Theoret. chim. Acta (Berl.) 20, 303—316 (1971)

## *Commentationes*

# On the Importance of Scale and Polarization of the Atomic Orbital Basis for LCAO Calculations of Electronic Intensities

AA. E. HANSEN and E. NØRBY SVENDSEN

Department of Physical Chemistry, H. C. Ørsted Institute
University of Copenhagen, Copenhagen, Denmark

Received August 24, 1970

The importance of scale and polarization of the atomic basis set for LCAO calculations of the intensities of electronic transitions is investigated using the molecular hydrogen ion, $H_2^+$, as a model. The transitions under consideration are the $1\sigma_g - 1\sigma_u$, the $1\pi_u - 1\pi_g$ and the $1\sigma_g - 1\pi_u$ excitations of this ion, and the electric dipole transition moments are calculated for a range of nuclear separations using the dipole length, the dipole velocity, the dipole acceleration and the time-derivative of the dipole acceleration formulations. For the $1\sigma_g - 1\sigma_u$ and the $1\pi_u - 1\pi_g$ excitations scaling and/or polarization are found very efficient for the improvement of the calculated transition moments for small internuclear separations for all the dipole formulations, whereas only the dipole length and the dipole velocity results are well-behaved for large separations. For the $1\sigma_g - 1\pi_u$ excitation scaling is found to be more important than polarization for all internuclear separations.

Die Bedeutung der Skalierung und der Polarisation atomarer Basisfunktionen für LCAO-Berechnungen der Intensitäten elektronischer Übergänge wird am Wasserstoffmolekülion, $H_2^+$, als Modell untersucht. Die betrachteten Übergänge sind der $1\sigma_g - 1\sigma_u$, der $1\pi_u - 1\pi_g$ und der $1\sigma_g - 1\pi_u$-Übergang dieses Ions. Die zugehörigen Dipolübergangsmomente werden für eine Reihe von Kernabständen berechnet, wobei die Dipollänge, die Dipolgeschwindigkeit, die Dipolbeschleunigung und die zeitliche Ableitung der Dipolbeschleunigung zu Grunde gelegt werden. Für die $1\sigma_g - 1\sigma_u$ und die $1\pi_u - 1\pi_g$-Anregung findet man, daß Skalierung und/oder Polarisation sehr wirksam für eine Verbesserung der berechneten Übergangsmomente bei kleinen Kernabständen sind. Dies gilt für alle Dipolformulierungen, während sich für große Kernabstände nur die Dipollänge und die Dipolgeschwindigkeit richtig verhalten. Für den $1\sigma_g - 1\pi_u$-Übergang ist die Skalierung bei allen Kernabständen wichtiger als die Polarisation.

Etude de l'influence de l'échelle et de la polarisation de la base atomique sur les calculs LCAO des intensités des transitions électroniques, en utilisant l'ion moléculaire $H_2^+$ comme modèle. On considère les transitions $1\sigma_g - 1\sigma_u$, $1\pi_u - 1\pi_g$ et $1\sigma_g - 1\pi_u$; les moments dipolaires de transition sont calculés pour un éventail de séparations nucléaires en utilisant les différentes formulations: longueur dipolaire, vitesse dipolaire, accélération dipolaire et dérivée par rapport au temps de l'accélération dipolaire. Pour les excitations $1\sigma_g - 1\sigma_u$ et $1\pi_u - 1\pi_g$ les facteurs précités ont une grande importance pour l'amélioration des moments de transition calculés à faible séparation nucléaire dans toutes les formulations, alors qu'à grande séparation nucléaire seules la longueur et la vitesse donnent des résultats convenables. Pour l'excitation $1\sigma_g - 1\pi_u$ l'échelle est un facteur plus important que la polarisation à toutes distances internucléaires.

## 1. Introduction

The linear combination of atomic orbitals (LCAO) molecular orbital approximation forms a time-honoured basis for the calculation of molecular electronic energies and wave functions, but the calculation of the intensities of electronic transitions from such wave functions has met with mainly qualitative, rather than quantitative, success. Basically, this can be blamed on two features of theoretical intensity calculations. Firstly, the operators associated with the various equivalent formulations [1–3] of the theoretical intensity are all unbound [4, 5]. Therefore, minor, in principle even infinitesimal, inaccuracies in the wave functions may lead to large errors in computed results. Secondly, these operators emphasize different aspects of the wave functions [6, 7], so that they generally yield rather different results for the predicted intensity of a particular transition when approximate wave functions are used. However, these statements are so general that they provide little direct clue to the reason for the quantitatively unsatisfactory results which are often obtained when LCAO wave functions are used as basis for electronic intensity calculations.

The influence of correlation effects on the calculation of electronic intensities has been the subject of a number of recent publications (see Refs. [8–11] and references therein) and the importance of ground state correlation, in particular, is firmly established. In the present communication we shall study another aspect of the LCAO calculation of intensities, namely, the importance of choosing the proper scale and polarization for the atomic orbitals which form the basis for LCAO wave functions. As our model we take the simplest molecular electronic system, the molecular hydrogen ion, $H_2^+$, thereby avoiding the complications of correlation effects, and the transitions under consideration are the $1\sigma_g - 1\sigma_u$, the $1\pi_u - 1\pi_g$ and the $1\sigma_g - 1\pi_u$ excitations of this ion.

