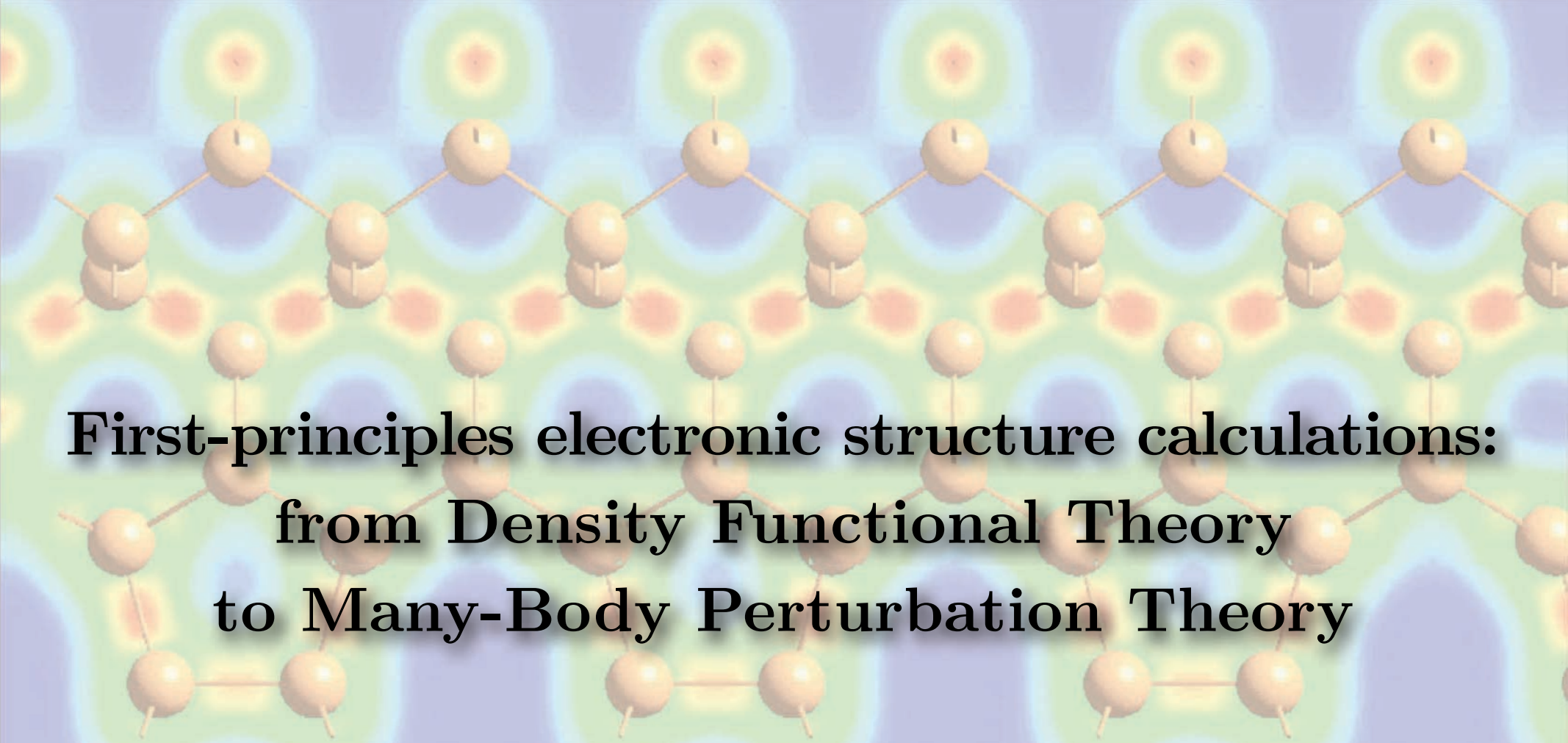


First-principles electronic structure calculations: from Density Functional Theory to Many-Body Perturbation Theory

School on "Computational Modelling of Materials"

Gian-Marco Rignanese

Antwerpen, 2 december 2010

ETSF

fnrs

Born-Oppenheimer approximation

- Let us consider a crystalline solid with N_e electrons et N_N nuclei, the system will be completely quantum-mechanically described by its **wavefunction** Ψ:

$$\Psi = \Psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e}, \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_{N_N}\right)$$

  where $\mathbf{r}_i$ ($i = 1, ..., N_e$) and $\mathbf{R}_\alpha$ ($\alpha = 1, ..., N_N$) are the coordinates of the electrons and of the nuclei, respectively.

- As the nuclei are much heavier (hence slower) than the electrons ($M_\alpha >> 1$), their respective dynamics can be decoupled. Hence, the wavefunction of the system can be broken into its electronic and nuclear components:

$$\Psi = \psi^e\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e}\right) \times \psi^N\left(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_{N_N}\right)$$

Electronic N-body problem

- In practice, its assumed that the nuclei positions can be considered as fixed when studying the electrons dynamics.
  In order to obtain the electronic wavefunction ψ^e, one has to solve the **Schrödinger equation** of the electronic system:

$$\hat{H}^e_{\{\mathbf{R}\}}\psi^e = E^e_{\{\mathbf{R}\}}\psi^e$$

  in which the **Hamiltonian** writes:

$$\hat{H}^e_{\{\mathbf{R}\}} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN}$$

  with

$$\hat{T}_e = \sum_{i=1}^{N_e} -\frac{1}{2}\nabla^2_{\mathbf{r}_i}$$

$$\hat{V}_{ee} = \frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{N_e,N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \qquad \hat{V}_{eN} = \sum_{i=1}^{N_e}\sum_{\alpha=1}^{N_N} \frac{-Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|}$$

Variational Quantum Monte Carlo

- Basically, it is impossible to solve this Schrödinger equation for more than two electrons analytically.
- A first class of numerical methods relies on the variational principle for the ground-state energy of the electronic system:

$$E^e_{\{\mathbf{R}\}} = \frac{\langle \psi^e | \, \hat{H}^e_{\{\mathbf{R}\}} \, | \psi^e \rangle}{\langle \psi^e \, | \, \psi^e \rangle}$$

- Namely, for any arbitrary function ϕ, called trial-wavefunction, its expectation value E_ϕ , which is defined as:

$$E_\phi = \frac{\langle \phi | \, \hat{H}^e_{\{\mathbf{R}\}} \, | \phi \rangle}{\langle \phi \, | \, \phi \rangle}$$

  is such that $E_\phi \geq E^e_{\{\mathbf{R}\}}$ and it reaches its minimum when:

$$\frac{\delta E_\phi}{\delta \phi} = 0$$

Variational Quantum Monte Carlo

- This variational principle can be exploited to approach the ground-state energy as much as possible.
- A trial-wavefunction $\phi(a)$ depending on one or more parameters is chosen. The different many-dimensional integrals are evaluated numerically (Monte Carlo methods) so as to obtain :

$$E(a) = \frac{\langle \phi(a) | \, \hat{H}^e_{\{\mathbf{R}\}} \, | \phi(a) \rangle}{\langle \phi(a) \, | \, \phi(a) \rangle}$$

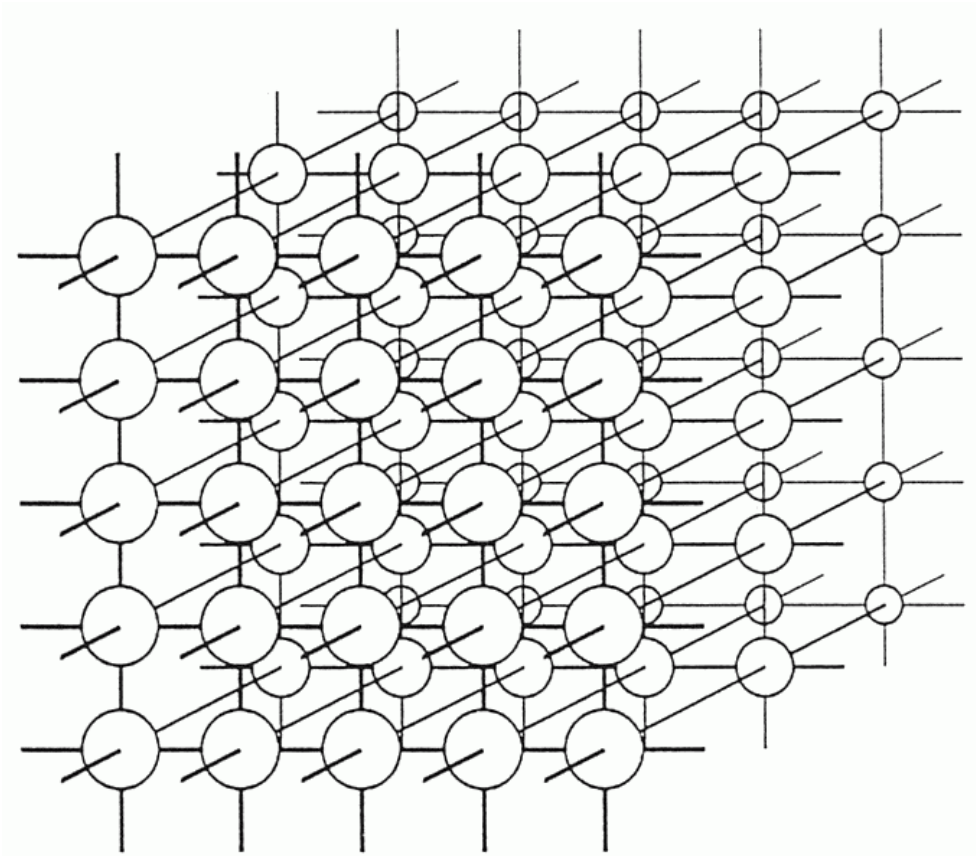
- The minimum is then located by varying the parameter(s):

$$\frac{\partial E(a)}{\partial a} = 0$$

- The choice of the trial-wavefunction is obviously very critical.

