

**Summary Secs. 2.1-2.3:
Structure factors and such things ...**

2.1 The interaction operator - revisited

Starting point:

The two-particle interaction operator \hat{V} in the **occupation number representation**

("second quantization"):

$$\hat{V}^{II} = \frac{1}{2} \sum_{\alpha\beta} \int \int d^3r d^3r' V(\mathbf{r} - \mathbf{r}') \hat{\psi}_\alpha^\dagger(\mathbf{r}) \hat{\psi}_\beta^\dagger(\mathbf{r}') \hat{\psi}_\beta(\mathbf{r}') \hat{\psi}_\alpha(\mathbf{r}). \quad (1)$$

The **electron density operator** in the first and second quantization:

$$\hat{\rho}^I(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i), \quad (2)$$

$$\hat{\rho}^{II}(\mathbf{r}) = \sum_{\alpha} \int d^3r' \hat{\psi}_\alpha^\dagger(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \hat{\psi}_\alpha(\mathbf{r}') = \sum_{\alpha} \hat{\psi}_\alpha^\dagger(\mathbf{r}) \hat{\psi}_\alpha(\mathbf{r}). \quad (3)$$

With

$$\sum_{\alpha\beta} \hat{\psi}_\alpha^\dagger(\mathbf{r}) \hat{\psi}_\beta^\dagger(\mathbf{r}') \hat{\psi}_\beta(\mathbf{r}') \hat{\psi}_\alpha(\mathbf{r}) = \sum_{\alpha\beta} \hat{\psi}_\alpha^\dagger(\mathbf{r}) \hat{\psi}_\alpha(\mathbf{r}) \hat{\psi}_\beta^\dagger(\mathbf{r}') \hat{\psi}_\beta(\mathbf{r}') - \sum_{\alpha} \hat{\psi}_\alpha^\dagger(\mathbf{r}) \hat{\psi}_\alpha(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')$$

one gets

$$\hat{V}^{II} = \frac{1}{2} \int d^3r d^3r' V(\mathbf{r} - \mathbf{r}') [\hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}') \hat{\rho}(\mathbf{r})].$$

The contribution of the **potential energy** to the ground state energy of the multi-electron system,

$$E_{pot} = \langle \Psi_0 | \hat{V} | \Psi_0 \rangle,$$

reads as

$$E_{pot} = \frac{1}{2} \int \int d^3r d^3r' V(\mathbf{r} - \mathbf{r}') [\langle \Psi_0 | \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle - \delta(\mathbf{r} - \mathbf{r}') \langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle] \quad (4)$$

where Φ_0 is the wavefunction of the **full-interacting** electron gas.

The next statement is valid for all **homogeneous** systems, **no matter how complicated Ψ_0 may be:**

$$\langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle = n_0 = \frac{N}{\Omega}.$$

Definition of the **density deviation operator**

$$\check{\rho}(\mathbf{r}) \equiv \hat{\rho}(\mathbf{r}) - n_0 \quad \text{what means that} \quad \langle \Psi_0 | \check{\rho}(\mathbf{r}) | \Psi_0 \rangle = 0. \quad (5)$$

Eqs. (4) and (5) yield

$$E_{pot} = \frac{1}{2} \int \int d^3r d^3r' V(\mathbf{r} - \mathbf{r}') [\langle \Psi_0 | \check{\rho}(\mathbf{r}) \check{\rho}(\mathbf{r}') | \Psi_0 \rangle + n_0^2 - n_0 \delta(\mathbf{r} - \mathbf{r}')] . \quad (6)$$

A further definition:

the **time-ordered density-density correlation function:**

$$\langle \Psi_0 | \hat{T} [\check{\rho}_H(x) \check{\rho}_H(x')] | \Psi_0 \rangle \quad (7)$$

with $x \equiv \mathbf{r}t$ and $x' \equiv \mathbf{r}'t'$.

As demonstrated in Appendix 4 of this lecture, this function **equals** - apart of the simple factor $i\hbar$ - the previously described **polarization function Π :**

$$\langle \Psi_0 | \hat{T} [\check{\rho}_H(x) \check{\rho}_H(x')] | \Psi_0 \rangle \equiv i\hbar \Pi(x, x'). \quad (8)$$

For $t > t'$, this expression reads

$$\langle \Psi_0 | \check{\rho}_H(\mathbf{r}, t) \check{\rho}_H(\mathbf{r}', t') | \Psi_0 \rangle = i\hbar \Pi(\mathbf{r}t, \mathbf{r}'t').$$

The left side of the above equation can be written as

$$\langle \Psi_0 | e^{i\hat{H}t/\hbar} \check{\rho}(\mathbf{r}) e^{-i\hat{H}(t-t')/\hbar} \check{\rho}(\mathbf{r}') e^{-i\hat{H}t'/\hbar} | \Psi_0 \rangle$$

and further

$$e^{-i\hat{E}_0(t-t')/\hbar} \langle \Psi_0 | \check{\rho}(\mathbf{r}) e^{-i\hat{H}(t-t')/\hbar} \check{\rho}(\mathbf{r}') | \Psi_0 \rangle .$$

For the limit $(t - t') \rightarrow 0^+$, one finally gets

$$\langle \Psi_0 | \check{\rho}(\mathbf{r}) \check{\rho}(\mathbf{r}') | \Psi_0 \rangle = i\hbar \lim_{(t-t') \rightarrow 0^+} \Pi(\mathbf{r}t, \mathbf{r}'t'). \quad (9)$$