In order to investigate the effect of scale and polarization for the intensities of these transitions we compare the results of calculations in which the LCAO functions are built from three different types of atomic orbitals. These three types of orbitals are: simple Slater orbitals, scaled Slater orbitals and scaled and polarized Slater orbitals, respectively. The wave functions necessary for these calculations are available in the work of Miller and Lykos [12] who reported individual variational optimisations of the relevant orbitals. The pertinent details and notations for the wave functions are summarized in Sect. 2. The intensities are calculated using four equivalent formulations of the electric dipole transition moment, viz. the ones referred as the dipole length, the dipole velocity, the dipole acceleration and the time-derivative of the dipole acceleration [2, 3] expressions. All calculations are carried out at a number of different internuclear separations, and the results are compared with the very accurate values obtained by Bates *et al.* [13, 14]. In this way, the present calculations illustrate how well the results of the individual dipole formulations can be brought to converge towards the correct results by the type of systematic improvements in the basis orbitals, which are considered here.

Molecular orbital calculations of the intensities of transitions in the molecular hydrogen ion, as function of the internuclear separation, have been reported previously by Bates *et al.* [13, 14] and by Lamb, Young, and LaPaglia [17].

We shall return to a comparison with their results in Sect. 4. A set of model calculations were reported recently by Danz and Harris [25], who approximated the molecular potential by a double square well. In their calculations, which differ from the present by the use of approximate transition energies, these authors compare the exact intensities for the transitions in the double well potential with the results of a molecular orbital analogy, in which the wave functions are linear combinations of the solutions for the separate wells. Their model includes a polarization-like effect for the wave functions and they do not observe any significant improvements in the intensities of the $1\sigma_g \rightarrow 1\sigma_u$ analogous excitation, in marked contrast to the present findings.

The plan of the paper is the following. We summarize the features of the wave functions in Sect. 2, and the general expression for the various dipole formulations of the intensity are given in Sect. 3, the details concerning the operators being referred to Appendix 1. The results are presented and discussed in Sect. 4, and Sect. 5 contains concluding remarks. Finally the computational details are given in Appendix 2.

## 2. Wave Functions

The LCAO molecular orbital wave functions which are used as the basis for the present calculations are those reported by Miller and Lykos [12]. We shall briefly summarize the pertinent features of these functions and refer to the paper by Miller and Lykos for the detailed presentation. The molecular orbitals for the four states $1\sigma_g$, $1\sigma_u$, $1\pi_u$, and $1\pi_g$ can be written

$$\sigma = N_\pm[\sigma_a(\xi) \pm \sigma_b(\xi)], \tag{1a}$$

$$\pi = N'_\pm[\pi_a(\xi') \pm \pi_b(\xi')] \tag{1b}$$

where the plus combination corresponds to the gerade state in the $\sigma$-orbitals, Eq. (1a), and to the ungerade state in the $\pi$-orbitals, Eq. (1b). The atomic orbitals on atom $a$ are of the form:

$$\sigma_a(\xi) = c_1\, 1s_a(\xi) + c_2\, 2p\sigma_a(\xi), \tag{2a}$$

$$\pi_a(\xi') = c'_1\, 2p\pi_a(\xi') + c'_2\, 3d\pi_a(\xi'), \tag{2b}$$

and similar expressions hold for the orbitals on atom $b$.

We shall use three different levels of complexity for the atomic orbitals. These are respectively,

1) primitive orbitals:

$$c_1 = c'_1 = 1\,; \quad c_2 = c'_2 = 0\,; \quad \xi = 1.0\,; \quad \xi' = 0.50,$$

2) scaled orbitals:

$$c_1 = c'_1 = 1\,; \quad c_2 = c'_2 = 0\,; \quad \xi \text{ and } \xi' \text{ variationally optimized,}$$

and

3) polarized orbitals:

$$\text{all parameters} \quad (c_1, c_2, \xi) \quad \text{and} \quad (c'_1, c'_2, \xi') \quad \text{variationally optimized.}$$

All the parameters required for these functions are given for a range of internuclear separation by Miller and Lykos [12]. In their terminology the scaled function 2, and the polarized functions, 3, are referred to as one- and two-parameter functions respectively.

In addition to the functions 1, 2, and 3 Miller and Lykos included "charge deformed" atomic orbitals. For the $\sigma$-type functions, Eq. (2a), this amounts to the addition of a $3d\sigma(\xi)$ atomic orbital. An estimate of the influence of this additional distortion is included in Sect. 4.

## 3. Matrix Elements for the Electric Dipole Transition Moment

The ordinary intensity of a transition between electronic states $k$ and $l$ is proportional to the square of the so-called electric dipole transition moment, $\boldsymbol{Q}(k,l)$. Here we shall compare the results of four of the equivalent expressions for $\boldsymbol{Q}(k,l)$, the respective $z$-components of which can be written (in atomic units) as

dipole length:

$$Q_1^z(k,l) = \langle \Psi_k | z | \Psi_l \rangle \; ; \quad (z)\,, \tag{3}$$

dipole velocity:

$$Q_2^z(k,l) = (E_l - E_k)^{-1} \left\langle \Psi_k \left| \frac{\partial}{\partial z} \right| \Psi_l \right\rangle \; ; \quad (\dot{z})\,, \tag{4}$$

