x') = \varepsilon_i \phi_i(x)$$

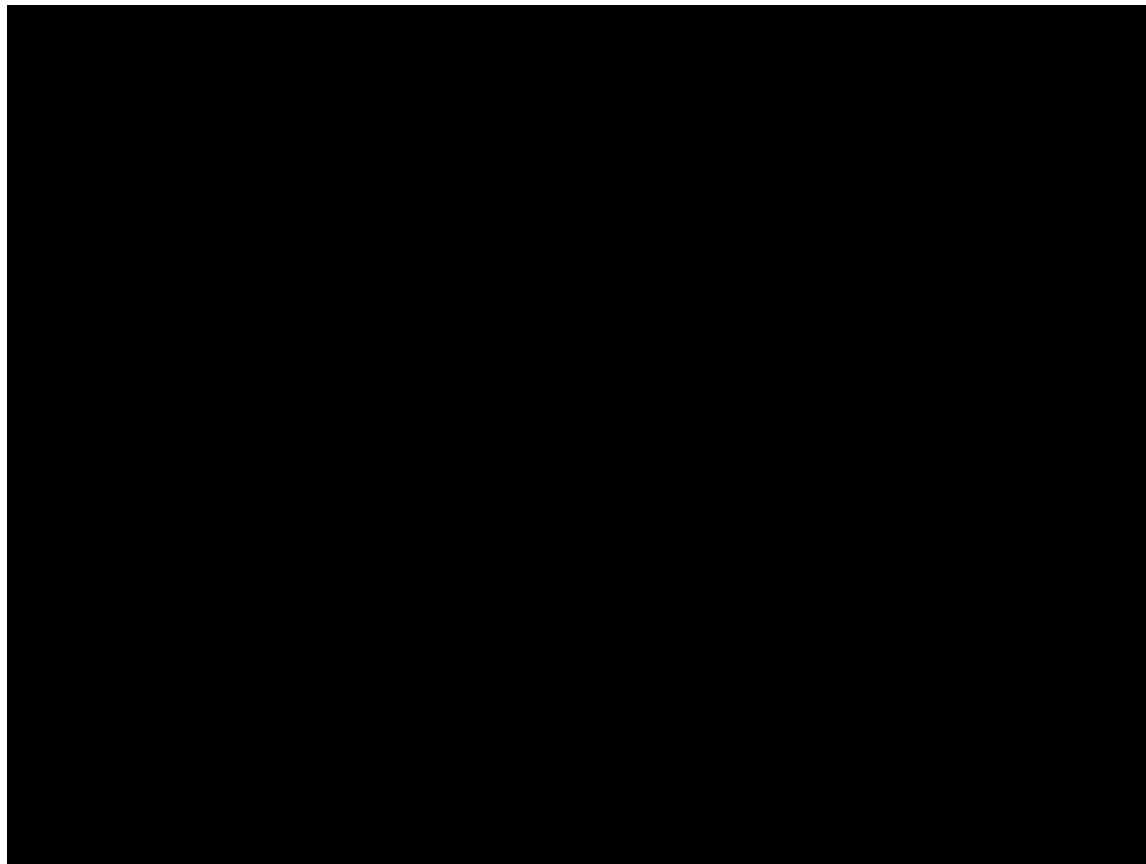
Spatially nonlocal exact exchange operator

Hartree-Fock approximation

- Lowest level of MBPT
- Reasonable computational expense allows for practical real-time evolution
- Models exchange exactly
- Neglects all electron correlation

How accurate is the electron density from Hartree-Fock?

Correlated system: perturbed 2-electron singlet



Many-body perturbation theory

- Screen the exchange potential in order to model correlation
- Common way of screening is the *GW* approximation
- Self-consistent *GW* approximation corresponds to an approximate wavefunction beyond a single Slater Determinant

Quasiparticle equations

$$\left(-\frac{1}{2} \frac{d^2}{dx^2} + v_{\text{ext}}(x) + v_{\text{H}}(x) \right) \phi_i(x, \omega_i) + \int dx' \Sigma_{\text{xc}}(x, x', \omega_i) \phi_i(x', \omega_i) = \omega_i \phi_i(x, \omega_i)$$

↑
Spatially nonlocal, frequency-dependent self energy

The frequency dependence excites the single-particle orbitals out of their ground state, thus the system is no longer described by a single Slater Determinant

