

## Interferences in Elastic Chiral Electron Scattering

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Asymmetric quantities in elastic scattering of electrons by optically active molecules, collectively denoted as  $\mathbf{A}$ , and  $\mathbf{A}_s$ , have been treated within the potential scattering model; the direct and spin-orbit interactions are partitioned by constituent atoms. In-plane components of the  $W(\theta)$  function, which account for  $\mathbf{A}_s$ , have been discussed from a general point of view. Interference structure will always be observed in the angular dependence of the components. Since the energy as well as angular dependence of the components are determined by interferences that are nearly destructive, the values of the components are inevitably very sensitive to approximation schemes adopted. A comparison with other interference phenomena is also made.

## I. INTRODUCTION

Elastic chiral electron scattering, or elastic scattering of electrons by optically active molecules,<sup>1</sup> is unique in the sense that it is characterized by asymmetric quantities that change sign for L- and D-isomers. That is,

$$\mathbf{A}_L = -\mathbf{A}_D, \quad (1)$$

where  $\mathbf{A}$  collectively denotes such quantities. According to Farago,<sup>2</sup> they are manifested in the following processes:

(i) In-plane polarization of initially unpolarized electrons.

Its observation has been attempted unsuccessfully.<sup>3</sup>

(ii) Difference in transmission of electrons of opposite helicity.

This has been observed for camphor at an electron energy of 5 eV.<sup>4</sup>

(iii) The rotation angle  $\Psi$  of the transverse polarization observed for transmitted electrons. These are illustrated in Fig. 1, where a comparison is made with analogous quantities for polarized light.<sup>5</sup>

Recently, a practicable theoretical treatment of these quantities was reported.<sup>6</sup> It was

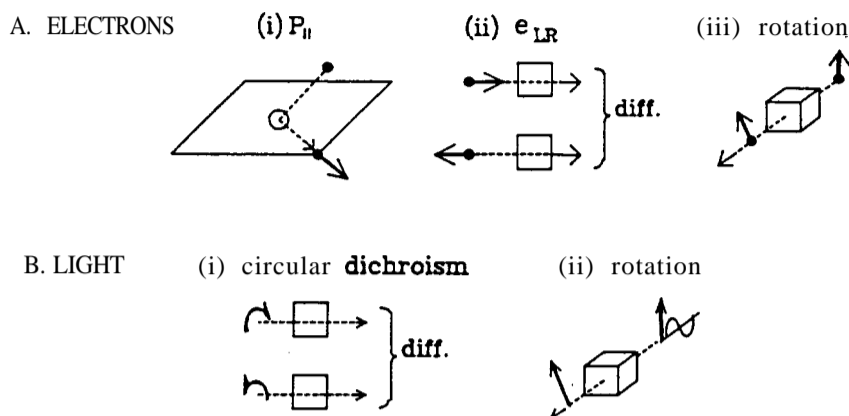


FIG. 1. Electron scattering processes that can manifest asymmetry for D- and L-isomers. Thick arrows: polarization components, sphere and cube: target. Similar processes for light polarization are also shown.

based on the potential scattering model in which molecules were regarded as comprising of non-overlapping spherically symmetric potentials' into which spin-orbit potentials were incorporated. The double scattering mechanism involving spin-orbit interaction was first suggested by Kessler.\* Asymmetry was thus assumed to originate from this interaction, which were accounted for by the function  $W(\theta)$ . Emphasis was placed more on the derivation of explicit symmetry relations such as Eq. (1) than on rigor. Thus in this paper we shall attempt to elucidate the structure of the solution, keeping approximations as little as possible.

The approach is an extension of the two-body potential scattering model involving spin-orbit interaction, for which the  $2 \times 2$  scattering amplitude is written as<sup>8</sup>

$$f(\mathbf{k}_f, \mathbf{k}_i) = f(\mathbf{k}_f, \mathbf{k}_i) \mathbf{1} + i \boldsymbol{\sigma} \cdot \hat{\mathbf{k}}_f \times \hat{\mathbf{k}}_i g(\mathbf{k}_f, \mathbf{k}_i) \quad (2)$$

where  $f$  and  $g$  are called the direct-scattering and spin-flip amplitudes, respectively,  $\mathbf{k}_i$  and  $\mathbf{k}_f$  are initial and final wave vectors of the electrons, respectively,  $\mathbf{1}$  is a unit  $2 \times 2$  matrix, and  $\boldsymbol{\sigma}$  denotes Pauli spin matrices. Eq. (2) leads to the well known formulae for the differential cross section and spin polarization for electrons with initial polarization  $P_i$ :<sup>8</sup>

