Beyond DFT: *GW*-type approaches to electronic structure

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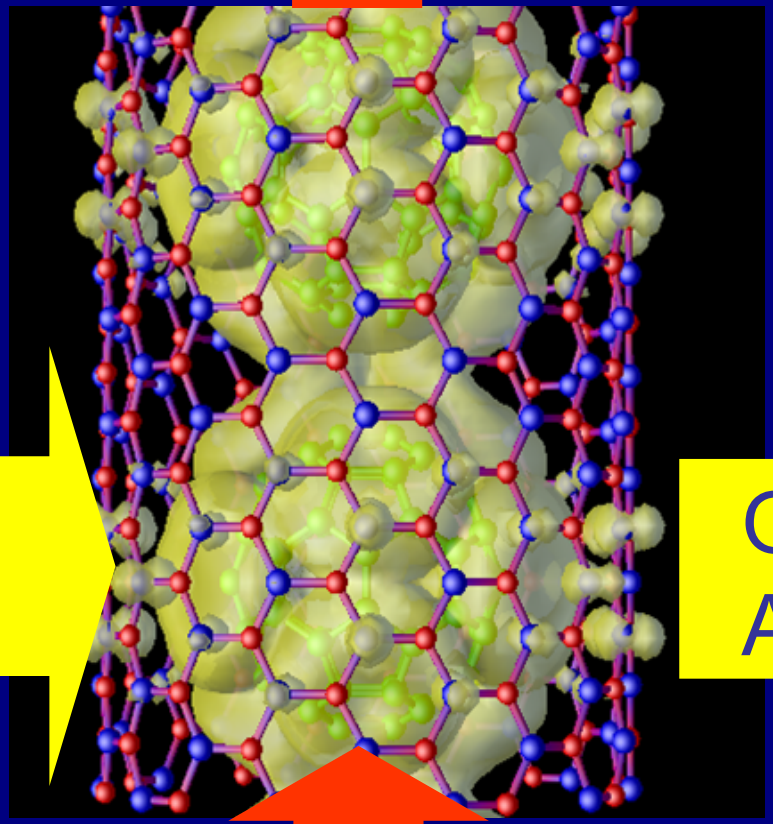
Outline

- Introduction to many-body perturbation theory
- MBPT vs DFT
- *GW* approximation
- Spectral properties

The Aim: Accurate excited-state properties of complex systems

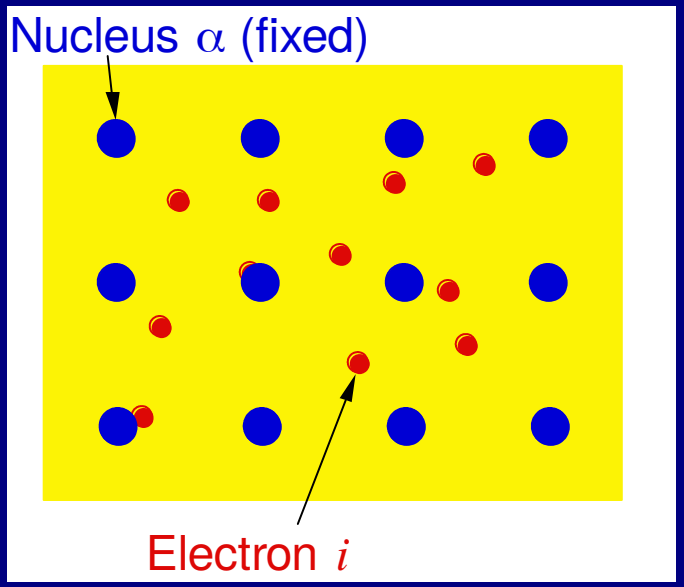


- E.g. Boron nitride nanotube containing C_{60} molecules
  (Rubio and Marques)

Optical Absorption

$I(V)$

The Basic Problem



- Electrons interact with each other as well as with the nuclei!

Why is the many-electron problem hard in QM?

- Consider silicon crystal (10^{23} electrons)

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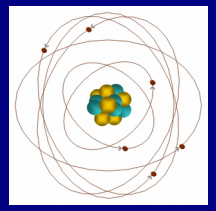
- No, let's make it easy: silicon *atom* (14 electrons)



- Wave function of the electrons: $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{14})$
- Suppose we store Ψ on a 10×10×10 grid for each $\mathbf{r}$
- Need to store $1000^{14}=10^{42}$ values
- 10^{33} DVDs (10^{26} lorry-loads)!

Why is the many-electron problem hard in QM?

- ~~Consider silicon crystal (10^{23} electrons)~~
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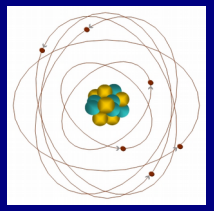
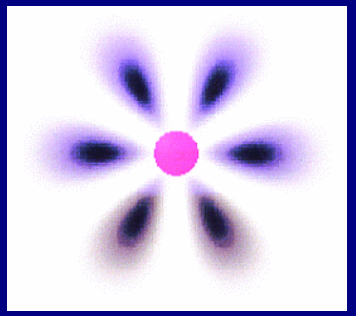
NEED TO APPROXIMATE!



