

Scattering of electrons by long linear molecules. The effect of approximate translational symmetry

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A general theory is considered of the scattering of electrons by a long linear chain in three-dimensional space; the chain consists of a large number of identical cells. Such a system has a translational symmetry, which is unusual in scattering problems. However, the symmetry is only approximate, because of the finiteness of the chain. Scattering by finite chains consisting of N cells (polymer molecules) can be observed, the cross section being averaged over the chain orientations (the analog of powder diagrams in x-ray structure analysis). As $N \rightarrow \infty$, the averaged differential cross section changes discontinuously at the angles $\theta_m = 2 \arcsin(\pi m / kd)$ (k is the momentum, d is the cell length, and m is an integer). The magnitude of the discontinuity is of the same order as the cross section itself at θ_m . For long but finite chains, the singularities become less pronounced and the discontinuity is replaced by a sharp increase, the derivative of the differential cross section with respect to angle increasing linearly with increase in N . A model calculation is carried out for chains consisting of wells of zero radius, and the results are compared with the general theory.

1. INTRODUCTION. ELEMENTARY THEORY

In the present work we consider the general theory of scattering by an object of a new type—a long linear chain in three-dimensional space, consisting of a large number of identical cells. Such an object has translational symmetry, which is unusual for scattering problems; however, the symmetry is approximate because of the finite length of the chain. Nevertheless, this symmetry leads to the appearance of characteristic features in the differential and total scattering cross sections. In what follows, we shall speak of the quantum mechanical scattering of the particles (electrons), although the theory that is developed is also applicable to the scattering of electromagnetic waves, neutrons, and so on.

Scattering from an infinite chain will be understood by us in the following limiting sense. For a finite linear chain, it is expedient to have in mind two asymptotic regions in coordinate space. The first region is characterized by distances that are much greater than the distance between neighboring scattering centers, and much smaller than the dimensions of the chain. The second (external) asymptotic region is so defined that the wave function in it is represented in the form of a plane incident wave and a spherical scattered wave. For an infinite chain, only the first asymptotic region exists and the behavior of the wave function in this region is close to the behavior of the wave function in the first asymptotic region for a very long finite chain.

A chain of infinite length has exact translational symmetry and scattering from it takes place along the generatrices of cones whose axes coincide with the axis of the chain (Fig. 1, where we have for simplicity drawn only one such cone). For the cone with number m , the momentum vector k of the scattered electron satisfies the equation

$$qd = 2m\pi, \quad m = 0, \pm 1, \dots \quad (1)$$

where $q = k - k_0$ is the transferred momentum, k_0 is the initial momentum of the emerging electron, and d is the period of the chain. The meaning of (1) is that the component of the transferred momentum in the direction of the chain should be a multiple of the period of the re-

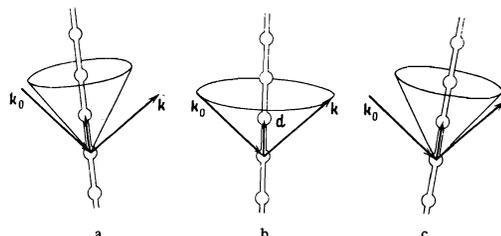


FIG. 1. Scattering of electrons from a long chain takes place in the direction of the generatrices of the cones. On all the drawings, the angle between the vectors k and k_0 is equal to θ_m . It is seen from the drawings that for all mutual orientations of the vectors k_0 and d , the m -th cone makes a contribution to the scattering only at angles $\theta > \theta_m$.

ciprocal lattice for the considered periodic structure (the chain).

Scattering by chains of finite length, of N cells, is observable (polymer molecules). If the molecules of the target are randomly oriented, then the experimentally measured quantity is the cross section averaged over the orientations of the chain in space (the analog of powder diagrams in x-ray structure analysis). It is just this sort of cross section that we are concerned with here.

For a cone with a given number m , we can introduce the limiting scattering angle θ_m :

$$\theta_m = 2 \arcsin(m\pi/kd), \quad m = 1, 2, \dots \quad (2)$$

Figure 1b shows the mutual orientations of the vectors k and d such that scattering takes place at the angle θ_m (and also at larger angles—along another cone). If we now vary the direction of the axis of the molecule in arbitrary fashion (Figs. 1a, 1c), then the scattering will take place at larger angles. Thus, averaged over the orientations of the chain, the m -th cone gives a contribution to the scattering only at angles larger than θ . To make more precise the character of the singularity that arises at $\theta = \theta_m$, a more detailed analysis is necessary, and is given below.