$$Q(\theta, P_i) = |f|^2 + |g|^2 2 \sin^2 \theta + 2 P_i \cdot \hat{\mathbf{n}} \sin \theta \operatorname{Im}(fg^*) \quad (3a)$$

$$\mathbf{P} = P_i - 2 \sin \theta \frac{\operatorname{Im}(f^*g)}{Q(\theta, P_i)} \hat{\mathbf{n}} + 2 \sin \theta \frac{\operatorname{Re}(f^*g)}{Q(\theta, P_i)} P_i \hat{\mathbf{r}}_i \times \hat{\mathbf{n}} \quad (3b)$$

where  $\mathbf{n} = \hat{\mathbf{k}}_i \times \hat{\mathbf{k}}_f$  and  $\theta$  is the scattering angle. The  $\operatorname{Im}(f^*g)$  and  $\operatorname{Re}(f^*g)$  factors can be understood as interferences between  $f$  and  $g$ . This is an elementary example of interference playing an important role in scattering by polarized electrons. Hereafter we shall discuss

some aspects of interference in the scattering by chiral molecules within our potential scattering model.

## II. ASYMMETRY IN CHIRAL ELECTRON SCATTERING

### 11-I. Potential Scattering Approach

We adopt a potential-scattering approach; the scattering potential comprises of spherically symmetric atomic potentials which do not overlap one another. Furthermore, we assume that scattering amplitudes for these potentials are already available. They are of the form similar to Eq. (2), but not necessarily obtained for free atoms. It may turn out to be necessary to take into account other potential regions outside the atomic potentials as in the so-called multiple scattering model,<sup>9</sup> but the results within the present model serve as a guide to more sophisticated treatments.

We then proceed following the treatment of Ref. 6. The spinor scattering amplitude for this system takes the form of a sum,  $\sum_{\alpha} F_{\alpha}$ , where

$$F_{\alpha} = \exp(-i\mathbf{k}_f \cdot \mathbf{r}_{\alpha}) \int d\Omega_{\mathbf{q}} f_{\alpha}(\mathbf{k}_f, \mathbf{k}\hat{\mathbf{q}}) \Gamma_{\alpha}(\mathbf{k}\hat{\mathbf{q}}) \quad (4)$$

Here  $f_{\alpha}(\mathbf{k}_f, \mathbf{k}\hat{\mathbf{q}})$  is defined for atom  $\alpha$  within the molecule, and  $\Gamma$  will be treated in Sec. III.

It is convenient to work with the matrix  $F_{\alpha}$  defined by

$$F_{\alpha} = F_{\alpha} \chi, \quad (5)$$

where the spinor  $\chi$  takes the form

$$\chi = \begin{bmatrix} \chi_+ \\ \chi_- \end{bmatrix} \quad (6)$$

$\chi_{\pm}$  being probability amplitudes for spin-up and spin-down electrons. The quantization axis is taken in the direction of  $\mathbf{n}$  and x-axis is taken along  $\mathbf{k}_i$ . The spin-flip amplitude  $g_{\alpha}$  is well approximated by a lowest-order partial amplitude  $A_{l=1}$  that is,

$$g_{\alpha}(\mathbf{k}_f, \mathbf{k}_i) \approx \Delta_{1,a} \quad (7)$$

which is independent of the scattering angle. An analog of Eq. (2) holds for the matrix amplitude,

$$F_{\alpha} = \sqrt{4\pi} \exp(-\mathbf{k} \cdot \mathbf{r}_{\alpha}) [\sqrt{4\pi} U_{\alpha 0} \mathbf{1} + \Delta_{1,a} \boldsymbol{\sigma} \cdot U_{\alpha}] \quad (8)$$

where  $\mathbf{K} = \mathbf{k}_f - \mathbf{k}_i$ , and  $U_{\alpha 0}$  and  $U_{\alpha}$  remain to be determined from  $\Gamma_{\alpha}$ .

## II-2. The $W(\theta)$ function and asymmetry

The  $W(\theta)$  function is defined by

$$W(\theta) = 2(4\pi)^{3/2} \sum_{\alpha, \alpha'=1}^n \Delta_{1,\alpha} \langle \exp(-\mathbf{K} \cdot \mathbf{r}_{\alpha\alpha'}) U_{\alpha} U_{\alpha'}^* \rangle_{\text{av}} \quad (9)$$

where  $\mathbf{r}_{\alpha\beta} = \mathbf{r}_{\alpha} - \mathbf{r}_{\beta}$  and  $\langle \rangle_{\text{av}}$  denotes orientation average.  $W(\theta)$  is in general complex-valued. This is an extension of Eq. (2) to molecular scattering, since the replacements

$$U_{\alpha 0} \leftarrow \frac{1}{4\pi} f, \quad \Delta_{1,\alpha} \leftarrow i \frac{1}{\sqrt{4\pi}} g \sin\theta \hat{\mathbf{n}}$$

lead to

$$W(\theta)_{\text{atomic}} = 2i (fg^*) \sin\theta \hat{\mathbf{n}}, \quad (10)$$

and hence to Eq. (3) if use is made of Eqs. (11) and (13) below.

