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EXACTLY-SOLVABLE STATISTICAL PROBLEMS FOR ELECTRON SCATTERING FROM THE MANY-PARTICLE DISORDERED SYSTEMS

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Abstract

The amplitude and the cross-section of elastic electron scattering from the multicentred systems are obtained as a result of an exact solution of the task of scattering in the case of one Coulomb and any number of short-range potentials. The statistical theory of line-shape of a narrow resonance in electron energy loss spectra of many-particle disordered systems is developopped within the correlational expansion method.

Introduction.

Charge-particle beam spectroscopy has been a valuable technique for exploring both electronic and atomic (molecular) structure in the different type of many-particle disordered systems within the wide spectra of aggregate states [1-5].

Two modern types of charge-beam spectroscopies, namely, elastic scattering of low-energy electrons and electron-energy loss spectroscopy (EELS) would be considered within the present paper with help of quantum-statistical approach. It is possible to formulate a general theory of both the kinds of scattering, but because of a many-body problem, the formal expressions require some additional approximation both for the electronic density and for atomic (molecular) many particle distribution functions, before they are useful for calculation. This approximation must be determined by the atomic (molecular) species and the deterministic conditions of the system. The development as well as applications to many problems of molecular and nuclear physics of both the theories can be find in the previous publications of the author. Therefore the first aim of this paper is to give (demonstrate) the possibility of an exact solution of the quantum-statistical problem for elastic electron scattering from multicentred system. Namely, the amplitude and the cross-section of scattering are obtained as a result of an exact solution of quantum problem in the case of a multicentred pseudopotential in which one Coulomb and any number of short-range potential are included.

The second goal of this paper will be to develop the statistical approach to the description of narrow resonance line-shape in EELS from disordered systems. The direct reconstruction of a disordered systems by EELS is an important technique by virtue of its wide applicability. The theory for this problem requires only simple expressions that connect the inelastic cross-section with the structural characteristics of the system. We develop this treatment around a correlational expansion method.

Thus, two exact solvable problems of scattering from many particle systems taking into account both quantum and statistical aspects would be considered within this paper.

1. Elastic electron scattering from the multicentred potential.

The aim of the present chapter is to calculate the amplitude and the cross section of elastic electron scattering from the system in which one Coulomb and any number of short range potentials are included. Within this problem the model of zero-radius potential (ZRP) [6-9] will be used with the role of a multicentred pseudopotential. The task was stimulated by the problem of interpretation of the electron-scattering experiments for the complex molecular ions, ionized gases and low-ionized plasma [10,11] on one hand. And on the other hand – by the problem of generalization and developing of the theories of scattering from single Coulomb centre with short range potential well [12-14] and from the superposition of ZRP [15-22] separately. A selected model of pseudopotential has been used in view of successfull applications of the ZRP in the numerical calculation of electron scattering from hydrogen molecule [23] and also, due to possibility of exact solution of the task in this case.

Consider the elastic scattering of a monochromatic electron beam with energy E from the multicentred target which include single Coulomb and N short-ranges potentials where the last ones describe as a superposition of ZRP. Let us assume the target particles as structured and being at rest during the elementary act of scattering. Putting the point $\vec{0}$ of the coordinate system in the Coulomb centre and following the general theory of ZRP [6-9] we shall write the stationary Schrodinger equation for all the system: electron plus target in the next dimensionless form

$$(1) \qquad \left[-\frac{1}{2}\Delta\vec{r} + \frac{s}{r} - E + 2\pi\sum_{j=1}^{N} l_j\delta(\vec{r}-\vec{R}_j)\frac{\partial}{\partial\tau_j}\tau_j\right]\Psi(\vec{r};\{\vec{R}\}) = 0$$

where: $\tau_j = |\vec{r}-\vec{R}_j|$ is the length of scattering for j-th ZRP; $S = \mp 1$ for the actractive and the repulsive Coulomb potentials, respectively; $\Psi(\vec{r};\{\vec{R}\})$ is the wave function of all the system, which includes dependance from all coordinates of the target particles $\{R\} = \vec{R}_1, \ldots, \vec{R}_N$ as parameters. In (1) and further Coulomb system of units will be used in which $\dfrac{\hbar^2}{me^2Z}$ and $\dfrac{me^4Z^2}{\hbar^2}$ are the scales of length and energy respectively, $\Delta_{\vec{r}} \equiv \dfrac{d^2}{d\vec{r}^2}$.

