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

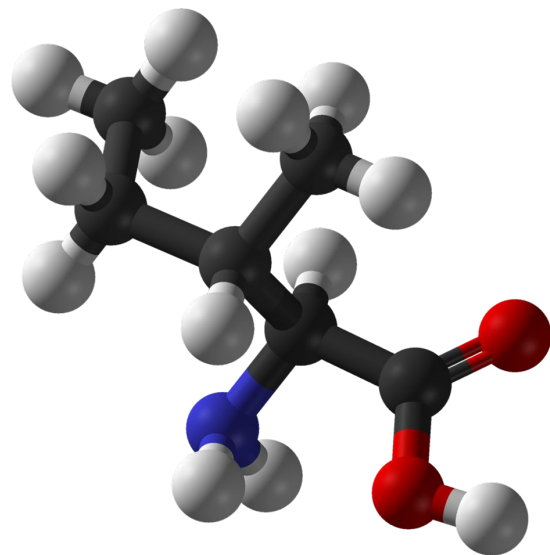**Matt Hodgson, Jack Wetherell and Rex Godby**

Max Planck Institute of Microstructure Physics, Halle, Germany
The University of York, Heslington, York, UK

I use the Born-Oppenheimer approximation

What are our aims?

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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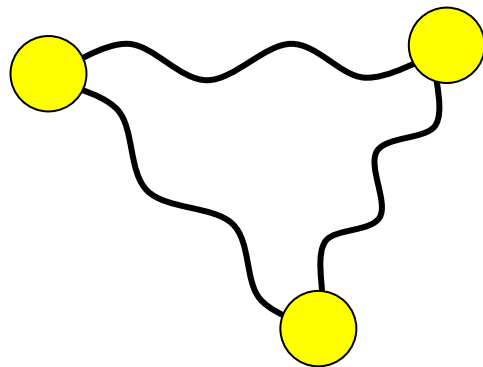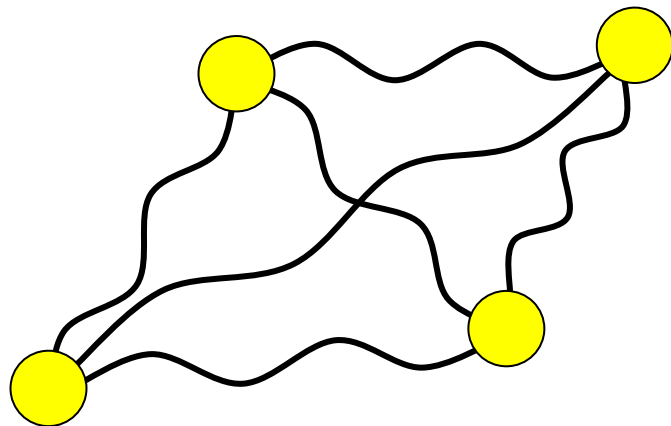
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So what's the problem?

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

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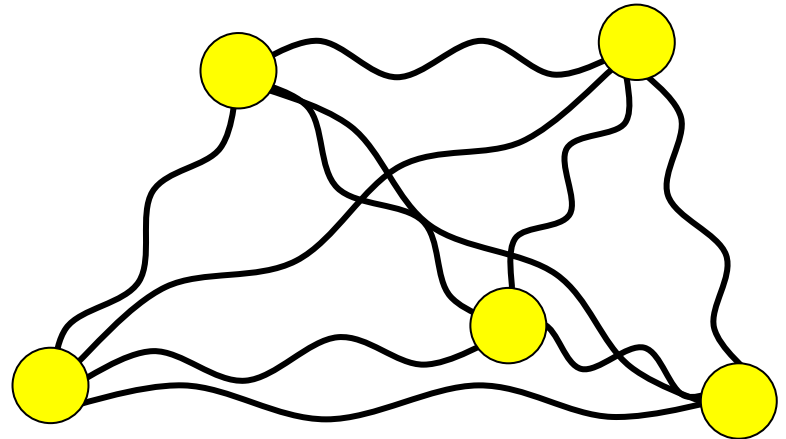
$$\Psi(x_1, x_2, x_3, x_4)$$

So what's the problem?

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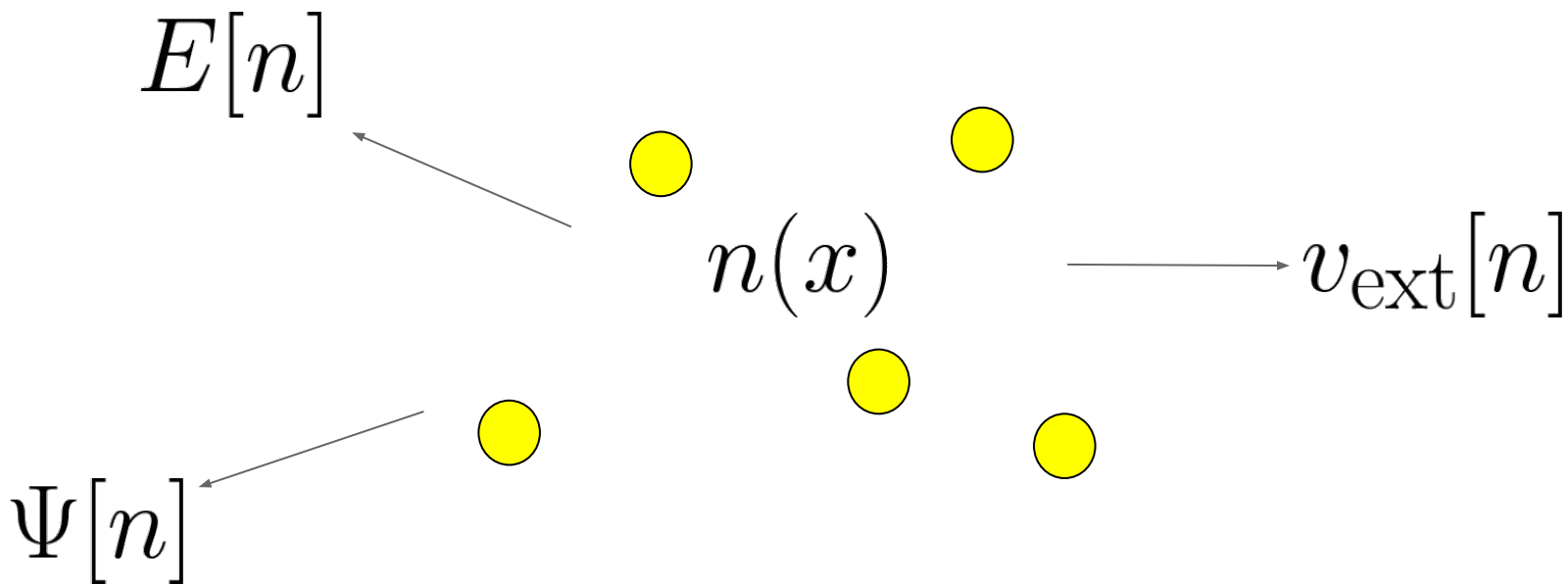quickly becomes impossible to calculate