dipole acceleration:

$$Q_3^z(k,l) = (E_l - E_k)^{-2} \left\langle \Psi_k \left| \frac{\partial}{\partial z} V(r) \right| \Psi_l \right\rangle \; ; \quad (\ddot{z})\,, \tag{5}$$

and time-derivative of dipole acceleration [2, 3, 15]

$$Q_4^z(k,l) = (E_l - E_k)^{-3} \langle \Psi_k | \hat{O}_4^z | \Psi_l \rangle \; ; \quad (\dddot{z})\,, \tag{6a}$$

where

$$\hat{O}_4^z = \left( \frac{\partial}{\partial z} \operatorname{grad} V(r) \right) \cdot \hat{V} + \frac{1}{2} \frac{\partial}{\partial z} (\operatorname{div} \operatorname{grad} V(r)) \tag{6b}$$

with similar expressions for the $x$- and $y$-components. In these equations $\Psi_k$ and $\Psi_l$ are the time-independent electronic wave functions and $E_k$ and $E_l$ are the energies for the two states. $V(r)$ is the static potential energy of the electron, and the symbols $(z)$, $(\dot{z})$ etc. are used as labels in the tables of results in Sect. 4. $(x)$, $(\dot{x})$ etc. are similarly used to label the results for $x$-axis polarized excitations.

The explicit form of the operators in Eqs. (3)–(6) are given in Appendix 1. The operator in the matrix element in Eq. (6) contains high derivatives of the potential which, for the conventional point nuclei coulomb potential, leads to the operator [2, 3, 15] being non-(anti)hermitean[1]. We have shown recently [15]

---

[1] Since we are working with transition moment operators on real form the operators in Eqs. (4) and (6) are antihermitean rather that hermitean. The operator $\hat{O}_4$ without $\delta$-function contributions is therefore, in fact, non-antihermetian.

for a single center coulomb potential, that the (anti)hermitean character can be restored if suitable $\delta$-functions and $\delta$-function derivatives are introduced by means of a cut-off in the potential. An analogous procedure can be applied in the case of the two-center coulomb potential in $H_2^+$. The details of this are given in Appendix 1, where it is also shown that the operator in Eq. (5), which again depends explicitly upon the potential, is for all practical purposes unaffected by the cut-off. The $\delta$-function terms which are introduced into the operator (6b) contribute to the calculations of the dipole transition moments for the $1\sigma_g - 1\sigma_u$ and the $1\sigma_g - 1\pi_u$ excitations, for which one or both of the orbitals have finite densities at the nuclei. The importance of these $\delta$-function contributions is illustrated by some representative examples in Appendix 2.

## 4. Results

The results of the present calculations of the electric dipole transition moments of the $1\sigma_g - 1\sigma_u$, the $1\pi_u - 1\pi_g$ and the $1\sigma_g - 1\pi_u$ excitations in the molecular hydrogen ion are given in Tables 1, 2, and 3 for a range of values of the internuclear separation $R$. In all cases the transition energies which are required in Eqs. (4, 5, 6) are the accurate energy differences taken from the work of Bates,

Table 1. *Dipole transition moment for the* $1\sigma_g - 1\sigma_u$ *excitation*[a]

| $R$ | [b] | Wave functions[c] | | | |
|---|---|---|---|---|---|
| | | primitive | scaled | polarized | accurate[d] |
| 1.0 | $z$ | 0.975 | 0.724 | 0.665 | 0.674 |
| | $\dot{z}$ | 0.539 | 0.617 | 0.624 | |
| | $\ddot{z}$ | 0.801 | 0.713 | 0.683 | |
| | $\dddot{z}$ | 0.839 | 1.03 | 0.813 | |
| 2.0 | $z$ | 1.23 | 1.17 | 1.04 | 1.05 |
| | $\dot{z}$ | 0.768 | 0.855 | 1.04 | |
| | $\ddot{z}$ | 1.24 | 1.33 | 0.987 | |
| | $\dddot{z}$ | −0.912 | 0.507 | 0.905 | |
| 4.0 | $z$ | 2.16 | 2.03 | 1.88 | 1.88 |
| | $\dot{z}$ | 1.24 | 1.20 | 1.86 | |
| | $\ddot{z}$ | 6.63 | 6.24 | 1.19 | |
| | $\dddot{z}$ | −27.5 | −26.7 | 9.14 | |
| 6.0 | $z$ | 3.15 | 3.00 | 2.89 | 2.86 |
| | $\dot{z}$ | 1.63 | 1.61 | 2.83 | |
| | $\ddot{z}$ | 64.1 | 60.8 | 12.7 | |
| | $\dddot{z}$ | −507 | −543 | 209 | |
| 8.0 | $z$ | 4.00 | 4.00 | 3.93 | 3.85 |
| | $\dot{z}$ | 2.03 | 2.03 | 3.71 | |
| | $\ddot{z}$ | 991 | 990 | −300 | |
| | $\dddot{z}$ | — | — | —[e] | |

[a] All values in a.u.

[b] See Sect. 3 for the notation used for the dipole formulations.

[c] See Sect. 2 for the notation used for the wave functions.

[d] Calculated from the intensities given in Ref. [13].

[e] These results could not be obtained with any numerical significance.

