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On the Evaluation of Electric and Magnetic Dipole Transition Moments in the ZDO Approximation

AAGE E. HANSEN

Department for Physical Chemistry, University of Copenhagen, Denmark

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The implications of the ZDO approximation for the evaluation of electric and magnetic dipole transition moments are analyzed using an overlap ordered expansion of the type proposed by FISCHER-HJALMARS. The relative merits of electric dipole length and electric dipole velocity matrix elements are discussed from the point of view of their use in conjunction with the ZDO approximation.

Die Folgerungen aus der ZDO-Näherung für die Berechnung elektrischer und magnetischer Dipolübergangsmomente werden mit Hilfe einer geordneten Entwicklung der Überlappungsmatrix, wie von FISCHER-HJALMARS vorgeschlagen, untersucht. Die relativen Vorzüge der Benutzung von Matrixelementen des Dipolmomentoperators einerseits und des Impulsoperators andererseits werden im Rahmen der ZDO-Näherung diskutiert.

Analyse des implications de l'approximation du recouvrement différentiel nul dans l'évaluation des moments de transition dipolaire électrique et magnétique, en utilisant un développement en série selon les puissances du recouvrement du type de celui proposé par FISCHER-HJALMARS. Les mérites relatifs des éléments de matrice des opérateurs longueur dipolaire électrique et vitesse dipolaire électrique sont discutés du point de vue de leur utilisation dans le cadre de l'approximation à recouvrement différentiel nul.

1. Introduction

One prominent approximation in current molecular orbital calculations on larger molecules is the so-called zero-differential-overlap (ZDO) approximation [*11*, *14*] according to which the number and types of molecular integrals to be evaluated are reduced considerably by formally neglecting the overlap distribution for atomic orbitals on different centers. It has repeatedly been argued [*3*, *6*, *8*, *12*] that the use of the ZDO approximation amounts to a reinterpretation of the basis set of atomic orbitals used for the construction of the molecular orbitals such that this basis set should be a Løwdin orthogonalized orbital set [*5*] rather than a non-orthogonal set of e.g. Slater-type orbitals.

FISCHER-HJALMARS [*3*] has recently derived explicit expressions for such orthogonalized orbitals and for the energy matrix elements between them in terms of the original, non-orthogonal set of orbitals. This derivation is based upon an ordered expansion of the overlap matrix for the relevant orbitals, and it appeared in the course of the derivation that nearest neighbour matrix elements for some one-electron operators differ in magnitude and sign when evaluated respectively in the orthogonal and in the non-orthogonal orbital basis. This difference is obtained already by taking first order terms in the overlap-ordered expansion into account.

It is, on the other hand, common usage to calculate the one-electron matrix elements which arise in the evaluation of electric and magnetic dipole transition moments [2] for electronic excitations in molecular systems from a non-orthogonal atomic orbital set at the same time as the ZDO approximation is invoked for the determination of the wavefunctions. It therefore seems relevant to investigate whether differences similar to those found by FISCHER-HJALMARS [3] for some one-electron energy operator matrix elements can be expected to appear for the operators used in the calculations of electric and magnetic dipole transition moments. This is of particular importance for theoretical calculations of the natural optical rotatory power since in this case the relative signs of the electric and magnetic dipole transition moments are of ultimate importance [9].

FISCHER-HJALMARS' derivations [3] are made under the assumption that each atomic center in the molecules contributes only one atomic orbital to the molecular orbitals used in the description of the mobile electrons. This is, however, not the case if for instance $n - \pi^+$ excited states of ketones or heteroaromatics are considered. In these cases at least two atomic orbitals must be taken explicitly into account for some of the atoms. We shall therefore consider the evaluation of the matrix elements pertinent for the electric and magnetic dipole transition moments for two different molecular systems. Firstly, the case treated by FISCHER-HJALMARS [3] in which the basis set of orbitals contains one orbital per atom. Secondly, the situation where the molecular orbitals are built from two mutually orthogonal sets of atomic orbitals where some atoms contribute two orbitals. The analysis is in both cases carried out to first order in a nearest-neighbour overlap integral only since the discrepancies observed by FISCHER-HJALMARS are revealed in this order of approximation as mentioned above.