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

Density functional theory

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

Density functional theory

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$$E[n]$$

$$n(x)$$
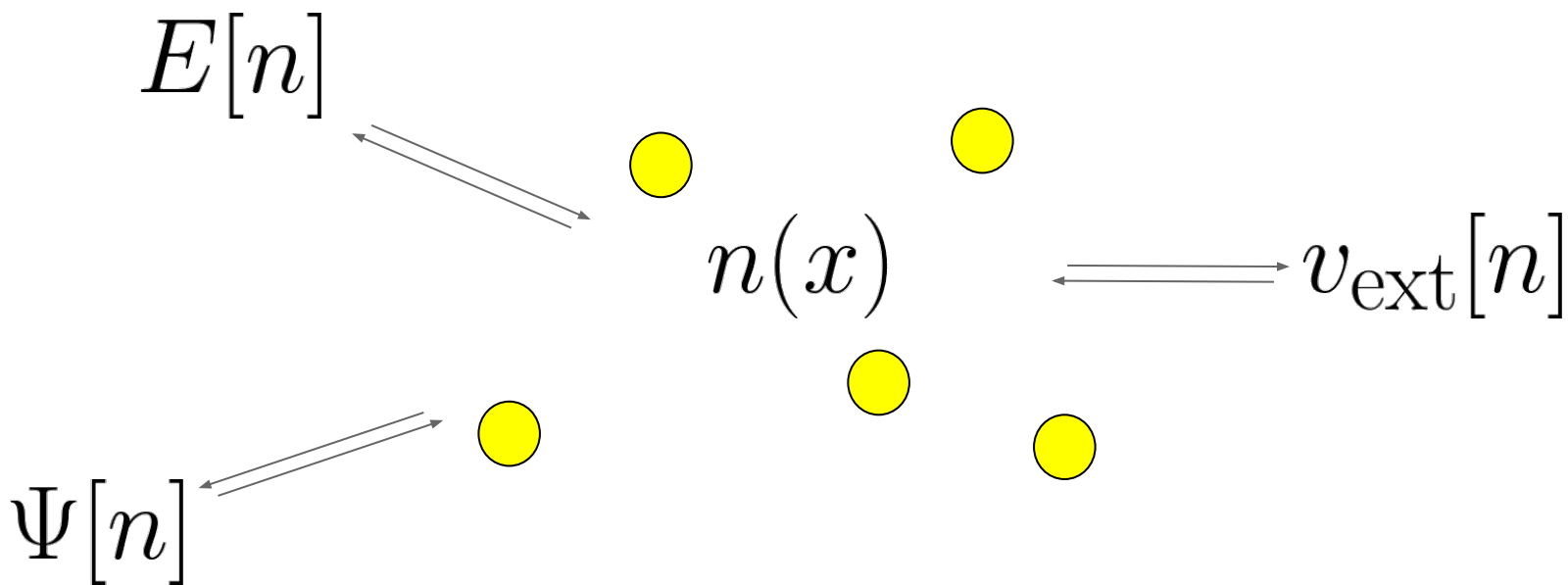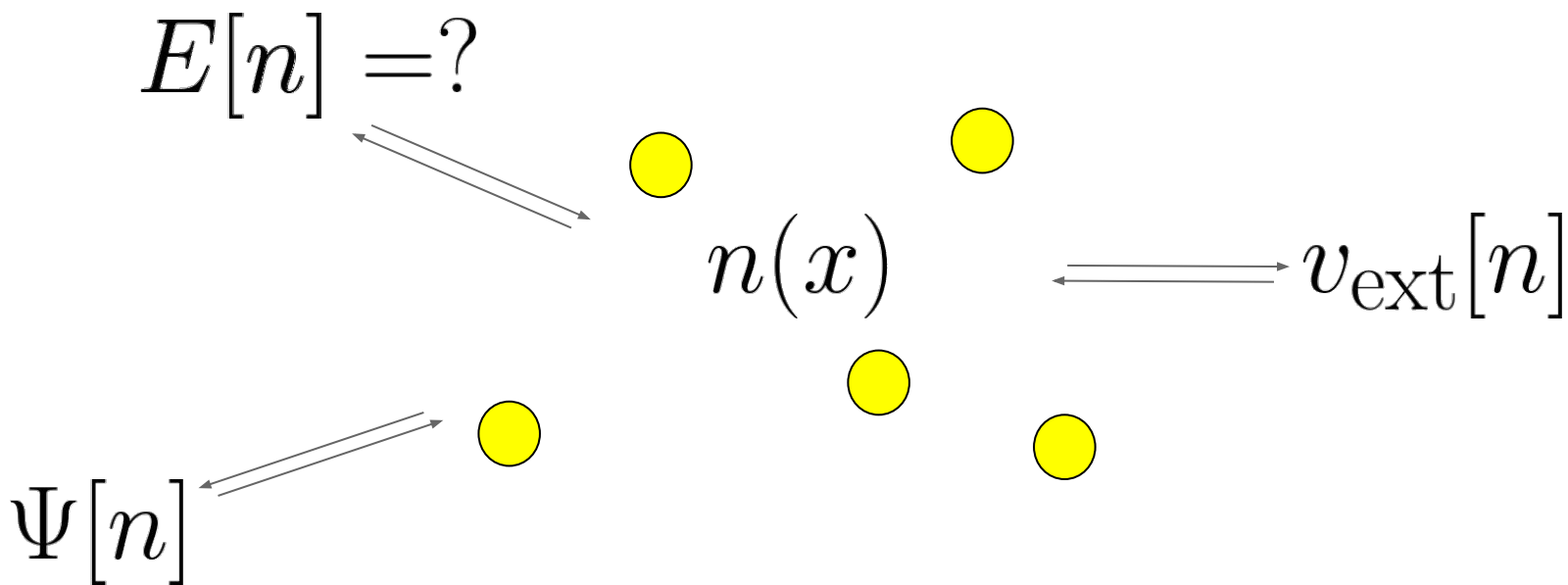
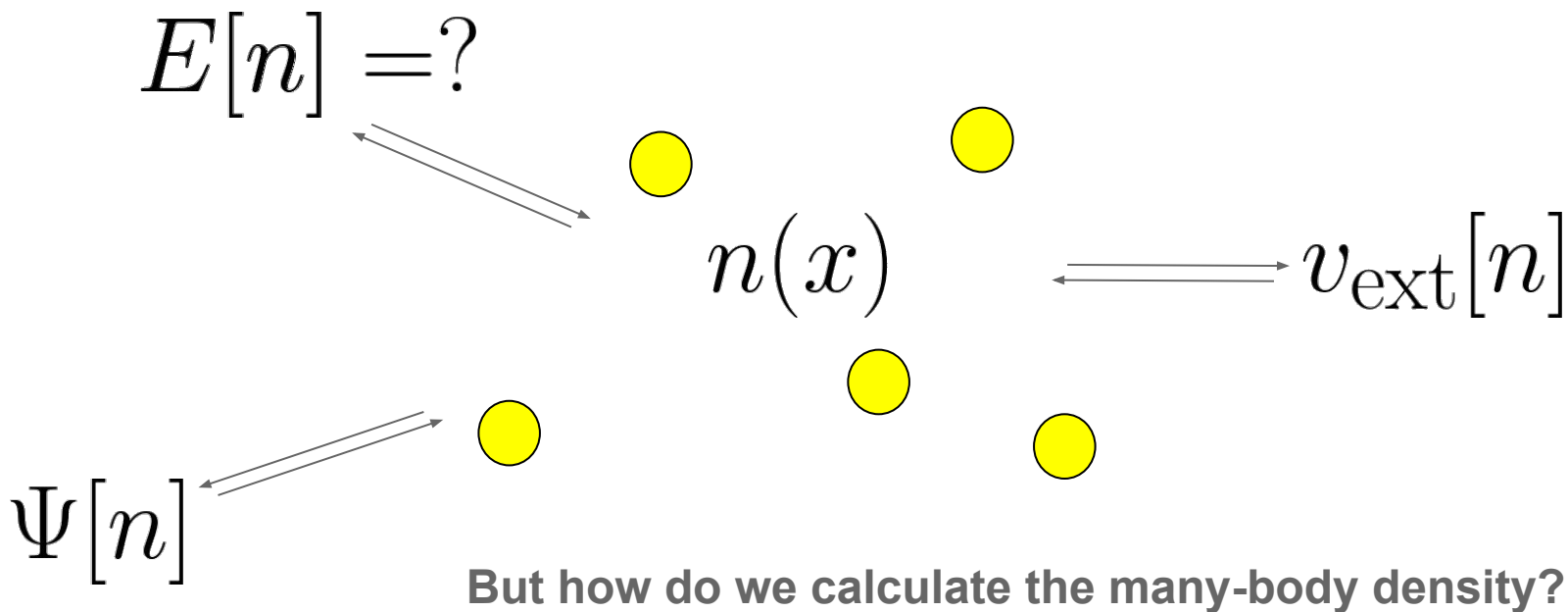$$v_{\text{ext}}[n]$$

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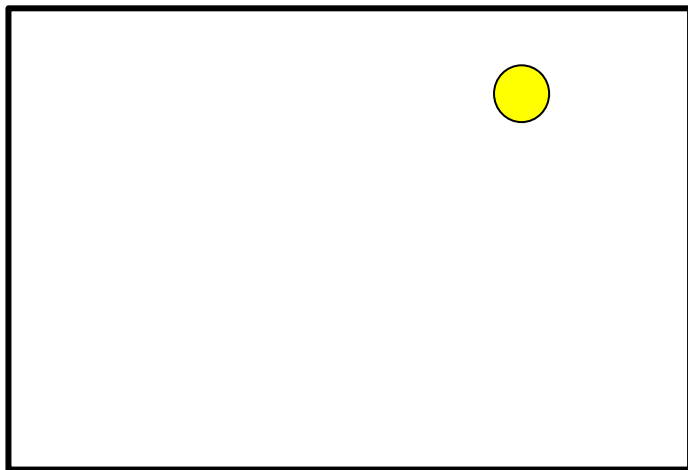
$$E[n] = ?$$

$$n(x)$$

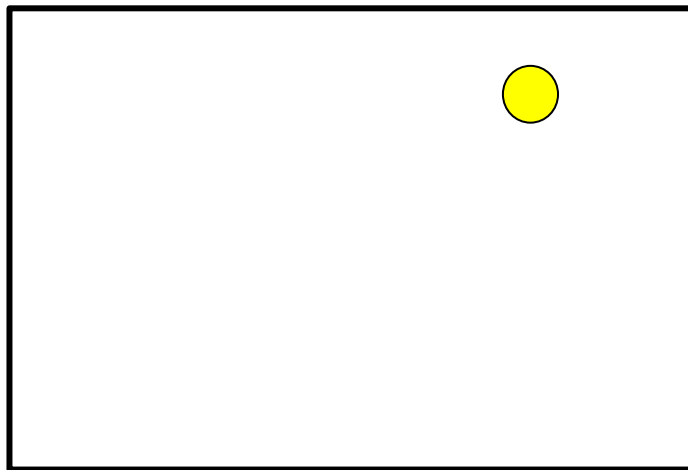$$v_{\text{ext}}[n]$$

$$\Psi[n]$$

But how do we calculate the many-body density?