Quantum Strategies

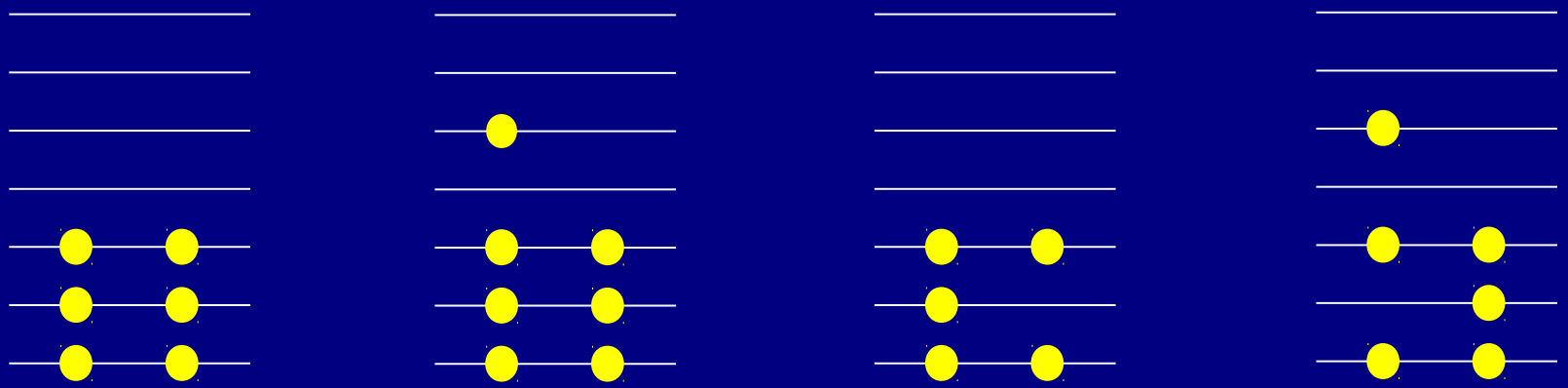
- One-electron Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\,\psi(\mathbf{r}) = E\,\psi(\mathbf{r})$$



- Account for other electrons through an *effective* potential felt by each electron
- Density-functional theory: $V(\mathbf{r}) \rightarrow V_{\text{eff}}(\mathbf{r})$
- Many-body perturbation theory: $V(\mathbf{r}) \rightarrow \Sigma(\mathbf{r},\mathbf{r}',E)$

Electronic Excitations



$|\, N,0\rangle$ $|\, N{+}1,s\,\rangle$ $|\, N{-}1,s\,\rangle$ $|\, N,s\,\rangle$

MBPT vs. DFT

MBPT vs. DFT

Many-body perturbation theory (e.g. *GW*)

- Based on Green's functions
- Self-energy theories give one-particle *G*, e.g. electron addition/removal
- Natural domain: quasiparticle energies, band structure, spectral function
- Similar diagrammatic theories for two-particle *G*, e.g. optical absorption
- Other applications: ground state total energy, etc.

MBPT vs. DFT (2)

DFT

- Natural domain (of ordinary DFT): ground state total energy
- TDDFT permits study of time-evolution (e.g. excited states) of *N*-electron system
- Treatment of exchange and correlation in DFT involves approximation, often based on the HEG / WIEG