Quasiparticle equations

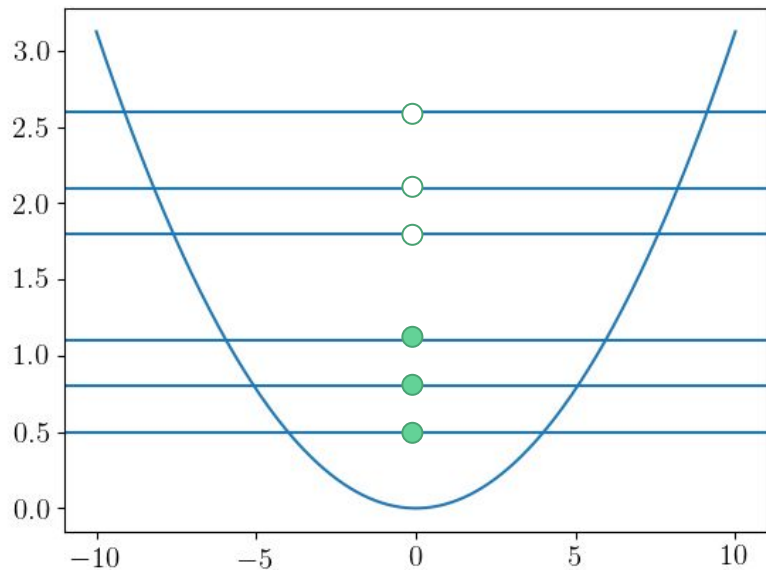
$$\left(-\frac{1}{2} \frac{d^2}{dx^2} + v_{\text{ext}}(x) + v_{\text{H}}(x) \right) \phi_i(x, \omega_i) + \int dx' \Sigma_{\text{xc}}(x, x', \omega_i) \phi_i(x', \omega_i) = \omega_i \phi_i(x, \omega_i)$$

↑
Spatially nonlocal, frequency-dependent self energy

Usually the **Green's function** equation (Dyson equation) is used over these equations; for finite systems they are equivalent

The Green's function G

t



$$G(x, x', t' - t)$$

t'

