Correlation and X-ray Scattering. I. Density Matrix Formulation

By Robert Benesch and Vedene H. Smith, Jr

Department of Chemistry, Queen's University, Kingston, Ontario, Canada

Equations suitable for obtaining values of the coherent and total intensities of X-ray radiation scattered by N-electron atomic systems are developed from the 1- and 2-particle density matrices. Although electron scattering within the first Born approximation can be treated in the same fashion, a separate consideration of this problem is not required since the scattered electron and X-ray intensities are related by equations well established in the literature.

The general formalism presented here is such that it easily allows the computation of X-ray scattering factors and intensities to extend beyond the Hartree–Fock approximation, thereby incorporating electron correlation effects. Evaluation of the relevant equations requires the natural orbitals or the natural spin orbitals and the natural geminals or the natural spin geminals. These can always be obtained from the 1- and 2-particle density matrix analyses of the N-electron wavefunction Ψ_g characterizing the atomic state. In the event that Ψ_g is approximated by a single Slater determinant, the equation for the total scattered X-ray intensity reduces to the familiar Waller–Hartree result.

1. Introduction

The purpose of this paper is to formulate the problem of X-ray scattering from atomic systems in terms of the 1- and 2-particle density matrices. Electron scattering within the first Born approximation is amenable to a similar development. However, results obtained for the X-ray case can be applied directly to this problem *via* relationships given by Morse (1932). § 2 is devoted mainly to the development of the density matrix formalism for X-ray scattering, whereas § 3 illustrates that the usual Waller–Hartree (1929) theory is a special case of this formalism.

2. Theory

A. General remarks

In order to introduce the density matrix formulation, we will briefly review a few necessary equations. If the N-electron atomic system is initially in a state described by the wavefunction Ψ_g, the expression for the total intensity of X-ray radiation observed at an angle ω with respect to the scattering plane is given (Waller & Hartree, 1929) by

$$I_t(\omega) = \sum_n a_n \langle \Psi_g | P_n | \Psi_n \rangle \langle \Psi_n | P_n^* | \Psi_g \rangle \,. \quad (1)$$

The summation in (1) extends over all electronic states (represented by Ψ_n) for which the energy differences $E_n - E_g$ are less than the energy of the incident radiation. The scattering operator P_n has the definition

$$P_n = \sqrt{I_{cl}} \sum_j \exp \{ i[\kappa S - k_s(E_n - E_g)/h\nu_{inc}] \cdot r_j \} \quad (2)$$

where the summation is over all electrons in the system. In a non-relativistic treatment the parameters a_n are

the Breit–Dirac recoil factors.* The scattering vector S, $|S| = 2 \sin(\omega/2)$, represents the difference between unit vectors in the directions of the incident and scattered X-rays whereas the vector k_s in the scattered direction has a magnitude determined from the conservation of energy principle. The propagation constant κ has a magnitude of $2\pi/\lambda$. The classical expression I_{cl} for the total intensity of radiation scattered by a free electron initially at rest is given by Thomson (1906).

With the assumption that no energy transfer occurs between the incident radiation and the scattering system, the summation in (1) reduces to

$$I_c(\omega) = \langle \Psi_g | P | \Psi_g \rangle \langle \Psi_g | P^* | \Psi_g \rangle$$
$$= |\langle \Psi_g | P | \Psi_g \rangle|^2 \quad (3)$$

for the coherent intensity I_c. Note that the operator P has the definition given by (2) but with $E_n = E_g$. With the assumptions that the incident X-ray frequency ν_{inc} is greater than the atomic K-shell absorption frequency and that $\nu_n \sim \nu_{inc}$, Waller & Hartree (1929) invoked the closure relation in (1) to obtain the zero-order expression (zero-order in incident X-ray energy)

$$I_t(\omega)/I_{cl} = \langle \Psi_g | PP^* | \Psi_g \rangle$$
$$= \langle \Psi_g | |P|^2 | \Psi_g \rangle \quad (4)$$

for the total scattered intensity I_t. The scattering operator P has the same definition as employed in (3). Unless the incident photon energy $h\nu_{inc}$ is greater than the excited state energies E_n for all n, use of the closure relation is not strictly valid. For some incident energies or for heavy atoms this is clearly the case, as pointed

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* These factors (Breit, 1924) are defined in terms of the incident and scattered X-ray frequencies as $a_n = (\nu_n/\nu_{inc})^3$ with $h(\nu_{inc} - \nu_n) = E_n - E_g$ where ν_{inc} is the frequency of the incident X-ray radiation. In terms of the incident X-ray energies these factors represent third order corrections to $I_t(\omega)$.

out by Bonham (1965). Thus Bonham (1965) has obtained correction terms to $I_t(\omega)/I_{cl}$ (for X-ray scattering and for electron scattering within the first Born approximation) through third order in the incident X-ray energy and to first order in the nuclear charge Z. The errors in $I_t(\omega)/I_{cl}$ for X-rays are smallest at small scattering angles since the correction term $\Delta I_t(\omega)$ for a given atomic system and given incident energy can be reduced (Bonham, 1965) to a power series involving sin $(\omega/2)$.

As the total scattered intensity is composed of coherent and incoherent components, the zero-order contribution to the incoherent part can be determined from their difference

$$I_i(\omega) = I_t(\omega) - I_c(\omega)$$
$$= \langle \Psi_g || P |^2 | \Psi_g \rangle - |\langle \Psi_g | P | \Psi_g \rangle|^2 . \qquad (5)$$

In terms of the scattering variable μ, $\mu = \kappa S$, the usual notation employed for the quantities introduced above is

$$I_t(\mu)/I_{cl} = F^2(\mu) + S(\mu) \qquad (6a)$$
$$I_c(\mu)/I_{cl} = F^2(\mu) \qquad (6b)$$
$$I_i(\mu)/I_{cl} = S(\mu) \qquad (6c)$$

where $S(\mu)$ and $F(\mu)$ are known as the incoherent scattering factor and the atomic form factor (coherent scattering factor) respectively. For spherically symmetric electron distributions, F and S depend only on the magnitude of μ, $|\mu| = 4\pi$ sin $(\omega/2)/\lambda$.