Variational Quantum Monte Carlo

- Moreover, the N_e-electrons wavefunction soon becomes an object very difficult to handle in a computer.
- For instance, the wavefunction of the oxygen atom (with 8 electrons) defined on a 10×10×10 real space-grid is an object which consists of 10^{24} real numbers.



Note: in classical mechanics, the very same system is fully described by 48 real numbers (the positions and the velocities of the 8 electrons).

Independent electron approximation

- In fact, electron-electron interactions are the real problem. Assuming that these are negligible w.r.t. the electron-ion interactions, the problem simplifies to:

$$\hat{H}^e_{\{\mathbf{R}\}}\psi^e = E^e_{\{\mathbf{R}\}}\psi^e \text{ with } \hat{H}^e_{\{\mathbf{R}\}} = \hat{T}_e + \hat{V}_{eN}$$

$$\sum_{i=1}^{N_e}\left[-\frac{1}{2}\nabla^2_{\mathbf{r}_i} + V_{ext}(\mathbf{r}_i)\right]\psi^e = E^e_{\{\mathbf{R}\}}\psi^e$$

$$\text{with } V_{ext}(\mathbf{r}) = \sum_{\alpha=1}^{N_N}\frac{-Z_\alpha}{|\mathbf{r}-\mathbf{R}_\alpha|}$$

- The form of the Hamiltonian calls for a separation of variables. The N_e-electrons wavefunction can be replaced by the product of N_e 1-electron wavefunctions:

$$\psi^e(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e}) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_{N_e}(\mathbf{r}_{N_e})$$

Independent electron approximation

- The 1-electron wavefunctions are the solutions of a 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

- The total electronic energy can be written as the sum of the electronic eigenenergies:

$$E^e_{\{\mathbf{R}\}} = \sum_{i=1}^{N_e} \epsilon_i$$

- The **electrons** are **independent**.
- This is the starting point of a second class of numerical methods, which originate from quantum chemistry.

Hartree approximation

- The **Hartree approximation** assumes that the N_e-electrons wavefunction can be replaced by the product of N_e 1-electron wavefunctions even when the electron-electron interactions are not neglected.
- It can be shown that the 1-electron wavefunctions are the solutions of the following 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + \sum_{\substack{j=1 \\ j\neq i}}^{N_e} \hat{J}_j \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

where $\hat{J}_j$ is the **Coulomb operator** defined by:

$$\hat{J}_j \phi_i(\mathbf{r}) = \left\{ \int \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_j(\mathbf{r}') d\mathbf{r}' \right\} \phi_i(\mathbf{r})$$

Hartree approximation

- The electronic eigenenergies can be written as:

$$\epsilon_i = \langle \phi_i | -\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) | \phi_i \rangle + \sum_{\substack{j=1 \\ j\neq i}}^{N_e} J_{ij}$$

where $$J_{ij} = \int \phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r})\phi_j(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

- So that the total electronic energy writes:

$$E^e_{\{\mathbf{R}\}} = \langle \psi^e | \hat{H}^e_{\{\mathbf{R}\}} | \psi^e \rangle = \sum_{i=1}^{N_e} \langle \phi_i | -\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) | \phi_i \rangle + \frac{1}{2} \sum_{\substack{i,j=1 \\ j\neq i}}^{N_e,N_e} J_{ij}$$

$$= \sum_{i=1}^{N_e} \epsilon_i - \frac{1}{2} \sum_{\substack{i,j=1 \\ j\neq i}}^{N_e,N_e} J_{ij}$$

Hartree approximation

- The 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + \sum_{\substack{j=1 \\ j\neq i}}^{N_e} \hat{J}_j \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

where $\hat{J}_j \phi_i(\mathbf{r}) = \left\{ \int \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_j(\mathbf{r}') d\mathbf{r}' \right\} \phi_i(\mathbf{r})$

is almost identical (a part from the self-interaction) to:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

with $V_H(\mathbf{r})$, the **Hartree potentiel**, defined by:

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

where $n(\mathbf{r}) = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2$ is the electronic density.

Hartree approximation

- In this case, the total electronic energy is written as:

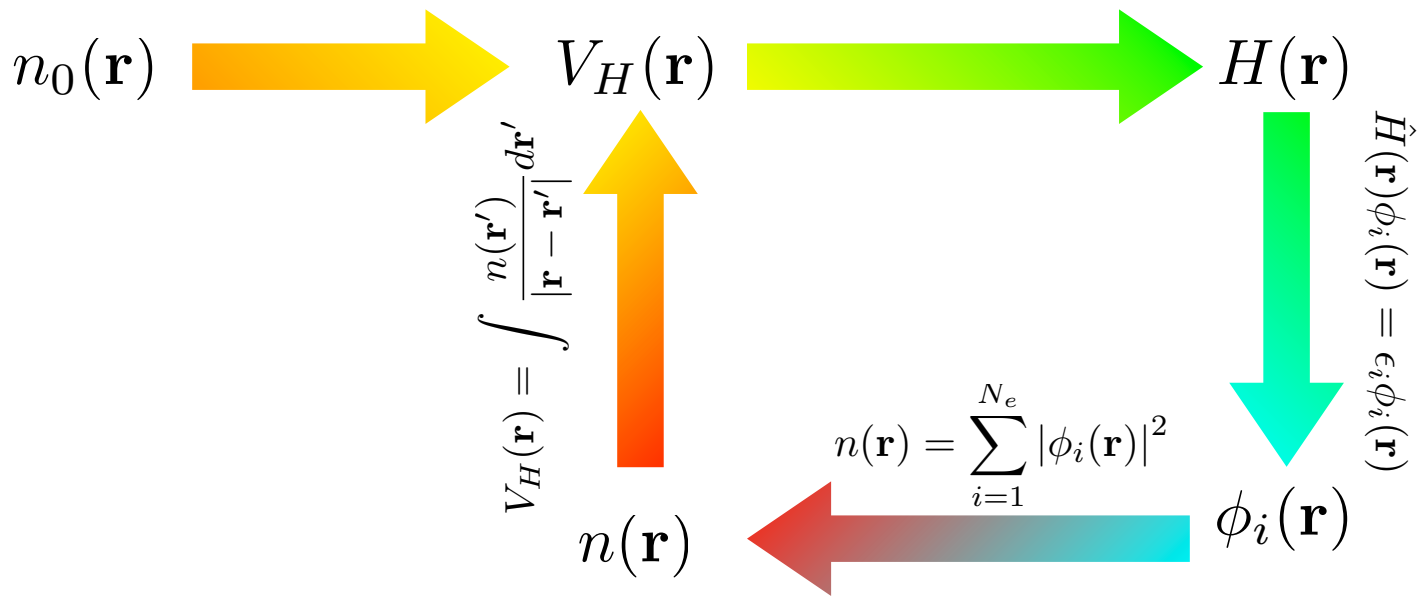
$$E^e_{\{\mathbf{R}\}} = \sum_{i=1}^{N_e} \epsilon_i - E_H$$

where E_H is the **Hartree energy**, defined by:

$$E_H = \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Hartree approximation

- However, there is a new difficulty:
  - to obtain the Hartree potential $V_H(\mathbf{r})$, the electronic density $n(\mathbf{r})$ and hence all the wavefunctions $\phi_i(\mathbf{r})$ are needed
  - to obtain the wavefunctions $\phi_i(\mathbf{r})$, the Hartree potential $V_H(\mathbf{r})$ is required
- In practice, one starts from a trial electronic density and then iterates the equations until **self-consistency** is reached:



Hartree-Fock approximation

- In order to take Pauli exclusion principle into account, the product of N_e 1-electron wavefunctions should be replaced by a **Slater determinant**:

$$\psi^e(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e}) = \frac{1}{\sqrt{!N_e}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_{N_e}(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_{N_e}(\mathbf{r}_2) \\ \vdots & \vdots & & \vdots \\ \phi_1(\mathbf{r}_{N_e}) & \phi_2(\mathbf{r}_{N_e}) & \cdots & \phi_{N_e}(\mathbf{r}_{N_e}) \end{vmatrix}$$

That is the **Hartree-Fock approximation**.

