INELASTIC SCATTERING OF FAST ELECTRONS
AND THE STRUCTURE OF THE SCATTERING MOLECULES.
I. THE ELECTRONIC INELASTIC SCATTERING FACTOR

V. I. Bazhanov

The relationship between the intensity of the inelastic scattering of fast electrons by a molecular gas and the matrix elements of the electronic transitions has been given in the Born approximation of scattering theory and in the Born–Oppenheimer approximation for the wave function of a molecule. It has been shown that experimental data from the study of the total scattering and the scattering accompanied only by purely vibrational transitions of the molecule can be used to obtain a function \( S(s) \) which depends on the one- and two-electron density functions of the scattering molecules.

The recently realized possibility of studying experimentally the inelastic scattering of fast electrons by a molecular gas enables important information to be obtained on the structure of the scattering molecules. The experiment can be carried out in such a way that by determining separately the intensity of the total and elastic scattering it is possible to obtain as their difference the intensity of the inelastic scattering of the electrons by the molecules

\[
I_I(s) = I_T(s) - I_E(s).
\]

Here \( I_I(s) \) is the intensity of the total scattering, \( I_E(s) \) is the intensity of the elastic scattering, and \( s \) is the modulus of the change in the wave vector of the scattered electrons.

The generally accepted method for calculating \( I_I(s) \) and \( I_E(s) \) involves the use of the Born approximation of the theory of scattering and (for the calculation of \( I_I(s) \)) the principle of completeness of the system of molecular wave functions. As can be shown in this case, the inelastic scattering factor \( S(s) \), related to \( I_I(s) \) [1], is determined by the electron density of the ground electronic state of the molecule. Nevertheless it is clear that the intensity of inelastic scattering contains information on the energy transitions of the molecule due to collisions with fast electrons. Thus for a more detailed description of the scattering process it is necessary to relate the function \( S(s) \) to the matrix elements of the energy transitions of the molecule. We shall carry out the argument using the Born approximation of the theory of scattering.

We write for the differential cross section of inelastic scattering, at which the molecule passes from the ground state to some excited state, the familiar expression [2]:

$$\frac{d\sigma}{d\Omega} = (2/a_0)^2 |\langle \Psi_0 | L | \Psi_k \rangle|^2.$$  

Here, $\Psi_0$ is the wave function of the ground state, and $\Psi_k$ is the wave function of the excited state

$$L = \sum_{i=1}^{N} Z_i \exp (i\mathbf{s}, \mathbf{R}_i) - \sum_{\nu=1}^{M} \exp (i\mathbf{s}, \mathbf{r}_\nu);$$

$N$ is the number of nuclei in the molecule; $M$ is the number of electrons in the molecule; $Z_i$ is the charge of the $i$-th nucleus; $\mathbf{R}_i$ is the radius vector of the $i$-th nucleus; and $\mathbf{r}_\nu$ is the radius vector of the $\nu$-th electron.

We shall assume that the Born–Oppenheimer approximation holds, that is

$$\Psi_n (\mathbf{r}, \mathbf{R}) = \Phi_\alpha (\mathbf{r}, \mathbf{R}) \varphi_{\alpha n} (\mathbf{R}).$$

Here, $\Phi_\alpha (\mathbf{r}, \mathbf{R})$ is the wave function of the $\alpha$-th electronic state, $\varphi_{\alpha n} (\mathbf{R})$ is the wave function of the $n$-th vibrational state in the $\alpha$-th electronic state, $\{\mathbf{r}\}$ is the set of coordinates of the electron, and $\{\mathbf{R}\}$ is the set of internal coordinates.

In this case the cross section of inelastic scattering will be determined by matrix elements of the following form:

$$a_{\alpha \nu m} = \left\langle \Phi_\alpha (\mathbf{r}, \mathbf{R}) \varphi_{\alpha n} (\mathbf{R}) \sum_{i=1}^{N} Z_i \exp (i\mathbf{s}, \mathbf{R}_i) \Phi_\alpha (\mathbf{r}, \mathbf{R}) \varphi_{\alpha n} (\mathbf{R}) \right\rangle,$$

$$b_{\alpha \nu m} = \left\langle \Phi_\alpha (\mathbf{r}, \mathbf{R}) \varphi_{\alpha n} (\mathbf{R}) \sum_{\nu=1}^{M} \exp (i\mathbf{s}, \mathbf{r}_\nu) \Phi_\alpha (\mathbf{r}, \mathbf{R}) \varphi_{\alpha n} (\mathbf{R}) \right\rangle.$$ 

We assume that scattering takes place on an assembly of molecules which are in the ground electronic state but in different vibrational states, and oriented in different ways. In this case, for the calculation of the intensity of total scattering, it is necessary to carry out the summation with respect to all cross sections and to average the result obtained with respect to the assembly of scattering molecules and with respect to their orientations:

$$s^e_{\nu m} (s) = C \left( \sum_{\alpha=0}^{\infty} W_n \sum_{m=0}^{\infty} \left| a_{\alpha \nu m} (s) - b_{\alpha \nu m} (s) \right|^2 \right)^{\text{orient}}.$$  

Here, $W_n$ is the Boltzmann factor, $C$ is an instrument constant, and $<...>_{\text{orient}}$ denotes averaging with respect to all orientations of the scattering molecules.

In addition,

$$s^e_{\nu m} (s) = C \left( \sum_{n=0}^{\infty} W_n \left| a_{\alpha \nu n} (s) - b_{\alpha \nu n} (s) \right|^2 \right)^{\text{orient}}.$$  

This means that for the intensity of inelastic scattering, with allowance for Eqs. (1), (7), and (8), it is possible to obtain the following expression:

$$s^t_{\nu m} (s) = C |S(s) + S^h (s)|;$$

where

$$S (s) = \left( \sum_{\alpha=1}^{\infty} \left| a_{\alpha \nu m} (s) - b_{\alpha \nu m} (s) \right|^2 \right)^{\text{orient}};$$

$$S^V (s) = \left( \sum_{n=0}^{\infty} W_n \left[ \left( \sum_{m=0}^{\infty} |a_{\alpha \nu m} (s) - b_{\alpha \nu m} (s)|^2 \right) - |a_{\alpha \nu n} (s) - b_{\alpha \nu n} (s)|^2 \right] \right)^{\text{orient}};$$

(here, $S(s)$ is the electronic, and $S^V(s)$ is the vibrational inelastic scattering factor).

Since the electronic wave functions are orthogonal, we obtain from Eq. (5) the following relationship:

$$a_{\alpha \nu m} (s) = \tilde{a}_{\alpha \nu m} (s) \delta_{\alpha \nu},$$