The problem of electron scattering from free atoms has been treated in detail by Morse (1932). Within the first Born approximation and to the level of approximation outlined above for X-ray scattering, Morse gives the zero-order expression

$$I_t^e(\mu)/I_{cl} = \frac{4}{\mu^4} [N^2 - 2NF(\mu) + \bar{S}(\mu)] \qquad (6d)$$

for the total electron intensity scattered at an angle ω with respect to the scattering plane. In our notation N is the number of electrons, $F(\mu)$ is the coherent X-ray scattering factor while $\bar{S}(\mu) = I_t(\mu)$ represents the total intensity of scattered X-ray radiation. The expression I_{cl} is given by Rutherford's (1911) law. Since the expression for the coherently scattered electron intensity can also be written in terms of its X-ray counterpart (Morse, 1932),

$$I_c^e(\mu) = f_e^2(\mu) = \frac{4}{\mu^4} [N - F(\mu)]^2 \qquad (6e)$$

(6d) can be rewritten as

$$I_t^e(\mu)/I_{cl} = \frac{4}{\mu^4} \{(N - F(\mu))^2 + S(\mu)\} \qquad (6f)$$

where $S(\mu)$ is just the incoherent X-ray scattering factor. The total, coherent and incoherent electron intensities can therefore be obtained from their X-ray counterparts except at $\omega = 0$ (i.e. $\mu = 0$) where (6e) and (6f) are undefined. For $\omega = 0$ the expression

$$I_c^e(0)/I_{cl} = [f_e(0)]^2 = [\tfrac{1}{3}\langle r^2 \rangle]^2 \qquad (6g)$$

may be obtained from Ibers' (1958) formula for $f_e(0)$. As correction terms to $I_t(\mu)/I_{cl}$ for X-ray and electron scattering can be found elsewhere (Bonham, 1965), the density matrix formalism for X-ray scattering will be based on (3) and on (4) for the coherent and total intensities, respectively. For incident electrons of velocity v, (6e) to (6g) should be multiplied by $\beta^{-1/2}$ where $\beta = 1 - (v/c)^2$.

B. Density matrix formulation

For any normalized N-electron wavefunction Ψ_g, the p-particle density matrix is defined (Löwdin, 1955) as

$$\Gamma^{(p)}(1,2\ldots,p|1',2',\ldots,p')$$

$$= \binom{N}{p} \int \Psi_g(1,2,\ldots N)\Psi_g^*(1',2',\ldots,p',$$

$$p+1,\ldots,N)dp+1\ldots dN \qquad (7a)$$

where $\binom{N}{p}$ represents the binomial coefficient. In (7a) the integration is over the combined space-spin coordinates of electrons $p+1, p+2, \ldots, N$. The following properties of $\Gamma^{(p)}$ arise from its definition:

$$\Gamma^{(p)}(1,2,\ldots,p|1',2',\ldots,p')$$

$$= \Gamma^{*(p)}(1',2',\ldots,p'|1,2,\ldots,p) \text{ (Hermitean)} \qquad (7b)$$

$$\Gamma^{(p)}(1,2,\ldots,p|1',2',\ldots,p')$$

$$= -\Gamma^{(p)}(2,1,\ldots,p|1',2',\ldots,p')$$

$$= -\Gamma^{(p)}(1,2,\ldots,p|2',1',\ldots,p')$$

$$\text{(Antisymmetric)} \qquad (7c)$$

$$\int \Gamma^{(p)}(1,2,\ldots,p|1,2,\ldots,p)d1\,d2\ldots dp = \binom{N}{p}$$

$$\text{(Finite trace)} . \qquad (7d)$$

If Ω is any many-particle operator which can be written in terms of zero, one-, two-, three-, $\ldots$ many-particle contributions Ω_0, Ω_1, Ω_{12}, Ω_{123} $\ldots$,

$$\Omega = \Omega_0 + \sum_i \Omega_i + \frac{1}{2!} \sum_{i,j} \Omega_{ij} + \frac{1}{3!} \sum_{i,j,k} \Omega_{ijk} + \ldots \qquad (8)$$

its expectation value $\langle \Omega \rangle$ takes the form (Löwdin, 1955)

$$\langle \Omega \rangle = \Omega_0 + \int \Omega_1 \Gamma^{(1)}(1|1')d1 + \int \Omega_{12}\Gamma^{(2)}(1,2|1',2')d1d2$$

$$+ \int \Omega_{123}\Gamma^{(3)}(1,2,3|1',2',3')d1d2d3 + \ldots . \qquad (9)$$

According to convention (Löwdin, 1955), the operators Ω_1, Ω_{12}, Ω_{123} which appear in the integrands of (9) work only on the unprimed variables. One then sets $1' = 1, 2' = 2, 3' = 3, \ldots$ and carries out the integrations.

In order to cast I_t/I_{cl} in the form indicated by (9), we rewrite (4) as

$$I_t(\mu)/I_{cl} = \int \Psi_g^* \sum_{i=1}^{N} \hat{1}\Psi_g(d\tau) + 2\int \Psi_g^*[\tfrac{1}{2}\sum_{j,k}'$$

$$\times \exp \{i\boldsymbol{\mu} \cdot (\mathbf{r}_j - \mathbf{r}_k)\}]\Psi_g(d\tau)$$

$$= N + 2 \int \Psi_g^*(1, 2, \dots, N)[\tfrac{1}{2} \sum_{j,k}'$$

$$\times \exp \{i\boldsymbol{\mu} \cdot (\mathbf{r}_j - \mathbf{r}_k)\}]\Psi_g(1, 2, \dots, N)$$

$$\times d\tau_1 d\tau_2 \dots d\tau_N \qquad (10)$$

where $\hat{1}$ denotes the unit operator and the prime indicates summation over all $j \neq k$. In terms of the 2-matrix (10) may be written as

$$I_t(\boldsymbol{\mu})/I_{\mathrm{cl}} = N + 2 \int \exp\{i\boldsymbol{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\}$$
$$\times \Gamma^{(2)}(1,2|1',2')\mathrm{d}1\mathrm{d}2 \qquad (11a)$$

where the integration is over both the space and spin coordinates of electrons 1 and 2.