Combining Eqs. (6) and (9), the **potential energy** of the electron ground state can be written as

$$E_{pot} = \frac{1}{2} \lim_{(t-t') \rightarrow 0^+} \int \int d^3r d^3r' V(\mathbf{r}-\mathbf{r}') [i\hbar\Pi(\mathbf{r}t; \mathbf{r}'t') + n_0^2 - n_0\delta(\mathbf{r}-\mathbf{r}')] .$$

A Fourier transform from $(\mathbf{r}t)$ to $(\mathbf{k}\omega)$ has the result

$$E_{pot} = \frac{1}{2} \lim_{\eta \rightarrow 0} \int \int d^3r d^3r' \frac{1}{\Omega} \sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} V(\mathbf{k}) \\ \times \left[i\hbar \frac{1}{2\pi\Omega} \sum_{\mathbf{q}} e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} \int d\omega e^{-i\omega\eta} \Pi(\mathbf{q}, \omega) + n_0^2 - n_0\delta(\mathbf{r}-\mathbf{r}') \right] .$$

Evaluating the integrals over \mathbf{r} and \mathbf{r}' (see page 69 of the german lecture notes) leads to the formula

$$E_{pot} = \frac{n_0^2 V(0)\Omega}{2} + \sum_{\mathbf{q}} \left[\frac{i\hbar}{4\pi} \int_{-\infty}^{+\infty} d\omega e^{-i\omega\eta} V(\mathbf{q})\Pi(\mathbf{q}, \omega) - \frac{n_0}{2} V(\mathbf{q}) \right] . \quad (10)$$

- The first term of Eq. (10) containing $V(0)$ can be interpreted as the **Hartree** contribution. As already discussed at the beginning of this lecture, for **homogeneous** electron gases, this contribution to the energy exactly cancels with the energy due to interactions of the electrons with the (jellium-like smeared) ion lattice of the solid. Mathematically, this fact is expressed by $V(0) = 0$.

- Here it has to be emphasized that the Fourier coefficients $\Pi(\mathbf{q}, \omega)$ in Eq. (10) mean **the complete polarisation function, including all repetitions**.

Remember the general relation between the **total** and the **proper (irreducible)** polarisation functions $\Pi(\mathbf{q}, \omega)$ and $\Pi^{pr}(\mathbf{q}, \omega)$:

$$\Pi^{total} \cdot V = \Pi^{pr} \cdot V + (\Pi^{pr} \cdot V)^2 + \dots = \frac{1}{1 - \Pi^{pr}V} - 1 = \frac{1}{\kappa} - 1$$

or, more precisely,

$$\Pi^{total}(\mathbf{q}, \omega) V(\mathbf{q}) = \frac{1}{\kappa(\mathbf{q}, \omega)} - 1 . \quad (11)$$

Inserting Eq. (11) into Eq. (10) with $V(\mathbf{q}) = 4\pi e^2/q^2$ and $V(0) = 0$ results to

$$E_{pot} = - \sum_{\mathbf{q}} \left[\frac{2\pi n_0 e^2}{q^2} - \frac{i\hbar}{4\pi} \int_{-\infty}^{+\infty} d\omega e^{-i\omega\eta} \left(\frac{1}{\kappa(\mathbf{q}, \omega)} - 1 \right) \right].$$

Now, as we often do during this lecture, the **"important" relation**

$$\left(\frac{1}{\kappa(\mathbf{q}, \omega)} \right)^T = 1 + \frac{1}{\pi} \int_0^\infty d\sigma \Im \left(\frac{1}{\kappa(\mathbf{q}, \sigma)} \right)^T \left\{ \frac{1}{\sigma - \omega - i\eta} + \frac{1}{\sigma + \omega - i\eta} \right\} \quad (12)$$

is used:

$$+ \frac{i\hbar}{4\pi^2} \int_0^\infty d\sigma \Im \left(\frac{1}{\kappa(\mathbf{q}, \sigma)} \right) \underbrace{\int d\omega e^{-i\omega\eta} \left\{ \frac{1}{\omega - \sigma + i\eta} - \frac{1}{\omega + \sigma - i\eta} \right\}}_{=-2\pi i},$$

and further

$$E_{pot} = - \sum_{\mathbf{q}} \left[\frac{2\pi n_0 e^2}{q^2} + \frac{\hbar}{2\pi} \int_0^\infty d\sigma \Im \left(\frac{1}{\kappa(\mathbf{q}, \sigma)} \right) \right]. \quad (13)$$

2.2 The Pauli-Hellmann-Feynman Theorem

In this section, we deal with the calculation of the energy E_0 of **the ground state of a full-interacting homogeneous electron gas**:

$$E_0 = \langle \Psi_0 | \hat{T} + \hat{V} | \Psi_0 \rangle, \quad (14)$$

where the second term describes the expectation value of the interaction operator containing the Coulomb interaction between the electrons:

$$\hat{V} \leftarrow \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}.$$

W. Pauli and other authors proposed to take the "e²" not simply as a physical constant, but **as coupling constant λ** of the interaction:

- $\lambda = 0$ \rightarrow no interaction
- $\lambda = e^2$ \rightarrow full interaction

