

## Summary Secs. 2.4, 2.5: Theory versus Experiment

The theoretical results (momentum density, correlation energy, pair correlation function etc.) of electrons in solid media discussed so far were not fully convincing: we observed partially strong deviations from the QMC standard, violations of basic conditions concerning the electron-electron pair correlation etc.

Remember:    **Basic aspects of the previous calculations**

- use of trivialized external potentials  
→ **jellium approximation**
- use of the simplest approximation for the polarisation of the electron gas  
→ **random phase approximation**

Of course, the following questions will be central for the following sections:

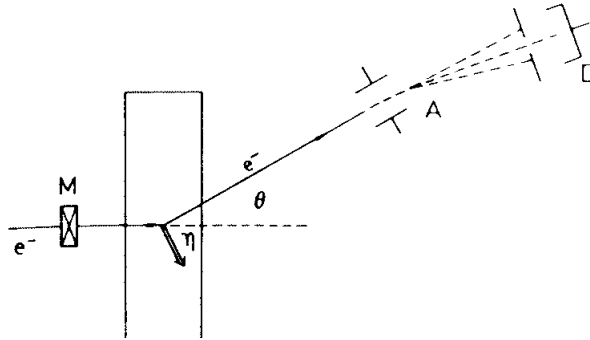
- the role of "beyond-jellium" effects
- the role of "beyond-RPA" effects

**In what direction is it most reasonable to invest brain and computer power?**

The answer to this question is hoped to be got from **confrontations "theory versus experiment"**.

## Important experiments

- Electron Energy Loss Spectroscopy EELS:



Scheme of an EELS spektrometer (H. Raether). The energy loss  $\Delta E$  of electrons that are scattered by the angle  $\Theta$  is measured by the energy analyzer (A) and the detector (D). M is a monochromator.

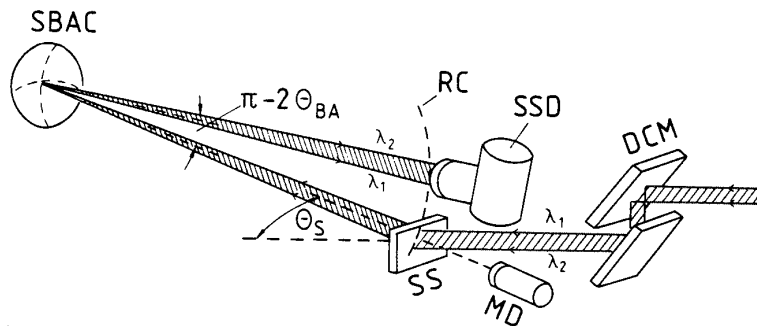
A monoenergetic electron beam ( $E > 30$  keV) penetrates a thin metal layer. The incoming particles undergo scattering processes with the electrons of the sample (electron-hole and plasmon excitations). The probability of the corresponding momentum and energy transfers is proportional to the **dynamical structure factor**  $S(\mathbf{q}, \omega)$  (the "loss function"), and therefore also proportional to

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

EELS is mainly used for momenta  $|\mathbf{q}| < q_c$ .

For more informations see, e.g., the review article by H. Raether, *Springer tracts in modern physics*, Springer, Berlin, 1980, Vol. 88.

- Inelastic X-ray Scattering Spectroscopy IXSS:



Scheme of an IXSS spectrometer (W. Schülke).

DCM = double-crystal monochromator, SS = scattering sample, SBC = spherically bent analyzing crystal, SSD = solid-state detector, RC = Rowland circle.

Measurements of the momentum and energy distribution of x-rays which undergo inelastic Compton scattering with electrons of the sample. The distribution of the intensity of the outgoing x-rays is described by the differential cross section

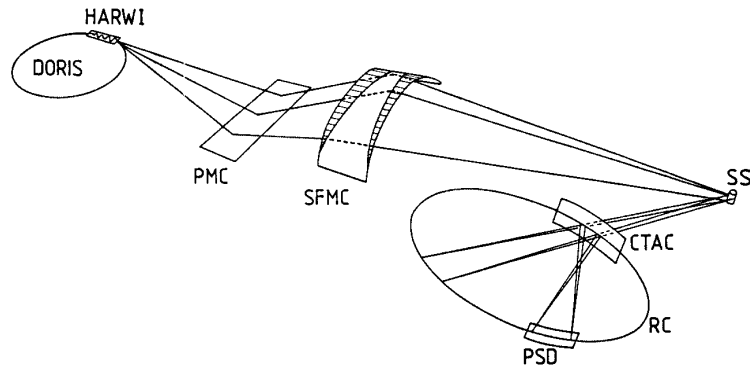
$$\frac{d^2\sigma}{d\Omega d\omega_2} \propto \frac{\omega_2}{\omega_1} S(\mathbf{q}, \omega),$$