At this point in our development of the density matrix formalism we note that $\exp \{i\boldsymbol{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\}$ is a spin-free operator and strictly of a multiplicative nature. We therefore dispense with the primed 'bookkeeping' notation in (11a) and in subsequent equations which refer to X-ray quantities, but we will continue to carry the spin coordinates in these equations. For an evalution of (11a) we use the diagonal representation of $\Gamma^{(2)}$ in terms of its eigenfunctions, the *natural spin geminals* (NSG),

$$\Gamma^{(2)}(1,2|1',2') = \sum_{i=1}^{r} \lambda_i g_i(1,2)g_i^*(1',2'). \qquad (11b)$$

This representation of $\Gamma^{(2)}$ leads to the expression

$$I_t(\boldsymbol{\mu})/I_{\mathrm{cl}} = N + 2 \sum_{j=1}^{r} \lambda_j \int \exp \{i\boldsymbol{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\}$$
$$g_j(1,2)g_j^*(1,2)\mathrm{d}1\mathrm{d}2 \qquad (12)$$

for the total intensity of scattered X-ray radiation. The expansion coefficients λ_j which appear in (12) are the eigenvalues (pair-occupation numbers) of $\Gamma^{(2)}$ while the summation limit r, the 2-rank (Ando, 1963) of Ψ_g, is the number of non-zero eigenvalues of $\Gamma^{(2)}$.

It is easily shown that the expression for the coherent intensity I_c can be written as

$$I_c(\boldsymbol{\mu})/I_{\mathrm{cl}} = \left| \int \exp \{i\boldsymbol{\mu} \cdot \mathbf{r}\}\gamma(1|1)\mathrm{d}1 \right|^2 \qquad (13)$$

where $\gamma(1|1)$ denotes the 1-particle density matrix. In terms of the eigenfunctions of $\gamma(1|1)$, the *natural spin orbitals* (NSO), (13) may be written as

$$I_c(\boldsymbol{\mu})/I_{\mathrm{cl}} = \left| \sum_{j=1}^{g} \gamma_j \int \exp \{i\boldsymbol{\mu} \cdot \mathbf{r}\}\chi_j(1)\chi_j^*(1)\mathrm{d}1 \right|^2 \qquad (14)$$

where γ_j indicates the eigenvalue (occupation number) of the jth NSO $\chi_j(\mathbf{r}, s)$. The manner in which the NSO and the NSG are obtained from many-electron wavefunctions has been discussed at length by Löwdin (1955), by Barnett & Shull (1967) and by others.

Although (12) and (14) are completely general, they may be evaluated at zero scattering angle without explicit knowledge of the $\{\chi_i\}$ or the $\{g_i\}$. Since the $\{g_i\}$ are mutually orthonormal, (12) reduces to

$$I_t(0)/I_{\mathrm{cl}} = N + 2 \sum \lambda_t$$
$$= N + 2\binom{N}{2}$$
$$= N^2$$

with the same result holding for $I_c(0)/I_{\mathrm{cl}}$. This result is consistent with the usual observation that at zero scattering angle the scattered X-ray radiation is coherent while the intensity has a magnitude equal to the square of the number of electrons.

C. Application to atomic states

In order to further develop equations (12) and (14), we must consider the structure of $\gamma(1|1')$ and $\Gamma^{(2)}(1,2|1',2')$. Bingel (1960) has demonstrated that if Ψ_g is an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ with eigenvalues S and M respectively, then the 1-matrix $\gamma(1|1')$ may be expressed as

$$\gamma(1|1') = \gamma_+(\mathbf{r}|\mathbf{r}') \, \alpha(s) \, \alpha^*(s') + \gamma_-(\mathbf{r}|\mathbf{r}') \, \beta(s) \, \beta^*(s') \qquad (15)$$

provided that Ψ_g can be represented as a sum of products of space and spin functions. In (15) the $\gamma_\pm$ are the spatial components of $\gamma(1|1')$ while α and β indicate the usual spin functions. The spin-orbital treatment (Löwdin, 1955) allows $\gamma(1|1')$ to be expanded in terms of its NSO's and (14) is a consequence of this expansion. Since $\exp\{i\boldsymbol{\mu} \cdot \mathbf{r}\}$ is a spin-independent operator we may also write the coherent intensity expression in terms of the eigenfunctions (the natural orbitals, NO's) of the charge density matrix,

$$\bar{\gamma}(\mathbf{r}) = \gamma_+(\mathbf{r}|\mathbf{r}) + \gamma_-(\mathbf{r}|\mathbf{r}),$$

as

$$I_c(\boldsymbol{\mu})/I_{\mathrm{cl}} = |\sum_k \bar{\gamma}_k \int \exp \{i\boldsymbol{\mu} \cdot \mathbf{r}\}\bar{\chi}_k(\mathbf{r})\bar{\chi}_k^*(\mathbf{r})\mathrm{d}^3 r|^2 . \qquad (16)$$

However, the occupation numbers $\{\bar{\gamma}_k\}$ of the NO's $\{\bar{\chi}_k\}$ appearing in (16) are not necessarily the same as the $\{\gamma_k\}$ which appear in (14).

Further development and evaluation of (14) or (16) requires explicit knowledge of the occupation numbers and of the NSO's or NO's. Although any set of one-electron functions would be appropriate, we assume for convenience that the NO's or the NSO's are expanded in a finite sum of normalized Slater-type orbitals (STO's) φ_j. In particular, the NO's may be expressed as

$$\bar{\chi}_n(\mathbf{r}) = \sum_{j=1}^{m} \varphi_j(\mathbf{r})b_{jn} \qquad (17a)$$

$$\varphi_j(\mathbf{r}) = N_j R_j(r) \, Y_{l_j}^{m_j}(\theta, \varphi) \qquad (17b)$$

$$N_j R_j(r) = \frac{(2\alpha_j)^{n_j + 1/2}}{[(2n_j)!]^{1/2}} r^{n_j - 1} \exp \{-\alpha_j r\} \qquad (17c)$$