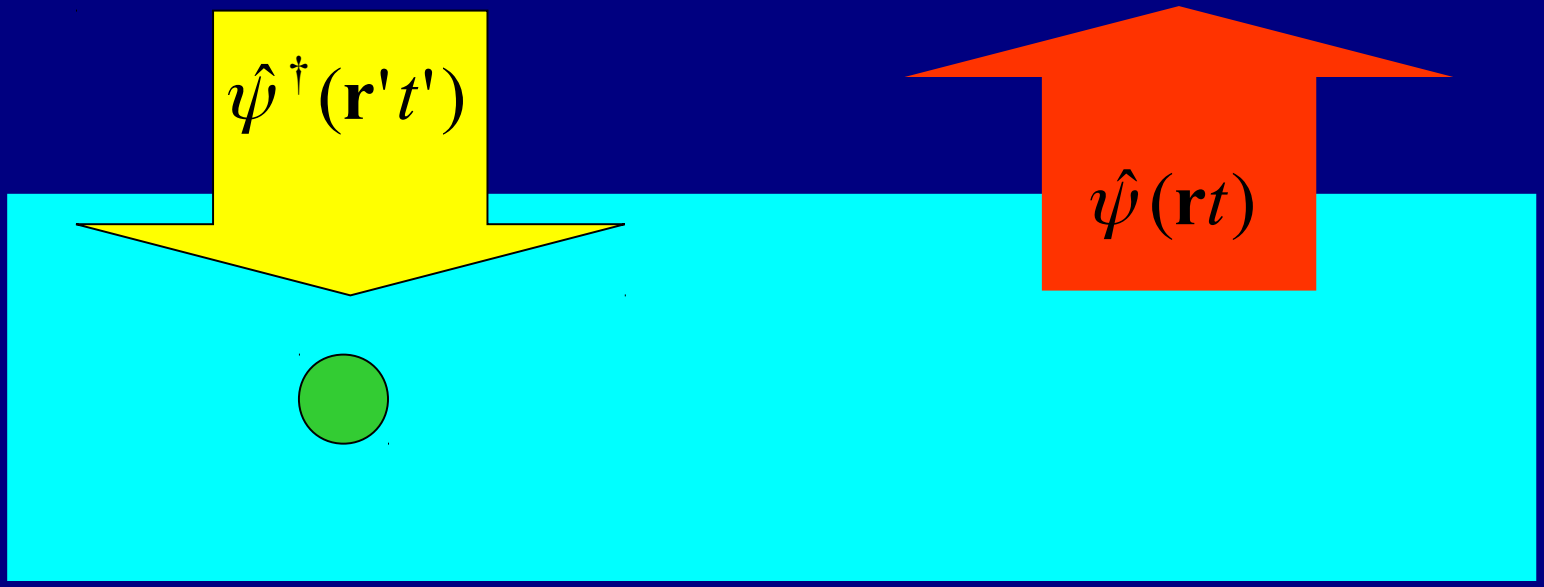
MBPT vs. DFT

Method	Advantages	Disadvantages
DFT / TDDFT (mainly for ground-state total energy and time-evolution)	Inexpensive (esp. density-based functionals)	XC functional pathological and can be difficult to approximate sufficiently accurately
GW etc. (mainly for excited-state properties)	Description of XC explicit diagrammatic series, better behaved	Can be expensive

Many-Body Perturbation Theory

The Green's function *G*

$$G(\mathbf{x},\mathbf{x}';t-t') \equiv -i\left\langle N\left|T[\hat{\psi}(\mathbf{x},t)\hat{\psi}^{+}(\mathbf{x}',t')]\right|N\right\rangle$$



Green's Functions and Self-Energies

- *G* obeys a very similar equation to the Green's function of the Kohn-Sham electrons in DFT, but with the non-local, time-dependent Σ replacing V_{xc}:

$$\left(i\frac{\partial}{\partial t} - \{h + V_{\mathrm{H}} + \Sigma_{\mathrm{xc}}\} \right) G(xt;x't') = \delta(x-x')\,\delta(t-t')$$

$$\left(i\frac{\partial}{\partial t} - \{h + V_{\mathrm{H}} + V_{\mathrm{xc}}\} \right) G_{\mathrm{KS}}(xt;x't') = \delta(x-x')\,\delta(t-t')$$