Hartree-Fock approximation

- It can be shown that the 1-electron wavefunctions are the solutions of the following 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + \sum_{\substack{j=1 \\ j\neq i}}^{N_e} (\hat{J}_j - \hat{K}_j) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

where $\hat{J}_j$ is the **Coulomb operator** defined by:

$$\hat{J}_j \phi_i(\mathbf{r}) = \left\{ \int \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}') d\mathbf{r}' \right\} \phi_i(\mathbf{r})$$

and $\hat{K}_j$ is the **exchange operator** defined by:

$$\hat{K}_j \phi_i(\mathbf{r}) = \left\{ \int \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}') d\mathbf{r}' \right\} \phi_j(\mathbf{r})$$

Hartree-Fock approximation

- The electronic eigenenergies can be written as:

$$\epsilon_i = \langle \phi_i | -\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) | \phi_i \rangle + \sum_{\substack{j=1 \\ j\neq i}}^{N_e} (J_{ij} - K_{ij})$$

where $J_{ij} = \int \phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r})\phi_j(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$

and $K_{ij} = \int \phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_j(\mathbf{r})\phi_i(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$

- So that the total electronic energy is:

$$E^e_{\{\mathbf{R}\}} = \langle \psi^e | \hat{H}^e_{\{\mathbf{R}\}} | \psi^e \rangle = \sum_{i=1}^{N_e} \epsilon_i - \frac{1}{2} \sum_{\substack{i,j=1,N_e \\ j\neq i}}^{N_e,N_e} (J_{ij} - K_{ij})$$

Hartree-Fock approximation

- The 1-electron Schrödinger equation::

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + \sum_{\substack{j=1 \\ j\neq i}}^{N_e} (\hat{J}_j - \hat{K}_j) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

  is identical (here, the self-interaction cancel in J and K) to:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + \hat{V}_x \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

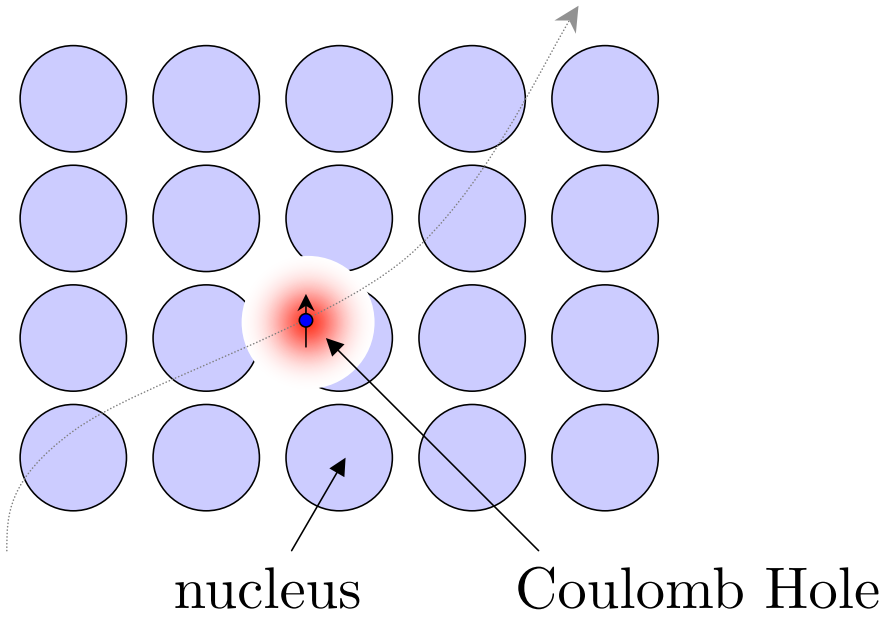
  with $\hat{V}_x$, the **exchange potential operator**, defined by:

$$\hat{V}_x \phi_i(\mathbf{r}) = \sum_{j=1}^{N_e} \left\{ \int \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}') d\mathbf{r}' \right\} \phi_j(\mathbf{r})$$

  It is a non-local operator.

Hartree-Fock approximation

- However, the Hartree-Fock approximation does not take **electronic correlation** into account. For instance, an electron traveling in a solid will repel the other electrons; and, as a result, a positive (due to the nuclei) charge cloud, called **Coulomb hole**, will be created around it. This cloud screens the Coulomb interaction between the electrons.



Post-Hartree-Fock methods

- **Configuration Interaction** (CI): the N_e-electrons wavefunction is approximated by a linear combination of Slater determinants (including 1-electron wavefunctions associated to excited states).
- **Coupled Cluster** (CC): the N_e-electrons wavefunction is obtained by applying an exponential of the excitation operator on the Slater determinant (hence producing a linear combination of excited Slater determinants).
- **Møller-Plasset** (MP): the N_e-electrons wavefunction is obtained by means of perturbation theory in terms of the correlation potential (i.e. the difference between the exact Hamiltonian exact and the one of Hartree-Fock approximation). The correlation potential does not contribute in first-order to the exact electronic energy. The higher-order terms are written on basis of doubly-excited Slater determinants (singly-excited do not contribute).

Density Functional Theory

- **Hohenberg-Kohn Theorem**

  Let us consider all possible Schrödinger equation for N_e electrons which only differ by the external potential $V_{ext}(\mathbf{r})$:

$$\left[\hat{T}_e + \hat{V}_{ee} + \sum_{i=1}^{N_e} V_{ext}(\mathbf{r}_i)\right] \psi^e = E^e_{\{\mathbf{R}\}} \psi^e$$

  The electronic density of the ground-state $n(\mathbf{r})$ defined by:

$$n(\mathbf{r}) = N_e \int \left[\psi^e(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e})\right]^* \psi^e(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e}) d\mathbf{r}_2 \ldots d\mathbf{r}_{N_e}$$

  determines uniquely the external potential $V(\mathbf{r})$, modulo a global constant.

- The external potential is thus a functional of the density.

Density Functional Theory

- It is also the case for all the quantities which can be formally obtained once the potential is fixed modulo a global constant (for instance, the wavefunctions of the ground-state), hence the name of the theory (acronym: DFT).

- Moreover, if the arbitrary constant for the external potential is fixed through a simple condition (for instance, the potential goes to zero when the distance goes to infinity), the total electronic energy is also a functional of the density:

$$E^e_{\{\mathbf{R}\}} = E[n]$$

  Indeed, the Hamiltonian is uniquely defined by specifying the external potential, and its expectation value gives the total electronic energy.

Density Functional Theory

- Starting from the variational principle, it is possible to gain insight about this energy functional:

$$
\begin{aligned}
E^e_{\{\mathbf{R}\}} &= \min_{\phi} \left\{ \langle \phi | \, \hat{H} \, | \phi \rangle \right\} = \min_{n} \left\{ \min_{\phi \to n} \left\{ \langle \phi | \, \hat{H} \, | \phi \rangle \right\} \right\} \\
&= \min_{n} \left\{ \min_{\phi \to n} \left\{ \langle \phi | \, \hat{T}_e + \hat{V}_{ee} + \sum_{i=1}^{N_e} V_{ext}(\mathbf{r}_i) \, | \phi \rangle \right\} \right\} \\
&= \min_{n} \left\{ \min_{\phi \to n} \left\{ \langle \phi | \, \hat{T}_e + \hat{V}_{ee} \, | \phi \rangle \right\} + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \right\} \\
&= \min_{n} \left\{ F[n] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \right\}
\end{aligned}
$$

where $F[n] = \min_{\phi \to n} \left\{ \langle \phi | \, \hat{T}_e + \hat{V}_{ee} \, | \phi \rangle \right\}$ is a universal functional of the density, but it is **not known explicitly**.

Density Functional Theory

- In fact, $F[n]$ represents an important part of the total electronic energy. It is thus critical to make a reasonable approximation for it in order to obtain a good value for $E[n]$

- **Kohn** and **Sham** tried to establish a connection with a system of non-interacting electrons with the same electronic density:

$$F[n] = \min_{\phi \to n} \left\{ \langle \phi | \, \hat{T}_e + \hat{V}_{ee} \, | \phi \rangle \right\} \longrightarrow T_0[n] = \min_{\phi \to n} \left\{ \langle \phi | \, \hat{T}_e \, | \phi \rangle \right\}$$

  The kinetic energy is a known functional $T_0[n]$ of the density. Moreover, the functional for the associated Hartree energy is also known explicitly:

$$E_H[n] = \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Density Functional Theory

- If this two pieces are substracted from $F[n]$, the rest represents a much smaller part of the total electronic energy. This difference is called **exchange-correlation energy functional**:

$$E_{xc}[n] = F[n] - T_0[n] - E_H[n]$$

  Indeed, it should contain an exchange term (see Hartree-Fock) and a correlation term. But, it also contains the difference between the kinetic energies of the systems of interacting and non-interacting electrons.

- Moreover, it is much easier to obtain a reasonable approximation for it (see below). Let us suppose that this functional is known.

Density Functional Theory

- The problem has now turned into minimizing the functional :

$$E[n] = T_0[n] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n]$$

  under constraint of a fixed number of electrons: $\int n(\mathbf{r}) d\mathbf{r} = N_e$

- Introducing Lagrange multipliers, one has to solve:

$$\frac{\delta \left(E[n] - \lambda \left[\int n(\mathbf{r}) d\mathbf{r} - N_e \right] \right)}{\delta n} = 0$$

$$\frac{\delta T_0[n]}{\delta n} + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n} = \lambda$$

Density Functional Theory

- This equation is strictly equivalent to that of a system of non-interacting electrons with the same electronic density in an external potential, called **Kohn-Sham potential**:

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \underbrace{\int \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'}_{V_H(\mathbf{r})} + \underbrace{\frac{\delta E_{xc}[n]}{\delta n}}_{V_{xc}(\mathbf{r})}$$

  where $V_{xc}(\mathbf{r})$ is the **exchange-correlation potential**.

- It is thus also equivalent to solve the 1-electron Schrödinger equation self-consistently:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{KS}(\mathbf{r})\right] \phi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS} \phi_i^{KS}(\mathbf{r})$$

  with the electronic density $n(\mathbf{r}) = \sum_{i=1}^{N_e} \left[\phi_i^{KS}(\mathbf{r})\right]^* \phi_i^{KS}(\mathbf{r})$

Density Functional Theory

- By construction, when self-consistency is reached, the electronic density and hence the total energy will be the exact ones (assuming the exchange-correlation functional to be exact).
- However, the Kohn-Sham wavefunctions and eigenenergies correspond to a fictitious set of independent electrons, so they do not correspond to any exact quantity.
- The solution of the Kohn-Sham self-consistent system of equations is equivalent to the minimization of

$$E[\{\phi_i\}] = \sum_i \left\langle \phi_i \left| -\frac{1}{2}\nabla^2 \right| \phi_i \right\rangle + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n]$$

under constraints of orthonormalization $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ for the occupied orbitals.

