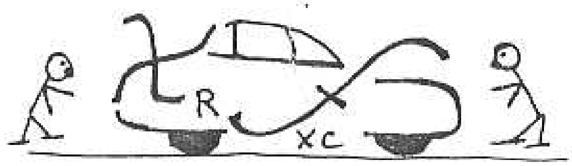
Robert van Leeuwen 27.7.99

χ_R and f_{xc} :

A glance under the hood:.
... and in the trunk.



References

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- G.D. Mahan, Many-Particle Physics (sum rules)
- E.K.U. Gross, W. Kohn, PRL 55, 2850 (1985) (f_{xc})
- D. Mearns, W. Kohn, Phys. Rev. A 35, 4796 (1987) ($\check{\chi}_R$)
- A.L. Fetter, J.D. Walecka, Quantum Theory of Many-Particle Systems (response theory)

Linear Response Theory

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \qquad , \qquad i\partial_t |\Psi_S\rangle = \hat{H}|\Psi_S\rangle$$

In the interaction picture

$$|\Psi_I\rangle = e^{i\hat{H}_0 t}\,|\Psi\rangle$$

$$\hat{V}_I(t) = e^{i\hat{H}_0 t}\,\hat{V}(t)\,e^{-i\hat{H}_0 t}$$

The Schrödinger eqn. becomes : $i\partial_t |\Psi_I\rangle = \hat{V}_I(t)\,|\Psi_I\rangle$

Integration yields

$$|\Psi_I\rangle(t) = |\Psi_I\rangle(t_0) - i\int_{t_0}^{t} dt'\,\hat{V}_I(t')\,|\Psi_I\rangle(t')$$

$$= |\Psi_I\rangle(t_0) - i\int_{t_0}^{t} dt'\,\hat{V}_I(t')\,|\Psi_I\rangle(t_0) + (-i)^2\int_{t_0}^{t} dt'\int_{t_0}^{t'} dt''\,\hat{V}_I(t')\hat{V}_I(t'')\,|\Psi_I\rangle(t_0) + \ldots$$

The change in the expectation value of an operator $\hat{A}$, due to the perturbation $\hat{V}(t)$ becomes:

@ Assuming the perturbation is turned on at t_0

$$\delta\langle\hat{A}(t)\rangle = \langle\Psi(t)|\hat{A}|\Psi(t)\rangle - \langle\Psi(t_0)|\hat{A}|\Psi(t_0)\rangle =$$

$$= -i\int_{t_0}^{t} dt'\,\langle\Psi(t_0)|\,[\hat{A}_{H_0}(t),\hat{V}_I(t')]\,|\Psi(t_0)\rangle +$$

$$+ (-i)^2\int_{t_0}^{t} dt'\int_{t_0}^{t'} dt''\,\langle\Psi(t_0)|\,[[\hat{A}_{H_0}(t),\hat{V}_I(t')],\hat{V}_I(t'')]\,|\Psi(t_0)\rangle + \ldots$$

where $\hat{A}_{H_0}(t) = e^{i\hat{H}_0 t}\,\hat{A}\,e^{-i\hat{H}_0 t}$

Let us now look at the density response : $\hat{A} = \hat{n}(r)$

and $\hat{V}_I(t) = \int d^3r\,\hat{n}_{H_0}(r,t)\,\delta v(r,t)$

δv = a small perturbing potential

and $\delta v = 0$ for $t < t_0$.

$$\rightarrow \quad \delta\langle \hat{n}(rt)\rangle = \int_{t_0}^{+\infty} dt' \int d^3r' \, \chi_R^{(1)}(rt, r't')\, \delta v(r't') \; +$$

$$+ \int_{t_0}^{+\infty} dt' \int_{t_0}^{+\infty} dt'' \int d^3r' d^3r'' \, \chi_R^{(2)}(rt, r't', r''t'')\, \delta v(r't')\, \delta v(r''t'') + \ldots$$

where we defined

$$i\chi_R^{(1)}(rt, r't') = \theta(t-t') \langle \Psi_0 | [\hat{n}_{H_0}(rt), \hat{n}_{H_0}(r't')] | \Psi_0 \rangle$$

$$i^2 \chi_R^{(2)}(rt, r't', r''t'') = \theta(t-t')\theta(t'-t'') \langle \Psi_0 | [[\hat{n}_{H_0}(rt), \hat{n}_{H_0}(r't')], \hat{n}_{H_0}(r''t'')] | \Psi_0 \rangle$$

$$\vdots$$

($\chi_R^{(1)}(rt, r't')$ is the retarded linear density response function

In the following we will write $\chi_R^{(1)} = \chi_R$ and $\hat{H}_0 = \hat{H}$, i.e.

$$\underline{\underline{\chi_R(rt, r't') = -i\,\theta(t-t') \langle \Psi_0 | [\hat{n}_H(rt), \hat{n}_H(r't')] | \Psi_0 \rangle}}$$

<u>Pole structure of χ_R</u>

From the definition of χ_R we have

$$i\chi_R(rt, r't') = \langle \Psi_0 | \hat{n}_H(rt)\hat{n}_H(r't') - \hat{n}_H(r't')\hat{n}_H(rt) | \Psi_0 \rangle$$

$$= \sum_s \Big\{ e^{i(E_0 - E_{N,s})(t-t')} \langle \Psi_0 | \hat{n}(r) | N,s \rangle \langle N,s | \hat{n}(r') | \Psi_0 \rangle$$

$$- e^{-i(E_0 - E_{N,s})(t-t')} \langle \Psi_0 | \hat{n}(r') | N,s \rangle \langle N,s | \hat{n}(r) | \Psi_0 \rangle \Big\}$$

Where $\hat{H}\,|N,s\rangle = E_{N,s}\,|N,s\rangle$

N - particle eigenstates (labeled by s) of the unperturbed Hamiltonian $\hat{H}$.