Electric dipole transition moments can be calculated on the basis of either the electric dipole length operator or the linear momentum operator (also called the dipole velocity operator) [2]. For exact wavefunctions the two procedures must lead to identical results, whereas inaccurate wavefunctions may lead to notably different results for the two operators, and it is a point of current interest and discussion which of the two procedures to use in any particular case [4, 15, 17]. We shall therefore in the present communication consider the two procedures separately and then ultimately compare their relative merits from the point of view of their use in conjunction with the ZDO approximation.

2. One Orbital per Atom

a) Orbitals and general matrix elements

We shall in this section briefly recapitulate the pertinent parts of FISCHER-HJALMARS' derivations [3]. Consider a non-orthogonal set of atomic orbitals, χ_p, which are assumed real. It is further assumed that no two orbitals are on the same center and that all nearest neighbour overlap integrals are of approximately the same magnitude. From this set of orbitals one can obtain a set of orthogonalized orbitals [5], λ_p, by the equation

$$\boldsymbol{\lambda} = \boldsymbol{\chi} \cdot \boldsymbol{S}^{-1/2} \tag{1}$$

where $\boldsymbol{\lambda}$ and $\boldsymbol{\chi}$ are row matrices of the respective orbitals and $\boldsymbol{S}$ is the overlap matrix with elements:

$$S_{pq} = \int \chi_p \, \chi_q d\tau \, .$$

This overlap matrix can to first order in a nearest neighbour overlap integral be written

$$\boldsymbol{S} = \mathbf{1} + \boldsymbol{a}$$

where $\mathbf{1}$ is a unit matrix and $\boldsymbol{a}$ is a symmetric matrix with elements:

$$a_{p,q} = S_{p,p+1} \cdot \delta_{p+1,q} + S_{p,p-1} \cdot \delta_{p-1,q} \, . \tag{2}$$

A next-nearest neighbour overlap is of the order of magnitude of the square of a nearest neighbour overlap and can hence consistently be neglected here [*3*]. The matrix $\boldsymbol{S}^{-1/2}$ is then readily found to first order as:

$$\boldsymbol{S}^{-1/2} = \mathbf{1} - \tfrac{1}{2} \boldsymbol{a} \tag{3}$$

and (1), (2) and (3) can be combined to give the following expression for an orbital λ_p belonging to the orthogonalized set

$$\begin{aligned} \lambda_p &= \sum_k \chi_k \, [\boldsymbol{S}^{-1/2}]_{kp} = \sum_k \chi_k (\delta_{kp} - \tfrac{1}{2} a_{k,p}) \\ &= \chi_p - \tfrac{1}{2} S_{p,p-1} \, \chi_{p-1} - \tfrac{1}{2} S_{p,p+1} \, \chi_{p+1} \, . \end{aligned} \tag{4}$$

This orbital is essentially as well localized as the orbital λ_p; the additional small terms contribute the extra nodes which assure the required first order orthogonality to the neighbouring orbitals in the set.

The following general relations between matrix elements of a one electron operator, M, evaluated in respectively the λ and the χ basis are then obtained by straightforward application of Eq. (4). The next-nearest neighbour matrix element (7) in the λ basis is included in order to ascertain that no non-negligible terms arise in this matrix element.

