

On the Differential Cross Section for X-Ray Inelastic Scattering

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A formal formulation of the differential cross section for x-ray inelastic scattering is given for a real solid, in particular, in terms of the polarization propagator and the inverse dielectric function. The differential cross section is related to the causal functions of electron properties rather than those retarded functions.

Key words: Differential cross section; real metals; theory; x-ray inelastic scattering.

A few years ago, the present author formulated the differential cross section for x-ray inelastic scattering in a unified way such that core electrons as well as valence electrons were treated on an equal basis [1].¹ This formulation aided explanation of the then unresolved x-ray Raman scattering problem. In this paper, the differential cross section will be expressed in terms of causal rather than retarded functions in model-independent form. The results are similar in form to the Nozières-Pines [2] results for an electron gas in the dielectric formulation.

Several results of this paper have been reported previously or used separately in papers published elsewhere [3, 4]. It is, however, desirable to present the entire formulation in a systematic way, although the formulation is a trivial one to those who are familiar with Schwinger's many-body formulation and the spectral function technique.

In previous papers [1, 5] it was shown that the differential cross section for x-ray inelastic scattering is given by the double four-dimensional Fourier transform of the electron charge (or current) correlation:

$$\sigma(k \rightarrow k') \equiv C(k, k') (\epsilon \cdot \epsilon')^2 \int \int d^4x d^4y \langle \Delta\rho(x) \Delta\rho(y) \rangle \exp [-i(k - k')(x - y)], \quad (1-a)$$

where k and k' are the four-vectors consisting of the wave vectors and the energies of the incoming and the outgoing photons, respectively, and ϵ and ϵ' are their polarization directions. The quantity $C(k, k')$ is defined by

$$C(k, k') = (2\pi)^{-4} (e^2/m)^2 (kk')^{-1}. \quad (1-b)$$

The function $\rho(x)$ is the electron charge operator and $\Delta\rho(x)$ is given by

$$\Delta\rho(x) = \rho(x) - \langle \rho(x) \rangle, \quad (2)$$

where $\langle Q \rangle$ indicates the expectation value of an operator Q with respect to the ground (Fermi vacuum) state of the electron system. This ground state² is a Heisenberg state of the electron system in the absence of radiation fields [1]. Units are such that $\hbar = c = 1$ and the metric is $kx = \mathbf{k} \cdot \mathbf{r} - |k|t$ if the four vectors are given by $k = (\mathbf{k}, |k|)$ and $x = (\mathbf{r}, t)$.

Since the charge correlation in eq (1) is defined by the Fermi vacuum expectation value of the system of electrons per se, one can proceed via the standard approach for many interacting electron problems to calculate it. In particular, we use Schwinger's action principle [6] by adding an external c -number source function to the Hamiltonian density of the electron system. The Hamiltonian density due to the external source, $U(x)$, is given by

$$\mathcal{H}_S(x) = U(x) \psi^+(x) \psi(x), \quad (3)$$

where $\psi(x)$ is the electron field operator and $\psi^+(x)$ is its adjoint. Then the action principle gives

$$i \frac{\delta \langle Q(1) \rangle}{\delta U(2)} = \langle T[Q(1) \psi^+(2) \psi(2)] \rangle - \langle Q(1) \rangle \langle \psi^+(2) \psi(2) \rangle \quad (4)$$

¹Figures in brackets indicate the literature references at the end of this paper.

²At finite temperatures, the ground state average $\langle \dots \rangle$ must be replaced by an average over a grand canonical ensemble.

where the variable, say 1, is short for $x_1 = (\mathbf{r}_1, t_1)$; $Q(x)$ is any operator in the Heisenberg representation; the symbol $T[\dots]$ implies the time ordering operation for fermions. The electron Green's function is defined by

$$G(12) = (-i) \langle T[\psi(1)\psi^+(2)] \rangle. \quad (5)$$

From this, the vacuum expectation value of the electron charge operator, $\rho(x)$, is given by

$$\langle \rho(1) \rangle = \langle \psi^+(1_+)\psi(1) \rangle = (-i)G(1, 1_+), \quad (6)$$

where 1_+ indicates the four vector $(\mathbf{r}_1, t_1 + 0)$.

If we substitute (6) into (4), we obtain

$$iS(12) = i \frac{\delta \langle \rho(1) \rangle}{\delta U(2)} = \frac{\delta G(1, 1_+)}{\delta U(2)} = \langle T[\Delta\rho(1) \cdot \Delta\rho(2)] \rangle. \quad (7)$$

This quantity is a causal Green's function, while the quantity in eq (1) is merely a time correlation. These two are, of course, different functions. However, there is a definite mathematical relation between them in the spectral representation [7, 8], provided that translational time invariance holds. In our electron system, this invariance holds since the total Hamiltonian of the electron system is thought of as being time independent.