Table 2. *Dipole transition moment for the* $1\pi_u - 1\pi_g$ *excitation*[a]

| $R$ | [b] | Wave functions[c] | | | |
|---|---|---|---|---|---|
| | | primitive | scaled | polarized | accurate[d] |
| 2.0 | $z$ | 2.38 | 1.55 | 1.39 | 1.42 |
| | $\dot{z}$ | 1.01 | 1.32 | 1.45 | |
| | $\ddot{z}$ | 1.26 | 1.57 | 1.43 | |
| | $\dddot{z}$ | 1.34 | 0.985 | 1.46 | |
| 4.0 | $z$ | 2.78 | 2.43 | 1.97 | 2.00 |
| | $\dot{z}$ | 1.36 | 1.57 | 2.02 | |
| | $\ddot{z}$ | 2.08 | 2.49 | 1.95 | |
| | $\dddot{z}$ | 1.07 | 0.304 | 2.07 | |
| 6.0 | $z$ | 3.40 | 3.27 | 2.62 | |
| | $\dot{z}$ | 1.70 | 1.70 | 2.61 | |
| | $\ddot{z}$ | 3.78 | 4.20 | 2.60 | |
| | $\dddot{z}$ | 0.275 | $-0.912$ | 2.95 | |
| 8.0 | $z$ | 4.16 | 4.12 | 3.39 | |
| | $\dot{z}$ | 1.97 | 1.82 | 3.25 | |
| | $\ddot{z}$ | 7.42 | 7.76 | 3.21 | |
| | $\dddot{z}$ | $-2.62$ | $-3.94$ | 5.68 | |

[a] All values in a.u.

[b] See Sect. 3 for the notation used for the dipole formulations.

[c] See Sect. 2 for the notation used for the wave functions.

[d] Calculated from the intensities given in Ref. [14].

Ledsham, and Stewart [16], and the details about the evaluation of the matrix elements are given in Appendix 2. For comparison Tables 1, 2, and 3 include the values for the transition moments which can be deduced from the very accurate intensities calculated by Bates *et al.* [13, 14]. These authors, and more recently Lamb, Young, and LaPaglia [17], have also reported calculations of the transition moments of these excitations in the dipole length and the dipole velocity formulations using simple, unscaled Slater orbitals. Wherever direct comparison is possible, our results labelled primitive agree with the values given previously. In addition to calculations based upon unscaled Slater orbitals Lamb, Young, and LaPaglia [17] performed a series of dipole length and dipole velocity intensity calculations using Gaussian type orbitals. In these calculations a certain degree of polarization was introduced by placing a single Gaussian orbital in the middle of the molecule. For small internuclear separations their results are quite similar to our results with polarized Slater type orbitals, whereas for larger separations their results resemble the ones obtained with unscaled Slater type orbitals.

The $1\sigma_g - 1\sigma_u$ and the $1\pi_u - 1\pi_g$ transitions, Tables 1 and 2, both belong to the class of parallel polarized excitations which Mulliken [18] named charge-transfer excitations, and the two tables show the same qualitative features. (In comparing the two tables it should be observed that the $\pi$-orbitals are much more extended in space than are the $\sigma$-orbitals so that, for example, a distance $R$ of 8 a.u., which is considered a large separation for the $1\sigma_g - 1\sigma_u$ transition, is, in fact, a physically small to intermediate separation for the $1\pi_u - 1\pi_g$ transition.)

Considering first the results for the primitive orbitals for these charge-transfer transitions, Tables 1 and 2 show that all the dipole formulations lead to results of the right order of magnitude for small internuclear separations. For larger values of $R$, only the dipole length results converge towards the correct values, while the dipole velocity results converge towards half the correct values [13]. The results from the two remaining dipole formulations are quite unacceptable for larger $R$. In fact, it can be shown that for the primitive orbitals and for large separations the transition moment in the dipole acceleration formulation becomes proportional to $\exp(2R)$ multiplied by $R^{-4}$. The results obtained with scaled orbitals show that scaling is rather effective at small $R$ for the dipole length and the dipole velocity formulations, but has negligible influence at large internuclear separations, as might have been expected. With scaled and polarized orbitals we obtain good agreement, for the whole range of separations, between the correct results and those obtained in the dipole length and the dipole velocity formulations. The polarized orbitals also lead to considerable improvements in the results from the dipole acceleration and the time derivative of the dipole acceleration formulations for small values of $R$, but the transition moments obtained at large $R$ are still unacceptable.

Turning to the perpendicularly polarized excitations $1\sigma_g - 1\pi_u$, Table 3, we observe firstly that all the dipole formulations lead to results of the right order of magnitude for the whole range of internuclear separations. This feature can be ascribed to the fact that the dipole transition moment for this excitation is largely dominated by the one-center contribution arising from the allowed