$$\begin{aligned} \int \lambda_p M \lambda_p d\tau &= \langle \lambda_p \mid M \mid \lambda_p \rangle \\ &= \langle \chi_p \mid M \mid \chi_p \rangle - \tfrac{1}{2} S_{p,p-1} \, [\langle \chi_p \mid M \mid \chi_{p-1} \rangle + \langle \chi_{p-1} \mid M \mid \chi_p \rangle] - \\ &\quad - \tfrac{1}{2} S_{p,p+1} \, [\langle \chi_p \mid M \mid \chi_{p+1} \rangle + \langle \chi_{p+1} \mid M \mid \chi_p \rangle] \end{aligned} \tag{5}$$

$$\begin{aligned} \int \lambda_p M \lambda_{p+1} d\tau &= \langle \lambda_p \mid M \mid \lambda_{p+1} \rangle \\ &= \langle \chi_p \mid M \mid \chi_{p+1} \rangle - \tfrac{1}{2} S_{p,p+1} \, [\langle \chi_p \mid M \mid \chi_p \rangle + \langle \chi_{p+1} \mid M \mid \chi_{p+1} \rangle] \end{aligned} \tag{6}$$

$$\begin{aligned} \int \lambda_p M \lambda_{p+2} d\tau &= \langle \lambda_p \mid M \mid \lambda_{p+2} \rangle \\ &= \langle \chi_p \mid M \mid \chi_{p+2} \rangle - \tfrac{1}{2} S_{p,p+1} \, \langle \chi_{p+1} \mid M \mid \chi_{p+2} \rangle - \\ &\quad - \tfrac{1}{2} S_{p+1,p+2} \, \langle \chi_p \mid M \mid \chi_{p+1} \rangle = o(S^2) \, . \end{aligned} \tag{7}$$

One electron matrix elements involving two non-orthogonal orbitals χ_p and χ_q can be expected to be at most of the same order as the corresponding overlap integral. All elements connecting non-nearest neighbour orbitals are therefore neglected in (5) and (6) whereas we have kept the leading next-nearest neighbour term in (7) in order to show that the three largest terms in the expansion of this integral are all of second order. Non-nearest neighbour matrix elements are therefore neglected in both the λ and the χ basis in the present discussion.

b) Electric and magnetic dipole transition moments

As mentioned in the introduction two different operators can be used for the evaluation of the intensity of an electric dipole transition, the two being respectively the electric dipole length operator [*2*]:

$$e\mathfrak{r} = e(\mathfrak{i}\,x + \mathfrak{j}\,y + \mathfrak{k}\,z) \tag{8}$$

where e is the electronic charge, and the linear momentum operator [*2*]:

$$\mathfrak{p} = -\,i\hbar\,\hat{\nabla} = -\,i\hbar\left(\mathfrak{i}\,\frac{\partial}{\partial x} + \mathfrak{i}\,\frac{\partial}{\partial y} + \mathfrak{k}\,\frac{\partial}{\partial z}\right). \tag{9}$$

The operator for the magnetic dipole transition moment is the angular momentum operator [*2*]:

$$\begin{aligned} \mathfrak{l} &= -\,i\hbar\,(\mathfrak{r} \times \hat{\nabla}) \\ &= -\,i\hbar\left[\mathfrak{i}\left(y\,\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y}\right) + \mathfrak{j}\left(z\,\frac{\partial}{\partial x} - x\,\frac{\partial}{\partial z}\right) + \mathfrak{k}\left(x\,\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x}\right)\right]. \end{aligned} \tag{10}$$

The hermitean character of the three operators gives the following relations:

$$\langle \chi_p \mid e\mathfrak{r} \mid \chi_q \rangle = \langle \chi_q \mid e\mathfrak{r} \mid \chi_p \rangle \tag{11a}$$

$$\langle \chi_p \mid \mathfrak{p} \mid \chi_q \rangle = \langle \chi_q \mid \mathfrak{p} \mid \chi_p \rangle^* = -\,\langle \chi_q \mid \mathfrak{p} \mid \chi_p \rangle \tag{11b}$$

