THE INTERACTIONS OF MOLECULES

WITH

THE ELECTROMAGNETIC FIELD

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ABSTRACT

The way in which the macroscopic description of the interaction of the electromagnetic field with matter is related to the microscopic viewpoint has been known for many years. Two distinct steps are necessary to establish the connection. Firstly one has to develop a descriptive scheme that accounts for the dynamical behaviour of microscopic systems qua matter under the influence of the field which involves the construction of a model of matter, and secondly there is the problem of calculating the averages over a large number of microsystems of the quantities predicted by the dynamical scheme. The latter problem is essentially one of statistical mechanics.

This thesis is concerned with the first aspect of the problem, that is the construction of a dynamical scheme to describe the interaction of the electromagnetic field with matter which we view as being composed of spatially separated aggregates of point charges called 'molecular systems'. The theory is illustrated with some examples of the type of calculations that are possible within this scheme. We make no attempt to discuss the associated problems in statistical mechanics.

The conventional theory of the interaction of radiation with molecules has been standardized for many years. There are however some unsatisfactory features about it which very largely stem from the problems associated with the invariance of the

hamiltonian under gauge transformations and the consequent freedom of choice of gauge. As shown by Power and Zienau (Phil. Trans. Roy. Soc. 1959, A251, 427) there exists a unique unitary transformation which eliminates the difficulties and casts the hamiltonian into a form in which the molecular multipoles are explicitly displayed. They also showed the extent to which earlier versions of the multipole hamiltonian were inexact about the definition of the fields involved. Power and Zienau however considered only dipolar and quadrupolar terms explicitly and it is desirable to extend the theory to encompass multipoles of arbitrary order. Moreover a proper account of the functional dependence of the canonical variables implied by the existence of the gauge transformations seems to be lacking in the case of molecular quantum electrodynamics.

The first part of the thesis therefore is concerned with the problem of deriving in a consistent non-relativistic approximation the modified hamiltonian for general electric and magnetic multipolar interactions with the electromagnetic field. We start from the microscopic Maxwell-Lorentz theory of charged particles which we develop in a form that is in close analogy to the macroscopic theory of dielectrics. We then postulate a lagrangian from which the field and particle equations of motion may be recovered under suitable assumptions using the calculus of variations. This procedure however forces us to introduce the electromagnetic field 4-potential and thus there are more dynamical variables than degrees of freedom. To

proceed to the hamiltonian therefore requires a discussion of the singular (degenerate) nature of the lagrangian and we use the theory first developed by Dirac (Can. J. Math. 1950, 2, 147) since this is the most direct way of performing calculations with lagrangians that exhibit degeneracy. Essentially the procedure consists of eliminating the dynamical variables that are not required in the account of the dynamical behaviour of the system, and when this is done the originally singular canonical scheme becomes regular as required. With a suitable lagrangian and the use of the Coulomb gauge condition to define a specific Lie algebra for the dynamical variables, the hamiltonian that finally emerges is the required generalization of the multipole hamiltonian. The importance of the Coulomb gauge condition is that it enables us to identify the canonical momentum with the transverse electric field strength operator to within a constant. The gauge condition is therefore an integral part of the theory. Having started from a non-relativistic classical lagrangian, the spin interaction terms are naturally absent from the hamiltonian and must be added, if required, in an ad hoc fashion.

The second section of the thesis is concerned with the use of the theory within the context of perturbation theory based on an expansion of the resolvent operator of the complete hamiltonian. In Chapter 3 we give a detailed account of the calculation of the optical rotation angle of a molecule in terms of the properties of its constituent groups which we assume are electronically isolated. For simplicity at this stage the

interaction potential is limited to the dipole approximation. Diagrammatic perturbation theory is used to simplify the calculation as much as possible. The final results of the calculation are in general agreement with those in the literature but the method seems to give a particularly clear account of the physical processes involved. In Chapter 4 we consider the complete multipole hamiltonian and examine the properties of its matrix elements in order to assess the feasibility of extending calculations in the dipole approximation to include higher multipoles. Some interesting new integral representations of the interaction terms are developed which may be useful in calculations. We conclude that there is no difficulty in generalizing calculations if the process in question involves real photons, but that in general 'virtual' photon processes may only be dealt with if a cut-off for the field energy is introduced. We note that if the theory is to be consistent with our original restriction to the non-relativistic case then a cut-off is required but we do not analyse such a theory.

Finally in the Discussion we attempt to assess our formulation of the multipole hamiltonian in relation to other versions and find agreement only with Power (Introductory Quantum Electrodynamics, 1964) though of course our final hamiltonian is not limited to quadrupolar terms. By extending the analysis of the integral representation of the electric multipole term in the hamiltonian, which we developed in Chapter 4, we are able to give a fully quantum mechanical

justification of the unitary transformation operator employed by Power and Zienau (1959) and Power (1964). Our argument follows from the recognition that the phase of probability amplitudes may be altered in the presence of an electromagnetic field ('Bohm-Aharonov' effect). In short the multipole hamiltonian is related to the conventional hamiltonian by a unitary operator that changes the phase of the state vectors of the two descriptions by an amount that corresponds to formally moving every particle of a molecular aggregate to the centre of mass of the aggregate (or vice versa to go from the multipole description to the conventional one) in the presence of an electromagnetic field described by a given vector potential. We conclude by discussing some of the difficulties inherent in the current theory of molecular quantum electrodynamics which appear to be of a fundamental nature since they arise from our manner of describing charged particles.

"Au terme dernier, vous m'apprenez que cet univers prestigieux et bariolé se réduit à l'atome et que l'atome lui-même se réduit à l'électron. Tout ceci est bon et j'attends que vous continuiez. Mais vous me parlez d'un invisible système planétaire où des électrons gravitent autour d'un noyau. Vous m'expliquez ce monde avec une image. Je reconnais alors que vous en êtes venus à la poésie: je ne connaîtrai jamais. Ai-je le temps de m'en indigner? Vous avez déjà changé de théorie. Ainsi cette science qui devait tout m'apprendre finit dans l'hypothèse, cette lucidité sombre dans la métaphore, cette incertitude se résout en oeuvre d'art."

Albert Camus 'Le Mythe de Sisyphe' 1942.

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CONTENTS

CHAPTER 1

INTRODUCTION

The conventional formulation of the non-covariant quantum theory of the interaction of radiation with matter is in terms of the electromagnetic potentials [1, 2] in contrast to the semi-classical theories in which molecular multipoles and the field strengths are introduced explicitly (see, for example [3]). Nevertheless, it is well known that it is possible to develop a quantum theory that involves the field strengths and which is in close correspondence with the semi-classical theory: the new hamiltonian which may be obtained from the usual hamiltonian by a unitary transformation, [4 - 6] , has several significant advantages over the latter.

In the usual formulation of the interaction of radiation with bound charges, the covariant Lorentz gauge leads to difficulties and is given up in favour of the Coulomb gauge, since one may then dispense with the longitudinal part of the electric field strength and use instead the electrostatic interaction energy of the charges. The propagation function for the vector potential in this gauge however, contains false static precursor signals, which arise because a neutral atom or molecule still acts as a source of an electrostatic field even after the removal of the Coulomb interaction between the charges, and this feature may require special attention in calculations. The canonical transformation developed by Power and Zienau is designed to remove just these spurious terms from the theory,

and as a consequence when the new hamiltonian is used in conjunction with perturbation theory, considerable simplification occurs in calculations since there are no longer any false terms of this type to be eliminated [6 - 11]

Power and Zienau emphasized the importance of considering the field and matter as a closed dynamical system, but treated only dipolar and quadrupolar terms explicitly: later attempts, [12 - 14], to extend the formalism to include multipolar interactions of higher order have not conformed with this requirement and to this extent these derivations are unsatisfactory. Furthermore the redundancy of the field variables is handled by using a Coulomb gauge condition just as in Fermi's original solution of the canonical formulation of electrodynamics [1] , and it would be desirable to remove this device. We note also that there is more than purely theoretical interest in multipolar interactions, especially in the context of interpreting birefringence phenomena [15, 16] .

In view of this we have re-examined the problem of deriving in a consistent non-relativistic framework the modified hamiltonian for general electric and magnetic multipolar interactions with the radiation field. We start from a classical action principle and the associated lagrangian, proceed canonically to the hamiltonian, and quantize the latter in the normal way. Such a route is

still probably fundamental to any quantum procedure [17, 18] : the hamiltonian is required because it seems to be essential for even the simplest systems, and because quantization procedures that avoid a hamiltonian are apparently of limited generality; the lagrangian is required to express the action principle, and to provide the link with the hamiltonian.

In electrodynamics it is a familiar difficulty that the momentum conjugate to the scalar potential vanishes, so that the method of passing from the lagrangian to the hamiltonian is not unique. Thus, since the electromagnetic potentials are to some extent arbitrary, their use as dynamical variables gives rise to more variables than degrees of freedom. Historically it has been the practice to impose gauge conditions on the potentials in a way that enables the normal transition from the lagrangian to the hamiltonian to be made: the gauge condition has then to be used as a supplementary condition in the theory [1] .

A more general and powerful hamiltonian theory in which the supplementary conditions arise as a consequence of the formalism has however been devised [17 - 22] , and this theory is ideal for the problem at hand. In the first part of this thesis we shall show how a proper consideration of the degeneracy of a particular lagrangian leads quickly to a hamiltonian for the interaction of molecules with the electromagnetic field. With a suitable

choice of lagrangian, the hamiltonian that finally emerges is the desired generalization of the multipolar hamiltonian of Power. We shall see that the rôle of the Coulomb gauge condition is merely to define a particular Lie algebra for the essential dynamical variables.

The second section of the thesis is devoted to a detailed account of an example of the usual type of calculation that is performed in electrodynamics using perturbation theory. We use the multipole hamiltonian in conjunction with the S-matrix theory described by Atkins and Barron [9] to calculate the optical rotation angle of a molecule in terms of the properties of its constituent groups which are assumed to be electronically isolated, i.e. we neglect exchange effects. This model of an optically active molecule has been used by many authors and our results are in general agreement with those in the literature [23 - 26]. We restrict ourselves to the simplest case where the groups interact in pairs, and where the individual subsystems are non-identical. The calculation is sufficient, however, to illustrate the physical processes involved in a way that is not possible with some other methods.

In Chapter 4 we recall briefly some details of perturbation theory based on the resolvent operator and thus show how calculations of energy shifts in electrodynamics (e.g. [7]) are related to the S-matrix theory calculations. We

next examine the complete multipole hamiltonian in some detail and illustrate its use in the context of the calculation on optical activity described in the previous chapter. In particular we examine the details of calculating the isotropic spatial average of the probability amplitudes derived from the S-matrix theory, and the problems associated with including higher multipolar interactions in virtual photon processes. We conclude that the generalization of calculations involving real photons so as to take account of higher multipoles is straightforward, but that some care is required with calculations that involve virtual photons.

We then discuss the physical content of the general theory and the relationship of the multipole hamiltonian to the more usual one. In particular we find a new form for the unitary transformation operator constructed by Power and Zienau [6] which permits some clarification of the physical ideas behind their argument. Finally we attempt to assess the current status of molecular quantum electrodynamics in relation to the accepted methods of quantum theory and spectroscopy.

CHAPTER 2

THE MULTIPOLE HAMILTONIAN

2.1 The Maxwell-Lorentz Theory.

The essential conceptual framework of the classical theory of charged particles is due to Lorentz who developed a microscopic theory of electrodynamics in which the interaction between the charges is mediated by the electromagnetic field [27] . If suitable statistical averaging procedures are invoked, the known macroscopic laws of electrodynamics, for example the Maxwell equations, may be deduced from the Lorentz theory. The main feature of the theory is the important rôle of the electromagnetic field, and although Lorentz found difficulties with notions such as the structure of the charged particles, his theory is the precursor of all modern classical and quantum theories of electrodynamics [28, 29] . We shall therefore begin with an account of the essentials of the Maxwell-Lorentz theory.

Since our ultimate aim is to describe the interaction of light with molecular systems we confine ourselves to a non-relativistic approximation throughout; that is, the theory is appropriate for particles with velocities of magnitudes v that satisfy the inequality $(v/c)^2 \ll 1$, where c is the velocity of light. This approximation is a necessary consequence of the fact that there is no known covariant extension of the Dirac equation to molecular systems. The microscopic Maxwell-Lorentz equations

however have no non-relativistic reduction since the velocity of light is involved explicitly in the Newtonian inequality, so that a theory of charged particles in interaction with the electromagnetic field can have a non-relativistic approximation only in so far as the particles are concerned. We shall find moreover that the tensor notation and the natural units system ($c = 1$) employed in covariant electrodynamics may be usefully maintained in parts of the non-relativistic theory, since they afford a particularly concise notation.

The electromagnetic field is described by the 4-potential a_μ : $a_o = \phi$, the scalar potential, and the a_r ($r = 1, 2, 3$) constitute the vector potential $\underset{\sim}{a}$. As is well known, it is possible to construct the skew-symmetric tensor field

$$f_{\mu\nu} = a_{\nu,\mu} - a_{\mu,\nu} \tag{2.1}$$

where an index preceded by a comma denotes the differentiation $y_{,\mu} = (\partial y/\partial x^\mu)$, with $x_o = t$, the time variable, and $(x_1, x_2, x_3) = \underset{\sim}{r}$, the spatial variable, and we employ the metric tensor $g^{\mu\nu}$ with $g^{00} = 1$, $g^{11} = g^{22} = g^{33} = -1$, $g^{\mu\nu} = 0$ if $\mu \neq \nu$. In terms of the tensor $f_{\mu\nu}$, the microscopic Maxwell-Lorentz equations for the free field are written,

$$f_{\mu\nu}{}^{,\rho} + f_{\nu\rho}{}^{,\mu} + f_{\rho\mu}{}^{,\nu} = 0 \tag{2.2}$$

$$f_{\mu\nu}{}^{,\nu} = 0 \tag{2.3}$$

where if the electric field strength $\underset{\sim}{e}$ with the three components e_r, and the magnetic induction $\underset{\sim}{b}$, with the three components b_r are introduced,

$$f_{\mu r} = -\delta_{\mu o} e_r - \epsilon_{\mu rs} b^s \tag{2.4}$$

$\epsilon_{\mu rs}$ being the Levi-Civita tensor density but with $\epsilon_{ors} = 0$.

In order to describe the interaction of the electromagnetic field with matter we introduce the current-charge 4-vector j_μ; $j_o = \rho$, the charge density and j_r $(r = 1, 2, 3)$ the current density. Thus we may write

$$f_{\mu\nu}{}^{,\nu} = -j_\mu \tag{2.5}$$

for a field in interaction with a given charge-current distribution. Note that the antisymmetry of the tensor $f_{\mu\nu}$ leads at once to the result that the 4-divergence of j_μ vanishes, so that equation (2.5) is consistent with the law of conservation of charge. When closed, non-conducting systems are considered, it is convenient to introduce a tensor field $p_{\mu\nu}$ which describes the polarization of matter by the electromagnetic field, and instead of equation (2.5) write

$$(f_{\mu\nu} + p_{\mu\nu})^{,\nu} = 0 \tag{2.6}$$

which is the microscopic analogue of the Maxwell equation of a dielectric. By inspection we see that for consistency we must have

$$p_{\mu\nu}{}^{,\nu} = j_\mu \,. \tag{2.7}$$

The components of the tensor $p_{\mu\nu}$, which is skew-symmetric, are given by

$$p_{\mu r} = -\delta_{\mu o} p_r + \epsilon_{\mu rs}\, m^s \tag{2.8}$$

where the p_r are the components of the electric polarization, $\underset{\sim}{p}$, of the matter, and the m_s are the components of its magnetization $\underset{\sim}{m}$.

We suppose that an elementary charge has no structure and so may be taken to be a point particle characterized solely by its charge e, and its mass m. If we introduce the position vector $\underset{\sim}{r}$, and the momentum $\underset{\sim}{P}$ of the charge then its equation of motion in a specified electromagnetic field ($\underset{\sim}{e}$, $\underset{\sim}{b}$) is given by Newton's second law with the Lorentz force,

$$\dot{\underset{\sim}{P}} = e\left\{\underset{\sim}{e}(\underset{\sim}{r}) + \dot{\underset{\sim}{r}} \wedge \underset{\sim}{b}(\underset{\sim}{r})\right\} \tag{2.9}$$

which in the non-relativistic approximation reduces to the familiar form

$$m\ddot{\underset{\sim}{r}} = e\left\{\underset{\sim}{e}(\underset{\sim}{r}) + \dot{\underset{\sim}{r}} \wedge \underset{\sim}{b}(\underset{\sim}{r})\right\} . \tag{2.10}$$

Equations (2.5), or equivalently (2.6), and (2.10) together constitute the basic equations of the Maxwell-Lorentz theory. It is important to realize that these equations are strictly valid only for specified charge distributions and fields respectively, for it is clear that the sources and fields must in fact be driven through

each others motion. The 'radiation damping' corrections that should be added to equation (2.10) are however $0\left\{(v/c)^3\right\}$ and so may be legitimately neglected in a non-relativistic theory [28].

It is of course well known that when the coupled equations of motion (2.6), (2.10) are generalized to the many particle case, stable solutions that correspond to the aggregates of charged particles which we characterize as molecular systems, cannot be found. This fact was of great importance in the development of the quantum theory. We shall nevertheless at this point introduce certain features that pertain to molecular systems in the expectation that the resultant internal inconsistency of the theory so produced will be eliminated by the introduction of the quantum theoretical axioms (the existence of acceptable solutions in the resulting quantum theory is of course another question altogether!). And when we speak of 'molecules' in the following (classical) theoretical development it will be with tacit appeal to this expectation.

We shall restrict our considerations to neutral molecular systems treating the molecules and electromagnetic field as a closed dynamical system, and take equations (2.6) and (2.10) as the basic equations of the theory. These equations are not however in the most convenient form for obtaining a quantum theory, but given an explicit

representation of the components of the tensor $p_{\mu\nu}$, it should be possible to derive both equations from a single variational principle, and so reformulate the theory in the framework of canonical classical mechanics. We may then obtain at once a quantum theory in the Heisenberg representation.

Let us assume that the molecules are sufficiently stable for the designation of their component particles to be meaningful: molecule $\underline{a}$ will be supposed to consist of n_a ($n_a > 1$) particles of charge e_{ai} and mass m_{ai} situated at the positions $\underset{\sim}{R}_{ai}(t)$, $i = 1, 2, \ldots\ldots n_a$. Thus we may now introduce the following mass weighted coordinates

$$\left\{ \sum_i m_{ai} \right\} \underset{\sim}{r}_a = \left\{ \sum_i m_{ai} \underset{\sim}{R}_{ai} \right\} \tag{2.11}$$

$$\underset{\sim}{q}_{ai} + \underset{\sim}{r}_a = \underset{\sim}{R}_{ai} \tag{2.12}$$

Clearly, $\underset{\sim}{r}_a$ is the position vector of the centre of mass of molecule $\underline{a}$ and $\underset{\sim}{q}_{ai}$ is the position of $\underline{i}$ in $\underline{a}$ relative to this centre. The condition of electrical neutrality of each molecule is expressed by $e_a \equiv \sum_i e_{ai} = 0$.

The charge and current densities for the system are [30],

$$\rho(\underset{\sim}{r},t) = \sum_{a,i} e_{ai}\, \delta(\underset{\sim}{R}_{ai} - \underset{\sim}{r}) \tag{2.13}$$

$$\underset{\sim}{j}(\underset{\sim}{r},t) = \sum_{a,i} e_{ai}\, \dot{\underset{\sim}{R}}_{ai}\, \delta(\underset{\sim}{R}_{ai} - \underset{\sim}{r}) \tag{2.14}$$

Since we may use the expression:

$$\delta(\underset{\sim}{R}_{ai} - \underset{\sim}{r}) = \exp(-\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})\,\delta(\underset{\sim}{r}_a - \underset{\sim}{r}) \tag{2.15}$$

where $\underset{\sim}{\partial} = \partial/\partial\underset{\sim}{r}$, we may write

$$\rho(\underset{\sim}{r},t) = \sum_{a,i} e_{ai} \exp(-\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})\,\delta(\underset{\sim}{r}_a - \underset{\sim}{r}) \tag{2.16}$$

$$\underset{\sim}{j}(\underset{\sim}{r},t) = \sum_{a,i} e_{ai} (\dot{\underset{\sim}{q}}_{ai} + \dot{\underset{\sim}{r}}_a) \exp(-\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})\,\delta(\underset{\sim}{r}_a - \underset{\sim}{r}). \tag{2.17}$$

These have the form of multipole series (when the exponentials are expanded), except that the molecular multipole moments are defined in a coordinate system in which the molecule is instantaneously at rest. In the non-relativistic theory this condition is obtained at once, since $\dot{\underset{\sim}{q}}_{ai} \gg \dot{\underset{\sim}{r}}_a$ and the galileian transformation may be used to write $\dot{\underset{\sim}{R}}_{ai} \sim \dot{\underset{\sim}{q}}_{ai}$. This transformation is assumed to be valid, and the $\underset{\sim}{q}_{ai}$ will thus be regarded as the dynamical coordinates of the particles.

From the definition of j_μ and $p_{\mu\nu}$ we obtain the familiar expressions

$$\rho(\underset{\sim}{r},t) = -\partial^r p_r(\underset{\sim}{r},t) \tag{2.18}$$

$$j_r(\underset{\sim}{r},t) = p_r{}'^{o}(\underset{\sim}{r},t) + \epsilon_{rst}\,\partial^s m^t(\underset{\sim}{r},t) \tag{2.19}$$

and so from equations (2.16) and (2.18)

$$p_r(\underset{\sim}{r},t) = \sum_{a,i} e_{ai} \sum_{n=0}^{\infty} \left\{(-1)^n/(n+1)!\right\} q_{air} (\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^n\,\delta(\underset{\sim}{r}_a - \underset{\sim}{r}). \tag{2.20}$$

The form of the vector field $\underset{\sim}{m}(\underset{\sim}{r},t)$ may be determined from equations (2.18) and (2.19) since in the non-relativistic

approximation the time dependence of the polarization field $\underset{\sim}{p}$ is due solely to the $\underset{\sim}{q}_{ai}$:

$$p_r'^{o} = (\partial p_r/\partial q_{ais})\dot{q}_{ais}$$

$$= \sum_{a,i} e_{ai} \sum_n \left\{(-1)^n/(n+1)!\right\} \left\{\dot{q}_{air}(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial}) + nq_{air}(\dot{\underset{\sim}{q}}_{ai}\cdot\underset{\sim}{\partial})\right\}$$

$$\times (\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\delta(\underset{\sim}{r}_a - \underset{\sim}{r}) \qquad (2.21)$$

and so

$$(j - p'^{o})_r = \sum_{a,i} e_{ai} \sum_n \left\{(-1)^{n+1} n/(n+1)!\right\} \left\{\underset{\sim}{\partial}\wedge(\underset{\sim}{q}_{ai}\wedge\dot{\underset{\sim}{q}}_{ai})\right.$$

$$\left.\times (\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\delta(\underset{\sim}{r}_a - \underset{\sim}{r})\right\}_r \qquad (2.22)$$

Consequently, from equation (2.19) we find that

$$\underset{\sim}{m}(r,t) = \sum_{a,i} e_{ai} \sum_n \left\{ (-1)^{n+1} n/(n+1)!\right\} (\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}$$

$$\times (\underset{\sim}{q}_{ai}\wedge\dot{\underset{\sim}{q}}_{ai})\,\delta(\underset{\sim}{r}_a - \underset{\sim}{r}) \qquad (2.23)$$

and equations (2.20) and (2.23) constitute the required non-relativistic multipole expansions for the polarization and magnetization of the system (c.f. [29]).