By doing so, one gets a **variable** interaction operator that is **linearly** dependent on λ :

$$\hat{V}(\lambda) = \lambda \cdot \hat{V}_0, \quad (15)$$

and Eq. (14) changes to

$$E_0(\lambda) = \langle \Psi_0(\lambda) | \hat{T} + \lambda \hat{V}_0 | \Psi_0(\lambda) \rangle.$$

Derivating this expression with respect to λ leads to

$$\begin{aligned} \frac{\partial E_0(\lambda)}{\partial \lambda} &= \langle \Psi_0(\lambda) | \hat{V}_0 | \Psi_0(\lambda) \rangle + \\ &+ \langle \frac{\partial \Psi_0(\lambda)}{\partial \lambda} | \hat{H} | \Psi_0(\lambda) \rangle + \langle \Psi_0(\lambda) | \hat{H} | \frac{\partial \Psi_0(\lambda)}{\partial \lambda} \rangle \\ &= \langle \Psi_0(\lambda) | \hat{V}_0 | \Psi_0(\lambda) \rangle + E_0(\lambda) \underbrace{\frac{\partial}{\partial \lambda} \langle \Psi_0(\lambda) | \Psi_0(\lambda) \rangle}_{=0}. \end{aligned}$$

Using Eq.(15), one further gets

$$\frac{\partial E_0(\lambda)}{\partial \lambda} = \frac{1}{\lambda} \langle \Psi_0(\lambda) | \hat{V}(\lambda) | \Psi_0(\lambda) \rangle, \quad (16)$$

and an integration of this expression with respect to λ yields

$$\int_{\lambda=0}^{e^2} d\lambda \frac{\partial E_0(\lambda)}{\partial \lambda} = E_0(\lambda = e^2) - E_0(\lambda = 0) = E_0 - \tilde{E}_0,$$

the difference between the ground state energies **of the interacting (E_0) and the non-interacting particle system (\tilde{E}_0)**.

Using Eqs. (16) and (13), one gets

$$E_0 = \tilde{E}_0 + \int_{\lambda=0}^{e^2} \frac{d\lambda}{\lambda} \langle \Psi_0(\lambda) | \hat{W}(\lambda) | \Psi_0(\lambda) \rangle$$

and

$$E_0 = 2 \sum_{|\mathbf{k}| \leq k_F} \frac{\hbar^2 k^2}{2m} - \sum_{\mathbf{q}} \int_{\lambda=0}^{e^2} \frac{d\lambda}{\lambda} \left[\frac{2\pi n_0 \lambda}{q^2} + \frac{\hbar}{2\pi} \int_0^\infty d\sigma \Im \left(\frac{1}{\kappa_\lambda(\mathbf{q}, \sigma)} \right) \right]. \quad (17)$$

This is a formula of extraordinary importance, because it enables the calculation of the ground state energy of the interacting electron gas only on the basis of its dielectric function.

2.3 Structure factors and pair correlation

The so-called **dynamical structure factor** $S(\mathbf{q}, \omega)$ of an interacting electron gas is easily obtained by a trivial new-formulation of Eq. (17):

$$E_0 = 2 \sum_{|\mathbf{k}| \leq k_F} \frac{\hbar^2 k^2}{2m} + 2\pi n_0 \sum_{\mathbf{q}} \frac{1}{q^2} \int_0^{e^2} d\lambda \left[-1 + \frac{1}{2\pi} \int_0^\infty d\sigma \underbrace{\left(-\frac{\hbar q^2}{2\pi \lambda n_0} \right) \mathfrak{S} \left(\frac{1}{\kappa_\lambda(\mathbf{q}, \sigma)} \right)}_{S_\lambda(\mathbf{q}, \sigma)} \right]$$

with

$$S_{\lambda=e^2}(\mathbf{q}, \omega) \equiv S(\mathbf{q}, \omega) = -\frac{\hbar q^2}{2\pi e^2 n_0} \mathfrak{S} \left(\frac{1}{\kappa(\mathbf{q}, \omega)} \right). \quad (18)$$

The eminent importance of this **real** quantity comes from its relations to **scattering experiments**:

- The dynamical structure factor is strongly correlated to the probability $P(\mathbf{q}, \omega)$ for an incoming particle to undergo a "change of momentum" ($\hbar\mathbf{q}$) and a "change of energy" ($\hbar\omega$), caused by its interaction by the electronic system:

$$P(\mathbf{q}, \omega) = \frac{n_0}{\Omega} \left[\frac{v(\mathbf{q})}{\Omega} \right]^2 S(\mathbf{q}, \omega),$$

where $v(\mathbf{q})$ means the Fourier transform of the interaction potential between the incoming particle and the electrons.

- For $T = 0$ K, the system can only absorb energy from the test particle; therefore, one has the relation

$$S(\mathbf{q}, \omega) = 0 \quad \text{für} \quad \omega < 0.$$

- Based on Eq. (18), the dynamical structure factor $S(\mathbf{q}, \omega)$ enables an experimental control of theoretically obtained dielectric functions $\kappa(\mathbf{q}, \omega)$ by inelastic scattering experiments as **electron energy loss spectroscopy EELS** or **inelastic x-ray scattering spectroscopy IXSS** etc.