$$\langle \chi_p \mid \mathfrak{l} \mid \chi_q \rangle = \langle \chi_q \mid \mathfrak{l} \mid \chi_p \rangle^* = -\,\langle \chi_q \mid \mathfrak{l} \mid \chi_p \rangle \tag{11c}$$

where we have utilized that the operators (9) and (10) are purely imaginary whereas the orbitals are assumed real. For the diagonal elements of the last two operators we therefore obtain:

$$\langle \chi_p \mid \mathfrak{p} \mid \chi_p \rangle = 0 \tag{12a}$$

$$\langle \chi_p \mid \mathfrak{l} \mid \chi_p \rangle = 0 \tag{12b}$$

in agreement with the well-known result that an electron in a state described by a real wavefunction does not carry any linear or angular momentum. Eqs. (11) and (12) can then be employed in conjunction with (5) and (6) to give the *first order* relations between diagonal and nearest neighbour matrix elements of the operators (8) to (10) evaluated in the λ and χ bases. One intermediate step is given in each of the following equations and the particular relations, (11a) to (12b), which go into the reductions are indicated in sharp parentheses.

Diagonal elements:

$$\begin{aligned} \langle \lambda_p \mid e\mathfrak{r} \mid \lambda_p \rangle &= \langle \chi_p \mid e\mathfrak{r} \mid \chi_p \rangle - S_{p,p-1}\,\langle \chi_p \mid e\mathfrak{r} \mid \chi_{p-1} \rangle - S_{p,p+1}\,\langle \chi_p \mid e\mathfrak{r} \mid \chi_{p+1} \rangle \\ &= \langle \chi_p \mid e\mathfrak{r} \mid \chi_p \rangle \qquad \text{[from (11a)]} \end{aligned} \tag{13a}$$

$$\begin{aligned} \langle \lambda_p \mid \mathfrak{p} \mid \lambda_p \rangle = \langle \chi_p \mid \mathfrak{p} \mid \chi_p \rangle &- \\ -\,\tfrac{1}{2}\,S_{p,p-1}\,[\langle \chi_p \mid \mathfrak{p} \mid \chi_{p-1} \rangle + \langle \chi_{p-1} \mid \mathfrak{p} \mid \chi_p \rangle] &- \\ -\,\tfrac{1}{2}\,S_{p,p+1}\,[\langle \chi_p \mid \mathfrak{p} \mid \chi_{p+1} \rangle + \langle \chi_{p+1} \mid \mathfrak{p} \mid \chi_p \rangle] &= 0 \\ \text{[from (11b) and (12a)]} \end{aligned} \tag{13b}$$

$$\begin{aligned} \langle \lambda_p \mid \mathfrak{l} \mid \lambda_p \rangle = \langle \chi_p \mid \mathfrak{l} \mid \chi_p \rangle &- \\ -\,\tfrac{1}{2}\,S_{p,p-1}[\langle \chi_p \mid \mathfrak{l} \mid \chi_{p-1} \rangle + \langle \chi_{p-1} \mid \mathfrak{l} \mid \chi_p \rangle] &- \\ -\,\tfrac{1}{2}\,S_{p,p+1}[\langle \chi_p \mid \mathfrak{l} \mid \chi_{p+1} \rangle + \langle \chi_{p+1} \mid \mathfrak{l} \mid \chi_p \rangle] &= 0\,. \\ \text{[from (11c) and (12b)]} \end{aligned} \tag{13c}$$