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: $3 \cdot k$
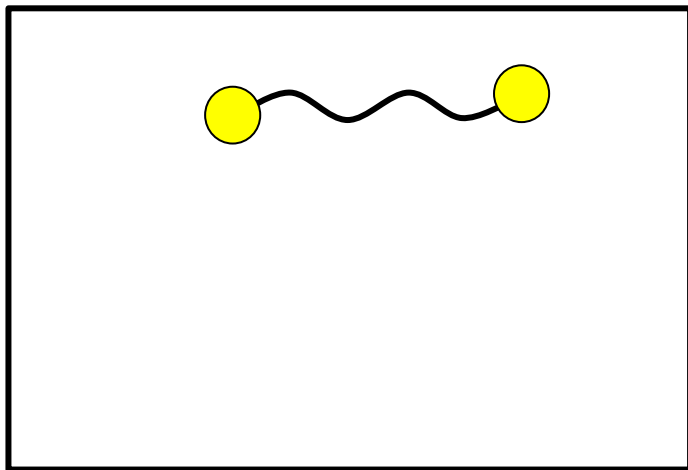
Many-body system
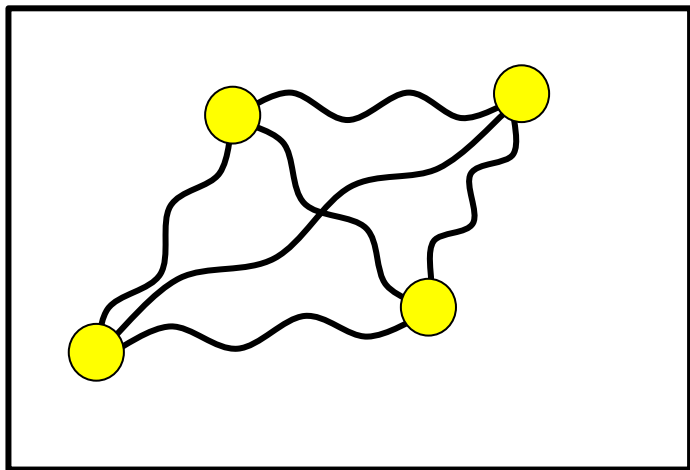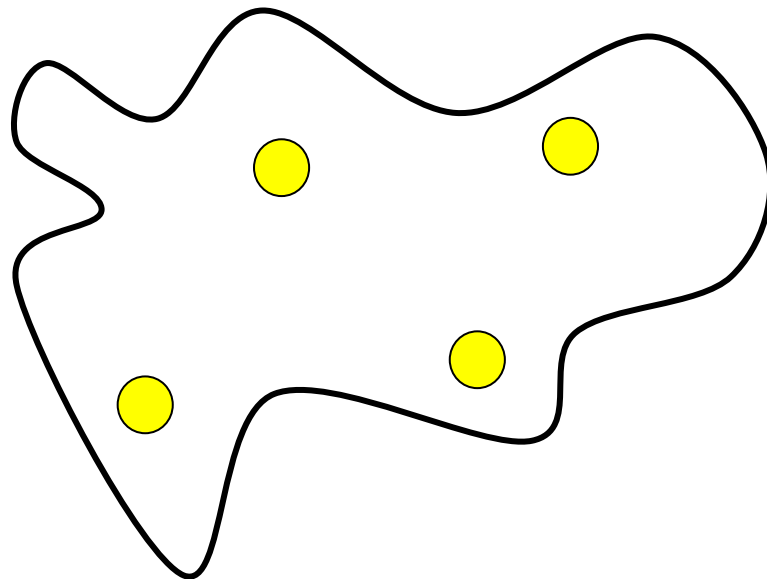
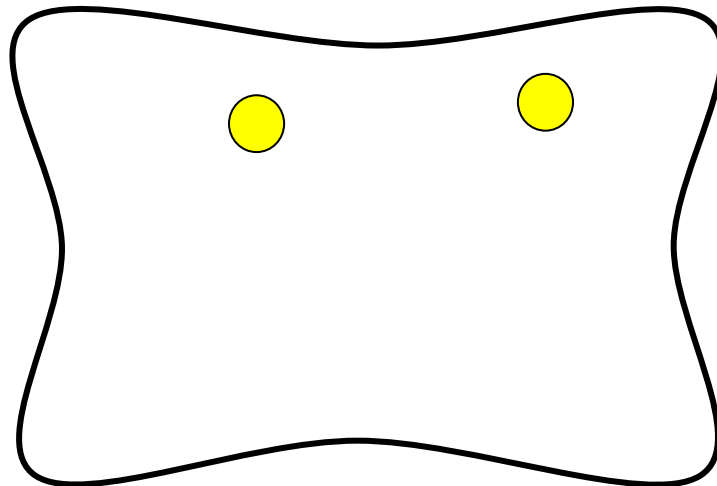**Kohn-Sham system**

The electron densities are the same

Computational scaling: k^4

Computational scaling: $4 \cdot k$
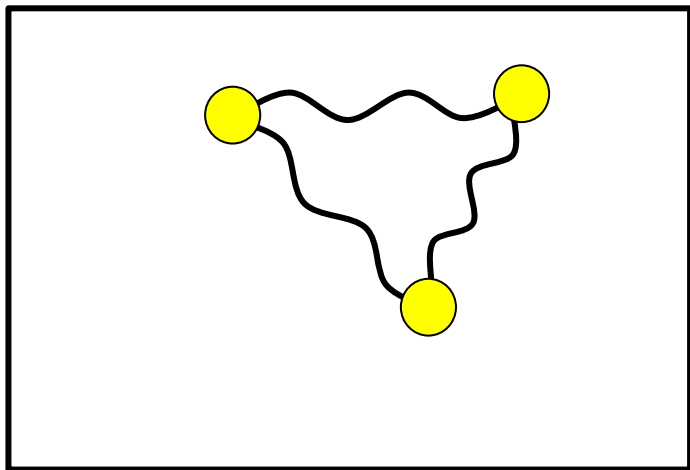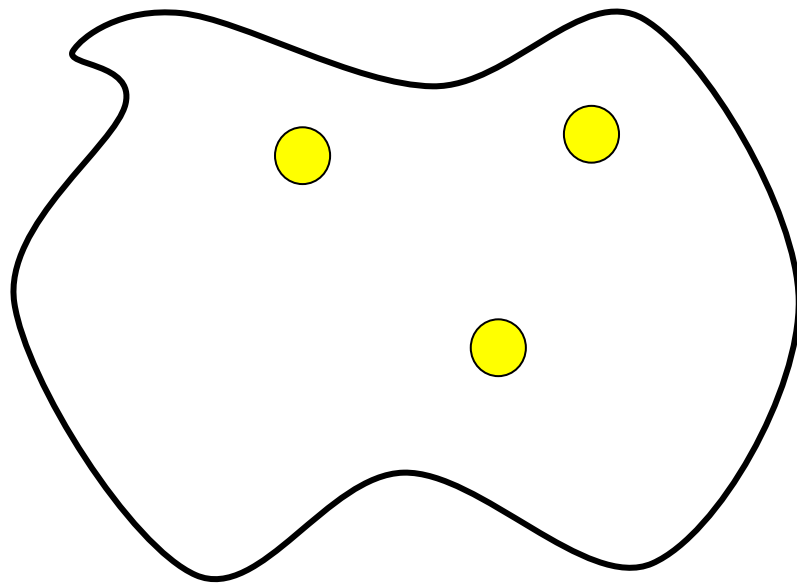
Many-body system
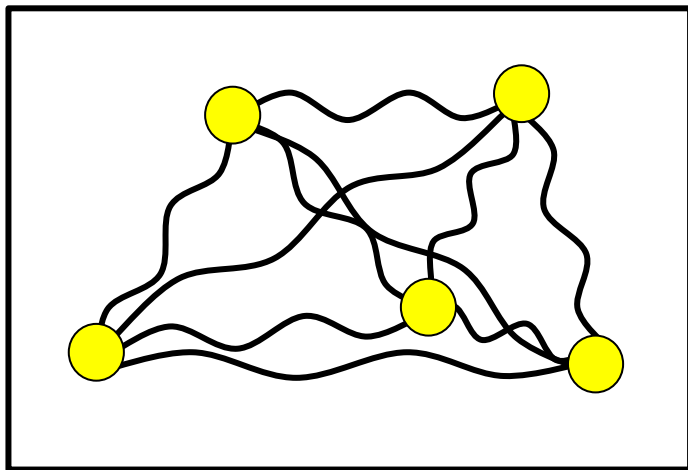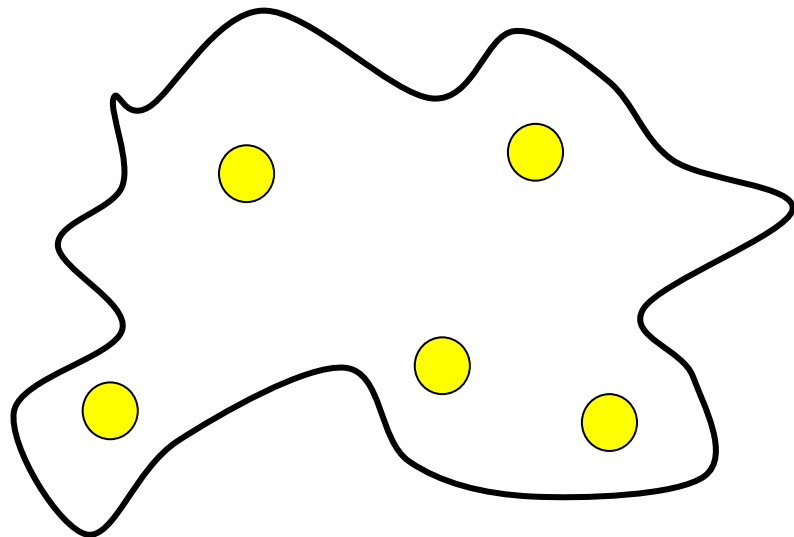
Kohn-Sham system