with  $\hbar\omega = \hbar(\omega_1 - \omega_2)$  and  $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$ , where  $\omega_1$ ,  $\omega_2$  and  $\mathbf{k}_1$ ,  $\mathbf{k}_2$  mean the energies and the momenta of the outgoing x-rays.

As the EELS technique, this method enables **the direct measurement of the dynamical structure factor  $S(\mathbf{q}, \omega)$** .

Literature: W. Schülke, Nucl. Inst. and Methods **A280**; W. Schülke, H. Schulte-Schrepping, and J. R. Schmitz, Phys. Rev. **47**, 12426 (1993); A. G. Eguluz, A. Fleszar, J. A. Gaspar, Nucl. Inst. and Methods **B96**, 550 (1995); A. G. Eguluz, Int. J. Quantum Chemistry **30**, 1457 (1996); A. G. Eguluz, W. Ku, J. M. Sullivan, J. Phys. Chem. of Solids **61**, 383 (2000).

- Compton Scattering CS:



Scheme of a Compton spectrometer, Hamburger Synchrotronstrahlungslabor (W. Schülke). PMC = plane monochromator crystal, SFMC = sagittal focusing monochromator crystal, SS = scattering sample, CTAC = Cauchois-type analyzer crystal, PSD = position-sensitive detector, RC = Rowland circle.

For this experiment, one has the following relation between the differential cross section and the **momentum density of electrons**  $n(\mathbf{p})$  within the solid material:

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \int d^3p n(\mathbf{p}) \delta\left(\omega - \frac{\hbar q^2}{2m} - \frac{\mathbf{p} \cdot \mathbf{q}}{m}\right).$$

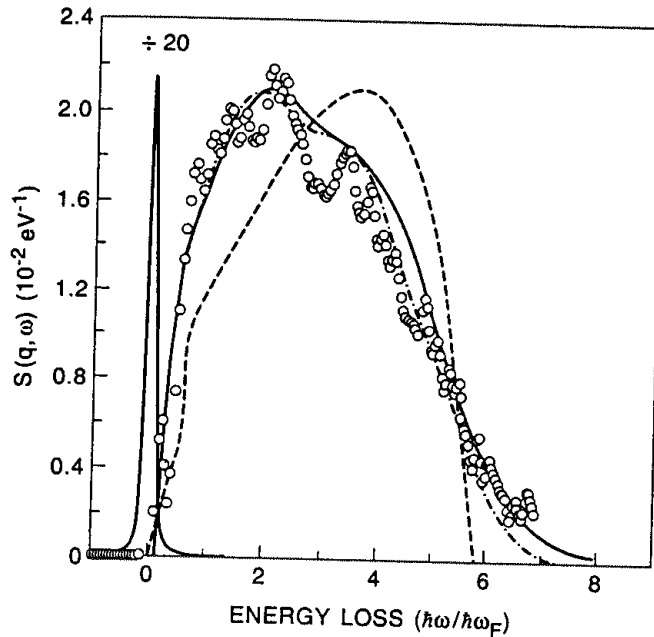
However, this equation also demonstrates a shortcoming of the CS technique: one does not obtain the three-dimensional momentum density  $n(p_x, p_y, p_z)$ , but only the one-dimensional projection of  $n(\mathbf{p})$  along a special direction  $\mathbf{q}$  (a one-dimensional Compton profile).

An important precondition for a high momentum- and energy resolution of IXSS and CS data is the availability of very intensive x-rays in form of **synchrotron radiation**. Such x-ray sources exist in Europe (Hamburg, Trieste, Grenoble), in the US (Brookhaven etc.), in Japan ("photon factories"), etc.

## Comparison experiment-theory for fcc Al

- **Why aluminum?** There is a general agreement that the (valence) electrons of this metal are almost perfectly **jellium-like**.
- Therefore, it can be expected that deviations between experimental and theoretical results are mainly due to **beyond-RPA effects** and not to **beyond-jellium** effects.
- Are these expectations realistic?