Of course, starting from $S(\mathbf{q}, \omega)$, one can define the **static structure factor**

$$S_{\lambda=e^2}(\mathbf{q}) \equiv \frac{1}{2\pi} \int_0^\infty d\omega S(\mathbf{q}, \omega) = -\frac{\hbar q^2}{4\pi^2 e^2 n_0} \int_0^\infty d\omega \Im \left(\frac{1}{\kappa(\mathbf{q}, \omega)} \right), \quad (19)$$

leading to the following relation to the ground-state energy:

$$E_0 = 2 \sum_{|\mathbf{k}| < k_F} \frac{\hbar^2 k^2}{2m} + 2\pi n_0 \sum_{\mathbf{q}} \frac{1}{q^2} \int_{\lambda=0}^{e^2} d\lambda [S_\lambda(\mathbf{q}) - 1]. \quad (20)$$

A relation between this static structure factor and the expectation value of the density-density correlation operator:

Remember Eq. (9):

$$\langle \Psi_0 | \check{\rho}(\mathbf{r}) \check{\rho}(\mathbf{r}') | \Psi_0 \rangle = i\hbar \lim_{(t-t') \rightarrow 0^+} \Pi^{total}(\mathbf{r}t, \mathbf{r}'t').$$

Including the Fourier transform of $\Pi(\mathbf{r} - \mathbf{r}', t - t')$, one gets

$$\langle \Psi_0 | \check{\rho}(\mathbf{r}) \check{\rho}(\mathbf{r}') | \Psi_0 \rangle = \lim_{\eta \rightarrow 0^+} \frac{i\hbar}{2\pi\Omega} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \int d\omega e^{-i\omega\eta} \Pi^{total}(\mathbf{q}, \omega),$$

and by inserting Eq. (11) with $V(\mathbf{q}) = 4\pi e^2/q^2$, yields

$$\langle \Psi_0 | \check{\rho}(\mathbf{r}) \check{\rho}(\mathbf{r}') | \Psi_0 \rangle = \lim_{\eta \rightarrow 0^+} \frac{i\hbar}{2\pi\Omega} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \int d\omega e^{-i\omega\eta} \frac{q^2}{4\pi e^2} \left(\frac{1}{\kappa(\mathbf{q}, \omega)} - 1 \right).$$

The integration over ω can be performed "as usual", i.e., by the help of Eq. (12), and the result of this calculation is

$$\frac{1}{n_0} \langle \Psi_0 | \check{\rho}(\mathbf{r}) \check{\rho}(\mathbf{r}') | \Psi_0 \rangle = \frac{1}{\Omega} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \left[-\frac{\hbar q^2}{4\pi^2 e^2 n_0} \int_0^\infty d\omega \Im \left(\frac{1}{\kappa(\mathbf{q}, \omega)} \right) \right].$$

A comparison of this result with Eq. (19) immediately leads to

$$\langle \Psi_0 | \check{\rho}(\mathbf{r}) \check{\rho}(\mathbf{r}') | \Psi_0 \rangle = \frac{1}{\Omega} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} [n_0 S(\mathbf{q})] = n_0 S(\mathbf{r} - \mathbf{r}'). \quad (21)$$

Again, a new function:

The pair correlation function $g(\mathbf{r}, \mathbf{r}')$ describes how the probability to detect a particle at \mathbf{r} is reduced by a "correlation partner" at \mathbf{r}' :

$$g(\mathbf{r}, \mathbf{r}') = \frac{\langle \Psi_0 | \sum_{i,j \neq i}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) | \Psi_0 \rangle}{\langle \Psi_0 | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | \Psi_0 \rangle \langle \Psi_0 | \sum_j \delta(\mathbf{r}' - \mathbf{r}_j) | \Psi_0 \rangle}, \quad (22)$$

where the operator in the numerator can be written as

$$\left(\sum_i \delta(\mathbf{r} - \mathbf{r}_i) \right) \left(\sum_j \delta(\mathbf{r}' - \mathbf{r}_j) \right) - \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_i).$$

Remember the density operator $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$.

By using this definition, Eq. (22) reads

$$g(\mathbf{r}, \mathbf{r}') = \frac{\langle \Psi_0 | \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle - \langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \langle \Psi_0 | \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle}{\langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \langle \Psi_0 | \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle} \delta(\mathbf{r} - \mathbf{r}'). \quad (23)$$

As already known, for a homogeneous electron gas, one has

$$\langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle = n_0,$$

leading to

$$g(\mathbf{r}, \mathbf{r}') = \frac{\langle \Psi_0 | \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle}{n_0^2} - \frac{\delta(\mathbf{r} - \mathbf{r}')}{n_0}.$$

If we use here the - also previously installed - *density deviation operator*

$$\check{\rho}(\mathbf{r}) = \hat{\rho}(\mathbf{r}) - n_0,$$

one gets the final result for jellium:

$$g(\mathbf{r} - \mathbf{r}') = 1 + \frac{\langle \Psi_0 | \check{\rho}(\mathbf{r}) \check{\rho}(\mathbf{r}') | \Psi_0 \rangle}{n_0^2} - \frac{\delta(\mathbf{r} - \mathbf{r}')}{n_0}. \quad (24)$$

By comparing Eqs. (21) and (24), one gets immediately **an important relation between pair correlation function and static structure factor**:

$$g(\mathbf{r} - \mathbf{r}') = 1 + \frac{1}{n_0} [S(\mathbf{r} - \mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')]$$

or, taking into account that all Fourier coefficients of a Dirac distribution are 1,

$$g(\mathbf{r} - \mathbf{r}') = 1 + \frac{1}{N} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} [S(\mathbf{q}) - 1] . \quad (25)$$

