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IONIZATION OF THE HYDROGEN ATOM BY ELECTRON IMPACT WITH ALLOWANCE FOR THE EXCHANGE

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It is shown that, in the problem considered, allowance for the exchange in the first approximation of the perturbation theory is made very simply and improves considerable the agreement between calculation and experiment. The formula obtained also makes it possible to deal with the limiting case of classical exchange scattering.

THE problem of the ionization of an atom by electron impact is basically very similar to the problem of the excitation of an atom. However, in making the calculations, it is necessary to use continuous spectrum functions, and the ionization problem is much more complex. For this reason, until very recently, calculations have been limited to the Born-approximation framework. Nevertheless, near the threshold, which is the most interesting region from the point of view of applications, the electron exchange and polarization effects may play a considerable role.

In the present work, it is shown that the method used earlier[1] to calculate the exchange effect in the excitation of atoms makes it possible to allow for this effect easily in the ionization problem treated in the first approximation of the perturbation theory. The polarization effects have not been considered in that earlier paper. However, if the exchange is allowed for, the role played by the polarization is usually considerably less, a fact which has been mentioned many times in the literature.

Let us now turn to the calculations. In the Born-Oppenheimer approximation, the total ionization cross section averaged over spins is

$$\bar{\sigma} = {}^1\!/_4\sigma^+ + {}^3\!/_4\sigma^-, \tag{1}$$

$$\sigma^\pm = \frac{k'}{k}\int |f(\mathbf{k}', \varkappa) \pm g(\mathbf{k}', \varkappa)|^2 \, d\omega_{k'} d\varkappa, \tag{2}$$

the direct and exchange scattering amplitudes f and g being given by

$$f(\mathbf{k}', \varkappa) = \frac{1}{2\pi}\int e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}_2}\bar{\psi}_\varkappa(\mathbf{r}_1)\,\psi_0(\mathbf{r}_1)\,\frac{d\tau_1\,d\tau_2}{r_{12}}, \tag{3}$$

$$g(\mathbf{k}', \varkappa) = \frac{1}{2\pi}\int e^{i(\mathbf{k}\mathbf{r}_2-\mathbf{k}'\mathbf{r}_1)}\bar{\psi}_\varkappa(\mathbf{r}_2)\,\psi_0(\mathbf{r}_1)\,\frac{d\tau_1\,d\tau_2}{r_{12}}. \tag{4}$$

Here, **k**, **k**′ and κ are, respectively, the momenta of the electron approaching the atom, scattered by it and knocked-out of it; ψ_0 and ψ_K are the functions of the initial and final states of the atom (we shall use the atomic units throughout).

Integration with respect to τ_2 in Eq. (3) is carried out in the usual way and gives the scattering amplitude in the Born approximation:

$$f(\mathbf{k}', \varkappa) = 2|\mathbf{k} - \mathbf{k}'|^{-2}V_{0\varkappa}(\mathbf{k} - \mathbf{k}'); \qquad V_{0\varkappa}(\mathbf{q}) = \langle\psi_\varkappa|e^{i\mathbf{q}\mathbf{r}}|\psi_0\rangle. \tag{5}$$

Integration with respect to τ_2 in Eq. (4) is much more complex. However, as shown earlier,[1] there is no need to calculate this integral exactly. It is sufficient to calculate the first term of the expansion of g in reciprocal powers of k, since the initial expression for the exchange scattering amplitude is valid only in the first approximation of the perturbation theory, and, consequently, only this first term of the expansion has any real meaning.

To find this term, we shall use the asymptotic equation[1]

$$\int \varphi(\mathbf{r}_1)\frac{e^{i\mathbf{k}\mathbf{r}_1}}{r_{12}}\,d\tau_1 = \frac{4\pi}{k^2}e^{i\mathbf{k}\mathbf{r}_2}\varphi(\mathbf{r}_2) + O(k^{-3}), \tag{6}$$

where $\varphi(\mathbf{r})$ is a function which varies slowly compared with $\exp(i\mathbf{k}\cdot\mathbf{r})$. In contrast to the excitation problem, it is necessary to allow only for the fact that at high collision energies we can have ionization acts in which the electron knocked-out of the atom carries away considerable energy. In this case, ψ_K includes a rapidly oscillating factor which should be separated explicitly. Bearing in mind that