Platzman et al., 1992:



IXSS measurements of  $S(\mathbf{q}, \omega)$  in Al for  $q/k_F=1.7$  (open circles), compared with the two-particle-hole theory of Mukhopadhyay *et al* (solid line) for  $q/k_F=1.6$ , and with the jellium RPA theory (dashed line).

P. M. Platzman, E. D. Isaacs, H. Williams, P. Zschack, and G. E. Ice, Phys. Rev. B **46**, 12943 (1992); G. Mukhopadhyay, R. K. Kalia, and K. S. Singwi, Phys. Rev. Lett. **34**, 950 (1975).

- The measurement has been performed for the relatively large wavenumber  $q/k_F=1.7$ , i.e., within the electron-hole scattering region.
- The jellium RPA curve is surprisingly wrong (no high-energy tail, position of the maximum too high, **no double-peak structure**).
- An old theory by Mukhopadhyay et al including "beyond-jellium" aspects as electron-hole exchange is evidently much more successful.
- Platzman's conclusion:  
*(The Al) measurements confirm the existence of strong non-random-phase-approximation-like correlations in an electron liquid where **bandstructure effects are unimportant.***

Platzman et al., 1992; **theory: Fleszar et al., 1995**

Remarkably, based on the same experimental results, one reads **quite different conclusions** in A. Fleszar, A. A. Quong, and A. G. Eguiluz, Phys. Rev. Lett. **74**, 590 (1995):

*For many years, efforts to explain a double peak observed in the dynamical structure factor  $S(\mathbf{q}; \omega)$  of aluminum – an archetype of jellium electronic behavior – via inelastic x-ray scattering have concentrated on many-body mechanisms for the uniform electron liquid. **On the basis of a first-principles evaluation of  $S(\mathbf{q}; \omega)$  for Al crystal we show that the double peak is an intrinsic feature of the response of noninteracting electron-hole pairs.** Many-electron effects, in the form of a vertex correction for the irreducible polarizability, are found to substantially improve the agreement with experiment of the calculated loss intensities.*

The following three diagrams are taken out of this paper. In order to understand the results properly, it is important to clearly understand what theoretical curves are presented by the authors.

The central quantity is, of course, the **dynamical structure factor of the electron gas** as it has been defined in Sec. 2.3 of this lecture. In the following, we use the random phase approximation (RPA):

$$S(\mathbf{q}, \omega) = -\frac{2\hbar}{v(\mathbf{q})n_0} \Im \left( \frac{1}{\kappa^{RPA}(\mathbf{q}, \omega)} \right).$$

Using the well-known relation between the dielectric function  $\kappa$  and the *proper* polarisation function  $\Pi^{pr}$ , one obtains

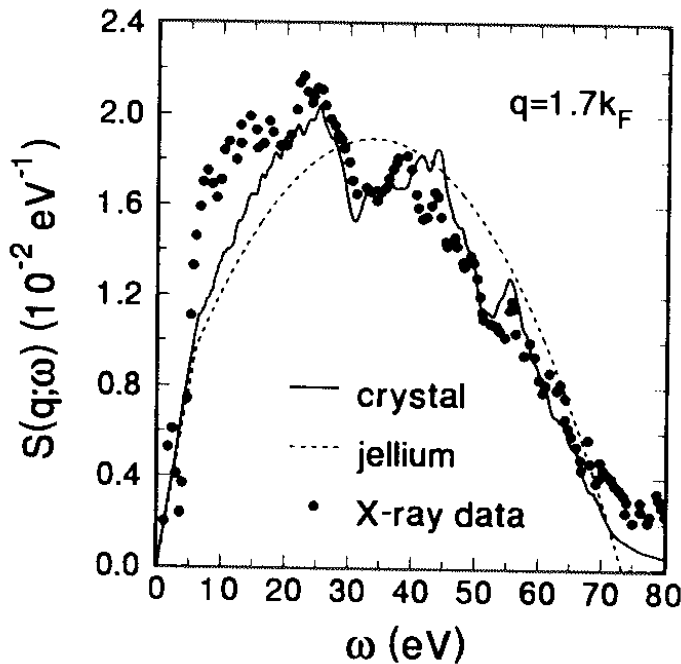
$$S(\mathbf{q}, \omega) = -\frac{2\hbar}{v(\mathbf{q})n_0} \Im \left( \frac{1}{1 - v(\mathbf{q})\Pi^{pr}(\mathbf{q}, \omega)} \right)$$

where  $\Pi^{pr}$  always means the RPA.