At absolute zero,³ the spectral relationship between the time correlation and the causal function is given by

$$\langle \Delta\rho(1)\Delta\rho(2) \rangle_\omega = -2\text{Im}[(-i)\langle T[\Delta\rho(1)\Delta\rho(2)] \rangle_\omega], \quad (8)$$

where $\langle \dots \rangle_\omega$ implies the spectral intensity (the Fourier transform using a basis of $\exp[-i\omega(t_1 - t_2)]$) of the function $\langle \dots \rangle$, and the symbol Im denotes "the imaginary part of". Since the differential cross section, eq (1), contains the quantity given by eq (8), we now study the properties of the causal function eq (7).

The electron system which we are dealing with must represent that of a real crystal. In such a system translational invariance may not hold for spatial coordinates. Therefore we deal with quantities, such as eq (7), as they are written, in terms of space-time coordinates; but not in terms of their Fourier transform until we reach the very end. The electron Green's function, $G(12)$, satisfies the electron Green's function equation:

$$G^{-1}(1\bar{1})G(\bar{1}2) = G(1\bar{1})G^{-1}(\bar{1}2) = \delta(12), \quad (9)$$

where the convention for integrations applies to the repeated variables with a bar. The vertex function for electron-electron interaction (not a radiation part) is defined by

$$\Gamma_U(12; 3) = \frac{\delta G^{-1}(12)}{\delta U(3)} \quad (10)$$

The quantity G^{-1} can be given in terms of the total average potential, $V(1)$, of the system and the self-energy operator $\Sigma(12)$:

$$G^{-1}(12) = \left[i \frac{\partial}{\partial t_1} + \frac{\nabla^2(1)}{2m} + \sum_n Z_n v_c(1, \mathbf{R}_n) + \mathcal{E}_f \right] \delta(12) - V(1) \delta(12) - \Sigma(12), \quad (11)$$

and

$$V(1) = U(1) - i v_c(1\bar{1}) G(\bar{1}\bar{1}_+), \quad (12)$$

where \mathbf{R}_n denotes the position of the nucleus n , $Z_n |e|$ is the charge of the n th nucleus, v_c is the instantaneous Coulomb interaction, and \mathcal{E}_f is the Fermi energy. The self energy operator Σ is given by

$$\Sigma(12) = -i v_c(1\bar{1}) G(\bar{1}2) \Gamma_U(\bar{2}2; \bar{1}_+). \quad (13)$$

The time ordered product of $\Delta\rho$ has been connected to the variational derivative of the electron Green's function by eq (7). In terms of the vertex function, eq (10), we can write

$$S(12) = i G(1\bar{1}) \Gamma_U(\bar{1}\bar{2}; 2) G(\bar{2}1_+). \quad (14)$$

This expression provides a way of calculating the charge correlation from eq (7). However, there is another way [9] to express it, emphasizing the dynamic properties of interacting electrons. Such dynamic properties of electrons can be characterized by a generalized dielectric or inverse dielectric function of the system, which represents the true response of the system, including the dynamic screening effect of electron interactions. The inverse dielectric function can be defined by

$$\epsilon^{-1}(12) = \frac{\delta V(1)}{\delta U(2)}. \quad (15)$$

Then we obtain

$$S(12) = P(1\bar{1}) \epsilon^{-1}(\bar{1}2), \quad (16)$$

where P is the irreducible polarization propagator [9, 10]. This propagator is now given in terms of a new dressed vertex function Γ by

$$P(12) = i G(1\bar{1}) \Gamma(\bar{1}2; 2) G(\bar{2}1_+), \quad (17)$$

where

$$\Gamma(12; 3) = \frac{\delta G^{-1}(12)}{\delta V(3)}. \quad (18)$$

³ At finite temperatures, the right-hand side of eq (8) should be multiplied by the following factor

$$f(\omega, T) = \frac{1}{1 + \eta \exp[-\omega/kT]}, \quad (8')$$

where T is absolute temperature, k is Boltzmann's constant and η is -1 for fermions.

We have thus calculated the causal function $S(12)$ originally defined by eq (7). We have also found that the spectral intensity of the time correlation is related to that of the causal function by relation (8). Since the differential cross section (1-a) is given by the Fourier transform of the electron charge time-correlation, it is now possible to calculate the differential cross section (1-a) from the causal function $S(12)$ through eq (16). We write the double Fourier transform of function $F(12)$ as follows:

$$F(12) = \int \frac{d\omega}{2\pi} \frac{d\mathbf{k}_1}{(2\pi)^3} \frac{d\mathbf{k}_2}{(2\pi)^3} F(\mathbf{k}_1, \mathbf{k}_2; \omega) \exp [i\mathbf{k}_1 \mathbf{r}_1 - i\mathbf{k}_2 \mathbf{r}_2 - i\omega(t_1 - t_2)]. \quad (19)$$

