Many-Body Perturbation Theory

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Outline

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What are we heading for?

Reminder: One oscillator in medium

The problem:

$$\frac{d^2x}{dt^2} + 2\gamma\frac{dx}{dt} + \omega_0^2 x = F(t).$$

Fourier Transform of Green's function equation:

$$\left[-\omega^2 - 2i\gamma\omega + \omega_0^2\right] G(\omega) = 1$$

Poles at $\omega = -i\gamma \pm \sqrt{-\gamma^2 + \omega_0^2}$. Spectral function:

$$A(\omega) = -\frac{1}{2\pi i}\left[G^*(\omega) - G(\omega)\right] = \frac{1}{\pi}\frac{\Gamma(\omega)}{(\omega^2 - \omega_0^2)^2 + \Gamma^2(\omega)}$$

with $\Gamma(\omega) = 2\gamma\omega$.

What are we heading for?

Self-energy and Dyson equation

Unperturbed oscillator:

$$\left[-\omega^2 + \omega_0^2\right] G_0(\omega) = 1$$

...in medium:

$$\left[-\omega^2 - 2i\gamma\omega + \omega_0^2\right] G(\omega) = 1$$

$$G^{-1}(\omega) = G_0^{-1}(\omega) - 2i\gamma\omega$$

Dyson equation:

$$G(\omega) = G_0(\omega) + G_0(\omega)\Sigma(\omega)G(\omega)$$

with $\Sigma(\omega) = 2i\omega\gamma$: "Self-energy".

The one-particle Green's function

In principle we know G .....

Definition and meaning of G (at 0 K, ground state):

$$G(\mathbf{x},t;\mathbf{x}',t') = -i < \Psi_0 | T\left[\psi(\mathbf{x},t)\psi^\dagger(\mathbf{x}',t')\right] |\Psi_0 >$$

Insert a complete set of $N+1$ or $N-1$-particle states. This yields

$$\begin{aligned} G(\mathbf{x},t;\mathbf{x}',t') &= -i\sum_j f_j(\mathbf{x}) f_j^*(\mathbf{x}') e^{-i\varepsilon_j(t-t')} \times \\ &\times \left[\Theta(t-t')\Theta(\varepsilon_j-\mu) - \Theta(t'-t)\Theta(\mu-\varepsilon_j)\right]; \end{aligned}$$

$\varepsilon_j = E(N+1,j) - E(N,0)$ or $E(N,0) - E(N-1,j)$ for $\varepsilon_j > \mu (< \mu)$, and

$$f_j(\mathbf{x}) = \begin{cases} \langle N,0 | \psi(\mathbf{x}) | N+1,j \rangle, & \varepsilon_j > \mu \\ \langle N-1,j | \psi(\mathbf{x}) | N,0 \rangle, & \varepsilon_j < \mu \end{cases}$$

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How to get G?

Straightforward?

$$G(\mathbf{x}, t; \mathbf{x}', t') = -i < \Psi_0 | T \left[\psi(\mathbf{x}, t) \psi^\dagger(\mathbf{x}', t') \right] | \Psi_0 >$$

$$|\Psi_0 > = ???$$

Interacting ground state!

Perturbation Theory?

Time-independent perturbation theories: messy. .Textbooks: adiabatically switched on interaction, Gell-Mann-Low theorem, Wick's theorem, expansion (diagrams). Lots of diagrams.....

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How to get G?

Learn from oscillator?

Green's function

$$\frac{d^2 G_0(t-t_0)}{dt^2} + \omega_0^2 G_0(t-t_0) = \delta(t-t_0)$$

Equation of motion

Equation of Motion

$$G(\mathbf{x},t;\mathbf{x}',t') = -i < \Psi_0 | T\left[\psi(\mathbf{x},t)\psi^\dagger(\mathbf{x}',t')\right] | \Psi_0 >$$

$$(\partial/\partial t)G = ???$$

$$(\partial/\partial t)\psi(\mathbf{x},t) = i[\hat{H}, \psi(\mathbf{x},t)]$$

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Functional approach to the MB problem