where the $Y_l^m(\theta, \varphi)$ are the usual normalized spherical harmonics. A similar expansion can be used for the NSO's $\chi_n(\mathbf{r}, s)$ by including a spin function $f_j(s)$ in the definition (17b). Thus the expression for I_c can in all generality be written as

$$I_c(\mathbf{\mu})/I_{c1} = |\sum_{n=1}^{\bar{q}} \sum_{j=1}^{p_n} \sum_{k=1}^{p_n} \bar{\gamma}_n b_{kn} b_{jn}^* \int \exp\{i\mathbf{\mu} \cdot \mathbf{r}\}$$

$$\times \varphi_k(\mathbf{r})\varphi_j^*(\mathbf{r})d^3r|^2 \qquad (18)$$

where p_n is the number of STO's employed in the expansion of the nth NO. Had we used the NSO's rather than the NO's, (18) would contain factors $\langle f_j(s)|f_k(s)\rangle$ arising from the spin integrations. If the NO's are expanded in a basis other than a STO set, knowledge of the transformation matrix connecting the two basis sets allows (18) to be used for the computation of $I_c(\mathbf{\mu})$.

As for the case of the 1-matrix, McWeeny & Kutzelnigg (1968) have demonstrated* that if Ψ_g is an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ with eigenvalues S and M; then $\Gamma^{(2)}$ may be expressed as a linear combination of spatial and spin factors,

$$\Gamma^{(2)}(1,2|1',2') = P_t(aa^* + bb^* + cc^*) + P_s dd^*$$
$$+ C_1(S,M)[T_1^{(1)}(aa^* - bb^*)$$
$$+ T_2^{(1)}(cd^* + dc^*) + T_3^{(1)}(dc^* - cd^*)]$$
$$+ C_2(S,M)[T^{(2)}(aa^* + bb^* - 2cc^*)] . \qquad (19)$$

The P's are the symmetric (singlet) and antisymmetric (triplet) spatial components of $\Gamma^{(2)}$ while the C's are certain vector coupling coefficients and the T's are various 2-particle spatial functions; all are defined in the paper cited above. The $a(s_1,s_2)$, $b(s_1,s_2)$, $c(s_1,s_2)$ denote the three triplet spin states while $d(s_1,s_2)$ represents the singlet spin state. As pointed out by McWeeny & Kutzelnigg (1968), the eigenfunctions of $\Gamma^{(2)}$ are of pure symmetric or antisymmetric character only if the terms in cd^* and dc^* vanish. These authors also remark that this is generally true only for singlet states or for states with $M = 0$.

We now examine the implications of (19) with respect to the expression for I_t. Since $\exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\}$ is spin independent and only of a multiplicative nature, insertion of (19) into (11a) and summation over the spin coordinates of electrons 1 and 2 gives

$$I_t(\mathbf{\mu})/I_{c1} = 2\left\{\int \exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\}[3P_t(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1\mathbf{r}_2)\right.$$
$$\left. + P_s(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)]d^3r_1 d^3r_2\right\} + N . \qquad (20)$$

An evaluation of the total intensity expression therefore requires only the natural geminals (NG's). The NG's are either purely symmetric (singlet) or antisymmetric (triplet) with respect to interchange of their coordinates since they are the respective eigenfunctions of the singlet and triplet spatial 2-matrices $P_s(\mathbf{r}_1\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)$ and $P_t(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)$ which occur in the decomposition (19). Before casting the total intensity expression in terms of the NG's, it is observed that summation over spin coordinates in (12) yields an expression wherein

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* For a discussion of the structure and symmetry properties of both γ and $\Gamma^{(2)}$ the reader may refer to McWeeny (1960) and to McWeeny & Kutzelnigg (1968).

non-vanishing matrix elements of $\exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\}$ only occur between the symmetric or antisymmetric spatial components of the NSG's. Matrix elements occurring for instance between singlet-triplet coupled NSG components vanish due to the spin independence of the scattering operator.

We now consider the formulation of I_t in terms of the NG's. For convenience the NG's are expanded in a sum of 2-electron configurations*

$$\bar{g}_j(\mathbf{r}_1,\mathbf{r}_2) = \sum_{k=1}^{m} X_{(k)}(\mathbf{r}_1,\mathbf{r}_2)C_{kj} \quad (k)=k_1,k_2 . \qquad (21)$$

The expression for the total scattered X-ray intensity can therefore be written as

$$I_t(\mathbf{\mu})/I_{c1} = N + 2\sum_{n=1}^{r} \sum_{j=1}^{m} \sum_{k=1}^{m} \lambda_n C_{jn} C_{kn}^* \left\{\int \exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 \right.$$
$$\left. -\mathbf{r}_2)\} X_{(j)}(\mathbf{r}_1,\mathbf{r}_2) X_{(k)}^*(\mathbf{r}_1,\mathbf{r}_2)d^3r_1 d^3r_2\right\} \qquad (22)$$

where m is the number of configurations involved in the expansion of the nth natural geminal. In order to define matrix elements as either 'diagonal' or 'non-diagonal' (22) is recast in the form

$$I_t(\mathbf{\mu})/I_{c1} = N + 2\sum_{n=1}^{r} \sum_{k=1}^{m} \lambda_n |C_{jn}|^2 \int$$
$$\times \exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\} |X_{(k)}(\mathbf{r}_1,\mathbf{r}_2)|^2 d^3r_1 d^3r_2$$
$$+ 4\sum_{n=1}^{r} \sum_{j=1}^{m} \sum_{k>j}^{m} \lambda_n C_{jn} C_{kn}^* \int \exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\}$$
$$\times X_{(j)}(\mathbf{r}_1,\mathbf{r}_2) X_{(k)}^*(\mathbf{r}_1,\mathbf{r}_2) d^3r_1 d^3r_2 . \qquad (23)$$

Discussion of the form taken by the matrix elements appearing in (18) and (23) is reserved for the next two sections.