We can obtain the differential cross section for the electrons with initial polarization  $P_i$ :

$$Q(\theta, P_i) = \sum_{\alpha, \alpha'=1}^n \langle \text{Tr}(F_{\alpha} \rho F_{\alpha'}) \rangle_{\text{av}} = Q(\theta, 0) + P_i \cdot \text{Re}[W(\theta)] \quad (11)$$

where  $\rho$  is the density matrix and  $Q(\theta, 0)$  is the differential cross section for unpolarized electrons.

For transmission experiments the integrals of  $Q$  and  $W$  over scattering angles are useful, and they are defined by

$$\langle Q \rangle = \int d\Omega Q(\theta, 0) \quad (12a)$$

$$\langle W \rangle = \int d\Omega W(\theta) \quad (12b)$$

In terms of  $W(\theta)$  the above-mentioned asymmetric quantities can be calculated:

(i) Polarization of initially unpolarized electrons.

This is given by setting  $P_i = 0$  in the following equation:

$$P_f(\theta, P_i) \approx P_i + \frac{\text{Re}[W(\theta)] - \text{Im}[W(\theta)] \times P}{Q(\theta, P_i)} \quad (13)$$

(ii) Asymmetry in the transmission of electrons of opposite helicity,  $P_{\parallel}$ , and  $-P_{\parallel}$ ,

$$e_{DL} = \frac{\langle Q(+P_{\parallel} \hat{\mathbf{x}}) \rangle - \langle Q(-P_{\parallel} \hat{\mathbf{x}}) \rangle}{\langle Q(+P_{\parallel} \hat{\mathbf{x}}) \rangle + \langle Q(-P_{\parallel} \hat{\mathbf{x}}) \rangle} = P_{\parallel} \frac{\text{Re}[\langle W \rangle]}{\langle Q \rangle} \quad (14)$$

(iii) The rotation angle  $\Psi$  of the transverse polarization for transmitted electrons:

$$\Psi \approx P_{\perp} \frac{\text{Im}[\langle W \rangle]}{\langle Q \rangle} \quad (15)$$

Here  $P_{\parallel}$  and  $P_{\perp}$  are longitudinal and transverse components of  $\mathbf{P}_i$ , and  $\mathbf{P}_i$  is decomposed into

$$\mathbf{P}_i = P_{\parallel} \hat{\mathbf{X}} + P_{\perp} \hat{\mathbf{Z}}, \quad (16)$$

where  $\hat{\mathbf{X}} (= \hat{\mathbf{x}})$  and  $\hat{\mathbf{Z}}$  are fixed in space. From these examples we see that in-plane components of  $\mathbf{W}(\theta)$ , i.e.,  $W_x(\theta)$  and  $W_y(\theta)$ , are most important.

### 11-2. Calculation of $\Gamma$

The meaning of Eq. (9) is unclear since  $U_{\alpha 0}$  and  $U_{\alpha}$  depend on geometry of the molecule as well as intramolecular multiple electron scattering, and so these quantities should be expressed in closed forms.

The scattering is treated by McRae's LEED approach extended to molecules and expressed in the spinor form. McRae's original method is to start with Lax's set of coupled equations for the wave functions  $\psi_{\alpha}(\mathbf{r})$ , which are expressed in terms of the momentum representation  $\Gamma$ . As spinor components this can be written as

$$\psi_{\alpha\pm}(\mathbf{r}) = \int d\Omega_s \Gamma_{\alpha\pm}(s) \exp[i\mathbf{k}s \cdot (\mathbf{r} - \mathbf{r}_{\alpha})] \quad (17)$$

The spinor  $\psi_{\alpha}$  obeys the so-called Lax's coupled equations:

$$\psi_{\alpha} = \phi_i + \sum_{\beta(\neq\alpha)}^n \frac{1}{d} \mathbf{t}_{\beta} \psi_{\beta} \quad (\alpha = 1, 2, \dots, n) \quad (18)$$

where  $n$  is the number of constituent atoms,  $\phi_i$  the incident wave,  $\mathbf{t}_{\alpha}$  the  $2 \times 2$  two-body  $\mathbf{t}$ -matrix for scattering by atom  $\alpha$  and  $1/d$  the free-particle Green function.

