Theoret. chim. Acta (Berl.) 16, 217—225 (1970)

On the Equivalence of Different Hamiltonians for the Semi-Classical Radiation Theory

AAGE E. HANSEN

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

Received August 11, 1969

Four different expressions for the electric dipole transition moment are currently available. In this paper, the Hamiltonians appropiate for these expressions are derived by classical, infinitesimal transformations. The derivations are restricted to the electric dipole approximation and all second and higher order terms in the field strengths are neglected. The equivalence of these Hamiltonians, within the stated approximations, shows that none of the formalisms can be given any formal priority. The differences which arise when approximate wave functions are used are briefly discussed in the light of the present work.

Für elektrische Dipole-Übergangsmomente sind bislang vier verschiedene Ausdrücke bekannt. In dieser Arbeit werden die entsprechenden Hamilton-Operatoren mittels klassischer Infinitesimaltransformationen hergeleitet. Dabei beschränkt man sich auf die Dipol-Glieder und vernachlässigt alle höheren Multipole. Die Gleichwertigkeit dieser Hamilton-Operatoren innerhalb der benutzten Näherung zeigt, daß keinem dieser Formalismen irgend eine Priorität gegeben werden kann. Die Unterschiede, die sich bei verschiedenen Näherungsansätzen für die Wellenfunktion ergeben, werden kurz diskutiert.

On dispose de quatre expressions différentes pour le moment de transition électrique dipolaire. Dans cet article des transformations infinitésimales classiques sont employées pour obtenir les hamiltoniens correspondant à ces expressions. Seule, l'approximation dipolaire est retenue et tous les termes de champ du second ordre et d'ordre supérieur sont négligés. Dans le cadre de ces approximations, l'équivalence de ces hamiltoniens montre qu'aucun des formalismes n'a de priorité formelle. Les différences que l'on voit apparaître par l'emploi de fonctions d'onde approchées sont brièvement discutées à la lumière du présent travail.

1. Introduction

The theoretical expression for the intensity of an electronic transition in an atom or molecule can be given in a number of different ways [1–3] within the electric dipole approximation. These expressions differ in the form of the dipole transition moment Q_{kl} for the excitation from the electronic state k to the electronic state l. The three usual expressions are (in atomic units), dipole length:

$$Q_{kl}^{L} = \langle \Psi_k | \sum_{\nu} \boldsymbol{r}_{\nu} | \Psi_l \rangle \tag{1a}$$

dipole velocity:

$$Q_{kl}^{V} = (E_l - E_k)^{-1} \langle \Psi_k | \sum_{\nu} \hat{\nabla}_{\nu} | \Psi_l \rangle \tag{1b}$$

dipole acceleration:

$$Q_{kl}^{A}=(E_l-E_k)^{-2}\langle\Psi_k|\sum_{\nu}(\mathrm{grad}_{\nu}V)|\Psi_l\rangle \tag{1c}$$

where ν runs over all the electrons and V is the (static) potential of the system. Ψ_k and Ψ_l are the time-independent wave functions for the two states and E_k and E_l are their energies. Chen [3] has recently used a quantum mechanical hypervirial theorem to generate a fourth dipole expression for the special case of a single electron in a spherically symmetric potential. This expression represents the time-derivative of the dipole acceleration and is therefore a natural extension of the sequence in Eqs. (1).

The equivalence of the four dipole expressions is usually proven in quantum mechanics by some operator manipulations [1,3] (also called hypervirial theorems) which are in fact applications of the Heisenberg equations of motion [4]. In the reference quoted above Chen has shown how such hypervirial theorems can be used, in principle, to generate an infinite number of equivalent dipole expressions. Several points should be noted in connection with the usual proof. Firstly, it hinges on the requirement that the wave functions Ψ_k and Ψ_l be exact solutions to the time-independent Schrödinger equation for the unperturbed system. Secondly, since the sundry expressions traditionally are derived from the velocity form, Eq. (1b), this may leave the impression that Eq. (1b) is somehow superior to the others when used in conjunction with approximate wave functions. Finally, these operator manipulations deal directly with the matrix elements in Eqs. (1) and therefore do not disclose the form of the semiclassical Hamiltonians corresponding to the four alternative formulations.

