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FREQUENCY MOMENTS: FINE STRUCTURE OF X-RAY SPECTRA IN METALS AND OTHER APPLICATIONS

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Fine structure of the edges of X-ray lines (absorption, emission, photoemission) in metals is admitted to frequently possess an asymptotic power law singularity $I(\omega) \to A(\omega - \omega_{\text{edge}})^{-\alpha}$ on the line threshold due to the analogue of the infrared catastrophe. This happens due to the quasicontinuity of energy spectra of metals. In this paper the leading term of this power law's exponent is combined with first exact frequency moments of the relevant spectrum. The moments are obtained from an exact explicit expression and the use is made of the results of the power moments' problem on the half-axis to restore approximate line forms beyond the edge asymptotic region: i.e. to find the so-called generalized power law $I(\omega) = C\omega^{-\alpha(\omega)}$. Applying the method to a model alkali metal we show that the postasymptotic form strongly depends on the long-range asymptotics of the potential of a core hole (where an electron excited by a quantum has been). Later on Tchebycheff-Markov inequality is shown which enables us to find some parameters of spectra with a number of absorption and nonabsorption regions. This method also requires only a few first moments. It can be applied to spectra for wide frequency regions.

1. Introduction

Fine structure of the lines of X-ray spectra in metals has been regarded as an exquisite problem of the many-body quantum theory for the last 30 years – since the edge forms of them were found by Mahan and proved analytically by Nozieres and DeDominicis (MND) [1] to be conspicuous. The set of atomic spectral lines of deep electronic levels (not collectivized in the condensed state) for metals is transformed into a set of the following complexes: a threshold (edge) of each line on "intensity-frequency" plots is followed by a curve with the asymptotical form $I(\omega) = C_0|\omega|^{\beta}$ for absorption ($\omega > 0$) [emission ($\omega < 0$)], and for photoemission – $P(-\omega) = c(-\omega)^{\sigma-1}, \omega > 0$; ω is measured from the corresponding thresholds (see figure 1, for example). This form is called a power law (PL). Obviously cases of $\beta < 0$ and $\sigma < 1$ correspond to a threshold singularity. The values of the exponents β, σ were proved to depend on the specific structure of a metal (which includes the atomic core structure). Later on Anderson, Friedel and Hopfield [1] explained the physical core of this essentially many-particle problem, generally considered on the basis of the one-particle approximation.

The model suggested to describe the process implies that an incident quantum interacts with a deep atomic residue level instantaneously, i.e. at $t = t_0 = 0$ (t – time measured from the moment when "quantum –

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system" interaction began, t_0 – the moment when configuration is believed to settle locally) an electron is assumed to have been already excited and a hole exists where the electron has been. In fact, t_0 is finite, but much smaller than any time parameter substantial for this problem (frequencies $\omega > \omega_{\text{plasma}}$). The period of time when all the interactions with the external field and the creation of the hole took place is therefore neglected, only their result is taken into account: the potential of the hole (core-hole potential) is V. It is also supposed that this $\mathrm{d}V/\mathrm{d}t = 0$: the potential does not change thereafter. Thus, too slow influences – lattice, surface, dynamic screening ($\omega \ll \omega_{\text{plasma}}$) – are excluded too. Despite these limitations, the model explains experimental data for prethreshold regions adequately. Of course, semiphenomenological nature of V is helpful, V being easily adjusted to fit experimental plots.

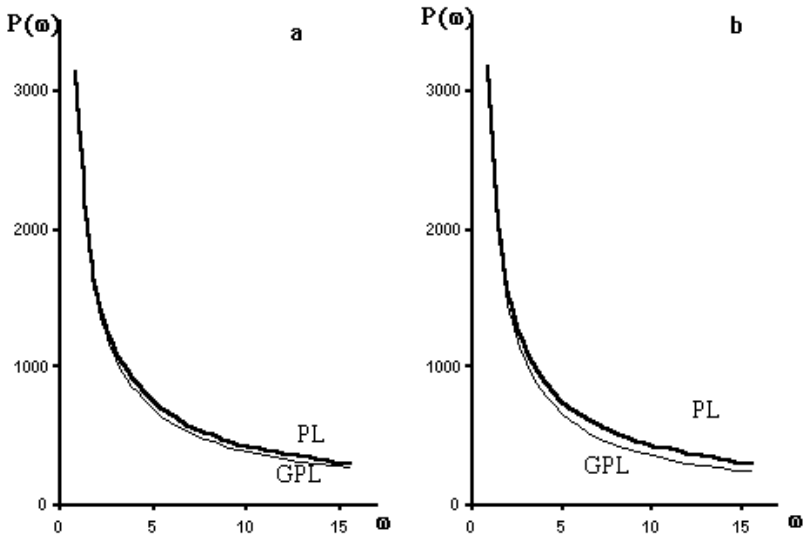

Figure 1. Restored X-ray photoemission generalized power laws (GPL) and the corresponding power laws (PL) $c\omega^{\sigma-1}$ for (**a**) nonsingular in $\boldsymbol{k} = 0$ potential and (**b**) singular in $\boldsymbol{k} = 0$ potential. Frequency-energy units – $10^{-3}E_{\mathrm{F}}$, intensity: $\int_0^\infty P(\omega)\mathrm{d}\omega = 2\pi$.

