PHYSICS

I. B. BERSUKER

1957

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Abstract

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PHYSICS

I. B. BERSUKER

ON THE THEOREM ON THE SUM OF OSCILLATOR STRENGTHS FOR ALKALI METALS

(Presented by Academician V. A. Fock, 12 XII 1956)

In the work of V. A. Fock ([1]) it was shown that, for a system with one optical electron outside a closed shell (of the alkali-metal atom type), the sum of the oscillator strengths for electron transitions observed experimentally must be greater than unity, since it does not include the negative oscillator strengths that are not realized in practice (but do enter the sum theorem) for transitions to the inner occupied states of the core. In addition, a certain small correction g is introduced by taking account of the exchange-energy operator in the equation of the valence electron. Thus, the sum of the experimentally measured oscillator strengths is

$$\sum_{n',l'}{}' f_{nl}^{n'l'} = 1 - \sum_{n_i l''} f_{nl}^{n_i l''} + g, \tag{1}$$

where $f_{nl}^{n_i l'}$ are the oscillator strengths for purely theoretical transitions to the inner states of the core, and the prime on the sum on the left-hand side of the equation means that these transitions are excluded from it.

Calculations by formula (1) gave, for Na,

$$\sum_{n'}{}' f_{30}^{n'2} = 1 - f_{30}^{21} + g \quad \left(f_{30}^{21} = -0.037, \quad g = -0.006\right),$$

which corresponded to the experimental data available earlier.

New, more accurate data on the measurement of oscillator strengths in alkali metals, obtained by the dispersion method ([2–4]), give, however, for Na

$$\sum_{n'} f_{30}^{n'1} = 1.26,$$

which does not agree with calculations by formula (1).

On the other hand, the author of the present article has shown ([5]) that in systems of a certain kind, to which the alkali metals also belong, for transitions of the optical electron under the influence of the perturbation of an electromagnetic wave a correction must be introduced into the expression itself for the transition probability and, consequently, for the oscillator strength. Indeed, the usual formula for the probability of a dipole transition is derived under the assumption that the perturbation of the optical electron in the field $\vec{\mathcal{E}}$ of a light wave is the expression

$$W = -(\vec{\mathcal{E}}, \mathbf{D}) = e(\vec{\mathcal{E}}, \mathbf{r}). \tag{2}$$

However, in the equation of the valence electron of an alkali atom

$$[\hat{H}(\mathbf{r}) + V(\mathbf{r})]\psi - \hat{A}\psi = E\psi \tag{3}$$

in the field of a light wave, in addition to the appearance of the perturbation W, the screening potential $V(\mathbf{r})$ and the exchange operator $\hat{A}$ also change as a result of deformation of the "ψ-cloud" of the inner electrons. Neglect of the influence of these changes on the transition of the optical electron is, in our opinion, unjustified.

Allowance for the influence of the core on the transitions of the optical electron under the perturbation by an electromagnetic wave can be made, as shown in the work, by introducing an additional periodic perturbation W' in the form of the potential energy of the optical electron in the field of the non-inertially polarized field of the core wave. For the case of alkali and similar atoms, it is expedient to choose the additional perturbation in the following form:

$$W' = \begin{cases} \dfrac{e(\mathbf{P}, \mathbf{r})}{r_0^3}, & r \leqslant r_0, \\ \dfrac{e(\mathbf{P}, \mathbf{r})}{r^3}, & r \geqslant r_0, \end{cases} \tag{4}$$

where r_0 is the radius of the core; $\mathbf{P} = \alpha\vec{\mathcal{E}}$ is the dipole moment of the core; α is its polarizability. (4) corresponds to the field of a uniformly polarized dielectric sphere (it is assumed that the wavelength is much larger than the dimensions of the system).

The total perturbation of the optical electron in the field of the light wave is

$$W + W' = e(\vec{\mathcal{E}}, \mathbf{r} + \vec{\chi}), \tag{5}$$

where

$$\vec{\chi} = \begin{cases} \dfrac{\alpha}{r_0^3}\mathbf{r}, & r \leqslant r_0, \\ \alpha\dfrac{\mathbf{r}}{r^3}, & r \geqslant r_0. \end{cases} \tag{6}$$

In accordance with (5), in the expression for the transition probability it is necessary to take the matrix element not only of the radius vector, but of the sum $\mathbf{r} + \vec{\chi}$, and the expression for the oscillator strength takes the form:

$$f_{nl}^{n'l'} = \frac{1}{3g_{nl}} \frac{Q_{nln'l'}}{4l_{\max}^2 - 1} (E_{n'l'} - E_{nl}) \left[\int_0^\infty (r + \chi) f_{nl}(r) f_{n'l'}(r)\, dr\right]^2. \tag{7}$$

Here g_{nl} is the statistical weight of the initial state; $l_{\max}$ is the larger of l, l'; $Q_{nln'l'}$ is a constant summed over the different states of the initial and final levels.