To determine the 1-particle Green's function

$$[\omega - h_0]G(\omega) + i\int vG_2(\omega) = 1$$

where $h_0 = -\frac{1}{2}\nabla^2 + v_{ext}$ is the independent particle Hamiltonian.
The 2-particle Green's function describes the motion of 2 particles.
Unfortunately, hierarchy of equations

$$\begin{array}{ccc} G_1(1,2) & \leftarrow & G_2(1,2;3,4) \\ G_2(1,2;3,4) & \leftarrow & G_3(1,2,3;4,5,6) \\ \vdots & \vdots & \vdots \end{array}$$

Self-energy

Perturbation theory starts from what is known to evaluate what is not known, hoping that the difference is small...
Let's say we know $G_0(\omega)$ that corresponds to the Hamiltonian h_0
Everything that is unknown is put in

$$\Sigma(\omega) = G_0^{-1}(\omega) - G^{-1}(\omega)$$

This is the definition of the self-energy
Thus,

$$[\omega - h_0]G(\omega) - \int \Sigma(\omega)G(\omega) = 1$$

to be compared with

$$[\omega - h_0]G(\omega) + i \int vG_2(\omega) = 1$$

Functional derivation of the MB problem

Trick due to Schwinger (1951):
introduce a small external potential $U(3)$, that will be made equal to zero at the end, and calculate the variations of G_1 with respect to U

$$\frac{\delta G_1(1,2)}{\delta U(3)} = -G_2(1,3;2,3) + G_1(1,2)G_1(3,3).$$

$$\begin{aligned} i\int d3v(1,3)G_2(1,3;2,3) &= -i\int d3v(1,3)G_1(3,3)G_1(1,2) \\ &\quad +i\int d3v(1,3)\frac{\delta G_1(1,2)}{\delta U(3)} \end{aligned}$$

$$\begin{aligned} i\int d3v(1,3)G_2(1,3;2,3) &= \int d3v(1,3)\rho(3)G_1(1,2) \\ &\quad +i\int d3\Sigma(1,3)G_1(3,2) \end{aligned}$$

Functional definition of the self-energy

Self-energy

$$\Sigma(1,2) = -i \int d3d4v(1^+,3)G(1,4)\frac{\delta G^{-1}(4,2)}{\delta U(3)}$$

Vertex function

$$\Gamma(1,2;3) = -\frac{\delta G^{-1}(1,2)}{\delta U(3)}$$

Dyson equation

$$G^{-1}(1,2) = G_0^{-1}(1,2) - U(1)\delta(1,2) - V_H(1)\delta(1,2) - \Sigma(1,2)$$

Vertex equation

$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \int d4d5d6d7 \left[-iv(1,4)\delta(1,2)\delta(4,5) + \frac{\delta\Sigma(1,2)}{\delta G(4,5)}\right] G(4,6)G(7,5)\Gamma(6,7;3)$$

Functional definition of the self-energy

Exact equations

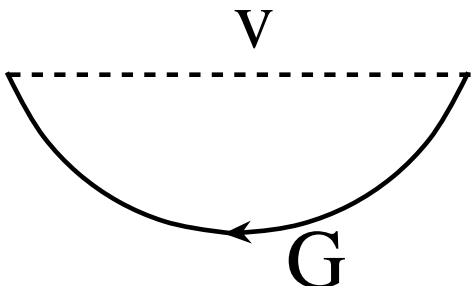
$$G^{-1} = G_0^{-1} - \Sigma$$

$$\Sigma = iGv\Gamma$$

$$\Gamma = 1 + \left[-iv + \frac{\delta\Sigma}{\delta G}\right] GG\Gamma$$

$$\Gamma^{(0)} = 1$$

$$\Sigma^{(1)} = iGv = \Sigma_x$$



$\longrightarrow$ **Hartree Fock** approximation

Hartree Fock

Hartree Fock is better than nothing!

2 masses, 1 spring: coordinate transformation $\Longrightarrow$ independent modes

We are looking for quite good quasiparticles.