Equation (1) is nonclosed, including, together with $\Psi(\vec{r};\{\vec{R}\})$ also N-unknown functions $\{\Psi(\vec{R}_j;\{\vec{R}\})\}$. Taking into account the physical properties of the wave functions, eqn. (1) will be considered together with typical boundary conditions in the following form

$$\frac{1}{\tau_j \Psi} \frac{\partial}{\partial \tau_j} (\tau_j \Psi)|_{\tau_j \to 0} = -\frac{1}{l_j} \equiv -x_j, \; j = 1, \ldots, N. \tag{2}$$

Introducing the Green function for the Schrodinger equation with Coulomb potential unperturbed by the short-range potentials in the closed form which was firstly obtained by Hostler and Pratt [9, 24-26]

(3)

$$G(\vec{r}, \vec{r}') = \frac{\Gamma(1-\eta)}{2\pi |\vec{r} - \vec{r}'|} \left(\frac{\partial}{\partial ikx} - \frac{\partial}{\partial iky} \right) W_{\eta, \frac{1}{2}}(-ikx) M_{\eta, \frac{1}{2}}(-iky),$$

$$k = \sqrt{2E}, \; x = r + r' + |\vec{r} - \vec{r}'|, \; y = r + r' - |\vec{r} - \vec{r}'|,$$

we can write an exact solution of (1), namely

$$\Psi(\vec{r}; \{\vec{R}\}) = \psi^{+}(\vec{r}) + \sum_{j=1}^{N} \tilde{\Psi}(\vec{R}_j; \{\vec{R}\}) G(\vec{r}, \vec{R}_j), \tag{4}$$

where

$$\psi^{+}(\vec{r}) = e^{-S\frac{\pi}{2k}} \Gamma(1 + S\frac{i}{k}) e^{i\vec{k}\vec{r}} F\left(-S\frac{i}{k}, 1, i(kr - \vec{k}\vec{r})\right), \tag{5}$$

is the Coulomb wave function for continuos spectrum; $\Gamma(z)$ is the gamma-function, $W_{\eta, \frac{1}{2}}(-ikx)$ and $M_{\eta, \frac{1}{2}}(-iky)$ are Witteker functions; $F\left(-S\frac{i}{k}, 1, i(kr - \vec{k}\vec{r})\right)$ is generate hypergeometrical function; $\eta = S\frac{i}{k}$.

The set of coefficients $\{\tilde{\Psi}(\vec{R}_j; \{\vec{R}\})\}$ can be determined as a result of the solution of a sistem of algebric equations which follows from (2) and (4). We represent here just the final result of this calculations, namely

$$\tilde{\Psi}(\vec{R}_j; \{\vec{R}\}) = \frac{\Delta_j}{\Delta}, \tag{6}$$

where

$$(7)\qquad \Delta = \begin{vmatrix} \xi(R_1)+x_1 & 2\pi G(\vec{R}_1,\vec{R}_2) & \dots & 2\pi G(\vec{R}_1,\vec{R}_N) \\ 2\pi G(\vec{R}_2,\vec{R}_1) & \xi(\vec{R}_2)+x_2 & \dots & 2\pi G(\vec{R}_2,\vec{R}_N) \\ \dots\dots & \dots\dots & \dots & \dots\dots \\ 2\pi G(\vec{R}_N,\vec{R}_1) & 2\pi G(\vec{R}_N,\vec{R}_2) & \dots & \xi(R_N)-x_N \end{vmatrix}.$$

$$(7)\qquad \Delta_j = \begin{vmatrix} \xi(R_1)+x_1 & -2\pi\psi^+(\vec{R}_1) & \dots & \xi(\vec{R}_N)+x_N \\ 2\pi G(\vec{R}_2,\vec{R}_1) & -2\pi\psi^+(\vec{R}_2) & \dots & 2\pi G(\vec{R}_2,\vec{R}_N) \\ \dots\dots & \dots\dots & \dots & \dots\dots \\ 2\pi G(\vec{R}_N,\vec{R}_1) & -2\pi\psi^+(\vec{R}_N) & \dots & \xi(R_N)-x_N \end{vmatrix}.$$

and

$$(8)\qquad \xi(R_j) = 2\pi\frac{\partial}{\partial\tau_j}\tau_j G(\vec{r},\vec{R}_j)|_{\tau_j\to 0}$$

To emphasise that the model values of our problem espressions (4,6,7) are obtained without any additional approximations and thus, represent an exact solution.

Using the known asymptotic properties of $\psi^+(\vec{r})$, $W_{\eta,\frac{1}{2}}(Z)$, $M_{\eta,\frac{1}{2}}(Z)$ [27, 28], with the help of (4,6,7), we obtain the expression for the wave function of scattered electron Ψ_{SC} in the following form

$$(9)\qquad \Psi_{sc}(\vec{r},\{\vec{R}\}) = [f_C(\vartheta)+f_{C;1,\dots,N}]\frac{\exp\left(ikr-\frac{i}{k}ln2kr\right)}{r},$$

where

$$(10)\qquad f_c(\vartheta) = -\frac{1}{2k^2\sin^2\frac{\vartheta}{2}}\cdot\frac{\Gamma\left(1+\frac{i}{k}\right)}{\Gamma\left(1-\frac{i}{k}\right)}\exp\left(-\frac{2i}{k}ln\sin\frac{\vartheta}{2}\right),$$

is Coulomb amplitude and ϑ is the angle of scattering.

