EXCITATION OF ALKALI METAL ATOMS

L. VAĬNSHTEĬN, V. OPYKHTIN, and L. PRESNYAKOV

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

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A previously developed model[3] is extended to the case of excitation of an arbitrary atom. Excitation of the alkali metals by electron impact is studied on the basis of this model and by the close coupling method. For nonresonance levels excitation at the threshold proceeds mainly via an intermediate level. The excitation cross section is explained satisfactorily by the model for $E > 3\Delta E$, and for all values of E in the case of a resonance level.

1. INTRODUCTION

In several recently published calculations of cross sections for inelastic collisions between electrons and atoms attempts to refine the Born approximation within the framework of conventional perturbation theory with a separation of variables were not successful. There is an increased discrepancy between the calculated and experimental cross sections when distortions of the incoming and scattered waves are taken into account. Also, an exact solution of the system of equations for several levels, as in [1,2], improves the agreement with experiment to such a small degree that little success can be expected in this direction.

In our opinion failure has resulted from the fact that the initial approximation takes into account the attraction between the incident electron and the atom, which is not important in the process under consideration. The distance between the optical and external (free) electrons is actually the principal factor in the inelastic scattering, and due to the polarization of the atom this distance remains practically unreduced when the external electron is attracted by the nucleus.

On the basis of earlier considerations[3] a model was proposed for use in calculating the cross sections for inelastic collisions, where the repulsion between the external and optical electrons is most prominent. A wave function with unseparated variables was used for the system. Cross sections for the excitation[3] and ionization[4] of the ground-state hydrogen atom calculated in this manner were found to be in very good agreement with experiment.

In calculating the excitation of alkali metal atoms the relatively small separations of levels must be kept in mind. Here close coupling begins to play an important part, since it can ensure the correct normalization of the cross sections and allows the inclusion of transitions via intermediate levels. Therefore the Born approximation with close coupling (but neglecting distortions) can be used to analyze the excitation processes of alkali metals. It should be emphasized, however, that this method, while indicating qualitative effects directly, does not necessarily lead to quantitatively correct results.

In the present work we have applied the model of [3] and the Born approximation with close coupling to the calculation of the excitation of alkali metal atoms. An electronic computer was used for all calculations. The radial functions of the optical electron were determined semi-empirically taking account of exchange;[5] these are similar to the Hartree-Fock functions.

2. APPLICATION OF THE MODEL TO A COMPLEX ATOM

The entire discussion in [3] pertains to the hydrogen atom, with the complete wave function of the system represented by

$$\Psi = \varphi(\mathbf{r}_1) g(\mathbf{r}_1, \mathbf{r}_2), \tag{1}$$

where φ is the unperturbed wave function of the atomic electron, and $g(\mathbf{r}_1, \mathbf{r}_2)$ describes the mutual scattering of the optical and external electrons and of their center of mass on the nucleus. It was found useful to introduce the effective velocity-dependent charge ζ. The function g satisfies the equation

$$\left[\frac{1}{2}\Delta_R + \frac{1}{2}\Delta_\rho + \frac{\zeta}{R} - \frac{\zeta}{\rho} + k_0^2\right] g = 0, \tag{2}$$

$$\zeta = k_0/(k_0+|\varepsilon_0|^{1/2}),\ \rho = \frac{1}{2}(\mathbf{r}_2-\mathbf{r}_1),\ \mathbf{R} = \frac{1}{2}(\mathbf{r}_2+\mathbf{r}_1), \quad (3)$$

where ϵ_0 is the energy of the atomic electron and k_0 is the momentum of the incident electron. Atomic units and Rydberg energy units are used here and in what follows.

The aforesaid method can be applied directly to an arbitrary atom described by the single-electron approximation, whereby it is assumed that the optical electron moves in the field of the atom core, which is not changed when the optical electron undergoes transitions. As previously, g is represented by (2); however, in the term ζ/R we would have to take into account the incomplete screening of the nucleus by the core. Therefore $\zeta = \zeta(R)$ and its form in (3) is approached only for $R \to \infty$. However, in order to retain a simple analytic form of g we shall hereinafter assume for all R that

$$\zeta = \text{const} = k_0(k_0+|\varepsilon_0|^{1/2})^{-1}.$$

Taking the foregoing into account, all results in [3] are applied directly to alkali metal atoms. The case of more complex atoms becomes somewhat more involved because the addition of angular momenta and spins must be taken into account. It is found that the method used in [3] to calculate the exchange part of the transition integral requires separate handling of the spatial and spin parts of the matrix element. Therefore a general formula of the cross section for the transition

$$\gamma_0(L_pS_p)n_0l_0L_0S_0 - \gamma_0(L_pS_p)n_1l_1L_1S_1$$

can be given only if the radial, angular, and spin factors are separated explicitly. Omitting the fairly laborious calculations, we present the result:

$$\sigma = \frac{8\pi a_0^2}{k_0^2}\sum_\lambda c_\lambda \int_{k_0-k_1}^{k_0+k_1}\frac{dq}{q^3}\left|\int_0^\infty P_0(r)P_1(r)j_\lambda(qr)\,dr\right|^2\Phi(q), \quad (4)$$

$$\Phi(q) = \delta_{S_0S_1}\left[f^2(\nu, X) - \frac{q^2}{k_0^2}f(\nu, X)f\left(\nu, \frac{1}{4}\right)\right] + \frac{2S_1+1}{2(2S_p+1)}\frac{q^4}{k_0^4}f^2\left(\nu, \frac{1}{4}\right) \quad (5)$$

$$f(\nu, z) = \frac{\pi\nu}{\sinh\pi\nu}F(-i\nu, i\nu, 1, z),$$

$$X = \left[\frac{\Delta\varepsilon+q^2}{\Delta\varepsilon+3q^2}\right]^2,\quad \nu = (k_0+|\varepsilon_0|^{1/2})^{-1}, \quad (6)$$

$$c_\lambda = (2L_1+1)\begin{Bmatrix}\lambda & l_1 & l_0\\ L_p & L_0 & L_1\end{Bmatrix}^2(2\lambda+1)(2l_0+1)(2l_1+1) \times \begin{pmatrix}\lambda & l_0 & l_1\\ 0 & 0 & 0\end{pmatrix}^2. \quad (7)$$

Here $\Delta\epsilon = \epsilon_1 - \epsilon_0 = k_0^2 - k_1^2$ is the excitation energy, P_0 and P_1 are the radial functions of the optical electron, F is a hypergeometric function, and j_λ is a spherical Bessel function. Equation (4) was derived on the basis of the same assumptions as in [3], together with the orthogonality of all one-electron atomic functions of the initial and final states. With $\Phi(q) = 1$, Eq. (4) becomes a Born approximation. With f = 1, Eqs. (4) and (5) extend Ochkur's formulas [6] to a complex atom.

The foregoing formulas were used to calculate the cross sections for a large number of transitions in alkali metals. The accompanying table gives the cross sections for resonance levels calculated in the Born approximation and with our model; x_1 is the momentum of a scattered electron in threshold units:

$$x_1 = k_1/k_{\text{thr}} = [(k_0^2-\Delta\varepsilon)/\Delta\varepsilon]^{1/2}. \quad (8)$$

The cross sections for the excitation of the 5p resonance level and of the next term 6p involved in the principal series of Rb are shown in the figure.

3. EFFECT OF CLOSE COUPLING

The close coupling of open scattering channels [1] plays an important role in the excitation of alkali metal atoms. An expansion in partial waves is needed to take account of close coupling. We have excluded distortion and exchange [2] for the reasons discussed in the Introduction. The cross section for excitation from the ground state is

$$\sigma = \sum_{\tilde{l}_0\tilde{l}_1}\sigma_{\Gamma_0\Gamma_1} = \frac{\pi a_0^2}{k_0^2}\sum_{\tilde{l}_0\tilde{l}_1}(2\tilde{l}_0+1)|T_{\Gamma_0\Gamma_1}|^2, \quad (9)$$

where $\Gamma = nlk\tilde{l}$ is the set of quantum numbers of the atomic and external electrons. The matrix $T_{\Gamma_0\Gamma_1}$ depends on the asymptotic behavior of the radial functions $\mathcal{F}_\Gamma(r)$ satisfying the equations [8]

$$\left[\frac{d}{dr^2} - \frac{\tilde{l}(\tilde{l}+1)}{r^2} + k^2\right]\mathcal{F}_\Gamma = \sum_{n'l'\tilde{l}'}u_{\Gamma\Gamma'}\mathcal{F}_{\Gamma'}, \quad (10)$$

$$\mathcal{F}_\Gamma(0) = 0,\quad \mathcal{F}_\Gamma \sim \frac{1}{k}\left[\sin\left(kr - \frac{\tilde{l}\pi}{2}\right)\delta_{\Gamma_0\Gamma} + T_{\Gamma_0\Gamma}\exp\left(ikr - i\frac{\tilde{l}\pi}{2}\right)\right],\quad r\to\infty. \quad (11)$$

[1] In the case of hydrogen the close coupling of open channels is unimportant; the principal correction of the cross section results from coupling with closed channels.

[2] In the case of very close coupling the omission of the diagonal potentials is not so obviously justified. However, we shall be interested mainly in the qualitative properties of the cross sections, which depend entirely on the nondiagonal potentials.

