



# Spectroscopy of linear and circular polarized light with the exact semiclassical light–matter interaction

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## Contents

1. Introduction	40
2. Transition moments	42
2.1 Transition moment of linearly polarized light	42
2.2 Transition moment of elliptically polarized light	44
3. General oscillator and rotatory strengths of the Jones vector	46
3.1 General oscillator strength of the Jones vector	47
3.2 General rotatory strength of the Jones vector	47
4. The multipole expansion approximation	49
4.1 The electric-dipole term	49
4.2 The electric-quadrupole and magnetic-dipole terms	50
5. Length gauge	52
6. Selection rules	57
7. Isotropically averaged oscillator and rotatory strengths	60
8. Evaluation of the integrals for the transition moments	65
8.1 Faster evaluation of the integrals for the transition moments	69
9. Connection with experiments	70
10. Summary	73
Acknowledgments	73
References	74

## Abstract

We present the theory and the analytical and numerical solution for the calculation of the oscillator and rotatory strengths of molecular systems using a state-specific formalism. For a start, this is done in the context of the exact semiclassical light–matter interaction in association with electronic wave functions expanded in a Gaussian basis. The reader is guided through the standard approximations of the field, e.g., the use of commutators, truncation of Taylor expansions, and the implications of these are discussed in parallel. Expressions for the isotropically averaged values are derived, recovering the isotropic oscillator strength in terms of the transition electric-dipole moment, and the isotropic rotatory strength in terms of the transition electric-dipole and magnetic-dipole moments. This chapter gives a detailed description of the computation of the integrals over the plane wave in association with Gaussian one-particle basis sets. Finally, a brief description is given of how the computed oscillator and rotatory strengths are related to the quantities commonly used and discussed in experimental studies.



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## 1. Introduction

Quantum chemistry has, by improving theoretical methods, striven to achieve quantitative accuracy in simulating chemical and physical phenomena of molecular systems. One of these challenges has been that of reproducing experimental spectroscopic data, both in the optical (UV/Vis) and X-ray energy range. For the last 30–40 years the advancement of *ab initio* simulations has been significant and today the energies of electronic transitions can be predicted with an impressive accuracy. However, there are still issues with respect to the quantitative, and also the qualitative, accuracy of predicted oscillator and rotatory strengths (i.e., the intensities) of these transitions [1]. Over the years, research has been assessing the role of using the dipole-moment approximation in the length or momentum gauge (see, for example, Refs. [2–10]), the impact of different basis sets, and the role of origin independence [11]. The latter has in particular been analyzed in terms of methods based on multipole expansions grouped in ways such that the result should be origin independent—which can be achieved if all terms are expressed in the same gauge [12]. Recent independent developments have demonstrated that the integrals associated with the exact semiclassical operator are trivial to express and incorporate in standard quantum chemistry program packages [13, 14]. This offers new insight and potential to investigate the impact and effects of the dipole approximation, and others, which have been used in the last century.

In the past few years, our group, and others, has been involved in some of these developments [11–17]. In this endeavor, it has from time to time felt that the literature has been inadequate, incomplete, or not adapted to modern formalism as it is used in the *ab initio* electronic structure community. Hence, in this chapter, a somewhat detailed description of the theory and computer implementation details of simulating oscillator and rotatory strengths, as it stands today, will be presented. This will be done in the frame of a state-specific theory. That is, not using the so-called response theory [18] to evaluate the transition properties but rather a state-interaction formalism [19, 20]. As a complement to this chapter, the reading of the review by Pecul and Ruud on the matter on computing optical rotation and electronic circular dichroism is recommended [1]. In that report, the dependence of the computed rotatory strength, evaluated in the conventional electric-dipole-magnetic-dipole approximation, is discussed with respect to the selection of basis sets, the inclusion of electron correlation, issues of the equilibrium molecular structure, role of vibrations, and finally solvent effects. In this presentation of the field, as originally described by Rosenfeld [21], the workhorse equations and their origin will be presented, as used in a state-specific formalism. Initially the relationship between the oscillator strength and the shape of the time-independent part of the perturbation added to the Hamiltonian will be discussed. The starting expression for the time-dependent perturbation will be the semiclassical operator for the matter-light interaction—the interaction between the electromagnetic field of a photon and the electrons in a molecule. At this point, the concept of general polarization—as expressed in, for example, the special cases of linear or circular polarized light—will be introduced in the concept of Jones vectors describing the polarization [22]. The operator, describing the light-matter interaction, is added to the one-component Schrödinger equation creating an ad hoc two-component Pauli formalism. The reader will then be guided through the various standard approximations that are commonly used. These are, for example, truncated multipole expansions of the exponential expression for the light-matter interaction, and the use of commutators to change gauge to a convenient form. This chapter will discuss in some detail the impact of these standard procedures along with common misconceptions and choice of proper gauges. Furthermore, the use of length vs velocity (or momentum) gauge and the selection rules will be analyzed. Expressions for isotropically averaged oscillator and rotatory strengths, and the integrals required for the exact expression of the light-matter interaction will be derived. In relationship to the latter it will be discussed how these

calculations can be done in an efficient way in association with X-ray spectroscopy simulations. Before the concluding summary a brief section will outline the connection between the computed properties and experiments.



## 2. Transition moments

Transition intensities, oscillator and rotatory strengths are computed from transition moments, the values of which are closely related to the polarization of the incident light. In this section, the expressions for the transition moment, in the special cases of linear and elliptically polarized light, will be presented. These equations will facilitate the derivation of the expressions for the oscillator strength, and, in the latter case, an expression for the rotatory strength will also be presented. The case of general polarization will be treated in the next section.

### 2.1 Transition moment of linearly polarized light

We present here a derivation of transition moment and oscillator strength for linearly polarized light, which is just a shortened version of the corresponding section in Ref. [12], noting that the authors in that reference used Gaussian units, while we use SI (or commensurate) units.

If we represent the electromagnetic field as a monochromatic, linearly polarized plane wave with scalar and vector field (the Coulomb gauge):

$$\begin{aligned}\phi(\mathbf{r}, t) &= 0 \\ \mathbf{A}(\mathbf{r}, t) &= -A_0 \cos(\mathbf{k} \cdot \mathbf{r} - 2\pi\nu t) \mathcal{E}\end{aligned}\quad (1)$$

the electric and magnetic fields are given by:

$$\begin{aligned}\mathbf{E}(\mathbf{r}, t) &= A_0 \sin(\mathbf{k} \cdot \mathbf{r} - 2\pi\nu t) 2\pi\nu \mathcal{E} \\ \mathbf{B}(\mathbf{r}, t) &= A_0 \sin(\mathbf{k} \cdot \mathbf{r} - 2\pi\nu t) (\mathbf{k} \times \mathcal{E})\end{aligned}$$

Here  $\mathbf{k}$  is the wave vector, with norm  $|\mathbf{k}| = \frac{2\pi\nu}{c}$  and pointing in the direction of propagation, while  $\mathcal{E}$  is a unit vector orthogonal to  $\mathbf{k}$ , representing the polarization direction.

This electromagnetic field can be introduced in the molecular Hamiltonian. For weak fields, terms quadratic in  $A_0$  can be neglected, and the effect of the external field can be separated from the unperturbed Hamiltonian  $\hat{H}_0$  as:

$$\hat{H} = \hat{H}_0 + \hat{U}(t)$$

$$\hat{U}(t) = -\frac{e}{m_e} \sum_i \mathbf{A}(\mathbf{r}_i, t) \cdot \hat{\mathbf{p}}_i - \frac{g_e e}{2m_e} \sum_i \mathbf{B}(\mathbf{r}_i, t) \cdot \hat{\mathbf{s}}_i,$$

where the index  $i$  refers to the electrons. Substituting the expressions for  $\mathbf{A}$  and  $\mathbf{B}$ , and the sine and cosine as exponentials, we get

$$\hat{U}(t) = \hat{U} \exp(-i2\pi\nu t) + \hat{U}^* \exp(i2\pi\nu t)$$

$$\hat{U} = \frac{eA_0}{2m_e} \sum_i \left[ \exp(i\mathbf{k} \cdot \mathbf{r}_i) (\mathcal{E} \cdot \hat{\mathbf{p}}_i) + i \frac{g_e}{2} \exp(i\mathbf{k} \cdot \mathbf{r}_i) (\mathbf{k} \times \mathcal{E}) \cdot \hat{\mathbf{s}}_i \right]$$

with  $\hat{\mathbf{p}}$  and  $\hat{\mathbf{s}}$  being the electronic momentum and spin operators. Under the assumption that the system is initially in state 0 and that the perturbation is turned on instantly at  $t = 0$  (sudden approximation), we can apply what Fermi called “golden rule #2” to obtain the transition rate to state  $n$ :

$$\Gamma_{0n}(\nu) = \frac{2\pi}{\hbar} |\langle 0 | \hat{U} | n \rangle|^2 \rho(h\nu)$$

$$= \frac{A_0^2}{4\hbar^2} |T_{0n}|^2 \delta(\nu - \nu_{0n}),$$
(2)

where the density of states  $\rho$  is replaced with a Dirac delta function. The transition moments  $T_{0n}$  are thus defined as:

$$T_{0n} = \frac{e}{m_e} \sum_i \left\langle 0 \left| \exp(i\mathbf{k} \cdot \mathbf{r}_i) (\mathcal{E} \cdot \hat{\mathbf{p}}_i) + i \frac{g_e}{2} \exp(i\mathbf{k} \cdot \mathbf{r}_i) [(\mathbf{k} \times \mathcal{E}) \cdot \hat{\mathbf{s}}_i] \right| n \right\rangle$$
(3)

with dimensions of charge times velocity. Note that  $T_{0n}$  is, in general, a complex-valued scalar, that depends on the  $\mathbf{k}$  and  $\mathcal{E}$  vectors. Here the first term expresses the orbital angular interaction with the electromagnetic field of the photon, whereas the second term is the explicit interaction of the individual intrinsic spin of the electrons with the same electromagnetic field. By applying the identity  $(\mathbf{k} \times \mathcal{E}) \cdot \hat{\mathbf{s}}_i = \mathcal{E} \cdot (\hat{\mathbf{s}}_i \times \mathbf{k})$ ,  $T_{0n}$  can also be written as:

$$T_{0n} = \frac{e}{m_e} \mathcal{E} \cdot \sum_i \left\langle 0 \left| \exp(i\mathbf{k} \cdot \mathbf{r}_i) \left[ \hat{\mathbf{p}}_i + i \frac{g_e}{2} (\hat{\mathbf{s}}_i \times \mathbf{k}) \right] \right| n \right\rangle$$
(4)

The transition rate is obviously dependent on the strength of the field,  $A_0$ . A more intrinsic property of the particular transition is its cross section, which is obtained by dividing  $\Gamma_{0n}$  by the flux (photons per time, per area). The intensity of the wave (energy per time, per area) can be calculated as the time average of the Poynting vector:

$$\mathbf{S} = \frac{1}{\mu_0} (\mathbf{E} \times \mathbf{B})$$

$$I(\nu) = \nu \int_0^{1/\nu} |\mathbf{S}| dt = 2\pi^2 c \epsilon_0 \nu^2 A_0^2,$$

where the integration is done over one period. Therefore, the frequency-integrated cross section is given by:

$$\sigma_{0n}^\nu = \int \frac{\Gamma_{0n}(\nu) h\nu}{I(\nu)} d\nu = \frac{|T_{0n}|^2}{2c\epsilon_0 h\nu_{0n}}$$

and this result can be compared with the cross section of a classical electron oscillator:

$$\sigma_{\text{clas}}^\nu = \frac{e^2}{4m_e c \epsilon_0} \quad (5)$$

defining the dimensionless oscillator strength ( $f$ ) as the quotient:

$$f_{0n} = \frac{\sigma_{0n}^\nu}{\sigma_{\text{clas}}^\nu} = \frac{2m_e}{e^2 \Delta E_{0n}} |T_{0n}|^2 \quad (6)$$

and this is still an expression dependent on the specific  $\mathbf{k}$  and  $\mathcal{E}$  vectors of the electromagnetic field, but not on  $A_0$ .