We now assert that the following lagrangian

$$L = \tfrac{1}{2}\sum_{a,i} m_{ai}\dot{\underset{\sim}{q}}_{ai}^2 - \tfrac{1}{2}\int d\tau \left\{\tfrac{1}{2} f_{\mu\nu} f^{\mu\nu} + p_{\mu\nu} f^{\mu\nu}\right\} \qquad (2.24)$$

in which the dynamical variables are the $\underset{\sim}{q}_{ai}$, the a_μ, and their time derivatives $\dot{\underset{\sim}{q}}_{ai}$ and $a_\mu'^{o}$, when used in conjunction with Hamilton's principle [31] , leads to the Maxwell equation (2.6), and to the Lorentz force law in the form

$$m_{ai}\ddot{\underline{q}}_{ai} = e_{ai}\left\{ \underline{e}(\underline{R}_{ai}) + \dot{\underline{q}}_{ai} \wedge \underline{b}(\underline{R}_{ai}) \right\} \qquad (2.25)$$

provided that we make independent variations of the field and particle variables (see Appendix I for a detailed account). Equation (2.24) is therefore a suitable, though not unique, lagrangian from which to develop the theory. It has the usual structure of lagrangians for coupled systems in that the first two terms refer to separate parts of the total system (particles and field respectively) whilst the last term accounts for the coupling between the particles and the field. An apparently disadvantageous feature of this last term is that it involves derivative coupling. In a non-relativistic theory however the principle of minimal electromagnetic coupling loses the important physical significance which it bears in the covariant quantized field theory [32] for the difficulties associated with derivative coupling no longer appear.

In order to proceed to a quantum theory one must now construct a hamiltonian, but since this lagrangian is independent of the velocities $a_o{}'^{o}$, the normal procedures cannot be invoked: such a situation corresponds to a theory involving a degenerate lagrangian, and so the canonical procedures first devised by Dirac [19, 20] must be used.

2.2 Degenerate Lagrangians and the Canonical Formalism.

The theory of degenerate lagrangians was first studied by Dirac [19] and though more rigorous and comprehensive theories have since been developed [18, 21] we shall employ his procedure since it is the most direct method of calculation for the problem at hand. For the sake of simplicity we shall discuss dynamical systems with a finite number (n) of degrees of freedom that may be described by a lagrangian $L = L(q_n, \dot{q}_n, t)$: the extension $n \to \infty$ is straightforward [17] .

From the variation of the action principle one may deduce the Euler-Lagrange equations,

$$(d/dt)(\partial L/\partial \dot{q}_i) = (\partial L/\partial q_i) \qquad i = 1, 2, \ldots\ldots n. \tag{2.26}$$

In the familiar case of elementary dynamics, these equations may be solved for the accelerations $\ddot{q}_i$ in terms of the coordinates and velocities, and one is led to the Hessian matrix $\underset{\sim}{J}$:

$$\underset{\sim}{J}\,\underset{\sim}{\ddot{q}} = \underset{\sim}{B} \tag{2.27}$$

where

$$\underset{\sim}{J} = \left|\left|\partial^2 L/\partial \dot{q}_i \partial \dot{q}_j\right|\right| \tag{2.28}$$

$$B_i = (\partial L/\partial q_i) - (\partial^2 L/\partial \dot{q}_i \partial t) - (\partial^2 L/\partial \dot{q}_i \partial q_j)\dot{q}_j \tag{2.29}$$

and $\underset{\sim}{B}$ and $\underset{\sim}{\ddot{q}}$ are n x 1 column matrices. It is possible for the Hessian matrix to have a rank less than n, in which

case L is said to be degenerate. Degeneracy reduces the differential order of some of the Lagrange equations and introduces the possibility that some equations may no longer be independent of the others: the remaining second order Lagrange equations can no longer be solved for all the accelerations. Whereas for physical systems of finite n the usual theory is sufficient, field theories almost invariably involve degenerate lagrangians and the concomitant degenerate variational problem [18, 21, 22] . The dynamical consequences of the degeneracy may most conveniently be examined in the canonical formalism; furthermore in this way one also obtains a basis for quantization because the Poisson brackets of the canonical dynamical variables define a Lie algebra suited to the quantization procedure.

Initially the domain of the lagrangian is taken to be the space R of $(2n + 1)$-dimensions : $R = (t, q_n, \dot{q}_n)$. The momentum conjugate to the coordinate q_i is defined in the normal manner by

$$p_i = \partial L/\partial \dot{q}_i \qquad i = 1, 2, \ldots\ldots n \tag{2.30}$$

and this expression may be regarded as a mapping of R into the $(2n + 1)$-dimensional phase space $P = (t, q_n, p_n)$. In the usual case the Hessian matrix, which now may be written $\| \partial p_i/\partial \dot{q}_j \|$, has rank n and the mapping is one to one, at least locally. In the degenerate case the rank of J is reduced from n to $n - r$, and so there must exist

r distinct relations of the form

$$\phi_\nu(t, q, p) = 0 \qquad \nu = 1, 2, \ldots\ldots r. \tag{2.31}$$

In this case the mapping of R into P is many to one (degenerate) and the whole of R is mapped on to the points of a $(2n + 1 - r)$-dimensional hypersurface, S, embedded in P. The equations $\phi_\nu = 0$ are the 'constraint equations' of Dirac's theory [19], and since they are valid only in S they are called 'weak equations' and the equality = is replaced by $\approx$ to imply this restricted validity; equations that are true irrespective of these conditions are 'strong equations' and written with the normal equality sign. Thus equation (2.31) is written

$$\phi_\nu(t, q, p) \approx 0 \tag{2.31a}$$

The hamiltonian, H, may still be defined by the normal relation,

$$H(p, q) \approx p\dot{q} - L \tag{2.32}$$

but the relation must be written as a weak equation because the coordinates and momenta are restricted by equations (2.31a). In Dirac's theory one seeks the further relations that ensure that the ϕ_ν are true for all times: these conditions may further delimit the dimensions of the hypersurface to which the actual physical motion is confined; this new space we write S'. Thus one is led to a set of coherence conditions ϕ'_μ $(\mu = 1, 2, \ldots\ldots\ldots s;\ n \geqslant s \geqslant r)$ which satisfy $\dot{\phi}_\mu' \approx [\phi_\mu, H] \approx 0$, and which enable one to define the hamiltonian in S' as a strong equation. The resulting

hamiltonian may however contain a number (not greater than s) of arbitrary terms which arise because not all the canonical dynamical variables are independent and so they cannot determine uniquely the state of the system.

A fundamental classification of the dynamical variables is into the sets 'first class' and 'second class': a dynamical variable $v(p, q)$ is first class if its Poisson brackets with all the constraints vanish at least weakly, otherwise it is second class. It may be shown that constraints that are themselves first class are relations that generate invariance groups of the system; that is, their importance is that they may be used as generating functions of contact transformations that leave unaltered the physical state of the system. It is just these quantities that give rise to the arbitrary terms in the total hamiltonian since the existence of invariant relations is closely related to the functional dependence of the dynamical variables. Finally we note that a dynamical variable may only correspond to a physical observable if it belongs to the set of first class observables.

2.3 The Hamiltonian.

For a finite dimensional system the momentum conjugate to the coordinate q_{ai} is defined in the normal way to be $(\partial L/\partial \dot{q}_{ai})$; for an infinite dimensional field the momentum densities are the coefficients of $\delta q(x)^{,0}$ in the variation of the lagrangian with respect to the velocities:

$$\delta_{vel} L = \int d\tau p(x) \delta q(x)^{,0}. \tag{2.33}$$

Consequently, if we employ the lagrangian of equation (2.24), the momentum conjugate to a_μ which is written π^μ, is defined by the relation

$$\delta_{vel} L = \int d\tau \pi_\mu \delta a^{\mu,0} = \int d\tau (f_{\mu 0} + p_{\mu 0}) \delta a^{\mu,0} \tag{2.34}$$

so that

$$\pi_\mu = f_{\mu 0} + p_{\mu 0} \tag{2.35}$$

The field potential and its conjugate momentum satisfy the equal time Poisson bracket relations ($x = x_1, x_2, x_3$),

$$\left[a_\mu(x), a^\nu(x')\right] = \left[\pi_\mu(x), \pi^\nu(x')\right] = 0 \tag{2.36}$$

$$\left[a_\mu(x), \pi^\nu(x')\right] = g_\mu^\nu \delta^3(x - x'). \tag{2.37}$$

Since both $p_{\mu\nu}$ and $f_{\mu\nu}$ are antisymmetric it follows from equation (2.35) that

$$\pi_0(x) \approx 0 \tag{2.38}$$

which is an equation of the type (2.31a) and is, therefore, a constraint equation. The remaining momenta (π_r) and the equations of motion derived from the Euler-Lagrange equations

must now be written as weak equations [19, 20] .

In order to determine $\underset{\sim}{p}_{ai}$ it should be observed that the velocity $\dot{\underset{\sim}{q}}_{ai}$ occurs in the relation defining the magnetization and in the first term in L; thus the expression for $\underset{\sim}{p}_{ai}$ may be written

$$\underset{\sim}{p}_{ai} \approx m_{ai}\dot{\underset{\sim}{q}}_{ai} + \underset{\sim}{Q}_{ai} \tag{2.39}$$

with

$$\underset{\sim}{Q}_{ai} = e_{ai}\sum_{n}\left\{n/(n+1)!\right\}\ (\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\underset{\sim}{b}(\underset{\sim}{r}_a)\wedge \underset{\sim}{q}_{ai} \tag{2.40}$$

where we have employed the relation

$$\int dx\ f(x)\ (d/dx)^n\ \delta(x - x') = (-1)^n\left\{(d/dx)^n\ f(x)\right\}_{x = x'} \tag{2.41}$$

and for brevity $\partial^n\underset{\sim}{b}(\underset{\sim}{r})\Big|_{\underset{\sim}{r} = \underset{\sim}{r}_a}$ has been written $\partial^n\underset{\sim}{b}(\underset{\sim}{r}_a)$.

The fundamental Poisson brackets for the particle variables are

$$\begin{aligned}\left[q_{air'}\ q_{bj}{}^{s}\right] &= \left[p_{air'}\ p_{bj}{}^{s}\right] = 0\\ \left[q_{air'}\ p_{bj}{}^{s}\right] &= \delta_{ab}\delta_{ij}\ g_r^s\end{aligned} \tag{2.42}$$

and we note that in rectangular cartesian coordinates g_r^s is equal to δ_{rs}.

With these results the hamiltonian may be written as

$$\begin{aligned}H \approx \sum_{a,i}\underset{\sim}{p}_{ai}\cdot\dot{\underset{\sim}{q}}_{ai} &+ \int d\tau\,\pi_\mu a^{\mu,o} - \tfrac{1}{2}\sum_{a,i} m_{ai}\dot{q}_{ai}^2\\ &+ \tfrac{1}{2}\int d\tau\left(\tfrac{1}{2}f_{\mu\nu}f^{\mu\nu} + \bar{p}_{\mu\nu}f^{\mu\nu}\right)\end{aligned} \tag{2.43}$$

The bar over $p_{\mu\nu}$ signifies that it still contains the velocities $\dot{q}_{ai}$: it is convenient to eliminate these at a later stage. If the weak equations (2.35) and (2.39) are inserted, and the relations

$$f_{ro}a^{r,o} + \tfrac{1}{2}f_{ro}f^{ro} = -\tfrac{1}{2}f_{ro}f^{ro} + f_{ro}a^{o,r} \tag{2.44}$$

$$\bar{p}_{ro}a^{r,o} + \bar{p}_{ro}f^{ro} = \bar{p}_{ro}a^{o,r} \tag{2.45}$$

$$\int d\tau \pi_r a^{o,r} = -\int d\tau \pi_r{}^{,r} a^o \tag{2.46}$$

are employed, the hamiltonian may be written

$$H \approx \tfrac{1}{2}\sum_{a,i}(1/m_{ai})(p_{ai}^2 - Q_{ai}^2) + \tfrac{1}{2}\int d\tau(\tfrac{1}{2}f_{rs}f^{rs} + \bar{p}_{rs}f^{rs})$$

$$+ \tfrac{1}{2}\int d\tau(2\pi_r\bar{p}^{ro} - \pi_r\pi^r - \bar{p}_{ro}\bar{p}^{ro}) - \int d\tau\, a^o\pi_r{}^{,r} . \tag{2.47}$$

The velocities are now eliminated from $\bar{p}_{rs}$. First we observe that $\bar{p}_{ro} = p_{ro}$ and $\bar{p}_{or} = p_{or}$ because no velocities occur in the first row and column of the matrix $||p_{\mu\nu}||$. Combining equations (2.23) and (2.39) we obtain

$$\underset{\sim}{m}(\underset{\sim}{r}) = \sum_{a,i}(e_{ai}/m_{ai})\sum_n\left\{(-1)^{n+1}n/(n+1)!\right\}(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}$$

$$\times\,(\underset{\sim}{q}_{ai}\wedge\underset{\sim}{p}_{ai} - \underset{\sim}{q}_{ai}\wedge\underset{\sim}{Q}_{ai})\,\delta(\underset{\sim}{r}_a - \underset{\sim}{r}) \tag{2.48}$$

and observe that

$$\tfrac{1}{2}\int d\tau\, \bar{p}_{rs}f^{rs} = -\int d\tau\, \underset{\sim}{m}\cdot\underset{\sim}{b} . \tag{2.49}$$

The second term in $\underset{\sim}{m}(\underset{\sim}{r})$ contributes to this integral the quantity

$$\int d\tau \sum_{a,i} (e_{ai}/m_{ai}) \sum_n \left\{ (-1)^{n+1} n/(n+1)! \right\} (\underset{\sim}{q}_{ai} . \underset{\sim}{\partial})^{n-1}$$

$$\times \ (\underset{\sim}{q}_{ai} \wedge \underset{\sim}{Q}_{ai}) . \underset{\sim}{b}(\underset{\sim}{r}) \, \delta(\underset{\sim}{r}_a - \underset{\sim}{r})$$

$$= \sum_{a,i} (e_{ai}/m_{ai}) \sum_n \left\{ n/(n+1)! \right\} (\underset{\sim}{q}_{ai} . \underset{\sim}{\partial})^{n-1} (\underset{\sim}{q}_{ai} \wedge \underset{\sim}{Q}_{ai}) . \underset{\sim}{b}(\underset{\sim}{r}_a)$$

$$= \sum_{a,i} (Q_{ai}^2/m_{ai}) \qquad (2.50)$$

The first term in $\underset{\sim}{m}(\underset{\sim}{r})$ contributes what we shall call $\frac{1}{2}\int d\tau p_{rs} f^{rs}$, or $-\int d\tau \underset{\sim}{m}' . \underset{\sim}{b}$, and so the hamiltonian may be written entirely in terms of the canonical variables as

$$H \approx \tfrac{1}{2} \sum_{a,i} (1/m_{ai})(p_{ai}^2 + Q_{ai}^2) + \tfrac{1}{2} \int d\tau (\tfrac{1}{2} f_{rs} f^{rs} + p_{rs} f^{rs})$$

$$+ \tfrac{1}{2} \int d\tau (2 \pi_r p^{ro} - \pi_r \pi^r - p_{ro} p^{ro}) - \int d\tau a^o \pi_r{}' {}^r \ . \qquad (2.51)$$

The consistency relations imposed by equation (2.38) must now be determined: the condition required is that which ensures that π_o vanishes at all times. Since the equation of motion of a dynamical variable Ω may be written $\Omega'^{o} \approx [\Omega, H]$ we may deduce that

$$\pi_o{}' {}^o \approx \pi_r{}' {}^r \ , \qquad (2.52)$$

and the latter term must vanish at least weakly for consistency. Now the Maxwell-Lorentz equations may be written as the weak equations

$$(f_{\mu\nu} + p_{\mu\nu})' {}^{\nu} \approx 0 \qquad (2.53)$$

and since $\pi_r \approx f_{ro} + p_{ro}$ it follows that the constraint

$$\pi_r{}'^r \approx 0 \tag{2.54}$$

is consistent with the field equations. Since this equation too must be true for all times, $\left[\pi_r{}'^r, H\right]$ must vanish: in Appendix II we give the proof that this bracket reduces to $0 = 0$, and so adds no further information, but is consistent as required. Equations (2.38) and (2.54) are the only constraint equations, and it is simple to show using the fundamental Poisson bracket relations (2.36, 2.37) that

$$\left[\pi_0(x), \pi^0(x')\right] = \left[\pi_0(x), \pi_r{}'^r(x')\right] = \left[\pi_r{}'^r(x), \pi_s{}'^s(x')\right] = 0 , \tag{2.55}$$

that is the constraints are <u>first class</u>. According to the general theory the total hamiltonian, H', may be obtained by adding all the first class constraints with arbitrary coefficients to the hamiltonian H (because the first class constraints commute with all physical observables and so the motion generated by H' remains in S'). The new hamiltonian is therefore defined in S' by the strong equation

$$H' = H + \int d\tau u(x) \pi_0(x) + \int d\tau v(x) \pi_r{}'^r(x), \tag{2.56}$$

$u(x)$ and $v(x)$ being arbitrary functions of space and time. When this hamiltonian is used the equation of motion of a dynamical variable Ω may be written as the strong equation

$$\Omega'^0 = \left[\Omega, H'\right] . \tag{2.57}$$

If Ω is chosen to be a^0, the equation of motion (2.57) implies that the time variation of a^0 is arbitrary, since

$$a^{0,0}(x) = \left[a^0, H'\right] = u(x) \tag{2.58}$$

and $u(x)$ is an arbitrary function. Now we have already seen that $\pi^0 \approx 0$ always, and so neither a^0 nor π^0 are of interest in describing the system and may therefore be discarded from the theory. If a new arbitrary coefficient $w(x) = v(x) - a^0(x)$ is introduced, the hamiltonian may be rewritten in the form

$$H' = \tfrac{1}{2}\sum_{a,i}(1/m_{ai})(p_{ai}^2 + Q_{ai}^2) + \tfrac{1}{2}\int d\tau(\tfrac{1}{2}f_{rs}f^{rs} + p_{rs}f^{rs})$$
$$+ \tfrac{1}{2}\int d\tau(2\pi_r p^{ro} - \pi_r \pi^r - p_{ro}p^{ro}) + \int d\tau\, w(x)\pi_r{}^{,r}. \tag{2.59}$$

This hamiltonian is sufficient to give the equations of motion for all the variables of physical interest: the variables a^0 and π^0 no longer appear or play any rôle in the theory. Since, however, the field variable a_r appears in H' only through its curl (in f_{rs}) there remains the possibility of a general gauge transformation in which a_r is replaced by $a_r + \chi_{,r}$, χ being any scalar function of x.

In a quantum theory one has no rules for the construction of the function $w(x)$, but it may be eliminated by a procedure first ingeniously prescribed by Dirac [19] and rationalized in later theories [21]. We

recall that the term involving w(x) appears because the constraint equation $\pi_r{}'^r \approx 0$ was first class and so could be used as a generator of infinitesimal transformations in the surface S' that left the physical state unchanged. If a supplementary condition on the potentials a_r is introduced it may be written as a further constraint equation $\phi(a_r) \approx 0$, and if ϕ is chosen so that its Poisson bracket with $\pi_r{}'^r$ is not zero, then the latter constraint is no longer first class and we must eliminate the term in w(x) since $\pi_r{}'^r$ may now induce migrations away from S'. Thus the term in w(x) must be discarded and we shall be left with the problem of quantizing a canonical system involving two second class constraints. This is the type of problem that Dirac [19] was the first to solve: the essential point of his theory is the redefinition of the Poisson brackets of the dynamical variables so that the new Poisson bracket of a dynamical variable with the (now) second class constraints vanishes. This enables us to write the second class constraints as strong equations. The new Poisson brackets (the Dirac brackets) still lead to the required equations of motion and preserve the Lie algebra of the dynamical variables.

In the present theory we shall study the use of the Coulomb gauge condition $a_r{}'^r \approx 0$, although it is evident that a less comprehensive supplementary condition such as $a_1{}'^1 \approx 0$ would suffice to make $\pi_r{}'^r \approx 0$ a second class constraint: any gauge condition may be introduced at this

point and the subsequent analysis modified accordingly.

Let us write the two second class constraints as

$$\phi_1(x) = \pi_r{}'^{,r} \approx 0$$

$$\phi_2(x) = a_s{}'^{,s} \approx 0 \tag{2.60}$$

and so construct the elements of a matrix $\underline{c}(x, x'')$ from the Poisson brackets

$$c_{ij}(x, x'') = \left[\phi_i(x), \phi_j(x'')\right] \qquad i, j = 1, 2. \tag{2.61}$$

This matrix has non-zero elements of the form

$$\left[\phi_1(x), \phi_2(x'')\right] = \partial^2 \delta^3(x - x'') \tag{2.62}$$

which follows from the definition of the fundamental Poisson brackets, equation (2.37). The unique inverse of the matrix $\underline{c}$ exists in S' and is defined by

$$\int d\tau\, c_{ij}(x'', x) c^{-1}_{ji'}(x, x') = \delta_{ii'} \delta^3(x' - x'') \tag{2.63}$$

From equations (2.62) and (2.63) one obtains the elements of the inverse matrix as

$$c^{-1}_{11} = c^{-1}_{22} = 0$$

$$c^{-1}_{12}(x', x'') = -c^{-1}_{21}(x', x'') = (1/4\pi)|x' - x''|^{-1} \tag{2.64}$$

Following Dirac [19] we now define the 'Dirac' bracket of two dynamical variables f and g, $\left[f, g\right]^*$ as

$$\begin{aligned}\left[f, g\right]^* &= \left[f, g\right] - \int d\tau d\tau' \left[f, \phi_i(x)\right] c^{-1}_{ij}(x, x') \left[\phi_j(x'), g\right] \\ &= \left[f, g\right] - (1/4\pi) \int d\tau d\tau' \Big\{ \left[f, \phi_1(x)\right] \left[\phi_2(x'), g\right] \\ &\qquad - \left[f, \phi_2(x)\right] \left[\phi_1(x'), g\right] \Big\} |x - x'|^{-1}. \end{aligned} \tag{2.65}$$

It is easy to verify that the Dirac bracket of a dynamical variable f with either $\dot{\varphi}_1$ or $\dot{\varphi}_2$ vanishes, and so equations (2.60) may be written as strong equations. Furthermore using equation (2.65) it is obvious that the brackets in equation (2.36) are unchanged but that

$$\left[a^r(x),\ \pi^s(x')\right]^* = g^{rs}\delta^3(x-x') - (1/4\pi)\partial^r\partial^s|x-x'|^{-1}$$

and so

$$\left[a^r(x),\ \pi_s(x')\right]^* = g^{\perp}(x-x')^r_s \tag{2.66}$$

where $\underset{\sim}{g}^{\perp}$ is the metric tensor form of the transverse delta dyadic $\delta^{\perp}_{rs}$ (see, for example, [7]).