Is the HF particle a good quasiparticle?

Was the Kohn-Sham one a good one?

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Wavefunctions methods

Hartree-Fock method: variationally best Slater determinant

$$\Phi_{N,0}(\mathbf{r}_1, ..., \mathbf{r}_N) \propto \begin{vmatrix} \phi_1(\mathbf{r}_1) & \dots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_2) \\ \vdots & & \vdots \\ \phi_1(\mathbf{r}_N) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

made of N one-particle wavefunctions ϕ_i.

$$\mathcal{L} = \langle \Phi | \mathcal{H} | \Phi \rangle - \sum_i \epsilon_i^{\mathrm{HF}} \int d\mathbf{r} |\phi_i(\mathbf{r})|^2$$

$$\Rightarrow h^{\mathrm{HF}} \phi_i = \epsilon_i^{\mathrm{HF}} \phi_i$$

ϵ_i^{HF} obtained as N Lagrange multipliers

Hartree-Fock method

Valence Photoemission:

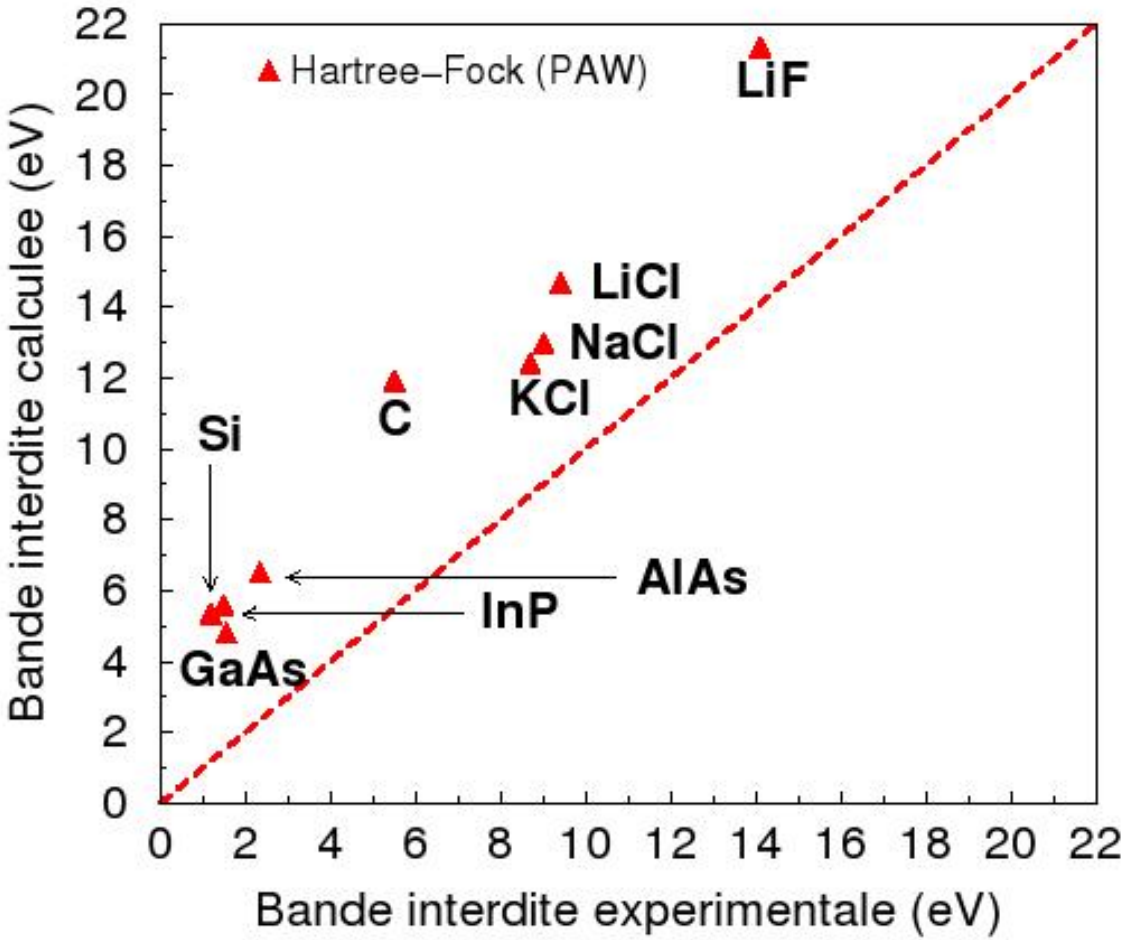
$$|N-1,i\rangle \propto \begin{vmatrix} \phi_1(\mathbf{r}_1) & \dots & \phi_{i-1}(\mathbf{r}_1) & \phi_{i+1}(\mathbf{r}_1) & \dots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \dots & \phi_{i-1}(\mathbf{r}_2) & \phi_{i+1}(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_2) \\ \vdots & & \vdots & & & \\ \phi_1(\mathbf{r}_{N-1}) & \dots & \phi_{i-1}(\mathbf{r}_{N-1}) & \phi_{i+1}(\mathbf{r}_{N-1}) & \dots & \phi_N(\mathbf{r}_{N-1}) \end{vmatrix}$$