Local Density Approximation

- Let us come back to the problem of finding a reasonable approximation for the exchange-correlation energy functional.

- It is possible to show that this functional of the density can be written as the integral over the whole space of the density multiplied by the local exchange-correlation energy per electron:

$$E_{xc}[n] = \int n(\mathbf{r})\, \varepsilon_{xc}(\mathbf{r}, n) d\mathbf{r}$$

- The Local Density Approximation (acronym: LDA), due to Kohn and Sham, consists in assuming that the local exchange-correlation energy per electron only depends on the local density and that it is equal to that of an homogeneous electron gas with the same density (in a neutralizing background – the "jellium"):

$$\varepsilon_{xc}^{LDA}(\mathbf{r}, n) = \varepsilon_{xc}^{\mathrm{hom}}(n(\mathbf{r}))$$

Local Density Approximation

- The exchange part can be calculated analytically:

$$\varepsilon_x^{\text{hom}}(n(\mathbf{r})) = -\frac{3}{4\pi}\left[3\pi^2 n(\mathbf{r})\right]^{1/3}$$

- The correlation part is obtained from accurate numerical simulations beyond DFT (e.g. Quantum Monte Carlo)

Table 1. *Physical Review* Articles with more than 1000 Citations Through June 2003

Publication	# cites	Av. age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL **45**, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR **108**, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL **19**, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB **12**, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR **124**, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP **57**, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP **54**, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB **13**, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

Beyond LDA

- Globally, LDA works very well (hence, it is widely used). However, in some particular cases (for instance, the hydrogen bond), it clearly shows its limits.

- Considerable efforts are dedicated to improving this approximation. One of the tracks that are pursued is to include a dependence on the gradients of the local density:

$$E_{xc}^{\text{approx}}[n] = \int n(\mathbf{r})\, \varepsilon_{xc}^{\text{approx}} \left(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \nabla^2 n(\mathbf{r}) \right) d\mathbf{r}$$

  This is the **generalized gradients approximation** (acronym: GGA).

- In this case, there is no model (such as the homogeneous electron gas) for which an analytic expression can be obtained.

Beyond LDA

- There exists a wide variety of GGA functionals which have been constructed trying to account for various sum rules (acronyms: PBE, PW86, PW91, LYP, ...).

- Another kind of approximation consists in obtaining a local form for the exchange potential by deriving the exchange term that appears in the Hartree-Fock approximation. This approach is referred to as **exact exchange** (acronym: EXX).

- Another approximation consists in suppressing the self-interaction which is present in the Hartree term (acronym: SIC).

- Finally, there are **hybrid functionals** which are obtained by mixing (using an empirically adjusted parameter) a part of exact exchange and an approximated part (acronyms: B3LYP, HSE, ...).

DFT and the band gap problem

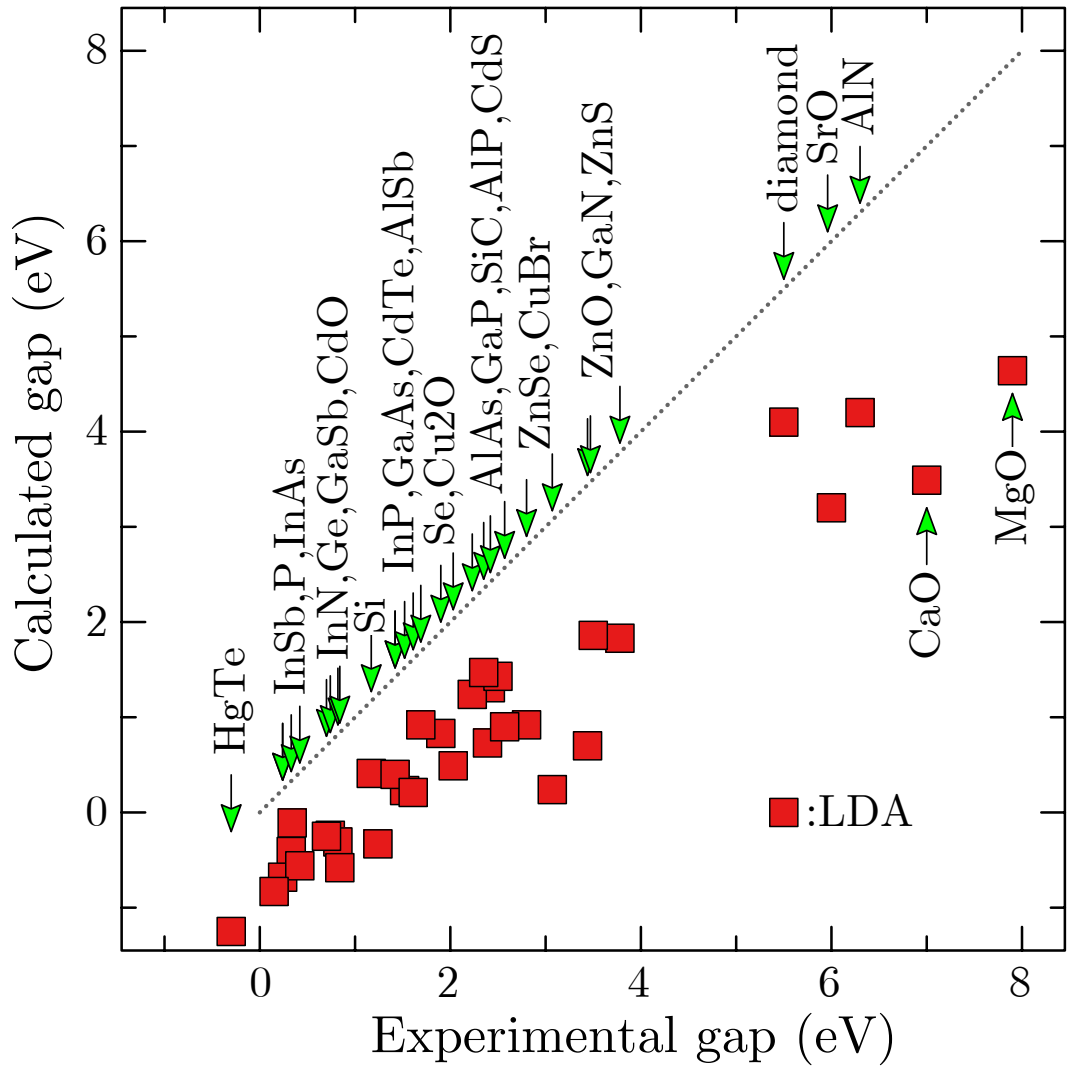
- The Density Functional Theory can (in principle) be used to compute exactly all the ground-state properties by solving the Kohn-Sham equation:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\phi^{KS}_{n\mathbf{k}}(\mathbf{r}) = \epsilon^{KS}_{n\mathbf{k}}\phi^{KS}_{n\mathbf{k}}(\mathbf{r})$$

  As already indicated, there is no direct physical interpretation for the Kohn-Sham eigenenergies (these are simply Lagrange multipliers).

- However, the electronic bandstructures obtained within DFT (LDA or GGA) are in quite good agreement with the experimental data. The most notable exception is the **band gap** which is **systematically underestimated** by 30-50% (or even 100%). This problem is related to the existence of a discontinuity in the derivative of the exchange-correlation potential functional.

DFT and the band gap problem



[adapted from van Schilfgaarde *et al.*, PRL **96**, 226402 (2006)]

Many-Body Perturbation Theory

- Green's function theory and the quasiparticle concept (acronym: MBPT=Many-Body Perturbation Theory) constitute an elegant alternative to DFT which allows to solve this problem.

- The 1-particle Green's function $G(\mathbf{r}, t, \mathbf{r}', t')$ of a system of N_e electron can be interpreted as the probability amplitude to detect an electron at point $\mathbf{r}$ and time t when an electron has been added to the system at point $\mathbf{r}'$ and time t' (if $t > t'$) or to detect a hole at point $\mathbf{r}$ and time t when an electron has been added to the system at point $\mathbf{r}'$ and time t' (if $t' > t$).

- The 1-particle Green's function can be used to obtain many properties of the system of N_e electrons (many-body) such as the ground-state energy and the 1-particle excitation energies (such as $N_e \rightarrow N_e + 1$ or $N_e \rightarrow N_e - 1$).

Many-Body Perturbation Theory

- Most often, it is more convenient to work with the Fourier transform of the 1-particle Green's function:

$$G(\mathbf{r},\mathbf{r}',\omega) = \int G(\mathbf{r},t,\mathbf{r}',t')e^{i\omega(t-t')}d(t-t')$$

- The physical meaning of the 1-particle Green's function can also be approached through its **Lehman representation**:

$$G(\mathbf{r},\mathbf{r}',\omega) = \sum_{n\mathbf{k}} \frac{\phi_{n\mathbf{k}}(\mathbf{r},\omega)\phi^*_{n\mathbf{k}}(\mathbf{r}',\omega)}{\omega - E_{n\mathbf{k}}(\omega)}$$

where the $\phi_{n\mathbf{k}}$ are the solutions of the **quasiparticle equation**:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\phi_{n\mathbf{k}}(\mathbf{r},\omega)$$
$$+ \int \Sigma(\mathbf{r},\mathbf{r}',\omega)\,\phi_{n\mathbf{k}}(\mathbf{r}',\omega)d\mathbf{r}' = E_{n\mathbf{k}}(\omega)\phi_{n\mathbf{k}}(\mathbf{r},\omega)$$

for ω=$E_{n\mathbf{k}}(\omega)$.