In the limit of negligible intramolecular multiple scattering the amplitude  $\mathbf{F}_{\alpha}$  should reduce to the form similar to Eq. (2), and so the lowest-order expression of  $\Gamma$  is

$$\begin{aligned} \Gamma_{\alpha}(s)_{\text{lowest-order}} &= \exp(i\mathbf{k} \cdot \mathbf{r}_{\alpha}) \delta(s - \mathbf{k}_i) \chi \\ &= \exp(i\mathbf{k}_i \cdot \mathbf{r}_{\alpha}) \sum Y_{lm}(\hat{\mathbf{k}}_i) Y_{lm}^*(\hat{s}) \chi \end{aligned} \quad (19)$$

which suggests the following expansion,

$$\Gamma_{\alpha\pm}(s) = \exp(i\mathbf{k} \cdot \mathbf{r}_{\alpha}) \sum A_{lm\pm} Y_{lm}^*(\hat{s}) \quad (20)$$

where coefficients  $A_{\pm}$ 's depend implicitly on the orientation of the molecule, or a set of Eulerian angles,  $\omega$ . With Eqs. (4) and (20), the spinor amplitude  $\mathbf{F}_{\alpha\pm}$  becomes

$$\begin{aligned} F_{\alpha\pm} &= \sqrt{4\pi} \exp(-i\mathbf{K} \cdot \mathbf{r}_{\alpha}) \sqrt{4\pi} \sum_{l=0}^{\infty} T_{l,\alpha} \sum_{m=-l}^l A_{\alpha lm\pm} Y_{lm}^*(\hat{\mathbf{k}}_f) \\ &\quad + i \frac{1}{\sqrt{3}} \Delta_{1,\alpha} [-\sin\theta \sigma_x A_{\alpha 10\pm} + \cos\theta \sigma_y A_{\alpha 10\pm} + \sin\theta \sigma_z A_{\alpha 1\pm} + \cos\theta \sigma_z A_{\alpha 1\pm}^-] \end{aligned} \quad (21)$$

where

$$A_{\alpha_1 \pm}^+ = (A_{\alpha_{11} \pm} + A_{\alpha_{1-1} \pm})/\sqrt{2} \quad (22a)$$

$$A_{\alpha_1 \pm}^- = (A_{\alpha_{11} \pm} - A_{\alpha_{1-1} \pm})/\sqrt{2}i \quad (22b)$$

Equation (21) shows that  $A_{\alpha_{10} \pm}$ 's give rise to the in-plane components of W(6), which are of our interest. Note also that no serious approximations have been introduced so far into the solution.

The equations for  $A_{\alpha lm \pm}$  have been worked out:

$$\begin{aligned} A_{\alpha lm \pm} = & Y_{lm}(\hat{k}_i) \chi_{\pm} + 4\pi i^{l+1} k \sum_{\beta(\neq \alpha)=1}^n \exp(-i\mathbf{k}_i \cdot \mathbf{r}_{\alpha\beta}) Y_{lm}(\mathbf{r}_{\alpha\beta}) \sum_{l'=0}^{\infty} i^{l'} T_{l',\beta} H_{l',l}(kr_{\alpha\beta}) \\ & \times \sum_{m=-l'}^{l'} A_{\beta l' m' \pm} Y_{l' m'}^*(\hat{\mathbf{r}}_{\alpha\beta}) + \frac{4\pi}{3} i^l k \sum_{\beta(\neq \alpha)=1}^n \exp(-i\mathbf{k}_i \cdot \mathbf{r}_{\alpha\beta}) \Delta_{1,\beta} [A_{\beta_{11} \pm} Y_{11}^*(\hat{\mathbf{r}}_{\alpha\beta}) \\ & - A_{\beta_{1-1} \pm} Y_{1-1}^*(\mathbf{r}_{\alpha\beta})] \times H_{1,l}(kr_{\alpha\beta}) Y_{lm}(\hat{\mathbf{r}}_{\alpha\beta}) \\ & + \frac{4\sqrt{2}\pi}{3} i^l k \sum_{\beta(\neq \alpha)=1}^n \exp(-i\mathbf{k}_i \cdot \mathbf{r}_{\alpha\beta}) \Delta_{1,\beta} [A_{\beta_{10} \mp} Y_{1\pm 1}^*(\hat{\mathbf{r}}_{\alpha\beta}) - A_{\beta_{1\mp 1} \mp} Y_{10}^*(\hat{\mathbf{r}}_{\alpha\beta})] \\ & \times H_{1,l}(kr_{\alpha\beta}) Y_{lm}(\hat{\mathbf{r}}_{\alpha\beta}) \quad (\alpha = 1, 2, \dots, n) \end{aligned} \quad (23)$$

where  $T_{l\alpha}$  is the direct-scattering partial amplitude for  $l$ th wave, and use has been made of the approximation

$$Y_{\lambda\mu}(\hat{\mathbf{R}}_{\alpha\beta}) \cong Y_{\lambda\mu}(\hat{\mathbf{r}}_{\alpha\beta}) \quad (24)$$

with  $\mathbf{R}_{\alpha\beta} = \mathbf{r}_{\alpha\beta} + \rho_{\alpha}$ .