In the limit when $R \to \infty$ expression (16) generates the following form $f_{c=1,2,} \Rightarrow f_{c=1} + f_2$ which includes results (14,15). Without any difficulty this scheme can be extrapolated on a higher order complexes.

The differential cross section of scattering which is given by the next formula

$$\frac{d\sigma}{d\Omega} = |f_c + f_{C;1,\dots,N}|^2 \tag{17}$$

must be correctly averaged all over the configurations $\{\vec{R}\}$. In particular, following [29, 30] this averaging can be realized with the help of correlational expansion of the $\langle \frac{d\sigma}{d\Omega} \rangle$ in the doubly-irriducible series, every p-th fragment of which represents an averaged contribution to $\langle \frac{d\sigma}{d\Omega} \rangle$ due to scattering from the $(1+p)$ particle complexes which includes one Coulomb and p-th ZRP centres, namely

$$\langle \frac{d\sigma}{d\Omega} \rangle = |f_c|^2 + \sum_{p=1}^{N} \frac{N(N-1)\dots(N-p+1)}{p!V^p} \times$$

$$\int \cdots \int \left\{ \left| \sum_{j=1}^{p} f_{C;j} \right|^2 - \left| \sum_{j=1}^{p} f_j \right|^2 + \left[f_c \left(\sum_{j=1}^{p} f_{C;j} - \sum_{j=1}^{p} f_j \right) \right]^* \right\} H_p^{(C;1,\dots,p)}(\vec{R}_1, \dots, \vec{R}_p) d\vec{R}_1 \dots d\vec{R}_p, \tag{18}$$

where the set of the irreducible density particle functions $\{H_p^{(C;1,\dots,p)}(\vec{R}_1, \dots, \vec{R}_p\}$ (form factors of the particle complexes) must be determined from alternative sources [29, 30] (see also next chapter).

2. Electron energy loss spectroscopy (EELS). Statistical theory of line-shape for localized excitation.

The double-differential inelastic cross sections have been studied extensively [1-5], particularly in spectral line wings that correspond to electronic excitation within a single molecule.

The inelastic cross section in this region has usually been explained with impact or quasi-static theories of spectral line broadening, taking into account the electron-electron correlation but without considering the internuclear or intermolecular correlations. Because the wing region of a spectral line is formed primarily by the short-range interactions between an excited molecule with its environment, these theories were adequate for explaining dense systems where the intermolecular correlations are saturated. But in cases where the resonance is narrow, for example, in small-angle scattering in low temperature systems with small Doppler width, the intermolecular contributions become non negligible. Consider a monochromatic beam of fast electrons ($E \sim 10^3 eV$) that is inelastically scattered at a fixed angle $\vartheta \leq 1^0$ by energy losses (ε) in the narrow $\varepsilon \sim 10^{-2} \div 10^{-1} eV$ neighborhood of distinctive narrow resonance.

This corresponds to excitation of a single molecule in one of its first excited states. In a simple disordered system of symmetrical molecules with volume V and temperature $T \sim 10^2 K$, the scattering process may be described with in the Born's approximation [9, 31, 32]. In this approximation the excited electronic level contributes primarily to the sum under the electronic state.

Now, we shall suppose that the target molecules may be considered as being at rest during scattering and that the excited level degenerates. We want to emphasize that the broadening of the spectral resonance is due to the effects of molecular motion and backscattering $\tilde{\Delta}[\tilde{\Delta} \sim (mk_b TE\vartheta/M)^{1/2}]$ where m and M are the masses of electron and molecule, respectively, for the parameter values of our problem, $\tilde{\Delta} \leq 10^{-3} eV$. In our problem the bound charge of the target molecules distributes not only in the region of localization of one single molecule but over the entire system volume. Therefore, the expression for the inelastic cross section must be averaged over all the molecular configurations with the

Gibbs distribution function. The resulting quantum-mechanical expression for the second differential cross section of the electron scattering, $\frac{d^2S}{d\varepsilon}$ (or the cross section of energy losses $I_\vartheta(\varepsilon)$), with reference to the volume of system V is

$$I_\vartheta(\varepsilon) \equiv \frac{d^2\delta}{d\varepsilon d\vartheta} = \frac{1}{V}\left[\frac{e}{E\vartheta^2}\right]^2 \left\langle \sum_{(\alpha)} |\rho^{(N)}_{10,\alpha}(\vec{q};\{\vec{R}\})|^2 \times \right. \tag{19}$$
$$\left. \times\delta[E_{1\alpha}(\{\vec{R}\}) - E_0(\{\vec{R}\}) - \varepsilon]\right\rangle ,$$

where $\rho^{(N)}_{10,\alpha}(\vec{q};\{\vec{R}\})$ is the Fourier transformation of the matrix element from the charge density operator; $\vec{q}$ is the impulse of scattering; $\{\vec{R}\} = \vec{R}_1, \dots, \vec{R}_N$ are the coordinates of the center of mass of the N molecules; $E_{1\alpha}(\{\vec{R}\})$ and $E_0(\{\vec{R}\})$ are respectively the energy of the final and initial states of the system in the adiabatic approximation. The sum from α goes over all the excited states of the system, which gives rise to the distinctive level of the isolated molecule; $\delta[\dots]$ is the Dirac δ function and the angular brackets denotes a Gibbs distribution average.

