Modelling electronic and optical properties
Background
• Photo-emission
• Inverse Photo-emission
• Optical absorption
- Photo-emission
- Inverse Photo-emission
- Optical absorption

\[ h\nu \]

N-1 excitations
• Photo-emission
• Inverse Photo-emission
• Optical absorption
- Photo-emission
- Inverse Photo-emission
- Optical absorption

Electronic structure
• Photo-emission
• Inverse Photo-emission
• Optical absorption
• Photo-emission
• Inverse Photo-emission
• Optical absorption

Im dielectric tensor

(b)
Divide the problem in 3 steps

Ground State
Ground State  N-1, N+1 excitations
Ground State  N-1, N+1 excitations
Ground State  N-1, N+1 excitations  N excitations
Ground State  N-1, N+1 excitations  N excitations

Electron-Hole interaction
Ground State  N-1, N+1 excitations  N excitations

Polarised medium
• “Gap” = E(N+1) + E(N-1) - 2E(N)
• Optical excitations = E(N)* - E(N)
• “Gap” = E(N+1) + E(N-1)-2E(N)

• Optical excitations = E(N)*-E(N)
• Periodic boundary conditions and Bloch theorem

• Hamiltonian model ###
The Many-Body Problem

N-electrons interacting through the Coulomb potential:

\[ H = \sum_{i=1}^{N} T(x_i) + \sum_{i \neq j=1}^{N} V(x_i, x_j) + \sum_{\alpha}^{N} \sum_{i=1}^{N} V_{ext}(x_i, R_\alpha) \]
• What is the problem with DFT?
The Kohn-Sham scheme

It is possible to define an auxiliary system of $N$ non-interacting electrons such that the GS density of the auxiliary system is equal to the GS of $N$ interacting electrons.

The Kohn-Sham orbitals have \textit{a priori} no physical meaning.

Self-Consistent determination of the density.

\[
\left(-\frac{1}{2} \nabla^2 + v_{\text{eff}}(r) - \epsilon_j\right) \varphi_j(r) = 0, \\
\]

\[
n(r) = \sum_{j=1}^{N} |\varphi_j(r)|^2
\]
• Density Functional Theory (mean field theory) : Ground State density

• Green Functions (Many-Body Perturbation theory)
Many-Body Problem in terms of Green functions

The Feynman rules for finding the contribution of $n$th order perturbation theory are simpler.

The use of Green functions imply the loss of detailed information although they still contain:

1.) The expectation value of any single-particle operator in the ground state
2.) The ground state energy
3.) The excitation spectrum.
The Quasi-Particle concept

Suppose an interaction invariant under translation and a system spatially uniform.

The quantities 1, 2, ..., depend only on coordinate differences thus a four dimensional Fourier transform can be defined.

Dyson Equation in Fourier space:

\[ G(k) = G^0(k) + G^0(k)\Sigma(k)G(k) \]

\[ G(k) = \frac{1}{[G^0(k)]^{-1} - \Sigma(k)} \]

\[ G(k, \omega) = \frac{1}{\omega - \epsilon^0_k - \Sigma(k, \omega)} \]
Approximations to the self-energy
Hartree

Single-particle equation, solvable, shifts non-interacting particle energies.

\[ F[\tilde{n}(r)] = T_s[\tilde{n}(r)] + \frac{1}{2} \int \frac{\tilde{n}(r)\tilde{n}(r')}{|r-r'|} \, drdr' + E_{xc}[\tilde{n}(r)] \]

"\[ \sum \]"
Hartree-Fock

Creation of an electron/hole at the vacuum level that propagates filling a mean bare-coulomb-interacting electronic see
Beyond

Converge with the **bare Coulomb** potential is very long and difficult ~ Multiple SCF Configuration Interaction ...

UNAFFORDABLE but for small molecules

Expansion with a **screened Coulomb** potential:

**Hedin Equations** or **GWΓ**
GWΓ

Set of five equations to be solved self-consistently

\[ G(12) = G^0(12) + \int d3d4G^0(13)\Sigma(34)G(42) \]

\[ P(12) = -i \int G(23)G(42)\Gamma(341)d(34) \]

\[ W(12) = \nu(12) + \int W(13)P(34)\nu(42)d(34) \]

\[ \Sigma(12) = i \int W(1^+3)G(14)\Gamma(423)d(34) \]

\[ \Gamma(123) = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(673)d4567 \]
Vertex corrections, or the filled bubble

Response of the system when an interacting electron-hole pair is created

\[ P(1, 2) = -i \int G(23)G(42)\Gamma(341)d(34) \]