Cross sections for resonance transitions (in units of πa_0^2)

x_1	Li, $2s-2p$		Na, $3s-3p$		K, $4s-4p$		Rb, $5s-5p$		Cs, $6s_{1/2}-6p_{1/2}$		Cs, $6s_{1/2}-6p_{3/2}$	
	Born approx.	Model of [3]	Born approx.	Model of [3]	Born approx.	Model of [3]	Born approx.	Model of [3]	Born approx.	Model of [3]	Born approx.	Model of [3]
0.2	55.6	7.1	43.0	5.57	67.9	6.28	76.8	6.51	35.3	2.48	6.07	4.46
0.4	97.1	13.7	75.6	10.7	121	12.3	138	12.8	63.1	4.94	110	8.83
0.6	120	19.3	96.7	15.4	155	18.4	176	19.3	80,5	7.51	141	13,6
0.8	127	23.9	10.5	19.8	171	24.8	194	26.3	88.6	10.4	157	19.0
1.2	119	30.8	102	27.7	169	37.7	192	40.7	87.5	16.4	157	30.7
1.6	101	34.9	89.2	32.7	149	47.1	170	51.5	77.1	21.2	140	39.7
2,0	83.7	36.2	75.4	34.6	126	51.6	145	57.0	65.5	23.9	120	45.3
2.8	58.2	33.7	53.6	32.6	90.8	51.0	104	56.0	47.0	24.4	86.2	45.8
3.6	42.3	29.0	39.4	28.1	67.1	45.1	76.6	50.7	34.6	22.0	63.9	41.3
4.4	32,0	24,3	30.1	23.6	51.4	38.6	58.7	43.6	26.5	19.1	49.3	35.7
5.2	25.1	20,4	23.7	19.8	40.6	32.7	46.4	37.1	21.0	16.3	38.8	30.6

We shall use the following notation: n_0s for the ground state, n_0p for the resonance level, and nl for other levels. In the case of transitions from the ground state the existence of close coupling leads to the following two effects.

A very high probability exists that a resonance level will be excited (the $n_0s - n_0p$ transition). In the Born approximation the probability becomes greater than unity (the partial cross sections exceed the theoretical limit). This result is obviated by close coupling; the hermiticity of the system (10) makes the matrix $\mathbf{S} = \mathbf{T} + \mathbf{I}$ unitary for all the considered channels. The cross section for the $n_0s - n_0p$ transition then becomes considerably smaller than the Born approximation result. At the same time the cross sections for other levels, although only weakly coupled to the ground state, decrease (by about the same factor). This decrease can be called a normalization effect. In order to arrive at the normalization effect for the $n_0s - np$ transition, we must in (10) retain three equations for

$$\Gamma_0 = n_0 s k_0 l_0, \quad \Gamma_1 = nlk_1 l_1, \quad \Gamma_2 = n_0 p k_2 l_2$$

and set $u_{\Gamma_1\Gamma_2} = 0$. (The equations suffice for a resonance transition.)

In order to excite nl levels, in addition to the normalization effect transitions via an intermediate level n_0p[3)] with $u_{\Gamma_1\Gamma_2} \neq 0$ can be important. Since the $n_0s - n_0p$ and $n_0p - nl$ transitions are much more highly probable than the $n_0s - nl$ transition, as a rule, the cross section for excitation via the intermediate level can be considerably larger than the cross section for direct excitation.