The quantity  $H_{1,l}(kr_{\alpha\beta})$  is defined from the expansion for Hankel functions of the first kind:

$$h_l^{(1)}(k|\mathbf{r}_{\alpha\beta} + \rho_{\alpha}|) \cong 4\pi \sum (-1)^\lambda H_{l,\lambda}(kr_{\alpha\beta}) j_\lambda(k\rho_{\alpha}) Y_{\lambda\mu}(\hat{\mathbf{r}}_{\alpha\beta}) Y_{\lambda\mu}^*(\hat{\rho}_{\alpha}) \quad (25)$$

and is given from Eq. (A4) of Ref. 6. The accuracy of the expansion has been examined for the values of

$$\begin{aligned} (kr_{\alpha\beta}, k\rho_{\alpha}, l) = & (50, 10, 1), (50, 10, 5), (50, 10, 10), (50, 10, 20); (10, 1, 1), \\ & (10, 2, 1), (10, 3, 1); (10, 1, 5), (10, 2, 5), (10, 3, 5); (10, 1, 10), (10, 2, 10), \\ & (10, 3, 10), \end{aligned}$$

leading to the conclusion that Eq. (25) is valid for

$$r_{\alpha\beta} > l \rho_{\alpha} \quad (26)$$

which is just the condition for Eq. (24) to be valid.

To solve Eq. (23), we set

$$\begin{bmatrix} A_{\alpha lm+} \\ A_{\alpha lm-} \end{bmatrix} = (A_{\alpha lm} \mathbf{1} + \mathbf{a}_{\alpha lm} \cdot \boldsymbol{\sigma}) \begin{bmatrix} \chi_+ \\ \chi_- \end{bmatrix} \quad (27)$$

It seems to be fair to assume that

$$|\mathbf{a}_{\alpha lm, u}| \ll |A_{\alpha lm}| \quad (u = x, y, z) \quad (28)$$

because even if the quantities in either side are of a similar magnitude, the left-hand side will have an extra phase factor of the form  $\exp(-i\mathbf{k}_i \cdot \mathbf{r}_{\alpha\beta})$ , contributing less to  $W(0)$ . We then have that

$$\begin{aligned} A_{\alpha lm} &= Y_{lm}(\hat{\mathbf{k}}_i) \\ &+ 4\pi i^{l+1} k \sum_{\beta(\neq\alpha)=1}^n \exp(-i\mathbf{k}_i \cdot \mathbf{r}_{\alpha\beta}) Y_{lm}(\mathbf{r}_{\alpha\beta}) \sum_{l'=0}^{\infty} i^{l'} T_{l' \beta} H_{l', l}(kr_{\alpha\beta}) \\ &\times \sum_{m'=-l'}^{l'} A_{\beta l' m'} Y_{l' m'}^*(\hat{\mathbf{r}}_{\alpha\beta}) \end{aligned} \quad (29)$$

which, correct to  $O(\Delta_{1\alpha})$ , ought to be obeyed also by the coefficients for scattering by unpolarized electrons. That is, the validity may be tested from elastic scattering by ordinary molecules.

The  $A_{\alpha lm\pm}$  term of Eq. (21) actually contains the terms involving Pauli spin matrices, which are accounted for by  $\mathbf{a}_{\alpha lm}$ 's. From the assumption (28), we may ignore this contribution so that Eq. (21) can be evaluated in terms of the  $A_{\alpha lm}$  coefficients:

$$U_{\alpha_0} = \sum_{l=0}^{\infty} T_{l, \alpha} \times \sum_{m=-l}^l A_{\alpha lm} Y_{lm}^*(\hat{\mathbf{k}}_f) \quad (30a)$$

$$U_{\alpha x} = -i \frac{1}{\sqrt{3}} \sin\theta A_{\alpha_{10}} \quad (30b)$$

$$U_{\alpha y} = i \frac{1}{\sqrt{3}} \cos\theta A_{\alpha_{10}} \quad (30c)$$

$$U_{\alpha z} = i \frac{1}{\sqrt{3}} \sin\theta A_{\alpha_{1+}} - i \frac{1}{\sqrt{3}} \cos\theta A_{\alpha_{1-}} \quad (30d)$$