The electron densities are the same

Computational scaling: k^5

Computational scaling: $5 \cdot k$

Kohn-Sham theory

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

$$\left(-\frac{1}{2} \frac{\mathrm{d}^2}{\mathrm{d}x^2} + v_\mathrm{s}(x) \right) \phi_i(x) = \varepsilon_i \phi_i(x) \qquad n(x) = \sum_i |\phi_i(x)|^2$$

$$v_\mathrm{s}(x) = v_\mathrm{ext}(x) + v_\mathrm{H}(x) + v_\mathrm{xc}(x)$$

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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

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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

The Green's function G

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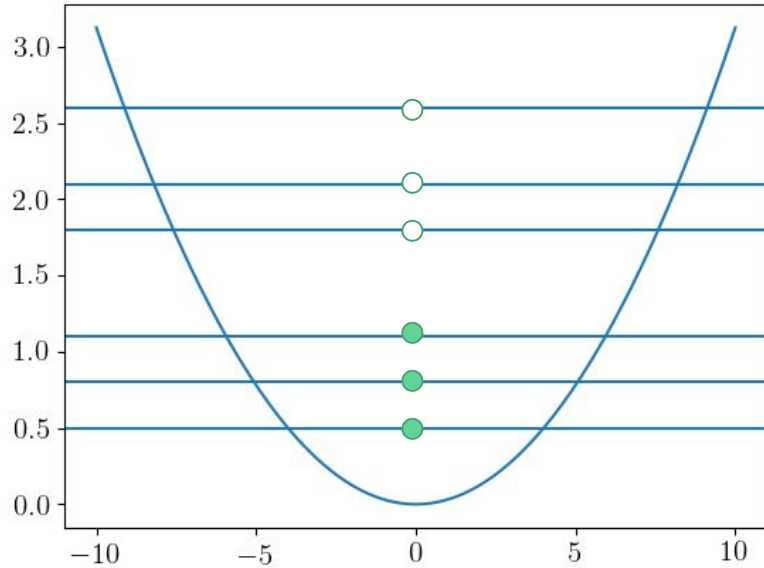
$G(x, x', t' - t)$

t'

The *GW* equations

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

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The *GW* approximation
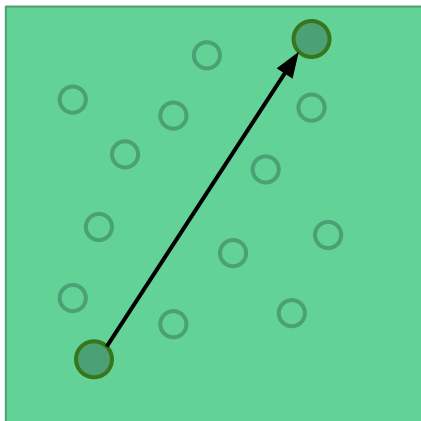
No Screening: Hartree-Fock

$$\Sigma_{xc} = Gv$$

$$P = 0$$
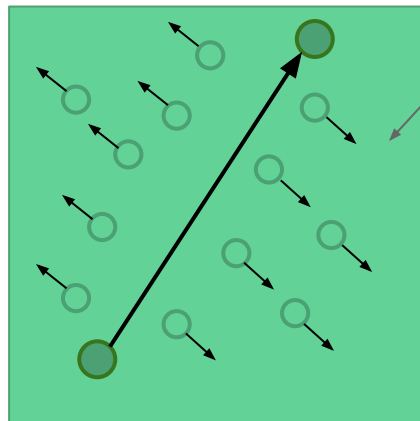
Excitations

Screening: *GW*

$$\Sigma_{xc} = GW$$

$$P = GG$$

$$\left\{\phi_i^0, \epsilon_i^0\right\}$$

$$G_0$$

$$P$$

$$n \leftarrow G \qquad W$$

$$\Sigma$$

$$\left\{\phi_i^{QP}, \epsilon_i^{QP}\right\}$$
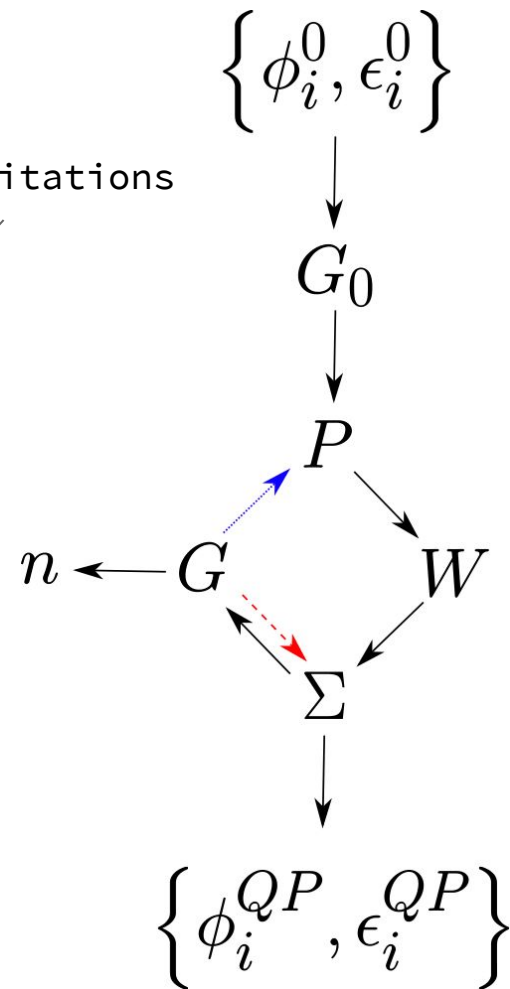
GW approximation

- 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"

Generalised Kohn-Sham theory

"Wavefunction theory meets density functional theory"

Kohn-Sham theory

$$E = \min_{n \to N} \left(T_s[n] + U[n] + E_{\text{xc}}[n] + \int n(x) v_{\text{ext}}(x) dx \right)$$
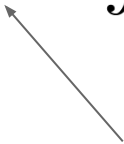
Generalised Kohn-Sham theory

"Wavefunction theory meets density functional theory"

Kohn-Sham theory

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Yields local potential

Generalised Kohn-Sham theory

"Wavefunction theory meets density functional theory"

Generalised Kohn-Sham theory

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

Yields nonlocal potential

Yields local potential

Generalised Kohn-Sham theory

An example: the Hartree-Fock equations:

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

Generalised Kohn-Sham theory

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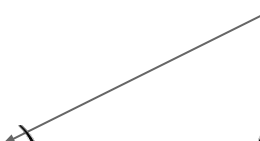
Hartree-Fock-Kohn-Sham equations:

Spatially local potential
adds (some) correlation

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

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 within this auxiliary system 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...