The potential's sudden switching shifts the mean field of the system and thus perturbs its energy spectrum, mainly, of course, the conduction band. This means that the quantum energy is not absorbed completely by the deep level electron being excited, a part of the energy is taken to perturb the background electron density. Similar ideas apply, for example, to a many-electron atom, but the latter has no Fermi surface with thermodynamically infinite number of particles on it. The analogue of the infrared catastrophe happens here: one-particle energy spectrum of a metal is quasicontinuous; that is, almost no energy is required to excite a particle on the Fermi surface. Thus, any amount of "spare" energy (not taken to excite a core electron) can create, however, many one-particle excitations, just as it happens to infrared photons in QED. This formal infinity manifests itself here as observable – the conduction band response follows $(\Delta t)^{-\sigma}$ (t – time) instead of $\mathrm{e}^{-\Delta t}$ that one may expect for relaxation. The latter corresponds to a finite number of one-particle transitions across a finite energy gap.

This results in $I \propto \int t^{-\sigma} \exp(-\mathrm{i}\omega t)\mathrm{d}t \propto \omega^{\sigma-1}$. Here σ depends on the core-hole potential and one-particle states density on the Fermi surface (see (3)).

It may be worth mentioning that, though an apparently singular form had been seen on $I(\omega)$-plots much earlier, no idea of edge singularity occured to researchers, besides the values of β and σ could be measured only with a synchrotron as a radiation source.

One of the issues which are of interest here is the problem of the generalized power law (GPL), i.e. the line form beyond its threshold asymptotical region, where the simple power law fails to hold, but the model is still applicable. Generally GPL is represented as $c\omega^{\sigma(\omega)-1}$ for photoemission [or $\beta(\omega)$ for absorption (emission)].

In this work a method of finding the GPL for photoemission spectra is presented (it can be easily adjusted to the absorption-emission case). The method is based on a general exact expression for a spectrum form [2]. Despite being general, explicit, one-particle, independent of wave basis etc., its direct application is hardly possible, only singular asymptotics can be found. However, its form enables us to obtain expressions for frequency moments [3].

In section 2 we shall restore the GPL by making use of the first four moments and the known edge asymptotics. We shall apply the expression to a model alkali metal and phenomenological core-hole potentials. It will be shown how line forms depend on long range asymptotics of the potentials.

In section 3 another application of the moments method is presented. Unlike the method in section 2, this one allows to find characteristics of spectra in wide frequency regions (regions of absorption and nonabsorption), but not very suitable for specific forms of single lines.

2. The generalized power law

We take the exact explicit expression for absorption (emission) intensity [2] (thereafter atomic units are used):

$$I(\omega) = \int_0^\infty P(t) I_0(t) \exp(-\mathrm{i}\omega t)\mathrm{d}t, \tag{1}$$

$$I_{\mathrm{P}}(\epsilon) = RP(\omega = W - \epsilon); R, W = \mathrm{const}. \tag{2}$$

Here the Laplace image of the first factor in the integrand describes the photoemission intensity as (2), where R and W are fixed for a specific line (transition). That is, the line form for photoemission is described by the Laplace-transform of $P(t)$ with the reversed ω-axis and shifted zero. In what follows we shall refer to $P(\omega)$ as a photoemission spectrum. $P(t)$ and $I_0(t)$ are built on the matrix elements of H_0 and H, one-particle hamiltonians of the initial and final states respectively, $H = H_0 + V$, where V is a one-particle core-hole potential, I_0 also contains transition matrix elements (e.g. dipole D_{ik}); the expressions for them are quite cumbersome (in [3] there are also the first four frequency moments of I and P).

Discussing, for instance, photoemission one uses a perturbation series in V. Then up to the second order in V when $t \to \infty$

$$P(t) \to \exp[-\mathrm{i}\sum_{i \leqslant N} V_{ii} t + A^{(2)}(t)]; \tag{3}$$

$$A^{(2)}(t) = -\sum_{i\leqslant N,k>N} |V_{ik}|^2 \int_0^t \mathrm{d}s(t-s)\exp[\mathrm{i}(E_i-E_k)s])$$
$$\to -\sigma\{\mathrm{i}\Xi t + \mathrm{i}\frac{\pi}{2} + \ln t + F + \gamma + 1\},$$
$$\sigma = 2[2\pi]^{-6}\int \mathrm{d}o_1 \int \mathrm{d}o_2 |V_{k_1k_2}|^2 \frac{k^4}{E_k'^2}|_{E=E_\mathrm{F}}. \quad (4)$$