where  $A_{\alpha_{1\pm}}$ 's are defined by the relations similar to Eq. (22). We thus have

$$\langle \exp(-i\mathbf{K} \cdot \mathbf{r}_{\alpha\alpha'}) U_{\alpha x} U_{\alpha'0} \rangle_{av}$$

$$\begin{aligned}
&= \frac{4\pi}{\sqrt{3}} \text{sine} \sum_{\alpha\beta\alpha'} \sum_{l'l'm} i^{l'} T_{l',\beta} T_{l',\alpha}^* H_{l',1}(kr_{\alpha\beta}) Y_{lm}^*(\hat{\mathbf{k}}_f) \sum_L c_{l'1Lm'0} \\
&\quad \mathbf{x} \langle \exp[-i(\mathbf{k}_f \cdot \mathbf{r}_{\alpha\alpha'} + \mathbf{k}_i \cdot \mathbf{r}_{\beta\alpha'})] A_{\beta l' m'} A_{\alpha' l m}^* Y_{L,-m'}(\hat{\mathbf{r}}_{\alpha\beta}) \rangle_{\text{av}} \quad (31)
\end{aligned}$$

where  $A_{\alpha'10}$  has been calculated from Eq. (29), and  $c_{l'1Lm'0}$  is given in Ref. 6.

#### II-4. Behavior of $W(\theta)$

Further approximations were introduced in Ref. 6, but a more rigorous treatment is possible. Since  $\mathbf{k}_i$  and  $\mathbf{k}_f$  are perpendicular to the quantization axis, the first term in the right hand side of Eq. (29) vanishes unless  $l+m = \text{even}$ . Hence

$$|A_{\alpha lm}| \text{ (with } l+m = \text{odd)} \ll |A_{\alpha lm}| \text{ (with } l+m = \text{even)} \quad (32)$$

to lowest order. This relation may be invalid on resonances where the effects of the  $Y_{lm}(\hat{\mathbf{k}}_i)$  term become negligible, leading to a significant amount of asymmetric quantities  $A$ . This is consistent with the experimental finding<sup>3,4</sup> that asymmetry is enhanced on resonances.

By successively substituting the left-hand side into the right-hand side of Eq. (29), we obtain the following expression:

$$\begin{aligned}
A_{\alpha lm} &= Y_{lm}(\hat{\mathbf{k}}_i) p_{\alpha lm} + \Delta p_{\alpha lm} \\
&\quad + \sum_{\beta(\neq\alpha)=1}^n \exp(-i\mathbf{k}_i \cdot \mathbf{r}_{\alpha\beta}) [Y_{lm}(\hat{\mathbf{k}}_i) G_{\alpha\beta,lm} + \Delta G_{\alpha\beta,lm}] \quad (33)
\end{aligned}$$

where the  $\Delta p$  and AG terms, originating from  $A_{\alpha lm}$ 's with  $l+m = \text{odd}$ , tend to vanish if Eq. (32) is valid, that is, they may be significant only on resonances. Explicit forms of  $\mathbf{p}$ ,  $\mathbf{Ap}$ ,  $\mathbf{G}$  and AG are yet to be calculated, but the form of Eq. (33) is sufficient for our purposes,

If Eq. (32) holds, then we effectively have  $l'+m' = \text{even}$  in Eq. (29) so that  $L+m' = \text{odd}$ . It can be shown that terms without the phase factor which arise from  $A_{\beta l' m'} A_{\alpha' l m}^*$  contribute to  $\langle \rangle_{\text{av}}$  of Eq. (31). Thus the  $\langle \rangle_{\text{av}}$  involves sums over four atomic indices, which is compatible with the fact that optically active molecules must have at least four atoms. Equation (1) will also be proved if explicit forms of  $\mathbf{p}$ ,  $\mathbf{Ap}$ ,  $\mathbf{G}$  and AG are inserted.

On the other hand, if Eq. (32) is not obeyed, there also remain sums over three atomic indices involving  $Y_{L-m}$ 's that are even with respect to inversion. Then it may be possible that Eq. (1) holds only approximately, depending on the magnitude of these sums. For the moment it is not clear whether this means a peculiar resonance phenomenon or this indicates a shortcoming of the present treatment.

