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# *EFFECTIVE CROSS SECTIONS FOR THE EXCHANGE EXCITATION OF ATOMS AND IONS BY ELECTRON IMPACT*

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A method is proposed for the calculation of the cross sections for excitation of intercombinational transitions, based on the use of orthogonalized wave functions of the outer electron. It is shown that, in contrast to the Born-Oppenheimer method, the present method is equivalent to a first-order perturbation theory. The excitation cross sections are given for the transitions H(1s → 2s), He(1s$^1$S → 2p$^3$P), C$^{2+}$(2s$^1$S → 2p$^3$P), He(1s$^1$S → 2s$^3$S), He(2s$^3$S → 2s$^1$S), Li$^+$(1s$^1$S → 2s$^3$S), C$^{4+}$(1s$^1$S → 2s$^3$S).

THE solution of many problems in the gas-discharge plasma physics and in astrophysics requires information on the effective cross sections for the excitation, by electron impact, of intercombinational transitions in atoms and ions. As is known, for transitions between levels of the same multiplicity, the Born method gives fairly good results even at low energies. However, when exchange effects are included within the framework of the Born-Oppenheimer (B.O.) method, the results become quite unsatisfactory. Nevertheless, the excitation of intercombinational transitions is possible (within the framework of LS coupling) only because of exchange effects. Results considerably better than those given by the B.O. method are sometimes obtained for neutral atoms by a modification proposed by Ochkur:[1] the amplitude of the exchange scattering is expanded in a series of powers of 1/k and only the first nonvanishing term is retained in this expansion. Subsequent generalization of the Ochkur method to the case of ions meets with considerable difficulties because it leads to the total exclusion of the effects of the long-range Coulomb field. An attempt to "normalize" the cross section, for example, by the R-matrix method,[2] also gives rise to difficulties.

As is known, an important limitation of the B.O. method is the use of nonorthogonal wave functions in the initial and final states. We can easily show that, as a consequence, the B.O. method does not represent the first order of the standard perturbation theory. We shall consider a method for calculating the intercombinational transition cross sections, based on the use of orthogonalized wave functions.

For simplicity, we shall first consider the scattering of electrons by hydrogen atoms; all the results can be generalized easily to any other atoms and ions. Since intercombinational transitions are the main interest, we shall consider only the exchange component of the scattering amplitude.

In the B.O. method, the exchange component of the inelastic scattering amplitude is governed by the matrix element (atomic units are used):

$$\langle \Phi_1(\mathbf{r}_2, \mathbf{r}_1) | V | \Phi_0(\mathbf{r}_1, \mathbf{r}_2) \rangle, \tag{1}$$

$$\Phi_i(\mathbf{r}_\alpha, \mathbf{r}_\beta) = \varphi_i(\mathbf{r}_\alpha) F_i(\mathbf{r}_\beta), \qquad V = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{r_2}, \tag{2}$$

where $\varphi_i$ are the atomic wave functions and $F = \exp(i\mathbf{k}\cdot\mathbf{r})$ (For an ion, F is the Coulomb function). The indices 0 and 1 represent the initial and final states. Obviously, the functions $\Phi_0(\mathbf{r}_1, \mathbf{r}_2)$ and $\Phi_1(\mathbf{r}_2, \mathbf{r}_1)$, defined by Eq. (2), are not orthogonal. Therefore, we shall replace them with new functions, in which the wave functions of the outer electron are orthogonalized by the atomic wave functions:

$$G_0 = F_0 - \langle F_0 | \varphi_1 \rangle \varphi_1, \quad G_1 = F_1 - \langle F_1 | \varphi_0 \rangle \varphi_0, \tag{3a}$$

$$\Phi_i(\mathbf{r}_\alpha, \mathbf{r}_\beta) = \varphi_i(\mathbf{r}_\alpha) G_i(\mathbf{r}_\beta). \tag{3b}$$

In general, it is sufficient to orthogonalize only the function F in order to make $\Phi_0(\mathbf{r}_1, \mathbf{r}_2)$ and $\Phi_1(\mathbf{r}_2, \mathbf{r}_1)$ orthogonal. However, we can show that if both functions are orthogonalized, then an expression of the type of Eq. (1) is a first-order perturbation theory with an unperturbed Hamiltonian additive with respect to the variables $\mathbf{r}_1$ and $\mathbf{r}_2$. We shall consider this in detail.