Here summation runs over one-particle states, the Nth level divides free and occupied states at $T=0$, i.e. $E_i \leqslant E_\mathrm{F}, E_k > E_\mathrm{F}$, γ is Euler constant. The values of Ξ and F should be calculated numerically:

$$\Xi = -\frac{1}{\sigma}\sum_{i<N,k>N} \frac{|V_{ik}|^2}{E_k - E_i}, \quad (5)$$

$$F = \ln[D\bar{D}/(D+\bar{D})] + \sum_{i<n,k>n} \frac{|V_{ik}|^2/\sigma - [\frac{\mathrm{d}\nu(E_i)}{\mathrm{d}E}\frac{\mathrm{d}\nu(E_k)}{\mathrm{d}E}]^{-1}/4}{(E_k-E_i)^2}, \quad (6)$$

where D is the distance "lower edge of the conduction band – Fermi level", $\bar{D}$ – "upper edge of the conduction band – Fermi level", $\nu(E)$ is the density of one-particle states (spin variables are included, 1/4 compensates this degree of freedom). Note that in (5) the first term is $O(1)$ and the second one is $O(10^{-2})$, but the latter is very important. Here the frequency is measured from the one-particle threshold. Note that frequency shift $\sum V_{ii} - \sigma\Xi$ is negative (less energy is required to excite a photoelectron).

Thus, the asymptotic singularity at $\omega \to 0$ is described because $e^{-\sigma \ln t} = t^{-\sigma}$. For absorption (emission) an additional power term arises and changes $\sigma \to \beta$.

A difference between (1) and (2) should be mentioned. Whereas (1) is a general expression for the whole spectrum, at least within the limitations of the model, (2) describes only some vicinity of a specific threshold, other lines require other constants R and W. This, however, is not substantial because even for (2) other lines require other core-hole potentials.

Rigorous expressions are, though, too complicated for further straightforward analysis. The authors of [1] solved coupled integral equations to obtain a GPL. There is another method connected with the theory of functions: the method of moments. In this way one combines the asymptotics at 0 with the asymptotics at infinity. The striking example of such approach is the formula of Drude-Lorentz from the conduction theory of metals which uses only the static value of conductivity and its zeroth moment. Thus one gets an approximate line form sparing some computational efforts, at least. Besides, a number of results can be obtained directly from the values of the moments.

For example, for photoemission the average frequency (measured from a one-particle line position – W) and centred moments

$$p_n^c \equiv \langle(\omega-\omega_0)^n\rangle \equiv \int_0^\infty (\omega-\omega_0)^n P(\omega)\mathrm{d}\omega$$

are [3]

$$\omega_0 = \sum_{i<N} V_{ii}. \quad (7)$$

$$p_2^c = \sum_{i<N;k>N} |V_{ik}|^2; \tag{8}$$

$$p_3^c = \sum_{i<N;k>N} (\epsilon_k - \epsilon_i)|V_{ik}|^2 - \sum_{i,j<N;k,l>N} [V_{ik}V_{kj}V_{ji} - V_{il}V_{lk}V_{ki}]; \tag{9}$$

$$p_4^c = \sum_{i<N;k>N} (\epsilon_k - \epsilon_i)^2|V_{ik}|^2 - 2\sum_{i,j<N;k,l>N} \{(\epsilon_k - \epsilon_i)[V_{ik}V_{kj}V_{ji} - V_{il}V_{lk}V_{ki}] + V_{ik}V_{kj}V_{jl}V_{li}\} + \sum_{i,j,m<N;k,l,n>N} (V_{ij}V_{jm}V_{mk}V_{ki} + V_{ik}V_{kl}V_{ln}V_{ni} - 2V_{ij}V_{jk}V_{kl}V_{li}) + 3[p_2^c]^2. \tag{10}$$

To restore the line form we shall use the known results of the frequency moments problem on semi-axis (Stiltjes problem) [4]. An unknown weight function $\rho(z)$ exists with a number of known power moments

$$\int_0^\infty t^k \rho(t)\mathrm{d}t = s_k. \quad k = 0 \ldots N. \tag{11}$$

Two sets of the polynomials: $Q_n(t)$ and conjugate $P_n(t)$ – should be constructed

$$Q_{2\nu}(z) = \frac{1}{\Delta_{\nu-1}^{(1)}} \det ||z^k s_k \ldots s_{k+\nu-1}||_0^\nu, \quad \Delta_k^{(1)} = \det ||s_{i+j+1}||_0^k; \tag{12}$$

$$Q_{2\nu+1}(z) = -\frac{1}{\Delta_{\nu-1}} \det ||z^{k+1} s_{k+1} \ldots s_{k+\nu}||_0^\nu, \quad \Delta_k = \det ||s_{i+j}||_0^k;$$

$$P_n(z) = \int_0^\infty \frac{Q_n(t) - Q_n(z)}{t - z}\mathrm{d}t.$$

Then

$$I_\rho^n(z) \equiv \frac{P_m(z) + \omega(z)P_l(z)}{Q_m(z) + \omega(z)Q_l(z)} \overset{n\to\infty}{\longrightarrow} I_\rho(z) \equiv \int_0^\infty \frac{\rho(t)\mathrm{d}t}{z - t}; \tag{13}$$

