Reply to the Preceeding Comment on the Zeeman-Effect in Rotational Spectroscopy

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In the preceeding note Howard and Moss present serious criticism of our paper „Zur Theorie des Zeeman-Effekts in Rotationsspektren“ [1]. Their criticism is based upon a difference in sign in the final Hamiltonian and on the belief that our way of performing the transformation of gauge is incorrect. We believe that their criticism is unjustified in both cases.

In their note the authors give a Hamiltonian which reduces to our Hamiltonian, when they — as we have done — considered only electrically neutral molecules.

The authors did not realize that the "difference in sign" was due to a printing error, which was corrected in a footnote of a second paper [2].

The only remaining difference, i. e. the neglection of the m/M terms in our derivation was discussed in detail in our paper and we still believe that it is justified as far as rotational spectroscopy is concerned.

As far as the transformation of gauge is concerned, we would like to state the following. It is well known, that a wide variety of transformations of gauge is permissible and that these transformations may be explicitly time dependent (aus in our case) without changing the magnetic and electric field strengths.

Since the sequence of equations in our paper might have caused some confusion about the stage at which the transformation is performed, we would like to restate in other words our line of thinking.

Our approach is based upon the assumption that the origin of the molecular coordinate system moves with constant velocity $\boldsymbol{v}_0$ on a straight line.

As we have pointed out we are well aware of the fact that this assumption does not hold rigorously but is only an approximation which we believe to be quite good in the case of neutral molecules.

Starting point was the Lagrangian [Eq. (2) in [1]] in a laboratory frame:

$$\text{(a)} \qquad \mathcal{L} = \tfrac{1}{2}\sum_n m_n \boldsymbol{v}_n'^2 + \frac{1}{2c}\sum_n q_n \boldsymbol{v}_n'(\boldsymbol{H}\times\boldsymbol{r}_n') - V'.$$

Using the vector relations *

$$\boldsymbol{r}_n' = \boldsymbol{r}_0 + \boldsymbol{r}_n, \qquad \boldsymbol{v}_n' = \boldsymbol{v}_0 + \boldsymbol{v}_n, \qquad \boldsymbol{r}_0 = \boldsymbol{v}_0 \cdot t$$

where $\boldsymbol{r}_0$ is the position vector of the origin of the translational coordinate system with respect to the laboratory fixed system.

Equation (a) may be written as:

$$\text{(b)} \qquad \mathcal{L} = \tfrac{1}{2}\sum_n m_n \boldsymbol{v}_0^2 + \sum_n m_n \boldsymbol{v}_n \cdot \boldsymbol{v}_0 + \tfrac{1}{2}\sum_n m_n \boldsymbol{v}_n^2 + \frac{1}{2c}\sum_n q_n(\boldsymbol{v}_0+\boldsymbol{v}_n)(\boldsymbol{H}\times\boldsymbol{r}_n) + \frac{1}{2c}\sum_n q_n(\boldsymbol{v}_0+\boldsymbol{v}_n)(\boldsymbol{H}\times\boldsymbol{r}_0) - V'.$$

In order to eliminate the part $\frac{1}{2c}\sum q_n(\boldsymbol{v}_0+\boldsymbol{v}_n)\cdot(\boldsymbol{H}\times\boldsymbol{r}_0)$. (a) is written using new potentials

$$A_{n\,\text{new}} = A_{n\,\text{old}} - \text{grad}_n\,\chi = A_{n\,\text{old}} - \tfrac{1}{2}(\boldsymbol{H}\times\boldsymbol{v}_0\,t),$$

$$\varphi_{\text{new}} = \varphi_{\text{old}} + \frac{1}{c}\frac{\partial\chi}{\partial t} = \varphi_{\text{old}} + \frac{1}{2c}\sum(\boldsymbol{H}\times\boldsymbol{v}_0)\cdot\boldsymbol{r}_n'$$

where

$$A_{n\,\text{old}} = \tfrac{1}{2}(\boldsymbol{H}\times\boldsymbol{r}_n')$$

and

$$\chi = \tfrac{1}{2}\sum(\boldsymbol{H}\times\boldsymbol{v}_0\,t)\cdot\boldsymbol{r}_n' = \tfrac{1}{2}\sum(\boldsymbol{H}\times\boldsymbol{v}_0\,t)\cdot\boldsymbol{r}_n$$

(the x' component of grad_n is $\partial/\partial x_n'$).