Koopmans theorem:

$$\epsilon_i = \langle N,0|\mathcal{H}|N,0\rangle - \langle N-1,i|\mathcal{H}|N-1,i\rangle$$

The ϵ_i do have a physical meaning.

....but gaps in solids are usualy severely overestimated:
Si: measured 3.4 eV, Hartree-Fock 8 eV
VO_2: measured 0.6 eV, Hartree-Fock $>$ 5 eV
table taken from Brice Arnaud:



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Approximation: **No relaxation** of the other orbitals

Hartree-Fock method

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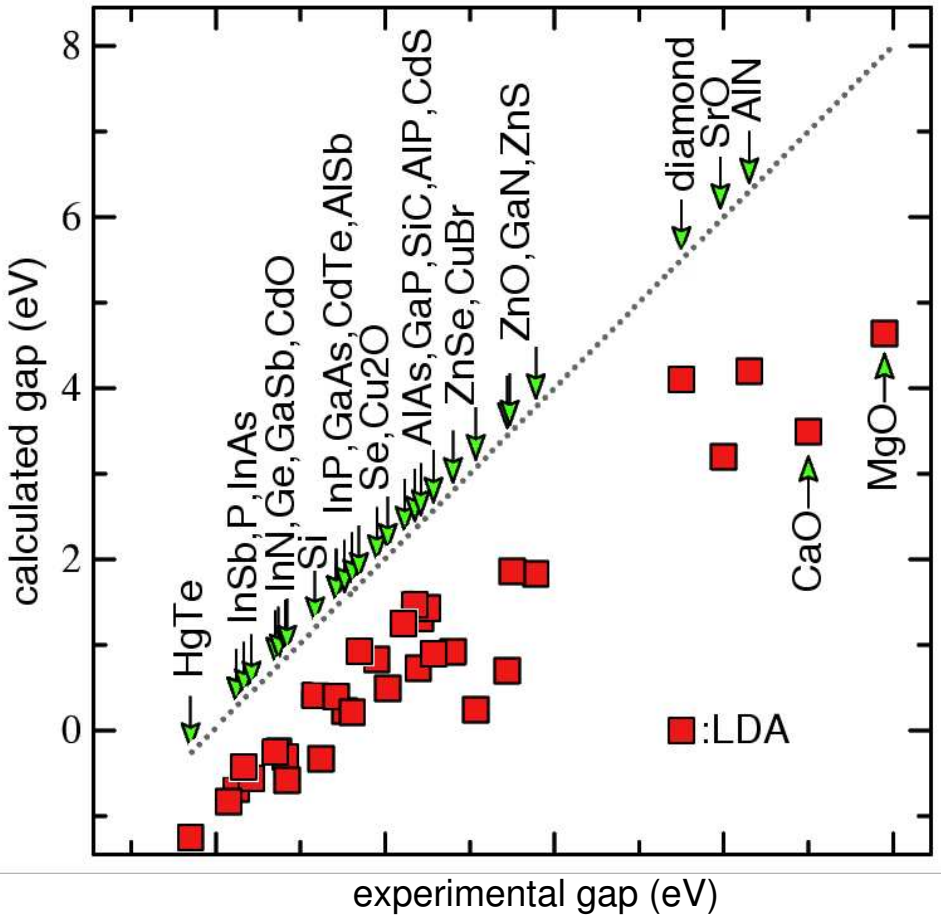
Approximation: **No relaxation** of the other orbitals