Combining the equations (25) and (19), one obtains the result

$$g(\mathbf{r} - \mathbf{r}') = 1 - \frac{1}{N} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \left[\frac{\hbar q^2}{4\pi^2 e^2 n_0} \int_0^\infty d\omega \Im \left(\frac{1}{\kappa(\mathbf{q}, \omega)} \right) + 1 \right] . \quad (26)$$

This equation offers an important possibility to check the quality of calculated approximations of the *dielectric function* $\kappa(\mathbf{q}, \omega)$. Fact is that the *pair correlation function* $g(\mathbf{r} - \mathbf{r}')$ must obey the following conditions:

- As for all **probability functions**, the condition

$$g(\mathbf{r} - \mathbf{r}') \geq 0 \quad \text{für alle } \mathbf{r}, \mathbf{r}' \quad (27)$$

has to be fulfilled.

- The condition

$$g(\mathbf{r} - \mathbf{r}') \rightarrow 1 \quad \text{für} \quad |\mathbf{r} - \mathbf{r}'| \rightarrow \infty \quad (28)$$

has also a simple physical interpretation: there is obviously no correlation between particles with infinitely large distances. Consequently, the probability to find the first particle at \mathbf{r} **will not be reduced** by the second particle.

2.3.1 Structure factor and pair correlation in the RPA

In the last sections, we discussed how the static structure factor of an interacting electron gas (19), its ground-state energy (20), and its pair correlation function (25) can be calculated only by the knowledge of the function

$$\Im \left(\frac{1}{\kappa(\mathbf{q}, \omega)} \right) :$$

$$S_\lambda(\mathbf{q}) = -\frac{\hbar q^2}{4\pi^2 e^2 n_0} \int_0^\infty d\omega \Im \left(\frac{1}{\kappa_\lambda(\mathbf{q}, \omega)} \right), \quad (19)$$

$$E_0 = 2 \sum_{|\mathbf{k}| < k_F} \frac{\hbar^2 k^2}{2m} + 2\pi n_0 \sum_{\mathbf{q}} \frac{1}{q^2} \int_{\lambda=0}^{e^2} d\lambda [S_\lambda(\mathbf{q}) - 1]. \quad (20)$$

$$g(\mathbf{r} - \mathbf{r}') = 1 + \frac{1}{N} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} [S(\mathbf{q}) - 1]. \quad (25)$$

The only approximation of the dielectric function discussed until now is the *random phase approximation* RPA:

$$\Im \left(\frac{1}{\kappa} \right) \approx \Im \left(\frac{1}{\kappa^{RPA}} \right)$$

However, this approximation is by no means the simplest one, as we can learn from the Dyson expansion of $(1/\kappa^{RPA})$:

$$\begin{aligned} \Im \left(\frac{1}{\kappa^{RPA}} \right) &= \Im \left(\frac{1}{1 - V \Pi^{pr(RPA)}} \right) = \Im (1 + V \Pi^{pr(RPA)} + \dots) \\ &\approx V \Im \Pi^{pr(RPA)}. \end{aligned} \quad (29)$$

Including a previously given result for $\Im \Pi^{pr(RPA)}$ (see Sec. 1.6 of this lecture), one gets

$$\begin{aligned} V(\mathbf{q}) \Im \Pi^{pr(RPA)}(\mathbf{q}, \omega) &= -\frac{2\pi}{\hbar(2\pi)^3} \left(\frac{4\pi e^2}{q^2} \right) \int d^3k \Theta(k_F - k) \Theta(|\mathbf{k} + \mathbf{q}| - k_F) \\ &\times [\delta(\omega + \omega_{\mathbf{k}}^0 - \omega_{\mathbf{k}+\mathbf{q}}^0) + \delta(\omega - \omega_{\mathbf{k}}^0 + \omega_{\mathbf{k}+\mathbf{q}}^0)]. \end{aligned}$$

Inserting this into Eq. (19) leads to the integral

$$\int_0^\infty d\omega [\delta(\omega + \omega_{\mathbf{k}}^0 - \omega_{\mathbf{k}+\mathbf{q}}^0) + \delta(\omega - \omega_{\mathbf{k}}^0 + \omega_{\mathbf{k}+\mathbf{q}}^0)] = 1,$$

and to the **simplest static structure factor**:

$$S^0(\mathbf{q}) = \frac{1}{4\pi^3 n_0} \int d^3k \Theta(k_F - k) \Theta(|\mathbf{k} + \mathbf{q}| - k_F),$$

what can be analytically evaluated (see Appendix 5) to

$$S^0(\mathbf{q}) = S^0(q) = \begin{cases} \frac{3}{2} \frac{q}{2k_F} - \frac{1}{2} \left(\frac{q}{2k_F} \right)^3 & \text{für } 0 < q \leq 2k_F, \\ 1 & \text{für } q \geq 2k_F. \end{cases} \quad (30)$$

How do the corresponding ground state energy of the electron gas and the pair correlation look like?

