A Comment on Zeeman Effects in Rotation Spectra

B. J. HOWARD and R. E. MOSS

Department of Chemistry, The University, Southampton, SO 9 5 NH, England

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Recently SUTTER et al. [1] obtained a Hamiltonian for a molecule in the presence of a constant external electromagnetic field. (A similar Hamiltonian has been developed [2], but including molecular vibrations, relativistic corrections and allowance for the fact that the molecular centre of gravity differs from the nuclear centre of gravity.) We believe that the Hamiltonian of Sutter et al. is not correct, since they make two errors of principle in performing their gauge transformation.

They start with a Lagrangian expressed in terms of the particle positions, $\boldsymbol{r}_n'$, in a space-fixed coordinate system. Each particle is associated with an external vector potential, $\boldsymbol{A}_n' = \frac{1}{2}\boldsymbol{H} \wedge \boldsymbol{r}_n'$, where $\boldsymbol{H}$ is the constant external magnetic field. At this stage a gauge transformation may be performed:

$$\boldsymbol{A}_n' \rightarrow \boldsymbol{A}_n' - \nabla_n \chi\,, \tag{1}$$

where χ is a scalar fuction and the operator ∇_n corresponds to the momentum of particle n and operates only on the components of $\boldsymbol{r}_n'$; this is permissible, because each particle has associated with it both a vector potential, $\boldsymbol{A}_n'$, and an appropriate operator, ∇_n. However, before making a gauge transformation they expressed the Lagrangian in a molecular coordinate system in which the coordinates $\boldsymbol{r}_n'$ were replaced by $\boldsymbol{r}_0$, the position of the molecular centre of gravity, rotational coordinates and $\boldsymbol{r}_j$, the electron positions relative to the molecular centre of gravity. Associated with each of these new coordinates there is a new operator corresponding to the new momentum. The individual nuclei can no longer be thought of as having their own vector potentials and the concept of a "translational" and a "rotational" vector potential, both of which will depend on the nuclear charges, must be introduced. A gauge transformation of these potentials can now be performed, but only if the appropriate translational and rotational operators are used. Sutter et al. introduce errors in their analysis by associating a vector potential with each individual nucleus after transforming to the molecular coordinate system.

When a gauge transformation is performed on a vector potential as in (1), the corresponding scalar potential, φ, is also modified:

$$\varphi \rightarrow \varphi + (1/c)\,(\partial\chi/\partial t)\,, \tag{2}$$

where t is the time. Sutter et al. maintain that $(\partial\chi/\partial t)$ is non-zero, since their choice of χ depends on $\boldsymbol{r}_0$ and the molecule is translating. We believe that $(\partial\chi/\partial t)$ is zero, since $\boldsymbol{r}_0$ does not depend on time explicitly. Let us consider the simpler, but equivalent, problem of a moving particle with instantaneous position $\boldsymbol{r}$, and consider the effect (2) of a gauge transformation on the external scalar potential, φ, at the point $\boldsymbol{r}$. Even if χ is a function of $\boldsymbol{r}$, $(\partial\chi/\partial t)$ is zero, since $\boldsymbol{r}$ is a fixed point. The fact that $\boldsymbol{r}$ is also the instantaneous position of a moving particle is not relevant; the velocity of the particle cannot affect the external potential at its instantaneous position. The only way in which φ can be changed is for χ to have explicit time-dependence, which in this case would involve $\boldsymbol{H}$ being time-dependent.

Using their terminology we believe the final Hamiltonian should be:

$$\begin{aligned}\mathcal{H} = {} & \tfrac{1}{2}\,\boldsymbol{\pi}^t \cdot \boldsymbol{M}^{-1} \cdot \boldsymbol{\pi} + \tfrac{1}{2}\,(\boldsymbol{P}-\boldsymbol{L})^t \cdot \boldsymbol{I}^{-1} \cdot (\boldsymbol{P}-\boldsymbol{L}) \\ & + \tfrac{1}{2}\sum_j \boldsymbol{p}_j^t \cdot \boldsymbol{m}^{-1} \cdot \boldsymbol{p}_j + V' \\ & - (e/4\,c)\,[(\boldsymbol{P}-\boldsymbol{L})^t \boldsymbol{I}^{-1} \boldsymbol{S}\,\boldsymbol{\Phi} \cdot \boldsymbol{H} + \boldsymbol{H}^t \boldsymbol{\Phi}^t \boldsymbol{S}\,\boldsymbol{I}^{-1}\,(\boldsymbol{P}-\boldsymbol{L})] \\ & + (e/2\,m\,c)\,\boldsymbol{L}^t \boldsymbol{\Phi}\,\boldsymbol{H} - (1/2\,M\,c)\sum_j \boldsymbol{p}_j^t\,\mu\,\boldsymbol{\Phi} \cdot \boldsymbol{H} \\ & + (e^2/8\,c^2)\,\boldsymbol{H}^t \boldsymbol{\Phi}^t \boldsymbol{S} \cdot \boldsymbol{I}^{-1} \boldsymbol{S}\,\boldsymbol{\Phi}\,\boldsymbol{H} \\ & + (e^2/8\,m\,c^2)\,\boldsymbol{H}^t \boldsymbol{\Phi}^t \boldsymbol{s}'\,\boldsymbol{\Phi}\,\boldsymbol{H} \\ & - (1/M\,c)\,\boldsymbol{\pi}^t \boldsymbol{\Phi}^t \mu\,\boldsymbol{\Phi}\,\boldsymbol{H} + (1/2\,M\,c^2)\,\boldsymbol{H}^t \boldsymbol{\Phi}^t \mu^t \mu\,\boldsymbol{\Phi}\,\boldsymbol{H},\end{aligned} \tag{3}$$

where $\boldsymbol{s}'$ is similar to $\boldsymbol{s}$ in Ref. [1] but a_j, b_j and c_j are to be replaced by $a_j + (m/M\,e)\,\mu_a$, $b_j + (m/M\,e)\,\mu_b$ and $c_j + (m/M\,e)\,\mu_c$ respectively. This Hamiltonian differs from that of Sutter et al. in that the "rotational" vector potential has the opposite sign and the vector potential associated with electron j is more complex. For the "translational" vector potential the two errors in the gauge transformation compensate one another and the conclusion that there is an effective transverse Stark electric field in unaffected. For light species this could well be up to 10 volt cm^{-1} for an external magnetic field of 30 kG and for molecules with linear Stark effects it will lead to line broadening, if the experiment involves random translational motion. However, in molecular beam studies with velocity selection it could lead to a detectable shift or splitting of lines and would have to be considered in electric dipole moment determinations.

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

[2] B. J. HOWARD and R. E. MOSS, Mol. Phys. **19**, 433 [1970]. — B. J. HOWARD and R. E. MOSS, Mol. Phys., to be published.