Nearest neighbour elements:

$$\begin{aligned}\langle \lambda_p \mid e\mathfrak{r} \mid \lambda_{p+1}\rangle &= \langle \chi_p \mid e\mathfrak{r} \mid \chi_{p+1}\rangle - \\ &\quad - \tfrac{1}{2}\, S_{p,p+1}[\langle \chi_p \mid e\mathfrak{r} \mid \chi_p\rangle + \langle \chi_{p+1} \mid e\mathfrak{r} \mid \chi_{p+1}\rangle]\end{aligned} \tag{14a}$$

$$\begin{aligned}\langle \lambda_p \mid \mathfrak{p} \mid \lambda_{p+1}\rangle &= \langle \chi_p \mid \mathfrak{p} \mid \chi_{p+1}\rangle - \\ &\quad - \tfrac{1}{2}\, S_{p,p+1}[\langle \chi_p \mid \mathfrak{p} \mid \chi_p\rangle + \langle \chi_{p+1} \mid \mathfrak{p} \mid \chi_{p+1}\rangle] \\ &= \langle \chi_p \mid \mathfrak{p} \mid \chi_{p+1}\rangle \qquad \text{[from (12a)]}\end{aligned} \tag{14b}$$

$$\begin{aligned}\langle \lambda_p \mid \mathfrak{l} \mid \lambda_{p+1}\rangle &= \langle \chi_p \mid \mathfrak{l} \mid \chi_{p+1}\rangle - \\ &\quad - \tfrac{1}{2}\, S_{p,p+1}[\langle \chi_p \mid \mathfrak{l} \mid \chi_p\rangle + \langle \chi_{p+1} \mid \mathfrak{l} \mid \chi_{p+1}\rangle] \\ &= \langle \chi_p \mid \mathfrak{l} \mid \chi_{p+1}\rangle \,. \qquad \text{[from (12b)]}\end{aligned} \tag{14c}$$

It should be noted that (13b) and (13c) are correct to all orders of approximation since the λ orbitals are real by definition [compare (12a) and (12b)]. Furthermore, in (14b) and (14c) the terms containing $S_{p,p+1}$ vanish identically.

In (13a) and (14a) we have used that a two center dipole length matrix element $\langle \chi_p \mid \mathfrak{r} \mid \chi_q\rangle$ can be reduced to an overlap integral [*10*], although the orbitals entering the overlap integral are not necessarily identical to the orbitals in the transition moment integral. From an order of magnitude point of view the correction terms in (13a) are hence of second order and are consequently neglected. The terms in (14a) are on the other hand all of first order in the overlap, and even though they tend to cancel they will in general leave a small, but non-vanishing, first order value for the matrix element $\langle \lambda_p \mid \mathfrak{r} \mid \lambda_{p+1}\rangle$. The nearest neighbour elements of the dipole length operator are therefore significantly different in magnitude and will, depending on the actual orbitals, in some cases, also be different in sign when evaluated in the two bases. This result is similar to what was found by FISCHER-HJALMARS for kinetic and potential energy operators, and it is in noteworthy contrast to the results obtained for the other matrix elements considered in (13) and (14).

The element (14a) will, however, often appear along with the non-vanishing diagonal element (13a) in any actual calculation of a dipole transition moment $(\varphi_k \mid \mathfrak{r} \mid \varphi_l)$ between two molecular orbitals

$$\varphi_k = \sum_p c_{kp}\, \lambda_p$$

and

$$\varphi_l = \sum_q c_{lq}\, \lambda_q \,.$$

This is seen from the first order expansion

$$\langle \varphi_k \mid \mathfrak{r} \mid \varphi_l\rangle = \sum_p \left[c_{kp}\, c_{lp} \langle \lambda_p \mid \mathfrak{r} \mid \lambda_p\rangle + (c_{kp}\, c_{lp+1} + c_{kp+1}\, c_{lp}) \langle \lambda_p \mid \mathfrak{r} \mid \lambda_{p+1}\rangle\right] . \tag{15}$$

This means that the nearest neighbour element can, for most purposes, be neglected compared to the diagonal terms, but it may be included in more accurate treatments by evaluating the terms in (14a).