The term ... **response of noninteracting electron-hole pairs** means the simple approximation

$$S(\mathbf{q}, \omega) = -\frac{2\hbar}{v(\mathbf{q})n_0} \Im \left( 1 + v(\mathbf{q})\Pi^{pr}(\mathbf{q}, \omega) + [v(\mathbf{q})\Pi^{pr}(\mathbf{q}, \omega)]^2 + \dots \right) \\ \approx -\frac{2\hbar}{n_0} \Im \Pi^{pr}(\mathbf{q}, \omega) = S^0(\mathbf{q}, \omega).$$

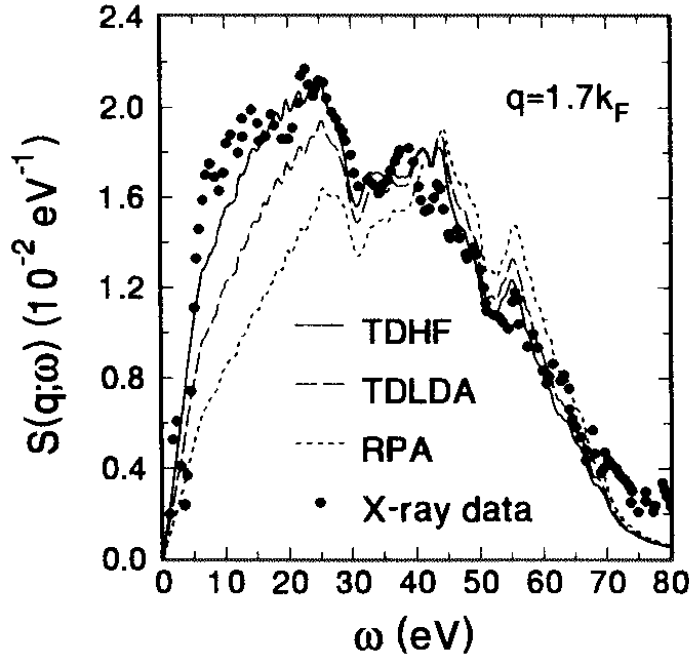
In the literature,  $S^0(\mathbf{q}, \omega)$  is used to be called the **non-interacting structure factor of the electron gas**.



Theoretical results of the non-interacting structure factor  $S^0(\mathbf{q}, \omega)$  in Al, compared to the x-ray data by Platzman *et al* (1992).

- The dashed line means the **jellium result** of  $S^0(\mathbf{q}, \omega)$  for  $r_s=2.07$  Bohr units: no "double-peak structure" appears.
- The full line ("crystal") is also based on the approximation  $S^0(\mathbf{q}, \omega)$ , **but the electron wavefunctions are no more jellium-like plane waves but crystal-like Bloch waves** ("beyond jellium", see in detail in chapter 3 of this lecture). The corresponding result is by no means a satisfying description of the experiment, but it shows quite well some of its features, especially the "double-peak structure".

