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On the Calculation of Phosphorescence Oscillator Strength

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It is pointed out that one of the two commonly used expressions for calculating the oscillator strength of phosphorescence transitions is incomplete. By using the adequate transition operator, a correction term is added to one of the two expressions which then become analytically equivalent up to second order in the fine structure constant.

(Keywords: Oscillator strength; Phosphorescence)

Zur Berechnung der Phosphoreszenzoszillatorenstärke

Es wird darauf hingewiesen, daß eine der beiden in der Literatur gebräuchlichen Formeln zur Berechnung der Phosphoreszenzoszillatorenstärke unvollständig ist. Wird jedoch unter Berücksichtigung des adäquaten Übergangsmomentoperators ein Korrekturterm hinzugefügt, werden die beiden Formeln analytisch äquivalent bis zu Termen zweiter Ordnung in der Feinstrukturkonstante.

On treating singlet-triplet radiative transitions one usually assumes a total *Hamiltonian* H, whereby the nonrelativistic kinetic and potential energy operator H_0 of the nuclei and the electrons has been extended by the spin-orbit operator H_{so}

$$H = H_0 + H_{so} \tag{1}$$

If spin-orbit coupling can be assumed to be a small perturbation, the wavefunctions for the total *Hamiltonian* can be set up by first order perturbation theory as linear combinations of spin-pure eigenfunctions $|^1k>$ and $|^3n>$ of H_0 of different multiplicity and energy ${}^1E_k^0$ and ${}^3E_n^0$

$$|^{(1)}S> = |^1S> - \sum_n \sum_q^3 \frac{<{}^3n_q|H_{so}|^1S>}{{}^3E_n^0 - {}^1E_S^0} |^3n_q> \tag{2a}$$

$$|^{(3)}T_q> = |^3T_q> - \sum_k \frac{<{}^1k|H_{so}|^3T_q>}{{}^1E_k^0 - {}^3E_T^0} |^1k> \tag{2b}$$

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The wave functions of the phosphorescent triplet state and of the singlet ground state are marked by multiplicities set in round brackets denoting spin-impure states (*Hameka* 1967). The triplet components are indicated by q. The singlet-triplet oscillator strength is given by the transition matrix element between the two spin-impure states

$$f = \frac{2}{9} \frac{1}{\Delta E_{ST}} \sum_{q}^{3} | < {}^{(1)}S | \vec{\pi} | {}^{(3)}T_q > |^2 \tag{3}$$

The three triplet components are assumed to be equally populated. Atomic units are used throughout.

Now the question arises which transition operator is adequate for spin-forbidden transitions (*Hameka* 1965, *Hameka* and *Goodman* 1965, *Lohr* 1966, *Lohr* 1972, *Englman* 1966, *Chiu* 1968, *Goodman* and *Laurenzi* 1968, *Drake* 1972). *Hameka* and *Goodman* (1965) used the total electronic momentum operator and discussed the transformation of matrix elements of the momentum operator to matrix elements over the electric dipole moment operator for spin-forbidden transitions. *Lohr* (1966) pointed out, that the extended *Hamiltonian* (1) contains the momentum not only in the kinetic energy part, but also in the spin-orbit term. Recalling that the operator for the interaction with the radiation field is derived by substituting the linear momentum by the mechanical momentum in the *Hamiltonian*, *Lohr* proposed an effective transition operator to be used for spin-forbidden transitions, which accounts for the momentum dependency of the spin-orbit operator. H_{so} will now be specified as a sum of effective one-electron operators of the form

$$H_{so} = \frac{\alpha^2}{2} \sum_j \sum_A \zeta_{Aj} (\vec{r}_{Aj} \times \vec{P}_j) \cdot \vec{S}_j \tag{4}$$

where the summation over j and A includes all electrons and nuclei respectively. $\vec{P}_j$ is the momentum operator and $\vec{S}_j$ the spin operator for electron j; α is the fine structure constant and ζ_{Aj} denotes

$$\zeta_{Aj} = \frac{Z_A^{\text{eff}}}{r_{Aj}^3} \tag{5}$$

Rewriting (4) as

$$H_{so} = \frac{\alpha^2}{2} \sum_j \sum_A \zeta_{Aj} (\vec{S}_j \times \vec{r}_{Aj}) \cdot \vec{P}_j \tag{6}$$

a correction term is derived from the spin-orbit operator to be added to the usual momentum operator valid for spin-allowed transition. Hence,

the effective transition operator is given by

$$\vec{\pi} = \sum_j \vec{P}_j + \frac{\alpha^2}{2} \sum_j \sum_A \zeta_{Aj} (\vec{S}_j \times \vec{r}_{Aj}) \tag{7}$$

