# ON THE ROLE OF INTERMEDIATE STATES IN THE EXCITATION OF ATOMS BY ELECTRON IMPACT

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In a number of cases the calculation of the cross section for the excitation of atoms by electron impact in the first Born approximation leads to an error which is unusual for this approximation: the calculated cross section is smaller than the experimental one. It is shown that such a situation arises when the probability for the direct excitation is relatively small and the transition via a virtual level in second order perturbation theory plays an important role. An approximate formula for the calculation of the cross section in second order is obtained. Calculations for the quadrupole transitions in He and Ne with account of a single virtual level lead to results with an error which is "typical" for the Born method.

1. The cross sections for the excitation of atoms by electron impact are in most cases (at least in applications) calculated in the Born approximation. As is known, this approximation is rigorously proven only for large energies of the incident electron. Nevertheless, the available experimental data show that even for small energies $E \sim (2-3)\Delta E$ ($\Delta E$ is the excitation energy) the errors of the Born method are not too large: the cross section comes out 1.5 to 2 times too large in the region of the maximum. For the following it is convenient to call this error the "standard error of the Born method." For many applications this type of accuracy is completely acceptable.

Until now it has not been possible to give a more exact method for the calculation of cross sections which is applicable for a wide class of transitions and energies. The methods based on a formal mathematical extension of the theory (for example, the known strong coupling theory) are, as a rule, unsuccessful because of the extremely slow convergence of the method. One must therefore analyze the situation by starting from more perspicuous physical ideas.

The standard error of the Born method is mainly due to the repulsion of the external and atomic electrons. This repulsion leads to an increase of the mean distance between the electrons and hence to a decrease of the inelastic scattering cross section.[1)] One of the possible methods to take account of the repulsion is the model proposed in [1]. However, this model is applicable only to transitions from the ground state.

In a number of cases other effects become important, which are not included in the Born approximation. Here the error of the calculation turns out to be different from the standard error. One of the well known examples is the so-called "violation of the normalization" of the cross section when the partial cross section $\sigma(l)$ calculated in Born approximation exceeds considerably the theoretical limit set by the particle current conservation. This situation usually occurs in transitions between close levels. A fully satisfactory method of overcoming this difficulty is the "normalization" method based on the use of the R matrix.[2] The "normalization" procedure allows one to calculate the cross section for transitions between close-lying levels with an error which does not exceed the standard error of the Born method, whereas the cross section may come out too high by an order of magnitude without normalization.

In the present paper we consider another important case of the violation of the above-mentioned standard error: transitions for which the Born method yields a cross section which is small for one reason or another. Here the transition goes with great probability via an intermediate state in second order perturbation theory. For example, the cross section for the quadrupole transition 1s – 3d will in first order Born approximation be smaller than the cross section for the transition 1s – 2p – 3d in second order (with a dipole transition in each step). It is important to emphasize that we are speaking of the calculation of the leading term in the perturbation series and not of the correction of second order to the Born approximation. By physical arguments one singles out from the sum over intermediate states one or two terms. Thus in transitions from the ground state of the atom that resonance level is especially important which is excited with a probability close to unity during the time of passage of the electron.

The calculation of the corrections of second order in cases where the first-order term is dominant is,

[1)] We note in this connection the principal difference between the elastic and inelastic scattering. The polarization of the atom owing to the repulsion of the electrons leads, as is known, to an additional attraction between the electron and the atom as a whole, i.e., to an increase in the elastic scattering cross section. However, for the inelastic scattering the most important role is played not by the attraction of the electron to the center of the atom but by the effective distance between the external and atomic electrons, which increases owing to the repulsion. Thus one and the same effect influences the elastic scattering in the opposite manner.

according to the philosophy discussed above, of little promise. In this case one must sum overall intermediate states, which is connected with very great mathematical difficulties. Moreover, this sum contains terms describing at least three different effects: the attraction of the electron by the average field of the atom ($U_{00}$, $U_{11}$), the coupling of the different channels ($U_{0a}$, $U_{a1}$), and the polarization of the atom ($U_{0a}$, $U_{a1}$ for the states a which are energy-forbidden). The description of these effects requires a different accuracy of calculation and depends differently on the higher orders of perturbation theory. The situation is here still far from clear. It can only be said that a second-order correction is hardly realistic if it is close to the first-order term, as was the case in [3].

In conclusion we note a circumstance which can lead to misunderstandings in the comparison of theory and experiment. Transitions via intermediate levels lead, in the cases of interest to us, to an increase of the cross section, i.e., their effect is opposite in sign to the repulsion effect. Thus an accidental compensation may occur. Such a situation obtains in the excitation of the D levels of He: the Born approximation cross section turns out to be somewhat smaller than the experimental one. (The calculation for the 3D level was carried out in [4]; cf. also Fig. 1 for the 4D level.) However, if one takes account of the repulsion of the electrons, for example, by the method [1], then the cross section comes out considerably below the experimental value.[2)]

Below we consider the excitation of atoms via an intermediate level in the simplified version of the second Born approximation.