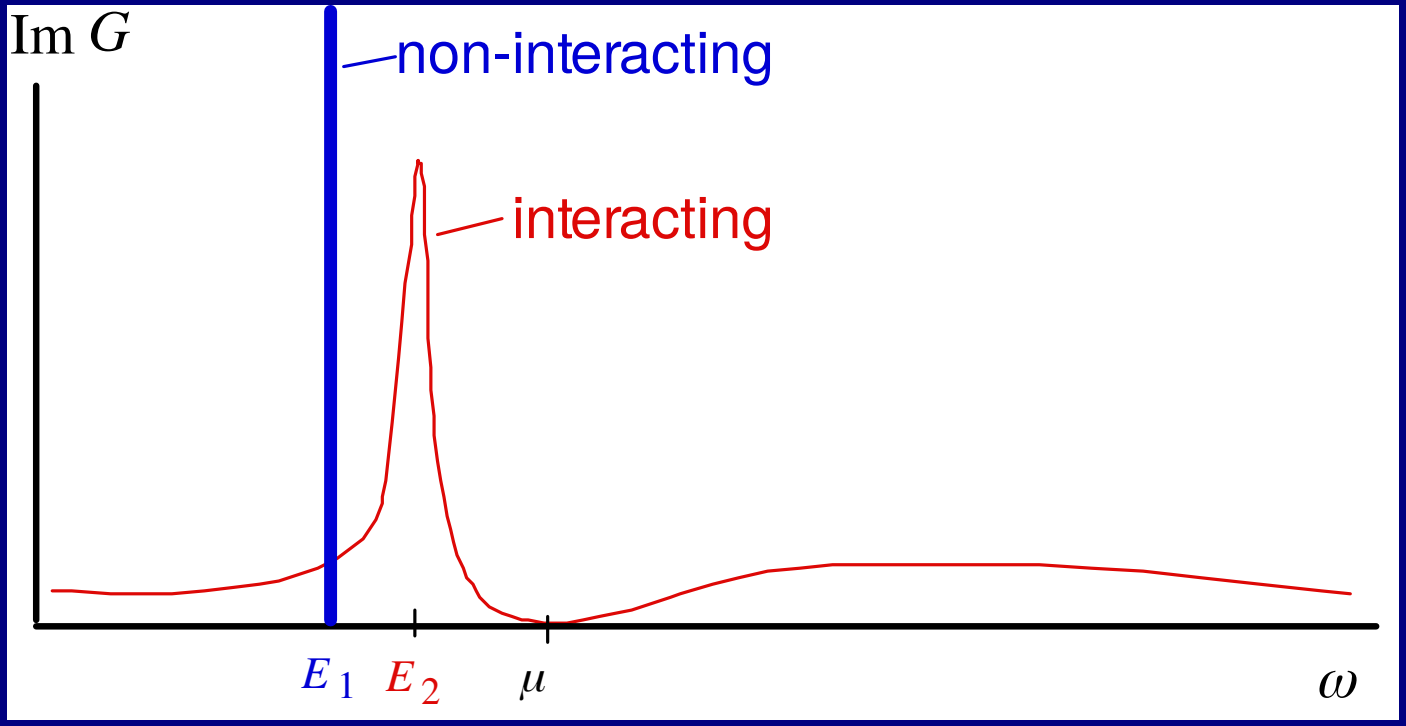
Lehmann Representation for *G*

$$G(\mathbf{r},\mathbf{r}',\omega)=\sum_s \frac{f_s(\mathbf{r})f_s{}^*(\mathbf{r}')}{\omega-\varepsilon_s \mp i\delta} \quad , \quad \varepsilon_s <> \mu$$

$$f_s(\mathbf{r})=\begin{cases}\left\langle N\middle|\hat{\psi}(\mathbf{r})\middle|N+1,s\right\rangle, & \varepsilon_s = E_{N+1,s}-E_N \ (>\mu)\\ \left\langle N-1,s\middle|\hat{\psi}(\mathbf{r})\middle|N\right\rangle, & \varepsilon_s = E_N-E_{N-1,s} \ (<\mu)\end{cases}$$

- *s* labels the excited states of the *N*+1 or *N*-1-electron systems
- *G* has its poles at each energy with which an electron can be added/removed

Spectral function and quasiparticles from Im *G*



$$\left[-\tfrac{1}{2}\nabla^2 + V_{\text{ext}} + V_{\text{Hartree}} + \Sigma_{\text{xc}}(\varepsilon) - \varepsilon\right]\psi(\mathbf{r}) = 0)$$

Hedin's Equations

$$
\begin{aligned}
\Sigma(1,2) &= \mathrm{i}\int W\left(1^{+},3\right) G(1,4)\,\Gamma(4,2,3)\,\mathrm{d}(3,4) \\
P(1,2) &= -\mathrm{i}\int G(2,3)\,G(4,2)\,\Gamma(3,4,1)\,\mathrm{d}(3,4) \\
W(1,2) &= v(1,2)+\int W(1,3)\,P(3,4)\,v(4,2)\,\mathrm{d}(3,4) \\
\Gamma(1,2,3) &= \delta(1,2)\,\delta(1,3) \\
&+ \int \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)\,G(7,5)\,\Gamma(6,7,3)\,\mathrm{d}(4,5,6,7)
\end{aligned}
$$

- Exact closed equations for *G*, Σ etc.