In this paper we shall follow instead an approach that originated with Goeppert-Mayer [5], who derived a time-dependent Hamiltonian which leads directly to the dipole length expression, Eq. (1a). This Hamiltonian was obtained by what amounts to a canonical transformation of the traditional Hamiltonian [4] corresponding to Eq. (1b). This transformation was independently discovered by Richards [6] and later extended to all orders in a multipole expansion by Fiutak [7]. Fiutak [7] and Power *et al.* [8] have gone beyond the semi-classical approximation and considered the result of applying the transformation to the complete Hamiltonian for field plus electronic system.

All these articles have considered only the transformation from the dipole velocity form, Eq. (1b) to the dipole length form, Eq. (1a). Power [2] has recently pointed out that the "Schwinger-transformation" in the theory of mass-renormalization leads to an interaction between particles and field which corresponds to the dipole acceleration form, Eq. (1c). In this discussion we shall consider the classical analogue of the Schwinger-transformation in order to adhere as closely as possible to the spirit of the semi-classical theory of radiation. At the same time the transformation to the fourth dipole expression appears as a natural extension. The sequence of equivalent Hamiltonians can in this way, in principle, be extended *ad libitum* by successive transformations. This approach therefore parallels the discussion by Chen [3] in which an infinite number of equivalent dipole moment expressions are generated by quantum mechanical hypervirial theorems.

We shall accordingly in Sect. 2 first briefly reiterate the Goeppert-Mayer transformation, which leads to the dipole length Hamiltonian, and subsequently perform the transformation to the dipole acceleration Hamiltonian. The transformation to Chen's dipole expression [3] will be considered in Sect. 3, and it will be shown explicitly that the present approach reproduces the result derived by Chen for an electron in a spherically symmetric potential. In the course of this transformation it will prove convenient to introduce a vector field which does not appear to have any precedence in electromagnetic theory. The discussions in Sects. 2 and 3 are kept entirely within the electric dipole approximation [1, 4]. In the concluding section some comments will be added concerning the fact that the various expressions for the dipole transition moment in general lead to significantly different results when approximate wave functions are employed.

2. The Three Hamiltonians Corresponding to Eqs. (1a, b, c)

The classical, non-relativistic Hamiltonian for a system of n electrons in the combined field from one or more space-fixed nuclei and an externally applied radiation field is conventionally written [4, 9]

$$H=\frac{1}{2m}\sum_{\nu}|\boldsymbol{p}_{\nu}-\varepsilon\frac{e}{c}\boldsymbol{A}_{\nu}|^{2}+V(q) \tag{2}$$

where $\boldsymbol{A}_{\nu}$ is the vector potential of the external field at the position of electron ν and ε is a smallness-parameter which indicates that the applied field is considered a weak perturbation on the bound motion of the particles. $V(q)$ is the internal static potential where q stands for all the cartesian coordinates of the electrons, the origin of the coordinate system being conveniently chosen within the region of bound motion. The linear momentum $\boldsymbol{p}_{\nu}$ of electron ν is given by

$$\boldsymbol{p}_{\nu}=m\boldsymbol{v}_{\nu}+\varepsilon\frac{e}{c}\boldsymbol{A}_{\nu}\,. \tag{3}$$

Finally, we have assumed that the field is described in the Coulomb (or radiation-) gauge

$$\operatorname{div}\boldsymbol{A}=0 \tag{4}$$

so that the vector potential is purely transverse and the scalar potential φ of the radiation field is zero.

We shall now invoke the electric dipole approximation according to which the value of the vector potential at the position of electron ν, $\boldsymbol{A}_{\nu}=\boldsymbol{A}(q_{\nu},t)$, is put equal to its value at the origin of the coordinate system, hence

$$\boldsymbol{A}_{\nu}(t)=\boldsymbol{A}^{0}(t)\,. \tag{5}$$

The Hamiltonian (2) can then be expanded retaining only first order terms in ε:

$$H=\frac{1}{2m}\sum_{\nu}|\boldsymbol{p}_{\nu}|^{2}+V(q)-\varepsilon\frac{e}{mc}\boldsymbol{A}^{0}\cdot\sum_{\nu}\boldsymbol{p}_{\nu}\,. \tag{6}$$

The quantum translation of the linear momentum $\boldsymbol{p}_\nu$ is $-i\hbar\hat{\nabla}_\nu$ and a time-dependent perturbation method based on the Hamiltonian (6) leads therefore in a well-known way [4] to the dipole velocity expression (1b) for the transition moment.