2. We consider the excitation of an atom by electron impact from the state 0 to the state 1. The cross section can be written in the form (we use atomic units with Rydberg units for the energy)

$$\sigma = \frac{a_0^2}{8\pi g_0 k_0^2} \int_{k_0-k_1}^{k_0+k_1} q\,dq \cdot \sum_{M_a M_1} \left| \sum_a \int d\mathbf{r} e^{i\mathbf{q}\mathbf{r}} W_{1a}(\mathbf{r}) U_{a0}(\mathbf{r}) \right|^2, \qquad (1)$$

where $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_1$; $\mathbf{k}_1$ is the wave vector of the external electron, M is the projection of the angular momentum of the atom on the z axis, and $g_0$ is the statistical weight of the initial state. The matrix elements of the potentials U and W are taken with respect to the coordinate of the atomic electrons $\mathbf{r}_j$. The matrix element $W_{1a}$ includes the nondiagonal polarization potential:[5]

$$W = 1 + W^{II} + \ldots, \quad W^{II} = \int d\mathbf{x} U(\mathbf{r}-\mathbf{x}) G_a(x) e^{i\mathbf{k}_1\mathbf{x}}, \qquad (2)$$

$$G_a(x) = -\frac{\exp\{ik_a x\}}{4\pi x}, \quad k_a^2 + E_{a0} = k_1^2 + E_{10} = k_0^2, \qquad (3)$$

where $G_a$ is the Green's function of the operator $\nabla^2$, $E_i$ is the energy of the i-th state of the atom, and $E_{ij} = E_i - E_j$; the first term in W corresponds to the Born approximation. In accordance with the task we set ourselves in Sec. 1, we retain one term in the sum over intermediate states a in (1). Moreover, we assume that $E_0 < E_a < E_1$.

Let us consider first a single-electron atom and leave out the interaction with the nucleus in U:[3)]

$$U = \frac{2}{|\mathbf{r}-\mathbf{r}_1|} \equiv \frac{2}{\rho}, \quad W^{II} = \int d\mathbf{x} \frac{2}{|\rho - \mathbf{x}|} G_a(x) e^{i\mathbf{k}_1\mathbf{x}}. \qquad (4)$$

The calculation of the second-order term $W^{II}$ is connected with serious calculational difficulties. For $k_1 \to 0$ the expression for $W^{II}$ simplifies considerably. Using the spectral representation of the Green's function $G_a$ we obtain

$$\int \frac{d\mathbf{x}}{|\rho-\mathbf{x}|} G_a(x) = -\frac{1}{8\pi^3} \int \frac{d\mathbf{x}}{|\rho-\mathbf{x}|} \int d\mathbf{k} \frac{e^{i\mathbf{k}\mathbf{x}}}{k^2 - k_a^2 - i\varepsilon} = -\frac{\exp\{ik_a\rho\} - 1}{k_a^2 \rho}.$$

Hence, for $k_1 \to 0$, $k_a^2 \to E_{1a}$

$$W^{II} = \frac{2}{E_{1a}\rho}(1 - \exp[i(E_{1a})^{1/2}\rho]), \quad k_1 \to 0. \qquad (5)$$

This formula indicates, incidentally, the region of applicability of the known adiabatic approximation, where one assumes [6]

$$G_a(x) = \frac{1}{E_a} \delta(x), \quad W^{II} = \frac{1}{E_a} U. \qquad (6)$$

If $E_{1a}$ is sufficiently large, the rapidly oscillating exponential in (5) can be neglected and (5) goes over into (6). The adiabatic approximation is widely used in the theory of elastic scattering, but in problems of inelastic scattering it has essentially not yet been employed.[4)]

For large k it is not possible to obtain an expression which is as simple as (5). It can, however, be shown, for example with the help of the quasiclassical approximation, that the operator $W^{II}$ becomes pure imaginary and decreases like $k^{-1}$.[7] The simplest extrapolation formula satisfying this condition and going over into (5) for $k_1 \to 0$ has the form

$$W^{II} = \frac{2}{k_a \rho}\left[\frac{1}{k_a}(1 - \cos\sqrt{E_{1a}}\rho) - \frac{i}{\sqrt{E_{1a}}}\sin\sqrt{E_{1a}}\rho\right]. \qquad (7)$$

The comparison of a number of examples with the results of numerical calculations showed that (7) gives good results over the whole range of energies.[7] The generalization to the many-electron atom and the inclusion of the interaction with the nucleus (the latter is necessary when the atomic wave functions are not orthogonal) is elementary:

$$U \to \sum_j \left[\frac{1}{\rho_j} - \frac{1}{r}\right],$$

$$W^{II} \to \sum_j [W^{II}(\rho_j) - W^{II}(r)]. \qquad (8)$$

For actual calculations one must separate the angular and radial parts in $U_{a0}$ and $W^{II}_{1a}$. With the use of approximation (7) this problem is not very difficult, since the expansion of expressions of the type (7) in spherical functions is well known. The final formulas for $\sigma$ are given in the Appendix.