## 2.2 Transition moment of elliptically polarized light

More generally, the electromagnetic field of a photon, moving in the direction described by the wave vector,  $\mathbf{k}$ , is carried by two perpendicular polarization directions, as described by the unit vectors  $\mathcal{E}_1$  and  $\mathcal{E}_2$ . For these vectors holds the relation  $\mathcal{E}_2 = (\mathbf{k} \times \mathcal{E}_1) / |\mathbf{k}|$ . In general, the amplitude and phase of the electromagnetic field in these two polarization directions differ. A general normalized polarization vector in terms of a Jones vector is expressed as

$$\mathcal{E} = \cos(\psi) \mathcal{E}_1 + \sin(\psi) \exp(i\eta) \mathcal{E}_2, \quad (7)$$

where  $\psi$  accounts for the relative amplitude of the electromagnetic field in the two polarization directions, and  $\eta$  describes their relative phase.

This general polarization easily reduces to the linear polarization for  $\eta = 0, \pi$ , where the two waves are in phase. Here  $\eta$  defines the starting polarization direction along the direction defined by the angle  $\psi$  relative to  $\mathcal{E}_1$ . We here see that if  $\psi$  is equal to 0 or  $\pi$  then the plane wave will be polarized along  $\mathcal{E}_1$  while for  $\psi$  equal to  $\pm\frac{\pi}{2}$  the polarization will be along  $\mathcal{E}_2$ .

Regular circular polarized light appears for  $\eta = \pm\frac{\pi}{2}$  with  $\psi = \pm\frac{\pi}{4}, \pm\frac{3\pi}{4}$  since here the two plane waves are exactly out of phase with the same amplitude. There are of course only two types of circularly polarized light, so the different choices of  $\eta$  and  $\psi$  will always give either left or right-circularly polarized light, but with different initial polarization directions hence the eight combinations. More complicated pulses like elliptically polarized light, where polarization amplitudes are different, simply come by choosing  $\eta = \pm\frac{\pi}{2}$  and  $\psi \neq \pm\frac{\pi}{4}, \pm\frac{3\pi}{4}$ .

The total transition moment is similarly given by:

$$T_{0n}(\psi, \eta) = \cos(\psi) T_{0n}(\mathcal{E}_1) + \sin(\psi) \exp(i\eta) T_{0n}(\mathcal{E}_2), \quad (8)$$

where  $T_{0n}(\mathcal{E}_1)$  and  $T_{0n}(\mathcal{E}_2)$  are obtained according to Eq. (3). We here immediately see that if the transition moment in Eq. (3) for a simple plane wave can be calculated then it is trivial to extend it to any elliptically polarized wave described by Eq. (7).

As it was said before, the transition moment is a complex quantity, but we note in passing that one should be careful when identifying which are the real and imaginary components of the transition moment—an entity which is not an observable; the square norm of the transition moment is real and it is an observable. Additionally, the wave functions are only known to within a complex factor. Hence, it is strictly impossible to uniquely identify the real and complex parts of the transition moment. For all practical purposes the transition moment can be structured into the form

$$T_{0n} = \exp(i\alpha)(T_{0n}^{\circ} + iT_{0n}^{\epsilon}), \quad (9)$$

where  $T^{\epsilon}$  and  $T^{\circ}$ , the even and odd components are those of the Taylor expansion of  $\exp(i\mathbf{k} \cdot \mathbf{r}_i)$  (see Eq. (16) in which the even terms are real and the odd terms are imaginary). Since in Eq. (3) the exponential is

multiplied by an imaginary quantity ( $\hat{p}_i$  or  $i$ ), their contribution to the total transition moment is real for the odd component and imaginary for the even one. As we are interested in the square norm of the transition moment, we will ignore the complex factor in the expression above, and when we mention the real and imaginary parts of the transition moment we are referring, respectively, to the odd and even terms in the Taylor expansion of the exponential expression.

Circular dichroism spectra are obtained as the difference in absorption between left and right-circularly polarized light. It is straightforward to define the difference in transition rates, or oscillator strengths

$$\Delta\Gamma_{0n}(\nu) = \Gamma_{0n}^L(\nu) - \Gamma_{0n}^R(\nu) = \frac{A_0^2}{4\hbar^2} (|T_{0n}^L|^2 - |T_{0n}^R|^2) \delta(\nu - \nu_{0n})$$

$$\Delta f_{0n} = f_{0n}^L - f_{0n}^R = \frac{2m_e}{e^2 \Delta E_{0n}} (|T_{0n}^L|^2 - |T_{0n}^R|^2),$$

where the superscripts L and R refer to left and right circular polarization. This difference is commonly reported as a “rotatory strength,”  $R_{0n}$ , for which the exact expression will be given in [Section 9](#), but for now it is enough to assume:

$$R_{0n} \propto (|T_{0n}^L|^2 - |T_{0n}^R|^2)$$



### 3. General oscillator and rotatory strengths of the Jones vector

The aim of this section is to give a general expression based on the Jones vector [22] and then to connect this to the expression from the plane-wave transition moment to show how easy it is to implement a general transition moment once the transition moment from a plane wave can be calculated.

The quantities relevant for oscillator and rotatory strengths from the transition moment in Eq. (8) based on the Jones vector in Eq. (7) will here be formulated in terms of transition moments of a pair of orthogonal plane waves. In this way we will demonstrate how simple it is to implement the effect of a general wave.



### 3.1 General oscillator strength of the Jones vector

If we use the transition moment of the Jones vector from Eq. (8): in the transition rate, from Eq. (2),

$$\begin{aligned}
 \Gamma_{0n}^J &= \frac{A_0^2}{4\hbar^2} |T_{0n}^J|^2 \delta(\nu - \nu_{0n}) \\
 |T_{0n}^J|^2 &= [\cos(\psi) T_{0n}(\mathcal{E}_1) + \sin(\psi) \exp(i\eta) T_{0n}(\mathcal{E}_2)] \\
 &\quad \times [\cos(\psi) T_{0n}(\mathcal{E}_1) + \sin(\psi) \exp(i\eta) T_{0n}(\mathcal{E}_2)]^* \\
 &= \cos^2(\psi) |T_{0n}(\mathcal{E}_1)|^2 + \sin^2(\psi) |T_{0n}(\mathcal{E}_2)|^2 \\
 &\quad + \cos(\psi) \sin(\psi) [T_{0n}(\mathcal{E}_1) \exp(-i\eta) T_{0n}(\mathcal{E}_2)^* + \exp(i\eta) T_{0n}(\mathcal{E}_2) T_{0n}(\mathcal{E}_1)^*] \\
 &= \cos^2(\psi) |T_{0n}(\mathcal{E}_1)|^2 + \sin^2(\psi) |T_{0n}(\mathcal{E}_2)|^2 \\
 &\quad + 2 \cos(\psi) \sin(\psi) [\cos(\eta) \operatorname{Re}(T_{0n}(\mathcal{E}_1) T_{0n}(\mathcal{E}_2)^*) \\
 &\quad + \sin(\eta) \operatorname{Im}(T_{0n}(\mathcal{E}_1) T_{0n}(\mathcal{E}_2)^*)] \tag{10}
 \end{aligned}$$

four distinct terms appear. The first two terms in Eq. (10) are the regular oscillator strength for a plane wave in the two polarization directions  $\mathcal{E}_1$  and  $\mathcal{E}_2$  multiplied by the square of their amplitude, respectively. These two regular terms are independent of the phase difference  $\eta$  between them. The last two terms in Eq. (10) are formed by the cross terms between the two polarization directions and are dependent on both amplitude ratio and the phase difference between the two plane waves. The first of these terms in Eq. (10) depends on the real part, and the second on the imaginary part of the product between the transition moments. From these last products it is therefore obvious that all terms in Eq. (10) are real and that the sum is positive. Since the phase  $\eta$  only appears in the last two terms in Eq. (10), only these two terms can give nonzero contributions to a difference spectrum like the circular dichroism.

Since the relative amplitude and phase, determined by  $\psi$  and  $\eta$ , respectively, are input parameters that form a certain linear combination of transition moments of plane waves, as shown in Eq. (10), calculating the oscillator strength of any pulse is simple if one can calculate the transition moment for a plane wave. The calculation of the transition moment of a plane wave in a Gaussian basis set is shown in [Section 8](#).

### 3.2 General rotatory strength of the Jones vector

The rotatory strength is proportional to the differential transition rate and arising from the measurement of two different pulses with the same direction

of propagation. Taking the difference in the square of the transition moments between two Jones vectors from Eq. (10)

$$\begin{aligned}
|T_{0n}^J(\psi, \eta)|^2 - |T_{0n}^J(\psi', \eta')|^2 &= (\cos^2(\psi) - \cos^2(\psi'))|T_{0n}(\mathcal{E}_1)|^2 \\
&+ (\sin^2(\psi) - \sin^2(\psi'))|T_{0n}(\mathcal{E}_2)|^2 + 2\cos(\psi)\sin(\psi)[\cos(\eta)\operatorname{Re}(T_{0n}(\mathcal{E}_1)T_{0n}(\mathcal{E}_2)^*) \\
&+ \sin(\eta)\operatorname{Im}(T_{0n}(\mathcal{E}_1)T_{0n}(\mathcal{E}_2)^*)] - 2\cos(\psi')\sin(\psi')[\cos(\eta')\operatorname{Re}(T_{0n}(\mathcal{E}_1)T_{0n}(\mathcal{E}_2)^*) \\
&+ \sin(\eta')\operatorname{Im}(T_{0n}(\mathcal{E}_1)T_{0n}(\mathcal{E}_2)^*)]
\end{aligned} \tag{11}$$

we see that a difference spectrum can be obtained in many different ways.

For pulses with equal amplitudes,  $\psi = \psi'$ , we see that only the relative phase matters

$$\begin{aligned}
|T_{0n}^J(\psi, \eta)|^2 - |T_{0n}^J(\psi, \eta')|^2 &= 2\cos(\psi)\sin(\psi) \times [(\cos(\eta) - \cos(\eta'))\operatorname{Re}(T_{0n}(\mathcal{E}_1)T_{0n}(\mathcal{E}_2)^*) \\
&+ (\sin(\eta) - \sin(\eta'))\operatorname{Im}(T_{0n}(\mathcal{E}_1)T_{0n}(\mathcal{E}_2)^*)]
\end{aligned}$$

and that there will be an absolute maximum in the difference from the relative phase when  $\eta' = \eta + \pi$  for a given  $(\psi, \eta)$

$$\begin{aligned}
|T_{0n}^J(\psi, \eta)|^2 - |T_{0n}^J(\psi, \eta + \pi)|^2 &= 4\cos(\psi)\sin(\psi) \\
&\times [\cos(\eta)\operatorname{Re}(T_{0n}(\mathcal{E}_1)T_{0n}(\mathcal{E}_2)^*) + \sin(\eta)\operatorname{Im}(T_{0n}(\mathcal{E}_1)T_{0n}(\mathcal{E}_2)^*)]
\end{aligned} \tag{12}$$

and zero when  $\eta = \eta'$ . The difference will of course have a maximum when the two plane waves are of equal amplitude, which is at  $\psi = \pm\frac{\pi}{4}, \pm\frac{3\pi}{4}$ . Setting  $\eta = \frac{\pi}{2}$  and using the amplitude ratio for the maximum, the regular circular dichroism dependence on the transition matrix elements appears when taking the difference between the transition rates from Eq. (10)

$$(\Gamma_{0n}^J - \Gamma_{0n}^{J'})_{\text{circ}} = \frac{A_0^2}{2\hbar^2} \operatorname{Im}(T_{0n}(\mathcal{E}_1)T_{0n}(\mathcal{E}_2)^*)\delta(\nu - \nu_{0n}). \tag{13}$$

Furthermore, we see that with elliptically polarized light the circular dichroism spectrum from Eq. (13) can be reproduced but with lower rotatory strength since  $\psi \neq \pm\frac{\pi}{4}, \pm\frac{3\pi}{4}$ . Taking  $\eta = 0$  we see a difference between two plane polarized waves with perpendicular polarization directions known as linear dichroism or diattenuation

$$(\Gamma_{0n}^J - \Gamma_{0n}^{J'})_{\text{lin}} = \frac{A_0^2}{2\hbar^2} \operatorname{Re}(T_{0n}(\mathcal{E}_1)T_{0n}(\mathcal{E}_2)^*)\delta(\nu - \nu_{0n}). \tag{14}$$

The difference between the two plane polarized waves in Eq. (14) will, however, be zero for isotropically averaged systems and is therefore best suited for oriented systems.