Table 3. *Dipole transition moment for the* $1\sigma_g - 1\pi_u$ *excitation*[a]

| $R$ | [b] | Wave functions[c] | | | |
|---|---|---|---|---|---|
| | | primitive | scaled | polarized | accurate[d] |
| 2.0 | $x$ | 0.783 | 0.733 | 0.768 | 0.726 |
| | $\dot{x}$ | 0.422 | 0.716 | 0.704 | |
| | $\ddot{x}$ | 0.317 | 0.730 | 0.743 | |
| | $\dddot{x}$ | 0.125 | 1.01 | 1.03 | |
| 4.0 | $x$ | 0.794 | 0.930 | 0.938 | 0.885 |
| | $\dot{x}$ | 0.631 | 0.867 | 0.875 | |
| | $\ddot{x}$ | 0.546 | 0.945 | 0.949 | |
| | $\dddot{x}$ | 0.289 | 1.62 | 0.803 | |
| 6.0 | $x$ | 0.761 | 0.880 | 0.892 | |
| | $\dot{x}$ | 0.709 | 0.874 | 0.872 | |
| | $\ddot{x}$ | 0.674 | 0.957 | 0.945 | |
| | $\dddot{x}$ | 0.507 | 1.50 | 0.865 | |
| 8.0 | $x$ | 0.734 | 0.802 | 0.794 | |
| | $\dot{x}$ | 0.724 | 0.817 | 0.800 | |
| | $\ddot{x}$ | 0.719 | 0.874 | 0.853 | |
| | $\dddot{x}$ | 0.669 | 1.15 | 1.18 | |

[a] All values in a.u.

[b] See Sect. 3 for the notation used for the dipole formulations.

[c] See Sect. 2 for the notation used for the wave functions.

[d] Calculated from the intensities given in Ref. [14].

$1s-2p$ atomic transition. It is further observed that, except for the fourth dipole formulation (Eq. (6)), scaling appears quite efficient as a means of improving the calculated transition moments, while polarization of the orbitals leads to only minor corrections. This again appears reasonable in view of the importance of the one-center contributions to the intensity.

The unsatisfactory results which are obtained from the dipole acceleration and the time-derivative of the dipole acceleration transition moments for the charge-transfer excitations at large separation suggest the possibility that higher order distortions of the atomic orbital basis are required. However, calculation of the dipole acceleration transition moment for the $1\sigma_g - 1\sigma_u$ excitation for an $R$ of 8 a.u. using the charge-deformed orbitals given by Miller and Lykos [12] shows no improvement over the value given in Table 1 for the polarized orbitals. On the contrary, we calculate a value of $-406$ a.u., to be compared to $-300$ a.u. (Table 1), so that charge-deformation, in the sense employed by Miller and Lykos [12], does not appear to introduce the type of change necessary for these transition moment calculations.

## 5. Concluding Remarks

Tables 1, 2, and 3 provide ample illustration of the statements in the introduction concerning the general features of electronic intensity calculations. Clearly, at large internuclear separations the wave functions involved in the calculation of the charge-transfer intensities differ only infinitesimally from the exact wave functions, and yet some of the dipole formulations lead to totally erroneous results. Even the quite accurate polarized wave functions do not yield reliable results for two of the dipole formulations, and, as mentioned in Sect. 4, the more accurate charge-deformed orbitals actually lead to worse results.

It also emerges that the results from the dipole length and the dipole velocity formulation are more well behaved than are those from the other two dipole formulations. The same grouping has been found by Chong [19] in a comparison of the results from the four dipole formulations for some transition involving states with non-vanishing angular momenta in the He-like isoelectronic series.

The implication of the present results is that the search for appropriate atomic basis functions for LCAO calculations of electronic intensities must allow some degree of individual optimisation for the states involved in the pertinent transitions. More specifically, only the dipole length and the dipole velocity formulations appear to provide reasonably reliable results for "economy size" atomic orbital basis functions, and for these two formulations individual scaling is rather efficient at small internuclear distances. Polarization effects must be invoked for the dipole velocity transition moment in the case of charge-transfer excitations at large distances.

## Appendix 1

The operators for the matrix elements in the dipole length and the dipole velocity expressions, Eqs. (3) and (4), Sect. 3, are

$$\hat{O}_1^z = \hat{O}_1^z(a) = z_a = z_b + R = \hat{O}_1^z(b) + R\,, \tag{I:1a}$$

$$\hat{O}_1^x = \hat{O}_1^x(a) = x_a = x_b = \hat{O}_1^x(b)\,, \tag{I:1b}$$

and

$$\hat{O}_2^z = \hat{O}_2^z(a) = \frac{\partial}{\partial z_a} = \frac{\partial}{\partial z_b} = \hat{O}_2^z(b)\,, \qquad \text{(I:2a)}$$

$$\hat{O}_2^x = \hat{O}_2^x(a) = \frac{\partial}{\partial x_a} = \frac{\partial}{\partial x_b} = \hat{O}_2^x(b)\,, \qquad \text{(I:2b)}$$

where $R$ is the internuclear separation and where the local coordinate systems on atoms $a$ and $b$ are right-handed with $z$-axes along the internuclear axis. Atomic units are used throughout. Using the conventional point nuclei potential

$$V = -\frac{1}{r_a} - \frac{1}{r_b} \qquad \text{(I:3)}$$

the operators for the dipole acceleration expression, Eq. (5), become:

$$\hat{O}_3^z = \frac{\partial V}{\partial z} = \hat{O}_3^z(a) + \hat{O}_3^z(b)\,, \qquad \text{(I:4a)}$$

where

$$\hat{O}_3^z(a) = \frac{\cos\theta_a}{r_a^2}\,; \quad \hat{O}_3^z(b) = \frac{\cos\theta_b}{r_b^2}\,, \qquad \text{(I:4b)}$$

and

$$\hat{O}_3^x = \frac{\partial V}{\partial x} = \hat{O}_3^x(a) + \hat{O}_3^x(b)\,, \qquad \text{(I:5a)}$$

where

$$\hat{O}_3^x(a) = \frac{\sin\theta_a \cos\varphi}{r_b^2}\,; \quad \hat{O}_3^x(b) = \frac{\sin\theta_b \cos\varphi}{r_b^2}\,. \qquad \text{(I:5b)}$$

It is shown at the end of this appendix that the complications resulting from the $\delta$-function contributions, which are considered in the following, are of no practical significance in the operator (I:4, 5).