Let H be the total Hamiltonian of a system consisting of an atom and an outer electron and $H_0$ be the unperturbed Hamiltonian. We shall write $H_0$ in the form

$$H_0 = H_1 + H_2; \quad H_i = -{}^1\!/_2\nabla_i^2 - 1/r_i + v_i. \tag{4}$$

Then in the first-order perturbation theory, the exchange interaction amplitude is given by Eq. (1), where $\Phi_0$ and $\Phi_1$ are the eigenfunctions of the operator $H_0$ and

$$V = H - H_0 = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - v_1 - v_2. \tag{5}$$

In the B.O. method it is necessary to assume that $v_1 = 0$, $v_2 = 1/r_2$. However, then $\Phi_1$ cannot be an eigenfunction of $H_0$ because the operator $H_2$ does not have bound states. The use of the function $\Phi_1$, defined in Eq. (2), represents a summation of some (obviously not very successful) sub-series in the perturbation theory series.

We can also use the so-called "symmetrical" method, in which $v_1 = v_2 = 0$, i.e., $\Phi_0$, $\Phi_1$ are the eigenfunctions of the same Hamiltonian, and, consequently, Eq. (1) represents the first-order perturbation theory. The shortcoming of this method is the Coulomb distortion of the wave functions of a free electron for large values of r, which yields a non-zero cross section at the excitation threshold. For ions of high multiplicity this disadvantage is of little importance.

The functions $\Phi$, defined in Eq. (3b), are also functions of the same Hamiltonian but, in contrast to the "symmetrical" method, the functions $G_0$ and $G_1$ have the correct asymptote (a plane wave for a neutral atom).

The existence of the Hermitian operators $H_1(\mathbf{r}_1)$ and $H_2(\mathbf{r}_2)$ with the eigenfunctions $\varphi_0(\mathbf{r}_0)$, $G_1(\mathbf{r}_1)$ are $\varphi_1(\mathbf{r}_2)$, $G_0(\mathbf{r}_2)$, respectively, is ensured by the orthogonality conditions $\langle G_0 | \varphi_1\rangle = \langle G_1 | \varphi_0 \rangle = 0$. We can easily see that the potentials $v_1$ and $v_2$ are then nonlocal. This, however, is not important because, in view of the orthogonality of the one-electron functions, the operators $v_i$ do not make a direct contribution to the matrix element of the transition, i.e., instead of Eq. (1) we have

$$\left\langle \varphi_1(\mathbf{r}_2) G_1(\mathbf{r}_1) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \varphi_0(\mathbf{r}_1) G_0(\mathbf{r}_2) \right\rangle. \tag{6}$$

Obviously the functions (3a) correspond to the simplest possible variant of the perturbation theory. The functions $G_0$ and $G_1$ are nonorthogonal and, consequently, they cannot be the eigenfunctions of one Hermitian Hamiltonian ($H_1$ or $H_2$). Therefore, using functions (3a), it is not possible to find an unperturbed Hamiltonian of the type given by Eq. (4) for direct scattering. Since the main interest lies in intercombinational transitions, we shall not consider this problem in detail. We shall mention only that, in principle, this shortcoming may be overcome by a suitable selection of nonlocal operators $v_1$ and $v_2$.

The proposed method can be applied without difficulty to any atom or ion [in the case of ions F represents the Coulomb wave functions in Eq. (3a)]. The amplitude of the "exchange" scattering is given by the same formula (6),[1] if the angular momentum of the atomic core is equal to zero. In the case of an atomic core with arbitrary orbital angular momentum $L_p$, and spin $S_p$, it is possible to obtain the exchange scattering amplitude in a closed form only by separation of the radial and angular variables. Let us assume that an atom is described by the quantum numbers $\gamma$, $L_p$, $S_p$, n, $l$, L, S ($\gamma$, $L_p$, $S_p$ are the quantum numbers of the atomic core) and let the outer electron have an angular momentum k and a spin $\lambda$. The initial and final states are distinguished by the indices 0 and 1. We shall assume that the one-electron atomic functions are orthonormalized. For intercombinational transitions ($S_0 \neq S_1$) only the exchange scattering amplitude is not equal to zero and the total cross section for the 0—1 transition is

$$\sigma = \sum_{\lambda_0\lambda_1} \sigma_{\lambda_0\lambda_1}, \tag{7}$$

$$\sigma_{\lambda_0\lambda_1} = \frac{2\pi^3 k_1}{k_0^3}\,\frac{(2S_1+1)(2L_1+1)}{(2S_p+1)(2L_p+1)} \sum_{L_T} \left| \sum_{\varkappa} a_\varkappa C_{\varkappa L_T} y_\varkappa \right|^2, \tag{8}$$