D. Matrix elements involving natural orbitals

For present purposes the determination of the coherent scattering factor F involves an evaluation of the operator $\exp\{i\mathbf{\mu} \cdot \mathbf{r}\}$ over a STO basis. Since the coherent scattering factor is just the square root of the coherent intensity, the expression for $F(\mathbf{\mu})$ arising from (18) can be expressed as

$$F(\mathbf{\mu}) = \sum_{n=1}^{\bar{q}} \bar{\gamma}_n f_n(\mathbf{\mu}) \qquad (24a)$$

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* The $X_{(k)}(\mathbf{r}_1,\mathbf{r}_2)$ notation signifies a two-electron configuration constructed from STO's $\varphi_{k_1}(\mathbf{r})$, $\varphi_{k_2}(\mathbf{r})$. For symmetric NG's $X_{(k)}$ can be represented by a 2×2 permanent, or a linear combination of 2×2 permanents,

$$P_{(k)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left\{\varphi_{k_1}(\mathbf{r}_1)\varphi_{k_2}(\mathbf{r}_2) + \varphi_{k_1}(\mathbf{r}_2)\varphi_{k_2}(\mathbf{r}_1)\right\}$$

while for *antisymmetric* NG's $X_{(k)}$ can be represented by a 2×2 *determinant*, or a linear combination of 2×2 determinants,

$$D_{(k)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left\{\varphi_{k_1}(\mathbf{r}_1)\varphi_{k_2}(\mathbf{r}_2) - \varphi_{k_1}(\mathbf{r}_2)\varphi_{k_2}(\mathbf{r}_1)\right\} .$$

If Ψ_g represents a state with z component of spin $M = 0$, then the NSG's are equal to the NG's multiplied by an appropriate 2-particle spin function.

with

$$f_n(\mathbf{\mu}) = \sum_{j=1}^{p_n} \sum_{k=1}^{p_n} b_{kn} b_{jn}^* f_{jk}(\mathbf{\mu}) \qquad (24b)$$

and

$$f_{jk}(\mathbf{\mu}) = \int \exp\{i\mathbf{\mu} \cdot \mathbf{r}\} \, \varphi_k(\mathbf{r}) \, \varphi_j^*(\mathbf{r}) \, d^3r . \qquad (24c)$$

To evaluate (24c) the expansion of $\exp\{i\mathbf{\mu} \cdot \mathbf{r}\}$ in terms of spherical harmonics and spherical Bessel functions may be employed

$$\exp\{i\mathbf{\mu} \cdot \mathbf{r}\} = 4\pi \sum_{p=0}^{\infty} \sum_{m=-p}^{+p} i^p j_p(\mu r) \, Y_p^m(\theta,\varphi) \, Y_p^{*m}(\alpha,\beta) . \quad (24d)$$

Here $j_p(\mu r)$ are spherical Bessel functions, $\mathbf{\mu} = (\mu,\alpha,\beta)$ and $\mathbf{r} = (r,\theta,\varphi)$. Substitution of (24d) and (17b) into (24c) and integration over θ,φ yields

$$f_{jk}(\mathbf{\mu}) = \sum_p i^p [4\pi(2p+1)]^{1/2} N_j N_k \, Y_p^{*m_j - m_k}(\alpha,\beta)$$
$$\times C^p(l_j m_j ; l_k m_k) \langle J_{pjk} \rangle \qquad (24e)$$

where the C^p are the usual Condon–Shortley coefficients,

$$C^p(l_j, m_j ; l_k m_k) = \left(\frac{2}{2p+1} \right)^{1/2}$$
$$\int_{-1}^{1} P_p^{m_j - m_k}(X) \, P_{l_j}^{m_j}(X) \, P_{l_k}^{m_k}(X) dX \qquad (24f)$$

and the remaining term in (24e) has the definition

$$\langle J_{pjk} \rangle = \int_0^{\infty} R_j(r) R_k(r) j_p(\mu r) r^2 dr . \qquad (24g)$$

If NSO's rather than NO's were used to evaluate the expression for $F(\mathbf{\mu})$, then (24e) would be multiplied by $S_{jk} = \langle f_j(s) | f_k(s) \rangle$. However, for an atomic state that is an eigenfunction of $\hat{S}_z$, $S_{jk} = 1$.

We note the following points of simplification in the expansion (24e).*

(1) For an atomic state which is an eigenfunction of $\hat{L}_z$, all the STO's used in the expansion of a given NO can be characterized by the same m_l value so that only $m_j = m_k = \bar{m}$ appears in (24e).

(2) For atomic S-states the NO's are further characterized by the angular momentum quantum number l.

(3) If a definite direction for $\mathbf{\mu}$ may be chosen, the selection rule $\delta(m_j, m_k)$ results.

(4) If the charge distribution is spherically symmetric (Bartell & Gavin, 1964) or if one averages over random orientations of $\mathbf{\mu}$ (i.e. an integration over α,β) the expansion (24e) reduces to the zero-order term involving $j_0(\mu r) = \sin(\mu r)/\mu r$ and $\delta(m_j, m_k)$.

E. Matrix elements involving natural geminals

In § 2C it was mentioned that individual NSG's constructed for a singlet state (or a state with $M = 0$) were either symmetric or antisymmetric under ex-

* Angular factors for integration involving STO's of s-, p-, d- and f-type symmetries are listed in Table 1 of Benesch & Malli (1968).

change of spatial coordinates. In general, NSG's constructed for a state with arbitrary S, M values do not exhibit this simple spatial symmetry. However, the total intensity expression written in terms of the NSG's yields matrix elements which only involve their spatially symmetric or antisymmetric components. On the other hand the NG's are of either singlet or triplet symmetry and the total intensity expression was therefore formulated in terms of the NG's. Since the NG's are either symmetric or antisymmetric regardless of the S, M values of the atomic state, we shall restrict our attention to NG's constructed for a singlet state. For such a state the symmetric 2-electron configurations appearing in the NG expansion (21) can be represented by

$$X_{(k)}(\mathbf{r}_1, \mathbf{r}_2) = P_{(k)}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_k(\mathbf{r}_1)\varphi_k(\mathbf{r}_2) \quad (k_1 = k_2) \quad (25a)$$

$$= \frac{1}{\sqrt{2}} [\varphi_{k_1}(\mathbf{r}_1)\varphi_{k2}(\mathbf{r}_2) + \varphi_{k_1}(\mathbf{r}_2)\varphi_{k_2}(\mathbf{r}_1)] \quad (k_1 \neq k_2) . \quad (25b)$$