The operator appropriate to the fourth dipole expression, the time derivative of the dipole acceleration formulation, is, according to Eq. (6b),

$$\hat{O}_4^z = \hat{O}_{4,1}^z + \hat{O}_{4,2}^z \qquad \text{(I:6)}$$

with

$$\hat{O}_{4,1}^z = \left(\frac{\partial}{\partial z}\operatorname{grad} V(\boldsymbol{r})\right) \cdot \hat{\boldsymbol{V}} \qquad \text{(I:7a)}$$

and

$$\hat{O}_{4,2}^z = \frac{1}{2}\,\frac{\partial}{\partial z}\left(\operatorname{div}\operatorname{grad} V(\boldsymbol{r})\right) \qquad \text{(I:7b)}$$

for a $z$-axis polarized excitation. The operator for $x$-polarized excitations is obtained by substituting $x$ for $z$ in Eqs. (I:6, 7).

In the hydrogen molecular ion the potential is a sum of two terms

$$V = V_a + V_b\,, \qquad \text{(I:8)}$$

$V_a$ and $V_b$ representing the potentials due to two nuclei $a$ and $b$ respectively. The operators Eqs. (I:7) can then be written:

$$\hat{O}_{4,1}^z = \hat{O}_{4,1}^z(a) + \hat{O}_{4,1}^z(b) \qquad \text{(I:9a)}$$

and

$$\hat{O}^z_{4,2} = \hat{O}^z_{4,2}(a) + \hat{O}^z_{4,2}(b)\,, \tag{I:9b}$$

with

$$\hat{O}^z_{4,1}(a) = \left(\frac{\partial}{\partial z_a}\operatorname{grad}_a V_a\right)\cdot \hat{\nabla}_a \tag{I:10a}$$

and

$$\hat{O}^z_{4,2}(a) = \frac{1}{2}\,\frac{\partial}{\partial z_a}(\operatorname{div}_a \operatorname{grad}_a V_a)\,. \tag{I:10b}$$

Corresponding expressions result for the operators associated with nucleus $b$.

As discussed in Refs. [2, 3, 15] the point nucleus potential Eq. (I:3) leads to the operator (I:6) having non-(anti)hermitean character with respect to states with non-vanishing density at the nuclei. Consistent with our work on the single center coulomb potential [15] we shall use the modified potentials

$$V_a = -\frac{1}{r_a}h(r_a-\varepsilon)\,; \qquad V_b = -\frac{1}{r_b}h(r_b-\varepsilon) \tag{I:11}$$

where $h(r-\varepsilon)$ is the Heaviside unit function whose derivative is the Dirac $\delta$-function $\delta(r-\varepsilon)$ [20]. The operators corresponding to (I:10a, b) are now obtained by inserting the potentials (I:11) and taking the limit $\varepsilon$ going to zero. The resulting expressions are:

$$\begin{aligned}\hat{O}^z_{4,1}(a) = {} & \left[-\frac{3}{r_a^3} + \frac{3}{r_a^2}\delta(r_a) - \frac{1}{r_a}\delta'(r_a)\right]\cos\theta_a\sin\theta_a\cos\varphi\,\frac{\partial}{\partial x_a}\\ & + \left[-\frac{3}{r_a^3} + \frac{3}{r_a^2}\delta(r_a) - \frac{1}{r_a}\delta'(r_a)\right]\cos\theta_a\sin\theta_a\sin\varphi\,\frac{\partial}{\partial y_a}\\ & + \left[\left(-\frac{1}{r_a^3} + \frac{1}{r_a^2}\delta(r_a)\right)(3\cos^2\theta_a - 1) - \frac{\cos^2\theta_a}{r_a}\delta'(r_a)\right]\frac{\partial}{\partial z_a}\,;\end{aligned} \tag{I:12a}$$

and

$$\hat{O}^z_{4,2}(a) = \frac{1}{2}\left[\frac{1}{r_a^2}\delta'(r_a) - \frac{1}{r_a}\delta''(r_a)\right]\cos\theta_a\,, \tag{I:12b}$$

with analogous expressions for the operators on atom $b$. The corresponding operator for $x$-axis polarized excitations are:

$$\begin{aligned}\hat{O}^x_{4,1}(a) = {} & \left[\left(\frac{1}{r_a^3} - \frac{1}{r_a^2}\delta(r_a)\right)\left(-\frac{3}{2}\sin^2\theta_a\cos2\varphi + \frac{1}{2}(3\cos^2\theta_a - 1)\right)\right.\\ & \left. - \frac{\sin^2\theta_a\cos^2\varphi}{r_a}\delta'(r_a)\right]\frac{\partial}{\partial x_a}\\ & + \left[-\left(\frac{1}{r_a^3} + \frac{1}{r_a^2}\delta(r_a)\right)\frac{3}{2}\sin^2\theta_a\sin2\varphi - \frac{\sin^2\theta_a\sin2\varphi}{2r_a}\delta'(r_a)\right]\frac{\partial}{\partial y_a}\\ & + \left[\left(-\frac{3}{r_a^3} + \frac{3}{r_a^2}\delta(r_a) - \frac{1}{r_a}\delta'(r_a)\right)\cos\theta_a\sin\theta_a\cos\varphi\right]\frac{\partial}{\partial z_a}\,;\end{aligned} \tag{I:13a}$$

and

$$\hat{O}^x_{4,2}(a) = \frac{1}{2}\left[\frac{1}{r_a^2}\,\delta'(r_a) - \frac{1}{r_a}\,\delta''(r_a)\right]\sin\theta_a\cos\varphi\,. \tag{I:13b}$$

The end point $\delta$-functions are defined such that

$$\int_0^\infty \delta(r)\,dr = 1\,,$$

and it is found in the actual calculations that most of the $\delta$-function derivatives in the operator (I:12, 13) can be converted into $\delta$-functions by use of the relation [21]

$$x^n\delta^{(m)}(x) = (-1)^n\frac{m!}{(m-n)!}\,\delta^{(m-n)}(x)\,; \qquad m \geqq n\,. \tag{I:14}$$

We shall terminate this appendix by showing that the use of the modified potentials, Eq. (I:11), has no practical consequence for the dipole acceleration operators, Eq. (I:4, 5), despite the fact that these operators depend explicitly upon the form of the electrostatic potential. Considering the operator $\hat{O}^z_3(a)$, Eq. (I:4b), we get:

$$\hat{O}^z_3(a) = \frac{\partial}{\partial z_a}\,V_a = \left[\frac{1}{r_a^2} - \frac{1}{r_a}\,\delta(r_a)\right]\cos\theta_a \tag{I:15}$$

by inserting the potential (I:11). However, any actual integration involving the $\delta$-function part of (I:15) can be carried out in spherical polar coordinates referred to the same nucleus as the operator. The angular integration is always convergent and the radial integration yields

$$\int R_i\frac{1}{r_a}\,\delta(r_a)\,R_j r_a^2\,dr_a = \int R_i R_j r_a\,\delta(r_a)\,dr_a \tag{I:16}$$

where $R_i$ and $R_j$ are the radial functions for the two orbitals involved. These orbitals may be situated on any nucleus in the system, including nucleus $a$, the only important feature of $R_i$ and $R_j$ being that they are both non-infinite everywhere. We can therefore use the operator relation [20]

$$x\,\delta(x) = 0$$

which makes the integral (I:16) vanish identically. We have therefore shown that for any one-, two- or three-center integral involving non-infinite orbitals the contributions from the $\delta$-function in Eq. (I:15) vanish identically. This then, is the justification for the neglect of the $\delta$-function terms in Eqs. (I:4, 5), which are in the form commonly quoted [1, 6, 7] for this formalism.

## Appendix 2

The matrix elements in the dipole transition moments in Eqs. (3)–(6) are reduced to matrix elements over single Slater type orbitals by inserting the wave functions Eqs. (1, 2). The resulting matrix elements are of one of the following three types:

$$\mathrm{I} = \langle a | \hat{O}(a) | a' \rangle , \tag{II:1}$$

$$\mathrm{II} = \langle a | \hat{O}(b) | a' \rangle , \tag{II:2}$$

$$\mathrm{III} = \langle a | \hat{O}(a) | b' \rangle , \tag{II:3}$$

where $a$ and $a'$ are Slater type orbitals centered at atom $a$ and $\hat{O}(i)$ is a transition moment operator referred to a coordinate system at atom $i$. The various pertinent operators $\hat{O}(i)$ are discussed in Appendix 1.

The purely one-center integrals, type I, are evaluated on closed form for all orbitals and operators. For the matrix elements II and III it is convenient to divide the operators into two groups:

$$\begin{array}{llllll} \text{group 1:} & \hat{O}_1^x(i), & \hat{O}_1^z(i), & \hat{O}_2^x(i), & \hat{O}_2^z(i)\,; & i = a, b, \\ \text{group 2:} & \hat{O}_3^x(i), & \hat{O}_3^z(i), & \hat{O}_4^x(i), & \hat{O}_4^z(i)\,; & i = a, b \end{array}$$

(see Eqs. (I:1, 2) and (I:12, 13)). Wherever a partial derivative appears in one of the operators, the differentiation is performed analytically and the resulting Slater orbital derivative is treated as a new orbital.

Group 1 operators:

Integrals of type II are calculated on closed form using the relations (I:1, 2), whereas the integrals of type III are evaluated numerically by use of a modification of a two-dimensional Gauss quadrature routine written by Johansen [22]. The integration uses a 32 times 32 points integration mesh with an over-all scale factor gauged by testing the normalisation of the orbitals. The accuracy was further tested by calculating a number of overlap integrals and comparing these with reliable sources.