$$\psi_\varkappa(\mathbf{r}) = (2\pi)^{-3/2}e^{\pi/2\varkappa}\Gamma(1 + i/\varkappa)\,e^{i\varkappa r}F(i/\varkappa;\ 1;\ -i(\varkappa r + \varkappa\mathbf{r})) \tag{7}$$

and that at high values of κ we have

$$F(i/\varkappa;\ 1;\ -i(\varkappa r+\boldsymbol{\varkappa}\mathbf{r}))=1+O(\varkappa^{-1}\ln\varkappa), \tag{8}$$

we obtain from Eqs. (4) and (6)

$$g(\mathbf{k}',\boldsymbol{\varkappa})=2|\mathbf{k}-\boldsymbol{\varkappa}|^{-2}V_{0\varkappa}(\mathbf{k}-\mathbf{k}')+O(k^{-3}). \tag{9}$$

Finally, substituting Eqs. (5) and (9) into Eq. (2), we arrive at the following expression for the differential ionization cross section:

$$d\sigma^{\pm}=4\frac{k'}{k}\left(\frac{1}{|\mathbf{k}-\mathbf{k}'|^2}\pm\frac{1}{|\mathbf{k}-\boldsymbol{\varkappa}|^2}\right)^2|V_{0\varkappa}(\mathbf{k}-\mathbf{k}')|^2\,d\omega_{k'}\,d\boldsymbol{\varkappa}. \tag{10}$$

Formula (10) is interesting because, first of all, it makes it possible to go over simply to the classical limit. In fact, for $\kappa \gg 1$, the matrix element $V_{0\kappa}(\mathbf{q})$, considered as a function of $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ and κ, has a sharp maximum at $\mathbf{q} = \kappa$.[2,3] However, since $\mathbf{k} - \kappa = \mathbf{k}'$, Eq. (10) becomes

$$d\sigma^{\pm}=\frac{8\pi}{k^2}\left(\frac{1}{q^2}\pm\frac{1}{k'^2}\right)^2|V_{0\varkappa}(q)|^2\,q\,dq\,d\omega_{\varkappa}\varkappa^2 d\varkappa. \tag{11}$$

Carrying out the integrations with respect to ω_{κ} and q (if $q \approx \kappa$, the latter integration is carried out easily analytically) and averaging over spins, we obtain the following result:

$$d\sigma=\frac{\pi}{E}\left[\frac{1}{\varepsilon^2}-\frac{1}{\varepsilon(E'-\varepsilon)}+\frac{1}{(E'-\varepsilon)^2}\right]d\varepsilon. \tag{12}$$

Here, $\epsilon = \kappa^2/2$, $E = k^2/2$, and $E' = E - 1/2$. For $\epsilon \gg 1$, Eq. (12) becomes identical with the result obtained usually[3] by the free-electron approximation.

The transition from Eq. (11) to Eq. (12) may be obtained more simply by the following formal assumption. Using the strongly resonant nature of $|V_{0K}(\mathbf{q})|^2$, we can replace in Eq. (11) the integration with respect to q for fixed κ by the integration with respect to κ for fixed q. Moreover, the integration with respect to κ may be extended to all values of κ, including the summation over a discrete spectrum. However, using the density of the system of functions ψ_K, we have

$$\int|V_{0\varkappa}(\mathbf{q})|^2\,d\boldsymbol{\varkappa}=\int\bar{\psi}_0(\mathbf{r}')\psi_0(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}')\,d\tau\,d\tau'=1$$

and, consequently,

$$d\sigma^{\pm}=\frac{8\pi}{k^2}\left(\frac{1}{\varkappa^2}\pm\frac{1}{k'^2}\right)^2\varkappa\,d\varkappa. \tag{13}$$

Here, again, we use the condition $q \approx \kappa$. Averaging over spins leads directly to Eq. (12).