While there are many ways a difference spectrum can be obtained from Eq. (11), the linear and circular dichroism spectra in Eqs. (13) and (14) are the most prominent and give the clearest signal and interpretation since the terms in Eq. (11) are clearly separated and the difference is at a maximum.



## 4. The multipole expansion approximation

Here we will start to introduce the standard approximations so that we will ultimately arrive at the prevailing standard expression of the oscillator and rotatory strengths. The first approximation is to ignore the direct coupling of the electromagnetic field of the photon with the intrinsic spin of the electrons, something which, probably, is fine for singlet states. However, one could possibly suspect that this would be of some significance for systems with transition metals in which higher multiplicities—open-shell structure—are predominant. Thus, we approximate Eq. (3) by

$$T_{0n} \approx \frac{e}{m_e} \sum_i \langle 0 | \exp(i\mathbf{k} \cdot \mathbf{r}_i) (\mathcal{E} \cdot \hat{\mathbf{p}}_i) | n \rangle \quad (15)$$

We proceed further by approximating the exponential operator using a Taylor expansion, truncated at a specific order of the wave vector,

$$\exp(i\mathbf{k} \cdot \mathbf{r}_i) = 1 + i(\mathbf{k} \cdot \mathbf{r}_i) - \frac{1}{2!}(\mathbf{k} \cdot \mathbf{r}_i)^2 - i\frac{1}{3!}(\mathbf{k} \cdot \mathbf{r}_i)^3 + \dots \quad (16)$$

Here we note an automatic separation of the components of the operator into even/real and odd/imaginary terms. In this respect, we will have that the leading terms of the two components of the transition moment are identified as (i) the electric-dipole term, and (ii) the combined electric-quadrupole and magnetic-dipole terms. Let us dwell a bit on these two terms before we continue the analysis of the oscillator and rotatory strengths.

### 4.1 The electric-dipole term

The electric-dipole term of the transition moment—the leading term of the even parts—is computed (in velocity gauge) as

$$T_{0n}^{\mu p}(\mathcal{E}) = \frac{e}{m_e} \mathcal{E} \cdot \sum_i \langle 0 | \hat{\mathbf{p}}_i | n \rangle$$

Assuming local potentials and using the hypervirial theorem [23]

$$[\mathbf{r}_i, \hat{H}_0] = \frac{i\hbar}{m_e} \hat{\mathbf{p}}_i \quad (17)$$

we can recast the expression for the electric-dipole term into the length gauge

$$T_{0n}^{\mu^p}(\mathcal{E}) = T_{0n}^{\mu}(\mathcal{E}) = i \frac{\Delta E_{0n}}{\hbar} \mathcal{E} \cdot \langle 0 | \hat{\boldsymbol{\mu}} | n \rangle, \quad (18)$$

where  $\hat{\boldsymbol{\mu}} = -e \sum_i \hat{\mathbf{r}}_i$  is the dipole-moment operator in length gauge. Since the Hamiltonian is unique only up to a gauge transformation there is not a single preferred Hamiltonian and the Hamiltonian in the length and velocity gauge are in that sense completely equal. In finite basis sets, the gauges are, however, not equal and neither are the electric-dipole terms in Eq. (18), although one gauge cannot be said to be an approximation of the other gauge. The choice of gauge should therefore be performed before any approximations are introduced. This point is discussed further in Section 5 with respect to the transformation to the length gauge. Since we in this section follow the standard derivation the multipole expansion is performed first and gauge transformation second even if it should be the other way around.

## 4.2 The electric-quadrupole and magnetic-dipole terms

These terms, due to the first-order contribution of the Taylor expansion—the leading term of the odd parts—of the exponential operator with respect to the wave vector, is in its raw form expressed as

$$T_{0n}^{(1)}(\mathcal{E}) = \frac{e}{m_e} \sum_i \langle 0 | i(\mathbf{k} \cdot \mathbf{r}_i)(\mathcal{E} \cdot \hat{\mathbf{p}}_i) | n \rangle$$

This term can be recast into a symmetric and an antisymmetric term by the following substitution,

$$\begin{aligned} (\mathbf{k} \cdot \mathbf{r}_i)(\mathcal{E} \cdot \hat{\mathbf{p}}_i) &= \frac{1}{2} [(\mathbf{k} \cdot \mathbf{r}_i)(\hat{\mathbf{p}}_i \cdot \mathcal{E}) + (\mathbf{k} \cdot \hat{\mathbf{p}}_i)(\mathbf{r}_i \cdot \mathcal{E})] \\ &\quad + \frac{1}{2} [(\mathbf{k} \cdot \mathbf{r}_i)(\hat{\mathbf{p}}_i \cdot \mathcal{E}) - (\mathbf{k} \cdot \hat{\mathbf{p}}_i)(\mathbf{r}_i \cdot \mathcal{E})] \end{aligned} \quad (19)$$

The symmetric and antisymmetric parts will now be rearranged into the electric-quadrupole and magnetic-dipole terms, respectively. Following the same route as Bernadotte et al. [12] we express the contribution to

the transition moment from the electric-quadrupole term (using implicit Einstein summation for the Cartesian indices,  $\alpha, \beta$ )

$$\begin{aligned} T_{0n}^{Q^p}(\mathcal{E}) &= \frac{ie}{2m_e} \sum_i \langle 0 | (\mathbf{k} \cdot \mathbf{r}_i) (\hat{\mathbf{p}}_i \cdot \mathcal{E}) + (\mathbf{k} \cdot \hat{\mathbf{p}}_i) (\mathbf{r}_i \cdot \mathcal{E}) | n \rangle \\ &= \frac{ie}{2m_e} k_\alpha \mathcal{E}_\beta \sum_i \langle 0 | r_{i,\alpha} \hat{p}_{i,\beta} + \hat{p}_{i,\alpha} r_{i,\beta} | n \rangle \end{aligned}$$

Using the hypervirial theorem from Eq. (17), an alternative operator in length gauge can be expressed as

$$\hat{Q}_{\alpha,\beta} = -\frac{e}{2} \sum_i r_{i,\alpha} r_{i,\beta} + r_{i,\alpha} r_{i,\beta}$$

which for exact wave functions is equal to the electric-quadrupole operator in the velocity gauge

$$T_{0n}^{Q^p}(\mathcal{E}) = T_{0n}^Q(\mathcal{E}) = -\frac{\Delta E_{0n}}{\hbar} k_\alpha \mathcal{E}_\beta \langle 0 | \hat{Q}_{\alpha,\beta} | n \rangle \quad (20)$$

since the multipole expansions in the different gauges are termwise identical. In finite basis sets, the electric-quadrupole in the two gauges in Eq. (20) will differ.

For the antisymmetric term, we note that, since  $\mathcal{E}$  and  $\mathbf{k}$  are orthogonal, we may rewrite it as

$$(\mathbf{k} \cdot \mathbf{r}_i) (\hat{\mathbf{p}}_i \cdot \mathcal{E}) - (\mathbf{k} \cdot \hat{\mathbf{p}}_i) (\mathbf{r}_i \cdot \mathcal{E}) = (\mathbf{k} \times \mathcal{E}) (\mathbf{r}_i \times \hat{\mathbf{p}}_i)$$

This gives that the transition moment due to the magnetic-dipole term is expressed as

$$\begin{aligned} T_{0n}^{m'}(\mathcal{E}) &= \frac{ie}{2m_e} \sum_i \langle 0 | (\mathbf{k} \cdot \mathbf{r}_i) (\hat{\mathbf{p}}_i \cdot \mathcal{E}) - (\mathbf{k} \cdot \hat{\mathbf{p}}_i) (\mathbf{r}_i \cdot \mathcal{E}) | n \rangle \\ &= \frac{ie}{2m_e} (\mathbf{k} \times \mathcal{E}) \sum_i \langle 0 | (\mathbf{r}_i \times \hat{\mathbf{p}}_i) | n \rangle \end{aligned} \quad (21)$$

$$= -i (\mathbf{k} \times \mathcal{E}) \langle 0 | \hat{\mathbf{m}}' | n \rangle, \quad (22)$$

where the orbital magnetic-dipole operator is defined as

$$\hat{\mathbf{m}}' = -\frac{e}{2m_e} \sum_i (\mathbf{r}_i \times \hat{\mathbf{p}}_i)$$

Note that this term is now similar in shape to the term describing the interaction of the electromagnetic field of the photon and the intrinsic angular

momentum—the spin—of the electrons (see the second term in the RHS of Eq. (3)). The term above, however, is associated with the orbital angular momentum— $\hat{l}$  rather than  $\hat{s}$ . Furthermore, we note that this term is in the velocity gauge and not in the length gauge, even if it is normally incorrectly used in connection with the length gauge. The correct magnetic-dipole operator in the length gauge is given in Eq. (27) in Section 5.

We therefore have that

$$T_{0n}^{(1)}(\mathcal{E}) = T_{0n}^{Qp}(\mathcal{E}) + T_{0n}^{m'}(\mathcal{E})$$

Higher order terms can be obtained in a similar fashion, but they are not necessary for our purposes here.



## 5. Length gauge

In the literature, the length gauge is often the favored choice when performing calculations. However, since the interaction in the minimal coupling picture with some external electromagnetic field (EMF) is most naturally written in the velocity gauge, a gauge transformation from the velocity to the length gauge is then needed. While any measurable result is gauge independent for the exact solution, this is not so once approximations in the basis set are performed. The choice of gauge like the Coulomb or Lorenz gauge, needed to fix the internal degrees of freedom in the EMF, or the choice between velocity and length gauge is therefore motivated by the numerical performance in a given gauge. The numerical performance of a given gauge, however, depends on the choice of basis set and correlation methods, which can visibly be demonstrated for simple systems [25]. The numerically best performing gauge in a given basis set for molecular systems may be strongly dependent on the nature of the transitions and can be very difficult to predict a priori. This means that it is not a given that the same gauge will be the best gauge for all transitions in a system.

For higher order multipole expansions it has been incorrectly stated that the oscillator strengths in the length gauge cannot be origin independent in finite basis sets [12, 15, 16]. This misconception arises from the incorrect derivation of the length gauge ubiquitous in the literature, which is in fact a mixed gauge,<sup>a</sup> where the electric multipoles are in the length gauge, but the magnetic multipoles remain untransformed in the velocity gauge. Since the length and velocity gauge differ in finite basis sets, due to different

<sup>a</sup> The mixed gauge is a bit of a misnomer since it cannot be related to a proper gauge via a gauge transformation and is therefore not a proper gauge.

integrands, the mixed gauge, not being a proper gauge, will not be origin independent since the origin independence of the multipole expansion relies on exact cancelation [11, 12, 15].

For the lowest order contribution to the rotatory strengths origin independence can be obtained in the mixed gauge by using London atomic orbitals (LAO) [1, 25–29] since LAOs are correct to first order in the external magnetic field, however, by using the correct length gauge the need for LAOs can be eliminated. The mixed gauge, as shown in Eq. (33), using LAOs is usually the favored choice when calculating CD spectra using response theory since it gives zero in the static limit in response theory whereas the velocity gives nonzero [30].