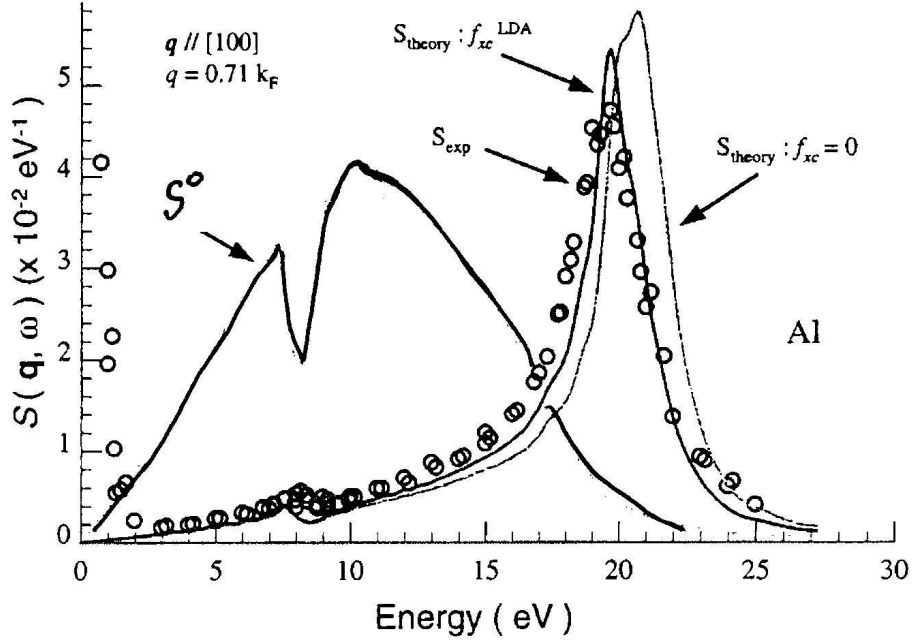




Calculated **interacting** structure factors  $S(\mathbf{q}, \omega)$  for Al. "RPA" is the pure random phase approximation, and "TDLDA" and "TDHF" mean RPA results **including local field factors**  $F(\mathbf{q})$ . All are "crystal" curves, i.e., based on electron Bloch waves.

Experimental points: Platzman *et al* (1992).

- In comparison to the previous diagram, the discussion of this figure starts with a disappointment: the "crystal" curve of the **low-level approximation**  $S^0(\mathbf{q}, \omega)$  showed a rather good agreement with experiment. It could be expected that the corresponding **full RPA**  $S(\mathbf{q}, \omega)$  gives an even better result. However, this is not the case: the RPA curve in the above figure shows the expected "double-peak structure" but lies considerably below the experimental data.
- How is this possible? How can an obviously improved theory [ $S(\mathbf{q}, \omega)$  instead of  $S^0(\mathbf{q}, \omega)$ ] lead to poorer results?
- The answer is given by the curves TDHFA and TDLDA that are based on polarisation functions  $\Pi(\mathbf{q}, \omega)$  **beyond RPA**, including correlation effects between the excited electron-hole pairs which are modeled by so-called **local field factors** (see Sec. 2.6).
- Obviously, the TDLDA and TDHFA corrections compensate errors that appear in the RP approximation.



Comparison of a measured IXSS spectrum of Al (Larson *et al*, 1996, empty circles) for a wave vector transfer  $|\mathbf{q}|=0.71k_F$  ( $\mathbf{q}$  is along the (100) direction) with calculations of the Bloch-based dielectric matrix for  $f_{xc}=0$  (no dynamical correlation effects), and  $f_{xc}$  evaluated in the LDA. **Note:**  $f_{xc}(\mathbf{q}, \omega) = -v(\mathbf{q}) F(\mathbf{q}, \omega)$ .

- In this last figure of the Al series, the relatively small wave number means that - unlike the previous figures - the physics is no more dominated by electron-hole excitations but by **collective (plasmonic) excitations** of the electron gas.
- It is clear that such a plasmon peak as shown by experiment can **in principle not be described by a non-interacting approximation to the structure factor as  $S^0(\mathbf{q}, \omega)$** .
- On the other hand, the full RP approximation  $S(\mathbf{q}, \omega)$  without any local field correction ( $f_{xc} = 0$ ) already gives a relatively good result.
- The inclusion of such a correction of the TDLDA type ( $f_{sc}^{LDA} \neq 0$ ) significantly increases the agreement between theory and experiment.

Resume: **even for a jellium-like metal like Al, a satisfying agreement between theory and experiment can only be achieved if the structure factor  $S(\mathbf{q}, \omega)$  contains both bandstructure and correlation (beyond-RPA) effects.**

## Summary Sec. 2.6: Beyond RPA: the local-field factor

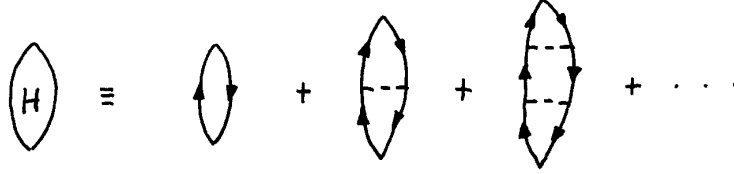
Starting from the RPA of the proper polarisation function  $\Pi^{pr,RPA}(\mathbf{q}, \omega)$ , a corresponding function **beyond RPA** can be obtained by the expression

$$\Pi^{pr}(q, \omega) = \frac{\Pi^{pr,RPA}(q, \omega)}{1 + V(q)F(q, \omega)\Pi^{pr,RPA}(q, \omega)}$$

where the generally wavenumber- and frequency-dependent function  $F(\mathbf{q}, \omega)$  is called the **dynamical local-field factor (LFF)**:

$$F(\mathbf{q}, \omega) \equiv 0 \quad \rightarrow \quad \Pi^{pr}(\mathbf{q}, \omega) = \Pi^{pr,RPA}(\mathbf{q}, \omega).$$