3. In Fig. 1, the cross sections for the excitation of the levels $4^1D$ and $4^1S$ from the ground state, calculated in first Born approximation ($\sigma^I$) and in second order via the intermediate level $2^1P$ ($\sigma^{II}$) are compared with the experimental data ($\sigma_{exp}$). Unfortun-

[2)] In [4] the interaction of the levels 3P and 3D was also considered, which turned out to be small. This result is very natural, but the use of the R matrix method in this paper calls for some objections.

[3)] The factor 2 arises from the use of Rydberg units for the energy.

[4)] For elastic scattering $E_1 = E_0 < E_a$. In (6) one must replace $E_{1a}$ by $-E_{a0}$.

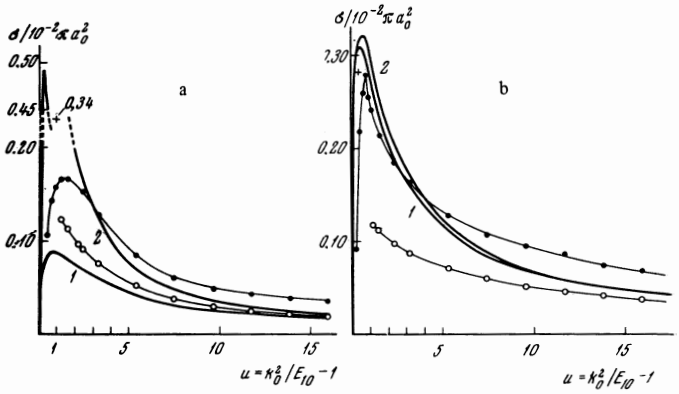


FIG. 1. Cross section for the transitions a–$1^1S$–$4^1D$ and b–$1^1S$–$4^1S$ in He. The curves were obtained 1–in first Born approximation and 2–with account of the transition via the level $2^1P$ in second order. Experimental points: ○–[8], ●–[9], and +–[10].

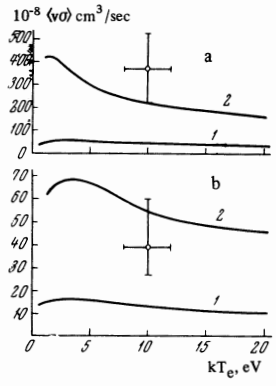


FIG. 2. Excitation rate as a function of energy; a–for the transition 5s′–5d′ and b–for the transition 5s′–6d′ in Ne. 1–first Born approximation, 2–with account of the transition via the level 5p′ in second order. The experimenta data are from [11] with the indicated errors for the measurement of ⟨vσ⟩ and $T_e$.

ately, the results of the experiments of the experiments of different authors differ considerably from each other. Nevertheless, qualitatively the situation is clear. For the excitation of the level $4^1S$ the value of $\sigma_{exp}$ is smaller than $\sigma^I$ by a factor of about $^2/_3$ (in the region of the maximum), which corresponds to the standard error of the Born method. As was to be expected, the inclusion of the second order does not here affect the result: $\sigma^{II} \approx \sigma^I$. This is connected with the fact that the probability for the transition $2^1P - 4^1S$ is small (the general rule for transitions with $\Delta L = -1$).

In the case of the excitation of the level $4^1D$ even the smallest of the $\sigma_{exp}$ is noticeably larger than $\sigma^I$ in the region of the maximum.[5)] On the other hand, the value of $\sigma^{II}$ is larger than $\sigma_{exp}$, which at least qualitatively corresponds to the standard error of the Born method. The error is rather large: in the maximum $\sigma^{II}$ exceeds $\sigma_{exp}$ by a factor of about 4 as compared with the results of [8] and by a factor of 2 to 3 as compared with [9,10]. Since the cross sections in [9,10] at large energies do not approach the Born cross section, one must apparently give preference to the results of [8]. It is not surprising that the error in the second order is larger than the standard error of the usual Born method. Here we have a cumulation of errors in the two stages of the process, as it were. However, the constancy of the sign of the error makes it possible to account for it qualitatively in applications.