In electron scattering by a molecule, the periodicity of the potential is disturbed by the oscillations of the nuclei. The order of magnitude of the displacement of

the atoms Δ from their equilibrium position can be estimated from the formula

$$\Delta \sim (kTN)^{1/2} / \omega_0 M^{1/2}, \quad (3)$$

where T is the temperature of the gas target, k is Boltzmann's constant, ω_0 is the frequency of oscillation for a single bond in the chain, and M is the mass of the atoms. In order that the interference picture not be distorted, it is necessary to require satisfaction of the condition

$$k\Delta \ll \pi. \quad (4)$$

On the other hand, singularities are observed in the cross section if

$$kd > \pi. \quad (5)$$

The model calculations given in this paper indicate that the interference effects are clearly pronounced even for not very large N , when the condition $\Delta/d \ll 1$ is satisfied. In this case, by choosing the energy of the incident electrons ($E \gtrsim 150$ eV), we can bring about simultaneous satisfaction of the conditions (4) and (5) and observe experimentally the characteristic singularities of the differential cross section that are established here.

2. GENERAL THEORY

It is convenient to start out from the integral form of the Schrödinger equation for the wave function of the incident electron $\psi_{k_0}(\mathbf{r})$:

$$\psi_{k_0}(\mathbf{r}) = e^{i\mathbf{k}_0 \cdot \mathbf{r}} - \int \frac{e^{i\mathbf{k}' \cdot \mathbf{r} - r'}}{2\pi |\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}') \psi_{k_0}(\mathbf{r}') d\mathbf{r}', \quad (6)$$

where $V(\mathbf{r})$ is the interaction potential of the electron with a chain of finite length.¹⁾

We assume that the wave function $\psi_{k_0}(\mathbf{r})$ satisfies approximately the Bloch condition

$$\psi_{k_0}(\mathbf{r} + m\mathbf{d}) = e^{im\mathbf{k} \cdot \mathbf{d}} \psi_{k_0}(\mathbf{r}) \quad (7)$$

if both the vectors \mathbf{r} and $\mathbf{r} + m\mathbf{d}$ lie in the region where the potential $V(\mathbf{r})$ differs from zero. The quasimomentum \mathbf{k} in (7) should be so chosen that the inhomogeneous term (the plane wave) on the right hand side of Eq. (6) also satisfies the condition (7), whence

$$\mathbf{k} \cdot \mathbf{d} = \mathbf{k}_0 \cdot \mathbf{d}.$$

As usual, we find the scattering amplitude f by considering the asymptotic behavior of the right hand side of (6) for the case $r \gg Nd$. Using (7) and (8) as well as the periodicity of the potential $V(\mathbf{r})$, we obtain, after simple transformations,

$$f(\mathbf{k}_0, \mathbf{k}, \mathbf{d}) = \frac{\sin(Nq\mathbf{d}/2)}{\sin(q\mathbf{d}/2)} B_N(\mathbf{k}_0, \mathbf{k}, \mathbf{d}), \quad (9)$$

$$B_N(\mathbf{k}_0, \mathbf{k}, \mathbf{d}) = -\frac{1}{2\pi} \int e^{-i\mathbf{k}' \cdot \mathbf{r}'} V(\mathbf{r}') \psi_{k_0}(\mathbf{r}') d\mathbf{r}'. \quad (10)$$

where the integration is carried out only over a single (central) cell. We use the following notation: θ is the angle between the vectors \mathbf{k} and \mathbf{k}_0 (i.e., the scattering angle); ϑ is the angle between \mathbf{d} and \mathbf{q} ; φ is the angle between the plane in which the vectors \mathbf{d} and \mathbf{q} lie, and the vector $\mathbf{k} + \mathbf{k}_0$. Then B_N is some function of the angles $B_N(\theta, \vartheta, \varphi)$.

It makes sense to introduce the differential cross section averaged over the orientations²⁾ of \mathbf{d} and referred to a single cell of the chain:

$$\sigma_N(\theta) = \frac{1}{4\pi N} \int_0^\pi \int_0^{2\pi} |f(\mathbf{k}_0, \mathbf{k}, \mathbf{d})|^2 \sin \theta \, d\vartheta \, d\varphi. \quad (11)$$