A. Seidl, A. Görling, P. Vogl, J. A. Majewski, and M. Levy Phys. Rev. B **53**, 3764

Hybrid functionals

- Hybrid functionals are within generalised Kohn-Sham theory

- They are known to give good quasiparticle energies and electron densities [1,2,3]

- 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] Refaely-Abramson, S. and Baer, R. and Kronik, L., Phys. Rev. B **84**, 075144 (2011)

[3] 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 quasiparticle energies (and densities) 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...
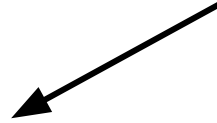
iDEA code

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

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Define a 1/2/3 electron model
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Compute **exact** (time-dependent), fully-correlated
many-body wavefunction and density

Reverse engineer **exact** density to give **exact**
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iDEA

iDEA code

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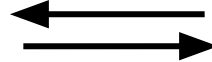
Available approximations:

- 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)

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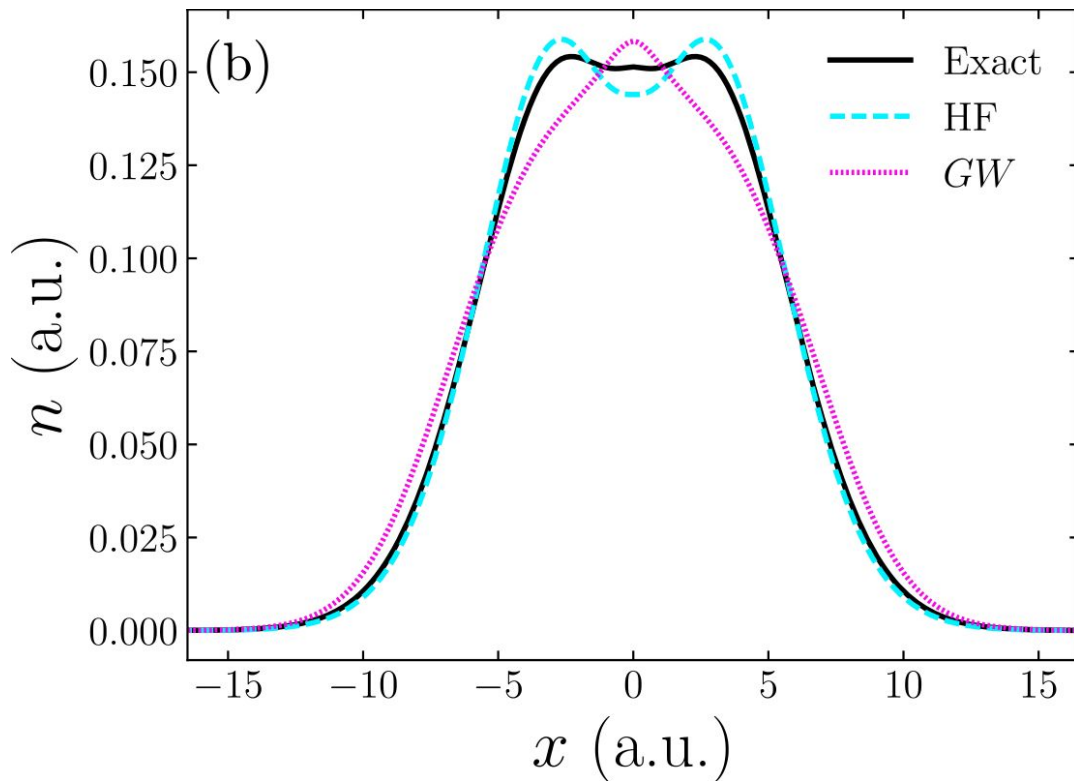**approximate** (time-dependent) Kohn-Sham
potential

Available approximations:

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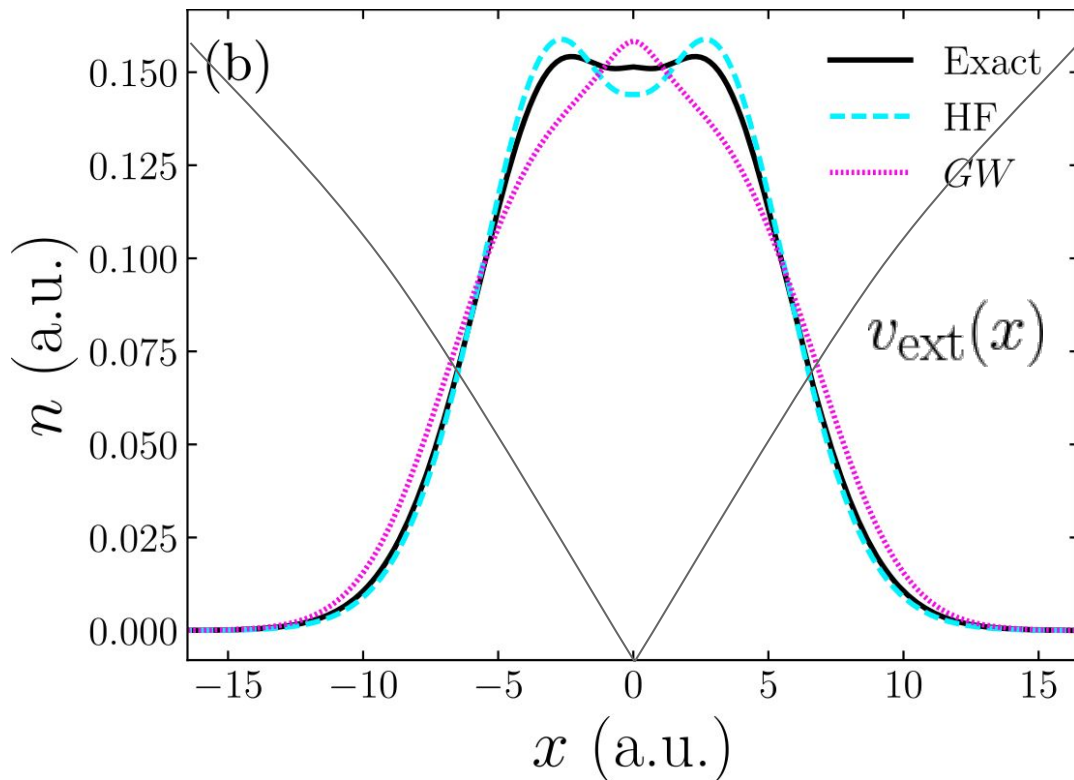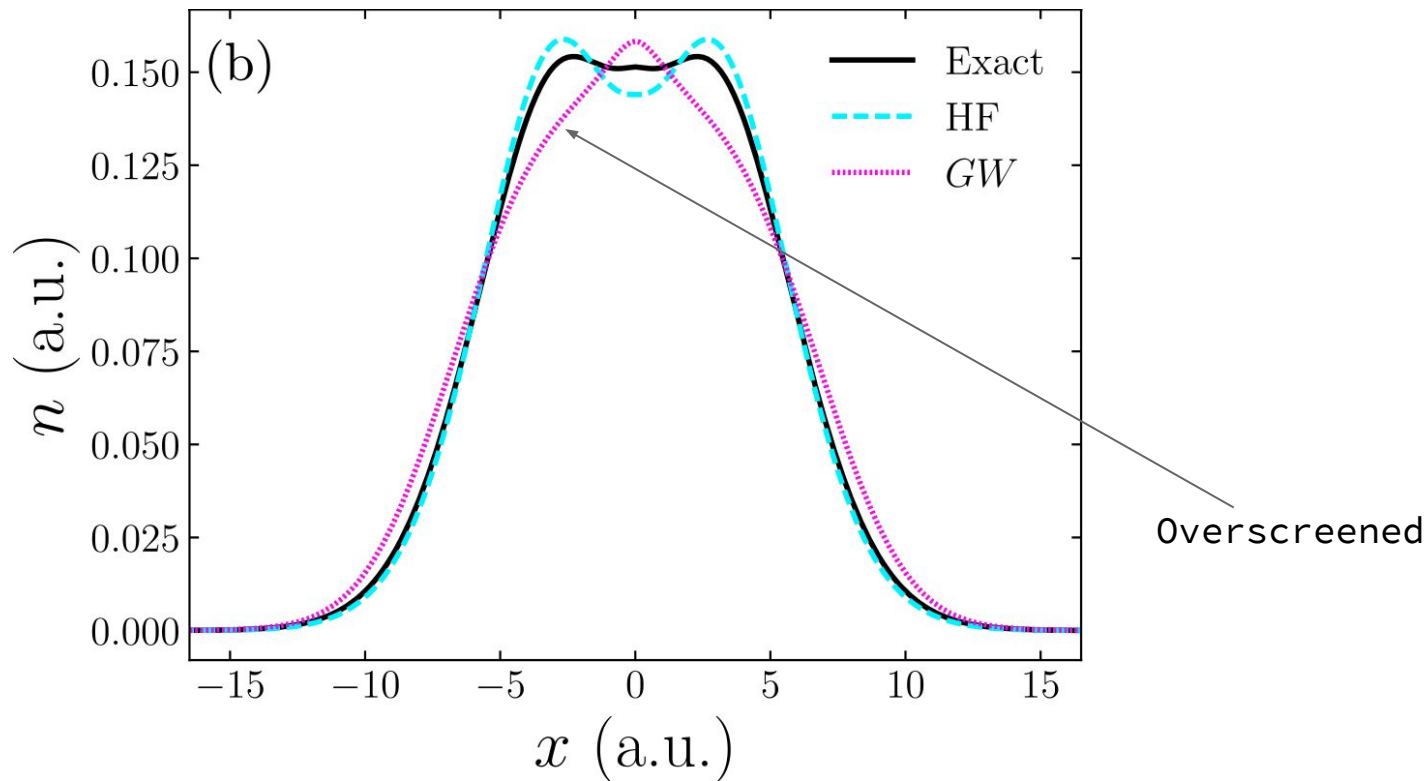- Many-body perturbation theory (HF, G0W0, GW0, COHSEX, scGW, GW+ssc)

How accurate is the density from MBPT?

