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Some New Relationships between the Molecular Electron Densities and the Intensities of Electrons and X-Rays Scattered by Gases

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Some new relations connecting the molecular electron densities and the intensities of electrons and X-rays scattered by gases have been derived by integrating analytically the scattered intensities multiplied by some functions of the momentum transfer, s, over ds.

The intensities of the electrons and X-rays scattered by gases have been known to provide information on atomic or molecular electron densities.[1] It has been proved that, in principle, the unique three-dimensional electron densities of molecules can not be derived directly from the one-dimensional scattering intensities.[2] However, the qualities of given molecular wave functions can be examined by comparing the experimental intensities with the theoretical ones calculated from the wave functions. Because of the considerably long computing time needed for such calculations, however, the theoretical scattering intensities based on molecular wave functions have been reported for only a very limited number of molecules.

A more convenient way of making such an examination is to make use of the integral relationships between the scattering intensities and the electron densities in molecules. A close connection between the integrated intensities of the total electron scattering and the total energies of molecules proved by Tavard *et al.* is an example of such a relationship.[3,4] Some relationships have also been reported by Bonham, who has mentioned the existence of other, similar relations.[5] These relations are obtained as the integral transforms of the scattering intensities by several kernels, which are functions involving momentum transfer, s. The purpose of the present paper is to present some new relations connecting the molecular electron densities with the scattered intensities by means of the integral transformation of the intensities, as well as to bring together the relations thus far reported in the form of analytical integration.

If the four σ functions are defined in terms of the elastic and total intensities of electrons (ED) and X-rays (XR) scattered by a free molecule as follows:[1,5]

$$\sigma_{\mathrm{E}}^{\mathrm{ED}}(s) = s^4 I_{\mathrm{E}}^{\mathrm{ED}}(s) - \sum_i Z_i^2, \tag{1}$$

$$\sigma_{\mathrm{T}}^{\mathrm{ED}}(s) = s^4 I_{\mathrm{T}}^{\mathrm{ED}}(s) - \sum_i Z_i^2 - N, \tag{2}$$

$$\sigma_{\mathrm{E}}^{\mathrm{XR}}(s) = I_{\mathrm{E}}^{\mathrm{XR}}(s), \tag{3}$$

$$\sigma_{\mathrm{T}}^{\mathrm{XR}}(s) = I_{\mathrm{T}}^{\mathrm{XR}}(s) - N, \tag{4}$$

to the first Born approximation, they are expressed in connection with the electron density in the molecule by:

$$\sigma_{\mathrm{E}}^{\mathrm{ED}}(s) = \sigma_{\mathrm{nn}}(s) - \sum_i Z_i^2 + \sigma_{\mathrm{ne}}(s) + \sigma_{\mathrm{E}}^{\mathrm{XR}}(s), \tag{5}$$

$$\sigma_{\mathrm{T}}^{\mathrm{ED}}(s) = \sigma_{\mathrm{nn}}(s) - \sum_i Z_i^2 + \sigma_{\mathrm{ne}}(s) + \sigma_{\mathrm{T}}^{\mathrm{XR}}(s), \tag{6}$$

where:

$$\sigma_{\mathrm{nn}}(s) - \sum_i Z_i^2 = \sum_{i\neq j}\sum Z_i Z_j \langle \mathrm{j}_0(sr_{ij})\rangle_{\mathrm{vib}}, \tag{7}$$

$$\sigma_{\mathrm{ne}}(s) = -2\sum_i Z_i \left\langle \int \mathrm{d}\boldsymbol{r}\, \mathrm{j}_0(sr)\, \rho(\boldsymbol{r}+\boldsymbol{r}_i) \right\rangle_{\mathrm{vib}}, \tag{8}$$

$$\sigma_{\mathrm{E}}^{\mathrm{XR}}(s) = \left\langle \int \mathrm{d}\boldsymbol{r}\, \mathrm{j}_0(sr) \int \mathrm{d}\boldsymbol{r}'\, \rho(\boldsymbol{r}')\, \rho(\boldsymbol{r}+\boldsymbol{r}') \right\rangle_{\mathrm{vib}}, \tag{9}$$

and

$$\sigma_{\mathrm{T}}^{\mathrm{XR}}(s) = \left\langle \int \mathrm{d}\boldsymbol{r}\, \mathrm{j}_0(sr)\, \rho_{\mathrm{c}}(\boldsymbol{r}) \right\rangle_{\mathrm{vib}}. \tag{10}$$

Here, the subscripts E and T denote elastic and total respectively; s is the momentum transfer given by $(4\pi/\lambda)\sin(\theta/2)$ (λ: wavelength, θ: scattering angle); N, the total number of electrons in the molecule; $\boldsymbol{r}_i$, the position vector of the i-th atom; Z, the atomic number; r_{ij}, an interatomic distance; $\mathrm{j}_0(x)$, the zero-order spherical Bessel function, $\sin x/x$; $\rho(\boldsymbol{r})$, the one-electron density, and $\rho_{\mathrm{c}}(\boldsymbol{r})$, the electron-pair correlation density; the brackets, $\langle\ \rangle_{\mathrm{vib}}$, denote the averaging over thermal vibration.