Equation (19) is the generalization of the one particle expression for the cross section of inelastic electron scattering [9] in the case where we consider the disordered system as a single larger molecule.

Following ref. [30-32] let us expand the total energy loss scattering cross section $I_{\vartheta,N}(\varepsilon)$ in a correlational series. The terms of this series represent the contribution to the cross section by isolated many-particle fluctuational complexes of different ranges. Using the identical representation for

$$I_{\vartheta,N}(\varepsilon;\{\vec{R}\}) = \sum_{i=1}^{N} Q_{\vartheta,1}(\varepsilon,\vec{R}_i) + \sum_{i=1}^{N}\sum_{j=i+1}^{N} Q_{\vartheta,2}(\varepsilon;\vec{R}_i,\vec{R}_j) + \tag{20}$$
$$+\sum_{i=1}^{N}\sum_{j=i+1}^{N}\sum_{k=i+1}^{N} Q_{\vartheta,3}(\varepsilon;\vec{R}_i,\vec{R}_j,\vec{R}_k) + \dots + Q_{\vartheta,N}(\varepsilon;\{\vec{R}\}),$$

where

$$\begin{aligned} Q_{\vartheta,S}(\varepsilon;\vec{R}_1,\dots,\vec{R}_s) &= (-1)^S\sum_{j=1}^{S} I_{\vartheta,1}(\varepsilon;\vec{R}_j)+ \\ &+(-1)^{S-2}\sum_{i=1}^{S}\sum_{j=i+1}^{S} I_{\vartheta,2}(\varepsilon;\vec{R}_i,\vec{R}_j)+\dots+I_{\vartheta,S}(\varepsilon;\vec{R}_1,\dots,\vec{R}_s) \end{aligned} \tag{21}$$

is the irriducible part of the scattering cross section by the s-particle complex $\vec{R}_1,\dots,\vec{R}_s$; $I_\vartheta(\varepsilon)=\langle I_{\vartheta,N}\rangle$. In tqimit of a thermodynamic average, Eqn. (20) becomes

$$\begin{aligned} I_\vartheta(\varepsilon) &= a(\vartheta)\sum_{s=1}^{\infty}\frac{h^s}{s=1}\int\dots\int\Bigg[\sum^{\nu_s}\alpha=1Z_{s,\alpha}(\vec{q};\vec{R}_1,\dots,\vec{R}_s)\times \\ &\times\delta(\varepsilon+\mu_{s,\alpha}(\vec{R}_1,\dots,\vec{R}_s))- \\ &-\frac{S!}{(S-1)!}\sum^{\nu_{s-1}}\alpha=1Z_{s-1,\alpha}(\vec{q};\vec{R}_1,\dots,\vec{R}_{s-1})\times \\ &\times\delta(\varepsilon+\mu_{s-1,\alpha}(\vec{R}_1,\dots,\vec{R}_{s-1}))+\frac{s!}{(s-2)!2!}\times \\ &\times\sum^{\nu_{s-2}}\alpha=1Z_{s-2,\alpha}(\vec{q};\vec{R}_1,\dots,\vec{R}_{s-2})\delta(\varepsilon\mu_{s-2,\alpha}(\vec{R}_1,\dots,\vec{R}_{s-2}))- \\ &-(-1)^sSZ_1(\vec{q};\vec{R}_s)\Bigg]\,g_s(\vec{R}_1,\dots,\vec{R}_s)d\vec{R}_1\dots d\vec{R}_s. \end{aligned} \tag{22}$$

Here $h=\dfrac{N}{V}$ is the particle density, $\{g_s(\vec{R}_1,\dots,\vec{R}_s)\}$ are s-particle dstribution functions [33], and $\mu_{s,\alpha}(\vec{R}_1,\dots,\vec{R}_s)$ are the single excitation energy shifts due to intermolecular interactions in s-particle complexes. Also,

$$a(\vartheta)\equiv\left[\frac{e}{E\vartheta^2}\right]^2,$$

$$Z_{s,\alpha}(\vec{q};\vec{R}_1,\dots,\vec{R}_s)\equiv|\rho^{(s)}_{10,\alpha}(\vec{q};\vec{R}_1,\dots,\vec{R}_s)|^2$$

Note that the functions $\{I_{\vartheta,S}(\varepsilon;\vec{R}_1,\dots,\vec{R}_s)\}$ or $\{Q_{\vartheta,s}(\varepsilon;\vec{R}_1,\dots,\vec{R}_s)\}$ are symmetric and

$$I_{\vartheta,1}(\varepsilon;\vec{R})=Q_{\vartheta,1}(\varepsilon;\vec{R})$$

is independent of $\vec{R}$. In Eqn. (22), the sum from 1 to ν_s covers all states of s-particle complexes.