$\rho(x) = -\frac{1}{\pi}\Im[I(x + i0)]$ ($m = 2n$ or $m = 2n + 2$, $l = 2n + 1$). Here $\omega(z)$ is a Nevanlinna function, an arbitrary function that must be represented as

$$\omega(z) = d + \int_0^\infty \frac{\psi(t)\mathrm{d}t}{t - z}, \quad d \geqslant 0, \quad \int_0^\infty (1 + t)^{-1}\psi(t)\mathrm{d}t < \infty \tag{14}$$

with an arbitrary d and a nonnegative $\psi(t)$ that satisfy, of course, the restrictions of (14).

The results of the moments problem provide an approximate function to have the fixed first moments automatically. The Nevanlinna function should be chosen in order to satisfy some additional conditions; for this case the power law asymptotic behaviour is the same.

Obviously, $Q_{2n}(t) = 1 + O(t)$, $P_{2n}(t) = O(1)$, $P_{2n+1}(t) = -1 + O(t)$, $Q_{2n+1}(t) = O(t)$ when $t \to 0$. That is why, for photoemission, the function

$$\omega_{\mathrm{id}}(x) = -c\pi x^{\sigma-1}\{\cot[\pi\sigma] - \mathrm{i}\} \tag{15}$$

(c – the preexponential of the corresponding power law, "id" stands for ideal – the ideal power law) seems to suit us as a Nevanlinna one: obviously it

gives $\rho(x) = cx^{\sigma-1} + O(t^\sigma)$. However, for photoemission with $\sigma = o(1)$ and absorption-emission with $\beta \sim -1$ the denominator of (13) contains $d(t) = 1 + At^\sigma + Bt^{2\sigma}$ with $A, B \sim 1$ which grows too fast in the vicinity of 0 ($\sigma \ll 1$). Such behaviour, in fact, would deprive the power law of any meaning, the preexponential c of GPL is not constant even for $\omega \sim 10^{-8}$eV (!). For the values $\beta \sim 0$ $\omega_{\rm id}$ is suitable, but our further expressions are not less convenient even for the latter case.

There is an inverse method: we can find a certain $\omega_{\rm lin}$ (15) ("lin" stands for linear) from

$$-\omega_{\rm id} = I^n_\rho(\omega_{\rm lin}) + O(t), \tag{16}$$

that is, supposing that (13) is an equation for an unknown function $\omega_{\rm lin}$ up to the terms linear in t. Thus, the power law will hold automatically up to the linear terms because, as we have said, $-1/(\pi\Im[\omega_{\rm id}])$ produces the power law. To write the equation explicitly we just omit all linear terms of higher orders. However, the function $\omega_{\rm lin}$ obtained from the equation (16) has no representation (14). It is, though, its behaviour at $z = x + {\rm i}0$ with $x > 0$ that is of significance. We can introduce new $\tilde\psi$ and $\tilde\omega$ and assume

$$\tilde\psi(x) \stackrel{(14)}{=} \Im[\tilde\omega(x + {\rm i}0)]/\pi \equiv \Im[\omega_{\rm lin}(x + {\rm i}0)] \tag{17}$$

i.e. on the positive real half-axis. Integrating (14) with $\psi(x)$ from (17), one gets $\Re[\tilde\omega(x + {\rm i}0)]$. Thus, found $\tilde\omega$ complies with all the restrictions and differs minimally from $\omega_{\rm lin}$ on the positive real semi-axis (its imaginary part simply coincides with it). This function should be put into the imaginary part of (13) divided by $-\pi$, hence:

$$\rho_{\rm app}(x) = \frac{\Im[\tilde\omega(x)]}{\pi[(Q_m(x) + \Re[\tilde\omega(x)]Q_l(x))^2 + (\Im[\tilde\omega(x)]Q_l(x))^2]}; \tag{18}$$

$$\begin{aligned}\tilde\omega(z) \quad = \quad & \frac{c\pi}{\Im(G)}\left[\left(\frac{Gz^{\sigma-1}}{1 - Gz^\sigma} - \frac{G^{1/\sigma}}{\sigma(1 - zG^{1/\sigma})}\right)(1 + z(q_1p_2 + q_2))\right. \\ & \left. -\frac{1-\sigma}{\sigma}\right]\end{aligned} \tag{19}$$

with $G = -c\pi q_1(ctg[\pi\sigma] - {\rm i})$ (see that $G^{1/\sigma}$ is real), where $p_2 = P_{2n}(0)$ and $q_1 = Q'_{2n+1}(0), q_2 = Q'_{2n}(0)$ [Q'_k – derivative of Q_k].