$$a_\varkappa = \left[\frac{(2\lambda_0+1)(2\lambda_1+1)}{(2\varkappa+1)}\right]^{1/2} \begin{pmatrix} l_0 & \varkappa & \lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda_0 & \varkappa & l_1 \\ 0 & 0 & 0 \end{pmatrix};$$

$$C_{\varkappa L_T} = [(2\varkappa+1)(2L_T+1)(2L_p+1) \times (2l_0+1)(2l_1+1)]^{1/2} \begin{Bmatrix} \lambda_0 & l_1 & \varkappa \\ L_0 & L_p & l_0 \\ L_T & L_1 & \lambda_1 \end{Bmatrix}, \tag{9}$$

$$y_\varkappa = \int_0^\infty \int_0^\infty R_{n_0 l_0}(r_1) g_{k_0\lambda_0}(r_2) \frac{r_<^\varkappa}{r_>^{\varkappa+1}} R_{n_1 l_1}(r_2) g_{k_1\lambda_1}(r_1)\, dr_1 dr_2,$$

where the quantities in parentheses and in braces represent the well-known 3j and 9j symbols.

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[1] We note that the expression (6) is symmetrical with respect to the initial and final states and, therefore, in the present case, we do not have the well-known post–prior indeterminacy which is characteristic of the B.O. method when approximate atomic wave functions are used.

Here $R_{nl}/r$ and $g_{kl}/r$ are the radial components of the wave functions of the optical and outer electrons; according to Eq. (3a),

$$\begin{aligned} g_{k_0\lambda_0} &= f_{k_0\lambda_0} - \langle f_{k_0\lambda_0} | R_{n_1l_1}\rangle R_{n_1l_1}\delta_{l_1\lambda_0},\ g_{k_1\lambda_1} \\ &= f_{k_1\lambda_1} - \langle f_{k_1\lambda_1} | R_{n_0l_0}\rangle R_{n_0l_0}\delta_{l_0\lambda_1}, \end{aligned} \tag{10}$$

where $f_{k\lambda}/r$ is the normalized, to $\delta(k - k')$, radial component of a plane wave or a Coulomb function.

If one of the angular momenta $L_p$, $l_0$, $l_1$ is equal to zero or if we are interested in a cross section which represents the sum over $L_0$ or $L_1$, the summation over $L_T$ can be made explicitly. We can easily show that in this case the result remains correct if we make the substitution

$$\sum_{L_T} \Big| \sum_{\varkappa} a_\varkappa C_{\varkappa L_T} y_\varkappa \Big|^2 \to \sum_{\varkappa} |a_\varkappa y_\varkappa|^2. \tag{11}$$

Figure 1 shows the results of calculations carried out using various methods and the experimental data for the cross section of the 1s → 2s transition in the H atom. This example is given purely for illustration, since a direct transition is possible and the role of the exchange is relatively small.

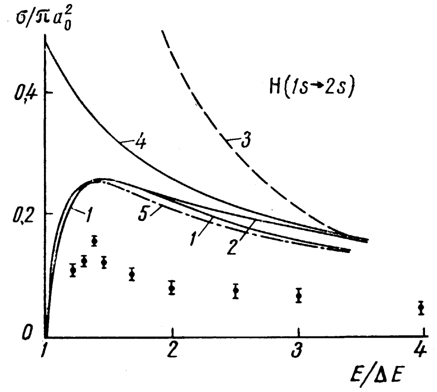

FIG. 1. Cross sections for the excitation of the 1s → 2s transition in the H atom: 1) orthogonalized function method; 2) Born method; 3) Born–Oppenheimer approximation; 4) "symmetrical" method; 5) Ochkur method; ●—experimental values. [3]

The method proposed in the present paper can be applied to neutral atoms and to ions. Since it is based on a first-order perturbation theory, its accuracy increases with increase of the ion charge.[2)] Unfortunately, there are no experimental data on the excitation of intercombinational transitions in ions by electron impact. Reliable experimental data for intercombinational transitions in neutral atoms (with allowance for possible cascades, re-absorption, etc.) are available only for the He atom.[4,5]

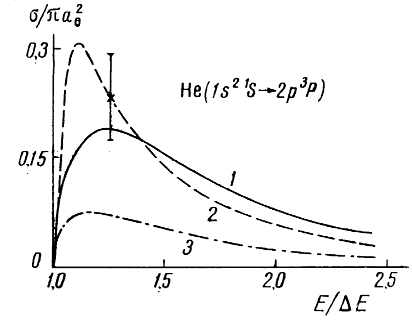

FIG. 2. Cross sections for the excitation of the transition $1s^2\ {}^1S \to 1s2p\ {}^3P$ in the He atom: 1) orthogonalized function method; 2) Born–Oppenheimer method; 3) Ochkur method; ×—experimental values. [4]