M. Gatti

Hedin's Equations

$$\Sigma(1,2) = \mathrm{i}\int$$

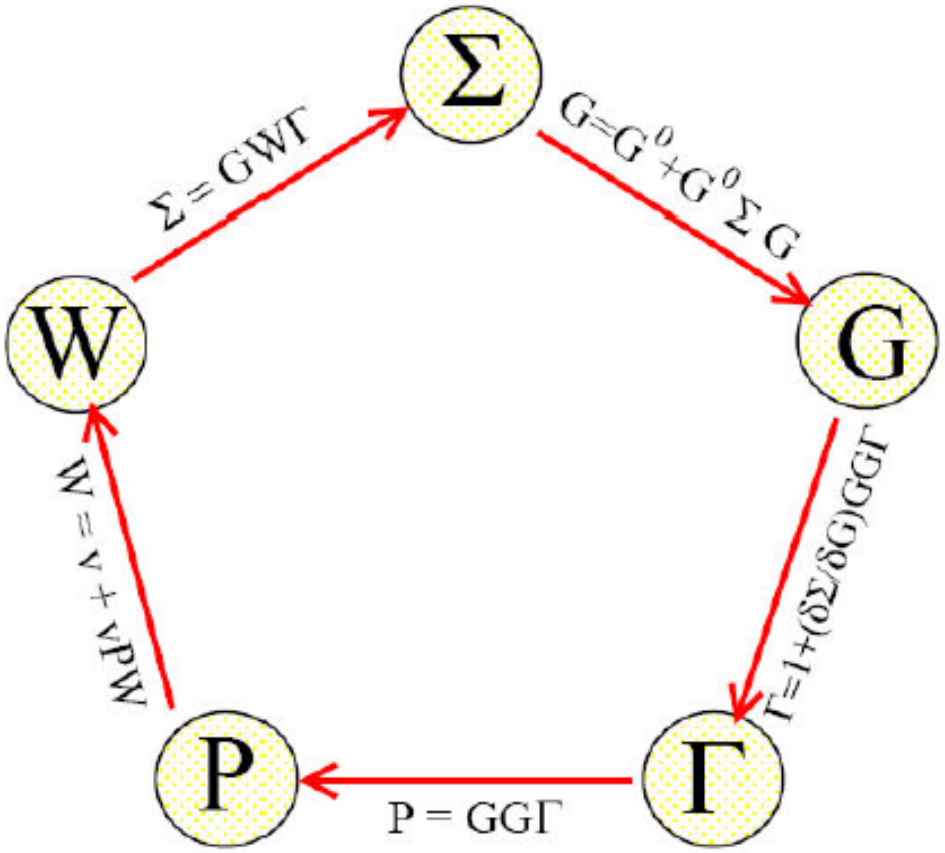
$$P(1,2) = -\mathrm{i}$$

$$W(1,2) = v($$

$$\Gamma(1,2,3) = \delta($$

$$+ \int$$

, 7)



M. Gatti

- Exact close

The *GW* Approximation

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- Iterate Hedin's equations once starting with Σ=0

$$
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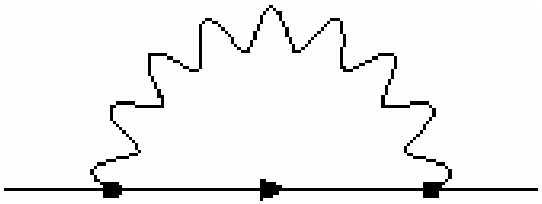
\end{aligned}
$$

The *GW* Approximation



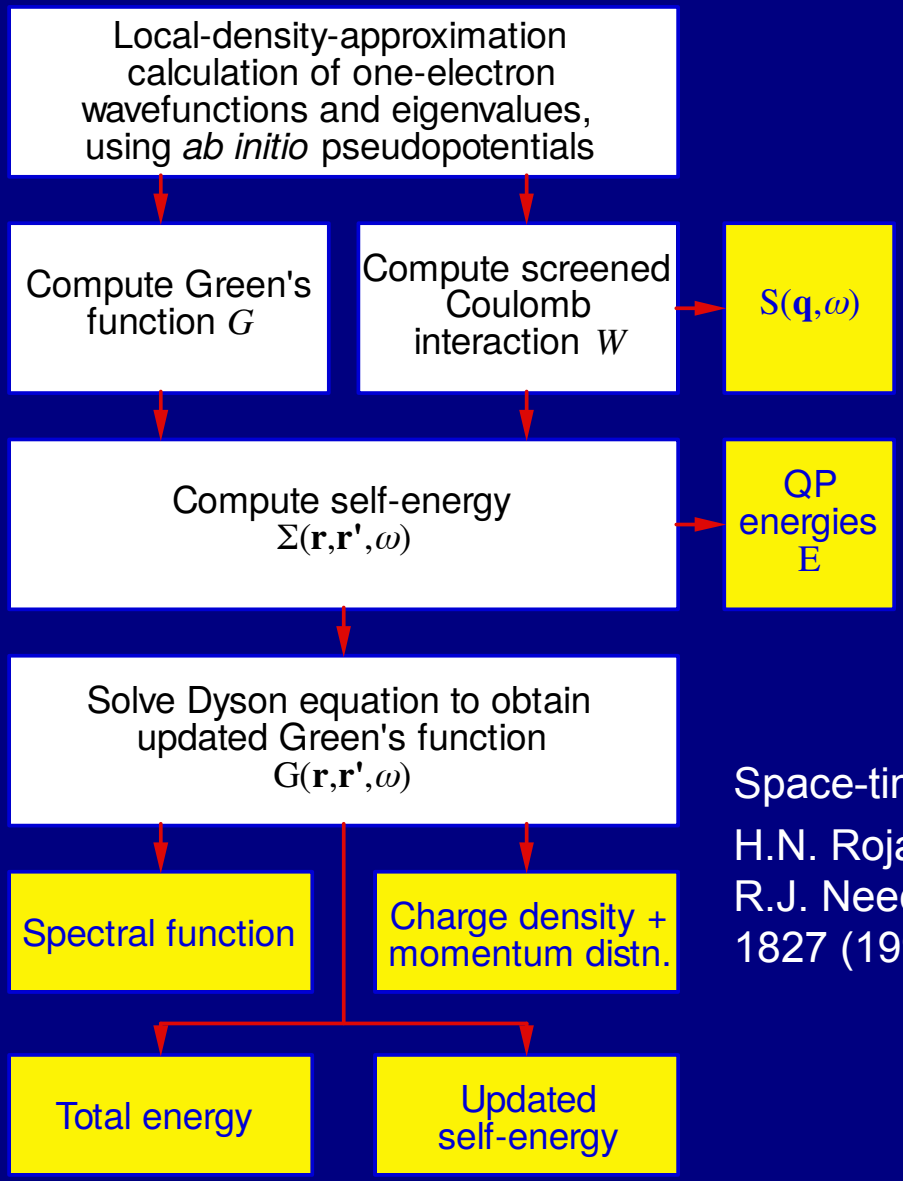
$$\Sigma(\mathbf{x},\mathbf{x}';\omega) = \frac{i}{2\pi}\int W(\mathbf{x},\mathbf{x}';\omega')G(\mathbf{x},\mathbf{x}';\omega+\omega')e^{i\delta\omega'}d\omega'$$