Expressions (18), (15), (12) together with the definitions of the constants q_1, q_2, p_2, G constitute the proposed method of restoring line forms. The moments are to be recalculated to a new centre – threshold, therefore Ξ is needed: it, as one can see, coincides with the multiplied by (-1) average frequency measured from the threshold (compare (3) and (7)) – in what follows we shall take its absolute value as Ξ (it is negative).

There are some important inequalities that we have mentioned before: all the determinants Δ_k and $\Delta^{(1)}_k$ must be positive. This leads, for example to nontrivial

$$\begin{aligned} p^c_3\Xi + \Xi^2 p^c_2 - (p^c_2)^2 \quad &> \quad 0, \\ p^c_2 p^c_4 - (p^c_3)^2 - (p^c_2)^3 \quad &> \quad 0. \end{aligned} \tag{20}$$

We purpose to describe the photoemission intensity of an alkali metal which, as it is known, is described by a free electrons' model quite adequately. A hypothetical model metal was chosen with one electron per elementary cell and a spherical first Brilloin zone. Plane waves are basis $\phi(\boldsymbol{r}) = (\Omega)^{-1/2}\exp(\mathrm{i}\boldsymbol{kr})$ (Ω – volume of the system), the dispersion law $\epsilon = k^2/2$. Obviously, only one parameter is left – electron density or the effective interelectron radius r_s. Let $r_\mathrm{s} = 3.93$ (it is r_s of natrium).

A core-hole potential has not yet been defined. In fact, this choice lies beyond the framework of the MND model, the core of the model consisting in the notion of a suddenly arising local perturbation considered invariable thereafter. Thus, one neglects both quick processes of creating the potential ($\omega > \max[\omega_\mathrm{plasma}, E_\mathrm{F}]$) and slow relaxation ($\omega \ll E_\mathrm{F}$). Therefore, V is to be introduced into the model as an external rather phenomenological expression (a set of matrix elements). Rigorous treatment of the "quantum - metal" interaction would provide such a formula. However, the treatment is impossible or else no model like the MND one with an intermediary potential would be necessary.

We used a semi-phenomenological way of defining a potential. If we discuss the excitation of a $2s$-electron in natrium (L-line) then the initial notion should consist in the potential of an absent $2s$-electron. But its Coulomb "tail" is impermissible (the effect was believed to be local). Obviously, some partial screening takes place. Certainly, as one should expect, Lindhardt's screening

$$V_\mathrm{2s}(q) = -\frac{4\pi}{q^2}\frac{(1-q^2)(1-2q^2)}{(q^2+1)^4}, \tag{21}$$

$$\chi(q) = (k_\mathrm{F}/\pi^2)\left[\frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|\right]; x = \frac{q}{2k_\mathrm{F}},$$

$$V(q) = V_\mathrm{2s}(q)\frac{q^2}{q^2 + 4\pi Z\chi(q)}. \tag{22}$$

(Lindhardt – $Z = 1$) holds when $t \to \infty$ proves too strong ($\sigma = 0.03$ whereas experiments [1] give $\sigma = 0.20$). To "adjust" screening one may purely phenomenologically put $Z = 0.348$. We also tested a semiphenomenological local-field-like correction factor to the Lindhardt chaotic phases approximation: $Z = f(q)$. The local electron density near the hole ($r \sim a_\mathrm{B} \Leftrightarrow k > k_\mathrm{F}$) may have already settled while at greater distances ($k \ll k_\mathrm{F}$) it may even not start to react: $f(0) \ll f(k_\mathrm{F})$ (keep in mind that we are defining a potential created by quick processes). Assuming that the problem has a limited number of values and laws connected with the unusual readjustment of the conduction band, one finds $Z = Z_0(q/2k_\mathrm{F})^\sigma$ not too superficial. To obtain $\sigma = 0.20$ we put $Z_0 = 0.516$; $Z_0 = O(1)$ seems to confirm that this is at least sensible.

We found the first five moments (s_4 including) of the photoemission spectrum for the two screened potentials (21) and the preexponentials. The latter are equal to

$$c = 2\pi\exp\left[-\sigma(F+\gamma+1]\right)/\Gamma(\sigma),$$

$\Gamma(x)$ being a gammma-function, F, γ taken from (3)-(5).

$$Z = \mathrm{const} : c = 2.001; \tag{23}$$

$$\begin{aligned} \Xi &= 0.0157; p_2^c = 7.06 \cdot 10^{-4}; p_3^c = 4.83 \cdot 10^{-5}; p_4^c = 5.59 \cdot 10^{-6}; \\ Z &= \text{const} \cdot q^{0.2} : c = 1.985 \\ \Xi &= 0.0142; p_2^c = 6.11 \cdot 10^{-4}; p_3^c = 4.11 \cdot 10^{-5}; p_4^c = 4.48 \cdot 10^{-6}. \end{aligned} \tag{24}$$

(atomic units $1 \equiv 2Ry$) and built the line forms for $n = 4$. They are presented in figure 1 (units – E_{F}): the line forms and the power law for each potential.