In Fig. 2 we compare the results of the calculation with the experimental data of Khaĭkin [11] for transitions between excited states of Ne. Since the experiment was performed in a plasma, the excitation rates averaged over the Maxwell distribution are given. In this case $\sigma_{exp}$ exceeds $\sigma^I$ by considerably more than in the case of He. The inclusion of the transitions via the intermediate level 5p′ removes this discrepancy for the main part (within the experimental error). It is possible that other intermediate levels also give significant, although smaller contributions. To our knowledge, Khaĭkin [11] was the first to measure the cross section for transitions between excited and not even neighboring levels ($\Delta n^* > 1$, where $n^* = E$ is the effective principal quantum number). The above comparison shows that for such transitions the first Born approximation may be useless even for $u = E/\Delta E \sim 20$. At the same time the cross sections for transitions between neighboring excited levels ($\Delta n^* < 1$) are apparently well described by the Born method with a correction for the normalization already for $u \sim 5 - 10$.[12] The inclusion of an appropriately chosen intermediate level makes the error of the calculated cross section of the order of the standard error even for $\Delta n^* > 1$. However, the question of the transitions with $\Delta n \gg 1$ remains open.

## APPENDIX

For the separation of the radial and angular variables in U and W we use the known formulas:

$$\frac{1}{\rho} \equiv \frac{1}{|\mathbf{r}-\mathbf{r}_1|} = \sum_{\lambda\mu} \frac{4\pi}{2\lambda+1} \frac{r_<^\lambda}{r_>^{\lambda+1}} Y_{\lambda\mu}(\hat{r}) Y_{\lambda\mu}^*(\hat{r}_1),$$

$$\frac{\cos\alpha\rho}{\rho} = -4\pi\alpha \sum_{\lambda\mu} j_\lambda(\alpha r_<) n_\lambda(\alpha r_>) Y_{\lambda\mu}(\hat{r}) Y_{\lambda\mu}^*(\hat{r}_1),$$

$$\frac{\sin\alpha\rho}{\rho} = 4\pi\alpha \sum_{\lambda\mu} j_\lambda(\alpha r) j_\lambda(\alpha r_1) Y_{\lambda\mu}(\hat{r}) Y_{\lambda\mu}^*(\hat{r}_1),$$

where $j_\lambda$ and $n_\lambda$ are the spherical Bessel and Neumann functions, and $r_<$ and $r_>$ are the smaller and larger of the variables r and $r_1$. For the atomic wave functions we use the one-electron approximation. Below we give the formulas for the complete cross section (including all terms) for the transition between two electron configurations $l_0^N - l_0^{N-1} l_1$ with account of the first and second orders of perturbation theory with one intermediate level $l_0^{N-1} l_a$:

$$\sigma = \sum_\varkappa \frac{2N}{k_0^2} \int_{k_0-k_1}^{k_0+k_1} q\,dq \left| \int_0^\infty j_\varkappa(qr) \left[ C_{\varkappa y_{10}} y_{10}^\varkappa + \frac{1}{k_a} \sum_{\lambda\lambda'} C_{\varkappa\lambda\lambda'} \times \left( \frac{1}{k_a} y_{1a}^\lambda + \frac{\sqrt{E_{1a}}}{k_a} z_{1a}^\lambda - i v_{1a}^\lambda \right) \right] r^2\,dr \right|^2,$$

$$y_{1a}^\lambda(r) = 2 \int_0^\infty P_1(r_1) P_a(r_1) \left[ \frac{r_<^\lambda}{r_>^{\lambda+1}} - \delta_{\lambda 0} \frac{1}{r} \right] dr_1,$$

$$z_{1a}^\lambda(r) = 2(2\lambda+1) \int_0^\infty P_1(r_1) P_a(r_1) [j_\lambda(x_<) n_\lambda(x_>) - \delta_{\lambda_a} n_0(x)]\,dr_1,$$

$$v_{1a}^\lambda(r) = 2(2\lambda+1) j_\lambda(x) \int_0^\infty P_1(r_1) P_a(r_1) [j_\lambda(x_1) - \delta_{\lambda 0}]\,dr_1,$$

5)The calculation with account of the repulsion of the electrons by the method [1] yields a value of σ which is considerably smaller than $\sigma_{exp}$. In the case of the $4^1S$ this method leads to good agreement with experiment.

$$x_i = \sqrt{E_{1a}}\, r_i,$$

$$C_\varkappa = \left(\frac{2l_1+1}{2\varkappa+1}\right)^{1/2} \begin{pmatrix} \varkappa & l_0 & l_1 \\ 0 & 0 & 0 \end{pmatrix}$$

$$C_{\varkappa\lambda\lambda'} = (-1)^{l_a}(2l_a+1)\begin{pmatrix} \varkappa & \lambda & \lambda' \\ 0 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} \lambda & l_1 & l_a \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \lambda' & l_a & l_0 \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} \varkappa & \lambda & \lambda' \\ l_a & l_0 & l_1 \end{Bmatrix}.$$


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