where $\mathbf{x} \equiv (\mathbf{r},\xi)$ is space+spin

In the time domain

$$\Sigma(\mathbf{x},\mathbf{x}';t-t') = iW(\mathbf{x},\mathbf{x}';t-t')G(\mathbf{x},\mathbf{x}';t-t')$$

W is the dynamically screened Coulomb interaction between electrons



Space-time method:

H.N. Rojas, RWG and R.J. Needs, Phys. Rev. Lett. **74** 1827 (1995)

Spectral Properties

G_0W_0 Band Structures of Insulators

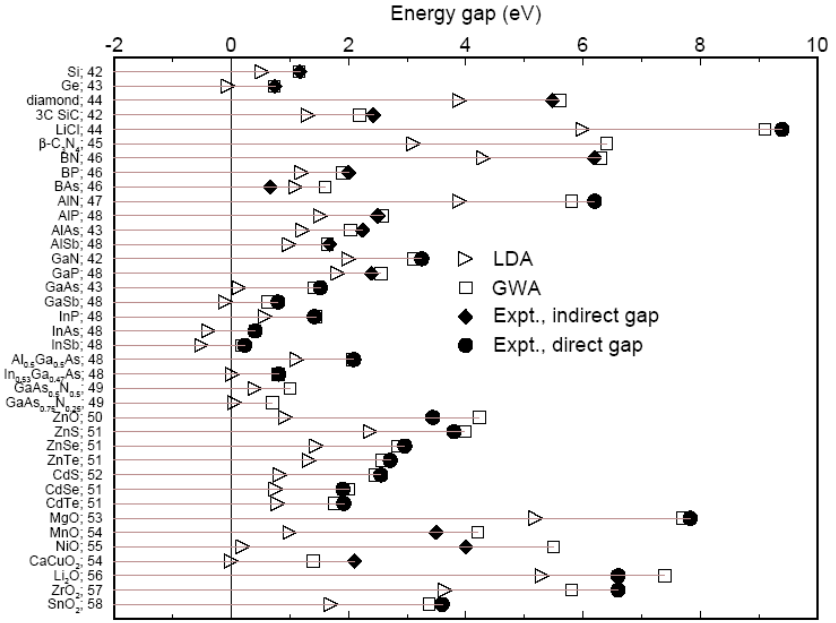
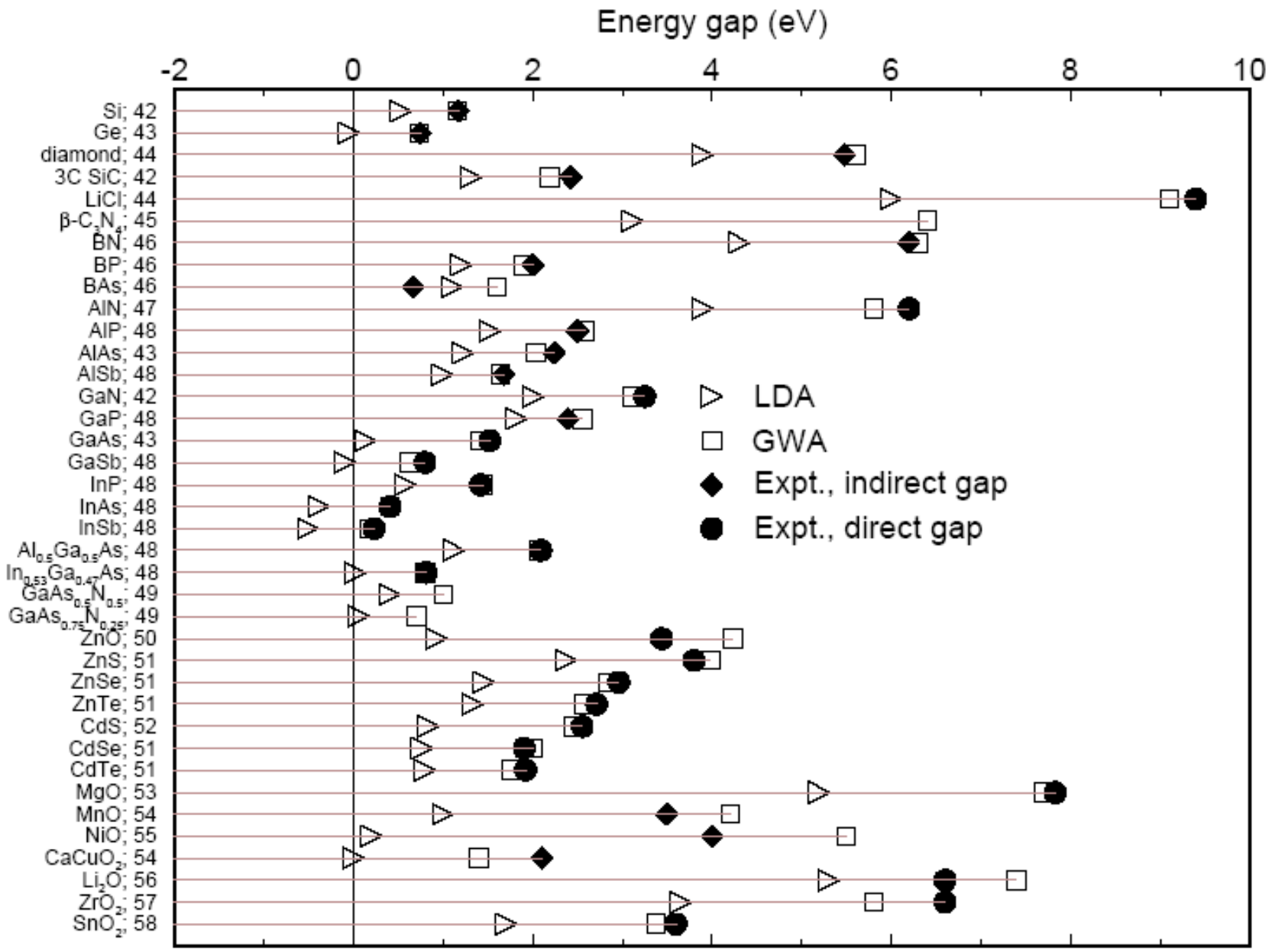