Many-Body Perturbation Theory

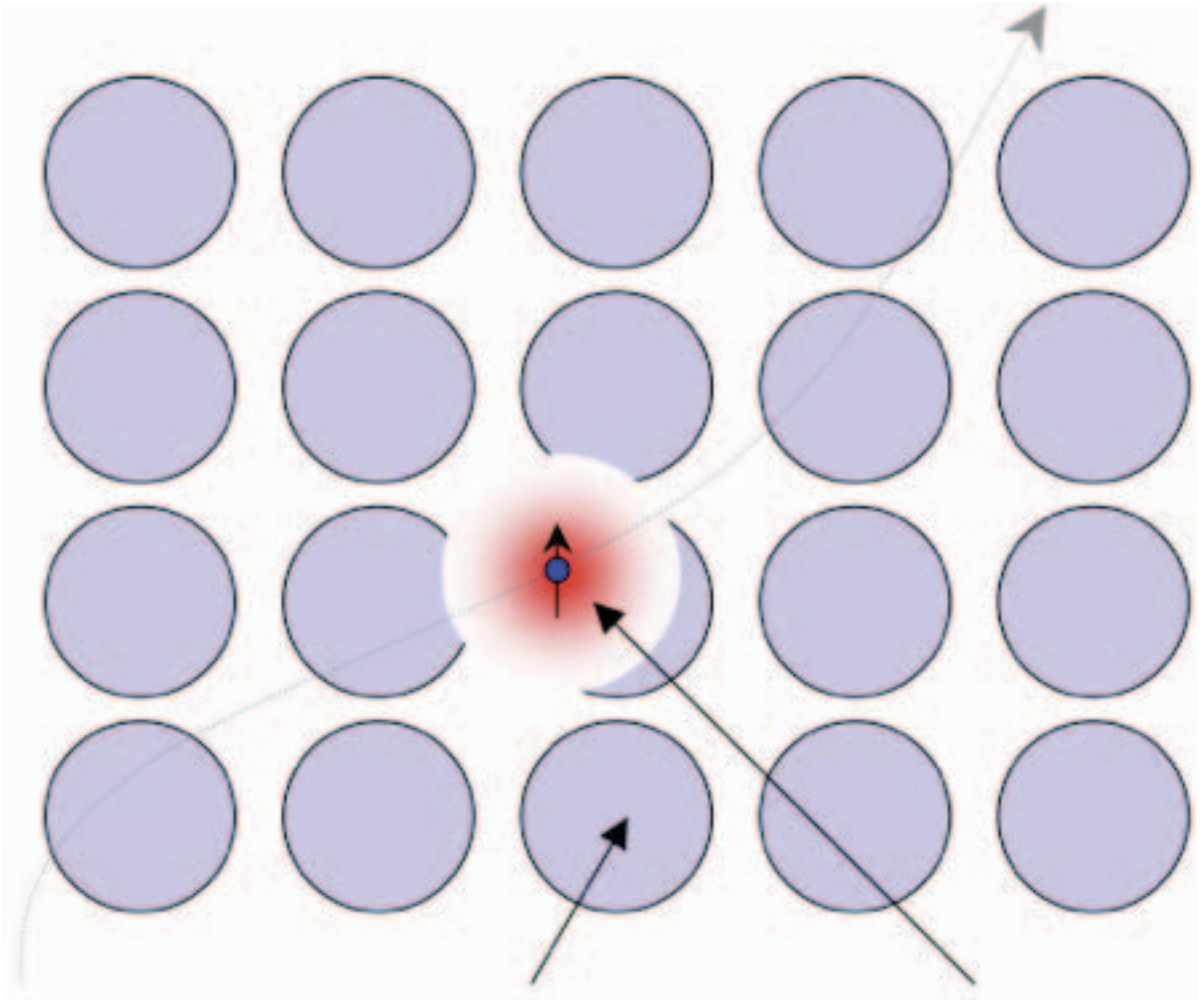
- The **self-energy operator** Σ contains all the many-body exchange and correlation effects. It is non-local, non-hermitian, and energy-dependent, the principal difficulty being to find a reasonable approximation for it.

- In general, the eigenvalues $E_{n\mathbf{k}}$ are complex. Their real part can be interpreted as a quasiparticle energy $\epsilon^{QP}_{n\mathbf{k}}$ whereas their imaginary part is related to the lifetime of the quasiparticle:

$$\text{Im } E_{n\mathbf{k}}(\omega) = 1/\tau^{QP}$$

- An intuitive picture of the quasiparticle concept consists in considering that when a "bare" particle (an electron or a hole) enters in a system of interacting electrons, it perturbs the other particles in its neighborhood and hence it gets "dressed" with a charged (positive or negative) cloud and hence becomes a quasiparticle.

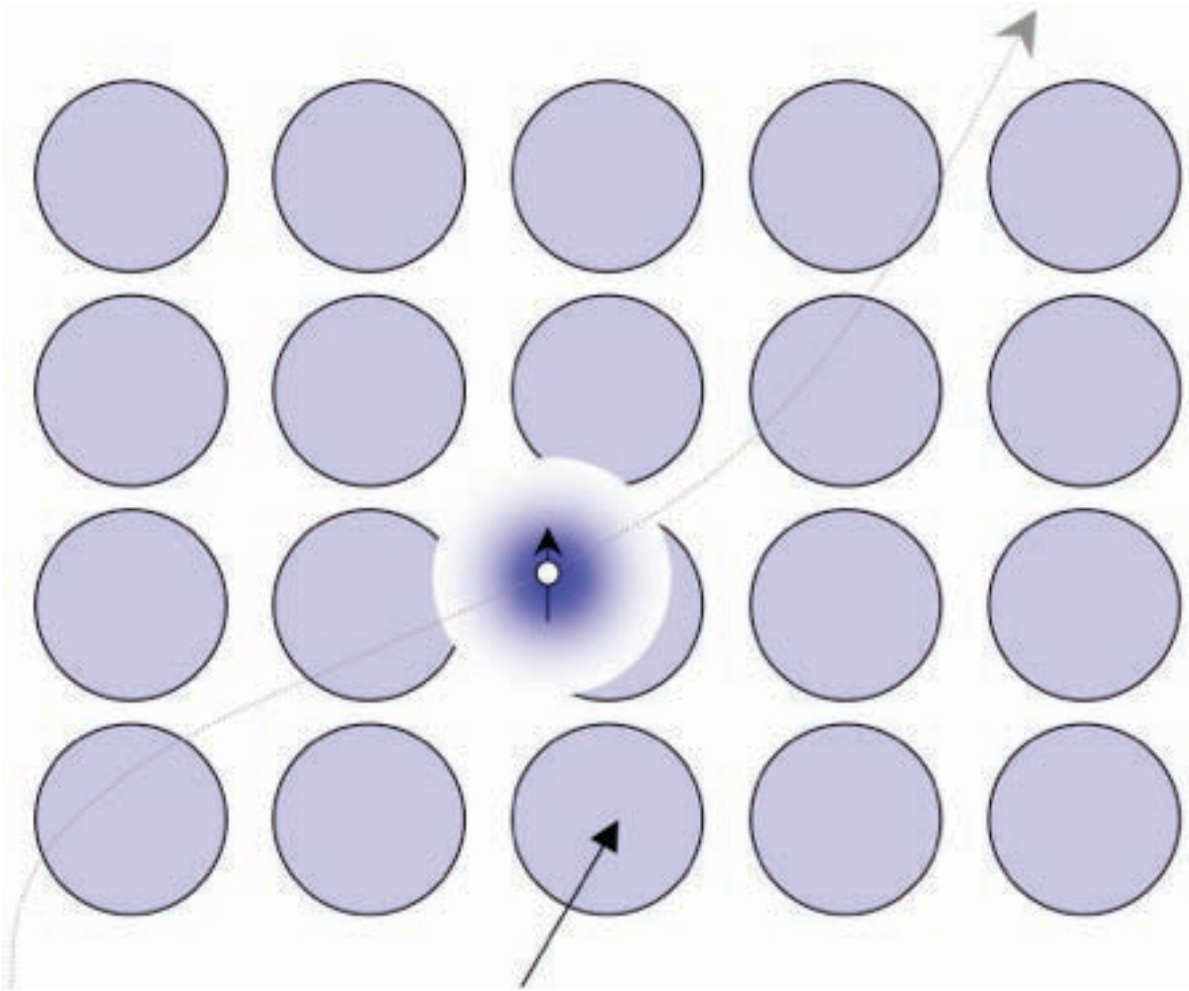
Many-Body Perturbation Theory



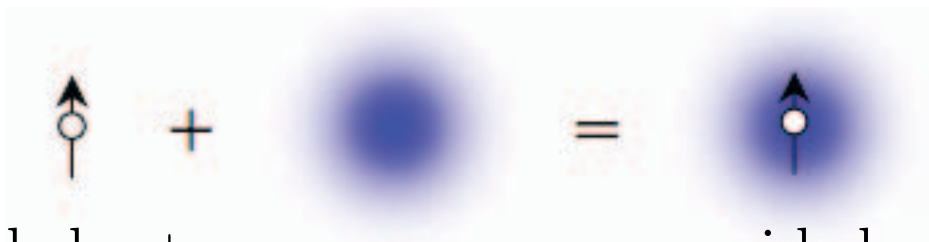
nucleus Coulomb hole

electron: $-e$ quasi-electron: $-e/\varepsilon$

Many-Body Perturbation Theory



nucleus



hole: $+e$ quasi-hole: $+e/\varepsilon$

Many-Body Perturbation Theory

- In many cases, it is possible to describe the (strongly) interacting electrons using these weakly interacting quasiparticles.