The GW equations

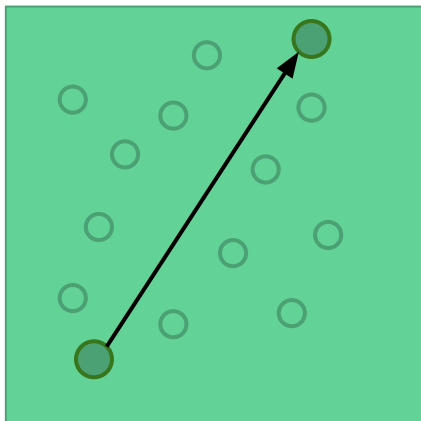
$$G = G_0 + G_0 \Sigma G$$

$$\Sigma = V_H + iGW$$

$$P = iGG$$

$$W = v + vPW$$

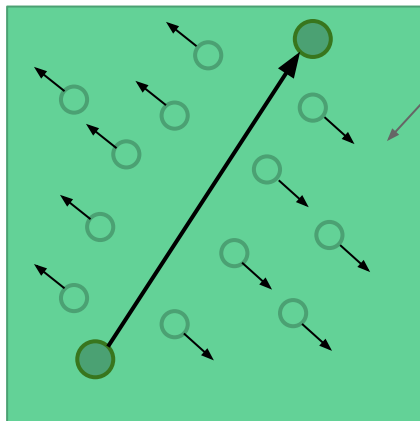
The GW approximation



No Screening: Hartree-Fock

$$\Sigma_{xc} = Gv$$

$$P = 0$$

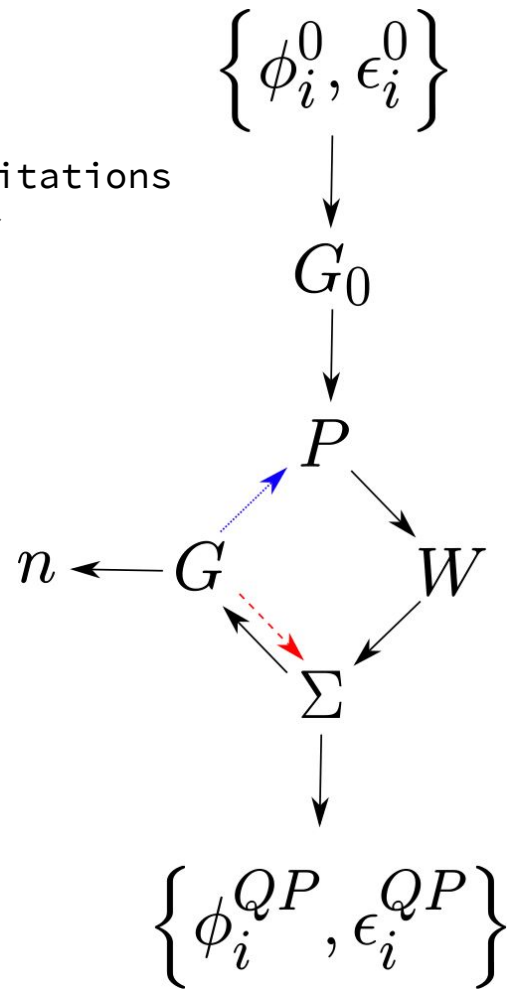


Screening: GW

$$\Sigma_{xc} = GW$$

$$P = GG$$

Excitations



GW approximation

- Models correlation by screening the exchange potential – correlation is not exact!
- Relatively computationally expensive – corrections beyond *GW* are very computationally expensive (vertex corrections)
- Good for calculating quasiparticle energies unless the system is strongly correlated
- How good is the corresponding electron density?

***GW* approximation**

Is there a computationally cheap way to correct the *GW* approximation for strongly correlated systems?

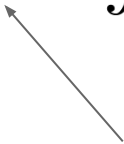
Generalised Kohn-Sham theory

“Wavefunction theory meets density functional theory”

Kohn-Sham theory

$$E = \min_{n \rightarrow N} \left(T_s[n] + U[n] + E_{xc}[n] + \int n(x)v_{\text{ext}}(x)dx \right)$$

Yields local potential



Generalised Kohn-Sham theory

“Wavefunction theory meets density functional theory”

Kohn-Sham theory

$$E = \min_{\{\phi_i\} \rightarrow n} \left(T_s[n] + S[\{\phi_i\}] + R[n] + \int n(x)v_{\text{ext}}(x)dx \right)$$

Yields nonlocal potential

Yields local potential

Generalised Kohn-Sham theory

An example: let's return to the Hartree-Fock equations:

$$\left(-\frac{1}{2} \frac{d^2}{dx^2} + v_{\text{ext}}(x) + v_{\text{H}}(x) \right) \phi_i(x) + \int dx' \Sigma_{\text{x}}(x, x') \phi_i(x') = \varepsilon_i \phi_i(x)$$

Hartree-Fock-Kohn-Sham equations:

Spatially local potential
adds (some) correlation

$$\left(-\frac{1}{2} \frac{d^2}{dx^2} + v_{\text{ext}}(x) + v_{\text{H}}(x) + v_{\text{c}}(x) \right) \phi_i(x) + \int dx' \Sigma_{\text{x}}(x, x') \phi_i(x') = \varepsilon_i \phi_i(x)$$

“An ‘exactification’ of the Hartree-Fock equations”

...in terms of the density

Generalised Kohn-Sham theory

- For certain **given** nonlocal potentials, e.g., Fock exchange, there is a corresponding **spatially local potential** which ensures an exact density
- Full correlation effects are not taken into account as GKS theory still restricts the wavefunction to a single Slater Determinant
- However, the quasiparticle energies may be good if the Fock operator is screened...

Hybrid functionals

- Hybrid functionals are within generalised Kohn-Sham theory
- They are known to give good quasiparticle energies and electron densities [1,2]
- As the Fock operator is screened they are akin to many-body perturbation theory

[1] M. G. Medvedev, I. S. Bushmarinov, J. Sun, J. P. Perdew, and K. A. Lyssenko, *Science* 355, 49 (2017)

[2] A. R. Elmaslmane, J. Wetherell, M. J. P. Hodgson, K. P. McKenna, and R. W. Godby *Phys. Rev. Materials* **2**, 040801(R)

So far...

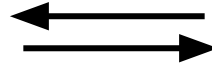
- We want accurate densities and quasiparticle energies for correlated systems
- Very expensive to add corrections to the GW approximation within MBPT
- Generalised Kohn-Sham theory *suggests* a computationally cheap way to correct GW – a spatially local potential used in conjunction with the spatially nonlocal self energy
- And we still don't know how good the GW density is...

iDEA code

Define a 1/2/3 electron model
system in 1D with a
(time-dependent) external potential

Compute **exact** (time-dependent), fully-correlated
many-body wavefunction and density

Compute **approximate** (time-dependent) density
and Kohn-Sham potential



Reverse engineer **exact** density to give **exact**
(time-dependent) Kohn-Sham potential

Reverse engineer **approximate** density to give
approximate (time-dependent) Kohn-Sham
potential