Figure 2 shows the exictation functions for the intercombinational transition $1s\,{}^1S \to 2p\,{}^3P$ in the He atom. Semi-empirical atomic wave functions were used in the calculations.[3)] Figure 2 gives also the value of the maximum cross section according to Zapesochnyĭ's measurements.[4] However, the excitation function obtained in [4] decreases more slowly than do the functions given in Fig. 2. It is difficult to understand such a slow decrease on the basis of the existing theories. A value of $0.29 \times 10^{-2}\pi a_0^2$, obtained by extrapolation of the data for transitions to higher levels, has been reported in [5] for the E = 108 eV cross section. The method given in the present paper, the Ochkur method, and the B. O. method give for this energy the values of 0.44, 0.16, and $0.3 \times 10^{-2}\pi a_0^2$, respectively; the experimental value is [4] $0.1\pi a_0^2$.

The cross section for the excitation of the metastable level $2s\,{}^3S$ has been measured only over a very narrow range of energies (≈1–2 eV) [6] and it is pointless to compare these

**Table I**

| | Theory | | Experiment | |
|---|---|---|---|---|
| | o.f. | Och.[1] | [4] | [5] |
| $2\,{}^3P$ | $180^0$ | $740^{-1}$ | $260^0$ | — |
| $3\,{}^3P$ | $610^{-1}$ | $171^{-1}$ | $120^{-1}$ | $110^{-1}$ |
| $4\,{}^3P$ | $261^{-1}$ | $660^{-2}$ | $455^{-3}$ | — |
| $5\,{}^3P$ | $164^{-1}$ | $372^{-2}$ | $680^{-4}$ | — |

Note. Cross sections are given in units of $\pi a_0^2$. The order and the mantissa of a number are given; for example, $180^0$ represents $0.180 \times 10^0$.

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[2)] The Coulomb potential is proportional to Z, the perturbation $1/|r_1 - r_2|$ is independent of Z, and $v_i \sim (Z + 1)/Z$.

[3)] The results obtained by us using the Ochkur method differ slightly (≈20%) from those given in [1] because of a difference in the atomic wave functions employed.

Table II

| $E/\Delta E$ | He ($2s\,^3S \to 2s\,^1S$) | | | | | He ($1s\,^1S \to 2s\,^3S$) | | | Li$^+$ ($1s\,^1S \to 2s\,^3S$) | | C$^{4+}$ ($1s\,^1S \to 2s\,^3S$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | o.f. | o.f. norm. | B.O. | B.O. norm. | Och. | o.f. | B.O. | Och. | o.f. | B.O. | o.f. | B.O. |
| 1.04 | $126^{+2}$* | $420^{+1}$ | $123^{+2}$ | $417^{+1}$ | $113^{+3}$ | $710^{-2}$ | $500^{0}$ | $167^{-1}$ | $280^{0}$ | $179^{+1}$ | $294^{0}$ | $248^{0}$ |
| 1.16 | $209^{+2}$ | $480^{+1}$ | $171^{+2}$ | $485^{+1}$ | $155^{+3}$ | $173^{-1}$ | $705^{0}$ | $290^{-1}$ | $220^{0}$ | $111^{+1}$ | $234^{0}$ | $191^{0}$ |
| 1.36 | $238^{+2}$ | $585^{+1}$ | $148^{+2}$ | $600^{+1}$ | $134^{+3}$ | $246^{-1}$ | $610^{0}$ | $322^{-1}$ | $153^{0}$ | $560^{0}$ | $167^{0}$ | $106^{0}$ |
| 1.64 | $228^{+2}$ | $657^{+1}$ | $111^{+2}$ | $653^{+1}$ | $920^{+2}$ | $257^{-1}$ | $400^{0}$ | $272^{-1}$ | $995^{-1}$ | 246 | 109 | $555^{-1}$ |
| 2.44 | $163^{+2}$ | $620^{+1}$ | $848^{+1}$ | $456^{+1}$ | $326^{+2}$ | $168^{-1}$ | $116^{0}$ | $129^{-1}$ | $370^{-1}$ | $430^{-1}$ | $417^{-1}$ | $174^{-1}$ |
| 3.56 | $906^{+1}$ | $455^{+1}$ | $730^{+1}$ | $400^{+1}$ | $108^{+2}$ | $803^{-2}$ | $284^{-1}$ | $507^{-2}$ | $135^{-1}$ | $900^{-2}$ | $157^{-1}$ | $720^{-2}$ |
| 5.00 | $447^{+1}$ | $287^{+1}$ | $443^{+1}$ | $286^{+1}$ | $398^{+1}$ | $346^{-2}$ | $710^{-2}$ | $200^{-2}$ | $523^{-2}$ | $264^{-2}$ | $655^{-2}$ | $335^{-2}$ |
| 14.00 | | | | | | $153^{-3}$ | $940^{-4}$ | | $236^{-3}$ | $162^{-3}$ | $308^{-3}$ | $250^{-3}$ |
| 28.00 | | | | | | $150^{-4}$ | $970^{-5}$ | | $250^{-4}$ | $236^{-4}$ | $388^{-4}$ | $350^{-4}$ |
| 47.00 | | | | | | $254^{-5}$ | $220^{-5}$ | | $550^{-5}$ | $516^{-5}$ | $810^{-5}$ | $780^{-5}$ |