Returning to Eq. (10), we must point out that a similar but more complex formula was proposed earlier by Peterkop[4], who showed that, for a certain choice of the phase $\eta(\mathbf{k}', \kappa)$, the scattered electron functions for the exact direct and exchange amplitudes in the ionization case are related by

$$f(\mathbf{k}',\boldsymbol{\varkappa})=g(\boldsymbol{\varkappa},\mathbf{k}'), \tag{14}$$

which, in an obvious way, leads to the following expression for the scattering cross section

$$d\sigma^{\pm}=4\frac{k'}{k}\left|\frac{\exp\{-i\Delta(\mathbf{k}',\boldsymbol{\varkappa})\}}{|\mathbf{k}-\mathbf{k}'|^2}V_{0\varkappa}(\mathbf{k}-\mathbf{k}')\pm\frac{\exp\{-i\Delta(\boldsymbol{\varkappa},\mathbf{k}')\}}{|\mathbf{k}-\boldsymbol{\varkappa}|^2}V_{0k'}(\mathbf{k}-\boldsymbol{\varkappa})\right|d\omega_{k'}\,d\boldsymbol{\varkappa}. \tag{15}$$

Here, $\Delta(\mathbf{k}', \kappa) = \eta - \eta'$, and η' is the phase corresponding to the Born approximation.

The considerations on which Peterkop[4] based his choice of the quantity $\Delta(\mathbf{k}', \boldsymbol{\kappa}) = \arg\Gamma(1 + i/k')$ cannot be regarded as fully satisfactory since they are associated with the behavior of the expression (5) near the threshold. This selection can, however, be justified by noting in addition that, if $\kappa \gg 1$, precisely this definition of $\Delta(\mathbf{k}', \boldsymbol{\kappa})$ makes both Eq. (15) and Eq. (10) give the correct transition to the classical limit. However, compared with Eq. (10), Eq. (15) is not only more complex but has another deficiency. Both formulas are obtained on the assumption that, after scattering, the system is described by the product of a plane wave and a Coulomb function of the continuous spectrum. It is clear that this approximation is closer to an exact description of the problem if the plane wave corresponds to the faster of two electrons. In the second term of Eq. (15), the plane wave corresponds to the slower electron, and the Coulomb function to the faster electron, since when the exchange is allowed for, k′ is always greater than κ. This gives rise to an additional error whose importance increases with the role of the exchange term.

Considering now the calculation of the total ionization cross section, we shall recall that Eq. (10) is rigorously valid only for sufficiently high collision energies. The use of this formula for calculations near the threshold, like the use of the standard Born formula in this region, is only a more or less successful approximation. Therefore, we shall not calculate the total ionization cross section using Eq. (10) exactly, but we shall replace the latter by a very similar but much simpler expression

$$d\sigma^{\pm}=4\frac{k'}{k}\left(\frac{1}{q^2}\pm\frac{1}{k^2-\varkappa^2}\right)^2|V_{0\varkappa}(\mathbf{q})|^2\,d\omega_{k'}\,d\boldsymbol{\varkappa}. \tag{16}$$

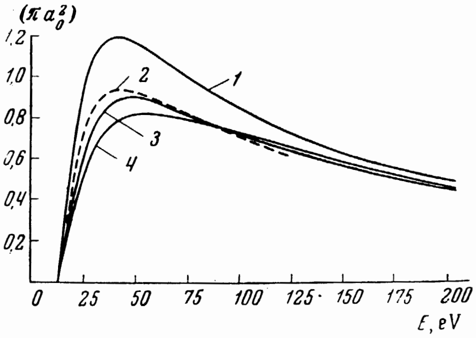
This substitution is suggested by Eq. (11). The substitution may be justified for high-energy collisions by the following considerations. The main contribution to the cross section is made by collisions with small energy transfer. However, in this case, κ has little effect on the magnitude of the exchange term which, in turn, contributes only a small correction to the main effect. In the opposite limiting case of the maximum possible energy transfer, due to the condition $q \approx \kappa$ and the energy relationship

$$k^2 - 1 = k'^2 + \varkappa^2 = 2E' \tag{17}$$

we have $|\mathbf{k} - \kappa|^2 = \kappa^2$, while it follows from Eq. (12) that $k^2 - \kappa^2 = \kappa^2 + 1$ (if the exchange is allowed for, the range of κ is given by the inequality $0 \leq \kappa^2 \leq E'$). Thus, Eq. (16) is identical with Eq. (10) also when $\kappa \gg 1$.