3. Two Mutually Orthogonal Sets of Atomic Orbitals

a) Orbitals and general matrix elements

We shall in this section consider a molecular system which has an inherent symmetry such that the pertinent molecular orbitals can be constructed from two mutually orthogonal sets of atomic orbitals, and we shall restrict the considerations to p-orbitals in real form but without any restrictions on the radial parts. It is assumed that no two orbitals belonging to the same set are centered on the same atom, whereas two orbitals from different sets may be associated with one atom. Each of the two sets can now be orthogonalized separately by Eq. (1) since there are no elements in the overlap matrix connecting orbitals of different sets. This gives according to (4) the following expressions for the two resulting sets of orthogonalized orbitals (a prime is used to distinguish between members of different sets):

$$\lambda_p = \chi_p - \tfrac{1}{2} S_{p,p-1}\, \chi_{p-1} - \tfrac{1}{2} S_{p,p+1}\, \chi_{p+1} \tag{4}$$

$$\lambda'_p = \chi'_p - \tfrac{1}{2} S'_{p,p-1}\, \chi'_{p-1} - \tfrac{1}{2} S'_{pp,+1}\, \chi'_{p+1}\,. \tag{16}$$

Matrix elements involving orbitals belonging exclusively to one set are identical to those derived in Section 1, and we can therefore concentrate on one- and two-center integrals in which both primed and unprimed orbitals are represented. The localized character of the λ orbitals makes it possible to retain the terminology one- respectively two-center terms meaning terms containing orbitals which have their peak values at the same or at different centers. Two-center terms others than nearest neighbour elements are neglected for reasons analogous to those outlined in the discussion of Eq. (7). The one-center and nearest neighbour two-center matrix elements of a one-electron operator M are then:

$$\begin{aligned}\langle \lambda_p \mid M \mid \lambda'_p \rangle = {} & \langle \chi_p \mid M \mid \chi'_p \rangle - \\ & - \tfrac{1}{2} [S_{p,p-1} \langle \chi_{p-1} \mid M \mid \chi'_p \rangle + S'_{p,p-1} \langle \chi_p \mid M \mid \chi'_{p+1} \rangle] - \\ & - \tfrac{1}{2} [S_{p,p+1} \langle \chi_{p+1} \mid M \mid \chi'_p \rangle + S'_{p,p+1} \langle \chi_p \mid M \mid \chi'_{p+1} \rangle]\end{aligned} \tag{17}$$

and

$$\begin{aligned}\langle \lambda_{p+1} \mid M \mid \lambda'_p \rangle = {} & \langle \chi_{p+1} \mid M \mid \chi'_p \rangle - \\ & - \tfrac{1}{2} [S_{p,p+1} \langle \chi_p \mid M \mid \chi'_p \rangle + S'_{p,p+1} \langle \chi_{p+1} \mid M \mid \chi'_{p+1} \rangle]\,.\end{aligned} \tag{18}$$

b) *Electric and magnetic dipole transition moments*

The three operators under consideration are given in Eqs. (8), (9) and (10), and the following relations result directly from the properties of the operators and from the fact that the basis sets are restricted to real orbitals with the same l-value,

$$\langle \chi_p \mid e\mathfrak{r} \mid \chi'_p \rangle = 0 \tag{19a}$$

$$\langle \chi_p \mid \mathfrak{p} \mid \chi'_p \rangle = 0\,. \tag{19b}$$

Eqs. (19a) and (19b) reflect the Laporte rule of atomic spectroscopy [*1*]. The matrix elements of the angular momentum operator are discussed later.

The relations between the pertinent one- and two-center matrix elements are given below. It is in all cases assumed that two-center integrals are at most of the same order as the overlap integral between parallel orbitals on the two atoms. The correction terms in (17) are therefore neglected.