In terms of these Fourier transforms, eq (8) gives

$$N(\mathbf{k}_1, \mathbf{k}_2; \omega) = -2 \operatorname{Im} S(\mathbf{k}_1, \mathbf{k}_2; \omega), \quad (20)$$

where $N(\mathbf{k}_1, \mathbf{k}_2; \omega)$ is the Fourier transform of the charge correlation $\langle \Delta\rho(x)\Delta\rho(y) \rangle$. It is convenient at this stage to introduce two experimental variables. One is the momentum transfer κ which is given by both the energy (or wave-length λ_{in}) of the incoming x rays and the scattering angle θ . The other is the energy transfer E which is the energy loss of the outgoing x rays. These quantities are defined by

$$\kappa = \mathbf{k} - \mathbf{k}'; |\kappa| \approx (4\pi/\lambda_{\text{in}}) \sin(\theta/2) \quad (21)$$

and

$$E = |\mathbf{k}| - |\mathbf{k}'|. \quad (22)$$

Then the differential cross section (1-a) is rewritten in terms of the double Fourier transform of the charge correlation, $N(\kappa, \kappa, E)$ as

$$\sigma(k \rightarrow k') = \sigma(\kappa, E) = \frac{C(k, k')}{(\epsilon \cdot \epsilon')^2} \int dt N(\kappa, \kappa; E). \quad (23)$$

It should be noted that the differential cross section defined by (1-a) is the *total* transition probability instead of the customary transition probability per unit time (i.e., rate). As seen from (23), the customary transition rate $\bar{\sigma}(\kappa, E)$ is given by the integrand of eq (23) since the integrand turns out to be time independent:

$$\sigma(\kappa, E) = \int dt \bar{\sigma}(\kappa, E). \quad (24)$$

Finally the customary differential cross section is given via eq (20) by

$$\bar{\sigma}(\kappa, E) = (-2) C(kk') (\epsilon \cdot \epsilon')^2 \operatorname{Im} \left[\int \frac{d^3k}{(2\pi)^3} P(\kappa, \bar{\mathbf{k}}; E) \epsilon^{-1}(\bar{\mathbf{k}}, \kappa; E) \right], \quad (25)$$

where the Fourier transform of eq (16) is used to express $S(\kappa, \kappa, E)$. This expression has been used to calculate the inelastic scattering profiles at different scattering angles in both the Hartree-Fock and the random phase approximations [3, 4].

As mentioned previously, the present formulation is model-independent and also holds for real crystals. In such crystals, periodic spatial translational invariance may not hold, thus forbidding the use of a Fourier series-integral expansion. As seen in the expression of the differential cross section, the final result is given by the double Fourier transforms of the physical quantities. Even in the crystal with imperfect spatial translational invariance, one can always expand the nonlocal functions by the double Fourier integrals as we have shown here.

Another advantage of the present result is found in its capability of separating, for instance, the core electron contribution from the valence electron contribution, thus filling in the gap between the modern x-ray inelastic theory and the traditional Waller-Hartree expression [11]. This separation can be done, because the polarization propagator, P , can be expressed as a sum of two terms: $P = P_{\text{core}} + P_{\text{valence}}$. It is also possible to deal with the interaction of electrons in crystals realistically through a proper decomposition of the P : for instance, $P = P_{\text{diagonal}} + P_{\text{nondiagonal}}$.

As a final point, note that, substituting expression (12) into (15), we obtain

$$\epsilon^{-1}(12) = \delta(12) + v_c(1\bar{1})S(\bar{1}2). \quad (15')$$

The Coulomb potential, $v_c(12)$, is instantaneous and a function of $1-2$. Therefore, the Fourier transform of v_c can be diagonalized. Utilizing this property, one may express the imaginary part of $S(12)$ by that of $\epsilon^{-1}(12)$, like in an electron gas model.

References

- [1] Kuriyama, M., Acta. Cryst. **A27**, 634 (1971).
- [2] Nozières, P., and Pines, D., Phys. Rev. **113**, 1254 (1959).
- [3] Cohen, G. G., Alexandropoulos, N. G., and Kuriyama, M., Solid State Comm. **10**, 95 (1972).
- [4] Alexandropoulos, N. G., Cohen, G. G. and Kuriyama, M., Phys. Rev. Letters **33**, 699 (1974).
- [5] Kuriyama, M., and Alexandropoulos, N. G., J. Phys. Soc. Japan **31**, 561 (1971).
- [6] Schwinger, J., Proc. Nat. Acad. Sci. **37**, 452 and 455 (1951).
- [7] Martin, P. C. and Schwinger, J., Phys. Rev. **115**, 1342 (1959).
- [8] Zubarev, D. N., Soviet Phys USPEKHI **3** No. 3, 320 (1960).
- [9] Hedin, L., Phys. Rev. **139**, A796 (1965).
- [10] Engelsberg, S., and Platzman, P. M., Phys. Rev. **148**, 103 (1966).
- [11] Waller, I. and Hartree, D. R., Proc. Roy. Soc. **A124**, 119 (1929).

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