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

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Underscreened

Overscreened
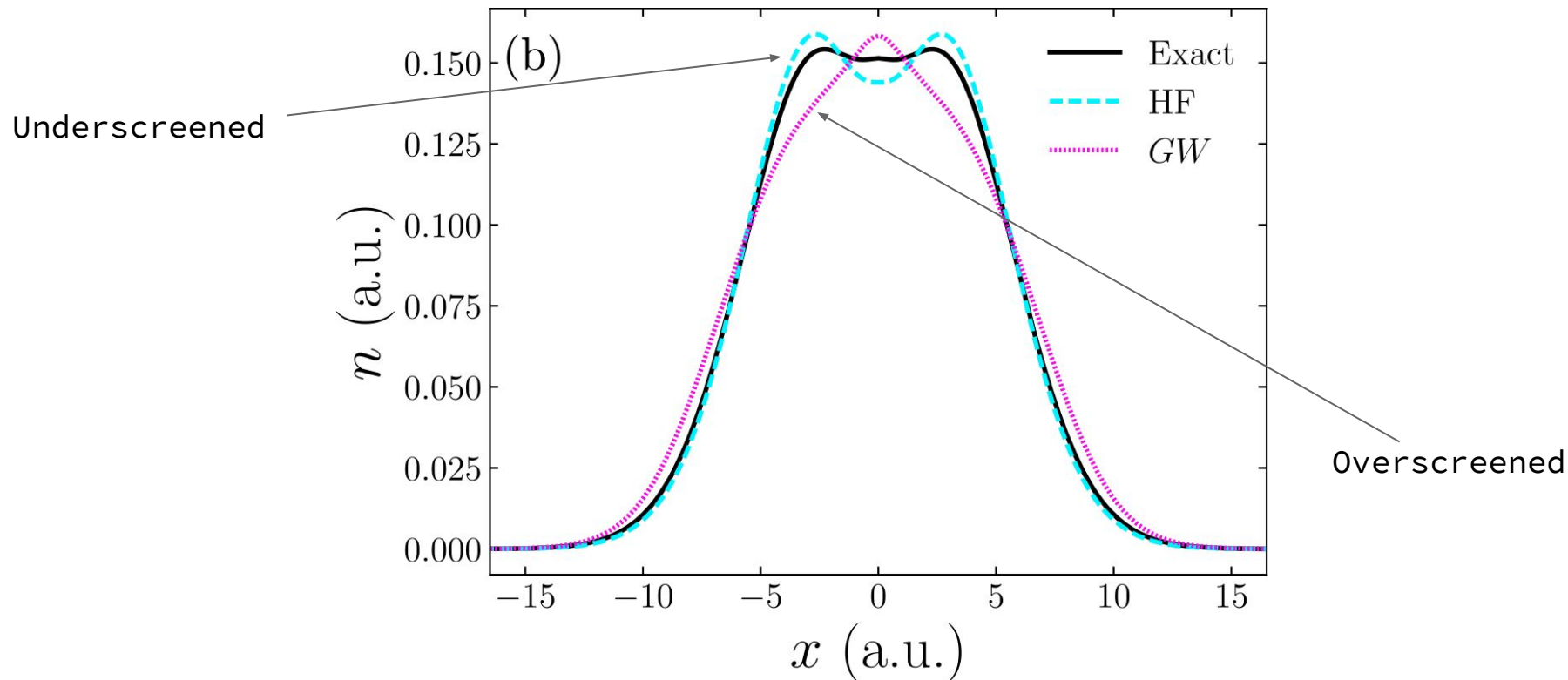
Approximations made within the *GW* approximation

$$\Sigma = V_{\mathrm{H}} + iGW \qquad\qquad P = iGG$$
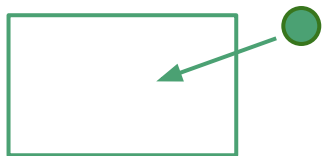
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The self-screening error

What is the energy required to add an electron to an empty box?
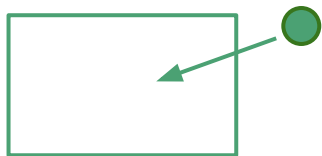
The LUMO of the zero-electron system:

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

$$\hat{H} = \hat{T}_{\mathrm{s}} + v_{\mathrm{ext}} + v_{\mathrm{H}} + v_{\mathrm{xc}}$$

The self-screening error

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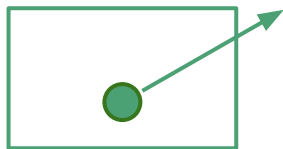$$\hat{H}\phi_0 = \varepsilon_0\phi_0$$

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

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

The self-screening error

What is the energy required to remove the electron?

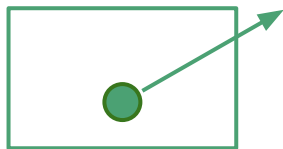The HOMO of the one-electron system:

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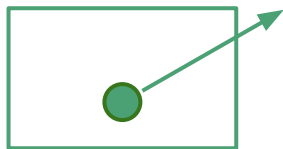
$$\hat{H}\phi_0 = \varepsilon_0\phi_0$$

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

The self-screening error

What is the energy required to remove the electron?

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$$v_\mathrm{xc} \neq -v_\mathrm{H}$$

The self-screening error

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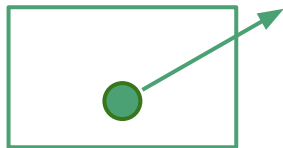
$$\hat{H}\phi_0 = \tilde{\varepsilon}_0 \phi_0$$

$$\hat{H} = \hat{T}_{\mathrm{s}} + v_{\mathrm{ext}} + v_{\mathrm{SS}}$$

$$v_{\mathrm{xc}} \neq -v_{\mathrm{H}}$$

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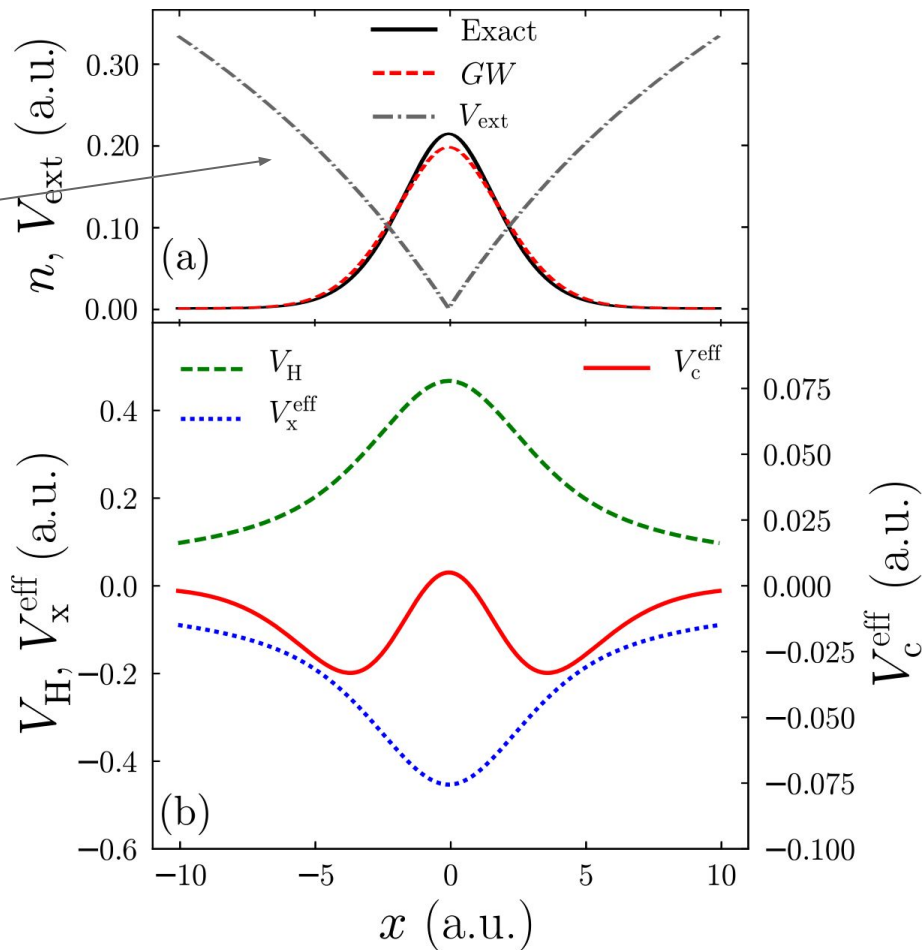
W. Nelson, P. Bokes, P. Rinke, and R. W. Godby, Phys. Rev. A. 75, 032505 (2007).