One finds the representation

$$\chi_R(r,r';t-t') = -i\,\theta(t-t')\sum_s e^{-i\Omega_{N,s}(t-t')} f_{N,s}(r) f^*_{N,s}(r') + c.c.$$

where
$$\begin{cases} f_{N,s}(r) = \langle \Psi_0 | \hat{n}(r) | N,s \rangle \\ \Omega_{N,s} = E_{N,s} - E_0 = \text{excitation energies of } \hat{H} \end{cases}$$

(Note: $\sum_s$ denotes an integration over s in the continous part of the spectrum)

We observe: 1. χ_R only depends on $t-t'$. This is because $\hat{H}$ is time-independent

2. χ_R is a real function

Fourier transforms:
$$\begin{cases} \tilde{\chi}_R(r,r';\omega) = \int_{-\infty}^{+\infty} d\tau\, e^{i\omega\tau} \chi_R(r,r';\tau) \\ \chi_R(r,r';\tau) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau} \tilde{\chi}_R(r,r';\omega) \end{cases}$$

χ_R is real and therefore $\tilde{\chi}_R^*(r,r';\omega) = \tilde{\chi}_R(r,r';-\omega)$

$$\rightarrow \begin{cases} \mathrm{Re}\,\tilde{\chi}_R(r,r';\omega) = \mathrm{Re}\,\tilde{\chi}_R(r,r';-\omega) & \text{even} \\ \mathrm{Im}\,\tilde{\chi}_R(r,r';\omega) = -\mathrm{Im}\,\tilde{\chi}_R(r,r';-\omega) & \text{odd} \end{cases}$$

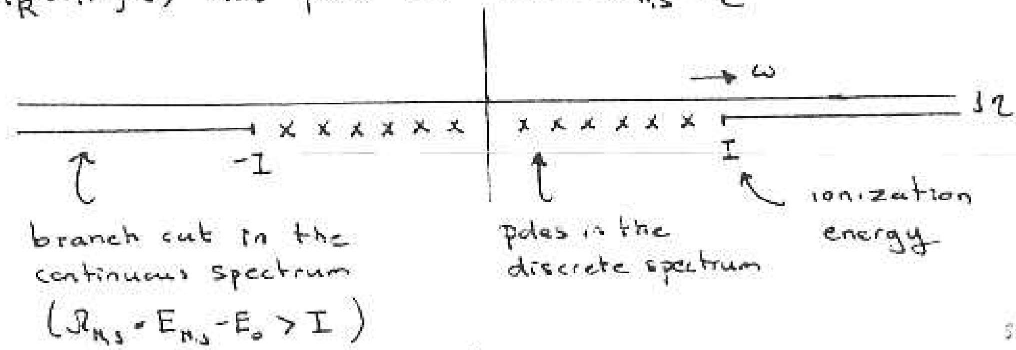
Using:
$$\theta(\tau) = \lim_{\eta\to 0^+} \frac{-1}{2\pi i} \int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega\tau}}{\omega + i\eta}$$

we can do the fourier transform of χ_R and find

$$\tilde{\chi}_R(r,r';\omega) = \lim_{\eta\to 0^+} \sum_s \left\{ \frac{f_{N,s}(r) f^*_{N,s}(r')}{\omega - \Omega_{N,s} + i\eta} - \frac{f^*_{N,s}(r) f_{N,s}(r')}{\omega + \Omega_{N,s} + i\eta} \right\}$$

$$+ \frac{f_s^*(r) f_s(r')}{-\omega - \Omega_s - i\eta}$$

$\tilde{\chi}_R(r,r';\omega)$ has poles at $\omega = \pm\Omega_{n,s} - i\eta$



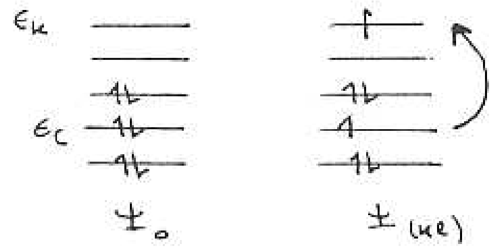
All poles are in the lower half plane

$\rightarrow$ $\tilde{\chi}_R(r,r';\omega)$ is an analytic function for $\mathrm{Im}\,\omega > 0$.