With respect to the operator $\exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\}$ for total scattering, the expansion (23) incorporates the following 'diagonal' matrix elements:

$$\text{M.E.} = \langle P_{(k)}(\mathbf{r}_1, \mathbf{r}_2) | \exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\} | P_{(k)}(\mathbf{r}_1, \mathbf{r}_2) \rangle$$
$$= |f_{kk}|^2 \qquad (26a)$$

$$\text{M.E.} = \langle P_{(k)}(\mathbf{r}_1, \mathbf{r}_2) | \exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\} | P_{(k)}(\mathbf{r}_1, \mathbf{r}_2) \rangle$$
$$= f_{k_1 k_1} f_{k_2 k_2} + |f_{k_1 k_2}|^2 . \qquad (26b)$$

The matrix elements (26a,b) follow from the definitions (25a,b) respectively. Note that the $f_{k_1 k_2}$ introduced in (26) involve only two STO's,

$$f_{k_1 k_2}(\mathbf{\mu}) = \int \exp\{i\mathbf{\mu} \cdot \mathbf{r}\} \varphi_{k_2}(\mathbf{r}) \varphi_{k_1}^*(\mathbf{r}) d^3r$$

and is therefore defined by the expansion (24e). The following symmetry properties of the $f_{k_1 k_2}$ should be noted:

$$f_{k_1 k_2} = f_{k_2 k_1} \neq f_{k_2 k_1}^* \qquad (27a)$$
$$f_{k_1 k_2}^* = f_{k_2 k_1}^* \neq f_{k_2 k_1} . \qquad (27b)$$

The self-adjoint property of $\exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\}$ along with the symmetry properties (27a) and (27b) will now lead to a new selection rule involving the orbital angular momentum quantum number l_k.

The subscripts in (25a,b) will be changed in order to obtain the 'non-diagonal' matrix elements appearing in (23). From (25a) we find

$$\text{M.E.} = \langle P_{(k)}(\mathbf{r}_1, \mathbf{r}_2) | \exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\} | P_{(j)}(\mathbf{r}_1, \mathbf{r}_2) \rangle$$
$$= f_{jk} f_{kj}^*$$
$$= |f_{jk}|^2 , \qquad (28a)$$

whereas from (25b)

$$\text{M.E.} = \langle P_{(k)}(\mathbf{r}_1, \mathbf{r}_2) | \exp\{i\mathbf{\mu} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\} | P_j(\mathbf{r}_1, \mathbf{r}_2) \rangle$$
$$= \frac{1}{2}(f_{k_1 j_1} f_{k_2 j_2}^* + f_{k_1 j_2} f_{k_2 j_1}^*$$
$$+ f_{k_2 j_1} f_{k_1 j_2}^* + f_{k_2 j_2} f_{k_1 j_1}^*) . \qquad (28b)$$

In (28b) three cases must be considered.

Case 1: $|l_{j_1}-l_{k_1}|+|l_{k_2}-l_{j_2}|$ odd; and

$|l_{k_1}-l_{j_2}|+|l_{k_2}-l_{j_1}|$ odd:

M.E. $= 0$ (29a)

Case 2: $|l_{k_1}-l_{j_1}|+|l_{k_2}-l_{j_2}|$ even; and

$|l_{k_1}-l_{j_2}|+|l_{k_2}-l_{j_1}|$ even:

M.E. $= f_{k_1 j_1}f_{k_2 j_2}+f_{k_1 j_2}f_{k_2 j_1}$ (29b)

Case 3: $|l_{k_1}-l_{j_1}|+|l_{k_2}-l_{j_2}|$ odd or even; and

$|l_{k_1}-l_{j_2}|+|l_{k_2}-l_{j_1}|$ odd or even:

M.E. $= f_{k_1 j_1}f_{k_2 j_2}$ or $f_{k_1 j_2}f_{k_2 j_1}$. (29c)

With regard to the 'non-diagonal' matrix elements obtained from (25a) and (25b),

M.E. $= \langle P_{(k)}(\mathbf{r}_1,\mathbf{r}_2)| \exp\{i\boldsymbol{\mu}\cdot(\mathbf{r}_1-\mathbf{r}_2)\}|P_{(j)}(\mathbf{r}_1,\mathbf{r}_2)\rangle$

the same considerations which led to (29a-29c) give

M.E. $= 0$, or (30a)

M.E. $= \sqrt{2}f_{kj_1}f_{kj_2}$. (30b)

The selection rules indicated in (29a-29c) have not been observed before. They occur because the NG's were expanded in configurations involving the non-orthogonal (for similar angular symmetries) STO basis.

Configurations constructed for an antisymmetric (triplet) NG must be of the type

$D_{(k)}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}\{\varphi_{k_1}(\mathbf{r}_1)\varphi_{k_2}(\mathbf{r}_2)-\varphi_{k1}(\mathbf{r}_2)\varphi_{k2}(\mathbf{r}_1)\}$ (31)

and can be shown to yield only the 'diagonal' matrix elements

M.E. $= f_{k_1 k_1}f_{k_2 k_2}-|f_{k_1 k_2}|^2$ (32a)

and the 'non-diagonal' elements

M.E. $= 0$ (32b)

M.E. $= f_{k_1 j_1}f_{k_2 j_2}-f_{k_1 j_2}f_{k_2 j_1}$ (32c)

M.E. $= f_{k_1 j_1}f_{k_2 j_2}$ or $-f_{k_1 j_2}f_{k_2 j_1}$. (32d)

In order to further evaluate the formulae involving $|f_{ij}|^2$ terms which for instance appear in (26a), (28a) and (32a), we must consider the possibility of a non-spherical configuration. (Open shells involving p^n, d^n, f^n configurations are illustrative examples.) If the configuration does not exhibit spherical symmetry, then from (24e) $|f_{ij}|^2$ obviously depends on the orientation of the scattering vector S, $(\boldsymbol{\mu}=\kappa \mathbf{S})$. For a p-type orbital oriented in an arbitrary direction, McWeeny (1951) demonstrated that the scattering from such an orbital is completely defined by two quantities $f_\parallel$ and $f_\perp$ and an angle β between S and the orbital axis. In this notation $f_\parallel$ is the scattering factor when S is parallel

to the orbital axis and $f_\perp$ represent the scattering factors when S is perpendicular to the orbital axis.