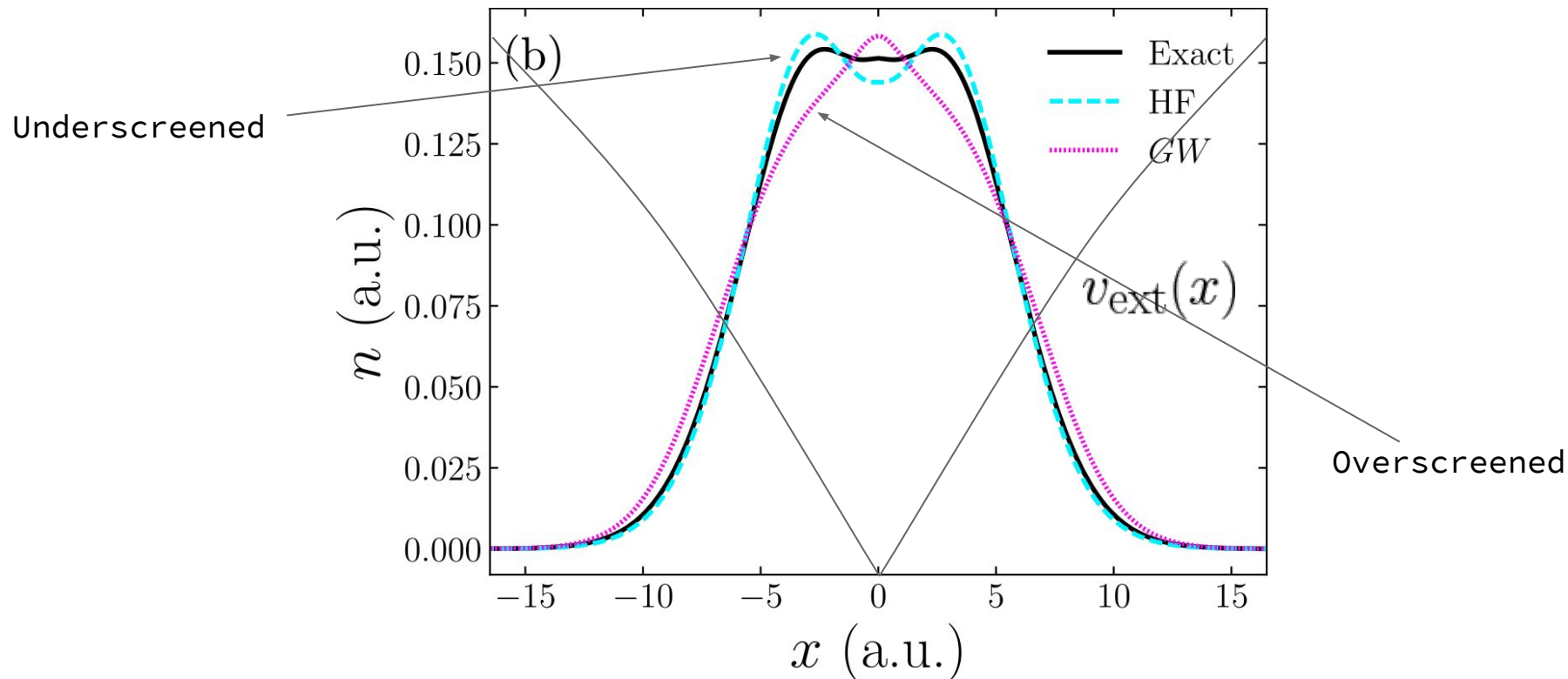
Available approximations:



- No interacting
- DFT and TDDFT – (generalised) Kohn-Sham (LDA, some novel methods)
- Hybrid functionals
- Many-body perturbation theory (HF, G0W0, GW0, COHSEX, scGW, GW+ssc)

How accurate is the density from MBPT?

Correlated system 'atom': 2 *same-spin* electrons



Approximations made within the *GW* approximation

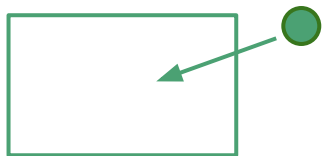
$$\Sigma = V_{\text{H}} + iGW$$

~~$$P = iGG$$~~

The self-screening error

What is the energy required to add an electron to an empty box?

The LUMO of the zero-electron system:



$$\hat{H}\phi_0 = \varepsilon_0\phi_0$$

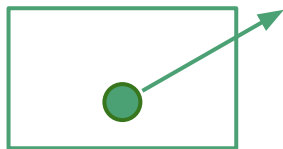
$$\hat{H} = \hat{T}_s + v_{\text{ext}}$$

$$v_{\text{H}} = v_{\text{xc}} = 0$$

The self-screening error

What is the energy required to remove the electron?