The expression in square brackets in Eqn. (22) describes irreducible s-particle contributions to the inelastic scattering cross section. The parameters are fixed and adopted (vide supra) for disordered systems. Each term of Eqn. (22) is a functional of density and temperature as the functions $\{g_s\}$ are functionals of these parameters.

In moderate density systems we can terminate the series (22) after a finite number of terms. For example, if we take only the first two terms into account, we obtain an expression for the inelastic cross-section of two atom quasi-molecules. The regular part is equal to

$$I_\vartheta(\varepsilon) = \frac{1}{2} a(\vartheta) h^2 \int g_2(R) \sum_{(\alpha)} Z_{2,\alpha}(\vec{q}, \vec{R}) \times \times \delta(\varepsilon + \mu_{2,\alpha}(\vec{R})) d\vec{R}. \tag{23}$$

The quasi molecule complexes consist of two atoms of the same element, one of which is in an excited state. The electronic states are divided into two groups, even (g) and odd (u), in accordance with the property of the wavefunctions. Even states conserve sign under inversion in the plane of symmetry; odd states change sign. In Eqn. (23) α may be equal to (g) or (u).

Using zero-order perturbation theory and neglecting overlap interactions, the wavefunctions of the ground state $\Psi_0(\{\vec{r}\}, \vec{R})$ and the excited states $\Psi_{1,\alpha}(\{\vec{r}\}, \vec{R})$ may be written:

$$\Psi_0(\{\vec{r}\}, \vec{R}) = \psi_0([\vec{r}_1])\psi_0([\vec{r}_2 - \vec{R}]),$$

$$\Psi_{1,\alpha}(\{\vec{r}\}, \vec{R}) = \frac{1}{\sqrt{2}} \{\psi_0([\vec{r}_1])\psi_1([\vec{r}_2 - \vec{R}]) \pm \psi_1([\vec{r}_1])\psi_0(\vec{r}_2 - \vec{R}])\} \tag{24}$$

Here $\psi_0([\vec{r}_1])$ and $\psi_1([\vec{r}_2 - \vec{R}])$ are wavefunctions of isolated atoms. Also $\{\vec{r}\}$ is the set of electronic variables of the pair of atoms; $[\vec{r}_1]$ and $[\vec{r}_2 - \vec{R}]$ are, respectively, the set of electronic coordinates of the first and the second atom: the ±sign corresponds to $\alpha = g$ and $\alpha = u$. Taking the Fourier transform of the charge density operator

$$\rho^{(2)}_{10,\alpha}(\vec{q},\vec{R}) = \sum_{(e)} \int \dots \int e^{-i\vec{q}\vec{r}e} \Psi^{*}_{1,\alpha}(\{\vec{r}\},\vec{R}) \Psi_0(\{\vec{r}\},\vec{R}) \{d\vec{r}\}, \tag{25}$$

and expression (24), we obtain

$$Z_{2,\alpha}(\vec{q};\vec{R}) = 2Z_1(\vec{q}) \begin{cases} \cos^2\left(\dfrac{1}{2}\vec{q}\vec{R}\right), & \alpha = g, \\ \sin^2\left(\dfrac{1}{2}\vec{q}\vec{R}\right), & \alpha = g. \end{cases} \tag{26}$$

Now we determine $\mu_{2,\alpha}(R)$, which is equal to $E^{(\alpha)}_{10}(R) - E_{00}(R)$, where $E^{(\alpha)}_{10}$ and $E_{00}(R)$ are the ground and excited state interatomic interaction energies of the two particle fluctuational complexes in the adiabatic approximation.

Now we need to determine which excited states are dipole allowed. For this purpose, we want to find the value for the crossing transition probability. In the dipole approximation the interatomic interaction is described by an operator $\hat{V}$:

$$\hat{V} = \frac{(\vec{d}_1 \cdot \vec{d}_2) - 3(\vec{d}_1 \cdot \vec{h})(\vec{d}_2 \cdot \vec{h})}{R^3} \tag{27}$$

which is the dipole-dipole interaction operator. Here $\vec{d}_1$ and $\vec{d}_2$ are the dipole moments of both atoms and $\vec{h}$ is the unit direction vector between both atomic charge centers. For example, consider a $1S$ ground state and a $1P$ excited state for which the transition is dipole allowed. The matrix element of the operator $\hat{V}$, which are given by

$$\begin{gathered} V^{(\alpha)}_{1i}(R) \equiv \langle \Psi_{1,i\alpha} | \hat{V} | \Psi_{1,i\alpha} \rangle = \\ \int \dots \int \Psi^{*}_{1i,\alpha}(\{\vec{r}_j\},\vec{R}) \hat{V} \Psi_{1i,\alpha}(\{\vec{r}_j\},\vec{R}) \{d\vec{r}_j\}, \end{gathered} \tag{28}$$

may be calculated by using the wavefunctions (24) namely,

$$V^{(\alpha)}_{1i}(R) = \pi_{i\alpha} \frac{d^2_{1\alpha}}{R^3}, \tag{29}$$

where

$$\pi_{i\alpha}=\begin{cases}-2,\ \alpha=g,\ i=z,\\ 1,\ \alpha=g,\ i=x,y,\\ 2,\ \neq=u,\ i=z,\\ -1,\alpha=u,\ i=x,y.\end{cases}$$

