Classical Calculations of Charge Transfer Cross Sections*

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This paper describes results obtained thus far in a recently initiated critical examination[1] of the utility of Gryżinski's classical procedures[2] for estimating charge transfer cross sections. To grasp the significance of our work, it is necessary first to recognize that Gryzinski's prescription for computing charge transfer cross sections requires à priori knowledge of each of the following essentially distinct items:

(i) The cross section $\sigma_{\Delta E}^{eff}(v_1,v_2)$ for producing an energy transfer ΔE in the collision of two charged particles of unequal masses m_1,m_2 (in charge transfer the masses respectively of the incident ion and of the electron) moving with arbitrary velocities $\vec{v}_1,\vec{v}_2$ in the laboratory system, averaged over all orientations of $\vec{v}_1,\vec{v}_2$ for fixed speeds v_1,v_2.

(ii) The range of energy transfer -- from $(\Delta E)_\ell$ to $(\Delta E)_u$ -- within which there can be significant probability of electron capture, remembering that the physically observed charge transfer cross section (as a function of incident ion speed v_1 for specified speed v_2 of the captured electron in its initially bound orbit) is

$$\sigma_{10}(v_1,v_2) = \int_{(\Delta E)_\ell}^{(\Delta E)_u} d(\Delta E)\sigma_{\Delta E}^{eff}(v_1,v_2) \qquad (1)$$

(iii) The distribution in speeds $f(v_2)dv_2$ of the initially bound to-be-captured electrons, in each of the orbits from which capture can take place.

(iv) In each of the orbits from which capture can take place, the effective number N_e of electrons (e.g., presumably one in H, two in He) which independently can collide with -- and be captured by -- the incident ion.

In terms of the above items (i) - (iv), our contribution can be described as follows:

(1) We have "improved" on Gryzinski's original formulation by employing in Eq. (1) the exact formula[3] for $\sigma_{\Delta E}^{eff}$ instead of the approximate expression Gryzinski suggests. It is not evident that use of the exact $\sigma_{\Delta E}^{eff}$ actually improves the agreement between theory and experiment. However employment of the exact formula eliminates uncertainties concerning the effects of approximating $\sigma_{\Delta E}^{eff}$, therewith permitting somewhat less equivocal evaluation of the utility of Gryzinski's prescription. As a matter of fact, with the exact $\sigma_{\Delta E}^{eff}$ Eq. (1) can be integrated in closed form. For instance, if for all $0 \leqslant (\Delta E)_\ell \leqslant \Delta E \leqslant (\Delta E)_u$

$$\Delta E \leqslant \frac{4m_1 m_2}{(m_1 + m_2)^2} \left(E_1 - E_2 - \left|E_1 \frac{v_2}{v_1} - E_2 \frac{v_1}{v_2}\right|\right) \tag{2}$$

(where E_1, E_2 are the kinetic energies of the particles) then for an incident simply charged ion

$$\sigma_{10} = \frac{\pi}{3} \frac{e^4}{v_1^2 v_2} \left[- \frac{2v_2^3}{(\Delta E)^2} - \frac{6v_2}{m_2 \Delta E} \right] \Bigg|_{(\Delta E)_u}^{(\Delta E)_\ell} \tag{3}$$

Similar formulas for σ_{10} hold when the alternative inequalities[3] to Eq. (2) are obeyed throughout the allowed range of ΔE, or when the inequalities change as ΔE increases the range from $(\Delta E)_\ell$ to $(\Delta E)_u$.

(2) We have examined various possibilities for $(\Delta E)_\ell$ and $(\Delta E)_u$, in addition to the limits specifically proposed by Gryzinski,[2] which were

$$(\Delta E)_\ell = \tfrac{1}{2} m v_1^2 + U_2 - U_1 \qquad (4a)$$

$$(\Delta E)_u = \tfrac{1}{2} m v_1^2 + U_2 + U_1 \qquad (4b)$$

where U_2, U_1 respectively are the ionization potentials of the transferring electron in its initial and final bound orbits. Alternatives to (4a) are especially needed when $U_1 \geqslant U_2$, in which event Eq. (1) makes σ_{10} infinite at incident ion energies $\frac{1}{2} m_1 v_1^2 \leqslant U_1 - U_2$. It is true that Gryzinski[2] proposes a geometrical upper bound to the cross section, but it is not clear that the proposed bound is well-founded or generally useful. In any event, the ΔE limits of Eq. (4) cause σ_{10} computed from Eq. (1) to be inconsistent with detailed balancing. For this reason we suggest that σ_{10} be computed from Eq. (1) only when $U_2 \geqslant U_1$; otherwise the desired classical estimate of σ_{10} for electron capture by ion 1 from atom 2 is to be found by detailed balancing from the classically estimated -- using Eq. (1) -- σ_{10} for electron capture by ion 2 from atom 1. With this procedure the value of $(\Delta E)_\ell$ actually employed in Eq. (1) always is $\geqslant 0$, and the resultant σ_{10} always is finite, except at zero energy when $U_2 = U_1$ (resonant charge transfer).

(3) Calculations of σ_{10} have been performed and (whenever possible) compared with experiment for protons incident on the noble gases, and for protons incident on the alkali atoms. The approximate as well as the exact expressions for $\sigma_{\Delta E}^{eff}$ have been employed, and alternatives to Eqs. (4) have been examined. The utility of the suggestion that σ_{10} be estimated from detailed balancing when $U_2 \leqslant U_1$ also has been tested. The sequence of

of charge transfer collisions from the alkalis are particularly useful for this purpose. This sequence has the further advantage that there is no room for argument concerning the value of N_e defined in (iv) above; surely $N_e = 1$ for the alkalis. The values of N_e seemingly are equally well known (they are > 1 of course) for the noble gas sequence. We also have examined the behavior of σ_{10} from Eq. (1) for charge transfer into excited states of the impinging proton; in such reactions we must understand how to weigh -- within Gryzinski's classical framework -- the fact that for capture into an orbit of energy $U_1 = -13.6/n^2$ there are available n^2 independent quantum mechanical final states. All calculations have assumed the only significant v_2 satisfies $\frac{1}{2} m v_2^2 = U_2$, i.e., that $f(v_2)$ of (iii) is a δ-function.

Results of the above calculations will be illustrated and discussed. Because the variety of possible charge transfer reactions is so great, we do not feel that these limited investigations should be the sole basis for sweeping generalizations concerning the utility of Gryzinski's procedures for estimating charge transfer cross sections. It does seem fair to say, however, that our experience suggests these procedures are significantly less useful for charge transfer than for ionization by electrons, where Bauer and Bartky[4] feel Gryzinski's methods are reliable to within a factor of about three.

References

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