Noninteracting case

$$f_{N,(kl)}(r) = \langle \Psi_0 | \hat{n}(r) | \Psi_{(kl)} \rangle$$

$\hookrightarrow$ singly excited Slater determinant



$$\Omega_{kl} = \epsilon_k - \epsilon_l = E_{N,(kl)} - E_0$$

Expand field operators in single particle eigenstates

$$\hat{\Psi}(r) = \sum_j \varphi_j(r)\, \hat{a}_j \qquad \hat{\Psi}^+(r) = \sum_j \varphi_j^*(r)\, \hat{a}_j^+$$

$$\rightarrow \hat{n}(r) = \hat{\Psi}^+(r)\hat{\Psi}(r) = \sum_{ij} \varphi_i^*(r)\varphi_j(r)\, \hat{a}_i^+ \hat{a}_j$$

$$\rightarrow f_{N,(kl)}(r) = \sum_{ij} \varphi_i^*(r)\varphi_j(r) \langle \Psi_0 | \hat{a}_i^+ \hat{a}_j | \Psi_{(kl)} \rangle$$

$\hookrightarrow$ nonzero if $\begin{cases} j = k, & k > N \\ i = l, & l \leq N \end{cases}$

With occupation number $\mu_i = \begin{cases} 1 & i \leq N \\ 0 & i > N \end{cases}$

we find: $f_{N,(kl)}(r) = \mu_l (1 - \mu_k)\, \varphi_l^*(r) \varphi_k(r)$

We find

$$\tilde{\chi}_{0,R}(r,r';\omega) = \lim_{\eta\to 0^+} \sum_{kl} \Big\{ \mu_l(1-\mu_k)\, \frac{\varphi_l^*(r)\varphi_k(r)\varphi_l(r')\varphi_k^*(r')}{\omega-(\epsilon_k-\epsilon_l)+i\eta}$$

$$- \mu_l(1-\mu_k)\, \frac{\varphi_l(r)\varphi_k^*(r)\varphi_l^*(r')\varphi_k(r')}{\omega+(\epsilon_k-\epsilon_l)+i\eta} \Big\}$$

↳ interchange k and l in the second part

$$\rightarrow \tilde{\chi}_{0,R}(r,r';\omega) = \lim_{\eta\to 0^+} \sum_{kl} (\mu_l-\mu_k)\, \frac{\varphi_k(r)\varphi_l^*(r)\varphi_k^*(r')\varphi_l(r')}{\omega-(\epsilon_k-\epsilon_l)+i\eta}$$

Noninteracting retarded density response function

For a time reversal invariant system we can always choose the states $|N,s\rangle$ and $|\Psi_0\rangle$ to be real.

Then: $\quad f_{N,s}(r) = f^*_{N,s}(r) \quad$ and

$$\tilde{\chi}_R(r,r',\omega) = \sum_s f_{N,s}(r) f_{N,s}(r') \left\{ \frac{1}{\omega-\Omega_{N,s}+i\eta} - \frac{1}{\omega+\Omega_{N,s}+i\eta} \right\}$$

With the formula $\quad \displaystyle\lim_{\eta\to 0} \frac{1}{\omega+i\eta} = P\left(\frac{1}{\omega}\right) - i\pi\,\delta(\omega)$,

↳ principle value (distribution)

we obtain

$$\mathrm{Re}\,\tilde{\chi}_R(r,r';\omega) = \sum_s f_{N,s}(r) f_{N,s}(r')\, P\left(\frac{1}{\omega-\Omega_{N,s}} - \frac{1}{\omega+\Omega_{N,s}}\right) =$$

$$= \sum_s f_{N,s}(r) f_{N,s}(r')\, P\left(\frac{2\Omega_{N,s}}{\omega^2-\Omega_{N,s}^2}\right)$$

and

$$\mathrm{Im}\,\tilde{\chi}_R(r,r';\omega) = -\pi \sum_s f_{N,s}(r) f_{N,s}(r') \left[\delta(\omega-\Omega_{N,s}) - \delta(\omega+\Omega_{N,s})\right]$$

$\mathrm{Re}\,\tilde{\chi}_R$ and $\mathrm{Im}\,\tilde{\chi}_R$ are resp. even and odd functions of ω

We see immediately that

$$\mathrm{Re}\,\tilde{\chi}_R(r,r';\omega) = -P\int_{-\infty}^{+\infty} d\omega' \frac{1}{\pi} \frac{\mathrm{Im}\,\tilde{\chi}_R(r,r';\omega')}{\omega-\omega'}$$

This is one of the Kramers-Kronig relations. The other one is:

$$\mathrm{Im}\,\tilde{\chi}_R(r,r';\omega) = P\int_{-\infty}^{+\infty} d\omega' \frac{1}{\pi} \frac{\mathrm{Re}\,\tilde{\chi}_R(r,r';\omega')}{\omega-\omega'}$$

With use of: $\delta(s-t) = \frac{1}{\pi^2}\int_{-\infty}^{+\infty} \frac{1}{(x-s)(x-t)}\,dx$ this can also be explicitly verified.

<u>Kramers-Kronig theorem:</u>

If $f(\omega)$ is analytic for $\mathrm{Im}\,\omega > 0$ and $|f(\omega)| \to 0$ $(\omega\to\infty)$ then:

$$\begin{cases} \mathrm{Re}\,f(\omega) = -\frac{1}{\pi} P\int_{-\infty}^{+\infty} d\omega' \frac{\mathrm{Im}\,f(\omega')}{\omega-\omega'} \\ \mathrm{Im}\,f(\omega) = \frac{1}{\pi} P\int_{-\infty}^{+\infty} d\omega' \frac{\mathrm{Re}\,f(\omega')}{\omega-\omega'} \end{cases}$$

We can therefore always construct $\tilde{\chi}_R$ from $\mathrm{Re}\,\tilde{\chi}_R$ or $\mathrm{Im}\,\tilde{\chi}_R$.