Here $i=x,\ y,\ z$ are the three perpendicular orientation of angular momentum. If $i=Z$, the angular momentum and the axis of the quasi-molecule are colinear. Finally, using Eqs.(23) and (29), we obtain

$$I_\vartheta(\varepsilon)=\frac{2}{3}\pi a(\vartheta)\frac{d_{1\alpha}^2}{\varepsilon^2}Z_1(q)h^2\sum_{s=-2}^{2}[1+sgh(s)\times \\ \times\frac{\sin qRs}{qR_s}\Bigg]\theta(R_s)g_2(R_s), \tag{30}$$

where

$$\theta(x)=\begin{cases}1,\ x>0,\\ 0,\ x<0,\ R_s=\left[-S\dfrac{d_{1\alpha}^2}{\varepsilon}\right]^{\frac{1}{3}}.\end{cases} \tag{31}$$

Let us consider a dipole forbidden transition, for example, the $1S$ to $2S$ transition. This transition has a probability that is zero to first order and is dependent only upon the interatomic separation. In this case $\mu_{2,\alpha}(R)\simeq-\dfrac{C_\alpha}{R^\sigma}$, where C_α is the atomic constant. We obtain

$$I_\vartheta(\varepsilon)=\frac{a(\vartheta)}{8\pi}Z_1(q)h^2\left[\sum_\nu\frac{R_\nu^2\left[1+\dfrac{\sin qR_\nu}{qR_\nu}\right]}{\left|\dfrac{d\mu_{2,g}(R)}{dR}\Big|_{R=R_\nu(\varepsilon)}\right|}\times\right. \\ \left.\times\ g_2[R_\nu(\varepsilon)]+\sum_{\nu'}\frac{R_\nu^2\left[1+\dfrac{\sin qR_\nu}{qR_\nu}\right]}{\left|\dfrac{d\mu_{2,g}(R)}{dR}\Big|_{R=R_\nu(\varepsilon)}\right|}g_2[R_{\nu'}(\varepsilon)]\right], \tag{32}$$

where R_ν and $R_{\nu'}$ are the solutions of the equations

$$\begin{aligned} &\mu_{2,g}(R) = \hbar(\omega - \omega_1) = -\varepsilon, \\ &\mu_{2,u}(R) = \hbar(\omega - \omega_1) = -\varepsilon, \\ &\mu_{2,\alpha}(R) = -C_\alpha / R^\sigma. \end{aligned} \tag{33}$$

In general if one of the terms in parentheses has a divisible root $\tilde{\omega}$, then in the limit $\omega \to \tilde{\omega}$, it will be sharply peaked. Corresponding sharp peaks will appear in the electron energy loss spectrum. These singular points are analogous to Van Hove singularities for the spectral density of states. Suppose that for such a frequency interval there exists a solution for only one of the equations in (33). Then, for the corresponding interval of the distances, we can directly determine the value of $g_2(R(\omega))$ by using Eqs. (32) and (33). If the splitting of the distinguishing level is negligible,

$$|\mu_{2,g}(R) - \mu_{2,u}(R)| \sim \tilde{\Delta} \ll \frac{1}{2} |\mu_{2,g}(R) + \mu_{2,u}(R)|, \tag{34}$$

we obtain a semplified form of the Eqs. (32):

$$\begin{aligned} I_\vartheta(\varepsilon) &= \frac{a(\vartheta)}{4\pi} h^2 Z_1(\vec{q}) R^2 \left| \frac{dR}{d\varepsilon} \right| g_2(R(\varepsilon)), \\ \mu_{2,\alpha}(R) &= \mu(R(\varepsilon)) = -\varepsilon = -\frac{C}{R^\sigma}. \end{aligned} \tag{35}$$

Expression (35) can be rewritten in the form

$$I_\vartheta(\varepsilon) = \frac{C^{\frac{1}{2}}}{24\pi} a(\vartheta) Z_1(\vec{q}) \varepsilon^{-\frac{3}{2}} h^2 g_2 \left[\left(\frac{c}{\varepsilon} \right)^{\frac{1}{\sigma}} \right] \tag{36}$$

In the ideal-gas limit, when $g_2 = 1$, $I_\vartheta(\varepsilon) \sim \varepsilon^{-\frac{3}{2}}$ [34]. Expressions (30-35) allow $g_2(R)$ to be directly determined for the individual points in simple disordered systems. This supplants the usual procedure that involves the revers Fourier tramsform of the scattering structures factors.

Due to the irregular convergence of the Fourier series, this usual procedure does not readily produce an easy determination of $g_2(R)$ [35].