It is convenient to consider the derivative $\tilde{\sigma}_N'(\theta)$, for which we obtain by integrating by parts and with the help of (9) and (11)

$$\begin{aligned} \tilde{\sigma}_N'(\theta) = & \frac{1}{8\pi N} \operatorname{ctg} \frac{\theta}{2} \frac{\sin^2(Nq\mathbf{d}/2)}{\sin^2(q\mathbf{d}/2)} \int_0^\pi |B_N(\theta, 0, \varphi)|^2 \\ & + |B_N(\theta, \pi, \varphi)|^2 d\varphi + \frac{1}{4\pi N} \int_0^\pi \int_0^{2\pi} \frac{\sin^2(Nq\mathbf{d}/2)}{\sin^2(q\mathbf{d}/2)} \left\{ \frac{\partial}{\partial \theta} |B_N|^2 \right. \\ & \left. + \frac{1}{2 \sin \theta} \operatorname{ctg} \frac{\theta}{2} \frac{\partial}{\partial \theta} (\cos \theta |B_N|^2) \right\} \sin \theta \, d\vartheta \, d\varphi. \end{aligned} \quad (12)$$

The singularities which are characteristic for scattering from long linear moleculars are connected with the first component in (12) (the second component is bounded as $N \rightarrow \infty$ and at $\theta \neq 0$). Actually, the function

$$\delta_p(x, N) = \sin^2(Nx) / (\pi N \sin^2 x) \quad (13)$$

has a δ -like character at large N , with maxima at the points $x = m\pi$ ($m = 0, \pm 1, \pm 2, \dots$), and

$$\delta_p(m\pi, N) = N/\pi, \quad (14)$$

$$\lim_{N \rightarrow \infty} \delta_p(x, N) = \delta_p(x) = \sum_{m=-\infty}^{\infty} \delta(x + m\pi). \quad (15)$$

It then follows that upon increase in θ , the cross section $\tilde{\sigma}_\infty(\theta)$ increases jumpwise at the points θ_m (2):

$$(\Delta \tilde{\sigma})_m = \tilde{\sigma}_\infty(\theta_m + 0) - \tilde{\sigma}_\infty(\theta_m - 0) = \frac{1}{2m} \{ |B_\infty(\theta_m, 0, \varphi)|^2 + |B_\infty(\theta_m, \pi, \varphi)|^2 \}. \quad (16)$$

The quantities $|B_\infty|^2$ in (16) actually do not depend on φ by virtue of the properties of the spherical set of coordinates ($\vartheta = 0, \pi$). The value of the jump in the cross section generally has the same order as the cross section itself at the point θ_m . By means of (9), (11), and (15) it is not difficult to obtain for $\tilde{\sigma}_\infty(\theta)$ a formula that contains the indicated discontinuities:

$$\tilde{\sigma}_\infty(\theta) = \sum_m \frac{1}{4kd \sin(\theta/2)} \int_0^{2\pi} \left| B_\infty \left(\theta, \arccos \frac{m\pi}{kd \sin(\theta/2)}, \varphi \right) \right|^2 d\varphi. \quad (17)$$

The summation is carried out here over all integer m (positive and negative) such that $|m|\pi < 2kd \sin(\theta/2)$. When θ passes through the value θ_m , the number of terms in the sum changes, and this is indeed the cause of the discontinuity.

For large but finite N , the function $\tilde{\sigma}_N(\theta)$ increases sharply in the neighborhood of the point θ_m , by an amount $(\Delta \tilde{\sigma})_m$, and the derivative $\tilde{\sigma}_N'(\theta_m)$ increases linearly with increase of N (see (12), (14)):

$$\tilde{\sigma}_N'(\theta_m) |_{N \rightarrow \infty} = N \frac{kr\ell}{2\pi} \cos \frac{\theta_m}{2} (\Delta \tilde{\sigma})_m + O(1). \quad (18)$$

The forward scattering cross section increases linearly with increasing N :

$$\tilde{\sigma}_N(0) |_{N \rightarrow \infty} = \frac{N}{4\pi} \int_0^\pi \int_0^{2\pi} |B_N(0, \theta, \varphi)|^2 \sin \theta \, d\vartheta \, d\varphi + O(1), \quad (19)$$

which follows directly from (9) and (11).