At this point we may summarize: the new hamiltonian is given by

$$H'' = \tfrac{1}{2}\sum_{a,i}(1/m_{ai})(p^2_{ai} + Q^2_{ai}) + \tfrac{1}{2}\int d\tau\,(\tfrac{1}{2}f_{rs}f^{rs} + p_{rs}f^{rs})$$
$$+ \tfrac{1}{2}\int d\tau\,(2\pi_r p^{ro} - \pi_r\pi^r - p_{ro}p^{ro}) \tag{2.67}$$

together with the conditions

$$\left[a_r(x),\ a^s(x')\right]^* = \left[\pi_r(x),\ \pi^s(x')\right]^* = \left[q_{air},\ q_{bj}{}^s\right]^*$$
$$= \left[p_{air},\ p_{bj}{}^s\right]^* = 0,$$
$$\left[q_{air},\ p_{bj}{}^s\right]^* = \delta_{ab}\delta_{ij}g^s_r$$
$$\left[a_r(x),\ \pi^s(x')\right]^* = g^{\perp}(x-x')^s_r\,, \tag{2.68}$$

and

$$a_s{}'{}^s(x) = \pi_r{}'{}^r(x) = 0. \tag{2.69}$$

These equations constitute the desired classical canonical description of the field in interaction with a distribution of 'molecules' in a form in which the redundant dynamical variables a_o and π_o have been discarded.

In order to make the transition to a quantum theory the conventional steps may be taken: the variables $\underset{\sim}{q}_{ai}$, $\underset{\sim}{p}_{ai}$, $\underset{\sim}{a}(x)$, and $\underset{\sim}{\pi}(x)$ are reinterpreted as operators, and the non-zero Poisson brackets (or in this case, the Dirac brackets) of the classical theory are replaced by their quantum counterparts, the commutators

$$\left[q_{air}, p^s_{bj}\right] = i\hbar\,\delta_{ab}\,\delta_{ij}g^s_r \tag{2.70}$$

$$\left[a^r(x), \pi_s(x')\right] = i\hbar g^{-1}(x - x')^r_s \,. \tag{2.71}$$

This introduces the usual ambiguities into the theory in connection with the ordering of the operators: the magnetization operator $\underset{\sim}{m}'$ suffers in this way, and the simplest manner in which its Hermiticity may be ensured is to symmetrize it and write it as

$$\underset{\sim}{m}'(\underset{\sim}{r}) = \sum_{a,i}(e_{ai}/2m_{ai})\sum_n\left\{(-1)^{n+1}n/(n+1)!\right\}\left\{(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}(\underset{\sim}{q}_{ai}\wedge\underset{\sim}{p}_{ai})\right.$$
$$\left. + (\underset{\sim}{q}_{ai}\wedge\underset{\sim}{p}_{ai})(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\right\}\delta(\underset{\sim}{r}_a - \underset{\sim}{r}). \tag{2.72}$$

The equations (2.69) become operator identities in the quantum theory and there are no supplementary conditions on the state vector. Finally the hamiltonian may be cast into a familiar form if π_s, the conjugate of a^r in equation (2.71), is replaced by $-\dot{\xi}_o e^i_s$ and equations (2.4)

and (2.8) used to write H" as

$$H'' = \tfrac{1}{2}\sum_{a,i}(1/m_{ai})p_{ai}^2 + \tfrac{1}{2}\varepsilon_o\int d\tau(\underset{\sim}{e}^{\perp}.\underset{\sim}{e}^{\perp} + c^2\underset{\sim}{b}.\underset{\sim}{b})$$
$$+ (1/2\varepsilon_o)\int d\tau p^2 - \int d\tau\, \underset{\sim}{m}'.\underset{\sim}{b} - \int d\tau\, \underset{\sim}{p}.\underset{\sim}{e}^{\perp} + \tfrac{1}{2}\sum_{a,i}(1/m_{ai})Q_{ai}^2. \tag{2.73}$$

Factors of c and ε_o, the vacuum permittivity, have been written explicitly, and the multipolar interaction is apparent in the last three terms. The identification of $\underset{\sim}{\Pi}$ with $\underset{\sim}{e}^{\perp}$ to within a multiplicative factor follows as a consequence of equation (2.68), c.f. [7] .

In the preceding sections we have developed a non-relativistic quantum mechanical hamiltonian for molecules in interaction with the electromagnetic field: the hamiltonian in equation (2.73) is the desired generalization of the multipole hamiltonian of Power [7] . From this point one may proceed in the conventional manner to the applications of the type discussed by Power and Zienau for spectral line shapes [6] , the applications to molecular interactions discussed by Power [7] ,and the application to the photon scattering description of optical birefringence and ellipsometry described by Atkins et al. [9, 10, 33] . The extension of these calculations to the description of the interaction of multipoles of arbitrary order may be developed in a simple and analogous manner.

In the following chapter we shall give a detailed

account of the application of the method of Atkins and Barron [9] to the description of the optical activity of a molecule in terms of the properties of its constituent groups. We shall confine the discussion to the same approximations as were made in the author's published account of this calculation [11] , and defer until chapter 4 the discussion of the modifications required when the complete multipole expansion is used.

CHAPTER 3

ON THE THEORY OF OPTICAL ACTIVITY

3.1 Introduction.

Optical rotation and circular dichroism are both manifestations of optical activity. The former, familiar phenomenon occurs when a plane polarized beam of light passes through a medium and reappears with a different plane of polarization; frequently the emergent beam has acquired some degree of elliptical polarization as a result of absorption by the medium and this phenomenon is circular dichroism. The quantum mechanical theory of optical rotation was first formulated by Rosenfeld [34] who used a semi-classical argument to calculate the interaction between an electromagnetic wave and a molecule. In this formalism the optical activity is a consequence of the retardation of the radiation field over the space occupied by the active molecule. The rotation angle, θ, for unit path length of a solution containing N molecules per unit volume is

$$\theta = (2/3)N\hbar\omega^2\mu_0\rho(\omega)_{vv} \qquad v = 1, 2, 3. \tag{3.1}$$

where μ_0 is the vacuum permeability and the gyration tensor $\underline{\rho}(\omega)$ is defined as

$$\rho(\omega)_{uv} = \mathrm{Im}\sum_f d^u_{mf} m^v_{mf} (E^2_{mf} - \hbar^2\omega^2)^{-1} \tag{3.2}$$

where $\underline{d}$ and $\underline{m}$ are the electric and magnetic dipole operators, m the molecular ground state, f the molecular excited states, and $E_{mf} = E_m - E_f$, their energy separation. Equation (3.1)

should be modified to accommodate a local field correction: usually one assumes that this is related to the refractive index of the medium through, for example, the Lorentz correction. From the pseudo-scalar nature of $\varrho(\omega)_{VV}$ the restriction of optical activity to molecules lacking reflection and inversion symmetry is immediate and well known.

The computation of $\underset{\sim}{\varrho}(\omega)$ can be performed in practice only by using a limited basis set, and this has been the scheme used in such calculations (see, for example, [35] , [36]). One may distinguish two distinct classes of optically active molecules [37] : a few molecules, such as hexahelicene, are 'inherently dissymmetric' and must be discussed in terms of a Rosenfeld type equation; the majority of molecules, however, owe their activity to the dissymmetric juxtaposition of symmetric (i.e. inherently optically inactive) subsystems. These molecules are commonly discussed on the basis of two models: the 'coupled oscillator' theory initiated by Kirkwood [23] , and the 'one-electron' theory of Condon, Altar and Eyring [38] . These theories emphasize different aspects of the coupling between the subsystems (groups) that arise because each group experiences the electric fields of the others. A general first order perturbation treatment of the Rosenfeld equation has shown the two mechanisms to be complementary, and both should be considered in a full treatment of a molecule's optical activity [24] , [25] .

The subject of a recent series of papers [9], [10], has been the formulation of the theory of optical birefringence phenomena on a fully quantum mechanical model. The phenomena were treated in terms of the scattering of polarized photons from molecules in a fluid medium. This 'natural' description of the process was expressed quantitatively in terms of the scattering matrix (S-matrix) and the reaction matrix (R-matrix). The polarizations of the incident and emergent beams of light were expressed in terms of the Stokes parameters S_μ, which were evaluated as the expectation values of the Stokes operators Σ_μ. In this way the elements of the R-matrix may be related to the polarization characteristics of the light beam. The structure of the R-matrix may conveniently be recalled by using diagrammatic perturbation theory [8], [9].

Just as the Rosenfeld equation has been extended to the computation of the activity of molecules in the manner already described, it is interesting to see whether the scattering formalism may be extended in a similar way. Recent work of the author's published elsewhere has shown that this is in fact possible [11], [39], and in the following we shall relate this calculation to the general theory described in the previous chapter.

We follow the philosophy of Kirkwood's original paper [23] and assume that a molecule may be divided into

a number of electronically independent groups. This approximation (the neglect of electron exchange between the groups) is implicit in all current theories of optical activity and in the absence of accurate molecular wave functions appears to be unavoidable. Without the use of this approximation moreover we would not be able to avail ourselves of the multipole hamiltonian derived in the preceding chapter in view of the assumptions necessary to obtain a representation of the tensor $p_{\mu\nu}$. We shall see that within the context of the perturbation theoretic version of non-relativistic quantum electrodynamics, the optical activity of a molecule arises as a result of the exchange of virtual photons between the molecular subsystems that are involved in the scattering of a photon from the external field. As discussed by Power [7], the use of the multipole hamiltonian enables one to describe all electromagnetic interactions in terms of the exchange of fully retarded transverse photons, and calculations are simplified in so far as the Coulomb interaction between the groups is automatically accommodated in the new interaction potential.

3.2 The Quantum Mechanical Model.

We assume that the molecules are in an infinitely dilute fluid solution, so that the solvent is important only through the appearance of its refractive index in the local field correction, and its effect on the conformation of the solute. The molecule is divided into n electronically independent groups, and the electron exchange between the groups is assumed to be negligible, so that the groups can only interact with each other through space via the electromagnetic field. If we transform the system hamiltonian in to the interaction representation, then provided the coupling between electrons in different groups is much weaker than that between electrons in the same group we may write

$$H = H_o + V \tag{3.3}$$

where H_o is the sum of all isolated group and external field hamiltonians, and V is the interaction of the groups with the field. In this representation the operators referring to the separate parts of the total system formally obey uncoupled equations of motion and so we are able to obtain explicit representations of the field operators. The only difference between our expansion of the field variables and earlier ones [7 - 9] is the trivial modification due to the choice of different units (we use S.I. rather than Gaussian

units).

We shall retain initially only the leading terms of V which from equations (2.20), (2.23) and (2.73) may be written

$$V' = \sum_s V(s) = \sum_s -\underset{\sim}{d}(s).\underset{\sim}{e}^{1}(s) - \underset{\sim}{m}(s).\underset{\sim}{b}(s) \qquad (3.4)$$

where $\underset{\sim}{d}(s)$ and $\underset{\sim}{m}(s)$ are the electric and magnetic dipole moment operators of group $\underline{s}$ defined as

$$\underset{\sim}{d}(s) = \sum_i e_{si}\underset{\sim}{q}_{si} \qquad (3.5)$$

$$\underset{\sim}{m}(s) = \tfrac{1}{2}\sum_i (e_{si}/m_{si})(\underset{\sim}{q}_{si} \wedge \underset{\sim}{p}_{si}) \qquad (3.6)$$

respectively. The fields are evaluated at the centre of mass of group $\underline{s}$ because of the delta functions in $p_{\mu\nu}$ and the spatial integrations in equation (2.73). It is clear that this approximation for V is valid only if the retardation over the extension of the group is such that the field may be assumed to be uniform and thus have negligible spatial derivatives. We defer to chapter 4 consideration of the more general case when these conditions are no longer valid, for example when the inequality $\langle q \rangle \ll \lambda$, where $\langle q \rangle$ is the 'radius' of a group and λ is the reduced vacuum wavelength of the radiation, no longer holds. No such dimensional limitation is applied to the separation of the group centres, and the difference in retardation at different groups is an essential requirement for optical activity if the individual groups are not themselves active.

The state vector $|0\rangle$ for the ground state of the molecular system may be written as a product of isolated group state vectors:

$$|0\rangle = \prod_{s=1}^{n} |m_s\rangle , \tag{3.7}$$

where $|m_s\rangle$ is the ground state of the group $\underline{s}$. In the zero-order Born-Oppenheimer approximation [40] the groups are placed at their equilibrium separation. The total state of the field and molecule in the remote past is, in the notation of Atkins and Barron [9] :

$$\Psi(-\infty) = |0, \lambda[n_\lambda]\rangle \tag{3.8}$$

with

$$(H_o - E_o)\Psi(-\infty) = 0. \tag{3.9}$$

For the optical activity calculation we require the amplitude of the probability that a photon originally (at $t = -\infty$) polarized along the $\hat{e}(1)$ direction will be found polarized along $\hat{e}(2)$, the direction orthogonal to $\hat{e}(1)$, long after it has been scattered from a molecule (i.e. at $t = +\infty$).

The original state vector $\Psi(-\infty)$ evolves in time according to the structure of the S-matrix. If the S-matrix is replaced by its definition in terms of the R-matrix and only processes involving two external field photons (one in, one out) are considered, then after an infinite time interval the state vector $\Psi(-\infty)$ will have evolved into the state $\Psi(\infty)$, and from this the optical rotation angle per unit

path length is found to be

$$\Theta = (NV/hcn_\lambda^{\frac{1}{2}}) \text{ Im } R^{(o)}_{\lambda'\lambda} \tag{3.10}$$

where

$$R^{(o)}_{\lambda'\lambda} = \left\langle o,\lambda[n_\lambda - 1]\,\lambda'[1]\right| R \left| \; o,\lambda[n_\lambda]\right\rangle \; . \tag{3.11}$$

In deriving this expression for Θ, one uses the fact that the rotation angle due to each molecular scattering event is independent of the initial polarization parameters of the light beam, so that the total angle from N scattering events is just N x the rotation angle due to one event. The matrix element $R^{(o)}_{\lambda'\lambda}$ contains all the information relating to the scattering process and to the interaction between the groups. An exact evaluation of $R^{(o)}_{\lambda'\lambda}$ is not however possible since the total system is described by the hamiltonian of equation (2.73) which cannot be diagonalized, and so we resort to perturbation theory and the adiabatic theorem.

We shall consider the simplest case which occurs when the energy of the field is far from a molecular resonance, and when the constituent groups of the molecule are non-identical. Then R is related to the retarded Green function G^o by the equation

$$R = V + VG^oR \tag{3.12}$$

which may be solved by iteration:

$$R = V + VG^oV + VG^oVG^oV + VG^oVG^oVG^oV + \ldots\ldots \tag{3.13}$$

$$G^{o} = (E - H^{o} + i\eta)^{-1} \tag{3.14}$$

The positive infinitesimal in G^{o} ensures that all the interactions preserve causality and are fully retarded. In terms of diagrams, this means that the photon propagator lines are all directed forward in time, and if this requirement is kept in mind we may drop the positive imaginary infinitesimal since it is only important near a molecular resonance. The series in equation (3.13) is then essentially a Rayleigh-Schrodinger perturbation expansion. We shall only continue the perturbation series up to fourth order, which corresponds to the retention of only those diagrams that contain no more than four vertices. Since two of the vertices are involved in the description of the scattering of the light beam, this means that we limit ourselves to pair-wise interactions between groups.

The molecules move randomly in solution, and so the optical rotation angle is determined by the isotropic spatial average of the R-matrix. This has the following consequences: since the processes are limited to those involving two real photons, one of the external field vertices must be associated with the field operator $\underset{\sim}{e}^{\perp}$ and the other with $\underset{\sim}{b}$ [9]. Thus we shall have to consider diagrams that have the generic form shown in Figure 1a, where the horizontal lines represent the evolution in time of the groups labelled $\underline{a}$ and $\underline{b}$, and within the box all chronological orderings of the

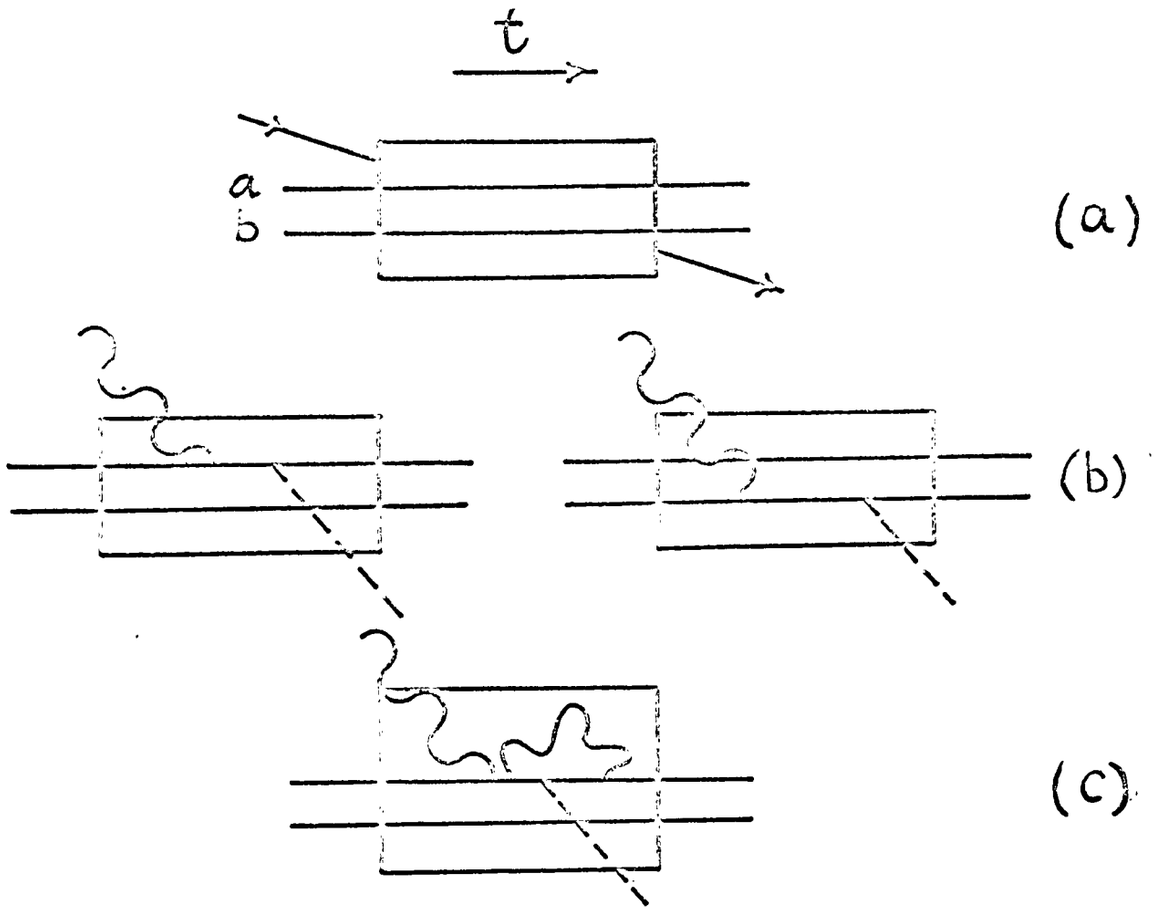

Figure 1

a) schematic form of diagrams that contribute to optical activity.

b) typical second-order diagrams that contribute to $\Theta_{internal}$.

c) a typical fourth-order renormalization diagram.

interaction vertices are implied. When the groups are themselves optically active we may have diagrams based on the generic structures shown in Figure 1b. Such systems involve no photon transfer, and have essentially been considered already [9] . Their contribution to the rotation angle corresponds to the internal activity of an isolated group, and vanishes unless the group is dissymmetric:

$$\Theta_{\text{internal}} = (2/3)N\hbar\omega^2\mu_o \sum_{s=1}^{n} \underset{\sim}{\varrho}(s,\omega)_{vv} \qquad (3.15)$$

where $\underset{\sim}{\varrho}(s,\omega)$ is the gyration tensor of group $\underline{s}$. In fourth order these graphs may be modified by self-energy contributions, for example that shown in Figure 1c. We shall, however, assume that all fundamental quantities have their experimental values, and not deal with the renormalization programme explicitly.

When the groups are not intrinsically active, rotation can occur only if photons are transferred between groups, and so a transfer vertex must be introduced on each line in all possible chronological sequences. The convention concerning the polarization of the external photon lines, that those with polarization along $\hat{e}(1)$ are drawn above the molecular line and those with polarization along $\hat{e}(2)$ below it, will not be maintained for the internal, virtual photons since we shall later sum over their polarizations.

Two types of diagrams may be distinguished:

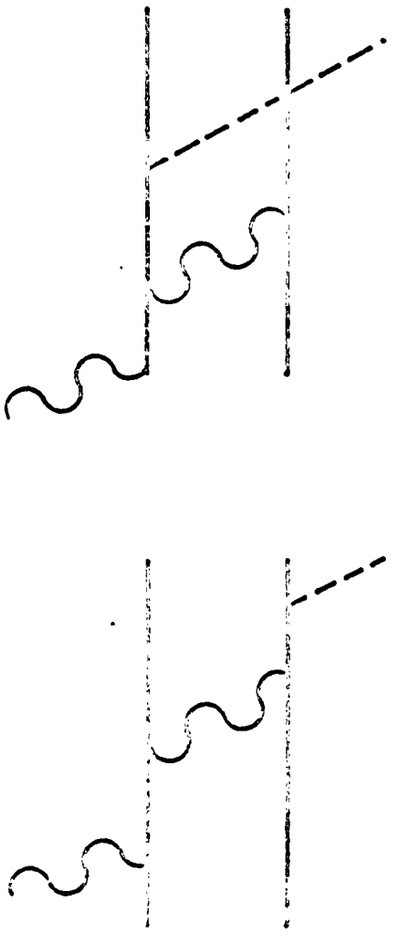

Figure 2

Typical Type A and Type B diagrams.

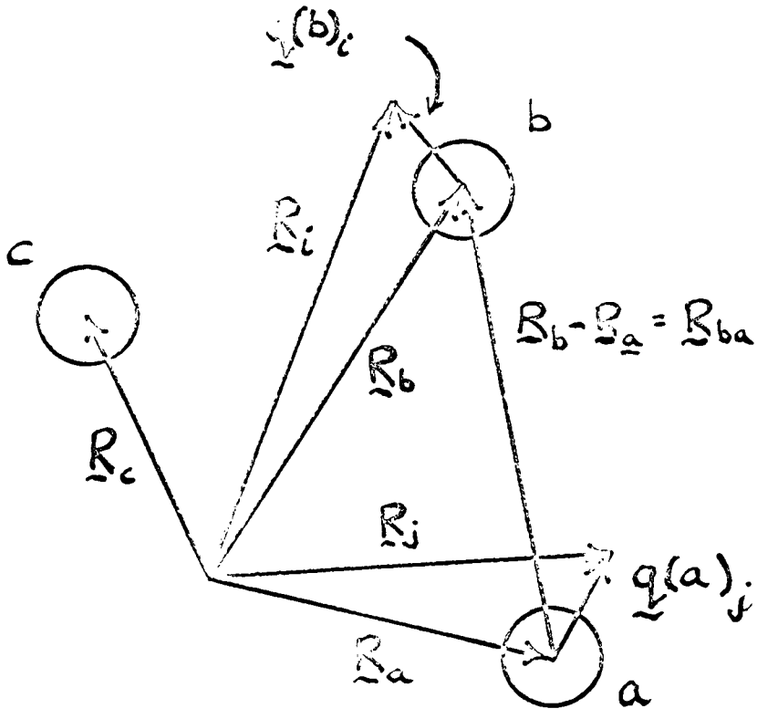

Figure 3.