Another way of expressing this is:

<u>Spectral Representation of $\tilde{\chi}_R$</u>

$$\tilde{\chi}_R(r,r';\omega) = \int_{-\infty}^{+\infty} d\omega' \frac{A(r,r';\omega')}{\omega-\omega'+i\eta}$$

Spectral function:

$$A(r,r';\omega) = \sum_s \left\{ f_{N,s}(r) f^*_{N,s}(r')\,\delta(\omega-\Omega_{N,s}) - f^*_{N,s}(r) f_{N,s}(r')\,\delta(\omega+\Omega_{N,s}) \right\}$$

If A is real $(f_{N,s} = f^*_{N,s})$

then:

$$\begin{cases} A(r,r';\omega) = \sum_s f_{N,s}(r) f_{N,s}(r')\left[\delta(\omega-\Omega_{N,s}) - \delta(\omega+\Omega_{N,s})\right] \\ A(r,r';\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,\tilde{\chi}_R(r,r';\omega) \end{cases}$$

Knowledge of the spectral function determines $\tilde{\chi}_R$.

Large-ω-behavior of $\tilde{\chi}_R$ and sum rules

$$\tilde{\chi}_R(r,r';\omega) = \lim_{\eta\to 0^+} \sum_s f_{N,s}(r) f_{N,s}(r') \left[\frac{1}{\omega - \Omega_{N,s} + i\eta} - \frac{1}{\omega + \Omega_{N,s} + i\eta} \right]$$

$$= \sum_s f_{N,s}(r) f_{N,s}(r') \left[\frac{2\Omega_{N,s}}{\omega^2} + \frac{2\Omega_{N,s}^3}{\omega^4} + \dots \right] \quad (\omega \to \infty)$$

$$= \frac{c_1}{\omega^2} + \frac{c_3}{\omega^4} + \frac{c_5}{\omega^6} + \dots \quad (\omega \to \infty)$$

For odd n we have

$$c_n = 2 \sum_s (\Omega_{N,s})^n f_{N,s}(r) f_{N,s}(r') = -\frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega\, \omega^n \,\mathrm{Im}\, \tilde{\chi}_R(r,r',\omega)$$

(For c_1 we can write

$$c_1 = \sum_s \Omega_{N,s} \left(f_{N,s}(r) f_{N,s}(r') + f_{N,s}(r') f_{N,s}(r) \right) =$$

$$c_1 = \sum_s \Big\{ \langle \Psi_0 | \hat{n}(r) | N,s \rangle (E_{N,s} - E_0) \langle N,s | \hat{n}(r') | \Psi_0 \rangle +$$
$$\langle \Psi_0 | \hat{n}(r') | N,s \rangle (E_{N,s} - E_0) \langle N,s | \hat{n}(r) | \Psi_0 \rangle \Big\}$$

$$c_1 = \langle \Psi_0 | \hat{n}(r) \hat{H} \hat{n}(r') | \Psi_0 \rangle - \langle \Psi_0 | \hat{n}(r) \hat{n}(r') \hat{H} | \Psi_0 \rangle$$
$$+ \langle \Psi_0 | \hat{n}(r') \hat{H} \hat{n}(r) | \Psi_0 \rangle - \langle \Psi_0 | \hat{H} \hat{n}(r') \hat{n}(r) | \Psi_0 \rangle,$$

($$c_1 = -\langle \Psi_0 | [[\hat{H}, \hat{n}(r)], \hat{n}(r')] | \Psi_0 \rangle$$

Similarly for c_3 one finds:

$$c_3 = -\langle \Psi_0 | [[\hat{H}, [\hat{H}, [\hat{H}, \hat{n}(r)]]], \hat{n}(r')] | \Psi_0 \rangle$$

We therefore have

$$-\frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega\, \omega \,\mathrm{Im}\, \tilde{\chi}_R(r,r';\omega) = -\langle \Psi_0 | [[\hat{H}, \hat{n}(r)], \hat{n}(r')] | \Psi_0 \rangle = c_1$$

This is known as the f-sum rule

We further have

$$-\frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega\, \omega^3 \, \mathrm{Im}\, \tilde{\chi}_R(r,r';\omega) = -\langle\Psi_0|[\hat{H},[\hat{H},[\hat{H},\hat{n}(r)]],\hat{n}(r')]|\Psi_0\rangle = c_3$$

third frequency sum rule

c_1 can be rewritten as:

$$c_1 = -\langle\Psi_0|[[\hat{H},\hat{n}(r)],\hat{n}(r')]|\Psi_0\rangle = i\langle\Psi_0|[\nabla\cdot\hat{j}(r),\hat{n}(r')]|\Psi_0\rangle$$

$$= i\nabla_r\cdot\langle\Psi_0|[\hat{j}(r),\hat{n}(r')]|\Psi_0\rangle = i\nabla_r(i\nabla_{r'}(\delta(r'-r)\,n(r')))$$

$$= -\nabla_r\cdot\nabla_{r'}(\delta(r'-r)\,n(r'))$$

The f-sum rule becomes:

$$-\frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega\, \omega \, \mathrm{Im}\, \tilde{\chi}_R(r,r';\omega) = -\nabla_r\cdot\nabla_{r'}(\delta(r-r')\,n(r'))$$

c_3 can also be worked out and leads to expressions involving the stress-momentum tensor.