- The electronic excitations such as $N_e \rightarrow N_e + 1$ or $N_e \rightarrow N_e - 1$ correspond to quasiparticles with long lifetimes and the imaginary part can be neglected, leading to the **Dyson equation**:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\phi^{QP}_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',\omega = \epsilon^{QP}_{n\mathbf{k}})\,\phi^{QP}_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = \epsilon^{QP}_{n\mathbf{k}}\phi^{QP}_{n\mathbf{k}}(\mathbf{r})$$

- This equation is similar to the DFT Kohn-Sham one:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\phi^{KS}_{n\mathbf{k}}(\mathbf{r}) = \epsilon^{KS}_{n\mathbf{k}}\phi^{KS}_{n\mathbf{k}}(\mathbf{r})$$

Many-Body Perturbation Theory

- The similarity between the Dyson equation:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\phi^{QP}_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',\omega=\epsilon^{QP}_{n\mathbf{k}})\,\phi^{QP}_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = \epsilon^{QP}_{n\mathbf{k}}\phi^{QP}_{n\mathbf{k}}(\mathbf{r})$$

  and the DFT Kohn-Sham one:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\phi^{KS}_{n\mathbf{k}}(\mathbf{r}) + V_{xc}(\mathbf{r})\phi^{KS}_{n\mathbf{k}}(\mathbf{r}) = \epsilon^{KS}_{n\mathbf{k}}\phi^{KS}_{n\mathbf{k}}(\mathbf{r})$$

  suggests to treat the difference between Σ et V_{xc} as a perturbation with respect to the Kohn-Sham calculations.

- In fact, the approximation $\phi^{QP}_{n\mathbf{k}}(\mathbf{r}) \simeq \phi^{KS}_{n\mathbf{k}}(\mathbf{r})$ is very reasonable for many materials so that we can write:

$$\epsilon^{QP}_{n\mathbf{k}} = \epsilon^{KS}_{n\mathbf{k}} + \left\langle \phi^{KS}_{n\mathbf{k}} \middle| \Sigma(\mathbf{r},\mathbf{r}',\omega=\epsilon^{QP}_{n\mathbf{k}}) - V_{xc}(\mathbf{r}) \middle| \phi^{KS}_{n\mathbf{k}} \right\rangle$$

Many-Body Perturbation Theory

- Since the self-energy Σ operator depends on the energy:

$$\epsilon_{n\mathbf{k}}^{QP} = \epsilon_{n\mathbf{k}}^{KS} + \left\langle \phi_{n\mathbf{k}}^{KS} \middle| \Sigma(\mathbf{r}, \mathbf{r}', \omega = \epsilon_{n\mathbf{k}}^{QP}) - V_{xc}(\mathbf{r}) \middle| \phi_{n\mathbf{k}}^{KS} \right\rangle$$

  this non-linear equation should in principle be solved self-consistently. In practice, the self-energy operator Σ is linearized:

$$\left\langle \Sigma(\omega = \epsilon_{n\mathbf{k}}^{QP}) \right\rangle = \left\langle \Sigma(\omega = \epsilon_{n\mathbf{k}}^{KS}) \right\rangle + \left(\epsilon_{n\mathbf{k}}^{QP} - \epsilon_{n\mathbf{k}}^{KS} \right) \left\langle \left. \frac{\partial \Sigma(\omega)}{\partial \omega} \right|_{\omega = \epsilon_{n\mathbf{k}}^{KS}} \right\rangle$$

- Hence, defining the **renormalization constant** $Z_{n\mathbf{k}}$ as:

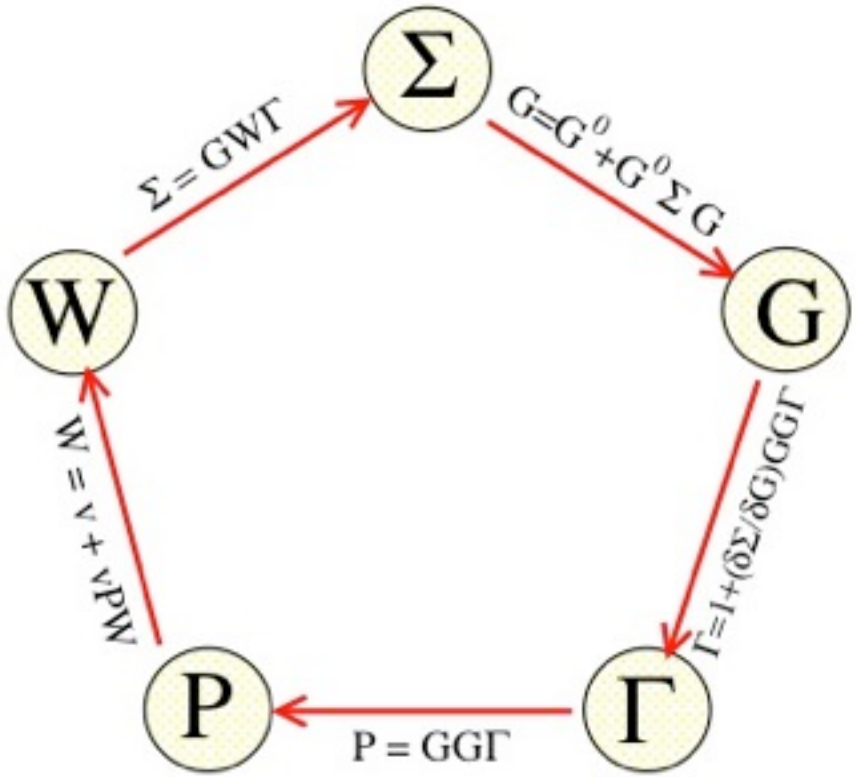
$$Z_{n\mathbf{k}} = \left(1 - \frac{\partial \left\langle \phi_{n\mathbf{k}}^{KS} \middle| \Sigma(\omega) \middle| \phi_{n\mathbf{k}}^{KS} \right\rangle}{\partial \omega} \right)^{-1}$$

  the linearized equation to solve becomes:

$$\epsilon_{n\mathbf{k}}^{QP} = \epsilon_{n\mathbf{k}}^{KS} + Z_{n\mathbf{k}} \left\langle \phi_{n\mathbf{k}}^{KS} \middle| \Sigma(\mathbf{r}, \mathbf{r}', \omega = \epsilon_{n\mathbf{k}}^{KS}) - V_{xc}(\mathbf{r}) \middle| \phi_{n\mathbf{k}}^{KS} \right\rangle$$

GW and $GW\Gamma$ approximations

- Hedin devised a systematic way to calculate the self-energy Σ operator using Green's functions theory. The scheme consists of five coupled integral equations, the so-called **Hedin's equations**, based on the single particle Green function G, the screened Coulomb interaction W, the polarizability P, and the vertex function Γ .



GW and *GWΓ* approximations

- In order to solve the Hedin's equations, one possible strategy could be to start from the top of the pentagon, with Σ=0.

- The **independent-particle Green function** G^0 is given by:

$$G^0(\mathbf{r},\mathbf{r}',\omega) = \sum_{n\mathbf{k}} \frac{\phi^{DFT}_{n\mathbf{k}}(\mathbf{r}) \left[\phi^{DFT}_{n\mathbf{k}}(\mathbf{r})\right]^*}{\omega - \epsilon^{DFT}_{n\mathbf{k}} + i\delta\,\mathrm{sgn}(\epsilon^{DFT}_{n\mathbf{k}} - \mu)}$$

  where μ is chemical potential and δ a positive infinitesimal.

- The **vertex function** Γ, which describes the propagation of an interacting electron-hole pair through the system, is simply Γ=δ. In other words, all the orders beyond the 0th are neglected in the perturbative expansion of Γ.

GW and *GWT* approximations

- The polarizability is given by the **independent-particle** or **Random Phase Approximation** (RPA) **polarizability**:

$$P^0(\mathbf{r},\mathbf{r}',\omega) = \frac{-i}{2\pi}\int G^0(\mathbf{r},\mathbf{r}',\omega-\omega')G^0(\mathbf{r}',\mathbf{r},\omega)e^{-i\delta\omega'}d\omega'$$

$$\varepsilon(\mathbf{r},\mathbf{r}',\omega) = \delta(\mathbf{r},\mathbf{r}') - \int \frac{P^0(\mathbf{r},\mathbf{r}'',\omega)}{|\mathbf{r}''-\mathbf{r}'|d\mathbf{r}''}$$

- The **screened Coulomb interaction** W, which takes into account the screening hole around electrons that weakens their interaction, is:

$$W^0(\mathbf{r},\mathbf{r}',\omega) = \int \frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$

GW and $GW\Gamma$ approximations

- Finally, the self-energy is given by:

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int G^0(\mathbf{r}, \mathbf{r}', \omega - \omega') W^0(\mathbf{r}, \mathbf{r}', \omega) e^{-i\delta\omega'} d\omega'$$

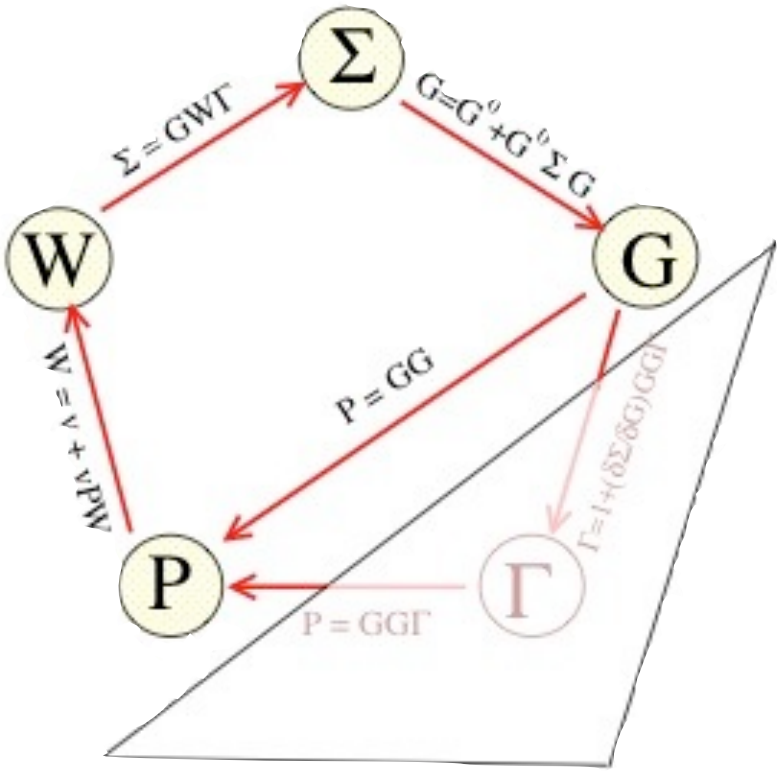
- In principle, this process should be iterated until full self-consistent resolution of Hedin's equations is reached.