The molecular coordinate system.

Type A: diagrams with two vertices on each group line (as in Figure 2a);

Type B: diagrams with three vertices on one line and only one on the other (as in Figure 2b).

We shall see that the Type A diagrams give rise to what are usually called the 'coupled oscillator' or the 'dynamic coupling' terms, whereas Type B diagrams generate the 'one-electron' or 'static-coupling' terms [24], [41]. We emphasize however that the total rotation angle is the observable, whereas although the separation of the matrix element $R^{(o)}_{\lambda'\lambda}$ into contributions from different diagrams is computationally useful, the individual diagrams have in general no physical meaning.

The coordinate system that we shall use to specify the relative disposition of the groups is shown in Figure 3 and is essentially the one used in the previous chapter: $\underline{a}$, $\underline{b}$.. ... label the groups and $\underline{i}$, $\underline{j}$... label the electrons in the groups. The incident light beam has a circular frequency ω, whilst the exchanged photon has a wave vector $\underline{k}$ and hence a circular frequency kc. To calculate the R-matrix to a given order all topologically inequivalent diagrams of that order are constructed, and Wallace's algorithm is used to interpret them [8], [9].

3.3 Evaluation of Type A Diagrams.

It is easy to deduce that there are forty eight topologically inequivalent diagrams of Type A which must be evaluated, but the properties of the operators involved will enable them to be reduced to only two types of matrix elements in the algebraic interpretations of the diagrams. Moreover, the energy factors may be grouped into two types, which pair specifically with the numerators to give only two terms ultimately. There are three types of vertex to consider:

$V_{in}^{(s)}$: an entry vertex on line $\underline{s}$

$V_{T}^{(s)}$: a transfer vertex on line $\underline{s}$

$V_{out}^{(s)}$: an exit vertex on line $\underline{s}$.

The existence of forty eight fundamental diagrams is based on the observation that if V_{in} occurs on line $\underline{a}$ then $V_{T}^{(a)}$ must occur either before or after the vertex, and project a photon forward in time onto line $\underline{b}$. If $V_{T}^{(a)}$ occurs before $V_{in}^{(a)}$ the vertex $V_{T}^{(b)}$ may occur either between $V_{T}^{(a)}$ and $V_{in}^{(a)}$, or after $V_{in}^{(a)}$; whereas if $V_{T}^{(a)}$ occurs after $V_{in}^{(a)}$, $V_{T}^{(b)}$ may occur only after $V_{T}^{(a)}$. Therefore in each case time is divided into four ordered segments, and $V_{out}^{(b)}$ may occur in any one of those. This is illustrated in Figure 4. The twelve diagrams so generated must be doubled, because either V_{in} or V_{out} may be a magnetic vertex, and then doubled again

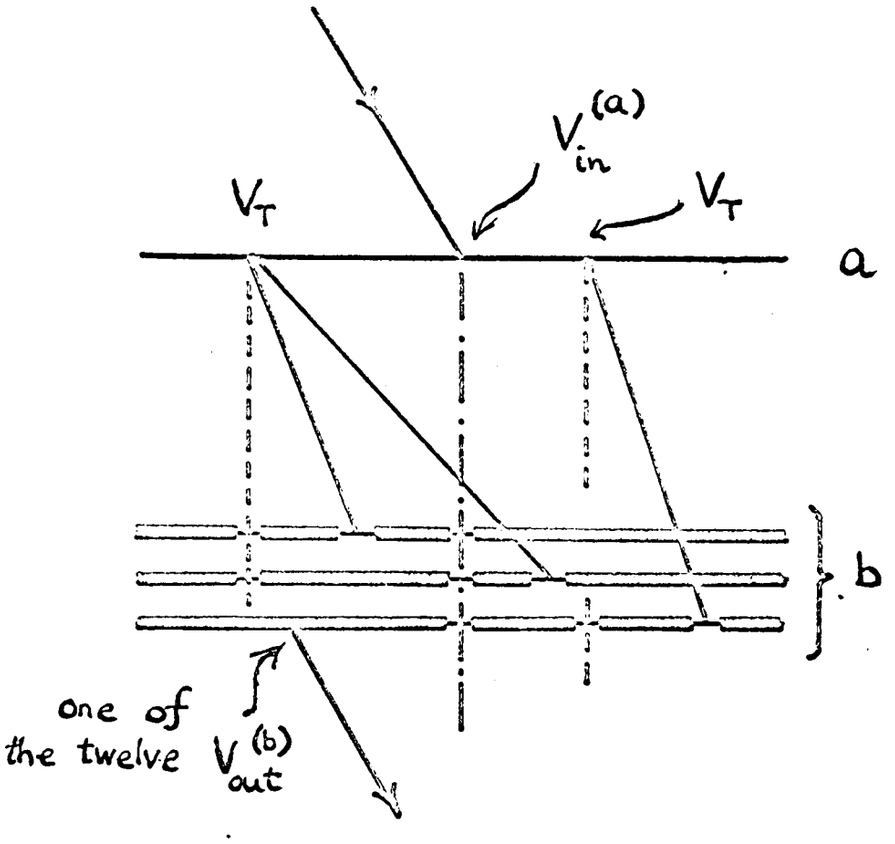

Figure 4

The ordered time intervals in the fourth-order diagrams.

because V_{in} may occur on line $\underline{b}$, in which case V_{out} must be on line $\underline{a}$.

As an illustration we interpret the diagram shown in Figure 5. According to the algorithm the numerator, $\mathcal{N}$, is given by

$$\mathcal{N} = B\sum_{\underline{k}}\sum_{f,f'} k\underline{d}(a)_{mf}\underline{m}(b)_{f'm}:\hat{e}(1)\hat{e}(1) \times \langle f|\underline{d}(a).\hat{e}(\alpha)e^{-i\underline{k}.\underline{R}a}|m\rangle\langle m|\underline{d}(b).\hat{e}(\alpha)e^{i\underline{k}.\underline{R}b}|f'\rangle \tag{3.17}$$

and the denominator, $\mathcal{D}$, by

$$\mathcal{D} = \{E(a)_{mf} + \hbar\omega\}\{E(a)_{mf} + E(b)_{mf'} - \hbar\omega - \hbar kc\}\{E(b)_{mf'} - \hbar\omega\} \tag{3.18}$$

The constant B has the value

$$B = \hbar^2\omega c^4\mu_o^2 n_\lambda^{\frac{1}{2}}/4V^2. \tag{3.19}$$

In equation (3.17) we have not retained the exponential factors associated with the external field interaction vertices because $\exp(\pm ir/\lambda\!\!\!^{-})\sim 1$, c.f. page 39: the corresponding factors for the internal photon vertices must be retained because all values of $\underline{k}$ are encountered. The summation over the polarization states of the transferred photon is carried out by means of the formula [7] :

$$\sum_{\alpha=1,2}\hat{e}(\alpha)\hat{e}(\alpha) = \underline{1} - \hat{k}\hat{k} \tag{3.20}$$

where $\underline{1}$ is the unit dyadic and $\hat{k} = \underline{k}/k$. Next, we recognize that whilst the electric and magnetic dipole moment operators are referred to an axis system fixed in the

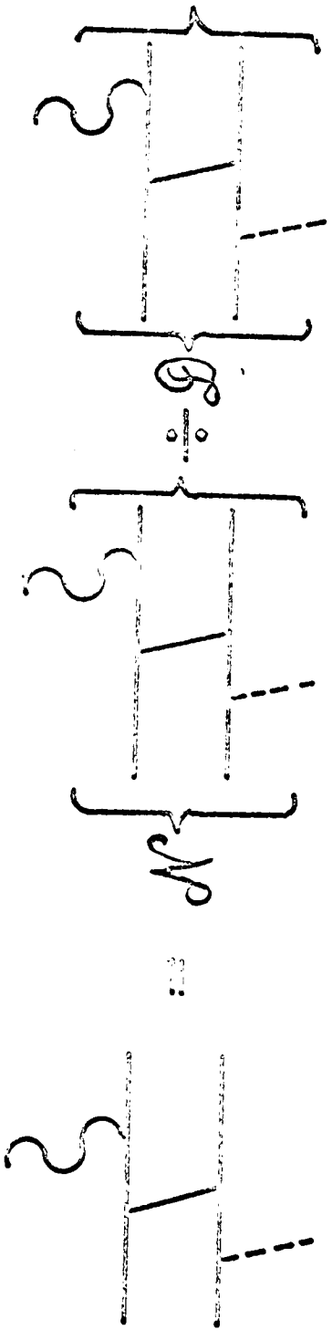

Figure 5

The Type A diagram discussed in the text.

molecule, the unit vectors $\hat{e}(1)$ and $\hat{e}(2)$ are referred to a system fixed in space by the properties of the light beam. In a solution in the absence of an external field the molecules tumble, and so we may make use of the isotropic averages:

$$\left\langle \underset{\sim}{a}.\hat{e}(u)\underset{\sim}{b}.\hat{e}(v)\right\rangle = \tfrac{1}{3}\delta_{uv}\underset{\sim}{a}.\underset{\sim}{b} \tag{3.21}$$

If equations (3.17), (3.20) and (3.21) are used, the average of the numerator may be written

$$\langle \mathcal{N}\rangle = \tfrac{1}{3}B\sum_{\underset{\sim}{k}}\sum_{f,f'} kd(a)^{u}_{mf}d(a)^{v}_{fm}d(b)^{t}_{mf'}m(b)^{u}_{f',m}(\underset{\sim}{1} - \hat{k}\hat{k})_{vt}e^{-i\underset{\sim}{k}.\underset{\sim}{R}ab} \tag{3.22}$$

where $\underset{\sim}{R}ab = \underset{\sim}{R}a - \underset{\sim}{R}b$ is the vector displacement of the group $\underline{a}$ from group $\underline{b}$ (see Figure 3). The summation over $\underset{\sim}{k}$ is replaced by an integration using the density of states factor,

$$\sum_{\underset{\sim}{k}} \rightarrow (V/8\pi^3)\int dk\, d\Omega(\underset{\sim}{k})k^2 \quad . \tag{3.23}$$

Therefore the entire integral over $\underset{\sim}{k}$ may be written

$$L_{vt} \equiv \int_0^\infty dk \int d\Omega(\underset{\sim}{k})k^3(\underset{\sim}{1} - \hat{k}\hat{k})_{vt}\exp(-i\underset{\sim}{k}.\underset{\sim}{R}ab) \tag{3.24}$$

$$= 4\pi\, \mathrm{Im}\int_0^\infty dk\, \hat{T}_{vt}(\underset{\sim}{R}ab;k) \tag{3.25}$$

where the tensor $\hat{\underset{\sim}{T}}(R_{ab};k)$ is defined by

$$\hat{\underset{\sim}{T}}(R_{ab};k) \equiv (\partial\partial - \underset{\sim}{1}\partial^2)(e^{ikR_{ab}}/4\pi\xi_o R_{ab}), \tag{3.26}$$

and $\partial \equiv \nabla_{R_{ab}}$. $\hat{\underset{\sim}{T}}(R_{ab};k)$ is the Fourier transform of the tensor $\hat{\underset{\sim}{T}}(R_{ab};\tau)$ which is defined through the commutator of the electric field strength operators,

$$-i\hbar\hat{T}_{vt}(R_{ab};\tau) = \left[e^{\perp}_{v}(R_a,\tau), e^{\perp}_{t}(R_b,0)\right] \qquad (3.27)$$

and is the singular function governing the propagation of the transverse electric field strength, and corresponds to the retarded electric field of a classical dipole oscillator [13] . This result is obtained from equation (3.24) by performing the angular integral and then noting that exp(ikR)/R is the Green function at infinity of the wave equation, so that we may replace k^2 by $-\delta^2$ [42] . We also note that the imaginary part of the tensor $\hat{T}(R_{ab};k)$, which is a generalized susceptibility tensor, determines the energy dissipation that occurs when one of the groups is perturbed by the other (c.f. [13] , [43]). Collecting together equations (3.19), (3.22 - 3.25) we obtain

$$\langle W \rangle = (\hbar^2\omega c^2\mu_o n_\lambda^{\frac{1}{2}}/6\pi V)\sum_{f,f'}\int_0^\infty dk\; d(a)^u_{mf}d(a)^v_{fm}d(b)^t_{mf'}m(b)^u_{f'm}$$

$$\times \text{Im}\;\hat{T}_{vt}(R_{ab};k). \qquad (3.28)$$

A close examination of the structure of the diagrams enables one to devise the relation that is illustrated in Figure 6a. A broken line (----) connecting the diagrams implies that the time orderings within the boxes, although arbitrary, is the same in each case. As an example of this rule we have the connexion shown in Figure 6b. This rule means that we may combine two diagrams as shown in Figure 6c, and so define the imaginary part of a diagram, indicated by

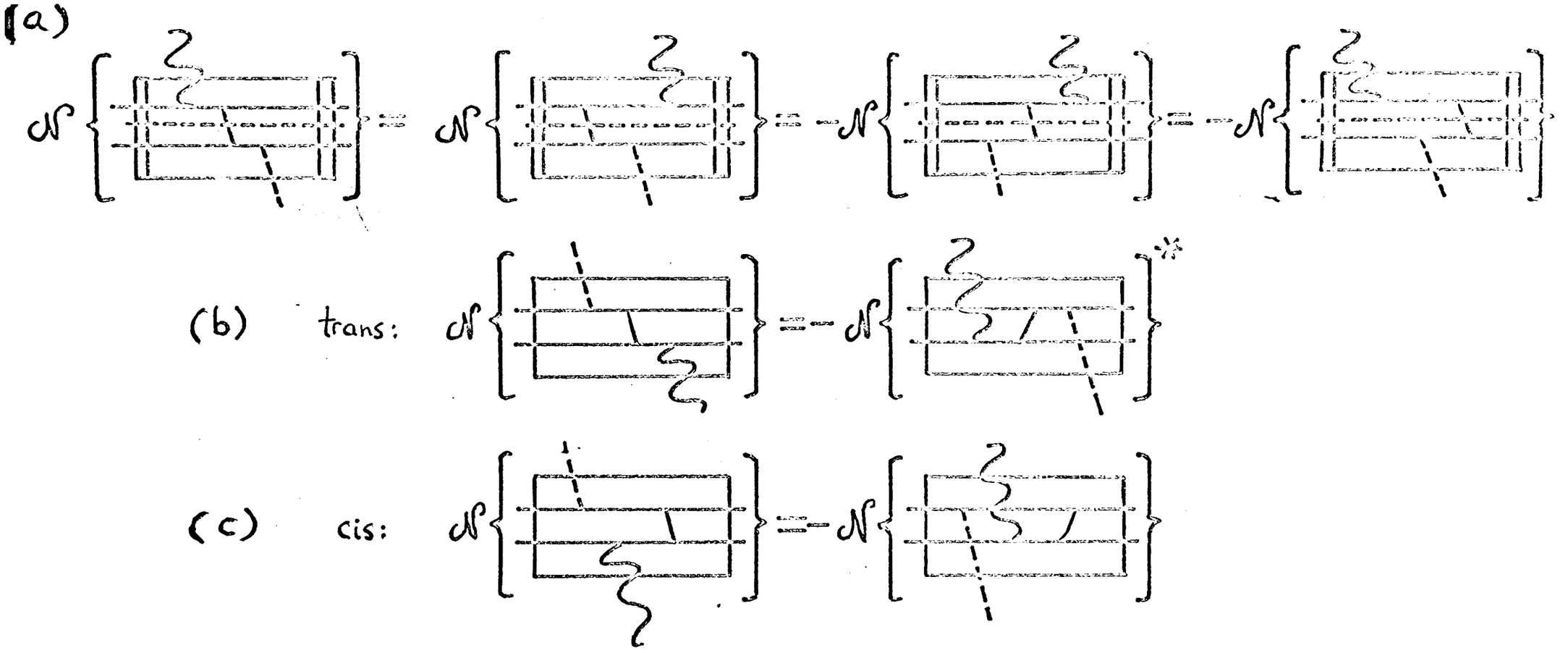

Figure 7

Symmetry rules for the numerators of the algebraic interpretations of the Type A diagrams.

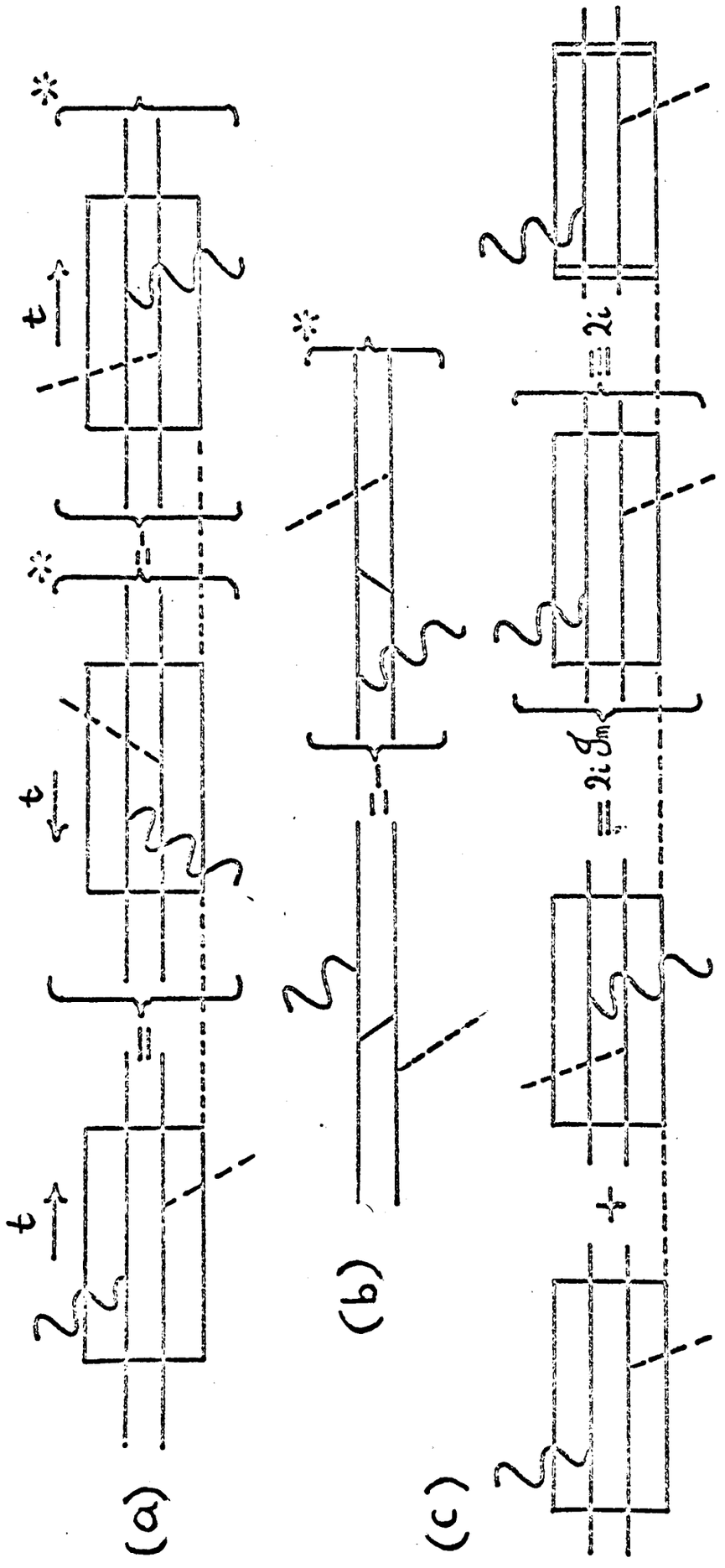

Figure 6

General symmetry rules for Type A diagrams.

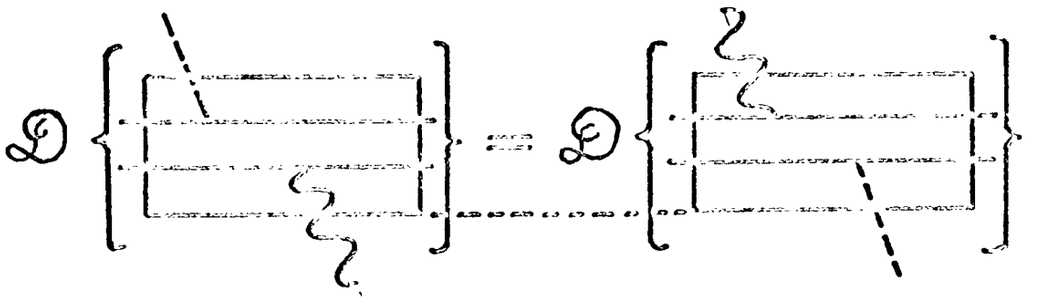

Figure 8

Symmetry rule for the denominators of the algebraic interpretations of the Type A diagrams.

double vertical lines. Furthermore the numerators of various types of diagram are connected as shown in Figure 7a, where the broken horizontal line implies that any relative ordering between the molecular lines may be taken, but the time ordering on a particular line must be as depicted. The diagrams may also be divided into cis and trans types, depending on whether V_{in} and V_{out} occur on the same side of the two V_T vertices, or whether V_{in} and V_{out} occur on opposite sides of the V_T-V_T connexion. This division enables the two relations shown in Figures 7b and 7c to be used. For all types of diagram the denominators are connected by the rule shown in Figure 8: this relation, together with the two preceding, enables the magnetic vertex to be transferred between the lines.