We have to stress that here the line forms were correctly restored up to linear in ω terms. This does not mean that the farther line form is wrong, it just means that it is unreliable. It contains peaks near Ξ. We cannot state that the peaks are to be made smooth by further approximations, though this also happens, but the measure of smoothening requires research. The value of the linear term in Q_4, for example, is of the order 10^2, which means that restoring holds up to $\omega < 0.01Ry \sim 0.1E_{\mathrm{F}}$. Observing that the GPL is connected with $S(E, E') \equiv \int\int |V_{kk'}|^2 \mathrm{d}o\mathrm{d}o'\nu(E)\nu(E')$ at least to the second order in V, we see that for a semielliptical or rectangular zone and $V = \text{const}$ (as in [1]) $S(E, E')$ has but the only maximum at $E = E' = E_{\mathrm{F}}$. But for other V and $\nu(E)$ this may not hold, and, if S possesses a maximum (even a local one) at $E = E_1, E' = E_2, E_1, E_2 \neq E_{\mathrm{F}}$, then a peak at $\omega \simeq E_1, E_2$ is possible. Partial confirmation of this statement was obtained by restoring the line form for a rectangular and semielliptical state density and constant V. We did not show this in figures, so that there are not too many lines in them, but $\sigma(\omega)$-plots (see further) for this case are much smoother than those for other cases (though, peaks arise here too, but far from the threshold: $\sim E_{\mathrm{F}}$).

Discussing the results on the background of experimental data is rather difficult because, though the data are not scarce, their precision is far from what is needed for any comparison. Singular exponents are obtained, but any deviations from power laws are not. So one can only compare theoretical predictions with numerical models or argue whether an experimental value corresponds to a model because the model is wrong or because the value was measured at frequencies where a curve follows not the power law but the GPL. For example, the authors of [1] claim that $\sigma = 0.20$ for natrium was obtained [5] too far from its threshold where the GPL goes lower than the power law (i.e. $\sigma(\omega)$ grows for $\omega/E_{\mathrm{F}} < 1$). To prove this they solved integral equations numerically for the contact type potential $V_{kK} = -V$ (V – a positive constant) and semielliptical $\nu(E) \propto (E_{\mathrm{F}}^2 - E^2)^{1/2}$ or the rectangular state density: $N(E) = \text{const}(0 < E < 2E_{\mathrm{F}}); N(E) = 0(E < 0, E > 2E_{\mathrm{F}})$.

Our results show that the significance of the GPL's deviation strongly depends on the long-range asymptotics of potentials. We have got different types of σ's behaviour for the two potentials. $\sigma(\omega)$ was calculated as

$$\sigma(x) = 1 + \frac{\ln\left[\rho_{\mathrm{app}}(x)/c\right]}{\ln x}. \tag{25}$$

We concluded that the longer is the range of the potential (the more prominent the peak of its k-transform is in $k = 0$), the closer it follows the corresponding power law. We also discussed a test example of the contact type $-V$ (i.e. the transform of the overlocalized $A\delta(\boldsymbol{r})$) with $\sigma = 0.2$:

$$\begin{aligned} V &= \text{const}; \ c = 1.774; \\ \Xi &= 0.0215; \ p_2^c = 1.264 \cdot 10^{-3}; p_3^c = 1.063 \cdot 10^{-4}; p_4^c = 9.07 \cdot 10^{-5}. \end{aligned} \tag{26}$$

which produces $\sigma(\omega)$ that lies even further from the power law than the short range potential's one. Dependencies $\sigma(\omega)$ are presented in figure 2. Such conclusion is not as trivial as it can appear. The extremal long range case should be just an overall shift of the mean field, the corresponding spectral line is a δ-like peak, nothing like a power law can occur here. That is obvious from the physical sense of the phenomenon: the singular form is created by multiple electron excitations across the Fermi surface, but those can happen only if matrix elements $V_{kk'}$ with $E(k) < E_{\mathrm{F}}$, $E(k') > E_{\mathrm{F}}$ (not diagonal in occupation number) are nonzero, which is not the case for $\delta(\boldsymbol{k}-\boldsymbol{k}')$ – a matrix element of $V(\boldsymbol{r}) = \mathrm{const}$. On the other hand, the power law cannot certainly hold forever, the line has finite moments, and the power law does not.