The first LFF has been proposed by Hubbard<sup>1</sup> and can be directly be interpreted as a so-called **ladder expansion** of the proper RP polarisation graph:



Such infinite sum of diagrams including zero, one, two... electron-hole interactions via a bare Coulomb potential can be approximately described by the **Hubbard approximation** of the proper polarisation function

$$\Pi^{pr,H}(q, \omega) = \frac{\Pi^{pr,RPA}(q, \omega)}{1 + V(q)F^H(q)\Pi^{pr,RPA}(q, \omega)}$$

including the **static LFF**

$$F^H(q) = \frac{q^2}{2(q^2 + k_F^2)}.$$

Hubbard's idea was the starting point of enormous theoretical efforts of numerous authors to find better and practically feasible LFF to improve the quality of polarisation functions.

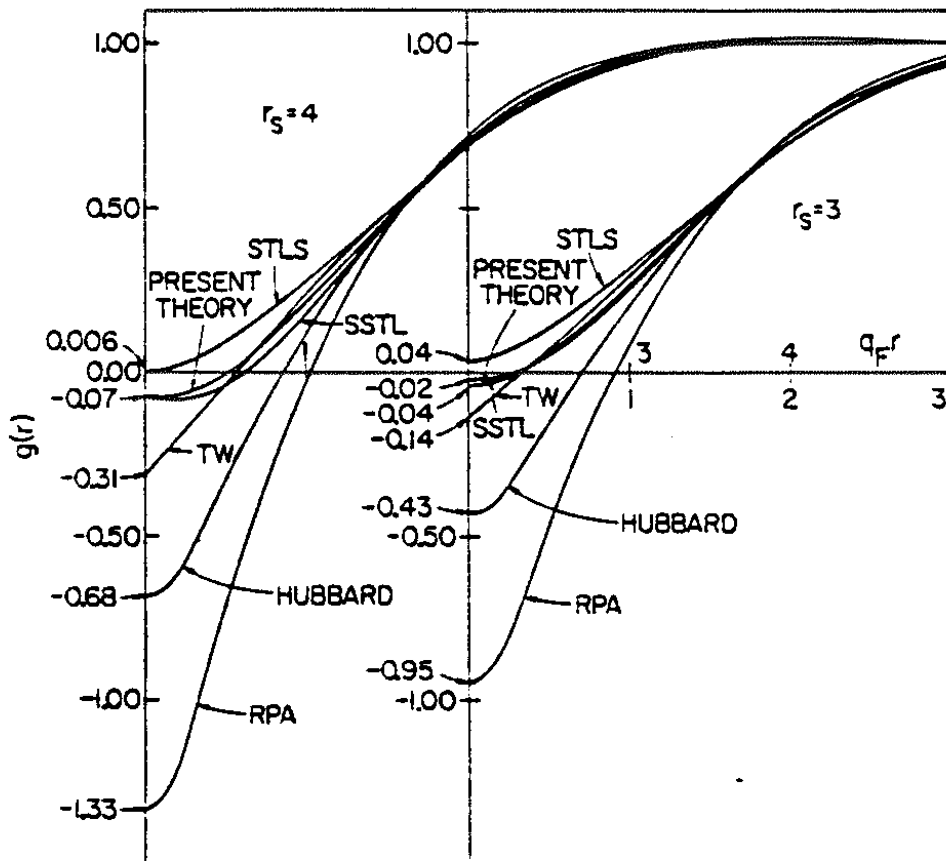
<sup>1</sup>J. Hubbard, Proc. Roy. Soc. **A 240**, 539 (1957); **A 243**, 336 (1957).

It is not the aim of this section to give an extensive overview on all these proposals; only some important milestones during the last fifty years shall be mentioned here:

H = Hubbard 1957, STLS = Singwi, Tosi, Land, Sjölander 1968, SSTL = Singwi, Sjölander, Tosi, Land 1970, TW = Toigo and Woodruff 1971, VS = Vashishta and Singwi 1972.

- Remember: each of the above local-field factors leads to a "beyond-RPA" polarisation function  $\Pi(\mathbf{q}, \omega)$  and, consequently, to a corresponding new dielectric function  $\kappa(\mathbf{q}, \omega)$ .
- The quality of each dielectric function can be tested by calculating the corresponding **pair correlation function  $g(r)$** , due to the general condition of  $g(r)$  that reads

$$g(r) \geq 0 \quad \text{for all } r \quad \text{and} \quad g(r \rightarrow \infty) = 1.$$



Pair correlation  $g(r)$  for  $r_s = 3$  and 4 Bohr units for the various theoretical descriptions of  $\Pi(q, \omega)$  and  $\kappa(q, \omega)$  given above.