Summing expression (7) with the aid of the expanded Schrödinger equation for the radial part of the valence-electron wave function, and also using the expansion $(r + \chi) f_{nl} = \sum_{n'} c_{n'} f_{n'l'}$, and all the other transformations usually used in deriving the theorem on the sum of oscillator strengths, we arrive at the expressions:

$$\sum_{n'} f_{nl}^{n'l+1} = \frac{(2l+3)(l+1)}{3(2l+1)} \left[1 + \left(2\frac{\alpha}{r_0^3} + \frac{\alpha^2}{r_0^6}\right) \int_0^{r_0} [f_{nl}(r)]^2\, dr - \frac{4\alpha l}{2l+3} \int_{r_0}^\infty [f_{nl}(r)]^2 \frac{dr}{r^3} + 2\alpha^2 \frac{l+3}{2l+3} \int_{r_0}^\infty [f_{nl}(r)$$

$$\sum_{n'} f_{nl}^{n'l-1} = \frac{(1-2l)l}{3(2l+1)} \left[1 + \left(2\frac{\alpha}{r_0^3} + \frac{\alpha^2}{r_0^6}\right) \int_0^{r_0} [f_{nl}(r)]^2\, dr + 4\alpha \frac{l+1}{2l-1} \int_{r_0}^\infty [f_{nl}(r)] \frac{dr}{r^3} - 2\alpha^2 \frac{2-l}{2l-1} \int_{r_0}^\infty [f_{nl}(r)]^2 \frac{\alpha}{r} \tag{8}$$

where g' denotes the exchange correction with allowance for the additional perturbation.

For the principal series of alkali metals and atoms similar to them, $l = 0$, and

$$\sum_{n'} f_{n0}^{n'1} = 1 + \left(2\frac{\alpha}{r_0^3} + \frac{\alpha^2}{r_0^6}\right) \int_0^{r_0} [f_{nl}(r)]^2 dr + 2\alpha^2 \int_{r_0}^\infty [f_{nl}(r)]^2 \frac{dr}{r^6} + g', \tag{9}$$

whence, for the sum of oscillator strengths of only the experimentally observed transitions, we obtain

$$\sum_{n'}{}' f_{n0}^{n'1} = 1 + \left(2\frac{\alpha}{r_0^3} + \frac{\alpha^2}{r_0^6}\right)\int_0^{r_0}[f_{nl}(r)]^2 dr + 2\alpha^2\int_{r_0}^{\infty}[f_{nl}(r)]^2\frac{dr}{r^6} - \sum_{n_i<n} f_{n0}^{n_i 1} + g'. \tag{10}$$

Calculations by formula (10) for Na, K, Ca^+, using tabulated wave functions for the optical and inner electrons from works ([6–9]), are given in Table 1. For comparison, the results of calculations by formula (1) and the experimental data (where available) are also given there. The polarizability of the corresponding ion was taken as α. The radius of the core r_0 was chosen as the mean value of the radius of the outermost of the inner orbits. The exchange correction, which for systems of the type considered is very small ([1]), was not taken into account for K and Ca^+, while for Na it was taken without allowance for additional perturbation (according to the data of work ([1])).

Table 1

Atom	$\sum_{n'} f_{n0}^{n'1}$, by formula (1)	$\sum_{n'} f_{n0}^{n'1}$, by formula (10)	$\sum_{n'} f_{n0}^{n'1}$, experiment
Na	1.031	1.248	1.26
K	1.135	1.269	–
Ca^+	1.187	1.453	–
Cs	–	–	1.21

From Table 1 it is seen that the discrepancy between the results of the present work and experiment for Na is less than 1%. This can serve as confirmation of our proposition that, for forced transitions in alkali metals and atoms similar to them, the atomic characteristic "oscillator strength" is the expression (7).

In conclusion I take the opportunity to express my deep gratitude to Yu. E. Perlin for his constant interest in the work and valuable discussions.

Beltsy State Pedagogical Institute

Received
29 XII 1955

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Note: Figure translations are in progress. See original paper for figures.