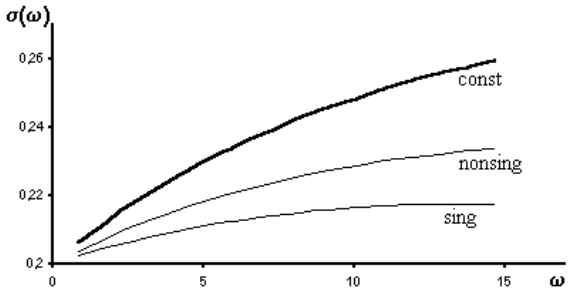

Figure 2. Generalised power law $\sigma(\omega)$ calculated from figure 1 (a,b).as $P(\omega) = c\omega^{\sigma(\omega)-1}$ for constant, nonsingular and singular potentials. Frequency-energy units – $10^{-3}E_{\mathrm{F}}$, intensity: $\int_0^\infty P(\omega)\mathrm{d}\omega = 2\pi$.

Thus, we state that, researchers [1] being right, the measure of GPL deviation and uncertainty of experimental values of σ substantially depend on the long range asymptotics of the core-hole potential.

And, certainly, we obtained a prethreshold line form. Note that calculating moments is much easier than solving integral equations numerically; for some cases (contact-type included) almost all the moments can be found analytically. The method appears applicable at least near the threshold ($\omega \ll E_{\mathrm{F}}$).

Some remarks should be made here concerning the form of $\sigma(\omega)$ farther from the threshold. We cannot claim that nonlinear parts of the curves in figure 2 do not result from our method faults. We have, obviously, $\mathrm{d}^2\sigma/\mathrm{d}\omega^2 < 0$. However, this holds only for $\omega > 10^{-3}$. For $\omega < 10^{-3}$, in fact, $\mathrm{d}^2\sigma/\mathrm{d}\omega^2 > 0$; we do not present it in the figure, because there is no appropriate scale to show this slight curving, even a logarithmic one is not enough. This partially coincides with the results [1] for the mentioned contact-type $-V$: $\sigma(\omega)$-curves have $\mathrm{d}^2\sigma/\mathrm{d}\ln\omega^2 > 0$. However, there the authors do not mention if the stronger $\mathrm{d}^2\sigma/\mathrm{d}\omega^2 > 0$ holds. At $\omega \simeq 10^{-3}$ the trend changes (for stronger potentials it may happen farther). It must happen just because $\mathrm{d}^2\sigma/\mathrm{d}\omega^2 > 0$ cannot hold too far from the edge, the frequency moments being finite, so $\sigma(\omega)$ must become negative sooner or later, probably somewhere near Ξ.

3. Tchebycheff-Markov inequality

Restoring line forms, as described above, is satisfactory when three relevant parameters – a threshold position, a power law exponent and a preexponential – are given from outside, e.g., calculated analytically from any general expression. However, this is not always possible, sometimes even regions of

nonabsorption in a spectrum are not clearly defined. There are cases when such information could be drawn from a small number of the first frequency moments [6,4]. Here another "subproblem" of the moments problem can be made use of: Tchebycheff-Markov inequality. This holds for a nonnegative function $f(x)$ with given moments $s_0, \ldots, s_N$.

$$l(x) \equiv \sum_{x_i<x} \eta_i(x) \leqslant \int_0^{x-0} f(y)\mathrm{d}y \leqslant \int_0^{x+0} f(y)\mathrm{d}y \leqslant \sum_{x_i<x} \eta_i(x) + \eta_x \equiv u(x), \tag{27}$$

where functions $\eta_i(x), \eta_x, x_i(x)$ can be obtained from the set of equations

$$s_k = x^k \eta_x + \sum_{i=1}^{n(N)} x_i^k \eta_i, \quad k = 0, 1, \ldots, R(N). \tag{28}$$

Here, for even N $n = N/2$ and (a) $R = N$; (b) $R = N-1, x_1 = 0$ and for odd N (a) $n = (N-1)/2, R = N-1$; (b) $n = (N+1)/2, R = N, x_1 = 0$. The case's (a) or (b) choice depends on x. One is to take the case with $\eta_i \geqslant 0, \eta_x \geqslant 0, x_i \geqslant 0$. There exists a unique solution of the type.

For $N = 4$ we defined the set of minors

$$\begin{aligned} D_2 &= s_0 s_2 - s_1^2; \quad D_3 = s_0 s_3 - s_1 s_2; \\ D_4' &= s_0 s_4 - s_2^2; \quad D_4 = s_1 s_3 - s_2^2; \\ D_5 &= s_1 s_4 - s_2 s_3; \quad D_6 = s_2 s_4 - s_3^2. \end{aligned} \tag{29}$$

For x_i the following equations were obtained

$$x_i^2 a(x) + x_i b(x) + c(x) = 0, \quad i = 1, 2, \tag{30}$$

$$x_2 = \frac{s_3 - s_2 x}{s_2 - s_1 x}; \quad x_1 = 0. \tag{31}$$

where

$$\begin{aligned} a(x) &= x^2 D_2 - x D_3 + D_4, b(x) = x^2 D_3 - x D_4' + D_5, \\ c(x) &= x^2 D_4 - x D_5 + D_6, \end{aligned} \tag{32}$$