The field strengths at the positions of the n-th particle are not changed:

$$\boldsymbol{H}_{n\,\text{new}} = \text{rot}_n\,A_{n\,\text{new}} = \text{rot}_n\,\boldsymbol{A}_{n\,\text{old}} - \tfrac{1}{2}\,\text{rot}_n(\boldsymbol{H}\times\boldsymbol{v}_0\,t) = \text{rot}_n\,\boldsymbol{A}_{n\,\text{old}} = H_{n\,\text{old}},$$

$$\boldsymbol{E}_{n\,\text{new}} = -\frac{1}{c}\frac{\partial \boldsymbol{A}_{n\,\text{new}}}{\partial t} - \text{grad}_n\,\varphi_{\text{new}} = -\frac{1}{c}\frac{\partial \boldsymbol{A}_{n\,\text{old}}}{\partial t} + \frac{1}{2c}(\boldsymbol{H}\times\boldsymbol{v}_0) - \text{grad}_n\,\varphi_{\text{old}} - \frac{1}{2c}(\boldsymbol{H}\times\boldsymbol{v}_0) = \boldsymbol{E}_{n\,\text{old}},$$

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[1] D. SUTTER, A. GUARNIERI, and H. DREIZLER, Z. Naturforsch. **25 a**, 222 [1970].

[2] D. SUTTER and A. GUARNIERI, Z. Naturforsch. **25 a**, 1036 [1970].

* For the sake of simplicity it is assumed that the translational system coincides at time $t=0$ with the laboratory frame.

With the transformed "new" potential we have:

$$\text{(a}'\text{)} \quad \mathcal{L} = \tfrac{1}{2} \sum m_n \boldsymbol{v_n}'^2 + \frac{1}{2\,c} \sum q_n v_n' (\boldsymbol{H} \times \boldsymbol{r}_n) - V' - \frac{1}{2\,c} \sum q_n (\boldsymbol{H} \times \boldsymbol{v}_0)\, \boldsymbol{r}_n\,,$$

$$\text{(b}'\text{)} \quad \mathcal{L} = \tfrac{1}{2} \sum m_n \boldsymbol{v}_0^2 + \sum m_n \boldsymbol{v}_0 \cdot \boldsymbol{v_n} + \tfrac{1}{2} \sum m_n \boldsymbol{v_n}^2 + \frac{1}{2\,c} \sum q_n \boldsymbol{v_n} \cdot (\boldsymbol{H} \times \boldsymbol{r_n}) - V' + \frac{1}{c} \sum q_n \boldsymbol{v}_0 \cdot (\boldsymbol{H} \times \boldsymbol{r_n}).$$

Up to this point $\boldsymbol{r}_0$ is the position of the origin of a coordinate system which "by chance" moves through space very close to the origin of the molecular system.

At this stage we introduced our approximation by identifying the origin of the molecular coordinate system with the origin of our "$\boldsymbol{v}_0$-reference-system".

This leads to Eq. (11) in [1] where $\boldsymbol{v}_0$ should be thought of as a constant velocity.

Even after neglection of the „Mitbewegung des Kerngerüstes" i. e. the m/M terms, there is still some coupling left which prevents $\boldsymbol{v}_0$ from being a constant of the motion. In a classical picture this coupling [part (g) of Eq. (11) in [1]] would cause the molecular center of mass to move on a small circle around the $\boldsymbol{r}_0$ position. The radius of this circle may be easily estimated to be in the order of 10^{-13} cm by using a rotational frequency of 30 GHz, a dipole moment of 1 Debye and a molecular mass of 50 amu.

Although this is a very small perturbation we have made allowance for it by giving $\boldsymbol{r}_0$ free as a variable of the system. The reason for our doing so is the fact that rotational frequencies are involved and not only the much higher "electronic frequencies". We have to admit that this step which leads from Eq. (11) to Eq. (12) of our paper should have been discussed in some detail.

By giving $\boldsymbol{r}_0$ (and $\boldsymbol{v}_0$) free as variables of the molecular system the final Hamiltonian is slightly improved in so far, as part (25 i) in [1], which gives a contribution to the susceptibility is included.

Proceeding in a more consequent manner the "constant" overall translational energy should have been dropped after Eq. (11) and the contribution due to the "translational Lorentz forces" (11 g) should have been treated as a potential energy. In this case the final Hamiltonian [Eq. (25) in [1]] would have been simplified in so far as (25 a) and (25 i) would disappear. In part (25 h) the translational momentum $\boldsymbol{\pi}$ would have to be replaced by $\boldsymbol{\pi} = M\boldsymbol{v}_0$.

Comparing the two ways which lead to the Hamiltonian of a neutral molecule rotating in an external magnetic field we believe that although our way uses an approximation and some physical intuition it is more easy to follow than the more formal approach of Howard and Moss who missed the "translational Lorentz force Stark effect" in their first paper [3].

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[3] Mol. Phys. **19**, 433 [1970].

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