Assuming:

\[ \Gamma(123) = \delta(12)\delta(13) \]
RPA, or the empty bubble

Response of the system when a non-interacting electron-hole pair is created

\[ P(1, 2) = -i G(12) G(21) \]
Hedin Equations within GW approximation

\[ G(12) = G^0(12) + \int d3d4 G^0(13) \Sigma(34) G(42) \]

\[ P(12) = -iG(12)G(21) \]

\[ W(12) = v(12) + \int W(13)P(34)v(42)d(34) \]

\[ \Sigma(12) = iW(1^+2)G(12) \]

Creation of an electron/hole at the vacuum level that propagates filling a polarized electronic see
GW \sim \text{Hartree-Fock with a "dressed" self-energy}

#The dress (W) is non-local, energy dependent
Ground State  N-1, N+1 excitations  N excitations

DFT  GW  BSE
4-point polarizability

\[ P^0(1, 1'; 2, 2') = -iG(1', 2')G(2, 1) \]

\[ P(1, 1', 2, 2') = P^0(1, 1', 2, 2') + \]
\[ + \int P^0(1, 1', 3, 3') W(3, 3', 4, 4') P(4, 4', 2, 2') d3d3' d4d4' \]
4-point polarizability

Quasi-particle state basis:

\[
S(x_1, x_{1'}, x_2, x_{2'}) = \sum_{(n_1, n_{1'})(n_2, n_{2'})} \psi_{n_1}^*(x_1) \psi_{n_{1'}}(x_{1'}) \psi_{n_2}(x_2) \phi_{n_{2'}}^*(x_{2'}) S(n_1, n_{1'})(n_2, n_{2'})
\]

Dyson equation

\[
\bar{P}(n_1, n_{1'})(n_2, n_{2'}) = \bar{P}^0(n_1, n_{1'})(n_2, n_{2'}) + \bar{P}^0(n_1, n_{1'})(n_3, n_{3'}) \Xi(n_3, n_{3'})(n_4, n_{4'}) \bar{P}(n_4, n_{4'})(n_2, n_{2'})
\]

Modified polarizability (reducible)

\[
\Xi(n_1, n_{1'})(n_2, n_{2'}) =
- \int dx_1 dx_{1'} \psi_{n_1}(x_1) \psi_{n_{1'}}^*(x_{1'}) W(x_1, x_{1'}) \psi_{n_2}(x_1) \psi_{n_{2'}}^*(x_{1'}) +
+ \int dx_1 dx_{1'} \psi_{n_1}(x_1) \psi_{n_{1'}}^*(x_{1'}) v(x_1, x_{1'}) \psi_{n_2}(x_{1'}) \psi_{n_{2'}}^*(x_{1'})
\]
The Bethe-Salpeter Equation

Effective 2-particle Hamiltonian:

\[ H_{(n_1,n_1')(n_2,n_2')}^{2p} = (\epsilon_{n_1'} - \epsilon_{n_1}) \delta_{(n_1,n_2)(n_1',n_2')} + (f_{n_1} - f_{n_1'}) \Xi_{(n_1,n_1')(n_2,n_2')} \]

Equivalent eigenvalue equation

\[ \sum_{(n_1,n_1')(n_2,n_2')} H_{(n_1,n_1')(n_2,n_2')}^{2p} A_{(n_2,n_2')}^\mu = E^\mu A_{(n_1,n_1')}^\mu \]
Ground State  N-1, N+1 excitations  N excitations

DFT  GW  BSE
free e-h gap

Binding energy

Absorption edge
optical gap

N+1 excitations

e-h pairs

N-1 excitations

Energy
Optical defect signature
Charge -1

Energy

Density Of States

Perfect crystal
Charge +1

Diagram showing energy levels and density of states for a perfect crystal.
formation of e-h pairs
formation of e-h pairs
formation of e-h pairs
Charge $-I_{hv}$
Charge $-I_{hv}$
Charge +1

hv

Perfect crystal

Energy

Density Of States

Perfect crystal
Charge +1
defects create absorption bands within the band gap
Disorder in semiconductors and insulators
Defects and doping

Possible mixing
ODC’s Band structure and optical properties within GW-BSE
SiODC

Quasi-dark exciton
SiODC

7.6-7.7 eV
transition from A to a localized state in conduction
defect absorption bands are ill defined and are inside the rumour of A’-C transitions
SiODC vs GeODC

The graph shows the optical absorption and DOS (density of states) for a-SiO2, GeODC(l), and SiODC(l) materials. The graph highlights the energy levels and defect states in these materials, with specific labels for the Anderson localized states (A), unoccupied defect levels (B), and conduction band (C).