The self-screening error
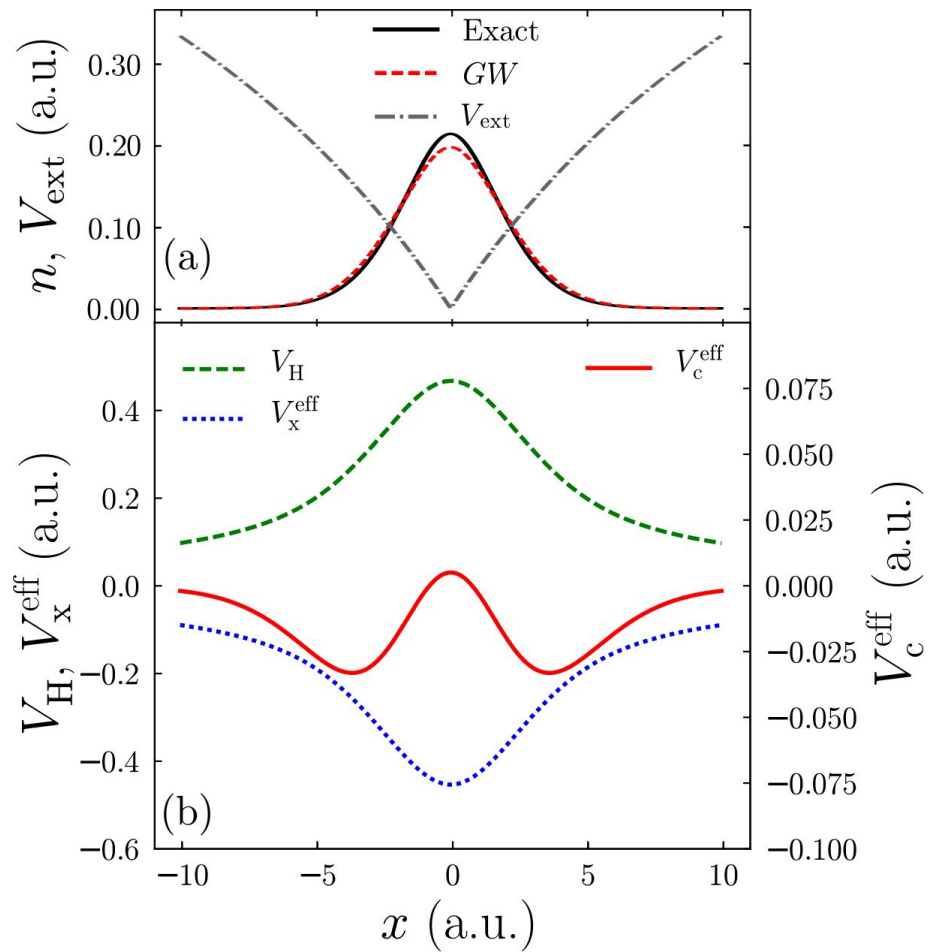
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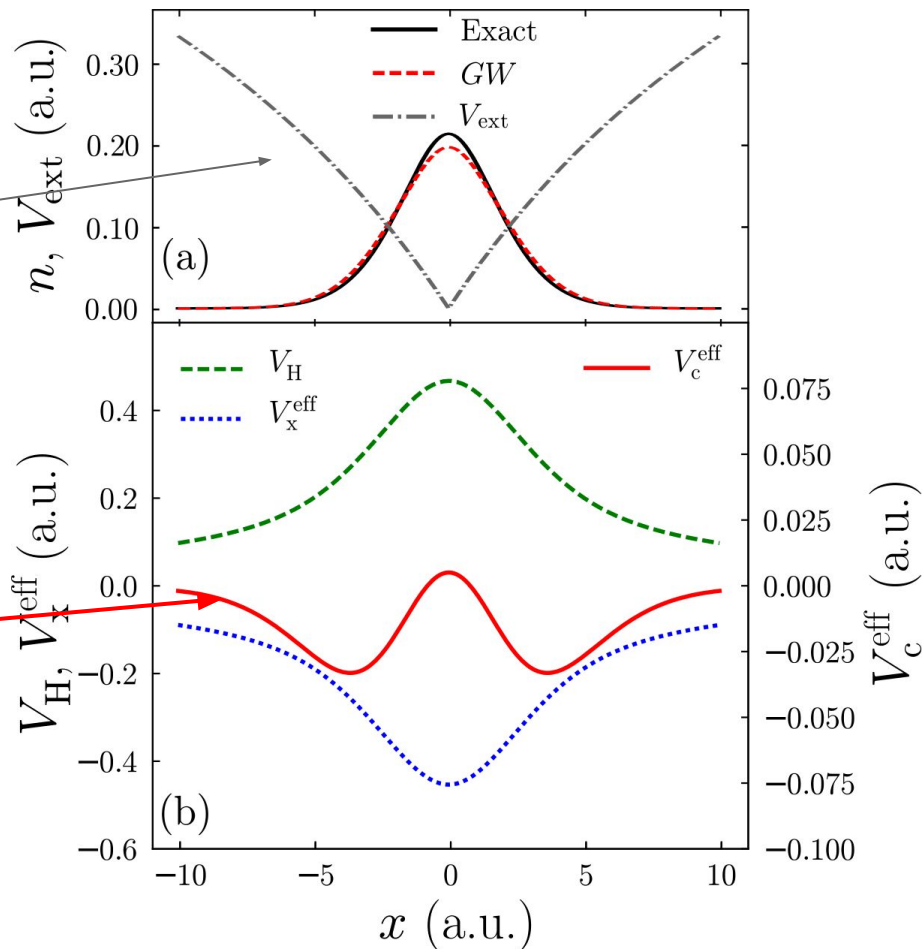
One-electron system (RPA is exact)

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)

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

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)

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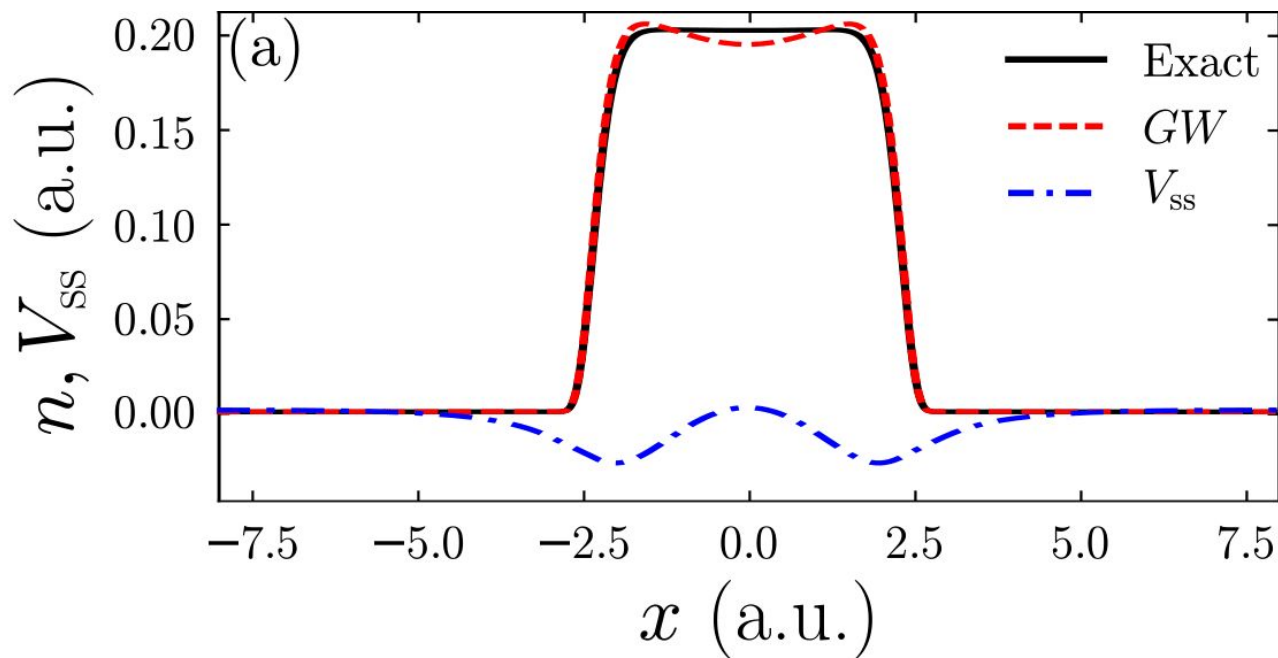Spatially nonlocal self-energy