Polarization

From $\delta n(rt) = \int_{-\infty}^{+\infty} dt' \int d^3r'\, \chi_R(r,r';t-t')\,\delta v(r't')$

$(\delta v = 0\ ,\ t < t_0)$

we find by Fourier transforming

$$\delta\tilde{n}(r\omega) = \int d^3r'\, \tilde{\chi}_R(r,r';\omega)\,\delta\tilde{v}(r'\omega)$$

Polarization $\vec{P}(\omega) = \int d^3r\, \vec{r}\,\delta\tilde{n}(r\omega) =$

$$= \int d^3r \int d^3r'\, \vec{r}\,\tilde{\chi}_R(r,r';\omega)\,\delta\tilde{v}(r'\omega)$$

Dipole field: $\begin{cases} \delta v(rt) = \vec{r}\cdot\vec{E}(t) \\ \delta\tilde{v}(r\omega) = \vec{r}\cdot\vec{\tilde{E}}(\omega) \end{cases}$

$$\rightarrow \quad P_i(\omega) = \sum_j \alpha_{ij}(\omega)\,\tilde{E}_j(\omega)$$

where $\quad \alpha_{ij}(\omega) = \int d^3r \int d^3r' \;\; x_i\, \tilde{\alpha}_R(r,r';\omega)\, x_j$

$\alpha_{ij}(\omega)$ = linear polarizability tensor

If we define $\quad F_s^{(i)} = \int d^3r \;\; x_i \langle \Psi_0 | \hat{n}(r) | N,s\rangle = \langle \Psi_0 | \hat{x}_i | N,s\rangle$

position operator

then

$$\alpha_{ij}(\omega) = \lim_{\eta \to 0^+} \sum_s F_s^{(i)} F_s^{(j)} \left\{ \frac{1}{\omega - \Omega_{N,s} + i\eta} - \frac{1}{\omega + \Omega_{N,s} + i\eta} \right\}$$

$$= \sum_s \frac{2\Omega_{N,s} F_s^{(i)} F_s^{(j)}}{\omega^2 - \Omega_{N,s}^2} - i\pi \sum_s F_s^{(i)} F_s^{(j)} \left[\delta(\omega - \Omega_{N,s}) - \delta(\omega + \Omega_{N,s}) \right]$$

Fermi's Golden Rule yields a relation between $\mathrm{Im}\,\alpha_{ij}(\omega)$ and the photoabsorption cross section.

$$\sigma_{ij}(\omega) = \frac{4\pi\omega}{c}\,\mathrm{Im}\,\alpha_{ij}(\omega)$$

From the f-sumrule we have

$$\int_{-\infty}^{+\infty} d\omega \;\; \omega \;\; \mathrm{Im}\,\alpha_{ij}(\omega) = \pi \langle \Psi_0 | [[\hat{H},\hat{x}_i],\hat{x}_j] | \Psi_0 \rangle$$

$\hat{x}_i = \int d^3r \; x_i\, \hat{n}(r) = \sum_k^N (x_i)_k \quad$ position operator

N = number of electrons

Further we have

$$[[\hat{H},\hat{x}_i],\hat{x}_j] = -i\,[\hat{p}_i,\hat{x}_j] = -\delta_{ij} N$$

We obtain $\quad -\frac{2}{\pi} \int_0^{+\infty} d\omega \;\; \omega \;\; \mathrm{Im}\,\alpha_{ij}(\omega) = \delta_{ij} N$

This yields a sumrule for the photo-ionization cross section

$$\int_0^{+\infty} d\omega \;\; \sigma_{ij}(\omega) = \frac{2\pi^2 N}{c}\,\delta_{ij}$$

Another sumrule follows from the Kramers-Kronig relation at $\omega = 0$.

$$\mathrm{Re}\,\tilde{\chi}_R(r,r',0) = \frac{2}{\pi}\int_0^{+\infty} d\omega' \,\frac{1}{\omega'}\,\mathrm{Im}\,\tilde{\chi}_R(r,r';\omega')$$

This yields

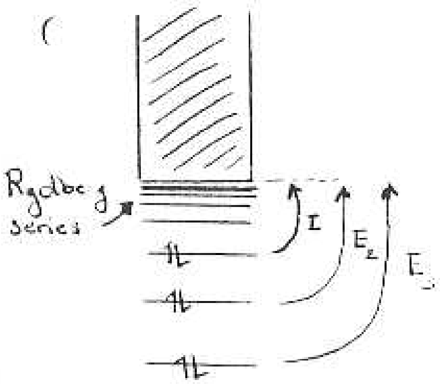
$$\int_0^{+\infty} d\omega \,\frac{1}{\omega}\,\mathrm{Im}\,\alpha_{ij}(\omega) = \alpha_{ij}(0)\,\frac{\pi}{2}$$