"PRESENT THEORY" means Vashishta and Singwi, 1972.

- As it has been already discussed in Sec. 2.3.1, the *random-phase approximation* violates the condition  $g(r) \geq 0$  for small values of  $r$ ; this violation increases with increasing electron density parameter  $r_s$ .
- It is clear that Hubbard's correction to the RPA is not able to clarify the situation, **but his idea goes - evidently - into the right direction.**
- Many of the more elaborated local-field factors mentioned above (especially STLS, SSTL, and VS) fulfill (or are nearly to fulfill) the condition  $g(r) \geq 0$  for all values of  $r$ .
- The second condition  $g(r \rightarrow \infty) = 1$  is fulfilled by all pair correlation factors shown in the above figure.

In some of the diagrams concerning Al shown above, some of the  $S(\mathbf{q}, \omega)$  curves have been calculated by using static local-field factors named TDLDA and TDHF:

- **TDLDA** means **time-dependent local-density approximation**, and the corresponding LLF reads

$$F^{TDLDA}(\mathbf{q}) = -V(q) \int d^3x e^{-i\mathbf{q}\cdot\mathbf{x}} \frac{dV_{xc}(\mathbf{x})}{dn(\mathbf{x})},$$

where  $V_{xc}(\mathbf{x})$  means the LDA to the exchange-correlation potential in the crystal potential. Details about this function see, e.g., Zangwill and Soven, Phys. Rev. A **21**, 1561 (1980).

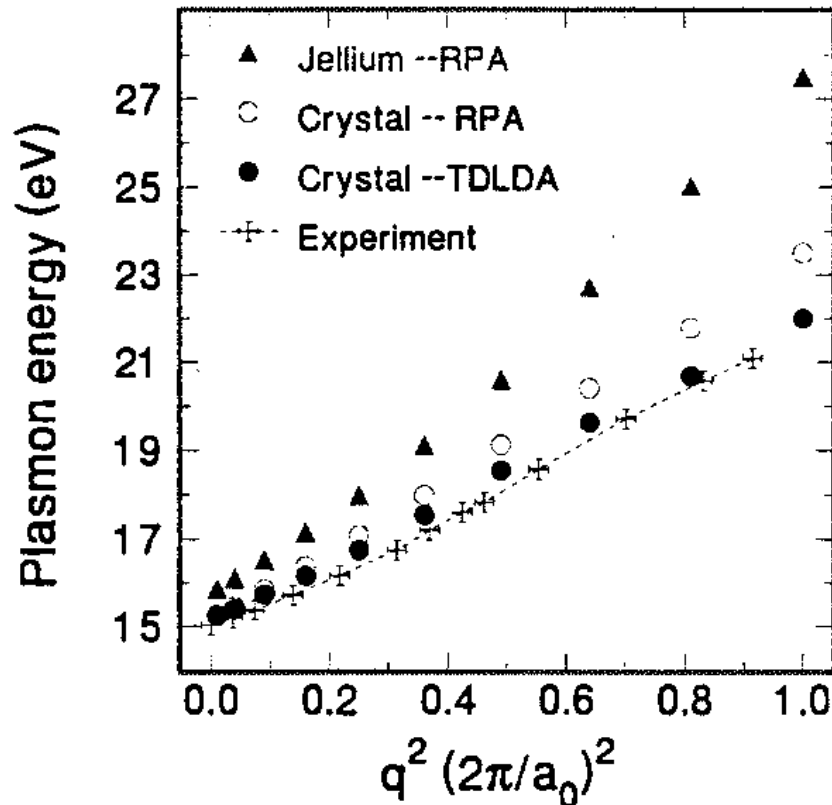
- The second approach **TDHF = time-dependent Hartree-Fock** is described in F. Brosens, J. T. Devreese, and L. F. Lemmens, Phys. Rev. B **21**, 1363 (1980).

## Plasmon dispersion in metals: Al

Theory: A. G. Eguiluz, A. Fleszar, and J. A. Gaspar,  
Nucl. Inst. and Meth. B **96**, 550 (1995)

Experiment (EELS): J. Sprösser-Prou, A.vom Felde,  
and J. Fink, PRB **40**, 5799 (1989).