Spatially local correction

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

Constructing the LDA

$$\varepsilon_{\mathrm{ssc}} = E_{\mathrm{exact}} - E_{GW}$$

Constructing the LDA

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

$$\varepsilon_{\mathrm{ssc}} = E_{\mathrm{exact}} - E_{GW}$$
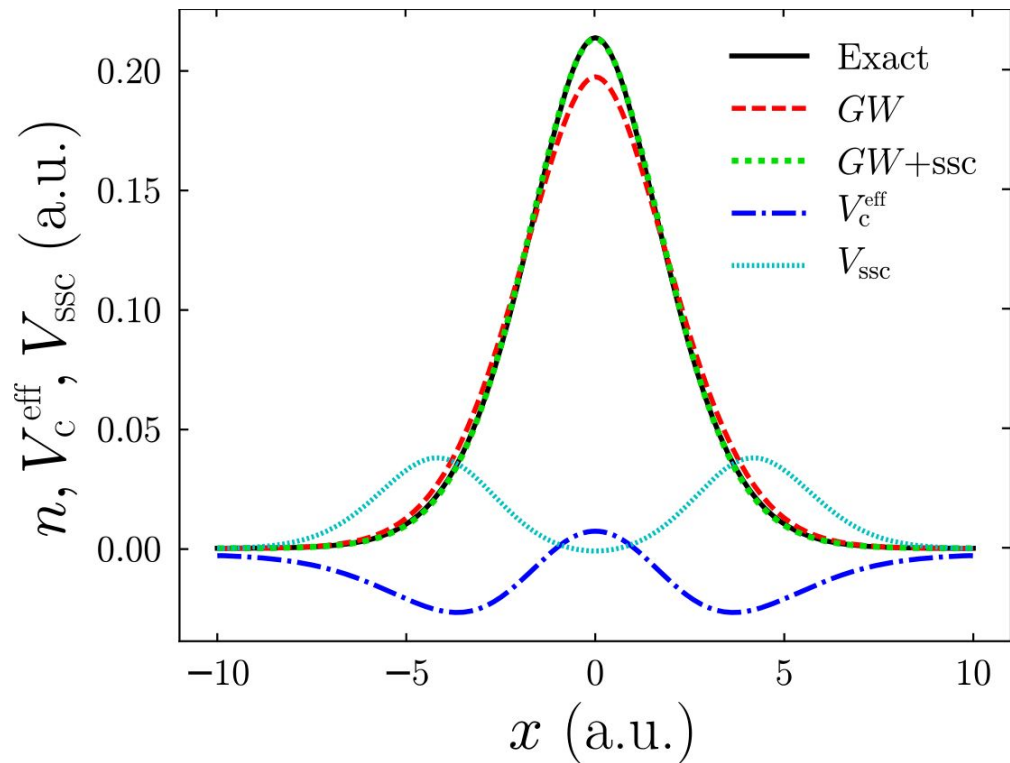
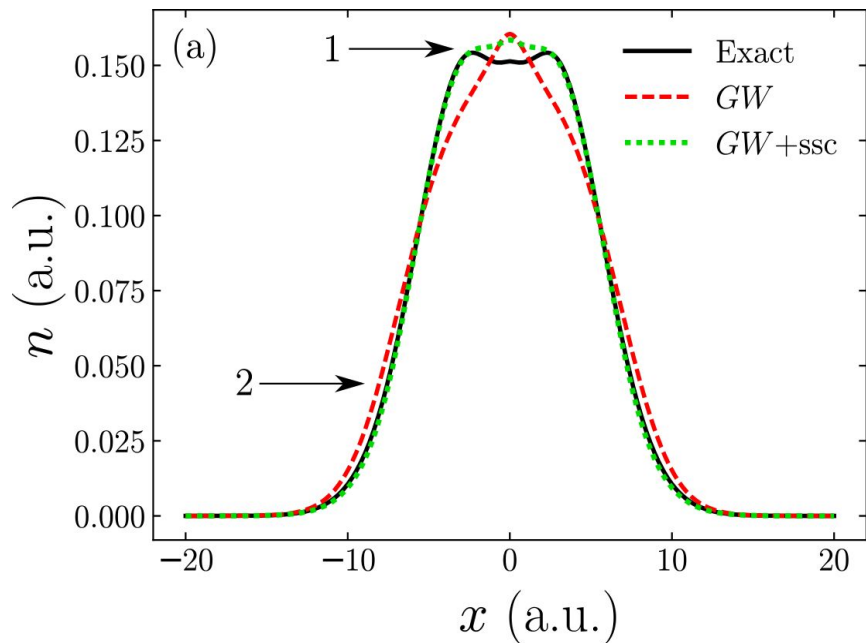$$a = 4.09268, b = 9.20609, c = 0.53652$$
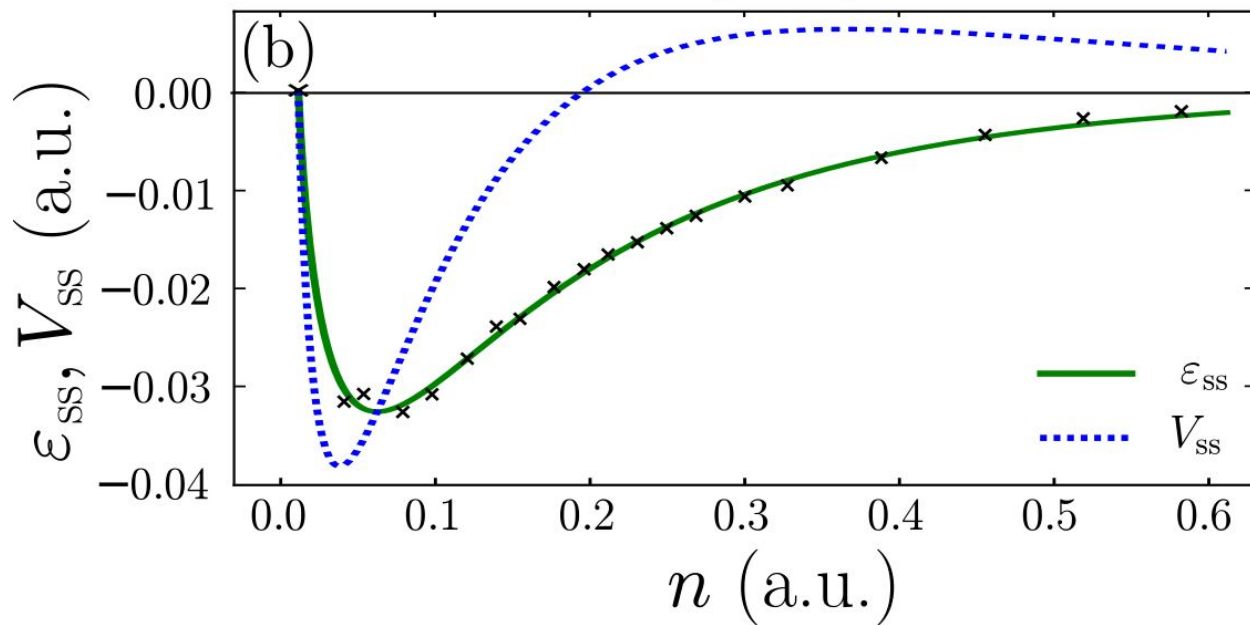
Performance for model systems
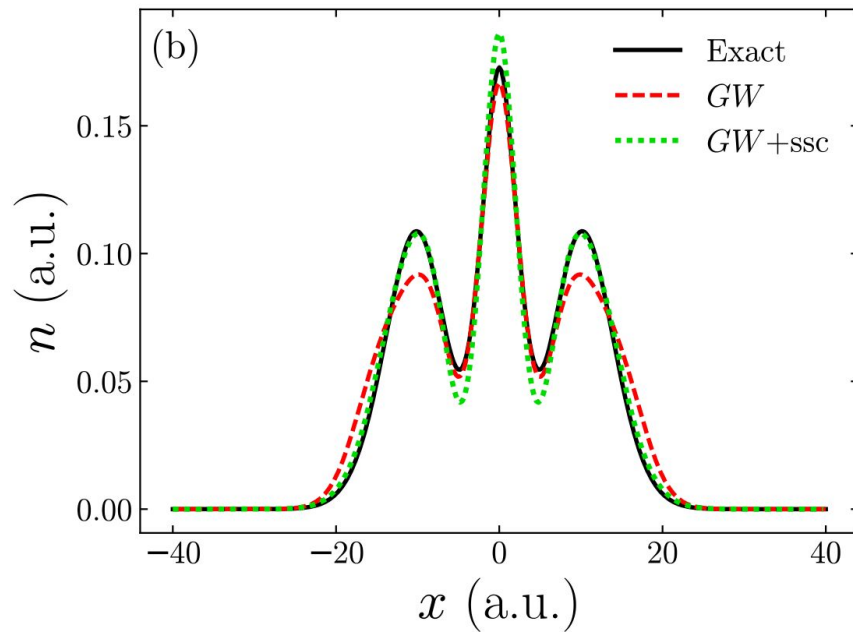
One-electron atom (again)

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	*GW*	*GW*+ssc	Exact
1	0.908	0.900	0.900
2	0.624	0.610	0.611
3	0.662	0.641	0.642

Conclusions

1. Methods which combine a nonlocal potential with a local correcting potential are 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. In tests the ionisation potential and density are corrected via our simple self-screening correction – how good is the spectral function?

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