*The order and mantissa of the number are given; for example, $126^{+2}$ represents $0.126 \times 10^{+2}$.

results with the first-order perturbation theory. As far as the levels lying above the $2p\,^3P$ level are concerned, we have to allow for transitions through intermediate ($2\,^3P$ or $2\,^3S$) levels in order to calculate their excitation cross sections. The role of such transitions has been considered in[7] for alkali metal atoms. This effect can be allowed for only in higher orders of the perturbation theory, and this meets with very serious computational difficulties. A similar situation obtains also in the case of "direct" transitions, for which the Born method can give seriously wrong results for levels lying above the $2p\,^1P$ level. Thus, the calculations carried out by us show that the Born cross section for the $3d\,^1D$ level is 1.5 times smaller than the experimental value, although it is known that the Born method normally gives overestimated results.

In view of this, there is little point in comparing the experimental values with the cross sections for higher levels, obtained in the first-order perturbation theory. Nevertheless we shall mention an observation, which seems very strange. Extremely small values of the excitation cross sections of the $np\,^3P$ levels have been reported in[4,8]. Table I lists the values of the maximum cross sections obtained experimentally[4,8] and calculated by the orthogonalized function (c.f. method), proposed in the present paper, and by the Ochkur method (Och.). It is not clear whether this effect can be explained by the influence of one intermediate level.

Figure 3 shows the cross sections for the transition $2\,^1S \to 2\,^3P$ in the $C^{2+}$ ion. In this case the cross section may be greater than the theoretical limit. Therefore, we normalized the partial cross sections by the R-matrix method.[2] In our case, the normalized cross section is

$$\sigma^{N}_{\lambda_0\lambda_1} = \sigma_{\lambda_0\lambda_1}\left[1+\frac{k^2\sigma_{\lambda_0\lambda_1}}{4(2\lambda_0+1)}\right]^{-2}, \qquad (12)$$

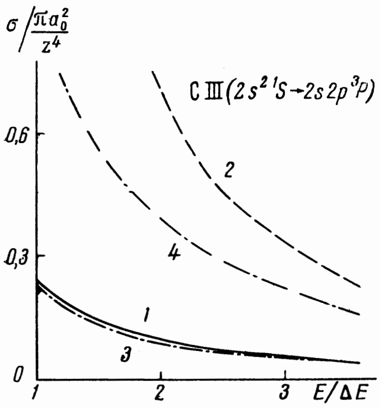

FIG. 3. Cross sections for the excitation of the transition $2s^2\,^1S \to 2s2p\,^3P$ in the $C^{2+}$ ion: 1) orthogonalized function method; 2) Born–Oppenheimer method; 3) orthonormalized function method; 4) normalized Born–Oppenheimer method.

where $\sigma_{\lambda_0\lambda_1}$ is the usual cross section obtained using Eqs. (7)—(9) or from the corresponding formulas of the B.O. method.

Table II gives the cross sections for the $2\,^3S \to 2\,^1S$ transition in the He atom. In this case the Ochkur method (Och.) gives a cross section which is even greater than the B. O. value. Table II includes also the results obtained by the o.f. method and by the B.O. method, with and without normalization. The same table includes the cross sections for the transition $1s\,^1S \to 2s\,^3S$ in the He atom and some helium-like ions. As expected, the difference between the B.O. method and the o.f. method decreases as the ion charge Z increases.

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25