Figure 3: Comparison of characteristic direct and indirect LDA, GWA, and experimental energy gaps for all semiconductors and insulators for which first-principles GWA calculations have been reported. GWA corrects most of the LDA band gap underestimation over more than one order of magnitude in the experimental band gap. The values for MnO, ZnO, and $CaCuO_2$ are from model-GWA calculations, which are accurate to within 0.4 eV. The discrepancy between GWA and experiment for LiO_2 results from the neglect of excitonic effects. The experimental value for BAs is tentative. The references for the LDA, GWA, and experimental values are listed after the element symbols.

From "Quasiparticle calculations in solids", W.G. Aulbur, L. Jönsson and J.W. Wilkins, Solid State Physics **54** 1 (2000)

[also available in preprint form at http://www.physics.ohio-state.edu/~wilkins/vita/publications.html#reviews]



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Self-Consistency

Fully self-consistent

$\Sigma = iGW$: Conserving

Partially self-consistent

$\Sigma = iGW_0$: Conserving

Non-self-consistent

$\Sigma = iG_0W_0$: Non-conserving

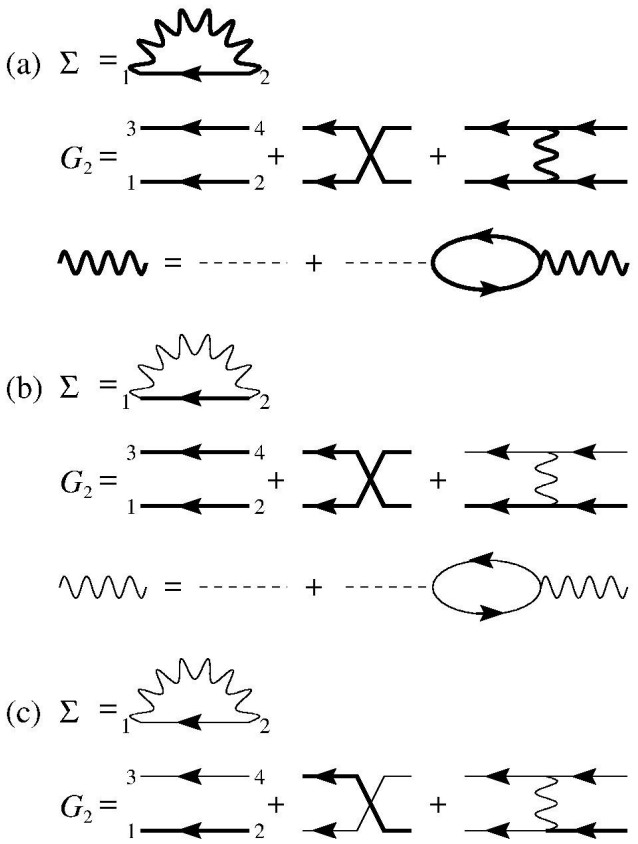
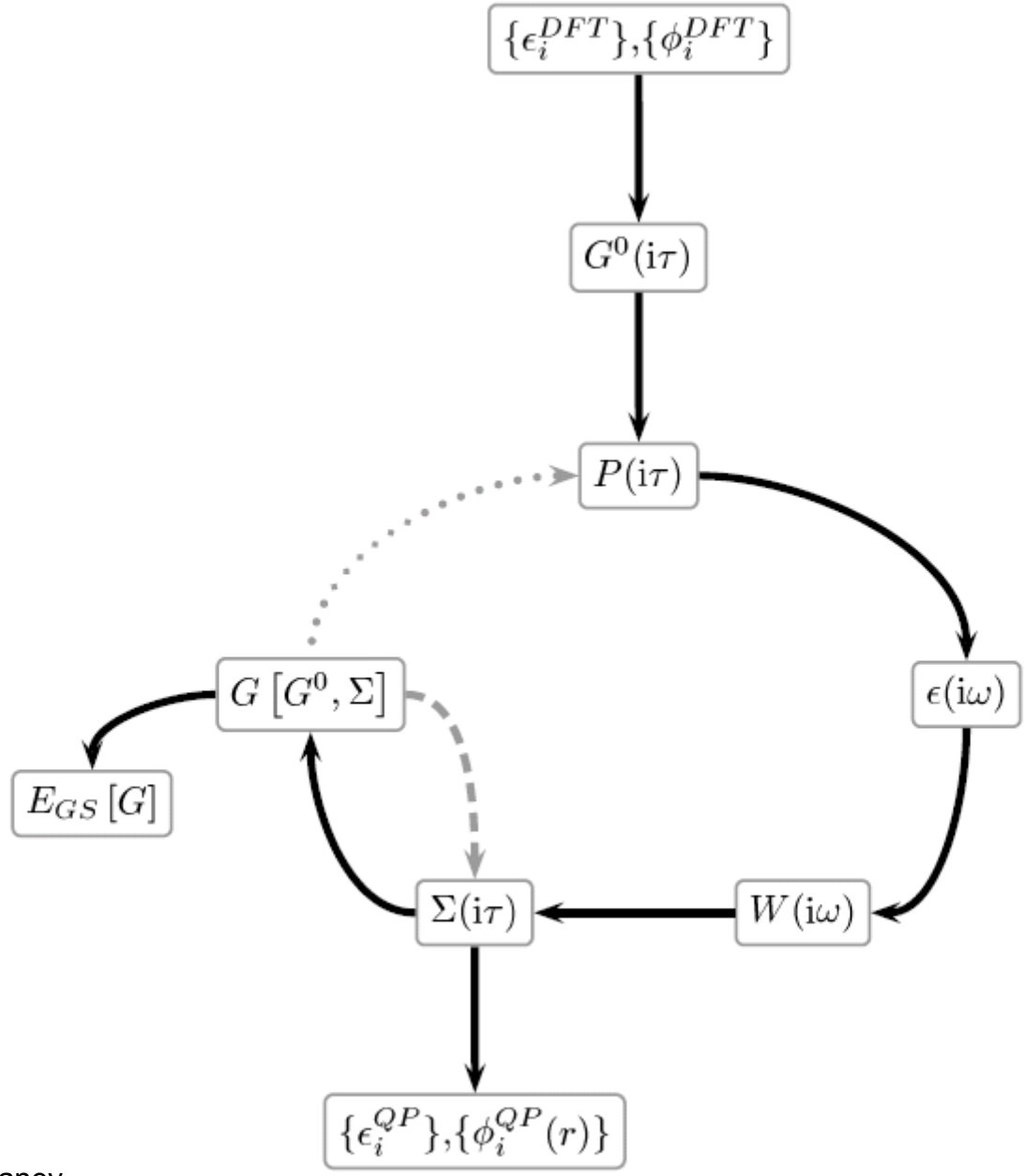


FIG. 1. Diagrammatic representation of the self-energy $\Sigma(x_1, x_2)$ and the corresponding two-particle Green function $G_2(x_1, x_3; x_2, x_4)$ in (a) the fully self-consistent GW approximation, (b) the partially self-consistent GW_0 approximation, and (c) the non-self-consistent G_0W_0 approximation.

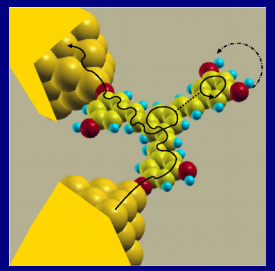
Arno Schindlmayr, Pablo García-González and RWG



Kris Delaney

Summary: The Status of *GW*

- Routine spectral properties
- Total energy
- *GW* + vertex corrections
- *GW*-level approaches to optical absorption; quantum conductance; quantum transport; time-dependent problems
- DFT insight from *GW:*
  TDDFT / orbital functionals



Further Reading

- "Interacting Electrons", Richard M. Martin, Lucia Reining and David M. Ceperley, Cambridge University Press (2016)
  Amazon In UoY Library
- "Quasiparticle calculations in solids", W.G. Aulbur, L. Jönsson and J.W. Wilkins, Solid State Physics **54** 1 (2000)
  http://www.physics.ohio-state.edu/~wilkins/vita/gw_review.ps

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