One-center elements:

$$\langle \lambda_p \mid e\mathfrak{r} \mid \lambda'_p \rangle = \langle \chi_p \mid e\mathfrak{r} \mid \chi'_p \rangle = 0; \qquad \text{[from (19a)]} \tag{20a}$$

$$\langle \lambda_p \mid \mathfrak{p} \mid \lambda'_p \rangle = \langle \chi_p \mid \mathfrak{p} \mid \chi'_p \rangle = 0; \qquad \text{[from (19b)]} \tag{20b}$$

$$\langle \lambda_p \mid \mathfrak{l} \mid \lambda'_p \rangle = \langle \chi_p \mid \mathfrak{l} \mid \chi'_p \rangle\,. \tag{20c}$$

Two-center elements:

$$\begin{aligned}\langle\lambda_{p+1}\,|\,e\mathfrak{r}\,|\,\lambda_p\rangle &= \langle\chi'_{p+1}\,|\,e\mathfrak{r}\,|\,\chi'_p\rangle - \\ &\quad -\tfrac{1}{2}\,[S_{p,p+1}\langle\chi_p\,|\,e\mathfrak{r}\,|\,\chi'_p\rangle + S'_{p,p+1}\langle\chi_{p+1}\,|\,e\mathfrak{r}\,|\,\chi'_{p+1}\rangle] \\ &= \langle\chi_{p+1}\,|\,e\mathfrak{r}\,|\,\chi'_p\rangle; \qquad \text{[from (19a)]}\end{aligned} \tag{21a}$$

$$\begin{aligned}\langle\lambda_{p+1}\,|\,\mathfrak{p}\,|\,\lambda'_p\rangle &= \langle\chi_{p+1}\,|\,\mathfrak{p}\,|\,\chi'_p\rangle - \\ &\quad -\tfrac{1}{2}\,[S_{p,p+1}\langle\chi_p\,|\,\mathfrak{p}\,|\,\chi'_p\rangle + S'_{p,p+1}\langle\chi_{p+1}\,|\,\mathfrak{p}\,|\,\chi'_{p+1}\rangle] \\ &= \langle\chi_{p+1}\,|\,\mathfrak{p}\,|\,\chi'_p\rangle; \qquad \text{[from (19b)]}\end{aligned} \tag{21b}$$

$$\begin{aligned}\langle\lambda_{p+1}\,|\,\mathfrak{l}\,|\,\lambda_p\rangle &= \langle\chi'_{p+1}\,|\,\mathfrak{l}\,|\,\chi_p\rangle - \\ &\quad -\tfrac{1}{2}\,[S_{p,p+1}\langle\chi_p\,|\,\mathfrak{l}\,|\,\chi'_p\rangle + S'_{p,p+1}\langle\chi_{p+1}\,|\,\mathfrak{l}\,|\,\chi'_{p+1}\rangle]\,.\end{aligned} \tag{21c}$$

The expressions for the matrix elements of the electric dipole transition moments (20a, b) and (21a, b) are in general valid to first order only, however, symmetry restrictions may in many cases make the integrals vanish identically. The one-center magnetic dipole moment integral (20a) is non-vanishing for p-orbitals. This is seen by noting the effect of the components of the angular momentum operator Eq. (10) on a set of *equivalent* p-orbitals. Considering the component $\mathfrak{l}_x = -\,i\hbar\left(y\,\dfrac{\partial}{\partial z} - z\,\dfrac{\partial}{\partial y}\right)$ one obtains

$$\mathfrak{l}_x\mathfrak{p}_x = 0 \tag{22a}$$

$$\mathfrak{l}_x\mathfrak{p}_y = i\hbar\,\mathfrak{p}_z \tag{22b}$$

$$\mathfrak{l}_x\mathfrak{p}_z = -\,i\hbar\,\mathfrak{p}_y\,. \tag{22c}$$

At least one component of the operator (10) will hence "turn" χ'_p into a p-orbital with a component along the direction of χ_p, thereby giving (20c) a non-zero value (except in the unusual case where the two orbitals happen to be radially orthogonal). By the same token the two center magnetic moment integral $(\chi_p\,|\,\mathfrak{l}\,|\,\chi'_{p+1})$ appearing in Eq. (21c) is equal to $i\hbar$ times an overlap integral since at least one component of $\mathfrak{l}$ will turn χ'_{p+1} into an orbital parallel to χ_p. The two terms in (21c) are hence of approximately the same magnitude and the phases are such that they in general tend to cancel if the overlaps $S_{p,p+1}$ and $S'_{p,p+1}$ are both non-vanishing. In fact, the right hand side of (21c) vanishes identically for p-orbitals perpendicular to the internuclear axis if χ_p is equivalent to χ'_p for all p.