For the study of the dependence of the total cross section on the momentum k

$$\tilde{\sigma}_N = 2\pi \int_0^\pi \tilde{\sigma}_N(\theta) \sin \theta \, d\theta \quad (20)$$

it is convenient to consider the derivative $d\tilde{\sigma}_N/dk$, which, with the help of (9), (11), and (20), can be represented in the form

$$\frac{d\tilde{\sigma}_N}{dk} = \frac{8\pi}{k} \tilde{\sigma}_N(\pi) + \frac{1}{2N} \int_0^\pi \int_0^{2\pi} \frac{\sin^2(Nq\mathbf{d}/2)}{\sin^2(q\mathbf{d}/2)} \left\{ \frac{\partial}{\partial k} |B_N|^2 \right\}$$

$$-\frac{4}{k} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin^2 \frac{\theta}{2} |B_N|^2 \right) \sin \theta \, d\theta \sin \vartheta \, d\vartheta \, d\varphi. \quad (21)$$

It follows from (17) that if we reach the point $k_m = m\pi/d$ by increasing k , then a term of the form

$$\frac{1}{4kd} \int_0^{2\pi} \left\{ \left| B_\infty \left(\pi, \arccos \frac{m\pi}{kd}, \varphi \right) \right|^2 + \left| B_\infty \left(\pi, \arccos \left(-\frac{m\pi}{kd} \right), \varphi \right) \right|^2 \right\} d\varphi \quad (22)$$

is added to the expression for $\tilde{\sigma}_N(\pi)$ on the right side of (21) at $N = \infty$. Thus, the quantity $d\tilde{\sigma}_\infty/dk$ changes jumpwise at $k = k_m$.

The relation (7), on which the derivations of this section are based, are valid only for an infinite chain. In the case of finite N , the greatest deviations from (7) take place near the ends of the chain. We shall show that the condition (7) is satisfied exactly in the framework of the Born approximation, and also when multiple scattering from different cells of the chain is neglected. The latter approximation is valid if each cell represents a potential center with the dimensions small in comparison with d , and $kd \gg 1$. On the other hand, the values of ψ_{k_0} inside the region of action of the potential approach the values of ψ_{k_0} for an infinite chain with increasing N , and the latter values satisfy the condition (7).

3. SCATTERING FROM A CHAIN OF POTENTIALS OF ZERO RADIUS

We now consider the scattering of electrons from a chain of identical potentials of zero radius, placed at the point $\mathbf{r}_m = m\mathbf{d}$. The bound states for this system, in the case of an infinite chain, were considered earlier by Demkov and Subramanian^[1] (see also^[2,3]). The wave function of the electrons satisfies the Schrödinger equation for a free particle, and the boundary condition (see, for example, ^[1])

$$\psi(\mathbf{r})|_{|\mathbf{r}-\mathbf{r}_m| \rightarrow 0} = A_m \left(\frac{1}{|\mathbf{r}-\mathbf{r}_m|} + \alpha \right) + O(|\mathbf{r}-\mathbf{r}_m|) \quad (23)$$

is specified at the points \mathbf{r}_m . Here the parameter α characterizes the depth of the well. The function $\psi_{k_0}(\mathbf{r})$ is of the form

$$\psi_{k_0}(\mathbf{r}) = e^{i\mathbf{k}_0 \cdot \mathbf{r}} + \sum_m A_m \frac{e^{i\mathbf{k}_0 \cdot (\mathbf{r}-\mathbf{r}_m)}}{|\mathbf{r}-\mathbf{r}_m|}. \quad (24)$$

The scattering problem reduces in this case to a linear algebraic system. The numerical calculations that we have carried out for different values of N and of the parameters of the problem kd and αd are in excellent agreement with the results of the general theory and allow us to assess the magnitude of the effects. Some results for the differential cross sections are given in Fig. 2, where the arrows indicate the values of the scattering angles at which the theory predicts discontinuities in the cross section. The linear dependence on N in Eq. (18) is also well confirmed by our model calculation. So far as effects in the total scattering cross section are concerned, they turn out to be very small in comparison with the cross section itself in the cases considered.

For an infinite chain we have $A_m = e^{im\kappa d} B_\infty$ and, with the help of (23), (24) and (8), we can find B_∞ in explicit form:

$$B_\infty = d \{ \alpha d + \ln(2 \cos kd - 2 \cos \alpha d) \}^{-1}. \quad (25)$$

It is convenient to consider the function $B_\infty(25)$ in the

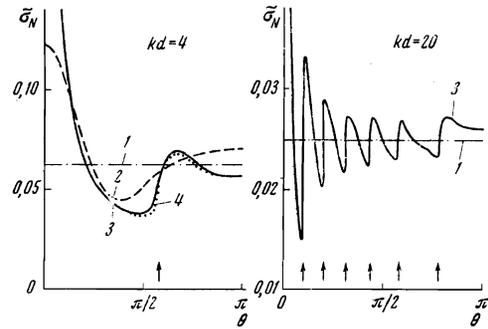


FIG. 2. The differential cross section (in units of d^2) averaged over the orientations for scattering of electrons by a chain of potentials of zero radius ($\alpha d = 0.01$) for different values of N and kd : 1— $N = 1$; 2— $N = 6$; 3— $N = 10$; 4— $N = 16$.

complex k plane at a fixed value of the parameter κ . The characteristic singularity is the presence in the function (25) of an infinite number of branch points of logarithmic character

$$k_n^{(n)} = 2\pi n/d \pm \kappa, \quad n = 0, \pm 1, \pm 2, \dots \quad (26)$$

We draw the cuts vertically downward from the branch points.