Group 2 operators:

The integrals containing the $\delta$-function parts of the operators $O_4^x(i)$ and $O_4^z(i)$ are calculated on closed form, whereas the integrals containing the remaining parts of these operators and the integrals over the operators $O_3^x(i)$ and $O_3^z(i)$ are expressed in terms of the integrals

$$U = \int x_a \frac{P_l^m(\cos\theta_a)}{r_a^{l+1}} x_b \, dv , \tag{II:4}$$

$$V = \int x_a \frac{P_l^m(\cos\theta_b)}{r_b^{l+1}} x_a' \, dv , \tag{II:5}$$

where $x_a$ and $x_b$ are Slater type orbitals.

These $U$ and $V$ integrals are calculated by a modification of a routine written by J. P. Dahl. The expansions and computations in this routine are similar to methods described by Barnett [23] and Pitzer, Kern, and Lipscomb [24].

The importance of the $\delta$-function contributions in the calculation of the time-derivative of the dipole acceleration transition matrix elements is illustrated by the following set of values:

$$\langle 1\sigma_g | \hat{O}_4^x | 1\pi_u \rangle = 0.03801\,, \tag{II:6a}$$

$$\langle 1\pi_u | \hat{O}_4^x | 1\sigma_g \rangle = -0.03818\,, \tag{II:6b}$$

$$\langle 1\sigma_g | \hat{O}_4^x - (\delta) | 1\pi_u \rangle = 0.1117\,, \tag{II:7a}$$

$$\langle 1\pi_u | \hat{O}_4^x - (\delta) | 1\sigma_g \rangle = 0.2776\,, \tag{II:7b}$$

where $\hat{O}_4^x - (\delta)$ means the part of the operator $\hat{O}_4^x$ which does not contain $\delta$-function contributions. These values for the matrix elements are calculated for $R$ equal to 2 a.u. using the primitive orbital basis set. In order to get the transition moment quoted in Table 3 the matrix element (II:6a) must be divided by the excitation energy to the third power. Eqs. (II:6a, b) show that the operator is properly (anti)hermitean and the agreement between the numerical values indicates the accuracy of the integration. The difference between the values in Eqs. (II:6) and Eqs. (II:7) show clearly the non-trivial contribution of the $\delta$-function parts of the operators.

*Acknowledgement.* The authors are grateful to Drs. J. P. Dahl and H. Johansen for the gifts of the computer routines mentioned in Appendix 2, and for numerous valuable discussions. The computations were carried out at the IBM 7094 installation at the Northern Europe University Computing Center (NEUCC) at Lundtofte, Denmark. We are grateful to the center for providing the computation time free of charge.

## References

1. Bethe, H. A., Salpeter, E. E.: Quantum mechanics of one and two-electron atoms. Berlin-Göttingen-Heidelberg: Springer 1957.
2. Chen, J. C. Y.: J. chem. Physics **40**, 615 (1964).
3. Hansen, Aa. E.: Theoret. chim. Acta (Berl.) **16**, 217 (1970).
4. Löwdin, P. O.: Annu. Rev. physic. Chem. **11**, 107 (1960).
5. Bazley, N. W., Fox, D. W.: Rev. mod. Physics **35**, 712 (1963).
6. Chandrasekhar, S.: Astrophysic. J. **102**, 223 (1945).
7. Ehrenson, S., Philipson, P. E.: J. chem. Physics **34**, 1224 (1961).
8. LaPaglia, S. R., Sinanoğlu, O.: J. chem. Physics, **44**, 1888 (1966).
9. Hansen, Aa. E.: Molecular Physics **13**, 425 (1967).
10. Harris, R. A.: J. chem. Physics **50**, 3947 (1969).
11. Kelly, H. P.: In: Adv. chem. Physics Vol. 14, ed. I. Prigogine. New York: Interscience Publishers 1969.
12. Miller, R. L., Lykos, P. G.: J. chem. Physics **37**, 993 (1962).
13. Bates, D. R.: J. chem. Physics **19**, 1122 (1951).
14. — Darling, R. T. S., Hawe, S. C., Stewart, A. L.: Proc. physic. Soc. (London) A **66**, 1124 (1954).
15. Hansen, Aa. E., Svendsen, E. Nørby: Chem. Physics Letters **5**, 483 (1970).
16. Bates, D. R., Ledsham, K., Stewart, A. L.: Phil. Trans. Roy. Soc. **246**, 215 (1953).
17. Lamb, W., Young, R., LaPaglia, S. R.: J. chem. Physics **49**, 2868 (1968).
18. Mulliken, R. S.: J. chem. Physics **7**, 20 (1939).
19. Chong, D. P.: J. chem. Physics **48**, 1413 (1968).
20. Friedman, B.: Principles and techniques of applied mathematics. New York: Wiley 1956.

21. Lighthill, M. J.: Introduction to fourier analysis and generalized functions. Cambridge: Cambridge University Press 1958.
22. Johansen, H.: Algol programs for molecular calculations. Copenhagen: 1965.
23. Barnett, M. P.: In: Methods in computational physics, Vol. 2, ed. S. Fernbach and M. Rotenberg. New York: Academic Press 1963.
24. Pitzer, R. M., Kern, C. W., Lipscomb, W. N.: J. chem. Physics **37**, 267 (1962).
25. Danz, J., Harris, R. A.: J. chem. Physics **52**, 5261 (1970).

Dr. Aage E. Hansen
Department of Physical Chemistry
H. C. Ørsted Institute
Universitetsparken 5
København Ø, Denmark