Kohn-Sham

Band gaps of semiconductors and insulators



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

$\longrightarrow$ underestimated

Density Functional Theory

DFT well assessed for the structure of solids

BUT

$$\mathcal{L} = \langle \Phi | \mathcal{H}^{\mathrm{KS}} | \Phi \rangle - \sum_i \epsilon_i^{\mathrm{KS}} \int d\mathbf{r} |\phi_i^{\mathrm{KS}}(\mathbf{r})|^2$$

$$\Rightarrow h^{\mathrm{KS}}(\mathbf{r})\phi_i^{\mathrm{KS}}(\mathbf{r}) = \epsilon_i^{\mathrm{KS}}\phi_i^{\mathrm{KS}}(\mathbf{r})$$

ϵ_i^{KS} obtained as N Lagrange multipliers

Kohn-Sham energies **cannot** be interpreted as removal/addition energies:

Koopman's theorem doesn't hold, not so clear how to fix that!

Beyond Hartree-Fock?

Exact equations

$$G^{-1} = G_0^{-1} - \Sigma$$

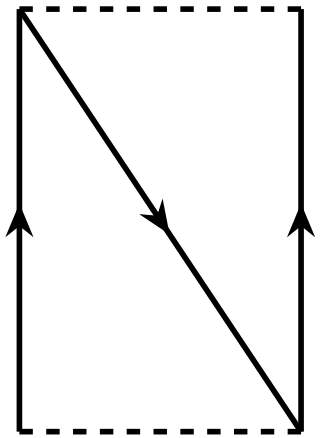
$$\Sigma = iGv\Gamma$$

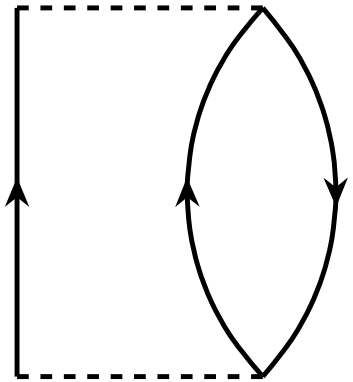
$$\Gamma = 1 + \left[-iv + \frac{\delta\Sigma}{\delta G}\right] GG\Gamma$$

$$\Sigma^{(1)} = iGv$$

$$\Gamma^{(1)} = 1 + ivGGv + ivGvG$$

$$\Sigma^{(2)} = \Sigma_x - GvGGv - GvGvG$$





$\longrightarrow$ 2nd order in v **[cf. MP2]**

Outline

What to do when screening is important?

In a solid, screening can be very important and an order-by-order treatment inadequate.

New fundamental quantity: the screened interaction

GW origins

PHYSICAL REVIEW VOLUME 139, NUMBER 3A 2 AUGUST 1965

New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem*

LARS HEDIN†
Argonne National Laboratory, Argonne, Illinois
(Received 8 October 1964; revised manuscript received 2 April 1965)