The relations in this section are all derived under the assumption of two delocalized molecular orbital sets, whereas conventional treatments of $n-\pi^+$ excitations, e.g. in ketones [*7, 16*], assume a delocalized π system but a single localized n orbital. The latter case is represented by setting $S'_{p,q} = \delta_{p,q}$ leaving only $\lambda'_p = \chi'_p$ for that particular orbital. The correspondingly simplified versions of Eqs. (17) through (21) are obtained by neglecting all $S'_{p,q}$ retaining only the unprimed $S_{p,q}$. The only integral which is affected by this is the two-center integral (21c) in which the cancellation of terms discussed above is contingent upon the non-vanishing values of both $S_{p,p+1}$ and $S'_{p,p+1}$. If only $S_{p,p+1}$ is retained the last term is only approximately half the value of the first term and one obtains

$$\langle\lambda_{p+1}\,|\,\mathfrak{l}\,|\,\lambda'_p\rangle \approx \tfrac{1}{2}\,S_{p,p+1}\langle\chi_p\,|\,\mathfrak{l}\,|\,\chi'_p\rangle \tag{23}$$

yielding a non-neglicible first order contribution.

This discussion shows that the only matrix element which is affected by the orthogonalisation in the case of two mutually orthogonal basis sets is the magnetic transition moment (21c) for which special caution should be exercised. Eq. (21c) is, however, correct to first order and can be employed to give the actual value of the integral in any particular case.

4. Conclusion

According to (13), (14), (20) and (21) it is consistent, to first order in a typical nearest neighbour overlap integral, to use non-orthogonal atomic orbitals for the evaluation of molecular electric and magnetic dipole transition moments at the same time as the ZDO approximation is invoked for the calculation of the corresponding energies, except for two integrals. These two are the nearest neighbour matrix elements of respectively the dipole length operator, Eq. (8), in the case where the atomic orbitals belong to the same basis set, section 2 Eq. (14a), and the magnetic moment (angular momentum) operator, Eq. (10), in the case where the orbitals belong to two different, mutually orthogonal basis sets, section 3 Eqs. (21c) and (23). Both of these matrix elements are of first order when evaluated from non-orthogonal orbitals. The nearest-neighbour dipole length integral, (14a), can in the ZDO approximation be neglected for most purposes, as discussed in section 2b, whereas it appears necessary to estimate the value of the two-center magnetic moment integral (21c) in each case. It should be remembered that the non-nearest neighbour two-center transition moment integrals are in general of second order and that their inclusion, for the sake of consistency, requires explicit consideration of the second order terms which are neglected in this discussion.

A second piece of information which can be gained from the derivations concerns the relative merits of the electric dipole length operator (8) and the linear momentum operator (9) in the calculation of electric dipole transition intensities. The two procedures will in general yield different results when approximate wavefunctions are used. It was noted in Section 2b that the first order terms vanish identically in the expansion of the dipole velocity matrix elements, (13b) and (14b), whereas the nearest neighbour dipole length element, (14a), still contains a small first order contribution in the orthogonalized basis. From this point of view the relations therefore suggest an advantage in using dipole velocity matrix elements rather than dipole length elements in conjunction with the ZDO approximation, unless the proper value of (14a) is assessed by actual calculation.

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Dr. A. E. Hansen
Department of Physical Chemistry
University of Copenhagen
Universitetsparken 5
Copenhagen, Denmark