- In practice, this is very cumbersome...

- Often, real calculations stop after one round.
  This is the **non-self-consistent GW approximation** or **G^0W^0 approximation**.

GW and GWT approximations

- Alternatively, the self-consistency can obtained within a reduced set of equations short-cutting the vertex function, leading to the **GW approximation**:



- The assumption that:

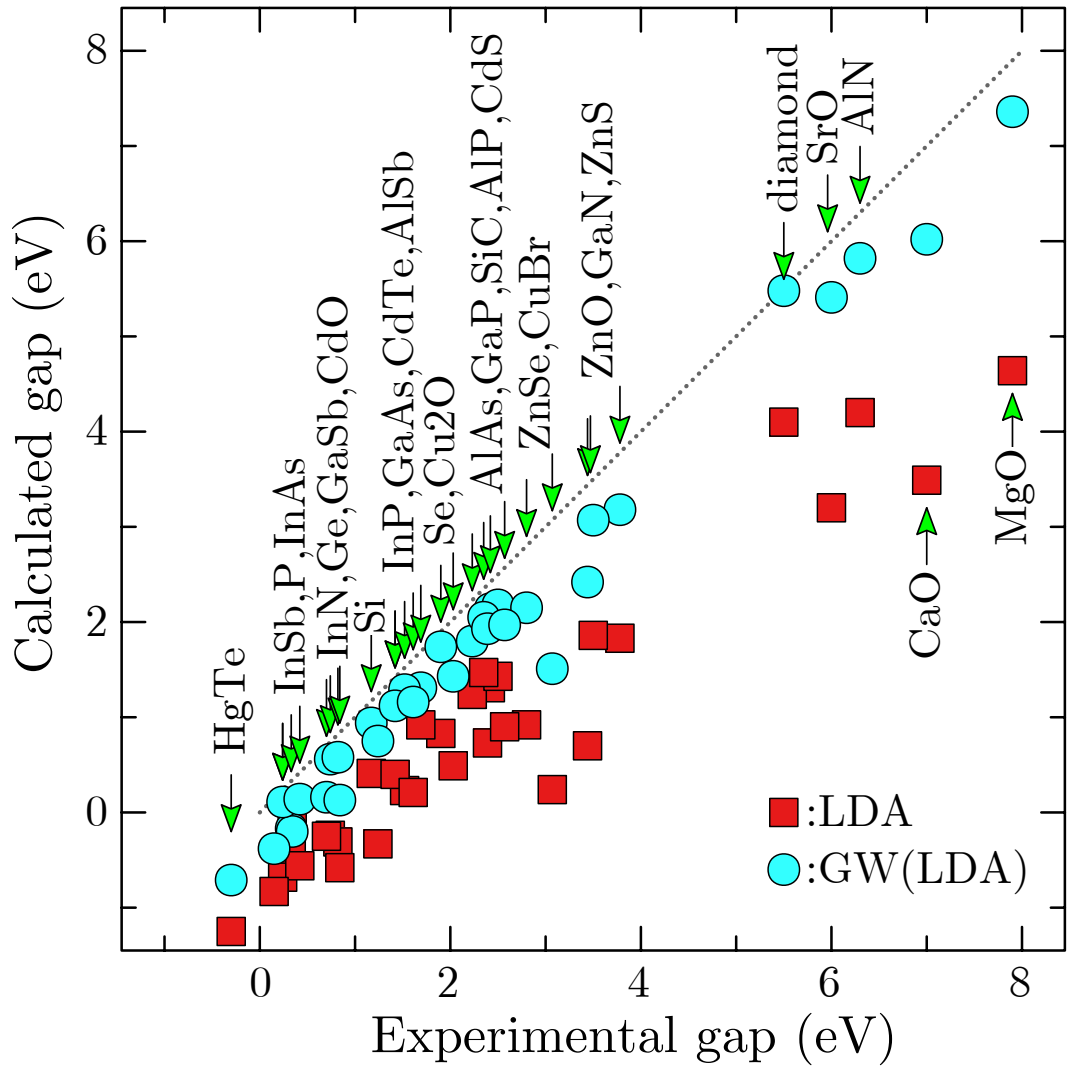
$$\phi_{n\mathbf{k}}^{QP}(\mathbf{r}) \simeq \phi_{n\mathbf{k}}^{DFT}(\mathbf{r})$$

still holds so that the self-consistency only consists in updating the eigenvalues.

- This approximation may, in principle, be improved using an approximate **vertex correction Γ**. For instance, Γ can been estimated using DFT.

The band gap within *GW*

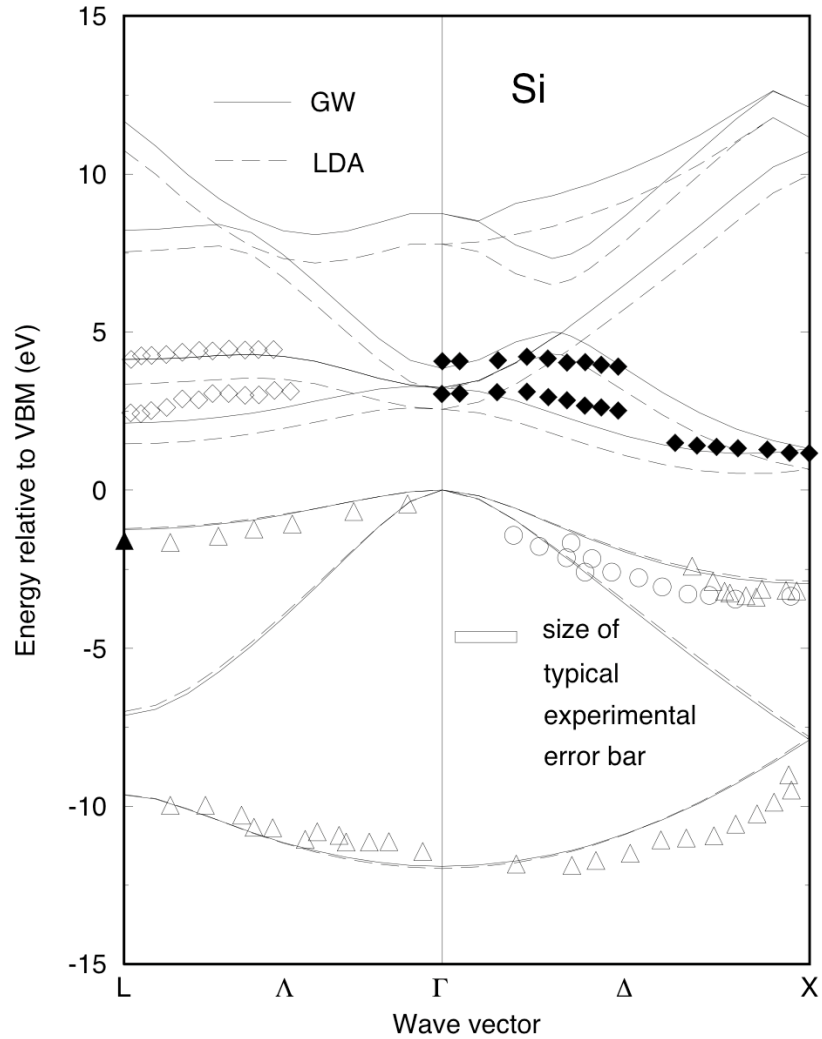
- The agreement with experiments is in much better!



[adapted from van Schilfgaarde *et al.*, PRL **96**, 226402 (2006)]

The band gap within *GW*

- The calculated band structures are in excellent agreement with those measured experimentally.