For low collision energies, this substitution again does not give rise to any singularities and its validity in the immediate vicinity of the threshold is self-evident. Moreover, for small energy transfer, the angular distribution of the electrons knocked-out from the atom is close to isotropic. Then, it can be easily shown that the expansion of the quantity $|\mathbf{k} - \kappa|^{-2}$ as a series in powers of κ, after averaging over all directions of the vector $\boldsymbol{\kappa}$, does not contain terms linear in κ. The quadratic terms, as shown by the calculations, are small, even at an energy of 40—50 eV corresponding to the maximum cross section, for the values of κ which are of prime importance. Therefore, we may expect that both formulas always give similar results (this was confirmed by detailed rough calculations). However, calculations of the velocity distribution of the knocked-out electrons and of the total ionization cross section, by means of formula (16), in contrast to formulas (10) and, in particular, (15), need only the same number of calculations as those for the case without allowance for the exchange.

From the point of view of the calculation of the total ionization cross section, there is no need to worry about the correct approximation in formula (10) in the region of large values of κ, since this region makes only a small contribution. Therefore, bearing in mind what has been said above, we can, in general, neglect the quantity κ^2 in the denominator of the exchange term so that Eq. (10) becomes identical with the formula for the excitation probability. Calculations show that the cross section obtained then in the region of the maximum is about 2% smaller than that given by Eq. (6). At high energies these results differ even less. This, once again, confirms the weak dependence of the expression considered here on the terms quadratic in κ.



Cross section for the ionization of the hydrogen atom by electron impact: 1) calculation without allowance for the exchange; 2) calculation, using Eq. (15), carried out by Peterkop; [4] 3) calculation, using Eq. (16); 4) Fite and Brackmann's experiments. [6]

The table lists the cross sections σ^+, σ^-, $\bar{\sigma}$ calculated using Eq. (16), as well as the ionization cross section σ found without allowance for the exchange. The latter is in complete agreement with the calculations carried out earlier by Dalgarno (cf. [5]). The figure shows the values of $\bar{\sigma}$ calculated without allowance for the exchange, Peterkop's results and the results of Fite and Brackmann's measurements[6]. It is evident from the figure that allowance for the exchange by means of Eq. (16) improves the calculated results without going outside the framework of the first approximation in the perturbation theory and without complicating the calculations compared with the exchange-free case. This result is particularly

Cross section for the ionization of the hydrogen atom by electron impact (in πa_0^2 units)

E, eV	$\sigma+$	$\sigma-$	$\bar{\sigma}$	σ	E, eV	$\sigma+$	$\sigma-$	$\bar{\sigma}$	σ
15	0.26	0.01	0.07	0.10	100	1.09	0.59	0.72	0.85
20	1.23	0.12	0,40	0.60	150	0,78	0.50	0.57	0.64
25	1,70	0.28	0,63	0,92	200	0.61	0.42	0.47	0,52
30	1.87	0,40	0,74	1.09	250	0.50	0.37	0.40	0.43
35	1.89	0,49	0,83	1.16	300	0,42	0.32	0.35	0.37
40	1,86	0,55	0,88	1.19	400	0.32	0,27	0.28	0.29
50	1,72	0.62	0.89	1,17	600	0.22	0,19	0,20	0,21
60	1.56	0.64	0.87	1.11	1000	0.14	0.13	0,13	0,13
80	1.30	0,63	0.80	0.97					

satisfactory if we bear in mind that the symmetric and antisymmetric cross sections σ^+ and σ^- for low collision energies differ considerably from $\overline{\sigma}$.

It is possible that because of the inconsistency of the exchange term in Eq. (15), some improvement in the results compared with Peterkop's calculations is not accidental.

Finally, we note that formulas of type (10) or (16) can, of course, be applied to the calculation of the ionization cross section of any atom. We note also that in the case of an atom having terms of various multiplicity, the ionization cross sections not averaged over spins may be useful for the extrapolation of the excitation functions calculated for discrete levels to higher values of the principal quantum number, in the same way as was done by McCarroll[5] for hydrogen.

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