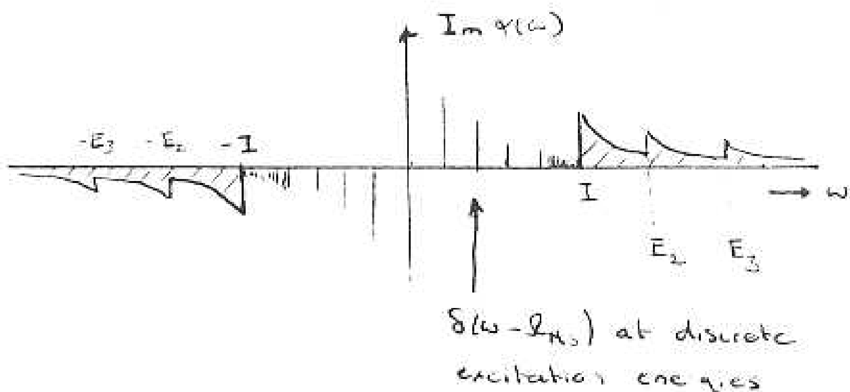
static polarizability

Let us take a system with only an $\alpha_{zz}(\omega)$-component.

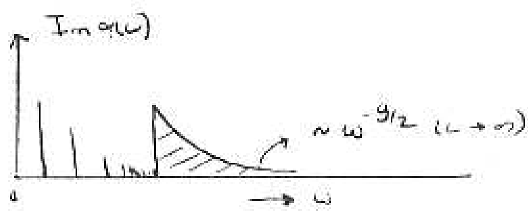
$P_z(\omega) = \alpha(\omega)\,\tilde{E}_z(\omega)$

How does $\mathrm{Im}\,\alpha(\omega)$ typically look like?

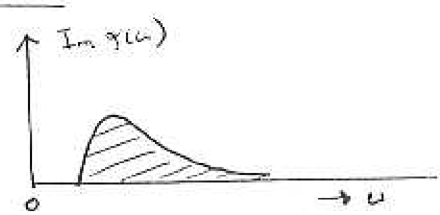




$\omega > I$: electrons can be excited into the continuum (photoelectric effect)



H-atom



H^--atom

H^- has only one bound state and no Rydberg series

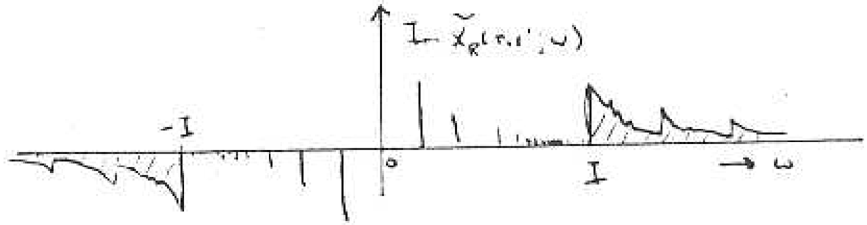
$\rightarrow$ the sharp ionization edge disappears.

How will $\operatorname{Im} \tilde{\chi}_R(r,r',\omega)$ typically look like? (finite system)

Recall that

$$\left\{ \begin{array}{l} \tilde{\chi}_R(r,r';\omega) = \displaystyle\int_{-\infty}^{+\infty} d\omega' \, \frac{A(r,r';\omega)}{\omega - \omega' + i\eta} \\[2ex] A(r,r',\omega) = -\frac{1}{\pi} \operatorname{Im} \tilde{\chi}_R(r,r',\omega) \end{array} \right.$$

From the previous results we can infer that $\operatorname{Im} \tilde{\chi}_R(r,r',\omega)$ for a finite neutral Coulomb system (atom, molecule) looks somewhat like: (r, r' fixed)



This gives a qualitative picture of the spectral function A, which determines the full density response $\tilde{\chi}_R$

With the information we have gathered on $\tilde{\chi}_R$ we can now discuss the properties of f_{xc}.

f_{xc}

$$f_{xc}(rt, r't') = \frac{\delta v_{xc}(rt)}{\delta n(r't')} \qquad v_{xc} = xc\text{-potential}$$

Kohn-Sham potential: $\quad v_s = v + \int \frac{n}{r_{12}} + v_{xc}$

Then

$$\chi_R = \frac{\delta n}{\delta v} = \int \frac{\delta n}{\delta v_s} \cdot \frac{\delta v_s}{\delta v} = \int \chi_{R,0} \left(\delta + \int \frac{\delta n}{\delta v} \frac{1}{r_{12}} + \int f_{xc} \frac{\delta n}{\delta v} \right)$$

$$= \chi_{R,0} + \chi_{R,0} \left(\frac{1}{r_{12}} + f_{xc} \right) \chi_R \quad , \qquad \chi_{R,0} = \frac{\delta n}{\delta v_s}$$

In Fourier space

$$\tilde{\chi}_R(r,r';\omega) = \tilde{\chi}_{R,0}(r,r';\omega) + \int d^3y\, d^3y'\, \tilde{\chi}_{R,0}(ry;\omega) \left[\frac{1}{|y-y'|} + \tilde{f}_{xc}(yy',\omega) \right] \tilde{\chi}_R(y'r';\omega)$$

This is a Dyson-like Eqn. for $\tilde{\chi}_R$.
Formally solving for $\tilde{f}_{xc}$ yields:

$$\tilde{f}_{xc}(r,r',\omega) = \tilde{\chi}_{R,0}^{-1}(r,r';\omega) - \tilde{\chi}_R^{-1}(r,r';\omega) - \frac{1}{|r-r'|}$$

Let us study the properties of $\tilde{\chi}_R^{-1}$.