The HOMO of the one-electron system:



$$\hat{H}\phi_0 = \tilde{\epsilon}_0\phi_0$$

$$\hat{H} = \hat{T}_S + v_{\text{ext}} + v_{\text{SS}}$$

$$v_{\text{XC}} \neq -v_{\text{H}}$$

When we use the exact P , we screen the exchange and so the potentials no longer cancel!

So with screening the electron screens its own removal!

The self-screening error

- When we screen the exchange operator we model correlation, but also reduce the self-interaction correction
- If the exchange operator were to be screened exactly within the *GW* approximation, this self-interaction error would remain
- This remaining error is termed the **self-screening error** as it can be thought of each electron screening its own presence

P. Romaniello, S. Guyot, and L. Reining, J. Chem. Phys. 131, 154111 (2009).

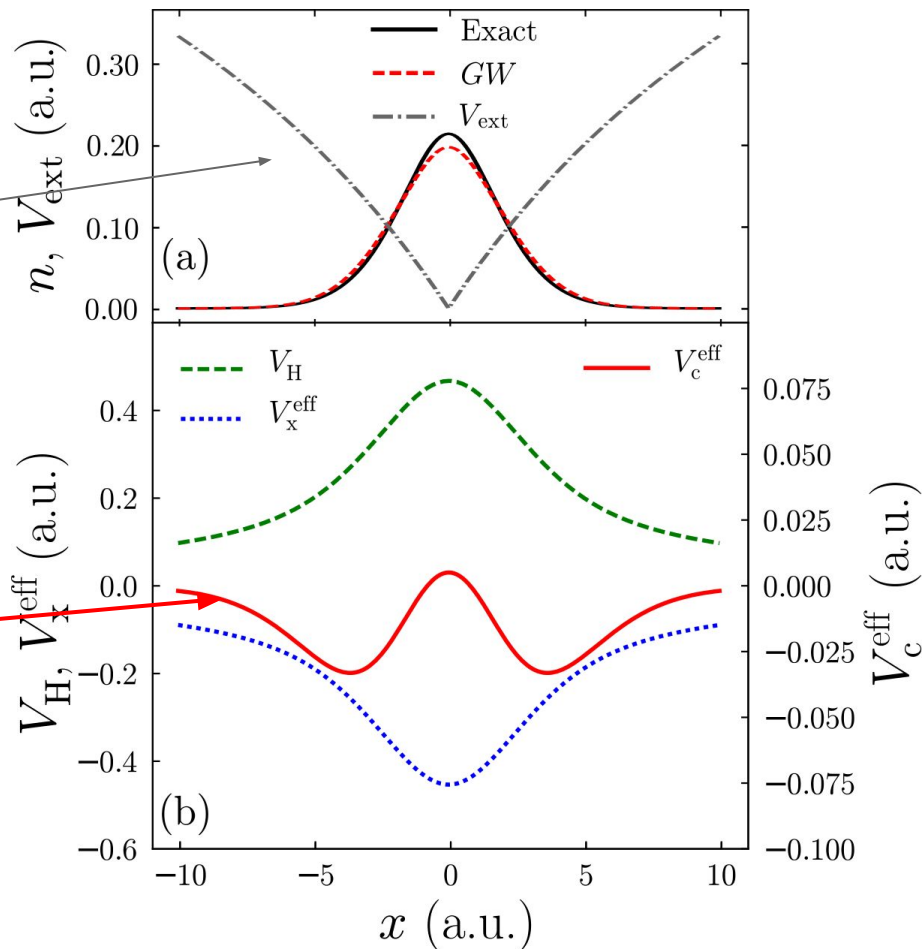
W. Nelson, P. Bokes, P. Rinke, and R. W. Godby, Phys. Rev. A. 75, 032505 (2007).

The self-screening error

One-electron system (RPA is exact)

$$V^{\text{eff}}(x) = \frac{1}{\phi(x)} \int \Sigma(x, x', \varepsilon) \phi(x') dx'$$

'Self-screening potential'



Our self-screening correction

We force the addition and removal energies to be correct with a spatially local potential – our self-screening correction (ssc)

$$\Sigma_{GW+ssc}(x, x', \omega) = \Sigma_{GW}(x, x', \omega) + V_{ssc}[n](x)$$

Spatially nonlocal self-energy



Spatially local correction

Not within generalised Kohn-Sham as wavefunction is beyond a single Slater Determinant