Consider now a canonical transformation in which the coordinates and momenta $\boldsymbol{q}_\nu$ and $\boldsymbol{p}_\nu$ are transformed into new variables $\boldsymbol{Q}_\nu$ and $\boldsymbol{P}_\nu$ which differ from the original ones by infinitesimal amounts only. Such a transformation is effected by a generating function [9]

$$F_2 = \sum_\nu \boldsymbol{q}_\nu \cdot \boldsymbol{P}_\nu + \varepsilon \sum_\nu G_\nu \tag{7}$$

where ε again is a smallness-parameter and G_ν is a single particle generating function which depends on the old coordinates $\boldsymbol{q}_\nu$ and the new momenta $\boldsymbol{P}_\nu$ of electron ν. The equations of transformation can then be written [9]

$$\boldsymbol{p}_\nu = \boldsymbol{P}_\nu + \varepsilon \frac{\partial}{\partial \boldsymbol{q}_\nu} G_\nu , \tag{8a}$$

$$\boldsymbol{Q}_\nu = \boldsymbol{q}_\nu + \varepsilon \frac{\partial}{\partial \boldsymbol{P}_\nu} G_\nu , \tag{8b}$$

$$K = H + \varepsilon \sum_\nu \frac{\partial}{\partial t} G_\nu , \tag{8c}$$

where K is the transformed Hamiltonian.

In the Goeppert-Mayer transformation [5] the generating function is taken as

$$G_\nu = \frac{e}{c} \boldsymbol{A}^0(t) \cdot \boldsymbol{q}_\nu . \tag{9}$$

The transformed dynamical variables are then by Eqs. (8a, b):

$$\boldsymbol{p}_\nu = \boldsymbol{P}_\nu + \varepsilon \frac{e}{c} \boldsymbol{A}^0(\mathrm{t}) , \tag{10a}$$

$$\boldsymbol{Q}_\nu = \boldsymbol{q}_\nu , \tag{10b}$$

and the transformed Hamiltonian becomes

$$K = \frac{1}{2m} \sum \left| \boldsymbol{P}_\nu + \varepsilon \frac{e}{c} \boldsymbol{A}^0 \right|^2 + V(q) - \varepsilon \frac{e}{mc} \boldsymbol{A}^0 \cdot \sum_\nu \boldsymbol{P}_\nu + \varepsilon \frac{e}{c} \left(\frac{\partial}{\partial t} \boldsymbol{A}^0 \right) \cdot \sum_\nu \boldsymbol{q}_\nu$$

or to first order in ε

$$K = \frac{1}{2m} \sum_\nu |\boldsymbol{P}_\nu|^2 + V(q) - \varepsilon e \boldsymbol{E}^0(t) \cdot \sum_\nu \boldsymbol{q}_\nu \tag{11}$$

where we have used the fact that the electric field is given by

$$\boldsymbol{E} = -\frac{1}{c} \frac{\partial}{\partial t} \boldsymbol{A} \tag{12}$$

and $\boldsymbol{E}^0$ is the value of $\boldsymbol{E}$ at the origin. According to Eqs. (3) and (10a) the linear momentum is

$$\boldsymbol{P}_\nu = m\boldsymbol{v}_\nu . \tag{13}$$

The Hamiltonian (11), which is in the form derived by Goeppert-Mayer [5], is conceptually by far the simplest starting point for a semi-classical radiation theory in the dipole approximation. The simplifications, as compared to Eq. (6), are two-fold. Firstly, the coordinates and momenta in Eq. (11) are identical with the usual mechanical variables [according to Eqs. (10b) and (13)] whereas the momenta in Eq. (6) are explicitly field-dependent according to Eq. (3). The second simplification is that the term representing the interaction between the applied field and the particles has an elementary physical interpretation, being the energy of an electric dipole moment in an electric field. A time-dependent perturbation approach based on the Hamiltonian (11) leads therefore to the dipole length expression, Eq. (1a).

The Hamiltonian appropiate for the dipole acceleration formalism is obtained from the Hamiltonian (6) by use of a generating function of the form

$$G'_\nu = \frac{e}{mc^2}\boldsymbol{\Pi}^0(t)\cdot \boldsymbol{P}'_\nu \tag{14}$$

where $\boldsymbol{\Pi}^0(t)$ is the electric Hertz vector at the origin. Eq. (14) is the classical analogue of the Schwinger transformation [2]. The vector potential is then given as[1]

$$\boldsymbol{A} = \frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{\Pi} \tag{15}$$