For the ground-state energy, one has to evaluate

$$\begin{aligned} E_0 &= 2 \sum_{|\mathbf{k}| < k_F} \frac{\hbar^2 k^2}{2m} + 2\pi n_0 \sum_{\mathbf{q}} \frac{1}{q^2} \int_{\lambda=0}^{e^2} d\lambda [S^0(q) - 1] \\ &= 2 \sum_{|\mathbf{k}| < k_F} \frac{\hbar^2 k^2}{2m} + \frac{N e^2}{\pi} \int_0^\infty dq [S^0(q) - 1]. \end{aligned} \quad (31)$$

The first term represents the

kinetic energy of the non-interacting electron gas:

$$T_0 = 2 \sum_{|\mathbf{k}| < k_F} \frac{\hbar^2 k^2}{2m} = N \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} = \underbrace{\left(\frac{\hbar^2}{2m a_B^2} \right)}_{=1 \text{ Ry}} N \frac{3}{5} \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^2} = N \frac{2.21}{r_s^2} \text{ Ry},$$

and the second term in Eq. (31) gives the

potential energy of the interacting electrons

$$V_0 = -N \frac{3e^2 k_F}{4\pi} = -N \frac{3}{2\pi} \left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{r_s} = -N \frac{0.916}{r_s},$$

(r_s in $a_B = \text{Bohr units}$).

The total energy *per particle* reads

$$\begin{aligned} E_0/N = (T_0 + V_0)/N &= \left\{ \frac{3}{5} \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^2} - \frac{3}{2\pi} \left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{r_s} \right\} \text{Ry} \\ &= \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} \right) \text{Ry}. \end{aligned} \quad (32)$$

This is exactly the result of the Hartree-Fock theory.

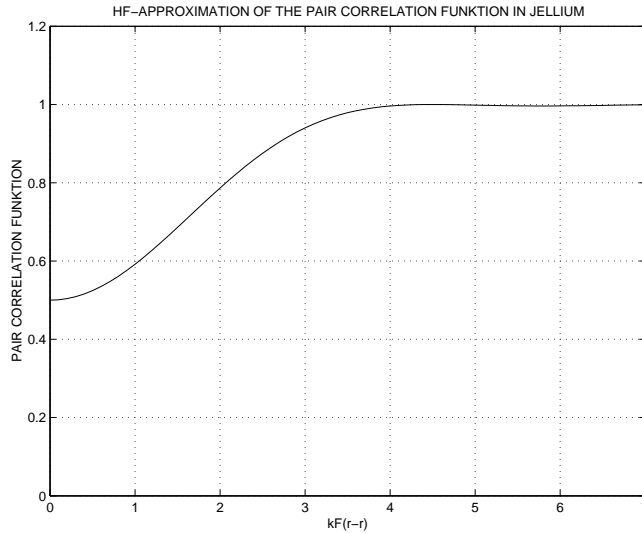
This statement also holds for the corresponding pair correlation function.

Inserting $S^0(q)$, Eq. (30), into the formula (25), one gets

$$g^0(\mathbf{r} - \mathbf{r}') = 1 + \frac{1}{N} \sum_{|\mathbf{q}| \leq 2k_F} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \left[\frac{3}{2} \frac{q}{2k_F} - \frac{1}{2} \left(\frac{q}{2k_F} \right)^3 - 1 \right]$$

and after some elementary mathematical treatment

$$g^0(\mathbf{r} - \mathbf{r}') = g^0(|\mathbf{r} - \mathbf{r}'|) = 1 - \frac{9}{2} \left(\frac{\sin \xi - \xi \cos \xi}{\xi^3} \right)^2 \quad \text{with} \quad \xi \equiv k_F |\mathbf{r} - \mathbf{r}'|. \quad (33)$$



According to this graphical representation, Eq. (33) describes the **exchange hole** around an electron, i.e., **the reduced probability of the presence of spin-parallel electrons around an electron.**

This behavior is also typically *Hartree-Fock-like*; therefore, the result g^0 is the HF approximation of a pair correlation function.

The next step for a better electron theory is evident:

Instead of the simple approximation (29), the total Dyson-result of $\Im(1/\kappa)^{RPA}$ has to be inserted into the energy equation (20):

Instead of

$$E_0^{RPA} = 2 \sum_{|\mathbf{k}| \leq k_F} \frac{\hbar^2 k^2}{2m} - \sum_{\mathbf{q}} \int_{\lambda=0}^{e^2} \frac{d\lambda}{\lambda} \left[\frac{2\pi n_0 \lambda}{q^2} + \frac{\hbar}{2\pi} \int_0^\infty d\omega V_\lambda(\mathbf{q}) \Im \Pi^{pr(RPA)}(\mathbf{q}, \omega) \right]$$

one has to calculate

$$E_0^{RPA} = 2 \sum_{|\mathbf{k}| \leq k_F} \frac{\hbar^2 k^2}{2m} - \sum_{\mathbf{q}} \int_{\lambda=0}^{e^2} \frac{d\lambda}{\lambda} \left[\frac{2\pi n_0 \lambda}{q^2} + \frac{\hbar}{2\pi} \int_0^\infty d\omega \Im \left(\frac{1}{\kappa_\lambda^{RPA}(\mathbf{q}, \omega)} \right) \right]. \quad (34)$$

Such calculations have already been performed some decades ago, e.g., by W. Macke [Z. Naturf. **5a**, 192 (1950)], by M. Gell-Mann and K. Brueckner [Phys. Rev. **106**, 364 (1960)], by L. Onsager *et al* [Ann. Physik (Leipzig) **18**, 71 (1966)], by R.F. Bishop und K.H. Lührmann [Phys. Rev. B **26**, 5523 (1982)] etc.