[from Aulbur *et al.*, Solid State Physics **54**, 1 (2000)]

Self-consitency in the GW approximation

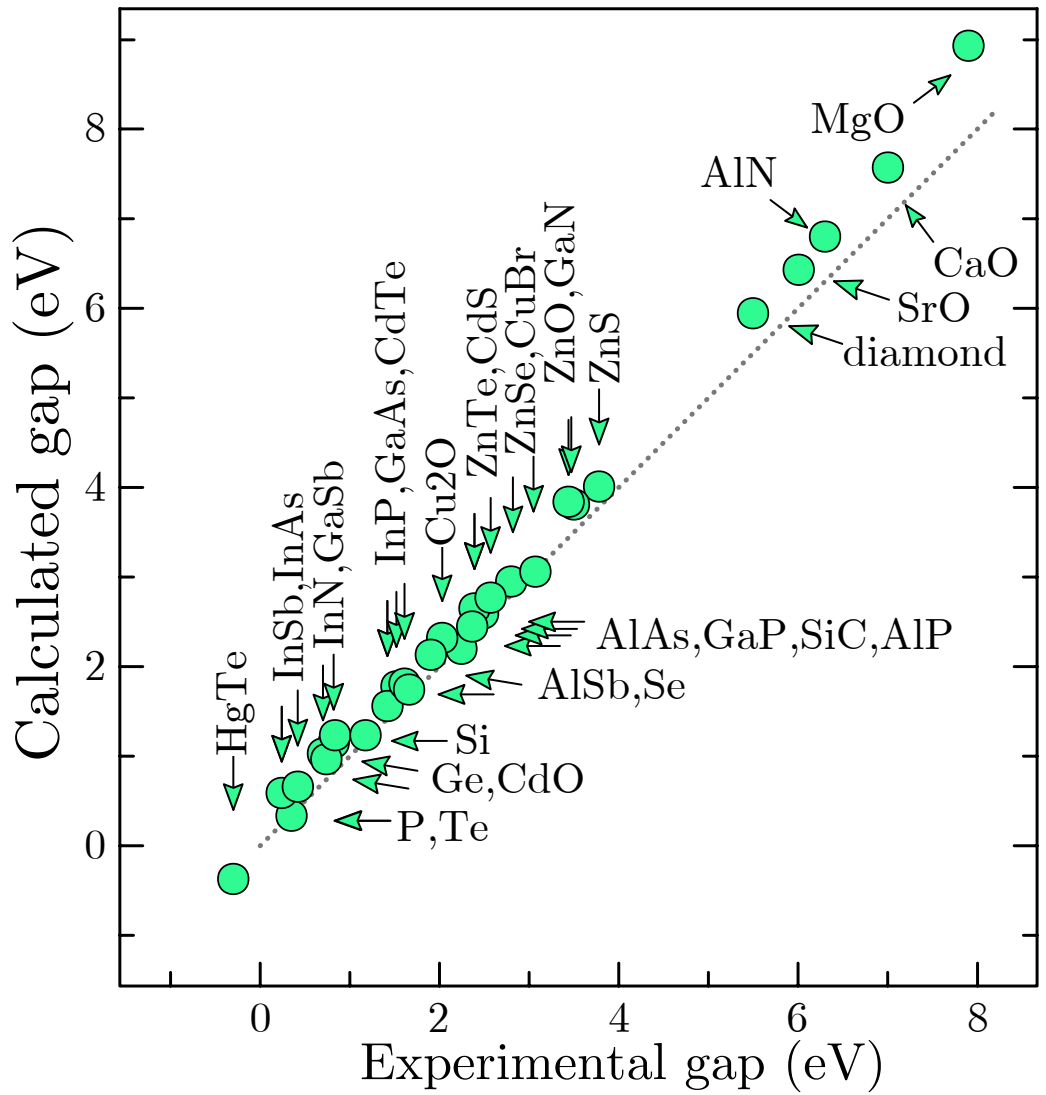
- It may happen that the DFT wavefunctions are not adequate, these need to be updated as well in the self-consistent cycle by diagonalizing the self-energy operator. The problem is that the self-energy operator is not hermitian and energy dependent.
- A smart method has thus been devised, the **Quasiparticle Self-consistent GW (QSGW)**, which allows to overcome these problems [S. V. Faleev, M. van Schilfgaarde, and T. Kotani, Phys. Rev. Lett. **93**, 126406 (2004)]:

$$\langle \phi_i | \Sigma | \phi_j \rangle = \frac{1}{2} \Re \left[\langle \phi_i | \Sigma(\epsilon_i) | \phi_j \rangle + \langle \phi_i | \Sigma(\epsilon_j) | \phi_j \rangle \right]$$

where $\Re$ means that one only retains the hermitian part of the matrix. Along with self-consistency, the diagonal elements of the self-energy are better and better approximations to the true GW diagonal terms, as each of them is finally evaluated for the correct GW energy.

Self-consitency in the GW approximation

- The QSGW band gap is slightly bigger than the experimental one.



[adapted from van Schilfgaarde et al., PRL **96**, 226402 (2006)]

Self-consitency in the *GW* approximation

PRL **99,** 246403 (2007) PHYSICAL REVIEW LETTERS week ending 14 DECEMBER 2007

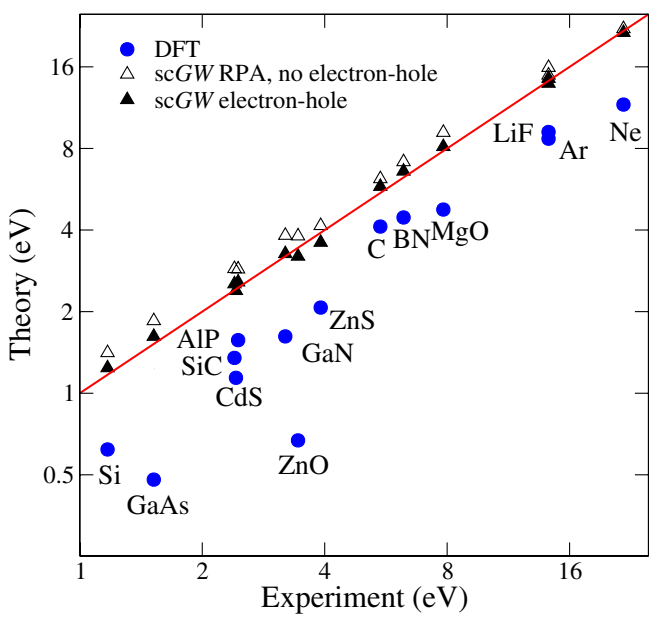
Accurate Quasiparticle Spectra from Self-Consistent *GW* Calculations with Vertex Corrections

M. Shishkin, M. Marsman, and G. Kresse

Faculty of Physics, Universität Wien and Center for Computational Materials Science, Sensengasse 8/12, A-1090 Wien, Austria

(Received 21 June 2007; published 12 December 2007)

Self-consistent calculations, maintaining only the quasiparticle part of the Green's function , are reported for a wide class of materials, including small gap semiconductors and large gap insulators. We show that the inclusion of the attractive electron-hole interaction via an effective nonlocal exchange correlation kernel is required to obtain accurate band gaps in the framework of self-consistent calculations. If these are accounted for via vertex corrections in , the band gaps are found to be within a few percent of the experimental values.



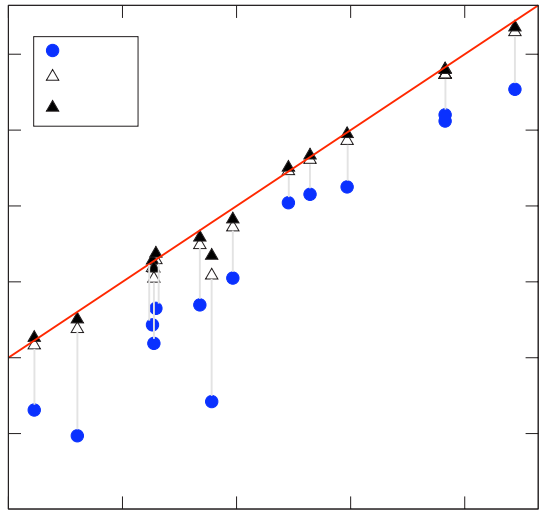
The static screening properties calculated from gradient corrected functionals in the random phase approximation agree very well with the self-consistently determined screening properties in the method. This offers a convenient shortcut and legitimates the often applied approximation.

Self-consitency in the GW approximation

Self-consistent GW calculations for semiconductors and insulators

M. Shishkin* and G. Kresse
Institut für Materialphysik and Centre for Computational Materials Science, Universität Wien, A 1090 Wien, Austria
(Received 22 November 2006; revised manuscript received 5 April 2007; published 4 June 2007)

We present GW calculations for small and large gap systems comprising typical semiconductors (Si, SiC, GaAs, GaN, ZnO, ZnS, CdS, and AlP), small gap semiconductors (PbS, PbSe, and PbTe), insulators (C, BN, MgO, and LiF), and noble gas solids (Ar and Ne). It is shown that the G_0W_0 approximation always yields too small band gaps. To improve agreement with experiment, the eigenvalues in the Green's function G (GW_0) and in the Green's function and the dielectric matrix (GW) are updated until self-consistency is reached. The first approximation leads to excellent agreement with experiment, whereas an update of the eigenvalues in G and W gives too large band gaps for virtually all materials. From a pragmatic point of view, the GW_0 approximation thus seems to be an accurate and still reasonably fast method for predicting quasiparticle energies in simple sp-bonded systems. We furthermore observe that the band gaps in materials with shallow d states (GaAs, GaN, and ZnO) are systematically underestimated. We propose that an inaccurate description of the static dielectric properties of these materials is responsible for the underestimation of the band gaps in GW_0, which is itself a result of the incomplete cancellation of the Hartree self-energy within the d shell by local or gradient corrected density functionals.



) (

Summary

- The interaction between matter and radiation creates electronic excitations which determine many properties of materials.
- The theoretical prediction of these excitations is quite complicated: it is a many-body problem.
- DFT maps the many-body problem onto a system of non-interacting fictitious particles. The KS eigenvalues compare rather well with experiment with the notable exception of the band-gap which is typically 30-50% smaller than in experiments.
- Within MBPT, the response of strongly interacting particles is described in terms of weakly interacting quasiparticles. The resulting band gaps compare much better with experiment.