To begin with, the integral of this type:

$$\Lambda(\alpha,\lambda) = \int_0^\infty \mathrm{d}s\, \sigma(s)\, s^\alpha \mathrm{e}^{-\lambda s}, \quad \lambda > 0 \tag{11}$$

will be considered. The factor, $\mathrm{e}^{-\lambda s}$, acts as a damping factor to reduce the error due to the termination of the integral. This type of integral has been mentioned in the literature[5] for the case where α is an integer. In general, for $\alpha \leqq -1$, the integral diverges, but for $\alpha > -1$ the integral can be expressed in terms of a hypergeometric function, ${}_2\mathrm{F}_1$.[6] By the use of the properties of ${}_2\mathrm{F}_1$, the integrals for the four kinds of σ are reduced to:[7]

$$\Lambda_{\mathrm{E}}^{\mathrm{ED}}(\alpha,\lambda) = \sum_{i\neq j}\sum Z_i Z_j \langle \mathrm{L}(\alpha,\lambda,r_{ij})\rangle_{\mathrm{vib}}$$
$$-2\sum_i Z_i \left\langle \int \mathrm{d}\boldsymbol{r}\, \mathrm{L}(\alpha,\lambda,r)\, \rho(\boldsymbol{r}+\boldsymbol{r}_i) \right\rangle_{\mathrm{vib}} + \Lambda_{\mathrm{E}}^{\mathrm{XR}}(\alpha,\lambda), \tag{12}$$

$$\Lambda_{\mathrm{T}}^{\mathrm{ED}}(\alpha,\lambda) = \sum_{i\neq j}\sum Z_i Z_j \langle \mathrm{L}(\alpha,\lambda,r_{ij})\rangle_{\mathrm{vib}}$$
$$-2\sum_i Z_i \left\langle \int \mathrm{d}\boldsymbol{r}\, \mathrm{L}(\alpha,\lambda,r)\, \rho(\boldsymbol{r}+\boldsymbol{r}_i) \right\rangle_{\mathrm{vib}} + \Lambda_{\mathrm{T}}^{\mathrm{XR}}(\alpha,\lambda), \tag{13}$$

$$\Lambda_{\mathrm{E}}^{\mathrm{XR}}(\alpha,\lambda) = \left\langle \int \mathrm{d}\boldsymbol{r}\, \mathrm{L}(\alpha,\lambda,r) \int \mathrm{d}\boldsymbol{r}'\, \rho(\boldsymbol{r}')\, \rho(\boldsymbol{r}+\boldsymbol{r}') \right\rangle_{\mathrm{vib}}, \tag{14}$$

$$\Lambda_{\mathrm{T}}^{\mathrm{XR}}(\alpha,\lambda) = \left\langle \int \mathrm{d}\boldsymbol{r}\, \mathrm{L}(\alpha,\lambda,r)\, \rho_{\mathrm{c}}(\boldsymbol{r}) \right\rangle_{\mathrm{vib}}, \tag{15}$$

with

$$\mathrm{L}(\alpha,\lambda,r) = \frac{1}{r}\,\frac{\Gamma(\alpha+1)}{(r^2+\lambda^2)^{\alpha/2}}\,\frac{\sin(\alpha\varphi)}{\alpha}, \quad \alpha > -1, \tag{16}$$

$$\varphi = \tan^{-1}\!\left(\frac{r}{\lambda}\right).$$

In the sense

$$\Sigma(\alpha) = \int_0^\infty \mathrm{d}s\sigma(s)s^\alpha = \lim_{\lambda\to 0}\int_0^\infty \mathrm{d}s\sigma(s)s^\alpha \mathrm{e}^{-\lambda s}, \tag{17}$$

$\Sigma_{\mathrm{T}}^{\mathrm{ED}}(\alpha)$ *etc.* are obtained by replacing $\mathrm{L}(\alpha,\lambda,r)$ in Eqs. 12—15 by:

$$F(\alpha,r) = \frac{\Gamma(\alpha+1)\sin(\alpha\pi/2)}{r^{\alpha+1}\quad\quad\alpha}, \quad 2>\alpha>-1, \tag{18}$$

and

$$F(2,r) = \frac{\pi}{r^2}\delta(r), \quad \alpha=2.$$

The result for $\Sigma_{\mathrm{T}}^{\mathrm{ED}}(0)$ is Tavard's energy relationship,[3,4] and those for $\alpha=1$ and 2 have already been given in the literature.[1,5] For $\alpha>2$, the integral over ds will diverge.