The results of these papers have been published mainly in form of numerical tables, analytical expressions are only existing for the *high-density limit* $r_s \rightarrow 0$:

$$\lim_{r_s \rightarrow 0} \frac{E_0^{RPA}}{N} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.0622 \ln r_s - 0.142 \text{ Ry} \quad (35)$$

where the coefficient 0.0622 corresponds to $2(1 - \ln 2)\pi^2$.

Remember: All energy terms *beyond* the Hartree-Fock terms are (per definition) denoted as **correlation terms**:

$$\lim_{r_s \rightarrow 0} \frac{E_{corr}^{RPA}}{N} = 0.0622 \ln r_s - 0.142 \text{ Ry}. \quad (36)$$

Now back to the main question:

What's about the quality of the dielectric function and the related quantites in the RPA and other approximations?

Concerning the correlation energy of the homogeneous electron gas, theoretical results are usually compared

- not with *real* experiments,
- but with Quantum Monte-Carlo (QMC) experiments:

D.M. Ceperley, *Phys. Rev.* **18**, 3126 (1978).

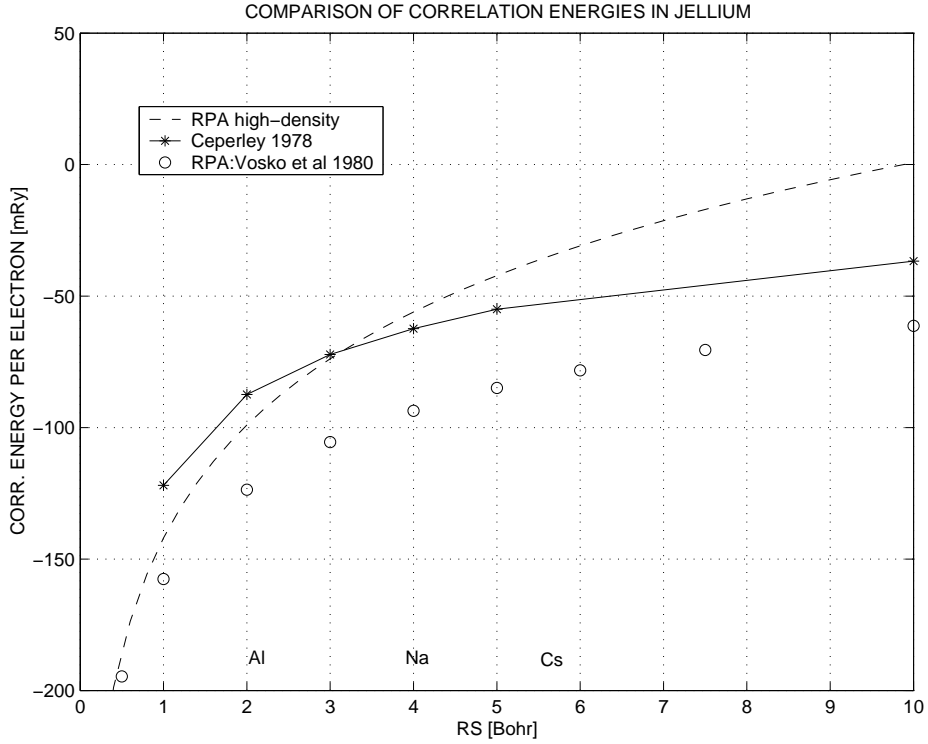
D.M. Ceperley and B.J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980)

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S.H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).

G. Ortiz and P. Ballone, *Phys. Rev. B* **50**, 1391 (1994).

G. Ortiz, M. Harris, and P. Ballone, *Phys. Rev. Lett.* **82**, 5317 (1999).



Correlation energies as a function of r_s . A comparison of various theoretical approximations with the QMC standard.

- Note: the practically most interesting region of r_s is $2 \geq r_s \geq 6$ (relevant for many interesting metals).
- The solid line with (*) shows QMC results by Ceperley et al. (1978).
- The dashed line means "high-density results", according to Eq. (36). As previously mentioned, this formula is only correct in the limit of $r_s \rightarrow 0$. Therefore, no reliable results can be expected within the "metallic region".
- The circles belong to a numerical evaluation of Eq. (34), i.e., based on a RPA of $\Im(1/\kappa)$ for the whole r_s region. This curve nicely approaches the "high density curve" for small r_s , and it also shows a reasonable behavior for higher values of r_s . Nevertheless, its correlation energies lie significantly below the corresponding QMC results.