According to Eqs. (8) the transformed variables are now

$$\boldsymbol{p}_\nu = \boldsymbol{P}'_\nu \tag{16a}$$

or from Eqs. (3) and (15)

$$\boldsymbol{P}'_\nu = m\boldsymbol{v}_\nu + \varepsilon\frac{e}{c^2}\frac{\partial}{\partial t}\boldsymbol{\Pi}^0 \tag{16b}$$

and

$$\boldsymbol{Q}'_\nu = \boldsymbol{q}_\nu + \varepsilon\frac{e}{mc^2}\boldsymbol{\Pi}^0 . \tag{16c}$$

The Hamiltonian is transformed into

$$K' = \frac{1}{2m}\sum_\nu |\boldsymbol{P}'_\nu|^2 + V(q) - \varepsilon\frac{e}{mc}\boldsymbol{A}^0\cdot\sum_\nu \boldsymbol{P}'_\nu + \varepsilon\frac{e}{mc^2}\left(\frac{\partial}{\partial t}\boldsymbol{\Pi}^0\right)\cdot\sum_\nu \boldsymbol{P}'_\nu$$

to first order in ε. Eq. (15) makes the last two terms vanish and we get:

$$K' = \frac{1}{2m}\sum_\nu |\boldsymbol{P}'_\nu|^2 + V(q) \tag{17}$$

---

[1] Since we consider the radiation field in a source-free region the magnetic Hertz vector can be put equal to zero, and the field is determined exclusively by the electric Hertz vector [10].

where it remains to insert the transformed coordinates from Eq. (16c):

$$\boldsymbol{q}_\nu = \boldsymbol{Q}'_\nu - \varepsilon \frac{e}{mc^2} \boldsymbol{\Pi}^0(t).$$

The vector $\boldsymbol{\Pi}^0$ is constant in space and the potential $V(q)$ can therefore be expanded in a Taylor series around Q'. Retaining only first order terms in ε this gives:

$$V(q) = V(Q') - \varepsilon \frac{e}{mc^2} \boldsymbol{\Pi}^0 \cdot \sum_\nu (\mathrm{grad}_\nu V). \tag{18}$$

Since $\boldsymbol{Q}'_\nu$ differs only infinitesimally from $\boldsymbol{q}_\nu$, the gradient of the potential can be computed with respect to the original cartesian coordinates q. Combining Eqs. (17) and (18) the transformed Hamiltonian can be written

$$K' = \frac{1}{2m} \sum_\nu |\boldsymbol{P}'_\nu|^2 + V(Q') - \varepsilon \frac{e}{mc^2} \boldsymbol{\Pi}^0 \cdot \sum_\nu (\mathrm{grad}_\nu V) \tag{19}$$

where the variables are defined in Eqs. (16).

Eq. (19) represents the desired Hamiltonian for the dipole acceleration formalism since a time-dependent perturbation treatment based on this Hamiltonian will lead to transition probabilities in terms of the dipole expression Eq. (1c). The present derivation shows that the field quantity which appears in the perturbation term is the electric Hertz vector $\boldsymbol{\Pi}$. It should be noticed that the coordinates and momenta are all explicitly field-dependent in this formulation [see Eqs. (16)]. However, the field quantities enter in such a way that the momentum $\boldsymbol{P}'_\nu$ is in fact equal to the mass times the time-derivative of the generalized coordinate $\boldsymbol{Q}'_\nu$.

3. The Hamiltonian Appropiate for the Fourth Dipole Expression

The transformation from the dipole acceleration Hamiltonian (19) to the Hamiltonian appropiate for Chen's dipole expression [3] can be effected by a generating function of the form

$$G''_\nu = -\frac{e}{mc^3} \boldsymbol{T}^0(t) \cdot (\mathrm{grad}_\nu V) \tag{20}$$

where $\boldsymbol{T}^0$ is the constant term in a Taylor expansion of a field $\boldsymbol{T}$ defined by

$$\boldsymbol{\Pi} = -\frac{1}{c} \frac{\partial}{\partial t} \boldsymbol{T}, \tag{21}$$

$\boldsymbol{\Pi}$ being the electric Hertz vector. The author knows of no previous discussion of a field of this sort. We shall not, however, investigate the properties of this field any further here, but only add that there will be a non-trivial gauge problem associated with the field (considering the complexity of the gauge problem for the Hertz vectors [10, 11]).