$\tilde{\chi}_R$ is a real function in the discrete spectrum $(-I < \omega < I)$ if $\omega \neq \Omega_{Ms}$. Then $\tilde{\chi}_R(r,r';\omega)$ is a real Hermitian integral kernel with a complete set of eigenstates

$$\int d^3r'\, \tilde{\chi}_R(r,r';\omega)\, \varphi_k(r'\omega) = \lambda_k(\omega)\, \varphi_k(r\omega)$$

Since $\tilde{\chi}_R(r,r';\omega) = \tilde{\chi}_R(r,r';-\omega)$ for these frequencies we have $\lambda_k(\omega) = \lambda_k(-\omega)$. The eigenfunctions can be chousen to be real and satisfy $\varphi_k(r\omega) = \varphi_k(r,-\omega)$

For $(-I < \omega < I)$, $\omega \neq R_{KS}$ we can therefore write

$$\begin{cases} \tilde{\chi}_R(r,r';\omega) = \sum_k \lambda_k(\omega)\, \varphi_k(r\omega)\, \varphi_k(r'\omega) \\ \tilde{\chi}_R^{-1}(r,r';\omega) = \sum_k \frac{1}{\lambda_k(\omega)}\, \varphi_k(r\omega)\, \varphi_k(r'\omega) \end{cases}$$

The function $\varphi_k(r\omega)$ corresponds to a potential variation that yields a density variation that is proportional to it.

If there is a $\omega = \bar{\omega}$ such that $\lambda_k(\bar{\omega}) = 0$ (and thus also $\lambda_k(-\bar{\omega}) = 0$), then

$$\delta\tilde{v}(r\omega) = \mu\left(\delta(\omega-\bar{\omega}) + \delta(\omega+\bar{\omega})\right) \varphi_k(r\omega)$$

yields

$$\delta\tilde{n}(r\omega) = \int d^3r'\, \tilde{\chi}_R(r,r';\omega)\, \delta\tilde{v}(r'\omega) =$$

$$= \mu\left(\delta(\omega+\bar{\omega}) + \delta(\omega-\bar{\omega})\right) \lambda_k(\omega)\, \varphi_k(r\omega) = 0$$

In that case

$$\delta v(rt) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, \tilde{v}(r\omega)\, e^{-i\omega t} = \frac{\mu}{2\pi} \varphi_k(r\bar{\omega}) \left(e^{i\bar{\omega}t} + e^{-i\bar{\omega}t}\right)$$

$$= \frac{\mu}{\pi} \varphi_k(r\bar{\omega}) \cos(\bar{\omega}t)$$

This is a plane wave field that exists at all times and does not correspond to a suith-on at t_0.

For a $\delta v(rt)$ of the form $\delta v(rt) = \theta(t-t_0)\, \delta w(rt)$ $(\delta w \neq C(t))$ one always has $\delta n \neq 0$. This follows directly from the proof of the Runge-Gross theorem.

We can now write $(-I < \omega < I)$

$$\tilde{f}_{xc}(r,r';\omega) = \sum_k \left\{ \frac{1}{\lambda_{o,k}(\omega)} \varphi_{o,k}(r\omega)\varphi_{o,k}(r'\omega) - \frac{1}{\lambda_k(\omega)} \varphi_k(r\omega)\varphi_k(r'\omega) \right\} - \frac{1}{|r-r'|}$$

Where similarly $\int d^3r' \, \tilde{\alpha}_{o,R}(r,r';\omega)\, \varphi_{o,k}(r'\omega) = \lambda_{o,k}(\omega)\, \varphi_{o,k}(r\omega)$

$\tilde{f}_{xc}(r,r';\omega)$ has poles where $\lambda_k(\bar{\omega}) = 0$ or $\lambda_{o,k}(\bar{\omega}) = 0$.

$\tilde{\chi}_R$ and $\tilde{\chi}_{o,R}$ have both a discrete spectrum for $-I < \omega < I$ since the ionization potentials of the full and the Kohn-Sham system are identical, $I = I_o$.

We therefore conclude

$\tilde{f}_{xc}(r,r';\omega)$ is real for $-I < \omega < I$, $\omega \neq \bar{\omega}$.