(31) applies to regions of x where either of x_i found from (30) proves negative. Those are, obviously, $a(x), c(x) > 0, b(x) < 0$ and $a(x), c(x) < 0, b(x) > 0$. For ηs we have

$$\eta_x = -\frac{s_1(x_1 + x_2) - s_2 - s_0 x_1 x_2}{(x - x_1)(x - x_2)}; \tag{33}$$

$$\eta_1 = -\frac{s_1(x + x_2) - s_2 - s_0 x x_2}{(x - x_1)(x_2 - x_1)}; \tag{34}$$

$$\eta_2 = \frac{s_1(x + x_1) - s_2 - s_0 x x_1}{(x - x_2)(x_2 - x_1)}. \tag{35}$$

$$\tag{36}$$

The method can be very helpful in finding regions of nonabsorption. If the boundaries $u(x)$ and $l(x)$ coincide and are constant, the conclusion is obvious: there is no absorption in this region of a spectrum.

Naturally, this method can hardly add much to the single line form, especially, the singular one. And really, boundaries (27) prove too loose. They "pinpoint" the line for the described models only for $\omega \simeq 0.1 \simeq E_{\mathrm{F}}$ which is no surprise for the only zone $\sim E_{\mathrm{F}}$ wide. Only some hints can be drawn from $Av(x) = [u(x) + l(x)]/2$. Certainly, the average of the boundaries does not have to coincide with the line form, but it is worth mentioning that this average for the short range potential lies lower than $F(x) = \int_0^{\omega} cx^{\sigma-1}\mathrm{d}x$ with the relevant c [except for $\omega \simeq 0$ where $Av(0) \neq 0$, and $F(0) = 0$], and $Av(x)$ for the long range potential lies higher than $F(x)$ in a certain region $\omega_1 < \omega < \omega_2, \omega_1, \omega_2 \neq 0$. This appears to confirm our general conclusions, i.e. these are no sequences of an apparently arbitrary choice of a Nevanlinna function.

To complete the Tchebycheff-Markov inequality's description, we mention that some differential characteristics of a spectrum can be found from the so-called coarse grained density

$$\bar{I}(x) = \frac{1}{\Delta}\int_{x-\Delta/2}^{x+\Delta/2} I(y)\mathrm{d}y,$$

which is bounded by $T(x) < I(x) < S(x)$ with

$$\begin{aligned}
S(x) &= \frac{1}{\Delta}\left[u(\frac{\Delta}{2} - x) + u(\frac{\Delta}{2} + x)\right], \qquad (37)\\
T(x) &= \frac{1}{\Delta}\left[l(\frac{\Delta}{2} - x) + l(\frac{\Delta}{2} + x)\right], \quad x \leqslant \frac{\Delta}{2},\\
S(x) &= \frac{1}{\Delta}\left[u(x + \frac{\Delta}{2}) - l(x - \frac{\Delta}{2})\right],\\
T(x) &= \max\left(0, \frac{1}{\Delta}\left[l(x) + \frac{\Delta}{2}) - u(x - \frac{\Delta}{2})\right]\right), \quad x \geqslant \frac{\Delta}{2}.
\end{aligned}$$

Obviously, this is a coarse definition of a derivative. Choosing interval Δ one should look for a compromise between smaller grains and the bounded interval: the smaller are the grains, the bigger is the distance between the boundaries.

This method sometimes produces quite exact line forms, especially for smooth and finite functions. That is why these coarse-grained boundaries are even less suitable for restoring an edge singularity form.

The inequalities can be applied to the MND problem if a number of different lines are discussed simultaneously and one aims at estimating their thresholds, respective intensities and frequency tails. For a specific application see [6].

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ЧАСТОТНІ МОМЕНТИ: ТОЧНА СТРУКТУРА РЕНТГЕНІВСЬКИХ СПЕКТРІВ МЕТАЛІВ ТА ІНШІ ЗАСТОСУВАННЯ

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Визнано, що краї ліній рентгенівських спектрів металів (поглинання, висилання, фотоемісія) мають нетривіальну форму: $I(\omega) \propto |\omega - \omega_{\rm edge}|^{-\alpha}$, яку ще називають степеневим законом. Цей закон виконується асимтотично при $\omega \to \omega_{\rm edge}$ в околі порогу. Таку незвичайну поведінку було пояснено як прояв аналогу інфрачервоної катастрофи, який є результатом раптової зміни середнього поля системи. До цього поля додається потенціал дірки в кістяку (де раніше був збуджений з глибокого рівня електрон). В даній статті обговорено метод відновлення форми лінії поза межами асимтотичної ділянки, де вважається справедливим так званий узагальнений степеневий закон: $I = c\omega^{\alpha(\omega)}$. З цією метою ми комбінуємо відомий показник сингулярності α з кількома першими частотними моментами, які знайдено з повного точного виразу для усього спектра. Ми показуємо, що $\alpha(\omega)$ сильно залежить від форми зони провідності та від асимтотики поля кістякової дірки на великих відстанях .