On the other hand, *Chiu* (1968) as well as *Goodman* and *Laurenzi* (1968), have shown that the dipole length operator $\vec{R} = \sum_j \vec{r}_j$ is the correct transition operator

$$\vec{\pi} = i\,[(H_0 + H_{so}),\, \vec{R}] \tag{8a}$$

and hence for eigenfunctions of the *Breit-Pauli-Hamiltonian*

$$\vec{\pi} = i\,\Delta E_{ST}\,\vec{R} \tag{8b}$$

Now, in so far as the spin-impure functions (2) set up by first order perturbation theory can be assumed to be eigenfunctions of the *Breit-Pauli-Hamiltonian*, the operator containing the dipole length has to be used. Taking $\vec{\pi}$ as in (8b) and substituting the linear combinations (2) in the matrix elements in (3), one obtains the familiar expression for the singlet-triplet oscillator strength [see for example *Goodman* and *Laurenzi* (1968)]:

$$f = \frac{2}{9}\Delta E_{ST} \sum_q^3 \Big| \sum_k \frac{1}{{}^1E_k^0 - {}^3E_T^0} \langle {}^1k \,|\, H_{so} \,|\, {}^3T_q \rangle \langle {}^1S \,|\, \vec{R} \,|\, {}^1k \rangle - \sum_n \frac{1}{{}^3E_n^0 - {}^1E_S^0} \langle {}^3n_q \,|\, H_{so} \,|\, {}^1S \rangle \langle {}^3T_q \,|\, \vec{R} \,|\, {}^3n_q \rangle \Big|^2 \tag{9}$$

If, however, one substitutes first the linear combinations of spin-pure functions in the transition matrix element, the correct operator $\vec{\pi}$ to be used is the effective operator (7), since the basis functions are eigenfunctions of H_0 and not of the total *Hamiltonian* (1). Thus, another formula for the oscillator strength results

$$f = \frac{2}{9}\frac{1}{\Delta E_{ST}} \sum_q^3 \Big| \quad i \sum_k{}' \frac{{}^1E_k^0 - {}^1E_S^0}{{}^1E_k^0 - {}^3E_T^0} \langle {}^1k \,|\, H_{so} \,|\, {}^3T_q \rangle \langle {}^1S \,|\, \vec{R} \,|\, {}^1k \rangle - i \sum_n{}' \frac{{}^3E_T^0 - {}^3E_n^0}{{}^3E_n^0 - {}^1E_S^0} \langle {}^3n_q \,|\, H_{so} \,|\, {}^1S \rangle \langle {}^3T_q \,|\, \vec{R} \,|\, {}^3n_q \rangle + \frac{\alpha^2}{2} \langle {}^1S \,|\, \sum_j \sum_A \zeta_{Aj} (\vec{S}_j \times \vec{r}_{Aj}) \,|\, {}^3T_q \rangle \Big|^2 \tag{10}$$

The prime indicates that the summands containing the moment of the ground state and of the emitting triplet state are to be excluded. Without the integral in the last line, such a formula has been derived by *Hameka* (1967). The additional term allows a direct coupling between

the spin-pure emitting triplet and the spin-pure singlet ground state (*Lohr* 1972).

An alternative derivation of (10) may be obtained starting from (8a). The matrix elements of the commutator $[H_0, \vec{R}]$ are given by *Heisenberg*'s equation of motion (see *Schiff* 1955)

$$[H_0, \vec{R}]_{lm} = \frac{\vec{P}_{lm}}{i} \tag{11}$$

where $\vec{P}_{lm}$, for eigenfunctions of H_0, can be further transformed

$$\vec{P}_{lm} = -i\,(E^0_m - E^0_l)\,\vec{R}_{lm} \tag{12}$$

For the commutator $[H_{so}, \vec{R}]$ a closed formula may be derived

$$[H_{so}, \vec{R}] = -i\frac{\alpha^2}{2}\sum_j\sum_A \zeta_{Aj}(\vec{S}_j \times \vec{r}_{Aj}) \tag{13}$$

Collecting matrix elements of (11) and (12), respectively, as well as those for the commutator (13) and discarding higher order terms, the expression (10) for the oscillator strength is obtained again.

The analytical equivalence up to terms of order α^2 of the two expressions (9) and (10) can be shown in the case of a complete basis $\{^1k\}$ and $\{^3n\}$. If ΔE_{ST} is approximated by $(^1E^0_S - {}^3E^0_T)$, formula (10) may be rewritten so that it differs from (9) by the terms

$$\frac{\alpha^2}{2} <^1S|\sum_j\sum_A \zeta_{Aj}(\vec{S}_j \times \vec{r}_{Aj})|^3T_q> + i\sum_k <^1S|\vec{R}|^1k><^1k|H_{so}|^3T_q> - i\sum_n <^1S|H_{so}|^3n_q><^3n_q|\vec{R}|^3T_q> \tag{14}$$

Using the resolution of the identity

$$1 = \sum_k |^1k><^1k| + \sum_n\sum_q |^3n_q><^3n_q|$$

and revoking (13), the second and third term in (14) can be seen to cancel exactly the commutator contribution.

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