If these symmetry relations are used to collect the numerators and denominators, the R-matrix element for the pair of groups, $(\underline{a}, \underline{b})$ is found to be

$$\langle R_{\lambda'\lambda} \rangle = (2i\hbar^2\omega c^2 \mu_o n_\lambda^{\frac{1}{2}}/3\pi V) \sum_{f,f'} \int_0^\infty dk \left\{ \tau^-(a,b)_{vt} G^+(k) + \tau^+(a,b)_{vt} G^-(k) \right\} \text{Im } T(R_{ab};k)_{vt} \qquad (3.29)$$

with the definitions

$$\tau^{\pm}(a,b)_{vt} \equiv u^{\pm}(a,b)\, d(a)^v_{fm} d(b)^t_{mf'}, \qquad (3.30)$$

$$u^{\pm}(a,b) \equiv \underset{\sim}{d}(a)_{mf} \cdot \underset{\sim}{m}(b)_{f'm} \pm \underset{\sim}{m}(a)_{mf} \cdot \underset{\sim}{d}(b)_{f'm} \qquad (3.31)$$

$$G^{\pm}(k) \equiv \frac{\hbar\omega\left\{E(a)_{mf} \pm E(b)_{mf'}\right\}}{\left\{E(a)^2_{mf} - \hbar^2\omega^2\right\}\left\{E(b)^2_{mf'} - \hbar^2\omega^2\right\}\left\{\hbar\omega - \hbar kc\right\}} \tag{3.32}$$

The integral over k may be written

$$I^{\pm} = \int_0^{\infty} dk\, G^{\pm}(k)\, \mathrm{Im}\, \hat{T}(R_{ab};k)$$

$$= \frac{\hbar\omega\left\{E(a)_{mf} \pm E(b)_{mf'}\right\}(\delta\delta - \underset{\sim}{1}\delta^2)}{\hbar c\left\{E(a)^2_{mf} - \hbar^2\omega^2\right\}\left\{E(b)^2_{mf'} - \hbar^2\omega^2\right\}} \mathrm{Im}(1/4\pi\xi_o R_{ab}) \int_0^{\infty} \frac{dk\, e^{ikR_{ab}}}{(\omega/c - k)} \tag{3.33}$$

where the singularity in the integrand is avoided by the prescription of taking the principal part of the integral. The integral may be expressed in terms of the sine and cosine integrals [44], and we find

$$I^{\pm} = \frac{\hbar\omega\left\{E(a)_{mf} \pm E(b)_{mf'}\right\}}{\hbar c\left\{E(a)^2_{mf} - \hbar^2\omega^2\right\}\left\{E(b)^2_{mf'} - \hbar^2\omega^2\right\}} \underset{\sim}{\mathcal{T}}(a,b;x). \tag{3.34}$$

In this expression we write

$$x = R_{ab}/\chi \tag{3.35}$$

and define the tensor $\underset{\sim}{\mathcal{T}}$ through the following scheme:

$$\underset{\sim}{\mathcal{T}}(a,b;x) = (1/4\pi\xi_o R^3_{ab})\underset{\sim}{\mathcal{R}}(a,b;x) \tag{3.36}$$

$$\underset{\sim}{\mathcal{R}}(a,b;x) = G_1(x)\,\underset{\sim}{1} - G_2(x)\,\hat{R}_{ab}\hat{R}_{ab} \tag{3.37}$$

$$G_1(x) = -J_o(x) - x\left\{1 - K_o(x)\right\} + x^2 J_o(x) \tag{3.38}$$

$$G_2(x) = -3J_o(x) - x\left\{1 - 3K_o(x)\right\} + x^2 J_o(x) \tag{3.39}$$

$$J_o(x) = \sin x\, Ci\, x - \cos x\, si\, x - \pi \cos x \qquad (3.40)$$

$$K_o(x) = \cos x\, Ci\, x + \sin x\, si\, x + \pi \sin x \qquad (3.41)$$

where $\hat{R}_{ab} = \underset{\sim}{R}_{ab}/R_{ab}$.

The integral $I^{\pm}$ may now be inserted into the expression for the R-matrix element, and if we sum over all groups in the molecule, we obtain in view of the Hermiticity of the operators, the expression

$$\left\langle R^{(o)}_{\lambda'\lambda} \right\rangle = (4i\hbar^2\omega^2 c\mu_o n_\lambda^{\frac{1}{2}}/3\pi V)\, Im \sum_{a\neq b} \sum_{f,f'} E(a)_{mf} \left\{E(a)^2_{mf} - \hbar^2\omega^2\right\}^{-1}$$

$$x \left\{E(b)^2_{mf'} - \hbar^2\omega^2\right\}^{-1} d(a)^u_{mf} d(a)^v_{fm} d(b)^t_{mf'} m(b)^u_{f',m} \tau(a,b;x)_{vt} \qquad (3.42)$$

Therefore using equation (3.10) we obtain the rotation angle for unit path length of solution containing N molecules per unit volume as

$$\theta_A = (2/3\pi) N\hbar\omega^2\mu_o \sum_{a\neq b} A(a)_{uv} P(b)_{tu} \tau(a,b;x)_{vt} \qquad (3.43)$$

The tensors $\underset{\sim}{A}$ and $\underset{\sim}{P}$ are defined by,

$$A(s)_{uv} = 2 \sum_f \frac{E(s)_{mf} d(s)^u_{mf} d(s)^v_{fm}}{\left\{E(s)^2_{mf} - \hbar^2\omega^2\right\}} \qquad (3.44)$$

$$P(s)_{uv} = Im \sum_f \frac{d(s)^u_{mf} m(s)^v_{fm}}{\left\{E(s)^2_{mf} - \hbar^2\omega^2\right\}} \qquad (3.45)$$

and may be related to the polarizability and gyration tensors

of the groups $(\underset{\sim}{\alpha}, \underset{\sim}{\rho})$ if we express the operators $\underset{\sim}{d}$ and $\underset{\sim}{m}$ in coordinate systems centred on the individual groups (c.f. [23]). Under a spatial translation by an amount $\underset{\sim}{R}$, the operators transform as follows:

$$d^u_{mf} \longrightarrow d^u_{mf} \tag{3.46}$$

$$m^u_{mf} \longrightarrow m^u_{mf} + (i/2\hbar c) E_{mf} \in_{uvt} R^v d^t_{mf} \tag{3.47}$$

so that

$$A(s)_{uv} \longrightarrow \alpha(s)_{uv} \tag{3.48}$$

$$P(s)_{uv} \longrightarrow \rho(s)_{uv} - (1/4\hbar c) \in_{tuw} R^t_s \alpha(s)_{vw}. \tag{3.49}$$

The rotation angle may therefore be written as,

$$\theta_A = (2N\hbar\omega^2\mu_o/3\pi) \sum_{a\neq b} \alpha(a,\omega)_{uv}\, \rho(b,\omega)_{tu}\, \tau(a,b;x)_{vt}$$
$$- (N\mu_o\omega/6\pi\hbar) \in_{tuw} \sum_{a\neq b} R^t_b\, \alpha(a,\omega)_{uv}\, \alpha(b,\omega)_{ws}\, \tau(a,b;x)_{vs}. \tag{3.50}$$

Let us now examine the behaviour of the tensor $\underset{\sim}{\tau}(a,b;x)$ defined through equations (3.36) to (3.41). The functions si x, and Ci x may be expressed as follows [44] :

$$\mathrm{si}\, x = -(\pi/2) + \sum_{n=0} (-1)^n x^{2n+1}/(2n+1)(2n+1)! \tag{3.51}$$

$$\mathrm{Ci}\, x = \gamma + \ln x + \sum_{n=0} (-1)^n x^{2n}/2n(2n)! \tag{3.52}$$

where γ is Euler's constant and so in the limit of small x we find

$$G_1(0) \equiv \lim_{x\to 0} G_1(x) = \pi/2 \tag{3.53}$$

$$G_2(0) \equiv \lim_{x\to 0} G_2(x) = 3\pi/2 \tag{3.54}$$

and therefore we may write

$$\mathcal{R}(a,b;x) = (\pi/2)\left\{\gamma_1(x)\underset{\sim}{1} - 3\gamma_2(x)\hat{R}_{ab}\hat{R}_{ab}\right\} \tag{3.55}$$

where the γ_i are defined as

$$\gamma_1(x) \equiv 2G_1(x)/\pi \tag{3.56}$$

$$\gamma_2(x) \equiv 2G_2(x)/3\pi \tag{3.57}$$

and clearly have the property

$$\lim_{x\to 0} \gamma_1(x) = \lim_{x\to 0} \gamma_2(x) \equiv 1. \tag{3.58}$$

The importance of retardation effects may be most easily seen from the magnitudes of the deviations of the γ_i from unity: we write $\delta\gamma_i = \gamma_i - 1$ and illustrate the variation of $\delta\gamma_i$ for small arguments in Figure 9. It is clear that over the intergroup distances that are physically important, the retardation corrections are essentially negligible. For example with $R_{ab}\sim 1.0\text{nm}$, $\lambda\sim 300\text{nm}$ we obtain $x\sim 0.02$, and thus $\delta\gamma_1(x) = -2.1 \times 10^{-4}$ and $\delta\gamma_2(x) = +8.6 \times 10^{-3}$, so that we may replace $\underset{\sim}{\mathcal{T}}$ by its classical counterpart $\underset{\sim}{T}$,

$$\underset{\sim}{T} = (1/4\pi\epsilon_o R_{ab}^3)(\underset{\sim}{1} - 3\hat{R}_{ab}\hat{R}_{ab}) \tag{3.59}$$

The first term of equation (3.50) thus corresponds to the term g^1 derived by Kirkwood [23] whilst the second term is

Figure 9

The behaviour of $\delta\gamma_i(x)$ for small values of the retardation parameter x.

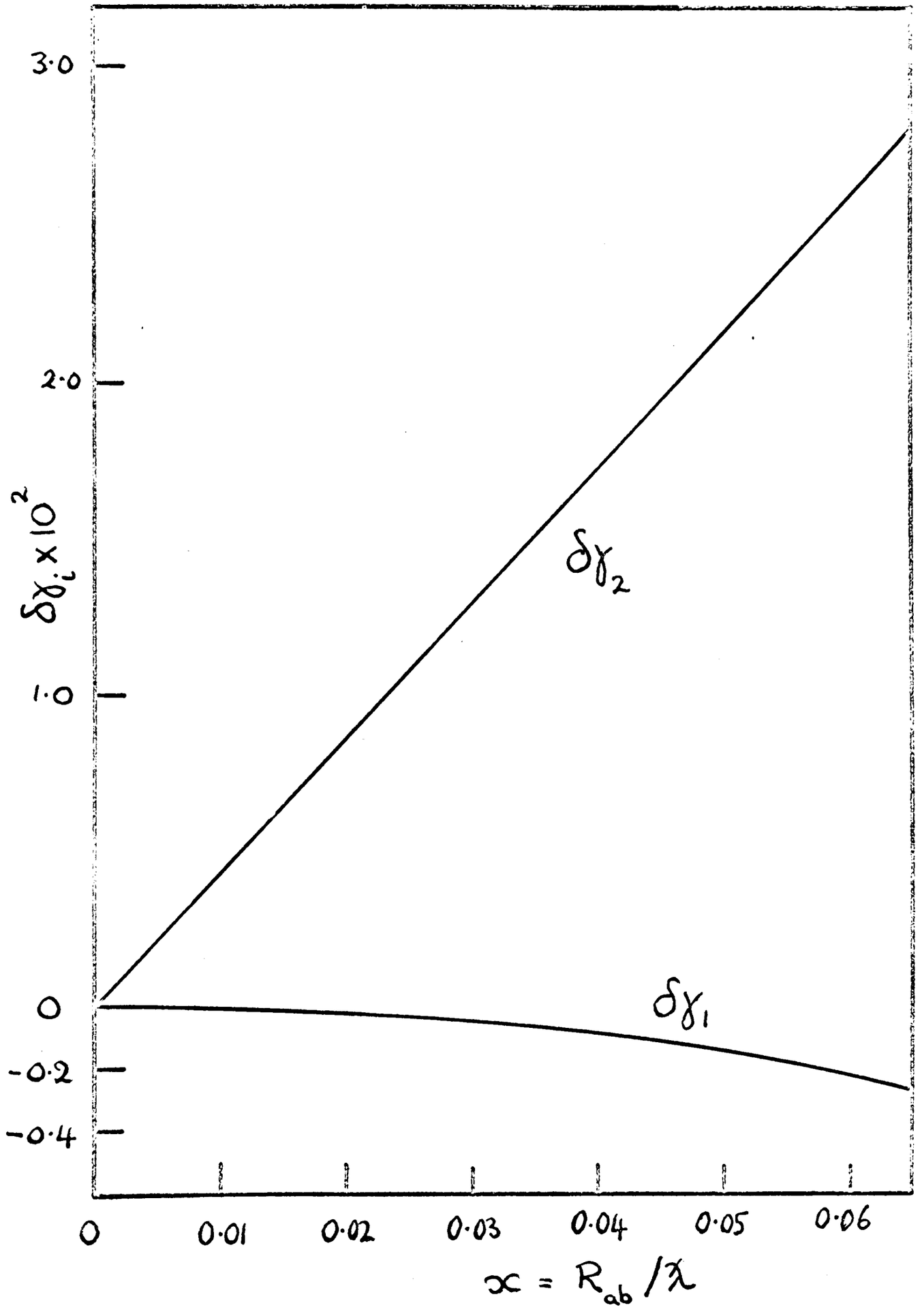
3·0
2·0
1·0
0
-0·2
-0·4
$\delta\gamma_i \times 10^2$
$\delta\gamma_2$
$\delta\gamma_1$
0
0·01
0·02
0·03
0·04
0·05
0·06
$x = R_{ab}/\lambda$

Figure 9

his 'polarizability' formula for the rotation angle. If the subsystems are optically inactive, $\underset{\sim}{\rho}(s) = 0$, so that the first term does not contribute. In general however when higher multipoles are considered this term will not vanish (see, for example [45]).

3.4 Evaluation of Type B Diagrams.

The diagrams to be considered now are those with unequal numbers of vertices on the group lines. It is clear that if the photon scattering occurs on line a then $V_T^{(b)}$ must correspond to the diagonal elements of the interaction potential. A discussion similar to that used in the preceding section shows that there are also forty eight topologically inequivalent diagrams of Type B that must be considered. We shall assume that the scattering takes place from group a: alternative possibilities are taken into account automatically in the final sum over groups. The manipulations follow through analogously to those in §3, and as an example we state the final interpretation of the diagram shown in Figure 2b:

$$\left\langle R^{(o)}_{\lambda'\lambda} \right\rangle = (\hbar^2\omega c^2 \mu_o n_\lambda^{\frac{1}{2}}/6\pi V) \sum_{f,f'} \int_o^\infty dk\; m(a)^u_{mf'} d(a)^v_{f'f} d(a)^u_{fm} d(b)^t_{mm}$$

$$\times \mathfrak{D}^{-1}_{ff'} \operatorname{Im} \hat{T}(R_{ab};k)_{vt} \qquad (3.60)$$

where

$$\mathfrak{D}_{ff'} = \left\{E(a)_{mf} + \hbar\omega\right\}\left\{E(a)_{mf'} + \hbar\omega - \hbar kc\right\}\left\{E(a)_{mf'} + \hbar\omega\right\} \qquad (3.61)$$

The summation over f and f' is restricted by the requirement that no two complete intermediate states (molecule + field) in an R-matrix element be the same.

The set of diagrams may again be divided into cis and trans types, depending on whether V_{in} and V_{out} occur on the same side or opposite sides of $V_T^{(a)}$. The position of the two external field-molecule vertices relative to $V_T^{(b)}$ is immaterial. Using the properties of the R-matrix elements under the interchange of the labels f and f' we obtain the rules shown in Figure 10. In the diagram the box signifies that the order of absorption and emission, polarization, and type of transition (electric or magnetic) of the external interaction vertices, although arbitrary, is the same in both cases. The interchange of the boxes in Figure 10b indicates that the two diagrams are related by interchanging the external magnetic and electric field vertices: the other features of the interactions (polarization and chronological order) remain the same. The diagrams thus have similar properties to those used in the S-matrix description of the Faraday effect [10], and a similar regrouping procedure is used here.

Far from resonance the R-matrix is pure imaginary [9], and after some simple but tedious algebra we obtain the R-matrix element as

$$\left\langle R^{(o)}_{\lambda'\lambda} \right\rangle = -(4i\hbar^2\omega^2 c\mu_o n_\lambda^{\frac{1}{2}}/3\pi V)\,\mathrm{Im}\sum_{f,f'}\int_0^\infty dk\, k^{-1}\left\{ \frac{d(a)^v_{f'f}\, d(b)^t_{mm}\, u^-(a,a)^*}{E(a)_{ff'}\left\{E(a)^2_{mf} - \hbar^2\omega^2\right\}} \right.$$

$$\left. + \frac{d(a)^v_{mf}\, d(b)^t_{mm}\, v^-(a,a)^*}{E(a)_{mf'}\left\{E(a)^2_{mf} - \hbar^2\omega^2\right\}} \right\} \mathrm{Im}\,\hat{T}(R_{ab};k)_{vt} \qquad (3.62)$$

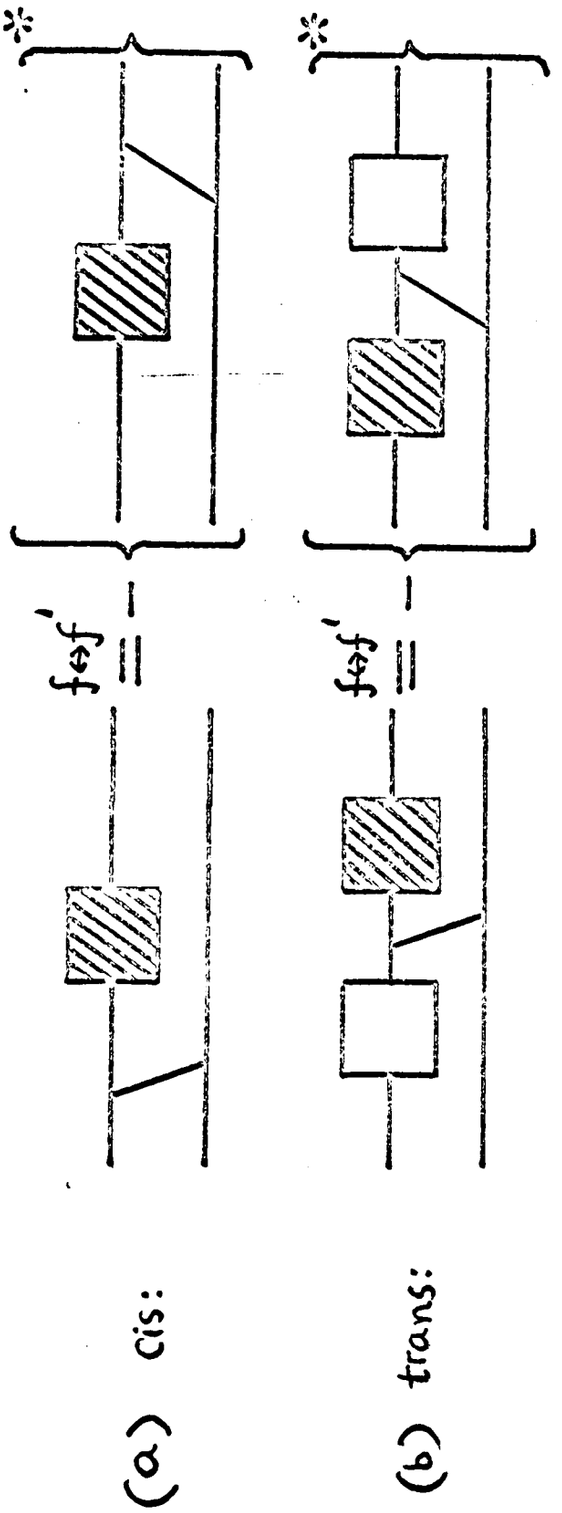

Figure 10

General symmetry rules for Type B diagrams.

where $u^{-}(a,a)$ is defined through equation 3.31 and

$$v^{-}(a,a) \equiv \underset{\sim}{m}(a)_{ff'} \cdot \underset{\sim}{d}(a)_{mf} - \underset{\sim}{d}(a)_{ff'} \cdot \underset{\sim}{m}(a)_{mf}. \tag{3.63}$$

The integral over k may be written

$$I_{vt} = \int_0^\infty dk\, k^{-1}\, \mathrm{Im}\, \hat{T}(R_{ab};k)_{vt} \tag{3.64}$$

$$= (\underset{\sim}{\partial}\underset{\sim}{\partial} - \underset{\sim}{1}\,\partial^2)_{vt}(4\pi\epsilon_o R_{ab})^{-1}\int_0^\infty dk\, k^{-1}\, \sin(kR_{ab})$$

$$= -(1/2\epsilon_o)\left\{\delta^{11}_{vt}(\underset{\sim}{R}_{ab}) - \delta_{vt}\,\delta(\underset{\sim}{R}_{ab})\right\} \tag{3.65}$$

In this equation $\delta^{11}(\underset{\sim}{R}_{ab})$ is the longitudinal delta function, and it represents the longitudinal (static) part of the singular dyadic field. For $R_{ab} \neq 0$, a physical constraint in the context of our theory, $\delta^{11}(\underset{\sim}{R}_{ab})$ yields the instantaneous electrical field strength at $\underset{\sim}{R}_{ab}$ due to an electric dipole at the origin. Therefore equation 3.65 becomes, [46] ,

$$I_{vt} = -(\pi/2)T(a,b)_{vt} \tag{3.66}$$

where $\underset{\sim}{T}(a,b)$ is the classical dipole coupling tensor defined in equation 3.59. This result does not contradict our remarks after equation 3.27 but is a consequence of the special form of the integral over $\underset{\sim}{k}$ in which the external field frequency does not appear. Substitution of equation 3.66 into equation 3.62, summation over all the groups in the molecule, and use of equation 3.10 yields the rotation angle per unit path length through a solution containing N molecules per unit volume as

$$\theta_B' = (\tfrac{2}{3}N\hbar\omega^2\mu_0)\sum_{a\neq b}\sum_{f,f'}\left\{E(a)_{mf}^2 - \hbar^2\omega^2\right\}^{-1} T(a,b)_{vt}\ \mathrm{Im}$$

$$x\left\{E(a)^{-1}_{ff'}d(a)^v_{f'f}d(b)^t_{mm}u^-(a,a)^* + E(a)^{-1}_{mf}d(a)^v_{mf}d(b)^t_{mm}v^-(a,a)^*\right\} \qquad (3.67)$$

The symbol * is the usual symbol for the complex conjugation operation.