We here want to stress that the mixed gauge is not a proper gauge and that there is no gauge transformation relating the Hamiltonian in the mixed gauge to the Hamiltonians in the proper gauges like the velocity and length gauge. Not being a proper gauge also means that gauge invariant properties, like the origin independence, are no longer conserved once approximations are introduced.

We will here derive the expression for the transition moment of a plane wave in the length gauge using the hypervirial theorem [23], since all other types of waves can be expressed as simple linear combinations of plane waves. The time-independent and spin-free perturbation operator for a plane wave in the velocity gauge

$$\hat{U}_p = \frac{eA_0}{2m_e} \sum_i \exp(i\mathbf{k} \cdot \mathbf{r}_i) (\mathcal{E} \cdot \hat{\mathbf{p}}_i)$$

can be transformed, using the hypervirial theorem from Eq. (17) to the length gauge

$$\hat{U}_r = -\frac{ieA_0}{2\hbar} \sum_i \exp(i\mathbf{k} \cdot \mathbf{r}_i) (\mathcal{E} \cdot [\mathbf{r}_i, \hat{H}_0]). \quad (23)$$

The gauge transformation using the hypervirial theorem in Eq. (17), however, only holds for local potentials and exact wave functions. In the finite basis sets used in numerical calculations, the hypervirial theorem is only approximate. However, we cannot conclude that the velocity gauge will always outperform the length gauge or the other way around, since the result from the exact Hamiltonian is invariant to any gauge transformation and therefore no preferred Hamiltonian exists. Since the gauges differ in

different basis sets and exact transformations between these finite basis sets are not possible to perform, the choice of gauge should therefore be made before any approximations or multipole expansions are invoked. While it may sound trivial that the gauge should be chosen before any approximations are carried out, this is a very common mistake in the scientific literature which we believe has led to a lot of confusion and erroneous conclusions about the length gauge, proper gauge transformations, and conservation of gauge invariant properties.

It is well known that the oscillator strengths for the exact expression in the velocity gauge are origin independent. The origin independence of the oscillator strengths can be easily shown by moving the origin from  $\mathbf{O}$  to  $\mathbf{O} + \mathbf{a}$

$$\begin{aligned} |T_{0n}(\mathbf{O} + \mathbf{a})|_p^2 &= \langle 0 | \exp(i\mathbf{k} \cdot (\mathbf{r} - \mathbf{a})) (\mathcal{E} \cdot \hat{\mathbf{p}}) | n \rangle \langle n | \exp(-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{a})) (\mathcal{E} \cdot \hat{\mathbf{p}}) | 0 \rangle \\ &= \langle 0 | \exp(i\mathbf{k} \cdot \mathbf{r}) (\mathcal{E} \cdot \hat{\mathbf{p}}) | n \rangle \langle n | \exp(-i\mathbf{k} \cdot \mathbf{r}) (\mathcal{E} \cdot \hat{\mathbf{p}}) | 0 \rangle \exp(i\mathbf{k} \cdot (\mathbf{a} - \mathbf{a})) \\ &= |T_{0n}(\mathbf{O})|^2. \end{aligned} \quad (24)$$

Since the hypervirial theorem does not affect the origin independence of the oscillator strengths in the length gauge these are then also origin independent

$$\begin{aligned} |T_{0n}(\mathbf{O} + \mathbf{a})|_r^2 &= \frac{-m_e^2}{\hbar^2} \langle 0 | \exp(i\mathbf{k} \cdot (\mathbf{r} - \mathbf{a})) (\mathcal{E} \cdot [(\mathbf{r} - \mathbf{a}), \hat{H}_0]) | n \rangle \\ &\quad \times \langle n | \exp(-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{a})) (\mathcal{E} \cdot [(\mathbf{r} - \mathbf{a}), \hat{H}_0]) | 0 \rangle \\ &= |T_{0n}(\mathbf{O})|^2 \end{aligned} \quad (25)$$

since  $\hat{H}_0$  commutes with  $\mathbf{a}$ . While the hypervirial theorem only holds for complete basis sets, the origin independence in the length gauge is still preserved in finite basis sets since this only relies on finding the eigenstates of  $\hat{H}_0$  [11].

By performing a multipole expansion of the perturbation operator in the length gauge from Eq. (23)

$$\begin{aligned} \hat{U}_r &= -\frac{ieA_0}{2\hbar} \sum_i \exp(i\mathbf{k} \cdot \mathbf{r}_i) (\mathcal{E} \cdot [\mathbf{r}_i, \hat{H}_0]) \\ &= -\frac{ieA_0}{2\hbar} \sum_i \left( 1 + i(\mathbf{k} \cdot \mathbf{r}_i) - \frac{1}{2}(\mathbf{k} \cdot \mathbf{r}_i)^2 + \dots \right) (\mathcal{E} \cdot [\mathbf{r}_i, \hat{H}_0]) \end{aligned} \quad (26)$$

the different terms in the multipole expansion can be identified. For the exact solution the multipole expansion in the length and velocity gauges are termwise identical, when using the same origin, while in all other cases



the gauges differ. For the zeroth order in Eq. (26), we find the familiar electric-dipole expression in the length gauge

$$T_{0n}^{(0)} = -i\frac{1}{\hbar}\langle 0|\mathcal{E}\cdot[\mathbf{r},\hat{H}_0]|n\rangle = -i\frac{\Delta E_{0n}}{\hbar}\langle 0|\mathcal{E}\cdot\mathbf{r}|n\rangle,$$

where  $\Delta E_{0n}$  is the energy difference between the two states. Writing the first order in terms of a symmetric and antisymmetric part with respect to the interchange of  $\mathbf{k}$  and  $\mathcal{E}$ , like in Eq. (19), the first-order electric and magnetic terms can be identified

$$\begin{aligned} T_{0n}^{(1)} &= -\frac{ie}{\hbar}\sum_i\langle 0|i(\mathbf{k}\cdot\mathbf{r}_i)(\mathcal{E}\cdot[\mathbf{r}_i,\hat{H}_0])|n\rangle \\ &= \frac{e}{2\hbar}\sum_i\left[\langle 0|(\mathbf{k}\cdot\mathbf{r}_i)([\mathbf{r}_i,\hat{H}_0]\cdot\mathcal{E})+(\mathbf{k}\cdot[\mathbf{r}_i,\hat{H}_0])(\mathbf{r}_i\cdot\mathcal{E})|n\rangle\right. \\ &\quad \left.+\langle 0|(\mathbf{k}\cdot\mathbf{r}_i)([\mathbf{r}_i,\hat{H}_0]\cdot\mathcal{E})-(\mathbf{k}\cdot[\mathbf{r}_i,\hat{H}_0])(\mathbf{r}_i\cdot\mathcal{E})|n\rangle\right] \\ &= \frac{\Delta E_{0n}}{2\hbar}k_\alpha\mathcal{E}_\beta\langle 0|e\sum_i r_{i,\alpha}r_{i,\beta}|n\rangle + \frac{e}{2\hbar}(\mathbf{k}\times\mathcal{E})\sum_i\langle 0|[\mathbf{r}_i,\hat{H}_0]|n\rangle \\ &= T_{0n}^Q + T_{0n}^{mf}. \end{aligned}$$

The symmetric term  $T_{0n}^Q$  is the usual electric-quadrupole term while the anti-symmetric term  $T_{0n}^{mf}$  is the magnetic-dipole term, both in the length gauge. The commutator in  $T_{0n}^{mf}$  cannot be replaced by the momentum operator using the hypervirial theorem from Eq. (17) for finite basis sets and therefore must be evaluated directly.

In the literature, when trying to show that the multipole expansion in the length gauge is not origin independent, the magnetic terms are always taken in the velocity gauge. The magnetic dipole in the velocity gauge from Eq. (21) will, when moving the origin, give a distance dependent electric-dipole transition moment in the velocity gauge; however, when using  $T_{0n}^{mf}$  a distance dependent electric-dipole transition moment in the length gauge instead appears

$$\begin{aligned} T_{0n}^{mf}(\mathbf{O}+\mathbf{a}) &= \sum_i\langle 0|(\mathbf{r}_i-\mathbf{a})\times[(\mathbf{r}_i-\mathbf{a}),\hat{H}_0]|n\rangle \\ &= \sum_i\langle 0|\mathbf{r}_i\times[\mathbf{r}_i,\hat{H}_0]-\mathbf{a}\times[\mathbf{r}_i,\hat{H}_0]+\mathbf{r}_i\times[-\mathbf{a},\hat{H}_0]+\mathbf{a}\times[\mathbf{a},\hat{H}_0]|n\rangle \\ &= T_{0n}^{mf}(\mathbf{O})-\varepsilon_{\alpha\beta\gamma}a_\beta\Delta E_{0n}\sum_i\langle 0|r_{i,\gamma}|n\rangle \end{aligned}$$

(27)

which is orthogonal to the direction of the movement as indicated by the Levi-Civita tensor. Using the Bernadotte et al. [12] proof of the termwise origin independence for the oscillator strengths in the multipole expansion in the velocity gauge, the origin independence in the length gauge follows from exactly the same arguments since in the correct length gauge, all lower order terms arising from shifting the origin will remain in the length gauge. For the rotatory strength we also see that the tensor averaging will eliminate any contribution from the electric-dipole term in Eq. (27), and therefore become origin independent for the exact same reasons as in the velocity gauge. The fact that the origin independence for oscillator and rotatory strengths are gauge invariant properties is not surprising since these rely on exact cancelation on terms from the multipole expansion and a gauge transformation of course does not change which terms should cancel.

The origin dependence of the individual terms in the multipole expansion also shows that there is no single separation between electric and magnetic transitions with all possible choices of origin since the electric and magnetic contributions are transformed into each other with any shift of the origin. Furthermore, it is not possible to measure the contribution from any of the terms in the multipole expansion and the statements of the measurement of electric-dipole or -quadrupole oscillator strengths are not physically possible. All these interpretations rely on special choices of origin or origins. It is numerically quite easy to show that even small displacements of the origin can introduce very large higher order terms in the multipole expansion [15] and thereby invalidate any interpretation of the different terms in the multipole expansion.

The major problem in using the length gauge for anything other than the electric terms is the evaluation of  $[\mathbf{r}_i, \hat{H}_0]$ , since for the magnetic dipole  $T_{0n}^{m'}$  or for the exact semiclassical expression in Eq. (25), the usual trick of applying  $\hat{H}_0$  on both the bra or the ket to get the energies of the eigenstates of  $\hat{H}_0$  does not appear to be directly possible. The evaluation of the integrals over these operators involving a commutator with  $\hat{H}_0$  is therefore nonstandard. For the kinetic energy part of  $\hat{H}_0$  the integrals do not differ significantly from those described in Section 8, since these all can be reduced to a sum of integrals of the form shown in Eq. (37). The two-electron Coulomb interaction can be reduced to a form similar to that used for a mixed Gaussian and plane-wave basis set as shown by Čarský and Poláček [31, 32]. Due to this more cumbersome evaluation of the integrals for the transition moments in the length gauge, it is doubtful that the length gauge will be useful for anything above the dipole approximation.



## 6. Selection rules

First, a very brief historical introduction to the standard selection rules for absorption/emission and CD active electronic transitions will be presented along with the connection to group theory. This is followed by a discussion of the dependence of the selection rules with respect to the choice of origin with an emphasis on the physical interpretation of the transition. Along the way, we will compare the multipole expansion to the full exponential operator.