Freeman (1959) employed group-theoretical methods for describing the scattering from open shells involving p^n and d^n configurations. By a transformation of the one-electron state functions, the vector S is brought parallel to the z axis in the rotated reference frame. In this fashion Freeman (1959) obtained results for p-type orbitals which are equivalent to those of McWeeny (1951). In addition, Freeman derived formulae for matrix elements involving d^n configurations. However, Freeman's method has the disadvantage in that it yields orbitals in the rotated reference frame which are no longer eigenfunctions of the angular momentum operators.

For non-spherical configurations we can always simplify the computation of matrix elements by averaging over random orientations of S, as pointed out by Pohler & Hanson (1965). This procedure involves multiplication of (24e) by its complex conjugate and integrating the result over the surface of the unit sphere (i.e. integration over α, β). However, $\delta(m_j,m_k)$ is no longer a valid selection rule.

One final word regarding the form taken by the f_{ij} is in order. If the STO's have the same orbital angular momentum quantum numbers $(l_i=l_j)$ but different principal quantum numbers $(n_i\neq n_j)$ an initial assumption of spherical symmetry or an averaging procedure for non-spherical configurations again leads to the $\delta(m_j,m_k)$ selection rule. Furthermore, only $j_0(\mu r)$ will be involved in the computation of f_{ij}. Both of these observations follow from an integration of (24e) over the surface of the unit sphere.

3. A special case: reduction to the Waller–Hartree equation

By approximating the N-electron wavefunction Ψ_g with a single Slater determinant constructed from a basis set $\{\mu_j\}$ of orthonormal spin-orbitals, Waller & Hartree (1929) have shown that

$$I_t(\boldsymbol{\mu})/I_{cl}=N+\sum_{j=1}^{N}\sum_{k\neq j}^{N}(f_{jj}f_{kk}^*-|f_{jk}|^2)$$ (33a)

$$=N+|\sum_{j=1}^{N}f_{jj}|^2-\sum_{j=1}^{N}|f_{jj}|^2-\sum_{j=1}^{N}\sum_{k\neq j}^{N}|f_{jk}|^2$$ (33b)

where

$$f_{jk}=\int \exp\{i\boldsymbol{\mu}\cdot\mathbf{r}\}\,\mu_k(\mathbf{r})\mu_j^*(\mathbf{r})\mathrm{d}^3 r \times \delta(\eta_j,\eta_k).$$ (33c)

The spin functions are denoted by η.

If Ψ_g is approximated by a single Slater determinant, then the density matrix and Waller–Hartree formalisms must be equivalent. In order to demonstrate their equivalence, we must know the form taken by the 2-matrix. For a single normalized Slater determinant constructed from some non-orthogonal spin orbital

basis $\{\varphi_j\}$, Löwdin (1955) has shown that the p-particle density matrix is completely determined by a knowledge of the 1-matrix, namely

$$p!\Gamma^{(p)}\,(1,2,\ldots,p|1',2',\ldots,p')$$

$$=\begin{vmatrix} \varrho(1|1')\varrho(1|2')\ldots\varrho(1|p') \\ \varrho(2|1')\varrho(2|2')\ldots\varrho(2|p') \\ \cdot\quad\cdot\quad\ldots\quad\cdot \\ \cdot\quad\cdot\quad\ldots\quad\cdot \\ \cdot\quad\cdot\quad\ldots\quad\cdot \\ \cdot\quad\cdot\quad\ldots\quad\cdot \\ \varrho(p|1')\varrho(p|2')\ldots\varrho(p|p') \end{vmatrix} \quad (34)$$

where the 1-matrix ϱ has the representation

$$\varrho(1|1')=\varrho(r_1,\eta_1|r_1',\eta_1')=\sum_{k=1}^{N}\sum_{l=1}^{N}\varphi_l(r_1,\eta)\varphi_k^*(r_1',\eta')d^{-1}(l,k) \quad (35)$$

in the non-orthogonal φ basis. The various $d(m,n)$ are the non-orthogonality or overlap integrals,

$$d(m,n)=\int\varphi_n(r)\varphi_m^*(r)d^3r\times\delta(\eta_n,\eta_m)\ .$$

Now the basis set $\{\varphi_j(r,\eta)\}$ can always be orthonormalized without changing the nature of the approximate wavefunction Ψ_g. The orthonormal spin-orbital basis $\{\Psi_k\}$ chosen by Löwdin (1955) for casting the 1-matrix in diagonal form is

$$\Psi_j=\sum_n\varphi_n d^{-1/2}(n,j) \quad (36)$$

(symmetric orthonormalization procedure) where the $d^{-1/2}(l,k)$ are elements of the unitary matrix $d^{-1/2}$ which diagonalizes ϱ. The 1-matrix now has the diagonal representation

$$\varrho(1|1')=\sum_{j=1}^{N}\Psi_j(1)\Psi_j^*(1')\ . \quad (37)$$

It must be pointed out that diagonalization of ϱ does not affect expectation values calculated from ϱ or from any of the $\Gamma^{(p)}$ since the density matrices belong to a class of operators known as trace operators. A well-known property of the trace is that $\mathrm{tr}(AB)=\mathrm{tr}(BA)$. Thus if U is any unitary transformation, $UU^{-1}=U^{-1}U$, it immediately follows that

$$\mathrm{tr}(U^{-1}\Gamma^{(p)}U)=\mathrm{tr}(U^{-1}U\Gamma^{(p)})=\mathrm{tr}(\Gamma^{(p)}UU^{-1})=\mathrm{tr}(\Gamma^{(p)})\ . \quad (38)$$

Although the expression (34) for $\Gamma^{(p)}$ is a special case, (38) is true for a general $\Gamma^{(p)}$.