### Plasmon dispersion in Al



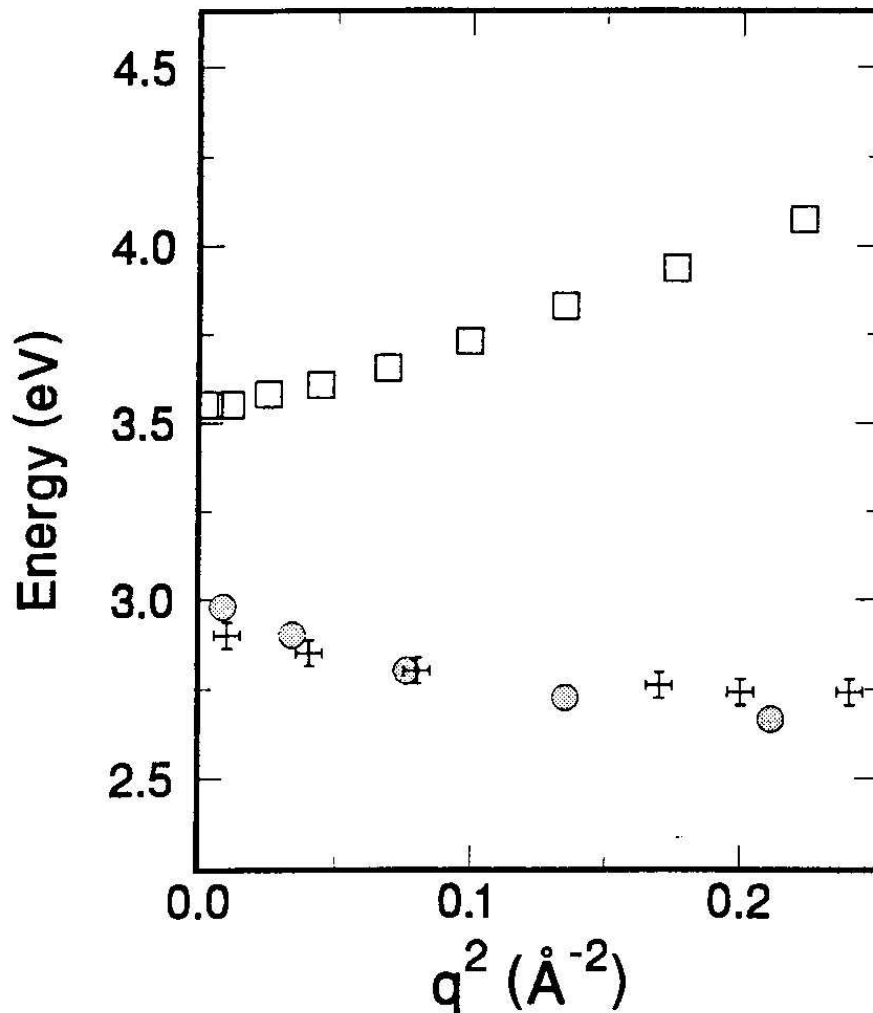
Plasmon dispersion in Al along the direction [100]. The figure shows calculated RPA and TDLDA dispersion curves for Al "crystal", and the RPA curve for jellium with  $r_s=2.07$  Bohr units.

- There is a large difference between the theoretical "jellium-RPA" result and the experimental data.
- Going **beyond jellium**, the "crystal-RPA" result (based on electron Bloch states) reduces this difference significantly.
- If one goes both **beyond jellium** and **beyond RPA** (by using a TDLDA local-field factor), one gets an almost perfect agreement between theory and experiment.

## Plasmon dispersion in metals: Cs

Theory: A. G. Eguiluz,  
Int.J. Quant. Chem. **30**, 1457 (1996).

Experiment (EELS): J. Sprösser-Prou, A.vom Felde,  
and J. Fink, PRB **40**, 5799 (1989).



Plasmon dispersion in Cs along the direction [110].

Squares: the jellium-RPA curve with  $r_s=5.6$  Bohr units,  
circles: the crystal-RPA curve including the TDLDA local-field factor, crosses: experimental data.

- The theoretical "jellium-RPA" result is quantitatively and qualitatively different to the experimental data.
- Going both beyond jellium and beyond RPA, the agreement between theory and experiment including the negative slope of the dispersion curve for small  $|q|$  is convincing.