The generating function (20) transforms the primed coordinates and momenta, Eqs. (16), into new variables given by

$$\boldsymbol{Q}''_\nu = \boldsymbol{Q}'_\nu , \tag{22a}$$

$$\boldsymbol{P}'_\nu = \boldsymbol{P}''_\nu + \varepsilon \frac{\partial}{\partial \boldsymbol{Q}'_\nu} G''_\nu = \boldsymbol{P}''_\nu + \varepsilon \frac{\partial}{\partial \boldsymbol{q}_\nu} G''_\nu , \tag{22b}$$

where the last step in (22b) is allowed because $\boldsymbol{Q}'_\nu$ and $\boldsymbol{q}_\nu$ differ by infinitesimal amounts only. For the ith cartesian component of the momentum Eq. (22b) becomes:

$$P'_{\nu i} = P''_{\nu i} - \varepsilon \frac{e}{mc^3} \boldsymbol{T}^0 \cdot \left[\frac{\partial}{\partial q_{\nu i}} (\mathrm{grad}_\nu V) \right] . \tag{22c}$$

The transformed Hamiltonian is then found from Eqs. (8c), (19) and (20) and turns out to be

$$\begin{aligned} K'' = \frac{1}{2m} \sum_\nu |\boldsymbol{P}'_\nu|^2 + V(Q'') - \varepsilon \frac{e}{mc^2} \boldsymbol{\Pi}^0 \cdot \sum_\nu (\mathrm{grad}_\nu V) \\ - \varepsilon \frac{e}{mc^3} \left(\frac{\partial}{\partial t} \boldsymbol{T}^0 \right) \cdot \sum_\nu (\mathrm{grad}_\nu V) . \end{aligned} \tag{23}$$

The definition of the auxiliary field $\boldsymbol{T}$, Eq. (21), makes the last two terms cancel and the only step left is to insert the transformed momenta from Eqs. (22). The resulting Hamiltonian can be written in the form

$$K'' = \frac{1}{2m} \sum_\nu |\boldsymbol{P}''_\nu|^2 + V(Q'') - \varepsilon \frac{e}{m^2 c^3} \boldsymbol{T}^0 \cdot \sum_\nu \mathscr{V}_\nu \boldsymbol{P}''_\nu . \tag{24}$$

Where $\mathscr{V}_\nu$ is a symmetric, second order tensor[2] with components:

$$(\mathscr{V}_\nu)_{ij} = \frac{\partial^2}{\partial q_{\nu i} \partial q_{\nu j}} V(q) . \tag{25}$$

In order to show that the perturbation term in the Hamiltonian (24) correctly reproduces Chen's expression for the dipole transition moment, we shall consider specifically the case of a single electron in a spherically symmetric potential:

$$V = - \frac{e^2}{r} \tag{26}$$

and furthermore assume that the field is linearly polarized along the z-direction so that

$$\boldsymbol{T}^0(t) = T^0_z(t) \boldsymbol{k} .$$

The perturbation term in (24) is in that case equal to

$$\frac{e}{m^2 c^3} T^0_z \left[\left(\frac{\partial}{\partial z} \,\mathrm{grad}\, V \right) \cdot \boldsymbol{P}'' \right] . \tag{27}$$

---

[2] We are working exclusively in cartesian coordinates and the distinction between covariant and contravariant quantities can therefore be disregarded.

In a quantum mechanical translation the momentum $\boldsymbol{P}''$ becomes $-i\hbar\hat{V}$ and the term in square brackets in (27) is turned into an operator[3]

$$\left(\frac{\partial}{\partial z}\operatorname{grad} V\right)\cdot \boldsymbol{P}'' \to -i\hbar\left(\frac{\partial}{\partial z}\operatorname{grad} V\right)\cdot\hat{V}.$$

If now the central potential (26) is inserted, this operator becomes

$$-i\hbar\left(\frac{1}{r^3}\frac{\partial}{\partial z}-\frac{3z}{r^4}\frac{\partial}{\partial r}\right) \tag{28}$$

which is identical to the operator in the dipole expression derived by Chen [3] by means of the off-diagonal quantum mechanical hypervirial theorem.

We have now shown that the Hamiltonian (24) does indeed lead to the fourth alternative formulation of the dipole transition moment. The derivation has furthermore shown that the field quantity which appears in the interaction term in this formulation must obey a relation of the form (21). The choice of constant and sign in (21) is of course arbitrary.

It should be noted that the perturbation terms in the Hamiltonians (19) and (24) may have strong singularities which can impose restrictions on the states the formulations can be applied to. In the case of the operator (28), which is valid in a central coulomb potential, Chen [3] has in fact shown that the singularity has the consequence that only excitations between states with orbital angular momenta different from zero can be treated.