In the literature, the selection rules are presented in terms of transition multipole moments (usually up to first order in the wave vector) and are derived to be valid for atoms and small molecular system exhibiting symmetry, when the ratio of the wavelength of the light to the molecular size is large. The original selection rules for transitions between electronic states date back to the work by Laporte and Meggers for such rules for centrosymmetric species [33]. These selection rules state that for an electronic transition to be allowed the spin must be conserved ( $\Delta S = 0$  for spin-allowed transitions) and the orbital angular momentum must change ( $\Delta L = \pm 1$ ). The latter condition is, for noncentrosymmetric species, translated so that the transition dipole moment is nonzero for allowed transitions, where the intensity of the transition is proportional to  $|\boldsymbol{\mu}|^2$ . For a transition to be CD active, the first requirement is, of course, that it should be a dipole-allowed transition. Additionally, as already understood from Rosenfeld's work, the transition should carry a nonzero magnetic-dipole moment [21]. This is not all, the CD activity is proportional to  $\text{Im}(\boldsymbol{\mu} \cdot \mathbf{m})$ , hence, the relative directions of the magnetic and electric-dipole moments matter. It is also worth mentioning that for CD under anisotropic conditions the electric-quadrupole moment contributes too. A more detailed analysis of the selection rules for CD spectroscopy and the underlying mechanism behind the CD activity, based on the independent systems/perturbation (ISP) model, has been presented by Schipper and Alison [34].

Thus, to summarize, the selection rules for intense transitions, only in terms of transition multipole moments, are

1. the transition must be associated with a nonzero electric-dipole moment (for both absorption/emission and CD active transitions), and
2. a nonzero electric-quadrupole moment (only in case of anisotropic CD activity) and/or
3. a nonzero magnetic-dipole moment, and not orthogonal to the electric-dipole moment (a must for isotropic CD activity).

For atoms and molecules the spectroscopic selection rules depend on whether or not the value of the transition moment integral

$$T_{0n} = \int \Psi_0^* \hat{\Lambda} \Psi_n \, dr = \langle 0 | \hat{\Lambda} | n \rangle$$

is zero. Here  $\Psi_0^* \hat{\Lambda} \Psi_n$  is the transition moment function and  $\hat{\Lambda}$  the transition moment operator, which can be any term from the multipole expansion or the exact semiclassical operator in our case. Using group theory, it can be shown that the transition moment function must belong to the totally symmetric representation of the point group of the given atom or molecule to give an allowed transition for the  $\hat{\Lambda}$  and states in question. The selection rules derived from symmetry considerations can in this way give information about the magnitude, shape and symmetry of spectra. For molecules with some elements of symmetry it is therefore easy to predict what transitions are allowed and forbidden directly from the character table of the point group.

The selection rules will typically point to a specific dominating term in the multipole expansion and this term is then commonly ascribed as the physical origin of the transition, like the electric quadrupole [35]. The problem with this physical interpretation is that it is given with a specific choice of origin for the coordinate system and any displacement of the origin will give a different interpretation since no terms above the electric dipole of the multipole expansion are origin independent. Therefore, there can be no measurement of the individual terms in the multipole expansion. However, any origin displacement will of course not change what is measured and the symmetries and magnitude deduced from symmetry considerations of the multipole expansion will always automatically show up in the exact operator and for an origin independent truncation of the oscillator strength at or above the dominating term. The drawback of using the full exponential operator for isotropically averaged transition strengths instead is that all transitions are allowed and it is not obvious how, from simple considerations, the intensity and symmetry can be estimated a priori.

While the dipole approximation and the full exponential operator show origin independence, the reason for doing so is very different. First, in the dipole-moment approximation, the velocity gauge is trivially invariant to a translation of the origin, while the length gauge is invariant because of the orthogonality of the states (see Eq. (18), and replace  $\boldsymbol{\mu}$  with  $\boldsymbol{\mu} + \mathbf{a}$ ). Within the dipole-moment approximation, the selection rules for optically active

transitions are therefore invariant to the choice of origin, but only intense transitions can be seen, and all transitions are predicted to be CD inactive due to the lack of higher order terms. For the full exponential operator, on the other hand, it is noted that the origin dependence of the transition moment (see Eqs. (24) and (25)) can be expressed as

$$T(\mathbf{O} + \mathbf{a}) = \exp(i\mathbf{k} \cdot \mathbf{a}) T(\mathbf{O}), \quad (28)$$

where the origin is displaced by the vector  $\mathbf{a}$ . From this, it is obvious that the oscillator strength—proportional to the square norm of the transition moment—is independent of the selection of the origin. To proceed, it is noted that the exponential term in the expression above will rotate the real and imaginary components of the transition moment into each other. A complete interchange of the two components is accomplished when the projection of the displacement vector  $\mathbf{a}$  on the wave vector  $\mathbf{k}$  is equal to  $\frac{\pi}{2}$ . To put this into a context of UV/Vis and X-ray spectroscopy, the magnitude of the displacement for such an interchange is  $|\mathbf{a}| = 500\text{--}2000 \text{ \AA}$  and  $|\mathbf{a}| = 0.025\text{--}25 \text{ \AA}$ , respectively. Again, the oscillator strength is invariant to such rotations since the displacement term is just a complex phase. The rotatory strength is proportional to the difference between two oscillators strength, so it is also invariant to the selection of the origin.

For a truncated multipole moment scheme above the dipole things are, however, a bit more complicated due to the dependence of the selection of origin. While Bernadotte et al. have demonstrated that an origin-independent multipole-moment-based oscillator strength can be computed, the values of the individual components of the multipoles are not invariant to the selection of origin [12]. For a more informative view on this, examine the terms for a given order  $m$  in Eq. (28), starting by expanding both factors in orders of  $\mathbf{k}$ ,

$$T(\mathbf{O} + \mathbf{a}) = \sum_{n=0}^{\infty} \frac{i^n}{n!} (\mathbf{k} \cdot \mathbf{a})^n \sum_{m=0}^{\infty} T^{(m)}(\mathbf{O})$$

and then grouping the terms of a given total order  $m$ ,

$$\begin{aligned} T(\mathbf{O} + \mathbf{a}) &= \sum_{m=0}^{\infty} T^{(m)}(\mathbf{O} + \mathbf{a}) \\ T^{(m)}(\mathbf{O} + \mathbf{a}) &= \sum_{n=0}^m \frac{i^n}{n!} (\mathbf{k} \cdot \mathbf{a})^n T^{(m-n)}(\mathbf{O}). \end{aligned} \quad (29)$$

which contains contributions from all lower order terms. In this way the multipole expansion is order by order building the complex phase of the full exponential operator. From Eq. (29), we also notice that higher-order transition moment operators, which perhaps were zero at  $\mathbf{O}$  due to symmetry, may now even become intense due to large lower order terms. In fact, when the origin is moved, then for all transitions, where a lower order transition moment operator is allowed, we see that as  $|\mathbf{a}|$  approaches infinity,

$$\lim_{|\mathbf{a}| \rightarrow \infty} |T^{(m>0)}(\mathbf{O} + \mathbf{a})| = \infty \text{ if any } T^{(n<m)}(\mathbf{O}) \neq 0 \quad (30)$$

the different terms in the multipole expansion tends to infinity. Even for simple systems, like the transition from 1s to 2p in helium, which would only be dipole allowed, the displacement of the origin will suddenly give nonzero higher order terms

$$T^{(1)}(\mathbf{O} + \mathbf{a}) = T^{(1)}(\mathbf{O}) + i(\mathbf{k} \cdot \mathbf{a})T^{(0)}(\mathbf{O}). \quad (31)$$

The exact cancelation in the origin independent approach by Bernadotte et al., however, ensures that the sum in the oscillator strength is always finite [12].

While the mixing of electric and magnetic terms from the displacement of origin is reminiscent of the change of inertial frame in electrodynamics, there are, however, significant differences. The most important differences are that the electric and magnetic fields in electrodynamics are physical and always remain finite, whereas the transition moments are not, and therefore should not be treated as such.

To conclude, the selection rules can give great insight into the both qualitative and quantitative aspects of spectra. Making a physical interpretation from the selection rules based on the multipole expansion is, however, not possible due the nonphysical nature of the different terms in the multipole expansion as seen in Eq. (30). Even though the full exponential operator is not plagued by summation of unphysical terms, it unfortunately does not provide the same a priori insights.



## 7. Isotropically averaged oscillator and rotatory strengths

What will follow is the derivation of the isotropic values for the oscillator strength,  $f$ , and the factor  $|T^L|^2 - |T^R|^2$  used in CD spectroscopy. This can be done in either of two ways: (i) the wave vector and the

polarization vector are varied over all possible combinations for a fixed molecular frame, or (ii) the molecule is rotated around the three Euler angles for fixed direction of the wave vector. List et al. [17] adopted the latter view, while in this section we will employ the former. We will start with the averaging over all possible polarization directions,  $\mathcal{E}$ , given a fixed wave vector  $\mathbf{k}$ —the rotatory strength is independent of the selection of the polarization directions and thus requires no such averaging. Note that for the rest of this section the notation  $\langle \hat{x} \rangle = \sum_i \langle 0 | \hat{x}_i | n \rangle$  will be used for any transition property.

The oscillator strength can effectively be expressed as, see Eqs. (6) and (15),

$$f_{0n}(\mathbf{k}, \mathcal{E}) = \frac{2m_e}{e^2 \Delta E_{0n}} |\mathcal{E} \cdot \mathbf{T}'_{0n}|^2,$$

where  $\mathbf{T}'_{0n} = \frac{e}{m_e} \langle \exp(i\mathbf{k} \cdot \mathbf{r}_i) \hat{\mathbf{p}}_i \rangle$ . A general polarization direction can be expressed as

$$\mathcal{E}(\chi) = \cos(\chi) \mathcal{E}_1 + \sin(\chi) \mathcal{E}_2,$$

where the angle  $\chi$  defines any polarization vector in the plane of the two, arbitrarily chosen, orthogonal polarization vectors,  $\mathcal{E}_1$  and  $\mathcal{E}_2$ . That is, the oscillator strength is expressed as

$$f_{0n}(\mathbf{k}, \mathcal{E}(\chi)) = \frac{2m_e}{e^2 \Delta E_{0n}} |(\cos(\chi) \mathcal{E}_1 + \sin(\chi) \mathcal{E}_2) \cdot \mathbf{T}'_{0n}|^2.$$

The square can be expanded as:

$$|(\cos(\chi) \mathcal{E}_1 + \sin(\chi) \mathcal{E}_2) \cdot \mathbf{T}'_{0n}|^2 = A + B \cos(2\chi) + C \sin(2\chi), \text{ where}$$

$$A = \frac{1}{2} (|\mathcal{E}_1 \cdot \mathbf{T}'_{0n}|^2 + |\mathcal{E}_2 \cdot \mathbf{T}'_{0n}|^2),$$

$$B = \frac{1}{2} (|\mathcal{E}_1 \cdot \mathbf{T}'_{0n}|^2 - |\mathcal{E}_2 \cdot \mathbf{T}'_{0n}|^2), \text{ and}$$

$$C = \frac{1}{2} [(\mathcal{E}_1 \cdot \mathbf{T}'_{0n})(\mathcal{E}_2 \cdot \mathbf{T}'_{0n})^* + (\mathcal{E}_1 \cdot \mathbf{T}'_{0n})^*(\mathcal{E}_2 \cdot \mathbf{T}'_{0n})].$$

This is now followed by the averaging of the oscillator strength over all polarization directions, to obtain the oscillator strength for unpolarized light, but for a particular wave vector,

$$\begin{aligned}
f_{0n}(\mathbf{k})_{\text{unpol}} &= \frac{\int_0^{2\pi} f_{0n}(\mathbf{k}, \boldsymbol{\mathcal{E}}(\chi)) \, d\chi}{\int_0^{2\pi} d\chi} \\
&= \frac{m_e}{e^2 \Delta E_{0n}} (|\boldsymbol{\mathcal{E}}_1 \cdot \mathbf{T}'_{0n}|^2 + |\boldsymbol{\mathcal{E}}_2 \cdot \mathbf{T}'_{0n}|^2),
\end{aligned}$$

where the  $\cos(2\chi)$  and  $\sin(2\chi)$  terms trivially vanish upon integration.