A set of successively more accurate self-consistent equations for the one-electron Green's function have been derived. They correspond to an expansion in a screened potential rather than the bare Coulomb potential. The first equation is adequate for many purposes. Each equation follows from the demand that a corresponding expression for the total energy be stationary with respect to variations in the Green's function. The main information to be obtained, besides the total energy, is one-particle-like excitation spectra, i.e., spectra characterized by the quantum numbers of a single particle. This includes the low-excitation spectra in metals as well as configurations in atoms, molecules, and solids with one electron outside or one electron missing from a closed-shell structure. In the latter cases we obtain an approximate description by a modified Hartree-Fock equation involving a "Coulomb hole" and a static screened potential in the exchange term. As an example, spectra of some atoms are discussed. To investigate the convergence of successive approximations for the Green's function, extensive calculations have been made for the electron gas at a range of metallic densities. The results are expressed in terms of quasiparticle energies $E(\mathbf{k})$ and quasiparticle interactions $f(\mathbf{k},\mathbf{k}')$. The very first approximation gives a good value for the magnitude of $E(\mathbf{k})$. To estimate the derivative of $E(\mathbf{k})$ we need both the first- and the second-order terms. The derivative, and thus the specific heat, is found to differ from the free-particle value by only a few percent. Our correction to the specific heat keeps the same sign down to the lowest alkali-metal densities, and is smaller than those obtained recently by Silverstein and by Rice. Our results for the paramagnetic susceptibility are unreliable in the alkali-metal-density region owing to poor convergence of the expansion for f. Besides the proof of a modified Luttinger-Ward-Klein variational principle and a related self-consistency idea, there is not much new in principle in this paper. The emphasis is on the development of a numerically manageable approximation scheme.

Functional definition of the self-energy

Self-energy

$$\Sigma(1,2) = -i \int d3d4v(1^+,3)G(1,4)\frac{\delta G^{-1}(4,2)}{\delta U(3)}$$