Consider a model in which an excitation is localized on a single molecule and the probability of excitation exchange between molecules is negligible. This situation is a good model for a dipole-forbidden excitation, a situation where the resonance interaction between an excited molecule and a ground-state molecule decreases with the interatomic distance more rapidly than R^{-3}. We shall suppose that the excited level of a single molecule is generated. Then, using zero-order perturbation theory, we obtain

$$Z_{S,1}(\vec{q};\vec{R}_1,\dots,\vec{R}_s) \simeq Z_1(\vec{q}) \equiv |\rho^{(1)}_{1\alpha}(\vec{q})|^2, \alpha = S$$

$$\mu_{s,\alpha}(\vec{R}_1,\dots,\vec{R}_s) = \sum_{j=1}^{s-1} \mu(|\vec{R}_j - \vec{R}_\alpha|), \tag{37}$$

where $\vec{R}_S = \vec{0}$; $\mu(R)$ is the exchange of energy of the single excitation in a pair of molecules that shift the one from the other on vector $\vec{R}$; and α, in this case, means that the ecitation is localized at the molecule with number s. Due to the symmetry of the functions $\{g_s\}$, and the Fourier-reducing properties of the Dirac delta function, we can rewrite the expression (22) as

$$I_\vartheta(\varepsilon) = \hat{a}(\vartheta) Z_1(\vec{q}) \sum_{s=1}^{\infty} \frac{h^s}{(s-1)!} \int_{-\infty}^{\infty} d\tau \exp(-i\varepsilon\tau) \times$$

$$\times \int \dots \int \prod_{j=1}^{s-1} [\exp(-i\mu(\vec{R}_j)\tau) - 1] g_S(\vec{R}_1,\dots,\vec{R}_{s-1}) d\vec{R}_1 \dots d\vec{R}_{s-1}, \tag{38}$$

$$g_s(\vec{R}_1,\dots,\vec{R}_{s-1}) \equiv g_s(\vec{R}_1,\dots,\vec{R}_{s-1},\vec{0});\ \hat{a}(\vartheta) = \frac{a(\vartheta)}{2\pi}.$$

Thus, if $\mu(R)$ is a finite function [i.e., $\mu(R) = 0$ outside a sphere with radius $\Gamma_0 < \infty$], integration in Eqn. (39) goes over the volume of the sphere $V_0 = \frac{4\pi}{3}\Gamma_0^3$ with its center at the origin of the coordinate system. The series (38) for the finite function is generated in the finite sum (we can only put a finite number of molecules in a sphere with radius $\Gamma_0 < \infty$). This means that, starting with some number S_0, all the functions $\{g_S\}$ $(S > S_0)$ become zero for all $R_S \geq \Gamma_0$. To prove that the correlation series converges when $\mu(R)$ is not finite but only a rapidly decreasing function, it is sufficient to introduce the multiplier $\exp(-\tilde{\Delta}^2\tau^2)$ under the integral sign in Eqn. (38). This is necessary for including spectral line broadening due to molecular motion and backscattering.

If all the functions $\{g_s\}$ $(|g_s| < C < \infty)$ are uniformly limited, the convergence of the series (38) follows from

$$\begin{aligned} |I_\vartheta(\varepsilon)| &\leq a\vartheta)|Z_1(\vec{q})|nC\sum_{s=1}^{\infty}\frac{n^{s-1}}{(s-1)!}\times\int_{-\infty}^{\infty}d\tau\exp(-\tilde{\Delta}^2\tau^2)\times \\ &\times\int\cdots\int\prod_{j=1}^{S-1}|\exp(-i\mu(R_j)\tau)-1|d\vec{R}_1\ldots d\vec{R}_{S-1} = \\ &= a(\vartheta)|Z_1(\vec{q})|Cn\int_{-\infty}^{\infty}d\tau\exp[-\tilde{\Delta}^2\tau^2+ \\ &+n\int d\vec{R}|\exp(-i\mu(R)\tau)-1|] \end{aligned} \tag{39}$$

Because all of the functions under the integral sign in Eqn. (38) are infinitely differentiable with respect to ε, every part of (38) decreases more rapidly than any power of ε when $\varepsilon \to \pm\infty$. This is in accordance with the usual properties of Fourier integrals.