What follows now is the averaging over all possible directions of the wave vector. For the expression of the isotropically averaged oscillator and rotatory strength, using the exact description of the electromagnetic field of the interacting photon, no closed formula exists. Lebedev and coworkers [36–41], however, have devised a way of defining a grid by distributing quadrature points over a unit sphere. That is, over the polar and azimuthal angles,  $\theta$  and  $\phi$ , which gives the propagation directions included in the numerical integration for the incoming light. The numerically averaged isotropic oscillator strength, expressed as a sum over quadrature points, is compiled as

$$f_{0n}(k)_{\text{iso}} = \sum_i^{n_{\text{quad}}} w(\theta_i, \phi_i) f_{0n}(\mathbf{k}(\theta_i, \phi_i))_{\text{unpol}},$$

where  $w$  are the weights of the Lebedev numerical quadrature. In such an integration, the exact isotropic average can be systematically approximated. List et al. [17] have shown that this converges, in terms of oscillator strengths, very rapidly with the number of quadrature points.

Now we turn our attention to the isotropic expressions using a truncated multipole expansion to approximate the exact expression for the electromagnetic field of the photon. Here will be derived the lowest order expressions of the oscillator strength and the rotatory strength.

The oscillator strength is approximated, at zeroth order ( $\mathbf{T}'_{0n} \approx \frac{e}{m_e} \langle \hat{\mathbf{p}} \rangle$ ), as

$$f_{0n}(\mathbf{k})_{\text{unpol}} = \frac{1}{m_e \Delta E_{0n}} (|\boldsymbol{\mathcal{E}}_1 \cdot \langle \hat{\mathbf{p}} \rangle|^2 + |\boldsymbol{\mathcal{E}}_2 \cdot \langle \hat{\mathbf{p}} \rangle|^2).$$

Observe that the integrals are independent of the wave vector. The expression above is now integrated over all angles. This is done in terms of the following transformation matrix (expressing a unitary rotation), which will transform any vector  $\mathbf{r} = (x, y, z)$  such that all possible angles are accessed as the azimuthal and polar angles are varied within their ranges,



$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos(\phi) & -\sin(\phi) & 0 \\ \sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos(\theta) & 0 & \sin(\theta) \\ 0 & 1 & 0 \\ -\sin(\theta) & 0 & \cos(\theta) \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Starting with  $\mathbf{k}(\phi=0, \theta=0) = k\hat{\mathbf{e}}_z$ ,  $\mathcal{E}_1 = \hat{\mathbf{e}}_x$ , and  $\mathcal{E}_2 = \hat{\mathbf{e}}_y$  one finds the general relation between the wave vector and the two polarization vectors expressed as

$$\begin{aligned} \mathbf{k}(\phi, \theta) &= k(\cos(\phi)\sin(\theta)\hat{\mathbf{e}}_x + \cos(\phi)\cos(\theta)\hat{\mathbf{e}}_y + \sin(\phi)\hat{\mathbf{e}}_z) \\ \mathcal{E}_1(\phi, \theta) &= \cos(\phi)\cos(\theta)\hat{\mathbf{e}}_x + \sin(\phi)\cos(\theta)\hat{\mathbf{e}}_y - \sin(\phi)\hat{\mathbf{e}}_z \\ \mathcal{E}_2(\phi, \theta) &= -\sin(\phi)\hat{\mathbf{e}}_x + \cos(\phi)\hat{\mathbf{e}}_y. \end{aligned}$$

That is, the oscillator strength, averaged over all polarization directions and for a given propagation direction, is expressed as

$$f_{0n}(\mathbf{k}(\phi, \theta))_{\text{unpol}} = \frac{1}{m_e \Delta E_{0n}} (|\mathcal{E}_1(\phi, \theta) \cdot \langle \hat{\mathbf{p}} \rangle|^2 + |\mathcal{E}_2(\phi, \theta) \cdot \langle \hat{\mathbf{p}} \rangle|^2).$$

The averaged dipole approximation of the oscillator strength reads

$$f_{0n}(k)_{\text{iso}} = \frac{1}{2\pi^2} \int_0^{2\pi} d\phi \sin(\phi) \int_0^\pi d\theta f_{0,n}(\mathbf{k}(\phi, \theta))_{\text{unpol}}$$

and gives the standard isotropic value of the oscillator strength in the velocity gauge as

$$f_{0n, \text{iso}} = \frac{2}{3m_e \Delta E_{0n}} |\langle \hat{\mathbf{p}} \rangle|^2 \approx \frac{2m_e}{3e^2 \Delta E_{0n}} |\langle \mathbf{T}' \rangle|^2. \quad (32)$$

This can also be derived from the fact that the sum,  $f_{0n}(\mathbf{k}(\phi, \theta))_{\text{unpol}} + f_{0n}(\mathbf{k}(\phi, \theta + \frac{\pi}{2}))_{\text{unpol}} + f_{0n}(\mathbf{k}(\phi + \frac{\pi}{2}, \theta + \frac{\pi}{2}))_{\text{unpol}}$ , the sum of the oscillator strength in three arbitrarily chosen orthogonal directions, is invariant under any unitary transformation. This is trivially realized from the fact that  $|\langle \hat{\mathbf{p}} \rangle|^2$  is invariant to any such transformation.

Before introducing the multipole expansion for the isotropically averaged rotatory strength, it is worth to have a quick look at the contributions specific to a particular wave vector. At this point, we adopt the convention of assigning to L the values  $\psi = \frac{\pi}{4}, \eta = -\frac{\pi}{2}$ , and therefore  $\psi = \frac{\pi}{4}, \eta = \frac{\pi}{2}$  to R. An opposite convention would simply result in a change of sign. That is, the rotatory strength (using Eq. (12), for  $\psi = \frac{\pi}{4}$  and  $\eta = -\frac{\pi}{2}$ ), as a function of the wave vector, which is proportional to

$$\Delta_{0n}^{\text{L-R}}(\mathbf{k}) = |T_{0n}^{\text{L}}(\mathbf{k})|^2 - |T_{0n}^{\text{R}}(\mathbf{k})|^2 = 2[T_{0n}^e(\mathbf{k}, \mathcal{E}_2)T_{0n}^o(\mathbf{k}, \mathcal{E}_1) - T_{0n}^e(\mathbf{k}, \mathcal{E}_1)T_{0n}^o(\mathbf{k}, \mathcal{E}_2)],$$

where  $T_{0n}$  is split into the even and odd term contributions of the complex exponential operator (see Eq. (9)).

We proceed by introducing the first-order truncation of the multipole expansion of the exponential operator, that is,  $T^e \approx -iT^{(0)}$  and  $T^o \approx T^{(1)}$ . This would allow one to define a rotatory strength tensor, as a general expression to derive the rotatory strength for an arbitrary direction of the wave vector [42]. It is noted that the first-order term,  $T^{(1)}$ , arranged into the magnetic-dipole and an electric-quadrupole terms, allows the rotatory strength tensor to be written as a sum of a symmetric and an antisymmetric part—the electric-dipole-magnetic-dipole term and the electric-dipole-electric-quadrupole term. The latter is traceless and will not contribute under isotropic averaging. That is, to first order in  $\mathbf{k}$ , one has that

$$\begin{aligned} \Delta_{0n}^{\text{L-R}}(\mathbf{k}) &= 2 \left[ -iT_{0n}^{(0)}(\mathbf{k}, \boldsymbol{\mathcal{E}}_2) T_{0n}^{(1)}(\mathbf{k}, \boldsymbol{\mathcal{E}}_1) + iT_{0n}^{(0)}(\mathbf{k}, \boldsymbol{\mathcal{E}}_1) T_{0n}^{(1)}(\mathbf{k}, \boldsymbol{\mathcal{E}}_2) \right] \\ &= 2i \left[ T_{0n}^{\text{Q}^p}(\mathbf{k}, \boldsymbol{\mathcal{E}}_2) + T_{0n}^{m'}(\mathbf{k}, \boldsymbol{\mathcal{E}}_2) \right] T_{0n}^{\mu^p}(\mathbf{k}, \boldsymbol{\mathcal{E}}_1) \\ &\quad - 2i \left[ T_{0n}^{\text{Q}^p}(\mathbf{k}, \boldsymbol{\mathcal{E}}_1) + T_{0n}^{m'}(\mathbf{k}, \boldsymbol{\mathcal{E}}_1) \right] T_{0n}^{\mu^p}(\mathbf{k}, \boldsymbol{\mathcal{E}}_2) \\ &= \Delta_{0n}^{\text{L-R}}(\mathbf{k})^{\text{Q}^p} + \Delta_{0n}^{\text{L-R}}(\mathbf{k})^{m'} \end{aligned}$$

with the multipole terms derived in Section 4. To proceed with deriving the isotropic average the contribution due to the electric-quadrupole term,  $\Delta_{0n}^{\text{L-R}}(\mathbf{k})^{\text{Q}^p}$ , will be ignored, as mentioned above. Furthermore, note that the rotatory strength is not an explicit function of the polarization directions, however, they have to fulfill mutual orthogonality and both be orthogonal to the wave vector. Further, using the relationships  $\mathbf{k} \times \boldsymbol{\mathcal{E}}_1 = k\boldsymbol{\mathcal{E}}_2$ ,  $\mathbf{k} \times \boldsymbol{\mathcal{E}}_2 = -k\boldsymbol{\mathcal{E}}_1$ , and Eq. (22), we see that

$$\begin{aligned} T_{0n}^{m'}(\mathbf{k}, \boldsymbol{\mathcal{E}}_1) &= -ik(\boldsymbol{\mathcal{E}}_2 \cdot \langle \hat{\mathbf{m}}' \rangle) \\ T_{0n}^{m'}(\mathbf{k}, \boldsymbol{\mathcal{E}}_2) &= +ik(\boldsymbol{\mathcal{E}}_1 \cdot \langle \hat{\mathbf{m}}' \rangle) \end{aligned}$$

and obtain the expression

$$\Delta_{0n}^{\text{L-R}}(\mathbf{k})^{m'} = -2k \frac{e}{m_e} [(\boldsymbol{\mathcal{E}}_1 \cdot \langle \hat{\mathbf{m}}' \rangle)(\boldsymbol{\mathcal{E}}_1 \cdot \langle \hat{\mathbf{p}} \rangle) + (\boldsymbol{\mathcal{E}}_2 \cdot \langle \hat{\mathbf{m}}' \rangle)(\boldsymbol{\mathcal{E}}_2 \cdot \langle \hat{\mathbf{p}} \rangle)].$$

That is, for example, the rotatory strength expressed explicitly for a wave vector in the  $z$ -direction and the two polarization directions to be arbitrarily chosen to be in the  $x$ - and  $y$ -direction, respectively, gives the expression,

$$\Delta_{0n}^{\text{L-R}}(k\hat{e}_z)^{m'} = -2k\frac{e}{m_e} \left( \langle \hat{m}'_x \rangle \langle \hat{p}_x \rangle + \langle \hat{m}'_y \rangle \langle \hat{p}_y \rangle \right)$$

The isotropically averaged rotatory strength is now derived in a fashion very similar to that of the oscillator strength. In this way, one obtains the expression of the isotropic squared difference of the transition moments of right and left polarized light,

$$\Delta_{0n}^{\text{L-R}}(k)_{\text{iso}} = -\frac{4}{3}k\frac{e}{m_e} \langle \hat{\mathbf{p}} \rangle \cdot \langle \hat{\mathbf{m}}' \rangle.$$

Further replacement of  $k$  by  $\frac{\Delta E}{\hbar c}$  and of  $\frac{e}{m_e} \langle \hat{\mathbf{p}} \rangle$  by  $i\frac{\Delta E_{0n}}{\hbar} \langle \hat{\boldsymbol{\mu}} \rangle$ , as in Eq. (18), leads to

$$\Delta_{0n,\text{iso}}^{\text{L-R}} = -i\frac{4\Delta E^2}{3\hbar^2 c} \langle \hat{\boldsymbol{\mu}} \rangle \cdot \langle \hat{\mathbf{m}}' \rangle = \frac{4\Delta E^2}{3\hbar^2 c} \text{Im}(\langle \hat{\boldsymbol{\mu}} \rangle \cdot \langle \hat{\mathbf{m}}' \rangle), \quad (33)$$

since for real wave functions  $\langle \hat{\boldsymbol{\mu}} \rangle$  is pure real and  $\langle \hat{\mathbf{m}}' \rangle$  is pure imaginary. Note that this last form is in mixed length and velocity gauge, and therefore subject to origin dependence. The consequences of the mixed gauge were discussed further in [Section 5](#).