We must now invoke the restriction on the allowed complete intermediate states, since as it stands equation (3.67) contains forbidden terms. A close examination of the diagram interpretations shows that the terms to be excluded are of two types: those that are singular because one of the intermediate state propagators vanishes, and those that are finite but involve two identical complete intermediate states. We discard the singular terms immediately, and obtain the finite contribution in the following way. The restriction amounts to deciding what states the label $\underline{f}'$ may refer to, and we find that we must exclude the contribution when $|f'\rangle = |m\rangle$ from the first term in equation (3.67), whilst we must exclude the contribution when $|f'\rangle = |f\rangle$ from the second term. For non-degenerate states we may always choose real wavefunctions so that the diagonal elements of the operator $\underline{m}$ vanish, and the term to be subtracted reduces to,

$$A = (\tfrac{2}{3}N\hbar\omega^2\mu_0)\sum_{a\neq b}\mathrm{Im}\sum_f E(a)^{-1}_{mf}\left\{E(a)^2_{mf} - \hbar^2\omega^2\right\}^{-1}$$

$$x\, d(a)^v_{mf}d(b)^t_{mm}\left\{\underset{\sim}{d}(a)_{ff} - \underset{\sim}{d}(a)_{mm}\right\}.\underset{\sim}{m}(a)_{fm}T(a,b)_{vt} \qquad (3.68)$$

We now introduce the permanent moments of the groups defined by $\underset{\sim}{\mu}(s)_n \equiv \langle n | \underset{\sim}{d}(s) | n \rangle$, and subtract equation (3.68) from equation (3.67) and so obtain the rotation angle as,

$$\Theta_B = (2N\hbar\omega^2\mu_o/3)\mathrm{Im}\sum_{a\neq b}\sum_{f\neq f'}\left\{E(a)^2_{mf} - \hbar^2\omega^2\right\}^{-1} T(a,b)_{vt}$$

$$x\left\{E(a)^{-1}_{ff'}d(a)^v_{f'f}\mu(b)^t_m u^-(a,a)^* + E(a)^{-1}_{mf'}d(a)^v_{mf'}\mu(b)^t_m v^-(a,a)^*\right.$$

$$\left. - E(a)^{-1}_{mf}d(a)^v_{mf}\mu(b)^t_m\left\{\underset{\sim}{\mu}(a)_f - \underset{\sim}{\mu}(a)_m\right\}\cdot\underset{\sim}{m}(a)_{fm}\right\}. \qquad (3.69)$$

If we now use equations (3.46) and (3.47) we obtain Θ_B as a sum of terms identical in form to equation (3.69) with the operators referred to their respective groups, plus the following origin-dependent terms:

$$\Theta(\underset{\sim}{R}) = (N\mu_o\omega/6\lambda)\sum_{a\neq b}\sum_{f\neq f'}\left\{E(a)^2_{mf} - \hbar^2\omega^2\right\}^{-1}$$

$$x\ \underset{\sim}{R}_a\cdot\left[\left\{\underset{\sim}{d}(a)_{fm}\wedge\underset{\sim}{d}(a)_{mf'}\langle f'_a m_b|V(a,b)|f_a m_b\rangle\right.\right.$$

$$- \underset{\sim}{d}(a)_{fm}\wedge\underset{\sim}{d}(a)_{f'f}\langle m_a m_b|V(a,b)|f'_a m_b\rangle$$

$$\left.\left. - \underset{\sim}{d}(a)_{fm}\wedge\left\{\underset{\sim}{\mu}(a)_f - \underset{\sim}{\mu}(a)_m\right\}\langle m_a m_b|V(a,b)|f_a m_b\rangle\right\}\right] \qquad (3.70)$$

where we have introduced the notation

$$\langle f'_a m_b|V(a,b)|f_a m_b\rangle = \underset{\sim}{d}(a)_{f'f}\cdot\underset{\sim}{T}(a.b)\cdot\underset{\sim}{\mu}(b)_m. \qquad (3.71)$$

It is clear that the coordinate transformation has eliminated the energy dependence on the state $|f'\rangle$ so that we may use closure, with respect to this state, on the terms in braces in equation (3.70). If we now make use of our freedom to choose real wavefunctions for non-degenerate states then

we may write $\underset{\sim}{d}(s)_{mf} = \underset{\sim}{d}(s)_{fm}$ since $\underset{\sim}{d}(s)$ is a real operator and it is a simple matter to show that the entire expression for $\Theta(\underset{\sim}{R})$ vanishes identically [11] , whence Θ_B is translation invariant as required. Thus the total rotation angle is the sum of the expressions in equations (3.50) and (3.69) in which the operators are referred to coordinate systems fixed in the individual groups and this sum agrees with the result of Tinoco [24] , when the tiny retardation terms are neglected and the dipole approximation is used.

In the following chapter we shall examine the use of the complete multipole interaction potential in the perturbation theoretic formulation of calculations in non-covariant quantum electrodynamics, and in particular illustrate some of the difficulties that are encountered when one attempts to generalize the above calculation on optical activity. We shall see that there are difficulties associated with virtual photon processes and so we believe it to be worthwhile to demonstrate briefly how the calculations of Power et al. [7] , [47] on long range intermolecular forces, which involve the exchange of two virtual photons between molecular systems, fit in to the framework of diagrammatic perturbation theory based on Wallace's algorithm [8] , and the reaction operator $\underset{\sim}{R}$, defined in equation (3.12).

CHAPTER 4

GENERAL MULTIPOLAR INTERACTIONS IN PERTURBATION THEORY

4.1 Time Indepedent Perturbation Theory.

In the previous chapter we discussed at length a calculation of the optical activity of a molecule that was based on diagrammatic perturbation theory and the expansion of the reaction operator defined in equation (3.12). In this section we wish to indicate how calculations such as those of Power et al. on intermolecular forces [7], [47], can be formulated within the same framework, so that the comments of the following sections may be taken to apply to perturbation theory calculations in general.

The hamiltonian, H, for the total system satisfies the Schrödinger equation $(H - E)\Psi = 0$, where E is the energy eigenvalue, and Ψ the state vector. We assume that H may be split into two parts, $H = H_o + V$ (c.f. page 38), and that the eigenfunctions Ψ_a, of H_o are known; $(H_o - E_a)\Psi_a = 0$. This division of H serves to define the perturbation V. In the following we limit the discussion to the case when the spectrum of both H and H_o is discrete, and when Ψ and Ψ_a are not orthogonal.

The resolvent operator is defined by the equation

$$\mathcal{R}(E) = (H - E)^{-1} \tag{4.1}$$

in which we regard $\mathcal{R}(E)$ as a function of the complex energy variable E. $\mathcal{R}(E)$ is a bounded operator in the entire complex E-plane except for the points defining the spectrum of H, [48].

If we set

$$\mathcal{R}_o(E) = (H_o - E)^{-1} \tag{4.2}$$

then the use of a simple operator identity yields

$$\mathcal{R}(E) = \mathcal{R}_o(E) - \mathcal{R}_o(E)V\mathcal{R}(E). \tag{4.3}$$

The diagonal elements of $\mathcal{R}(E)$ in the unperturbed basis will be written as,

$$\langle \Psi_a | \mathcal{R}(E) | \Psi_a \rangle \equiv \mathcal{D}_a(E) \tag{4.4}$$

and if we introduce the notation

$$F_a(E) = \langle \Psi_a | \{ -V + V\mathcal{R}_o(E)V - \ldots\ldots \}' | \Psi_a \rangle \tag{4.5}$$

where the prime indicates that the complete set of unperturbed states except Ψ_a is to be inserted in the braces, then by calculating the diagonal and off-diagonal matrix elements of $\mathcal{R}(E)$, and using equation (4.3), it is a simple matter to show that, [48],

$$\mathcal{D}_a(E) = -\{E - E_a + F_a(E)\}^{-1} \tag{4.6}$$

In the Schrodinger representation the time development of the state $\Psi(t_o)$ is described by a unitary operator U so that

$$\Psi(t) = U(t - t_o)\Psi(t_o) \tag{4.7}$$

where

$$U(t - t_o) = \exp\left\{-iH(t - t_o)/\hbar\right\} \tag{4.8}$$

With the aid of the resolvent operator we may write equation

(4.8) in the form of a contour integral,

$$U(t - t_o) = -(1/2\pi i)\int_C dE\, \mathcal{R}(E) \exp\left\{-iE(t - t_o)/\hbar\right\} \qquad (4.9)$$

where the contour encircles the poles of $\mathcal{R}(E)$ and is closed in an anticlockwise sense. Equation (4.9) will enable us to calculate the energy difference between the unperturbed ground state and the true ground state of the system.

Suppose that at time $t = 0$, the ground state of the reference system is described by the state vector $|\Psi_o\rangle$. After a time t has elapsed, in the absence of interaction the new state vector will be simply $|\Psi_o\rangle \exp\left\{-iE_o t/h\right\}$. If however the perturbation is "switched on" at $t = 0$, the system will start to make transitions from the state $|\Psi_o\rangle$ to all possible excited states. The amplitude that the system after a time t is still in the (time-developed) ground state, is called the 'vacuum amplitude', $A(t)$, [49], and is clearly given by the inner product $A(t) = (|\Psi_o\rangle \exp\left\{-iE_o t/\hbar\right\}, |\Psi(t)\rangle)$. Using equation (4.7) we may write

$$A(t) = \langle \Psi_o | U(t) | \Psi_o \rangle \exp\left\{iE_o t/\hbar\right\} \qquad (4.10)$$

$$= (1/2\pi i) e^{iE_o t/\hbar} \int_C \frac{dE \exp(-iEt/\hbar)}{E - E_o + F_o(E)} \qquad (4.11)$$

by equations (4.4), (4.6) and (4.9). The relevant pole in the integrand is at $E = E_o - F_o(E)$, $\left\{\left[\mathcal{D}_o(E)\right]^{-1} = 0\right\}$, and so using the residue theorem we obtain

$$A(t) = \exp\left\{iF_o(E)t/\hbar\right\}. \qquad (4.12)$$

According to a theorem proved by Thouless [49], the energy difference ΔE, between the true and the unperturbed ground state energies is given by

$$\Delta E = E - E_o = i\hbar \left\{ \partial_t \ln A(t) \right\}_{t \to \infty(1 - i\epsilon)} \tag{4.13}$$

where ϵ is an infinitesimal chosen so that $\infty \times \epsilon = \infty$. From equations (4.12) and (4.13) we thus obtain the result that

$$\Delta E = - F_o(E). \tag{4.14}$$

The eigenvalue E which gives rise to a pole in $\mathcal{D}_o(E)$, equation (4.6), therefore corresponds to the true energy of the system. Since the eigenvalues of H are real the poles of $\mathcal{D}_o(E)$ must lie on the real E-axis, and so we may write $E \to \mathcal{E} + i\eta$ where the energy $\mathcal{E}$ is now taken as a real quantity. Equation (4.2) can thus be written as

$$\mathcal{R}_o(E) \longrightarrow (H_o - \mathcal{E} - i\eta)^{-1} = -G^o(\mathcal{E}) \tag{4.15}$$

where G^o is the Green function defined in equation (3.14). With this result we may write equation (4.5) as

$$-F_o(E) = \langle \Psi_o | \{ V + VG^oV + \ldots\ldots\ldots \}' | \Psi_o \rangle \tag{4.16}$$

$$= \langle \Psi_o | R | \Psi_o \rangle \tag{4.17}$$

where we have used the definition of the reaction operator, equation (3.12), so that finally

$$\underline{\Delta E = \langle \Psi_o | R | \Psi_o \rangle}. \tag{4.18}$$

It is evident that the iterative expansion of equation

(4.17) when evaluated in the (unperturbed) molecule + photon vacuum state, $|m, \lambda[0_\lambda]\rangle$ leads at once to the results of Power et al. [7], [47], and that if the unperturbed state Ψ_o is chosen as $|m, \lambda[n_\lambda]\rangle$, we obtain the perturbation energy of a molecule in an electromagnetic field as discussed by Atkins and Barron [9]. We thus see that the reaction operator R plays the central rôle in perturbation theory calculations.

4.2 The Multipolar Interaction Potential.

We now wish to generalize our discussion so as to include the case when the complete multipole expansion is retained in the interaction potential though we shall neglect those terms quadratic in the magnetic induction. We have therefore,

$$V = -\int d\tau\, \underset{\sim}{p}\cdot\underset{\sim}{e}^{\perp} - \int d\tau\, \underset{\sim}{m}'\cdot\underset{\sim}{b} \quad . \tag{4.19}$$

If the explicit representations of the polarization fields $\underset{\sim}{p}$ and $\underset{\sim}{m}$ are introduced into equation (4.19) and the integrations performed, we obtain,

$$+\int d\tau \underset{\sim}{p}\cdot\underset{\sim}{e}^{\perp} = \sum_{a,i} e_{ai} \sum_{n} \left\{1/(n+1)!\right\} (\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n} \underset{\sim}{q}_{ai}\cdot\underset{\sim}{e}^{\perp}(\underset{\sim}{r}_{a}) \tag{4.20}$$

$$+\int d\tau \underset{\sim}{m}'\cdot\underset{\sim}{b} = \sum_{a,i} (e_{ai}/2m_{ai}) \sum_{n} \left\{n/(n+1)!\right\} \left\{ (\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1} (\underset{\sim}{q}_{ai}\wedge\underset{\sim}{p}_{ai})\cdot\underset{\sim}{b}(\underset{\sim}{r}_{a}) + (\underset{\sim}{q}_{ai}\wedge\underset{\sim}{p}_{ai})(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\cdot\underset{\sim}{b}(\underset{\sim}{r}_{a}) \right\}. \tag{4.21}$$

These equations are rather cumbersome as they stand, but they may be cast into a more convenient form in the following way. If we note the identity $\int_{0}^{1} dy\, y^{n} \equiv (1/n+1)$, then equation (4.20) may be written as

$$+\int d\tau \underset{\sim}{p}\cdot\underset{\sim}{e}^{\perp} = \sum_{a,i}' e_{ai} \int_{0}^{1} dy\, \underset{\sim}{q}_{ai}\cdot\underset{\sim}{e}^{\perp}(\underset{\sim}{r}_{a} + y\underset{\sim}{q}_{ai}) \tag{4.20a}$$

as may be verified directly if $\underset{\sim}{e}^{\perp}(\underset{\sim}{r}_{a} + y\underset{\sim}{q}_{ai})$ is expanded as a Taylor series about $\underset{\sim}{r}_{a}$ and the order of integration and summation interchanged. This last step must be possible if the multipole representation is to have any meaning (c.f.

[12] where a similar integral representation is used but in a different context).

To obtain the corresponding integral expression for equation (4.21) we have only to note that the sum over $\underset{\sim}{n}$ in this equation starts from 0, so that because of the factor of $\underset{\sim}{n}$ in the numerator we may write the equation equally well as

$$\sum_{a,i}(e_{ai}/2m_{ai})\sum_{n=0}\left\{1/(n+2)n!\right\}\left\{(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n}(\underset{\sim}{q}_{ai}\wedge\underset{\sim}{p}_{ai})\cdot\underset{\sim}{b}(\underset{\sim}{r}_{a})\right.$$
$$\left. + (\underset{\sim}{q}_{ai}\wedge\underset{\sim}{p}_{ai})(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n}\cdot\underset{\sim}{b}(\underset{\sim}{r}_{a})\right\}$$
$$=\sum_{a,i}(e_{ai}/2m_{ai})\int_{0}^{1}dy\ y\left\{(\underset{\sim}{q}_{ai}\wedge\underset{\sim}{p}_{ai})\cdot\underset{\sim}{b}(\underset{\sim}{r}_{a}+y\underset{\sim}{q}_{ai})\right.$$
$$\left. + \underset{\sim}{b}(\underset{\sim}{r}_{a}+y\underset{\sim}{q}_{ai})\cdot(\underset{\sim}{q}_{ai}\wedge\underset{\sim}{p}_{ai})\right\}$$

where we have employed the same argument as above. We may write this expression concisely in the form of an anticommutator, and if we note that $(\underset{\sim}{q}_{ai}\wedge\underset{\sim}{p}_{ai})$ is in fact the angular momentum operator $\underset{\sim}{l}_{ai}$, then we obtain

$$+\int d\tau\,\underset{\sim}{m}'\cdot\underset{\sim}{b}=\sum_{a,i}(e_{ai}/2m_{ai})\int_{0}^{1}dy\ y\left\{l^{r}_{ai},b(\underset{\sim}{r}_{a}+y\underset{\sim}{q}_{ai})^{r}\right\}_{+}\qquad r=1,2,3. \tag{4.21a}$$

We see that equations (4.20a) and (4.21a) reduce to equations (3.5) and (3.6) respectively if the fields have no dependence on $\underset{\sim}{y}$ so that the $\underset{\sim}{y}$ integral is immediate. The physical significance of this fact may be exhibited more clearly in the case of equation (4.20a) in the following way. If we make the substitution $\underset{\sim}{r}=\underset{\sim}{r}_{a}+y\underset{\sim}{q}_{ai}$, then $d\underset{\sim}{r}=\underset{\sim}{q}_{ai}dy$

and so equation (4.20a) may be written as

$$+\int d\tau\, \underset{\sim}{p}.\underset{\sim}{e}^{\perp} = \sum_{a,i} e_{ai} \int_{\underset{\sim}{r}_a}^{\underset{\sim}{R}_{ai}} d\underset{\sim}{r}.\underset{\sim}{e}^{\perp}(\underset{\sim}{r}), \qquad (4.20b)$$

which is obviously the line integral of the transverse electric field strength evaluated along the path from the centre of mass $\underset{\sim}{r}_a$ to the particle coordinate $\underset{\sim}{R}_{ai}$, multiplied by the charge of the particle. If the electric field is essentially constant over the molecule, $\underset{\sim}{e}^{\perp}(\underset{\sim}{r})$ may be taken out of the integrand, so that the integral reduces to the vector displacement of $\underset{\sim}{R}_{ai}$ from $\underset{\sim}{r}_a$ i.e. $\underset{\sim}{q}_{ai}$, and the resulting expression is just the first term of the R.H.S. of equation (3.4). Presumably a similar argument applies to equation (4.21a) though we have not been able to find the corresponding line integral.

These results are of course independent of the representation we use, but if for definiteness we choose the interaction representation we may introduce the usual plane wave expansions of the fields $\underset{\sim}{e}(\underset{\sim}{r})$ and $\underset{\sim}{b}(\underset{\sim}{r})$ into the expressions for the multipole potential. In this case the spatial dependence of the fields is of the form $\underset{\sim}{A}(\underset{\sim}{r}_a)\exp(\pm i\underset{\sim}{k}.\underset{\sim}{q}_{ai})$ and so if we write $\langle q_{ai} \rangle$ for the average 'radius' of the molecular system, it is clear that the dipole approximation will be valid when $\langle q_{ai} \rangle / \lambda \to 0$, as we noted on page 39. If this condition does not obtain then the earlier calculations in the dipole approximation [7 - 10] must be suitably modified to take account of the contributions of the

higher multipoles. The generalization may be carried out quite simply using equations (4.20a) and (4.21a) provided that these more general potentials behave suitably under spatial averaging, and that virtual photon processes give rise to no difficulties. We shall examine these two questions in turn in the following sections. Note however that if we use equation (4.21a) we must appreciate two points; firstly, whilst the introduction of the anticommutator ensures the Hermiticity of the operator it is an arbitrary device which may not be reliable, and secondly, since in quantum mechanics the angular momentum operator $\underline{l}_{ai}$ in the coordinate representation is a differential operator that acts on $\underline{q}_{ai}$, we must perform the integral over $\underline{y}$ before evaluating the anticommutator.

4.3 On Spatial Averages Involving Multipoles of Arbitrary Order.

The S-matrix theory of optical birefringence [9, 10], was developed in the dipole approximation with the neglect of intermolecular forces. This latter assumption enabled the polarization characteristics of the emergent light beam to be calculated as the isotropic spatial average of the relevant R-matrix element unless molecular orientation was induced by the light beam or by an external field, in which case a Boltzmann weighted average was required. To extend the theory to include multipoles of arbitrary order it is however necessary to first re-examine the details of the averaging procedure. For simplicity we consider only two photon processes as it will become evident that all the earlier conclusions still hold in the general case.

Since the photon annihilation and creation operators will contribute only numerical factors to the R-matrix element we shall include them in the normalization factors and write explicitly only the essential parts of the expansions of the field variables,

$$\underset{\sim}{e}^{\perp}(\underset{\sim}{r}) = B\ \hat{e}(\pi)\exp(\pm i\underset{\sim}{k}.\underset{\sim}{r}) \tag{4.22}$$

$$\underset{\sim}{b}(\underset{\sim}{r}) = C\ \underset{\sim}{k}_{\lambda} \wedge \hat{e}(\pi)\exp(\pm i\underset{\sim}{k}.\underset{\sim}{r}) \tag{4.23}$$

where $\pi = 1$ or 2, and the vectors $\hat{e}(1)$, $\hat{e}(2)$ and $\underset{\sim}{k}_{\lambda}$ form an orthogonal set in the sense that

$$\hat{e}(1).\hat{e}(2) = \hat{e}(1).\underset{\sim}{k}_{\lambda} = \hat{e}(2).\underset{\sim}{k}_{\lambda} = 0$$

$$\underset{\sim}{k}_\lambda \wedge \hat{e}(1) = -k_\lambda \hat{e}(2)$$

$$\underset{\sim}{k}_\lambda \wedge \hat{e}(2) = k_\lambda \hat{e}(1) \qquad (4.24)$$

with $k_\lambda = |\underset{\sim}{k}_\lambda|$. B and C are the normalization constants which need not be further specified in this analysis.

When considering scattering from a single molecule $\underline{a}$, we may adopt the position vector of the centre of mass, $\underset{\sim}{r}_a$, as the coordinate origin, and so combining equations (4.20a) and (4.22), and (4.21a) and (4.23), we obtain the interaction potentials as,

$$V(\underset{\sim}{e}^{\perp}) = B\int_0^1 dy V(\underset{\sim}{e}^{\perp}_y) \; ; \; V(\underset{\sim}{b}) = C\int_0^1 y\,dy\,V(\underset{\sim}{b}_y) \qquad (4.25)$$

with

$$V(\underset{\sim}{e}^{\perp}_y) = \sum_i e_i \underset{\sim}{q}_i . \hat{e}(\pi)\exp(\pm iy\underset{\sim}{k}.\underset{\sim}{q}_i) \qquad (4.26)$$

$$V(\underset{\sim}{b}_y) = \sum_i (e_i/2m_i)\left\{\underset{\sim}{k}_\lambda \wedge \hat{e}(\pi)\right\}^r \left\{1_i^r, \exp(\pm iy\underset{\sim}{k}.\underset{\sim}{q}_i)\right\}_+ \qquad (4.27)$$

Let us assume that both photon interactions are caused by $V(\underset{\sim}{e}^{\perp})$ and are of $\hat{e}(1)$ polarization; as we shall see the results for all other cases may be deduced immediately from the analysis of this case. The part of the R-matrix element which is involved in the averaging may be written as (c.f. [9])

$$I = \left\langle m\left|\sum_i e_i \underset{\sim}{q}_i . \hat{e}(1)\exp(iy\underset{\sim}{k}.\underset{\sim}{q}_i)\right| f\right\rangle \left\langle f\left|\sum_j e_j \underset{\sim}{q}_j . \hat{e}(1)\exp(-iy'\underset{\sim}{k}.\underset{\sim}{q}_j)\right| m\right\rangle \qquad (4.28)$$

and as before, the average may be most easily performed with the aid of spherical tensors [9] .

We recall that in the spherical basis we have the

following relations for the components of a vector $\underset{\sim}{q}$;

$$\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}(1) = (i/\sqrt{2})(q^{1} + q^{-1}) \tag{4.29}$$

$$\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}(2) = -(1/\sqrt{2})(q^{1} - q^{-1}) \tag{4.30}$$

$$\underset{\sim}{q}\cdot\underset{\sim}{k}_{\lambda} = k_{\lambda}q^{0}. \tag{4.31}$$

We shall also require the transformation rule for spherical tensors of rank j under rotations,

$$A(j)^{m} = \sum_{m'} D^{(j)}_{mm'}(\Omega)A(j)^{m'} \tag{4.32}$$

where Ω specifies the Euler angles of the rotation, and $D(\Omega)$ is a Wigner rotation matrix, and the usual plane-wave expansion formula

$$\exp(\pm i\underset{\sim}{k}\cdot\underset{\sim}{r}) = \sum_{n}(\pm i)^{n}(2n+1)j_{n}(kr)D^{(n)}_{00}(\Omega) . \tag{4.33}$$

where $j_{n}(kr)$ is a spherical Bessel function [50] .