### III. INTERFERENCES

### III.-1 Interference Structure of the in-plane components of $W(\theta)$

From Eqs. (3 1) and (33) it follows that the in-plane component of  $W(\theta)$  can be written schematically in the following form :

$$W(\theta) = \sum_{\alpha\beta\gamma\delta} \sum_{l'l''} \sum_{\alpha'\beta'\gamma'} \Delta_{l\alpha} [\text{Amplitude}]_{\beta\gamma\delta/l'l''} [\text{Geometry}]_{\alpha\beta\gamma\delta,lm} \quad (34)$$

Here partial amplitudes involved in  $\langle \rangle_{av}$  have been factored out in some way, e.g., by setting  $G_{\alpha\beta,lm}(\omega) = G_{\alpha\beta,lm} G_{\alpha\beta,lm}(\omega)$  with  $\max |G_{\alpha\beta,lm}(\omega)| = 1$ , and the [Geometry] factor essentially derives from the  $\langle \rangle_{av}$  factor. Contributions of the  $\Delta p$  and AG terms are ignored. Precise expression of Eq. (34) is unimportant for the moment.

From this definition it is obvious that the following condition must hold for the asymmetry to be finite:

$$[\text{Geometry}]_{D\text{-isomer}} \neq - [\text{Geometry}]_{L\text{-isomer}} \neq 0 \quad (35)$$

Another factor, [Amplitude], is identical for D- and L-isomers by definition. However, [Geometry]  $\neq 0$ , is not obvious. For example, the previous treatment<sup>13</sup> would yield null asymmetry for imaginary chiral molecules of regular tetrahedral symmetry.<sup>14</sup> This difficulty would never occur for Eq. (34).

Equation (34) helps us consider interference structure. First, interference between scattering amplitudes is involved. This has already been encountered in the scattering of initially unpolarized electrons by atoms, which is accounted for by Eq. (3). For chiral molecules the interference is far more complex and more important.

It is easy to understand the importance: for optically inactive organic molecules having mirror reflection symmetry such as a methane derivative  $\text{CH}_2\text{ClBr}$ ,  $W(0)$  vanishes identically, but if one of the H atoms is replaced by another atom to give an optically active molecule  $\text{CHClBrI}$ , say, then  $W(0)$  becomes finite. Changes in atomic distances usually occur simultaneously, which may account for this behavior, but this is not essential.<sup>6</sup>

To see this more clearly, let us consider an imaginary tetrahedral molecule ABCD, the center atom being ignored. This must be the simplest one that can be conceived, since the summands in Eq. (34) contain the same geometry factor, which can be factored out. Actual numerical results were plotted in Fig. 1 of Ref. 6, where  $W(\theta)$  were evaluated using the double scattering approximation and the amplitude part was expressed in the form:

$$[\text{Amplitude}] = \begin{vmatrix} \Delta_{1,A} & f_A^* & T_{1,A} & T_{l,A} \\ \Delta_{1,B} & f_B^* & T_{1,B} & T_{l,B} \\ \Delta_{1,C} & f_C^* & T_{1,C} & T_{l,C} \\ \Delta_{1,D} & f_D^* & T_{1,D} & T_{l,D} \end{vmatrix}$$

Note that no running atomic indices are involved any more. Its value vanishes, i.e., interference is perfectly destructive if any two of atomic species are identical. Therefore a mere

change in atomic species induces finite asymmetry.

Second, we see interference originating from the [Geometry] factor. It must satisfy the following conditions for finite asymmetry:

- (a) To change sign on reflection or inversion.
- (b) To be of finite value only if four or more atoms are involved that do not lie in a plane.

Such a function has been derived in Ref. 6. It has the form

$$I_{LM}(\theta; \alpha\alpha'; \beta\gamma; \delta\beta') = \langle \exp(-ik_f \cdot r_{\alpha\alpha'}) Y_{LM}(\hat{r}_{\beta\gamma}) \exp(ik_i \cdot r_{\delta\beta'}) \rangle_{av} \quad (36)$$

where  $L + M = \text{odd}$ . This function has been shown to satisfy Conditions (a) and (b).<sup>6</sup> It was derived for isotropic coefficients in Eq. (33), and so it is very likely that one will encounter with more complicated forms of the [Geometry] factor.

To summarize, two types of chirality exist as illustrated in Fig. 2. For one type, chiral



FIG. 2. Two types of chirality: (1) chiral geometry and (2) chiral substitution. Same circles denote same atoms. If the atoms were of the same species, then Type (2) would become optically inactive, although the substitution actually induces a change in interatomic distances.

geometry, even a lowest-order calculation gives finite asymmetry, but for the other, chiral substitution, careful treatment is required to obtain rational results.

### III-2. Comparison with interferences in scattering by crystals

An asymmetry phenomenon similar to (i) mentioned above is not restricted only to optically active molecules. A large degree of in-plane polarization has been observed for the scattering by the surface of tungsten, when the scattering plane does not coincide with the symmetry plane of crystal (spin polarized LEED).<sup>15</sup> This has been treated by a model similar to, but somewhat cruder than, the present model.<sup>16</sup> Although the calculation was qualitative, a large degree of in-plane polarization was certainly obtained, and this behavior was ascribed to the difference in interference structure: In crystals atoms are located regularly so that in some scattering directions the interference can be constructive.