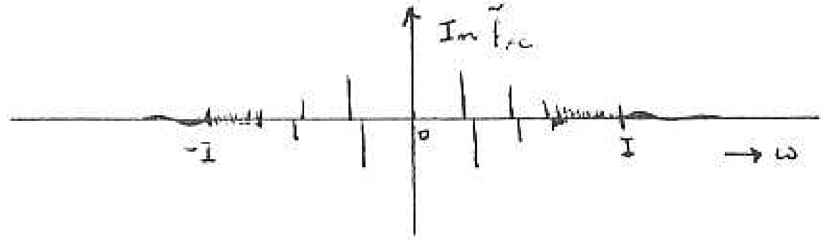
If we denote $\beta_k(\omega) = \left(\frac{d\lambda_k}{d\omega}(\omega) \right)^{-1}$ $\quad (\beta_k(\omega) = -\beta_k(-\omega))$

we find for $-I < \omega < I$ that (Kramers-Kronig)

$$-\frac{1}{\pi}\mathrm{Im}\, \tilde{f}_{xc}(r,r';\omega) = \sum_{k\ell} \Big\{ \delta(\omega - \bar{\omega}_{o,k\ell})\, \beta_{o,k}(\omega)\, \varphi_{o,k}(r\omega)\, \varphi_{o,k}(r'\omega) - \delta(\omega - \bar{\omega}_{k\ell})\, \beta_k(\omega)\, \varphi_k(r\omega)\, \varphi_k(r'\omega) \Big\}$$

where $\begin{cases} \lambda_k(\bar{\omega}_{k\ell}) = 0 , & \bar{\omega}_{k\ell} = \ell\text{'th pole } \lambda_k \\ \lambda_{o,k}(\bar{\omega}_{o,k\ell}) = 0 , & \bar{\omega}_{o,k\ell} = \ell\text{'th pole of } \lambda_{o,k} \end{cases}$

One can explicitly check that $\mathrm{Im}\, \tilde{f}_{xc}(r,r';\omega) = -\mathrm{Im}\, \tilde{f}_{xc}(r,r';$ as it must be since f_{xc} is a causal function.



Asymptotics of $\tilde{f}_{xc}$ for large ω

For $\tilde{\chi}_R$ we found: $\tilde{\chi}_R = \frac{c_1}{\omega^2} + \frac{c_3}{\omega^4} + O\left(\frac{1}{\omega^6}\right) \quad (\omega \to \infty)$

where $c_1(r,r') = -\nabla_r \cdot \nabla_{r'} \left(\delta(r-r') n(r') \right)$

For $\tilde{\chi}_R^{-1}$ we make the Ansatz

$$\tilde{\chi}_R^{-1} = \omega^2 a + b + O\left(\frac{1}{\omega^2}\right) \quad (\omega \to \infty)$$

We then find

$$\delta(x-r') = \int d^3r \, \tilde{\chi}_R^{-1}(x,r) \tilde{\chi}_R(r,r') =$$

$$= \int d^3r \, a(x,r) c_1(r,r') + \frac{1}{\omega^2} \int d^3r \left[b(x,r) c_1(r,r') + a(x,r) c_3(r,r') \right] + \ldots$$

This yields

$$\delta(x-r') = \int d^3r \, a(x,r) c_1(r,r') =$$

$$= -\int d^3r \, a(x,r) \nabla_r \nabla_{r'} \left(\delta(r-r') n(r') \right)$$

$$= \nabla_{r'} \left(n(r') \nabla_{r'} a(x,r') \right)$$

we further find

$$b(x,y) = -\int d^3r \, d^3r' \, a(x,r) c_3(r,r') a(r',y),$$

$a(x,r)$ is solution to $\quad \nabla_r \left(n(r) \nabla_r a(x,r) \right) = \delta(x-r)$

with boundary condition $\quad a(x,r) = a(r,x)$

a depends only on the density $n(r)$ and is therefore the same for $\tilde{\chi}_R$ and $\tilde{\chi}_{0,e}$!

For $\tilde{f}_{xc}$ we therefore find

$$\tilde{f}_{xc}(r,r';\omega) = b_0(r,r') - b(r,r') - \frac{1}{|r-r'|} + O\left(\frac{1}{\omega^2}\right)$$

$$(\omega \to \infty)$$

Now $\quad b_0(x,y) - b(x,y) = \int d^3r \int d^3r' \; a(x,r)\left[c_3(r,r') - c_{3,0}(r,r')\right] a(r',y)$

From the third frequency sum rule we therefore find

$$\tilde{f}_{xc}(x,y;+\infty) = -\frac{2}{\pi}\int d^3r\, d^3r' \; a(x,r)\left\{\int_0^\infty d\omega\, \omega^3\, \mathrm{Im}\left(\tilde{\chi}_R(rr',\omega) - \tilde{\chi}_{R,0}(rr';\omega)\right)\right\} a(r'y) - \frac{1}{|x-y|}$$

Since $\tilde{f}_{xc} \rightarrow \tilde{f}_{xc}(x,y;+\infty) \neq 0$ the function $\tilde{f}_{xc}$ does not satisfy the requirements of the Kramers-Kronig theorem. However the function $\tilde{f}_{xc}(r,r';\omega) - \tilde{f}_{xc}(rr';+\infty)$ does, We therefore find

$$\mathrm{Re}\, \tilde{f}_{xc}(rr';\omega) - \tilde{f}_{xc}(rr';+\infty) = -\frac{1}{\pi} P \int_{-\infty}^{+\infty} d\omega' \; \frac{\mathrm{Im}\, \tilde{f}_{xc}(rr';\omega')}{\omega - \omega'}$$

$$\mathrm{Im}\, \tilde{f}_{xc}(rr';\omega) = \frac{1}{\pi} P \int_{-\infty}^{+\infty} d\omega' \; \frac{\mathrm{Re}\, \tilde{f}_{xc}(rr',\omega) - \tilde{f}(rr';+\infty)}{\omega - \omega'}$$

(the last relation has already been used at page 14).