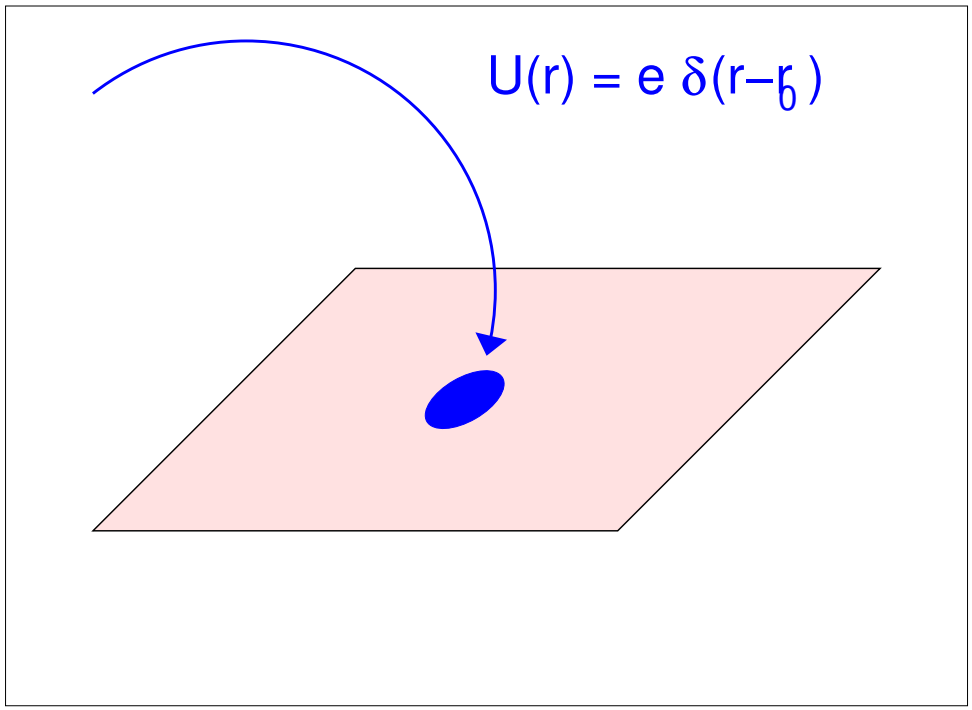
Vertex function

$$\Gamma(1,2;3) = -\frac{\delta G^{-1}(1,2)}{\delta U(3)}$$

Need for screening

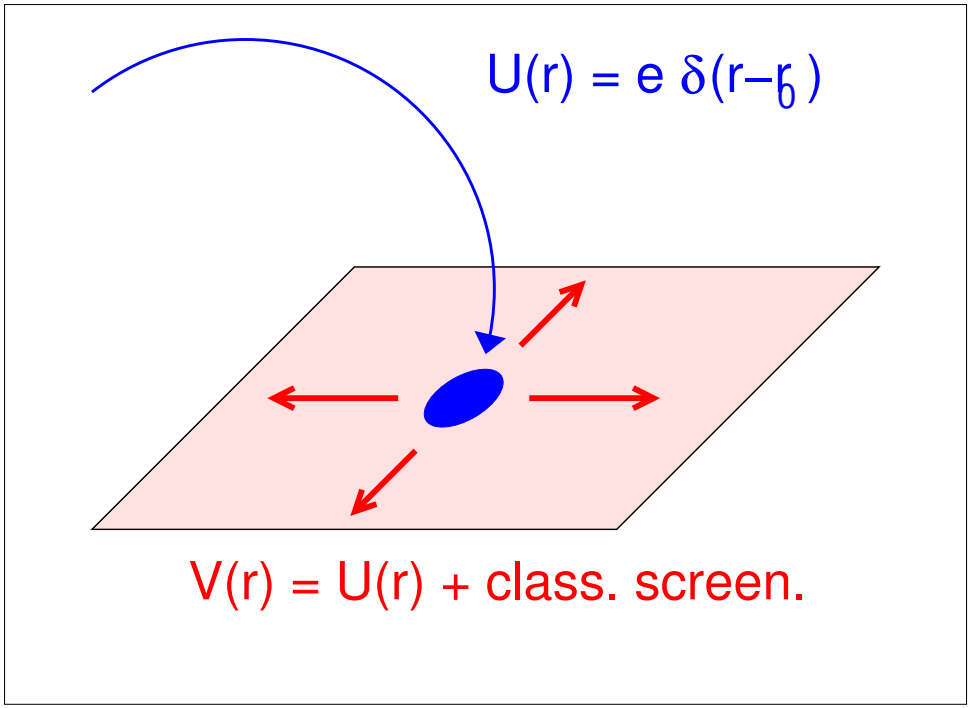
$$A[U]$$

variations of some operator with respect to a local bare perturbation: $\frac{\delta A}{\delta U}$



Need for screening

Purely classical interaction



$$V(1) = U(1) + \int d2v(1,2)\rho(2)$$

the variations of the charge density $\delta\rho$ tends to oppose to the perturbation.

Need for screening

better to work with $\frac{\delta A}{\delta V}$ than with $\frac{\delta A}{\delta U}$

$$\begin{aligned} \Gamma &= -\frac{\delta G^{-1}}{\delta U} \\ &= -\frac{\delta G^{-1}}{\delta V}\frac{\delta V}{\delta U} \\ &= -\frac{\delta G^{-1}}{\delta V}\varepsilon^{-1} \end{aligned}$$

where ε is the dielectric function of the medium.

Towards Hedin's equations

$$\Sigma = iGv\varepsilon^{-1}\tilde{\Gamma}$$

irreducible vertex

$$\begin{aligned}\tilde{\Gamma} &= -\frac{\delta G^{-1}}{\delta V} \\ &= 1 + \frac{\delta \Sigma}{\delta G} GG\tilde{\Gamma}\end{aligned}$$

screened Coulomb interaction

$$W = \epsilon^{-1} v$$

dielectric function

$$\epsilon = 1 - v\tilde{\chi}$$

irreducible polarizability

$$\tilde{\chi} = \frac{\delta \rho}{\delta V} = -iGG\tilde{\Gamma}$$

Hedin's equations

$$
\begin{aligned}
\Sigma &= iGW\tilde{\Gamma} \\
\tilde{\Gamma} &= 1 + \frac{\delta\Sigma}{\delta G} GG\tilde{\Gamma} \\
W &= \epsilon^{-1} v \\
\epsilon &= 1 - v\tilde{\chi} \\
\tilde{\chi} &= -iGG\tilde{\Gamma}
\end{aligned}
$$

Hedin's wheel