From (34) the 2-matrix has the form

$$2!\Gamma^{(2)}\,(1,2|1',2')=\begin{vmatrix}\varrho(1|1')\varrho(1|2')\\ \varrho(2|1')\varrho(2|2')\end{vmatrix} \quad (39)$$

and by application of (39), (37) and (11a) it immediately follows that the total intensity expression becomes

$$I_t(\mu)/I_{cl}=N+\sum_{j=1}^{N}\sum_{k=1}^{N}\int\Psi_j(1)\Psi_j^*(1)\exp\{i\mu\cdot(r_1-r_2)\}$$

$$\times\Psi_k(2)\Psi_k^*(2)\mathrm{d}l\mathrm{d}2-\sum_{j=1}^{N}\sum_{k=1}^{N}\int\Psi_j(1)\Psi_j^*(2)$$

$$\times\exp\{i\mu\cdot(r_1-r_2)\}\Psi_k(2)\Psi_k^*(1)\mathrm{d}l\mathrm{d}2 \quad (40)$$

after expansion of the determinant. Since the terms exactly cancel when $j=k$, the expression for I_t becomes

$$I_t(\mu)/I_{cl}=N+\sum_{j=1}^{N}\sum_{k\neq j}^{N}\left\{\int\exp\{i\mu\cdot r_1\}\Psi_j(1)\Psi_j^*(1)\mathrm{d}l\right.$$

$$\times\int\exp\{-i\mu\cdot r_2\}\Psi_k^*(2)\Psi_k(2)\mathrm{d}2$$

$$-\int\exp\{-i\mu\cdot r_2\}\Psi_j^*(2)\Psi_k(2)\mathrm{d}2$$

$$\left.\times\int\exp\{i\mu\cdot r_1\}\Psi_j(1)\times\Psi_k^*(1)\mathrm{d}l\right\}. \quad (41)$$

It is therefore apparent that (41) can be written as

$$I_t(\mu)/I_{cl}=N+\sum_{j\neq 1}^{N}\sum_{k\neq j}^{N}(f_{jj}f_{kk}^*-|f_{jk}|^2) \quad (42)$$

where the f_{jk} are defined as in (33c). However, (42) is just the familiar Waller–Hartree result. It is therefore evident that the density matrix and Waller–Hartree formulations of X-ray scattering are equivalent provided that the wavefunction Ψ_g is represented by a single Slater determinant.

4. Summary

Values of the coherent and total scattered X-ray intensities can be found from the 1- and 2-particle density matrix analysis of an arbitrary state function Ψ_g. These values can then be used to compute analogous electron intensities within the first Born approximation. Evaluation of the coherent scattering factor $F(\mu)$ was shown to involve only the spatial component of the 1-matrix. Therefore only the NO's are required when computing $F(\mu)$ values, but the NSO's may also be used by simply summing over the spin coordinates before applying the operator $\exp\{i\mu\cdot r\}$. The analysis of the total intensity expression was shown to involve only the purely symmetric and purely antisymmetric spatial components of the 2-matrix $\Gamma^{(2)}$. By assuming a convenient expansion for the symmetric and antisymmetric NG's, it was possible to find all the matrix elements of $\exp\{i\mu\cdot(r_1-r_2)\}$ regardless of the S, M values of the atomic state. Although the matrix elements (26–30) and (32) were derived for a particular representation of the NG's, they are the only ones required in practice provided the transformation matrix from an arbitrary basis to the basis of 2×2 STO configurations is known. The same observation holds for the matrix elements of $\exp\{i\mu\cdot r\}$. In practise, total intensity values may also be calculated from an NSG analysis of an arbitrary wavefunction by first summing over the spin coordinates, the results being equivalent to those given above.

The density matrix formalism developed here provides a general extension of the usual Waller–Hartree equations and therefore facilitates a study of the importance of effects other than electron exchange; that is, we are in a favorable position to assess the importance of electron correlation on X-ray scattering. This topic is treated in the next paper where we compare coherent and total intensity values obtained for the Be atom from the NSO and NSG analysis of a configuration interaction (CI) function, and from a two-configuration function, with those computed within the Waller–Hartree formalism from a HF function.

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Correlation and X-ray Scattering. II. Atomic Beryllium

BY ROBERT BENESCH AND VEDENE H. SMITH, JR.

Department of Chemistry, Queen's University, Kingston, Ontario, Canada

In order to assess the importance of correlation effects with respect to the Hartree–Fock (HF) results, values of the coherent, total and incoherent scattered X-ray intensities were computed for the ^1S ground state of atomic beryllium. Natural spin orbitals (NSO) and natural spin geminals (NSG) constructed from the accurate configuration interaction (CI) wavefunction of A. W. Weiss were used in the evaluation of these X-ray quantities from previously derived density matrix expressions. Values were also computed from the two-configuration wavefunction of Watson, which accounts for the $2s$–$2p$ near degeneracy effect. As expected, the CI results for the total intensity differ from their HF counterparts but the magnitudes of the absolute deviations are not as large as those observed for the coherent intensity values. Although the HF results for the coherent intensity are in reasonably good agreement with the CI values, conclusions based on the Møller–Plesset theorem must be made with caution. The largest percentage deviations between HF and CI results, however, are observed for the incoherent intensity. All calculations reported here were verified by the use of sum rules.

1. Introduction

In this paper we examine the effects of electron correlation on the coherent, incoherent and total intensities (the sum of the Compton and Rayleigh contributions) of scattered X-ray radiation. Total intensity values computed from Hartree–Fock (HF) wavefunctions are expected to be somewhat erroneous since an independent particle model (IPM) description of the atom assumes that the spatial coordinates of each electron are in fact independent of the spatial coordinates of

the remaining electrons. This neglect of the so-called 'Coulomb holes' associated with electron pairs can lead to errors when evaluating the total intensity expression since the scattering operator contains the inter-electron distances $r_{ij} = r_i - r_j$. These coulombic manifestations of correlation must not be confused with exchange effects since exchange terms, which do enter the IPM (Waller–Hartree, 1929) expression for the total scattered intensity, owe their existence only to the antisymmetric behaviour of the HF wavefunction. Thus antisymmetry leads to an exchange corre-