### III-3. Comparison with interferences in gas electron diffraction

Although spin polarization is usually not involved, gas electron diffraction is an example in which one takes advantage of interference structure in the cross section. Usually

the so-called molecular term having the form  $\sum f_\alpha f_\beta \sin Kr_{\alpha\beta} / Kr_{\alpha\beta}$  is analyzed to obtain information on interatomic distances. This term, however, is not of our interest since it suffices to use scattering amplitudes for free atoms.

Higher-order interference arising from a combination of three atoms is more important.<sup>17,18</sup> This is given from Eqs. (14) and (30):

$$Q(\theta)^{(2)} = \sum_{\alpha\alpha'\beta} \sum_{lm'l'm'} (4\pi)^2 Y_{lm}^*(\hat{k}_f) Y_{lm}(\hat{k}_i) Y_{l'm'}(\hat{k}_f) Y_{l'm'}^*(\hat{k}_i) \\ \times \langle \exp(-i\mathbf{k}_f \cdot \mathbf{r}_{\alpha\beta} + i\mathbf{k}_i \cdot \mathbf{r}_{\beta\alpha'}) p_{\alpha lm}(\omega) G_{\alpha\alpha', l'm'}^*(W) \rangle_{av} + c.c. \quad (37a)$$

$$= \sum_{\alpha\alpha'\beta} \sum_{lm} (2l+1) (2l'+1) P_l(\cos\theta) P_{l'}(\cos\theta) \\ \times \langle \exp(-i\mathbf{k}_f \cdot \mathbf{r}_{\alpha\beta} + i\mathbf{k}_i \cdot \mathbf{r}_{\beta\alpha'}) p_{l,l'}(W) G_{\alpha\alpha', l}^*(\omega) \rangle_{av} + c.c. \quad (37b)$$

where the second is obtained if the  $m$ -dependence of  $p_{\alpha lm}(\omega) G_{\alpha\alpha', l'm'}^*(\omega)$  can be ignored. The orientation dependence has been shown explicitly by  $\omega$ . A further approximation to ignore this  $\omega$ -dependence gives a poor result for the scattering at an energy of 10keV,<sup>17</sup> where the validity of Eqs. (24) and (26) is also questionable. Thus a study of this higher-order interference provides a test of the approximation schemes which may be adopted in the present approach if corresponding results based on a more exact treatment is available especially at lower energies.

#### III-4. Schematic representation of interferences

The interferences thus far discussed may be represented schematically as in Fig. 3, where a solid line corresponds to the propagation of electron waves and a dotted line to

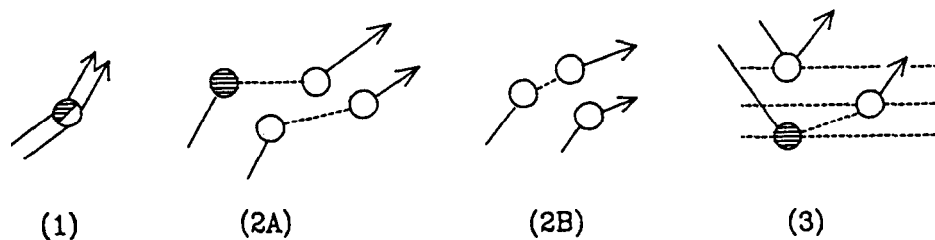


FIG. 3. Schematic representation of interferences. (1) electron-atom, (2A) electron-molecule (asymmetry), (2B) electron-molecule (higher-order term in gas electron diffraction), (3) electron-crystal. Solid line: propagation of electron wave, broken line: interatomic double scattering, open circle: direct scattering amplitude, shaded circle: spin-flip amplitude.

interatomic double scattering. For the sake of simplicity the diagrams show only double scattering events, which are a kind of approximation scheme since the amplitudes defined in Eq. (33) include all the events, which are difficult to express.

## IV. CONCLUSION

Asymmetry in chiral electron scattering has been treated within the potential scattering model in which spin-orbit interaction is partitioned by the constituent atoms. A quantitative and approximation-dependent discussion has been avoided but some conclusions can be drawn irrespective of possible approximations. That is, if partitioned spin-orbit interaction is a cause of asymmetry then interferences play an important role in the angular dependence and energy dependence. For example, the angular dependence will exhibit a complicated structure, and precise calculations of these quantities are very difficult because the interferences are affected by the approximations adopted.

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