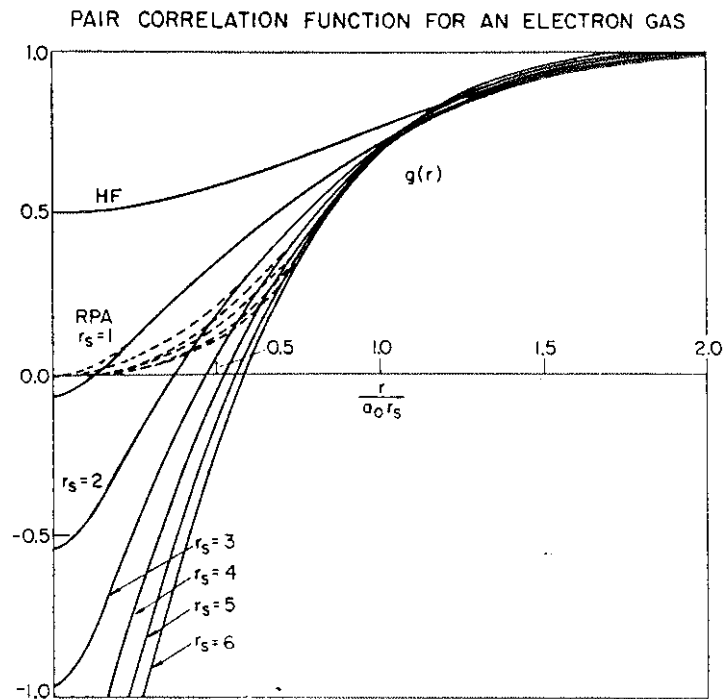
Resumee: Except for very small values of r_s , the random phase approximation is not able to describe properly the correlation energy in jellium.

A further, even more impressive argument for **severe deficiencies of RPA results** are calculations of the pair correlation function $g(|\mathbf{r} - \mathbf{r}'|)$, based on Eq. (26) including

$$\kappa(q, \omega) \approx \kappa^{RPA}(q, \omega).$$

Remember:

- $g(|\mathbf{r} - \mathbf{r}'|) \geq 0$
- $\lim_{|\mathbf{r} - \mathbf{r}'| \rightarrow \infty} g(|\mathbf{r} - \mathbf{r}'|) = 1$



The RPA for the pair correlation function in jellium for r_s from 1 to 6 [see L. Hedin, PR **139**, A805 (1965)].

Resume: Evidently, especially for small values of $|\mathbf{r} - \mathbf{r}'|$, all RPA curves violate the first condition mentioned above. This deficiency gets more and more dramatic for increasing values of r_s .

2.3.2 Sum rules for the dielectric function

The following is taken from: P. Ziesche und G. Lehmann, *Elektronentheorie der Metalle*, Springer, Berlin, 1983, p. 30f..

For the dielectric function $\kappa(q, \omega)$, the literature offers several **sum rules (SR)**. These are important because they enable a theoretical testing of different approximations of κ .

For a more extensive treatment of this subject and a more profound mathematical background see, e.g., D. Pines and P. Nozieres, *The Theory of Quantum Liquids*, Benjamin, New York, 1966, and A. Sjölander, *Nuovo Cimento* **23B**, 124 (1974).

- f -SR:

$$\int \frac{d\omega}{\pi} \Im \left(\frac{1}{\kappa(q, \omega)} \right) \omega = -\omega_p^2.$$

- Conductivity-SR:

$$\int \frac{d\omega}{\pi} \Im (\kappa(q, \omega)) \omega = \omega_p^2,$$

- Compressibility-SR:

$$\lim_{q \rightarrow 0} \int \frac{d\omega}{\pi} \Im (\kappa(q, \omega)) \frac{1}{\omega} = \lim_{q \rightarrow 0} K n_0 M \frac{\omega_p^2}{q^2},$$

- Screening-SR:

$$\lim_{q \rightarrow 0} \int \frac{d\omega}{\pi} \Im \left(\frac{1}{\kappa(q, \omega)} \right) \frac{1}{\omega} = -1 + \lim_{q \rightarrow 0} \frac{q^2}{K n_0 m \omega_p^2}.$$

The following relations give informations about the **high-frequency behavior** of κ :

$$\lim_{\omega \rightarrow \infty} \frac{1}{\kappa(q, \omega)} = 1 + \lim_{\omega \rightarrow \infty} \frac{\omega_p^2}{\omega^2} \quad \text{und} \quad \lim_{\omega \rightarrow \infty} \kappa(q, \omega) = 1 - \lim_{\omega \rightarrow \infty} \frac{\omega_p^2}{\omega^2}.$$

Further, there are some **compressibility theorems** as

$$\lim_{q \rightarrow 0} \kappa(q, 0) = 1 + K n_0 m \lim_{q \rightarrow 0} \frac{\omega_p^2}{q^2} \quad \text{und} \quad \lim_{q \rightarrow 0} \frac{1}{\kappa(q, 0)} = \lim_{q \rightarrow 0} \frac{q^2}{K n_0 m \omega_p^2}.$$

The above equations contain the following quantities: ω_p means the plasma frequency (see Sec. 1.6.1), n_0 and m are the electron density and the electron mass, and K is the *compressibility* of the electron gas which is defined by

$$K = \Omega \frac{\partial^2 E}{\partial \Omega^2}.$$

By the formula

$$\frac{K_0}{K} = 1 - \frac{\alpha^3}{\pi} r_s + \frac{\alpha^3}{6} r_s^4 \left[\frac{d^2 \epsilon_{corr}}{dr_s^2} - \frac{2}{r_s} \frac{d\epsilon_{corr}}{dr_s} \right],$$

this quantity is related to the correlation energy per electron ϵ_{corr} , with

$$\alpha = \left(\frac{4}{9\pi} \right)^{1/3}$$

and with K_0 , the compressibility of the free electron gas

$$K_0 = \frac{3}{2n_0 \epsilon_F^0}.$$