4. Concluding Remarks

The fact that the Hamiltonians (6), (11), (19), and (24) can be converted into each other by canonical transformations shows that they are entirely equivalent within the two stated approximations: a) the electric dipole approximation in which all field quantities are put equal to their value at the origin of the coordinate system, and b) the first-order perturbation approximation in which second and higher order terms in ε (and hence in the field strengths) are neglected. The electric dipole approximation is appropiate for most of ordinary absorption and emission spectroscopy, but it is insufficient for such areas as magnetic dipole transitions and natural optical rotatory power both of which require explicit consideration of the spacial variations of the field over the dimensions of the absorbing system [1, 12]. The neglect of higher order terms in the field strengths restricts the applicability of these Hamiltonians to single-photon processes, although it may be worthwhile to point out that the Goeppert-Mayer Hamiltonian (11) is in fact equivalent to the full Hamiltonian (2), in the dipole approximation. The Hamil-

---

[3] The operator should rigorously speaking contain an additional term $-\frac{1}{2}i\hbar\operatorname{div}(\partial\operatorname{grad}V/\partial z)$ $=-\frac{1}{2}i\hbar\frac{\partial}{\partial z}\operatorname{div}\operatorname{grad}V$ in order to warrant the hermitian properties [4]. However, the electrostatistic potential fulfills Laplace's equation $\operatorname{div}\operatorname{grad}V=0$ (except at the point nucleus), and this term therefore does not contribute to the operator (for r different from zero). The problem of the behaviour at the point nucleus is connected with Chen's observation [3] that transitions to or from s-orbitals can not be treated with this operator *(vide infra)*.

tonians (2) and (11) are therefore equally valid for a treatment of multi-photon processes [5, 13].

The equivalence of the four Hamiltonians means specifically that none of the formalisms can be considered more fundamental than the others, and they do indeed lead to identical intensities when the exact energy eigenfunctions for the unperturbed systems are used as basis for a time-dependent perturbation expansion. It is, on the other hand, a significant feature of the calculation of electronic transition probabilities that the sundry formalisms in general yield very different results for approximate wave functions (see Refs. [14] and [15] and references therein). The reason for this is that only for exact energy eigenstates do the different Hamiltonians lead to the same time-evolution. The use of approximate wave functions is therefore tantamount to an artificial admixture of some off-resonance character in the transitions. These off-resonance parts will contribute differently in the various formalisms [16], partly because of the neglect of higher order terms in the field quantities, and the computed intensities will hence in general be different.

Acknowledgement. The author is grateful to Drs. J. P. Dahl and J. S. Avery for valuable discussions and comments on the manuscript.

References

1. Bethe, H. A., Salpeter, E. E.: Quantum mechanics of one and two-electron atoms. Berlin-Göttingen-Heidelberg: Springer 1957.
2. Power, E. A.: Introductory quantum electrodynamics. London: Longmans, Green and Co Ltd. 1964.
3. Chen, J. C. Y.: J. chem. Physics **40**, 615 (1964).
4. Schiff, L. I.: Quantum mechanics. New York: McGraw-Hill 1968.
5. Goeppert-Mayer, M.: Ann. Physik **9**, 273 (1931).
6. Richards, P. I.: Physic. Rev. **73**, 254 (1948).
7. Fiutak, J.: Canad. J. Physics **41**, 12 (1963).
8. Power, E. A., Shail, R.: Proc. Cambridge philos. Soc. **55**, 87 (1959). – Zienau, S.: Philos. Trans. Roy. Soc. (London) A **251**, 54 (1958).
9. Goldstein, H.: Classical mechanics. Massachusetts: Addison-Wesley 1950.
10. Stratton, J. A.: Electromagnetic theory. New York: McGraw-Hill 1941.
11. Nisbet, A.: Proc. Roy. Soc. (London) A **231**, 250 (1955).
12. Moscowitz, A.: in: Advances chem. physics, vol. 4, Ed. I. Progogine, New York: Interscience Publishers 1962.
13. Peticolas, W. L.: Annu. Rev. physic. Chem. **18**, 233 (1967).
14. LaPaglia, S. R., Sinanoglu, O.: J. chem. Physics **44**, 1888 (1966).
15. Hansen, Aa. E.: Molecular Physics **13**, 425 (1967).
16. Paul, H., Frahm, J.: Ann. Physik **19**, 216 (1967).

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