## 8. Evaluation of the integrals for the transition moments

The evaluation of the integrals for the exact semiclassical light–matter interaction has been the major obstacle in the evaluation of the operator [12, 43]. It will be shown below that the exact semiclassical light–matter interaction of a plane wave can be thought of as a Fourier transformation of the overlap between basis functions in a Gaussian basis and that this can be solved analytically. The evaluation of the integrals is therefore very similar to those found for dynamic structure factors [43], matrix elements in a mixed Gaussian and plane wave basis set [31, 32, 44], London atomic orbitals or gauge invariant atomic orbitals (GIAO) [25–27, 29, 45–47], and similarities are shared with the plane wave representations of the electromagnetic field [48].

In order to evaluate the transition rate, Eq. (2), the matrix element of Eq. (3) needs to be evaluated. This can be generalized to the expression

$$\langle 0 | \hat{U} | n \rangle = \sum_{\mu\nu} U_{\mu\nu}^{AB} \gamma_{\mu\nu}^{AB}. \quad (34)$$

In Eq. (34),  $U_{\mu\nu}^{AB}$  is the integral matrix for the orbital bases  $A$  and  $B$  with indices  $\mu$  and  $\nu$  and likewise defined for the transition density matrix  $\gamma_{\mu\nu}^{AB}$  [49]. As in Section 4, we ignore the intrinsic spin contribution, i.e., we approximate Eq. (3) with Eq. (15). For a wave function expanded in Gaussians the individual terms in  $U_{\mu\nu}^{AB}$  from Eq. (34) correspond to evaluating integrals of the form

$$I_\lambda = \langle \chi_\mu | \exp(\pm i\mathbf{k} \cdot \mathbf{r}) \hat{p}_\lambda | \chi_\nu \rangle \quad (35)$$

for  $\lambda = x, y, z$ , where the real-valued atomic Cartesian basis functions  $\chi_\mu$  and  $\chi_\nu$  are expressed as

$$\begin{aligned} \chi_\mu(\mathbf{r}) &= \chi_{i,j,k}(\mathbf{r}, \alpha_\mu, \mathbf{A}) \\ &= (x - A_x)^i (y - A_y)^j (z - A_z)^k \exp(-\alpha_\mu |\mathbf{r} - \mathbf{A}|^2) \\ &= \chi_i(x, \alpha_\mu, A_x) \chi_j(y, \alpha_\mu, A_y) \chi_k(z, \alpha_\mu, A_z) \end{aligned}$$

in their different components, where  $i, j$ , and  $k$  represent the order of the Cartesian components  $x, y$ , and  $z$ , respectively. The integral in Eq. (35) can be factorized into three one-dimensional integrals

$$I_\lambda = I_\lambda^x \cdot I_\lambda^y \cdot I_\lambda^z,$$

where each  $I_\lambda^\tau$  is of the form

$$I_\lambda^\tau = \int_{-\infty}^{\infty} \chi_i(\tau, \alpha_\mu, A_\tau) \exp(\pm ik_\tau \tau) \hat{q}_{\tau\lambda} \chi_j(\tau, \alpha_\nu, B_\tau) d\tau, \quad \hat{q}_{\tau\lambda} = \begin{cases} \hat{p}_\lambda & \text{if } \tau = \lambda, \\ 1 & \text{if } \tau \neq \lambda. \end{cases}$$

Applying, for example, the differentiation operator  $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$  one finds

$$I_x^x = -i\hbar \int_{-\infty}^{\infty} \chi_i(x, \alpha_\mu, A_x) \exp(\pm ik_x x) \left[ j\chi_{j-1}(x, \alpha_\nu, B_x) - 2\alpha_\nu \chi_{j+1}(x, \alpha_\nu, B_x) \right] dx \quad (36)$$

that the integrals  $I_\lambda^\lambda$  can be expressed as a sum of two terms. From Eq. (36) it is seen that both terms, as well as those for  $\tau \neq \lambda$ , are of the form

$$J_\lambda = \int_{-\infty}^{\infty} \exp(\pm ik_\lambda \lambda) \chi_i(\lambda, \alpha_\mu, A_\lambda) \chi_j(\lambda, \alpha_\nu, B_\lambda) d\lambda. \quad (37)$$

Using the Gaussian product formula one notes that the expression in Eq. (37) is akin to a Fourier transformation of a Gaussian from real space  $\lambda$  to  $k_\lambda$  space. Integrals of the form in Eq. (37) can be solved analytically using recursive

formulas for the analytical Fourier representation of Gaussians or directly as a Fourier transformation of the overlap between two basis functions as shown by Lehtola et al. for dynamic structure factors [32, 43].

Since the Fourier transformation of a Gaussian is a new Gaussian, one can choose not to use the analytical form, but instead rewrite the integral in Eq. (37) to a form which can be easily evaluated by a standard Gauß–Hermite quadrature. Alternative approaches have been suggested, for example, by List et al. in which an extension to the McMurchie–Davidson procedure is suggested based on the individual integration of the real and imaginary part of the complex operator or by Tellgren and coworkers using magnetic field-dependent Hermite Gaussian functions [13, 50, 51]. To proceed with Gauß–Hermite quadrature, using the Gaussian product formula in Eq. (37), for  $\lambda = x$

$$\begin{aligned} J_x &= \int_{-\infty}^{\infty} \exp(\pm ik_x x) \chi_i(x, \alpha_\mu, A_x) \chi_j(x, \alpha_\nu, B_x) dx \\ &= \exp\left[-\frac{\alpha_\mu \alpha_\nu}{\zeta} (A_x - B_x)^2\right] \int_{-\infty}^{\infty} (x - A_x)^i (x - B_x)^j \exp(-\zeta(x - P_x)^2 \pm ik_x x) dx, \end{aligned} \quad (38)$$

where  $\zeta = \alpha_\mu + \alpha_\nu$  and  $P_x = (\alpha_\mu A_x + \alpha_\nu B_x)/\zeta$  one can complete the square in the exponent

$$J_x = \exp\left[-\frac{\alpha_\mu \alpha_\nu}{\zeta} (A_x - B_x)^2\right] \exp(\gamma) \int_{-\infty}^{\infty} (x - A_x)^i (x - B_x)^j \exp(-\zeta(x - Q_x)^2) dx, \quad (39)$$

where  $Q_x = P_x \pm ik_x/(2\zeta)$  and  $\gamma = \zeta(Q_x^2 - P_x^2)$ . Notice here that for mixed Gaussian and plane wave basis set expressions are similar to Eq. (38) [44].

Making a change of variables  $t = \sqrt{\zeta}(x - Q_x)$  the integral in Eq. (39) can now be transformed to

$$J_x = \Theta \lim_{S \rightarrow \infty} \int_{-\sqrt{\zeta}(S - Q_x)}^{\sqrt{\zeta}(S - Q_x)} \left(\frac{t}{\sqrt{\zeta}} + Q_x - A_x\right)^i \left(\frac{t}{\sqrt{\zeta}} + Q_x - B_x\right)^j \exp(-t^2) dt, \quad (40)$$

where

$$\Theta = \exp\left(-\frac{\alpha_\mu \alpha_\nu}{\zeta} (A_x - B_x)^2\right) \frac{\exp(\gamma)}{\sqrt{\zeta}}.$$

Defining the polynomial

$$f(t) = \Theta \left( \frac{t}{\sqrt{\zeta}} + Q_x - A_x \right)^i \left( \frac{t}{\sqrt{\zeta}} + Q_x - B_x \right)^j \quad (41)$$

Eq. (40) can be written a little more compact

$$J_x = \lim_{S \rightarrow \infty} \int_{-\sqrt{\zeta}(S-Q_x)}^{\sqrt{\zeta}(S-Q_x)} f(t) \exp(-t^2) dt. \quad (42)$$

Since the integral in Eq. (42) is analytic the integration is independent of the path and can therefore be split into

$$\begin{aligned} J_x &= \lim_{S \rightarrow \infty} \int_{-\sqrt{\zeta}(S-Q_x)}^{-\sqrt{\zeta}S} f(t) \exp(-t^2) dt \\ &\quad + \lim_{S \rightarrow \infty} \int_{-\sqrt{\zeta}S}^{\sqrt{\zeta}S} f(t) \exp(-t^2) dt \\ &\quad + \lim_{S \rightarrow \infty} \int_{\sqrt{\zeta}S}^{\sqrt{\zeta}(S-Q_x)} f(t) \exp(-t^2) dt. \end{aligned} \quad (43)$$

Since  $\sqrt{\zeta} > 0$  and due to the exponential decay of the integrand, as  $\text{Re}(t) \rightarrow \pm\infty$ , the first and last terms of the RHS of Eq. (43) vanish, leaving

$$J_x = \lim_{S \rightarrow \infty} \int_{-\sqrt{\zeta}S}^{\sqrt{\zeta}S} f(t) \exp(-t^2) dt = \int_{-\infty}^{\infty} f(t) \exp(-t^2) dt$$

to be evaluated. One can note that although  $t$  in general is complex it will only be integrated along the real axis. Thus, for all practical purposes, a standard Gauß–Hermite quadrature can be used. However, the coefficients of the polynomial, see Eq. (41), are complex. Hence, using the standard Gauß–Hermite nodes  $t_n$  and weights  $w_n$ , the integral is computed as

$$J_x = \sum_n w_n f(t_n)$$

or equivalently with the transformed quadrature nodes  $x_n = t_n/\sqrt{\zeta} + Q_x$

$$J_x = \Theta \sum_n w_n (x_n - A_x)^i (x_n - B_x)^j.$$

## 8.1 Faster evaluation of the integrals for the transition moments

The central problem, from a numerical perspective, with the exact operator in comparison to the multipole expansion is the need for a new set of integrals for every transition since every transition has a different resonance frequency and therefore also different  $k$ -vectors. For systems where only few transitions need to be calculated, this is not a problem, but, for example, in X-ray spectroscopy of transition metal complexes many hundreds or more transitions are involved and thus, calculating a new set of integrals for every transition quickly becomes cumbersome. It is therefore of interest to approximate the integrals in a way such that there is no need to recalculate them for every transition.