Our self-screening correction

We force the addition and removal energies to be correct with a spatially local potential – our self-screening correction (ssc)

$$\Sigma_{GW+ssc}(x, x', \omega) = \Sigma_{GW}(x, x', \omega) + V_{ssc}[n](x)$$

Spatially nonlocal self-energy



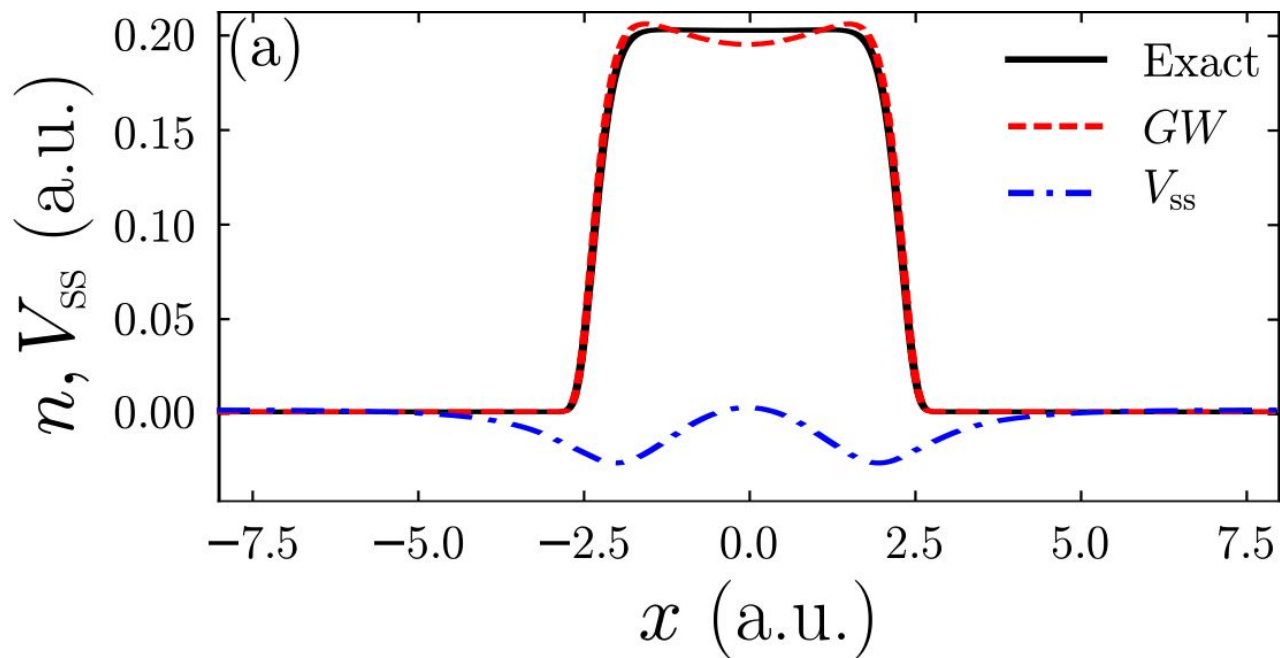
Spatially local correction

We approximate the spatially local potential with a local density approximation (LDA)...