If λ in Eq. 11 is replaced by a complex number $(\lambda+\mathrm{i}r')$, the integral over ds is expressed by a hypergeometric function, ${}_2\mathrm{F}_1$, of $-r'^2/(\lambda+\mathrm{i}r')^2$. By taking the imaginary part and letting λ tend to zero, in a sense similar to Eq. 17 we can obtain this integral:

$$\mathrm{J}(\alpha,r') = \int_0^\infty \mathrm{d}s\sigma(s)s^\alpha \mathrm{j}_0(sr'), \quad 2\geqq\alpha>0. \tag{19}$$

This is a modification of Weber-Schafheitlin's discontinuous integral.[9] A useful relationship is obtained only for $\alpha=2$.

$$\begin{aligned}\mathrm{J}_{\mathrm{T}}^{\mathrm{ED}}(2,r') &= \int_0^\infty \mathrm{d}s\sigma_{\mathrm{T}}^{\mathrm{ED}}(s)s^2\mathrm{j}_0(sr')\\ &= \frac{\pi}{2}\sum_{i\neq j}\sum Z_iZ_j\langle r'^{-2}\delta(r'-r_{ij})\rangle_{\mathrm{vib}}\\ &\quad -\pi\sum_i Z_i\left\langle\int \mathrm{d}\Omega_{\boldsymbol{r}'}\rho(\boldsymbol{r}'+\boldsymbol{r}_i)\right\rangle_{\mathrm{vib}}\\ &\quad +\frac{\pi}{2}\left\langle\int \mathrm{d}\Omega_{\boldsymbol{r}'}\rho_{\mathrm{c}}(\boldsymbol{r}')\right\rangle_{\mathrm{vib}}. \end{aligned} \tag{20}$$

Similar relations hold for the other scattering intensities, some of which have previously been reported in the literature.[10] The second and third terms of Eq. 20 are the averages over solid angles of the one-electron density around each nucleus and the electron-pair correlation density respectively. The latter is a radial inter-electron density function.[10]

In order to reduce termination errors, another integral:

$$\mathrm{M}(\alpha,\,\mu) = \int_0^\infty \mathrm{d}s\sigma(\mathrm{s})\mathrm{s}^\alpha\mathrm{e}^{-\mu s^2}, \quad \mu>0, \tag{21}$$

is considered, where $\mathrm{e}^{-\mu s^2}$ is a damping factor often used in the calculations of radial distribution curves in electron-diffraction studies of gas molecules. This integral can be obtained in terms of a confluent hypergeometric function, ${}_1\mathrm{F}_1$, of $r^2/4\mu$. For an even integer of α, $\mathrm{M}(\alpha,\mu)$ can conveniently be expressed by replacing $\mathrm{L}(\alpha,\lambda,r)$ in Eqs. 12—15 by the following $\mathrm{G}(\alpha,\mu,r)$:

$$\mathrm{G}(\alpha,\mu,r) = \frac{\partial^{(\alpha-2)/2}}{\partial\mu^{(\alpha-2)/2}}\left(\frac{1}{4}\sqrt{\frac{\pi}{\mu^3}}\mathrm{e}^{-r^2/4\mu}\right), \quad \alpha\geqq 2. \tag{22}$$

Finally, relationships based upon finite integrals:

$$\Sigma_0(n) = \int_a^b \mathrm{d}s\sigma(s)s^n, \tag{23}$$

and

$$\Lambda_0(n,\lambda) = \int_a^b \mathrm{d}s\sigma(s)s^n\mathrm{e}^{-\lambda s}, \tag{24}$$

may sometimes be used, where n is an integer. The functions, $\mathrm{F}_0(n,r)$ and $\mathrm{L}_0(n,\lambda,r)$, corresponding to $\mathrm{F}(n,r)$ and $\mathrm{L}(n,\lambda,r)$ are:

$$\begin{aligned} F_0(1,r) &= r^{-2}(\cos(ar) - \cos(br)),\\ F_0(2,r) &= r^{-1}(b^2\mathrm{j}_1(br) - a^2\mathrm{j}_1(ar)),\\ \mathrm{L}_0(n,\lambda,r) &= (-1)^{n-1}\frac{\partial^{n-1}}{\partial\lambda^{n-1}}\{[(\lambda\sin(ar)+r\cos(ar))\mathrm{e}^{-\lambda a}\\ &\quad -(\lambda\sin(br)+r\cos(br))\mathrm{e}^{-\lambda b}]/r(r^2+\lambda^2)\}, \quad n\geqq 1. \end{aligned} \tag{25}$$

The various quantities closely related to the molecular electron density are obtainable from the experimental intensities. Except for small α values, the accuracy of $\Sigma(\alpha)$ is limited mainly by experimental errors at large scattering angles and the termination error at $s_{\max}$. Such uncertainties are reducible by using $\mathrm{M}(\alpha,\mu)$ and $\Lambda(\alpha,\lambda)$ with an appropriate choice of the parameters, μ and λ. There is no termination-error problem in $\Sigma_0(n)$ and $\Lambda_0(n,\lambda)$.

Since the calculation of the right-hand side of the above equations takes much less computing time than the calculation of the scattering intensities themselves from the molecular wave functions, these relationships must be of great use. The $\mathrm{J}_{\mathrm{T}}^{\mathrm{ED}}(2,r')$ given by Eq. 20 is computed most easily; accordingly, it is most suitable for the first examination of a molecular wave function.

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