Using equation (4.29) we now transform I to the spherical basis, so that

$$\begin{aligned} I = -\tfrac{1}{2}\Big\{ &\langle m|\sum_{i} e_{i}q_{i}^{1}\exp(iy\underset{\sim}{k}\cdot\underset{\sim}{q}_{i})|f\rangle\langle f|\sum_{j} e_{j}q_{j}^{1}\exp(-iy'\underset{\sim}{k}\cdot\underset{\sim}{q}_{j})|f\rangle \\ &+\langle m|\sum_{i} e_{i}q_{i}^{-1}\exp(iy\underset{\sim}{k}\cdot\underset{\sim}{q}_{i})|f\rangle\langle f|\sum_{j} e_{j}q_{j}^{1}\exp(-iy'\underset{\sim}{k}\cdot\underset{\sim}{q}_{j})|f\rangle \\ &+\langle m|\sum_{i} e_{i}q_{i}^{1}\exp(iy\underset{\sim}{k}\cdot\underset{\sim}{q}_{i})|f\rangle\langle f|\sum_{j} e_{j}q_{j}^{-1}\exp(-iy'\underset{\sim}{k}\cdot\underset{\sim}{q}_{j})|f\rangle \\ &+\langle m|\sum_{i} e_{i}q_{i}^{-1}\exp(iy\underset{\sim}{k}\cdot\underset{\sim}{q}_{i})|f\rangle\langle f|\sum_{j} e_{j}q_{j}^{-1}\exp(-iy'\underset{\sim}{k}\cdot\underset{\sim}{q}_{j})|f\rangle\Big\}. \end{aligned} \tag{4.34}$$

Let us examine the third term of equation (4.34) which we call I', using equations (4.32) and (4.33);

$$I' = \sum_n \sum_{n'} \sum_{m_1} \sum_{m_2} i^{n-n'}(2n+1)(2n'+1)\left\langle m\left|\sum_i e_i q_i^{m_1} j_n(kyq_i)\right|f\right\rangle$$

$$\times \left\langle f\left|\sum_j e_j q_j^{m_2} j_{n'}(ky'q_j)\right|m\right\rangle D^{(1)}_{1m_1}(\Omega) D^{(1)}_{-1m_2}(\Omega) D^{(n)}_{00}(\Omega) D^{(n')}_{00}(\Omega). \tag{4.35}$$

Here we have chosen Ω as the angle between the (space fixed) vector $\underset{\sim}{k}$, and the (molecule fixed) vectors $\underset{\sim}{q}$.

The spatial average of I' may now be written as

$$\langle I' \rangle = \int I(\Omega) d\Omega \Big/ \int d\Omega \,. \tag{4.36}$$

To proceed further we use the contraction rule for the Wigner rotation matrices [50],

$$D^{(j)}_{mm'}(\Omega) D^{(j')}_{ss'}(\Omega) = \sum_J (2J+1) \begin{pmatrix} j & j' & J \\ m & s & M \end{pmatrix} \begin{pmatrix} j & j' & J \\ m' & s' & M' \end{pmatrix} D^{(J)}_{MM'}(\Omega)^*$$

where the $\begin{pmatrix} j & j' & J \\ m & s & M \end{pmatrix}$ are 3-j symbols, and the property

$$D^{(J)}_{MM'}(\Omega)^* = (-1)^{M-M'} D^{(J)}_{-M-M'}(\Omega)$$

to write

$$D^{(1)}_{1m_1}(\Omega) D^{(n)}_{00}(\Omega) = \sum_M (2M+1) \begin{pmatrix} 1 & n & M \\ 1 & 0 & m \end{pmatrix} \begin{pmatrix} 1 & n & M \\ m_1 & 0 & m' \end{pmatrix} D^{(M)}_{mm'}(\Omega)^* \tag{4.37}$$

and

$$D^{(1)}_{-1m_2}(\Omega) D^{(n')}_{00}(\Omega) = \sum_K (2K+1) \begin{pmatrix} 1 & n' & K \\ -1 & 0 & s \end{pmatrix} \begin{pmatrix} 1 & n' & K \\ m_2 & 0 & s' \end{pmatrix} (-1)^{s-s'} D^{(K)}_{-s-s'}(\Omega). \tag{4.38}$$

The conditions that ensure that the 3-j symbols in equations (4.37) and (4.38) do not vanish are

$$m = -1, \; m_1 = -m'$$

$$|n-1| \leqslant M \leqslant n+1 \ , \tag{4.37a}$$

$$s = 1, \quad m_2 = -s'$$

$$|n'-1| \leqslant K \leqslant n'+1 \ . \tag{4.38a}$$

The rotation matrices have the following orthogonality property,

$$\int d\Omega D^{(j)}_{mm'}(\Omega) D^{(j')}_{ss'}(\Omega)^* = 8\pi^2(2j+1)^{-1} \delta_{jj'} \delta_{ms} \delta_{m's'} \tag{4.39}$$

and so collecting together all these relations we obtain $\langle I' \rangle$ as

$$\langle I' \rangle = -\sum_n \sum_{n'} \sum_{m_1} \sum_{m_2} \sum_M \sum_K i^{n-n'} (2n+1)(2n'+1)(2K+1)(-1)^{m_2} \delta_{MK} \delta_{m_2 - m_1}$$

$$\times \begin{pmatrix} 1 & n & M \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & n & M \\ m_1 & 0 & -m_1 \end{pmatrix} \begin{pmatrix} 1 & n' & K \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & n' & K \\ m_2 & 0 & -m_2 \end{pmatrix}$$

$$\times \langle m | \sum_i e_i q_i^{m_1} j_n(kyq_i) | f \rangle \langle f | \sum_j e_j q_j^{m_2} j_{n'}(ky'q_j) | m \rangle \tag{4.40}$$

The sum over $\underline{m}_2$ is immediate and if we sum over $\underline{K}$ it is clear that for the inequalities in equations (4.37a) and (4.38a) to be satisfied we must have $\underline{n} = \underline{n}'$, which reduces the sum over $\underline{n}'$ to one term. Noting that the 3-j symbols have the following symmetry property

$$\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & M \end{pmatrix} = (-1)^{m_1+m_2+M} \begin{pmatrix} j_1 & j_2 & J \\ M & m_2 & m_1 \end{pmatrix} \tag{4.41}$$

we finally obtain $\langle I' \rangle$ as

$$\langle I' \rangle = -\sum_n \sum_{m_1} \sum_M (2n+1)^2(2M+1)(-1)^{m_1} \begin{pmatrix} 1 & n & M \\ 1 & 0 & -1 \end{pmatrix}^2 \begin{pmatrix} 1 & n & M \\ m_1 & 0 & -m_1 \end{pmatrix}^2$$

$$\times \langle m|\sum_i e_i q_i^{m_1} j_n(kyq_i)|f\rangle\langle f|\sum_j e_j q_j^{-m_1} j_n(ky'q_j)|m\rangle \qquad (4.42)$$

It is now quite straightforward to calculate the averages of the remaining terms in equation (4.34) and we find that the first and last terms vanish, whilst the average of the second term is exactly the same as the expression given in equation (4.42), so that

$$\langle I \rangle = \sum_n \sum_{m_1} \sum_M (2n+1)^2(2M+1)(-1)^{m_1} \begin{pmatrix} 1 & n & M \\ 1 & 0 & -1 \end{pmatrix}^2 \begin{pmatrix} 1 & n & M \\ m_1 & 0 & -m_1 \end{pmatrix}^2$$

$$\times \langle m|\sum_i e_i q_i^{m_1} j_n(kyq_i)|f\rangle\langle f|\sum_j e_j q_j^{-m_1} j_n(ky'q_j)|m\rangle \; . \qquad (4.43)$$

We may now summarize the rules for averages of matrix elements containing multipoles of arbitrary order:

i) if both photons have the same polarization then both interactions must be mediated by the same type of interaction potential i.e. both interactions must be either electric field induced, or magnetic field induced. We conclude therefore that

ii) for a polarization 'flip' to occur i.e. one photon of $\hat{e}(1)$ polarization and the other of $\hat{e}(2)$ polarization, one interaction must be associated with the electric field whilst the other is associated with the magnetic field (c.f. page 42),

iii) These rules only apply to isotropic spatial averages

of R-matrix elements. It is clear that these rules follow simply from the form of equations (4.29) and (4.30) which determine the signs of those terms that survive the spatial averaging, and from equation (4.24) which leads to rule (ii) because after using this equation the resulting quantity to be averaged is once more of the form of equation (4.28). An important feature of equation (4.43) is that it consists of a product of matrix elements of multipoles of the same order. The calculations of Atkins et al. [9, 10] may thus be generalized to include multipoles of arbitary order without great difficulty, and as far as these calculations are concerned the multipole hamiltonian is in no way inferior to the conventional gauge dependent interaction hamiltonian (c.v. [16], where the opposite opinion is expressed).

If however, we wish to extend the calculation on optical activity presented in the previous chapter to take account of higher multipoles, we require a slight extension of the above analysis. We may introduce the complete multipole hamiltonian into the algebraic interpretations of the diagrams but since it is no longer permissible to drop the exponential factors associated with the external field vertices, we shall have to deal with a 'two-centre' average. Equation (3.21) must now be modified to read

$$\langle M \rangle = \langle \underset{\sim}{a}.\hat{e}(u)\underset{\sim}{b}.\hat{e}(v)\exp(-i\underset{\sim}{\omega}.\underset{\sim}{R}_{ab}) \rangle \qquad (4.44)$$

where $\underset{\sim}{\omega}$ is the wave-vector of the incident radiation. This

average may be calculated using the techniques outlined above if the exponential factor is expanded using equation (4.33) which however introduces an extra summation into the calculation. From the properties of the spherical Bessel functions it is clear that for physically realistic values of ωR_{ab}, this sum will be dominated by the first term since $j_o(\omega R_{ab})$ is ~ 1, and all higher order Bessel functions are ~ 0 for small arguments ($\lesssim 0.3$). To this approximation therefore the average reduces to the expression we would have obtained by neglecting the exponential factor in the first place, so that in practice such 'two-centre' averages need not be considered, and the calculation with the complete multipole hamiltonian proceeds in close correspondence with the calculation outlined in Chapter 3.

4.4 Multipolar Interactions and Virtual Photon Processes.

We saw in Chapter 3 that the effect of the electric field of a neutral molecular system on a neighbouring group could be described in a natural way by means of the exchange of a virtual photon. This conclusion is also evident from calculations on long range intermolecular forces in which the exchange of two virtual photons accounts for the (retarded) dispersion forces between molecules [7], [47] . Only the dipole-dipole interaction has been considered so far however and we must now deal with the more general case when multipoles of arbitrary order are involved. We shall illustrate the extension of the theory in the context of the calculation described in Chapter 3.

If we use the multipole hamiltonian of equations (4.25) and (4.26), then the relevant part of the algebraic interpretation of the diagram shown in Figure 5 may be written as (c.f. page 50)

$$Q = \sum_{\underset{\sim}{k}} \sum_{f,f'} (k/w-k) \int_0^{'} dy \int_0^{'} dy' \; \langle f | \sum_i e_i \underset{\sim}{q}_i . \hat{e}(\alpha) \exp(-iy \underset{\sim}{k} . \underset{\sim}{q}_i) | m \rangle$$

$$\times \langle m' | \sum_j e_j \underset{\sim}{q}'_j . \hat{e}(\alpha) \exp(iy' \underset{\sim}{k} . \underset{\sim}{q}'_j) | f' \rangle \exp(-i \underset{\sim}{k} . \underset{\sim}{R}_{ab}) \qquad (4.45)$$

where the prime indicates that the appropriate quantity is associated with group b. As before we invoke equations (3.20) and (3.23) to write Q in the form

$$Q = \int_0^\infty dk \int d\Omega(\underset{\sim}{k})(k^3/w - k) \int_0^t dy \int_0^t dy' \; (\underset{\sim}{1} - \hat{k}\hat{k})_{vt} \exp(-i\underset{\sim}{k}.\underset{\sim}{R}_{ab})$$

$$\times \sum_{f,f'} \langle f|\sum_i e_i q_i^t \exp(-iy\underset{\sim}{k}.\underset{\sim}{q}_i)|m\rangle\langle m'|\sum_j e_j q_j'^v \exp(iy'\underset{\sim}{k}.\underset{\sim}{q}_j')|f'\rangle . \quad (4.46)$$

Note that we would obtain the corresponding expression for a Type B diagram by putting $w = 0$ and $f' = m'$.

It is very difficult to assess accurately the behaviour of this expression for $\underset{\sim}{Q}$ because we know nothing about the analytic properties of the molecular integrals and the sum over the excited states. If we suppose however that it is permissible to interchange the order of the integrations so as to perform the $\underset{\sim}{k}$ integral first, then it is clear that the integrand diverges at large $\underset{\sim}{k}$ values and so the calculation breaks down. But it may very well be that this manipulation is invalid because the integrand does not satisfy the requisite conditions of continuity in the variables. Then to effect the integral over the photon wave vector we are forced to use the expansion in equation (4.20) instead of equations (4.25) and (4.26), and if we do so we finally obtain an expression for $\underset{\sim}{Q}$ which consists of the sum of the expectation values of multipoles of increasing order contracted on to derivatives (of the same order) of the coupling tensor $\underset{\sim}{\mathcal{T}}(a,b;x)$ defined in equation (3.36), or alternatively when $w = 0$, derivatives of the tensor $\underset{\sim}{T}(a,b)$ defined in equation (3.59). The latter series is clearly an expansion of (e^2/R_{ij}) in inverse powers of R_{ab} (see Figure 3), and its expectation value has been

evaluated in several simple cases. Jansen, using Gaussian and simple exponential basis functions found that the series diverged for large values of $\underline{R}$ and was only asymptotic in the sense of Poincaré [51] . Presumably the corresponding series involving $\underset{\sim}{\tau}(a,b;x)$ would behave in a similar way.

There is therefore some doubt as to whether it is meaningful to extend calculations involving virtual photons in this way. We should however bear in mind that whilst the entire theory has been developed within the framework of the non-relativistic approximation and so cannot be expected to describe high energy phenomena, when dealing with virtual photons we are required to consider all values of $\underline{k}$ from 0 to ∞. A possible way to circumvent this difficulty in a manner consistent with the non-relativistic approximation is to introduce a finite upper limit, k_{max}, into the $\underline{k}$ integral. One usually chooses k_{max} to have a value about the Compton wavelength for an electron $(mc/\hbar)$ [7] , but this device can hardly be considered satisfactory in view of its ad hoc nature. We shall defer further comment until Chapter 5.

CHAPTER 5

DISCUSSION

In our development of the equations describing the coupled system of charged particles and the electromagnetic field (Chapter 2) we made the point that in the classical theory there were no solutions of these equations that corresponded to the aggregates of particles called 'molecular systems', but we expressed the hope that the introduction of the quantum theoretical axioms would change the nature of the solutions in the same way as is found for example in the elementary discussion of the hydrogen atom, when the transition from the classical to the quantum mechanical theory is made.

In Chapter 3 however we stated that the hamiltonian for the total system of molecules and field could not be diagonalized so that we would have to resort to perturbation theory to perform calculations. We then gave a detailed account of a calculation on the optical activity of molecular systems using quantum electrodynamics and the S-matrix theory of Atkins and Barron [9] within the context of the independent group model first introduced by Kirkwood [23] . In the dipole approximation we found agreement with the well known results of Tinoco [24] , but later found in Chapter 4 that if we attempted to generalize the calculations to take account of higher multipolar interactions between the individual subsystems we encountered difficulties associated with virtual photon processes.

In the following we wish to examine these problems

further but first it will be useful to indicate the close relationship between the multipole hamiltonian developed in Chapter 2, and the conventional hamiltonian expressed in terms of the vector potential and the kinetic momentum of the particles. Our later comments on the current state of molecular quantum electrodynamics will the be of quite general application.

We have already mentioned that the conventional quantum mechanical hamiltonian for the system of charged particles plus electromagnetic field is related to the multipole hamiltonian by a unitary transformation. This transformation has been discussed by several authors [4 - 7, 12 - 14] but only the account given by Power [7] can be regarded as satisfactory. Power and Zienau [6] showed that the earlier discussions of the transformation [4, 5] were incomplete because they were ambiguous about the exact definition of the electric field intensity operator (inter alia this criticism may also be made of the other derivations [12 - 14] mentioned above), but their account differs from the later published version [7] in that the two hamiltonians given in reference [6] contain a term $U(q_\alpha)$ which is supposed to describe the intramolecular electron-electron and electron-nuclear electrostatic interaction whereas this term is missing from the later version which we believe to be the correct one for the reasons outlined below. Although Fiutak [12] and Kielich [13] obtain multipole hamiltonians, both of them regard the

molecules as prescribed charge distributions interacting with an external field and thus their work is merely an extension of the earlier work of Goeppert-Mayer and Richards [4, 5]. Furthermore their considerations are restricted to a classical electromagnetic field as the external perturbation.

In the Coulomb gauge the conventional quantum mechanical hamiltonian for a system composed of charged particles and the electromagnetic field may be written as,

$$H = \tfrac{1}{2}\sum_{a,i}(1/m_{ai})p_{ai}^2 - \sum_{a,i}(e_{ai}/m_{ai})\underset{\sim}{p}_{ai}\cdot\underset{\sim}{a}(\underset{\sim}{R}_{ai}) + \tfrac{1}{2}\sum_{a,i}(e_{ai}^2/m_{ai})a(\underset{\sim}{R}_{ai})^2 + \tfrac{1}{2}\epsilon_o\int d\tau\,(\underset{\sim}{e}\cdot\underset{\sim}{e} + c^2\underset{\sim}{b}\cdot\underset{\sim}{b}) \qquad (5.1)$$

in the notation employed previously. The only points we wish to emphasize here are that $\underset{\sim}{e}$ is the total electric field intensity operator, and that in the Coulomb gauge the order of the factors $\underset{\sim}{p}_{ai}$ and $\underset{\sim}{a}(\underset{\sim}{R}_{ai})$ is immaterial since their commutator is proportional to Div$\underset{\sim}{a}$. We claim that the longitudinal part of the electric field intensity operator in this expression describes completely both the intramolecular and intermolecular electrostatic interactions. This follows from the fact that in this gauge $\underset{\sim}{e}^{\shortparallel}$ is equal to $-\nabla\phi$ and consequently it is a straightforward matter to demonstrate that

$$\int d\tau\,\underset{\sim}{e}^{\shortparallel}\cdot\underset{\sim}{e}^{\shortparallel} = \sum_{i>j} e_i e_j/R_{ij}\,, \quad R_{ij} = |\underset{\sim}{R}_i - \underset{\sim}{R}_j| \qquad (5.2)$$

where the sum is taken over all the particles (c.f. the discussion in Landau and Lifshitz, section 37: [52]), so that a term of the form $U(q_\alpha)$ would seem to be redundant. Equation (5.1) is to be compared with the multipole hamiltonian given in equation (2.73) which for convenience we repeat here,

$$H' = \tfrac{1}{2}\sum_{a,i}(1/m_{ai})p_{ai}^2 + \tfrac{1}{2}\epsilon_o\int d\tau(\underset{\sim}{e}^{\perp}.\underset{\sim}{e}^{\perp} + c^2\underset{\sim}{b}.\underset{\sim}{b}) - \int d\tau \underset{\sim}{m}'.\underset{\sim}{b}$$
$$- \int d\tau \underset{\sim}{p}.\underset{\sim}{e}^{\perp} + \tfrac{1}{2}\sum_{a,i}(1/m_{ai})Q_{ai}^2 + (1/2\epsilon_o)\int d\tau p^2 \,. \qquad (5.3)$$

In the Heisenberg representation at a given instant in time the two hamiltonians are related by a unitary transformation induced by the operator $\Lambda = \exp(-iS/\hbar)$ where

$$S = \int d\tau \underset{\sim}{p}(\underset{\sim}{x}).\underset{\sim}{a}(\underset{\sim}{x}) \,. \qquad (5.4)$$

subject to the condition $a_r{}'^r(\underset{\sim}{x}) = 0$, so that we may write

$$H(t)' = \Lambda H(t)\Lambda^{-1} \qquad (5.5)$$

$$|\Psi(t)\rangle' = \Lambda|\Psi(t)\rangle \,. \qquad (5.6)$$

A straightforward application of the argument given in section 4.2 (page 78) that lead from equation (4.20) to equation (4.20b) enables us to write the transformation operator in the form

$$\Lambda = \exp\left\{(i/\hbar)\sum_{a,i}e_{ai}\int_{\underset{\sim}{R}_{ai}}^{\underset{\sim}{r}_a} d\underset{\sim}{r}.\underset{\sim}{a}(\underset{\sim}{r})\right\} \qquad (5.7)$$

where we have changed the sign of the integral by inverting the limits; this is possible with a path integral provided always that we traverse the same path (note that Curl $\underset{\sim}{a}$ is the magnetic induction ($\underset{\sim}{b}$) which is not zero and so the value of the integral depends on the path traversed). Combining equations (5.6) and (5.7) we therefore obtain

$$|\Psi(t)\rangle' = \exp\left\{(i/\hbar)\sum_{a,i} e_{ai}\int_{\underset{\sim}{R}_{ai}}^{\underset{\sim}{r}_a} d\underset{\sim}{r}.\underset{\sim}{a}(\underset{\sim}{r})\right\}|\Psi(t)\rangle \quad . \qquad (5.8)$$

Equation (5.8) shows that the unitary transformation changes the phase of the state vector $|\Psi(t)\rangle$ in obvious analogy to the phase change first described by Aharonov and Bohm [53] ; in this case the phase changes by an amount that would arise from the transfer of each particle in an aggregate $\underset{\sim}{a}$ from its position at $\underset{\sim}{R}_{ai}$ to the centre of mass $\underset{\sim}{r}_a$, in the presence of the electromagnetic field described by the vector potential $\underset{\sim}{a}(\underset{\sim}{r})$. Since the centre of mass at $\underset{\sim}{r}_a$ is assumed to be at rest, it is clear that in the new description the effects that arose from the distribution of charges in each neutral aggregate must be incorporated elsewhere; that is, in the field. This view is consistent with and provides a physical picture of the process of incorporating the entire molecule and its fields in redefined modes of the electromagnetic field which was the idea that prompted Power and Zienau's original considerations [6] . Now clearly a term of the form $U(q_\alpha)$ would commute with Λ , but its occurrence in the new

hamiltonian H' would be inconsistent with the above interpretation of the transformation since as we have just seen this formally eliminates the finite extension of the molecular charge distribution $\underline{a}$, in favour of a superposition of point multipoles located at the centre of mass $\underline{r}_a$. Thus there appears to be no place for this term in either of the two hamiltonians.

We now observe that it is possible to invert the above interpretation of the transformation in the sense that if we wish to pass from the description afforded by H and $|\Psi(t)\rangle$ to the new description in terms of H' and $|\Psi(t)\rangle'$ then we need only recognize that a multipole expansion replaces the expression for a charge distribution of finite extent by an expression that is only defined at the centre of mass (e.g. $\underline{r}_a$) so that we are required to change the phase of the state vector $|\Psi(t)\rangle$ by an amount $(-S/\hbar)$ since the state vector is the probability amplitude that the components of the system will be found in some configuration at the time t. This phase change is precisely the effect of the unitary transformation induced by the operator Λ. We have therefore obtained an alternative method of finding the required transformation operator to the argument put forward by Power and Zienau which followed from an examination of the nature of the false static terms that occur in the expectation value of the transverse electric field intensity operator when the hamiltonian H in

equation (5.1) is employed [6] .