Constructing the LDA

$$\varepsilon_{\text{SSC}} = E_{\text{exact}} - E_{\text{GW}}$$

Set of one-electron systems

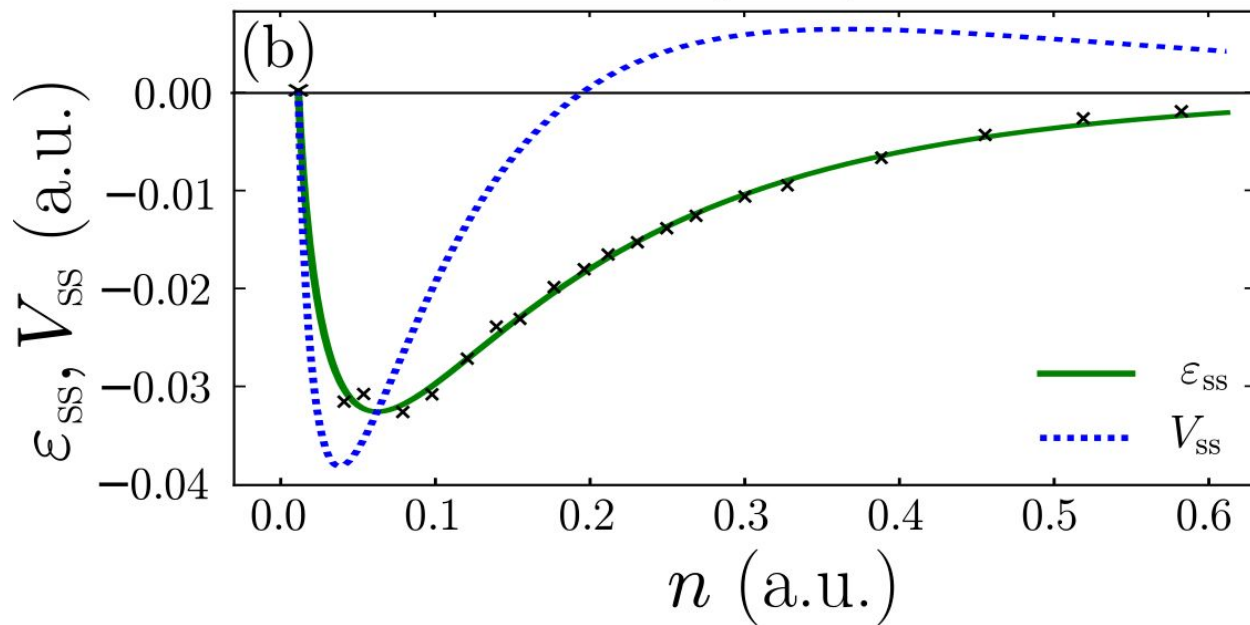


Constructing the LDA

$$\varepsilon_{\text{SSC}} = E_{\text{exact}} - E_{\text{GW}}$$

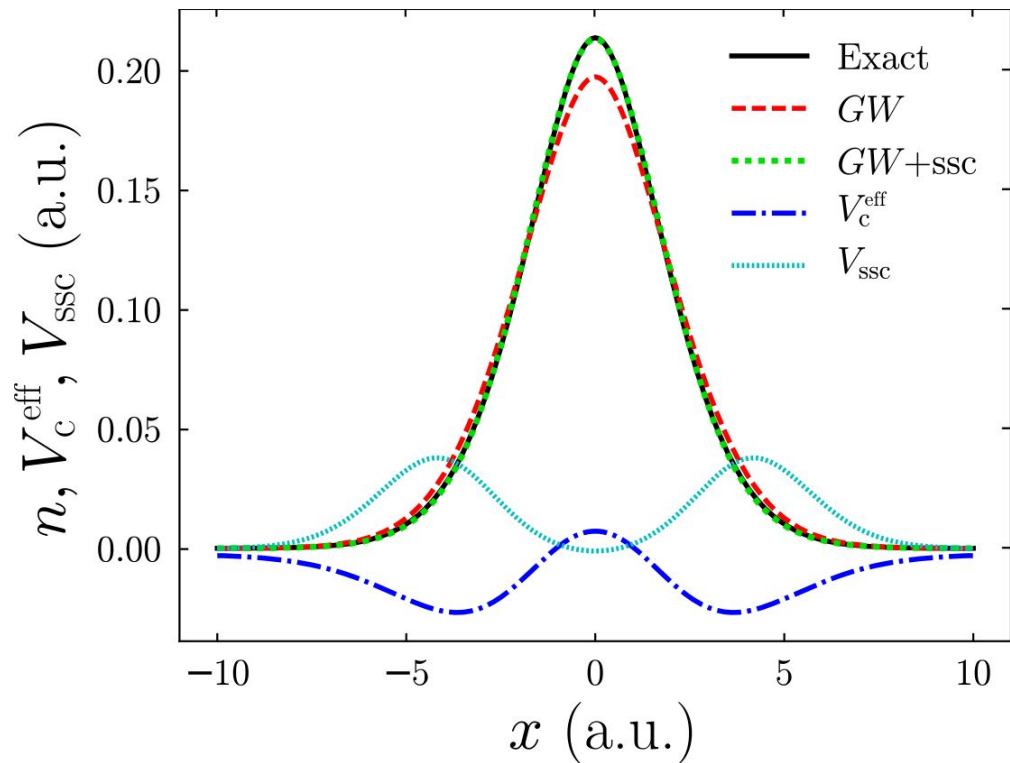
$$V_{\text{SSC}}[n(x)] = ane^{-bn^c} (2 - bcn^c)$$