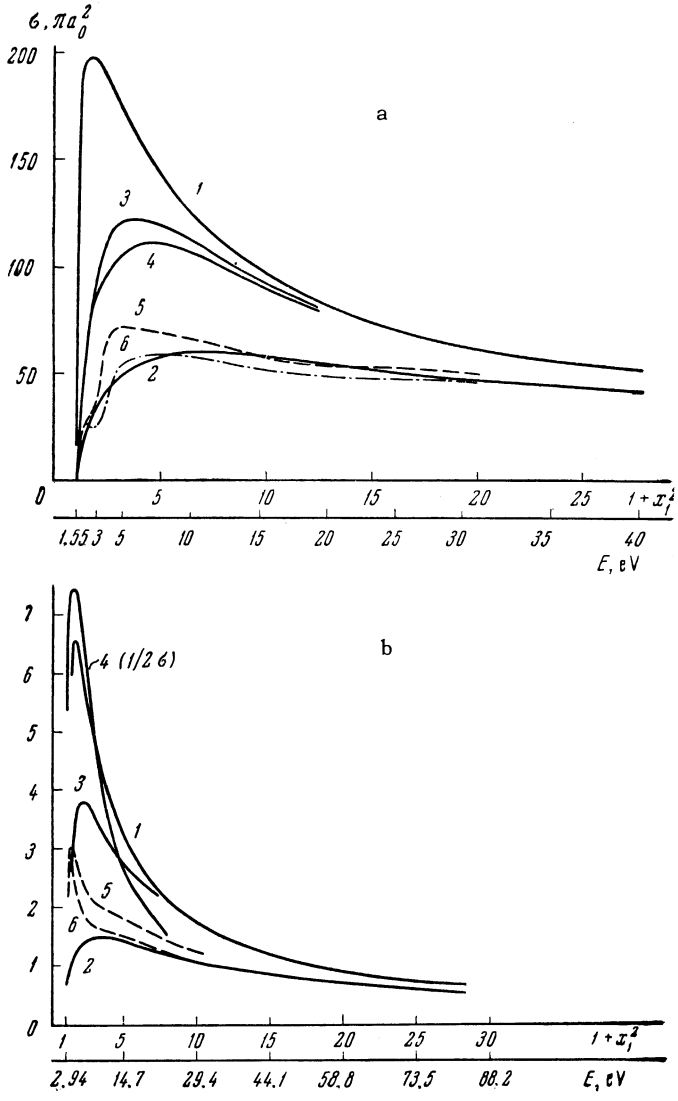
Numerical calculations confirm the existence of both the aforesaid effects. As an illustration, the accompanying figure shows the cross sections for the excitations of the 5p and 6p levels in Rb, calculated with 5s-5p-6p close coupling both with and without 5p-6p coupling. The normalization effect is seen to reduce both cross sections to about one-half in the vicinity of the maximum. The inclusion of 5p-6p coupling increases sharply the cross section for 6p excitation; the peak becomes very sharp and is reached near the threshold. The cross section for the 5s-5p transition exhibits relatively little variation, but a break in the excitation function appears at the threshold of the 6p channel.

Similar results are obtained for other levels and other alkali metals. The same should apply to ionization, but no specific calculations have been performed.

4. DISCUSSION OF RESULTS

In the two foregoing methods of calculating the effective cross sections different aspects of the phenomena are emphasized. It can be stated in the terminology of perturbation theory that in our model (Sec. 2) we consider the polarization of an atom by an external electron as involving all virtual levels without distinguishing any particular single level. On the other hand, the close coupling method takes into account one or more open channels, but neglects the polarization interaction of electrons. The latter effect is associated mainly with closed channels and greatly reduces the cross sections. Therefore the model must be supplemented by a qualitative close coupling effect, by transitions via an intermediate level. So long as such a combined procedure is unavailable, we can predict only qualitatively the difference between the excitation functions of the resonance and other levels in alkali metals, such as were recently observed experimentally in [7]. There the cross sections for the excitation of all levels except a resonance level exhibit a sharp peak and diminish by a factor of 2 to 3 at energies up to 30 eV. At the same time the cross sections for resonance transi-

[3)]This process could be called "Raman excitation" by analogy with the Raman scattering of light.



Cross sections for Rb transitions (a) 5s – 5p and (b) 5s – 6p. (1) Born approximation; (2) model of [3]; 5s-5p-6p close coupling with $u_{\Gamma_1\Gamma_2} = 0$; (4) 5s-5p-6p close coupling with $u_{\Gamma_1\Gamma_2} \neq 0$; (5) experimental results in [7]; (6) experimental results [7] after subtraction of cascade transitions.

tions exhibit flatter maxima and decrease by only 20% in the same energy region. This behavior has been observed qualitatively in [9-11]. As a single exception, in [12] the cross section for the resonance transition in the K atom decreases somewhat more rapidly.

We at present have no absolute measurements of the cross sections, so that only the energy dependence of the excitation functions can be compared with the theory. In addition, cascade transitions must be considered, even if only approximately. We adopt the following procedure. The experimental cross section at the maximum energy 30 eV is equated to the sum of cross sections for the direct and cascade excitations calculated using the discussed model. The figure shows that at this energy transitions via an intermediate level play only a small part. The figure also includes experimental curves 5 normalized in this manner.

The curves 6 were obtained by subtracting cross sections for cascade excitation. The figure shows that the experimental maximum of σ (for the 5s-6p) transition is about twice as large as the value calculated from the model. Assuming the same for the other nonresonance transitions, in the process of subtracting we multiplied the cross sections for cascade transitions when $E < 30$ eV by a factor increasing from 1 to 2 at the threshold. In both instances the cascade transitions played a relatively small part. The excitation function obtained for the 5s-5p resonance transition agrees well with the model. The cross section for the 5s-6p transition at the threshold differs greatly from the model, as was to be expected, but for $E > 3\Delta E$ there is good agreement. Although the foregoing method of treating experimental data is somewhat arbitrary, it can hardly lead to serious errors. It appears that any more reliable procedure would require absolute measurements of the cross sections for a large number of lines.

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