The choice of the physical sheet in the infinitely sheeted surface k is determined by the fact that the energies of the bound states, which are determined from the equation^[1]

$$\alpha d + \ln(2 \cos kd - 2 \cos \alpha d) = 0, \quad (27)$$

should be poles of the scattering amplitude (i.e., the functions B_∞). Thus, for k lying on the upper imaginary semi-axis of the physical sheet, one should take in Eq. (25), just as in (27), the principal value of the multivalued analytic function $\ln(x)$, which is denoted by $\ln(x)$. When moving along the real k axis, all the branch points should be bypassed in the upper half-plane. Consequently, if k is real and m branch points lie in the interval from zero to k ($k > 0$), then

$$B_\infty = d \{ \alpha d + \ln | 2 \cos kd - 2 \cos \alpha d | - im\pi \}^{-1}. \quad (28)$$

We note that Eq. (28) can also be obtained if, in the derivation of the expression for B_∞ (Eq. (25)), we take accurately into account the property of periodicity of the infinite sums that appear.

In the work of Subramanian and one of the authors,^[1] it was noted that Eq. (27), which determines the energy of the bound states as a function of the quasimomentum κ , can have a solution even for positive energies (i.e., for real k). However, the problem of the choice of sheets on the multi-sheeted energy surface was not considered in this case. The discussion given above shows that the indicated bands with positive energies are lacking at $k > \kappa$, since the corresponding poles of the scattering amplitude lie on distant nonphysical sheets of the complex energy surface. These poles will not appear, for example, in the scattering of particles by a finite or an infinite chain. So far as the interval $0 < k < \kappa$ is concerned, the function B_∞ on it can have a pole even on the physical sheet (for a corresponding choice of α). However, inasmuch as $\kappa d = k_0 \cdot d \leq k_0 d$ in the scattering problem, in accord with (8), the indicated pole will again not appear in the scattering cross section.

The validity of Eq. (28) is confirmed by numerical calculation. It can be verified, for example, that, for large N , the sum

$$\frac{1}{N} \sum_m |A_m|^2$$

tends to the value $|B_\infty|^2$, where B_∞ is determined from (25) and the values of the coefficients A_m are obtained by means of numerical solution of the scattering problem for finite chains. We must point out that a rigorous proof of convergence in this and similar cases turns out to be difficult even in the simplest model of potentials of zero radius.

4. CONCLUSION

In order that the considered deductions of the general theory be applicable to the specific problem of scattering of electrons from a polymer chain, satisfaction of the conditions of regularity and rectilinearity are necessary. These will unavoidably be violated for sufficiently long molecules. At the same time, the singularities in the scattering cross sections will be clearly pronounced only if the chain is not too short. Estimates show, however, that for N of the order of ten to twenty, these seemingly contradictory requirements can be reconciled.

It is interesting that scattering from a regular chain of potentials of zero radius of unequal depth also leads to singularities in the differential cross section, of the same type as obtained here. For such potentials, the interesting problem appears of the determination of the sequence of links of a biopolymer rectilinear chain from scattering data, and in particular from the values of the discontinuities in the differential cross section.

As a whole, it can be assumed that the problem of

scattering from a periodic one-dimensional chain possesses a number of qualitative singularities which distinguish it from other scattering problems and which admit of a clear physical interpretation. Hence, in addition to possible specific applications, this problem is interesting also from the general physical point of view.

Note added in proof (December 19, 1973). Recently, we became acquainted with the work in which similar problems were touched on: O. Kratky, *Monatshefte für Chemie*, **76**, 325 (1947). In this work, the scattering of x-rays by colloidal particles was considered only in an approximation equivalent to the Born method, without taking into account multiple scattering from different cells. The discontinuities of $\tilde{\sigma}_\infty(\theta)$ were obtained for infinite chains. However, for finite chains, no singularities of the functions $\tilde{\sigma}_N(\theta)$ were discovered and thus the transition from finite chains to infinite ones was not observed.

¹The atomic system of units is used.

²For simplicity, the chain is assumed to be axially symmetric in what follows, and therefore it is not necessary to average over rotations of the chain about its own axis.

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50