$$a = 4.09268, b = 9.20609, c = 0.53652$$



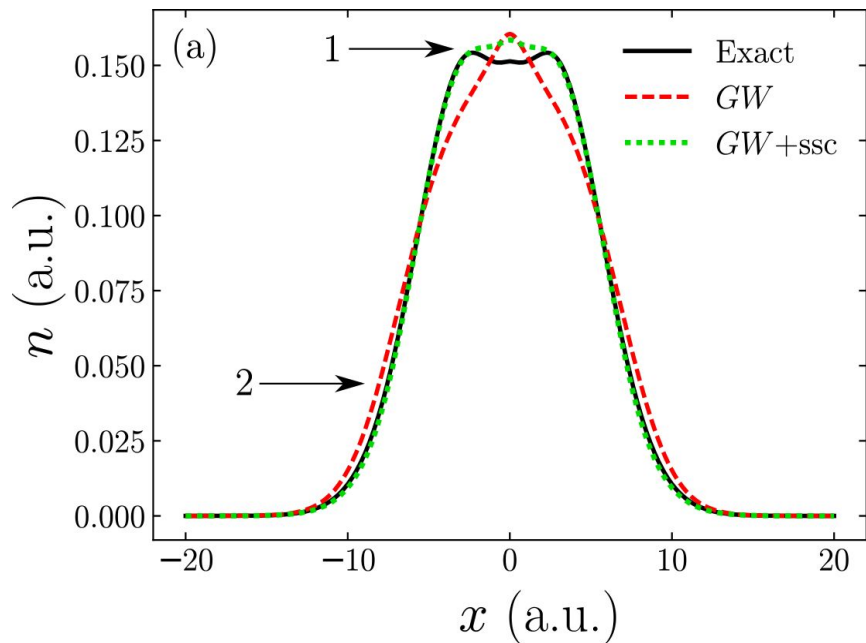
Performance for model systems

One-electron atom (again)

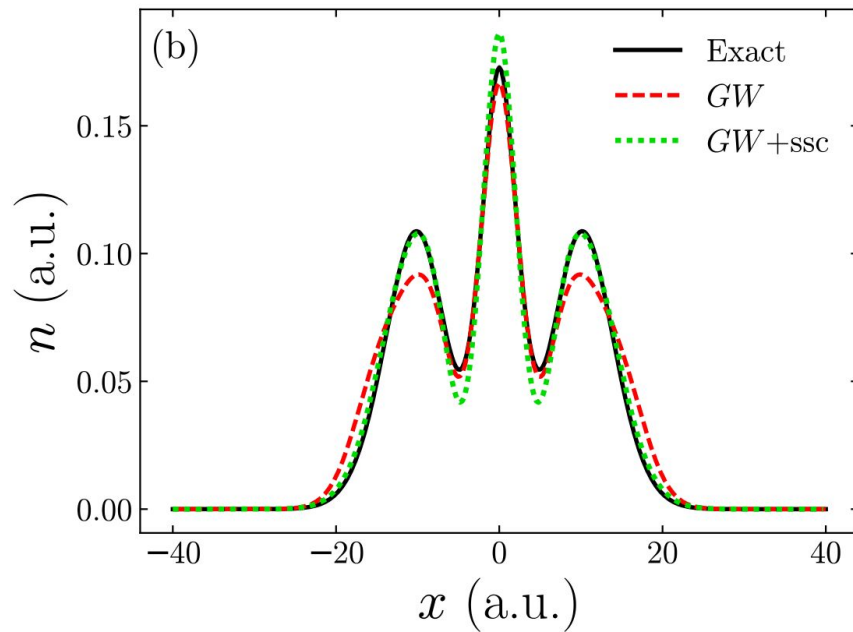


Performance for model systems

Correlated system: 2 *same-spin* electrons



Correlated system: 3 *same-spin* electrons



RPA is *not* exact for these systems with more than one electron

Performance for model systems

Ionisation Potentials
(Hartrees):

System	<i>GW</i>	<i>GW</i> +ssc	Exact
1	0.908	0.900	0.900
2	0.624	0.610	0.611
3	0.662	0.641	0.642

What about time-dependent densities?

- Currently no reliable way to get the real-time evolution of the density for strongly perturbed systems
- “Time-dependent generalized Kohn–Sham theory” Baer, R. & Kronik, L. Eur. Phys. J. B (2018) 91: 170
- Computationally efficient to use a single Slater Determinant but this requires an accurate local correlation potential!

Conclusions

1. Methods which combine a nonlocal potential with a local correcting potential look promising for modelling strongly correlated systems
2. We use a spatially local potential to correct the self-screening error within the *GW* approximation for simple correlated systems
3. More work is required to find a reliable way to yield time-dependent densities

J. Wetherell, M. J. P. Hodgson, and R. W. Godby *Phys. Rev. B* 97, 121102(R)

My webpage: www-users.york.ac.uk/~mjph501

My email: matthew.hodgson@mpi-halle.mpg.de

Extra slide

Time-dependent density functional theory

- Density functional theory was extended for dynamic systems in 1984 – Erich Runge and E. K. U. Gross Phys. Rev. Lett. **52**, 997
- Computationally efficient
- Often used to calculate optical absorption spectra
- Not so accurate for real-time evolution – more advanced approximation to the time-dependent Kohn-Sham exchange-correlation potential required