For distinguishing the correlational contribution in the inelastic cross section, we shall write the s-particle distribution function in the form of a series of irreducible contributions:

$$\begin{aligned} g_s(\vec{R}_1,\ldots,\vec{R}_{s-1}) &= 1+\sum_{i=1}^{S}\sum_{j=i+1}^{S}h_2(\vec{R}_i-\vec{R}_j)+ \\ &+\sum_{i=1}^{S}\sum_{j=i+1}^{S}\sum_{k=j+1}^{S}h_3(\vec{R}_i-\vec{R}_j;\vec{R}_i-\vec{R}_k)+ \\ &+\ldots+h_S(\vec{R}_1,\ldots,\vec{R}_{S-1}), \end{aligned} \tag{40}$$

where $\{h_S(\vec R_1, \dots, \vec R_{S-1})\}$ is the set of irriducible correlation functions:

$$
\begin{aligned}
&h_2(R) = g_2(R) - 1,\\
&h_3(\vec R, \vec R') = g_3(\vec R, \vec R') - g_2(R) - g_2(R') - g_2(|\vec R - \vec R'|) + 2,\\
&h_s(\vec R_1, \vec R_2, \dots, \vec R_{s-1}) = g_s(\vec R_1, \dots, \vec R_{s-1}) - g_{s-1}(\vec R_1, \dots, \vec R_{s-2}) -\\
&\qquad - \dots - (-1)^S (S-1).
\end{aligned}
\tag{41}
$$

Let us rewrite the expression (38) with the help of (40) and distinguish noncorrelation contributions and the corrections to them due to two-, three-,....,s-particle correlations. We obtain the noncorrelational term $I_\vartheta^{(0)}(\varepsilon)$, which describes the shift and the broadening of the spectral lines as a funtion of pressure in a gas approximation if we put all $\{g_s\} = 1$ in Eqn. (38). After summing the power series we obtain in this case

$$
\begin{aligned}
I_\vartheta^{(0)}(\varepsilon) &= a(\vartheta) Z_1(\vec q) n \int_{-\infty}^{\infty} d\tau \exp[-\varepsilon\tau +\\
&+ 4\pi h \int_0^{\infty} (e^{-i\mu(R)\tau} - 1) R^2 dR] \equiv \hat a(\vartheta) Z_1(\vec q) n M_\vartheta^{(0)}(\varepsilon).
\end{aligned}
\tag{42}
$$

If, for example we used in $\mu(R)$ only the long-range asymptote of this function, that is, $\mu(R) = -\dfrac{C}{R^\sigma}$ (if we consider dipole-forbidden excitation), we immediately obtain the expression derived by Margenau [34] and others [35], which describes the behavior of the spectral line of a molecule dissolved in an ideal gas:

$$
\begin{aligned}
I_\vartheta^{(0,M)}(\varepsilon) &= \hat a(\vartheta) Z_1(\vec q) n \lambda \varepsilon^{-\frac{3}{2}} \exp\left[-\frac{\pi\lambda^2}{\varepsilon}\right] =\\
&= \hat a(\vartheta) Z_1(\vec q) n M_\vartheta^{(0,M)}(\varepsilon),\\
\lambda &\equiv \frac{2}{3} \pi C^{\frac{1}{2}} n
\end{aligned}
\tag{43}
$$

In general, if we examine only the first two terms in Eqn. (40), after summing the corresponding power series that generate

Eqn. (38), we obtain

$$\begin{aligned}
I_\vartheta(\varepsilon) &= \hat{a}(\vartheta)Z_1(\vec{q})n\{M_\vartheta^{(0)}(\varepsilon) + n\int \Delta M_\vartheta^{(0)}(\varepsilon + \mu(\vec{R}))\times \\
&\times h_2(R)d\vec{R}+ \\
&+\frac{1}{2}n^2\int\int[\Delta M_\vartheta^{(0)}(\varepsilon + \mu(\vec{R}) + \mu(\vec{R}')) - \Delta M_\vartheta^{(0)}(\varepsilon + \mu(\vec{R}))- \\
&- \Delta M_\vartheta^{(0)}(\varepsilon + \mu(\vec{R}'))]h_2(|\vec{R} - \vec{R}'|)d\vec{R}d\vec{R}'\} \equiv \\
&\equiv \hat{a}(\vartheta)Z_1(\vec{q})nM_\vartheta^{(1)}(\varepsilon);\ \Delta M_\vartheta^{(0)} \equiv M_\vartheta^{(0)}(\varepsilon + \mu(R)) - M_\vartheta^{(0)}(\varepsilon)
\end{aligned} \tag{44}$$

In the next approximation

$$\begin{aligned}
I_\vartheta(\varepsilon) &= \hat{a}(\vartheta)Z_1(\vec{q})n\{M_\vartheta^{(1)}(\varepsilon) + \frac{1}{2}n^2\int\int[\Delta M_\vartheta^{(0)}(\varepsilon+ \\
&+ \mu(\vec{R}) + \mu(\vec{R}')) - \Delta M_\vartheta^{(0)}(\varepsilon + \mu(\vec{R})) - \Delta M_\vartheta^{(0)}(\varepsilon + \mu(\vec{R}'))]\times \\
&\times h_3(\vec{R}, \vec{R}')d\vec{R}d\vec{R}'\},
\end{aligned} \tag{45}$$

and so on. In Eqs. (44) and (45), $M_\vartheta^{(0)}(\varepsilon)$ is formally determined by Eqn. (42).

Thus, expressions such as (44) and (45) give the possibility for analytical (or numerical) calculation of corrections to expressions (42) and (43) in any order of correlation approximation.

The development of this theory and their applications can be find in [30].

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