Since we are usually only interested in transitions within a reasonably narrow energy window in comparison to the energy of the incoming light, it is interesting to look at the change of the value of the integral for energetically close transitions:

$$\begin{aligned}
 \Delta I_{\lambda}^{\tau} &= I_{\lambda}^{\tau}(k^a) - I_{\lambda}^{\tau}(k^b) \\
 &= \int_{-\infty}^{\infty} \chi_i(\tau, \alpha_{\mu}, A_{\tau}) [\exp(\pm i k_{\tau}^a \tau) - \exp(\pm i k_{\tau}^b \tau)] \hat{q}_{\tau\lambda} \chi_j(\tau, \alpha_{\nu}, B_{\tau}) d\tau \\
 &= \int_{-\infty}^{\infty} \chi_i(\tau, \alpha_{\mu}, A_{\tau}) \exp(\pm i k_{\tau}^a \tau) [1 - \exp(\pm i k_{\tau}^c \tau)] \hat{q}_{\tau\lambda} \chi_j(\tau, \alpha_{\nu}, B_{\tau}) d\tau,
 \end{aligned} \tag{44}$$

where  $k^c = k^b - k^a$ . Assuming  $k^a \approx k^b$  then  $k^c$  will be small and performing multipole expansions for  $k^c$  and  $k^a$  in Eq. (44) we find the first-order difference to be

$$\int_{-\infty}^{\infty} \pm \chi_i(\tau, \alpha_{\mu}, A_{\tau}) i k_{\tau}^c \tau \hat{q}_{\tau\lambda} \chi_j(\tau, \alpha_{\nu}, B_{\tau}) d\tau. \tag{45}$$

The first-order difference is therefore seen to be of first order in the transition moments for the multipole expansion and multiplied by a small number  $k^c$ . For the isotropically averaged oscillator strengths the difference is of second-order  $(k^c)^2$ . The result in Eq. (45) is, however, not so surprising since the  $k$ -vector first appears at the first order in the transition moments for the multipole expansion and the difference between two integrals with different  $k$ -vectors naturally must be there.

This suggests various level of approximation. The simplest idea, valid especially for intense dipole-allowed transition, is to simply neglect this

difference by grouping all transitions within a small relative energy interval and using the same integral for all those transitions. As a first-order correction, the linearity in  $k^{\ell}$  in Eq. (45) can be used by computing the integrals for the first and last transition of the energy interval and perform a linear interpolation to estimate their value for all transition energies within that interval.

It is important to note that while this approximation is motivated by a multipole expansion, it is significantly more accurate than the conventional multipole expansion, as long as the energy interval, and thus  $k^{\ell}$ , is kept small. This provides the user with simple and powerful error control.



## 9. Connection with experiments

Absorption spectra are measured as the absorbance ( $A$ ) versus the frequency ( $\nu$ ) of the electromagnetic radiation.<sup>b</sup> The absorbance is defined as the decimal logarithm of the ratio of the incident intensity ( $I_0$ ) and the transmitted intensity ( $I$ ), and within a range, it is linear with respect to the molar concentration ( $C$ ) and path length ( $l$ ), the proportionality constant being the molar extinction coefficient ( $\epsilon$ ; not to be confused with  $\epsilon_0$ , the vacuum permittivity):

$$A(\nu) = \log_{10} \frac{I_0(\nu)}{I(\nu)} = \epsilon(\nu)Cl$$

The experimental cross section for a particular absorption band can be obtained by integrating the area in a  $\epsilon$  vs  $\nu$  representation:

$$\sigma^{\nu} = \frac{\ln 10}{N_A} \int \epsilon(\nu) d\nu$$

from which the oscillator strength is obtained dividing by  $\sigma_{\text{clas}}^{\nu}$ , Eq. (5):

$$f = \frac{\sigma^{\nu}}{\sigma_{\text{clas}}^{\nu}} = \frac{4m_e c \epsilon_0}{N_A e^2} \ln 10 \int \epsilon(\nu) d\nu$$

The factor in front of the integral has the value of  $1.441 \times 10^{-18} \text{ mol s m}^{-2}$  or  $4.319 \times 10^{-9} \text{ mol cm L}^{-1}/(\text{c cm}^{-1})$

<sup>b</sup> Other quantities to identify the electromagnetic radiation are also possible, like wavelength ( $\lambda$ ), wave number ( $\bar{\nu}$ ), angular frequency ( $\omega$ ) or photon energy ( $E$ ); appropriate conversion factors would then need to be used in the following equations.



The computed oscillator strength (Eq. 6) becomes, within the dipole approximation and with isotropic averaging, in the velocity gauge (Eq. 32):

$$f_{\text{iso}}^p = \frac{2}{3m_e \Delta E_{0n}} |\langle \hat{\mathbf{p}} \rangle|^2 = \frac{2}{3\hbar^2 e^2} \Delta E_{0n} |\langle \hat{\boldsymbol{\mu}}_{0n}^p \rangle|^2$$

and in the length gauge:

$$f_{\text{iso}}^r = \frac{2m_e \Delta E_{0n}}{3\hbar^2} |\langle \hat{\mathbf{r}} \rangle|^2 = \frac{2}{3\hbar^2 e^2} \Delta E_{0n} |\langle \hat{\boldsymbol{\mu}}_{0n} \rangle|^2,$$

where  $\langle \boldsymbol{\mu} \rangle = -e \langle \hat{\mathbf{r}} \rangle$  and  $\langle \boldsymbol{\mu}^p \rangle = -\frac{ie\hbar}{m_e \Delta E} \langle \hat{\mathbf{p}} \rangle$  are the transition dipole moment in length and velocity gauge, respectively.<sup>c</sup>

From these, a dipole strength ( $D$ ), representing  $\langle \hat{\boldsymbol{\mu}}_{0n} \rangle^2$  or  $\langle \hat{\boldsymbol{\mu}}_{0n}^p \rangle^2$ , can be defined as:

$$D = \frac{3\hbar^2 e^2}{2m_e \Delta E_{0n}} f_{\text{iso}} = \frac{3\hbar c \epsilon_0}{\pi N_A} \ln 10 \int \frac{\epsilon(\nu)}{\nu} d\nu,$$

where the approximation  $\frac{1}{\nu_{0n}} \int \epsilon d\nu \simeq \int \frac{\epsilon}{\nu} d\nu$  has been used. The units of  $D$  are therefore those of an electric-dipole moment squared. The factor in front of the integral has the value of 1.022 C<sup>2</sup> mol or  $9.186 \times 10^{-3}$  D<sup>2</sup>/ (L mol<sup>-1</sup> cm<sup>-1</sup>).

Circular dichroism is measured as a difference between absorbance of left- and right-circularly polarized radiation. Similarly to the above, a difference oscillator strength can be obtained by integration of a differential spectral band:

$$\Delta f = \frac{4m_e c \epsilon_0}{N_A e^2} \ln 10 \int \Delta \epsilon(\nu) d\nu$$

In this case, the dipole approximation does not help, since that would trivially give  $\Delta f = 0$ . The first terms to contribute in the multipole expansion are the electric dipole–electric quadrupole and electric dipole–magnetic dipole, which results, after isotropically averaging, in:

$$\Delta f_{\text{iso}}^{fp} = \frac{4}{3m_e \hbar c} \langle \hat{\mathbf{p}} \rangle \cdot \langle \hat{\mathbf{r}} \times \hat{\mathbf{p}} \rangle = \frac{8m_e}{3\hbar^2 e^2 c} \Delta E_{0n} \text{Im}(\langle \hat{\boldsymbol{\mu}}_{0n}^p \rangle \cdot \langle \hat{\mathbf{m}}'_{0n} \rangle)$$

<sup>c</sup> In Ref. [12] the authors used the symbol  $\boldsymbol{\mu}^p$  for the imaginary quantity  $\frac{e}{m_e} \sum_i \mathbf{p}_i$ , which does not have the dimensions of an electric-dipole moment.

for the velocity gauge, and for a mixed gauge:

$$\Delta_{\text{iso}}^{f,r,p} = -i \frac{4\Delta E_{0n}}{3\hbar^2 c} \langle \hat{\mathbf{r}} \rangle \cdot \langle \hat{\mathbf{r}} \times \hat{\mathbf{p}} \rangle = \frac{8m_e}{3\hbar^2 e^2 c} \Delta E_{0n} \text{Im}(\langle \hat{\boldsymbol{\mu}}_{0n} \rangle \cdot \langle \hat{\mathbf{m}}'_{0n} \rangle)$$

The rotatory strength ( $R$ ) is defined to represent  $\text{Im}(\langle \hat{\boldsymbol{\mu}}_{0n} \rangle \cdot \langle \hat{\mathbf{m}}'_{0n} \rangle)$ , analogous to the dipole strength:

$$R = \frac{3\hbar^2 e^2 c}{8m_e \Delta E_{0n}} \Delta_{\text{iso}} = \frac{3\hbar c^2 \epsilon_0}{4\pi N_A} \ln 10 \int \frac{\Delta \epsilon(\nu)}{\nu} d\nu$$

The units of  $R$  are those of an electric dipole times a magnetic dipole. The factor in front of the integral has the value of  $7.660 \times 10^{-53} \text{ m s A}^2 \text{ mol}$  or  $2.296 \times 10^{-39} \text{ Fr cm erg G}^{-1}/(\text{L mol}^{-1} \text{ cm}^{-1})$ . The reduced rotatory strength  $[R]$  is defined as:

$$[R] = \frac{100}{\mu_D \mu_B} R$$

where  $\mu_D$  is a dipole of 1 D and  $\mu_B$  is the Bohr magneton; in other words,  $[R]$  is the value of the rotatory strength in units of  $10^{-2} \text{ D } \mu_B = 1.967 \times 10^{-3} \text{ au} = 9.274 \times 10^{-41} \text{ Fr cm erg G}^{-1}$ .

Another commonly used measure of circular dichroism is the ellipticity. Linearly polarized light can be represented by a superposition of left- and right-circularly polarized waves with equal amplitudes. When linearly polarized light incides on an optically active medium, the left- and right-circularly polarized components are absorbed differently, as indicated by  $\Delta \epsilon(\nu)$ , and the two components in the transmitted light do not have equal amplitude: it is elliptically polarized. The ellipticity angle ( $\theta$ ) is defined from the major and minor axes of the resulting ellipse, i.e.:

$$\tan \theta = \frac{A_0^R - A_0^L}{A_0^R + A_0^L},$$

where  $A_0^R$  and  $A_0^L$  are the magnitudes of the electric field vectors for the right- and left-circularly polarized components,  $\theta$  is zero for linearly polarized light ( $A_0^R = A_0^L$ ) and  $\frac{\pi}{4} = 45$  degrees for circularly polarized light ( $A_0^R = 0$  or  $A_0^L = 0$ ). Note that although  $\theta$  is an angle, it has no information about the rotation of the plane of polarization, which is associated with the phase change of the left and right components, but only on the fact that linearly polarized light becomes elliptically polarized. The difference in absorption is very small and  $\theta$  can be approximated as  $\tan \theta$  (in radians). As with absorbance, the ellipticity of the transmitted light is proportional to the

concentration and path length, so the molar ellipticity ( $[\theta]$ ) is defined, and can be directly related to  $\Delta\varepsilon$  (in degrees):

$$[\theta] = \frac{\theta}{Cl} \simeq \frac{\ln 10}{4} \frac{180}{\pi} \Delta\varepsilon$$

The factor has the value of 32.98 degrees. The units of  $\varepsilon$  are usually  $\text{L mol}^{-1} \text{cm}^{-1}$ , while those of  $[\theta]$  are more commonly  $\text{degree cm}^2 \text{dmol}^{-1}$ , which accounts for an additional factor of 100 normally found in conversion formulas.



## 10. Summary

In this chapter we have worked on the formalism for oscillator and rotatory strengths computed as transition properties in an approach based on explicitly expressed states.

The development of the formalism is based on the Jones vector approach to describe polarized light (where circular and linear polarized light are just two limits), and the use of the exact semiclassical operator describing the electromagnetic field of the interacting photon. Subsequently, this chapter discusses the origin, nature, and possible problems with different types of gauges—the velocity vs length gauge. This was followed by the introduction of the multipole expansion of the exponential expression for the electromagnetic field, which subsequently is subjected to a truncation. This chapter discusses the so-called selection rules, here both in the terminology of the conventional truncated multipole approach and also in terms of the exact operator along with the physical interpretation of the transitions. This chapter proceeds to derive the isotropic values for the oscillator and rotatory strengths. Furthermore, it is in some detail described how the integrals of the exact operator can be evaluated analytically in the Gauß–Hermite scheme. This was followed by a brief discussion of how the exact-operator approach can be substantially speeded up in the case of X-ray spectroscopy. Finally, the association between the experimentally observed quantities and the theory was presented.

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