It is of interest that this new interpretation of the transformation as a phase shift induced by the operator $\wedge$ is purely quantum mechanical in nature [54] : there is clearly no analogous classical interpretation of equations (5.6) and (5.7). We mention this point because the classical canonical transformation studied by Fiutak [12] is formally identical to equations (5.4) and (5.5). On the other hand there is a close connection between the classical lagrangians that lead to the two hamiltonians, since the lagrangian from which the hamiltonian H is derived may be written,

$$L = \tfrac{1}{2}\sum_{a,i} m_{ai}\dot{q}_{ai}^2 - \int d\tau\, j_\mu a^\mu - \tfrac{1}{4}\int d\tau\, f_{\mu\nu} f^{\mu\nu} \qquad (5.9)$$

and if we use the definition of j_μ and equations (2.1) and (2.7), it is not difficult to see that equations (2.24) and (5.9) differ only by a perfect time differential which is irrelevant as far as the variation of the action and the equations of motion are concerned. This perfect differential is in fact just S'^{o} where S is defined in equation (5.4). Furthermore there is an obvious analogy between the ansatz used by Power and Zienau [6] that the transformation should be such that $\wedge$ ensures that $\underset{\sim}{e}^{\perp}_{new} = \underset{\sim}{e}^{\perp}_{old} + \underset{\sim}{p}^{\perp}$, and the 'microscopic theory of dielectrics' which we took as one of our starting points (c.f. equation (2.6)).

We see from the above discussion that the electromagnetic

field plays a very important role in the description of the system in terms of H' and $|\Psi(t)\rangle'$, and that the particles are of less importance than in the conventional description. The usual Coulomb interaction terms in H (equation 5.2)) are in fact contained in the last term in equation (5.3), which is overall a self-energy term. Since we have used the Heisenberg representation in which attention is focussed on the operators rather than the wave function, and we have aimed at a description that exhibits explicitly the multipolar nature of the interaction between the electromagnetic field and molecular systems, it is hardly surprising that the notion of the 'electronic structure' of the molecules which forms the basis of all discussions of information derived from spectroscopy, makes no appearance at all in our formalism. Nevertheless we should still be able to relate the observables of spectroscopy to the expectation values of the field and particle operators. It is at this point however that we encounter the most important difficulty associated with electrodynamics. The fact is that there is no known set of basis functions in which the hamiltonian H (or H') is diagonal, so that we have no way of evaluating expectation values, and the question arises therefore as to the validity of the system of equations derived in Chapter 2.

Successful physical theories are by definition theories which when supplemented by the necessary correspondence rules describe observable phenomena in a satisfactory fashion.

Their importance is not that they 'explain' observations, an attribute which would necessarily involve circularity, but in their existence as logical deductive descriptive schemes. At first sight therefore it appears that the theory of molecular electrodynamics presented in Chapter 2 has a somewhat doubtful status, since we are not able to test it against observation, and therefore cannot justify the choice of the basic equation of the theory, the lagrangian of equation (2.24). We may however adopt perturbation theory to perform calculations for although there is the serious difficulty that we have no way of establishing the relationship of the perturbation theory solutions to the true solutions assuming that the latter exist, we may hopefully claim that the parent theory is satisfactory if the results of the perturbation theory are satisfactory.

A consideration of for example the hydrogen atom problem however shows that perturbation theory in electrodynamics has difficulties of its own. To a very high degree of accuracy the solution of the Dirac equation for an electron moving in the Coulomb field of a proton is in accord with the observed electronic spectrum of hydrogen. There is however a small splitting between levels of the atom with the same principal quantum number (e.g. the $^2 2S_{\frac{1}{2}}$ and $^2 2P_{\frac{1}{2}}$ levels) which is observed in the spectrum but not predicted by the theory; this is the so called Lamb shift. To account for the removal of the degeneracy of the levels one postulates that the electron

interacts with its own electric field, thereby causing a small energy shift. The theory however has now become part of electrodynamics since we have introduced the electromagnetic field. In the framework of perturbation theory the self-interaction may be pictured as the emission and reabsorption (or vice versa) of a 'virtual' photon. The explicit calculation of the energy shift due to this process leads one to divergent integrals which may be eliminated by carrying through the renormalization program, and in this way a finite splitting is predicted, the numerical magnitude of which is in good agreement with the observed value [55] .

One must recognize however that the renormalization program implies that the original primitive quantities of the theory such as the charge e_{ai} and mass m_{ai} of a particle are only parameters and are not to be identified with the experimental values, a situation which contrasts strongly with the conventional interpretation of the Schrodinger and Dirac equations even though they may be derived formally from quantum electrodynamics by making suitable approximations. Finally we note the curious way that the theory of electrodynamics is formulated: the lagrangian employed in Chapter 2 is built up from a term for the 'free' particles, a term for the 'free' field and a coupling term; and since there is nothing in the theory to determine the charge and mass spectrum of the particles involved in terms of fundamental constants, what does such a theory describe?

There are thus considerable difficulties associated with a strict interpretation of the theory of molecular electrodynamics. The above analysis shows that it is not really valid within the terms of the theory to suppose that an electromagnetic field (a light beam for example) can be switched on and off thereby causing a temporary perturbation of the molecule, though of course this is precisely the viewpoint of the experimentalist. The example of the hydrogen atom however suggests that it is a very good approximation to ignore self-interactions and if this is done then the perturbation theory becomes regular and reduces to the usual type. We thus have the situation that if we attempt to take account of the electromagnetic field properly we encounter physically insignificant but formally divergent quantities, whereas if we just regard the field as an external perturbation and do not worry about the logical consistency of the theory we are able to perform calculations quite successfully.

To conclude the discussion we would like to point out two features of the multipole hamiltonian. Firstly, the hamiltonian of equation (2.73) is gauge dependent in a non trivial sense even though it is apparently independent of the potentials. The point that is sometimes missed is that the canonical momentum and transverse electric field strength operators may be identified to within a multiplicative factor only because of the form of the commutation relation, equation (2.68) which was derived with the aid of the Coulomb gauge

condition. If we had chosen any other gauge condition in our analysis (page 28) we would still have obtained the hamiltonian of equation (2.67) but there would no longer be a clear interpretation of the canonical momentum operator $\underset{\sim}{\Pi}$, and it is unlikely that we would be able to find an explicit representation of this operator to use in perturbation theory. The fact that we nearly always use the perturbation theory described in Chapters 3 and 4 to perform calculations, rather than using the 'equations of motion' method is of course the main reason for the priveleged position of the Coulomb gauge condition in our theory.

A final point is that just as there is the difficulty of the gauge dependence of the perturbation terms, $\underset{\sim}{p}_{ai} \cdot \underset{\sim}{a}(\underset{\sim}{R}_{ai})$ and $a(\underset{\sim}{R}_{ai})^2$ which are derived from equation (5.1), so also there is the problem of the origin dependence of the multipolar interaction potential (c.f. section 4.2). The translation invariance of, for example, our results for the optical rotation angle, equations (3.50) and (3.69), is a consequence of the special form of these equations and could not have been guaranteed a priori for as is well known only the first non-zero multipole moment of a neutral system is origin independent.

APPENDIX I

Lagrangian Theory and the Equations of Motion.

We define a quantity S, called the action, by the integral relation

$$S = \int_{t_1}^{t_2} L(q, \dot{q}, t)dt \qquad (A.1)$$

and use the calculus of variations to find the extremum values of S for arbitrary variations of the coordinates and velocities. We now assert that for a suitable choice of L, the conditions that ensure that $\delta S = 0$, (the Euler-Lagrange equations) lead to the equations of motion for the system. For a system with a finite number of degrees of freedom the Euler-Lagrange equation is (c.f. equation (2.26)),

$$(d/dt)(\partial L/\partial \dot{q}) - (\partial L/\partial q) = 0. \qquad (A.2)$$

For systems with an infinite number of degrees of freedom such as a field, we modify the formalism slightly, and introduce a so called Lagrangian density $\mathcal{L} = \mathcal{L}(V, V'^{\alpha})$ in terms of the field variables V and their derivatives V'^{α}. The action integral is now written as

$$S = \int_{x_1}^{x_2} \mathcal{L}(V, V'^{\alpha})d\Omega \qquad d\Omega = d^3\underline{r}dt \qquad (A.3)$$

and the Euler-Lagrange condition is

$$(\partial \mathcal{L}/\partial V'^{\alpha})'^{\alpha} - (\partial \mathcal{L}/\partial V) = 0. \qquad (A.4)$$

According to equation (2.24) the lagrangian for electrodynamics

may be taken to be,

$$L = \tfrac{1}{2}\sum_{a,i} m_{ai}\dot{q}_{ai}^2 - \tfrac{1}{2}\int d\tau\left\{\tfrac{1}{2}f_{\mu\nu}f^{\mu\nu} + p_{\mu\nu}f^{\mu\nu}\right\} \qquad (A.5)$$

in which the dynamical variables for the particles are the $\underset{\sim}{q}_{ai}$ and the $\dot{\underset{\sim}{q}}_{ai}$, and we take the 4-potential a_μ as the field variable V. In making the variations of the action integral we assume that the field and particle variables are independent.

If we use the definition of the field tensor $f_{\mu\nu}$ in terms of the 4-potential, equation (2.1), and combine equations (A.4) and (A.5), the field equations $(f_{\mu\nu} + p_{\mu\nu})^{,\nu} = 0$ follow at once since only the first term in equation (A.4) contributes.

The equations of motion for the particles may be obtained from the lagrangian L' derived from L by omitting all terms that are independent of the particle variables and inserting the potentials in place of $\underset{\sim}{e}$, $\underset{\sim}{e} = -\dot{\underset{\sim}{a}} - \partial\phi$ c.f. equation (2.2). When the multipole expansions of p_r and m_r are introduced by means of equations (2.8), (2.20) and (2.23) and the integrations performed we obtain

$$\begin{aligned} L' = {} & \tfrac{1}{2}\sum_{a,i} m_{ai}\dot{q}_{ai}^2 - \sum_{a,i} e_{ai}\phi(\underset{\sim}{R}_{ai}) \\ & - \sum_{a,i} e_{ai}\sum_n \left\{1/(n+1)!\right\}(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^n \underset{\sim}{q}_{ai}\cdot\dot{\underset{\sim}{a}}(\underset{\sim}{r}_a) \\ & + \sum_{a,i} e_{ai}\sum_n \left\{n/(n+1)!\right\}(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\epsilon_{rst}\, b^r(\underset{\sim}{r}_a) q_{ai}^s \dot{q}_{ai}^t . \end{aligned} \qquad (A.6)$$

Since

$$\epsilon_{rsm}\epsilon_{rtv} = \delta_{st}\delta_{mv} - \delta_{sv}\delta_{mt} \qquad (A.7)$$

and

$$\dot{b}_r(\underset{\sim}{r}_a) = \epsilon_{rtv}\partial^t \dot{a}^v(\underset{\sim}{r}_a) \tag{A.8}$$

we may deduce that

$$(d/dt)(\partial L/\partial q^p_{ai}) = m_{ai}\ddot{q}_{aip} + e_{ai}\sum_n \left\{n/(n+1)!\right\}\left\{(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\epsilon_{rsp}b^r(\underset{\sim}{r}_a)q^s_{ai}\right.$$

$$+ \epsilon_{rsp}(n-1)(\dot{\underset{\sim}{q}}_{ai}\cdot\underset{\sim}{\partial})(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-2}q^s_{ai}b^r(\underset{\sim}{r}_a) + (\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^n\dot{a}_p(\underset{\sim}{r}_a)$$

$$\left. - (\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\partial_p\underset{\sim}{q}_{ai}\cdot\dot{\underset{\sim}{a}}(\underset{\sim}{r}_a)\right\} \tag{A.9}$$

and also

$$(\partial L/\partial q^p_{ai}) = -e_{ai}\partial_p\phi(\underset{\sim}{R}_{ai}) + e_{ai}\sum_n \left\{n/(n+1)!\right\}\left\{(n-1)(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-2}\epsilon_{rst}\right.$$

$$\times\ \partial_p b^r(\underset{\sim}{r}_a)q^s_{ai}\dot{q}^t_{ai} + \epsilon_{rpt}(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\dot{q}^t_{ai}b^r(\underset{\sim}{r}_a)\Big\}$$

$$-e_{ai}\sum_n \left\{1/(n+1)!\right\}\left\{n(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\partial_p\underset{\sim}{q}_{ai}\cdot\dot{\underset{\sim}{a}}(\underset{\sim}{r}_a) + (\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^n\dot{a}_p(\underset{\sim}{r}_a)\right\} \tag{A.10}$$

With the use of the relation in equation (A.7) these two expressions may be combined into an Euler-Lagrange equation of the form

$$m_{ai}\ddot{q}_{aip} + e_{ai}\partial_p\phi(\underset{\sim}{R}_{ai}) + e_{ai}(\partial/\partial t)a_p(\underset{\sim}{R}_{ai})$$

$$+ e_{ai}\sum_n \left\{n/(n+1)!\right\}(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-2}\left\{(n-1)\epsilon_{rsp}(\dot{\underset{\sim}{q}}_{ai}\cdot\underset{\sim}{\partial})q^s_{ai}b^r(\underset{\sim}{r}_a)\right.$$

$$\left. - (n-1)\epsilon_{rst}\partial_p q^s_{ai}\dot{q}^t_{ai}b^r(\underset{\sim}{r}_a) + 2\epsilon_{rsp}(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})\dot{q}^s_{ai}b^r(\underset{\sim}{r}_a)\right\} = 0. \tag{A.11}$$

But since according to equation (2.2) $\underset{\sim}{\partial}\cdot\underset{\sim}{b} = 0$, we may write

$$I_p \equiv \epsilon_{rsp}(\dot{\underset{\sim}{q}}_{ai}\cdot\underset{\sim}{\partial})q^s_{ai}b^r(\underset{\sim}{r}_a) - \epsilon_{rst}\partial_p q^s_{ai}\dot{q}^t_{ai}b^r(\underset{\sim}{r}_a) - \epsilon_{rsp}(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})\dot{q}^s_{ai}b^r(\underset{\sim}{r}_a)$$

$$= 0. \tag{A.12}$$

The proof of this result depends upon the relation

$$\partial_p(\dot{q}^p_{ai}q^s_{ai} - \dot{q}^s_{ai}q^p_{ai}) = \epsilon^{psu}\partial_p(\dot{\underset{\sim}{q}}_{ai} \wedge \underset{\sim}{q}_{ai})_u \qquad (A.13)$$

so that

$$I_p = \epsilon_{rsp}\epsilon_{tsu}\partial_t(\dot{\underset{\sim}{q}}_{ai} \wedge \underset{\sim}{q}_{ai})^u b^r(\underset{\sim}{r}_a) - \epsilon_{rst}\partial_p q^s_{ai}\dot{q}^t_{ai}b^r(\underset{\sim}{r}_a)$$

$$=(\delta_{rt}\delta_{pu} - \delta_{ru}\delta_{pt})\partial_t(\dot{\underset{\sim}{q}}_{ai} \wedge \underset{\sim}{q}_{ai})^u b^r(\underset{\sim}{r}_a) + \epsilon_{rts}\partial_p q^s_{ai}\dot{q}^t_{ai}b^r(\underset{\sim}{r}_a)$$

$$= 0 \qquad (A.14)$$

by virtue of $\underset{\sim}{\partial} . \underset{\sim}{b} = 0$.

With this result we may replace the term in braces in equation (A.11) by the expression

$$\epsilon_{rsp}(n+1)(\underset{\sim}{q}_{ai}.\underset{\sim}{\partial})\dot{q}^s_{ai}b^r(\underset{\sim}{r}_a)$$

and so the last term in equation (A.11) is equal to

$$-e_{ai}(\dot{\underset{\sim}{q}}_{ai} \wedge \underset{\sim}{b}(\underset{\sim}{R}_{ai}))_p$$

and we obtain the Lorentz force law

$$m_{ai}\ddot{\underset{\sim}{q}}_{ai} = e_{ai}\left\{\underset{\sim}{e}(\underset{\sim}{R}_{ai}) + \dot{\underset{\sim}{q}}_{ai} \wedge \underset{\sim}{b}(\underset{\sim}{R}_{ai})\right\} \qquad (A.15)$$

in agreement with equation (2.25). We conclude therefore that the lagrangian in equation (A.5) is indeed a suitable though not unique classical lagrangian from which we may develop the theory.

APPENDIX II

On the Consistency of the Constraint Equations.

We seek to prove that $\pi_r{}'^r \approx 0$ is true for all times, and so we must demonstrate that the Poisson bracket g disappears:

$$g = \left[\pi_r{}'^r(x),\ H\right] = \left[\pi_r(x),\ H\right]'^r \qquad (A.16)$$

The hamiltonian H is given by equation (2.51). From the basic Poisson bracket relations it is clear that the only terms that may contribute to the time variation of π_r are those that involve a^s, and so g may be written as $g_1 + g_2$, with

$$g_1 = \tfrac{1}{2}\sum_{a,i}(1/m_{ai})\left[\pi_r(x),\ Q_{ai}^2\right]'^r \qquad (A.17)$$

$$g_2 = \left\{\tfrac{1}{2}\int d\tau'\left[\pi_r(x),\ \tfrac{1}{2}f_{ts}(x')f^{ts}(x') + p_{ts}(x')f^{ts}(x')\right]\right\}'^r. \qquad (A.18)$$

g_1 may be cast into the form

$$g_1 = \sum_{a,i}(e_{ai}/m_{ai})\sum_n\left\{n/(n+1)!\right\}(\underset{\sim}{q}_{ai}\cdot\underset{\sim}{\partial})^{n-1}\partial^r \times \left[\pi_r(x),\ \left(b(\underset{\sim}{r}_a)\wedge\underset{\sim}{q}_{ai}\right)_s\right]Q_{ai}^s \qquad (A.19)$$

where $\partial^r = \partial/\partial x_r$. If $\partial/\partial r_a^s$ is written as ∂''_s and $r_a = x''$, the derivative of the Poisson bracket in g_1 may be written

$$\begin{aligned}\partial^r\left[\pi_r(x),\left(\underset{\sim}{b}(\underset{\sim}{r}_a)\wedge\underset{\sim}{q}_{ai}\right)_s\right] &= \epsilon_{suv}\epsilon_{upt}q_{ai}^v\partial^r\partial''^p\left[\pi_r(x),\ a^t(x'')\right]\\ &= \epsilon_{suv}\epsilon_{upt}g_r^t q_{ai}^v\partial^r\partial''^p\delta^3(x-x'')\\ &= -\epsilon_{suv}q_{ai}^v\left\{\underset{\sim}{\partial}\wedge\underset{\sim}{\partial}''\delta^3(x-x'')\right\}^u = 0, \qquad (A.20)\end{aligned}$$

because $\underset{\sim}{\partial}\wedge\underset{\sim}{\partial}''\delta^3(x-x'')$ vanishes.

g_2 may be written

$$g_2 = \left\{ \tfrac{1}{2} \int d\tau' \left[\pi_r(x),\ f^{ts}(x') \right] h_{ts}(x') \right\}_{,r} \tag{A.21}$$

with

$$h_{ts} = f_{ts} + p_{ts} = -h_{st}. \tag{A.22}$$

Using the definition of the field tensor, equation (2.1), we obtain the Poisson bracket in g_2 as

$$\left[\pi_r(x),\ f^{ts}(x') \right] = (g_r^t \delta'^s - g_r^s \delta'^t)\, \delta^3(x - x') \tag{A.23}$$

and so g_2 itself is

$$g_2 = \left\{ \tfrac{1}{2} \int d\tau' (g_r^t \delta'^s - g_r^s \delta'^t)\, \delta^3(x - x') h_{ts}(x') \right\}_{,r}$$

$$= h_{rs}{}^{,sr}(x) = 0 \tag{A.24}$$

since h_{rs} is antisymmetric. Thus, as both g_1 and g_2 disappear, so too does g, and $\pi_r{}^{,r} \approx 0$ remains true for all times.

Q.E.D.

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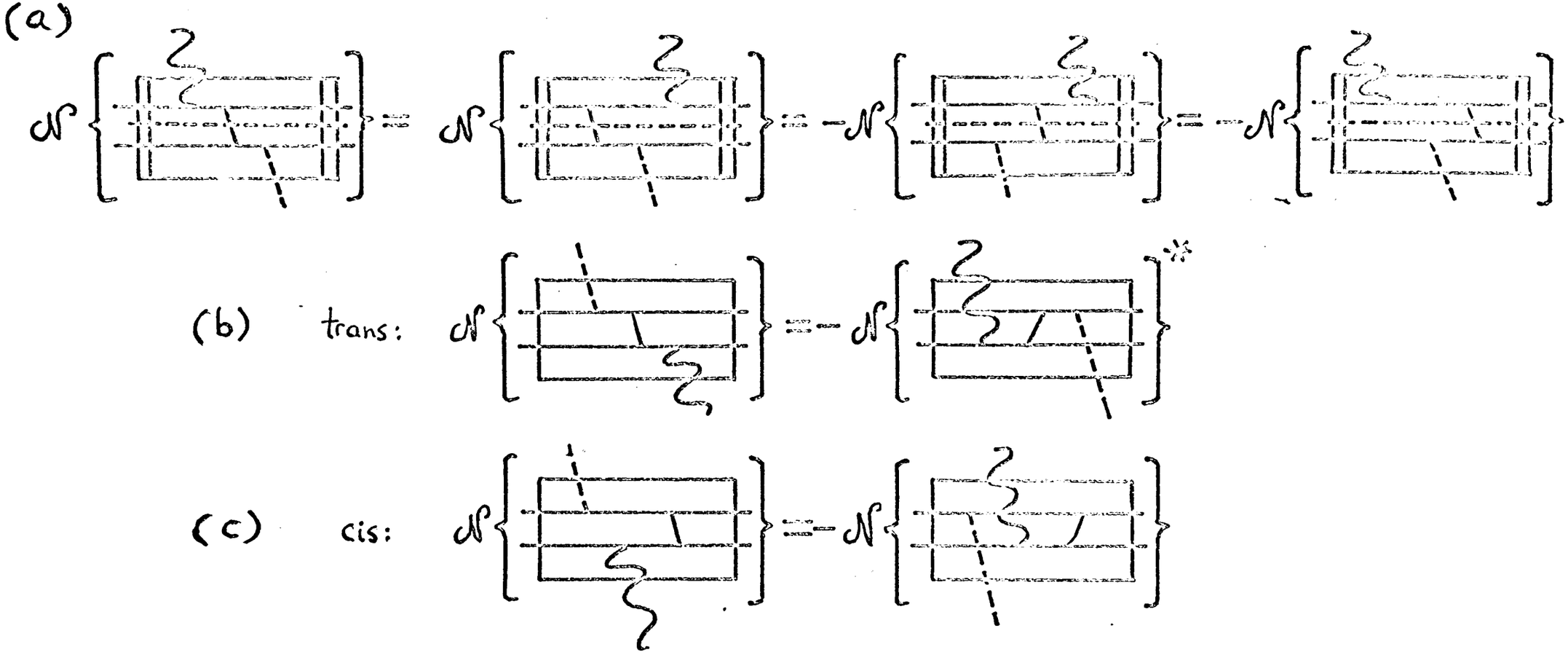

Figure 7

Symmetry rules for the numerators of the algebraic interpretations of the Type A diagrams.